B.Sc. (Honours) Part-I & II
Paper-I & III A

Topic: Thermodynamics

UG
Subject-Chemistry

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7.1 INTRODUCTION

Thermodynamics is a Greek word. Its literal meaning is motion or flow (dynamics) of heat (thermos). However, the term is used in a more general way. **Thermodynamics is the branch of science which deals with all changes in energy or transfers of energy that accompany physical and chemical processes.** It is concerned with interconversion of various forms of energy.

Chemical thermodynamics is the branch of thermodynamics which deals with the study of processes in which chemical energy is involved.

Or

Chemical thermodynamics is one of the branches of physical chemistry which deals with transport of heat either as a result of physical change or as a result of chemical change.

Chemical thermodynamics is concerned with the following questions:

(i) When two or more substances are put together, will they react?

(ii) If they do react, what energy changes will be associated with the reaction?

(iii) If a reaction occurs, at what concentrations of the reactants and their products will equilibrium be established?

Thermodynamics is not concerned with the total energy of the body but only with energy changes taking place during the transformation. The study of thermodynamics is based on three generalisations derived from experimental results. These generalisations are known as first, second and third law of thermodynamics based on human experience and there is no formal proof for them. Scientists are of the view that nothing contrary to these laws will ever occur.

Limitations of thermodynamics: (i) The laws of thermodynamics apply only to the matter in bulk, *i.e.*, macroscopic system and not to individual atoms or molecules of the macroscopic system. Thermodynamics does not deal with internal structure of atoms and molecules. (ii) Thermodynamics can only predict the feasibility or spontaneity of a process under a given set of conditions but does not tell anything about the rate at which the given process may proceed. It is only concerned with initial and final states of the system. For example, thermodynamics predicts that the reaction between oxygen and hydrogen is possible under ordinary conditions but does not tell whether the reaction is fast or slow.

7.2 TERMS USED IN THERMODYNAMICS

Before we study the laws of thermodynamics, it is necessary to define some of the basic terms which are frequently used in its discussion:

(i) System, Surroundings and Boundary: A system is defined as a specified part of the universe or specified portion of the matter which is under experimental investigation and the rest of the universe, *i.e.*, all other matter which can interact with the system, is surroundings.

Anything which separates system and surroundings is called **boundary.** The boundary may be real or imaginary; it may be rigid or non-rigid; it may be a conductor or a non-conductor of heat. The terms **diathermic wall** and **adiabatic wall** are used for conductor and non-conductor of heat boundaries respectively.

For example, a reaction is carried out in a beaker. The contents of the beaker constitute the system, beaker serves as boundary and the beaker, the air and anything else in the vicinity constitute the surroundings.

(ii) Types of System: There are three types of system:

(a) Isolated system: This type of system has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surroundings. A substance contained in an ideal thermos flask is an example of an isolated system.

(b) Closed system: This type of system can exchange energy in the form of heat, work or radiations but not matter with its surroundings. The boundary between system and surroundings is sealed but not insulated. For example, liquid in contact with vapour in a sealed tube forms a closed system. Heat can be transferred through the walls of the tube to the surroundings but total amount of matter remains the same as vapours cannot escape.

(c) Open system: This type of system can exchange matter as well as energy with surroundings. The boundary is not sealed and not insulated. Sodium reacting with water in an open beaker is an example of open system as hydrogen escapes and heat of the reaction is transferred to the surroundings.

On the basis of composition, there are two types of systems:

(1) Homogeneous system: A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one-phase only. Examples are: a pure single solid, liquid or gas, mixture of gases and a true solution.

(2) Heterogeneous system: A system is said to be heterogeneous when it is not uniform throughout, *i.e.*, it consists two or more phases. Examples are: ice in contact with water, two or more immiscible liquids, insoluble solid in contact with a liquid, a liquid in contact with vapour, etc.

(iii) Thermodynamic Properties: These are of two types:

(a) Intensive properties: The properties which do not depend upon the quantity of matter present in the system or size of the system are called **intensive properties.** Pressure, temperature, density, specific heat, surface tension, refractive index, viscosity, melting point, boiling point, volume per mole, concentration, etc., are the examples of intensive properties of the system.

(b) Extensive properties: The properties whose magnitude depends upon the quantity of matter present in the system are called **extensive properties.**

Extensive property is an additive property of the system. For a heterogeneous system consisting of several phases, the total value of extensive property will be equal to the sum of contributions from several phases.

The following are some salient features of these properties :

(i) In a system having two or more substances, the extensive property will depend not only on the independent variables but also on the number of moles of different components present in it.

(ii) If an extensive property is expressed per mole or per gram, it becomes intensive property. For example, mass and volume are extensive properties but density (mass per unit volume) and specific volume (volume per unit mass) are intensive properties.

(iii) The product, sum and ratio of intensive properties are also intensive properties. Let X and Y be two intensive properties, then $(X + Y)$; XY; $\frac{X}{Y}$; $\frac{\partial X}{\partial Y}$ are intensive properties.

(iv) Let X and Y be the two extensive properties, then

(a) $(X + Y)$ will also be an extensive variable.

(b) $\frac{X}{Y}$ and $\frac{\partial X}{\partial Y}$ will be intensive variables.

Extensive and intensive properties

Intensive properties	Extensive properties
Molarity	Heat capacity
Molality	Mass
Concentration	Volume
Density	Number of moles
Temperature	Gibbs free energy
Pressure	Enthalpy
Mole fraction	Entropy
Molar enthalpy	Internal energy
Molar entropy	
Refractive index	
Specific heat	
Viscosity	
Surface tension	
Dielectric constant	

When the total mass, temperature, volume, number of moles and composition have definite values, the system is said to be in a **definite state.** When there is any change in any one of these properties, it is said that the system has undergone a **change of state.**

(iv) State Functions or State Variables: Fundamental properties which determine the state of a system are referred to as **state variables** or **state functions** or **thermodynamic parameters.** The change in the state properties depends only upon the initial and final states of the system, but is independent of the manner in which the change has been brought about. In other words, the state properties do not depend upon a path followed.

Following are the state variables that are commonly used to describe the state of the thermodynamic system:

1. Pressure (P)
2. Temperature (T)
3. Volume (V)
4. Internal energy (E)
5. Enthalpy (H)
6. Entropy (S)
7. Free energy (G)
8. Number of moles (n)

(v) Thermodynamic Processes: When the thermodynamic system changes from one state to another, the operation is called a **process.** The various types of the processes are:

(a) Isothermal process: The process is termed **isothermal** if temperature remains fixed, *i.e.*, operation is done at constant temperature. This can be achieved by placing the system in a constant temperature bath, *i.e.*, thermostat. For an isothermal process $dT = 0$, *i.e.*, heat is exchanged with the surroundings and the system is not thermally isolated.

(b) Adiabatic process: If a process is carried out under such condition that no exchange of heat takes place between the system and surroundings, the process is termed **adiabatic.** The system is thermally isolated, *i.e.*, $dQ = 0$. This can be done by keeping the system in an insulated container, *i.e.*, thermos flask. In adiabatic process, the temperature of the system varies.

(c) Isobaric process: The process is known as **isobaric** in which the pressure remains constant throughout the change, *i.e.*, $dP = 0$.

(d) Isochoric process: The process is termed as **isochoric** in which volume remains constant throughout the change, *i.e.*, $dV = 0$.

(e) Cyclic process: When a system undergoes a number of different processes and finally returns to its initial state, it is termed **cyclic process.** For a cyclic process $dE = 0$ and $dH = 0$.

(f) Reversible process: A process which occurs infinitesimally slowly, *i.e.*, opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process, it is said to be **reversible process.** In fact, a reversible process is considered to proceed from initial state to final state through an infinite series of infinitesimally small stages and at every stage it is virtually in state of equilibrium. A reversible process is an ideal process and cannot be realised in practice.

(g) Irreversible process: When the process goes from initial to final state in single step in finite time and cannot be reversed, it is termed as **irreversible process.** In such a case equilibrium state exists only at the initial and final stages of the process. An irreversible process is spontaneous in nature. It is real and can be performed in practice. All natural processes are irreversible in nature.

Reversible process	Irreversible process
1. It is an ideal process and takes infinite time.	It is a spontaneous process and takes finite time.
2. The driving force is infinitesimally greater than the opposing force.	The driving force is much greater than the opposing force.
3. It is in equilibrium at all stages.	Equilibrium exists in the initial and final stages only.
4. Work obtained is maximum.	Work obtained is not maximum.
5. It is difficult to realise in practice.	It can be performed in practice.

Nature of Work and Heat

Work is a mode of energy transfer to or from a system with reference to the surroundings. If an object is displaced through a distance dx against a force of F, then the amount of work done is defined as

$$W = F \times dx$$

There are many types of work and all of them could be expressed as the product of two factors:

(i) an intensity factor,

(ii) a capacity factor.

Some of them are:

(a) Gravitational work $= (mg) \times h$

where, m = mass of body, g = acceleration due to gravity, h = height moved.

(b) Electrical work = charge × potential

$$= Q \times V$$

where, Q = charge, V = potential gradient.

(c) Mechanical work $= P_{ext}\ (V_2 - V_1) = P_{ext}\ \Delta V$

where, P_{ext} = external pressure, ΔV = increase or decrease in volume.

Work associated with change in volume of a system against external pressure is called mechanical work.

P_{ext} = intensity factor

ΔV = capacity factor

Work (w) is a path-dependent function, it is a manifestation of energy. Work done on a system increases the energy of the system and work done by the system decreases the energy of the system.

Work done on the system, $w = +$ ve

Work done by the system, $w = -$ ve

Heat may be defined as the quantity of energy which flows between a system and its surroundings on account of temperature difference. Heat always flows from high temperature to low temperature.

Heat absorbed or evolved, $\Delta Q = ms\,\Delta t$

where, m = mass of substance, s = specific heat

and Δt = temperature difference.

(i) Heat flowing into the system, ΔQ or $\Delta H = +$ ve.

The process in this case is endothermic in which the temperature of the system is raised and that of the surroundings is lowered.

(ii) Heat flowing out of the system, ΔQ or $\Delta H = -$ ve.

The process in this case is exothermic in which the temperature of the system is lowered and that of the surroundings is raised.

Units of Heat and Work: The unit of heat is calorie (cal). It is defined as the quantity of heat required to raise the temperature of one gram of water by 1°C.

Since, heat and work are interrelated, SI unit of heat is the joule (J).

$$1 \text{ joule} = 0.2390 \text{ cal}$$
$$1 \text{ calorie} = 4.184 \text{ J}$$
$$1 \text{ kcal} = 4.184 \text{ kJ}$$
$$1 \text{ litre-atm} = 101.3 \text{ J}$$
$$= 1.013 \times 10^9 \text{ erg}$$
$$= 24.206 \text{ cal}$$

SOME SOLVED EXAMPLES

Example 1. *A gas expands by 0.5 litre against a constant pressure of one atmosphere. Calculate the work done in joule and calorie.*

Solution: Work $= -P_{ext} \times$ volume change

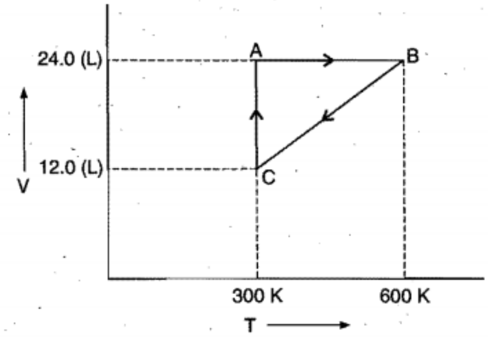
$$= -1 \times 0.5 = -0.5 \text{ litre-atm}$$
$$= -0.5 \times 101.328 \text{ J} = -50.664 \text{ J}$$
$$0.5 \text{ litre-atm} = -0.5 \times 24.20 \text{ cal} = -12.10 \text{ cal}$$

Example 2. *One mole of an ideal gas is put through a series of changes as shown in the graph in which A, B and C mark the three stages of the system. At each stage the variables are shown in the graph.*

(*a*) *Calculate the pressure at three stages of the system.*

(*b*) *Name the processes during the following changes:*

(*i*) *A to B* (*ii*) *B to C* (*iii*) *C to A and* (*iv*) *overall change.*



Solution: **(a) At stage *A*:**

$V = 24.0\,\text{L}; T = 300\,\text{K}; n = 1; R = 0.0821\,\text{litre-atm K}^{-1}\ \text{mol}^{-1}$

Substituting these values in the ideal gas equation,

$$PV = nRT,$$

$$P = \frac{1 \times 0.0821 \times 300}{24.0} = 1.026\,\text{atm}$$

At stage *B*: Volume remains the same but temperature changes from 300 K to 600 K. Thus, according to pressure law, the pressure will be doubled at *B* with respect to *A*.

$$\text{Pressure at } B = 2 \times 1.026 = 2.052\,\text{atm}$$

At stage *C*: Temperature is 300 K and volume is half that of stage *A*. Thus, according to Boyle's law, the pressure at *C* will be doubled with respect to *A*.

$$\text{Pressure at } C = 2 \times 1.026 = 2.052\,\text{atm}$$

(b) (i) During the change from *A* to *B*, volume remains constant, the process is **isochoric.**

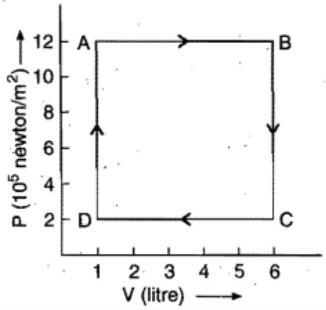
(ii) During the change from *B* to *C* the pressure remains constant, the process is **isobaric.**

(iii) During the change from *C* to *A*, the temperature remains constant, the process is **isothermal.**

(iv) Overall, the process is **cyclic** as it returns to initial state.

Example 3. *The diagram shows a P-V graph of a thermodynamic behaviour of an ideal gas. Find out from this graph (i) work done in the process* $A \to B, B \to C, C \to D$ *and* $D \to A$, *(ii) work done in the complete cycle* $A \to B \to C \to D \to A$.

Solution: (i) Work done in the process $A \to B$ (the process is expansion, hence work is done by the gas)



$$= -P \times dV = -12 \times 10^5 \times 5 \times 10^{-3}$$
$$= -6000\,\text{J}$$

Work done in the process $B \to C$ is zero as volume remains constant.

Work done in the process $C \to D$ (The process is contraction, hence work is done on the gas)

$$= P \times dV = 2 \times 10^5 \times 5 \times 10^{-3}$$
$$= 1000\,\text{J}$$

(ii) Work done in the process $D \to A$ is zero as volume remains constant.

Net work done in the whole cycle = − 6000 + 1000 = − 5000 J

i.e., net work is done by the gas.

Example 4. *Calculate the work done when* 1.0 *mole of water at* 373 *K vaporizes against an atmospheric pressure of* 1.0 *atmosphere. Assume ideal gas behaviour.*

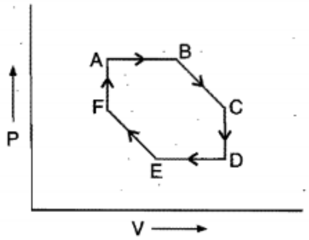
Solution: The volume occupied by water is very small and thus the volume change is equal to the volume occupied by one gram mole of water vapour.

$$V = \frac{nRT}{P} = \frac{1.0 \times 0.0821 \times 373}{1.0} = 31.0\,\text{litre}$$

$$W = -P_{\text{ext}} \times \Delta V = -(1.0) \times (31.0)\,\text{litre-atm}$$

$$= -(31.0) \times 101.3\,\text{J} = -3140.3\,\text{J}$$

Example 5. *Identify different steps in the following cyclic process:*



Temperature At A, B and F is T_1 and at C, D and E is T_2

$$T_1 > T_2$$

Solution: (i) $A \to B$ (Temperature and pressure are constant).

∴ It is **isothermal** and **isobaric** process.

(ii) $B \to C$: It is adiabatic expansion in which temperature falls from T_1 to T_2.

(iii) $C \to D$ (Temperature and volume are constant)

∴ This process is isothermal and isochoric.

(iv) $D \to E$ (Temperature and pressure are constant)

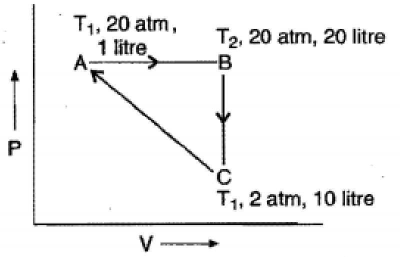
∴ It is isothermal and isobaric contraction.

(v) $E \to F$ (It is adiabatic compression in which temperature increases from T_2 to T_1).

(vi) $F \to A$ (Temperature and volume are constant).

∴ It is isothermal and isochoric process.

Example 6. *One mole of a monoatomic gas is subjected to following cyclic process:*



(*a*) *Calculate* T_1 *and* T_2.

(*b*) *Calculate* $\Delta E, q$ *and* W *in calories in each step of cyclic process.*

Solution: (a) At A **:**

$$PV = nRT$$

$$20 \times 1 = 1 \times 0.0821 \times T_1$$

$$T_1 = 243.6\,\text{K}$$

At B **:**

$$PV = nRT$$

$$20 \times 10 = 1 \times 0.0821 \times T_2$$

$$T_2 = 2436.05\,\text{K}$$

(b) Path AB **: Isobaric process** ($\Delta E = 0, q = W$)

$$W = P\Delta V = 20 \times 9 = 180 \text{ litre-atm}$$

$$= \frac{180 \times 101.3}{4.185}\,\text{cal}$$

$$= 4356.9\,\text{cal} \quad \text{(Work in compression is positive)}$$

Path BC **: Isochoric process**

$$W = 0$$

$$q_V = \Delta U = n\,C_V\,\Delta T = 1 \times \frac{3}{2} R \times (2436 - 243.6)$$

$$= \frac{3}{2} \times 2 \times 2192.4 = 6577.2\,\text{cal}$$

It is cooling process : $q_V = -6577.2\,\text{cal}$

Path CA**: It is isothermal compression** ΔE_0

$$q = W = 2.303\,nRT \log \frac{V_2}{V_1}$$

$$q = W = 2.303 \times 1 \times 2 \times \log \frac{10}{1} = 1122.02\,\text{cal}$$

7.3 INTERNAL ENERGY

Every system having some quantity of matter is associated with a definite amount of energy. This energy is known as internal energy. The exact value of this energy is not known as it includes all types of energies of molecules constituting the given mass of matter such as translational, vibrational, rotational, the kinetic and potential energy of the nuclei and electrons within the individual molecules and the manner in which the molecules are linked together, etc. The internal energy is denoted by E.

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \dots$$

Accurate measurements of some forms of energy which contribute to the absolute value of internal energy for a given substance in a given state is impossible. But one thing is certain that the internal energy of a particular system is a definite quantity at the given moment, irrespective of the manner by which it has been obtained. Internal energy like temperature, pressure, volume, etc., is a state function, *i.e.*, **total of all possible kinds of energy of a system is called its internal energy*.**

It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics, one is concerned only with energy change which occurs when the system moves from one state to another. Let ΔE be the difference of energy of the initial state (E_i) and the final state (E_f), then

$$\Delta E = E_f - E_i$$

ΔE is positive if $E_f > E_i$ and negative if $E_f < E_i$.

A system may transfer energy to or from the surroundings as heat or work or both.

Characteristics of Internal Energy

(i) Internal energy of a system is an extensive property.

(ii) Internal energy is a state property.

(iii) The change in the internal energy does not depend on the path by which the final state is reached.

(iv) There is no change in internal energy in a cyclic process.

Thermal Equilibrium and Zeroth Law of Thermodynamics

When a hot body is kept in contact with a cold body, the cold body warms up and the hot body cools down. The internal energy of the hot body decreases and that of cold body increases. The transfer of energy from the hot body to a cold body is a non-mechanical process. The energy that is transferred from one body to the other, without any mechanical work involved, is called **heat.**

Two bodies are said to be in *thermal equilibrium* if no transfer of heat takes place when they are placed in contact.

The temperature concept can be stated precisely by the fact that systems in thermal equilibrium with each other have the same temperature.

Courses of thermodynamics usually deal with the three laws : the first, second and third laws, which constitute the subject matter of thermodynamics. However, at present an ever increasing use is made in thermodynamics of the law of thermal equilibrium formulated by R. Fowler in 1931, *i.e.*, the *Zeroth law of thermodynamics.* This law was formulated after the first and the second laws had been enunciated.

This law states : *If two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.*

Conversely, the law can be stated as follows :

If three or more systems are in thermal contact with each other by means of diathermal walls and are all in thermal equilibrium together, then any two systems taken separately are in thermal equilibrium with each other.

Now let us consider three systems A, B and C as shown in Fig. 7.1. It is an experimental fact that if system A is in thermal

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*The word internal is often omitted and the word energy implies internal energy of a system.

equilibrium with system C and system B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other.

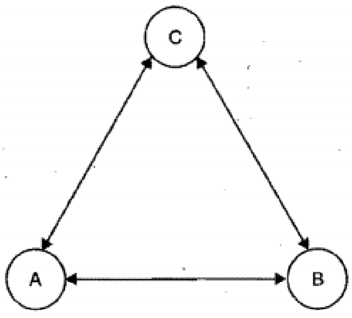


Fig. 7.1 Systems in thermal equilibrium

7.4 FIRST LAW OF THERMODYNAMICS

This law has been stated in various forms but is merely the law of conservation of energy. It was given by **Robert Mayer** and **Helmholtz.**

(i) Energy cannot be created or destroyed but it can be converted from one form to another.

(ii) The total energy of the universe is constant.

(iii) Whenever a quantity of one kind of energy disappears, an exactly equivalent quantity of energy in some other form must appear.

(iv) It is impossible to construct a perpetual motion machine which could produce work without consuming energy.

(v) The total energy of an isolated system remains constant though it may change from one form to another.

When a system is changed from initial state to the final state, it undergoes a change in the internal energy from E_i to E_f. Thus, ΔE can be written as:

$$\Delta E = E_f - E_i$$

The change in internal energy can be brought about in two ways:

(a) Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).

(b) By doing work on the system or the work done by the system.

Consider a system whose internal energy is E_1. If the system is supplied q amount of heat, the internal energy of the system will become $E_1 + q$. Now if work w is also done on the system, the final internal energy becomes E_2. Thus,

$$E_2 = E_1 + q + w$$

or $$E_2 - E_1 = q + w$$

or $$\Delta E = q + w$$

This is the mathematical statement of the first law of thermodynamics. In this statement, q is the heat absorbed and w is the work done on the system.

In case q is the heat absorbed and w the work done by the system, then the relationship becomes

$$\Delta E = q + (-w) = q - w$$

The first law of thermodynamics may also be stated as:

The net energy change of a closed system is equal to heat absorbed plus the work done on the system.

Or

The net energy change of a closed system is equal to heat absorbed minus the work done by the system.

Or

It is impossible to construct a mobile or perpetual machine that can work without consumption of any fuel energy.

Example 7. *If 500 calorie of heat energy are added to a system and the system does 350 calorie of work on the surroundings, what is the energy change of the system?*

Solution: Heat absorbed, $q = 500\,\text{cal}$

Work done by the system, $w = -350\,\text{cal}$

Applying the first law of thermodynamics,

$$\Delta E = q + w = 500 + (-350) = 150\,\text{calorie}$$

Example 8. *If 100 calorie of heat are added to the same system as in example 1 and a work of 50 calorie is done on the system, calculate the energy change of the system.*

Solution: Heat absorbed, $q = 100\,\text{cal}$

Work done on the system, $w = +50\,\text{cal}$

Applying the first law of thermodynamics,

$$\Delta E = q + w = (100 + 50) = 150\,\text{calorie}$$

In the above two examples, the final state is same but the paths adopted are different. Thus, the change in energy of the system depends on the initial and final states but does not depend on the path by which the final state has reached, q and w are, therefore, not state functions but ΔE is a state function.

Some useful conclusions drawn from the first law: $\Delta E = q + w$

(i) When a system undergoes a change $\Delta E = 0$, *i.e.*, there is no increase or decrease in the internal energy of the system, the first law of thermodynamics reduces to

$$0 = q + w$$

or $$q = -w$$

(heat absorbed from surroundings = work done by the system)

or $$w = -q$$

(heat given to surroundings = work done on the system)

(ii) If no work is done, $w = 0$ and the first law reduces to

$$\Delta E = q$$

i.e., increase in internal energy of the system is equal to the heat absorbed by the system or decrease in internal energy of the system is equal to heat lost by the system.

(iii) If there is no exchange of heat between the system and surroundings, $q = 0$, the first law reduces to

$$\Delta E = w$$

It shows that if work is done on the system, its internal energy will increase or if work is done by the system, its internal energy will decrease. This occurs in an adiabatic process.

(iv) In case of gaseous system, if a gas expands against the constant external pressure, P, let the volume change be ΔV. The mechanical work done by the gas is equal to $-P \times \Delta V$.

Substituting this value in $\Delta E = q + w$,

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

When $\Delta V = 0$,

$$\Delta E = q \text{ or } q_V$$

The symbol q_V indicates the heat change at constant volume.

Example 9. *A gas contained in a cylinder fitted with a frictionless piston expands against a constant pressure 1 atmosphere from a volume of 4 litre to a volume of 14 litre. In doing so, it absorbs 800 J thermal energy from surroundings. Determine ΔE for the process.*

Solution: Given, $q = 800\text{ J}$

$$\Delta V = (14 - 4) = 10\text{ litre}$$

$$w = -P \times \Delta V = -1 \times 10 = -10\text{ litre-atm}$$

But $0.082\text{ litre-atm} = 1.987\text{ cal}$

So, $$w = -\frac{10 \times 1.987}{0.082} = -242.3\text{ cal}$$

But $1\text{ calorie} = 4.184\text{ J}$

So, $$w = -242.3 \times 4.184 = -1013.7\text{ J}$$

Substituting the values in equation,

$$\Delta E = q + w = (800 - 1013.7) = -213.7\text{ J}$$

7.5 ENTHALPY

Heat content of a system at constant pressure is called **enthalpy** denoted by 'H'.

From first law of thermodynamics;

$$Q = E + PV \qquad \text{... (i)}$$

Heat change at constant pressure can be given as

$$\Delta Q = \Delta E + P\,\Delta V \qquad \text{... (ii)}$$

At constant pressure heat can be replaced by enthalpy.

$$\Delta H = \Delta E + P\,\Delta V \qquad \text{... (iii)}$$

Constant pressures are common in chemistry as most of the reactions are carried out in open vessels.

At constant volume, $\Delta V = 0$; thus equation (ii) can be written as

$$\Delta Q = \Delta E$$

$\therefore \Delta H$ = Heat change or heat of reaction (in chemical process) at constant pressure

ΔE = Heat change or heat of reaction at constant volume.

(i) In case of solids and liquids participating in a reaction,

$$\Delta H \approx \Delta E \;(P\,\Delta V \approx 0)$$

(ii) Difference between ΔH and ΔE is significant when gases are involved in a chemical reaction.

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

$$\boldsymbol{\Delta H = \Delta E + \Delta nRT}$$

Here, $$P\Delta V = \Delta nRT$$

Δn = Number of gaseous moles of products − Number of gaseous moles of reactants.

Using the above relation we can interrelate heats of reaction at constant pressure and at constant volume.

