

CHAPTER

7

CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

7.1 INTRODUCTION

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

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

Or

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

Chemical thermodynamics is concerned with the following questions:

- (i) When two or more substances are put together, will they react?
- (ii) If they do react, what energy changes will be associated with the reaction?
- (iii) If a reaction occurs, at what concentrations of the reactants and their products will equilibrium be established?

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

Limitations of thermodynamics: (i) The laws of thermodynamics apply only to the matter in bulk, i.e., macroscopic system and not to individual atoms or molecules of the macroscopic system. Thermodynamics does not deal with internal structure of atoms and molecules. (ii) Thermodynamics can only predict the feasibility or spontaneity of a process under a

given set of conditions but does not tell anything about the rate at which the given process may proceed. It is only concerned with initial and final states of the system. For example, thermodynamics predicts that the reaction between oxygen and hydrogen is possible under ordinary conditions but does not tell whether the reaction is fast or slow.

7.2 TERMS USED IN THERMODYNAMICS

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

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

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

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

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

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

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

surroundings but total amount of matter remains the same as vapours cannot escape.

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

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

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

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

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

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

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

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

The following are some salient features of these properties :

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

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

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

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

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

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

Extensive and intensive properties

Intensive properties	Extensive properties
Molarity	Heat capacity
Molality	Mass
Concentration	Volume

Density	Number of moles
Temperature	Gibbs free energy
Pressure	Enthalpy
Mole fraction	Entropy
Molar enthalpy	Internal energy
Molar entropy	
Refractive index	
Specific heat	
Viscosity	
Surface tension	
Dielectric constant	

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

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

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

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

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

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

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

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

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

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

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

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

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

Nature of Work and Heat

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

$$W = F \times dx$$

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

- (i) an intensity factor,
- (ii) a capacity factor.

Some of them are:

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

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

(b) Electrical work $= \text{charge} \times \text{potential}$
 $= Q \times V$

where, Q = charge, V = potential gradient.

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

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

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

P_{ext} = intensity factor

ΔV = capacity factor

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

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

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

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

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

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

and Δt = temperature difference.

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

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

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

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

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

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

$$1 \text{ joule} = 0.2390 \text{ cal}$$

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

$$1 \text{ kcal} = 4.184 \text{ kJ}$$

$$1 \text{ litre-atm} = 101.3 \text{ J}$$

$$= 1.013 \times 10^9 \text{ erg}$$

$$= 24.206 \text{ cal}$$

SOME SOLVED EXAMPLES

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

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

$$= -1 \times 0.5 = -0.5 \text{ litre-atm}$$

$$= -0.5 \times 101.328 \text{ J} = -50.664 \text{ J}$$

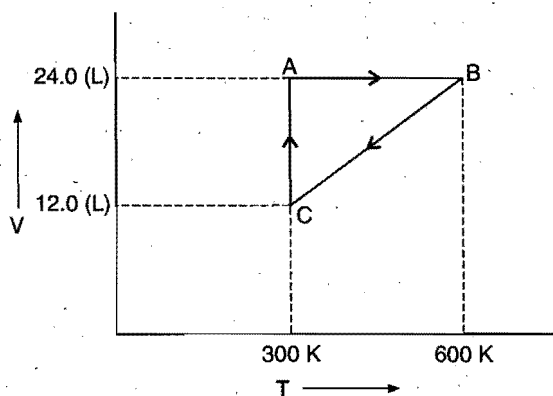
$$0.5 \text{ litre-atm} = -0.5 \times 24.20 \text{ cal} = -12.10 \text{ cal}$$

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

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

(b) Name the processes during the following changes:

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



Solution: (a) At stage A:

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

Substituting these values in the ideal gas equation,

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

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

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

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

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

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

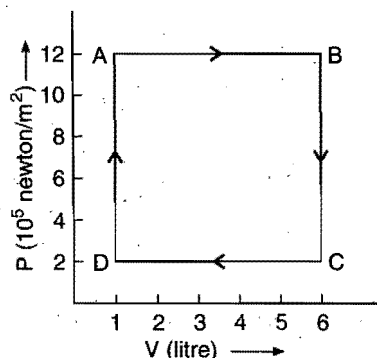
(ii) During the change from B to C the pressure remains constant, the process is **isobaric**.

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

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

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

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



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

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

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

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

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

$$\text{Net work done in the whole cycle} = -6000 + 1000 = -5000 \text{ J}$$

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

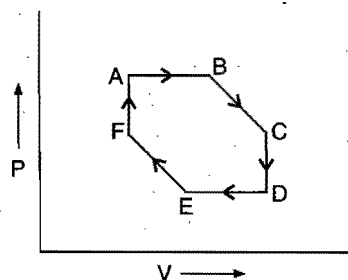
Example 4. Calculate the work done when 1.0 mole of water at 373 K vaporizes against an atmospheric pressure of 1.0 atmosphere. Assume ideal gas behaviour.

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

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

$$W = -P_{\text{ext}} \times \Delta V = -(1.0) \times (31.0) \text{ litre-atm} \\ = -(31.0) \times 101.3 \text{ J} = -3140.3 \text{ J}$$

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



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

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

$\therefore$ It is **isothermal** and **isobaric** process.

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

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

$\therefore$ This process is isothermal and isochoric.

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

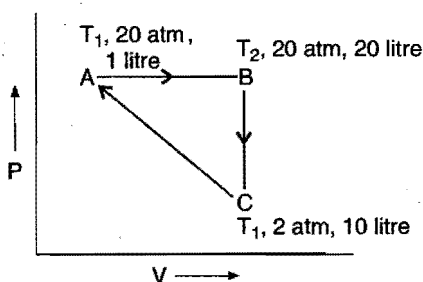
$\therefore$ It is isothermal and isobaric contraction.

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

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

$\therefore$ It is isothermal and isochoric process.

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



(a) Calculate T_1 and T_2 .

(b) Calculate ΔE , q and W in calories in each step of cyclic process.

Solution: (a) At A :

$$PV = nRT$$

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

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

At B :

$$PV = nRT$$

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

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

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

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

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

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

Path BC : Isochoric process

$$W = 0$$

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

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

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

Path CA : It is isothermal compression ΔE_0

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

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

7.3 INTERNAL ENERGY

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

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

Accurate measurements of some forms of energy which

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

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

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

$$\Delta E = E_f - E_i$$

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

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

Characteristics of Internal Energy

- Internal energy of a system is an extensive property.
- Internal energy is a state property.
- The change in the internal energy does not depend on the path by which the final state is reached.
- There is no change in internal energy in a cyclic process.

Thermal Equilibrium and Zeroth Law of Thermodynamics

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

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

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

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

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

Conversely, the law can be stated as follows :

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

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

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

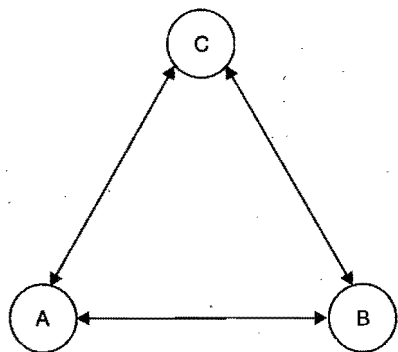


Fig. 7.1 Systems in thermal equilibrium

7.4 FIRST LAW OF THERMODYNAMICS

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

- (i) Energy cannot be created or destroyed but it can be converted from one form to another.
- (ii) The total energy of the universe is constant.
- (iii) Whenever a quantity of one kind of energy disappears, an exactly equivalent quantity of energy in some other form must appear.
- (iv) It is impossible to construct a perpetual motion machine which could produce work without consuming energy.
- (v) The total energy of an isolated system remains constant though it may change from one form to another.

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

$$\Delta E = E_f - E_i$$

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

- (a) Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).
- (b) By doing work on the system or the work done by the system.

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

$$E_2 = E_1 + q + w$$

$$\text{or } E_2 - E_1 = q + w$$

$$\text{or } \Delta E = q + w$$

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

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

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

The first law of thermodynamics may also be stated as:

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

Or

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

Or

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

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

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

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

Applying the first law of thermodynamics,

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

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

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

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

Applying the first law of thermodynamics,

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

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

Some useful conclusions drawn from the first law:

$$\Delta E = q + w$$

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

$$0 = q + w$$

or

$$q = -w$$

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

or

$$w = -q$$

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

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

$$\Delta E = q$$

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

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

$$\Delta E = w$$

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

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

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

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

When

$$\Delta V = 0,$$

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

The symbol q_V indicates the heat change at constant volume.

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

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

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

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

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

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

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

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

Substituting the values in equation,

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

7.5 ENTHALPY

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

From first law of thermodynamics;

$$Q = E + PV \quad \dots (i)$$

Heat change at constant pressure can be given as

$$\Delta Q = \Delta E + P \Delta V \quad \dots (ii)$$

At constant pressure heat can be replaced by enthalpy.

$$\Delta H = \Delta E + P \Delta V \quad \dots (iii)$$

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

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

$$\Delta Q = \Delta E$$

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

$\Delta E =$ Heat change or heat of reaction at constant volume.

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

$$\Delta H \approx \Delta E \quad (P \Delta V \approx 0)$$

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

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

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

Here,

$$P \Delta V = \Delta n RT$$

$\Delta n =$ Number of gaseous moles of products - Number of gaseous moles of reactants.

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

7.6 HEAT CAPACITY

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

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

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

At constant volume, $q = \Delta E$

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

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

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

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

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

and

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

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

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

For 1 mole of gas $PV = RT$.

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

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

or

$$P \Delta V = R$$

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

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

Atomicity	C_V	$C_P = C_V + R$	$\gamma = \frac{C_P}{C_V}$
Monoatomic He, Ne, Ar etc.	$\frac{3}{2}R$	$\frac{5}{2}R$	$\gamma = \frac{5/2R}{3/2R} = 1.66$
Diatomic $\text{O}_2, \text{N}_2, \text{H}_2, \text{Cl}_2$	$\frac{5}{2}R$	$\frac{7}{2}R$	$\gamma = \frac{7/2R}{5/2R} = 1.40$
Tri and polyatomic $\text{CO}_2, \text{NH}_3, \text{SO}_3, \text{NO}_2, \text{CH}_4$ etc.	$3R$	$4R$	$\gamma = \frac{4R}{3R} = 1.33$

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

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

7.7 EXPANSION OF AN IDEAL GAS

(i) Isothermal Expansion

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

$$\Delta E = 0$$

According to first law of thermodynamics,

$$\Delta E = q + w$$

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

$$q = -w$$

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

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

$$H = E + PV$$

$$\text{or } \Delta H = \Delta E + \Delta(PV)$$

$$\text{or } \Delta H = \Delta E + \Delta(nRT)$$

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

$$\Delta H = 0$$

Work done in reversible isothermal expansion

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

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

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

Since, the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced due to expansion is balanced by the absorption of heat from the

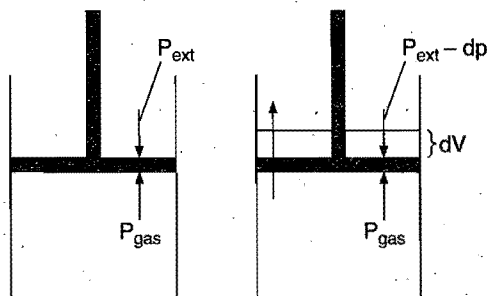


Fig. 7.2

surroundings and the temperature remains constant throughout the expansion.

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

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

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

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

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

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

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

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

At constant temperature, according to Boyle's law,

$$P_1 V_1 = P_2 V_2$$

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

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

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

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

Work done in irreversible isothermal expansion

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

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

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

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

(ii) Adiabatic Expansion

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

In expansion, work is done by the system on the surroundings, hence, w is negative. Accordingly ΔE is also negative, i.e.,

internal energy decreases and therefore, the temperature of the system falls. In case of compression, ΔE is positive, i.e., internal energy increases and therefore, the temperature of the system rises.

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

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

or $dE = C_V \cdot dT$... (i)

and for finite change $\Delta E = C_V \Delta T$... (ii)

So, $w = \Delta E = C_V \Delta T$... (iii)

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

Reversible adiabatic expansion

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

$$w = -P \Delta V \quad \dots (iv)$$

If ΔT is the fall in temperature, then

$$C_V \Delta T = -P \Delta V \quad \dots (v)$$

For very small change in reversible process,

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

$$C_V \cdot \frac{dT}{T} = -R \cdot \frac{dV}{V} \quad \dots (vi)$$

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

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

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

or $\log \frac{T_2}{T_1} = -\frac{R}{C_V} \log \frac{V_2}{V_1} = \frac{R}{C_V} \log \frac{V_1}{V_2} \quad \dots (vii)$

We know that, $C_P - C_V = R$

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

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

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

$$\begin{aligned} \log \frac{T_2}{T_1} &= (\gamma - 1) \log \frac{V_1}{V_2} \\ &= \log \left(\frac{V_1}{V_2} \right)^{\gamma-1} \quad \dots (viii) \end{aligned}$$

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

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

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

or $P_1 V_1^\gamma = P_2 V_2^\gamma \quad \dots (xi)$

or $PV^\gamma = \text{constant} \quad \dots (xii)$

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

Modifying the eq. (x),

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

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

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

From eq. (v),

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

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

Irreversible adiabatic expansion

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

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

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

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

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

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

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

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

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

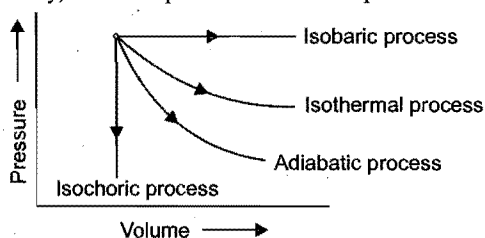


Fig. 7.3 (a)

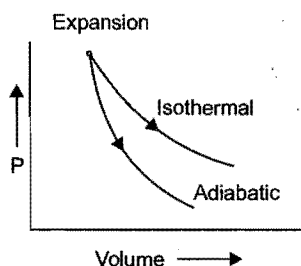


Fig. 7.3 (b)

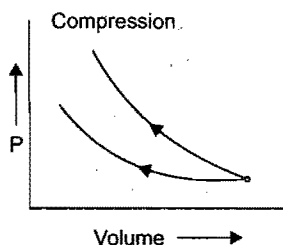


Fig. 7.3 (c)

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

$$\text{Work done on the gas, } w = -P_{\text{ext}}(V_f - V_i) \\ = +ve \text{ work,} \quad \text{Since } V_f < V_i$$

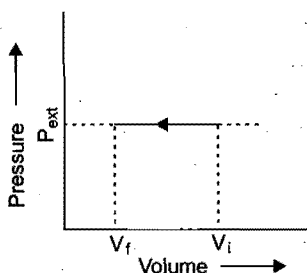


Fig. 7.4 Single step compression of ideal gas against external pressure P_{ext}

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

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

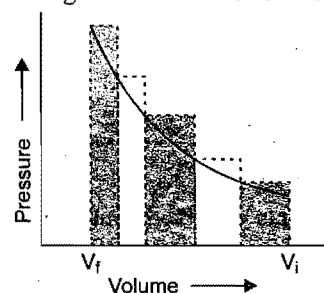


Fig. 7.5 Indicator diagram (P-V) plot in which the compression took place in the finite number of steps with varying pressure

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

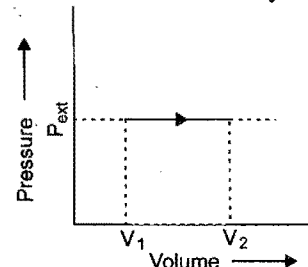


Fig. 7.6 Shaded area gives the work done by the gas when pressure remains constant

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

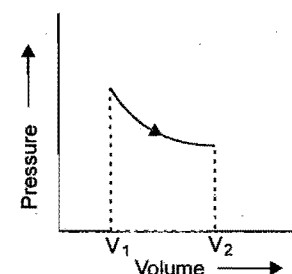


Fig. 7.7 Shaded area represents the work done by the gas when both pressure and volume vary

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

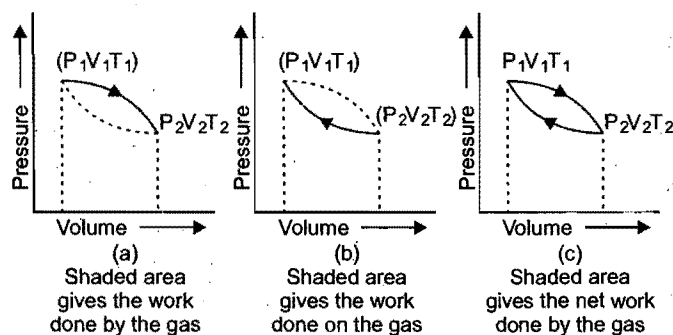


Fig. 7.8 Complete cyclic process of a gas

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

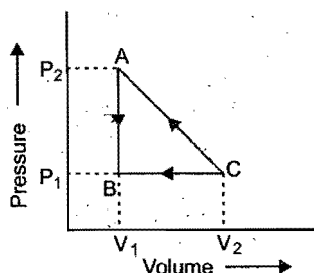


Fig. 7.9 The gas in closed cyclic process $ABCA$

Work done = Area of shaded triangle

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

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

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

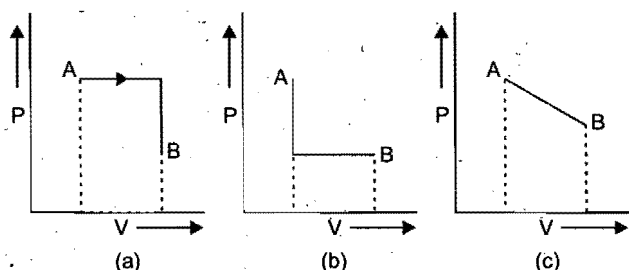


Fig. 7.10 Graphical proof that the work is not a state function

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

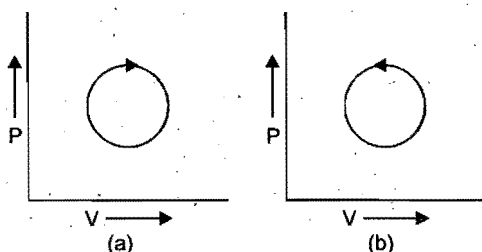


Fig. 7.11 Representation of closed cyclic process in clockwise and anti-clockwise direction

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

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

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

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

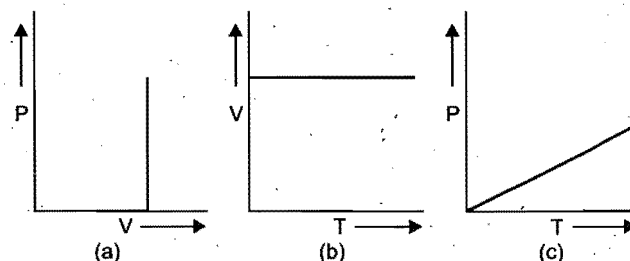


Fig. 7.12 Isochores of Ideal Gas

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

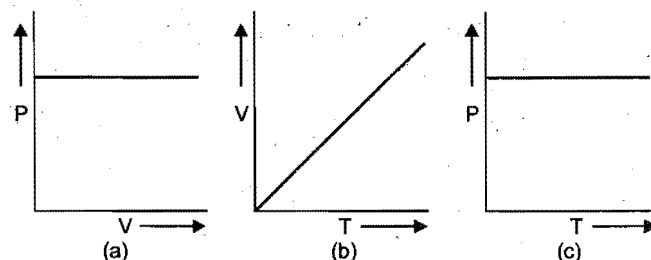


Fig. 7.13 Isobars of Ideal Gas

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

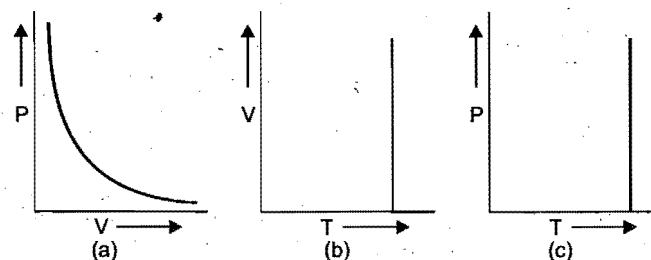


Fig. 7.14 Isotherm of Ideal Gas

7.9 JOULE-THOMSON EFFECT

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

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

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

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

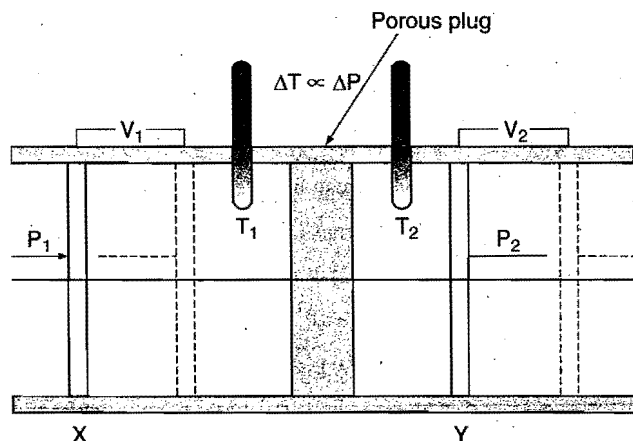


Fig. 7.15

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

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

The gas is compressed on left hand side. Thus, work is done on the gas. It is equal to $P_1 V_1$. The work done on right hand side by the gas is equal to $P_2 V_2$.

$$\text{Total work done by the gas} = P_1 V_1 - P_2 V_2$$

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

$$\begin{aligned}\Delta E &= P_1 V_1 - P_2 V_2 \\ E_2 - E_1 &= P_1 V_1 - P_2 V_2 \\ (E_2 + P_2 V_2) - (E_1 + P_1 V_1) &= 0\end{aligned}$$

$$\text{or } H_2 - H_1 = 0$$

$$\text{or } \Delta H = 0$$

Thus, Joule-Thomson effect occurs at constant enthalpy.

Joule-Thomson Coefficient

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

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

When μ has positive value, the gas cools on expansion. If it has negative value, the gas warms on expansion. Every gas has a definite value of temperature when the sign changes from negative to positive. This temperature is termed **inversion**

temperature. Most of the gases have inversion temperature near about room temperature and thus cool at room temperature when expansion is done. However, the inversion temperature for H_2 is -80°C . Thus, at room temperature hydrogen warms on expansion. In order to produce further cooling by Joule-Thomson effect in hydrogen, it is necessary that it should be first cooled to -80°C by other cooling devices.

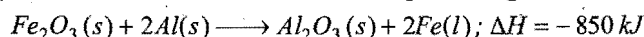
The value of inversion temperature has been calculated by using van der Waals' equation,

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

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

SOME SOLVED EXAMPLES

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



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

Solution: Mass of products

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

$$= 214 \text{ g}$$

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

$$= 257656 \text{ J} = 257.656 \text{ kJ}$$

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

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

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

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

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

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

Work done by the system,

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

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

$$= 15.3 \times 101.3 \text{ J} = 1549.89 \text{ J}$$

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

$$w = -1549.89 \text{ J}$$

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

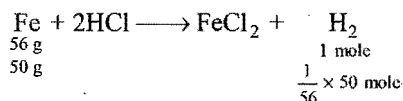
$$= 0.5 \times 40670 \text{ J} = 20335 \text{ J}$$

According to first law of thermodynamics,

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

Example 12. Calculate the work done when 50 g of iron is dissolved in HCl at 25°C in (i) a closed vessel and (ii) an open beaker when the atmospheric pressure is 1 atm.

Solution: (i) When the reaction is carried in a closed vessel, the change in volume is zero. Hence, the work done by the system will be zero. (ii) When iron dissolves in HCl, hydrogen is produced.



Volume of hydrogen produced at 25°C

$$= \frac{nRT}{P} = \frac{50}{56} \times \frac{0.0821 \times 298}{1} = 21.84 \text{ L}$$

This is equal to volume change when the reaction is carried in open beaker.

$$\begin{aligned} \text{Work done by the system} &= -P \Delta V = -1.0 \times 21.84 \\ &= -21.84 \text{ litre-atm} = -2212.39 \text{ J} \end{aligned}$$

Example 13. 5 mole of oxygen are heated at constant volume from 10°C to 20°C. What will be the change in the internal energy of gas? The molar heat of oxygen at constant pressure, $C_p = 7.03 \text{ cal mol}^{-1} \text{ deg}^{-1}$ and $R = 8.31 \text{ J mol}^{-1} \text{ deg}^{-1}$.

$$\begin{aligned} \text{Solution: } R &= 8.31 \text{ J mol}^{-1} \text{ deg}^{-1} = \frac{8.31}{4.18} \text{ cal mol}^{-1} \text{ deg}^{-1} \\ &= 1.99 \text{ cal mol}^{-1} \text{ deg}^{-1} \end{aligned}$$

$$\begin{aligned} \text{We know that, } C_p - C_v &= R \\ \text{or } C_v &= C_p - R = 7.03 - 1.99 = 5.04 \text{ cal mol}^{-1} \text{ deg}^{-1} \end{aligned}$$

Heat absorbed by 5 mole of oxygen in heating from 10°C to 20°C

$$= 5 \times C_v \times \Delta T = 5 \times 5.04 \times 10 = 252 \text{ cal}$$

Since, the gas is heated at constant volume, no external work is done,

$$\text{i.e., } w = 0$$

So, change in internal energy will be equal to heat absorbed,

$$\Delta E = q + w = 252 + 0 = 252 \text{ cal}$$

Example 14. Calculate the amount of work done by 2 mole of an ideal gas at 298 K in reversible isothermal expansion from 10 litre to 20 litre.

