

## THERMODYNAMICS



Classical thermodynamics... is the only physical theory of universal physical theory of universal content which I am convinced... will never be overthrown.

Albert Einstein



Rudolf Clausius  
(1822-1888)

### Learning Objectives:

After studying this unit, students will be able to

- distinguish between the system and surroundings
- define closed, open and isolated systems
- distinguish between state and path functions
- describe the relation between internal energy, work and heat
- state four laws of thermodynamics
- correlate internal energy change ( $\Delta U$ ) and enthalpy change ( $\Delta H$ ) and their measurement.
- calculate enthalpy changes for various types of reactions
- apply Hess's law to calculate lattice energy of crystals
- define spontaneous and non spontaneous processes
- establish the relationship between thermodynamic state functions enthalpy ( $H$ ), entropy ( $S$ ) and Gibbs free energy ( $G$ )
- list the factors that determines spontaneity of the process
- establish the link between  $\Delta G$  and spontaneity, and the relationship between  $\Delta G^0$  and equilibrium constant

## 7.1 Introduction

The term 'Thermodynamics' means flow of heat and is derived from the Greek 'Thermos' (heat) and 'dynamics' (flow). In our daily life, we come across many useful reactions such as burning of fuel to produce heat energy, flow of electrons through circuit to produce electrical energy, metabolic reactions to produce the necessary energy for biological functions and so on. Thermodynamics, the study of the transformation of energy, explains all such processes quantitatively and allows us to make useful predictions.

In the 19<sup>th</sup> century, scientists tried to understand the underlying principles of steam engine which were already in operation, in order to improve their efficiency. The basic problem of the investigation was the transformation of heat into mechanical work. However, over time, the laws of thermodynamics were developed and helped to understand the process of steam engine. These laws have been used to deduce powerful mathematical relationships applicable to a broad range of processes.

Thermodynamics evaluates the macroscopic properties (heat, work) and their inter relationships. It deals with properties of systems in equilibrium and is independent of any theories or properties of the individual molecules which constitute the system.

The principles of thermodynamics are based on three laws of thermodynamics. The first two laws (First and second law) summarise the actual experience of inter

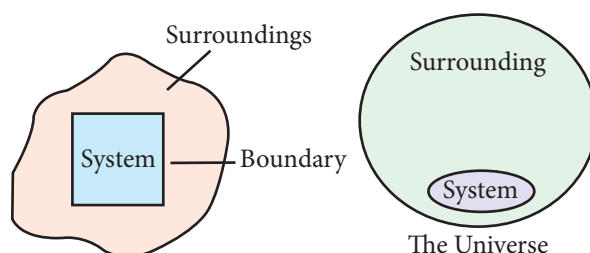
conversion of different forms of energy. The third law deals with the calculation of entropy and the unattainability of absolute zero Kelvin. Thermodynamics carries high practical values but bears certain limitations. It is independent of atomic and molecular structure and reaction mechanism. The laws can be used to predict whether a particular reaction is feasible or not under a given set of conditions, but they cannot give the rate at which the reaction takes place. In other words, thermodynamics deals with equilibrium conditions quantitatively, but does not take into account the kinetic approach to the equilibrium state.

## 7.2 System and Surrounding

Before studying the laws of thermodynamics and their applications, it is important to understand the meaning of a few terms used frequently in thermodynamics.

### System:

The universe is divided into two parts, the system and its surroundings. The system is the part of universe which is under thermodynamic consideration. It is separated from the rest of the universe by real or imaginary boundaries.



**Figure 7.1 System, surrounding & boundary Homogeneous and heterogeneous systems**

### Example:

The system may be water in a beaker, a balloon filled with air, an aqueous solution of glucose etc.

On the basis of physical and chemical properties, systems can be divided into two types.

A system is called homogeneous if the physical state of all its constituents are the same. Example: a mixture of gases, completely miscible mixture of liquids etc.

A system is called heterogeneous, if physical state of all its constituents is not the same.

Example: mixture of oil and water

### Surrounding:

Everything in the universe that is not the part of the system is called surroundings.

### Boundary:

Anything which separates the system from its surrounding is called boundary.

#### 7.2.1 Types of systems:

There are three types of thermodynamic systems depending on the nature of the boundary.

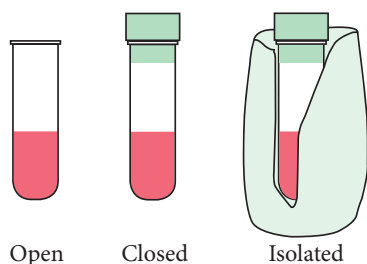


Figure 7.2 Types of Systems

### Isolated system:

A system which can exchange neither matter nor energy with its surroundings is called an isolated system. Here boundary is sealed and insulated. Hot water contained in a thermos flask, is an example for an isolated system. In this isolated system both energy (heat) and matter (water vapour) neither enter nor leave the system.

### Closed system:

A system which can exchange only energy but not matter with its surroundings is called a closed system. Here the boundary is sealed but not insulated. Hot water contained in a closed beaker is an example for a closed system. In this system energy (heat) is transferred to the surroundings but no matter (water vapour) can escape from this system. A gas contained in a cylinder fitted with a piston constitutes a closed system.

### Open system:

A System which can exchange both matter and energy with its surrounding is called an open system. Hot water contained in an open beaker is an example for open system. In this system both matter (water vapour) and energy (heat) is transferred to the surrounding.

All living things and chemical reactions are open systems because they exchange matter and energy with the surroundings.

## 7.2.2 Properties of the system:

### Intensive and extensive properties

Some of the properties of a system depend on its mass or size whereas other properties do not depend on its mass or size. Based on this, the properties of a system are grouped as *extensive* property and *intensive* property.

#### Extensive properties:

The property that depends on the mass or the size of the system is called an extensive property.

**Examples:** Volume, Number of moles, Mass, Internal energy, etc.,

#### Intensive properties:

The property that is independent of the mass or the size of the system is called an intensive property.

**Examples :** Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

**Table: 7.1 Typical List of Extensive and Intensive properties**

Extensive properties	Intensive properties
volume, mass, amount of substance (mole), energy, enthalpy, entropy, free energy, heat capacity	molar volume, density, molar mass, molarity, mole fraction, molality, specific heat capacity

## 7.2.3 Thermodynamic processes

The method of operation which can bring about a change in the system is called thermodynamic process. Heating, cooling, expansion, compression, fusion, vaporization etc., are some examples of a thermodynamic process.

### Types of processes:

A thermodynamic process can be carried out in different ways and under different conditions. The processes can be classified as follows:

#### Reversible process:

The process in which the system and surrounding can be restored to the initial state from the final state without producing any changes in the thermodynamic properties of the universe is called a reversible process. There are two important conditions for the reversible process to occur. Firstly, the process should occur infinitesimally slowly and secondly throughout the process, the system and surroundings must be in equilibrium with each other.

#### Irreversible Process:

The process in which the system and surrounding cannot be restored to the initial state from the final state is called an irreversible process. All the processes occurring in nature are irreversible processes. During the irreversible process the system and surroundings are not in equilibrium with each other.

### Adiabatic process:

An adiabatic process is defined as one in which there is no exchange of heat ( $q$ ) between the system and surrounding during the process. Those processes in which no heat can flow into or out of the system are called **adiabatic processes**. This condition is attained by thermally insulating the system. In an adiabatic process if work is done by the system its temperature decreases, if work is done on the system its temperature increases, because, the system cannot exchange heat with its surroundings.

For an adiabatic process  $q = 0$

### Isothermal process :

An isothermal process is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. The system exchanges heat with its surrounding and the temperature of the system remains constant. For this purpose the experiment is often performed in a thermostat.

For an isothermal process  $dT = 0$

### Isobaric process

An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

For an isobaric process  $dP = 0$ .

### Isochoric process

An isochoric process is defined as

the one in which the volume of system remains constant during its change from initial to final state. Combustion of a fuel in a bomb calorimeter is an example of an isochoric process.

For an isochoric process,  $dV = 0$ .

### Cyclic process:

When a system returns to its original state after completing a series of changes, then it is said that a cycle is completed. This process is known as a cyclic process.

For a cyclic process  $dU = 0$ ,  $dH = 0$ ,  $dP = 0$ ,  $dV = 0$ ,  $dT = 0$

**Table: 7.2 Overview of the process and its condition**

Process	Condition
Adiabatic	$q = 0$
Isothermal	$dT = 0$
Isobaric	$dP = 0$
Isochoric	$dV = 0$
Cyclic	$dE = 0$ , $dH = 0$ , $dP = 0$ , $dV = 0$ , $dT = 0$

### State functions, path functions:

#### State function

A thermodynamic system can be defined by using the variables  $P$ ,  $V$ ,  $T$  and  $n$ . A state function is a thermodynamic property of a system, which has a specific value for a given state and does not depend on the path (or manner) by which the particular state is reached.

**Example :** Pressure (P), Volume (V), Temperature(T), Internal energy (U), Enthalpy (H), free energy (G) etc.

### Path functions:

A path function is a thermodynamic property of the system whose value depends on the path by which the system changes from its initial to final states.

**Example: Work ( $w$ ), Heat ( $q$ ).**

Work ( $w$ ) will have different values if the process is carried out reversibly or irreversibly.

### Internal Energy (U)

The internal energy is a characteristic property of a system which is denoted by the symbol U. The internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The total energy of all molecules in a system is equal to the sum of their translational energy ( $U_t$ ), vibrational energy ( $U_v$ ), rotational energy ( $U_r$ ), bond energy ( $U_b$ ), electronic energy ( $U_e$ ) and energy due to molecular interactions ( $U_i$ ).

### Thus:

$$U = U_t + U_v + U_r + U_b + U_e + U_i$$

The total energy of all the molecules of the system is called internal energy. In thermodynamics one is concerned only with the change in internal energy ( $\Delta U$ ) rather than the absolute value of energy.

### Importance of Internal energy

The internal energy possessed by a substance differentiates its physical structure. For example, the allotropes of carbon, namely, graphite C(graphite) and diamond C(diamond), differ from each other because they possess different internal energies and have different structures.

### Characteristics of internal energy (U):

- The internal energy of a system is an extensive property. It depends on the amount of the substances present in the system. If the amount is doubled, the internal energy is also doubled.
- The internal energy of a system is a state function. It depends only upon the state variables (T, P, V, n) of the system. The change in internal energy does not depend on the path by which the final state is reached.
- The change in internal energy of a system is expressed as  $\Delta U = U_f - U_i$
- In a cyclic process, there is no internal energy change.  $\Delta U_{(cyclic)} = 0$
- If the internal energy of the system in the final state ( $U_f$ ) is less than the internal energy of the system in its initial state ( $U_i$ ), then  $\Delta U$  would be negative.  
$$\Delta U = U_f - U_i = -ve \quad (U_f < U_i)$$
- If the internal energy of the system in the final state ( $U_f$ ) is greater than the internal energy of the system in its initial state ( $U_i$ ), then  $\Delta U$  would be positive.  
$$\Delta U = U_f - U_i = +ve \quad (U_f > U_i)$$

## HEAT( $q$ )

The heat ( $q$ ) is regarded as an energy in transit across the boundary separating a system from its surrounding. Heat changes lead to temperature differences between system and surrounding. Heat is a path function.

### Units of heat:

The SI unit of heat is joule (J). Heat quantities are generally measured in calories (cal). A calorie is defined as the quantity of heat required to raise the temperature of 1 gram of water by  $1^{\circ}\text{C}$  in the vicinity of  $15^{\circ}\text{C}$ .

### Sign convention of heat:

The symbol of heat is  $q$ .

If heat flows into the system from the surrounding, energy of a system increases. Hence it is taken to be positive (+ $q$ ).

If heat flows out of the system into the surrounding, energy of the system decreases. Hence, it is taken to be negative (- $q$ ).

## Work( $w$ )

Work is defined as the force ( $F$ ) multiplied by the displacement( $x$ ).

$$-w = F \cdot x \quad \text{-----(7.1)}$$

The negative sign (-) is introduced to indicate that the work has been done by the system by spending a part of its internal energy.

The work,

- (i) is a path function.
- (ii) appears only at the boundary of the system.
- (iii) appears during the change in the state of the system.
- (iv) In thermodynamics, surroundings is so large that macroscopic changes to surroundings do not happen.

### Units of work:

The SI unit of work is joule (J), which is defined as the work done by a force of one Newton through a displacement of one meter ( $J = \text{Nm}$ ). We often use kilojoule ( $\text{kJ}$ ) for large quantities of work.  $1 \text{ kJ} = 1000 \text{ J}$ .

### Sign convention of work:

The symbol of work is ' $w$ '.

If work is done by the system, the energy of the system decreases, hence by convention, work is taken to be negative (- $w$ ).

If work is done on the system, the energy of the system increases, hence by convention, the work is taken to be positive (+ $w$ ).

### Pressure - volume work

In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as pressure-volume work, PV work or expansion work.

**Work involved in expansion and compression processes:**

In most thermodynamic calculations we are dealing with the evaluation of work involved in the expansion or compression of gases. The essential condition for expansion or compression of a system is that there should be difference between external pressure ( $P_{ext}$ ) and internal pressure ( $P_{int}$ ).

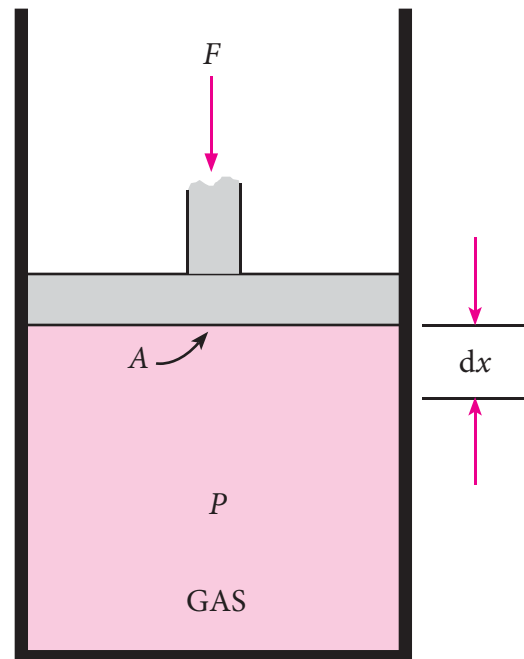
For understanding pressure-volume work, let us consider a cylinder which contains 'n' moles of an ideal gas fitted with a frictionless piston of cross sectional area A. The total volume of the gas inside is  $V_i$  and pressure of the gas inside is  $P_{int}$ .

If the external pressure  $P_{ext}$  is greater than  $P_{int}$ , the piston moves inward till the pressure inside becomes equal to  $P_{ext}$ . Let this change be achieved in a single step and the final volume be  $V_f$ .

In this case, the work is done on the system (+w). It can be calculated as follows

$$w = -F \cdot \Delta x \text{ ----- (7.2)}$$

where dx is the distance moved by the piston during the compression and F is the force acting on the gas.



**Figure 7.3 showing work involved in compression processes**

$$F = P_{ext} A \text{ ---- (7.3)}$$

*Substituting 7.3 in 7.2*

$$w = - P_{ext} \cdot A \cdot \Delta x$$

$$A \cdot \Delta x = \text{change in volume} = V_f - V_i$$

$$w = - P_{ext} \cdot (V_f - V_i) \text{ ----- (7.4)}$$

$$w = - P_{ext} \cdot (-\Delta V) \text{ ----- (7.5)}$$

$$= P_{ext} \cdot \Delta V$$

Since work is done on the system, it is a positive quantity.

If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation



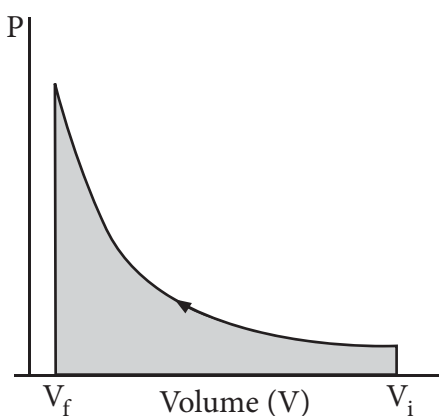
$$w_{rev} = - \int_{V_i}^{V_f} P_{ext} dV$$

In a compression process,  $P_{ext}$  the external pressure is always greater than the pressure of the system.

$$\text{i.e. } P_{ext} = (P_{int} + dP).$$

In an expansion process, the external pressure is always less than the pressure of the system

$$\text{i.e. } P_{ext} = (P_{int} - dP).$$



**Figure 7.4**

When pressure is not constant and changes in infinitesimally small steps (reversible conditions) during compression from  $V_i$  to  $V_f$ , the P-V plot looks like in fig 7.4 Work done on the gas is represented by the shaded area.

In general case we can write,

$P_{ext} = (P_{int} \pm dP)$ . Such processes are called reversible processes. For a compression process work can be related to internal pressure of the system under reversible conditions by writing equation

$$w_{rev} = - \int_{V_i}^{V_f} P_{int} dV$$

For a given system with an ideal gas

$$P_{int} V = nRT$$

$$P_{int} = \frac{nRT}{V}$$

$$w_{rev} = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$w_{rev} = - nRT \int_{V_i}^{V_f} \left( \frac{dV}{V} \right)$$

$$w_{rev} = - nRT \ln \left( \frac{V_f}{V_i} \right)$$

$$w_{rev} = - 2.303 nRT \log \left( \frac{V_f}{V_i} \right) \text{ ----- 7.6}$$

If  $V_f > V_i$  (expansion), the sign of work done by the process is negative.

If  $V_f < V_i$  (compression) the sign of work done on the process is positive.

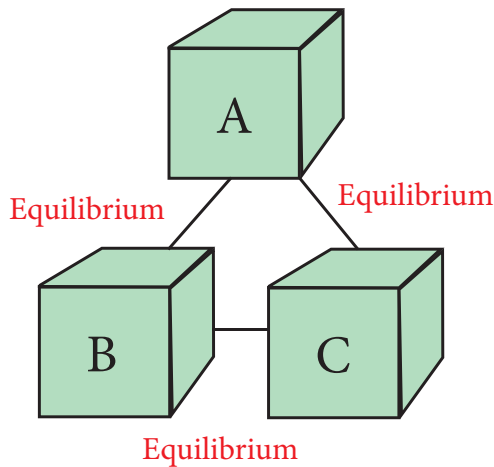
**Table: 7.3 Summary of sign conventions**

1.	If heat is absorbed by the system	:	$+q$
2.	If heat is evolved by the system	:	$-q$
3.	work is done by the system	:	$-w$
4.	work is done on the system	:	$+w$

### 7.3 Zeroth law of thermodynamics:

The zeroth law of thermodynamics, also known as the law of thermal equilibrium, was put forward much after the establishment of the first and second laws of thermodynamics. It is placed

before the first and second laws as it provides a logical basis for the concept of temperature of the system.



**Figure : 7.5 Zeroth law of thermodynamics:**

The law states that 'If two systems are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.

According to this law, if systems B and C separately are in thermal equilibrium with another system A, then systems B and C will also be in thermal equilibrium with each other. This is also the principle by which thermometers are used.

#### 7.4 First Law of Thermodynamics:

The first law of thermodynamics, known as the law of conservation of energy, states that the total energy of an isolated system remains constant though it may change from one form to another.

When a system moves from state 1 to state 2, its internal energy changes from  $U_1$  to  $U_2$ . Then change in internal energy

$$\Delta U = U_2 - U_1.$$

This internal energy change is brought about by the either absorption or evolution of heat and/or by work being done by/on the system.

Because the total energy of the system must remain constant, we can write the mathematical statement of the First Law as:

$$\Delta U = q + w \text{ -----(7.7)}$$

Where q - the amount of heat supplied to the system; w - work done on the system

Other statements of first law of thermodynamics

- (1) Whenever an energy of a particular type disappears, an equivalent amount of another type must be produced.
- (2) The total energy of a system and surrounding remains constant (or conserved)
- (3) "Energy can neither be created nor destroyed, but may be converted from one form to another".
- (4) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".
- (5) "Heat and work are two ways of changing a system's internal energy".

### 7.4.1 Mathematical statement of the first law

The mathematical statement of the first law of thermodynamics is

$$\Delta U = q + w \text{ ----- 7.7}$$

**Case 1 :** For a cyclic process involving isothermal expansion of an ideal gas,

$$\Delta U = 0.$$

$$\text{eqn (7.7)} \Rightarrow \therefore q = -w$$

In other words, during a cyclic process, the amount of heat absorbed by the system is equal to work done by the system.

**Case 2 :** For an isochoric process (no change in volume) there is no work of expansion. i.e.  $\Delta V = 0$

$$\begin{aligned} \Delta U &= q + w \\ &= q - P\Delta V \\ \Delta V &= 0 \\ \Delta U &= q_v \end{aligned}$$

In other words, during an isochoric process, the amount of heat supplied to the system is converted to its internal energy.

**Case 3 :** For an adiabatic process there is no change in heat. i.e.  $q = 0$ . Hence

$$q = 0$$

$$\text{eqn (7.7)} \Rightarrow \Delta U = w$$

In other words, in an adiabatic process, the decrease in internal energy

is exactly equal to the work done by the system on its surroundings.

**Case 4 :** For an isobaric process. There is no change in the pressure. P remains constant. Hence

$$\begin{aligned} \Delta U &= q + w \\ \Delta U &= q - P\Delta V \end{aligned}$$

In other words, in an isobaric process a part of heat absorbed by the system is used for PV expansion work and the remaining is added to the internal energy of the system.

#### Problem: 7.1

A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J of thermal energy from its surroundings. Determine the change in internal energy of system.

#### Solution:

Given data  $q = 400 \text{ J}$   $V_1 = 5 \text{ L}$   $V_2 = 10 \text{ L}$

$\Delta u = q - w$  (heat is given to the system (+q); work is done by the system(-w))

$$\begin{aligned} \Delta u &= q - PdV \\ &= 400 \text{ J} - 1 \text{ atm} (10-5)\text{L} \\ &= 400 \text{ J} - 5 \text{ atm L} \\ &[\therefore 1 \text{ L atm} = 101.33 \text{ J}] \\ &= 400 \text{ J} - 5 \times 101.33 \text{ J} \\ &= 400 \text{ J} - 506.65 \text{ J} \\ &= -106.65 \text{ J} \end{aligned}$$

## 7.5 Enthalpy (H)

The enthalpy (H), is a thermodynamic property of a system, is defined as the sum of the internal energy (U) of a system and the product of pressure and volume of the system. That is,

$$H = U + PV \text{ -----(7.8)}$$

It reflects the capacity to do mechanical work and the capacity to release heat by the system. When a process occurs at constant pressure, the heat involved (either released or absorbed) is equal to the change in enthalpy.

Enthalpy is a state function which depends entirely on the state functions T, P and U. Enthalpy is usually expressed as the change in enthalpy ( $\Delta H$ ) for a process between initial and final states at constant pressure.

$$\Delta H = \Delta U + P\Delta V \text{ -----(7.9)}$$

The change in enthalpy ( $\Delta H$ ) is equal to the heat supplied at the constant pressure to a system (as long as the system does no additional work).

$$\Delta H = q_p$$

In an endothermic reaction heat is absorbed by the system from the surroundings that is  $q > 0$  (positive). Therefore,  $\Delta H$  is also positive. In an exothermic reaction heat is evolved by the system to the surroundings that is,  $q < 0$  (negative). If  $q$  is negative, then  $\Delta H$  will also be negative.

### 7.5.1 Relation between enthalpy 'H' and internal energy 'U'

When the system at constant pressure undergoes changes from an initial state with  $H_1$ ,  $U_1$  and  $V_1$  to a final state with  $H_2$ ,  $U_2$  and  $V_2$  the change in enthalpy  $\Delta H$ , can be calculated as follows:

$$H = U + PV$$

In the initial state

$$H_1 = U_1 + PV_1 \text{ -----(7.10)}$$

In the final state

$$H_2 = U_2 + PV_2 \text{ -----(7.11)}$$

change in enthalpy is (7.11) - (7.10)

$$(H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V \text{ ----- (7.12)}$$

As per first law of thermodynamics,

$$\Delta U = q + w$$

Equation 7.12 becomes

$$\Delta H = q + w + P\Delta V$$

$$w = -P\Delta V$$

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

$$\Delta H = q_p \text{ ----- (7.13)}$$

$q_p$  - is the heat absorbed at constant pressure and is considered as heat content.

Consider a closed system of gases which are chemically reacting to form gaseous products at constant temperature

and pressure with  $V_i$  and  $V_f$  as the total volumes of the reactant and product gases respectively, and  $n_i$  and  $n_f$  as the number of moles of gaseous reactants and products, then,

For reactants (initial state) :

$$PV_i = n_i RT \text{ ----- (7.14)}$$

For products (final state) :

$$PV_f = n_f RT \text{ ----- (7.15)}$$

$$(7.15) - (7.14)$$

$$P (V_f - V_i) = (n_f - n_i) RT$$

$$P \Delta V = \Delta n_{(g)} RT \text{ ----- (7.16)}$$

Substituting in 7.16 in 7.12

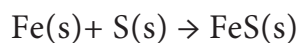
$$\Delta H = \Delta U + \Delta n_{(g)} RT \text{ ----- (7.17)}$$

### 7.5.2 Enthalpy Changes for Different Types of Reactions and Phase Transitions:

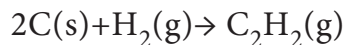
The heat or enthalpy changes accompanying chemical reactions is expressed in different ways depending on the nature of the reaction. These are discussed below.

#### Standard heat of formation

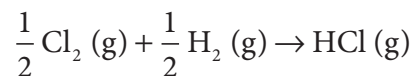
The standard heat of formation of a compound is defined as "the change in enthalpy that takes place when one mole of a compound is formed from its elements, present in their standard states (298 K and 1 bar pressure)". By convention the standard heat of formation of all elements is assigned a value of zero.



$$\Delta H_f^0 = -100.42 \text{ kJ mol}^{-1}$$



$$\Delta H_f^0 = +222.33 \text{ kJ mol}^{-1}$$



$$\Delta H_f^0 = -92.4 \text{ kJ mol}^{-1}$$

The standard heats of formation of some compounds are given in Table 7.4.

**Table: 7.4 standard heat of formation of some compounds**

Substance	$\Delta H_f^0$ (kJ mol <sup>-1</sup> )	Substance	$\Delta H_f^0$ (kJ mol <sup>-1</sup> )
H <sub>2</sub> O(l)	-242	CH <sub>4</sub> (g)	-74.85
HCl(g)	-92.4	C <sub>2</sub> H <sub>6</sub> (g)	-84.6
HBr(g)	-36.4	C <sub>6</sub> H <sub>6</sub> (g)	+49.6
NH <sub>3</sub> (g)	-46.1	C <sub>2</sub> H <sub>2</sub> (g)	+222.33
CO <sub>2</sub> (g)	-393.5	CH <sub>3</sub> OH(l)	-239.2

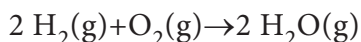
#### 7.6 Thermochemical Equations:

A thermochemical equation is a balanced stoichiometric chemical equation that includes the enthalpy change ( $\Delta H$ ). The following conventions are adopted in thermochemical equations:

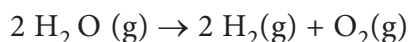
- (i) The coefficients in a balanced thermochemical equation refer to number of moles of reactants and products involved in the reaction.