7.6 HEAT CAPACITY

Heat capacity of a system is defined as the quantity of heat required to raise the temperature of the system by one degree. Let a very small quantity of heat dq be given to a system and the temperature of the system rises by dT.

Thus, $$\text{Heat capacity} = \frac{dq}{dT}$$

The heat capacity of a system, particularly in a gaseous system, determined at constant volume, is different from that determined at constant pressure.

At constant volume, $q = \Delta E$

So, Heat capacity at constant volume, $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

At constant pressure, $q = \Delta E + P\Delta V = \Delta H$

So, Heat capacity at constant pressure, $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

For 1 mole of a gas, heat capacities at constant volume and constant pressure are denoted by C_V and C_P, respectively. These are termed as molar heat capacities. Thus, for 1 mole of a gas,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

and $$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

The difference between C_P and C_V is equal to the work done by 1 mole of gas in expansion when heated through 1°C.

Work done by the gas at constant pressure = $P\,\Delta V$.

For 1 mole of gas $PV = RT$.

When temperature is raised by 1°C, the volume becomes $V + \Delta V$;

So, $$P(V + \Delta V) = R(T + 1)$$

or $$P\,\Delta V = R$$

Hence, $$C_P - C_V = P\,\Delta V = R$$

Ratio of heat capacity $\left(\gamma = \frac{C_P}{C_V}\right)$ depends on atomicity of gas.

Atomicity	C_V	$C_P = C_V + R$	$\gamma = \frac{C_P}{C_V}$
Monoatomic He, Ne, Ar etc.	$\frac{3}{2}R$	$\frac{5}{2}R$	$\gamma = \frac{5/2R}{3/2R} = 1.66$
Diatomic O_2, N_2, H_2, Cl_2	$\frac{5}{2}R$	$\frac{7}{2}R$	$\gamma = \frac{7/2R}{5/2R} = 1.40$
Tri and polyatomic CO_2, NH_3, SO_3 NO_2, CH_4 etc.	$3R$	$4R$	$\gamma = \frac{4R}{3R} = 1.33$

Let n_1 and n_2 moles of two non-reacting gases A and B are mixed then heat capacity of the mixture may be calculated as.

$$(C_V)_{\text{mixture}} = \frac{n_1\,(C_V)_1 + n_2\,(C_V)_2}{n_1 + n_2}$$

7.7 EXPANSION OF AN IDEAL GAS

(i) Isothermal Expansion

In an isothermal expansion, heat is allowed to flow into or out of the system so that temperature remains constant throughout the process of expansion. Since, for an ideal gas, the internal energy, ΔE, depends only on temperature, it follows that at constant temperature, the internal energy of the gas remains constant, *i.e.*, ΔE is zero.

$$\Delta E = 0$$

According to first law of thermodynamics,

$$\Delta E = q + w$$

Since, for isothermal process, $\Delta E = 0$, hence

$$q = -w$$

This shows that in isothermal expansion, the work is done by the system at the expense of heat absorbed. The magnitude of q or w depends on the manner in which the process of expansion is carried out, *i.e.*, whether it is carried reversibly or irreversibly.

Calculation of ΔH can be done according to the following equation:

$$H = E + PV$$

or $$\Delta H = \Delta E + \Delta(PV)$$

or $$\Delta H = \Delta E + \Delta(nRT)$$

Since, for isothermal process, ΔE and ΔT are zero respectively, hence,

$$\Delta H = 0$$

Work done in reversible isothermal expansion

Consider an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. The cylinder is not insulated. The external pressure, P_{ext}, is equal to pressure of the gas, P_{gas}. Let it be P.

$$P_{\text{ext}} = P_{\text{gas}} = P$$

If the external pressure is decreased by an infinitesimal amount dP, the gas will expand by an infinitesimal volume, dV. As a result of expansion, the pressure of the gas within the cylinder falls to $P_{\text{gas}} - dP$, *i.e.*, it becomes again equal to the external pressure and, thus, the piston comes to rest. Such a process is repeated for a number of times, *i.e.*, in each step the gas expands by a volume dV.

Since, the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced due to expansion is balanced by the absorption of heat from the surroundings and the temperature remains constant throughout the expansion.

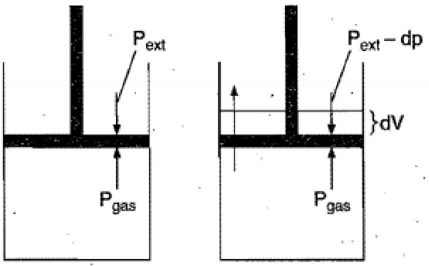


Fig. 7.2

The work done by the gas in each step of expansion can be given as,

$$d_w = -(P_{\text{ext}} - dP)\,dV = -P_{\text{ext}} \cdot dV = -P\,dV$$

$dP \cdot dV$, the product of two infinitesimal quantities, is neglected.

The total amount of work done by the isothermal reversible expansion of the ideal gas from volume V_1 to volume V_2 is, therefore,

$$w = -\int_{V_1}^{V_2} P\,dV$$

For an ideal gas, $$P = \frac{nRT}{V}$$

So, $$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

Integrating, $$w = -nRT \log_e \frac{V_2}{V_1} = -2.303nRT \log \frac{V_2}{V_1}$$

At constant temperature, according to Boyle's law,

$$P_1V_1 = P_2V_2$$

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

So, $$w = -2.303nRT \log \frac{P_1}{P_2}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with positive sign.

$$w_{\text{compression}} = 2.303nRT \log \frac{V_1}{V_2} = 2.303nRT \log \frac{P_2}{P_1}$$

Work done in irreversible isothermal expansion

Two types of irreversible isothermal expansions are observed, *i.e.*, (i) Free expansion and (ii) Intermediate expansion. In free expansion, the external pressure is zero, *i.e.*, work done is zero when gas expands in vacuum. In intermediate expansion, the external pressure is less than gas pressure. So, the work done when volume changes from V_1 to V_2 is given by

$$w = -\int_{V_1}^{V_2} P_{\text{ext}} \times dV = -P_{\text{ext}}(V_2 - V_1)$$

Since, P_{ext} is less than the pressure of the gas, the work done during intermediate expansion is numerically less than the work done during reversible isothermal expansion in which P_{ext} is almost equal to P_{gas}.

Maximum work: The work done by the system always depends upon the external pressure. The higher the value of P_{ext}, the more work is done by the gas. As P_{ext} cannot be more than P_{gas}, otherwise compression will occur, thus the largest value of P_{ext} can be equal to P_{gas}. Under this condition when expansion occurs, the maximum work is done by the gas on the surroundings.

(ii) Adiabatic Expansion

In adiabatic expansion, no heat is allowed to enter or leave the system, hence, $q = 0$. When this value is substituted in first law of thermodynamics, $\Delta E = q + w$, we get $\Delta E = w$.

In expansion, work is done by the system on the surroundings, hence, w is negative. Accordingly ΔE is also negative, *i.e.*, internal energy decreases and therefore, the temperature of the system falls. In case of compression, ΔE is positive, *i.e.,* internal energy increases and therefore, the temperature of the system rises.

The molar specific heat capacity at constant volume of an ideal gas is given by

$$C_V = \left(\frac{dE}{dT}\right)_V$$

or $$dE = C_V \cdot dT \qquad \text{... (i)}$$

and for finite change $$\Delta E = C_V \; \Delta T \qquad \text{... (ii)}$$

So, $$w = \Delta E = C_V \; \Delta T \qquad \text{... (iii)}$$

The value of ΔT depends upon the process whether it is reversible or irreversible.

Reversible adiabatic expansion

Let P be the external pressure and ΔV the increase in volume. Thus, the work done by the system is

$$w = -P \, \Delta V \qquad \text{... (iv)}$$

If ΔT is the fall in temperature, then

$$C_V \; \Delta T = -P \, \Delta V \qquad \text{... (v)}$$

For very small change in reversible process,

$$C_V \, dT = -P dV = -\frac{RT}{V} \cdot dV \quad \text{(for 1 mole of the gas)}$$

$$C_V \cdot \frac{dT}{T} = -R \cdot \frac{dV}{V} \qquad \text{... (vi)}$$

Integrating the above equation between temperatures T_1 and T_2 when corresponding values are V_1 and V_2,

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_V \; \log_e \frac{T_2}{T_1} = -R \, \log_e \frac{V_2}{V_1} = R \, \log_e \frac{V_1}{V_2}$$

or $$\log \frac{T_2}{T_1} = -\frac{R}{C_V} \log \frac{V_2}{V_1} = \frac{R}{C_V} \log \frac{V_1}{V_2} \qquad \text{... (vii)}$$

We know that, $$C_P - C_V = R$$

or $$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

or $$(\gamma - 1) = \frac{R}{C_V}$$

Putting the value of $\frac{R}{C_V}$ in eq. (vii),

$$\log \frac{T_2}{T_1} = (\gamma - 1) \log \frac{V_1}{V_2}$$

$$= \log \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \text{... (viii)}$$

or $$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \text{... (ix)}$$

or $$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1} \qquad \text{... (x)}$$

or $$\frac{P_1 V_1}{P_2 V_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1}$$

or $$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \qquad \text{... (xi)}$$

or $$PV^{\gamma} = \text{constant} \qquad \text{... (xii)}$$

Thus, knowing γ, V_1, V_2 and initial temperature, T_1, the final temperature, T_2, can be readily evaluated.

Modifying the eq. (x),

$$\frac{T_1}{T_2} = \left(\frac{\frac{RT_2}{P_2}}{\frac{RT_1}{P_1}}\right)^{\gamma - 1} = \left(\frac{P_1}{P_2} \cdot \frac{T_2}{T_1}\right)^{\gamma - 1}$$

or $$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{\gamma - 1} = \left(\frac{P_2}{P_1}\right)^{1 - \gamma} \qquad \text{... (xiii)}$$

Thus, knowing γ, P_1, P_2 and initial temperature, the final temperature, T_2, can be evaluated.

From eq. (v),

$$\text{Work done} = C_V \cdot \Delta T = C_V \, (T_2 - T_1) = \frac{R}{(\gamma - 1)} (T_2 - T_1)$$

$$\text{For } n \text{ moles} = \frac{nR}{(\gamma - 1)} (T_2 - T_1)$$

Irreversible adiabatic expansion

In free expansion, the external pressure is zero, *i. e.*, work done is zero. Accordingly, ΔE which is equal to w is also zero. If ΔE is zero, ΔT should be zero. Thus, in free expansion (adiabatically), $\Delta T = 0$, $\Delta E = 0$, $w = 0$ and $\Delta H = 0$.

In intermediate expansion, the volume changes from V_1 to V_2 against external pressure, P_{ext}.

$$w = -P_{\text{ext}} (V_2 - V_1) = -P_{\text{ext}} \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$$

$$= -P_{\text{ext}} \left(\frac{T_2 P_1 - T_1 P_2}{P_1 P_2}\right) \times R$$

or $$w = C_V \, (T_2 - T_1) = -RP_{\text{ext}} \left(\frac{T_2 P_1 - T_1 P_2}{P_1 P_2}\right)$$

Process	**Condition**	**Heat change *q***	**Internal energy change ΔU**	**Work done**
Free expansion	(U) constant	—	0	0 as $P = 0$
Isochoric	(V) constant	ΔU	$nC_V \, \Delta T$	0 as $\Delta V = 0$
Isothermal	(T) constant	$-W$	0	$2.303 \, nRT \log\left(\frac{V_2}{V_1}\right)$ $= 2.303 \, nRT \log\left(\frac{P_1}{P_2}\right)$

Isobaric	(P) constant	$nC_P\,\Delta T$	$nC_V\,\Delta T$	$P\,(V_2 - V_1)$ $= nR(T_2 - T_1)$
Adiabatic	(q) constant	0	$-W$	$C_V\,(T_1 - T_2)$ $= \frac{nR}{\gamma - 1}$ $(T_1 - T_2)$ $= \frac{1}{\gamma - 1}$ $(P_1V_1 - P_2V_2)$
Cyclic process	——	W	0	Area of cycle

7.8 GRAPHICAL REPRESENTATION OF VARIOUS THERMODYNAMIC PROCESSES AND THE CALCULATION OF WORK DONE BY GRAPHICAL METHODS

1. Graphically, different processes can be represented as follows.

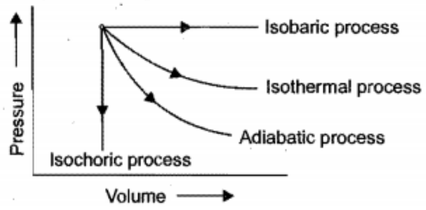


Fig. 7.3 (a)

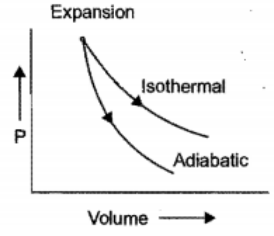


Fig. 7.3 (b)

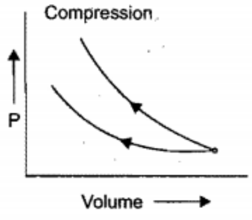


Fig. 7.3 (c)

2. Let a gas is compressed from V_i or V_f by an external pressure of P_{ext}. The work done on the gas can be calculated by the shaded area of the graph represented in following Fig. 7.4.

Work done on the gas, $w = -P_{\text{ext}}\ (V_f - V_i)$

$= +$ ve work, Since $V_f < V_i$

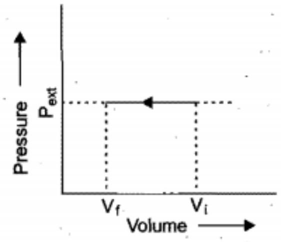


Fig. 7.4 Single step compression of ideal gas against external pressure P_{ext}

3. Let compression of gas takes place from volume V_i to V_f in the finite number of stages then the work done on the gas can be calculated by summing up the work of all stages.

Work done on the gas = Shaded area of the diagram.

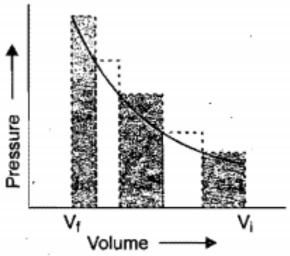


Fig. 7.5 Indicator diagram (*P-V*) plot in which the compression took place in the finite number of steps with varying pressure

4. Graphically, the work of expansion can also be determined. In case, if a graph is plotted between P and V, then the area under the curve gives the external work done by the gas.

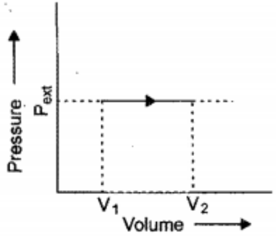


Fig. 7.6 Shaded area gives the work done by the gas when pressure remains constant

$$w_{\text{exp}} = -P_{\text{ext}}\ (V_2 - V_1)$$
$$= -\text{ ve work}$$

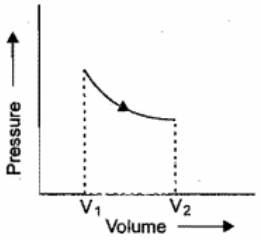
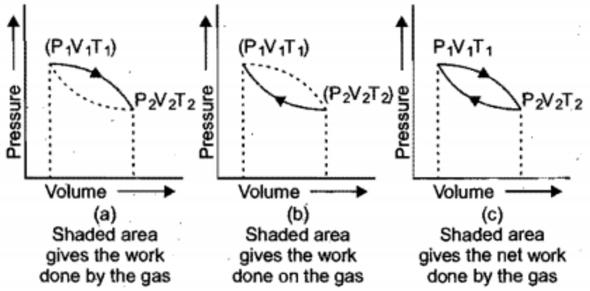


Fig. 7.7 Shaded area represents the work done by the gas when both pressure and volume vary

5. Work done by a gas undergoing cyclic process : It is determined with the help of following three graphs.



(a) Shaded area gives the work done by the gas

(b) Shaded area gives the work done on the gas

(c) Shaded area gives the net work done by the gas

Fig. 7.8 Complete cyclic process of a gas

6. Work done by the gas in a closed path *ABCA*.

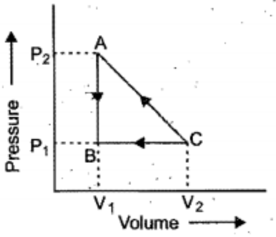


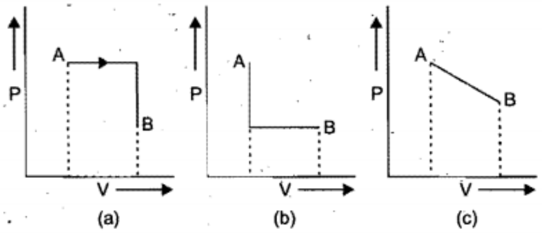
Fig. 7.9 The gas in closed cyclic process ABCA

$$\text{Work done} = \text{Area of shaded triangle}$$

$$= \frac{1}{2} \times \text{Length of base} \times \text{Length of perpendicular}$$

$$= \frac{1}{2} \times (V_2 - V_1)(P_2 - P_1)$$

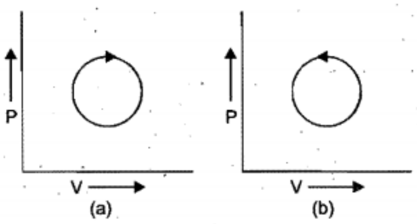
7. Let a system of gas passes from initial state *A* to *B* in following three ways. The work done by the gas will be calculated by the shaded area.



(a) (b) (c)

Fig. 7.10 Graphical proof that the work is not a state function

8. Work done in clockwise and anti-clockwise cyclic process :



(a) (b)

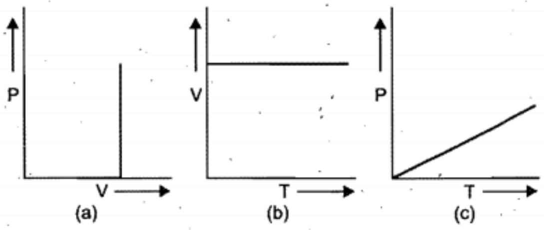
Fig. 7.11 Representation of closed cyclic process in clockwise and anti-clockwise direction

Shaded area represents the net work done in the cyclic process.

Case I : If the cyclic process is in clockwise direction then work done will be negative because the net work will be done by the system.

Case II : If the cyclic process is in anti-clockwise direction then work done will be positive because the net work is done on the system.

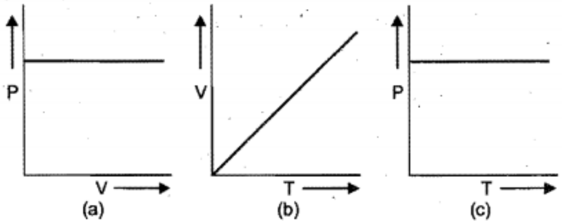
9. If the state of a system changes in such a way that its volume remains constant, the process is called isochoric. Following three plots represent isochoric process.



(a) (b) (c)

Fig. 7.12 Isochores of Ideal Gas

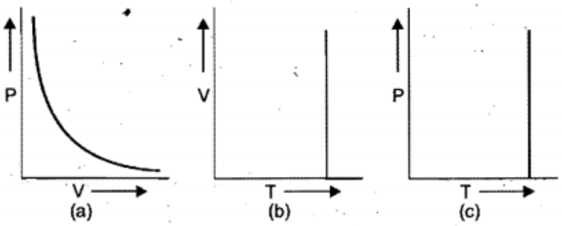
10. If the state of system changes in such a way that pressure is constant, the process is called isobaric.



(a) (b) (c)

Fig. 7.13 Isobars of Ideal Gas

11. If the state of a system changes in such a way that temperature remains constant, the process is called isothermal.



(a) (b) (c)

Fig. 7.14 Isotherm of Ideal Gas

7.9 JOULE-THOMSON EFFECT

An ideal gas is defined as the gas in which intermolecular forces of attraction are absent. If such a gas expands into vacuum adiabatically, no cooling is produced in the process, *i. e.*, there is no change in the internal energy which only depends upon the temperature.

However, when a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled. The greater the difference in pressure on the two sides, the higher shall be difference in temperature.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson effect.

The experimental set-up is shown in Fig. 7.15. It consists of a thermally insulated tube fitted with a porous plug and two weightless and frictionless pistons X and Y. Two sensitive thermometers are fitted on both the sides of the porous plug to record temperature.

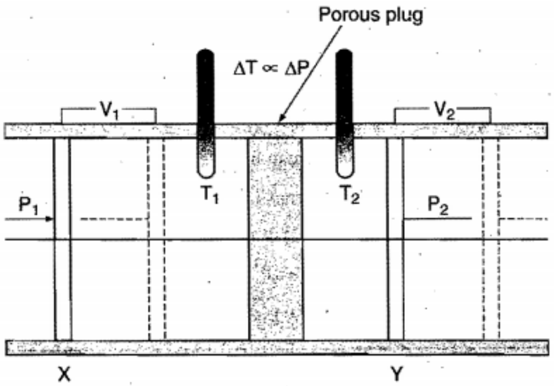


Fig. 7.15

Consider that a certain amount of the gas is passed through the porous plug by slow movement of piston X, *i.e.*, a volume V_1 of the gas at pressure P_1 be forced through the plug on the left side of the plug. The gas in the right hand chamber is allowed to expand to volume V_2 and pressure P_2 by moving the piston Y. The change in temperature is recorded from the thermometers.

Most of the gases are found to undergo cooling on expansion through the porous plug. However, helium and hydrogen are exceptions as these get warmed.

The gas is compressed on left hand side. Thus, work is done on the gas. It is equal to P_1V_1. The work done on right hand side by the gas is equal to P_2V_2.

$$\text{Total work done by the gas} = P_1V_1 - P_2V_2$$

As $q = 0$, the work done by the gas lowers its internal energy and consequently temperature falls.

$$\Delta E = P_1V_1 - P_2V_2$$

$$E_2 - E_1 = P_1V_1 - P_2V_2$$

$$(E_2 + P_2V_2) - (E_1 + P_1V_1) = 0$$

or $$H_2 - H_1 = 0$$

or $$\Delta H = 0$$

Thus, Joule-Thomson effect occurs at constant enthalpy.

Joule-Thomson Coefficient

The number of degrees of temperature change produced per atmospheric drop in pressure under constant enthalpy conditions when the gas is allowed to expand through porous plug is called **Joule-Thomson coefficient.** It is denoted by μ.

$$\mu = \frac{dT}{dP}$$

When μ has positive value, the gas cools on expansion. If it has negative value, the gas warms on expansion. Every gas has a definite value of temperature when the sign changes from negative to positive. This temperature is termed **inversion temperature.** Most of the gases have inversion temperature near about room temperature and thus cool at room temperature when expansion is done. However, the inversion temperature for H_2 is $-80°C$. Thus, at room temperature hydrogen warms on expansion. In order to produce further cooling by Joule-Thomson effect in hydrogen, it is necessary that it should be first cooled to $-80°C$ by other cooling devices.

The value of inversion temperature has been calculated by using van der Waals' equation,

$$T_i = \frac{2a}{Rb}$$

Thus, inversion temperature depends upon van der Waals' constants a and b of the gas.

SOME SOLVED EXAMPLES

Example 10. *1 mole of* Fe_2O_3 *and 2 mole of Al are mixed at temperature* $25°C$ *and the reaction is completed to give :*

$$Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(l);\ \Delta H = -850\ kJ$$

The liberated heat is retained within the products, whose combined specific heat over a wide temperature range is about $0.8\,Jg^{-1}\,K^{-1}$. *The melting point of iron is* $1530°C$. *Show that the quantity of heat liberated is sufficient to raise the temperature of the product to the melting point of iron in order to get it welded.*

Solution: Mass of products

$= \text{Mass of one mole } Al_2O_3 + \text{Mass of two mole Fe}$

$= 214\ g$

$$q = ms\,\Delta T = 214 \times 0.8 \times (1803 - 298)$$

$$= 257656\ J = 257.656\ kJ$$

Heat required is less than heat released, hence the temperature can be easily raised to the required value.

Example 11. *Calculate w and* ΔE *for the conversion of* 0.5 *mole of water at* $100°C$ *to steam at* 1 *atm pressure. Heat of vaporisation of water at* $100°C$ *is* $40670\ J\,mol^{-1}$.

Solution: Volume of 0.5 mole of steam at 1 atm pressure

$$= \frac{nRT}{P} = \frac{0.5 \times 0.0821 \times 373}{1.0} = 15.3\ L$$

$$\text{Change in volume} = \text{Vol. of steam} - \text{Vol. of water}$$

$$= 15.3 - \text{negligible} = 15.3\ L$$

Work done by the system,

$$w = P_{ext} \times \text{volume change}$$

$$= 1 \times 15.3 = 15.3\ \text{litre-atm}$$

$$= 15.3 \times 101.3\ J = 1549.89\ J$$

'w' should be negative as the work has been done by the system on the surroundings.

$$w = -1549.89\ J$$

Heat required to convert 0.5 mole of water at $100°C$ to steam

$$= 0.5 \times 40670\ J = 20335\ J$$

According to first law of thermodynamics,

$$\Delta E = q + w = 20335 - 1549.89 = 18785.11\ J$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 5 moles of an ideal gas at 27°C expands isothermally and reversibly from a volume of 6 L to 60 L. The work done in kJ is:
   (a) −14.7 (b) −28.72 (c) +28.72 (d) −56.72
   [**Ans.** (b)]
   [**Hint:** $w = -2.303nRT \log \frac{V_2}{V_1}$
   $$= -2.303 \times 5 \times 8.314 \times 300 \log \frac{60}{6}$$
   $$= -28.72 \text{ kJ}]$$

2. 10 moles of an ideal gas confined to a volume of 10 L is released into atmosphere at 300 K where the pressure is 1 bar. The work done by the gas is:
   $(R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1})$
   (a) 249 L bar (b) 259 L bar (c) 239 L bar (d) 220 L bar
   [**Ans.** (c)]
   [**Hint:** Initial volume, $V_1 = 10$ L
   $$V_2 \text{ (final)} = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$
   $$W = P\,\Delta V = 1 \times (249 - 10)$$
   $$= 239 \text{ L bar}]$$

3. 1 litre-atm work is approximately equal to:
   (a) 101.3 J (b) 8.314 J (c) 931 J (d) 19.2 J
   [**Ans.** (a)]
   [**Hint:** 0.0821 litre-atm = 8.314 J (values of gas constant)
   ∴ 1 litre-atm = 101.3 J]

4. A system absorbs 20 kJ heat and also does 10 kJ of work. The net internal energy of the system:
   (a) increases by 10 kJ (b) decreases by 10 kJ
   (c) increases by 30 kJ (d) decreases by 30 kJ
   [**Ans.** (a)]
   [**Hint:** $\Delta U = q + w = 20 - 10 = 10$ kJ]

5. One mole of a gas is heated at constant pressure to raise its temperature by 1°C. The work done in joules is:
   (a) − 4.3 (b) −8.314
   (c) −16.62 (d) unpredictable
   [**Ans.** (b)]
   [**Hint:** $w = -nR\,\Delta T$ or $w = -P\,\Delta V$
   $$= -1 \times 8.314 \times 1 = -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right)$$
   $$= -8.314 \text{ J}]$$

6. In open system:
   (a) there will be exchange of both matter and energy
   (b) there will be no exchange of matter and energy
   (c) there will be exchange of energy only
   (d) there will be exchange of matter only
   [**Ans.** (a)]
   [**Hint :** Open system has imaginary boundary, therefore, both energy and mass can be exchanged.]