Solution: Amount of work done in reversible isothermal expansion,

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

Given, $n = 2$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$, $V_2 = 20 \text{ L}$ and $V_1 = 10 \text{ L}$.

Substituting the values in above equation,

$$\begin{aligned} w &= -2.303 \times 2 \times 8.314 \times 298 \log \frac{20}{10} \\ &= -2.303 \times 2 \times 8.314 \times 298 \times 0.3010 = -3434.9 \text{ J} \end{aligned}$$

i.e., work is done by the system.

Example 15. 5 moles of an ideal gas expand isothermally and reversibly from a pressure of 10 atm to 2 atm at 300 K. What is the largest mass which can be lifted through a height of 1 metre in this expansion?

Solution: Work done by the system

$$\begin{aligned} &= -nRT \log_e \frac{P_1}{P_2} = -2.303nRT \log \frac{P_1}{P_2} \\ &= -2.303 \times 5 \times 8.314 \times 300 \log \frac{10}{2} = -20.075 \times 10^3 \text{ J} \end{aligned}$$

Let M be the mass which can be lifted through a height of 1 m.

Work done in lifting the mass

$$= Mgh = M \times 9.8 \times 1 \text{ J}$$

$$\text{So, } M \times 9.8 = 20.075 \times 10^3$$

$$M = 2048.469 \text{ kg}$$

Example 16. Two moles of an ideal monoatomic gas at NTP are compressed adiabatically and reversibly to occupy a volume of 4.48 dm³. Calculate the amount of work done, ΔE , final temperature and pressure of the gas. C_v for ideal gas = 12.45 J K⁻¹ mol⁻¹.

$$\text{Solution: For an ideal gas, } \gamma = \frac{C_p}{C_v} = 1.667$$

$$\text{Initial volume, } V_1 = 2 \times 22.4 = 44.8 \text{ dm}^3$$

$$\text{Initial pressure, } P_1 = 1 \text{ atm}$$

$$\text{Initial temperature, } T_1 = 273 \text{ K}$$

$$\text{Final volume, } V_2 = 4.48 \text{ dm}^3$$

Let the final pressure be P_2 and temperature be T_2 .

$$\text{Applying } P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\text{or } \frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^\gamma = \left(\frac{4.48}{44.8} \right)^{1.667}$$

$$\text{or } \frac{P_2}{P_1} = (10)^{1.667}$$

$$P_2 = (10)^{1.667} (P_1 = 1 \text{ given})$$

$$\log P_2 = 1.667 \log 10 = 1.667$$

$$P_2 = \text{antilog } 1.667 = 46.45 \text{ atm}$$

$$\text{Final temperature} = \frac{P_2 V_2}{P_1 V_1} \cdot T_1 = \frac{46.45 \times 4.48}{1 \times 44.8} \times 273$$

$$= 1268 \text{ K}$$

$$\text{Work done on the system} = n \cdot C_v \cdot \Delta T$$

$$= 2 \times 12.45 \times (1268 - 273)$$

$$= 2 \times 12.45 \times 995 = 24775.5 \text{ J}$$

From the first law of thermodynamics,

$$\Delta E = q + w = 0 + 24775.5 = 24775.5 \text{ J}$$

Example 17. A certain volume of dry air at NTP is expanded reversibly to four times its volume (a) isothermally (b) adiabatically. Calculate the final pressure and temperature in each case, assuming ideal behaviour.

$$\left(\frac{C_P}{C_V} \text{ for air} = 1.4 \right)$$

Solution: Let V_1 be the initial volume of dry air at NTP.

(a) **Isothermal expansion:** During isothermal expansion, the temperature remains the same throughout. Hence, final temperature will be 273 K.

$$\begin{aligned} \text{Since, } P_1 V_1 &= P_2 V_2 \\ P_2 &= \frac{P_1 V_1}{V_2} = \frac{1 \times V_1}{4V_1} = 0.25 \text{ atm} \end{aligned}$$

(b) **Adiabatic expansion:**

$$\begin{aligned} \frac{T_1}{T_2} &= \left(\frac{V_2}{V_1} \right)^{\gamma-1} \\ \frac{273}{T_2} &= \left(\frac{4V_1}{V_1} \right)^{1.4-1} = 4^{0.4} \\ T_2 &= \frac{273}{4^{0.4}} = 156.79 \text{ K} \end{aligned}$$

$$\begin{aligned} \text{Final pressure: } \frac{P_1}{P_2} &= \left(\frac{V_2}{V_1} \right)^{\gamma} \\ \frac{1}{P_2} &= \left(\frac{4V_1}{V_1} \right)^{1.4} = 4^{1.4} \\ P_2 &= \frac{1}{4^{1.4}} = 0.143 \text{ atm} \end{aligned}$$

Example 18. Calculate q , w , ΔE and ΔH for the reversible isothermal expansion of one mole of an ideal gas at 127°C from a volume of 10 dm^3 to 20 dm^3 .

Solution: Since, the process is isothermal,

$$\Delta E = \Delta H = 0$$

From first law of thermodynamics,

$$\Delta E = q + w = 0$$

$$q = -w$$

$$\begin{aligned} w &= -2.303nRT \log \frac{V_2}{V_1} \\ &= -2.303 \times 1 \times 8.314 \times 400 \log \frac{20}{10} \\ &= -2.303 \times 1 \times 8.314 \times 400 \times 0.3010 \\ &= -2305.3 \text{ J} \quad (\text{Work is done by the system}) \\ q &= -w = 2305.3 \text{ J} \quad (\text{Heat is absorbed by the system}) \end{aligned}$$

Example 19. A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against a constant pressure of 3.0 atm . The work done during expansion is used to heat 10.0 mole of water of

temperature 290.0 K . Calculate the final temperature of water (specific heat of water = $4.184 \text{ JK}^{-1} \text{ g}^{-1}$). (IIT 1993)

$$\begin{aligned} \text{Solution: } \text{Work done} &= P \times dV = 3.0 \times (5.0 - 3.0) \\ &= 6.0 \text{ litre-atm} = 6.0 \times 101.3 \text{ J} \\ &= 607.8 \text{ J} \end{aligned}$$

Let ΔT be the change in temperature.

$$\begin{aligned} \text{Heat absorbed} &= m \times s \times \Delta T \\ &= 10.0 \times 18 \times 4.184 \times \Delta T \end{aligned}$$

$$\text{Given, } P \times dV = m \times s \times \Delta T$$

$$\text{or } \Delta T = \frac{P \times dV}{m \times s} = \frac{607.8}{10.0 \times 18.0 \times 4.184} = 0.807$$

$$\text{Final temperature} = 290 + 0.807 = 290.807 \text{ K}$$

Example 20. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 litre to 5 litre . Calculate q , w , ΔE and ΔH for this process.

$$R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}, \log 2 = 0.30. \text{ Atomic weight of Ar} = 40. \quad (\text{IIT 1997})$$

$$\begin{aligned} \text{Solution: } w &= -2.303nRT \log \frac{V_2}{V_1} \\ &= -2.303 \times \frac{10}{40} \times 2 \times 300 \log \frac{5}{10} = 103.635 \text{ cal} \end{aligned}$$

$$\Delta E = 0$$

$$q = \Delta E - w$$

$$\therefore q = -w = -103.635 \text{ cal}$$

Example 21. Calculate the maximum work done in expanding 16 g of oxygen at 300 K and occupying a volume of 5 dm^3 isothermally until the volume becomes 25 dm^3 .

Solution: Reversible work is maximum work.

$$\begin{aligned} \therefore w &= -2.303nRT \log \left(\frac{V_2}{V_1} \right) \\ &= 2.303 \times \frac{16}{32} \times 8.314 \times 300 \log \frac{25}{5} = 2.01 \times 10^3 \text{ joule} \end{aligned}$$

Example 22. How much heat is required to change 10 g ice at 0°C to steam at 100°C ? Latent heat of fusion and vaporization for H_2O are 80 cal/g and 540 cal/g , respectively. Specific heat of water is 1 cal/g .

Solution: Total heat absorbed

$$\begin{aligned} &= \Delta H_{\text{fusion}} + \Delta H_{\text{temp. rise}} + \Delta H_{\text{vap.}} \\ &= 10 \times 80 + 10 \times 1 \times 100 + 10 \times 540 = 7200 \text{ cal} \end{aligned}$$

Example 23. A swimmer coming out of a pool is covered with a film of water weighing about 80 g . How much heat must be supplied to evaporate this water?

$$\begin{aligned} \text{Solution: } q &= mL \\ &= \frac{80}{18} \times 40.79 \\ &= 181.28 \text{ kJ} \end{aligned}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 5 moles of an ideal gas at 27°C expands isothermally and reversibly from a volume of 6 L to 60 L. The work done in kJ is:

(a) -14.7 (b) -28.72 (c) +28.72 (d) -56.72

[Ans. (b)]

[Hint: $w = -2.303nRT \log \frac{V_2}{V_1}$

$$= -2.303 \times 5 \times 8.314 \times 300 \log \frac{60}{6}$$

$$= -28.72 \text{ kJ}]$$

2. 10 moles of an ideal gas confined to a volume of 10 L is released into atmosphere at 300 K where the pressure is 1 bar. The work done by the gas is:

($R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$)

(a) 249 L bar (b) 259 L bar (c) 239 L bar (d) 220 L bar

[Ans. (c)]

[Hint: Initial volume, $V_1 = 10 \text{ L}$

$$V_2 (\text{final}) = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$

$$W = P \Delta V = 1 \times (249 - 10)$$

$$= 239 \text{ L bar}]$$

3. 1 litre-atm work is approximately equal to:

(a) 101.3 J (b) 8.314 J (c) 931 J (d) 19.2 J

[Ans. (a)]

[Hint: $0.0821 \text{ litre-atm} = 8.314 \text{ J}$ (values of gas constant)

$\therefore 1 \text{ litre-atm} = 101.3 \text{ J}]$

4. A system absorbs 20 kJ heat and also does 10 kJ of work. The net internal energy of the system:

(a) increases by 10 kJ (b) decreases by 10 kJ
(c) increases by 30 kJ (d) decreases by 30 kJ

[Ans. (a)]

[Hint: $\Delta U = q + w = 20 - 10 = 10 \text{ kJ}$

5. One mole of a gas is heated at constant pressure to raise its temperature by 1°C. The work done in joules is:

(a) -4.3 (b) -8.314
(c) -16.62 (d) unpredictable

[Ans. (b)]

[Hint: $w = -nR \Delta T$ or $w = -P \Delta V$

$$= -1 \times 8.314 \times 1 = -P \left(\frac{nRT_2}{P} - \frac{nRT_1}{P} \right)$$

$$= -8.314 \text{ J}]$$

6. In open system:

(a) there will be exchange of both matter and energy
(b) there will be no exchange of matter and energy
(c) there will be exchange of energy only
(d) there will be exchange of matter only

[Ans. (a)]

[Hint: Open system has imaginary boundary, therefore, both energy and mass can be exchanged.]

7.10 THERMOCHEMISTRY

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

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

Exothermic Reactions

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

At constant pressure,

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

At constant volume,

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

Endothermic Reactions

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

At constant pressure,

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

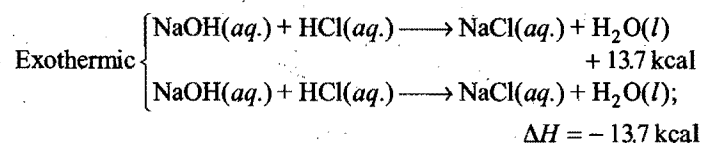
At constant volume,

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

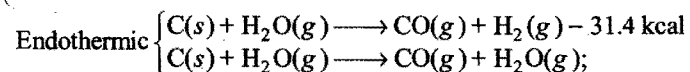
Sign conventions:

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

Exothermic and endothermic chemical equations can be represented as:



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



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

7.11 HEAT OF REACTION OR ENTHALPY OF REACTION

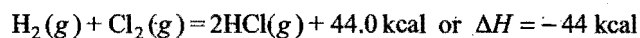
Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction

(or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically,

Enthalpy of reaction (or heat of reaction)

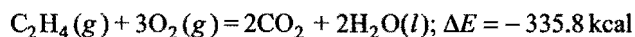
$$= \Delta H = \Sigma H_P - \Sigma H_R$$

For example, the equation



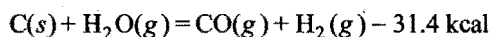
indicates that when 2 g of hydrogen (1 mole) completely reacts with 71 g of chlorine (1 mole) to form 73 g of HCl (2 mole), the amount of heat evolved is 44.0 kcal or the enthalpy decreases by 44.0 kcal or the reacting system loses 44.0 kcal of heat or the enthalpy change of the reaction, $\Delta H =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

Consider the following reaction:



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

Consider another reaction:



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

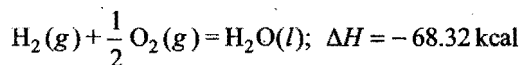
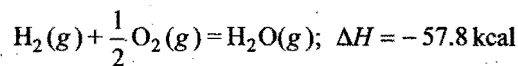
This reaction indicates that 1 mole of carbon (12 g) reacts with 1 mole of steam (18 g) to form 1 mole of CO and 1 mole of hydrogen and 31.4 kcal of heat is absorbed. The enthalpy of the system increases by 31.4 kcal or the total enthalpy of the products is 31.4 kcal more than the enthalpy of reactants.

Factors which Influence the Heat of Reaction

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

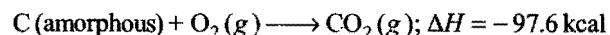
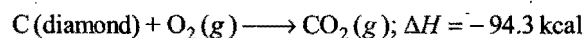
(i) **Physical state of reactants and products:** Heat energy is involved for changing the physical state of a chemical substance. For example, in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed.

Considering the following two reactions:

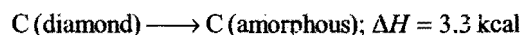


It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in second case is higher because heat is evolved when steam condenses. Hence, physical state always affects the heat of reaction.

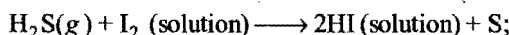
(ii) **Allotropic forms of the element:** Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous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



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



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



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

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

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

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

or

$$q_V + \Delta nRT = q_P$$

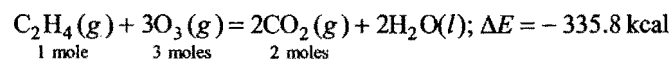
q_V = heat change at constant volume,

q_P = heat change at constant pressure.

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

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

Solution: The chemical equation for the combustion of C_2H_4 is



$$\text{No. of moles of reactants} = (1 + 3) = 4$$

$$\text{No. of moles of products} = 2$$

So,

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

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

and

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

Applying

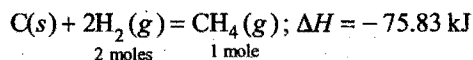
$$\Delta H = \Delta E + \Delta nRT$$

$$= -335.8 + (-2)(2 \times 10^{-3})(291)$$

$$= -336.964 \text{ kcal}$$

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

Solution: The equation for the formation of methane is



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

Given, $\Delta H = -75.83 \text{ kJ}$, $R = 8.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$

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

$$-75.83 = \Delta E + (-1)(8.3 \times 10^{-3})(300)$$

$$\begin{aligned} \text{So, } \Delta E &= -75.83 + 2.49 \\ &= -73.34 \text{ kJ} \end{aligned}$$

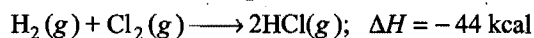
7.12 ENTHALPY OF FORMATION OR HEAT OF FORMATION

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

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



Enthalpy of formation of CO_2 is -97.6 kcal

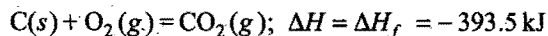


Thus, enthalpy of formation of HCl is -22 kcal per mol .

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

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

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



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

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

So, $\Delta H_f = \Delta H = H_p = \text{enthalpy of } \text{CO}_2 = -393.5 \text{ kJ}$

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

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

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

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

$$\text{i.e., } \Delta H^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

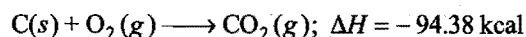
The heats of formation of all the elements in their standard states are arbitrarily assumed to be zero.

Intrinsic energy: It may be defined as:

Intrinsic energy = $-\text{Heat of formation}$

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

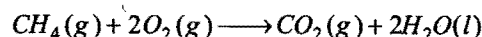
Let us consider the combustion of carbon.



When 1 mole CO_2 is formed, 94.38 kcal heat is evolved. It means, energy content of CO_2 is less than energy content of $\text{C}(s)$ and $\text{O}_2(g)$ by 94.38 kcal. Thus, intrinsic energy of CO_2 is 94.38 kcal.

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

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

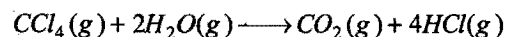


given, enthalpies of formation of CH_4 , CO_2 and H_2O are $-74.8 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-286.2 \text{ kJ mol}^{-1}$ respectively.

Solution:

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\ &= [\Delta H_f^\circ (\text{CO}_2) + 2\Delta H_f^\circ (\text{H}_2\text{O})] - [\Delta H_f^\circ (\text{CH}_4) + 2\Delta H_f^\circ (\text{O}_2)] \\ &= [-393.5 + 2 \times (-286.2)] - [-74.8 + 2 \times 0] \\ &= -393.5 - 572.4 + 74.8 \\ &= -891.1 \text{ kJ} \end{aligned}$$

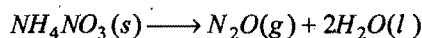
Example 27. The standard heats of formation at 298 K for $\text{CCl}_4(g)$, $\text{H}_2\text{O}(g)$, $\text{CO}_2(g)$ and $\text{HCl}(g)$ are -25.5 , -57.8 , -94.1 and $-22.1 \text{ kcal mol}^{-1}$ respectively. Calculate ΔH_{298}° for the reaction.



Solution:

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants}) \\ &= [\Delta H_f^\circ (\text{CO}_2) + 4\Delta H_f^\circ (\text{HCl})] - [\Delta H_f^\circ (\text{CCl}_4) + 2\Delta H_f^\circ (\text{H}_2\text{O})] \\ &= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2 \times (-57.8)] \\ &= -94.1 - 88.4 + 25.5 + 115.6 \\ &= -182.5 + 141.1 = -41.4 \text{ kcal} \end{aligned}$$

Example 28. The molar heat of formation of $\text{NH}_4\text{NO}_3(s)$ is -367.5 kJ and those of $\text{N}_2\text{O}(g)$ and $\text{H}_2\text{O}(l)$ are $+81.46 \text{ kJ}$ and -285.78 kJ respectively at 25°C and 1 atmospheric pressure. Calculate the ΔH and ΔE for the reaction,



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

$$= [\Delta H_f^\circ(\text{N}_2\text{O}) + 2 \times \Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{NH}_4\text{NO}_3)]$$

$$= 81.46 + 2 \times (-285.78) - (-367.5)$$

$$= 81.46 - 571.56 + 367.5$$

$$= -122.56 \text{ kJ}$$

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

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

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

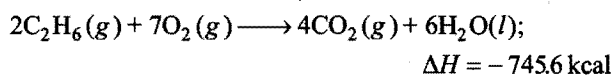
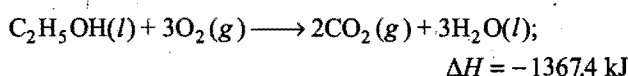
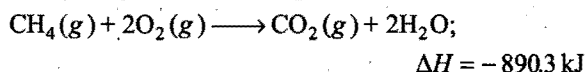
$$\Delta E = -122.56 - (1)(8.314 \times 10^{-3})(298)$$

$$= -122.56 - 2.477$$

$$= -125.037 \text{ kJ}$$

7.13 ENTHALPY OF COMBUSTION OR HEAT OF COMBUSTION

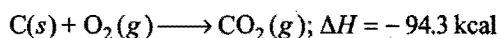
Enthalpy of combustion is the amount of heat evolved or decrease in enthalpy when 1 mole of the substance (compound or element) is completely oxidised. The enthalpy of combustion, i.e., ΔH is always negative. For example,



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

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

$$\text{C}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g); \Delta H = -26.0 \text{ kcal}$$



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

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

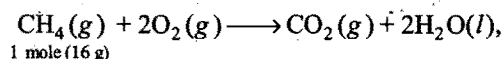
(i) Calorific values of foods and fuels: Energy is needed for the working of all machines. Even human body is no exception. Coal, petroleum, natural gas, etc., serve as the principal sources of energy for man-made machines, the food which we eat serves as a source of energy to our body. These substances undergo oxidation or combustion and release energy.

These substances are, therefore, termed as fuels. An adult requires 2500 to 3000 kcal of energy per day. Since, the values of enthalpies of combustion of different food articles are known, it becomes easy to calculate our daily requirements and thus select the articles of food so as to secure a balanced diet.

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

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

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



$$\Delta H_{\text{CH}_4} = -890.3 \text{ kJ}$$

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

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

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

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

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

Heat of reaction $= \Sigma$ Heat of combustion of reactants

$- \Sigma$ Heat of combustion of products

SOME SOLVED EXAMPLES

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

Solution: Molar mass of methane = 16

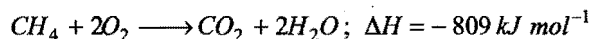
$$\text{Heat produced per gram of methane} = -\frac{890.3}{16} = -55.64 \text{ kJ}$$

Molar mass of butane = 58

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

Thus, methane has greater fuel efficiency than butane.

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



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

Solution: Energy consumption of 50 families per day
 $= 50 \times 20,000 \text{ kJ} = 1 \times 10^6 \text{ kJ}$

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

$1 \times 10^6 \text{ kJ}$ of energy will be obtained by burning methane

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

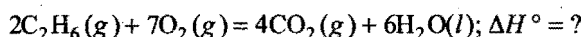
$$= 19.8 \text{ kg}$$

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

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

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

Solution: The required chemical equation for combustion of ethane is



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

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

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

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

$$= -376.4 - 409.8 + 42.2$$

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

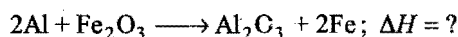
$$\frac{\Delta H^\circ}{2} = \text{Heat of combustion of ethane} = -\frac{744.0}{2} = -372.0 \text{ kcal}$$

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

$$H_f(\text{Al}_2\text{O}_3) = -399 \text{ kcal mol}^{-1}; H_f(\text{Fe}_2\text{O}_3) = -199 \text{ kcal mol}^{-1}$$

$$\text{Density of Fe}_2\text{O}_3 = 5.2 \text{ g/cm}^3; \text{Density of Al} = 2.7 \text{ g/cm}^3$$

Solution: The required equation is:



$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

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

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

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

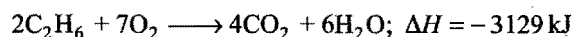
$$\text{At. mass of aluminium} = 27, \text{ Mol. mass of Fe}_2\text{O}_3 = 160$$

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

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

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

Solution: The equation for the combustion of C_2H_6 is:



$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

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

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

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

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

Example 34. The standard heats of formation of $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -76.2 , -398.8 and $-241.6 \text{ kJ mol}^{-1}$ respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under normal conditions. (IIT 1990)

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



$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

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

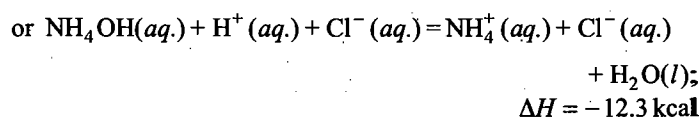
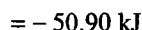
$$= -398.8 - 2 \times 241.6 - (-76.2) - 2 \times 0$$

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

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

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

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



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

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

Determination of Heat of Neutralisation

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

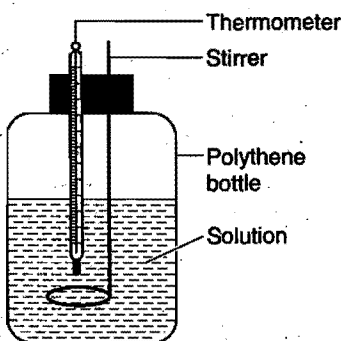


Fig. 7.16

Calculations:

Suppose, the initial temperature of acid and base = T_1

Final temperature of solution after mixing = T_2

Rise in temperature = $T_2 - T_1$

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

$Q = \text{Heat change in reaction} = \text{Mass of solution}$

$\times \text{sp. heat} \times (T_2 - T_1)$

Q is the heat evolved by the neutralisation.