- (ii) The enthalpy change of the reaction  $\Delta H_r$  has to be specified with appropriate sign and unit.
- (iii) When the chemical reaction is reversed, the value of  $\Delta H$  is reversed in sign with the same magnitude.
- (iv) The physical states (gas, liquid, aqueous, solid in brackets) of all species are important and must be specified in a thermochemical reaction, since  $\Delta H$  depends on the physical state of reactants and products.
- (v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also multiplied by the same number.
- (vi) The negative sign of  $\Delta H_r$  indicates that the reaction is exothermic and the positive sign of  $\Delta H_r$  indicates an endothermic reaction.

For example, consider the following reaction,



$$\Delta H_r^0 = -967.4 \text{ kJ}$$



$$\Delta H_r^0 = +967.4 \text{ kJ}$$

**Standard enthalpy of reaction ( $\Delta H_r^0$ ) from standard enthalpy of formation ( $\Delta H_f^0$ )**

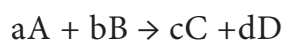
The standard enthalpy of a reaction is the enthalpy change for a reaction

when all the reactants and products are present in their standard states. Standard conditions are denoted by adding the superscript 0 to the symbol ( $\Delta H^0$ )

We can calculate the enthalpy of a reaction under standard conditions from the values of standard enthalpies of formation of various reactants and products. The standard enthalpy of reaction is equal to the difference between standard enthalpy of formation of products and the standard enthalpies of formation of reactants.

$$\Delta H_r^0 = \sum \Delta H_r^0(\text{products}) - \sum \Delta H_r^0(\text{reactants})$$

For a general reaction

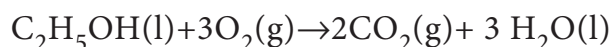


$$\Delta H_r^0 = \sum \Delta H_r^0(\text{products}) - \sum \Delta H_r^0(\text{reactants})$$

$$\Delta H_r^0 = \{c \Delta H_f^0(\text{C}) + d \Delta H_f^0(\text{D})\} - \{a \Delta H_f^0(\text{A}) + b \Delta H_f^0(\text{B})\}$$

### Problem : 7.2

The standard enthalpies of formation of  $\text{C}_2\text{H}_5\text{OH}(\text{l})$ ,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are -277, -393.5 and -285.5  $\text{kJ mol}^{-1}$  respectively. Calculate the standard enthalpy change for the reaction

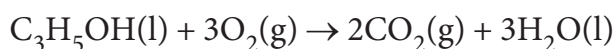


The enthalpy of formation of  $\text{O}_2(\text{g})$  in the standard state is Zero, by definition

### Solution:

For example, the standard enthalpy change for the combustion of ethanol can be calculated from the standard enthalpies of formation of  $\text{C}_2\text{H}_5\text{OH}(\text{l})$ ,  $\text{CO}_2(\text{g})$

and  $\text{H}_2\text{O}(\text{l})$ . The enthalpies of formation are  $-277$ ,  $-393.5$  and  $-285.5 \text{ kJ mol}^{-1}$  respectively.



$$\Delta H_r^0 = \left\{ (\Delta H_f^0)_{\text{products}} - (\Delta H_f^0)_{\text{reactants}} \right\}$$

$$\Delta H_r^0 = \left[ 2(\Delta H_f^0)_{\text{CO}_2} + 3(\Delta H_f^0)_{\text{H}_2\text{O}} \right] - \left[ 1(\Delta H_f^0)_{\text{C}_3\text{H}_5\text{OH}} + 3(\Delta H_f^0)_{\text{O}_2} \right]$$

$$\Delta H_r^0 = \left[ 2\text{mol}(-393.5)\text{kJ mol}^{-1} + 3\text{mol}(-285.5)\text{kJ mol}^{-1} \right]$$

$$- \left[ 1\text{mol}(-277)\text{kJ mol}^{-1} + 3\text{mol}(0)\text{kJ mol}^{-1} \right]$$

$$= [-787 - 856.5] - [-277]$$

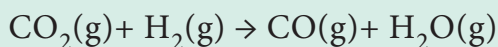
$$= -1643.5 + 277$$

$$\Delta H_r^0 = -1366.5 \text{ KJ}$$

### Evaluate Yourself - 1



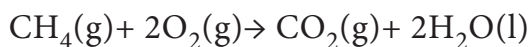
Calculate  $\Delta H_f^0$  for the reaction



given that  $\Delta H_f^0$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-111.31$  and  $-242 \text{ kJ mol}^{-1}$  respectively.

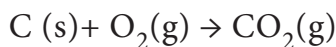
### Heat of combustion

The heat of combustion of a substance is defined as “The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen”. It is denoted by  $\Delta H_C$ . For example, the heat of combustion of methane is  $-87.78 \text{ kJ mol}^{-1}$



$$\Delta H_C = -87.78 \text{ kJ mol}^{-1}$$

For the combustion of carbon,



$$\Delta H_C = -394.55 \text{ kJ mol}^{-1}$$

Combustion reactions are always exothermic. Hence the enthalpy change is always negative.

### Molar heat capacities

When heat ( $q$ ) is supplied to a system, the molecules in the system absorb the heat and hence their kinetic energy increases, which in turn raises the temperature of the system from  $T_1$  to  $T_2$ . This increase ( $T_2 - T_1$ ) in temperature is directly proportional to the amount of heat absorbed and the mass of the substance. In other words,

$$q \propto m\Delta T$$

$$q = c m \Delta T$$

$$c = q/m \Delta T$$

The constant  $c$  is called heat capacity.

$$c = \left( \frac{q}{m(T_2 - T_1)} \right) \text{ ----- (7.18)}$$

when  $m=1 \text{ kg}$  and  $(T_2 - T_1) = 1 \text{ K}$  then the heat capacity is referred as specific heat capacity. The equation 7.18 becomes

$$c = q$$

Thus specific heat capacity of a

system is defined as “The heat absorbed by one kilogram of a substance to raise its temperature by one Kelvin at a specified temperature”.

The heat capacity for 1 mole of substance, is called molar heat capacity ( $c_m$ ). It is defined as “The amount of heat absorbed by one mole of the substance to raise its temperature by 1 kelvin”.

**Units of Heat Capacity:**

The SI unit of molar heat capacity is  $\text{JK}^{-1}\text{mol}^{-1}$

The molar heat capacities can be expressed either at constant volume ( $C_v$ ) or at constant pressure ( $C_p$ ).

According to the first law of thermodynamics

$$U = q + w \quad \text{or} \quad U = q - PdV$$

$$q = U + PdV \text{ -----(7.19)}$$

Differentiate (7.19) with respect to temperature at constant volume i.e  $dV=0$ ,

$$\left(\frac{\partial q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \text{ -----7.20}$$

Thus the heat capacity at constant volume ( $C_v$ ) is defined as the rate of change of internal energy with respect to temperature at constant volume.

Similarly the molar heat capacity at constant pressure ( $C_p$ ) can be defined as

the rate of change of enthalpy with respect to temperature at constant pressure.

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p \text{ ----- (7.21)}$$

**Relation between  $C_p$  and  $C_v$  for an ideal gas.**

From the definition of enthalpy

$$H=U+PV \text{ -----(7.8)}$$

for 1 mole of an ideal gas

$$PV = nRT \text{ -----(7.22)}$$

By substituting (7.22) in (7.8)

$$H = U + nRT \text{ ---- (7.23)}$$

Differentiating the above equation with respect to T,

$$\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + nR \frac{\partial T}{\partial T}$$

$$\begin{matrix} C_p = C_v + nR \text{ (1)} \\ C_p - C_v = nR \text{ .....(7.24)} \end{matrix} \left[ \begin{matrix} \because \left(\frac{\partial H}{\partial T}\right)_P = C_P \\ \text{and} \left(\frac{\partial U}{\partial T}\right)_V = C_V \end{matrix} \right]$$

At constant pressure processes, a system has to do work against the surroundings. Hence, the system would require more heat to effect a given temperature rise than at constant volume, so  $C_p$  is always greater than  $C_v$

**Calculation of  $\Delta U$  and  $\Delta H$**

For one mole of an ideal gas, we have



$$c_v = \frac{dU}{dT}$$

$$dU = C_V dT$$

For a finite change, we have

$$\Delta U = C_V \Delta T$$

$$\Delta U = C_V (T_2 - T_1)$$

and for  $n$  moles of an ideal gas we get

$$\Delta U = n C_V (T_2 - T_1) \text{----- (7.25)}$$

Similarly for  $n$  moles of an ideal gas we get

$$\Delta H = n C_P (T_2 - T_1) \text{----- (7.26)}$$

### Problem 7.3

Calculate the value of  $\Delta U$  and  $\Delta H$  on heating 128.0 g of oxygen from  $0^\circ \text{C}$  to  $100^\circ \text{C}$ .  $C_V$  and  $C_P$  on an average are 21 and 29  $\text{J mol}^{-1} \text{K}^{-1}$ . (The difference is  $8 \text{J mol}^{-1} \text{K}^{-1}$  which is approximately equal to  $R$ )

### Solution.

We know

$$\Delta U = n C_V (T_2 - T_1)$$

$$\Delta H = n C_P (T_2 - T_1)$$

Here  $n = \frac{128}{32}$  4 moles ;

$$T_2 = 100^\circ \text{C} = 373\text{K}; T_1 = 0^\circ \text{C} = 273\text{K}$$

$$\Delta U = n C_V (T_2 - T_1)$$

$$\Delta U = 4 \times 21 \times (373 - 273)$$

$$\Delta U = 8400 \text{ J}$$

$$\Delta U = 8.4 \text{ kJ}$$

$$\Delta H = n C_P (T_2 - T_1)$$

$$\Delta H = 4 \times 29 \times (373 - 273)$$

$$\Delta H = 11600 \text{ J}$$

$$\Delta H = 11.6 \text{ kJ}$$



### Evaluate Yourself -2

Calculate the amount of heat necessary to raise 180 g of water from  $25^\circ \text{C}$  to  $100^\circ \text{C}$ . Molar heat capacity of water is  $75.3 \text{ J mol}^{-1} \text{K}^{-1}$

### 7.7 Measurement of $\Delta U$ and $\Delta H$ using Calorimetry.

Calorimeter is used for measuring the amount of heat change in a chemical or physical change. In calorimetry, the temperature change in the process is measured which is directly proportional to the heat capacity. By using the expression  $C = q/m\Delta T$ , we can calculate the amount of heat change in the process. Calorimetric measurements are made under two different conditions

i) At constant volume ( $q_v$ )

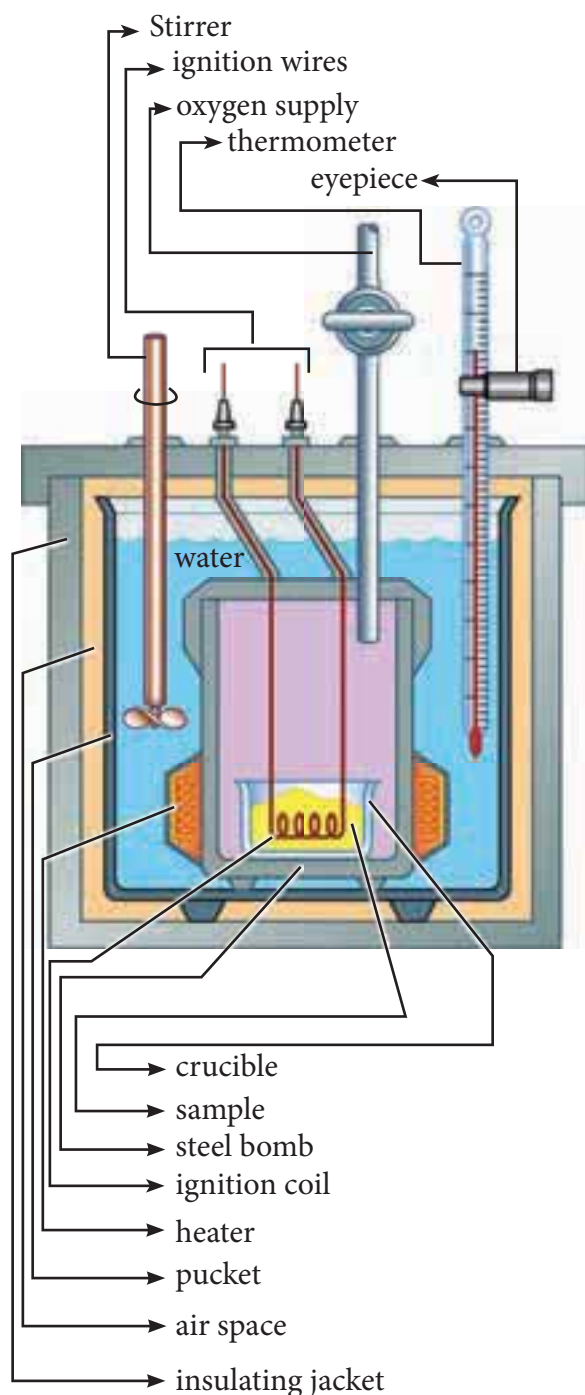
ii) At constant pressure ( $q_p$ )

#### (A) $\Delta U$ Measurements

For chemical reactions, heat evolved at constant volume, is measured

in a *bomb calorimeter*.

The inner vessel (the bomb) and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws.



**Figure 7.6 Bomb calorimeter**

A weighed amount of the substance is taken in a platinum cup connected with

electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurized with excess oxygen. The bomb is immersed in water, in the inner volume of the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly. The reaction is started by striking the substance through electrical heating.

A known amount of combustible substance is burnt in oxygen in the bomb. Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed. The change in temperature is measured using a Beckman thermometer. Since the bomb is sealed its volume does not change and hence the heat measurements is equal to the heat of combustion at a constant volume ( $\Delta U$ )<sub>c</sub>.

The amount of heat produced in the reaction ( $\Delta U$ )<sub>c</sub> is equal to the sum of the heat absorbed by the calorimeter and water.

Heat absorbed by the calorimeter

$$q_1 = k \cdot \Delta T$$

where  $k$  is a calorimeter constant equal to  $m_c C_c$  ( $m_c$  is mass of the calorimeter and  $C_c$  is heat capacity of calorimeter)

Heat absorbed by the water

$$q_2 = m_w C_w \Delta T$$

where  $m_w$  is molar mass of water

$C_w$  is molar heat capacity of water (4,184 kJ K<sup>-1</sup> mol<sup>-1</sup>)

$$\begin{aligned}\text{Therefore } \Delta U_c &= q_1 + q_2 \\ &= k \cdot \Delta T + m_w C_w \Delta T \\ &= (k + m_w C_w) \Delta T\end{aligned}$$

Calorimeter constant can be determined by burning a known mass of standard sample (benzoic acid) for which the heat of combustion is known ( $-3227 \text{ kJ mol}^{-1}$ )

The enthalpy of combustion at constant pressure of the substance is calculated from the equation (7.17)

$$\Delta H_C^0 (\text{pressure}) = \Delta U_C^0 (\text{Vol}) + \Delta n_g RT$$

### Applications of bomb calorimeter:

1. Bomb calorimeter is used to determine the amount of heat released in combustion reaction.
2. It is used to determine the calorific value of food.
3. Bomb calorimeter is used in many industries such as metabolic study, food processing, explosive testing etc.

### (b) $\Delta H$ Measurements

Heat change at constant pressure (at atmospheric pressure) can be measured using a coffee cup calorimeter. A schematic representation of a coffee cup calorimeter is given in Figure 7.7. Instead of bomb, a styrofoam cup is used in this calorimeter. It acts as good adiabatic wall and doesn't allow transfer of heat produced during the reaction to its surrounding. This entire heat energy is absorbed by the water inside the cup. This method can be used for the reactions where there is no

appreciable change in volume. The change in the temperature of water is measured and used to calculate the amount of heat that has been absorbed or evolved in the reaction using the following expression.

$$q = m_w C_w \Delta T$$

where  $m_w$  is the molar mass of water and  $C_w$  is the molar heat capacity of water ( $4184 \text{ kJ K}^{-1} \text{ mol}^{-1}$ )

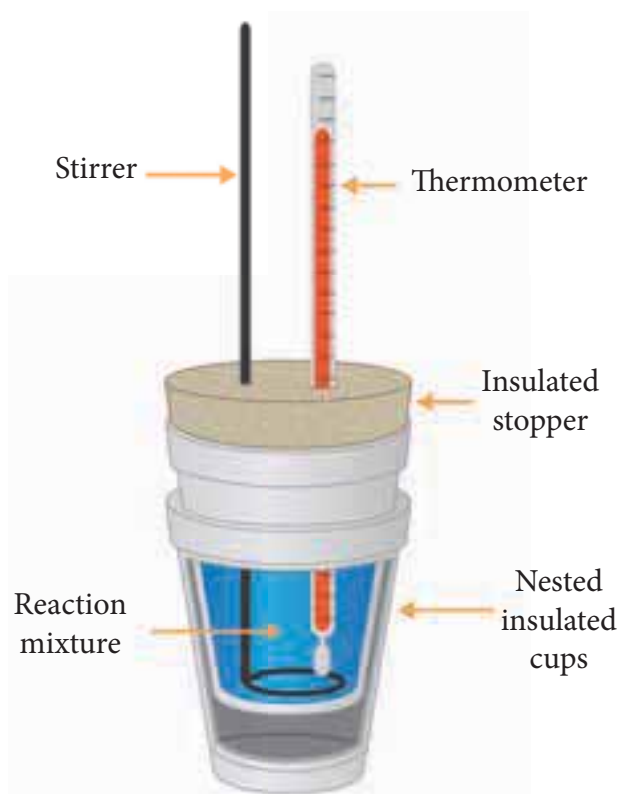
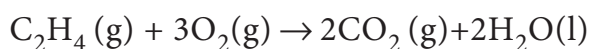


Figure 7.7 Coffee cup Calorimeter

### Problem 7.4

Calculate the enthalpy of combustion of ethylene at 300 K at constant pressure, if its heat of combustion at constant volume ( $\Delta U$ ) is  $-1406 \text{ kJ}$ .

The complete ethylene combustion reaction can be written as,



$$\Delta U = -1406 \text{ kJ}$$

$$\Delta n = n_{\text{p}(\text{g})} - n_{\text{r}(\text{g})}$$

$$\Delta n = 2 - 4 = -2$$

$$\Delta H = \Delta U + RT\Delta n_{\text{g}}$$

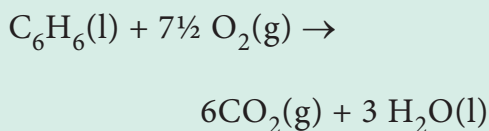
$$\Delta H = -1406 + (8.314 \times 10^{-3} \times 300 \times (-2))$$

$$\Delta H = -1410.9 \text{ kJ}$$

### Evaluate Yourself - 3



From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.



$$\Delta U \text{ at } 25^\circ \text{C} = -3268.12 \text{ kJ}$$

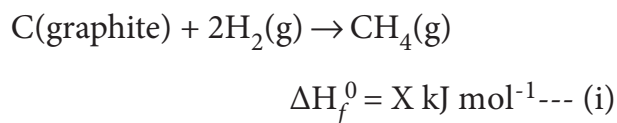
### Applications of the heat of combustion:

**(1) Calculation of heat of formation:** Since the heat of combustion of organic compounds can be determined with considerable ease, they are employed to calculate the heat of formation of other compounds.

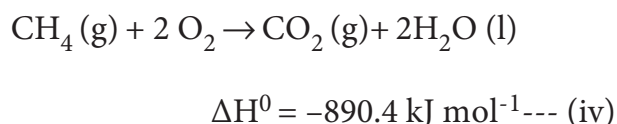
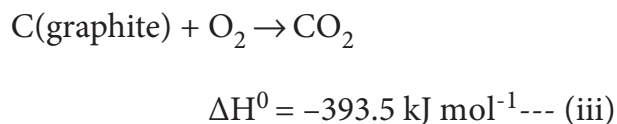
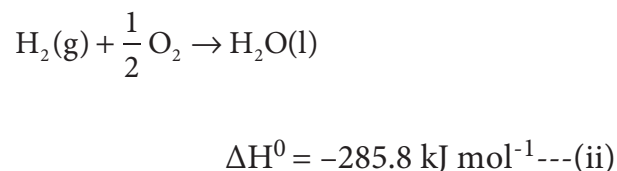
For example let us calculate the standard enthalpy of formation  $\Delta H_f^0$  of  $\text{CH}_4$  from the values of enthalpy of combustion for  $\text{H}_2$ ,  $\text{C}(\text{graphite})$  and  $\text{CH}_4$  which are  $-285.8$ ,  $-393.5$ , and  $-890.4 \text{ kJ mol}^{-1}$  respectively.

Let us interpret the information

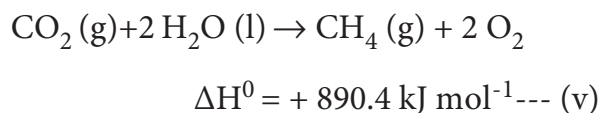
about enthalpy of formation by writing out the equations. It is important to note that the standard enthalpy of formation of pure elemental gases and elements is assumed to be zero under standard conditions. Thermochemical equation for the formation of methane from its constituent elements is,



Thermo chemical equations for the combustion of given substances are,



Since methane is in the product side of the required equation (i), we have to reverse the equation (iv)



In order to get equation (i) from the remaining,

$$(i) = [(ii) \times 2] + (iii) + (v)$$

$$X = [(-285.8) \times 2] + [-393.5] + [+890.4]$$

$$= -74.7 \text{ kJ}$$

Hence, the amount of energy required for the formation of 1 mole of methane is  $-74.7 \text{ kJ}$

The heat of formation methane =  $-74.7 \text{ kJ mol}^{-1}$

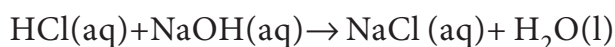
**(2) Calculation of calorific value of food and fuels:** The calorific value is defined as the amount of heat produced in calories (or joules) when one gram of the substance is completely burnt. The SI unit of calorific value is  $\text{J kg}^{-1}$ . However, it is usually expressed in  $\text{cal g}^{-1}$ .

### Heat of solution:

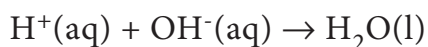
Heat changes are usually observed when a substance is dissolved in a solvent. The heat of solution is defined as the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.

### Heat of neutralisation:

The heat of neutralisation is defined as “The change in enthalpy when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base or vice versa in dilute solution”.



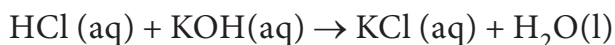
$$\Delta H = - 57.32 \text{ kJ}$$



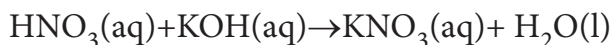
$$\Delta H = - 57.32 \text{ kJ}$$

The heat of neutralisation of a strong acid and strong base is around  $- 57.32 \text{ kJ}$ , irrespective of nature of acid or base used which is evident from the below

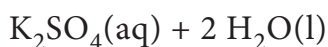
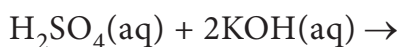
mentioned examples.



$$\Delta H = - 57.32 \text{ kJ}$$

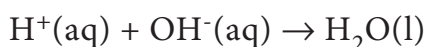


$$\Delta H = - 57.32 \text{ kJ}$$



$$\Delta H = - 57.32 \text{ kJ}$$

The reason for this can be explained on the basis of Arrhenius theory of acids and bases which states that strong acids and strong bases completely ionise in aqueous solution to produce  $\text{H}^+$  and  $\text{OH}^-$  ions respectively. Therefore in all the above mentioned reactions the neutralisation can be expressed as follows.

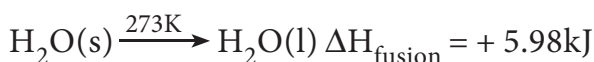


$$\Delta H = - 57.32 \text{ kJ}$$

### Molar heat of fusion

The molar heat of fusion is defined as “the change in enthalpy when one mole of a solid substance is converted into the liquid state at its melting point”.

For example, the heat of fusion of ice can be represented as

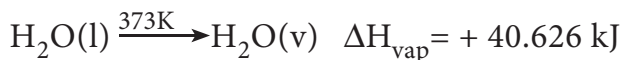


### Molar heat of vapourisation

The molar heat of vaporisation is defined as “the change in enthalpy when

one mole of liquid is converted into vapour state at its boiling point”.

For example, heat of vaporisation of water can be represented as



### Molar heat of sublimation

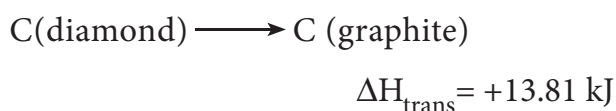
Sublimation is a process when a solid changes directly into its vapour state without changing into liquid state. Molar heat of sublimation is defined as “the change in enthalpy when one mole of a solid is directly converted into the vapour state at its sublimation temperature”. For example, the heat of sublimation of iodine is represented as



Another example of sublimation process is solid  $\text{CO}_2$  to gas at atmospheric pressure at very low temperatures.

### Heat of transition

The heat of transition is defined as “The change in enthalpy when one mole of an element changes from one of its allotropic form to another. For example, the transition of diamond into graphite may be represented as



Similarly the allotropic transitions in sulphur and phosphorous can be represented as follows,



$$\Delta H_{\text{trans}} = - 0.067 \text{ kJ}$$



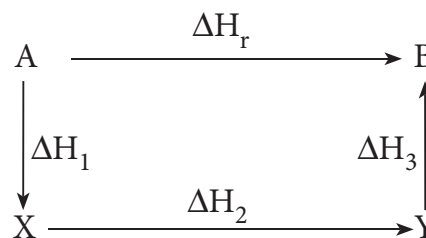
$$\Delta H_{\text{trans}} = - 4.301 \text{ kJ}$$

## 7.8 Hess's law of constant heat summation

We have already seen that the heat changes in chemical reactions are equal to the difference in internal energy ( $\Delta U$ ) or heat content ( $\Delta H$ ) of the products and reactants, depending upon whether the reaction is studied at constant volume or constant pressure. Since  $\Delta U$  and  $\Delta H$  are functions of the state of the system, the heat evolved or absorbed in a given reaction depends only on the initial state and final state of the system and not on the path or the steps by which the change takes place.

This generalisation is known as **Hess's law** and stated as:

The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps provided the initial and final states are same.



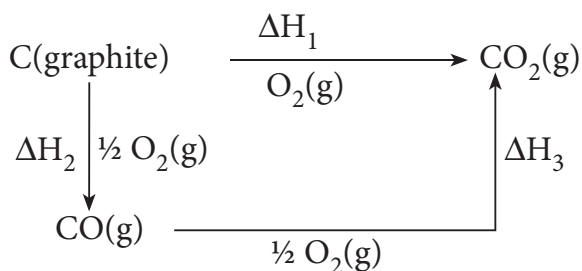
$$\Delta H_{\text{r}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

**Application of Hess's Law:** Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure. For example, it is very difficult to measure the heat of combustion of graphite to give pure  $\text{CO}$ .

However, enthalpy for the oxidation of graphite to  $\text{CO}_2$  and  $\text{CO}$  to  $\text{CO}_2$  can easily be measured. For these conversions, the heat of combustion values are  $-393.5 \text{ kJ}$  and  $-283.5 \text{ kJ}$  respectively.