7.10 THERMOCHEMISTRY

Thermochemistry is a branch of physical chemistry which is concerned with energy changes accompanying chemical transformations. It is also termed as chemical energetics. It is based on the first law of thermodynamics.

Chemical reactions are accompanied by evolution or absorption of heat energy. When reactants combine together to form new products, there is readjustment of energies. During a chemical reaction, the chemical bonds between atoms in the reactant molecules are rearranged in the product molecules, *i.e.*, chemical bonds in the reactants are broken down and new chemical bonds are formed in the products. Energy is needed to break the bonds of reactants and energy is released in the formation of new bonds of products.

Exothermic Reactions

Heat is evolved in these chemical reactions. It is possible when the bond energy of reactants is less than the bond energy of products.

At constant pressure,

$$\Delta H = (H_P - H_R) = -\text{ve}, \qquad i.e., \quad H_P < H_R$$

At constant volume,

$$\Delta E = (E_P - E_R) = -\text{ve}, \qquad i.e., \quad E_P < E_R$$

Endothermic Reactions

Heat is absorbed in these chemical reactions. It is possible when the bond energy of reactants is greater than the bond energy of products.

At constant pressure,

$$\Delta H = H_P - H_R = +\text{ve}, \qquad i.e., \quad H_P > H_R$$

At constant volume,

$$\Delta E = E_P - E_R = +\text{ve}, \qquad i.e., \quad E_P > E_R$$

Sign conventions:

	ΔQ	ΔE	ΔH
Exothermic	(−)	(−)	(−)
Endothermic	(+)	(+)	(+)

Exothermic and endothermic chemical equations can be represented as:

$$\text{Exothermic}\begin{cases}\text{NaOH}(aq.) + \text{HCl}(aq.) \longrightarrow \text{NaCl}(aq.) + H_2O(l) + 13.7 \text{ kcal} \\ \text{NaOH}(aq.) + \text{HCl}(aq.) \longrightarrow \text{NaCl}(aq.) + H_2O(l); \quad \Delta H = -13.7 \text{ kcal}\end{cases}$$

$$\text{Endothermic}\begin{cases}C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) - 31.4 \text{ kcal} \\ C(s) + H_2O(g) \longrightarrow CO(g) + H_2O(g); \quad \Delta H = +31.4 \text{ kcal}\end{cases}$$

7.11 HEAT OF REACTION OR ENTHALPY OF REACTION

Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction (or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically,

Enthalpy of reaction (or heat of reaction)

$$= \Delta H = \Sigma H_P - \Sigma H_R$$

For example, the equation

$$H_2(g) + Cl_2(g) = 2HCl(g) + 44.0 \text{ kcal} \quad \text{or} \quad \Delta H = -44 \text{ kcal}$$

indicates that when 2 g of hydrogen (1 mole) completely reacts with 71 g of chlorine (1 mole) to form 73 g of HCl (2 mole), the amount of heat evolved is 44.0 kcal or the enthalpy decreases by 44.0 kcal or the reacting system loses 44.0 kcal of heat or the enthalpy change of the reaction, $\Delta H = -44.0$ kcal.

Consider the following reaction:

$$C_2H_4(g) + 3O_2(g) = 2CO_2 + 2H_2O(l); \ \Delta E = -335.8 \text{ kcal}$$

The equation indicates that reaction has been carried between 1 mole of C_2H_4 and 3 mole of oxygen at constant volume and 25° C. The heat evolved is 335.8 kcal or the internal energy of the system decreases by 335.8 kcal.

Consider another reaction:

$$C(s) + H_2O(g) = CO(g) + H_2(g) - 31.4 \text{ kcal}$$

or $$\Delta H = 31.4 \text{ kcal}$$

This reaction indicates that 1 mole of carbon (12 g) reacts with 1 mole of steam (18 g) to form 1 mole of CO and 1 mole of hydrogen and 31.4 kcal of heat is absorbed. The enthalpy of the system increases by 31.4 kcal or the total enthalpy of the products is 31.4 kcal more than the enthalpy of reactants.

Factors which Influence the Heat of Reaction

There are a number of factors which affect the magnitude of heat of reaction.

(i) Physical state of reactants and products: Heat energy is involved for changing the physical state of a chemical substance. For example, in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed.

Considering the following two reactions:

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g); \ \Delta H = -57.8 \text{ kcal}$$

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l); \ \Delta H = -68.32 \text{ kcal}$$

It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in second case is higher because heat is evolved when steam condenses. Hence, physical state always affects the heat of reaction.

(ii) Allotropic forms of the element: Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous form is used.

$$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g); \ \Delta H = -94.3 \text{ kcal}$$

$$C(\text{amorphous}) + O_2(g) \longrightarrow CO_2(g); \ \Delta H = -97.6 \text{ kcal}$$

The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is termed as **heat of transition.**

$$C(\text{diamond}) \longrightarrow C(\text{amorphous}); \ \Delta H = 3.3 \text{ kcal}$$

(iii) Enthalpies of solution: Enthalpies of reaction differ when in one case dry substances react and in another case when the same substances react in solution. For example, in the reaction between hydrogen sulphide and iodine,

$$H_2S(g) + I_2(g) \longrightarrow 2HI + S; \quad \Delta H = -17.2 \text{ kcal}$$

$$H_2S(g) + I_2 \text{ (solution)} \longrightarrow 2HI \text{ (solution)} + S;$$

$$\Delta H = -21.93 \text{ kcal}$$

(iv) Temperature: Heat of reaction or enthalpy of reaction also depends on the temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature. Due to this reason, enthalpies of reaction are calculated and expressed at a standard temperature of 25° C or 298 K. However, if the reaction is not carried out at 25° C, the temperature at which the reaction is performed, is indicated.

(v) Reaction carried out at constant pressure or constant volume: When a chemical reaction occurs at constant volume, the heat change is called the enthalpy of reaction at constant volume. However, most of the reactions are carried out at constant pressure; the enthalpy change is then termed as the enthalpy of reaction at constant pressure. The difference in the values is negligible when solids and liquids are involved in a chemical change. But, in reactions which involve gases, the difference in two values is considerable. For this purpose see section 7.5.

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

or $$q_V + \Delta nRT = q_P$$

q_V = heat change at constant volume,

q_P = heat change at constant pressure.

Δn = total number of moles of products − total number of moles of reactants

Example 24. *The heat of combustion of ethylene at 18° C and at constant volume is −335.8 kcal when water is obtained in liquid state. Calculate the heat of combustion at constant pressure and at 18° C.*

Solution: The chemical equation for the combustion of C_2H_4 is

$$\underset{1 \text{ mole}}{C_2H_4(g)} + \underset{3 \text{ moles}}{3O_3(g)} = \underset{2 \text{ moles}}{2CO_2(g)} + 2H_2O(l); \ \Delta E = -335.8 \text{ kcal}$$

No. of moles of reactants = (1 + 3) = 4

No. of moles of products = 2

So, $$\Delta n = (2 - 4) = -2$$

Given, $\Delta E = -335.8$ kcal, $\Delta n = -2$, $R = 2 \times 10^{-3}$ kcal

and $$T = (18 + 273) = 291 \text{ K}$$

Applying
$$\Delta H = \Delta E + \Delta nRT$$
$$= -335.8 + (-2)(2 \times 10^{-3})(291)$$
$$= -336.964 \text{ kcal}$$

Example 25. *The enthalpy of formation of methane at constant pressure and 300 K is –75.83 kJ. What will be the heat of formation at constant volume?* $(R = 8.3\,J\,K^{-1}\,mol^{-1})$

Solution: The equation for the formation of methane is

$$C(s) + \underset{2\text{ moles}}{2H_2(g)} = \underset{1\text{ mole}}{CH_4(g)};\ \Delta H = -75.83\text{ kJ}$$

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

Given, $\Delta H = -75.83\text{ kJ}, R = 8.3\times10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1}, T = 300\text{K}$

Applying $\Delta H = \Delta E + \Delta nRT$

$$-75.83 = \Delta E + (-1)(8.3\times10^{-3})(300)$$

So, $\Delta E = -75.83 + 2.49$

$$= -73.34\text{ kJ}$$

7.12 ENTHALPY OF FORMATION OR HEAT OF FORMATION

The process in which a compound is formed from its constituent elements in their standard state is called **formation.**

The amount of heat absorbed or evolved when 1 mole of the substance is directly obtained from its constituent elements is called **heat of formation.**

$$C\text{ (amorphous)} + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -97.6\text{ kcal/mol}$$

Enthalpy of formation of CO_2 is –97.6 kcal

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g);\ \Delta H = -44\text{ kcal}$$

Thus, enthalpy of formation of HCl is –22 kcal per mol.

Standard enthalpy of formation: The enthalpy of formation depends upon the conditions of formation, *i.e.*, temperature, pressure and physical states (gas, solid or liquid) or allotropic state of the reactants. If all substances of the chemical reaction are in their standard states (*i.e.*, at 25° C or 298 K and 1 atmospheric pressure), the heat of formation or enthalpy of formation is called **standard heat of formation** or **standard enthalpy of formation.** It is denoted by ΔE_f° (volume constant) or ΔH_f° (pressure constant).

It is very difficult to determine absolute values of enthalpies of substances. However, relative enthalpies of substances can be determined if the enthalpies of free elements at 25° C and 1 atmospheric pressure are taken arbitrarily as zero.

Consider the reaction between carbon and oxygen at 25° C to form carbon dioxide under atmospheric pressure.

$$C(s) + O_2(g) = CO_2(g);\ \Delta H = \Delta H_f = -393.5\text{ kJ}$$

$$\therefore\ \Delta H_f = \Delta H = H_P - H_R = -393.5\text{ kJ}$$

$H_R = 0$, *i.e.*, enthalpies of free elements are taken as zero.

So, $\Delta H_f = \Delta H = H_P$ = enthalpy of $CO_2 = -393.5$ kJ

Thus, $\Delta H_f^\circ = -393.5$ kJ.

The compounds which have positive enthalpies of formation are called **endothermic compounds** and are less stable than the reactants. The compounds which have negative enthalpies of formation are known as **exothermic compounds** and are more stable than reactants.

The knowledge of standard heats of formation of various substances can be used to calculate the heats of reactions under standard conditions, *i.e.*, ΔH°.

$$\begin{array}{c}\Delta H^\circ\text{ for}\\ \text{the reaction}\end{array} = \begin{bmatrix}\text{Sum of the standard}\\ \text{heats of formation}\\ \text{of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard}\\ \text{heats of formation}\\ \text{of reactants}\end{bmatrix}$$

i.e., $$\Delta H^\circ = \Sigma\,\Delta H_{f\text{ (products)}}^\circ - \Sigma\,\Delta H_{f\text{ (reactants)}}^\circ$$

The heats of formation of all the elements in their standard states are arbitrarily assumed to be zero.

Intrinsic energy: It may be defined as:

Intrinsic energy = – Heat of formation

"Additional amount of energy which one gram mole of the compound possesses above that of its constituent elements."

Let us consider the combustion of carbon.

$$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -94.38\text{ kcal}$$

When 1 mole CO_2 is formed, 94.38 kcal heat is evolved. It means, energy content of CO_2 is less than energy content of $C(s)$ and $O_2(g)$ by 94.38 kcal. Thus, intrinsic energy of CO_2 is 94.38 kcal.

If we assume that intrinsic energy of elements is zero, then intrinsic energy of compound may be calculated in the form of heat of formation. Hence, intrinsic energy may not be considered as internal energy of the compound.

Example 26. *Calculate the enthalpy change for the following reaction:*

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

given, enthalpies of formation of CH_4, CO_2 *and* H_2O *are* –74.8 *kJ mol*$^{-1}$, –393.5 *kJ mol*$^{-1}$ *and* –286.2 *kJ mol*$^{-1}$ *respectively.*

Solution:

$$\Delta H^\circ = \Delta H_{f\text{ (products)}}^\circ - \Delta H_{f\text{ (reactants)}}^\circ$$

$$= [\Delta H_{f\,(CO_2)}^\circ + 2\Delta H_{f\,(H_2O)}^\circ] - [\Delta H_{f\,(CH_4)}^\circ + 2\Delta H_{f\,(O_2)}^\circ]$$

$$= [-393.5 + 2\times(-286.2)] - [-74.8 + 2\times 0]$$

$$= -393.5 - 572.4 + 74.8$$

$$= -891.1\text{ kJ}$$

Example 27. *The standard heats of formation at 298 K for* $CCl_4(g), H_2O(g), CO_2(g)$ *and* $HCl(g)$ *are –25.5, –57.8, –94.1 and –22.1 kcal mol*$^{-1}$ *respectively. Calculate* ΔH_{298}° *for the reaction.*

$$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$$

Solution:

$$\Delta H^\circ = \Delta H_{f\text{ (products)}}^\circ - \Delta H_{f\text{ (reactants)}}^\circ$$

$$= [\Delta H_{f(CO_2)}^\circ + 4\Delta H_{f(HCl)}^\circ] - [\Delta H_{f(CCl_4)}^\circ + 2\Delta H_{f(H_2O)}^\circ]$$

$$= [-94.1 + 4\times(-22.1)] - [-25.5 + 2\times(-57.8)]$$

$$= -94.1 - 88.4 + 25.5 + 115.6$$

$$= -182.5 + 141.1 = -41.4\text{ kcal}$$

Example 28. *The molar heat of formation of $NH_4NO_3(s)$ is -367.5 kJ and those of $N_2O(g)$ and $H_2O(l)$ are $+81.46$ kJ and -285.78 kJ respectively at 25° C and 1 atmospheric pressure. Calculate the ΔH and ΔE for the reaction,*

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$$

Solution: $\Delta H^\circ = \Delta H^\circ_{f\,(\text{products})} - \Delta H^\circ_{f\,(\text{reactants})}$

$$\begin{aligned} &= [\Delta H^\circ_{f\,(N_2O)} + 2\times\Delta H^\circ_{f\,(H_2O)}] - [\Delta H^\circ_{f\,(NH_4NO_3)}] \\ &= 81.46 + 2\times(-285.78) - (-367.5) \\ &= 81.46 - 571.56 + 367.5 \\ &= -122.56 \text{ kJ} \end{aligned}$$

We know that, $\Delta H = \Delta E + \Delta nRT$

or $\Delta E = \Delta H - \Delta nRT$

$\Delta n = 1;\ R = 8.314\times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1};\ T = 298\ \text{K}$

$$\begin{aligned} \Delta E &= -122.56 - (1)(8.314\times10^{-3})(298) \\ &= -122.56 - 2.477 \\ &= -125.037\ \text{kJ} \end{aligned}$$

7.13 ENTHALPY OF COMBUSTION OR HEAT OF COMBUSTION

Enthalpy of combustion is the amount of heat evolved or decrease in enthalpy when 1 mole of the substance (compound or element) is completely oxidised. The enthalpy of combustion, *i.e.*, ΔH is always negative. For example,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O; \quad \Delta H = -890.3\ \text{kJ}$$

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l); \quad \Delta H = -1367.4\ \text{kJ}$$

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l); \quad \Delta H = -745.6\ \text{kcal}$$

Since, 2 mole of C_2H_6 are involved, hence enthalpy of combustion of ethane

$$= -\frac{745.6}{2} = -372.8\ \text{kcal}$$

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\ \Delta H = -26.0\ \text{kcal}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -94.3\ \text{kcal}$$

The enthalpy of combustion of carbon is not –26.0 kcal as combustion is not complete because carbon monoxide can further be oxidised to carbon dioxide. The enthalpy of combustion of carbon is thus –94.3 kcal.

The enthalpies of combustion have a number of applications. Some of these are described below:

(i) Calorific values of foods and fuels: Energy is needed for the working of all machines. Even human body is no exception. Coal, petroleum, natural gas, etc., serve as the principal sources of energy for man-made machines, the food which we eat serves as a source of energy to our body. These substances undergo oxidation or combustion and release energy. These substances are, therefore, termed as fuels. An adult requires 2500 to 3000 kcal of energy per day. Since, the values of enthalpies of combustion of different food articles are known, it becomes easy to calculate our daily requirements and thus select the articles of food so as to secure a balanced diet.

The grading of food articles and various fuels can be done on the basis of the values of enthalpies of combustion.

The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energies per gram. It is known as calorific value. **The amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised.**

When methane burns, 890.3 kJ mol^{-1} of energy is released.

$$\underset{1\ \text{mole}\ (16\ \text{g})}{CH_4(g)} + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l),$$

$$\Delta H_{CH_4} = -890.3\ \text{kJ}$$

So, the calorific value of methane $= -\dfrac{890.3}{16} = -55.6\ \text{kJ/g}$

Calorific values of some important foodstuffs and fuels are given below:

Fuel	Calorific value (kJ/g)	Food	Calorific value (kJ/g)
Wood	17	Milk	3.1
Charcoal	33	Egg	6.7
Kerosine	48	Rice	16.7
Methane	55	Sugar	17.3
LPG	55	Butter	30.4
Hydrogen	150	Ghee	37.6

Out of the fuels listed, hydrogen has the highest calorific value. However, it is not used as domestic or industrial fuel due to some technical problems. Of the various constituents of our food, fats and carbohydrates serve as the main sources of energy. The calorific value of proteins is quite low.

(ii) Enthalpies of formation: Enthalpies of formation of various compounds, which are not directly obtained, can be calculated from the data of enthalpies of combustions easily by the application of Hess's law.

Heat of reaction = Σ Heat of combustion of reactants
− Σ Heat of combustion of products

SOME SOLVED EXAMPLES

Example 29. *The heats of combustion of CH_4 and C_4H_{10} are -890.3 kJ mol^{-1} and -2878.7 kJ mol^{-1} respectively. Which of the two has greater efficiency as fuel per gram?*

Solution: Molar mass of methane = 16

$$\text{Heat produced per gram of methane} = -\frac{890.3}{16} = -55.64\ \text{kJ}$$

Molar mass of butane = 58

$$\text{Heat produced per gram of butane} = -\frac{2878.7}{58} = -49.63\ \text{kJ}$$

Thus, methane has greater fuel efficiency than butane.

Example 30. *In a Gobar gas plant, gobar gas is formed by bacterial fermentation of animal refuse. It mainly contains methane and its heat of combustion is* $-809\ kJ\ mol^{-1}$ *according to following equation:*

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O;\ \Delta H = -809\ kJ\ mol^{-1}$$

How much gobar gas would have to be produced per day for a small village of 50 families, if it is assumed that each family requires 20,000 kJ of energy per day? The methane content in gobar gas is 80% by mass.

Solution: Energy consumption of 50 families per day

$$= 50 \times 20{,}000\ \text{kJ} = 1 \times 10^6\ \text{kJ}$$

809 kJ of energy is obtained by burning methane = 16 g

1×10^6 kJ of energy will be obtained by burning methane

$$= \frac{16}{809} \times 10^6 = 1.98 \times 10^4\ \text{g}$$

$$= 19.8\ \text{kg}$$

Since, methane content in gobar gas is 80% by mass, hence, the mass of gobar gas needed

$$= \frac{100}{80} \times 19.8 = 24.75\ \text{kg}$$

Example 31. *The standard molar heats of formation of ethane, carbon dioxide and liquid water are* −21.1, −94.1 *and* −68.3 *kcal respectively. Calculate the standard molar heat of combustion of ethane.*

Solution: The required chemical equation for combustion of ethane is

$$2C_2H_6(g) + 7O_2(g) = 4CO_2(g) + 6H_2O(l);\ \Delta H^\circ = ?$$

The equation involves 2 moles of C_2H_6; heat of combustion of ethane will be $= \dfrac{\Delta H^\circ}{2}$

$$\Delta H^\circ = \Delta H^\circ_{f\,(\text{products})} - \Delta H^\circ_{f\,(\text{reactants})}$$

$$= [4 \times \Delta H^\circ_{f\,(CO_2)} + 6\Delta H^\circ_{f\,(H_2O)}] - [2\Delta H^\circ_{f\,(C_2H_6)} + 7\Delta H^\circ_{f\,(O_2)}]$$

$$= [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 7 \times 0]$$

$$= -376.4 - 409.8 + 42.2$$

$$= -744.0\ \text{kcal}$$

$$\frac{\Delta H^\circ}{2} = \text{Heat of combustion of ethane} = -\frac{744.0}{2} = -372.0\ \text{kcal}$$

Example 32. *An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value per* cm^3 *of the mixture. Heats of formation and densities are as follows:*

$$H_{f\,(Al_2O_3)} = -399\ kcal\ mol^{-1};\ H_{f\,(Fe_2O_3)} = -199\ kcal\ mol^{-1}$$

$$Density\ of\ Fe_2O_3 = 5.2\ g/cm^3;\ Density\ of\ Al = 2.7\ g/cm^3$$

Solution: The required equation is:

$$2\text{Al} + \text{Fe}_2\text{O}_3 \longrightarrow \text{Al}_2\text{C}_3 + 2\text{Fe};\ \Delta H = ?$$

$$\Delta H = \Delta H_{f\,(\text{products})} - \Delta H_{f\,(\text{reactants})}$$

$$= [\Delta H_{f\,(\text{Al}_2\text{O}_3)} + 2\Delta H_{f\,(\text{Fe})}] - [2\Delta H_{f\,(\text{Al})} + \Delta H_{f\,(\text{Fe}_2\text{O}_3)}]$$

$$= (-399 + 2 \times 0) - [2 \times 0 + (-199)]$$

$$= -399 + 199 = -200\ \text{kcal}$$

At. mass of aluminium = 27, Mol. mass of Fe_2O_3 = 160

$$\text{Volume of reactants} = \frac{160}{5.2} + \frac{2 \times 27}{2.7} = 50.77\ \text{cm}^3$$

$$\text{Fuel value per cm}^3 = \frac{200}{50.77} = 3.92\ \text{kcal}$$

Example 33. *When 2 mole of* C_2H_6 *are completely burnt,* 3129 *kJ of heat is liberated. Calculate the heat of formation of* C_2H_6. ΔH_f *for* CO_2 *and* H_2O *are* −395 *kJ and* −286 *kJ respectively.*

Solution: The equation for the combustion of C_2H_6 is:

$$2\text{C}_2\text{H}_6 + 7\text{O}_2 \longrightarrow 4\text{CO}_2 + 6\text{H}_2\text{O};\ \Delta H = -3129\ \text{kJ}$$

$$\Delta H = \Delta H_{f\,(\text{products})} - \Delta H_{f\,(\text{reactants})}$$

$$= [4 \times \Delta H_{f\,(\text{CO}_2)} + 6 \times \Delta H_{f\,(\text{H}_2\text{O})}] - [2 \times \Delta H_{f\,(\text{C}_2\text{H}_6)} + 7\Delta H_{f\,(\text{O}_2)}]$$

$$-3129 = [4 \times (-395) + 6 \times (-286)] - [2 \times \Delta H_{f\,(\text{C}_2\text{H}_6)} + 7 \times 0]$$

or $$2 \times \Delta H_{f\,(\text{C}_2\text{H}_6)} = -167$$

So, $$\Delta H_{f\,(\text{C}_2\text{H}_6)} = -\frac{167}{2} = -83.5\ \text{kJ}$$

Example 34. *The standard heats of formation of* $CH_4(g)$, $CO_2(g)$ *and* $H_2O(g)$ *are* −76.2, −398.8 *and* −241.6 $kJ\ mol^{-1}$ *respectively. Calculate the amount of heat evolved by burning* $1\ m^3$ *of methane measured under normal conditions.* **(IIT 1990)**

Solution: The required equation for the combustion of methane is:

$$\text{CH}_4 + 2\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O};\ \Delta H = ?$$

$$\Delta H = \Delta H_{f\,(\text{products})} - \Delta H_{f\,(\text{reactants})}$$

$$= \Delta H_{f\,(\text{CO}_2)} + 2 \times \Delta H_{f\,(\text{H}_2\text{O})} - \Delta H_{f\,(\text{CH}_4)} - 2\Delta H_{f\,(\text{O}_2)}$$

$$= -398.8 - 2 \times 241.6 - (-76.2) - 2 \times 0$$

$$= -805.8\ \text{kJ mol}^{-1}$$

Heat evolved by burning 22.4 litre (1 mole) methane = −805.8 kJ. So, heat evolved by burning 1000 litre ($1\ \text{m}^3$) methane

$$= -\frac{805.8}{22.4} \times 1000 = -35973.2\ \text{kJ}$$

Example 35. *A gas mixture of* 3.67 *litre of ethylene and methane on complete combustion at* $25^\circ C$ *produces* 6.11 *litre of* CO_2. *Find out the heat evolved on burning* 1 *litre of the gas mixture. The heats of combustion of ethylene and methane are* −1423 *and* −891 $kJ\ mol^{-1}$ *at* $25^\circ C$. **(IIT 1991)**

Solution: $\underset{a\text{ litre}}{C_2H_4} + 3O_2 \longrightarrow \underset{2a\text{ litre}}{2CO_2} + 2H_2O$

$$\underset{(3.67-a)\text{ litre}}{CH_4} + 2O_2 \longrightarrow \underset{(3.67-a)\text{ litre}}{CO_2} + 2H_2O$$

Given, $2a + 3.67 - a = 6.11$

$$a = 2.44 \text{ litre}$$

$$\text{Volume of ethylene in mixture} = 2.44 \text{ litre}$$

$$\text{Volume of methane in mixture} = 1.23 \text{ litre}$$

$$\text{Volume of ethylene in 1 litre mixture} = \frac{2.44}{3.67} = 0.6649 \text{ litre}$$

$$\text{Volume of methane in 1 litre mixture} = \frac{1.23}{3.67} = 0.3351 \text{ litre}$$

24.45 litre of a gas at 25° C correspond to 1 mole.

Thus, heat evolved by burning 0.6649 litre of ethylene

$$= -\frac{1423}{24.5} \times 0.6649 = -38.69 \text{ kJ}$$

and heat evolved by burning 0.3351 litre of methane

$$= -\frac{891}{24.45} \times 0.3351 = -12.21 \text{ kJ}$$

So, total heat evolved by burning 1 litre of mixture

$$= -38.69 - 12.21$$

$$= -50.90 \text{ kJ}$$

7.14 ENTHALPY OF SOLUTION OR HEAT OF SOLUTION

The amount of heat evolved or absorbed when 1 mole solute is dissolved in excess of solvent (about 200 mole) is called **heat of solution.**

Some examples, of heat of solution are:

$$H_2SO_4(l) + aq. = H_2SO_4(aq.); \quad \Delta H = -20.2 \text{ kcal}$$

$$KCl(s) + aq. = KCl(aq.); \quad \Delta H = 4.4 \text{ kcal}$$

$$KOH(s) + aq. = KOH(aq.); \quad \Delta H = -13.3 \text{ kcal}$$

Heat of ideal solution is taken zero.

Generally, dissolution of substances in a solvent is a disintegration process. This process needs energy. In such cases, energy is absorbed, *i.e.*, ΔH is positive. But in some cases, besides the process of breaking or ionisation, there is hydrate formation. During hydration heat is evolved. The net result is that heat is either evolved or absorbed. There are also cases in which heat of separation of ions is just equal to the heat of hydration and there is very little heat effect as in the case of sodium chloride. The heat of solution of NaCl is very small as the heat of ionisation is nearly equal to the heat of hydration.