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

where, $x = \text{normality of the acid or base}$.

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

Solution: Total mass of solution = $150 + 150 = 300 \text{ g}$

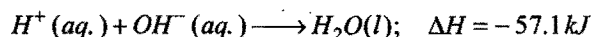
$Q = \text{Total heat produced} = 300 \times (28.77 - 25.35) \text{ cal}$
 $= 300 \times 3.42 = 1026 \text{ cal}$

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

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

So, heat of neutralisation = -13.68 kcal .

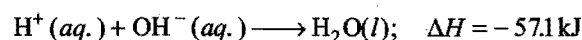
Example 37. Whenever an acid is neutralised by a base, the net reaction is



Calculate the heat evolved for the following experiments:

- 0.50 mole of HCl solution is neutralised by 0.50 mole of NaOH solution.
- 0.50 mole of HNO_3 solution is mixed with 0.30 mole of KOH solution.
- 100 mL of 0.2 M HCl is mixed with 100 mL of 0.3 M NaOH solution.
- 400 mL of 0.2 M H_2SO_4 is mixed with 600 mL of 0.1 M KOH solution.

Solution: According to the reaction,



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

- 0.50 mole $\text{HCl} \equiv 0.50 \text{ mole } \text{H}^+$ ions

0.50 mole $\text{NaOH} \equiv 0.50 \text{ mole } \text{OH}^-$ ions

On mixing, 0.50 mole of water is formed.

Heat evolved for the formation of 0.50 mole of water

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

- 0.50 mole $\text{HNO}_3 \equiv 0.50 \text{ mole } \text{H}^+$ ions

0.30 mole $\text{KOH} \equiv 0.30 \text{ mole } \text{OH}^-$ ions

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

Heat evolved in the formation of 0.3 mole of water

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

- 100 mL of 0.2 M HCl will give

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

and 100 mL of 0.3 M NaOH will give

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

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

Heat evolved in the formation of 0.02 mole of water

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

- 400 mL of 0.2 M H_2SO_4 will give

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

and 600 mL of 0.1 M KOH will give

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

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

Heat evolved in the formation of 0.06 mole of water
 $= 0.06 \times 57.1 = 3.426 \text{ kJ}$

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

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

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

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

Heat evolved during neutralisation

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

$$\therefore \text{Enthalpy of neutralisation} = -\frac{2858.5}{100} \times 1000 \times \frac{1}{0.50} \\ = -57.17 \text{ kJ}$$

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

(a) the heat change during mixing,

(b) the enthalpy change for the reaction,



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

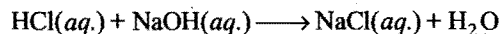
$$= \frac{MV}{1000} = \frac{1 \times 50}{1000} = 0.05$$

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

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

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

(b) The involved reaction is:



ΔH = Heat evolved per mol

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

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

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

$$x + y = 1 \quad \dots (i)$$

$$x \times 13.7 + y \times 12.7 = 13.5 \quad \dots (ii)$$

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

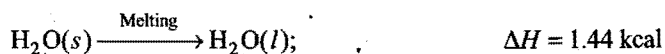
$$x = 0.8, y = 0.2$$

$$x : y = 4 : 1$$

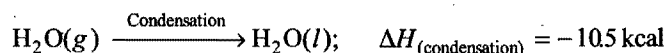
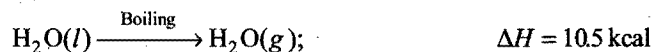
7.16 ENTHALPIES OF PHYSICAL CHANGES (Phase Changes)

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

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



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



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

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



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

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

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

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

$B \Delta H_1$ calorie, from B to $C \Delta H_2$ calorie and from C to $D \Delta H_3$ calorie. Total enthalpy change from A to D will be equal to the sum of enthalpies involved in various steps.

Total enthalpy change

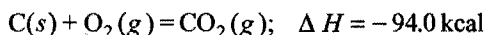
$$\Delta H_{\text{steps}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

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

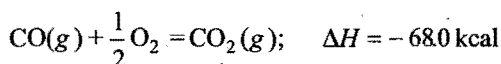
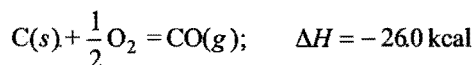
Hess's law can also be verified experimentally with the help of following examples:

(i) Formation of carbon dioxide from carbon:

First method: Carbon is directly converted into $\text{CO}_2(g)$.



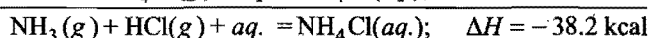
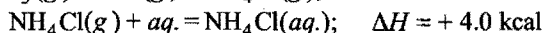
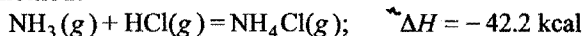
Second method: Carbon is first converted into $\text{CO}(g)$ and then $\text{CO}(g)$ into $\text{CO}_2(g)$, i.e., conversion has been carried in two steps:



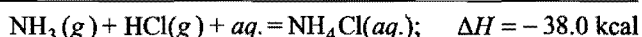
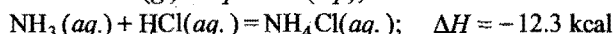
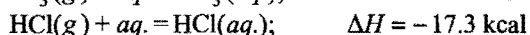
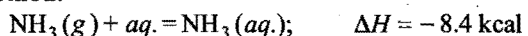
Total enthalpy change $\text{C}(s)$ to $\text{CO}_2(g)$; $\Delta H = -94.0 \text{ kcal}$

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

First method:



Second method:



Conclusions

- The heat of formation of compounds is independent of the manner of its formation.
- The heat of reaction is independent of the time consumed in the process.
- The heat of reaction depends on the sum of enthalpies of products minus sum of the enthalpies of reactants.
- Thermochemical equations can be added, subtracted or multiplied like algebraic equations.

Applications of Hess's Law

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

- For the determination of enthalpies of extremely slow reactions.
- For the determination of enthalpies of transformation of one allotropic form into another.
- For the determination of bond energies.

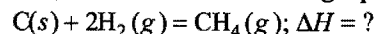
$$\Delta H_{\text{reaction}} = \Sigma \text{Bond energies of reactants}$$

$$- \Sigma \text{Bond energies of products}$$

- For the determination of resonance energy.
- For the determination of lattice energy.

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

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



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

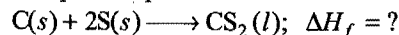
(a) By adding, subtracting and multiplying the various given thermochemical equations. Or

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

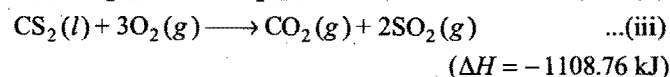
Note: In case of calculation of heat of formation, the enthalpies of free elements can be arbitrarily fixed as zero at 25°C and 1 atmospheric pressure.

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

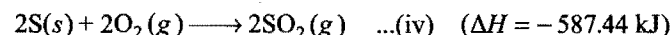
Solution: Required equation is



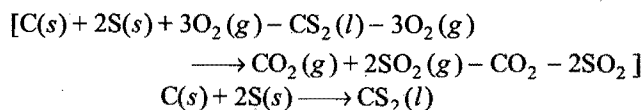
Given,



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



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

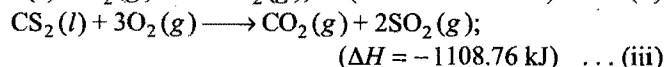


This is the required equation.

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

Standard heat of formation of $\text{CS}_2(l) = 128.02 \text{ kJ}$

Second method:



From eqs. (i) and (ii),

Enthalpy of $\text{CO}_2 = -393.3 \text{ kJ}$

Enthalpy of $\text{SO}_2 = -293.72 \text{ kJ}$

Enthalpy of $O_2 = 0$ (By convention)

ΔH of eq. (iii) = Enthalpies of products

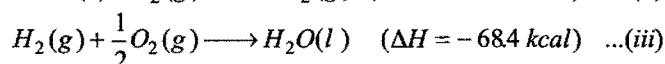
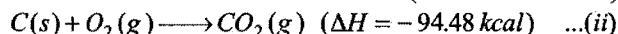
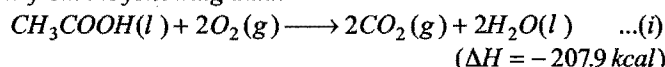
– Enthalpies of reactants

$$-1108.76 = -393.3 + 2 \times (-293.72) - \Delta H_{CS_2(l)}$$

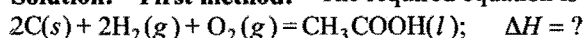
$$\Delta H_{CS_2(l)} = (1108.76 - 980.74) = 128.02 \text{ kJ}$$

Enthalpy of $CS_2(l) = 128.02 \text{ kJ}$

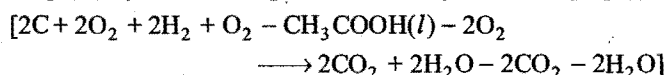
Example 42. Calculate the heat of formation of acetic acid from the following data:



Solution: First method: The required equation is



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



$$\Delta H_{CH_3COOH(l)} = 2 \times (-94.48) + 2 \times (-68.4) - (-207.9)$$

$$= -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

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

Enthalpy of $CO_2 = -94.48 \text{ kcal}$

Enthalpy of $H_2O = -68.4 \text{ kcal}$

Enthalpy of $O_2 = 0$ (by convention)

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

$$-207.9 = 2 \times (-94.48) + 2(-68.4) - \Delta H_{CH_3COOH(l)}$$

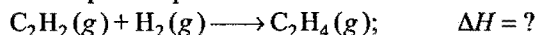
$$\Delta H_{CH_3COOH(l)} = -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

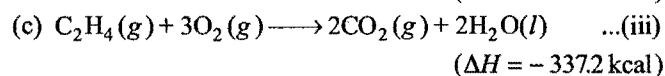
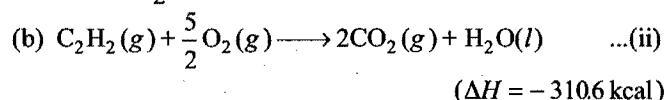
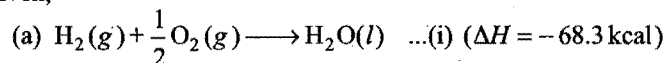
Example 43. Given the following standard heats of reactions:

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

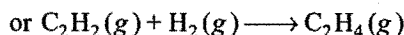
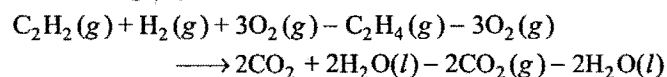
Solution: The required equation is



Given,



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



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

We know that,

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

or

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

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

and

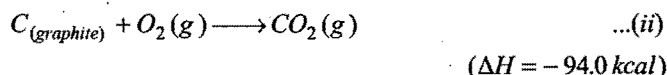
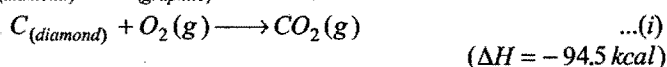
$$T = (25 + 273) = 298 \text{ K}$$

Substituting the values in above equation,

$$\Delta E = -41.7 - (-1)(2 \times 10^{-3})(298)$$

$$= -41.7 + 0.596 = -41.104 \text{ kcal}$$

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

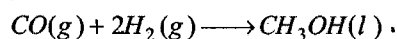


Solution: Subtracting eq. (ii) from (i), the required equation is obtained.

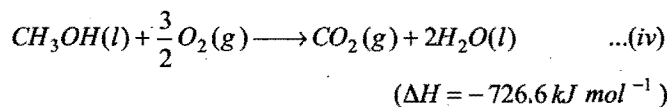
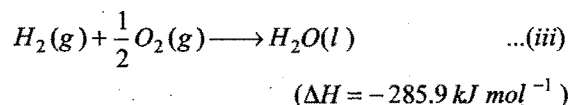
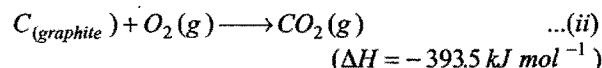
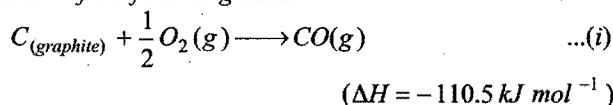
$$\Delta H_{\text{transformation}} = -94.5 - (-94.0)$$

$$= -94.5 + 94.0 = -0.5 \text{ kcal}$$

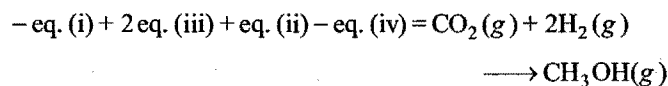
Example 45. Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gases under pressure in the presence of a catalyst. The reaction is



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

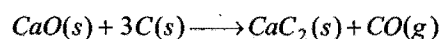


Solution: The required equation can be obtained in the following manner:



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

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



The heats of formation of $\text{CaO}(s)$, $\text{CaC}_2(s)$ and $\text{CO}(g)$ are -151.6 , -14.2 and -26.4 kcal respectively.

Solution: $\Delta H = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$

$$= [\Delta H_f^\circ (\text{CaC}_2) + \Delta H_f^\circ (\text{CO})] - [\Delta H_f^\circ (\text{CaO}) + 3\Delta H_f^\circ (\text{C})]$$

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

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

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

So, heat required for making 2000 g of

$$\text{CaC}_2 = \frac{111.0}{64} \times 2000 = 3468.75 \text{ kcal}$$

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

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

$$\Delta H = H_P - H_R$$

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

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

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

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

Integrating above differential equation within proper limit, we get:

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

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

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

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

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

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

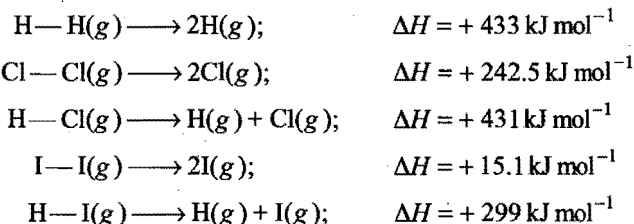
$$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_V$$

7.19 BOND ENERGY OR BOND ENTHALPIES

When a bond is formed between atoms, energy is released. Obviously same amount of energy will be required to break the

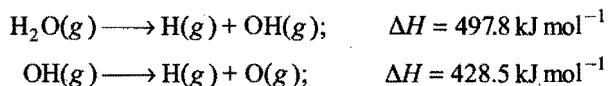
bond. The energy required to break the bond is termed bond dissociation energy. The more precise definition is:

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



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

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



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

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

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

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



Application of Bond Energy

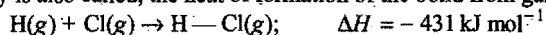
- Heat of a reaction = $\sum$ Bond energy of reactants
 $-\sum$ Bond energy of products

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

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

$$\text{Resonance energy} = \text{Experimental or actual heat of formation} - \text{Calculated heat of formation.}$$

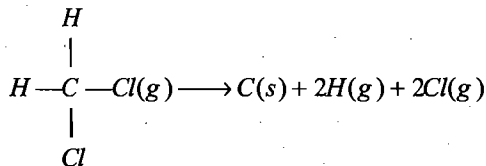
*Bond energy is also called, the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.



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

SOME SOLVED EXAMPLES

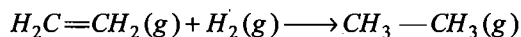
Example 47. Calculate the ΔH of the reaction,



Bond energy for C—H bond and C—Cl bond are 415 kJ and 326 kJ respectively.

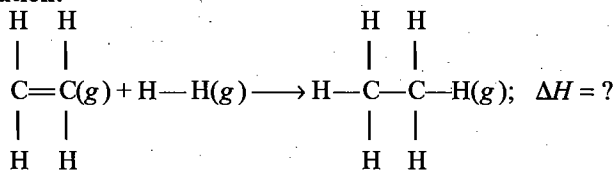
Solution: ΔH = Sum of bond energies of reactants
 – Sum of bond energies of products
 $= [2 \times (\text{C}-\text{H}) + 2 \times (\text{C}-\text{Cl})] - 0$
 (All the products are free atoms)
 $= 2 \times 415 + 2 \times 326$
 $= 830 + 652 = 1482 \text{ kJ}$

Example 48. Calculate the enthalpy of the following reaction:



The bond energies of C—H, C—C, C=C and H—H are 99, 83, 147 and 104 kcal respectively.

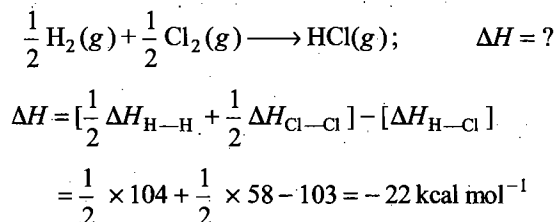
Solution: The reaction is:



ΔH = Sum of bond energies of reactants
 – Sum of the bond energies of products
 $= [\Delta H_{\text{C}=\text{C}} + 4 \times \Delta H_{\text{C}-\text{H}} + \Delta H_{\text{H}-\text{H}}]$
 $\quad - [\Delta H_{\text{C}-\text{C}} + 6 \times \Delta H_{\text{C}-\text{H}}]$
 $= (147 + 4 \times 99 + 104) - (83 + 6 \times 99) = -30 \text{ kcal}$

Example 49. The bond dissociation energies of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation of $\text{HCl}(\text{g})$.

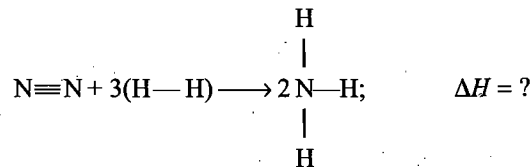
Solution: The required equation is



Example 50. Calculate the enthalpy of formation of ammonia from the following bond energy data:

(N—H) bond = 389 kJ mol^{-1} ; (H—H) bond = 435 kJ mol^{-1} and (N $\equiv$ N) bond = 945.36 kJ mol^{-1} .

Solution:



$$\Delta H = [\Delta H_{(\text{N} \equiv \text{N})} + 3 \times \Delta H_{(\text{H}-\text{H})}] - [6 \Delta H_{(\text{N}-\text{H})}]$$

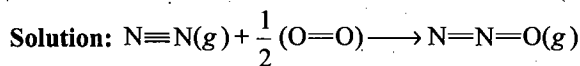
$$= 945.36 + 3 \times 435.0 - 6 \times 389.0 = -83.64 \text{ kJ}$$

$$\text{Heat of formation of } \text{NH}_3 = \frac{\Delta H}{2} = -\frac{83.64}{2} = -41.82 \text{ kJ mol}^{-1}$$

Example 51. Calculate the resonance energy of N_2O from the following data:

$$\Delta H_f^\circ \text{ of } \text{N}_2\text{O} = 82 \text{ kJ mol}^{-1}$$

Bond energy of N $\equiv$ N, N=N, O=O and N=O bonds is 946, 418, 498 and 607 kJ mol^{-1} respectively. (IIT 1991)



$$\Delta H_{f(\text{N}_2\text{O})} = [\Delta H_{(\text{N} \equiv \text{N})} + \frac{1}{2} \Delta H_{(\text{O}=\text{O})}] - [\Delta H_{(\text{N}=\text{O})} + \Delta H_{(\text{N}=\text{N})}]$$

$$= (946 + \frac{1}{2} \times 498) - (607 + 418)$$

$$= 946 + 249 - 607 - 418$$

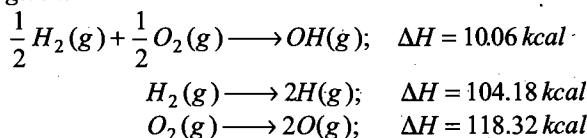
$$= 1195 - 1025 = 170 \text{ kJ mol}^{-1}$$

Resonance energy = Observed heat of formation

~ Calculated heat of formation

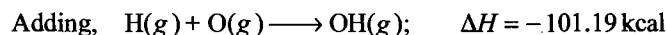
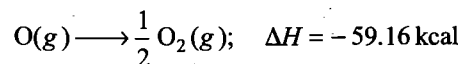
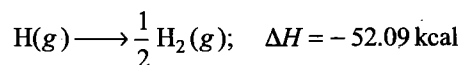
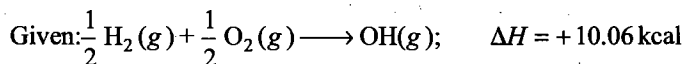
$$= 82 - 170 = -88 \text{ kJ mol}^{-1}$$

Example 52. The enthalpies for the following reactions at 25°C are given:



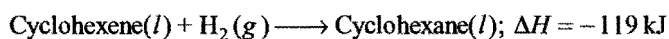
Calculate the O—H bond energy in the OH group.

Solution: Required equation is



Example 53. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are -156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is -119 kJ mol^{-1} . Use these data to estimate the magnitude of resonance energy of benzene.

(IIT 1996)

Solution:

Enthalpy of formation of cyclohexane(*l*) = -156 kJ mol^{-1}

$$\text{So, enthalpy of formation of cyclohexane} = -156 - (-119) \text{ kJ} \\ = -37 \text{ kJ mol}^{-1}$$

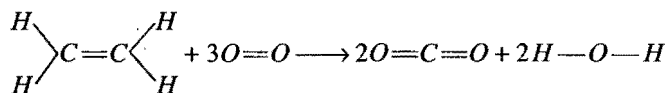
Since, $\Delta H_{\text{cyclohexane}}$ is -156 kJ mol^{-1} , we can say that for every double bond the energy decreases by an amount $+119 \text{ kJ mol}^{-1}$ and therefore for the introduction of three double bonds (present in benzene ring) the energy required

$$= 3 \times 119 \text{ kJ mol}^{-1} = 357 \text{ kJ mol}^{-1}$$

$$\text{Hence, theoretical } \Delta H_f \text{ for benzene} = (357 - 156) \text{ kJ mol}^{-1} \\ = 201 \text{ kJ mol}^{-1}$$

$$\text{Resonance energy} = \text{Theoretical } \Delta H_f - \text{Observed } \Delta H_f \\ = (201 - 49) \text{ kJ mol}^{-1} = 152 \text{ kJ mol}^{-1}$$

Example 54. Calculate heat of combustion of ethene:



from bond energy data: $\text{C}=\text{C}$, $\text{C}-\text{H}$, $\text{O}=\text{O}$, $\text{C}=\text{O}$, $\text{O}-\text{H}$

$$\text{BE kJ mol}^{-1}: \quad 619 \quad 414 \quad 499 \quad 724 \quad 460$$

Solution:

$$\Delta H = \text{Sum of bond energies of reactants}$$

$$- \text{Sum of bond energies of products}$$

$$= [\Delta H_{(\text{C}=\text{C})} + 4\Delta H_{(\text{C}-\text{H})} + 3 \times \Delta H_{(\text{O}=\text{O})}] \\ - [4 \times \Delta H_{(\text{C}=\text{O})} + 4 \times \Delta H_{(\text{O}-\text{H})}] \\ = [619 + 4 \times 414 + 3 \times 499] - [4 \times 724 + 4 \times 460] \\ = -964 \text{ kJ mol}^{-1}$$

Example 55. Using the data (all values are in kilocalorie per mole at 25°C) given below, calculate the bond energy of $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds.

$$\Delta H_{\text{combustion of ethane}}^\circ = -372.0$$

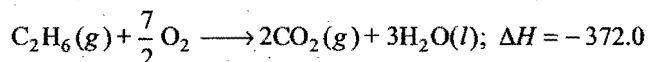
$$\Delta H_{\text{combustion of propane}}^\circ = -530.0$$

$$\Delta H^\circ \text{ for } \text{C}_{(\text{graphite})} \longrightarrow \text{C}(g) = +172.0$$

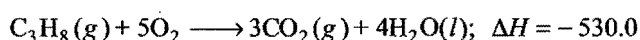
$$\text{Bond energy of } \text{H}-\text{H} \text{ bond} = +104.0$$

$$\Delta H_f^\circ \text{ of } \text{H}_2\text{O}(l) = -68.0$$

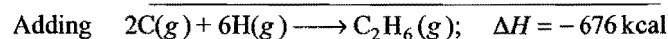
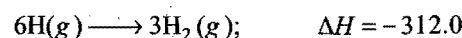
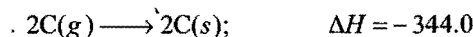
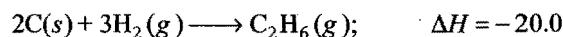
$$\Delta H_f^\circ \text{ of } \text{CO}_2(g) = -94.0$$

Solution:

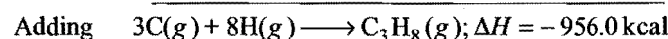
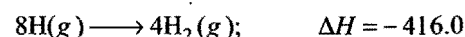
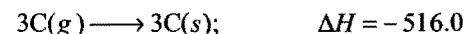
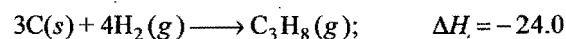
$$\Delta H_f^\circ (\text{C}_2\text{H}_6) = 2 \times (-94.0) + 3 \times (-68.0) + 372.0 = -20 \text{ kcal}$$



$$\Delta H_f^\circ (\text{C}_3\text{H}_8) = 2 \times (-94.0) + 4 \times (-68.0) + 530.0 = -24 \text{ kcal}$$



So, enthalpy of formation of $6\text{C}-\text{H}$ bonds and one $\text{C}-\text{C}$ bond is -676.0 kcal .