From these data the enthalpy of combustion of graphite to  $\text{CO}$  can be calculated by applying Hess's law.

The reactions involved in this process can be expressed as follows



According to Hess law,

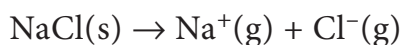
$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

$$-393.5 \text{ kJ} = X - 283.5 \text{ kJ}$$

$$X = -110.5 \text{ kJ}$$

## 7.9 Lattice energy ( $\Delta H_{\text{lattice}}$ )

Lattice energy is defined as the amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance. It is also referred as lattice enthalpy.



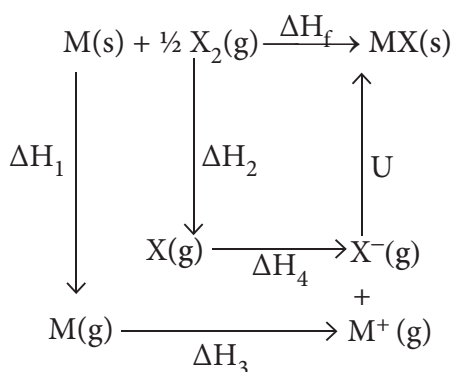
$$\Delta H_{\text{lattice}} = +788 \text{ kJ mol}^{-1}$$

From the above equation it is clear that  $788 \text{ kJ}$  of energy is required to separate  $\text{Na}^+$  and  $\text{Cl}^-$  ions from 1 mole of  $\text{NaCl}$ .

## Born - Haber cycle

The Born-Haber cycle is an approach to analyse reaction energies. It was named after two German scientists Max Born and Fritz Haber who developed this cycle. The cycle is concerned with the formation of an ionic compound from the reaction of a metal with a halogen or other non-metallic element such as oxygen.

Born-Haber cycle is primarily used in calculating lattice energy, which cannot be measured directly. The Born-Haber cycle applies Hess's law to calculate the lattice enthalpy. For example consider the formation of a simple ionic solid such as an alkali metal halide  $\text{MX}$ , the following steps are considered.



$\Delta H_1$  - enthalpy change for the sublimation  $\text{M(s)}$  to  $\text{M(g)}$

$\Delta H_2$  - enthalpy change for the dissociation of  $\frac{1}{2} \text{X}_2(\text{g})$  to  $\text{X(g)}$

$\Delta H_3$  - Ionisation energy for  $\text{M(g)}$  to  $\text{M}^+(\text{g})$

$\Delta H_4$  - electron affinity for the conversion of  $\text{X(g)}$  to  $\text{X}^-(\text{g})$

$U$  - the lattice enthalpy for the formation of solid  $\text{MX}$

$\Delta H_f$  - enthalpy change for the formation of solid  $\text{MX}$  directly from elements

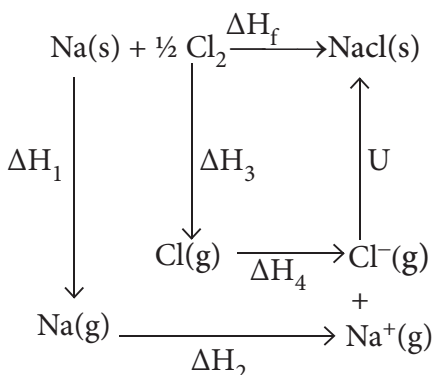
According to Hess's law of heat summation

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + U$$

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows:

Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Let us calculate the lattice energy of sodium chloride using Born-Haber cycle



$\Delta H_f$  = heat of formation of sodium chloride =  $-411.3 \text{ kJ mol}^{-1}$

$\Delta H_1$  = heat of sublimation of Na(S) =  $108.7 \text{ kJ mol}^{-1}$

$\Delta H_2$  = ionisation energy of Na(S) =  $495.0 \text{ kJ mol}^{-1}$

$\Delta H_3$  = dissociation energy of  $\text{Cl}_2$ (S) =  $244 \text{ kJ mol}^{-1}$

$\Delta H_4$  = Electron affinity of Cl(S) =  $-349.0 \text{ kJ mol}^{-1}$

U = lattice energy of NaCl

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \frac{1}{2} \Delta H_3 + \Delta H_4 + U$$

$$\therefore U = (\Delta H_f) - (\Delta H_1 + \Delta H_2 + \frac{1}{2} \Delta H_3 + \Delta H_4)$$

$$\Rightarrow U = (-411.3) - (108.7 + 495.0 + 122 - 349)$$

$$U = (-411.3) - (376.7)$$

$$\therefore U = -788 \text{ kJ mol}^{-1}$$

This negative sign in lattice energy indicates that the energy is released when sodium is formed from its constituent gaseous ions  $\text{Na}^+$  and  $\text{Cl}^-$

#### Evaluate Yourself - 4



When a mole of magnesium bromide is prepared from 1 mole of magnesium and 1 mole of liquid bromine, 524 kJ of energy is released.

The heat of sublimation of Mg metal is  $148 \text{ kJ mol}^{-1}$ . The heat of dissociation of bromine gas into atoms is  $193 \text{ kJ mol}^{-1}$ . The heat of vapourisation of liquid bromine is  $31 \text{ kJ mol}^{-1}$ . The ionisation energy of magnesium is  $2187 \text{ kJ mol}^{-1}$  and the electron affinity of bromine is  $-662 \text{ kJ mol}^{-1}$ . Calculate the lattice energy of magnesium bromide.

#### 7.10. Second Law of thermodynamics:

##### Need for the second law of thermodynamics:

We know from the first law of thermodynamics, the energy of the universe is conserved. Let us consider the following processes:



1. A glass of hot water over time loses heat energy to the surrounding and becomes cold.
2. When you mix hydrochloric acid with sodium hydroxide, it forms sodium chloride and water with evolution of heat.

In both these processes, the total energy is conserved and are consistent with the first law of thermodynamics. However, the reverse process i.e. cold water becoming hot water by absorbing heat from surrounding on its own does not occur spontaneously even though the energy change involved in this process is also consistent with the first law. However, if the heat energy is supplied to cold water, then it will become hot. i.e. the change that does not occur spontaneously and can be driven by supplying energy.

Similarly, a solution of sodium chloride does not absorb heat energy on its own, to form hydrochloric acid and sodium hydroxide. But, this process can not be driven even by supplying energy. From these kinds of our natural experiences, we have come to know that certain processes are spontaneous while the others are not, and some processes have a preferred direction. In order to explain the feasibility of a process, we need the second law of thermodynamics.

### 7.10.1 Various statements of the second law of thermodynamics

#### Entropy

The second law of thermodynamics introduces another state function called entropy. Entropy is a measure of the

molecular disorder (randomness) of a system. But thermodynamic definition of entropy is concerned with the change in entropy that occurs as a result of a process.

It is defined as,  $dS = dq_{\text{rev}} / T$

#### Entropy statement:

The second law of thermodynamics can be expressed in terms of entropy. i.e. “the entropy of an isolated system increases during a spontaneous process”.

For an irreversible process such as spontaneous expansion of a gas,

$$\Delta S_{\text{total}} > 0$$

$$\Delta S_{\text{total}} > \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\text{i.e. } \Delta S_{\text{universe}} > \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

For a reversible process such as melting of ice,

$$\Delta S_{\text{system}} = - \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{universe}} = 0$$

#### Kelvin-Planck statement:

It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink. The second law of thermodynamics explains why even an ideal, frictionless engine cannot convert 100% of its input heat into work. Carnot on his analysis of heat engines, found that the maximum efficiency of a heat engine which operates reversibly, depends only on the two temperatures between which it is operated.

Efficiency = work performed / heat absorbed

$$\eta = \frac{|q_h| - |q_c|}{|q_h|}$$

$q_h$  - heat absorbed from the hot reservoir

$q_c$  - heat transferred to cold reservoir

$$\eta = 1 - \frac{|q_c|}{|q_h|} \quad \text{--- (7.27)}$$

For a reversible cyclic process

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{system}} = - \Delta S_{\text{surroundings}}$$

$$\frac{q_h}{T_h} = \frac{-q_c}{T_c}$$

$$\frac{-T_c}{T_h} = \frac{q_c}{q_h}$$

$$\frac{T_c}{T_h} = \frac{|q_c|}{|q_h|} \quad \text{--- 7.28}$$

Sustituting 7.28 in 7.27

$$\Rightarrow \eta = 1 - \frac{T_c}{T_h} \quad \text{--- 7.29}$$

$$T_h \gg T_c$$

Hence,  $\eta < 1$

**efficiency in percentage can be expressed as**

$$\text{Efficiency in percentage} = \left[ 1 - \frac{T_c}{T_h} \right] \times 100$$

**Clausius statement:**

It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

### Problem: 7.10

If an automobile engine burns petrol at a temperature of  $816^\circ \text{C}$  and if the surrounding temperature is  $21^\circ \text{C}$ , calculate its maximum possible efficiency.

**Solution:**

$$\% \text{ Efficiency} = \left[ \frac{T_h - T_c}{T_h} \right] \times 100$$

Here

$$T_h = 816 + 273 = 1089 \text{ K};$$

$$T_c = 21 + 273 = 294 \text{ K}$$

$$\% \text{ Efficiency} = \left( \frac{1089 - 294}{1089} \right) \times 100$$

$$\% \text{ Efficiency} = 73\%$$

### Evaluate Yourself - 5



An engine operating between  $127^\circ \text{C}$  and  $47^\circ \text{C}$  takes some specified amount of heat from a high temperature reservoir. Assuming that there are no frictional losses, calculate the percentage efficiency of an engine.

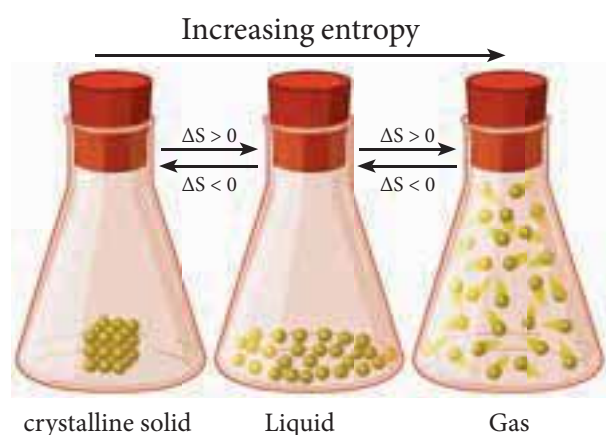
**Unit of entropy:**

The entropy (S) is equal to heat energy exchanged (q) divided by the temperature (T) at which the exchange takes place. Therefore, The SI unit of entropy is  $\text{JK}^{-1}$ .

**Spontaneity and Randomness**

Careful examination shows that in each of the processes viz., melting of ice and evaporation of water, there is an increase in randomness or disorder of the system. The water molecules in ice

are arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganised and can move more freely. The movement of molecules becomes freer in the liquid phase and even more free in the vapour phase. In other words, we can say that the randomness of the water molecules increases, as ice melts into water or water evaporates. Both are spontaneous processes which result in an increase in randomness (entropy).



**Figure 7.8 Illustration showing an increase in disorder.**

### Standard Entropy Change( $\Delta S^0$ ):

It is possible to calculate the actual entropy of a substance at any temperature above 0 K. The absolute entropy of a substance at 298 K and one bar pressure is called the standard entropy  $S^0$ . The third law of thermodynamics states, according to Nernst, that the absolute entropy of elements is zero only at 0 K in a perfect crystal, and standard entropies of all substances at any temperature above 0 K always have positive values. Once we know the entropies of different substances, we

can calculate the standard entropy change ( $\Delta S_r^0$ ) for chemical reactions.

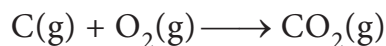
$$\Delta S_r^0 = \sum S_{\text{products}}^0 - \sum S_{\text{reactants}}^0 \quad \text{----- (7.30)}$$

### Standard Entropy of Formation:

Standard entropy of formation is defined as “the entropy of formation of 1 mole of a compound from the elements under standard conditions”. It is denoted as  $\Delta S_f^0$ . We can calculate the value of entropy of a given compound from the values of  $S^0$  of elements.

### Problem: 7.6

Calculate the standard entropy change for the following reaction ( $\Delta S_f^0$ ), given the standard entropies of  $\text{CO}_2(\text{g})$ ,  $\text{C}(\text{s})$ ,  $\text{O}_2(\text{g})$  as 213.6, 5.740 and 205  $\text{JK}^{-1}$  respectively.



$$\Delta S_r^0 = \sum S_{\text{products}}^0 - \sum S_{\text{reactants}}^0$$

$$\Delta S_r^0 = \{S_{\text{CO}_2}^0\} - \{S_{\text{C}}^0 + S_{\text{O}_2}^0\}$$

$$\Delta S_r^0 = 213.6 - [5.74 + 205]$$

$$\Delta S_r^0 = 213.6 - [210.74]$$

$$\Delta S_r^0 = 2.86 \text{ JK}^{-1}$$

### Evaluate Yourself- 6



Urea on hydrolysis produces ammonia and carbon dioxide. The standard entropies of urea,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$  are 173.8, 70, 213.5 and 192.5  $\text{J mole}^{-1}\text{K}^{-1}$  respectively. Calculate the entropy change for this reaction.

### Entropy change accompanying change of phase

When there is a change of state from solid to liquid (melting), liquid to vapour (evaporation) or solid to vapour (sublimation) there is a change in entropy. This change may be carried out at constant temperature reversibly as two phases are in equilibrium during the change.

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{rev}}}{T} \quad \text{----- (7.31)}$$

### Entropy of fusion:

The heat absorbed, when one mole of a solid melts at its melting point reversibly, is called molar heat of fusion. The entropy change for this process is given by

$$\Delta S_{\text{rev}} = \frac{dq_{\text{rev}}}{T}$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} \quad \text{----- (7.32)}$$

where  $\Delta H_{\text{fusion}}$  is Molar heat of fusion.  $T_f$  is the melting point.

### Entropy of vapourisation:

The heat absorbed, when one mole of liquid is boiled at its boiling point reversibly, is called molar heat of vapourisation. The entropy change is given by

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad \text{----- (7.33)}$$

where  $\Delta H_v$  is Molar heat of vaporisation.  $T_b$  is the boiling point.

### Entropy of transition:

The heat change, when one mole of a solid changes reversibly from one allotropic form to another at its transition temperature is called enthalpy of

transition. The entropy change is given

$$\Delta S_t = \frac{\Delta H_t}{T_t} \quad \text{----- (7.34)}$$

where  $\Delta H_t$  is the molar heat of transition,  $T_t$  is the transition temperature.

### Problem: 7.7

Calculate the entropy change during the melting of one mole of ice into water at 0° C and 1 atm pressure. Enthalpy of fusion of ice is 6008 J mol<sup>-1</sup>

#### Given:

$$\Delta H_{\text{fusion}} = 6008 \text{ J mol}^{-1}$$

$$T_f = 0^\circ \text{ C} = 273 \text{ K}$$



$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$\Delta S_{\text{fusion}} = \frac{6008}{273}$$

$$\Delta S_{\text{fusion}} = 22.007 \text{ J K}^{-1} \text{ mole}^{-1}$$

### Evaluate Yourself - 7



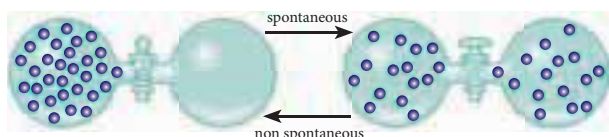
Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is 39.84 kJ mol<sup>-1</sup>

## 7.11 Gibbs free energy (G)

One of the important applications of the second law of thermodynamics is to predict the spontaneity of a reaction under a specific set of conditions. A reaction that occurs under the given set of conditions without any external driving force is called a spontaneous reaction. Otherwise, it is said to be non-spontaneous. In our day today life, we observe many spontaneous physical and chemical

processes, which includes the following examples.

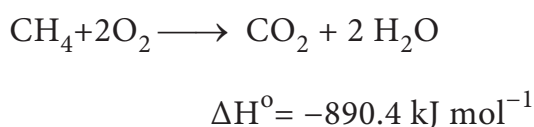
1. A waterfall runs downhill, but never uphill, spontaneously.
2. A lump of sugar dissolves spontaneously in a cup of coffee, but never reappears in its original form spontaneously.
3. Heat flows from hotter object to a colder one, but never flows from colder to hotter object spontaneously.
4. The expansion of a gas into an evacuated bulb is a spontaneous process, the reverse process that is gathering of all molecules into one bulb is not spontaneous.



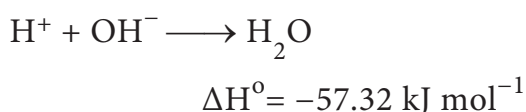
**Figure 7.9 Spontaneous process illustration**

These examples show that the processes that occur spontaneously in one direction, cannot take place in opposite direction spontaneously.

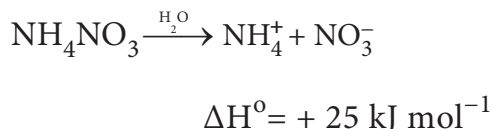
Similarly a large number of exothermic reactions are spontaneous. An example is combustion of methane.



Another example is acid-base neutralization reaction:



However, some endothermic processes are also spontaneous. For example ammonium nitrate dissolves in water spontaneously though this dissolution is endothermic.



From the above examples we can come to the conclusion that exothermicity favors the spontaneity but does not guarantee it. We cannot decide whether or not a chemical reaction will occur spontaneously solely on the basis of energy changes in the system. We know from second law of thermodynamics that in a spontaneous process, the entropy increases. But not all the processes which are accompanied by an increase in entropy are spontaneous. In order to predict the spontaneity of a reaction, we need some other thermodynamic function.

The second law of thermodynamics introduces another thermodynamic function called Gibbs free energy which finds useful in predicting the spontaneity of a reaction. The Gibbs free energy (G) was developed in the 1870's by Josiah Willard Gibbs. He originally termed this energy as the "available energy" to do work in a system. This quantity is the energy associated with a chemical reaction that can be used to do work.

Gibbs free energy is defined as below

$$G = H - TS \text{ ----- (7.35)}$$

Gibbs free energy (G) is an extensive property and it is a single valued

state function.

Let us consider a system which undergoes a change of state from state (1) to state (2) at constant temperature.

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T \Delta S \text{-----(7.36)}$$

Now let us consider how  $\Delta G$  is related to reaction spontaneity.

We know that

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

For a reversible process (equilibrium), the change in entropy of universe is zero.  $\Delta S_{\text{total}} = 0$  [ $\because \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$ ]

Similarly, for an equilibrium process  $\Delta G = 0$

For spontaneous process,  $\Delta S_{\text{total}} > 0$ , so

$$\Delta S_{\text{total}} > 0$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

$$\frac{\Delta H_{\text{sys}}}{T} - \Delta S_{\text{system}} > 0$$

$$\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} > 0$$

$$T \Delta S_{\text{sys}} - \Delta H_{\text{sys}} < 0$$

$$-(\Delta H_{\text{sys}} - T \Delta S_{\text{sys}}) > 0$$

$$-(\Delta G) > 0$$

hence for a spontaneous process,

$$\Delta G < 0$$

$$\text{i.e. } \Delta H - T \Delta S < 0 \text{-----(7.37)}$$

$\Delta H_{\text{sys}}$  is the enthalpy change of a reaction,  $T \Delta S_{\text{sys}}$  is the energy which is not available to do useful work. So  $\Delta G$  is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known

as the free energy of the reaction. For non spontaneous process,  $\Delta G > 0$

### Gibbs free energy and the net work done by the system:

For any system at constant pressure and temperature

$$\Delta G = \Delta H - T \Delta S \text{----- (7.36)}$$

We know that,

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

$$\therefore \Delta G = \Delta U + P \Delta V - T \Delta S$$

from first law of thermodynamics

$$\Delta U = q + w$$

from second law of thermodynamics

$$\Delta S = \frac{q}{T} \quad \Delta G = q + w + P \Delta V - T \left( \frac{q}{T} \right)$$

$$\Delta G = w + P \Delta V$$

$$-\Delta G = -w - P \Delta V \text{.....(7.38)}$$

But  $-P \Delta V$  represents the work done due to expansion against a constant external pressure. Therefore, it is clear that the decrease in free energy ( $-\Delta G$ ) accompanying a process taking place at constant temperature and pressure is equal to the maximum work obtainable from the system other than the work of expansion.

### 7.11.1 Criteria for spontaneity of a process

The spontaneity of any process depends on three different factors.

- If the enthalpy change of a process is negative, then the process is exothermic and may be spontaneous. ( $\Delta H$  is negative)
- If the entropy change of a process is positive, then the process may occur spontaneously. ( $\Delta S$  is positive)
- The gibbs free energy which is the

combination of the above two ( $\Delta H - T\Delta S$ ) should be negative for a reaction to occur spontaneously, i.e. the necessary condition for a reaction to be spontaneous is  $\Delta H - T\Delta S < 0$

**Table 7.5 Effect of Temperature on Spontaneity of Reactions:**

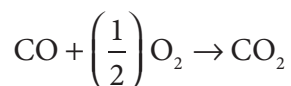
$\Delta H_r$	$\Delta S_r$	$\Delta G_r = \Delta H_r - T\Delta S_r$	Description	Example
-	+	- (at all T)	Spontaneous at all temperature	$2O_3(g) \rightarrow 3O_2(g)$
-	-	- (at low T)	spontaneous at low temperature	Adsorption of gases
		+ (at high T)	non-spontaneous at high temperature	
+	+	+ (at low T)	non-spontaneous at low temperature	Melting of a solid
		- (at high T)	spontaneous at high temperature	
+	-	+ (at all T)	non spontaneous at all temperatures	$2H_2O(g) + O_2(g) \rightarrow 2H_2O_2(l)$

The Table assumes  $\Delta H$  and  $\Delta S$  will remain the way indicated for all temperatures. It may not be necessary that way. The Spontaneity of a chemical reaction is only the potential for the reaction to proceed as written. The rate of such processes is determined by kinetic factors, outside of thermodynamical prediction.

### Problem: 7. 8

Show that the reaction  $CO + \left(\frac{1}{2}\right)O_2 \rightarrow CO_2$

at 300K is spontaneous. The standard Gibbs free energies of formation of  $CO_2$  and CO are  $-394.4$  and  $-137.2$   $\text{kJ mole}^{-1}$  respectively.



$$\Delta G_{(\text{reaction})}^0 = \sum G_{f(\text{products})}^0 - \sum G_{f(\text{reactants})}^0$$

$$\Delta G_{(\text{reaction})}^0 = [G_{CO_2}^0] - \left[ G_{CO}^0 + \frac{1}{2} G_{O_2}^0 \right]$$

$$\Delta G_{(\text{reaction})}^0 = -394.4 + [137.2 + 0]$$

$$\Delta G_{(\text{reaction})}^0 = -257.2 \text{ kJ mol}^{-1}$$

$\Delta G_{(\text{reaction})}$  of a reaction at a given temperature is negative hence the reaction is spontaneous.

### Evaluate Yourself - 8

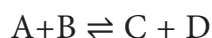


For a chemical reaction the values of  $\Delta H$  and  $\Delta S$  at 300K are  $-10 \text{ kJ mole}^{-1}$  and  $-20 \text{ J deg}^{-1} \text{ mole}^{-1}$  respectively. What is the value of  $\Delta G$  of the reaction? Calculate the  $\Delta G$  of a reaction at 600 K assuming  $\Delta H$  and  $\Delta S$  values are constant. Predict the nature of the reaction.

### 7.11.2 Relationship between standard free energy change ( $\Delta G^0$ ) and equilibrium constant ( $K_{eq}$ ):

In a reversible process, the system is in perfect equilibrium with its surroundings at all times. A reversible chemical reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with decrease in free energy, which is impossible. It is possible only if at equilibrium, the free energy of a system is minimum. Lets consider a general

equilibrium reaction



The free energy change of the above reaction in any state ( $\Delta G$ ) is related to the standard free energy change of the reaction ( $\Delta G^0$ ) according to the following equation.

$$\Delta G = \Delta G^0 + RT \ln Q \text{ -----(7.39)}$$

where  $Q$  is reaction quotient and is defined as the ratio of concentration of the products to the concentrations of the reactants under non equilibrium condition.

When equilibrium is attained, there is no further free energy change i.e.  $\Delta G = 0$  and  $Q$  becomes equal to equilibrium constant. Hence the above equation becomes.

$$\Delta G^0 = -RT \ln K_{eq}$$

This equation is known as Van't Hoff equation.

$$\Delta G^0 = -2.303 RT \log K_{eq} \text{ -----(7.40)}$$

We also know that

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 = - RT \ln K_{eq}$$

### Problem: 7.9

Calculate  $\Delta G^0$  for conversion of oxygen to ozone  $3/2 O_2 \rightleftharpoons O_{3(g)}$  at 298 K, if  $K_p$  for this conversion is  $2.47 \times 10^{-29}$  in standard pressure units.

### Solution:

$$\Delta G^0 = - 2.303 RT \log K_p$$

Where

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

$$K_p = 2.47 \times 10^{-29}$$

$$T = 298\text{K}$$

$$\Delta G^0 = -2.303(8.314)(298)\log(2.47 \times 10^{-29})$$

$$\Delta G^0 = 16300 \text{ Jmol}^{-1}$$

$$\Delta G^0 = 16.3 \text{ KJ mol}^{-1}$$

## 7.12 Third law of Thermodynamics

The entropy of a substance varies directly with temperature. Lower the temperature, lower is the entropy. For example, water above  $100^\circ \text{C}$  at one atmosphere exists as a gas and has higher entropy (higher disorder). The water molecules are free to roam about in the entire container. When the system is cooled, the water vapour condenses to form a liquid. The water molecules in liquid phase still can move about somewhat freely. Thus the entropy of the system has decreased. On further cooling, water freezes to form ice crystal. The water molecules in the ice crystal are highly ordered and entropy of the system is very low.

If we cool the solid crystal still further, the vibration of molecules held in the crystal lattice gets slower and they have very little freedom of movement (very little disorder) and hence very small entropy.

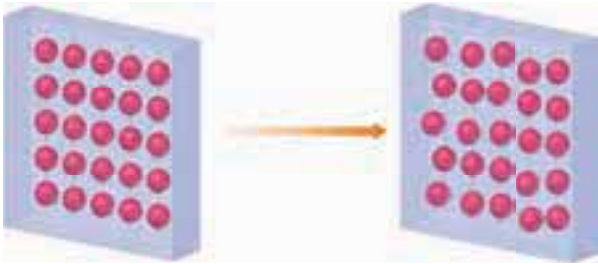
At absolute zero (0 K or  $-273\text{K}$ ), theoretically all modes of motion stop.



Absolute zero is a temperature that an object can get arbitrarily close to but absolute zero will remain unattainable.

Thus the third law of thermodynamics states that the entropy of pure crystalline substance at absolute zero is zero. Otherwise it can be stated as it is impossible to lower the temperature of an object to absolute zero in a finite number of steps. Mathematically,

$$\lim_{T \rightarrow 0} S = 0 \text{ for a perfectly ordered crystalline state.}$$



**Figure 7.10 Third law of Thermodynamics**

Crystals with defects (imperfection) at absolute zero, have entropy greater than zero. Absolute entropy of a substance can never be negative.