7.15 ENTHALPY OF NEUTRALISATION OR HEAT OF NEUTRALISATION

The heat of neutralisation (or enthalpy of neutralisation) is defined as the heat evolved or decrease in enthalpy when 1 gram equivalent of an acid is neutralised by 1 gram equivalent of a base in dilute solution. Some examples are:

Strong acid + Strong base = Salt + Water; $\Delta H = -13.7$ kcal

$$HNO_3(aq.) + NaOH(aq.) = NaNO_3(aq.) + H_2O(l); \quad \Delta H = -13.7 \text{ kcal}$$

$$HCl(aq.) + NaOH(aq.) = NaCl(aq.) + H_2O(l); \quad \Delta H = -13.75 \text{ kcal}$$

$$\frac{1}{2}H_2SO_4(aq.) + NaOH(aq.) = \frac{1}{2}Na_2SO_4(aq.) + H_2O(l); \quad \Delta H = -13.7 \text{ kcal}$$

It is observed that heat of neutralisation of a strong acid against a strong base is always nearly the same, *i.e.*, 13.7 kcal or 57 kJ, no matter what acid or base is employed. This constant value is explained with the help of theory of ionisation. Both acid and base are present in aqueous solution in the form of ions and when mixed, the following reaction occurs:

$$\underset{\text{Strong acid}}{H^+ + A^-} + \underset{\text{Strong base}}{B^+ + OH^-} = \underset{\text{Salt}}{B^+ + A^-} + H_2O; \ \Delta H = -13.7 \text{ kcal}$$

Cancelling the ions which are common on both the sides,

$$H^+ + OH^- = H_2O; \quad \Delta H = -13.7 \text{ kcal}$$

Thus, heat of neutralisation of a strong acid and a strong base is merely the heat of formation of water from H^+ and OH^- ions. This is the common reaction whenever a strong acid and a strong base are mixed and that is why the heat of neutralisation is same.

However, when a strong acid and a weak base or a weak acid and a strong base or a weak acid and a weak base are mixed in equivalent amount, the heat evolved or change in enthalpy is less than 13.7 kcal. This is shown in the following examples:

$$\underset{\text{Strong}}{HCl(aq.)} + \underset{\text{Weak}}{NH_4OH(aq.)} = NH_4Cl(aq.) + H_2O(l); \quad \Delta H = -12.3 \text{ kcal}$$

$$\underset{\text{Weak}}{HCN(aq.)} + \underset{\text{Strong}}{NaOH(aq.)} = NaCN(aq.) + H_2O(l); \quad \Delta H = -12.3 \text{ kcal}$$

$$\underset{\text{Weak}}{CH_3COOH(aq.)} + \underset{\text{Weak}}{NH_4OH(aq.)} = CH_3COONH_4(aq.) + H_2O(l); \quad \Delta H = -11.9 \text{ kcal}$$

The reason for the lower value is that part of the heat energy evolved is utilised in the complete ionisation of a weak acid or a weak base or both. Hence, the net heat of neutralisation is less than 13.7 kcal. The neutralisation of NH_4OH with HCl can be explained in the following way:

$$NH_4OH(aq.) = NH_4^+(aq.) + OH^-(aq.); \quad \Delta H = Q$$

and $NH_4^+(aq.) + Cl^-(aq.) + H^+(aq.) + OH^-(aq.) = NH_4^+(aq.) + Cl^-(aq.) + H_2O(l);$

$$\Delta H = -13.7 \text{ kcal}$$

or $NH_4OH(aq.) + H^+(aq.) + Cl^-(aq.) = NH_4^+(aq.) + Cl^-(aq.) + H_2O(l);$

$$\Delta H = -12.3 \text{ kcal}$$

So, $$Q - 13.7 = -12.3$$

or $$Q = 13.7 - 12.3 = 1.4 \text{ kcal}$$

Hence, 1.4 kcal of heat energy is absorbed for ionisation of NH_4OH which get subtracted from 13.7 kcal. Thus, the observed value of heat of neutralisation is not –13.7 kcal but –12.3 kcal.

Determination of Heat of Neutralisation

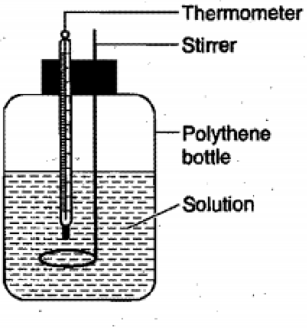


Fig. 7.16

The heat of neutralisation of an acid or base can be easily determined in the laboratory with the help of polythene or polystyrene bottle. Bottle is fitted with rubber cork through which a thermometer and a stirrer are fitted as shown in the Fig. 7.16. 100 mL each of acid and alkali of equal normality are taken in separate bottles. The temperature of each solution is regularly recorded. When constant temperature is attained, the alkali solution is added to the acid solution. The mixture is quickly stirred and the maximum temperature attained is noted.

Calculations:

Suppose, the initial temperature of acid and base $= T_1$

Final temperature of solution after mixing $= T_2$

Rise in temperature $= T_2 - T_1$

For the purpose of simplicity, the heat capacity of the bottle may be neglected as it is very small in comparison to that of solution. The specific heat capacity of the solution is assumed to be the same as that of water.

$$Q = \text{Heat change in reaction} = \text{Mass of solution} \times \text{sp. heat} \times (T_2 - T_1)$$

Q is the heat evolved by the neutralisation.

Therefore, the enthalpy of neutralisation $= \dfrac{Q}{100} \times 1000 \times \dfrac{1}{x}$

where, x = normality of the acid or base.

Example 36. *150 mL of 0.5 N nitric acid solution at 25.35° C was mixed with 150 mL of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be 28.77° C. Calculate the heat of neutralisation of nitric acid with sodium hydroxide.*

Solution: Total mass of solution = 150 + 150 = 300 g

$$Q = \text{Total heat produced} = 300 \times (28.77 - 25.35) \text{ cal}$$
$$= 300 \times 3.42 = 1026 \text{ cal}$$

$$\text{Heat of neutralisation} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5}$$
$$= \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68 \text{ kcal}$$

Since, heat is liberated, heat of neutralisation should be negative.

So, heat of neutralisation = – 13.68 kcal.

Example 37. *Whenever an acid is neutralised by a base, the net reaction is*

$$H^+(aq.) + OH^-(aq.) \longrightarrow H_2O(l); \quad \Delta H = -57.1 \, kJ$$

Calculate the heat evolved for the following experiments:

(i) *0.50 mole of HCl solution is neutralised by 0.50 mole of NaOH solution.*

(ii) *0.50 mole of HNO_3 solution is mixed with 0.30 mole of KOH solution.*

(iii) *100 mL of 0.2 M HCl is mixed with 100 mL of 0.3 M NaOH solution.*

(iv) *400 mL of 0.2 M H_2SO_4 is mixed with 600 mL of 0.1 M KOH solution.*

Solution: According to the reaction,

$$H^+(aq.) + OH^-(aq.) \longrightarrow H_2O(l); \quad \Delta H = -57.1 \text{ kJ}$$

when 1 mole of H^+ ions and 1 mole of OH^- ions are neutralised, 1 mole of water is formed and 57.1 kJ of energy is released.

(i) 0.50 mole HCl ≡ 0.50 mole H^+ ions

0.50 mole NaOH ≡ 0.50 mole OH^- ions

On mixing, 0.50 mole of water is formed.

Heat evolved for the formation of 0.50 mole of water

$$= 57.1 \times 0.5 = 28.55 \text{ kJ}$$

(ii) 0.50 mole HNO_3 ≡ 0.50 mole H^+ ions

0.30 mole KOH ≡ 0.30 mole OH^- ions

i.e., 0.30 mole of H^+ ions react with 0.30 mole of OH^- ions to form 0.30 mole of water molecules.

Heat evolved in the formation of 0.3 mole of water

$$= 57.1 \times 0.3 = 17.13 \text{ kJ}$$

(iii) 100 mL of 0.2 *M* HCl will give

$$\left(\frac{0.2}{1000} \times 100\right) = 0.02 \text{ mole of } H^+ \text{ ions}$$

and 100 mL of 0.3 *M* NaOH will give

$$\left(\frac{0.3}{1000} \times 100\right) = 0.03 \text{ mole of } OH^- \text{ ions}$$

i.e., 0.02 mole of H^+ ions react with 0.02 mole of OH^- ions to form 0.02 mole of water molecules.

Heat evolved in the formation of 0.02 mole of water

$$= 0.02 \times 57.1 = 1.142 \text{ kJ}$$

(iv) 400 mL of 0.2 *M* H_2SO_4 will give

$$\left(\frac{2 \times 0.2}{1000} \times 400\right) = 0.16 \text{ mole of } H^+ \text{ ions}$$

and 600 mL of 0.1 *M* KOH will give

$$\left(\frac{0.1}{1000}\times 600\right) = 0.06 \text{ mole of } OH^- \text{ ions}$$

i.e., 0.06 mole of H^+ ions react with 0.06 mole of OH^- ions to form 0.06 mole of water molecules.

Heat evolved in the formation of 0.06 mole of water

$$= 0.06 \times 57.1 = 3.426 \text{ kJ}$$

Example 38. *100 cm^3 of 0.5 N HCl solution at 299.95 K were mixed with 100 cm^3 0.5 N NaOH solution at 299.75 K in a thermos flask. The final temperature was found to be 302.65 K. Calculate the enthalpy of neutralisation of HCl. Water equivalent of thermos flask is 44 g.*

Solution: The initial average temperature of the acid and the base

$$= \frac{299.95 + 299.75}{2} = 299.85 \text{ K}$$

$$\text{Rise in temperature} = (302.65 - 299.85) = 2.80 \text{ K}$$

Heat evolved during neutralisation

$$= (100 + 100 + 44) \times 4.184 \times 2.8 = 2858.5 \text{ J}$$

$$\therefore \quad \text{Enthalpy of neutralisation} = -\frac{2858.5}{100} \times 1000 \times \frac{1}{0.50}$$

$$= -57.17 \text{ kJ}$$

Example 39. *When a student mixed 50 mL of 1 M HCl and 50 mL of 1 M NaOH in a coffee cup calorimeter, the temperature of the resultant solution increases from 21°C to 27.5°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the total volume of solution is 100 mL, its density 1 g mL^{-1} and that its specific heat is 4.18 J/g. Calculate :*

(*a*) *the heat change during mixing,*

(*b*) *the enthalpy change for the reaction,*

$$HCl(aq.) + NaOH(aq.) \longrightarrow NaCl(aq.) + H_2O(aq.)$$

Solution: (a) Number of moles of HCl and NaOH added

$$= \frac{MV}{1000} = \frac{1 \times 50}{1000} = 0.05$$

$$\text{Mass of mixture} = V \times d = 100 \times 1 = 100 \text{ g}$$

$$\text{Heat evolved, } q = ms\,\Delta T = 100 \times 4.18 \times (27.5 - 21.0)$$

$$= 100 \times 4.18 \times 6.5 \text{ J} = 2717 \text{ J} = 2.717 \text{ kJ}$$

(b) The involved reaction is:

$$\text{HCl}(aq.) + \text{NaOH}(aq.) \longrightarrow \text{NaCl}(aq.) + \text{H}_2\text{O}$$

$$\Delta H = \text{Heat evolved per mol}$$

$$= \frac{-2.717}{0.05} = -54.34 \text{ kJ}$$

Example 40. *The enthalpies of neutralisation of a strong acid HA and weaker acid HB by NaOH are −13.7 and −12.7 kcal/eq. When one equivalent of NaOH is added to a mixture containing 1 equivalent of HA and HB ; the enthalpy change was −13.5 kcal. In what ratio is the base distributed between HA and HB?*

Solution: Let x equivalent of HA and y equivalent of HB are taken in the mixture

$$x + y = 1 \qquad \ldots \text{(i)}$$

$$x \times 13.7 + y \times 12.7 = 13.5 \qquad \ldots \text{(ii)}$$

Solving eqs. (i) and (ii), we get

$$x = 0.8,\ y = 0.2$$

$$x : y = 4 : 1$$

7.16 ENTHALPIES OF PHYSICAL CHANGES (Phase Changes)

Heat energy is involved whenever a physical state of a substance is changed. Some important enthalpies of physical changes are defined below:

(i) Enthalpy of fusion: It is the enthalpy change in converting 1 mole of the substance from solid state to liquid state at its melting point. The enthalpy of fusion equals latent heat of fusion per gram multiplied by the molecular mass. The value of enthalpy of fusion gives an idea about the strength of the intermolecular forces operating in a solid. The values of enthalpies of fusion for ionic solids are much more than molecular solids in which molecules are held together by weak van der Waals' forces.

$$H_2O(s) \xrightarrow{\text{Melting}} H_2O(l); \qquad \Delta H = 1.44 \text{ kcal}$$

$$H_2O(l) \xrightarrow{\text{Freezing}} H_2O(s); \qquad \Delta H_{(\text{freezing})} = -1.44 \text{ kcal}$$

(ii) Enthalpy of vaporization: It is the enthalpy change in converting 1 mole of the substance from liquid state to gaseous state (or vapour state) at its boiling point.

$$H_2O(l) \xrightarrow{\text{Boiling}} H_2O(g); \qquad \Delta H = 10.5 \text{ kcal}$$

$$H_2O(g) \xrightarrow{\text{Condensation}} H_2O(l); \qquad \Delta H_{(\text{condensation})} = -10.5 \text{ kcal}$$

Enthalpy of vaporization of a liquid gives an idea about the strength of intermolecular forces operating between the molecules of the liquid.

(iii) Enthalpy of sublimation: Sublimation is the process in which a solid on heating is directly converted into vapour state. It is the heat change in converting 1 mole of a solid directly into its vapour at a given temperature below its melting point.

$$I_2(s) \longrightarrow I_2(g); \qquad \Delta H = 14.9 \text{ kcal}$$

The enthalpy of sublimation of a solid is equal to the sum of enthalpy of fusion and enthalpy of vaporization.

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

7.17 HESS'S LAW (The Law of Constant Heat Summation)

This law was presented by **Hess** in 1840. According to this law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, *i.e.*, the total enthalpy change is independent of intermediate steps involved in the change. The enthalpy change of a chemical reaction depends on the initial and final stages only. Let a substance A be changed in three steps to D with enthalpy change from A to

B ΔH_1 calorie, from B to C ΔH_2 calorie and from C to D ΔH_3 calorie. Total enthalpy change from A to D will be equal to the sum of enthalpies involved in various steps.

Total enthalpy change

$$\Delta H_{\text{steps}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Now if D is directly converted into A, let the enthalpy change be ΔH_{direct}. According to Hess's law $\Delta H_{\text{steps}} + \Delta H_{\text{direct}} = 0$, *i.e.*, ΔH_{steps} must be equal to ΔH_{direct} numerically but with opposite sign. In case it is not so, say ΔH_{steps} (which is negative) is more than ΔH_{direct} (which is positive), then in one cycle, some energy will be created which is not possible on the basis of first law of thermodynamics. Thus, ΔH_{steps} must be equal to ΔH_{direct} numerically.

Hess's law can also be verified experimentally with the help of following examples:

(i) Formation of carbon dioxide from carbon:

First method: Carbon is directly converted into $CO_2(g)$.

$$C(s) + O_2(g) = CO_2(g); \quad \Delta H = -94.0 \text{ kcal}$$

Second method: Carbon is first converted into $CO(g)$ and then $CO(g)$ into $CO_2(g)$, *i.e.*, conversion has been carried in two steps:

$$C(s) + \frac{1}{2}O_2 = CO(g); \qquad \Delta H = -26.0 \text{ kcal}$$

$$CO(g) + \frac{1}{2}O_2 = CO_2(g); \qquad \Delta H = -68.0 \text{ kcal}$$

Total enthalpy change $C(s)$ to $CO_2(g)$; $\quad \Delta H = -94.0$ kcal

(ii) Formation of ammonium chloride from ammonia and hydrochloric acid:

First method:

$$\begin{array}{rl} NH_3(g) + HCl(g) = NH_4Cl(g); & \Delta H = -42.2 \text{ kcal} \\ NH_4Cl(g) + aq. = NH_4Cl(aq.); & \Delta H = +4.0 \text{ kcal} \\ \hline NH_3(g) + HCl(g) + aq. = NH_4Cl(aq.); & \Delta H = -38.2 \text{ kcal} \end{array}$$

Second method:

$$\begin{array}{rl} NH_3(g) + aq. = NH_3(aq.); & \Delta H = -8.4 \text{ kcal} \\ HCl(g) + aq. = HCl(aq.); & \Delta H = -17.3 \text{ kcal} \\ NH_3(aq.) + HCl(aq.) = NH_4Cl(aq.); & \Delta H = -12.3 \text{ kcal} \\ \hline NH_3(g) + HCl(g) + aq. = NH_4Cl(aq.); & \Delta H = -38.0 \text{ kcal} \end{array}$$

Conclusions

(i) The heat of formation of compounds is independent of the manner of its formation.

(ii) The heat of reaction is independent of the time consumed in the process.

(iii) The heat of reaction depends on the sum of enthalpies of products minus sum of the enthalpies of reactants.

(iv) Thermochemical equations can be added, subtracted or multiplied like algebraic equations.

Applications of Hess's Law

(i) For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.

(ii) For the determination of enthalpies of extremely slow reactions.

(iii) For the determination of enthalpies of transformation of one allotropic form into another.

(iv) For the determination of bond energies.

$$\Delta H_{\text{reaction}} = \Sigma \text{ Bond energies of reactants} - \Sigma \text{ Bond energies of products}$$

(v) For the determination of resonance energy.

(vi) For the determination of lattice energy.

Thermochemical calculations: For making thermochemical calculations, the following points are kept in mind:

(i) Write down the required thermochemical equation. For example, if heat of formation of methane is to be determined, write down the following equation:

$$C(s) + 2H_2(g) = CH_4(g); \ \Delta H = ?$$

(ii) Try to obtain the required equation from the given data. This can be done in two ways:

(a) By adding, subtracting and multiplying the various given thermochemical equations. Or

(b) Heat of reaction = Total enthalpies of products − Total enthalpies of reactants

Note: In case of calculation of heat of formation, the enthalpies of free elements can be arbitrarily fixed as zero at 25° C and 1 atmospheric pressure.

Example 41. *Calculate the standard heat of formation of carbon disulphide (l). Given that the standard heats of combustion of carbon (s), sulphur (s) and carbon disulphide (l) are* –393.3, 293.7 *and* –1108.76 *kJ mol* $^{-1}$ *respectively.*

Solution: Required equation is

$$C(s) + 2S(s) \longrightarrow CS_2(l); \ \Delta H_f = ?$$

Given,

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad (\Delta H = -393.3 \text{ kJ}) \quad ...(i)$$

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad (\Delta H = -293.72 \text{ kJ}) \quad ...(ii)$$

$$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \quad ...(iii)$$
$$(\Delta H = -1108.76 \text{ kJ})$$

First method: Multiply the eq. (ii) by 2.

$$2S(s) + 2O_2(g) \longrightarrow 2SO_2(g) \quad ...(iv) \quad (\Delta H = -587.44 \text{ kJ})$$

Adding eqs. (i) and (iv) and subtracting eq. (iii),

$$[C(s) + 2S(s) + 3O_2(g) - CS_2(l) - 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) - CO_2 - 2SO_2]$$

$$C(s) + 2S(s) \longrightarrow CS_2(l)$$

This is the required equation.

Thus, $\Delta H_f = -393.3 - 587.44 + 1108.76 = 128.02$ kJ

Standard heat of formation of $CS_2(l) = 128.02$ kJ

Second method:

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad (\Delta H = -393.3 \text{ kJ}) \quad \ldots(i)$$

$$S(s) + O_2(g) \longrightarrow SO_2(g); \quad (\Delta H = -293.72 \text{ kJ}) \quad \ldots(ii)$$

$$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g);$$
$$(\Delta H = -1108.76 \text{ kJ}) \quad \ldots(iii)$$

From eqs. (i) and (ii),

Enthalpy of $CO_2 = -393.3$ kJ

Enthalpy of $SO_2 = -293.72$ kJ

$$\text{Enthalpy of } O_2 = 0 \qquad \text{(By convention)}$$

ΔH of eq. (iii) = Enthalpies of products − Enthalpies of reactants

$$-1108.76 = -393.3 + 2 \times (-293.72) - \Delta H_{CS_2(l)}$$
$$\Delta H_{CS_2(l)} = (1108.76 - 980.74) = 128.02 \text{ kJ}$$
$$\text{Enthalpy of } CS_2(l) = 128.02 \text{ kJ}$$

Example 42. *Calculate the heat of formation of acetic acid from the following data:*

$$CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \quad ...(i) \quad (\Delta H = -207.9 \; kcal)$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad (\Delta H = -94.48 \; kcal) \quad ...(ii)$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad (\Delta H = -68.4 \; kcal) \quad ...(iii)$$

Solution: First method: The required equation is

$$2C(s) + 2H_2(g) + O_2(g) = CH_3COOH(l); \qquad \Delta H = ?$$

This equation can be obtained by multiplying eq. (ii) by 2 and also eq. (iii) by 2 and adding both and finally subtracting eq. (i).

$$[2C + 2O_2 + 2H_2 + O_2 - CH_3COOH(l) - 2O_2 \longrightarrow 2CO_2 + 2H_2O - 2CO_2 - 2H_2O]$$
$$\Delta H_{CH_3COOH(l)} = 2 \times (-94.48) + 2 \times (-68.4) - (-207.9)$$
$$= -188.96 - 136.8 + 207.9$$
$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

Second method: From eqs. (ii) and (iii)

$$\text{Enthalpy of } CO_2 = -94.48 \text{ kcal}$$
$$\text{Enthalpy of } H_2O = -68.4 \text{ kcal}$$
$$\text{Enthalpy of } O_2 = 0 \text{ (by convention)}$$

ΔH of eq. (i) = Enthalpies of products − Enthalpies of reactants

$$-207.9 = 2 \times (-94.48) + 2(-68.4) - \Delta H_{CH_3COOH(l)}$$
$$\Delta H_{CH_3COOH(l)} = -188.96 - 136.8 + 207.9$$
$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

Example 43. *Given the following standard heats of reactions :*

(a) heat of formation of water = − 68.3 kcal, (b) heat of combustion of $C_2H_2 = -310.6$ kcal and (c) heat of combustion of ethylene = − 337.2 kcal. Calculate the heat of the reaction for the hydrogenation of acetylene at constant volume and at 25° C.

Solution: The required equation is

$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g); \qquad \Delta H = ?$$

Given,

(a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ ...(i) $(\Delta H = -68.3 \text{ kcal})$

(b) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$ ...(ii) $(\Delta H = -310.6 \text{ kcal})$

(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ ...(iii) $(\Delta H = -337.2 \text{ kcal})$

The required equation can be achieved by adding eqs. (i) and (ii) and subtracting (iii).

$$C_2H_2(g) + H_2(g) + 3O_2(g) - C_2H_4(g) - 3O_2(g) \longrightarrow 2CO_2 + 2H_2O(l) - 2CO_2(g) - 2H_2O(l)$$

or $C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$

$$\Delta H = -68.3 - 310.6 - (-337.2) = -378.9 + 337.2 = -41.7 \text{ kcal}$$

We know that,

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

or

$$\Delta E = \Delta H - \Delta nRT$$

$$\Delta n = (1 - 2) = -1, R = 2 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1}$$

and

$$T = (25 + 273) = 298 \text{ K}$$

Substituting the values in above equation,

$$\Delta E = -41.7 - (-1)(2 \times 10^{-3})(298)$$
$$= -41.7 + 0.596 = -41.104 \text{ kcal}$$

Example 44. *Determine the heat of transformation of $C_{(diamond)} \rightarrow C_{(graphite)}$ from the following data:*

$$C_{(diamond)} + O_2(g) \longrightarrow CO_2(g) \quad ...(i) \quad (\Delta H = -94.5 \; kcal)$$
$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g) \quad ...(ii) \quad (\Delta H = -94.0 \; kcal)$$

Solution: Subtracting eq. (ii) from (i), the required equation is obtained.

$$\Delta H_{\text{transformation}} = -94.5 - (-94.0)$$
$$= -94.5 + 94.0 = -0.5 \text{ kcal}$$

Example 45. *Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gases under pressure in the presence of a catalyst. The reaction is*

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l).$$

Determine the enthalpy of this reaction by an appropriate combination of the following data:

$$C_{(graphite)} + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad ...(i) \quad (\Delta H = -110.5 \; kJ \; mol^{-1})$$
$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g) \quad ...(ii) \quad (\Delta H = -393.5 \; kJ \; mol^{-1})$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad ...(iii) \quad (\Delta H = -285.9 \; kJ \; mol^{-1})$$
$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad ...(iv) \quad (\Delta H = -726.6 \; kJ \; mol^{-1})$$

Solution: The required equation can be obtained in the following manner:

$$-\text{eq. (i)} + 2\,\text{eq. (iii)} + \text{eq. (ii)} - \text{eq. (iv)} = CO_2(g) + 2H_2(g) \longrightarrow CH_3OH(g)$$

So, $\Delta H = 110.5 - 571.8 - 393.5 + 726.6 = -128.2 \text{ kJ mol}^{-1}$

Example 46. *How much heat will be required to make 2 kg of calcium carbide (CaC_2) according to the following reaction?*

$$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g)$$

The heats of formation of $CaO(s)$, $CaC_2(s)$ and $CO(g)$ are -151.6, -14.2 *and* -26.4 *kcal respectively.*

Solution: $\Delta H = \Sigma \Delta H^\circ_{f\,(\text{products})} - \Sigma \Delta H^\circ_{f\,(\text{reactants})}$

$$= [\Delta H^\circ_{f\,(\mathrm{CaC_2})} + \Delta H^\circ_{f\,(\mathrm{CO})}] - [\Delta H^\circ_{f\,(\mathrm{CaO})} + 3\Delta H^\circ_{f\,(\mathrm{C})}]$$

$$= [-14.2 - 26.4] - [-151.6 + 3 \times 0]$$

$$= -40.6 + 151.6 = 111.0 \text{ kcal}$$

For formation of 64 g of CaC_2 111.0 kcal of heat is required.

So, heat required for making 2000 g of

$$\mathrm{CaC_2} = \frac{111.0}{64} \times 2000 = 3468.75 \text{ kcal}$$

7.18 INFLUENCE OF TEMPERATURE ON THE HEAT OF REACTION OR KIRCHHOFF'S EQUATION

Let us consider a reaction occurring at constant pressure. Heat of reaction at constant pressure may be given as:

$$\Delta H = H_P - H_R$$

Differentiating the above equation with respect to 'T' at constant pressure, we get:

$$\left(\frac{d\Delta H}{dT}\right)_P = \left(\frac{dH_P}{dT}\right)_P - \left(\frac{dH_R}{dT}\right)_P$$

$$= (C_P)_P - (C_P)_R = \Delta C_P$$

or $$d(\Delta H) = \Delta C_P \, dT$$

Integrating above differential equation within proper limit, we get:

$$\int_{T_1}^{T_2} d\Delta H = \Delta C_P \int_{T_1}^{T_2} dT$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_P (T_2 - T_1)$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$$

Above equation is **Kirchhoff's equation.** It is used to calculate heat of reaction at a temperature provided it is known at another temperature.