So, enthalpy of formation of $8\text{C}-\text{H}$ and $2\text{C}-\text{C}$ bonds is -956 kcal .

Let the bond energy of $\text{C}-\text{C}$ be x and of $\text{C}-\text{H}$ be $y \text{ kcal}$.

$$\text{In ethane} \quad x + 6y = 676$$

$$\text{In propane} \quad 2x + 8y = 956$$

$$\text{On solving,} \quad x = 82 \text{ and } y = 99$$

Thus, bond energy of $\text{C}-\text{C} = 82 \text{ kcal}$ and
bond energy of $\text{C}-\text{H} = 99 \text{ kcal}$

Example 56. Using the bond enthalpy data given below, calculate the enthalpy of formation of acetone (*g*).

$$\text{Bond energy } \text{C}-\text{H} = 413.4 \text{ kJ mol}^{-1};$$

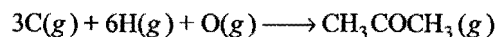
$$\text{Bond energy } \text{C}-\text{C} = 347.0 \text{ kJ mol}^{-1};$$

$$\text{Bond energy } \text{C}=\text{O} = 728.0 \text{ kJ mol}^{-1};$$

$$\text{Bond energy } \text{O}=\text{O} = 495.0 \text{ kJ mol}^{-1};$$

$$\text{Bond energy } \text{H}-\text{H} = 435.8 \text{ kJ mol}^{-1};$$

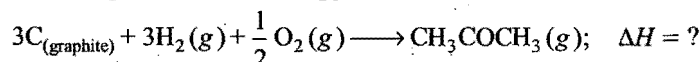
$$\Delta H_{\text{sub}} \text{C}(s) = 718.4 \text{ kJ mol}^{-1}$$

Solution:

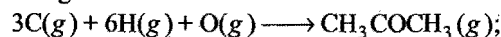
In acetone, six $\text{C}-\text{H}$ bonds, one $\text{C}=\text{O}$ bond and two $\text{C}-\text{C}$ bonds are present. Energy released in the formation of these bonds is

$$= -6 \times 413.4 - 728.0 - 2 \times 347.0 = -3902.4 \text{ kJ mol}^{-1}$$

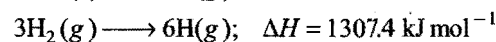
The equation of the enthalpy of formation of acetone is

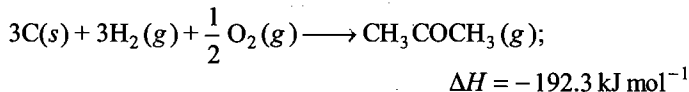
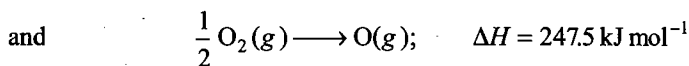


This equation can be obtained from the following equations by adding:



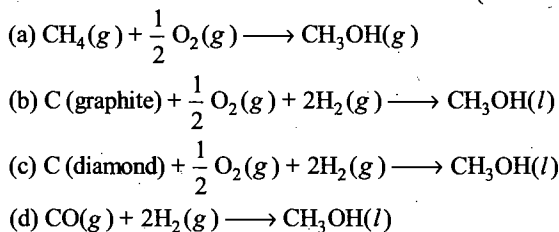
$$\Delta H = -3902.4 \text{ kJ mol}^{-1}$$





ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. ΔH_f° 298 K of methanol is given by the chemical equation:
(AIIMS 2005)



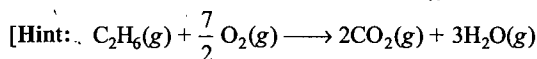
[Ans. (b)]

[Hint: In the process of formation, the compound must be formed from constituent elements in their standard state.]

8. The standard molar heat of formation of ethane, CO_2 and $\text{H}_2\text{O}(\text{l})$ are respectively -21.1 , -94.1 and -68.3 kcal. The standard molar heat of combustion of ethane will be:



[Ans. (a)]



$$\Delta H = 2\Delta H_f(\text{CO}_2) + 3\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_2\text{H}_6)$$

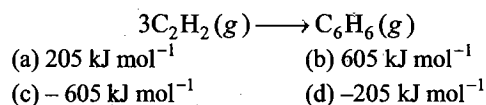
$$= 2(-94.1) + 3(-68.3) - (-21.1) = -372 \text{ kcal}]$$

9. When ethyne is passed through a red hot tube, then formation of benzene takes place:

$$\Delta H_f^\circ(\text{C}_2\text{H}_2)(\text{g}) = 230 \text{ kJ mol}^{-1}$$

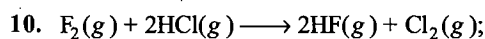
$$\Delta H_f^\circ(\text{C}_6\text{H}_6)(\text{g}) = 85 \text{ kJ mol}^{-1}$$

Calculate the standard heat of trimerisation of ethyne to benzene.



[Ans. (c)]

[Hint: $\Delta H_{\text{reaction}} = \Delta H_f^\circ(\text{C}_6\text{H}_6) - 3\Delta H_f^\circ(\text{C}_2\text{H}_2)$
 $= 85 - 3(230)$
 $= -605 \text{ kJ mol}^{-1}$]



$$\Delta H^\circ = -352.18 \text{ kJ}$$

$$\Delta H_f^\circ(\text{HF}) = -268.3 \text{ kJ}$$

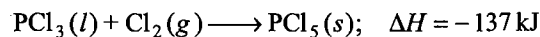
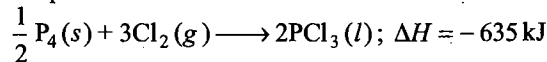
The heat of formation of HCl will be:



[Ans. (c)]

[Hint: $\Delta H_{\text{reaction}}^\circ = 2\Delta H_f^\circ(\text{HF}) - 2\Delta H_f^\circ(\text{HCl})$
 $-352.18 = 2 \times (-268.3) - 2x$
 $2x = 2(-268.3) + 352.18$
 $x = -92.21 \text{ kJ mol}^{-1}$]

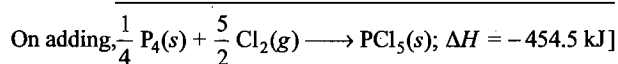
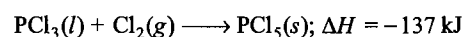
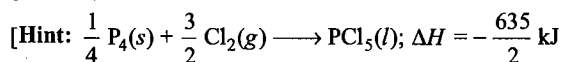
11. Given two processes:



The value of ΔH_f° of PCl_5 is:



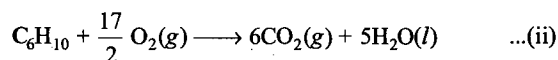
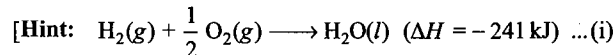
[Ans. (b)]



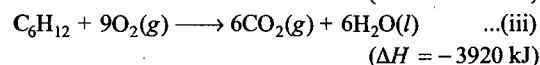
12. The enthalpy of combustion at 25°C of H_2 , cyclohexane (C_6H_{12}) and cyclohexene (C_6H_{10}) are -241 , -3920 and -3800 kJ/mol respectively. The heat of hydrogenation of cyclohexene is: [CBSE (Med.) 2006]



[Ans. (a)]

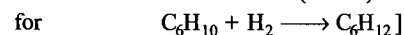


$$(\Delta H = -3800 \text{ kJ})$$

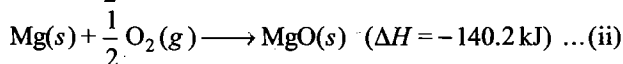
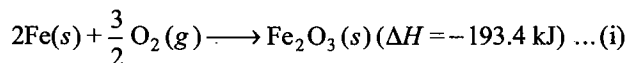


Eq. (i) + eq. (ii) - eq. (iii) gives

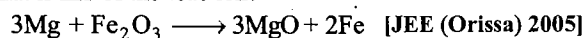
$$\Delta H = -241 - 3800 - (-3920) = -121 \text{ kJ}$$



13. Given that:

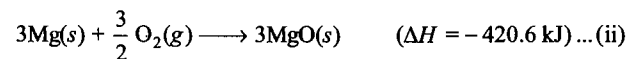
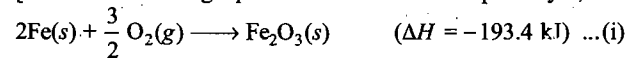


What is ΔH of the reaction?

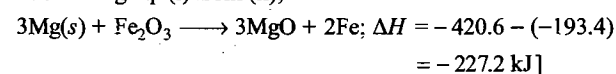


[Ans. (a)]

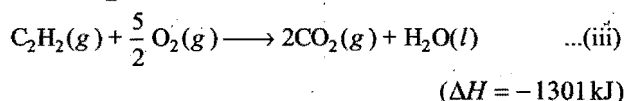
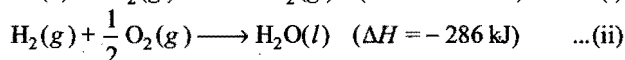
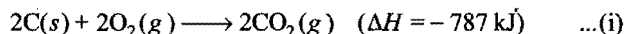
[Hint: Subtracting equation 1st from 2nd multiplied by 3,



Subtracting eq. (i) from (ii),



14. Given that:



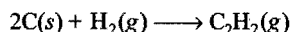
Heat of formation of acetylene is: [JEE (Orissa) 2005]

(a) -1802 kJ (b) +1802 kJ

(c) -800 kJ (d) +228 kJ

[Ans. (d)]

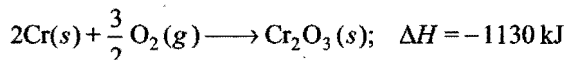
[Hint: Required equation is:



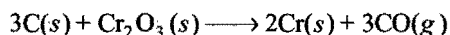
Eq. (i) + eq. (ii) - eq. (iii) gives

$$\Delta H = (-787) + (-286) - (-1301) \\ = +228 \text{ kJ}]$$

15. The enthalpy changes for two reactions are given by the equations:



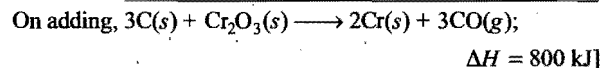
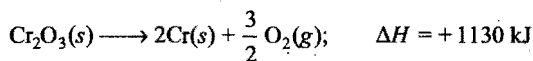
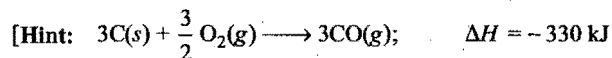
What is the enthalpy change in kJ for the following reaction?



(a) -1460 kJ (b) -800 kJ (c) +800 kJ (d) +1020 kJ

(e) +1460 kJ

[Ans. (c)]



16. The enthalpy change
- ΔH
- for the neutralisation of 1 M HCl by caustic potash in dilute solution at 298 K is: (DPMT 2005)

(a) 68 kJ

(b) 65 kJ

(c) 57.3 kJ

(d) 50 kJ

[Ans. (c)]

[Hint: Since, both HCl and KOH are strong, 57.3 kJ heat will be released.]

17. Enthalpy of neutralisation of the reaction between
- $CH_3COOH(aq.)$
- and
- $NaOH(aq.)$
- is
- $-13.2 \text{ kcal eq}^{-1}$
- and that of the reaction between
- $H_2SO_4(aq.)$
- and
- $KOH(aq.)$
- is
- $-13.7 \text{ kcal eq}^{-1}$
- . The enthalpy of dissociation of
- $CH_3COOH(aq.)$
- is:

(a) $-0.5 \text{ kcal eq}^{-1}$ (b) $+0.5 \text{ kcal eq}^{-1}$ (c) $-26.9 \text{ kcal eq}^{-1}$ (d) $+13.45 \text{ kcal eq}^{-1}$

[Ans. (b)]

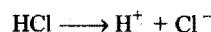
[Hint: Dissociation enthalpy of $CH_3COOH = 13.7 - 13.2 = 0.5 \text{ kcal eq}^{-1}$. Thus, 0.5 kcal eq^{-1} heat will be used to dissociate CH_3COOH completely.]

18. Calculate the enthalpy change when 50 mL of 0.01 M
- $Ca(OH)_2$
- reacts with 25 mL of 0.01 M HCl. Given that
- ΔH°
- neutralisation of a strong acid and a strong base is
- $140 \text{ kcal mol}^{-1}$
- .

(a) 14 kcal (b) 35 cal (c) 10 cal (d) 7.5 cal

[Ans. (b)]

$$[Hint: \text{Number of moles of HCl} = \frac{MV}{1000} = \frac{0.01 \times 25}{1000} \\ = 25 \times 10^{-5}]$$



$$n_{H^+} = 25 \times 10^{-5}$$

$$\text{Number of moles of } Ca(OH)_2 = \frac{MV}{1000} = \frac{0.01 \times 50}{1000} = 50 \times 10^{-5}$$

$$n_{OH^-} = 2 \times 50 \times 10^{-5} = 10^{-3}$$

In the process of neutralisation 25×10^{-5} mole H^+ will be completely neutralised

$$\therefore \Delta H = 140 \times 25 \times 10^{-5} \text{ kcal} = 0.035 \text{ kcal} = 35 \text{ cal}]$$

19. Equal volumes of 1 M HCl and 1 M
- H_2SO_4
- are neutralised by 1 M NaOH solution and x and y kJ/equivalent of heat are liberated respectively. Which of the following relations is correct?

(a) $x = 2y$ (b) $x = 3y$ (c) $x = 4y$ (d) $x = \frac{1}{2}y$

[Ans. (d)]

[Hint: Since, H_2SO_4 gives 2 moles H^+ while HCl gives 1 mole H^+ from 1 mole after ionisation. Hence, H_2SO_4 will release double amount of heat as compared to HCl,

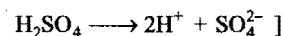
$$i.e., y = 2x \text{ or } x = \frac{y}{2}]$$

20. Which of the following acid will release maximum amount of heat when completely neutralised by strong base NaOH?

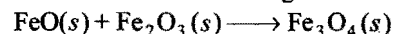
(a) 1 M HCl

(b) 1 M HNO_3 (c) 1 M $HClO_4$ (d) 1 M H_2SO_4

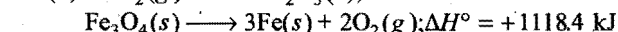
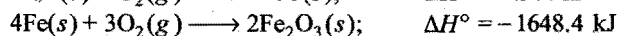
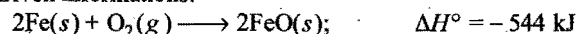
[Ans. (d)]

[Hint: Ionisation of H_2SO_4 gives double amount of H^+ ions as compared to other acids.

21. Determine the heat of the following reaction:

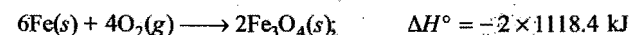
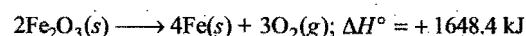
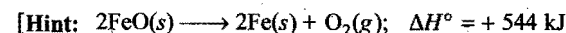


Given informations:

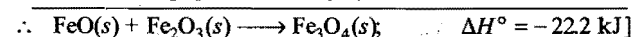


(a) -1074 kJ (b) -22.2 kJ (c) +249.8 kJ (d) +2214.6 kJ

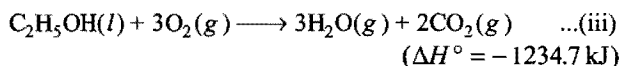
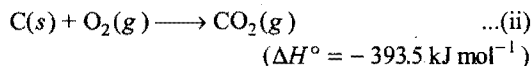
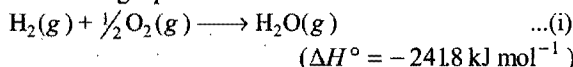
[Ans. (b)]



On adding,



22. Calculate the enthalpy of formation of ΔH_f for C_2H_5OH from tabulated data and its heat of combustion as represented by the following equations:

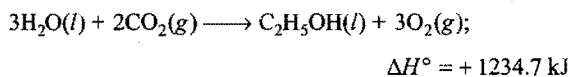
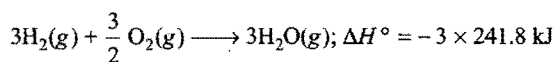
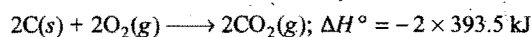
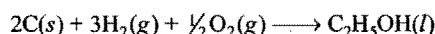


(a) $-2747.1 \text{ kJ mol}^{-1}$ (b) $-277.7 \text{ kJ mol}^{-1}$

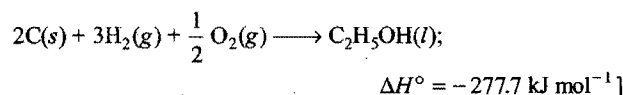
(c) $277.7 \text{ kJ mol}^{-1}$ (d) $2747.1 \text{ kJ mol}^{-1}$

[Ans. (b)]

[Hint: Required equation:



On adding,



23. Which of the following methods for calculation of heat of a reaction is not correct?

(a) $\Delta H_{\text{reaction}} = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ reactants}$

(b) $\Delta H_{\text{reaction}} = \sum (BE)_{\text{reactants}} - \sum (BE)_{\text{products}}$

(c) $\Delta H_{\text{reaction}} = \sum \Delta H_{\text{comb. (reactants)}} - \sum \Delta H_{\text{comb. (products)}}$

(d) $\Delta H_{\text{reaction}} = \sum \Delta H_{\text{solution (reactants)}} - \sum \Delta H_{\text{solution (products)}}$

[Ans. (d)]

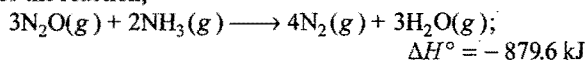
24. Heat of combustion of diamond and graphite are -94.5 kcal and -94 kcal/mol respectively. What will be the heat of transition from diamond to graphite?

(a) -0.5 kcal (b) $+0.5 \text{ kcal}$ (c) 1 kcal (d) -1 kcal

[Ans. (b)]

[Hint: $\Delta H = \Delta H_{\text{comb. (diamond)}} - \Delta H_{\text{comb. (graphite)}}$]

25. For the reaction,



If $\Delta H_f^\circ[NH_3(g)] = -45.9 \text{ kJ mol}^{-1}$;

$\Delta H_f^\circ[H_2O(g)] = -241.8 \text{ kJ mol}^{-1}$

then $\Delta H_f^\circ[N_2O(g)]$ will be:

(a) $+246 \text{ kJ}$ (b) $+82 \text{ kJ}$

(c) -82 kJ (d) -246 kJ

[Ans. (b)]

[Hint: $\Delta H_{\text{reaction}} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$

$$= 4 \Delta H_f^\circ[N_2] + 3 \Delta H_f^\circ[H_2O] - \{3 \Delta H_f^\circ[N_2O]$$

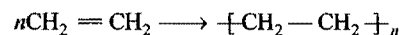
$$+ 2 \Delta H_f^\circ[NH_3]\}$$

26. The bond energies of $C=C$ and $C-C$ at 298 K are 590 and 331 kJ mol^{-1} respectively. The enthalpy of polymerisation per mole of ethylene is:

(a) -70 kJ (b) -72 kJ (c) 72 kJ (d) -68 kJ

[Ans. (b)]

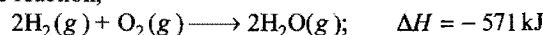
[Hint: The polymerisation of ethene may be represented as



one mole of $C=C$ bond is decomposed and two moles of $C-C$ bonds are formed per mole of ethene.

$\therefore \Delta H = 590 - 2 \times 331 = -72 \text{ kJ per mol of ethylene.}$

27. For the reaction,



bond energy of $(H-H) = 435 \text{ kJ}$; of $(O=O) = 498 \text{ kJ}$; then calculate the average bond energy of $(O-H)$ bond using the above data. (DCE 2005)

(a) 484 kJ (b) -484 kJ (c) 271 kJ (d) -271 kJ

[Ans. (a)]

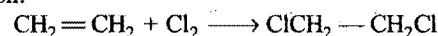
[Hint: $2(H-H) + O=O \longrightarrow 2(H-O-H)$

$$\Delta H = \sum (BE)_{\text{reactants}} - \sum (BE)_{\text{products}}$$

$$-571 = [2 \times 435 + 498] - 4 \times (BE)_{O-H}$$

$$(BE)_{O-H} = \frac{2 \times 435 + 498 + 571}{4} \approx 484 \text{ kJ}]$$

28. Use the bond energies in the table to estimate ΔH for this reaction:



Bond	C—C	C=C	C—Cl	C—H	Cl—Cl
Bond energy (kJ/mol)	347	612	331	414	243

(a) $\Delta H = -684 \text{ kJ}$

(b) $\Delta H = -154 \text{ kJ}$

(c) $\Delta H = +89 \text{ kJ}$

(d) $\Delta H = +177 \text{ kJ}$

[Ans. (b)]

[Hint:

$$\Delta H_{\text{reaction}} = \sum (BE)_{\text{reactants}} - \sum (BE)_{\text{products}}$$

$$= [(BE)_{C=C} + 4(BE)_{C-H} + (BE)_{Cl-Cl}]$$

$$- [4(BE)_{C-H} + 2(BE)_{C-Cl} + (BE)_{C-C}]$$

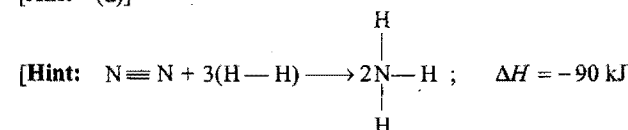
$$= [(BE)_{C=C} + (BE)_{Cl-Cl}] - [2(BE)_{C-Cl} + (BE)_{C-C}]$$

$$= [612 + 243] - [2 \times 331 + 347] = -154 \text{ kJ}]$$

29. Heat of formation of 2 moles of $NH_3(g)$ is -90 kJ ; bond energies of $H-H$ and $N-H$ bonds are 435 kJ and 390 kJ mol^{-1} respectively. The value of the bond energy of $N \equiv N$ will be:

(a) -472.5 kJ (b) -945 kJ (c) 472.5 kJ (d) 945 kJ mol^{-1}

[Ans. (d)]



$$\Delta H_{\text{reaction}} = \sum (BE)_{\text{reactants}} - \sum (BE)_{\text{products}}$$

$$-90 = [(BE)_{N \equiv N} + 3(BE)_{H-H}] - [6(BE)_{N-H}]$$

$$-90 = x + 3 \times 435 - 6 \times 390$$

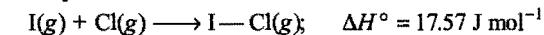
$$x = 945 \text{ kJ mol}^{-1}]$$

30. If values of ΔH_f° of $\text{ICl}(g)$, $\text{Cl}(g)$ and $\text{I}(g)$ are respectively 17.57, 121.34, 106.96 J mol^{-1} . The value of I—Cl (bond energy) in J mol^{-1} is:

(a) 17.57 (b) 210.73 (c) 35.15 (d) 106.96

[Ans. (b)]

[Hint: The process will be:



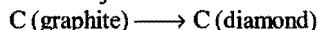
ΔH = Heat of atomisation of $\text{I}(g)$ and $\text{Cl}(g)$

– Bond energy of I—Cl bond

$$17.57 = 121.34 + 106.96 - x$$

$$x = 210.73 \text{ J mol}^{-1}$$

31. Calculate the ΔH in joules for:



from the following data:



[CET (J&K) 2006]

(a) 1900

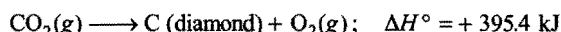
(b) -788.9×10^3

(c) 190000

(d) $+788.9 \times 10^3$

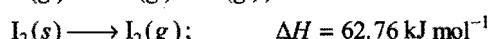
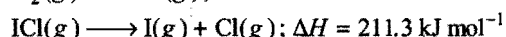
[Ans. (a)]

[Hint: $\text{C (graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g); \Delta H^\circ = -393.5 \text{ kJ}$



On adding, $\text{C (graphite)} \longrightarrow \text{C (diamond)}; \Delta H^\circ = +1900 \text{ J}$
 $= +1.9 \text{ kJ}$

32. The enthalpy changes for the following processes are listed below:



Given that, the standard states for iodine and chlorine are $\text{I}_2(s)$ and $\text{Cl}_2(g)$, the standard enthalpy of formation for $\text{ICl}(g)$ is: (AIEEE 2006)

(a) $-14.6 \text{ kJ mol}^{-1}$

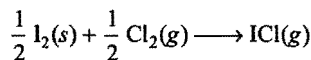
(b) $-16.8 \text{ kJ mol}^{-1}$

(c) $+16.8 \text{ kJ mol}^{-1}$

(d) $+244.8 \text{ kJ mol}^{-1}$

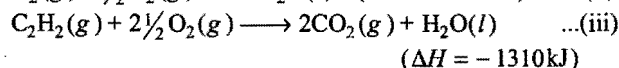
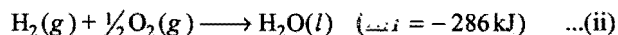
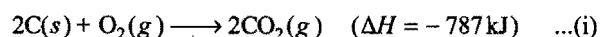
[Ans. (c)]

[Hint: The reaction is:



$$\begin{aligned} \Delta_f H_{\text{I—Cl}} &= \left[\frac{1}{2} \Delta H_{\text{I}_2(s) \rightarrow \text{I}_2(g)} + \frac{1}{2} \Delta H_{\text{I—I}} \right. \\ &\quad \left. + \frac{1}{2} \Delta H_{\text{Cl—Cl}} \right] - [\Delta H_{\text{I—Cl}}] \\ &= \left[\frac{1}{2} \times 62.76 + \frac{1}{2} \times 151 + \frac{1}{2} \times 242.3 \right] - [211.3] \\ &= 16.73 \text{ kJ mol}^{-1} \end{aligned}$$

33. Given that:



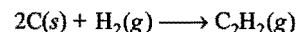
The heat of formation of acetylene is: (VITEEE 2007)

(a) $-1802 \text{ kJ mol}^{-1}$ (b) $+1802 \text{ kJ mol}^{-1}$

(c) $+237 \text{ kJ mol}^{-1}$ (d) -800 kJ mol^{-1}

[Ans. (c)]

[Hint: Required equation is:



It can be obtained by adding eqs. (i) and (ii) and then subtracting eq. (iii) from it.