## SUMMARY



The branch of science which deals the relation between energy, heat and work is called Thermodynamics. The main aim of the study of chemical thermodynamics is to learn (i) transformation of energy from one form into another form (ii) Utilization of various forms of energies.

**System:** A system is defined as any part of universe under consideration. There are three types of thermodynamic systems. They are (i) isolated system (ii) closed system and (iii) open system.

**Surrounding:** Everything in the universe that is not the part of the system is called surrounding.

**Boundary:** Anything which separates the system from its surrounding is called boundary.

**Thermodynamic Properties:** Any quantity that depends only on the state of system is called thermodynamic property of a system. There are two kinds of thermodynamic properties called (1) intensive - independent of the quantity of material and (2) extensive - directly proportional to the quantity of material. There are five basic thermodynamic properties. (U,H,S and G)

### Thermodynamic Processes:

Adiabatic process in which no heat transfer takes place ( $q = 0$ )

Isothermal process in which

temperature remains constant ( $dT = 0$ ).

Isobaric process in which pressure remains constant ( $dP = 0$ ).

Isochoric process in which volume remains constant ( $dV = 0$ ).

Cyclic process in which the system returns to its original state after completing a series of changes.

**Internal energy (U):** Internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The energy of a system of molecules is equal to the sum of its translational energy, vibrational energy, rotational energy, bond energy, electronic energy and energy due to molecular interactions.

**Heat:** Heat is regarded as the energy in transit across the boundary separating a system from its surrounding. Heat is a path function. The SI unit of heat is joule (J)

**Work :** Work is defined as the force (F) multiplied by the displacement  $-w = F \cdot x$ , work is measured in Joules, i.e the SI unit of work is Joule. During expansion or compression of a gas the work done is calculated by the relation  $w = -P\Delta V$ .

The sign conventions for heat and work are as follows:

If heat is absorbed by the system :  $+q$

If heat is evolved by the system : -q

If work is done by the system : -w

If work is done on the system : +w

### Laws of Thermodynamics:

**Zeroth law :** When two systems are separately in equilibrium with a third system, they are in equilibrium with each other.

**First law:** "Energy can neither be created nor destroyed, but may be converted from one form to another".

$$\Delta U = q + w.$$

Enthalpy is a thermodynamic property of a system. Enthalpy H is defined as the sum of the internal energy and pressure volume work.

$$H=U+PV. \text{ Enthalpy change, } \Delta H = \Delta U + \Delta n_g RT.$$

**Hess's law:** It states that "the enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps". Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure.

### Heat capacities: [ $C_p$ and $C_v$ ]

Heat capacity is defined as the amount of energy required to increase the temperature of one unit quantity of material by one degree, under specific conditions. It can be measured under two different conditions, namely,

(a) constant pressure  $C_p = dH/dT$

(b) constant volume  $C_v = dU/dT$

### Second law of thermodynamics:

The second law of thermodynamics helps us to predict whether the reaction is feasible or not and also tells the direction of the flow of heat.

To predict spontaneity of a process, a new thermodynamic quantity namely entropy (S) was introduced. Entropy is a measure of the randomness or disorderliness of the system.

Entropy statement: "whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the universe".

Kelvin-Planck statement: It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of that heat to a colder reservoir.

Clausius statement: This statement recognises that heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to spend some work.

### Gibbs Free Energy (G):

G is expressed as  $G=H-TS$ , free energy change of a process is given by the relation  $\Delta G= \Delta H-T\Delta S$ .

Standard free energy change and equilibrium constants are related by the equation  $\Delta G^0 = -RT\ln K_{eq}$

### Third law:

The entropy of a perfectly crystalline material at absolute zero is zero.

## EVALUATION



### I. Choose the best answer

- The amount of heat exchanged with the surrounding at constant temperature and pressure is given by the quantity
  - $\Delta E$
  - $\Delta H$
  - $\Delta S$
  - $\Delta G$
- All the naturally occurring processes proceed spontaneously in a direction which leads to
  - decrease in entropy
  - increase in enthalpy
  - increase in free energy
  - decrease in free energy
- In an adiabatic process, which of the following is true ?
  - $q = w$
  - $q = 0$
  - $\Delta E = q$
  - $P \Delta V = 0$
- In a reversible process, the change in entropy of the universe is
  - $> 0$
  - $\geq 0$
  - $< 0$
  - $= 0$
- In an adiabatic expansion of an ideal gas
  - $w = -\Delta u$
  - $w = \Delta u + \Delta H$
  - $\Delta u = 0$
  - $w = 0$
- The intensive property among the quantities below is
  - mass
  - volume
  - enthalpy
  - $\frac{\text{mass}}{\text{volume}}$
- An ideal gas expands from the volume of  $1 \times 10^{-3} \text{ m}^3$  to  $1 \times 10^{-2} \text{ m}^3$  at 300 K against a constant pressure at  $1 \times 10^5 \text{ Nm}^{-2}$ . The work done is
  - 900 J
  - 900 kJ
  - 270 kJ
  - 900 kJ
- Heat of combustion is always
  - positive
  - negative
  - zero
  - either positive or negative
- The heat of formation of CO and CO<sub>2</sub> are - 26.4 kCal and - 94 kCal, respectively. Heat of combustion of carbon monoxide will be
  - + 26.4 kcal
  - 67.6 kcal
  - 120.6 kcal
  - + 52.8 kcal

10.  $C(\text{diamond}) \rightarrow C(\text{graphite})$ ,  $\Delta H = -ve$ , this indicates that
- graphite is more stable than diamond
  - graphite has more energy than diamond
  - both are equally stable
  - stability cannot be predicted
11. The enthalpies of formation of  $Al_2O_3$  and  $Cr_2O_3$  are  $-1596 \text{ kJ}$  and  $-1134 \text{ kJ}$ , respectively.
- $\Delta H$  for the reaction  $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$  is
- $-1365 \text{ kJ}$
  - $2730 \text{ kJ}$
  - $-2730 \text{ kJ}$
  - $-462 \text{ kJ}$
12. Which of the following is not a thermodynamic function ?
- internal energy
  - enthalpy
  - entropy
  - frictional energy
13. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then
- $\Delta H > \Delta U$
  - $\Delta H - \Delta U = 0$
  - $\Delta H + \Delta U = 0$
  - $\Delta H < \Delta U$
14. Change in internal energy, when  $4 \text{ kJ}$  of work is done on the system and  $1 \text{ kJ}$  of heat is given out by the system is
- $+1 \text{ kJ}$
  - $-5 \text{ kJ}$
  - $+3 \text{ kJ}$
  - $-3 \text{ kJ}$
15. The work done by the liberated gas when  $55.85 \text{ g}$  of iron (molar mass  $55.85 \text{ g mol}^{-1}$ ) reacts with hydrochloric acid in an open beaker at  $25^\circ \text{C}$
- $-2.48 \text{ kJ}$
  - $-2.22 \text{ kJ}$
  - $+2.22 \text{ kJ}$
  - $+2.48 \text{ kJ}$
16. The value of  $\Delta H$  for cooling 2 moles of an ideal monatomic gas from  $125^\circ \text{C}$  to  $25^\circ \text{C}$  at constant pressure will be  $\left[ \text{given } C_p = \frac{5}{2} R \right]$
- $-250 R$
  - $-500 R$
  - $500 R$
  - $+250 R$
17. Given that  $C(g) + O_2(g) \rightarrow CO_2(g)$   $\Delta H^0 = -a \text{ kJ}$ ;  $2 CO(g) + O_2(g) \rightarrow 2CO_2(g)$   $\Delta H^0 = -b \text{ kJ}$ ; Calculate the  $\Delta H^0$  for the reaction  $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
- $\frac{b+2a}{2}$
  - $2a-b$
  - $\frac{2a-b}{2}$
  - $\frac{b-2a}{2}$

18. When 15.68 litres of a gas mixture of methane and propane are fully combusted at  $0^{\circ}\text{C}$  and 1 atmosphere, 32 litres of oxygen at the same temperature and pressure are consumed. The amount of heat of released from this combustion in kJ is ( $\Delta H_{\text{C}}(\text{CH}_4) = -890\text{ kJ mol}^{-1}$  and  $\Delta H_{\text{C}}(\text{C}_3\text{H}_8) = -2220\text{ kJ mol}^{-1}$ )
- a)  $-889\text{ kJ}$       b)  $-1390\text{ kJ}$       c)  $-3180\text{ kJ}$       d)  $-653.66\text{ kJ}$
19. The bond dissociation energy of methane and ethane are  $360\text{ kJ mol}^{-1}$  and  $620\text{ kJ mol}^{-1}$  respectively. Then, the bond dissociation energy of C-C bond is
- a)  $170\text{ kJ mol}^{-1}$       b)  $50\text{ kJ mol}^{-1}$       c)  $80\text{ kJ mol}^{-1}$       d)  $220\text{ kJ mol}^{-1}$
20. The correct thermodynamic conditions for the spontaneous reaction at all temperature is (NEET Phase - I)
- a)  $\Delta H < 0$  and  $\Delta S > 0$   
 b)  $\Delta H < 0$  and  $\Delta S < 0$   
 c)  $\Delta H > 0$  and  $\Delta S = 0$   
 d)  $\Delta H > 0$  and  $\Delta S > 0$
21. The temperature of the system, decreases in an \_\_\_\_\_
- a) Isothermal expansion      b) Isothermal Compression      c) adiabatic expansion  
 d) adiabatic compression
22. In an isothermal reversible compression of an ideal gas the sign of q,  $\Delta S$  and w are respectively
- a) +, -, -      b) -, +, -      c) +, -, +      d) -, -, +
23. Molar heat of vapourisation of a liquid is  $4.8\text{ kJ mol}^{-1}$ . If the entropy change is  $16\text{ J mol}^{-1}\text{ K}^{-1}$ , the boiling point of the liquid is
- a)  $323\text{ K}$       b)  $27^{\circ}\text{C}$       c)  $164\text{ K}$       d)  $0.3\text{ K}$
24.  $\Delta S$  is expected to be maximum for the reaction
- a)  $\text{Ca(S)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaO(S)}$   
 b)  $\text{C(S)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   
 c)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO(g)}$   
 d)  $\text{CaCO}_3(\text{S}) \rightarrow \text{CaO(S)} + \text{CO}_2(\text{g})$

25. The values of  $\Delta H$  and  $\Delta S$  for a reaction are respectively  $30 \text{ kJ mol}^{-1}$  and  $100 \text{ JK}^{-1} \text{ mol}^{-1}$ . Then the temperature above which the reaction will become spontaneous is
- a) 300 K                      b) 30 K                      c) 100 K                      d)  $20^{\circ} \text{ C}$
26. State the first law of thermodynamics.
27. Define Hess's law of constant heat summation.
28. Explain intensive properties with two examples
29. Define the following terms:
- a. isothermal process                      b. adiabatic process  
c. isobaric process                      d. isochoric process
30. What is the usual definition of entropy? What is the unit of entropy?
31. Predict the feasibility of a reaction when
- i) both  $\Delta H$  and  $\Delta S$  positive                      ii) both  $\Delta H$  and  $\Delta S$  negative  
iii)  $\Delta H$  decreases but  $\Delta S$  increases
32. Define is Gibbs's free energy.
33. Define enthalpy of combustion.
34. Define molar heat capacity. Give its unit.
35. Define the calorific value of food. What is the unit of calorific value?
36. Define enthalpy of neutralization.
37. What is lattice energy?
38. What are state and path functions? Give two examples.
39. Give Kelvin statement of second law of thermodynamics.
40. The equilibrium constant of a reaction is 10, what will be the sign of  $\Delta G$ ? Will this reaction be spontaneous?
41. Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.

42. State the third law of thermodynamics.
43. Write down the Born-Haber cycle for the formation of  $\text{CaCl}_2$
44. Identify the state and path functions out of the following: a) Enthalpy b) Entropy c) Heat d) Temperature e) Work f) Free energy.
45. State the various statements of second law of thermodynamics.
46. What are spontaneous reactions? What are the conditions for the spontaneity of a process?
47. List the characteristics of internal energy.
48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.
49. Calculate the work involved in expansion and compression process.
50. Derive the relation between  $\Delta H$  and  $\Delta U$  for an ideal gas. Explain each term involved in the equation.
51. Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.
52. List the characteristics of Gibbs free energy.
53. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at  $25^\circ\text{C}$  and normal pressure.
54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is  $2.5 \text{ kJ K}^{-1}$ . Calculate the enthalpy of combustion of the gas in  $\text{kJ mol}^{-1}$ .
55. Calculate the entropy change in the system, and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at  $77^\circ\text{C}$  to the surrounding at  $33^\circ\text{C}$ .
56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710J and expands to 2 litres. Calculate the entropy change in expansion process.
57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is  $28.4 \text{ JK}^{-1} \text{ mol}^{-1}$ . Calculate the melting point of sodium chloride.
58. Calculate the standard heat of formation of propane, if its heat of combustion is  $-2220.2 \text{ kJ mol}^{-1}$ . the heats of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-393.5$  and  $-285.8 \text{ kJ mol}^{-1}$  respectively.



59. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S. No	Liquid	Boiling points ( $^{\circ}\text{C}$ )	$\Delta\text{H}$ ( kJ mol $^{-1}$ )
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

60. For the reaction  $\text{Ag}_2\text{O}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g})$  :  $\Delta\text{H} = 30.56 \text{ kJ mol}^{-1}$  and  $\Delta\text{S} = 6.66 \text{ JK}^{-1} \text{ mol}^{-1}$  (at 1 atm). Calculate the temperature at which  $\Delta\text{G}$  is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

61. What is the equilibrium constant  $K_{\text{eq}}$  for the following reaction at 400K.



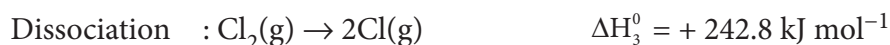
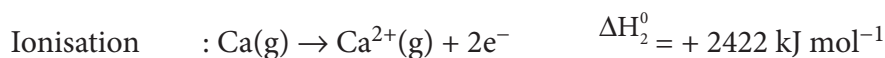
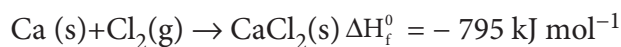
given that  $\Delta\text{H}^{\circ} = 77.2 \text{ kJ mol}^{-1}$  ;

and  $\Delta\text{S}^{\circ} = 122 \text{ JK}^{-1} \text{ mol}^{-1}$ .

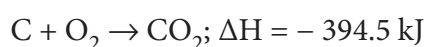
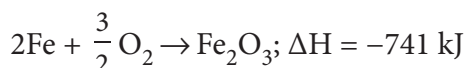
62. Cyanamide ( $\text{NH}_2\text{CN}$ ) is completely burnt in excess oxygen in a bomb calorimeter,  $\Delta\text{U}$  was found to be  $-742.4 \text{ kJ mol}^{-1}$ , calculate the enthalpy change of the reaction at 298K.  $\text{NH}_2\text{CN}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$   $\Delta\text{H} = ?$

63. Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C – H, C – C, C = C and H – H are 414, 347, 618 and 435 kJ mol $^{-1}$ .

64. Calculate the lattice energy of  $\text{CaCl}_2$  from the given data



65. Calculate the enthalpy change for the reaction  $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$  from the following data.



66. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne(A) , 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at 175°C, calculate  $\Delta G^0$  for the following equilibria.



67. At 33K,  $N_2O_4$  is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

68. The standard enthalpies of formation of  $SO_2$  and  $SO_3$  are  $-297 \text{ kJ mol}^{-1}$  and  $-396 \text{ kJ mol}^{-1}$  respectively. Calculate the standard enthalpy of reaction for the reaction:  $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$

69. For the reaction at 298 K :  $2A + B \rightarrow C$

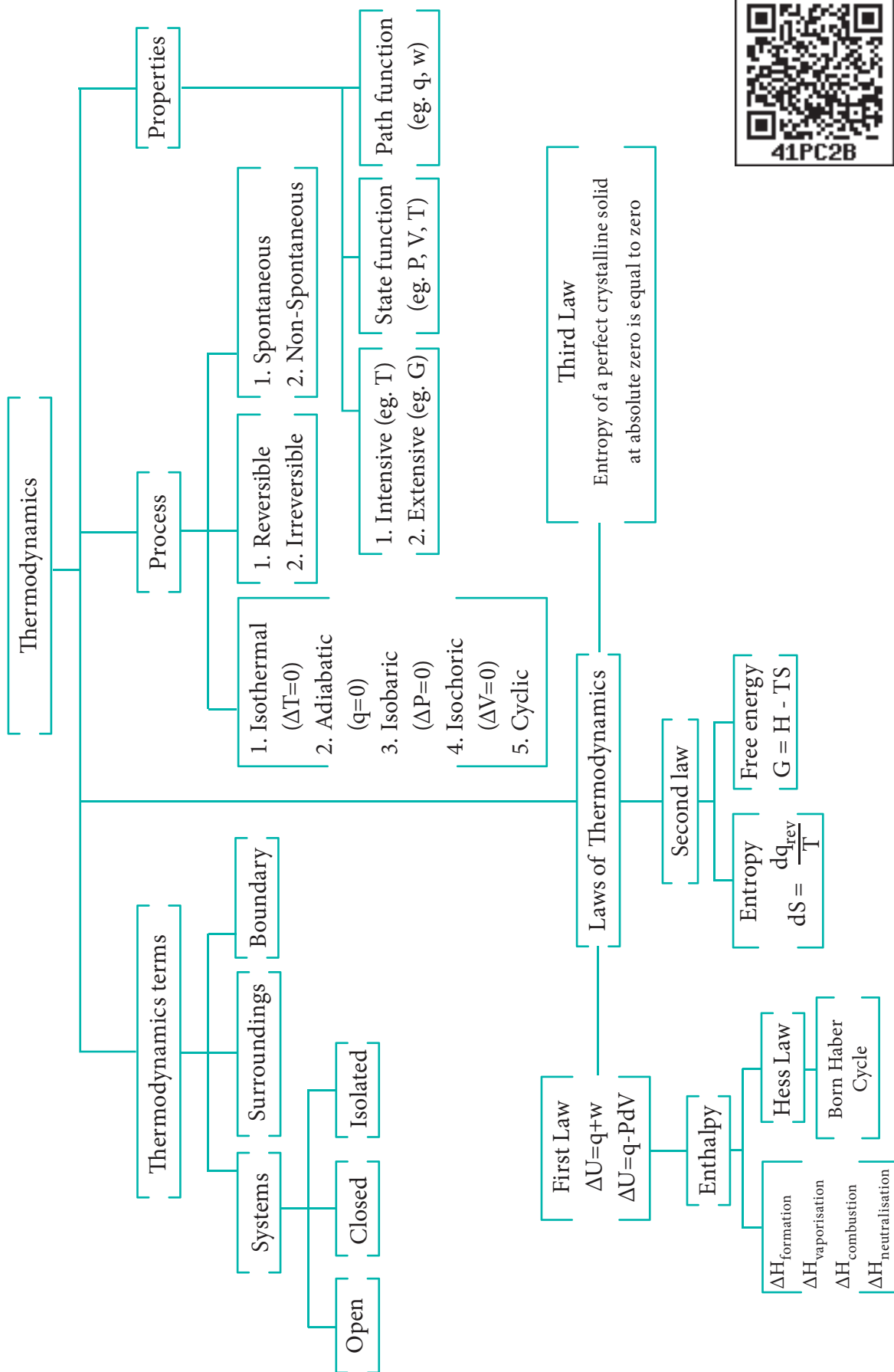
$\Delta H = 400 \text{ J mol}^{-1}$  ;  $\Delta S = 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$  Determine the temperature at which the reaction would be spontaneous.

70. Find out the value of equilibrium constant for the following reaction at 298K,  $2 NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2(aq) + H_2O(l)$  Standard Gibbs energy change,  $\Delta G_r^0$  at the given temperature is  $-13.6 \text{ kJ mol}^{-1}$ .

71. A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at 1 atm pressure produce 6.11 lit of carbondioxide. Find out the amount of heat evolved in kJ, during this combustion. ( $\Delta H_C(CH_4) = -890 \text{ kJ mol}^{-1}$  and ( $\Delta H_C(C_2H_4) = -1423 \text{ kJ mol}^{-1}$



## CONCEPT MAP



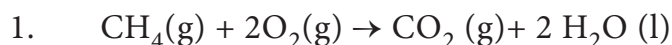
## EVALUATION



### I Choose the best answer

- (a) 40 ml of CO<sub>2</sub> gas
- (d) 200 u
- (c) assertion is true but reason is false
- (b) oxygen
- (a) 102 g
- (c)  $6.022 \times 10^{20}$
- (c) 16 %
- (c) 0.075
- (d) 1 mole of HCl
- (c)  $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2 \text{HCl}$
- (b)  $\text{P}_4 + 3 \text{NaOH} + 3 \text{H}_2\text{O} \rightarrow \text{PH}_3 + 3 \text{NaH}_2\text{PO}_2$
- (b) 52.7
- (d)  $6.022 \times 10^{24}$  molecules of water
- (a) NO
- (a)  $6.022 \times 10^{23}$
- (c)  $\text{S}_2\text{O}_4^{2-} < \text{SO}_3^{2-} < \text{S}_2\text{O}_6^{2-} < \text{SO}_4^{2-}$
- (c) molar mass of ferrous oxalate / 3
- (d) the mass of one mole of carbon
- (c) the ratio between the number of molecules in A to number of molecules in B is 2:1
- (a) 3.59 g
- (b)  $44 \text{ g mol}^{-1}$
- (c) both (a) & (b)
- (a) propene
- (a) relative atomic mass is 12 u
- (a)  ${}_6\text{C}^{12}$

### Key to the multiple choice questions



Content	$\text{CH}_4$	$\text{O}_2$	$\text{CO}_2$
Stoichiometric coefficient	1	2	1
Volume of reactants allowed to react	40 mL	80 mL	
Volume of reactant reacted and product formed	40 mL	80 mL	40 mL
Volume of gas after cooling to the room temperature	-	-	-

Since the product was cooled to room temperature, water exists mostly as liquid. Hence, option (a) is correct

2.

$$= \frac{(200 \times 90) + (199 \times 8) + (202 \times 2)}{200 \text{ u}} = 199.96$$

3. Correct reason: Total number of entities present in one mole of any substance is equal to  $6.022 \times 10^{23}$ .

4. Reaction 1 :  $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$   
 $2 \times 12 \text{ g carbon combines with } 32 \text{ g of oxygen. Hence,}$

$$\text{Equivalent mass of carbon} = \frac{2 \times 12}{32} \times 8 = 6$$

Reaction 2 :  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

$12 \text{ g carbon combines with } 32 \text{ g of oxygen. Hence,}$

$$\text{Equivalent mass of carbon} = \frac{12}{32} \times 8 = 3$$

5. Let the trivalent metal be  $\text{M}^{3+}$

Equivalent mass = mass of the metal / valance factor

$9 \text{ g eq}^{-1} = \text{mass of the metal} / 3 \text{ eq}$

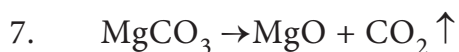
Mass of the metal = 27 g

Oxide formed  $\text{M}_2\text{O}_3$  ;

Mass of the oxide =  $(2 \times 27) + (3 \times 16)$

= **102 g**

6. Weight of the water drop = 0.018 g  
 No. of moles of water in the drop = Mass of water / molar mass  
 =  $0.018 / 18 = 10^{-3}$  mole  
 No of water molecules present in 1 mole of water =  $6.022 \times 10^{23}$   
 No. water molecules in one drop of water ( $10^{-3}$  mole) =  $6.022 \times 10^{23} \times 10^{-3}$   
 =  **$6.022 \times 10^{20}$**



$\text{MgCO}_3$  :  $(1 \times 24) + (1 \times 12) + (3 \times 16) = 84$  g

$\text{CO}_2$  :  $(1 \times 12) + (2 \times 16) = 44$  g

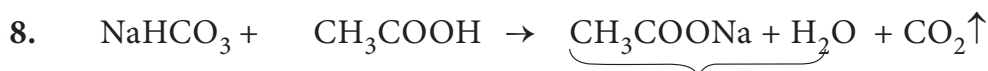
100 % pure 84 g  $\text{MgCO}_3$  on heating gives 44 g  $\text{CO}_2$

Given that 1 g of  $\text{MgCO}_3$  on heating gives 0.44 g  $\text{CO}_2$

Therefore, 84 g  $\text{MgCO}_3$  sample on heating gives 36.96 g  $\text{CO}_2$

Percentage of purity of the sample =  $\frac{100\%}{44 \text{ g CO}_2} \times 36.96 \text{ g CO}_2$   
 = 84 %

Percentage of impurity = **16 %**



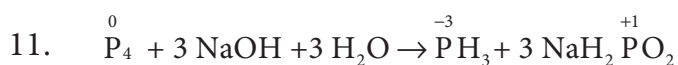
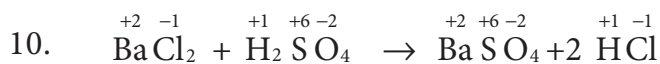
6.3 g + 30 g → 33 g + x

The amount of  $\text{CO}_2$  released, x = 3.3 g

No. of moles of  $\text{CO}_2$  released =  $3.3 / 44 = 0.075$  mol



Content	$\text{H}_2(\text{g})$	$\text{Cl}_2(\text{g})$	$\text{HCl}(\text{g})$
Stoichiometric coefficient	1	1	2
No. of moles of reactants allowed to react at 273 K and 1 atm pressure	22.4 L (1 mol)	11.2 L (0.5 mol)	-
No. of moles of reactant reacted and product formed	0.5	0.5	1
<b>Amount of HCl formed = 1 mol</b>			



12. The reduction reaction of the oxidising agent ( $\text{MnO}_4^-$ ) involves gain of 3 electrons. Hence the equivalent mass = (Molar mass of  $\text{KMnO}_4$ )/3 = 158.1/3 = 52.7

13. No. of moles of water present in 180 g  
 = Mass of water / Molar mass of water  
 = 180 g / 18 g mol<sup>-1</sup> = 10 moles

One mole of water contains

$$= 6.022 \times 10^{23} \text{ water molecules}$$

10 mole of water contains = 6.022 x 10<sup>23</sup> x 10 = 6.022 x 10<sup>24</sup> water molecules

14. 7.5 g of gas occupies a volume of 5.6 liters at 273 K and 1 atm pressure Therefore, the mass of gas that occupies a volume of 22.4 liters

$$= \frac{7.5 \text{ g}}{5.6 \text{ L}} \times 22.4 \text{ L} = 30 \text{ g}$$

Molar mass of NO (14+16) = 30 g

15. No. of electrons present in one ammonia ( $\text{NH}_3$ ) molecule (7 + 3) = 10

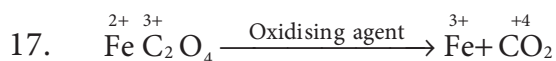
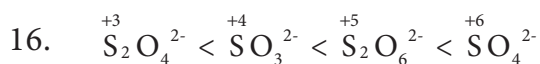
$$\begin{aligned} \text{No. of moles of ammonia} &= \frac{\text{Mass}}{\text{Molar mass}} \\ &= \frac{1.7 \text{ g}}{17 \text{ gmol}^{-1}} \\ &= 0.1 \text{ mol} \end{aligned}$$

No. of molecules present in 0.1 mol of ammonia

$$= 0.1 \times 6.022 \times 10^{23} = 6.022 \times 10^{22}$$

No. of electrons present in 0.1 mol of ammonia

$$= 10 \times 6.022 \times 10^{22} = 6.022 \times 10^{23}$$



$$n = 1 + 2(1) = 3$$

18. The mass of one mole of carbon

$$\begin{aligned} 19. \text{ No, of moles of oxygen} &= 8 \text{ g}/32 \text{ g} \\ &= 0.25 \text{ moles of oxygen} \\ \text{No. of moles of sulphur dioxide} &= 8 \text{ g} / 64 \text{ g} \\ &= 0.125 \text{ moles of sulphur dioxide} \\ \text{Ratio between the no. of molecules} &= 0.25: 0.125 \\ &= 2:1 \end{aligned}$$

20.  $\text{AgNO}_3 + \text{KCl} \rightarrow \text{KNO}_3 + \text{AgCl}$

50 mL of 8.5 % solution contains 4.25 g of  $\text{AgNO}_3$

No. of moles of  $\text{AgNO}_3$  present in 50 mL of 8.5 %  $\text{AgNO}_3$  solution

$$\begin{aligned} &= \text{Mass} / \text{Molar mass} \\ &= 4.25 / 170 \\ &= 0.025 \text{ moles} \end{aligned}$$

Similarly, No of moles of  $\text{KCl}$  present in 100 mL of 1.865 %  $\text{KCl}$  solution

$$\begin{aligned} &= 1.865 / 74.5 \\ &= 0.025 \text{ moles} \end{aligned}$$

So total amount of  $\text{AgCl}$  formed is 0.025 moles (based on the stoichiometry)

Amount of  $\text{AgCl}$  present in 0.025 moles of  $\text{AgCl}$

$$\begin{aligned} &= \text{no. of moles} \times \text{molar mass} \\ &= \mathbf{0.025 \times 143.5 = 3.59 \text{ g}} \end{aligned}$$

21. No. of moles of a gas that occupies a volume of 612.5 mL at room temperature and pressure ( $25^\circ \text{C}$  and 1 atm pressure)

$$\begin{aligned} &= 612.5 \times 10^{-3} \text{ L} / 24.5 \text{ Lmol}^{-1} \\ &= 0.025 \text{ moles} \end{aligned}$$

We know that,

$$\begin{aligned} \text{Molar mass} &= \text{Mass} / \text{no. of moles} \\ &= \mathbf{1.1 \text{ g} / 0.025 \text{ mol} = 44 \text{ g mol}^{-1}} \end{aligned}$$



22. No. of moles of carbon present in 6 g of C-12 = Mass / Molar mass

$$= 6/12 = 0.5 \text{ moles} = 0.5 \times 6.022 \times 10^{23} \text{ carbon atoms.}$$

No. of moles in 8 g of methane =  $8 / 16 = 0.5$  moles

$$= 0.5 \times 6.022 \times 10^{23} \text{ carbon atoms.}$$

No. of moles in 7.5 g of ethane =  $7.5 / 16 = 0.25$  moles

$$= 2 \times 0.25 \times 6.022 \times 10^{23} \text{ carbon atoms.}$$

23. Percentage of carbon in ethylene ( $C_2H_4$ ) =  $\frac{\text{mass of carbon}}{\text{Molar mass}} \times 100$   
$$= \frac{24}{28} \times 100 = 85.71\%$$

Percentage of carbon in propene ( $C_3H_6$ ) =  $\frac{36}{42} \times 100 = 85.71\%$

24. (a) relative atomic mass of C-12 is 12 u

25.  ${}_6C^{12}$

## II Key to brief answer questions:

32. Given :

The density of  $CO_2$  at 273 K and 1 atm pressure =  $1.965 \text{ kgm}^{-3}$

Molar mass of  $CO_2$  = ?