Change in heat of reaction due to per degree change in temperature is equivalent to heat capacity difference between reactant and product.

Kirchhoff's equation at constant volume may be given as:

$$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_V$$

7.19 BOND ENERGY OR BOND ENTHALPIES

When a bond is formed between atoms, energy is released. Obviously same amount of energy will be required to break the bond. The energy required to break the bond is termed bond dissociation energy. The more precise definition is:

The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, *i.e.*, to separate the atoms in the gaseous state under 1 atmospheric pressure and the specified temperature is called bond dissociation energy. For example,

$$\mathrm{H{-}H}(g) \longrightarrow 2\mathrm{H}(g); \qquad \Delta H = +433 \text{ kJ mol}^{-1}$$

$$\mathrm{Cl{-}Cl}(g) \longrightarrow 2\mathrm{Cl}(g); \qquad \Delta H = +242.5 \text{ kJ mol}^{-1}$$

$$\mathrm{H{-}Cl}(g) \longrightarrow \mathrm{H}(g) + \mathrm{Cl}(g); \qquad \Delta H = +431 \text{ kJ mol}^{-1}$$

$$\mathrm{I{-}I}(g) \longrightarrow 2\mathrm{I}(g); \qquad \Delta H = +15.1 \text{ kJ mol}^{-1}$$

$$\mathrm{H{-}I}(g) \longrightarrow \mathrm{H}(g) + \mathrm{I}(g); \qquad \Delta H = +299 \text{ kJ mol}^{-1}$$

The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present. When a molecule of a compound contains more than one bond of the same kind, the average value of the dissociation energies of a given bond is taken. **This average bond dissociation energy required to break each bond in a compound is called bond energy.***

Consider the dissociation of water molecule which consists of two O—H bonds. The dissociation occurs in two stages.

$$\mathrm{H_2O}(g) \longrightarrow \mathrm{H}(g) + \mathrm{OH}(g); \qquad \Delta H = 497.8 \text{ kJ mol}^{-1}$$

$$\mathrm{OH}(g) \longrightarrow \mathrm{H}(g) + \mathrm{O}(g); \qquad \Delta H = 428.5 \text{ kJ mol}^{-1}$$

The average of these two bonds dissociation energies gives the value of bond energy of O—H.

$$\text{Bond energy of O—H bond} = \frac{497.8 + 428.5}{2} = 463.15 \text{ kJ mol}^{-1}$$

Similarly, the bond energy of N—H bond in NH_3 is equal to one-third of the energy of dissociation of NH_3 and those of C—H bond in CH_4 is equal to one-fourth of the energy of dissociation of CH_4.

$$\text{Bond energy C—H} = \frac{1664}{4} = 416 \text{ kJ mol}^{-1}$$

$$[\mathrm{CH_4}(g) \longrightarrow \mathrm{C}(g) + 4\mathrm{H}(g);\ \Delta H = 1664 \text{ kJ mol}^{-1}]$$

Application of Bond Energy

1. Heat of a reaction = Σ Bond energy of reactants − Σ Bond energy of products

Note: In case of atomic species, bond energy is replaced by heat of atomization.

2. Determination of resonance energy: When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

Resonance energy = Experimental or actual heat of formation − Calculated heat of formation.

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*Bond energy is also called, the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.

$$\mathrm{H}(g) + \mathrm{Cl}(g) \rightarrow \mathrm{H{-}Cl}(g); \qquad \Delta H = -431 \text{ kJ mol}^{-1}$$

Bond energy of H—Cl = − (enthalpy of formation) = − (− 431) = + 431 kJ mol^{-1}

	Steps involved	Energy change
(a)	Solid sodium changes into gaseous sodium. Energy is absorbed. It is sublimation energy. $Na(s) + \text{sublimation energy} \longrightarrow Na(g)$	$+\Delta H_{sub}$
(b)	Gaseous sodium atoms change into gaseous sodium ions. In this step, energy equivalent to ionisation potential is absorbed. $Na(g) + IP \longrightarrow Na^+(g) + e$	$+IP$
(c)	Half mole of molecular chlorine dissociate into one mole of gaseous atomic chlorine. In this step, energy equivalent to one half of the dissociation energy is absorbed. $\frac{1}{2}Cl_2(g) + \frac{1}{2}D = Cl(g)$	$+\frac{1}{2}D$
(d)	Gaseous chlorine atoms change into chloride ions by acceptance of electrons. In this process, energy equivalent to electron affinity is released. $Cl(g) + e \longrightarrow Cl^-(g) + EA$	$-EA$
(e)	Sodium and chlorine ions are held together by electrostatic forces to form Na^+Cl^-. The energy equivalent to lattice energy is released.	U

Total energies involved in the above five steps

$$= \Delta H_{sub} + \frac{1}{2}D + IP - EA + U$$

Thus, according to Hess's law

$$-Q = \Delta H_{sub} + \frac{1}{2}D + IP - EA + U$$

Example 57. *Calculate the lattice energy for the reaction,*

$$Li^+(g) + Cl^-(g) \rightarrow LiCl(s)$$

from the following data:

$$\Delta H_{sub(Li)} = 160.67\, kJ\ mol^{-1};\ \frac{1}{2}D(Cl_2) = 122.17\, kJ\ mol^{-1}$$

$$IP(Li) = 520.07\, kJ\ mol^{-1};\ EA(Cl) = -365.26\, kJ\ mol^{-1}$$

and $$\Delta H_f^\circ(LiCl) = -401.66\, kJ\ mol^{-1}.$$

Solution: Applying the equation

$$-Q = \Delta H + \tfrac{1}{2}D + IP - EA + U$$

and substituting the respective values,

$$-401.66 = 160.67 + 122.17 + 520.07 - 365.26 + U$$

$$U = -839.31\, \text{kJ mol}^{-1}$$

Example 58. *When a mole of crystalline sodium chloride is prepared, 410 kJ of heat is produced. The heat of sublimation of sodium metal is 180.8 kJ. The heat of dissociation of chlorine gas into atoms is 242.7 kJ. The ionisation energy of Na and electron affinity of Cl are 493.7 kJ and −368.2 kJ respectively. Calculate the lattice energy of NaCl.*

Solution: Applying the equation

$$-Q = \Delta H_{sub} + \frac{1}{2}D + IP - EA + U$$

and substituting the respective values,

$$-410 = 108.8 + \frac{1}{2} \times 242.7 + 493.7 - 368.2 + U$$

$$U = -765.65\, \text{kJ mol}^{-1}$$

7.21 EXPERIMENTAL DETERMINATION OF THE HEAT OF REACTION

The heat evolved or absorbed in a chemical reaction is measured by carrying out the reaction in an apparatus called **calorimeter.** The principle of measurement is that heat given out is equal to heat taken, *i.e.*,

$$Q = (W + m) \times s \times (T_2 - T_1),$$

where, Q is the heat of the reaction (given out), W is the water equivalent of the calorimeter and m is the mass of liquid in the calorimeter and s its specific heat, T_2 is the final temperature and T_1 the initial temperature of the system. Different types of calorimeters are used but two of the common types are:

(i) Water calorimeter and

(ii) Bomb calorimeter

(i) Water calorimeter

It is a simple form of a calorimeter which can be conveniently used in the laboratory. It is shown in Fig. 7.18.

It consists of a large vessel A in which a calorimeter B is held on corks. In between the calorimeter and the vessel, there is a packing of an insulating material such as cotton wool. Inside the calorimeter there are holes through which a thermometer, a stirrer and the boiling tube containing reacting substances are fitted. A known amount of water is taken in the calorimeter. Known amounts of reacting substances are taken in the boiling tube. The heat evolved during the reaction will be absorbed by the water. The rise in temperature is recorded with the help of thermometer. The heat evolved is then calculated from the formula

$$(W + m) \times s \times (T_2 - T_1)$$

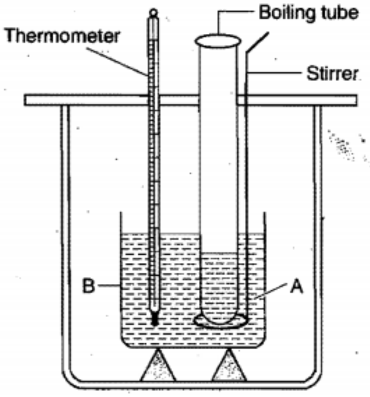


Fig. 7.18

(ii) Bomb calorimeter

This is commonly used to find the heat of combustion of organic substances. It consists of a sealed combustion chamber, called a bomb. A weighed quantity of the substance in a dish along with oxygen under about 20 atmospheric pressure is placed in the bomb which is lowered in water contained in an insulated copper vessel. The vessel is fitted with a stirrer and a sensitive thermometer. The arrangement is shown in Fig. 7.19.

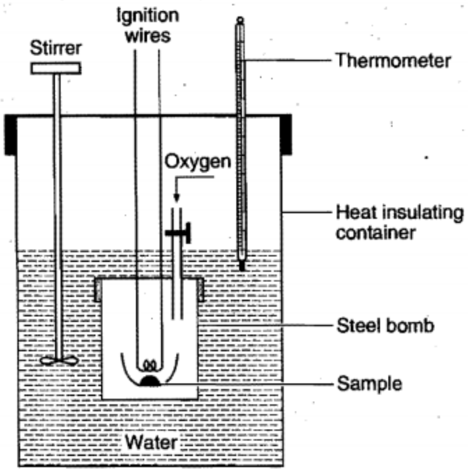


Fig. 7.19

The temperature of the water is noted and the substance is ignited by an electric current. After combustion, the rise in temperature of the system is noted. The heat of combustion can be calculated from the heat gained by water and calorimeter.

Since, the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE.

$$\Delta E = \frac{(W+m)(T_2 - T_1)\times s}{w_1} \times M \text{ kcal}$$

Where, M is the molecular mass of the substance and w_1 is the mass of substance taken.

ΔH can be calculated from the relation,

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

Example 59. *0.5 g of benzoic acid was subjected to combustion in a bomb calorimeter at 15°C when the temperature of the calorimeter system (including water) was found to rise by 0.55°C. Calculate the heat of combustion of benzoic acid (i) at constant volume and (ii) at constant pressure. The thermal capacity of the calorimeter including water was found to be 23.85 kJ.*

Solution: (i) Heat of combustion at constant volume, ΔE

= Heat capacity of calorimeter and its contents

$$\times \text{ rise in temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 23.85 \times 0.55 \times \frac{122}{0.5} = 3200.67 \text{ kJ}$$

i.e., $\Delta E = -3200.67 \text{ kJ mol}$

(ii) We know that, $\Delta H = \Delta E + \Delta nRT$

$$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l)$$

$\Delta n = 7 - 7.5 = -0.5$; $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}; $T = 288$ K

Substituting the values in the above equation,

$$\Delta H = -3200.67 + 8.314 \times 10^{-3} \times (-0.5) \times 288$$

$$= -3200.67 - 1.197 = -3201.867 \text{ kJ mol}^{-1}$$

Example 60. *A sample of 0.16 g CH_4 was subjected to combustion at 27° C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5° C. Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} and $R = 8.314\, J\, K^{-1}\, mol^{-1}$.* **(IIT 1998)**

Solution: (i) Heat of combustion at constant volume, ΔE = Heat capacity of calorimeter system × rise in temperature

$$\times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

i.e., $\Delta E = -885 \text{ kJ mol}^{-1}$

(ii) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta n = 1 - 3 = -2$, $T = 300$ K, $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}

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

$$= -885 + (-2) \times 8.314 \times 10^{-3} \times 300$$

$$= -885 - 4.988 = -889.988 \text{ kJ mol}^{-1}$$

Example 61. *The heat of combustion of ethane gas is −368 kcal/mol. Assuming that 60% of heat is useful, how many m^3 of ethane measured at NTP must be burned to supply heat to convert 50 kg of water at 10° C to steam at 100° C?*

Solution: Heat required per gram of water

$$= (90 + 540) \text{ cal} = 630 \text{ cal}$$

Total heat needed for 50 kg of water

$$= 50 \times 10^3 \times 630 \text{ cal}$$

As the efficiency is 60%, the actual amount of heat required

$$= \frac{50 \times 10^3 \times 630}{60} \times 100 = 52500 \text{ kcal}$$

No. of mole of ethane required to produce 52500 kcal

$$= \frac{52500}{368} = 142.663 \text{ mole}$$

Volume of 142.663 mole at NTP = 142.663 × 22.4

$$= 3195.65 \text{ litre} = 3.195 \text{ m}^3$$

7.22 LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

The essence of first law of thermodynamics is that all physical and chemical processes occur in such a way that the total energy of the system and surroundings is constant. The law correlates the various forms of energy, *i.e.*, their interconversion into one another in exactly equivalent amounts. The law has stood the test of time as no transformation has violated the principle of conservation of energy. However, the first law of thermodynamics has a number of limitations.

1. The law does not give any information about the direction in which flow of energy takes place. For example, if two systems *A* and *B* which are capable of exchanging heat are brought in contact with each other, the first law of thermodynamics will only tell us that one system loses energy and other system gains the same amount of energy. But the law fails to tell whether the heat will flow from system *A* to *B* or from system *B* to *A*. In order to predict the direction of the flow of heat, one more parameter, *i.e.*, temperature is required. The heat actually flows from a system which has higher temperature. The process continues till both the systems attain the same temperature. The law fails to answer why heat energy does not flow from cold system to hot system though the energy is conserved in this way also.
2. The law does not explain why the chemical reactions do not proceed to completion.
3. The law does not explain why natural spontaneous processes are irreversible.
4. The law does not contradict the existence of self-acting refrigerator.
5. The law does not contradict the existence of 100% efficient engine.
6. The difference between spontaneous and non-spontaneous processes is insignificant in view of the first law.

The answers to above limitations are provided by second law of thermodynamics. However, before we study this law, let us understand the terms **spontaneous, entropy** and **free energy.**

7.23 SPONTANEOUS AND NON-SPONTANEOUS PROCESSES

One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a reaction will occur when reactants are brought together under a special set of conditions (for example, at a certain temperature, pressure and concentration). A reaction that occurs under the given set of conditions is called a **spontaneous reaction.** If a reaction does not occur under specified conditions, it is said to be **non-spontaneous.**

The term spontaneity means the feasibility of a process. In nature, we observe many processes which occur of their own. For example, water flows down the hill without the help of any external agency, heat flows from a conductor at high temperature to another at low temperature, electricity flows from high potential to low potential. There are processes which require some initiation before they can proceed. But once initiated, they proceed by themselves. The burning of carbon, burning of fuels and petrol, etc., require some initiation. These processes are termed as spontaneous on account of their feasibility, *i.e.*, these can occur without the help of external work.

A process which has an urge or a natural tendency to occur either of its own or after proper initiation under the given set of conditions is known as spontaneous process.

Spontaneous process does not mean that it takes place **instantaneously.** It simply implies that the process has an urge to take place and is practically feasible. The actual speed of the process may vary from very low to extremely fast. The rusting of iron is a slow spontaneous process while the neutralisation reaction between an acid and an alkali is a fast spontaneous process. It is a matter of experience also that all natural processes are spontaneous and are **irreversible,** *i.e.*, move in one direction only. The reverse process which can be termed as non-spontaneous can be made to occur only by supplying external energy. For example, water can be made to flow upward by the use of some external agency or energy is always required to lift the ball from the ground. The natural (spontaneous) processes follow a non-equilibrium path and as such are irreversible but these processes proceed up to establishment of equilibrium. At equilibrium state, the process stops to occur any further. Heat flows from a hotter body to a colder body till the temperature of both bodies becomes equal; there is no further flow of heat and we say that the system has attained equilibrium. Some of the familiar examples of spontaneous processes are listed below:

(a) Spontaneous processes where no initiation is required

(i) Dissolution of sugar or salt in water

Sugar + water ⟶ Aqueous solution of sugar

Salt + water ⟶ Aqueous solution of salt

(ii) Evaporation of water from water reservoirs such as ponds, lakes, rivers, sea, open vessels, etc.

$$H_2O(l) \longrightarrow H_2O(g)$$

(iii) Flow of heat from a hot body to a cold body.

(iv) Mixing of different gases.

(v) Flow of water down a hill.

(vi) Reaction between $H_2(g)$ and $I_2(g)$ to form HI(*g*).

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

(vii) Reaction between nitric oxide gas and oxygen to form nitrogen dioxide.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

(viii) Melting of ice into water.

$$H_2O(s) \longrightarrow H_2O(l)$$

(ix) A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq.) + H_2(g)$$

(x) When a zinc rod is dipped in an aqueous solution of copper sulphate, copper is precipitated.

$$CuSO_4(aq.) + Zn(s) \longrightarrow ZnSO_4(aq.) + Cu(s)$$

(b) Spontaneous processes where initiation is required

(i) Reaction between H_2 and O_2: This reaction is initiated by passing electric spark through the mixture.

$$2H_2(g) + O_2(g) \xrightarrow[\text{spark}]{\text{Electric}} 2H_2O(l)$$

(ii) Coal burns in oxygen or air when ignited. Coal keeps on burning once initiated.

$$C(s) + O_2(g) \xrightarrow{\text{Ignition}} CO_2(g)$$

(iii) Methane burns with oxygen when ignited.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

(iv) A candle made up of wax burns only when ignited.

(v) Calcium carbonate evolves carbon dioxide upon heating.

$$CaCO_3(s) \xrightarrow{\text{Heat}} CaO(s) + CO_2(g)$$

A process which can neither occur by itself nor by initiation is called a non-spontaneous process.

Or

A process which has no natural tendency or urge to occur is said to be a non-spontaneous process.

Few examples of non-spontaneous processes are:

(i) Flow of heat from a cold body to a hot body.

(ii) Dissolution of gold or silver in water.

(iii) Flow of water from ground to overhead tank.

(iv) Hydrolysis of sodium chloride.

(v) Decomposition of water into hydrogen and oxygen.

(vi) Diffusion of gas from a low pressure to a high pressure.

It is not always true that non-spontaneous processes do not occur at all. Many of the non-spontaneous processes or changes can be made to take place when energy from some external source is supplied continuously throughout the change. (However, the processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the opposite direction). For example, the decomposition of water into hydrogen and oxygen (non-spontaneous process) can occur when electrical energy is supplied to water. The process stops when the passage of electrical energy is stopped.

Driving force for a spontaneous process: After having learnt about spontaneous processes, a very obvious question arises in our minds that why some processes are spontaneous? Obviously there must be some kind of driving force which is responsible for driving the process or a reaction in a particular direction.

The force which is responsible for the spontaneity of a process is called the driving force.

Let us now discuss the nature of the driving force.

1. Tendency to acquire minimum energy: We know that, *lesser is the energy, greater is the stability.* Thus, every system tends to acquire minimum energy. For example:

(i) Heat flows from high temperature to low temperature so that heat content of hot body becomes minimum.

(ii) Water flows down a hill or a slope to have minimum energy (potential).

(iii) A wound watch spring tends to unwind so that mechanical energy of watch becomes minimum.

All the above processes are spontaneous because of a tendency to acquire minimum energy.

It has been observed that most of the spontaneous chemical reactions are exothermic. For example:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -286.2 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -395 \text{ kJ mol}^{-1}$$

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

In exothermic reactions, heat is evolved from the system, *i.e.*, energy is lowered. Thus, exothermic reactions occur spontaneously on account of decrease in enthalpy of system ($\Delta H = -\text{ve}$).

Hence, it can be concluded that the negative value of ΔH may be the criterion of spontaneity.

Limitations of the criterion for minimum energy

(a) Spontaneous endothermic reactions or processes: A number of endothermic reactions and processes are known which are spontaneous, *i.e.*, when ΔH is +ve. Some examples are given below:

(i) Evaporation of water or melting of ice takes place by absorption of heat from surroundings, *i.e.*, these processes are endothermic ($\Delta H = +\text{ve}$).

$$H_2O(s) \longrightarrow H_2O(l); \quad \Delta H = +6.0 \text{ kJ mol}^{-1}$$

$$H_2O(l) \longrightarrow H_2O(g); \quad \Delta H = +44 \text{ kJ mol}^{-1}$$

(ii) The decomposition of $CaCO_3$ is non-spontaneous at room temperature but becomes spontaneous when the temperature is raised.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g); \ \Delta H = +178.3 \text{ kJ mol}^{-1}$$

(iii) Compounds like NH_4Cl, KCl, etc., dissolve in water by absorption of heat from water. Temperature of the water decreases.

$$NH_4Cl(s) + aq. \longrightarrow NH_4^+(aq.) + Cl^-(aq.); \quad \Delta H = +15.1 \text{ kJ mol}^{-1}$$

(iv) Dinitrogen pentoxide (N_2O_5) decomposes spontaneously at room temperature into NO_2 and O_2, although the reaction is highly endothermic.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g); \quad \Delta H = 219 \text{ kJ mol}^{-1}$$

(v) The decomposition of HgO becomes spontaneous on heating.

$$2HgO(s) \longrightarrow Hg(l) + O_2(g); \quad \Delta H = 90.3 \text{ kJ mol}^{-1}$$

(b) Occurrence of reversible reactions: A large number of reactions are reversible in nature. In these reactions, both forward and backward reactions occur simultaneously in spite of the fact that one reaction is exothermic ($\Delta H = -\text{ve}$) and other endothermic ($\Delta H = +\text{ve}$).

(i) $H_2(g) + I_2(g) \longrightarrow 2HI(g); \quad \Delta H = -\text{ve}$

$$2HI(g) \longrightarrow H_2(g) + I_2(g); \quad \Delta H = +\text{ve}$$

$$\overline{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$$

(ii) $$\begin{array}{ll} N_2(g)+3H_2(g) \longrightarrow 2NH_3(g); & \Delta H = -\text{ve} \\ 2NH_3(g) \longrightarrow N_2(g)+3H_2(g); & \Delta H = +\text{ve} \\ \hline N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g) & \end{array}$$

(c) Reactions having zero ΔH: A number of reactions are known in which neither energy is evolved nor absorbed, but these are spontaneous. For example, esterification of acetic acid is a spontaneous process. ΔH of this reaction is zero.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

(d) Exothermic reactions fail to achieve completion: Every exothermic reaction rarely proceeds to completion even though ΔH remains negative throughout. In fact, all spontaneous reactions proceed in a direction until an equilibrium is attained.

Since, some spontaneous reactions are exothermic and others are endothermic, it is clear that enthalpy alone cannot account for spontaneity. There must be some other factor responsible for spontaneity or feasibility of a process.

2. Tendency to acquire maximum randomness: There is another natural tendency that must be taken into account to predict the direction of spontaneity.

Nature tends to move spontaneously from a state of lower probability to one of higher probability, *i.e.*, things tend to change from organized to disorganized. To illustrate what this statement means, we consider a spontaneous process of intermixing of two inert gases for which ΔH is zero. Two different inert gases, let us say helium (He) and neon (Ne), are originally contained in different glass bulbs, separated by a stopcock as shown in Fig. 7.20(a). To make the system as **closed** one, the entire system is perfectly insulated.

When the valve is opened, the intermixing of the two inert gases occurs due to diffusion into one another. As the gases are inert, there is no chemical interaction between them, the heat change during intermixing is negligible. The process of intermixing is a spontaneous process. If the process is examined critically, it is observed that when the valve is opened, both the gases are provided larger volume to occupy, *i.e.*, each gas achieves its own most probable distribution, independent of the presence of other gas. The final distribution is clearly much more probable than the initial distribution. There is, however, another useful way of looking at this process. The system has gone from a highly ordered state (all the helium molecules on the left, all the neon molecules on the right) to a more disordered or random state. Mixed gases cannot be separated on their own. Thus, diffusion is a spontaneous process acquiring more randomness.

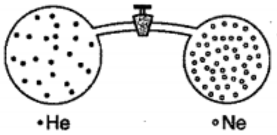


Fig. 7.20 (a)
Inert gases before mixing

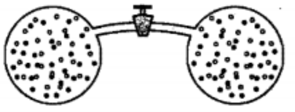


Fig. 7.20 (b)
Inert gases after mixing

In general, nature tends to move spontaneously from more ordered to more random states, or *a process proceeds spontaneously in a direction in which randomness of the system increases.*

Another example of achieving more randomness is the sugar dissolving in water. Before the solid sugar dissolves, the sugar molecules are organized in a crystal. As the molecules dissolve, they become distributed randomly and uniformly throughout the liquid. The opposite process never occurs, *i.e.*, sugar cubes do not form from the solution.

Thus, the second factor which is responsible for the spontaneity of a process is the tendency to acquire maximum randomness.

On the basis of second factor we may also explain the spontaneity of endothermic processes.

(i) *Decomposition of calcium carbonate*:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g); \quad \Delta H = +178.3 \text{ kJ mol}^{-1}$$

This process is spontaneous because the gaseous CO_2 produced is more random than solid calcium carbonate.

(ii) *Evaporation of water*:

$$H_2O(l) \longrightarrow H_2O(g); \quad \Delta H = +44 \text{ kJ mol}^{-1}$$

The gaseous state of a substance is more random than the liquid state. Thus, evaporation of water is spontaneous which proceeds in the direction of more randomness.

Similarly, fusion of ice is also spontaneous because the process again proceeds in the direction of more random state, *i.e.*, liquid state is more random in comparison to solid state.

$$H_2O(s) \longrightarrow H_2O(l); \quad \Delta H = +6.06 \text{ kJ mol}^{-1}$$

(iii) *Dissolution of NH_4Cl in water*:

$$NH_4Cl(s) + aq. \longrightarrow NH_4^+(aq.) + Cl^-(aq.); \quad \Delta H = +15.1 \text{ kJ mol}^{-1}$$

When solid $NH_4Cl(s)$ is dissolved in water, its ions become free. Free ions move randomly in all directions. Thus, the solution is a more random state as compared to solid NH_4Cl. Thus, the process of dissolution will be spontaneous because randomness increases on dissolution.

(iv) *Decomposition of mercuric oxide*:

$$2HgO(s) \longrightarrow 2Hg(l) + O_2(g); \quad \Delta H = +90.3 \text{ kJ mol}^{-1}$$

Here again the process will be spontaneous because the product is more random than reactant due to presence of gaseous O_2.

Limitations of the criterion for maximum randomness: Like energy factor, the randomness factor has also certain limitations. For example, in the liquefaction of a gas or in the solidification of a liquid, the randomness of the particles decreases but still these processes are spontaneous. Thus, like energy factor, randomness alone cannot be the sole criterion for the spontaneity of a process.

Overall tendency as driving force for a spontaneous process

From the above discussion, it is apparent that the spontaneous processes occur because of the two tendencies:

(i) Tendency of a system to achieve a state of minimum energy.

(ii) Tendency of a system to achieve a state of maximum randomness.

The overall tendency of a process to be spontaneous depends on the resultant of the above two factors. The resultant of the two tendencies or overall tendency for a process to occur is termed the **driving force.**

Here, it should be noted that these tendencies are independent of each other. Both may act in the same or in opposite directions in a process.