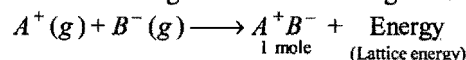
Heat of formation of acetylene

$$= (-787) + (-286) - (-1310)$$

$$= +237 \text{ kJ mol}^{-1}$$

7.20 DETERMINATION OF LATTICE ENERGY (Born-Haber Cycle)

Lattice energy of an ionic compound is defined as the amount of energy released when one mole of the compound is formed by the interaction of constituent gaseous cations and gaseous anions.



It is represented by the symbol, U . It is given negative sign as the energy is always released. Since, it is difficult to find the lattice energy by direct experiment, it is generally calculated by indirect method known as **Born-Haber cycle** which is based on Hess's law. The cycle can be easily explained by taking the example of the formation of sodium chloride (NaCl). The formation of sodium chloride can be schematically represented as:

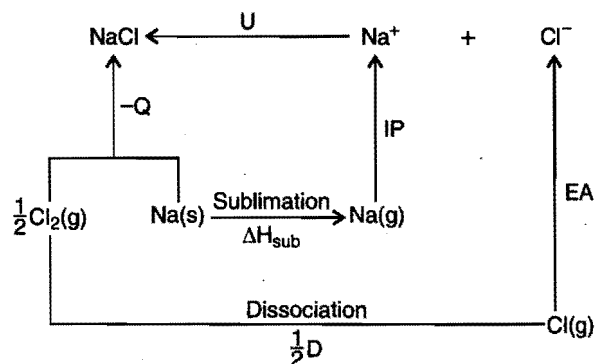


Fig. 7.17

The formation of sodium chloride can occur either by direct combination of sodium(s) and chlorine(g) or in various steps.

Let the heat of formation of sodium chloride by direct combination be $-Q$.

The various steps in the formation of NaCl are the following: In each step, either energy is absorbed or released.

Steps involved	Energy change
(a) Solid sodium changes into gaseous sodium. Energy is absorbed. It is sublimation energy. $\text{Na(s)} + \text{sublimation energy} \longrightarrow \text{Na(g)}$	$+\Delta H_{\text{sub}}$
(b) Gaseous sodium atoms change into gaseous sodium ions. In this step, energy equivalent to ionisation potential is absorbed. $\text{Na(g)} + IP \longrightarrow \text{Na}^+(\text{g}) + e$	$+IP$
(c) Half mole of molecular chlorine dissociate into one mole of gaseous atomic chlorine. In this step, energy equivalent to one half of the dissociation energy is absorbed. $\frac{1}{2} \text{Cl}_2(\text{g}) + \frac{1}{2} D = \text{Cl(g)}$	$+\frac{1}{2} D$
(d) Gaseous chlorine atoms change into chloride ions by acceptance of electrons. In this process, energy equivalent to electron affinity is released. $\text{Cl(g)} + e \longrightarrow \text{Cl}^-(\text{g}) + EA$	$-EA$
(e) Sodium and chlorine ions are held together by electrostatic forces to form Na^+Cl^- . The energy equivalent to lattice energy is released.	U

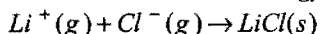
Total energies involved in the above five steps

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

Thus, according to Hess's law

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

Example 57. Calculate the lattice energy for the reaction,



from the following data:

$$\Delta H_{\text{sub}}(\text{Li}) = 160.67 \text{ kJ mol}^{-1}; \quad \frac{1}{2} D(\text{Cl}_2) = 122.17 \text{ kJ mol}^{-1}$$

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

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

Solution: Applying the equation

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

and substituting the respective values,

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

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

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

Solution: Applying the equation

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

and substituting the respective values,

$$-410 = 180.8 + \frac{1}{2} \times 242.7 + 493.7 - 368.2 + U$$

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

7.21 EXPERIMENTAL DETERMINATION OF THE HEAT OF REACTION

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

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

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

- Water calorimeter and
- Bomb calorimeter

(i) Water calorimeter

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

It consists of a large vessel A in which a calorimeter B is held on corks. In between the calorimeter and the vessel, there is a packing of an insulating material such as cotton wool. Inside the calorimeter there are holes through which a thermometer, a stirrer and the boiling tube containing reacting substances are fitted. A known amount of water is taken in the calorimeter. Known

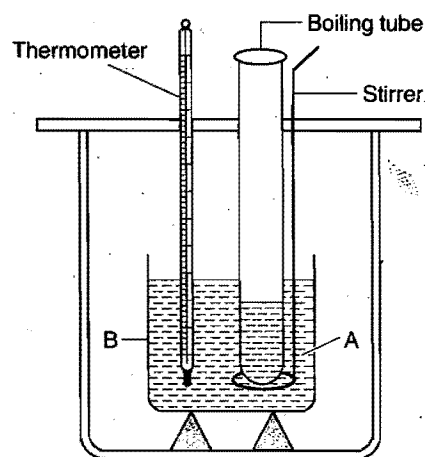


Fig. 7.18

amounts of reacting substances are taken in the boiling tube. The heat evolved during the reaction will be absorbed by the water. The rise in temperature is recorded with the help of thermometer. The heat evolved is then calculated from the formula

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

(ii) Bomb calorimeter

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

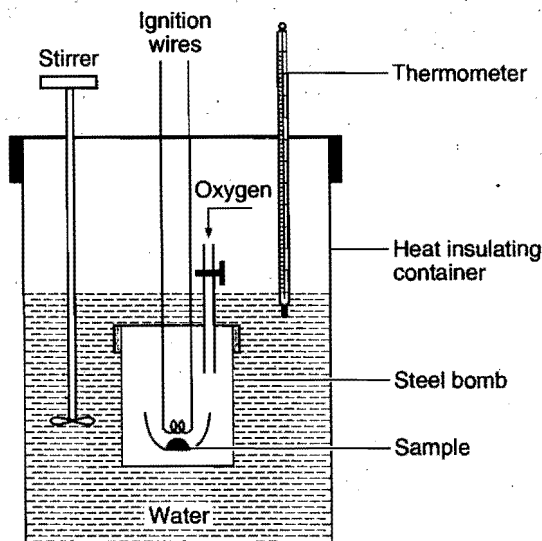


Fig. 7.19

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

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

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

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

ΔH can be calculated from the relation,

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

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

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

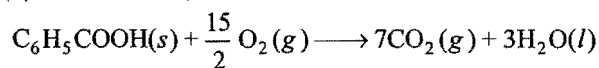
= Heat capacity of calorimeter and its contents

$$\times \text{rise in temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 23.85 \times 0.55 \times \frac{122}{0.5} = 3200.67 \text{ kJ}$$

$$\text{i.e.,} \quad \Delta E = -3200.67 \text{ kJ mol}^{-1}$$

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



$$\Delta n = 7 - 7.5 = -0.5; R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}; T = 288 \text{ K}$$

Substituting the values in the above equation,

$$\begin{aligned} \Delta H &= -3200.67 + 8.314 \times 10^{-3} \times (-0.5) \times 288 \\ &= -3200.67 - 1.197 = -3201.867 \text{ kJ mol}^{-1} \end{aligned}$$

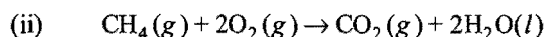
Example 60. A sample of 0.16 g CH_4 was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C . Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. (IIT 1998)

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

$$= \text{Heat capacity of calorimeter system} \times \text{rise in temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

$$\text{i.e.,} \quad \Delta E = -885 \text{ kJ mol}^{-1}$$



$$\Delta n = 1 - 3 = -2, T = 300 \text{ K}, R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

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

$$= -885 + (-2) \times 8.314 \times 10^{-3} \times 300$$

$$= -885 - 4.988 = -889.988 \text{ kJ mol}^{-1}$$

Example 61. The heat of combustion of ethane gas is -368 kcal/mol . Assuming that 60% of heat is useful, how many m^3 of ethane measured at NTP must be burned to supply heat to convert 50 kg of water at 10°C to steam at 100°C ?

Solution: Heat required per gram of water

$$= (90 + 540) \text{ cal} = 630 \text{ cal}$$

Total heat needed for 50 kg of water

$$= 50 \times 10^3 \times 630 \text{ cal}$$

As the efficiency is 60%, the actual amount of heat required

$$= \frac{50 \times 10^3 \times 630}{60} \times 100 = 52500 \text{ kcal}$$

No. of mole of ethane required to produce 52500 kcal

$$= \frac{52500}{368} = 142.663 \text{ mole}$$

Volume of 142.663 mole at NTP = 142.663×22.4

$$= 3195.65 \text{ litre} = 3.195 \text{ m}^3$$

7.22 LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

The essence of first law of thermodynamics is that all physical and chemical processes occur in such a way that the total energy of the system and surroundings is constant. The law correlates the

various forms of energy, *i.e.*, their interconversion into one another in exactly equivalent amounts. The law has stood the test of time as no transformation has violated the principle of conservation of energy. However, the first law of thermodynamics has a number of limitations.

1. The law does not give any information about the direction in which flow of energy takes place. For example, if two systems *A* and *B* which are capable of exchanging heat are brought in contact with each other, the first law of thermodynamics will only tell us that one system loses energy and other system gains the same amount of energy. But the law fails to tell whether the heat will flow from system *A* to *B* or from system *B* to *A*. In order to predict the direction of the flow of heat, one more parameter, *i.e.*, temperature is required. The heat actually flows from a system which has higher temperature. The process continues till both the systems attain the same temperature. The law fails to answer why heat energy does not flow from cold system to hot system though the energy is conserved in this way also.
2. The law does not explain why the chemical reactions do not proceed to completion.
3. The law does not explain why natural spontaneous processes are irreversible.
4. The law does not contradict the existence of self-acting refrigerator.
5. The law does not contradict the existence of 100% efficient engine.
6. The difference between spontaneous and non-spontaneous processes is insignificant in view of the first law.

The answers to above limitations are provided by second law of thermodynamics. However, before we study this law, let us understand the terms **spontaneous**, **entropy** and **free energy**.

7.23 SPONTANEOUS AND NON-SPONTANEOUS PROCESSES

One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a reaction will occur when reactants are brought together under a special set of conditions (for example, at a certain temperature, pressure and concentration). A reaction that occurs under the given set of conditions is called a **spontaneous reaction**. If a reaction does not occur under specified conditions, it is said to be **non-spontaneous**.

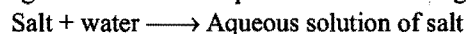
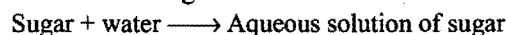
The term spontaneity means the feasibility of a process. In nature, we observe many processes which occur of their own. For example, water flows down the hill without the help of any external agency, heat flows from a conductor at high temperature to another at low temperature, electricity flows from high potential to low potential. There are processes which require some initiation before they can proceed. But once initiated, they proceed by themselves. The burning of carbon, burning of fuels and petrol, etc., require some initiation. These processes are termed as spontaneous on account of their feasibility, *i.e.*, these can occur without the help of external work.

A process which has an urge or a natural tendency to occur either of its own or after proper initiation under the given set of conditions is known as spontaneous process.

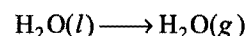
Spontaneous process does not mean that it takes place **instantaneously**. It simply implies that the process has an urge to take place and is practically feasible. The actual speed of the process may vary from very low to extremely fast. The rusting of iron is a slow spontaneous process while the neutralisation reaction between an acid and an alkali is a fast spontaneous process. It is a matter of experience also that all natural processes are spontaneous and are **irreversible**, *i.e.*, move in one direction only. The reverse process which can be termed as non-spontaneous can be made to occur only by supplying external energy. For example, water can be made to flow upward by the use of some external agency or energy is always required to lift the ball from the ground. The natural (spontaneous) processes follow a non-equilibrium path and as such are irreversible but these processes proceed up to establishment of equilibrium. At equilibrium state, the process stops to occur any further. Heat flows from a hotter body to a colder body till the temperature of both bodies becomes equal; there is no further flow of heat and we say that the system has attained equilibrium. Some of the familiar examples of spontaneous processes are listed below:

(a) Spontaneous processes where no initiation is required

(i) Dissolution of sugar or salt in water



(ii) Evaporation of water from water reservoirs such as ponds, lakes, rivers, sea, open vessels, etc.

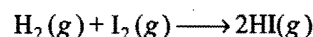


(iii) Flow of heat from a hot body to a cold body.

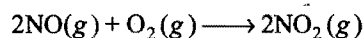
(iv) Mixing of different gases.

(v) Flow of water down a hill.

(vi) Reaction between $\text{H}_2(g)$ and $\text{I}_2(g)$ to form $\text{HI}(g)$.



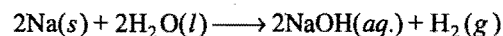
(vii) Reaction between nitric oxide gas and oxygen to form nitrogen dioxide.



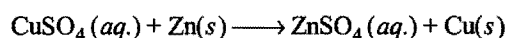
(viii) Melting of ice into water.



(ix) A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas.

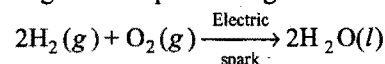


(x) When a zinc rod is dipped in an aqueous solution of copper sulphate, copper is precipitated.

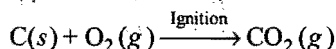


(b) Spontaneous processes where initiation is required

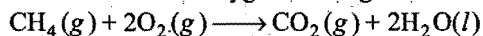
(i) Reaction between H_2 and O_2 : This reaction is initiated by passing electric spark through the mixture.



- (ii) Coal burns in oxygen or air when ignited. Coal keeps on burning once initiated.

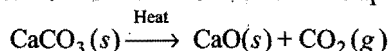


- (iii) Methane burns with oxygen when ignited.



- (iv) A candle made up of wax burns only when ignited.

- (v) Calcium carbonate evolves carbon dioxide upon heating.



A process which can neither occur by itself nor by initiation is called a non-spontaneous process.

Or

A process which has no natural tendency or urge to occur is said to be a non-spontaneous process.

Few examples of non-spontaneous processes are:

- (i) Flow of heat from a cold body to a hot body.
- (ii) Dissolution of gold or silver in water.
- (iii) Flow of water from ground to overhead tank.
- (iv) Hydrolysis of sodium chloride.
- (v) Decomposition of water into hydrogen and oxygen.
- (vi) Diffusion of gas from a low pressure to a high pressure.

It is not always true that non-spontaneous processes do not occur at all. Many of the non-spontaneous processes or changes can be made to take place when energy from some external source is supplied continuously throughout the change. (However, the processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the opposite direction). For example, the decomposition of water into hydrogen and oxygen (non-spontaneous process) can occur when electrical energy is supplied to water. The process stops when the passage of electrical energy is stopped.

Driving force for a spontaneous process: After having learnt about spontaneous processes, a very obvious question arises in our minds that why some processes are spontaneous? Obviously there must be some kind of driving force which is responsible for driving the process or a reaction in a particular direction.

The force which is responsible for the spontaneity of a process is called the driving force.

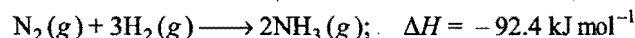
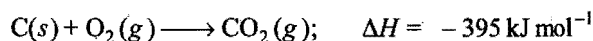
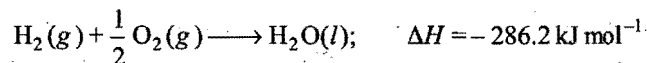
Let us now discuss the nature of the driving force.

1. Tendency to acquire minimum energy: We know that, *lesser is the energy, greater is the stability*. Thus, every system tends to acquire minimum energy. For example:

- (i) Heat flows from high temperature to low temperature so that heat content of hot body becomes minimum.
- (ii) Water flows down a hill or a slope to have minimum energy (potential).
- (iii) A wound watch spring tends to unwind so that mechanical energy of watch becomes minimum.

All the above processes are spontaneous because of a tendency to acquire minimum energy.

It has been observed that most of the spontaneous chemical reactions are exothermic. For example:



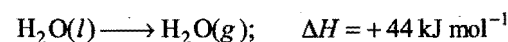
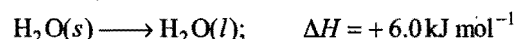
In exothermic reactions, heat is evolved from the system, i.e., energy is lowered. Thus, exothermic reactions occur spontaneously on account of decrease in enthalpy of system ($\Delta H = -ve$).

Hence, it can be concluded that the negative value of ΔH may be the criterion of spontaneity.

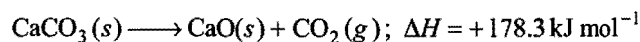
Limitations of the criterion for minimum energy

(a) Spontaneous endothermic reactions or processes: A number of endothermic reactions and processes are known which are spontaneous, i.e., when ΔH is +ve. Some examples are given below:

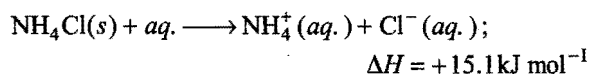
(i) Evaporation of water or melting of ice takes place by absorption of heat from surroundings, i.e., these processes are endothermic ($\Delta H = +ve$).



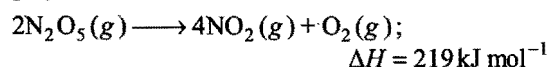
(ii) The decomposition of CaCO_3 is non-spontaneous at room temperature but becomes spontaneous when the temperature is raised.



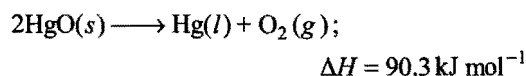
(iii) Compounds like NH_4Cl , KCl , etc., dissolve in water by absorption of heat from water. Temperature of the water decreases.



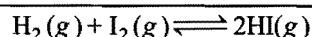
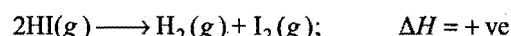
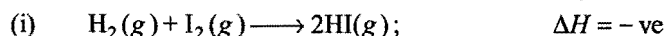
(iv) Dinitrogen pentoxide (N_2O_5) decomposes spontaneously at room temperature into NO_2 and O_2 , although the reaction is highly endothermic.

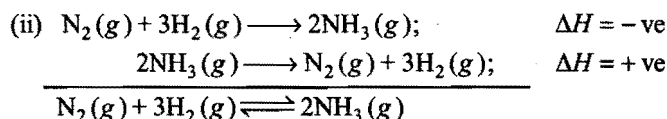


(v) The decomposition of HgO becomes spontaneous on heating.



(b) Occurrence of reversible reactions: A large number of reactions are reversible in nature. In these reactions, both forward and backward reactions occur simultaneously in spite of the fact that one reaction is exothermic ($\Delta H = -ve$) and other endothermic ($\Delta H = +ve$).





(c) **Reactions having zero ΔH :** A number of reactions are known in which neither energy is evolved nor absorbed, but these are spontaneous. For example, esterification of acetic acid is a spontaneous process. ΔH of this reaction is zero.



(d) **Exothermic reactions fail to achieve completion:** Every exothermic reaction rarely proceeds to completion even though ΔH remains negative throughout. In fact, all spontaneous reactions proceed in a direction until an equilibrium is attained.

Since, some spontaneous reactions are exothermic and others are endothermic, it is clear that enthalpy alone cannot account for spontaneity. There must be some other factor responsible for spontaneity or feasibility of a process.

2. Tendency to acquire maximum randomness: There is another natural tendency that must be taken into account to predict the direction of spontaneity.

Nature tends to move spontaneously from a state of lower probability to one of higher probability, *i.e.*, things tend to change from organized to disorganized. To illustrate what this statement means, we consider a spontaneous process of intermixing of two inert gases for which ΔH is zero. Two different inert gases, let us say helium (He) and neon (Ne), are originally contained in different glass bulbs, separated by a stopcock as shown in Fig. 7.20(a). To make the system as closed one, the entire system is perfectly insulated.

When the valve is opened, the intermixing of the two inert gases occurs due to diffusion into one another. As the gases are inert, there is no chemical interaction between them, the heat change during intermixing is negligible. The process of intermixing is a spontaneous process. If the process is examined critically, it is observed that when the valve is opened, both the gases are provided larger volume to occupy, *i.e.*, each gas achieves its own most probable distribution, independent of the presence of other gas. The final distribution is clearly much more probable than the initial distribution. There is, however, another

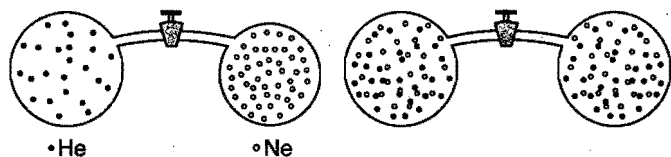


Fig. 7.20 (a)
Inert gases before mixing

Fig. 7.20 (b)
Inert gases after mixing

useful way of looking at this process. The system has gone from a highly ordered state (all the helium molecules on the left, all the neon molecules on the right) to a more disordered or random state. Mixed gases cannot be separated on their own. Thus, diffusion is a spontaneous process acquiring more randomness.

In general, nature tends to move spontaneously from more ordered to more random states, or a process proceeds

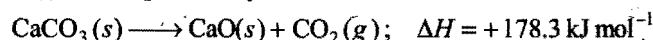
spontaneously in a direction in which randomness of the system increases.

Another example of achieving more randomness is the sugar dissolving in water. Before the solid sugar dissolves, the sugar molecules are organized in a crystal. As the molecules dissolve, they become distributed randomly and uniformly throughout the liquid. The opposite process never occurs, *i.e.*, sugar cubes do not form from the solution.

Thus, the second factor which is responsible for the spontaneity of a process is the tendency to acquire maximum randomness.

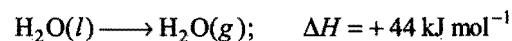
On the basis of second factor we may also explain the spontaneity of endothermic processes.

(i) **Decomposition of calcium carbonate:**



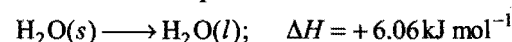
This process is spontaneous because the gaseous CO_2 produced is more random than solid calcium carbonate.

(ii) **Evaporation of water:**

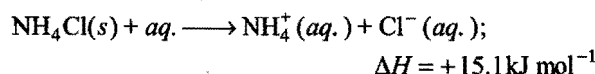


The gaseous state of a substance is more random than the liquid state. Thus, evaporation of water is spontaneous which proceeds in the direction of more randomness.

Similarly, fusion of ice is also spontaneous because the process again proceeds in the direction of more random state, *i.e.*, liquid state is more random in comparison to solid state.

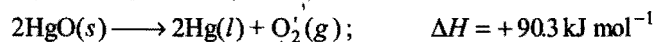


(iii) **Dissolution of NH_4Cl in water:**



When solid $\text{NH}_4\text{Cl}(\text{s})$ is dissolved in water, its ions become free. Free ions move randomly in all directions. Thus, the solution is a more random state as compared to solid NH_4Cl . Thus, the process of dissolution will be spontaneous because randomness increases on dissolution.

(iv) **Decomposition of mercuric oxide:**



Here again the process will be spontaneous because the product is more random than reactant due to presence of gaseous O_2 .

Limitations of the criterion for maximum randomness: Like energy factor, the randomness factor has also certain limitations. For example, in the liquefaction of a gas or in the solidification of a liquid, the randomness of the particles decreases but still these processes are spontaneous. Thus, like energy factor, randomness alone cannot be the sole criterion for the spontaneity of a process.

Overall tendency as driving force for a spontaneous process

From the above discussion, it is apparent that the spontaneous processes occur because of the two tendencies:

(i) Tendency of a system to achieve a state of minimum energy.

- (ii) Tendency of a system to achieve a state of maximum randomness.