At 273 K and 1 atm pressure, 1 mole of  $CO_2$  occupies a volume of 22.4 L

$$\begin{aligned} \text{Mass of 1 mole of } CO_2 &= \frac{1.965 \text{ Kg}}{1 \text{ m}^3} \times 22.4 \text{ L} \\ &= \frac{1.965 \times 10^3 \text{ g} \times 22.4 \times 10^{-3} \text{ m}^3}{1 \text{ m}^3} \\ &= 44.01 \text{ g} \end{aligned}$$

Molar mass of  $CO_2$  =  $44 \text{ gmol}^{-1}$

33.

Compound	Given no. of moles	No. of oxygen atoms
Ethanol - C <sub>2</sub> H <sub>5</sub> OH	1	1 × 6.022 × 10 <sup>23</sup>
Formic acid - HCOOH	1	2 × 6.022 × 10 <sup>23</sup>
Water - H <sub>2</sub> O	1	1 × 6.022 × 10 <sup>23</sup>
<b>Answer : Formic acid</b>		

$$\begin{aligned}
 34. \quad \text{Average atomic mass} &= \frac{(78.99 \times 23.99) + (10 \times 24.99) + (11.01 \times 25.98)}{100} \\
 &= \frac{2430.9}{100} \\
 &= 24.31 \text{ u}
 \end{aligned}$$

35. Reaction :  $x + y + z_2 \rightarrow xyz_2$ 

Question	Number of moles of reactants allowed to react			Number of moles of reactants consumed during reaction			Limiting reagent
	x	y	z <sub>2</sub>	x	y	z <sub>2</sub>	
(a)	200 atoms	200 atoms	50 molecules	50 atoms	50 atoms	50 molecules	z <sub>2</sub>
(b)	1 mol	1 mol	3 mol	1 mol	1 mol	1 mol	x and y
(c)	50 atom	25 atom	50 molecules	25 atom	25 atom	25 molecules	y
(d)	2.5 mol	5 mol	5 mol	2.5 mol	2.5 mol	2.5 mol	x

36. Given: mass of one atom =  $6.645 \times 10^{-23}$  g

$$\begin{aligned}
 \therefore \text{mass of 1 mole of atom} &= 6.645 \times 10^{-23} \text{ g} \times 6.022 \times 10^{23} \\
 &= 40 \text{ g}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \text{number of moles of element in 0.320 kg} &= \frac{1 \text{ mole}}{40 \text{ g}} \times 0.320 \text{ kg} \\
 &= \frac{1 \text{ mol} \times 320 \text{ g}}{40 \text{ g}}
 \end{aligned}$$

$$= 8 \text{ mol.}$$

38.

Compound	Molecular formula	Empirical formula
Fructose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	CH <sub>2</sub> O
Caffeine	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>4</sub> H <sub>5</sub> N <sub>2</sub> O

39. Given  $2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$

	Reactants		Products	
	Al	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	Fe
Amount of reactant allowed to react	324 g	1.12 kg	-	-
Number of moles allowed to react	$\frac{324}{27} = 12 \text{ mol}$	$\frac{1.12 \times 10^3}{160} = 7 \text{ mol}$	-	-
Stoichiometric Co-efficient	2	1	1	2
Number of moles consumed during reaction	12 mol	6 mol	-	-
Number of moles of reactant unreacted and number of moles of product formed	-	1 mol	6 mol	12 mol

Molar mass of  $\text{Al}_2\text{O}_3$  formed

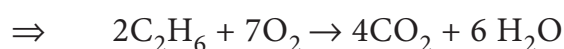
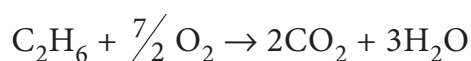
$$= 6 \text{ mol} \times 102 \text{ g mol}^{-1} \left[ \begin{array}{l} \text{Al}_2\text{O}_3 \\ (2 \times 27) + 3(\times 16) \\ 54 + 48 = 102 \end{array} \right] = 612 \text{ g}$$

Excess reagent =  $\text{Fe}_2\text{O}_3$

Amount of excess reagent left at the end of the reaction =  $1 \text{ mol} \times 160 \text{ g mol}^{-1}$

$$= 160 \text{ g} \left[ \begin{array}{l} \text{Fe}_2\text{O}_3 \\ (2 \times 56) + (3 \times 16) \\ 112 + 48 = 160 \end{array} \right] = 160 \text{ g}$$

40. Balanced equation for the combustion of ethane

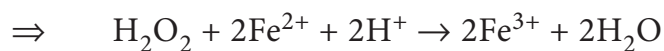
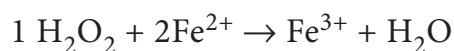
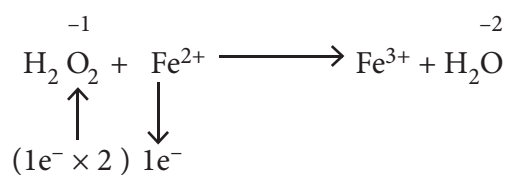


To produce 4 moles of  $\text{CO}_2$ , 2 moles of ethane is required

$\therefore$  To produce 1 mole (44 g) of  $\text{CO}_2$  required

$$\begin{aligned} \text{number of moles of ethane} &= \frac{2 \text{ mol ethane}}{4 \text{ mol CO}_2} \times \cancel{1 \text{ mol CO}_2} \\ &= \frac{1}{2} \text{ mole of ethane} \\ &= \mathbf{0.5 \text{ mole of ethane}} \end{aligned}$$

41.



42.

Element	Percentage	Atomic mass	Relative number of atoms	Simple ratio	Whole no.
C	76.6	12	$\frac{76.6}{12} = 6.38$	$\frac{6.38}{1.06} = 6$	6
H	6.38	1	$\frac{6.38}{1} = 6.38$	$\frac{6.38}{1.06} = 6$	6
O	17.02	16	$\frac{17.02}{16} = 1.06$	$\frac{1.06}{1.06} = 1$	1

$$\text{Empirical formula} = \text{C}_6 \text{H}_6 \text{O}$$

$$n = \frac{\text{Molar mass}}{\text{Calculated empirical formula mass}}$$

$$= \frac{2 \times \text{vapour density}}{94} = \frac{2 \times 47}{94} = 1$$

$$\therefore \text{molecular formula } (\text{C}_6\text{H}_6\text{O}) \times 1 = \text{C}_6\text{H}_6\text{O}$$

43.

Element	%	Relative no. of atoms	Simple ratio
Na	14.31	$\frac{14.31}{23} = 0.62$	$\frac{0.62}{0.31} = 2$
S	9.97	$\frac{9.97}{32} = 0.31$	$\frac{0.31}{0.31} = 1$
H	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.31} = 20$
O	69.5	$\frac{69.5}{16} = 4.34$	$\frac{4.34}{0.31} = 14$

$\therefore$  Empirical formula =  $\text{Na}_2 \text{S H}_{20} \text{O}_{14}$

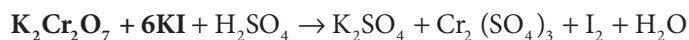
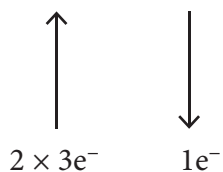
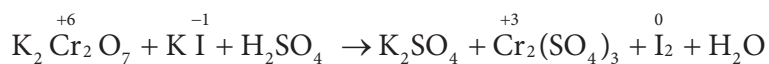
$$n = \frac{\text{molar mass}}{\text{calculated empirical formula mass}} = \frac{322}{322} = 1 \quad \left[ \begin{array}{l} \text{Na}_2 \text{S H}_{20} \text{O}_{14} \\ = (2 \times 23) + (1 \times 32) + (20 \times 1) + 14(16) \\ = 46 + 32 + 20 + 224 \\ = 322 \end{array} \right]$$

Molecular formula =  $\text{Na}_2 \text{S H}_{20} \text{O}_{14}$

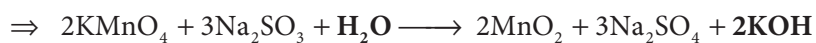
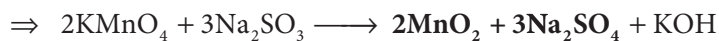
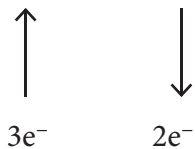
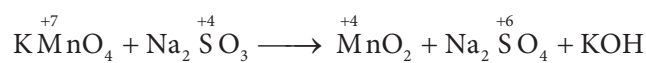
Since all the hydrogen in the compound present as water

$\therefore$  Molecular formula is  $\text{Na}_2 \text{SO}_4 \cdot 10\text{H}_2\text{O}$

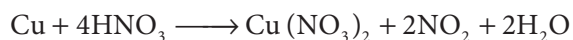
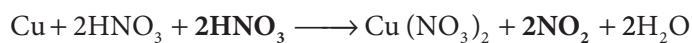
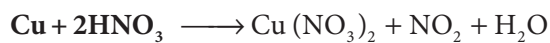
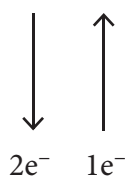
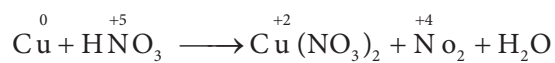
44. (i)



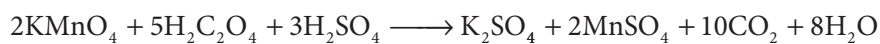
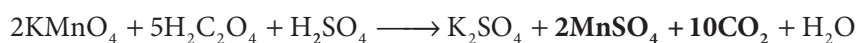
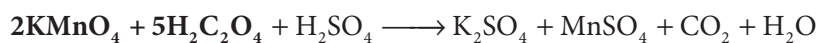
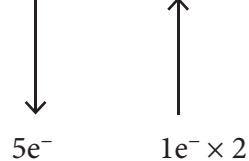
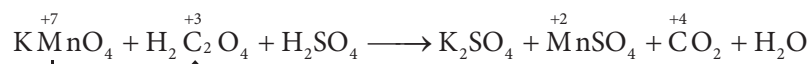
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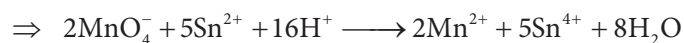
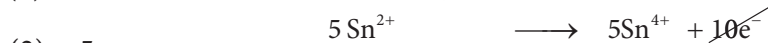
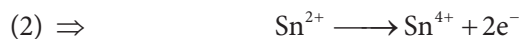
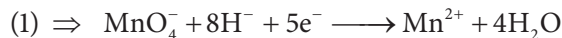
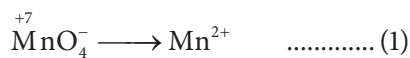
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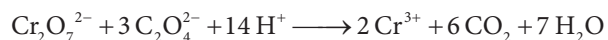
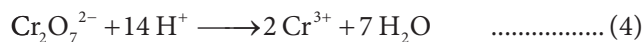
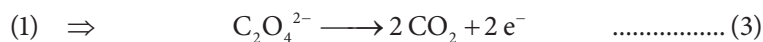
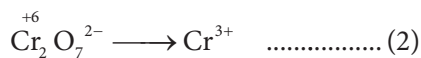
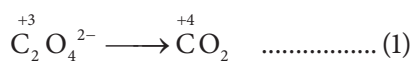
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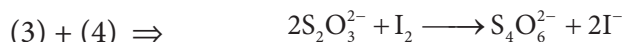
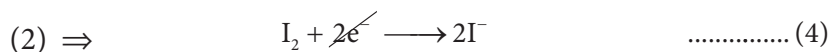
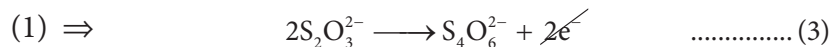
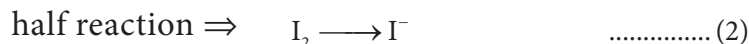
45. (i) Half reaction are



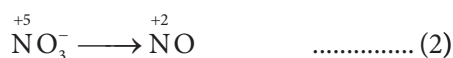
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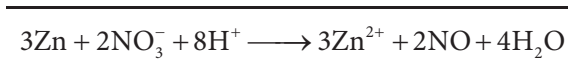
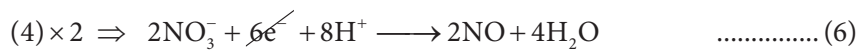
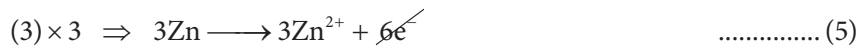
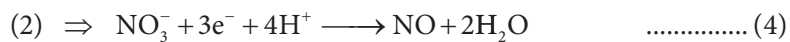


(iii)



(iv) Half reactions are







## Unit - 2

### Quantum Mechanical Model of Atom

Evaluate yourself:

1) Given: accelerated potential = 1 keV

The kinetic energy of the electron =  
the energy due to accelerating potential.

$$\frac{1}{2}mv^2 = eV$$

$$mv^2 = 2eV$$

$$m^2v^2 = 2meV \Rightarrow (mv)^2 = 2meV$$

$$\Rightarrow mv = \sqrt{2meV}$$

$$\text{de Broglie wavelength } \lambda = \frac{h}{mv}$$

$$\Rightarrow \lambda = \frac{h}{\sqrt{2meV}}$$

m = mass of the electron =  $9.1 \times 10^{-31}$  kg

h = Planck constant =  $6.626 \times 10^{-34}$  Js

1 eV =  $1.6 \times 10^{-19}$  J

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{\sqrt{2 \times 9.1 \times 10^{-31} \text{ kg} \times 1 \text{ keV}}}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ JS}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1 \times 10^3 \times 1.6 \times 10^{-19} \text{ kgJ}}}$$

$$\lambda = 3.88 \times 10^{-11} \text{ m}$$

$$\begin{aligned} [\because \frac{\text{Js}}{\sqrt{\text{J kg}}} &= \text{J}^{1/2} \text{kg}^{-1/2} \cdot \text{s} \\ &= (\text{kgm}^2 \text{s}^{-2})^{1/2} \cdot \text{kg}^{-1/2} \cdot \text{s} \\ &= \text{m}] \end{aligned}$$

2. Given

$$\Delta v = 5.7 \times 10^5 \text{ ms}^{-1} \quad \Delta x = ?$$

According to Heisenberg's uncertainty principle,  $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

$$\frac{h}{4\pi} = \frac{6.626 \times 10^{-34}}{4 \times 3.14} \text{ kgm}^2 \text{ s}^{-1}$$

$$\frac{h}{4\pi} = 5.28 \times 10^{-35}$$

$$\Delta x \cdot \Delta p \geq 5.28 \times 10^{-35}$$

$$\Delta x \cdot m \cdot \Delta v \geq 5.28 \times 10^{-35}$$

$$\Rightarrow \Delta x \geq \frac{5.28 \times 10^{-35} \text{ kgm}^2 \text{ s}^{-1}}{9.1 \times 10^{-31} \text{ kg} \times 5.7 \times 10^5 \text{ ms}^{-1}}$$

$$\Rightarrow \Delta x \geq 1.017 \times 10^{-10} \text{ m}$$

3.  $n = 4$

$l = 0, 1, 2, 3$

$\therefore$  4 sub shells s, p, d & f.

$l = 0 \ m_l = 0 \Rightarrow$  one 4s orbital.

$l = 1 \ m_l = -1, 0, +1 \Rightarrow$  three 4p orbitals.

$l = 2 \ m_l = -2, -1, 0, +1, +2 \Rightarrow$  five 4d orbitals.

$l = 3 \ m_l = -3, -2, -1, 0, +1, +2, +3 \Rightarrow$  seven 4f orbitals.

Over all 16 orbitals are possible.

4.

Orbital	n	l	Radial node $n - l - 1$	Angular node $l$	Total node $n - 1$
3d	3	2	0	2	2
4f	4	3	0	3	3

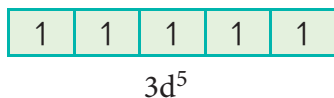
5.  $E_n = \frac{-13.6}{n^2} \text{eV}$

Second excited state

$n = 3 \quad \therefore E_3 = \frac{-13.6}{9} \text{eV}$   
 $E_3 = -1.51 \text{eV}$

6. Electronic configuration of  $\text{Fe}^{3+}$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

**Five unpaired electrons.**



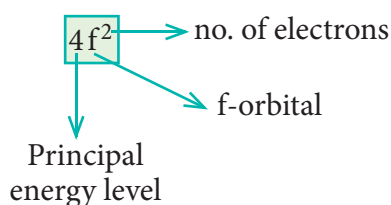
Electronic configuration of  $\text{Mn}^{2+}$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

$\therefore$  **Five unpaired electrons.**

Electronic configuration of Ar:  $1s^2 2s^2 2p^6 3s^2 3p^6$

**no unpaired electrons.**

7.



$$n = 4 ; f \text{ orbital } l = 3 \Rightarrow m_l = -3, -2, -1, 0, +1, +2$$

Out of two electrons, one electron occupies 4f orbital with  $m_l = -3$  and another electron occupies 4f orbital with  $m_l = -2$ .

$\therefore$  All the four quantum numbers for the two electrons are

Electron	n	l	$m_l$	$m_s$
$1e^-$	4	3	-3	+1/2
$2e^-$	4	3	-2	+1/2

8.

Electronic configuration of  $Fe^{3+}$  :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^5$

Electronic configuration of  $Ni^{2+}$  :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^8$

**$Fe^{3+}$  has stable  $3d^5$  half filled configuration.**

## EVALUATION

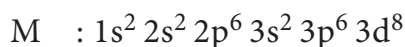
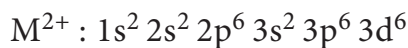


### I Choose the best answer:

- (c) 30
- (c)  $4.42 \times 10^{-18} \text{ J}$
- (b)  $\lambda_1 = 2\lambda_2$
- (d) Stark effect
- (b)
- (d)  $n=6$  to  $n=5$
- (a)
- (c)  $d_{z^2}, d_{x^2-y^2}$
- (b) Spin quantum number
- (b)  $[Xe]4f^7 6s^2$  ;  $[Xe]4f^7 5d^1 6s^2$  ;  $[Xe]4f^9 6s^2$
- (c)  $4l+2$
- (d)  $\sqrt{6} h/2\pi$
- (c) 2
- (c)
- (a) 9
- (a)  $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$
- (b) (ii),(iv) & (v)
- (b) 17
- (a) Zero
- (c)  $1/2m \sqrt{h/\pi}$
- (c)  $6.6 \times 10^{-31} \text{ cm}$
- (d) 0.4
- (d)  $-9E$
- (a)  $\hat{H}\psi = E\psi$
- (d)  $\Delta E \cdot \Delta X \geq h/4\pi$

**Key to multiple choice questions:**

1.



Atomic number = 26

Mass number = 56

No. of neutrons = 56 - 26 = 30

$$2. E = h\nu = hc/\lambda$$

$$= \frac{6.626 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{45 \times 10^{-9} \text{ m}}$$

$$= 4.42 \times 10^{-18} \text{ J}$$

3.

$$\frac{E_1}{E_2} = \frac{25 \text{ eV}}{50 \text{ eV}} = \frac{1}{2}$$

$$\frac{hc}{\lambda_1} \times \frac{\lambda_2}{hc} = \frac{1}{2}$$

$$2\lambda_2 = \lambda_1$$

4. Splitting of spectral lines in magnetic field is called Zeeman effect and splitting of spectral lines in electric field, is called Stark effect.

5. **Correct statement:** For  $n=1$ , the electron has more negative energy than it does for  $n=6$  which means that the electron is **strongly** bound in the smallest allowed orbit.

6.  $n = 6$  to  $n=5$

$$E_6 = -13.6 / 6^2 ; \quad E_5 = -13.6 / 5^2$$

$$E_6 - E_5 = (-13.6 / 6^2) - (-13.6 / 5^2)$$

$$= 0.166 \text{ eV atom}^{-1}$$

$$E_5 - E_4 = (-13.6 / 5^2) - (-13.6 / 4^2)$$

$$= 0.306 \text{ eV atom}^{-1}$$

9. Spin quantum number

For the first electron  $m_s = +\frac{1}{2}$

For the second electron  $m_s = -\frac{1}{2}$

10. Eu : [Xe]  $4f^7, 5d^0, 6s^2$

Gd : [Xe]  $4f^7, 5d^1, 6s^2$

Tb: [Xe]  $4f^9, 5d^0, 6s^2$

$$11. 2(2l+1) = 4l+2$$

12. Orbital angular momentum =  $\sqrt{l(l+1)} h/2\pi$  For d orbital =  $\sqrt{(2 \times 3)} h/2\pi = \sqrt{6} h/2\pi$

13.  $n = 3; l=1; m = -1$

either  $3p_x$  or  $3p_y$

i.e., Maximum two electrons can be accommodated either in  $3p_x$  or in  $3p_y$

14. No. of radial node =  $n-l-1$

No. of angular node =  $l$

for  $3p$  orbital

No. of angular node =  $l = 1$

No. of radial node =  $n-l-1 = 3-1-1 = 1$

15.  $n = 3; l = 0; m_l = 0$  - one s orbital

$n = 3; l = 1; m_l = -1, 0, 1$  - three p orbitals

$n = 3; l = 2; m_l = -2, -1, 0, 1, 2$  - five d Orbitals

Overall nine orbitals are possible.

16.  $n = 6$

According Aufbau principle,

$$6s \rightarrow 4f \rightarrow 5d \rightarrow 6p$$

$$ns \rightarrow (n-1)f \rightarrow (n-2)d \rightarrow np$$

17 (ii)  $l$  can have the values from 0 to  $n-1$

$n=2$ ; possible 'l' values are 0, 1 hence  $l = 2$  is not possible.

(iv) for  $l=0$ ;  $m=-1$  not possible

(v) for  $n=3$   $l = 4$  and  $m = 3$  not possible

18.  $n+l = 8$

Electronic configuration of atom with atomic number 105 is  $[Rn] 5f^{14} 6d^3 7s^2$

Orbital	(n+l)	No. of electrons
5f	$5+3 = 8$	14
6d	$6+2 = 8$	3
7s	$7+0 = 0$	2
<b>No of electrons = 14 + 3 = 17</b>		

19. Option (a) - Zero (Refer to Figure 2.9)

20.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta p \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta p^2 \geq \frac{h}{4\pi}$$

$$m^2 (\Delta v)^2 \geq \frac{h}{4\pi}$$

$$(\Delta v) \geq \sqrt{\frac{h}{4\pi m^2}}$$

$$\Delta v \geq \frac{1}{2m} \sqrt{\frac{h}{\pi}}$$

21.

$$m = 100 \text{ g} = 100 \times 10^{-3} \text{ kg}$$

$$v = 100 \text{ cm s}^{-1} = 100 \times 10^{-2} \text{ m s}^{-1}$$

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34} \text{ Js}^{-1}}{100 \times 10^{-3} \text{ kg} \times 100 \times 10^{-2} \text{ ms}^{-1}}$$

$$= 6.626 \times 10^{-33} \text{ ms}^{-1}$$

$$= 6.626 \times 10^{-31} \text{ cms}^{-1}$$

23.

$$E_n = \frac{-13.6}{n^2} \text{ eV atom}^{-1}$$

$$E_1 = \frac{-13.6}{(1)^2} = -13.6$$

$$E_3 = \frac{-13.6}{(3)^2} = -\frac{13.6}{9}$$

Givethat

$$E_3 = -E$$

$$-\frac{13.6}{9} = -E$$

$$-13.6 = -9E$$

$$\Rightarrow E_1 = -9E$$

## II Key to brief answer question:

27.  $n = 4$   $l = 0, 1, 2, 3$

four sub-shells  $\Rightarrow$  s, p, d, f

$l = 0$   $m_l = 0$ ; one 4s orbital.