Case I: *When enthalpy factor is absent then randomness factor decides spontaneity of a process.*

Case II: *When randomness factor is absent then enthalpy or energy factor decides spontaneity of a process.*

Case III: *When both factors take place simultaneously then magnitude of the tendencies becomes important to decide spontaneity.*

7.24 ENTROPY

Why do systems tend to move spontaneously to a state of maximum randomness or disorder? The answer is that a disordered state is more probable than an ordered state because the disordered state can be achieved in more ways. The following example illustrates the point. Suppose that you shake a box containing 10 identical coins and then count the number of heads (H) and tails (T). It is very unlikely that all the 10 coins will come up heads; *i.e.*, perfectly ordered arrangement is much less probable than the totally disordered state in which heads and tails come up randomly. The perfectly ordered state of 10 heads can be achieved in only one way and the totally disordered state can be achieved in 2^{10} (1024) ways, *i.e.*, the totally disordered state is 2^{10} times more probable than the perfectly ordered state. If the box contained 1 mol of coins, the perfectly ordered state would be only one, but the disordered states would be much higher ($2^{N_A} = 2^{6.02\times 10^{23}}$). It is thus, concluded that a change which brings about randomness is more likely to occur than one that brings about order. The extent of disorder or randomness is expressed by a property known as **entropy.**

Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.

Entropy is represented by the symbol 'S'. It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state. The change in entropy from initial to final state of a system is represented by ΔS. The entropy is a state function and depends only on the initial and final states of the system.

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

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

For a chemical reaction,

$$\Delta S = S_{\text{(products)}} - S_{\text{(reactants)}}$$

Mathematical Definition of Entropy

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature (isothermally).

$$\int dS = \frac{1}{T}\int \delta q_{\text{rev}}$$

or

$$\Delta S = \frac{q_{\text{rev}}}{T} \qquad \text{... (i)}$$

If heat is absorbed, then ΔS is positive (increase in entropy). If heat is evolved, ΔS is negative (decrease in entropy). The value of ΔS, like ΔE and ΔH, is a definite quantity and depends on the initial and final states of the system. It is independent of the manner in which the change has been brought about, *i.e.*, whether the change has been brought about reversibly or irreversibly.

Several factors influence the amount of entropy that a system has in a particular state. In general,

(i) The value of entropy depends on the mass of the system. Hence, it is an extensive property.

(ii) A liquid has a higher entropy than the solid from which it is formed. In a solid, the atoms, molecules or ions are fixed in position; in the liquid, these particles are free to move past one another, *i.e.*, liquid structure is more random and the solid more ordered.

(iii) A gas has a higher entropy than the liquid from which it is formed. When vaporization occurs, the particles acquire greater freedom to move about.

(iv) Increasing temperature of a substance increases its entropy. Raising the temperature increases the kinetic energy of the molecules (atoms or ions) and hence their freedom of motion. In the solid, the molecules vibrate with a greater amplitude at higher temperatures. In a liquid or a gas, they move about more rapidly.

In other words, the more heat the system absorbs, the more disordered it becomes. Furthermore, if heat is absorbed at low temperature, it becomes more disordered than when the same amount of heat is added at higher temperature.

Units of Entropy and Entropy Change

Since, entropy change is expressed by a heat term divided by temperature, it is expressed in terms of calories per degree, *i.e.*, cal K^{-1}. In SI units, the entropy change is expressed in terms of joules per degree, *i.e.*, J K^{-1}. Entropy is an extensive property, *i.e.*, it depends on the mass of the substance; hence units of entropy are expressed as cal deg^{-1} mol^{-1} (cal K^{-1} mol^{-1}) or joule deg^{-1} mol^{-1} (J K^{-1} mol^{-1}).

Spontaneity in Terms of Entropy Change

In an isolated system, such as mixing of gases, there is no exchange of energy or matter between the system and surroundings. However, the mixing of gases is accompanied by randomness, *i.e.*, there is increase in entropy. Therefore, it can be stated that **for a spontaneous process in an isolated system, the change in entropy is positive, *i.e.,* $\Delta S > 0$.**

However, if a system is not isolated, the entropy changes of both the system and surroundings are to be taken into account because system and surroundings together constitute the **isolated system.** Thus, the total entropy change (ΔS_{total}) is sum of the change in entropy of the system (ΔS_{system}) and the change in entropy of the surroundings ($\Delta S_{\text{surroundings}}$), *i.e.*,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad \text{... (ii)}$$

For a spontaneous process, ΔS_{total} must be positive, *i.e.*,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad \text{... (iii)}$$

ΔS_{total} is also termed as $\Delta S_{\text{universe}}$

During a spontaneous process, the entropy of the system goes on increasing till the system attains the equilibrium state, *i.e.*, entropy of the system becomes maximum and, therefore, no more increase in the entropy of the system is possible. The mathematical condition for equilibrium is,

$$\Delta S = 0 \,(\text{at equilibrium for an isolated system}) \quad \text{... (iv)}$$

If ΔS_{total} is negative, the direct process is non-spontaneous whereas the reverse process is spontaneous.

This can be illustrated by considering the entropy changes in the conversion of water to ice at three different temperatures. The relevent entropy changes for the system and surroundings and total change are given in the following table:

Temperature		ΔS_{system}	$\Delta S_{\text{surrounding}}$	ΔS_{total}
°C	K	$\text{J K}^{-1}\text{ mol}^{-1}$	$\text{J K}^{-1}\text{ mol}^{-1}$	$\text{J K}^{-1}\text{ mol}^{-1}$
− 1	272	− 21.85	+ 21.93	+ 0.08
0	273	− 21.99	+ 21.99	0.00
+ 1	274	− 22.13	+ 22.05	− 0.08

At 272 K: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$= -21.85 + 21.93 = +0.08 \text{ J K}^{-1}\text{ mol}^{-1}$$

$\therefore \quad \Delta S_{\text{process}} > 0 \quad$ at 272 K

Thus, *freezing of ice at 272 K, $H_2O(l) \rightarrow H_2O(s)$ will be spontaneous.*

At 273 K: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$= -21.99 + 21.99 = 0$$

$$\Delta S_{\text{total}} = 0$$

Thus, *at this temperature, water and ice will be at equilibrium.*

$$H_2O(l) \rightleftharpoons H_2O(s); \quad \Delta S = 0 \text{ at } 273 \text{ K} \quad (\text{at equilibrium})$$

At 274 K: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$= -22.13 + 22.05 = -0.08 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta S < 0$$

Thus, *freezing of water will be non-spontaneous at* 274 *K.*

$$H_2O(l) \longrightarrow H_2O(s) \qquad \Delta S < 0 \,(\text{non-spontaneous})$$

Entropy Change in Reversible Process

Consider an isothermal reversible process. In this process, let the system absorb q amount of heat from surroundings at temperature T. The increase in the entropy of the system will be

$$\Delta S_{\text{system}} = +\frac{q}{T}$$

On the other hand, surroundings lose the same amount of heat at the same temperature. The decrease in the entropy of the surroundings will

$$\Delta S_{\text{surroundings}} = -\frac{q}{T}$$

Total change in entropy = entropy change in system + entropy change in surroundings
of the process

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

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

When the reversible process is **adiabatic,** there will be no heat exchange between system and surroundings, *i.e.*, $q = 0$

$$\therefore \quad \Delta S_{\text{system}} = 0, \; \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

Entropy Change in Irreversible Processes

Consider a system at higher temperature T_1 and its surroundings at lower temperature T_2. 'q' amount of heat goes irreversibly from system to surroundings.

$$\therefore \quad \Delta S_{\text{system}} = -\frac{q}{T_1}$$

$$\Delta S_{\text{surroundings}} = +\frac{q}{T_2}$$

$$\Delta S_{\text{process}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= -\frac{q}{T_1} + \frac{q}{T_2} = q\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

But $T_1 > T_2$, $\therefore T_1 - T_2 = +\text{ve}$

or $\quad \Delta S_{\text{process}} > 0$

Hence, *entropy increases in an irreversible process.*

Entropy Change for Ideal Gases

Change in entropy for an ideal gas under different conditions may be calculated as:

(i) *When changes from initial state* (1) *to final state* (2):

$$\Delta S = 2.303 n C_V \log\left(\frac{T_2}{T_1}\right) + 2.303 nR \log\left(\frac{V_2}{V_1}\right)$$

(when T and V are variables)

$$\Delta S = 2.303 n C_P \log\left(\frac{T_2}{T_1}\right) + 2.303 nR \log\left(\frac{P_1}{P_2}\right)$$

(when T and P are variables)

(ii). *Entropy change for isothermal process*:

$$\Delta S = 2.303 nR \log\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = 2.303nR \log\left(\frac{P_1}{P_2}\right)$$

(iii) *Entropy change for isobaric process (at constant pressure)*:

$$\Delta S = 2.303n\,C_P \log\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = 2.303n\,C_P \log\left(\frac{V_2}{V_1}\right)$$

(iv) *Entropy change for isochoric process (at constant volume)*:

$$\Delta S = 2.303n\,C_V \log\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = 2.303n\,C_V \log\left(\frac{P_2}{P_1}\right)$$

(v) *Entropy change in mixing of ideal gases*: Let n_1 mole of gas A and n_2 mole of gas B are mixed; then total entropy change can be calculated as:

$$\Delta S = -2.303R[n_1 \log x_1 + n_2 \log x_2]$$

x_1, x_2 are mole fractions of gases A and B,

i.e., $$x_1 = \frac{n_1}{n_1 + n_2};\ x_2 = \frac{n_2}{n_1 + n_2}$$

$$\Delta S/\text{mol} = -2.303R\left[\frac{n_1}{n_1 + n_2}\log x_1 + \frac{n_2}{n_1 + n_2}\log x_2\right]$$

$$\Delta S/\text{mol} = -2.303R[x_1 \log x_1 + x_2 \log x_2]$$

Entropy change in adiabatic expansion will be zero, $\Delta S = 0$.

Physical Significance of Entropy at a Glance

1. Entropy as unavailable energy: Entropy is unavailable energy of the system.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature in K}}$$

2. Entropy and randomness: Entropy is a measure of disorderness or randomness in the system. Increase in entropy means change from an ordered to less ordered (or disordered) state.

3. Entropy and probability: Entropy may be defined as a function of probability of the thermodynamic state. Since, we know that both the entropy and thermodynamic probability increase simultaneously in a process, hence the state of equilibrium is the state of maximum probability.

Characteristics of Entropy

The important characteristics of entropy are summarised below:

(i) Entropy is an extensive property. It is difficult to determine the absolute value of entropy of a substance but its value depends on mass of the substance present in the system.

(ii) Entropy of a system is a state function. It depends on the state variables such as T, P, V and n which govern the state of the system.

(iii) The change in entropy taking place in going from one state to another state does not depend on the path adopted. It actually depends on the final and initial states of the system.

$$\text{Change in entropy, } \Delta S = S_{\text{final}} - S_{\text{initial}}$$

(iv) The entropy change for a cyclic process is zero.

(v) The entropy change in the equilibrium state is zero $(\Delta S = 0)$.

(vi) For natural processes, entropy of universe is increasing.

$$\Delta S_{\text{universe}} > 0$$

(vii) In a reversible process, ΔS_{total} or $\Delta S_{\text{universe}} = 0$ and therefore

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

(viii) For adiabatic reversible process,

$$\Delta S_{\text{system}} = \Delta S_{\text{surroundings}} = \Delta S_{\text{total}} = 0$$

In a spontaneous (irreversible process),

$$\Delta S_{\text{total}} \text{ or } \Delta S_{\text{universe}} > 0,$$

i.e., in spontaneous processes, there is always increase in entropy of the universe.

7.25 ENTROPY CHANGE DURING PHASE TRANSITIONS

Solid, liquid and gas are the three forms of a matter. The change of a substance from one form to another is known as **phase transformation.** Such changes occur at definite temperatures and are accompanied by entropy change. During these transformations either heat is absorbed or evolved, *i.e.*, the entropy either increases or decreases accordingly.

The entropy change for these transformations is given by

$$\Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T}$$

where, q_{rev} is the heat absorbed or evolved and T is the temperature of transition. q_{rev} is actually the molar enthalpy change of the substance.

(i) Entropy of fusion: The entropy of fusion is defined as the change in entropy when one mole of a solid substance changes into liquid form at the melting temperature.

The heat absorbed is equal to the latent heat of fusion

$$\Delta S_{\text{fusion}} = S_{\text{liquid}} - S_{\text{solid}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

For example, when ice melts, the change in entropy is given by

$$\Delta S_{\text{fusion (ice)}} = S_{\text{water}} - S_{\text{ice}} = \frac{\Delta H_{\text{fusion}}}{T_f} = \frac{6000\,\text{J mol}^{-1}}{273}$$

$$= 21.98\,\text{J K}^{-1}\,\text{mol}^{-1}$$

(ii) Entropy of vaporisation: It is defined as the change in entropy when one mole of the liquid substance changes into vapours (gas) at its boiling point.

$$\Delta S_{\text{vapour}} = S_{\text{vapour}} - S_{\text{liquid}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}}$$

Where, ΔH_{vapour} is the latent heat of vaporisation and T_{bp} is the boiling point.

For example, when water is converted into steam, the change in entropy is given by

$$\Delta S_{\text{vapour (water)}} = S_{\text{steam}} - S_{\text{water}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}} = \frac{40626\ \text{J mol}^{-1}}{373}$$

$$= 108.9\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(iii) Entropy of sublimation: Sublimation involves the direct conversion of a solid into its vapour. The entropy of sublimation is defined as the change in entropy when one mole of a solid changes into vapour at a particular temperature.

$$\Delta S_{\text{sub}} = S_{\text{vapour}} - S_{\text{solid}} = \frac{\Delta H_{\text{sub}}}{T}$$

Where, ΔH_{sub} = heat of sublimation at temperature T.

SOME SOLVED EXAMPLES

Example 62. *The enthalpy change, for the transition of liquid water to steam, ΔH_{vapour} is 40.8 kJ mol^{-1} at 373 K. Calculate entropy change for the process.*

Solution: The transition under consideration is:

$$H_2O(l) \longrightarrow H_2O(g)$$

We know that, $$\Delta S_{\text{vapour}} = \frac{\Delta H_{\text{vapour}}}{T}$$

Given, $$\Delta H_{\text{vapour}} = 40.8\ \text{kJ mol}^{-1}$$

$$= 40.8 \times 1000\ \text{J mol}^{-1}$$

$$T = 373\ \text{K}$$

Thus, $$\Delta S_{\text{vapour}} = \frac{40.8 \times 1000}{373} = 109.38\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Example 63. *What is entropy change for the conversion of one gram of ice to water at 273 K and one atmospheric pressure? ($\Delta H_{fusion} = 6.025\ kJ\ mol^{-1}$)*

Solution: $$\Delta H_{\text{fusion}} = 6.025 \times 1000\ \text{J mol}^{-1}$$

$$= \frac{6025}{18}\ \text{J g}^{-1} = 334.72\ \text{J g}^{-1}$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$= \frac{334.72}{273} = 1.226\ \text{J K}^{-1}\ \text{g}^{-1}$$

Example 64. *Calculate the enthalpy of vaporisation per mole for ethanol. Given, $\Delta S = 109.8\ J\ K^{-1}\ mol^{-1}$ and boiling point of ethanol is 78.5°C.*

Solution: We know that,

$$\Delta S_{\text{vapour}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}}$$

Given, $$\Delta S_{\text{vapour}} = 109.8\ \text{J K}^{-1}\ \text{mol}^{-1}$$

$$T_{\text{bp}} = 78.5 + 273 = 351.5\ \text{K}$$

Substituting these values in above equation, we get

$$109.8 = \frac{\Delta H_{\text{vapour}}}{351.5}$$

$$\Delta H_{\text{vapour}} = 38594.7\ \text{J mol}^{-1}$$

$$= 38.594\ \text{kJ mol}^{-1}$$

Example 65. *Calculate the entropy change for the following reversible process:*

$$\underset{1\ mol\ at\ 1\ atm}{\alpha\text{-}Tin} \rightleftharpoons \underset{1\ mol\ at\ 1\ atm}{\beta\text{-}Tin} \qquad at\ 13°\text{C}$$

($\Delta H_{trans} = 2090\ J\ mol^{-1}$)

Solution: $$\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T} = \frac{2090}{286}$$

$$= 7.3076\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Example 66. *At 0°C, ice and water are in equilibrium and enthalpy change for the process $H_2O(s) \rightleftharpoons H_2O(l)$ is $6\ kJ\ mol^{-1}$. Calculate the entropy change for the conversion of ice into liquid water.*

Solution: We know that for the process of fusion,

$$H_2O(s) \rightleftharpoons H_2O(l)$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$= \frac{6 \times 1000}{273} = 21.98\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Example 67. *The enthalpy of vaporisation of liquid diethyl ether $(C_2H_5)_2O$ is $26\ kJ\ mol^{-1}$ at its boiling point 35°C. Calculate $\Delta S°$ for conversion of :*

(*a*) *liquid to vapour,*
(*b*) *vapour to liquid at 35°C.*

Solution: (a) $$\Delta S_{\text{vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T_{\text{bp}}} = \frac{26000}{308}$$

$$= 84.42\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(b) $$\Delta S_{\text{condensation}} = -\Delta H_{\text{vaporisation}}$$

$$= -84.42\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Example 68. *Calculate entropy change when 10 moles of an ideal gas expands reversibly and isothermally from an initial volume of 10 litre to 100 litre at 300 K.*

Solution: $$\Delta S = 2.303 nR \log\left(\frac{V_2}{V_1}\right)$$

$$= 2.303 \times 10 \times 8.314 \log\left(\frac{100}{10}\right)$$

$$= 191.24\ \text{J K}^{-1}$$

Example 69. *Oxygen gas weighing 64 g is expanded from 1 atm to 0.25 atm at 30°C. Calculate entropy change, assuming the gas to be ideal.*

Solution:
$$n = \frac{w}{\text{m. wt.}} = \frac{64}{32} = 2$$
$$\Delta S = 2.303 nR \log\left(\frac{P_1}{P_2}\right)$$
$$= 2.303 \times 2 \times 8.314 \log\left(\frac{1}{0.25}\right)$$
$$= 23.053 \text{ J K}^{-1}$$

Example 70. *Calculate the change in entropy when 1 mole nitrogen gas expands isothermally and reversibly from an initial volume of 1 litre to a final volume of 10 litre at 27° C.*

Solution:
$$\Delta S = 2.303\, nR \log\left(\frac{V_2}{V_1}\right)$$
$$= 2.303 \times 1 \times 8.134 \log\left(\frac{10}{1}\right)$$
$$= 19.12 \text{ J K}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

34. For a liquid, enthalpy of fusion is 1.435 kcal mol^{-1} and molar entropy change is 5.26 cal $\text{mol}^{-1}\text{ K}^{-1}$. The melting point of the liquid is:

(a) 0°C (b) – 273°C
(c) 173 K (d) 100°C

[**Ans.** (a)]

[**Hint:** $\Delta S_{\text{fusion}} = \dfrac{\Delta H_{\text{fusion}}}{T_{\text{mp}}}$

$$5.26 = \frac{1.435 \times 1000}{T_{\text{mp}}}$$
$$T_{\text{mp}} = \frac{1435}{5.26} = 273 \text{ K},\ i.e., 0° \text{ C}]$$

35. Latent heat of vaporisation of water is 540 cal g^{-1} at 100°C. Calculate the entropy change when 1000 g water is converted to steam at 100°C.

(a) 1447 cal (b) 2447 cal (c) 3447 cal (d) 4447 cal

[**Ans.** (a)]

[**Hint:** $\Delta S_{\text{vap}} = \dfrac{\Delta H_{\text{vap}}}{T} = \dfrac{540 \times 1000}{373} = 1447 \text{ cal}$]

36. Enthalpy of fusion of water is 6.01 kJ mol^{-1}. The entropy change of 1 mole of ice at its melting point will be:

(a) 22 kJ mol^{-1} (b) 109 kJ mol^{-1}
(c) 44 kJ mol^{-1} (d) 11 kJ mol^{-1}

[**Ans.** (a)]

[**Hint:** $\Delta S_{\text{fusion}} = \dfrac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \dfrac{6.01 \times 1000}{273} = 22 \text{ kJ mol}^{-1}$]

37. For spontaneous process:

(a) $\Delta S_{\text{total}} = 0$ (b) $\Delta S_{\text{total}} > 0$
(c) $\Delta S_{\text{total}} < 0$ (d) none of these

[**Ans.** (b)]

[**Hint:** $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$
= + ve for spontaneous process]

38. Melting point of a solid is x K and its latent heat of fusion is 600 cal mol^{-1}. The entropy change for fusion of 1 mol solid is 2 cal $\text{mol}^{-1}\text{ K}^{-1}$. The value of x will be:

(a) 100 K (b) 200 K (c) 300 K (d) 400 K

[**Ans.** (c)]

[**Hint:** $\dfrac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \Delta S_{\text{fusion}}$

$$\frac{600}{T} = 2$$
$$T = 300 \text{ K}]$$

39. The entropy change involved in the conversion of 1 mole of liquid water at 373 K to vapour at the same temperature will be:

$$\Delta H_{\text{vap}} = 2.257 \text{ kJ/g}$$

(a) 0.119 kJ (b) 0.109 kJ
(c) 0.129 kJ (d) 0.120 kJ

[PMT (MP) 2007]

[**Ans.** (b)]

[**Hint:** $\Delta S = \dfrac{\Delta H_{\text{vap}}}{T} = \dfrac{2.257 \times 18}{373} = 0.109 \text{ kJ/g}$]

7.26 SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics tells us whether a given process can occur spontaneously and to what extent. It also helps us to calculate the maximum fraction of heat that can be converted into work in a given process.

The second law of thermodynamics like first law is a postulate and has not been derived from any prior concepts. It is stated in various forms. However, all the statements of second law have the same meaning.

1. Clausius statement: *"It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency."*

It means that work can always be completely converted into heat but heat cannot be converted completely into work without leaving some permanent change in the system or surroundings. For example, heat produced in heat engine is never fully utilized, as part of it is always lost to surroundings or in overcoming friction, etc. Thus, it can be said that *the complete conversion of heat into work is impossible without leaving some effect elsewhere.*

Or

It is not possible to convert heat into work without compensation.

Or

All forms of energy can be converted into heat energy but heat cannot be converted into other forms of energy fully by any process.

The other similar statements are:

2. Thomson statement: *The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work.*

3. Kelvin-Planck statement: *It is impossible by means of inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*

4. *It is impossible to construct a heat engine of 100 % thermal efficiency.*

5. Ludwig Boltzmann statement: In 1886, Ludwig Boltzmann gave a most useful statement of the second law of thermodynamics. *Nature tends to pass from a less probable to more probable state.*

The connection between entropy and the spontaneity of a reaction or a process is expressed by the second law of thermodynamics in a number of ways.

6. *All spontaneous processes or naturally occurring processes are thermodynamically irreversible. Without the help of an external agency, a spontaneous process cannot be reversed.*

For example, the mixing of non-reacting gases is a spontaneous process. But these cannot be separated from the mixture without the application of special methods.

Heat energy can flow from a hot body to a cold body of its own (spontaneously) but not from a cold body to a hot body unless the former is heated.

7. *The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.*

Since, the universe is made up of the system and the surroundings, the entropy change in the universe ($\Delta S_{\text{universe}}$) for any process is the sum of the entropy changes in the system (ΔS_{system}) and in the surroundings ($\Delta S_{\text{surroundings}}$). Mathematically, the second law of thermodynamics can be expressed as:

A spontaneous process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

An equilibrium process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For a spontaneous process, the law says that $\Delta S_{\text{universe}}$ must be greater than zero, but it does not place a restriction on either ΔS_{system} or $\Delta S_{\text{surroundings}}$. Thus, it is possible for either ΔS_{system} or $\Delta S_{\text{surroundings}}$ to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, $\Delta S_{\text{universe}}$ is zero, *i.e.*, ΔS_{system} and $\Delta S_{\text{surroundings}}$ must be equal in magnitude but opposite in sign.

Thus, *the entropy of the universe is continuously increasing.* The main ideas of the first and second law of thermodynamics may be summarised as:

First law states that the energy of the universe is constant whereas the second law states that the entropy of the universe is continuously increasing and tends to a maximum.

First law deals with the conservation of energy whereas the second law tells the direction of flow of energy.

For a reversible process,

$$dS = \frac{dq}{T} \quad \text{or} \quad dq = T\,dS$$

For an irreversible process,

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

$$\therefore \qquad dS \geq \frac{dq}{T}$$

This is the mathematical statement of second law of thermodynamics.

$dq = dE + P\,dV$ This is the mathematical statement of first law of thermodynamics

Combining both the laws of a reversible process,

$$T\,dS = dE + P\,dV$$

7.27 GIBBS FREE ENERGY, (*G*), CHANGE IN FREE ENERGY AND SPONTANEITY

As discussed earlier, there are two thermodynamic quantities that affect reaction spontaneity. One of these is enthalpy, *H*; the other is the entropy, *S*. The problem is to put these two quantities together in such a way as to arrive at a single function whose sign will determine whether a reaction is spontaneous. This problem was first solved more than a century ago by **J. Willard Gibbs,** who introduced a new quantity, now called the **Gibbs free energy** and given the symbol, *G*. Gibbs showed that for a reaction taking place at constant pressure and constant temperature, ΔG represents that portion of the total energy change that is available (*i.e.*, free) to do useful work. If, for example, ΔG for a reaction is – 300 kJ, it is possible to obtain 300 kJ of useful work from the reaction. Conversely, if ΔG is + 300 kJ, at least that much energy in the form of work must be supplied to make the reaction to take place. Gibbs free energy of a system is defined as:

"The thermodynamic quantity of the system, the decrease in whose value during a process is equal to useful work done by the system."

Mathematically, it may be defined as:

$$G = H - TS \qquad \text{... (i)}$$

where, H = enthalpy; S = entropy and T = absolute temperature.

We know that, $H = E + PV$ ... (ii)

From eqs. (i) and (ii),

$$G = E + PV - TS$$

Free energy change at constant temperature and pressure can be given as:

$$\Delta G = \Delta E + P\,\Delta V - T\,\Delta S$$

$$\Delta G = \Delta H - T\,\Delta S \qquad \text{... (iii)}$$

(Gibbs-Helmholtz equation)

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

Gibbs-Helmholtz equation is used to discuss the **driving force, *i.e.*, the overall criterion of spontaneity.**

[**Note:** Since, '*H*' and '*S*' are extensive property hence '*G*' will also be an extensive property. Moreover, Gibbs function '*G*' is a state function.]

Free Energy Change and Spontaneity

Let us consider a system which is not isolated from its surroundings. In this case, total entropy change can be calculated as:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \qquad \text{... (i)}$$

Let us consider the process at constant temperature and pressure. Let q_P amount of heat be given by the system to the surroundings.

$$(q_P)_{\text{surroundings}} = -(q_P)_{\text{system}} = -\Delta H_{\text{system}}$$

$$\Delta S_{\text{surroundings}} = \frac{(q_P)_{\text{surroundings}}}{T} = \frac{-\Delta H_{\text{system}}}{T} \qquad \text{... (ii)}$$

From equations (i) and (ii),

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

or $$T\ \Delta S_{\text{total}} = T\ \Delta S_{\text{system}} - \Delta H_{\text{system}}$$

or $$-T\ \Delta S_{\text{total}} = \Delta H_{\text{system}} - T\ \Delta S_{\text{system}} \qquad \text{... (iii)}$$

According to Gibbs-Helmholtz equation,

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

$$\therefore \qquad \Delta G_{\text{system}} = \Delta H_{\text{system}} - T\ \Delta S_{\text{system}} \qquad \text{... (iv)}$$

From equations (iii) and (iv),

$$\Delta G_{\text{system}} = -T\ \Delta S_{\text{total}}$$

We know that for spontaneous process, $\Delta S_{\text{total}} > 0$

$\therefore$ $\Delta G = -$ ve for spontaneous process.