The overall tendency of a process to be spontaneous depends on the resultant of the above two factors. The resultant of the two tendencies or overall tendency for a process to occur is termed the **driving force**.

Here, it should be noted that these tendencies are independent of each other. Both may act in the same or in opposite directions in a process.

Case I: When enthalpy factor is absent then randomness factor decides spontaneity of a process.

Case II: When randomness factor is absent then enthalpy or energy factor decides spontaneity of a process.

Case III: When both factors take place simultaneously then magnitude of the tendencies becomes important to decide spontaneity.

7.24 ENTROPY

Why do systems tend to move spontaneously to a state of maximum randomness or disorder? The answer is that a disordered state is more probable than an ordered state because the disordered state can be achieved in more ways. The following example illustrates the point. Suppose that you shake a box containing 10 identical coins and then count the number of heads (H) and tails (T). It is very unlikely that all the 10 coins will come up heads; i.e., perfectly ordered arrangement is much less probable than the totally disordered state in which heads and tails come up randomly. The perfectly ordered state of 10 heads can be achieved in only one way and the totally disordered state can be achieved in 2^{10} (1024) ways, i.e., the totally disordered state is 2^{10} times more probable than the perfectly ordered state. If the box contained 1 mol of coins, the perfectly ordered state would be only one, but the disordered states would be much higher ($2^{N_A} = 2^{6.02 \times 10^{23}}$). It is thus, concluded that a change which brings about randomness is more likely to occur than one that brings about order. The extent of disorder or randomness is expressed by a property known as **entropy**.

Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.

Entropy is represented by the symbol 'S'. It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state. The change in entropy from initial to final state of a system is represented by ΔS . The entropy is a state function and depends only on the initial and final states of the system.

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

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

For a chemical reaction,

$$\Delta S = S_{(\text{products})} - S_{(\text{reactants})}$$

Mathematical Definition of Entropy

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature (isothermally).

$$\int dS = \frac{1}{T} \int \delta q_{\text{rev}}$$

or

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad \dots (i)$$

If heat is absorbed, then ΔS is positive (increase in entropy). If heat is evolved, ΔS is negative (decrease in entropy). The value of ΔS , like ΔE and ΔH , is a definite quantity and depends on the initial and final states of the system. It is independent of the manner in which the change has been brought about, i.e., whether the change has been brought about reversibly or irreversibly.

Several factors influence the amount of entropy that a system has in a particular state. In general,

- (i) The value of entropy depends on the mass of the system. Hence, it is an extensive property.
- (ii) A liquid has a higher entropy than the solid from which it is formed. In a solid, the atoms, molecules or ions are fixed in position; in the liquid, these particles are free to move past one another, i.e., liquid structure is more random and the solid more ordered.
- (iii) A gas has a higher entropy than the liquid from which it is formed. When vaporization occurs, the particles acquire greater freedom to move about.
- (iv) Increasing temperature of a substance increases its entropy. Raising the temperature increases the kinetic energy of the molecules (atoms or ions) and hence their freedom of motion. In the solid, the molecules vibrate with a greater amplitude at higher temperatures. In a liquid or a gas, they move about more rapidly. In other words, the more heat the system absorbs, the more disordered it becomes. Furthermore, if heat is absorbed at low temperature, it becomes more disordered than when the same amount of heat is added at higher temperature.

Units of Entropy and Entropy Change

Since, entropy change is expressed by a heat term divided by temperature, it is expressed in terms of calories per degree, i.e., cal K^{-1} . In SI units, the entropy change is expressed in terms of joules per degree, i.e., J K^{-1} . Entropy is an extensive property, i.e., it depends on the mass of the substance; hence units of entropy are expressed as $\text{cal deg}^{-1} \text{mol}^{-1}$ ($\text{cal K}^{-1} \text{mol}^{-1}$) or $\text{joule deg}^{-1} \text{mol}^{-1}$ ($\text{J K}^{-1} \text{mol}^{-1}$).

Spontaneity in Terms of Entropy Change

In an isolated system, such as mixing of gases, there is no exchange of energy or matter between the system and surroundings. However, the mixing of gases is accompanied by randomness, i.e., there is increase in entropy. Therefore, it can be

stated that for a spontaneous process in an isolated system, the change in entropy is positive, i.e., $\Delta S > 0$.

However, if a system is not isolated, the entropy changes of both the system and surroundings are to be taken into account because system and surroundings together constitute the **isolated system**. Thus, the total entropy change (ΔS_{total}) is sum of the change in entropy of the system (ΔS_{system}) and the change in entropy of the surroundings ($\Delta S_{\text{surroundings}}$), i.e.,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad \dots \text{(ii)}$$

For a spontaneous process, ΔS_{total} must be positive, i.e.,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad \dots \text{(iii)}$$

ΔS_{total} is also termed as $\Delta S_{\text{universe}}$

During a spontaneous process, the entropy of the system goes on increasing till the system attains the equilibrium state, i.e., entropy of the system becomes maximum and, therefore, no more increase in the entropy of the system is possible. The mathematical condition for equilibrium is,

$$\Delta S = 0 \text{ (at equilibrium for an isolated system)} \quad \dots \text{(iv)}$$

If ΔS_{total} is negative, the direct process is non-spontaneous whereas the reverse process is spontaneous.

This can be illustrated by considering the entropy changes in the conversion of water to ice at three different temperatures. The relevant entropy changes for the system and surroundings and total change are given in the following table:

Temperature		ΔS_{system}	$\Delta S_{\text{surrounding}}$	ΔS_{total}
°C	K	$\text{J K}^{-1} \text{mol}^{-1}$	$\text{J K}^{-1} \text{mol}^{-1}$	$\text{J K}^{-1} \text{mol}^{-1}$
-1	272	-21.85	+21.93	+0.08
0	273	-21.99	+21.99	0.00
+1	274	-22.13	+22.05	-0.08

$$\begin{aligned} \text{At 272 K: } \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= -21.85 + 21.93 = +0.08 \text{ J K}^{-1} \text{mol}^{-1} \end{aligned}$$

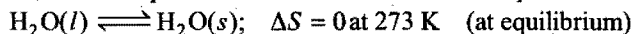
$$\therefore \Delta S_{\text{process}} > 0 \quad \text{at 272 K}$$

Thus, freezing of ice at 272 K, $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$ will be spontaneous.

$$\begin{aligned} \text{At 273 K: } \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= -21.99 + 21.99 = 0 \end{aligned}$$

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

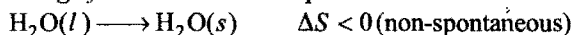
Thus, at this temperature, water and ice will be at equilibrium.



$$\begin{aligned} \text{At 274 K: } \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= -22.13 + 22.05 = -0.08 \text{ J K}^{-1} \text{mol}^{-1} \end{aligned}$$

$$\Delta S < 0$$

Thus, freezing of water will be non-spontaneous at 274 K.



Entropy Change in Reversible Process

Consider an isothermal reversible process. In this process, let the system absorb q amount of heat from surroundings at temperature T . The increase in the entropy of the system will be

$$\Delta S_{\text{system}} = + \frac{q}{T}$$

On the other hand, surroundings lose the same amount of heat at the same temperature. The decrease in the entropy of the surroundings will

$$\Delta S_{\text{surroundings}} = - \frac{q}{T}$$

Total change in entropy = entropy change in system + entropy change in surroundings

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= \frac{q}{T} - \frac{q}{T} = 0 \end{aligned}$$

When the reversible process is **adiabatic**, there will be no heat exchange between system and surroundings, i.e., $q = 0$

$$\therefore \Delta S_{\text{system}} = 0, \Delta S_{\text{surroundings}} = 0$$

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

Entropy Change in Irreversible Processes

Consider a system at higher temperature T_1 and its surroundings at lower temperature T_2 . ' q ' amount of heat goes irreversibly from system to surroundings.

$$\therefore \Delta S_{\text{system}} = - \frac{q}{T_1}$$

$$\Delta S_{\text{surroundings}} = + \frac{q}{T_2}$$

$$\begin{aligned} \Delta S_{\text{process}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= - \frac{q}{T_1} + \frac{q}{T_2} = q \left[\frac{T_1 - T_2}{T_1 T_2} \right] \end{aligned}$$

But $T_1 > T_2$, $\therefore T_1 - T_2 = +ve$

or $\Delta S_{\text{process}} > 0$

Hence, entropy increases in an irreversible process.

Entropy Change for Ideal Gases

Change in entropy for an ideal gas under different conditions may be calculated as:

(i) When changes from initial state (1) to final state (2):

$$\Delta S = 2.303n C_V \log \left(\frac{T_2}{T_1} \right) + 2.303nR \log \left(\frac{V_2}{V_1} \right)$$

(when T and V are variables)

$$\Delta S = 2.303n C_P \log \left(\frac{T_2}{T_1} \right) + 2.303nR \log \left(\frac{P_1}{P_2} \right)$$

(when T and P are variables)

(ii). Entropy change for isothermal process:

$$\Delta S = 2.303nR \log \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = 2.303nR \log \left(\frac{P_1}{P_2} \right)$$

(iii) Entropy change for isobaric process (at constant pressure):

$$\Delta S = 2.303n C_p \log \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = 2.303n C_p \log \left(\frac{V_2}{V_1} \right)$$

(iv) Entropy change for isochoric process (at constant volume):

$$\Delta S = 2.303n C_v \log \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = 2.303n C_v \log \left(\frac{P_2}{P_1} \right)$$

(v) Entropy change in mixing of ideal gases: Let n_1 mole of gas A and n_2 mole of gas B are mixed; then total entropy change can be calculated as:

$$\Delta S = -2.303R[n_1 \log x_1 + n_2 \log x_2]$$

x_1, x_2 are mole fractions of gases A and B,

$$i.e., \quad x_1 = \frac{n_1}{n_1 + n_2}; \quad x_2 = \frac{n_2}{n_1 + n_2}$$

$$\Delta S/\text{mol} = -2.303R \left[\frac{n_1}{n_1 + n_2} \log x_1 + \frac{n_2}{n_1 + n_2} \log x_2 \right]$$

$$\Delta S/\text{mol} = -2.303R[x_1 \log x_1 + x_2 \log x_2]$$

Entropy change in adiabatic expansion will be zero, $\Delta S = 0$.

Physical Significance of Entropy at a Glance

1. Entropy as unavailable energy: Entropy is unavailable energy of the system.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature in K}}$$

2. Entropy and randomness: Entropy is a measure of disorder or randomness in the system. Increase in entropy means change from an ordered to less ordered (or disordered) state.

3. Entropy and probability: Entropy may be defined as a function of probability of the thermodynamic state. Since, we know that both the entropy and thermodynamic probability increase simultaneously in a process, hence the state of equilibrium is the state of maximum probability.

Characteristics of Entropy

The important characteristics of entropy are summarised below:

- (i) Entropy is an extensive property. It is difficult to determine the absolute value of entropy of a substance

but its value depends on mass of the substance present in the system.

- (ii) Entropy of a system is a state function. It depends on the state variables such as T, P, V and n which govern the state of the system.
- (iii) The change in entropy taking place in going from one state to another state does not depend on the path adopted. It actually depends on the final and initial states of the system.

$$\text{Change in entropy, } \Delta S = S_{\text{final}} - S_{\text{initial}}$$

- (iv) The entropy change for a cyclic process is zero.
- (v) The entropy change in the equilibrium state is zero ($\Delta S = 0$).
- (vi) For natural processes, entropy of universe is increasing.

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

- (vii) In a reversible process, ΔS_{total} or $\Delta S_{\text{universe}} = 0$ and therefore

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

- (viii) For adiabatic reversible process,

$$\Delta S_{\text{system}} = \Delta S_{\text{surroundings}} = \Delta S_{\text{total}} = 0$$

In a spontaneous (irreversible process),

$$\Delta S_{\text{total}} \text{ or } \Delta S_{\text{universe}} > 0,$$

i.e., in spontaneous processes, there is always increase in entropy of the universe.

7.25 ENTROPY CHANGE DURING PHASE TRANSITIONS

Solid, liquid and gas are the three forms of a matter. The change of a substance from one form to another is known as **phase transformation**. Such changes occur at definite temperatures and are accompanied by entropy change. During these transformations either heat is absorbed or evolved, i.e., the entropy either increases or decreases accordingly.

The entropy change for these transformations is given by

$$\Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T}$$

where, q_{rev} is the heat absorbed or evolved and T is the temperature of transition. q_{rev} is actually the molar enthalpy change of the substance.

(i) Entropy of fusion: The entropy of fusion is defined as the change in entropy when one mole of a solid substance changes into liquid form at the melting temperature.

The heat absorbed is equal to the latent heat of fusion

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

For example, when ice melts, the change in entropy is given by

$$\begin{aligned} \Delta S_{\text{fusion (ice)}} &= S_{\text{water}} - S_{\text{ice}} = \frac{\Delta H_{\text{fusion}}}{T_f} = \frac{6000 \text{ J mol}^{-1}}{273} \\ &= 21.98 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

(ii) **Entropy of vaporisation:** It is defined as the change in entropy when one mole of the liquid substance changes into vapours (gas) at its boiling point.

$$\Delta S_{\text{vapour}} = S_{\text{vapour}} - S_{\text{liquid}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}}$$

Where, ΔH_{vapour} is the latent heat of vaporisation and T_{bp} is the boiling point.

For example, when water is converted into steam, the change in entropy is given by

$$\begin{aligned}\Delta S_{\text{vapour (water)}} &= S_{\text{steam}} - S_{\text{water}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}} = \frac{40626 \text{ J mol}^{-1}}{373} \\ &= 108.9 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

(iii) **Entropy of sublimation:** Sublimation involves the direct conversion of a solid into its vapour. The entropy of sublimation is defined as the change in entropy when one mole of a solid changes into vapour at a particular temperature.

$$\Delta S_{\text{sub}} = S_{\text{vapour}} - S_{\text{solid}} = \frac{\Delta H_{\text{sub}}}{T}$$

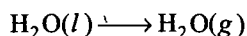
Where, ΔH_{sub} = heat of sublimation at temperature T .

••••• SOME SOLVED EXAMPLES •••••

Example 62. The enthalpy change, for the transition of liquid water to steam, ΔH_{vapour} is 40.8 kJ mol^{-1} at 373 K .

Calculate entropy change for the process.

Solution: The transition under consideration is:



We know that,
$$\Delta S_{\text{vapour}} = \frac{\Delta H_{\text{vapour}}}{T}$$

Given,
$$\begin{aligned}\Delta H_{\text{vapour}} &= 40.8 \text{ kJ mol}^{-1} \\ &= 40.8 \times 1000 \text{ J mol}^{-1} \\ T &= 373 \text{ K}\end{aligned}$$

Thus,
$$\Delta S_{\text{vapour}} = \frac{40.8 \times 1000}{373} = 109.38 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example 63. What is entropy change for the conversion of one gram of ice to water at 273 K and one atmospheric pressure? ($\Delta H_{\text{fusion}} = 6.025 \text{ kJ mol}^{-1}$)

Solution:
$$\begin{aligned}\Delta H_{\text{fusion}} &= 6.025 \times 1000 \text{ J mol}^{-1} \\ &= \frac{6025}{18} \text{ J g}^{-1} = 334.72 \text{ J g}^{-1} \\ \Delta S_{\text{fusion}} &= \frac{\Delta H_{\text{fusion}}}{T_f} \\ &= \frac{334.72}{273} = 1.226 \text{ J K}^{-1} \text{ g}^{-1}\end{aligned}$$

Example 64. Calculate the enthalpy of vaporisation per mole for ethanol. Given, $\Delta S = 109.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and boiling point of ethanol is 78.5°C .

Solution: We know that,

$$\Delta S_{\text{vapour}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}}$$

Given,
$$\Delta S_{\text{vapour}} = 109.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

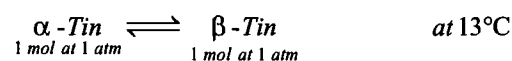
$$T_{\text{bp}} = 78.5 + 273 = 351.5 \text{ K}$$

Substituting these values in above equation, we get

$$109.8 = \frac{\Delta H_{\text{vapour}}}{351.5}$$

$$\begin{aligned}\Delta H_{\text{vapour}} &= 38594.7 \text{ J mol}^{-1} \\ &= 38.594 \text{ kJ mol}^{-1}\end{aligned}$$

Example 65. Calculate the entropy change for the following reversible process:

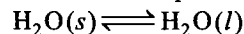


$$(\Delta H_{\text{trans}} = 2090 \text{ J mol}^{-1})$$

Solution:
$$\begin{aligned}\Delta S_{\text{trans}} &= \frac{\Delta H_{\text{trans}}}{T} = \frac{2090}{286} \\ &= 7.3076 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Example 66. At 0°C , ice and water are in equilibrium and enthalpy change for the process $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$ is 6 kJ mol^{-1} . Calculate the entropy change for the conversion of ice into liquid water.

Solution: We know that for the process of fusion,



$$\begin{aligned}\Delta S_{\text{fusion}} &= \frac{\Delta H_{\text{fusion}}}{T_f} \\ &= \frac{6 \times 1000}{273} = 21.98 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Example 67. The enthalpy of vaporisation of liquid diethyl ether ($\text{C}_2\text{H}_5)_2\text{O}$ is 26 kJ mol^{-1} at its boiling point 35°C . Calculate ΔS° for conversion of:

(a) liquid to vapour,

(b) vapour to liquid at 35°C .

Solution: (a)
$$\Delta S_{\text{vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T_{\text{bp}}} = \frac{26000}{308}$$

$$= 84.42 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b)
$$\begin{aligned}\Delta S_{\text{condensation}} &= -\Delta H_{\text{vaporisation}} \\ &= -84.42 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Example 68. Calculate entropy change when 10 moles of an ideal gas expands reversibly and isothermally from an initial volume of 10 litre to 100 litre at 300 K .

Solution:
$$\begin{aligned}\Delta S &= 2.303nR \log \left(\frac{V_2}{V_1} \right) \\ &= 2.303 \times 10 \times 8.314 \log \left(\frac{100}{10} \right) \\ &= 191.24 \text{ J K}^{-1}\end{aligned}$$

Example 69. Oxygen gas weighing 64 g is expanded from 1 atm to 0.25 atm at 30°C. Calculate entropy change, assuming the gas to be ideal.

Solution:

$$n = \frac{w}{\text{m. wt.}} = \frac{64}{32} = 2$$

$$\Delta S = 2.303nR \log \left(\frac{P_1}{P_2} \right)$$

$$= 2.303 \times 2 \times 8.314 \log \left(\frac{1}{0.25} \right)$$

$$= 23.053 \text{ J K}^{-1}$$

Example 70. Calculate the change in entropy when 1 mole nitrogen gas expands isothermally and reversibly from an initial volume of 1 litre to a final volume of 10 litre at 27°C.

Solution:

$$\Delta S = 2.303 nR \log \left(\frac{V_2}{V_1} \right)$$

$$= 2.303 \times 1 \times 8.134 \log \left(\frac{10}{1} \right)$$

$$= 19.12 \text{ J K}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

34. For a liquid, enthalpy of fusion is 1.435 kcal mol⁻¹ and molar entropy change is 5.26 cal mol⁻¹ K⁻¹. The melting point of the liquid is:

- (a) 0°C (b) -273°C
(c) 173 K (d) 100°C

[Ans. (a)]

[Hint: $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}}$]

$$5.26 = \frac{1.435 \times 1000}{T_{\text{mp}}}$$

$$T_{\text{mp}} = \frac{1435}{5.26} = 273 \text{ K, i.e., } 0^\circ \text{C}$$

35. Latent heat of vaporisation of water is 540 cal g⁻¹ at 100°C. Calculate the entropy change when 1000 g water is converted to steam at 100°C.

- (a) 1447 cal (b) 2447 cal (c) 3447 cal (d) 4447 cal

[Ans. (a)]

[Hint: $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{540 \times 1000}{373} = 1447 \text{ cal}$]

36. Enthalpy of fusion of water is 6.01 kJ mol⁻¹. The entropy change of 1 mole of ice at its melting point will be:

- (a) 22 kJ mol⁻¹ (b) 109 kJ mol⁻¹
(c) 44 kJ mol⁻¹ (d) 11 kJ mol⁻¹

[Ans. (a)]

[Hint: $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \frac{6.01 \times 1000}{273} = 22 \text{ kJ mol}^{-1}$]

37. For spontaneous process:

- (a) $\Delta S_{\text{total}} = 0$ (b) $\Delta S_{\text{total}} > 0$
(c) $\Delta S_{\text{total}} < 0$ (d) none of these

[Ans. (b)]

[Hint: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$
= + ve for spontaneous process]

38. Melting point of a solid is x K and its latent heat of fusion is 600 cal mol⁻¹. The entropy change for fusion of 1 mol solid is 2 cal mol⁻¹ K⁻¹. The value of x will be:

- (a) 100 K (b) 200 K (c) 300 K (d) 400 K

[Ans. (c)]

[Hint: $\frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \Delta S_{\text{fusion}}$]

$$\frac{600}{T} = 2$$

$$T = 300 \text{ K}$$

39. The entropy change involved in the conversion of 1 mole of liquid water at 373 K to vapour at the same temperature will be:

- (a) 0.119 kJ (b) 0.109 kJ
(c) 0.129 kJ (d) 0.120 kJ

[PMT (MP) 2007]

[Ans. (b)]

[Hint: $\Delta S = \frac{\Delta H_{\text{vap}}}{T} = \frac{2.257 \times 18}{373} = 0.109 \text{ kJ/g}$]

7.26 SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics tells us whether a given process can occur spontaneously and to what extent. It also helps us to calculate the maximum fraction of heat that can be converted into work in a given process.

The second law of thermodynamics like first law is a postulate and has not been derived from any prior concepts. It is stated in various forms. However, all the statements of second law have the same meaning.

1. Clausius statement: "It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency."

It means that work can always be completely converted into heat but heat cannot be converted completely into work without leaving some permanent change in the system or surroundings. For example, heat produced in heat engine is never fully utilized, as part of it is always lost to surroundings or in overcoming friction, etc. Thus, it can be said that *the complete conversion of heat into work is impossible without leaving some effect elsewhere.*

Or

It is not possible to convert heat into work without compensation.

Or

All forms of energy can be converted into heat energy but heat cannot be converted into other forms of energy fully by any process.

The other similar statements are:

2. Thomson statement: *The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work.*

3. Kelvin-Planck statement: *It is impossible by means of inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*

4. *It is impossible to construct a heat engine of 100% thermal efficiency.*

5. Ludwig Boltzmann statement: In 1886, Ludwig Boltzmann gave a most useful statement of the second law of thermodynamics. *Nature tends to pass from a less probable to more probable state.*

The connection between entropy and the spontaneity of a reaction or a process is expressed by the second law of thermodynamics in a number of ways.

6. *All spontaneous processes or naturally occurring processes are thermodynamically irreversible. Without the help of an external agency, a spontaneous process cannot be reversed.*

For example, the mixing of non-reacting gases is a spontaneous process. But these cannot be separated from the mixture without the application of special methods.

Heat energy can flow from a hot body to a cold body of its own (spontaneously) but not from a cold body to a hot body unless the former is heated.

7. *The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.*

Since, the universe is made up of the system and the surroundings, the entropy change in the universe ($\Delta S_{\text{universe}}$) for any process is the sum of the entropy changes in the system (ΔS_{system}) and in the surroundings ($\Delta S_{\text{surroundings}}$). Mathematically, the second law of thermodynamics can be expressed as:

A spontaneous process:

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

An equilibrium process:

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

For a spontaneous process, the law says that $\Delta S_{\text{universe}}$ must be greater than zero, but it does not place a restriction on either ΔS_{system} or $\Delta S_{\text{surroundings}}$. Thus, it is possible for either ΔS_{system} or $\Delta S_{\text{surroundings}}$ to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, $\Delta S_{\text{universe}}$ is zero, i.e., ΔS_{system} and $\Delta S_{\text{surroundings}}$ must be equal in magnitude but opposite in sign.

Thus, *the entropy of the universe is continuously increasing.* The main ideas of the first and second law of thermodynamics may be summarised as:

First law states that the energy of the universe is constant whereas the second law states that the entropy of the universe is continuously increasing and tends to a maximum.

First law deals with the conservation of energy whereas the second law tells the direction of flow of energy.

For a reversible process,

$$dS = \frac{dq}{T} \quad \text{or} \quad dq = T dS$$

For an irreversible process,

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

$$\therefore dS \geq \frac{dq}{T}$$

This is the mathematical statement of second law of thermodynamics.