$l = 1$   $m_l = -1, 0, +1$ ; three 4p orbitals.

$l = 2$   $m_l = -2, -1, 0, +1, +2$ ; five 4d orbitals.

$l = 3$   $m_l = -3, -2, -1, 0, +1, +2, +3$ ; seven 4f orbitals

Over all Sixteen orbitals.

28.

Orbital	n	l	Radial node $n - l - 1$	Angular node $l$
2s	2	0	1	0
4p	4	1	2	1
5d	5	2	2	2
4f	4	3	0	3

30. i) ground state

1	1	1	1	1
---	---	---	---	---

ii) maximum exchange energy

1	1	1	1	1
---	---	---	---	---

32.

Orbital	n	l
$3p_x$	3	1
$4d_{x^2-y^2}$	4	2

34.

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta p \geq 5.28 \times 10^{-35} \text{ Kg m}^2 \text{ s}^{-1}$$

$$\Delta x \cdot (m\Delta v) \geq 5.28 \times 10^{-35} \text{ Kg m}^2 \text{ s}^{-1}$$

Given  $\Delta v = 0.1\%$

$$v = 2.2 \times 10^6 \text{ ms}^{-1}$$

$$m = 9.1 \times 10^{-31} \text{ Kg}$$

$$\Delta v = \frac{0.1}{100} \times 2.2 \times 10^6 \text{ ms}^{-1}$$

$$= 2.2 \times 10^3 \text{ ms}^{-1}$$

$$\therefore \Delta x \geq \frac{5.28 \times 10^{-35} \text{ Kg m}^2 \text{ s}^{-1}}{9.1 \times 10^{-31} \text{ Kg} \times 2.2 \times 10^3 \text{ ms}^{-1}}$$

$$\Delta x \geq 2.64 \times 10^{-8} \text{ m}$$

35. Electronic configuration of oxygen

$$= 1s^2 \ 2s^2 \ 2p^4$$

$$\boxed{\uparrow\downarrow} \ \boxed{\uparrow\downarrow} \ \boxed{\uparrow\uparrow\downarrow}$$

$\therefore$  8<sup>th</sup> electron present in  $2p_x$  orbital and the quantum numbers are

$$n = 2, l = 1, m_l = \text{either } +1 \text{ or } -1 \text{ and } s = -1/2$$

Electronic configuration of chlorine =

$$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^5$$

$$\boxed{\uparrow\downarrow} \ \boxed{\uparrow\downarrow} \ \boxed{\uparrow\downarrow \ \uparrow\downarrow \ \uparrow\downarrow} \ \boxed{\uparrow\downarrow} \ \boxed{\uparrow\downarrow \ \uparrow\downarrow \ \uparrow}$$

$$3p_x \ 3p_y \ 3p_z$$

15<sup>th</sup> electron present in  $3p_z$  orbital and the quantum numbers are  $n = 3, l = 1, m_l = \text{either } +1 \text{ or } -1$  and  $m_s = +1/2$

36.

$$E_n = \frac{-13.6}{n^2} \text{ eV atom}^{-1}$$

$$n = 3 \ E_3 = \frac{-13.6}{3^2} = \frac{-13.6}{9} = -1.51 \text{ eV atom}^{-1}$$

$$n = 4 \ E_4 = \frac{-13.6}{4^2} = \frac{-13.6}{16} = -0.85 \text{ eV atom}^{-1}$$

$$\Delta E = (E_4 - E_3) = (-0.85) - (-1.51)$$

$$\text{eV atom}^{-1}$$

$$= (-0.85 + 1.51)$$

$$= \mathbf{0.66 \text{ eV atom}^{-1}}$$

$$(1 \text{ eV} = 1.6 \times 10^{-19} \text{ J})$$

$$\Delta E = 0.66 \times 1.6 \times 10^{-19} \text{ J}$$

$$\Delta E = 1.06 \times 10^{-19} \text{ J}$$

$$h\nu = 1.06 \times 10^{-19} \text{ J}$$

$$\frac{hc}{\lambda} = 1.06 \times 10^{-19} \text{ J}$$

$$\therefore \lambda = \frac{hc}{1.06 \times 10^{-19} \text{ J}}$$

$$= \frac{6.626 \times 10^{-34} \text{ JS} \times 3 \times 10^8 \text{ ms}^{-1}}{1.06 \times 10^{-19} \text{ J}}$$

$$\lambda = 1.875 \times 10^{-6} \text{ m}$$

37. Given : de Broglie wavelength of the tennis ball equal to 5400 Å.

$$m = 54 \text{ g}$$

$$v = ?$$

$$\lambda = \frac{h}{mV}$$

$$V = \frac{h}{m\lambda}$$

$$V = \frac{6.626 \times 10^{-34} \text{ JS}}{54 \times 10^{-3} \text{ Kg} \times 5400 \times 10^{-10} \text{ m}}$$

$$V = 2.27 \times 10^{-26} \text{ ms}^{-1}$$

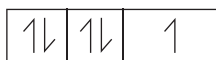
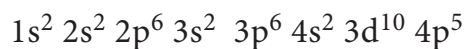
38.

n	l	Sub Energy levels	$m_l$ values	Number of orbitals
4	2	4d	-2, -1, 0, +1, +2	five 4d orbitals
5	3	5f	-3, -2, -1, 0, +1, +2, +3	seven 5f orbitals
7	0	7s	0	one 7s orbitals

41. no. of electrons : 35 (given)

no. of protons : 35

Electronic configuration



last electron present in  $4P_y$  orbital

$n = 4$   $l = 1$   $m_l = \text{either } +1 \text{ or } -1$   
and  $s = -1/2$

43.  $\text{He}^+ \rightarrow \text{He}^{2+} + e^-$

$$E_n = \frac{-13.6z^2}{n^2}$$

$$E_1 = \frac{-13.6(2)^2}{(1)^2} = -56.4$$

$$E_\infty = \frac{-13.6(2)^2}{(\infty)^2} = 0$$

$\therefore$  Required Energy for the given process =  $E_\infty - E_1 = 0 - (-56.4) = 56.4 \text{ eV}$

44.

	Atom	Uni-negative ion
number of electron	$x - 1$	$x$
number of protons	$x - 1$	$x - 1$
number of neutrons	$y$	$y$

Given that,  $y = x + 11.1\%$  of  $x$

$$= \left( x + \frac{11.1}{100}x \right) = x + 0.111x$$

$$y = 1.111x$$

mass number = 37

number of protons + number of neutrons = 37

$$(x - 1) + 1.111x = 37$$

$$x + 1.111x = 38$$

$$2.111x = 38$$

$$x = \frac{38}{2.111}$$

$$x = 18.009 \quad x = 18 \text{ (whole number)}$$

$$\therefore \text{Atomic number} = x - 1$$

$$= 18 - 1 = 17$$

Mass number = 37

Symbol of the ion  ${}_{17}^{37}\text{Cl}^-$

45)

$$r_n = \frac{(0.529)n^2}{z} \text{ \AA} \quad E_n = \frac{-13.6(z^2)}{n^2} \text{ eV atom}^{-1}$$

for  $\text{Li}^{2+}$   $z = 3$ Bohr radius for the third orbit ( $r_3$ )

$$\begin{aligned} &= \frac{(0.529)(3)^2}{3} \\ &= 0.529 \times 3 \\ &= 1.587 \text{ \AA} \end{aligned}$$

Energy of an electron in the fourth

$$\text{orbit } (E_4) = \frac{-13.6(3)^2}{(4)^2}$$

$$= -7.65 \text{ eV atom}^{-1}$$

46) Given

$$v = 2.85 \times 10^8 \text{ ms}^{-1}$$

$$m_p = 1.673 \times 10^{-27} \text{ Kg}$$

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34} \text{ kgm}^2 \text{ s}^{-1}}{1.673 \times 10^{-27} \text{ kg} \times 2.85 \times 10^8 \text{ ms}^{-1}}$$

$$\lambda = 1.389 \times 10^{-15} \Rightarrow \lambda = 1.389 \times 10^{-5} \text{ \AA}$$

$$[\because 1 \text{ \AA} = 10^{-10} \text{ m}]$$

47)  $m = 160 \text{ g} = 160 \times 10^{-3} \text{ kg}$ 

$$v = 140 \text{ km hr}^{-1} = \frac{140 \times 10^3}{60 \times 60} \text{ ms}^{-1}$$

$$v = 38.88 \text{ ms}^{-1}$$

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ Kg m}^2 \text{ s}^{-1}}{160 \times 10^{-3} \text{ Kg} \times 38.88 \text{ ms}^{-1}}$$

$$\lambda = 1.065 \times 10^{-34} \text{ m}$$

48)  $\Delta x = 0.6 \text{ \AA} = 0.6 \times 10^{-10} \text{ m}$ 

$$\Delta p = ?$$

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta p \geq 5.28 \times 10^{-35} \text{ kgm}^2 \text{ s}^{-1}$$

$$(0.6 \times 10^{-10}) \Delta p \geq 5.28 \times 10^{-35}$$

$$\Rightarrow \Delta p \geq \frac{5.28 \times 10^{-35} \text{ kgm}^2 \text{ s}^{-1}}{0.6 \times 10^{-10} \text{ m}}$$

$$\Delta p \geq 8.8 \times 10^{-25} \text{ kgms}^{-1}$$

49) Given  $\Delta x =$ 

$$\Delta v = ?$$

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\lambda \cdot (m\Delta v) \geq \frac{h}{4\pi}$$

$$\Delta v \geq \frac{h}{4\pi(m\lambda)}$$

$$\Delta v \geq \frac{h}{4\pi \times m \times \frac{h}{mv}} \quad \left[ \because \lambda = \frac{h}{mv} \right]$$

$$\Delta v \geq \frac{v}{4\pi}$$

Therefore,

$$\text{minimum uncertainty in velocity} = \frac{v}{4\pi}$$

50) Potential difference = 100V

$$= 100 \times 1.6 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{h}{\sqrt{2meV}}$$

$$= \frac{6.626 \times 10^{-34} \text{ Kg m}^2 \text{ s}^{-1}}{\sqrt{2 \times 9.1 \times 10^{-31} \text{ Kg} \times 100 \times 1.6 \times 10^{-19} \text{ J}}}$$

$$\lambda = 1.22 \times 10^{-10} \text{ m}$$

51)

n	l	$m_l$	sub energy level
4	2	0	4d
3	1	0	3p
5	1	any one value -1, 0, +1	5p
3	2	-2	3d



## Unit - 3

### Periodic classification of elements

#### Evaluate yourself

2. Atomic number : 120

IUPAC temporary symbol :  
Unbinilium

IUPAC temporary symbol : Ubn

Possible electronic configuration  
:[Og] 8s<sup>2</sup>

3. Electronic Configuration : (n - 1)d<sup>2</sup>  
ns<sup>2</sup>

for n = 5, the electronic configuration  
is,

1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>6</sup> 4d<sup>2</sup>  
5s<sup>2</sup> Atomic number : 40

4<sup>th</sup> group 5<sup>th</sup> period (d block element)  
= Zirconium

4. Electronic Configuration of  
Aluminium

$\text{Al}^{13}$   $1s^2$   $2s^2$   $2p^6$   $3s^2$   $3p^1$   
(n-2) (n-1) n

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	2	0.35	0.70
(n - 1)	8	0.85	6.80
(n - 2)	2	1	2.00
			9.50

∴ Effective nuclear charge = Z - S

= 13 - 9.5

(Z<sub>eff</sub>)<sub>Al</sub> = 3.5

Electronic Configuration of chlorine

$1s^2$   $2s^2$   $2p^6$   $3s^2$   $3p^5$   
n-2 n-1 n

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	6	0.35	2.1
(n - 1)	8	0.85	6.8
(n - 2)	2	1	2
		S =	10.9

∴ Effective nuclear charge = Z - S

= 17 - 10.9

(Z<sub>eff</sub>)<sub>Cl</sub> = 6.1

(Z<sub>eff</sub>)<sub>Cl</sub> > (Z<sub>eff</sub>)<sub>Al</sub> and. Hence r<sub>Cl</sub> < r<sub>Al</sub>.

5.

X<sup>3+</sup>, Y<sup>2+</sup>, Z<sup>-</sup> are isoelectronic.

∴ Effective nuclear charge is in the order (Z<sub>eff</sub>)<sub>Z<sup>-</sup></sub> < (Z<sub>eff</sub>)<sub>Y<sup>2+</sup></sub> < (Z<sub>eff</sub>)<sub>X<sup>3+</sup></sub> and

Hence, ionic radii should be in the order

r<sub>Z<sup>-</sup></sub> > r<sub>Y<sup>2+</sup></sub> > r<sub>X<sup>3+</sup></sub>

∴ The correct values are,

Species	Ionic radii
Z <sup>-</sup>	136
Y <sup>2+</sup>	64
X <sup>3+</sup>	49

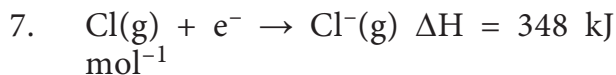
6. **Noble gases** : Ionisation energy ranging from 2372 KJmol<sup>-1</sup> to 1037 kJ mol<sup>-1</sup>.

For element X, the IE<sub>1</sub> value is in the

range of noble gas, moreover for this element both  $IE_1$  and  $IE_2$  are higher and hence X is the noble gas.

For Y, the first ionisation energy is low and second ionisation energy is very high and hence Y is most reactive metal.

For Z, both  $IE_1$  and  $IE_2$  are higher and hence it is least reactive.



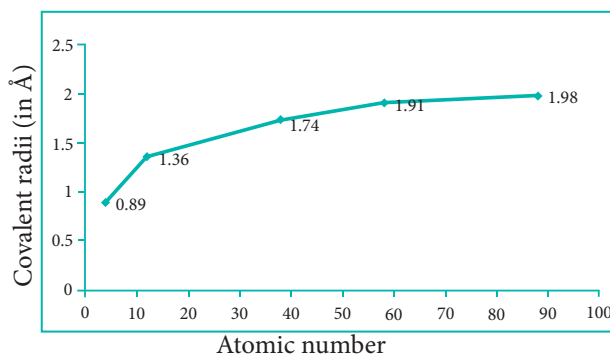
For one mole (35.5g) 348 kJ is released.

$\therefore$  For 17.5g chlorine,  $\frac{348 \text{ kJ}}{35.5 \text{ g}} \times 17.75 \text{ g}$  energy leased.

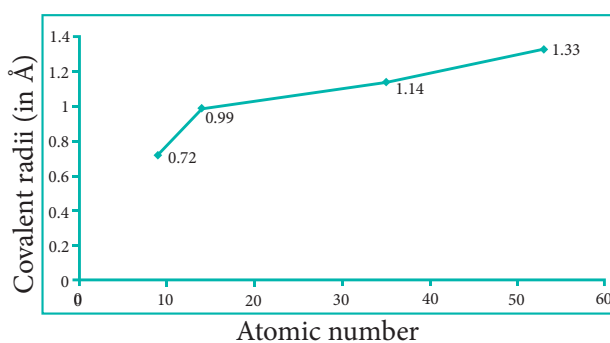
$$\therefore \text{The amount of energy released} = \frac{348}{2} = 174 \text{ kJ}$$

### Activitiy : 3.1

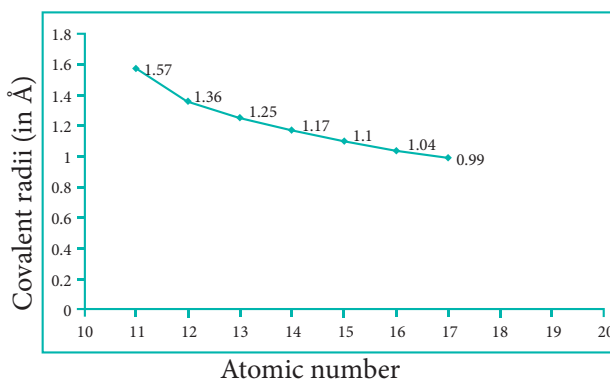
#### Covalent radii - 2nd group elements



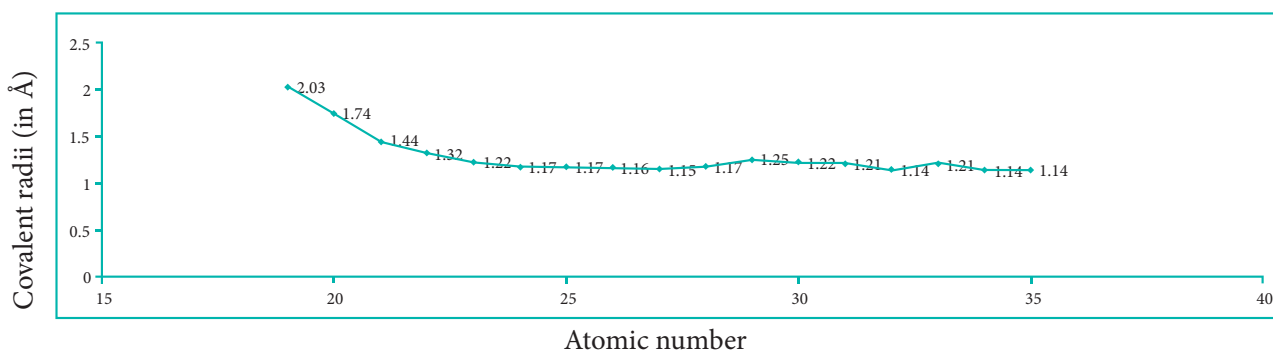
#### Covalent radii - 17<sup>th</sup> group elements



#### Covalent radii - 3<sup>rd</sup> period elements



#### Covalent radii - 4<sup>th</sup> period elements



## EVALUATION



### I Choose the best answer:

- (d) bismuth
- (b)  $AB_2$
- (d) f-block elements
- (a)  $I < Br < Cl < F$  (increasing electron gain enthalpy)
- (d) fluorine
- (c) Aluminium
- (b)  $Na < Al < Mg < Si < P$
- (a)
- (d)  $Ca < Al < C < O < F$
- (c)  $Cl > F > Br > I$
- (d) Hydrogen
- (c) Argon
- (a)  $Y > Z > X > A$
- (c)
- (a)  $1s^2, 2s^2, 2p^6, 3s^1$
- (a) Chlorine
- (c)  $+527 \text{ kcal mol}^{-1}$
- (a)  $s > p > d > f$
- (d) None of these
- (b)  $575 \text{ kJ mol}^{-1}$
- (a)
- (a) Generally increases
- (d) Be and Al



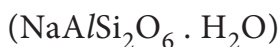
I Choose the best answer:

1. (c)
2. (c)  $\text{CO} + \text{H}_2$
3. (b)
4. (d) group one elements
5. (c)  $1p+2n$
6. (a) Palladium, Vanadium
7. (a)
8. (a) 1.2 g
9. (d) EDTA
10. (c)  $\text{CaCl}_2$
11. (a) sodium aluminium silicate
12. (a)
13. (c)  $\text{CrO}(\text{O}_2)_2$
14. (c)  $5/2$
15. (d) 8.4
16. (d)  $sp^3$  and  $sp^3$
17. (c) monobasic acid
18. (a) tetrahedrally by 4-H atoms
19. (b) intra-molecular hydrogen bonding and inter molecular hydrogen bonding
20. (c) both (a) & (b)
21. (c) amphoteric oxide

Key for multiple choice questions:

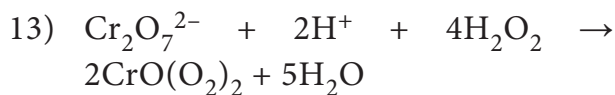
- 1) Option (c)  
**Correct statement :** Hydrogen has three isotopes of which **protium** is the most common.
- 2) Option (c)  
 $\text{CO} + \text{H}_2$  - Water gas
- 3) Option (b)  
**Correct statement :** Ortho isomer - one nuclear spin  
Para isomer - zero nuclear spin
- 4) Option (d)  
eg : Sodium hydride ( $\text{Na}^+ \text{H}^-$ )
- 5) Option (c)  
 ${}_1\text{T}^3 (1e^-, 1p, 2n)$
- 7) Option (a)  
 $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$
- 8) mass of deuterium =  $2 \times$  mass of protium  
If all the 1.2 g hydrogen is replaced with deuterium, the weight will become 2.4g. Hence the increase in body weight is  $(2.4 - 1.2 = 1.2 \text{ g})$   
Option (a)
- 9) EDTA (option (d))
- 10) Permanent hardness of water is due to the presence of the chlorides, nitrates and sulphates of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.  
Option (c)  $\text{CaCl}_2$

11) Zeolite is sodium aluminium silicate.

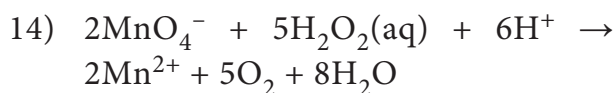


Option (a)

12) (a) 1 mL of  $\text{H}_2\text{O}_2$  will give 100ml  $\text{O}_2$  at STP.



Option (c)



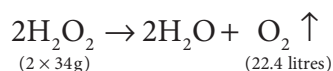
Option (c) 5/2 moles

15) Volume strength of hydrogen peroxide = Normality of hydrogen peroxide  $\times 5.6$

$$= 1.5 \times 5.6$$

$$= 8.4$$

Option (d)



Volume strength of Hydrogen peroxide

$$= \frac{\text{Normality} \times \text{Equivalent weight of } \text{H}_2\text{O}_2 \times 22.4}{68}$$

$$= \text{Normality} \times \left( \frac{17 \times 22.4}{68} \right)$$

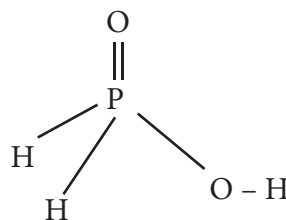
Volume strength of hydrogen peroxide

$$= \text{Normality} \times 5.6$$

16)  $\text{sp}^3$  and  $\text{sp}^3$

Option (d)

17) Hypophosphorus acid on reaction with  $\text{D}_2\text{O}$ , only one hydrogen is replaced by deuterium and hence it is mono basic

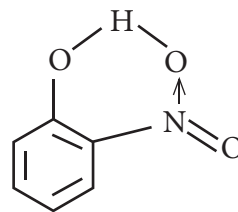


Option (c) monobasic acid

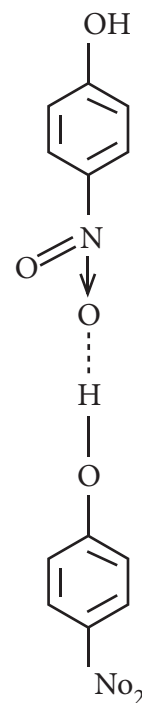
18) (a) tetrahedrally surrounded by 4 hydrogen atoms (refer 4.6 (a) Structure of ice)

19)

*o*-nitro phenol



*p*-nitro phenol



20) Option (c)

Heavy water is used as moderator as well as coolant in nuclear reactions.

21) Water is a amphoteric oxide.

Option (c)

## Unit - 5

### Alkali and Alkaline Earth Metals

#### EVALUATION



#### I Choose the best answer.

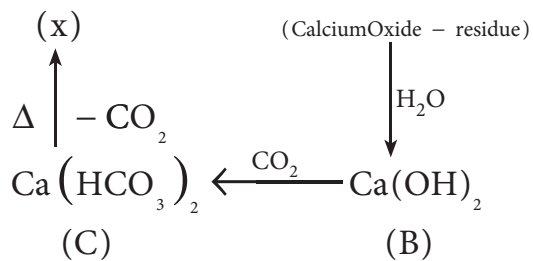
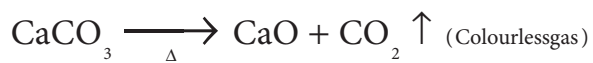
- (c) Density:  $\text{Li} < \text{K} < \text{Na} < \text{Rb} < \text{C}$
- (a)  $\text{Li}^+$  has minimum degree of hydration among alkali metal cations
- (d) none of these
- (b) Li
- (c) kerosene
- (a) superoxide and paramagnetic
- (c) Potassium carbonate can be prepared by solvay process
- (b) Magnesium
- (b)  $\text{MI} < \text{MBr} < \text{MCl} < \text{MF}$
- (a) Castners process
- (c)  $\text{Ca}(\text{CN})_2$
- (a)  $\text{MgCl}_2$
- (a) p-2, q-1, r-4, s-5, t-6, u-3
- (d) both assertion and reason are false
- (a)
- (b)  $\text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
- (c) Its salts are rarely hydrolysed
- (c) milk of lime
- (b)  $\text{NaHCO}_3$
- (b)  $\text{Ca}(\text{OH})_2$
- (a)  $\text{Ca}^{2+}$  ions are not important in maintaining the regular beating of the heart.
- (b)  $\text{CaF}_2$
- (a)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- (b)  $\text{CaNCN}$
- (d)  $\text{Li}_2\text{CO}_3$

#### Keys to multiple choice questions:

- Option (c)  
Potassium is lighter than sodium  
(Refer table 5.3)  
The correct order of density is  
 $\text{Li} < \text{K} < \text{Na} < \text{Rb} < \text{Cs}$   
 $0.54 < 0.86 < 0.97 < 1.53 < 1.90$  (in  $\text{g cm}^{-3}$ )
- Option (a)  
 $\text{Li}^+$  has maximum degree of hydration among alkali metal cations.  
 $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
- All these compounds reacts with alkali metals to evolve hydrogen gas.  
(d) none of these.
- hydration energy of  $\text{Li}^+$  is more and hence  $\text{Li}^+$  is stabilized in aqueous medium.  
(b) Li
- (c) Kerosene



20)



21)  $\text{Ca}^{2+}$  ion plays an important role in maintaining regular heart beat.

Option (a)

22) 'Blue john' –  $\text{CaF}_2$

(A variety of fluorite)

$\therefore$  Option (b)

23)  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$   $\therefore$  Option (a)

24)  $\text{CaC}_2 + \text{N}_2 \xrightarrow{1 \text{ atm}} \text{CaNCN}$   
nitrolium  
(or)  
Calcium cyanamide

$\therefore$  Option (b)

25)  $\text{Li}_2\text{CO}_3$  is least stable.

Option (d)



## Unit - 6 Gaseous State

Evaluate yourself:

1. Volume of freon ( $V_1$ ) =  $1.5 \text{ dm}^3$

Pressure ( $P_1$ ) =  $0.3 \text{ atm}$

'T' is constant

$P_2$  =  $1.2 \text{ atm}$

$V_2$  = ?