Thus, *for spontaneous process $T\ \Delta S_{total}$ should be positive or ΔG should be negative.*

Case I: Let entropy and energy, both factors are favourable for a process, *i.e.*, $\Delta H = -$ ve and $T\ \Delta S = +$ ve

$\therefore$ From $$\Delta G = \Delta H - T\ \Delta S$$
$$= (-\text{ve}) - (+\text{ve}) = -\text{ve}$$

Thus, $\Delta G = -$ *ve for spontaneous process.*

Case II: Let both energy and entropy factors oppose a process, *i.e.*, $\Delta H = +$ ve, $T\ \Delta S = -$ ve.

$\therefore$ From $$\Delta G = \Delta H - T\ \Delta S$$
$$= +\text{ve} - (-\text{ve}) = +\text{ve}$$

Thus, ΔG *is positive for a non-spontaneous process.*

Case III: Let both tendencies be equal in magnitude but opposite, *i.e.*,

$$\Delta H = +\text{ve} \quad \text{and} \quad T\ \Delta S = +\text{ve} \quad \text{and} \quad \Delta H = T\ \Delta S$$

$\therefore$ From $$\Delta G = \Delta H - T\ \Delta S$$
$$= 0$$

In this condition, the process is said to be at equilibrium.

Coupled Reactions

We know that the reactions which have $\Delta G = +$ ve are non-spontaneous. However, such reactions can be made spontaneous when coupled with a reaction having very large negative free energy of reaction,

e.g., $$2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g); \ \Delta G° = +1487 \text{ kJ/mol}$$

$$6CO(g) + 3O_2(g) \longrightarrow 6CO_2(g); \qquad \Delta G° = -1543.2 \text{ kJ/mol}$$

On adding, $$2Fe_2O_3(s) + 6CO(g) \longrightarrow 4Fe(s) + 6CO_2(g);$$
$$\Delta G° = -52.2 \text{ kJ/mol}$$

Thus, both reactions proceed simultaneously.

The free energy of a reaction is the chemical analogue of potential energy of mechanical systems. A body moves in the direction in which there is decrease in potential energy. Similarly, in chemical system, the substance moves in a direction in which there is decrease in free energy, *i.e.*, ΔG is negative.

In a chemical reaction, $\Delta G = G_{\text{products}} - G_{\text{reactants}}$. Thus, spontaneous changes occur with a decrease in free energy, *i.e.*, ΔG is negative.

To sum up, the criteria for spontaneity of a process in terms of ΔG is as follows:

(i) If ΔG is negative, the process is spontaneous.

(ii) If ΔG is zero, the system is in equilibrium. The process does not occur.

(iii) If ΔG is positive, the process does not occur in the forward direction. It may occur in the backward direction.

Conditions for ΔG to be negative or the process to be spontaneous

We know that, $\Delta G = \Delta H - T\ \Delta S$

ΔH	$T\Delta S$	Conditions	ΔG
–ve (favourable)	+ve (favourable)	(any)	–ve spontaneous
–ve (favourable)	–ve (unfavourable)	$\lvert \Delta H \rvert > (T\ \Delta S)$	–ve spontaneous
+ve (unfavourable)	+ve (favourable)	$\lvert T\ \Delta S \rvert > \lvert \Delta H \rvert$	–ve spontaneous

Role of Temperature on Spontaneity

In Gibbs-Helmholtz equation:

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

not only ΔH and ΔS but also temperature 'T' is a determining factor for spontaneity, *i.e.*, for ΔG to be –ve. Let us discuss exothermic and endothermic reactions to show the influence of temperature.

1. Exothermic processes: In exothermic reactions,

$$\Delta H = -\text{ve} \ \text{(favourable condition)}$$

Case I: When $T\ \Delta S$ is positive, *i.e.*, favourable, then ΔG will be negative and the process will be spontaneous at all temperatures.

Case II: When $T\ \Delta S$ is negative, *i.e.*, unfavourable, then ΔG will be negative when $|\Delta H| > |T\ \Delta S|$. To reduce the magnitude of $T\ \Delta S$, the temperature should be low. Thus, *exothermic reactions can be made favourable (when $T\ \Delta S = -$ ve) by lowering the temperature.*

2. Endothermic reactions: In endothermic reactions, $\Delta H = +$ ve (unfavourable conditions).

In case of endothermic reactions, ΔG will be negative when $|\Delta H| < |T\ \Delta S|$. To increase the magnitude of $T\ \Delta S$, temperature

(T) should be increased. Thus, *endothermic reactions can be made favourable by increasing the temperature.*

Thus, temperature also plays an important role in deciding the spontaneity of a reaction. A reaction which is non-spontaneous at low temperature becomes spontaneous at high temperature and *vice-versa.*

Sign of ΔH, ΔG and ΔS and prediction of spontaneity

ΔH	ΔS	ΔG	Remarks
–ve	+ve	–ve	Spontaneous at all temperatures
–ve	–ve	–ve (at low temperature)	Spontaneous
		+ve (at high temperature)	Non-spontaneous
+ve	+ve	+ve (at low temperature)	Non-spontaneous
		–ve (at high temperature)	Spontaneous
+ve	–ve	+ve	Non-spontaneous at all temperatures

		ΔH	
		+	–
ΔS	+	Spontaneous at high temperature and non-spontaneous at low temperatures	Spontaneous at all temperatures
	–	Non-spontaneous at all temperatures	Non-spontaneous at high temperatures and spontaneous at low temperatures

SOME SOLVED EXAMPLES

Example 71. *ΔH and ΔS for the reaction,*

$$Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g)$$

are $30.56\,kJ\,mol^{-1}$ and $66.0\,J\,K^{-1}\,mol^{-1}$ respectively. Calculate the temperature at which free energy change for the reaction will be zero. Predict whether the forward reaction will be favoured above or below this temperature.

Solution: We know that,

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

At equilibrium, $\Delta G = 0$

so that $0 = \Delta H - T\,\Delta S$

or $T = \dfrac{\Delta H}{\Delta S}$

Given that, $\Delta H = 30.56\text{ kJ mol}^{-1}$

$= 30560\text{ J mol}^{-1}$

$\Delta S = 66.0\text{ J K}^{-1}\text{ mol}^{-1}$

$$T = \frac{30560}{66} = 463\text{ K}$$

Above this temperature, ΔG will be negative and the process will be spontaneous in forward direction.

Example 72. *For the reaction,*

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Calculate ΔG at $700\,K$ when enthalpy and entropy changes are $-113.0\,kJ\,mol^{-1}$ and $-145\,J\,K^{-1}\,mol^{-1}$ respectively.

Solution: We know that, $\Delta G = \Delta H - T\,\Delta S$

Given, $\Delta H = -113\text{ kJ mol}^{-1}$

$= -113000\text{ J mol}^{-1}$

$\Delta S = -145\text{ J K}^{-1}\text{ mol}^{-1}$

$T = 700\text{ K}$

Substituting these values in the above equation,

we get $\Delta G = -113000 - 700 \times (-145)$

$= -11500\text{ J mol}^{-1}$

$= -11.5\text{ kJ mol}^{-1}$

Example 73. *In the reaction $A^+ + B \longrightarrow A + B^+$, there is no entropy change. If enthalpy change is $22\,kJ$ of A^+, calculate ΔG for the reaction.*

Solution: For the given reaction,

$\Delta H = 22\text{ kJ}, \Delta S = 0$

$\therefore$ From, $\Delta G = \Delta H - T\,\Delta S$

$\Delta G = 22 - T \times 0 = 22\text{ kJ mol}^{-1}$

Example 74. *ΔH and ΔS for the reaction $Br_2(l) + Cl_2(g) \rightarrow 2BrCl(g)$ are $29.37\,kJ$ and $104.0\,J\,K^{-1}$ respectively. Above what temperature will this reaction become spontaneous?*

Solution: According to Gibbs-Helmholtz equation,

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

For spontaneous process, $\Delta G < 0$

i.e., $\Delta H - T\,\Delta S < 0$

$T\,\Delta S > \Delta H$

$T > \dfrac{\Delta H}{\Delta S}$

$T > \dfrac{29.37 \times 1000}{104}$ $\quad T > 282.4\text{ K}$

Example 75. *Calculate the temperature at which liquid water will be in equilibrium with water vapour.*

$\Delta H_{vap} = 40.73\,kJ\,mol^{-1}$ and $\Delta S_{vap} = 0.109\,kJ\,mol^{-1}\,K^{-1}$

Solution: Given, $\Delta H = 40.73\text{ kJ mol}^{-1}$

$\Delta S = 0.109\text{ kJ mol}^{-1}\text{ K}^{-1}$

and $\Delta G = 0$

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

$0 = 40.73 - T \times 0.109$

$$T = \frac{40.73}{0.109} = 373.6\text{ K}$$

Example 76. *Zinc reacts with dilute hydrochloric acid to give hydrogen at 17° C. The enthalpy of the reaction is $-12.55\,kJ\,mol^{-1}$ of zinc and entropy change equals $5.0\,J\,K^{-1}\,mol^{-1}$ for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.*

Solution: Given, $\Delta H = -12.55\ \text{kJ mol}^{-1}$

$$\Delta S = 5.0\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$= 0.005\ \text{kJ K}^{-1}\ \text{mol}^{-1}$$
$$T = 17 + 273 = 290\ \text{K}$$

Applying
$$\Delta G = \Delta H - T\,\Delta S$$
$$= -12.55 - 0.005 \times 290$$
$$= -12.55 - 1.45 = -14.00\ \text{kJ mol}^{-1}$$

Since, ΔG is negative, the reaction will be spontaneous.

Example 77. *ΔH and ΔS for the system $H_2O\,(l) \rightleftharpoons H_2O(g)$ at 1 atmospheric pressure are 40.63 kJ mol $^{-1}$ and 108.8 J K $^{-1}$ mol $^{-1}$ respectively. Calculate the temperature at which the rates of forward and backward reactions will be the same. Predict the sign of free energy for this transformation above this temperature.*

Solution: Given, $\Delta H = 40.63\ \text{kJ mol}^{-1}$

$$\Delta S = 108.8\ \text{J K}^{-1}\ \text{mol}^{-1} = 0.1088\ \text{kJ K}^{-1}\ \text{mol}^{-1}$$

$\Delta G = 0$ (when the system is in equilibrium)

Applying
$$\Delta G = \Delta H - T\,\Delta S$$
$$0 = 40.63 - T \times 0.1088$$
$$T = \frac{40.63}{0.1088} = 373.4\ \text{K}$$

The sign of ΔG above 373 K, *i.e.*, say 374 K, may be calculated as follows:

Again applying
$$\Delta G = \Delta H - T\,\Delta S$$
$$= 40.63 - 374 \times 0.1088$$
$$= 40.63 - 40.69 = -0.06\ \text{kJ}$$

ΔG will be negative; hence, the reaction will be spontaneous.

Example 78. *For the reaction,*

$$SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl,$$

the enthalpy of reaction is 49.4 kJ and the entropy of reaction is $336\,J\ K^{-1}$. Calculate ΔG at 300 K and predict the nature of the reaction.

Solution:
$$\Delta G = \Delta H - T\,\Delta S$$
$$= 49.4 - (300 \times 336 \times 10^{-3})$$
$$= -51.4\ \text{kJ}$$

Since, the free energy change is negative, the given reaction is spontaneous.

Example 79. *The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below:*

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$
$$\Delta H^\circ_{300\,K} = -41.16\ kJ\ mol^{-1}$$
$$\Delta S^\circ_{300\,K} = -4.24 \times 10^{-2}\ kJ\ mol^{-1}$$
$$\Delta H^\circ_{1200\,K} = -32.93\ kJ\ mol^{-1}$$
$$\Delta S^\circ_{1200\,K} = -2.96 \times 10^{-2}\ kJ\ mol^{-1}$$

Calculate K_P at each temperature and predict the direction of reaction at 300 K and 1200 K, when $P_{CO} = P_{CO_2} = P_{H_2} = P_{H_2O} = 1$ atm at initial state.

Solution: At 300 K: $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$

$$= -41.16 - 300 \times (-4.24 \times 10^{-2})$$
$$= -28.44\ \text{kJ}$$

Since, ΔG° is negative hence reaction is spontaneous in forward direction,

$$\Delta G^\circ = -2.303\,RT \log K_P$$
$$-28.44 = -2.303 \times 8.314 \times 10^{-3} \times 300 \log K_P$$
$$K_P = 8.93 \times 10^4$$

At 1200 K: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= -32.93 - 1200(-2.96 \times 10^{-2}) = +2.59\ \text{kJ}$$

Positive value of ΔG° shows that the reaction is spontaneous in backward direction

$$\Delta G^\circ = -2.303\,RT \log K_P$$
$$2.59 = -2.303 \times 8.314 \times 10^{-3} \times 1200 \log K_P$$
$$K_P = 0.77$$

Example 80. *The standard Gibbs free energies for the reactions at 1773 K are given below:*

$$C(s) + O_2(g) \longrightarrow CO_2(g);\ \ \Delta G^\circ = -380\ kJ\ mol^{-1}$$
$$2C(s) + O_2(g) \rightleftharpoons 2CO(g);\ \ \Delta G^\circ = -500\ kJ\ mol^{-1}$$

Discuss the possibility of reducing Al_2O_3 and PbO with carbon at this temperature,

$$4Al + 3O_2(g) \longrightarrow 2Al_2O_3(s);\ \ \Delta G^\circ = -22500\ kJ\ mol^{-1}$$
$$2Pb + O_2(g) \longrightarrow 2PbO(s);\ \ \Delta G^\circ = -120\ kJ\ mol^{-1}$$

Solution: Let us consider the reduction of Al_2O_3 by carbon:

$$2\text{Al}_2\text{O}_3 + 3\text{C}(s) \longrightarrow 4\text{Al}(s) + 3\text{CO}_2(g);$$
$$\Delta G^\circ = -380 \times 3 + (22500) = +21360\ \text{kJ}$$
$$2\text{Al}_2\text{O}_3 + 6\text{C}(s) \longrightarrow 4\text{Al}(s) + 6\text{CO}(g);$$
$$\Delta G^\circ = -500 \times 3 + 22500 = +21000\ \text{kJ}$$

Positive values of ΔG° show that the reduction of Al_2O_3 is not possible by any of the above methods.

Now, let us consider the reduction of PbO.

$$2\text{PbO}(s) + \text{C} \longrightarrow 2\text{Pb} + \text{CO}_2;$$
$$\Delta G^\circ = +120 + (-380) = -260\ \text{kJ}$$
$$2\text{PbO}(s) + 2\text{C} \longrightarrow 2\text{Pb} + 2\text{CO};$$
$$\Delta G^\circ = +120 + (-500) = -380\ \text{kJ}$$

Negative value of ΔG° shows that the process is spontaneous and PbO can be reduced by carbon.

Example 81. *In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is:*

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Calculate standard Gibbs free energy change for the reaction that can be converted into electrical work. If standard enthalpy of combustion for methanol is $-726\,kJ\,mol^{-1}$; calculate the efficiency of conversion of Gibbs energy into useful work.

ΔG_f° for CO_2, H_2O, CH_3OH, O_2 are -394.36; -237.13; -166.27 and zero respectively.

Solution: The reaction for combustion of methanol is:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\begin{aligned}\Delta G^\circ_{\text{reaction}} &= [\Delta G_f^\circ\ CO_2(g) + 2\,\Delta G_f^\circ\ H_2O(l)] \\ &\quad - [\Delta G_f^\circ\ CH_3OH(l) + \frac{3}{2}\,\Delta G_f^\circ\ O_2(g)] \\ &= [-394.36 + 2(-237.13)] - [-166.27 + 0] \\ &= -702.35\ \text{kJ mol}^{-1}\end{aligned}$$

Efficiency of conversion of Gibbs free energy into useful work

$$= \frac{\Delta G^\circ_{\text{reaction}} \times 100}{\Delta H^\circ_{\text{reaction}}}$$

$$= \frac{-702.35 \times 100}{-726} = 96.7\%$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

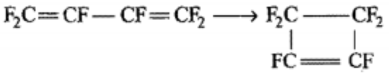
40. The free energy for a reaction having $\Delta H = 31400$ cal, $\Delta S = 32\ \text{cal K}^{-1}\ \text{mol}^{-1}$ at 1000°C is: **[JEE (Orissa) 2005]**

(a) –9336 cal (b) –7386 cal (c) –1936 cal (d) +9336 cal

[**Ans.** (a)]

[**Hint:** $\Delta G = \Delta H - T\,\Delta S = 31400 - 1273 \times 32 = -9336$ cal]

41.



For this reaction (ring closure), $\Delta H = -49\ \text{kJ mol}^{-1}$, $\Delta S = -40.2\ \text{J K}^{-1}\ \text{mol}^{-1}$. Upto what temperature is the forward reaction spontaneous?

(a) 1492°C (b) 1219°C (c) 946°C (d) 1080°C

[**Ans.** (c)]

[**Hint:** For spontaneous process,

$$\Delta G = \Delta H - T\,\Delta S \quad \text{(should be negative)}$$

$$\therefore \quad T > \frac{\Delta H}{\Delta S}$$

$$T > \frac{-49 \times 1000}{-40.2}$$

$$T > 1219\ \text{K},\ i.e.,\ 946^\circ\text{C}]$$

42. For the equilibrium reaction, the value of Gibbs free energy change is: **(DCE 2005)**

(a) > 0 (b) < 0 (c) = 0 (d) ≠ 0

[**Ans.** (c)]

[**Hint:** $\Delta G = 0$ at equilibrium]

43. At 0°C, ice and water are in equilibrium and $\Delta H = 6\,\text{kJ mol}^{-1}$. For this process:

$$H_2O(s) \rightleftharpoons H_2O(l)$$

The values of ΔS and ΔG for conversion of ice into liquid water at 0°C are:

(a) $-21.9\ \text{J K}^{-1}\ \text{mol}^{-1}$ and 0 (b) $0.219\ \text{J K}^{-1}\ \text{mol}^{-1}$ and 0

(c) $21.9\ \text{J K}^{-1}\ \text{mol}^{-1}$ and 0 (d) $0.0219\ \text{J K}^{-1}\ \text{mol}^{-1}$ and 0

[**Ans.** (c)]

[**Hint:** $\Delta G = 0$,

$$\therefore \quad \Delta H - T\Delta S = 0$$

$$\Delta S = \frac{\Delta H}{T} = \frac{6000}{273} = 21.9\ \text{J K}^{-1}\ \text{mol}^{-1}]$$

44. For a reaction:

$$Ag_2O(s) \rightleftharpoons 2Ag(s) + \frac{1}{2}O_2(g)$$

ΔH, ΔS and T are 40.63 kJ mol^{-1}; 108.8 J K^{-1} mol^{-1} and 373.4 K respectively. Predict the feasibility of the reaction.

(a) feasible (b) non-feasible

(c) remains at equilibrium (d) not predicted

[**Ans.** (c)]

[**Hint:** $\Delta G = \Delta H - T\,\Delta S$

$$= 40.63 \times 1000 - 373.4 \times 108.8 = 0]$$

45. For the homogeneous reactions:

$$xA + yB \longrightarrow lY + mZ$$

$\Delta H = -30\ \text{kJ mol}^{-1}$, $\Delta S = -100\ \text{J K}^{-1}\ \text{mol}^{-1}$.

At what temperature the reaction is at equilibrium? **[PMT (Kerala) 2006]**

(a) 50°C (b) 250°C (c) 100 K (d) 27°C

(e) 500 K

[**Ans.** (d)]

[**Hint:** $\Delta G = \Delta H - T\,\Delta S$

At equilibrium, $\Delta G = 0$

$$\therefore \quad T = \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{-100} = 300\ \text{K},\quad i.e.,\ 27^\circ\text{C}]$$

46. For the reaction $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$, ΔH and ΔS are -283 kJ and $-87\ \text{J K}^{-1}\ \text{mol}^{-1}$ respectively. It was intended to carry out this reaction at 1000, 1500, 3000 and 3500 K. At which of these temperatures would this reaction be thermodynamically spontaneous? **[PMT (Kerala) 2006]**

(a) 1500 and 3500 K (b) 3000 and 3500 K

(c) 1000, 1500 and 3000 K (d) 1500, 3000 and 3500 K

(e) At all of the above temperatures

[**Ans.** (c)]

[**Hint:** $\Delta G = \Delta H - T\,\Delta S$

At 1000 K, $\Delta G = -283 - (-1000 \times 0.087)$ (Spontaneous) $= -196$

At 1500 K, $\Delta G = -283 - (-1500 \times 0.087)$ (Spontaneous) $= -152.5$ kJ

At 3000 K, $\Delta G = -283 - (-3000 \times 0.087)$ (Spontaneous) $= -22$ kJ

At 3500 K, $\Delta G = -283 - (-3500 \times 0.087)$ (Non-spontaneous) $= +21.5$ kJ]

47. For a reaction,

$$\Delta H = +29\ \text{kJ mol}^{-1}; \quad \Delta S = -35\ \text{JK}^{-1}\ \text{mol}^{-1}$$

at what temperature, the reaction will be spontaneous? **[PMT (Haryana) 2007]**

(a) 828.7°C
(b) 828.7 K
(c) Spontaneous at all temperature
(d) Not possible

[**Ans.** (d)]

[**Hint:** $\Delta G = \Delta H - T\,\Delta S$

When $\Delta H = +$ ve, $\Delta S = -$ ve then ΔG will be positive and the reaction is non-spontaneous.]

7.28 STANDARD FREE ENERGY CHANGE

Just like enthalpy and internal energies, we cannot determine absolute value of *Gibbs free energy.* The standard free energy change can be determined and it is defined as *the free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted to products in their standard state.* It is denoted as $\Delta G°$; it can be related to standard enthalpy and entropy change in the following manner:

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

Like that of $\Delta H°$, $\Delta G°$ can be calculated from the standard free energies of formation of the products and the reactants.

$$\Delta G° = \Sigma G_f^\circ\ (\text{products}) - \Sigma G_f^\circ\ (\text{reactants})$$

$$= \begin{bmatrix}\text{Sum of standard free}\\ \text{energies of formation}\\ \text{of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of standard free}\\ \text{energies of formation}\\ \text{of reactants}\end{bmatrix}$$

Let us consider a general reaction:

$$n_1 A + n_2 B \longrightarrow n_3 L + n_4 M$$

$$\Delta G° = \Sigma G_f^\circ\ (\text{products}) - \Sigma G_f^\circ\ (\text{reactants})$$

$$= [n_3\,G_f^\circ(L) + n_4\,G_f^\circ(M)] - [n_1\,G_f^\circ(A) + n_2\,G_f^\circ(B)]$$

The standard free energy of formation (ΔG_f°) may be defined as *the free energy change when 1 mole of a compound is formed from its constituent elements in their standard state. The standard free energy of formation of an element in its standard state is assumed to be zero.*

Standard Gibbs Free Energy of Formation (kJ mol^{-1} at 298 K)

HCl	−95.27	C_4H_8 (*iso*-butene)	294
H_2O	−228.6	BaO	−528.4
H_2O_2	−103.3	$BaCO_3$	−1139
CO	−137.3	$BaSO_4$	−1465
CO_2	−394.4	CaO	−604.2
SO_2	−300.4	$Ca(OH)_2$	−896.6
SO_3	−370.4	$CaCO_3$	−1129
NO_2	51.84	CuO	−127
N_2O	104	NaCl	−384.0
NH_3	−16.6	KCl	−408.3
O_3	163.4	NH_4Cl	−203.0
NO	86.69	Al_2O_3	−1582.4
CH_4	−50.79	Fe_2O_3	−741.0
C_2H_6 (ethane)	229	ZnO	−318.2
C_3H_8 (propane)	270	SiO_2	−805
C_4H_{10} (*n*-butane)	310	PbO_2	−219
C_4H_{10} (*iso*-butane)	310	CH_3OH	−166.2
C_2H_2 (acetylene)	209.2	C_2H_5OH	−174.8
C_2H_4 (ethylene)	219.4	C_6H_6	−124.5
C_3H_6 (propylene)	266.9	CH_3COOH	−392
C_4H_8 (1-butene)	307.4		

Example 82. *Will the reaction,*

$$I_2(s) + H_2S(g) \longrightarrow 2HI(g) + S(s)$$

proceed spontaneously in the forward direction at 298 K, $\Delta G_f^\circ HI(g) = 1.8\ kJ\ mol^{-1}$, $\Delta G_f^\circ H_2S(g) = 33.8\ kJ\ mol^{-1}$?

Solution:

$$\Delta G° = \Sigma G_f^\circ(\text{products}) - \Sigma G_f^\circ(\text{reactants})$$

$$= [2G_f^\circ \text{HI}(g) + G_f^\circ \text{S}(s)] - [1 \times G_f^\circ \text{I}_2(s) + G_f^\circ \text{H}_2\text{S}(g)]$$

$$= [2 \times 1.8 + 0] - [0 + 33.8] = -30.2\ \text{kJ}$$

–ve value shows that the process is spontaneous in forward direction.

Example 83. *Compute the standard free energy of the reaction at 27° C for the combustion of methane using the given data:*

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Species	CH_4	O_2	CO_2	H_2O
$\Delta H_f^\circ\ /\ (kJ\ mol^{-1})$	−74.8	—	−393.5	−285.8
$S°/(J\ K^{-1}\ mol^{-1})$	186	205	214	70

Solution: $\Delta H° = \Delta H^\circ_{f\,(\text{CO}_2)} + 2\Delta H^\circ_{f\,(\text{H}_2\text{O})} - \Delta H^\circ_{f\,(\text{CH}_4)}$

$$= -393.5 + 2 \times (-285.8) - (-74.8)$$

$$= -890\ \text{kJ mol}^{-1}$$

$$\Delta S° = S^\circ_{(\text{CO}_2)} + 2S^\circ_{(\text{H}_2\text{O})} - S^\circ_{(\text{CH}_4)} - 2S^\circ_{(\text{O}_2)}$$

$$= 214 + 2 \times 70 - 186 - 2 \times 205$$

$$= -242\ \text{J K}^{-1}\text{mol}^{-1}$$

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

$$= -890 - 300 \times (-242 \times 10^{-3})$$

$$= -890 + 72.6 = -817.4\ \text{kJ mol}^{-1}$$

7.29 RELATIONSHIP BETWEEN STANDARD FREE ENERGY CHANGE ($\Delta G°$) AND EQUILIBRIUM CONSTANT

For any reversible reaction, $A + B \rightleftharpoons C + D$, the free energy change and standard free energy change are related with each other by the following relation:

$$\Delta G = \Delta G° + RT \log_e Q$$

where, R is universal constant; T is temperature and Q is reaction quotient $Q = \dfrac{[C][D]}{[A][B]}$.

At equilibrium state, $\Delta G = 0$ and $Q = K_{eq}$

$$0 = \Delta G° + RT \log_e K_{eq}$$

or $$\Delta G° = -RT \log_e K_{eq}$$

or $$\Delta G^\circ = -2.303RT \log K_{eq}$$

This equation helps in the calculation of K_{eq} if ΔG° of the reaction is known and *vice-versa*. The value of K_{eq} can give an idea about the extent of chemical reaction before the equilibrium is attained.