$dq = dE + P dV$ This is the mathematical statement of first law of thermodynamics

Combining both the laws of a reversible process,

$$T dS = dE + P dV$$

7.27 GIBBS FREE ENERGY, (G), CHANGE IN FREE ENERGY AND SPONTANEITY

As discussed earlier, there are two thermodynamic quantities that affect reaction spontaneity. One of these is enthalpy, H ; the other is the entropy, S . The problem is to put these two quantities together in such a way as to arrive at a single function whose sign will determine whether a reaction is spontaneous. This problem was first solved more than a century ago by **J. Willard Gibbs**, who introduced a new quantity, now called the **Gibbs free energy** and given the symbol, G . Gibbs showed that for a reaction taking place at constant pressure and constant temperature, ΔG represents that portion of the total energy change that is available (i.e., free) to do useful work. If, for example, ΔG for a reaction is -300 kJ, it is possible to obtain 300 kJ of useful work from the reaction. Conversely, if ΔG is $+300$ kJ, at least that much energy in the form of work must be supplied to make the reaction to take place. Gibbs free energy of a system is defined as:

"The thermodynamic quantity of the system, the decrease in whose value during a process is equal to useful work done by the system."

Mathematically, it may be defined as:

$$G = H - TS \quad \dots (i)$$

where, H = enthalpy; S = entropy and T = absolute temperature.

$$\text{We know that, } H = E + PV \quad \dots (ii)$$

From eqs. (i) and (ii),

$$G = E + PV - TS$$

Free energy change at constant temperature and pressure can be given as:

$$\begin{aligned} \Delta G &= \Delta E + P \Delta V - T \Delta S \\ \Delta G &= \Delta H - T \Delta S \quad \dots (iii) \end{aligned}$$

(Gibbs-Helmholtz equation)

Here,

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

Gibbs-Helmholtz equation is used to discuss the **driving force**, i.e., the overall criterion of spontaneity.

[Note: Since, ' H ' and ' S ' are extensive property hence ' G ' will also be an extensive property. Moreover, Gibbs function ' G ' is a state function.]

Free Energy Change and Spontaneity

Let us consider a system which is not isolated from its surroundings. In this case, total entropy change can be calculated as:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad \dots (i)$$

Let us consider the process at constant temperature and pressure. Let q_p amount of heat be given by the system to the surroundings.

$$(q_p)_{\text{surroundings}} = -(q_p)_{\text{system}} = -\Delta H_{\text{system}}$$

$$\Delta S_{\text{surroundings}} = \frac{(q_p)_{\text{surroundings}}}{T} = \frac{-\Delta H_{\text{system}}}{T} \quad \dots (ii)$$

From equations (i) and (ii),

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

$$\text{or } T \Delta S_{\text{total}} = T \Delta S_{\text{system}} - \Delta H_{\text{system}}$$

$$\text{or } -T \Delta S_{\text{total}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}} \quad \dots (iii)$$

According to Gibbs-Helmholtz equation,

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

$$\therefore \Delta G_{\text{system}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}} \quad \dots (iv)$$

From equations (iii) and (iv),

$$\Delta G_{\text{system}} = -T \Delta S_{\text{total}}$$

We know that for spontaneous process, $\Delta S_{\text{total}} > 0$

$\therefore \Delta G = -ve$ for spontaneous process.

Thus, for spontaneous process $T \Delta S_{\text{total}}$ should be positive or ΔG should be negative.

Case I: Let entropy and energy, both factors are favourable for a process, i.e., $\Delta H = -ve$ and $T \Delta S = +ve$

$$\therefore \text{From } \Delta G = \Delta H - T \Delta S$$

$$= (-ve) - (+ve) = -ve$$

Thus, $\Delta G = -ve$ for spontaneous process.

Case II: Let both energy and entropy factors oppose a process, i.e., $\Delta H = +ve$, $T \Delta S = -ve$.

$$\therefore \text{From } \Delta G = \Delta H - T \Delta S$$

$$= +ve - (-ve) = +ve$$

Thus, ΔG is positive for a non-spontaneous process.

Case III: Let both tendencies be equal in magnitude but opposite, i.e.,

$$\Delta H = +ve \text{ and } T \Delta S = +ve \text{ and } \Delta H = T \Delta S$$

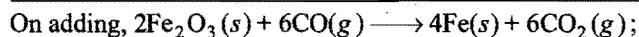
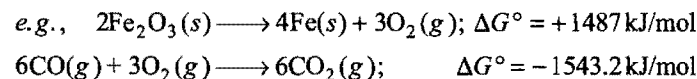
$$\therefore \text{From } \Delta G = \Delta H - T \Delta S$$

$$= 0$$

In this condition, the process is said to be at equilibrium.

Coupled Reactions

We know that the reactions which have $\Delta G = +ve$ are non-spontaneous. However, such reactions can be made spontaneous when coupled with a reaction having very large negative free energy of reaction,



$$\Delta G^\circ = -52.2 \text{ kJ/mol}$$

Thus, both reactions proceed simultaneously.

The free energy of a reaction is the chemical analogue of potential energy of mechanical systems. A body moves in the direction in which there is decrease in potential energy. Similarly, in chemical system, the substance moves in a direction in which there is decrease in free energy, i.e., ΔG is negative.

In a chemical reaction, $\Delta G = G_{\text{products}} - G_{\text{reactants}}$. Thus, spontaneous changes occur with a decrease in free energy, i.e., ΔG is negative.

To sum up, the criteria for spontaneity of a process in terms of ΔG is as follows:

- If ΔG is negative, the process is spontaneous.
- If ΔG is zero, the system is in equilibrium. The process does not occur.
- If ΔG is positive, the process does not occur in the forward direction. It may occur in the backward direction.

Conditions for ΔG to be negative or the process to be spontaneous

We know that, $\Delta G = \Delta H - T \Delta S$

ΔH	$T \Delta S$	Conditions	ΔG
-ve (favourable)	+ve (favourable)	(any)	-ve spontaneous
-ve (favourable)	-ve (unfavourable)	$ \Delta H > T \Delta S $	-ve spontaneous
+ve (unfavourable)	+ve (favourable)	$ T \Delta S > \Delta H $	-ve spontaneous

Role of Temperature on Spontaneity

In Gibbs-Helmholtz equation:

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

not only ΔH and ΔS but also temperature ' T ' is a determining factor for spontaneity, i.e., for ΔG to be -ve. Let us discuss exothermic and endothermic reactions to show the influence of temperature.

1. Exothermic processes: In exothermic reactions, $\Delta H = -ve$ (favourable condition)

Case I: When $T \Delta S$ is positive, i.e., favourable, then ΔG will be negative and the process will be spontaneous at all temperatures.

Case II: When $T \Delta S$ is negative, i.e., unfavourable, then ΔG will be negative when $|\Delta H| > |T \Delta S|$. To reduce the magnitude of $T \Delta S$, the temperature should be low. Thus, *exothermic reactions can be made favourable (when $T \Delta S = -ve$) by lowering the temperature.*

2. Endothermic reactions: In endothermic reactions, $\Delta H = +ve$ (unfavourable conditions).

In case of endothermic reactions, ΔG will be negative when $|\Delta H| < |T \Delta S|$. To increase the magnitude of $T \Delta S$, temperature

(T) should be increased. Thus, *endothermic reactions can be made favourable by increasing the temperature.*

Thus, temperature also plays an important role in deciding the spontaneity of a reaction. A reaction which is non-spontaneous at low temperature becomes spontaneous at high temperature and vice-versa.

Sign of ΔH , ΔG and ΔS and prediction of spontaneity

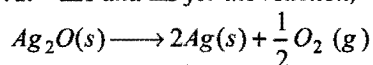
ΔH	ΔS	ΔG	Remarks
-ve	+ve	-ve	Spontaneous at all temperatures
-ve	-ve	-ve (at low temperature) +ve (at high temperature)	Spontaneous Non-spontaneous
+ve	+ve	+ve (at low temperature) -ve (at high temperature)	Non-spontaneous Spontaneous
+ve	-ve	+ve	Non-spontaneous at all temperatures

ΔH

		+	-
ΔS	+	Spontaneous at high temperature and non-spontaneous at low temperatures	Spontaneous at all temperatures
	-	Non-spontaneous at all temperatures	Non-spontaneous at high temperatures and spontaneous at low temperatures

SOME SOLVED EXAMPLES

Example 71. ΔH and ΔS for the reaction,



are $30.56 \text{ kJ mol}^{-1}$ and $66.0 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Calculate the temperature at which free energy change for the reaction will be zero. Predict whether the forward reaction will be favoured above or below this temperature.

Solution: We know that,

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

At equilibrium, $\Delta G = 0$

so that $0 = \Delta H - T \Delta S$

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

Given that, $\Delta H = 30.56 \text{ kJ mol}^{-1}$

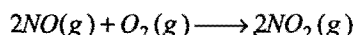
$$= 30560 \text{ J mol}^{-1}$$

$$\Delta S = 66.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = \frac{30560}{66} = 463 \text{ K}$$

Above this temperature, ΔG will be negative and the process will be spontaneous in forward direction.

Example 72. For the reaction,



Calculate ΔG at 700 K when enthalpy and entropy changes are $-113.0 \text{ kJ mol}^{-1}$ and $-145 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively.

Solution: We know that, $\Delta G = \Delta H - T \Delta S$

Given,

$$\Delta H = -113 \text{ kJ mol}^{-1}$$

$$= -113000 \text{ J mol}^{-1}$$

$$\Delta S = -145 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 700 \text{ K}$$

Substituting these values in the above equation,

$$\text{we get } \Delta G = -113000 - 700 \times (-145)$$

$$= -11500 \text{ J mol}^{-1}$$

$$= -11.5 \text{ kJ mol}^{-1}$$

Example 73. In the reaction $A^+ + B \longrightarrow A + B^+$, there is no entropy change. If enthalpy change is 22 kJ of A^+ , calculate ΔG for the reaction.

Solution: For the given reaction,

$$\Delta H = 22 \text{ kJ}, \Delta S = 0$$

$\therefore$ From,

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

$$\Delta G = 22 - T \times 0 = 22 \text{ kJ mol}^{-1}$$

Example 74. ΔH and ΔS for the reaction $\text{Br}_2(l) + \text{Cl}_2(g) \longrightarrow 2\text{BrCl}(g)$ are 29.37 kJ and 104.0 J K^{-1} respectively. Above what temperature will this reaction become spontaneous?

Solution: According to Gibbs-Helmholtz equation,

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

For spontaneous process, $\Delta G < 0$

i.e.,

$$\Delta H - T \Delta S < 0$$

$$T \Delta S > \Delta H$$

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

$$T > \frac{29.37 \times 1000}{104} \quad T > 282.4 \text{ K}$$

Example 75. Calculate the temperature at which liquid water will be in equilibrium with water vapour.

$$\Delta H_{\text{vap}} = 40.73 \text{ kJ mol}^{-1} \text{ and } \Delta S_{\text{vap}} = 0.109 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

Solution: Given, $\Delta H = 40.73 \text{ kJ mol}^{-1}$

$$\Delta S = 0.109 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

and

$$\Delta G = 0$$

Applying

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

$$0 = 40.73 - T \times 0.109$$

$$T = \frac{40.73}{0.109} = 373.6 \text{ K}$$

Example 76. Zinc reacts with dilute hydrochloric acid to give hydrogen at 17°C . The enthalpy of the reaction is $-12.55 \text{ kJ mol}^{-1}$ of zinc and entropy change equals $5.0 \text{ J K}^{-1} \text{ mol}^{-1}$ for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.

Solution: Given, $\Delta H = -12.55 \text{ kJ mol}^{-1}$

$$\Delta S = 5.0 \text{ J K}^{-1} \text{ mol}^{-1} \\ = 0.005 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 17 + 273 = 290 \text{ K}$$

Applying

$$\Delta G = \Delta H - T \Delta S \\ = -12.55 - 0.005 \times 290 \\ = -12.55 - 1.45 = -14.00 \text{ kJ mol}^{-1}$$

Since, ΔG is negative, the reaction will be spontaneous.

Example 77. ΔH and ΔS for the system $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$ at 1 atmospheric pressure are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Calculate the temperature at which the rates of forward and backward reactions will be the same. Predict the sign of free energy for this transformation above this temperature.

Solution: Given, $\Delta H = 40.63 \text{ kJ mol}^{-1}$

$$\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1} = 0.1088 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G = 0 \quad (\text{when the system is in equilibrium})$$

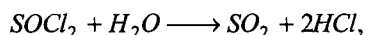
$$\text{Applying} \quad \Delta G = \Delta H - T \Delta S \\ 0 = 40.63 - T \times 0.1088 \\ T = \frac{40.63}{0.1088} = 373.4 \text{ K}$$

The sign of ΔG above 373 K, i.e., say 374 K, may be calculated as follows:

$$\text{Again applying} \quad \Delta G = \Delta H - T \Delta S \\ = 40.63 - 374 \times 0.1088 \\ = 40.63 - 40.69 = -0.06 \text{ kJ}$$

ΔG will be negative; hence, the reaction will be spontaneous.

Example 78. For the reaction,



the enthalpy of reaction is 49.4 kJ and the entropy of reaction is 336 J K^{-1} . Calculate ΔG at 300 K and predict the nature of the reaction.

$$\text{Solution:} \quad \Delta G = \Delta H - T \Delta S \\ = 49.4 - (300 \times 336 \times 10^{-3}) \\ = -51.4 \text{ kJ}$$

Since, the free energy change is negative, the given reaction is spontaneous.

Example 79. The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below:

$$\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \\ \Delta H_{300 \text{ K}}^\circ = -41.16 \text{ kJ mol}^{-1} \\ \Delta S_{300 \text{ K}}^\circ = -4.24 \times 10^{-2} \text{ kJ mol}^{-1} \\ \Delta H_{1200 \text{ K}}^\circ = -32.93 \text{ kJ mol}^{-1} \\ \Delta S_{1200 \text{ K}}^\circ = -2.96 \times 10^{-2} \text{ kJ mol}^{-1}$$

Calculate K_p at each temperature and predict the direction of reaction at 300 K and 1200 K , when $P_{\text{CO}} = P_{\text{CO}_2} = P_{\text{H}_2} = P_{\text{H}_2\text{O}} = 1 \text{ atm}$ at initial state.

$$\text{Solution: At } 300 \text{ K: } \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \\ = -41.16 - 300 \times (-4.24 \times 10^{-2}) \\ = -28.44 \text{ kJ}$$

Since, ΔG° is negative hence reaction is spontaneous in forward direction,

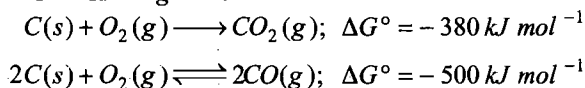
$$\Delta G^\circ = -2.303 RT \log K_p \\ -28.44 = -2.303 \times 8.314 \times 10^{-3} \times 300 \log K_p \\ K_p = 8.93 \times 10^4$$

$$\text{At } 1200 \text{ K: } \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \\ = -32.93 - 1200(-2.96 \times 10^{-2}) = +2.59 \text{ kJ}$$

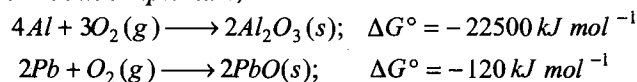
Positive value of ΔG° shows that the reaction is spontaneous in backward direction

$$\Delta G^\circ = -2.303 RT \log K_p \\ 2.59 = -2.303 \times 8.314 \times 10^{-3} \times 1200 \log K_p \\ K_p = 0.77$$

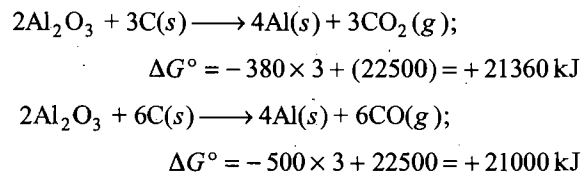
Example 80. The standard Gibbs free energies for the reactions at 1773 K are given below:



Discuss the possibility of reducing Al_2O_3 and PbO with carbon at this temperature,

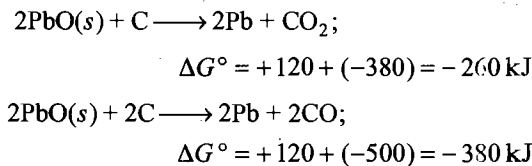


Solution: Let us consider the reduction of Al_2O_3 by carbon:



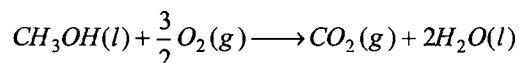
Positive values of ΔG° show that the reduction of Al_2O_3 is not possible by any of the above methods.

Now, let us consider the reduction of PbO .



Negative value of ΔG° shows that the process is spontaneous and PbO can be reduced by carbon.

Example 81. In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is:



[PMT (Haryana) 2007]

- (a) 828.7°C
 (b) 828.7 K
 (c) Spontaneous at all temperature
 (d) Not possible

[Ans. (d)]

[Hint: $\Delta G = \Delta H - T \Delta S$

When $\Delta H = +ve$, $\Delta S = -ve$ then ΔG will be positive and the reaction is non-spontaneous.]

7.28 STANDARD FREE ENERGY CHANGE

Just like enthalpy and internal energies, we cannot determine absolute value of Gibbs free energy. The standard free energy change can be determined and it is defined as the free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted to products in their standard state. It is denoted as ΔG° ; it can be related to standard enthalpy and entropy change in the following manner:

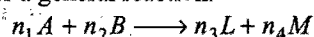
$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Like that of ΔH° , ΔG° can be calculated from the standard free energies of formation of the products and the reactants.

$$\Delta G^\circ = \sum G_f^\circ (\text{products}) - \sum G_f^\circ (\text{reactants})$$

$$= \left[\begin{array}{c} \text{Sum of standard free} \\ \text{energies of formation} \\ \text{of products} \end{array} \right] - \left[\begin{array}{c} \text{Sum of standard free} \\ \text{energies of formation} \\ \text{of reactants} \end{array} \right]$$

Let us consider a general reaction:



$$\Delta G^\circ = \sum G_f^\circ (\text{products}) - \sum G_f^\circ (\text{reactants})$$

$$= [n_3 G_f^\circ (L) + n_4 G_f^\circ (M)] - [n_1 G_f^\circ (A) + n_2 G_f^\circ (B)]$$

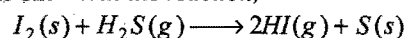
The standard free energy of formation (ΔG_f°) may be defined as the free energy change when 1 mole of a compound is formed from its constituent elements in their standard state. The standard free energy of formation of an element in its standard state is assumed to be zero.

Standard Gibbs Free Energy of Formation (kJ mol⁻¹ at 298 K)

HCl	-95.27	C ₄ H ₈ (iso-butene)	294
H ₂ O	-228.6	BaO	-528.4
H ₂ O ₂	-103.3	BaCO ₃	-1139
CO	-137.3	BaSO ₄	-1465
CO ₂	-394.4	CaO	-604.2
SO ₂	-300.4	Ca(OH) ₂	-896.6
SO ₃	-370.4	CaCO ₃	-1129
NO ₂	51.84	CuO	-127
N ₂ O	104	NaCl	-384.0
NH ₃	-16.6	KCl	-408.3
O ₃	163.4	NH ₄ Cl	-203.0
NO	86.69	Al ₂ O ₃	-1582.4
CH ₄	-50.79	Fe ₂ O ₃	-741.0
C ₂ H ₆ (ethane)	229	ZnO	-318.2

C ₃ H ₈ (propane)	270	SiO ₂	-805
C ₄ H ₁₀ (n-butane)	310	PbO ₂	-219
C ₄ H ₁₀ (iso-butane)	310	CH ₃ OH	-166.2
C ₂ H ₂ (acetylene)	209.2	C ₂ H ₅ OH	-174.8
C ₂ H ₄ (ethylene)	219.4	C ₆ H ₆	-124.5
C ₃ H ₆ (propylene)	266.9	CH ₃ COOH	-392
C ₄ H ₈ (1-butene)	307.4		

Example 82. Will the reaction,



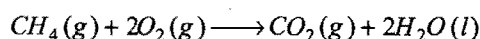
proceed spontaneously in the forward direction at 298 K, $\Delta G_f^\circ HI(g) = 1.8 \text{ kJ mol}^{-1}$, $\Delta G_f^\circ H_2S(g) = 33.8 \text{ kJ mol}^{-1}$?

Solution:

$$\begin{aligned} \Delta G^\circ &= \sum G_f^\circ (\text{products}) - \sum G_f^\circ (\text{reactants}) \\ &= [2G_f^\circ HI(g) + G_f^\circ S(s)] - [1 \times G_f^\circ I_2(s) + G_f^\circ H_2S(g)] \\ &= [2 \times 1.8 + 0] - [0 + 33.8] = -30.2 \text{ kJ} \end{aligned}$$

-ve value shows that the process is spontaneous in forward direction.

Example 83. Compute the standard free energy of the reaction at 27°C for the combustion of methane using the given data:



Species	CH ₄	O ₂	CO ₂	H ₂ O
$\Delta H_f^\circ / (\text{kJ mol}^{-1})$	-74.8	—	-393.5	-285.8
$S^\circ / (\text{J K}^{-1} \text{ mol}^{-1})$	186	205	214	70

$$\text{Solution: } \Delta H^\circ = \Delta H_f^\circ (CO_2) + 2\Delta H_f^\circ (H_2O) - \Delta H_f^\circ (CH_4)$$

$$\begin{aligned} &= -393.5 + 2 \times (-285.8) - (-74.8) \\ &= -890 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= S^\circ (CO_2) + 2S^\circ (H_2O) - S^\circ (CH_4) - 2S^\circ (O_2) \\ &= 214 + 2 \times 70 - 186 - 2 \times 205 \\ &= -242 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -890 - 300 \times (-242 \times 10^{-3}) \\ &= -890 + 72.6 = -817.4 \text{ kJ mol}^{-1} \end{aligned}$$

7.29 RELATIONSHIP BETWEEN STANDARD FREE ENERGY CHANGE (ΔG°) AND EQUILIBRIUM CONSTANT

For any reversible reaction, $A + B \rightleftharpoons C + D$, the free energy change and standard free energy change are related with each other by the following relation:

$$\Delta G = \Delta G^\circ + RT \log_e Q$$

where, R is universal constant; T is temperature and Q is reaction quotient $Q = \frac{[C][D]}{[A][B]}$.

At equilibrium state, $\Delta G = 0$ and $Q = K_{eq}$
 $0 = \Delta G^\circ + RT \log_e K_{eq}$
 or $\Delta G^\circ = -RT \log_e K_{eq}$

or

$$\Delta G^\circ = -2.303RT \log K_{eq}$$

This equation helps in the calculation of K_{eq} if ΔG° of the reaction is known and *vice-versa*. The value of K_{eq} can give an idea about the extent of chemical reaction before the equilibrium is attained.

Alternatively,

$$K = e^{-\Delta G^\circ/RT}$$

Equilibrium constant of unity implies that standard free energy change ΔG° is zero and that the positive values of ΔG° implies the equilibrium constant to be less than unit.

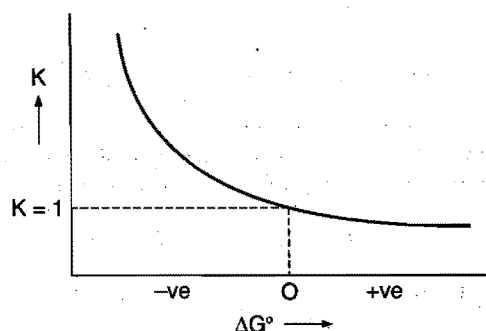


Fig. 7.21 Variation of equilibrium constant against standard free energy change

If we draw a graph of free energy against extent of reaction, we get U-shaped graph Fig. 7.22.