$\therefore P_1 V_1 = P_2 V_2$

$$\begin{aligned} \Rightarrow V_2 &= \frac{P_1 V_1}{P_2} \\ &= \frac{0.3 \text{ atm} \times 1.5 \text{ dm}^3}{1.2 \text{ atm}} \\ &= 0.375 \text{ dm}^3 \end{aligned}$$

$\therefore$  Volume decreased from  $1.5 \text{ dm}^3$   
to  $0.375 \text{ dm}^3$

2.  $V_1 = 0.375 \text{ dm}^3$        $V_2 = 0.125$

$P_1 = 1.05 \text{ atm}$        $P_2 = ?$

'T' - Constant

$P_1 V_1 = P_2 V_2$

$$\begin{aligned} \therefore P_2 &= \frac{P_1 V_1}{V_2} = \frac{1.05 \times 0.375}{0.125} \\ &= 3.15 \text{ atm} \end{aligned}$$

3.  $V_1 = 3.8 \text{ dm}^3$      $T_2 = 0^\circ\text{C} = 273 \text{ K}$

$T_1 = ?$        $V_2 = 2.27 \text{ dm}^3$

$$\begin{aligned} \frac{V_1}{T_1} &= \frac{V_2}{T_2} \quad T_1 = \left( \frac{T_2}{V_2} \right) \times V_1 \\ &= \frac{273 \text{ K}}{2.27 \text{ dm}^3} \times 3.8 \text{ dm}^3 \\ T_1 &= 457 \text{ K} \end{aligned}$$

4.  $V_1 = 7.05 \text{ dm}^3$        $V_2 = 2.35 \text{ dm}^3$

$n_1 = 0.312 \text{ mol}$        $n_2 = ?$

'P' and 'T' are constant

$$\begin{aligned} \therefore \frac{V_1}{n_1} &= \frac{V_2}{n_2} \\ \Rightarrow n_2 &= \left( \frac{n_1}{V_1} \right) \times V_2 \\ n_2 &= \frac{0.312 \text{ mol}}{7.05 \text{ dm}^3} \times 2.35 \text{ dm}^3 \\ n_2 &= 0.104 \text{ mol} \end{aligned}$$

Number of moles exhaled =

$0.312 - 0.104 = 0.208 \text{ moles}$

5)  $T_1 = 8^\circ\text{C} = 8 + 273 = 281 \text{ K}$

$P_1 = 6.4 \text{ atm}$        $V_1 = 2.1 \text{ mol}$

$T_2 = 25^\circ\text{C} = 25 + 273 = 298 \text{ K}$

$P_2 = 1 \text{ atm}$        $V_2 = ?$

$$\begin{aligned} \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ \Rightarrow V_2 &= \left( \frac{P_1 V_1}{T_1} \right) \times \frac{T_2}{P_2} \\ &= \frac{6.4 \text{ atm} \times 2.1 \text{ mol}}{281 \text{ K}} \times \frac{298 \text{ K}}{1 \text{ atm}} \\ V_2 &= 14.25 \text{ ml} \end{aligned}$$

6(a)

$$\left. \begin{array}{l} V_{\text{O}_2} = 12 \text{ dm}^3 \\ V_{\text{He}} = 46 \text{ dm}^3 \end{array} \right\} \begin{array}{l} T = 298 \\ P = 1 \text{ atm} \end{array} \text{ Constant}$$

$V_{\text{total}} = 5 \text{ dm}^3$

$$\begin{aligned} P_{\text{O}_2} &= x_{\text{O}_2} \times P_{\text{total}} & n_{\text{O}_2} &= \frac{1 \text{ mol}}{22.4 \text{ L}} \times 12 \text{ L} \\ x_{\text{O}_2} &= \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{He}}} & n_{\text{O}_2} &= 0.54 \text{ mol} \\ &= \frac{0.54}{0.54 + 2.05} & n_{\text{He}} &= \frac{1 \text{ mol}}{22.4 \text{ L}} \times 46 \text{ L} \\ &= \frac{0.54}{2.59} = 0.21 & n_{\text{He}} &= 2.05 \text{ mol} \end{aligned}$$

$$P_{\text{total}} \times V_{\text{total}} = 1 \text{ atm} \times 22.4 \text{ l}$$

$$\therefore P_{\text{total}} = \frac{1 \text{ atm} \times 22.4 \cancel{\text{ l}}}{5 \cancel{\text{ l}}}$$

$$P_{\text{total}} = 4.48 \text{ atm}$$

$$\therefore P_{\text{O}_2} = 0.21 \times 4.48 \text{ atm} \\ = 0.94 \text{ atm}$$

$$P_{\text{He}} = x_{\text{He}} \times P_{\text{total}}$$

$$x_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{O}_2} + n_{\text{He}}} \\ = \frac{2.05}{0.54 + 2.05}$$

$$x_{\text{He}} = \frac{2.05}{2.59} = 0.79$$

$$\therefore P_{\text{He}} = 0.79 \times 4.48 \text{ atm}$$

$$P_{\text{He}} = 3.54 \text{ atm}$$



$$P_{\text{total}} = 772 \text{ mm Hg}$$

$$P_{\text{H}_2\text{O}} = 26.7 \text{ mm Hg}$$

$$P_{\text{total}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

$$\therefore P_{\text{O}_2} = P_{\text{total}} - P_{\text{H}_2\text{O}}$$

$$P_1 = 26.7 \text{ mm Hg} \quad T_2 = 295 \text{ K}$$

$$T_1 = 300 \text{ K} \quad P_2 = ?$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow P_2 = \left( \frac{P_1}{T_1} \right) T_2 = \frac{26.7 \text{ mm Hg}}{300 \cancel{\text{ K}}} \times 295 \cancel{\text{ K}}$$

$$P_2 = 26.26 \text{ mm Hg}$$

$$\therefore P_{\text{O}_2} = 772 - 26.26 \\ = 745.74 \text{ mm Hg}$$

$$7) \quad t_1 = 1.5 \text{ minutes} \quad (\text{gas})_{\text{hydro carbon}}$$

$$t_2 = 4.73 \text{ minutes} \quad (\text{gas})_{\text{Bromine}}$$

$$\frac{\gamma_{\text{Hydrocarbon}}}{\gamma_{\text{Bromine}}} = \frac{t_{\text{Bromine}}}{t_{\text{Hydrocarbon}}}$$

( $\therefore$  Volume is constant)

$$= \frac{4.73 \text{ minutes}}{1.5 \text{ minutes}}$$

$$= 3.15$$

$$\frac{\gamma_{\text{Hydrocarbon}}}{\gamma_{\text{Bromine}}} = \sqrt{\frac{m_{\text{Bromine}}}{m_{\text{hydrocarbon}}}}$$

$$3.15 = \sqrt{\frac{159.8 \text{ gmol}^{-1}}{m_{\text{hydro carbon}}}}$$

$$= 3.15$$

Squaring on both sides and rearranging,

$$m_{\text{hydro carbon}} = \frac{159.8 \text{ g mol}^{-1}}{(3.15)^2}$$

$$m_{\text{hydro carbon}} = 16.1 \text{ gmol}^{-1}$$

$$\begin{array}{l} n(12) + (2n+2)1 = 16 \\ 12n + 2n + 2 = 16 \end{array} \quad \left[ \begin{array}{l} \therefore \text{general formula} \\ \text{for hydrocarbon} \\ \text{C}_n\text{H}_{2n+2} \end{array} \right]$$

$$14n = 16 - 2$$

$$14n = 14$$

$$n = 1$$

$\therefore$  The hydro carbon is  $\text{C}_1\text{H}_{2(1)+2} = \text{CH}_4$

8) Critical temperature of a gas is defined as the temperature above which it cannot be liquified even at high pressures.

$\therefore$  When cooling starts from 700 K,  $\text{H}_2\text{O}$  will liquify first, then followed by ammonia and finally carbondioxide will liquify.



I Choose the correct answer:

1. (d) at high pressure the intermolecular interactions become significant
2. (d) inversely proportional to the square root of its molecular weight
3. (c)  $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$
4. (b) exert no attractive forces on each other
5. (a) 1/3
6. (b) Boyle temperature
7. (c) diffusion
8. (b) near the hydrogen chloride bottle
9. (d) pressure and volume of the gas
10. (c)  $8.3 \text{ J mol}^{-1} \text{ K}^{-1}$
11. (a) Boyle's Law
12. (c)  $\text{NH}_3$
13. (d) I, II and III
14. (c)  $0.41 \text{ dm}^3$
15. (c) P
16. (b) 4
17. (c) 1/8
18. (b) 1/T
19. (a) P
20. (b)  $\text{NH}_3$
21. (c)  $\text{mol}^{-1} \text{ L}$  and  $\text{L}^2 \text{ atm mol}^{-2}$

22. (d) both assertion and reasons are false
23. (c)  $3.41 \text{ g L}^{-1}$
24. (c)
25. (d) HI

Keys to multiple choice questions:

5. mass of methane  
= mass of oxygen = a

$$\text{number of moles of methane} = \frac{a}{16}$$

$$\text{number of moles of Oxygen} = \frac{a}{32}$$

$$\begin{aligned} \text{mole fraction of Oxygen} &= \frac{\frac{a}{32}}{\frac{a}{16} + \frac{a}{32}} \\ &= \frac{\frac{a}{32}}{\frac{2a}{32} + \frac{a}{32}} \\ &= \frac{\frac{a}{32}}{\frac{3a}{32}} \\ &= \frac{1}{3} \end{aligned}$$

Partial pressure of oxygen

= mole fraction  $\times$  Total Pressure

$$= \frac{1}{3}P$$

6. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called Boyle temperature

8. Rate of diffusion  $\propto 1/\sqrt{m}$

$$m_{\text{NH}_3} = 17 ; m_{\text{HCl}} = 36.5$$

$$\gamma_{\text{NH}_3} > \gamma_{\text{HCl}}$$

Hence white fumes first formed near hydrogen chloride

12. Higher the value of 'a', greater the intermolecular force of attraction, easier the liquefaction.

**option (c) is correct**

14.

$$\text{Compressibility factor (z)} = \frac{PV}{nRT}$$

$$V = \frac{z \times nRT}{P}$$

$$= \frac{0.8697 \times 1 \times 8.314 \times 10^{-2} \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}{71 \text{ bar}}$$

$$V = 0.41 \text{ dm}^3$$

15.  $T_1 \quad T_2 = 2T_1$

$V_1 \quad V_2 = 2V_1$

$P_1 \quad P_2 = ?$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{V_2} = \frac{P_1 V_1}{T_1} \times \frac{2T_1}{2V_1}$$

$$P_2 = P_1$$

Option (c)

16.

$$\frac{\gamma_{\text{H}_2}}{\gamma_{\text{C}_n\text{H}_{2n+2}}} = \sqrt{\frac{m_{\text{C}_n\text{H}_{2n+2}}}{m_{\text{H}_2}}}$$

$$3\sqrt{3} = \sqrt{\frac{m_{\text{C}_n\text{H}_{2n+2}}}{2}}$$

Squaring on both sides and rearranging

$$27 \times 2 = m_{\text{C}_n\text{H}_{2n+2}}$$

$$54 = n(12) + (2n-2)(1)$$

$$54 = 12n + 2n - 2$$

$$54 = 14n - 2$$

$$n = (54+2)/14 = 56/14 = 4$$

17.

$$\frac{\gamma_{\text{O}_2}}{\gamma_{\text{H}_2}} = \sqrt{\frac{m_{\text{H}_2}}{m_{\text{O}_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4}$$

$$\gamma_{\text{O}_2} = \frac{1}{4} \gamma_{\text{H}_2}$$

The fraction of oxygen that escapes in the time required for one half of the hydrogen to escape is 1/8

18.

$$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad [\text{For an ideal gas } PV = nRT]$$

$$= \frac{1}{V} \left( \frac{\partial \left( \frac{nRT}{P} \right)}{\partial T} \right)_P$$

$$= \frac{nR}{PV} \left( \frac{\partial T}{\partial T} \right) = \frac{nR}{nRT} = \frac{1}{T}$$

19. Greater the 'a' value, easier the liquefaction

21.

$$an^2/V^2 = atm$$

$$a = atm \text{ L}^2/\text{mol}^2 = \text{L}^2 \text{ mol}^{-2} \text{ atm}$$

$$nb = L$$

$$b = L/\text{mol} = \text{L mol}^{-1}$$

22. **Correct Statement:** Critical temperature of  $\text{CO}_2$  is 304 K. It means that  $\text{CO}_2$  cannot be liquefied above 304 K, whatever the pressure may applied.

Pressure is inversely proportional to volume

23.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\text{Mass}}{\text{Volume}}$$

$$= \frac{m}{\left(\frac{nRT}{P}\right)} = \left(\frac{m}{n}\right) \frac{P}{RT}$$

$$= \text{Molar mass} \times \frac{P}{RT}$$

$$= 14 \text{ g mol}^{-1}$$

$$\frac{5 \text{ atm}}{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}$$

$$= 3.41 \text{ g L}^{-1}$$

24. For a fixed mass of an ideal gas  $V \propto T$   
 $P \propto 1/V$

and  $PV = \text{Constant}$

25. At a given temperature and pressure  
Volume  $\propto$  no. of moles

Volume  $\propto$  Mass / Molar mass

Volume  $\propto$  28 / Molar mass

i.e. if molar mass is more, volume is less. Hence HI has the least volume

## II Key to short answer questions:

46.  $T_1 = 15^\circ \text{C} + 273$        $T_2 = 38 + 273$

$T_1 = 288 \text{ K}$        $T_2 = 311 \text{ K}$

$V_1 = 2.58 \text{ dm}^3$        $V_2 = ?$

( $P = 1$  atm constant)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \left(\frac{V_1}{T_1}\right) \times T_2$$

$$= \frac{2.58 \text{ dm}^3}{288 \text{ K}} \times 311 \text{ K}$$

$V_2 = 2.78 \text{ dm}^3$  i.e. volume increased from  $2.58 \text{ dm}^3$  to  $2.78 \text{ dm}^3$

47.  $V_1 = 8.5 \text{ dm}^3$      $V_2 = 6.37 \text{ dm}^3$

$T_1 = ?$        $T_2 = 0^\circ \text{C} = 273 \text{ K}$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 \times \left(\frac{T_2}{V_2}\right) = T_1$$

$$T_1 = 8.5 \text{ dm}^3 \times \frac{273 \text{ K}}{6.37 \text{ dm}^3}$$

$$T_1 = 364.28 \text{ K}$$

48.  $n_A = 1.5 \text{ mol}$      $n_B = ?$

$V_A = 37.6 \text{ dm}^3$      $V_B = 16.5 \text{ dm}^3$

( $T = 298 \text{ K}$  constant)

$$\frac{V_A}{n_A} = \frac{V_B}{n_B}$$

$$n_A = \left(\frac{n_B}{V_A}\right) V_B$$

$$= \frac{1.5 \text{ mol}}{37.6 \text{ dm}^3} \times 16.5 \text{ dm}^3$$

$$= 0.66 \text{ mol}$$

49.  $n = 1.82 \text{ mole}$

$$V = 5.43 \text{ dm}^3$$

$$T = 69.5 + 273 = 342.5$$

$$P = ?$$

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$1.82 \text{ mol} \times$$

$$0.821 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$$

$$P = \frac{\times 342.5 \text{ K}}{5.43 \text{ dm}^3}$$

$$P = 94.25 \text{ atm}$$

50.

$$P_1 = 1.2 \text{ atm}$$

$$T_1 = 18^\circ \text{ C} + 273 = 291 \text{ K}$$

$$T_2 = 85^\circ \text{ C} + 273 = 358 \text{ K}$$

$$P_2 = ?$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = \left( \frac{P_1}{T_1} \right) \times T_2$$

$$= \frac{1.2 \text{ atm}}{291 \text{ K}} \times 358 \text{ K}$$

$$P_2 = 1.48 \text{ atm}$$

51.  $T_1 = 6^\circ \text{ C} + 273 = 279 \text{ K}$

$$P_1 = 4 \text{ atm} \quad V_1 = 1.5 \text{ ml}$$

$$T_2 = 25^\circ \text{ C} + 273 = 298 \text{ K}$$

$$P_2 = 1 \text{ atm} \quad V_2 = ?$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{4 \text{ atm} \times 1.5 \text{ ml} \times 298 \text{ K}}{279 \text{ K} \times 1 \text{ atm}}$$

$$V_2 = 6.41 \text{ ml}$$

52. Given,

$$V = 154.4 \times 10^{-3} \text{ dm}^3,$$

$$P = 742 \text{ mm of Hg}$$

$$T = 298 \text{ K} \quad m = ?$$

$$n = \frac{PV}{RT} = \frac{742 \text{ mm Hg} \times 154.4 \times 10^{-3} \text{ L}}{62 \text{ mm Hg L K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$$= 0.006 \text{ mol}$$

$$n = \frac{\text{Mass}}{\text{Molar mass}}$$

$$\text{Mass} = n \times \text{Molar mass}$$

$$= 0.006 \times 2.016$$

$$= 0.0121 \text{ g} = 12.1 \text{ mg}$$

53.

$$\frac{\gamma_{\text{unknown}}}{\gamma_{\text{N}_2}} = \frac{t_{\text{N}_2}}{t_{\text{unknown}}} = \sqrt{\frac{m_{\text{N}_2}}{m_{\text{unknown}}}}$$

$$\frac{84 \text{ sec}}{192 \text{ sec}} = \sqrt{\frac{14 \text{ g mol}^{-1}}{m_{\text{unknown}}}}$$

$$= \frac{14 \text{ g mol}^{-1}}{m_{\text{unknown}}}$$

$$m_{\text{unknown}} = 14 \text{ g mol}^{-1} \times \left( \frac{192 \text{ sec}}{84 \text{ sec}} \right)^2$$

$$m_{\text{unknown}} = 73.14 \text{ g mol}^{-1}$$

$$54. \quad m_{\text{O}_2} = 52.5 \text{ g} \quad P_{\text{O}_2} = ?$$

$$m_{\text{CO}_2} = 65.1 \text{ g} \quad P_{\text{CO}_2} = ?$$

$$T = 300 \text{ K} \quad P = 9.21 \text{ atm}$$

$$P_{\text{O}_2} = X_{\text{O}_2} \times \text{Total Pressure}$$

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{CO}_2}}$$

$$n_{\text{O}_2} = \frac{\text{Mass of O}_2}{\text{Molar mass of O}_2}$$

$$= \frac{52.5 \text{ g}}{32 \text{ g mol}^{-1}} = 1.64 \text{ mol}$$

$$n_{\text{CO}_2} = \frac{\text{Mass of CO}_2}{\text{Molar mass of CO}_2}$$

$$= \frac{65.1 \text{ g}}{44 \text{ g mol}^{-1}} = 1.48 \text{ mol}$$

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{O}_2} + n_{\text{CO}_2}} = \frac{1.64}{3.12} = 0.53$$

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{O}_2} + n_{\text{CO}_2}} = \frac{1.48}{3.12} = 0.47$$

$$P_{\text{O}_2} = X_{\text{O}_2} \times \text{Total pressure}$$

$$= 0.53 \times 9.21 \text{ atm} = 4.88 \text{ atm}$$

$$P_{\text{CO}_2} = X_{\text{CO}_2} \times \text{Total pressure}$$

$$= 0.47 \times 9.21 \text{ atm} = 4.33 \text{ atm}$$

55. Pressure of the gas in the tank at its melting point

$$T_1 = 298 \text{ K}; P_1 = 2.98 \text{ atm}; T_2 = 1100 \text{ K}; P_2 = ?$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow P_2 = \frac{P_1}{T_1} \times T_2$$

$$= \frac{2.98 \text{ atm}}{298 \text{ K}} \times 1100 \text{ K} = 11 \text{ atm}$$

At 1100 K the pressure of the gas inside the tank will become 11 atm. Given that tank can withstand a maximum pressure of 12 atm, the tank will start melting first.

## Unit - 7 Thermodynamics

### Evaluation Yourself

1. Calculate the  $\Delta H_r^0$  for the reaction  
 $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$

Given that  $\Delta H_f^0$  for  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-111.31$  and  $-242$   $\text{kJ mol}^{-1}$  respectively.

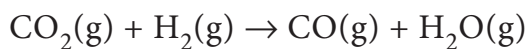
### Solution :

Given

$$\Delta H_f^0 \text{CO}_2 = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0 \text{CO} = -111.31 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0 (\text{H}_2\text{O}) = -242 \text{ kJ mol}^{-1}$$



$$\Delta H_r^0 = ?$$

$$\Delta H_r^0 = \sum (\Delta H_f^0)_{\text{products}} - \sum (\Delta H_f^0)_{\text{reactants}}$$

$$\Delta H_r^0 = [\Delta H_f^0 (\text{CO}) + \Delta H_f^0 (\text{H}_2\text{O})] - [\Delta H_f^0 (\text{CO}_2) + \Delta H_f^0 (\text{H}_2)]$$

$$\Delta H_r^0 = [-111.31 + (-242)] - [-393.5 + (0)]$$

$$\Delta H_r^0 = [-353.31] + 393.5$$

$$\Delta H_r^0 = 40.19$$

$$\Delta H_r^0 = +40.19 \text{ kJ mol}^{-1}$$

2. Calculate the amount of heat necessary to raise 180g of water from  $25^\circ\text{C}$  to  $100^\circ\text{C}$ . Molar heat capacity of water is  $75.3 \text{ J mol}^{-1} \text{ K}^{-1}$ .

### Solution :

Given :

number of moles of water n

$$= \frac{180 \text{ g}}{18 \text{ g mol}^{-1}} = 10 \text{ mol}$$

molar heat capacity of water

$$C_p = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_2 = 100^\circ\text{C} = 373 \text{ K}$$

$$T_1 = 25^\circ\text{C} = 298 \text{ K}$$

$$\Delta H = ?$$

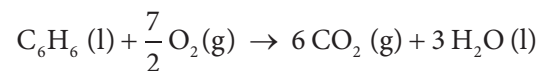
$$\Delta H = nC_p (T_2 - T_1)$$

$$\Delta H = 10 \text{ mol} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times (373 - 298) \text{ K}$$

$$\Delta H = 56475 \text{ J}$$

$$\Delta H = 56.475 \text{ kJ}$$

3. From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.



$$\Delta U \text{ at } 25^\circ\text{C} = -3268.12 \text{ kJ}$$

### Solution :

Given

$$T = 25^\circ\text{C} = 298 \text{ K} ;$$

$$\Delta U = -3268.12 \text{ kJ mol}^{-1}$$

$$\Delta H = ?$$

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

$$\Delta H = \Delta U + (n_p - n_r) RT$$



$$\Delta H = -3268.12 + \left(6 - \frac{7}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

$$\Delta U = -3268.12 + (2.5 \times 8.314 \times 10^{-3} \times 298)$$

$$\Delta U = -3268.12 + 6.19$$

$$\Delta U = -3261.93 \text{ kJ mol}^{-1}$$

4. When a mole of magnesium bromide is prepared from 1 mole of magnesium and 1 mole of liquid bromine, 524 kJ of energy is released.

The heat of sublimation of metal is  $148 \text{ kJ mol}^{-1}$ . The heat of dissociation of bromine gas into atoms is  $193 \text{ kJ mol}^{-1}$ . The heat of vapourisation of liquid bromine is  $31 \text{ kJ mol}^{-1}$ . The ionisation energy of magnesium is  $2187 \text{ kJ mol}^{-1}$  and electron affinity of bromine is  $-331 \text{ kJ mol}^{-1}$ . Calculate the lattice energy of magnesium bromide.

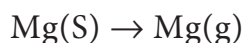
### Solution :

Given :



$$\text{MgBr}_2(\text{S}) \quad \Delta H_f^0 = -524 \text{ kJ mol}^{-1}$$

Sublimation :



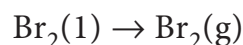
$$\Delta H_1^0 = +148 \text{ kJ mol}^{-1}$$

Ionisation :



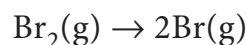
$$\Delta H_2^0 = 2187 \text{ kJ mol}^{-1}$$

Vapourisation :



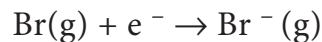
$$\Delta H_3^0 = +31 \text{ kJ mol}^{-1}$$

Dissociation :



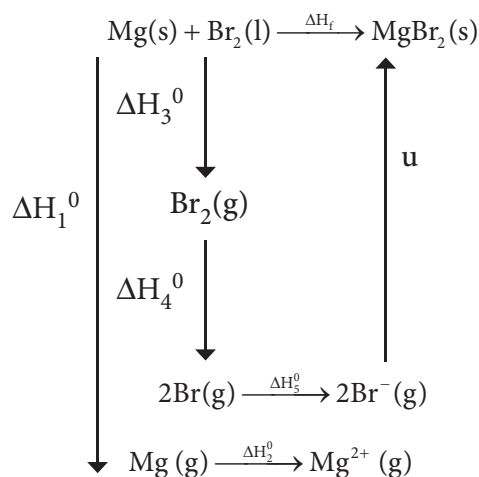
$$\Delta H_4^0 = +193 \text{ kJ mol}^{-1}$$

Electron affinity :



$$\Delta H_5^0 = -331 \text{ kJ mol}^{-1}$$

Solution :



$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + 2\Delta H_5 + u$$

$$-524 = 148 + 2187 + 31 + 193 + (2 \times -331) + u$$

$$-524 = 1897 + u$$

$$u = -524 - 1897$$

$$u = -2421 \text{ kJ mol}^{-1}$$

5. An engine operating between  $127^0 \text{ C}$  and  $47^0 \text{ C}$  takes some specified amount of heat from a high temperature reservoir. Assuming that there are no frictional losses,

calculate the percentage efficiency of an engine.

**Solution:**

Given

$$T_h = 127^\circ \text{C} = 127 + 273 = 400 \text{ K}$$

$$T_c = 47^\circ \text{C} = 47 + 273 = 320 \text{ K}$$

% efficiency  $\eta = ?$

$$\eta = \left[ \frac{T_h - T_c}{T_h} \right] \times 100$$

$$\eta = \left[ \frac{400 - 320}{400} \right] \times 100$$

$$\eta = \left[ \frac{80}{400} \right] \times 100$$

$$\eta = 20\%$$

6. Urea on hydrolysis produces ammonia and carbon dioxide. The standard entropies of urea,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$  as 173.8, 70, 213.5 and 192.5  $\text{J mol}^{-1} \text{K}^{-1}$  respectively. Calculate the entropy change.

**Solution:**

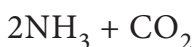
Given:

$$S^0(\text{urea}) = 173.8 \text{ J mol}^{-1} \text{K}^{-1}$$

$$S^0(\text{H}_2\text{O}) = 70 \text{ J mol}^{-1} \text{K}^{-1}$$

$$S^0(\text{CO}_2) = 213.5 \text{ J mol}^{-1} \text{K}^{-1}$$

$$S^0(\text{NH}_3) = 192.5 \text{ J mol}^{-1} \text{K}^{-1}$$



$$\Delta S_r^0 = \sum (S^0)_{\text{products}} - \sum (S^0)_{\text{reactants}}$$

$$\Delta S_r^0 = [2 S^0(\text{NH}_3) + S^0(\text{CO}_2)]$$

$$- [S^0(\text{urea}) + S^0(\text{H}_2\text{O})]$$

$$\Delta S_r^0 = [2 \times 192.5 + 213.5]$$

$$- [173.8 + 70]$$

$$\Delta S_r^0 = [598.5] - [243.8]$$

$$\Delta S_r^0 = 354.7 \text{ J mol}^{-1} \text{K}^{-1}$$

7. Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is 39.84  $\text{kJ mol}^{-1}$ .