Alternatively,

$$K = e^{-\Delta G^\circ / RT}$$

Equilibrium constant of unity implies that standard free energy change ΔG° is zero and that the positive values of ΔG° implies the equilibrium constant to be less than unit.

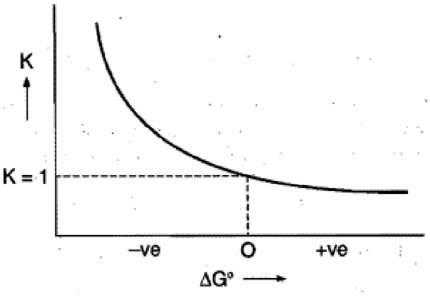


Fig. 7.21 Variation of equilibrium constant against standard free energy change

If we draw a graph of free energy against extent of reaction, we get U-shaped graph Fig. 7.22.

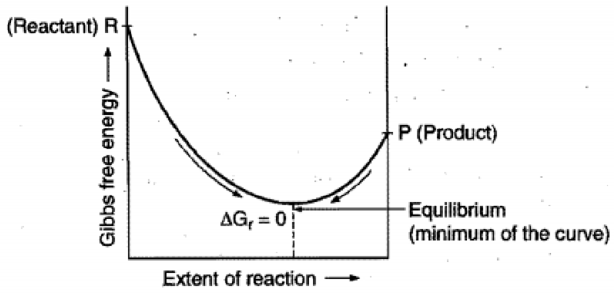


Fig. 7.22 Plot of free energy against extent of reaction

If the minimum in the curve lies closer to products, it means that reaction is in favour of products ($K >>> 1$). The reaction in this case will be closer to completion. On the other hand, if the minimum in the curve lies closer to the reactants, the reaction favours reactants ($K <<< 1$). The reaction in this case will be farthest from completion. (See. Fig. 7.23)

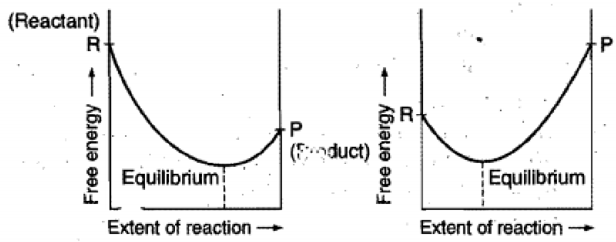


Fig. 7.23 Prediction of extent of reaction by the plot of free energy against extent of reaction

Example 84. *What is the equilibrium constant K_c for the following reaction at 400 K?*

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

$$\Delta H^\circ = 77.2\,kJ \text{ and } \Delta S^\circ = 122\,J\,K^{-1} \text{ at } 400\,K.$$

Solution: According to Gibbs-Helmholtz equation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= 77.2 - 400 \times 122 \times 10^{-3}$$
$$= 28.4 \text{ kJ} = 28.4 \times 10^3 \text{ J}$$

We know that, $\Delta G^\circ = -2.303RT \log K_c$

$$\therefore \quad \log K_c = \frac{-\Delta G^\circ}{2.303RT} = -\frac{28.4 \times 10^3}{2.303 \times 8.314 \times 400}$$
$$= -3.7081$$
$$K_c = \text{antilog } (-3.7081) = 1.958 \times 10^{-4}$$

Example 85. *For the equilibrium,*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \text{ at } 25^\circ C$$
$$K_c = 1.8 \times 10^{-7}$$

Calculate ΔG° for the reaction ($R = 8.314\,J\,K^{-1}\,mol^{-1}$).

Solution: We know that,

$$\Delta G^\circ = -2.303RT \log K_c$$
$$= -2.303 \times 8.314 \times 298 \log (1.8 \times 10^{-7})$$
$$= 38484 \text{ J mol}^{-1} = 38.484 \text{ kJ mol}^{-1}$$

Example 86. *The equilibrium constant at 25° C for the process:*

$$Co^{3+}(aq.) + 6NH_3(aq.) \rightleftharpoons [Co(NH_3)_6]^{3+}(aq.)$$

is 2×10^7.

Calculate the value of ΔG° at 25°C. ($R = 8.314\,J\,K^{-1}mol^{-1}$)

In which direction, the reaction is spontaneous when the reactants and products are in standard state?

Solution: We know that, $\Delta G^\circ = -2.303RT \log K_c$

Given, $K_c = 2 \times 10^7, T = 298\text{K}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Thus, from above equation,

$$\Delta G^\circ = -2.303 \times 8.314 \times 298 \log 2 \times 10^7$$
$$= -12023.4 \text{ J} = -12.023 \text{ kJ}$$

Example 87. *The equilibrium constant for the reaction,*

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \text{ at } 298\,K$$

is 73. Calculate the value of the standard free energy change ($R = 8314\,J\,K^{-1}\,mol^{-1}$).

Solution: We know that, $\Delta G^\circ = -2.303RT \log K_c$

Given, $K_c = 73, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T = 298 \text{ K}$

$\therefore$ From above equation,

$$\Delta G^\circ = -2.303 \times 8.314 \times 298 \log 73$$
$$= -10.632 \text{ kJ}$$

Example 88. *For the water gas reaction,*

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

the standard Gibbs free energy of reaction (at $1000\,K$) is -8.1 kJ/mol. Calculate its equilibrium constant.

Solution: We know that,

$$K = \text{antilog}\left(\frac{-\Delta G^\circ}{2.303RT}\right) \qquad \ldots \text{(i)}$$

Given that, $\Delta G^\circ = -8.1\,\text{kJ/mol}$

$R = 8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1}$

$T = 1000\,\text{K}$

Substituting these values in eq. (i), we get

$$K = \text{antilog}\left[\frac{-(-8.1)}{2.303 \times 8.314 \times 10^{-3} \times 1000}\right]$$

$$K = 2.65$$

Example 89. *Calculate ΔG° for the conversion of oxygen to ozone, $(3/2)O_2(g) \rightleftharpoons O_3(g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29}.*

Solution: We know that,

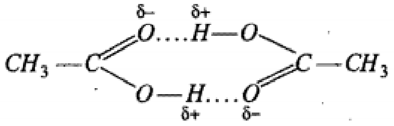
$$\Delta G^\circ = -2.303RT \log K_p$$

$$= -2.303 \times 8.314 \times 298 \log 2.47 \times 10^{-29}$$

$$= 163228\,\text{J/mol}$$

$$= 163.228\,\text{kJ/mol}$$

Example 90. *Acetic acid CH_3COOH can form a dimer $(CH_3COOH)_2$ in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5 kJ per mol of dimer*



If at 25° C, the equilibrium constant for the dimerization is 1.3×10^3. Calculate ΔS° for the reaction:

$$2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$$

Solution: $\Delta G^\circ = -2.303\,RT \log K$

$$= -2.303 \times 8.314 \times 298 \log (1.3 \times 10^3)$$

$$= -17767.688\,\text{J} = -17.767\,\text{kJ}$$

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

$$-17.767 = -66.5 - 298 \times \Delta S^\circ$$

$$\Delta S^\circ = \frac{-66.5 + 17.767}{298} = -0.163\,\text{kJ}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

48. What is ΔG° for this reaction?

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g);\ K_P = 4.42 \times 10^4 \text{ at } 25^\circ C$$

(a) -26.5 kJ mol^{-1} (b) -11.5 kJ mol^{-1}

(c) -2.2 kJ mol^{-1} (d) -0.97 kJ mol^{-1}

[Ans. (a)]

[Hint: $\Delta G^\circ = -2.303RT \log K_P$

$= -2.303 \times 8.314 \times 298 \log (4.42 \times 10^4)$

$= -26.5\ \text{kJ mol}^{-1}$]

49. What is the sign of ΔG° and the value of K for an electrochemical cell for which $E^\circ_{\text{cell}} = 0.80$ volt?

	ΔG°	K
(a)	$-$	> 1
(b)	$+$	> 1
(c)	$+$	< 1
(d)	$-$	< 1

[Ans. (a)]

[Hint: $\Delta G^\circ = -nFE^\circ$; $\Delta G^\circ = -2.303RT \log K$]

50. The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K?

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$$

(a) 8.4×10^{-5} (b) 7.1×10^{-9}

(c) 4.2×10^{-10} (d) 1.7×10^{-19}

[Ans. (a)]

[Hint: $K = \text{antilog}\left[\frac{-\Delta G^\circ}{2.303RT}\right]$

$= \text{antilog}\left[\frac{-78 \times 1000}{2.303 \times 8.314 \times 1000}\right]$

$= 8.4 \times 10^{-5}$]

51. Equilibrium constant for the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is $K_c = 50$ at 25°C.

The standard Gibbs free energy change for the reaction will be:

(a) -6.964 kJ (b) -9.694 kJ

(c) -4.964 kJ (d) -6.496 kJ

[Ans. (b)]

[Hint: $\Delta G^\circ = -2.303RT \log K_c$

$= -2.303 \times 8.314 \times 298 \log 50$

$= -9694\ \text{J} = -9.694\ \text{kJ}$]

52. Standard Gibbs free energy change ΔG° for a reaction is zero. The value of the equilibrium constant will be:

(a) 10 (b) 1 (c) 100 (d) ∞

[Ans. (b)]

[Hint: $\Delta G^\circ = -2.303RT \log K$

When $K = 1$, $\Delta G^\circ = 0$]

53. The standard free energy change of a reaction is $\Delta G^\circ = -115$ kJ at 298 K. Calculate the equilibrium constant K_P in $\log K_P$. ($R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$)

(a) 20.16 (b) 2.303 (c) 2.016 (d) 13.83

(VITEEE 2008)

[Ans. (a)]

[**Hint:** $\log K_P = \frac{-\Delta G^\circ}{2.303\,RT}$

$$= \frac{-(-115\times 1000)}{2.303\times 8.314\times 298}$$

$$= 20.16]$$

7.30 PHYSICAL SIGNIFICANCE OF GIBBS FREE ENERGY CHANGE (Free Energy and Useful Work)

According to first law of thermodynamics,

$$\Delta E = q - w \qquad \text{... (i)}$$

(–ve sign as the work is done by system)

Here, q is heat absorbed by the system and w is the work done by the system while ΔE is the change in internal energy. The work (w) actually includes two types of work, *i.e.*, $w_{\text{expansion}}$ (or $P\Delta V$) and $w_{\text{non-expansion}}$ (useful work). The two types of works can be understood by taking an example of the electrolysis of water to form $H_2(g)$ and $O_2(g)$ leading to an increase in the volume of the system. The work non-expansion (non-mechanical) is done to cause the decomposition of water while the work expansion (mechanical) is due to expansion in volume of the system. Thus, the electrical work is called non-pressure-volume work or non-expansion work or non-mechanical work. The non-expansion work is also known as useful work. Thus,

$$\Delta E = q - w_{\text{expansion}} - w_{\text{non-expansion}} \qquad \text{... (ii)}$$

$$= q - P\,\Delta V - w_{\text{non-expansion}} \qquad (\because w_{\text{expansion}} = P\,\Delta V)$$

or $$q = \Delta E + P\Delta V + w_{\text{non-expansion}} \qquad \text{... (iii)}$$

We know that,

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

or $$q = \Delta H + w_{\text{non-expansion}} \qquad \text{... (iv)}$$

According to second law of thermodynamics, for a reversible change taking place at constant temperature, T

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

or $$q_{\text{rev.}} = T\,\Delta S \qquad \text{... (v)}$$

Substituting in equation (iv)

$$T\,\Delta S = \Delta H + w_{\text{non-expansion}} \qquad \text{... (vi)}$$

or $$\Delta H - T\,\Delta S = -w_{\text{non-expansion}}$$

or $$\Delta G = -w_{\text{non-expansion}} \qquad (\because \Delta H - T\,\Delta S = \Delta G)$$

or $$-\Delta G = w_{\text{non-expansion}} = w_{\text{useful work}} \qquad \text{... (vii)}$$

Thus, *the decrease in Gibbs free energy is a measure of useful work or non-expansion work done by the system.* The greater the free energy change, the greater is the amount of work that can be obtained from the process. This relation is useful in assessing the electrical work that may be produced by electrochemical cells and fuel cells.

Free Energy Change and Electrical Work Done in a Cell

Free energy change in electrochemical cells is related to the electrical work done in the cell.

ΔG and emf of the cell (E) are related by the following relation:

$$\Delta G = -nFE$$

where, F = faraday = 96500 coulomb

E = emf of the cell

n = Number of moles of electrons involved in balanced electrochemical reaction

If the reactants and products are in their standard states, then

$$\Delta G^\circ = -nFE^\circ$$

when E° = standard emf of the cell.

Example 91. *The emf of the cell reaction,*

$$Zn(s) + Cu^{2+}(aq.) \longrightarrow Zn^{2+}(aq.) + Cu(s)$$

is 1.1 V. Calculate free energy change for the reaction. If enthalpy of the reaction is – 216.7 kJ mol^{-1}, calculate the entropy change for the reaction.

Solution: $-\Delta G^\circ = n\times F\times E^\circ = 2\times 96500\times 1.1 = 212.3$ kJ

$$\Delta G^\circ = -212.3 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-216.7-(-212.3)}{298}$$

$$= -0.01476 \text{ kJ K}^{-1}\text{ mol}^{-1}$$

$$= -14.76 \text{ J K}^{-1}\text{ mol}^{-1}$$

Example 92. *Calculate equilibrium constant for the following reaction:*

$$Cu(s) + 2Ag^{+}(aq.) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$$

At 25°C, $E^\circ_{cell} = 0.47$ volt, $R = 8.314\,J\,K^{-1}\,mol^{-1}$, $F = 96500$ coulomb.

Solution: Let us apply Nernst equation at equilibrium

$$E^\circ_{\text{cell}} = \frac{0.0591}{n}\log K_c$$

$$0.47 = \frac{0.0591}{2}\log K_c$$

$$K_c = \text{antilog}\left[\frac{0.47\times 2}{0.0591}\right]$$

$$= 8.5\times 10^{15}$$

7.31 ABSOLUTE ENTROPIES AND THIRD LAW OF THERMODYNAMICS

Third law of Thermodynamics was given by T.W. Richards, Walter Nernst and Max Planck. Some statements for third law of thermodynamics are given below:

Statement-1. *"Every substance has a finite positive entropy but at the absolute zero temperature the entropy may become zero and does so become in the case of perfectly crystalline solids."*

Because

Statement-2. *"Entropy of a solid or liquid approaches zero at the absolute zero of temperature."*

It can be mathematically expressed as

$$\lim_{T \to 0\,\text{K}} S \to 0$$

Because

Statement-3. *"It is impossible by any method, no matter how idealised it is, to reduce the temperature of any system to the absolute zero in a finite number of operations."*

Application of Third Law of Thermodynamics

The third law of thermodynamics has been useful in calculating the absolute entropies of solids, liquids and gases at different temperatures. Moreover, this law is also useful to calculate entropy changes of a chemical or physical process. Let us calculate absolute entropy.

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

$$dS = C_P \frac{dT}{T}$$

On integrating the above equation between temperature limits of 0 and T K, we get

$$S_T - S_0 = \int_0^T C_P \frac{dT}{T}$$

or $$S_T - S_0 = \int_0^T C_P \, d \ln T$$

From third law of thermodynamics, $S_0 = 0$

$$\therefore \quad S_T = \int_0^T C_P \, d \ln T$$

When entropy of one mole of a substance is expressed at 298 *K and* 1 *atm pressure, it is called* **standard entropy** *of that substance.* It is denoted by $S°$. The standard entropy change $\Delta S°$ for a chemical reaction can be calculated as

$$\Delta S° = \Sigma S°_{(\text{products})} - \Sigma S°_{(\text{reactants})}$$

$$= \begin{bmatrix}\text{Sum of the standard} \\ \text{entropies of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard} \\ \text{entropies of reactants}\end{bmatrix}$$

e.g., in the reaction:

$$C_2H_6(g) \longrightarrow H_2(g) + C_2H_4(g)$$

$$\Delta S° = \Sigma S°_{(\text{products})} - \Sigma S°_{(\text{reactants})}$$

$$= [S°_{H_2} + S°_{C_2H_4}] - [S°_{C_2H_6}]$$

Standard molar entropies in J/K mol at 298 K

Solids	Entropy	Solids	Entropy
C (graphite)	5.7	N_2	191.6
C (diamond)	2.4	O_2	205.1
Fe	27.3	CO_2	213.7
Pb	64.8	NO_2	240.1
Cu	33.1	N_2O_4	304.3
Al	96.2	NH_3	192.3
Fe_2O_3	87.4	CH_4	186.2
$CuSO_4 \cdot 5H_2O$	300.4	Hg	76.0
$C_{12}H_{22}O_{11}$ (sucrose)	360.8	H_2O	69.9
CaO	39.8	C_2H_5OH	160.7
$CaCO_3$ (calcite)	92.9	C_6H_6	173.3
H_2	130.7	CH_3COOH	159.8

Tephigraph

Graph of entropy of a substance against temperature is called tephigraph. In the following graph variation of entropy with temperature is represented:

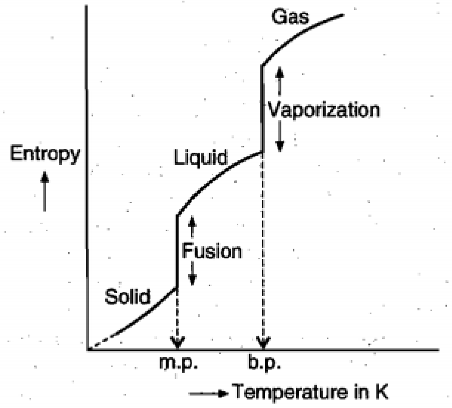


Fig. 7.24

From the graph it is clear that entropy of a substance increases with increase in temperature; there is sudden change in entropy at the stage of phase transformation.

Example 93. *Calculate* $\Delta G°$ *for the following reaction:*

$$CO(g) + (\frac{1}{2})O_2(g) \longrightarrow CO_2(g); \; \Delta H° = -282.84 \, kJ$$

Given,

$S°_{CO_2} = 213.8 \, J \, K^{-1} \, mol^{-1}$, $S°_{CO(g)} = 197.9 \, J \, K^{-1} \, mol^{-1}$, $S°_{O_2} = 205.0 \, J \, K^{-1} \, mol^{-1}$.

Solution: $\Delta S° = \Sigma S°_{(\text{products})} - \Sigma S°_{(\text{reactants})}$

$$= [S°_{CO_2}] - [S°_{CO} + \frac{1}{2} S°_{O_2}]$$

$$= 213.8 - [197.9 + \frac{1}{2} 205]$$

$$= -86.6 \, \text{J K}^{-1}$$

According to Gibbs-Helmholtz equation,

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

$$= -282.84 - 298 \times (-86.6 \times 10^{-3})$$

$$= -282.84 + 25.807$$

$$= -257.033 \, \text{kJ}$$

Example 94. *For the reaction;*

$$A(s) \longrightarrow B(s) + C(s)$$

calculate the entropy change at 298 K and 1 atm if absolute entropies (in $J \, K^{-1} \, mol^{-1}$*) are:*

$$A = 130, B = 203, C = 152$$

Solution: $\Delta S^\circ = \Sigma S^\circ_{\text{(products)}} - \Sigma S^\circ_{\text{(reactants)}}$

$$= [S^\circ_B + S^\circ_C] - [S^\circ_A]$$

$$= [203 + 152] - [130]$$

$$= 225\ \text{J K}^{-1}$$

7.32 CONVERSION OF HEAT INTO WORK—THE CARNOT CYCLE

Carnot, a French engineer, in 1824, employed merely theoretical and an imaginary reversible cycle known as Carnot cycle to demonstrate the maximum convertibility of heat into work.

The system consists of one mole of an ideal gas enclosed in a cylinder fitted with a piston which is subjected to a series of four successive operations. The four operations are:

(i) Isothermal reversible expansion
(ii) Adiabatic reversible expansion
(iii) Isothermal reversible compression
(iv) Adiabatic reversible compression

The four operations have been shown in Fig. 7.25.

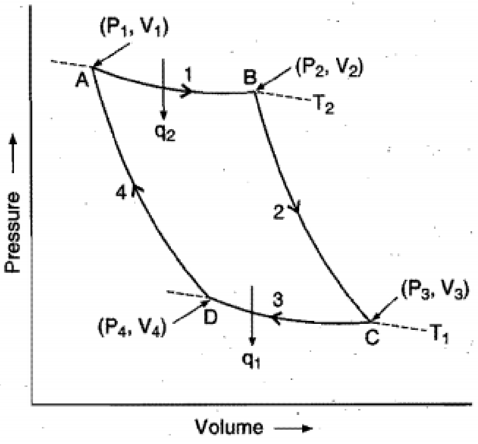


Fig. 7.25

First operation—Isothermal reversible expansion

The gas is allowed to expand reversibly and isothermally at the temperature T_2 through AB path. The volume V_1 (point A) increases to volume V_2 (point B). In this operation, let the heat absorbed by the system be q_2 (+ve) and the work done by the system on the surroundings be w_1 (−ve).

Since, the expansion is isothermal, $\Delta E = 0$. The heat absorbed, q_2, should be equal to the work done by the system on the surroundings, *i.e.*,

$$q_2 = -w_1 = RT_2 \log_e \frac{V_2}{V_1} \qquad \text{... (i)}$$

Second operation—Adiabatic reversible expansion

The gas is now allowed to expand reversibly and adiabatically through BC path. The volume increases from V_2 (point B) to volume V_3 (point C). In this operation, no heat is absorbed and thus, the work, w_2, is done by the system at the expense of internal energy, *i.e.*, the temperature of the system falls from temperature T_2 to temperature T_1.

$$\Delta E = -w_2 = -C_V (T_2 - T_1) \qquad \text{... (ii)}$$

Third operation—Isothermal reversible compression

The gas at point C is subjected to reversible isothermal compression at temperature T_1. The path followed is CD when the volume decreases from V_3 to V_4 (point D). In this operation work is done on the system and heat q_1 is given out by the system to surroundings.

$$-q_1 = w_3 = RT_1 \log_e \frac{V_4}{V_3} \qquad \text{... (iii)}$$

Fourth operation—Adiabatic reversible compression

Finally, the gas at point D is subjected to reversible adiabatic compression through the path DA at temperature T_1. The volume changes from V_4 to V_1, *i.e.*, the original volume is restored. The temperature increases from T_1 to T_2 (original temperature). The work done increases the internal energy of the system as $q = 0$.

$$w_4 = C_V (T_2 - T_1) \qquad \text{... (iv)}$$

The net heat absorbed, q, by the ideal gas in the cycle is given by

$$q = q_2 + (-q_1) = RT_2 \log_e \frac{V_2}{V_1} + RT_1 \log_e \frac{V_4}{V_3}$$

$$= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} \qquad \text{... (v)}$$

According to the expression governing adiabatic changes,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma - 1} \qquad \text{(For adiabatic expansion)}$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_4}\right)^{\gamma - 1} \qquad \text{(For adiabatic compression)}$$

or $$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

or $$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substituting the value of $\frac{V_3}{V_4}$ in eq. (v),

$$q = q_2 - q_1 = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1}$$

$$= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \qquad \text{... (vi)}$$

Similarly, net work done by the gas is given by

$$w = -w_1 - w_2 + w_3 + w_4$$

$$= RT_2 \log_e \frac{V_2}{V_1} - C_V (T_2 - T_1) + RT_1 \log_e \frac{V_4}{V_3} - C_V (T_2 - T_1)$$

$$= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4}$$

$$= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1}$$

$$= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \qquad \text{... (vii)}$$

Thus, $q = w$. For cyclic process, the essential condition is that net work done is equal to heat absorbed. This condition is satisfied in a Carnot cycle.

Calculation of thermodynamic efficiency of Carnot engine

Total work done from eq. (vii),

$$w = R(T_2 - T_1) \log_e \frac{V_2}{V_1}$$

and the heat absorbed at temperature T_2 from eq. (i),

$$q_2 = RT_2 \log_e \frac{V_2}{V_1}$$

Dividing both equations,

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = \text{Thermodynamic efficiency}$$

Thus, the larger the temperature difference between high and low temperature reservoirs, the more the heat converted into work by the heat engine.

Since, $\frac{T_2 - T_1}{T_2} < 1$, it follows that $w < q_2$. This means that only a part of heat absorbed by the system at the higher temperature is transformed into work. The rest of the heat is given out to surroundings. The efficiency of the heat engine is always less than 1. This has led to the following enunciation of the second law of thermodynamics.

It is impossible to convert heat into work without compensation.

Example 95. *Calculate the maximum efficiency of an engine operating between* $100°C$ *and* $25°C$.

Solution: Efficiency $= \frac{T_2 - T_1}{T_2}$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$\text{Efficiency} = \frac{373 - 298}{373} = \frac{75}{373} = 0.20 = 20\%$$

Example 96. *Heat supplied to a Carnot engine is* 453.6 *kcal. How much useful work can be done by the engine which works between* $10°C$ *and* $100°C$?

Solution: $T_2 = 100 + 273 = 373$ K; $T_1 = 10 + 273 = 283$ K;

$$q_2 = 453.6 \times 4.184 = 1897.86 \text{ kJ}$$

We know that,

$$w = q_2 \cdot \frac{T_2 - T_1}{T_2}$$

$$= 1897.86 \times \frac{(373 - 283)}{373}$$

$$= \frac{1897.86 \times 90}{373} = 457.92 \text{ kJ}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

54. For which of the following reactions, the entropy change will be positive? **[JEE (WB) 2008]**

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(b) $HCl(g) + NH_3(g) \rightleftharpoons NH_4Cl(s)$

(c) $NH_4NO_3(s) \rightleftharpoons N_2O(g) + 2H_2O(g)$

(d) $MgO(s) + H_2(g) \rightleftharpoons Mg(s) + H_2O(l)$

[Ans. (c)]

[Hint: $\Delta n_g = 3 - 0 = 3$,

Since $\Delta n_g > 0$, there will be increase in entropy change.]

55. If an endothermic reaction occurs spontaneously at constant temperature T and pressure P, then which of the following is true? **(VITEEE 2008)**

(a) $\Delta G > 0$ (b) $\Delta H < 0$ (c) $\Delta S > 0$ (d) $\Delta S < 0$

[Ans. (c)]

[Hint: $\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$\Delta S > 0$ for spontaneous process.]

56. Which is the correct expression that relates changes of entropy with the change of pressure for an ideal gas at constant temperature, among the following? **[PET (MP) 2008]**

(a) $\Delta S = nRT \ln \frac{P_2}{P_1}$ (b) $\Delta S = T(P_2 - P_1)$

(c) $\Delta S = nR \ln \left(\frac{P_1}{P_2}\right)$ (d) $\Delta S = 2.303\, nRT \ln \left(\frac{P_1}{P_2}\right)$

[Ans. (c)]

[Hint: From first law, $\Delta U = q - W$

$$0 = q - W \quad \text{(for isothermal process)}$$

$$q = W = PdV$$

$$dS = \frac{q}{T} = \frac{PdV}{T}$$

$$dS = nR\frac{dV}{V}$$

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

$\Delta S = nR \ln \left(\frac{P_1}{P_2}\right)$. Since $P_1V_1 = P_2V_2$ according to Boyle's law.]