**Solution:**

Given:

$$T_b = 351 \text{ K}$$

$$\Delta H_{\text{vap}} = 39840 \text{ J mol}^{-1}$$

$$\Delta S_v = ?$$

$$\Delta S_v = \frac{\Delta H_{\text{vap}}}{T_b}$$

$$\Delta S_v = \frac{39840}{351}$$

$$\Delta S_v = 113.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

8. For a chemical reaction the values of  $\Delta H$  and  $\Delta S$  at 300 K are  $-10 \text{ kJ mol}^{-1}$  and  $-20 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively. What is the value of  $\Delta G$  of the reaction? Calculate the  $\Delta G$  of a reaction at 600K assuming  $\Delta H$  and  $\Delta S$  values are constant. Predict the nature of the reaction.

**Solution:**

Given:

$$\Delta H = -10 \text{ kJ mol}^{-1} = -10000 \text{ J mol}^{-1}$$

$$\Delta S = -20 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 300 \text{ K}$$

$$\Delta G = ? \quad \times (-20 \times 10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1}$$

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

$$\Delta G = (-10 + 12) \text{ kJ mol}^{-1}$$

$$\Delta G = -10 \text{ kJ mol}^{-1} - 300 \text{ K} \times (-20 \times 10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = +2 \text{ kJ mol}^{-1}$$

$$\Delta G = (-10 + 6) \text{ kJ mol}^{-1}$$

The value of  $\Delta G$  is negative at 300K and the reaction is spontaneous, but at 600K the value  $\Delta G$  becomes positive and the reaction is non spontaneous.

$$\Delta G = -4 \text{ kJ mol}^{-1}$$

At 600 K

$$\Delta G = -10 \text{ kJ mol}^{-1} - 600 \text{ K}$$

## EVALUATION



### Evaluation:

I Choose the best answer:

- |  |  |
|--|--|
| 1. (b) $\Delta H$                            | 13. (d) $\Delta H < \Delta U$  |
| 2. (d) decrease in free energy               | 14. (c) + 3 kJ   |
| 3. (b) $q = 0$                               | 15. (a) - 2.48 kJ  |
| 4. (d) = 0                                   | 16. (b) - 500 R  |
| 5. (a) $w = -\Delta U$                       | 17. (d) $\frac{b-2a}{2}$   |
| 6. (d) $\frac{\text{mass}}{\text{volume}}$   | 18. (d) - 635.66 kJ  |
| 7. (a) - 900 J                               | 19. (c) 80 kJ mol <sup>-1</sup>  |
| 8. (b) negative                              | 20. (a) $\Delta H < 0$ and $\Delta S > 0$  |
| 9. (b) - 67.6 kcal                           | 21. (c) adiabatic expansion  |
| 10. (a) graphite is more stable than diamond | 22. (d) (-, -, +)  |
| 11. (d) - 462 kJ                             | 23. (b) 27 °C  |
| 12. (d) frictional energy                    | 24. (d) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ |
|  | 25. (a) 300K   |

**Keys to multiple choice questions:**

7.

$$w = -P \Delta V$$

$$w = - (1 \times 10^5 \text{ Nm}^{-2})$$

$$(1 \times 10^{-2} \text{ m}^3 - 1 \times 10^{-3} \text{ m}^3)$$

$$w = -10^5 (10^{-2} - 10^{-3}) \text{ Nm}$$

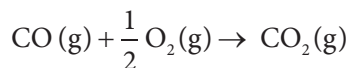
$$w = -10^5 (10 - 1) 10^{-3} \text{ J}$$

$$w = -10^5 (9 \times 10^{-3}) \text{ J}$$

$$w = -9 \times 10^2 \text{ J}$$

$$w = -900 \text{ J}$$

9.



$$\Delta H_C^0 (\text{CO}) = \Delta H_f (\text{CO}_2) - \Delta H_f (\text{CO}) + \Delta H_f (\text{O}_2)]$$

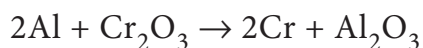
$$\Delta H_C^0 (\text{CO}) = \Delta H_f (\text{CO}_2) - \Delta H_f (\text{CO}) + \Delta H_f (\text{O}_2)]$$

$$\Delta H_C^0 (\text{CO}) = -94 \text{ KCal} - [-26.4 \text{ KCal} + 0]$$

$$\Delta H_C^0 (\text{CO}) = -94 \text{ KCal} + 26.4 \text{ KCal}$$

$$\Delta H_C^0 (\text{CO}) = -67.4 \text{ KCal}$$

11.



$$\Delta H_r^0 = [2\Delta H_f (\text{Cr}) + \Delta H_f (\text{Al}_2\text{O}_3)] - [2\Delta H_f (\text{Al}) + \Delta H_f (\text{Cr}_2\text{O}_3)]$$

$$\Delta H_r^0 = [0 + (-1596 \text{ kJ})]$$

$$- [0 + (-1134)]$$

$$\Delta H_r^0 = -1596 \text{ kJ} + 1134 \text{ kJ}$$

$$\Delta H_r^0 = -462 \text{ kJ}$$

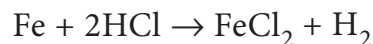
14.

$$\Delta U = q + w$$

$$\Delta U = -1 \text{ kJ} + 4 \text{ kJ}$$

$$\Delta U = +3 \text{ kJ}$$

15.



1 mole of Iron liberates 1 mole of Hydrogen gas

55.85 g Iron = 1 mole Iron

$$\therefore n = 1$$

$$T = 25^0 \text{ C} = 298 \text{ K}$$

$$w = -P \Delta V$$

$$w = -P \left( \frac{nRT}{P} \right)$$

$$w = -nRT$$

$$w = -1 \times 8.314 \times 298 \text{ J}$$

$$w = -2477.57 \text{ J}$$

$$w = -2.48 \text{ kJ}$$

16.

$$T_i = 125^0 \text{ C} = 398 \text{ K}$$

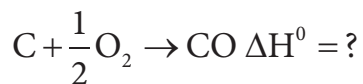
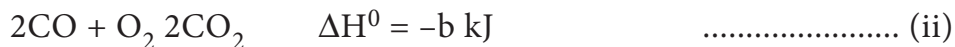
$$T_f = 25^0 \text{ C} = 298 \text{ K}$$

$$\Delta H = nC_p (T_f - T_i)$$

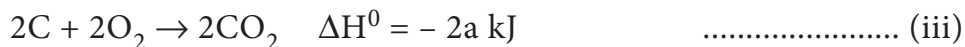
$$\Delta H = 2 \times \frac{5}{2} R (298 - 398)$$

$$\Delta H = -500 R$$

17.



(i)  $\times 2$



Reverse of equation (ii) will be



(iii) + (iv)



(v)  $\div 2$



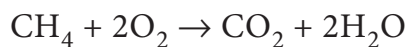
18.

Given :

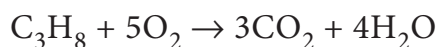
$$\Delta H_C (\text{CH}_4) = -890 \text{ kJ mol}^{-1}$$

$$\Delta H_C (\text{C}_3\text{H}_8) = -2220 \text{ kJ mol}^{-1}$$

Let the mixture contain  $x$  lit of  $\text{CH}_4$  and  $(15.68 - x)$  lit of propane.



$$x \quad \quad 2x$$



$$(15.68 - x) \quad \quad 5(15.68 - x)$$

$$\text{Volume of oxygen consumed} = 2x + 5(15.68 - x) = 32 \text{ lit}$$

$$2x + 78.4 - 5x = 32 \text{ l}$$

$$78.4 - 3x = 32$$

$$3x = 46.4 \text{ l}$$

$$x = 15.47 \text{ l}$$

Given mixture contains 15.47 lit of methane and 0.213 lit of propane, hence

$$\Delta H_c = \left[ \left( \frac{\Delta H_c (\text{CH}_4)}{22.4 \text{ lit}} \right) x \text{ lit} \right] + \left[ \left( \frac{\Delta H_c (\text{C}_3\text{H}_8)}{22.4 \text{ lit}} \right) (15.68 - x) \text{ lit} \right]$$

$$\Delta H_c = \left[ \left( \frac{-890 \text{ kJ mol}^{-1}}{22.4 \text{ lit}} \right) 15.47 \text{ lit} \right] + \left[ \left( \frac{-2220}{22.4 \text{ lit}} \right) 0.21 \text{ lit} \right]$$

$$\Delta H_c = [-614.66 \text{ kJ mol}^{-1}] + [-20.81 \text{ kJ mol}^{-1}]$$

$$\Delta H_c = 635.47 \text{ kJ mol}^{-1}$$

19.

$$4E_{\text{C-H}} = 360 \text{ kJ mol}^{-1}$$

$$E_{\text{C-H}} = 90 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} + 6 E_{\text{C-H}} = 620 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} + 6 \times 90 = 620 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} + 540 = 620 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} = 80 \text{ kJ mol}^{-1}$$

22. During compression, energy of the system increases, in isothermal condition, to maintain temperature constant, heat is liberated from the system. Hence q is negative.

During compression entropy decreases.

During compression work is done on the system, hence w is positive

23.

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

$$T_b = \frac{\Delta H_v}{\Delta S_v} = \frac{4800 \text{ J mol}^{-1}}{16 \text{ J mol}^{-1} \text{ K}^{-1}} = 300 \text{ K} = 27^\circ \text{C}$$

24. In  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ , entropy change is positive. In (a) and (b) entropy change is negative ; in (c) entropy change is zero.

25.

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

At 300K

$$\Delta G = 30000 \text{ J mol}^{-1} - 300 \text{ K} \\ \times 100 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = 0$$

above 300 K ;  $\Delta G$  will be negative  
and reaction becomes spontaneous.

### I Keys to the short answer questions:

53.

#### SOLUTION :

Given :

$$n = 2 \text{ moles}$$

$$V_i = 500 \text{ ml} = 0.5 \text{ lit}$$

$$V_f = 2 \text{ lit}$$

$$T = 25^\circ\text{C} = 298 \text{ K}$$

$$w = -2.303 nRT \log \left( \frac{V_f}{V_i} \right)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \\ \times \log \left( \frac{2}{0.5} \right)$$

$$w = -2.303 \times 2 \times 8.314 \\ \times 298 \times \log(4)$$

$$w = -2.303 \times 2 \times 8.314 \\ \times 298 \times 0.6021$$

$$w = -6871 \text{ J}$$

$$w = -6.871 \text{ kJ}$$

54.

#### SOLUTION :

Given :

$$T_i = 298 \text{ K}$$

$$T_f = 298.45 \text{ K}$$

$$k = 2.5 \text{ kJ K}^{-1}$$

$$m = 3.5 \text{ g}$$

$$M_m = 28$$

$$\text{heat evolved} = k \Delta T$$

$$= k (T_f - T_i)$$

$$= 2.5 \text{ kJ K}^{-1} (298.45 - 298) \text{ K}$$

$$= 1.125 \text{ kJ}$$

$$\Delta H_c = \frac{1.125}{3.5} \times 28 \text{ kJ mol}^{-1}$$

$$\Delta H_c = 9 \text{ kJ mol}^{-1}$$

55.

#### SOLUTION :

Given :

$$T_{\text{sys}} = 77^\circ\text{C} = (77 + 273) = 350 \text{ K}$$

$$T_{\text{surr}} = 33^\circ\text{C} = (33 + 273) = 306 \text{ K}$$

$$q = 245 \text{ J}$$

$$\Delta S_{\text{sys}} = \frac{q}{T_{\text{sys}}} = \frac{-245}{350} = -0.7 \text{ JK}^{-1}$$

$$\Delta S_{\text{surr}} = \frac{q}{T_{\text{surr}}} = \frac{+245}{306} = +0.8 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{univ}} = -0.7 \text{ JK}^{-1} + 0.8 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = 0.1 \text{ JK}^{-1}$$

56.

**SOLUTION :**

**Given :**

$$n = 1 \text{ mole}$$

$$P = 4.1 \text{ atm}$$

$$V = 2 \text{ Lit}$$

$$T = ?$$

$$q = 3710 \text{ J}$$

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

$$\Delta S = \frac{q}{\left(\frac{PV}{nR}\right)}$$

$$\Delta S = \frac{nRq}{PV}$$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm K}^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm K}^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$$\Delta S = 37.10 \text{ JK}^{-1}$$

57.

**SOLUTION:**

**Given :**

$$\Delta H_f(\text{NaCl}) = 30.4 \text{ kJ} = 30400 \text{ J mol}^{-1}$$

$$\Delta S_f(\text{NaCl}) = 28.4 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T_f = ?$$

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

$$T_f = \frac{\Delta H_f}{\Delta S_f}$$

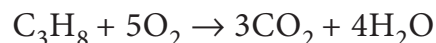
$$T_f = \frac{30400 \text{ J mol}^{-1}}{28.4 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$T_f = 1070.4 \text{ K}$$

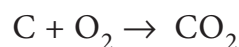
58.

**SOLUTION :**

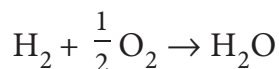
**Given**



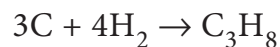
$$\Delta H_c^\circ = -2220.2 \text{ kJ mol}^{-1} \text{ -----(1)}$$



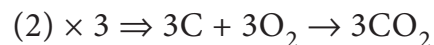
$$\Delta H_f^\circ = -393.5 \text{ kJ mol}^{-1} \text{ -----(2)}$$



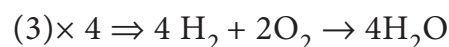
$$\Delta H_f^\circ = -285.8 \text{ kJ mol}^{-1} \text{ ----- (3)}$$



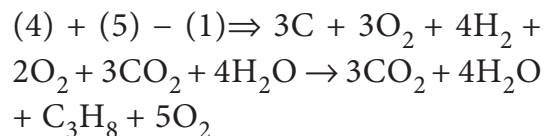
$$\Delta H_c^\circ = ?$$



$$\Delta H_f^\circ = -1180.5 \text{ kJ} \text{ -----(4)}$$

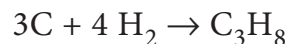


$$\Delta H_f^\circ = -1143.2 \text{ kJ} \text{ -----(5)}$$



$$\Delta H_f^\circ = -1180.5 - 1143.2$$

$$- (-2220.2) \text{ kJ}$$



$$\Delta H_f^\circ = -103.5 \text{ kJ}$$

Standard heat of formation of propane is  $\Delta H_f^\circ(\text{C}_3\text{H}_8) = -103.5 \text{ kJ}$



59.

S. No	Liquid	Boiling points ( $^{\circ}\text{C}$ )	$\Delta\text{H}$ ( kJ mol $^{-1}$ )
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

**SOLUTION :**

**For ethanol :**

**Given :**

$$T_b = 78.4^{\circ}\text{C} = (78.4 + 273)$$

$$= 351.4\text{ K}$$

$$\Delta H_v(\text{ethanol}) = + 42.4\text{ kJ mol}^{-1}$$

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

$$\Delta S_v = \frac{+ 42.4\text{ kJ mol}^{-1}}{351.4\text{ K}}$$

$$\Delta S_v = \frac{+ 42400\text{ J mol}^{-1}}{351.4\text{ K}}$$

$$\Delta S_v = +120.66\text{ J K}^{-1}\text{ mol}^{-1}$$

**For Toluene :**

**Given :**

$$T_b = 110.6^{\circ}\text{C} = (110.6+273)$$

$$= 383.6\text{ K}$$

$$\Delta H_v(\text{toluene}) = + 35.2\text{ kJ mol}^{-1}$$

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

$$\Delta S_v = \frac{+ 35.2\text{ kJ mol}^{-1}}{383.6\text{ K}}$$

$$\Delta S_v = \frac{+ 35200\text{ J mol}^{-1}}{383.6\text{ K}}$$

$$\Delta S_v = + 91.76\text{ J K}^{-1}\text{ mol}^{-1}$$

60.

**Solution :**

**Given :**

$$\Delta H = 30.56\text{ kJ mol}^{-1}$$

$$= 30560\text{ J mol}^{-1}$$

$$\Delta S = 6.66 \times 10^{-3}\text{ kJK}^{-1}\text{mol}^{-1}$$

$$T = ? \text{ at which } \Delta G = 0$$

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

$$0 = \Delta H - T\Delta S$$

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

$$T = \frac{30.56\text{kJmol}^{-1}}{6.66 \times 10^{-3}\text{kJK}^{-1}\text{mol}^{-1}}$$

$$T = 4589\text{ K}$$

(i) At 4589K ;  $\Delta G = 0$  the reaction is in equilibrium.

(ii) at temperature below 4598 K ,  $\Delta H > T \Delta S$

$\Delta G = \Delta H - T \Delta S > 0$ , the reaction in the forward direction, is non spontaneous. In other words the reaction occurs in the backward direction.

61.

**Solution :**

**Given**

$$T = 400\text{K}; \Delta H^0 = 77.2 \text{ kJ mol}^{-1} = 77200$$

$$\text{J mol}^{-1}; \Delta S^0 = 122 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta G^0 = -2.303 RT \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = \frac{\Delta G^0}{2.303 RT}$$

$$\log K_{\text{eq}} = -\frac{(\Delta H^0 - T\Delta S^0)}{2.303 RT}$$

$$\log K_{\text{eq}} = -\left(\frac{77200 - 400 \times 122}{2.303 \times 8.314 \times 400}\right)$$

$$\log K_{\text{eq}} = -\left(\frac{28400}{7659}\right)$$

$$\log K_{\text{eq}} = -3.7080$$

$$K_{\text{eq}} = \text{antilog}(-3.7080)$$

$$K_{\text{eq}} = 1.95 \times 10^{-4}$$

62.

**Solution :**

**Given**

$$T = 298\text{K}; \Delta U = -742.4 \text{ kJ mol}^{-1}$$

$$\Delta H = ?$$

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

$$\Delta H = \Delta U + (n_p - n_r) RT$$

$$\Delta H = -742.4 + \left(2 - \frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

$$= -742.4 + (0.5 \times 8.314 \times 10^{-3} \times 298)$$

$$= -742.4 + 1.24$$

$$= -741.16 \text{ kJ mol}^{-1}$$

63.

**Solution :**

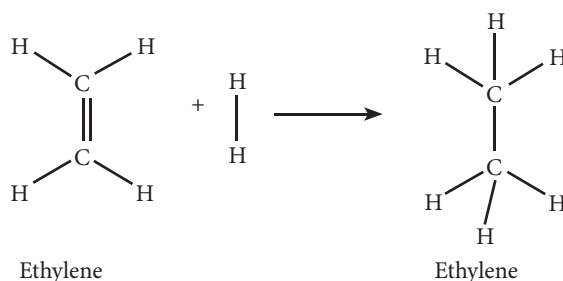
**Given :**

$$E_{\text{C-H}} = 414 \text{ kJ mol}^{-1}$$

$$E_{\text{C-C}} = 347 \text{ kJ mol}^{-1}$$

$$E_{\text{C=C}} = 618 \text{ kJ mol}^{-1}$$

$$E_{\text{H-H}} = 435 \text{ kJ mol}^{-1}$$



$$\Delta H_r = \Sigma (\text{Bond energy})_r - \Sigma (\text{Bond energy})_p$$

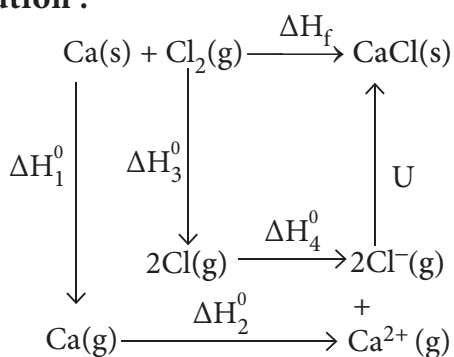
$$\Delta H_r = (E_{\text{C=C}} + 4E_{\text{C-H}} + E_{\text{H-H}}) - (E_{\text{C-C}} + 6E_{\text{C-H}})$$

$$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414))$$

$$\Delta H_r = 2709 - 2831$$

$$\Delta H_r = -122 \text{ kJ mol}^{-1}$$

64.

**Solution :**

$$\begin{aligned}
 \Delta H_f &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\
 &\quad + 2 \Delta H_4 + u \\
 -795 &= 121 + 2422 + 242.8 \\
 &\quad + (2 \times -355) + u \\
 -795 &= 2785.8 - 710 + u \\
 -795 &= 2075.8 + u \\
 u &= -795 - 2075.8 \\
 u &= -2870.8 \text{ kJ mol}^{-1}
 \end{aligned}$$

65.

**Solution :****Given :**

$$\begin{aligned}
 \Delta H_f(\text{Fe}_2\text{O}_3) &= -741 \text{ kJ mol}^{-1} \\
 \Delta H_f(\text{CO}) &= -137 \text{ kJ mol}^{-1} \\
 \Delta H_f(\text{CO}_2) &= -394.5 \text{ kJ mol}^{-1} \\
 \text{Fe}_2\text{O}_3 + 3\text{CO} &\rightarrow 2\text{Fe} + 3\text{CO}_2 \\
 \Delta H_r &=? \\
 \Delta H_r &= \Sigma(\Delta H_f)_{\text{products}} \\
 &\quad - \Sigma(\Delta H_f)_{\text{reactants}} \\
 \Delta H_r &= [2 \Delta H_f(\text{Fe}) + 3\Delta H_f(\text{CO}_2)] \\
 &\quad - [\Delta H_f(\text{Fe}_2\text{O}_3) + 3\Delta H_f(\text{CO})] \\
 \Delta H_r &= [0 + 3(-394.5)]
 \end{aligned}$$

$$- [-741 + 3(-137)]$$

$$\Delta H_r = [-1183.5] - [-1152]$$

$$\Delta H_r = -1183.5 + 1152$$

$$\Delta H_r = -31.5 \text{ kJ mol}^{-1}$$

66.

**Solution:****Given :**

$$T = 175^{\circ}\text{C} = 175 + 273 = 448\text{K}$$

Concentration of 1-pentyne

$$[\text{A}] = 1.3\%$$

Concentration of 2-pentyne

$$[\text{B}] = 95.2\%$$

Concentration of 1, 2-pentadiene

$$[\text{C}] = 3.5\%$$

At equilibrium

B A

$$95.2\% \quad 1.3\% \Rightarrow$$

$$K_1 = \frac{1.3}{95.2} = 0.0136$$

B C

$$95.2\% \quad 3.5\% \Rightarrow$$

$$K_2 = \frac{3.5}{95.2} = 0.0367$$

$$\Rightarrow \Delta G_1^{\circ} = -2.303 RT \log K_1$$

$$\Delta G_1^{\circ} = -2.303 \times 8.314 \times 448$$

$$\times \log 0.0136$$

$$\Delta G_1^{\circ} = +16010 \text{ J}$$

$$\Delta G_1^{\circ} = +16 \text{ kJ}$$

$$\Rightarrow \Delta G_2^{\circ} = -2.303 RT \log K_2$$

$$\Delta G_2^{\circ} = -2.303 \times 8.314 \times 448$$

$$\times \log 0.0367$$

$$\Delta G_2^0 = +12312 \text{ J}$$

$$\Delta G_2^0 = +12.312 \text{ kJ}$$

67.

**Solution:**

**Given :**

$$T = 33 \text{ K}$$



Initial concentration 100% 0

Concentration dissociated 50% -

Concentration remaining at equilibrium  
50% 100%

$$K_{\text{eq}} = \frac{100}{50} = 2$$

$$\Delta G^0 = -2.303 RT \log K_{\text{eq}}$$

$$\Delta G^0 = -2.303 \times 8.314 \times 33 \times \log 2$$

$$\Delta G^0 = -190.18 \text{ J mol}^{-1}$$

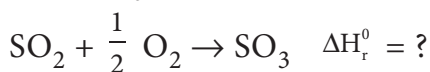
68.

**Solution :**

**Given :**

$$\Delta H_f^0 (\text{SO}_2) = -297 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0 (\text{SO}_3) = -396 \text{ kJ mol}^{-1}$$



$$\Delta H_r^0 = (\Delta H_f^0)_{\text{compound}}$$

$$- \sum (\Delta H_f^0)_{\text{elements}}$$

$$\Delta H_r^0 = \Delta H_f^0 (\text{SO}_3) - \left( \Delta H_f^0 (\text{SO}_2) + \frac{1}{2} \Delta H_f^0 (\text{O}_2) \right)$$

$$\Delta H_r^0 = -396 \text{ kJ mol}^{-1}$$

$$- (-297 \text{ kJ mol}^{-1} + 0)$$

$$\Delta H_r^0 = -396 \text{ kJ mol}^{-1} + 297$$

$$\Delta H_r^0 = -99 \text{ kJ mol}^{-1}$$

69.

**Solution:**

**Given :**

$$T = 298 \text{ K}$$

$$\Delta H = 400 \text{ J mol}^{-1} = 400 \text{ J mol}^{-1}$$

$$\Delta S = 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

if  $T = 2000 \text{ K}$

$$\Delta G = 400 - (0.2 \times 2000) = 0$$

if  $T > 2000 \text{ K}$

$\Delta G$  will be negative.

The reaction would be spontaneous only beyond 2000K

70.

**Solution :**

**Given :**

$$T = 298 \text{ K}$$

$$\Delta G_r^0 = -13.6 \text{ kJ mol}^{-1}$$

$$= -13600 \text{ J mol}^{-1}$$

$$\Delta G^0 = -2.303 RT \log K_{\text{eq}}$$

$$\log K_{\text{eq}} = \frac{-\Delta G^0}{2.303 RT}$$

$$\log K_{\text{eq}} = \frac{13.6 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$$\log K_{\text{eq}} = 2.38$$

$$K_{\text{eq}} = \text{antilog}(2.38)$$

$$K_{\text{eq}} = 239.88$$

71.

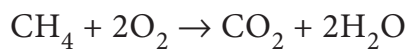
**Solution :**

**Given :**

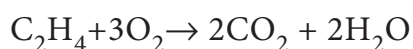
$$\Delta H_C (\text{CH}_4) = -890 \text{ kJ mol}^{-1}$$

$$\Delta H_C (\text{C}_2\text{H}_4) = -1423 \text{ kJ mol}^{-1}$$

Let the mixture contain  $x$  lit of  $\text{CH}_4$   
and  $(3.67 - x)$  lit of ethylene.



$$x \text{ lit} \quad \quad \quad x \text{ lit}$$



$$(3.67-x) \text{ lit} \quad \quad 2(3.67 - x) \text{ lit}$$

Volume of Carbondioxide formed =

$$x + 2(3.67-x) = 6.11 \text{ lit}$$

$$x + 7.34 - 2x = 6.11$$

$$7.34 - x = 6.11$$

$$x = 1.23 \text{ lit}$$

Given mixture contains 1.23 lit of methane and 2.44 lit of ethylene, hence

$$\Delta H_C = \left[ \frac{\Delta H_C (\text{CH}_4)}{22.4 \text{ lit}} \times (x) \text{ lit} \right]$$

$$+ \left[ \frac{\Delta H_C (\text{C}_2\text{H}_4)}{22.4 \text{ lit}} \times (3.67 - x) \text{ lit} \right]$$

$$\Delta H_C = \left[ \frac{-890 \text{ kJ mol}^{-1}}{22.4 \text{ lit}} \times 1.23 \text{ lit} \right]$$

$$+ \left[ \frac{-1423}{22.4 \text{ lit}} \times (3.67 - 1.23) \text{ lit} \right]$$

$$\Delta H_C = [-48.87 \text{ kJ mol}^{-1}]$$

$$+ [-155 \text{ kJ mol}^{-1}]$$

$$\Delta H_C = -203.87 \text{ kJ mol}^{-1}$$