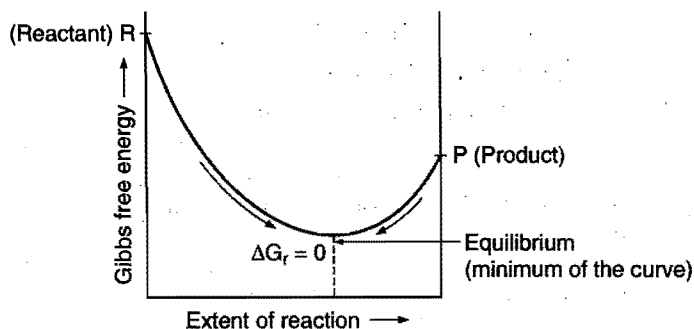


Fig. 7.22 Plot of free energy against extent of reaction

If the minimum in the curve lies closer to products, it means that reaction is in favour of products ($K \gg 1$). The reaction in this case will be closer to completion. On the other hand, if the

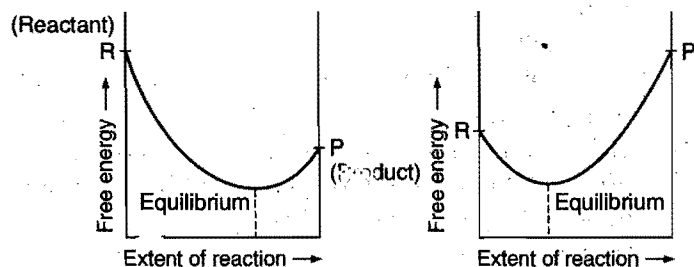
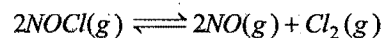


Fig. 7.23 Prediction of extent of reaction by the plot of free energy against extent of reaction

minimum in the curve lies closer to the reactants, the reaction favours reactants ($K \ll 1$). The reaction in this case will be farthest from completion. (See. Fig. 7.23)

Example 84. What is the equilibrium constant K_c for the following reaction at 400 K?



$$\Delta H^\circ = 77.2 \text{ kJ and } \Delta S^\circ = 122 \text{ J K}^{-1} \text{ at } 400 \text{ K.}$$

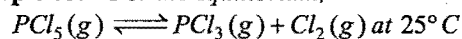
Solution: According to Gibbs-Helmholtz equation,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 77.2 - 400 \times 122 \times 10^{-3} \\ &= 28.4 \text{ kJ} = 28.4 \times 10^3 \text{ J} \end{aligned}$$

We know that, $\Delta G^\circ = -2.303RT \log K_c$

$$\begin{aligned} \therefore \log K_c &= \frac{-\Delta G^\circ}{2.303RT} = -\frac{28.4 \times 10^3}{2.303 \times 8.314 \times 400} \\ &= -3.7081 \\ K_c &= \text{antilog}(-3.7081) = 1.958 \times 10^{-4} \end{aligned}$$

Example 85. For the equilibrium,



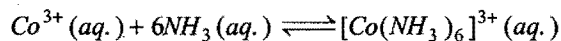
$$K_c = 1.8 \times 10^{-7}$$

Calculate ΔG° for the reaction ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

Solution: We know that,

$$\begin{aligned} \Delta G^\circ &= -2.303RT \log K_c \\ &= -2.303 \times 8.314 \times 298 \log (1.8 \times 10^{-7}) \\ &= 38484 \text{ J mol}^{-1} = 38.484 \text{ kJ mol}^{-1} \end{aligned}$$

Example 86. The equilibrium constant at 25°C for the process:



is 2×10^7 .

Calculate the value of ΔG° at 25°C . ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

In which direction, the reaction is spontaneous when the reactants and products are in standard state?

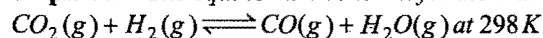
Solution: We know that, $\Delta G^\circ = -2.303RT \log K_c$

Given, $K_c = 2 \times 10^7$, $T = 298 \text{ K}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Thus, from above equation,

$$\begin{aligned} \Delta G^\circ &= -2.303 \times 8.314 \times 298 \log 2 \times 10^7 \\ &= -12023.4 \text{ J} = -12.023 \text{ kJ} \end{aligned}$$

Example 87. The equilibrium constant for the reaction,



is 73. Calculate the value of the standard free energy change ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

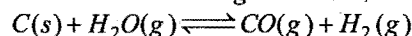
Solution: We know that, $\Delta G^\circ = -2.303RT \log K_c$

Given, $K_c = 73$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$

$\therefore$ From above equation,

$$\begin{aligned} \Delta G^\circ &= -2.303 \times 8.314 \times 298 \log 73 \\ &= -10.632 \text{ kJ} \end{aligned}$$

Example 88. For the water gas reaction,



the standard Gibbs free energy of reaction (at 1000 K) is -8.1 kJ/mol . Calculate its equilibrium constant.

Solution: We know that,

$$K = \text{antilog} \left(\frac{-\Delta G^\circ}{2.303RT} \right) \quad \dots (i)$$

Given that, $\Delta G^\circ = -8.1 \text{ kJ/mol}$

$$R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 1000 \text{ K}$$

Substituting these values in eq. (i), we get

$$K = \text{antilog} \left[\frac{-(-8.1)}{2.303 \times 8.314 \times 10^{-3} \times 1000} \right]$$

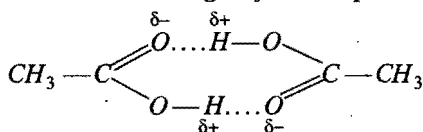
$$K = 2.65$$

Example 89. Calculate ΔG° for the conversion of oxygen to ozone, $(3/2)\text{O}_2(\text{g}) \rightleftharpoons \text{O}_3(\text{g})$ at 298 K, if K_p for this conversion is 2.47×10^{-29} .

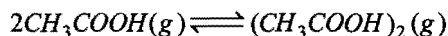
Solution: We know that,

$$\begin{aligned} \Delta G^\circ &= -2.303RT \log K_p \\ &= -2.303 \times 8.314 \times 298 \log 2.47 \times 10^{-29} \\ &= 163228 \text{ J/mol} \\ &= 163.228 \text{ kJ/mol} \end{aligned}$$

Example 90. Acetic acid CH_3COOH can form a dimer $(\text{CH}_3\text{COOH})_2$ in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5 kJ per mol of dimer



If at 25°C , the equilibrium constant for the dimerization is 1.3×10^3 . Calculate ΔS° for the reaction:



Solution: $\Delta G^\circ = -2.303 RT \log K$

$$\begin{aligned} &= -2.303 \times 8.314 \times 298 \log (1.3 \times 10^3) \\ &= -17767.688 \text{ J} = -17.767 \text{ kJ} \end{aligned}$$

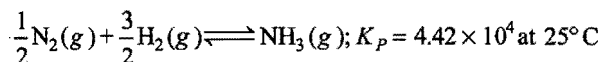
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-17.767 = -66.5 - 298 \times \Delta S^\circ$$

$$\Delta S^\circ = \frac{-66.5 + 17.767}{298} = -0.163 \text{ kJ}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

48. What is ΔG° for this reaction?



- (a) $-26.5 \text{ kJ mol}^{-1}$ (b) $-11.5 \text{ kJ mol}^{-1}$
(c) -2.2 kJ mol^{-1} (d) $-0.97 \text{ kJ mol}^{-1}$

[Ans. (a)]

[Hint: $\Delta G^\circ = -2.303RT \log K_p$

$$\begin{aligned} &= -2.303 \times 8.314 \times 298 \log (4.42 \times 10^4) \\ &= -26.5 \text{ kJ mol}^{-1} \end{aligned}$$

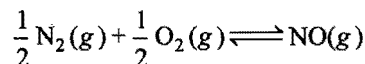
49. What is the sign of ΔG° and the value of K for an electrochemical cell for which $E^\circ_{\text{cell}} = 0.80 \text{ volt}$?

- | | ΔG° | K |
|-----|------------------|-------|
| (a) | - | > 1 |
| (b) | + | > 1 |
| (c) | + | < 1 |
| (d) | - | < 1 |

[Ans. (a)]

[Hint: $\Delta G^\circ = -nFE^\circ$; $\Delta G^\circ = -2.303RT \log K$]

50. The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K?



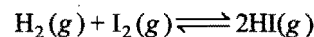
- (a) 8.4×10^{-5} (b) 7.1×10^{-9}
(c) 4.2×10^{-10} (d) 1.7×10^{-19}

[Ans. (a)]

[Hint: $K = \text{antilog} \left[\frac{-\Delta G^\circ}{2.303RT} \right]$

$$\begin{aligned} &= \text{antilog} \left[\frac{-78 \times 1000}{2.303 \times 8.314 \times 1000} \right] \\ &= 8.4 \times 10^{-5} \end{aligned}$$

51. Equilibrium constant for the reaction:



is $K_c = 50$ at 25°C .

The standard Gibbs free energy change for the reaction will be:

- (a) -6.964 kJ (b) -9.694 kJ
(c) -4.964 kJ (d) -6.496 kJ

[Ans. (b)]

[Hint: $\Delta G^\circ = -2.303RT \log K_c$

$$\begin{aligned} &= -2.303 \times 8.314 \times 298 \log 50 \\ &= -9694 \text{ J} = -9.694 \text{ kJ} \end{aligned}$$

52. Standard Gibbs free energy change ΔG° for a reaction is zero. The value of the equilibrium constant will be:

- (a) 10 (b) 1 (c) 100 (d) ∞

[Ans. (b)]

[Hint: $\Delta G^\circ = -2.303RT \log K$

When $K = 1$, $\Delta G^\circ = 0$]

53. The standard free energy change of a reaction is $\Delta G^\circ = -115 \text{ kJ}$ at 298 K. Calculate the equilibrium constant K_p in $\log K_p$. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

- (a) 20.16 (b) 2.303 (c) 2.016 (d) 13.83

(VITEEE 2008)

[Ans. (a)]

$$\begin{aligned}
 [\text{Hint: } \log K_p &= \frac{-\Delta G^\circ}{2.303 RT} \\
 &= \frac{-(-115 \times 1000)}{2.303 \times 8.314 \times 298} \\
 &= 20.16]
 \end{aligned}$$

7.30 PHYSICAL SIGNIFICANCE OF GIBBS FREE ENERGY CHANGE (Free Energy and Useful Work)

According to first law of thermodynamics,

$$\Delta E = q - w \quad \dots (i)$$

(-ve sign as the work is done by system)

Here, q is heat absorbed by the system and w is the work done by the system while ΔE is the change in internal energy. The work (w) actually includes two types of work, i.e., $w_{\text{expansion}}$ (or $P\Delta V$) and $w_{\text{non-expansion}}$ (useful work). The two types of works can be understood by taking an example of the electrolysis of water to form $H_2(g)$ and $O_2(g)$ leading to an increase in the volume of the system. The work non-expansion (non-mechanical) is done to cause the decomposition of water while the work expansion (mechanical) is due to expansion in volume of the system. Thus, the electrical work is called non-pressure-volume work or non-expansion work or non-mechanical work. The non-expansion work is also known as useful work. Thus,

$$\Delta E = q - w_{\text{expansion}} - w_{\text{non-expansion}} \quad \dots (ii)$$

$$= q - P\Delta V - w_{\text{non-expansion}} \quad (\because w_{\text{expansion}} = P\Delta V)$$

$$\text{or} \quad q = \Delta E + P\Delta V + w_{\text{non-expansion}} \quad \dots (iii)$$

We know that,

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

$$\text{or} \quad q = \Delta H + w_{\text{non-expansion}} \quad \dots (iv)$$

According to second law of thermodynamics, for a reversible change taking place at constant temperature, T

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

$$\text{or} \quad q_{\text{rev.}} = T \Delta S \quad \dots (v)$$

Substituting in equation (iv)

$$T \Delta S = \Delta H + w_{\text{non-expansion}} \quad \dots (vi)$$

$$\text{or} \quad \Delta H - T \Delta S = -w_{\text{non-expansion}}$$

$$\text{or} \quad \Delta G = -w_{\text{non-expansion}} \quad (\because \Delta H - T \Delta S = \Delta G)$$

$$\text{or} \quad -\Delta G = w_{\text{non-expansion}} = w_{\text{useful work}} \quad \dots (vii)$$

Thus, the decrease in Gibbs free energy is a measure of useful work or non-expansion work done by the system. The greater the free energy change, the greater is the amount of work that can be obtained from the process. This relation is useful in assessing the electrical work that may be produced by electrochemical cells and fuel cells.

Free Energy Change and Electrical Work Done in a Cell

Free energy change in electrochemical cells is related to the electrical work done in the cell.

ΔG and emf of the cell (E) are related by the following relation:

$$\Delta G = -nFE$$

where, F = faraday = 96500 coulomb

E = emf of the cell

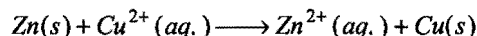
n = Number of moles of electrons involved in balanced electrochemical reaction

If the reactants and products are in their standard states, then

$$\Delta G^\circ = -nFE^\circ$$

when E° = standard emf of the cell.

Example 91. The emf of the cell reaction,



is 1.1 V. Calculate free energy change for the reaction. If enthalpy of the reaction is $-216.7 \text{ kJ mol}^{-1}$, calculate the entropy change for the reaction.

$$\text{Solution: } -\Delta G^\circ = n \times F \times E^\circ = 2 \times 96500 \times 1.1 = 212.3 \text{ kJ}$$

$$\Delta G^\circ = -212.3 \text{ kJ mol}^{-1}$$

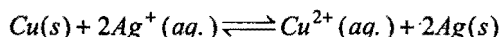
$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-216.7 - (-212.3)}{298}$$

$$= -0.01476 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$= -14.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example 92. Calculate equilibrium constant for the following reaction:



At 25°C , $E_{\text{cell}}^\circ = 0.47 \text{ volt}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $F = 96500 \text{ coulomb}$.

Solution: Let us apply Nernst equation at equilibrium

$$E_{\text{cell}}^\circ = \frac{0.0591}{n} \log K_c$$

$$0.47 = \frac{0.0591}{2} \log K_c$$

$$\begin{aligned}
 K_c &= \text{antilog} \left[\frac{0.47 \times 2}{0.0591} \right] \\
 &= 8.5 \times 10^{15}
 \end{aligned}$$

7.31 ABSOLUTE ENTROPIES AND THIRD LAW OF THERMODYNAMICS

Third law of Thermodynamics was given by T.W. Richards, Walter Nernst and Max Planck. Some statements for third law of thermodynamics are given below:

Statement-1. "Every substance has a finite positive entropy but at the absolute zero temperature the entropy may become zero and does so become in the case of perfectly crystalline solids."

Because

Statement-2. "Entropy of a solid or liquid approaches zero at the absolute zero of temperature."

It can be mathematically expressed as

$$\lim_{T \rightarrow 0 \text{ K}} S \rightarrow 0$$

Because

Statement-3. "It is impossible by any method, no matter how idealised it is, to reduce the temperature of any system to the absolute zero in a finite number of operations."

Application of Third Law of Thermodynamics

The third law of thermodynamics has been useful in calculating the absolute entropies of solids, liquids and gases at different temperatures. Moreover, this law is also useful to calculate entropy changes of a chemical or physical process. Let us calculate absolute entropy.

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

$$dS = C_P \frac{dT}{T}$$

On integrating the above equation between temperature limits of 0 and T K, we get

$$S_T - S_0 = \int_0^T C_P \frac{dT}{T}$$

or
$$S_T - S_0 = \int_0^T C_P d \ln T$$

From third law of thermodynamics, $S_0 = 0$

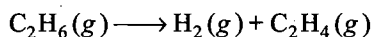
$$\therefore S_T = \int_0^T C_P d \ln T$$

When entropy of one mole of a substance is expressed at 298 K and 1 atm pressure, it is called **standard entropy** of that substance. It is denoted by S° . The standard entropy change ΔS° for a chemical reaction can be calculated as

$$\Delta S^\circ = \sum S^\circ_{(\text{products})} - \sum S^\circ_{(\text{reactants})}$$

$$= \left[\text{Sum of the standard entropies of products} \right] - \left[\text{Sum of the standard entropies of reactants} \right]$$

e.g., in the reaction:



$$\Delta S^\circ = \sum S^\circ_{(\text{products})} - \sum S^\circ_{(\text{reactants})}$$

$$= [S^\circ_{\text{H}_2} + S^\circ_{\text{C}_2\text{H}_4}] - [S^\circ_{\text{C}_2\text{H}_6}]$$

Standard molar entropies in J/K mol at 298 K

Solids	Entropy	Solids	Entropy
C (graphite)	5.7	N ₂	191.6
C (diamond)	2.4	O ₂	205.1
Fe	27.3	CO ₂	213.7
Pb	64.8	NO ₂	240.1
Cu	33.1	N ₂ O ₄	304.3
Al	96.2	NH ₃	192.3
Fe ₂ O ₃	87.4	CH ₄	186.2

CuSO ₄ · 5H ₂ O	300.4	Hg	76.0
C ₁₂ H ₂₂ O ₁₁ (sucrose)	360.8	H ₂ O	69.9
CaO	39.8	C ₂ H ₅ OH	160.7
CaCO ₃ (calcite)	92.9	C ₆ H ₆	173.3
H ₂	130.7	CH ₃ COOH	159.8

Tephigraph

Graph of entropy of a substance against temperature is called tephigraph. In the following graph variation of entropy with temperature is represented:

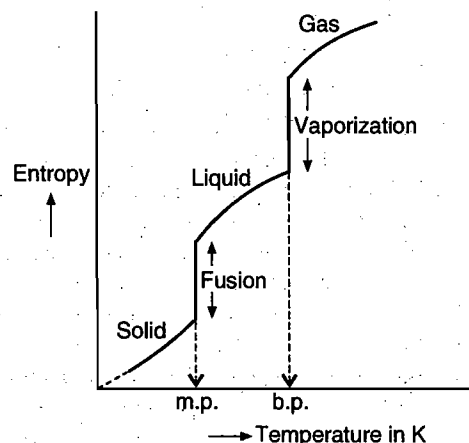
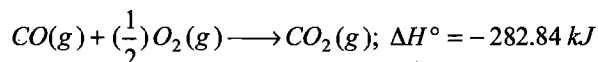


Fig. 7.24

From the graph it is clear that entropy of a substance increases with increase in temperature; there is sudden change in entropy at the stage of phase transformation.

Example 93. Calculate ΔG° for the following reaction:



Given,

$$S^\circ_{\text{CO}_2} = 213.8 \text{ J K}^{-1} \text{ mol}^{-1}, S^\circ_{\text{CO}(\text{g})} = 197.9 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$S^\circ_{\text{O}_2} = 205.0 \text{ J K}^{-1} \text{ mol}^{-1}.$$

Solution:
$$\Delta S^\circ = \sum S^\circ_{(\text{products})} - \sum S^\circ_{(\text{reactants})}$$

$$= [S^\circ_{\text{CO}_2}] - [S^\circ_{\text{CO}} + \frac{1}{2} S^\circ_{\text{O}_2}]$$

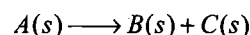
$$= 213.8 - [197.9 + \frac{1}{2} \times 205]$$

$$= -86.6 \text{ J K}^{-1}$$

According to Gibbs-Helmholtz equation,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -282.84 - 298 \times (-86.6 \times 10^{-3}) \\ &= -282.84 + 25.807 \\ &= -257.033 \text{ kJ} \end{aligned}$$

Example 94. For the reaction;



calculate the entropy change at 298 K and 1 atm if absolute entropies (in $\text{J K}^{-1} \text{ mol}^{-1}$) are:

$$A = 130, B = 203, C = 152$$

Solution: $\Delta S^\circ = \sum S^\circ_{(\text{products})} - \sum S^\circ_{(\text{reactants})}$

$$= [S^\circ_B + S^\circ_C] - [S^\circ_A]$$

$$= [203 + 152] - [130]$$

$$= 225 \text{ J K}^{-1}$$

7.32 CONVERSION OF HEAT INTO WORK—THE CARNOT CYCLE

Carnot, a French engineer, in 1824, employed merely theoretical and an imaginary reversible cycle known as Carnot cycle to demonstrate the maximum convertibility of heat into work.

The system consists of one mole of an ideal gas enclosed in a cylinder fitted with a piston which is subjected to a series of four successive operations. The four operations are:

- (i) Isothermal reversible expansion
- (ii) Adiabatic reversible expansion
- (iii) Isothermal reversible compression
- (iv) Adiabatic reversible compression

The four operations have been shown in Fig. 7.25.

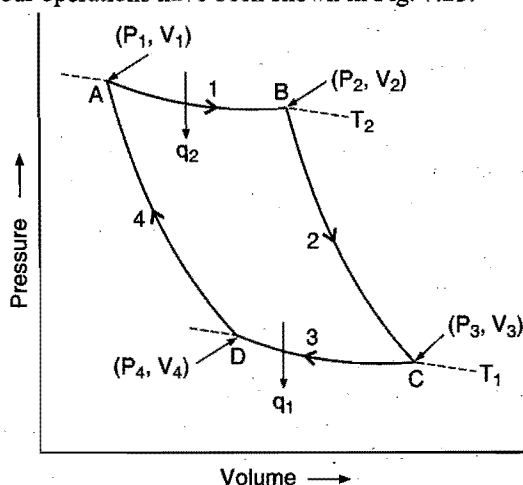


Fig. 7.25

First operation—Isothermal reversible expansion

The gas is allowed to expand reversibly and isothermally at the temperature T_2 through AB path. The volume V_1 (point A) increases to volume V_2 (point B). In this operation, let the heat absorbed by the system be q_2 (+ve) and the work done by the system on the surroundings be w_1 (-ve).

Since, the expansion is isothermal, $\Delta E = 0$. The heat absorbed, q_2 , should be equal to the work done by the system on the surroundings, i.e.,

$$q_2 = -w_1 = RT_2 \log_e \frac{V_2}{V_1} \quad \dots (i)$$

Second operation—Adiabatic reversible expansion

The gas is now allowed to expand reversibly and adiabatically through BC path. The volume increases from V_2 (point B) to

volume V_3 (point C). In this operation, no heat is absorbed and thus, the work, w_2 , is done by the system at the expense of internal energy, i.e., the temperature of the system falls from temperature T_2 to temperature T_1 .

$$\Delta E = -w_2 = -C_V (T_2 - T_1) \quad \dots (ii)$$

Third operation—Isothermal reversible compression

The gas at point C is subjected to reversible isothermal compression at temperature T_1 . The path followed is CD when the volume decreases from V_3 to V_4 (point D). In this operation work is done on the system and heat q_1 is given out by the system to surroundings.

$$-q_1 = w_3 = RT_1 \log_e \frac{V_4}{V_3} \quad \dots (iii)$$

Fourth operation—Adiabatic reversible compression

Finally, the gas at point D is subjected to reversible adiabatic compression through the path DA at temperature T_1 . The volume changes from V_4 to V_1 , i.e., the original volume is restored. The temperature increases from T_1 to T_2 (original temperature). The work done increases the internal energy of the system as $q = 0$

$$w_4 = C_V (T_2 - T_1) \quad \dots (iv)$$

The net heat absorbed, q , by the ideal gas in the cycle is given by

$$q = q_2 + (-q_1) = RT_2 \log_e \frac{V_2}{V_1} + RT_1 \log_e \frac{V_4}{V_3}$$

$$= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} \quad \dots (v)$$

According to the expression governing adiabatic changes,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2} \right)^{\gamma-1} \quad (\text{For adiabatic expansion})$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_4} \right)^{\gamma-1} \quad (\text{For adiabatic compression})$$

$$\text{or } \frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\text{or } \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substituting the value of $\frac{V_3}{V_4}$ in eq. (v),

$$q = q_2 - q_1 = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1}$$

$$= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \quad \dots (vi)$$

Similarly, net work done by the gas is given by

$$w = -w_1 - w_2 + w_3 + w_4$$

$$\begin{aligned}
 &= RT_2 \log_e \frac{V_2}{V_1} - C_V (T_2 - T_1) \\
 &\quad + RT_1 \log_e \frac{V_4}{V_3} - C_V (T_2 - T_1) \\
 &= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} \\
 &= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1} \\
 &= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \quad \dots \text{(vii)}
 \end{aligned}$$

Thus, $q = w$. For cyclic process, the essential condition is that net work done is equal to heat absorbed. This condition is satisfied in a Carnot cycle.

Calculation of thermodynamic efficiency of Carnot engine

Total work done from eq. (vii),

$$w = R(T_2 - T_1) \log_e \frac{V_2}{V_1}$$

and the heat absorbed at temperature T_2 from eq. (i),

$$q_2 = RT_2 \log_e \frac{V_2}{V_1}$$

Dividing both equations,

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = \text{Thermodynamic efficiency}$$

Thus, the larger the temperature difference between high and low temperature reservoirs, the more the heat converted into work by the heat engine.

Since, $\frac{T_2 - T_1}{T_2} < 1$, it follows that $w < q_2$. This means that only

a part of heat absorbed by the system at the higher temperature is transformed into work. The rest of the heat is given out to surroundings. The efficiency of the heat engine is always less than 1. This has led to the following enunciation of the second law of thermodynamics.

It is impossible to convert heat into work without compensation.

Example 95. Calculate the maximum efficiency of an engine operating between 100°C and 25°C .

Solution: Efficiency = $\frac{T_2 - T_1}{T_2}$

$$T_2 = 100 + 273 = 373\text{ K}$$

$$T_1 = 25 + 273 = 298\text{ K}$$

$$\text{Efficiency} = \frac{373 - 298}{373} = \frac{75}{373} = 0.20 = 20\%$$

Example 96. Heat supplied to a Carnot engine is 453.6 kcal. How much useful work can be done by the engine which works between 10°C and 100°C ?

Solution: $T_2 = 100 + 273 = 373\text{ K}$; $T_1 = 10 + 273 = 283\text{ K}$;

$$q_2 = 453.6 \times 4.184 = 1897.86\text{ kJ}$$

We know that,

$$\begin{aligned}
 w &= q_2 \cdot \frac{T_2 - T_1}{T_2} \\
 &= 1897.86 \times \frac{(373 - 283)}{373} \\
 &= \frac{1897.86 \times 90}{373} = 457.92\text{ kJ}
 \end{aligned}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

54. For which of the following reactions, the entropy change will be positive? [JEE (WB) 2008]

- (a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 (b) $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s})$
 (c) $\text{NH}_4\text{NO}_3(\text{s}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
 (d) $\text{MgO}(\text{s}) + \text{H}_2(\text{g}) \rightleftharpoons \text{Mg}(\text{s}) + \text{H}_2\text{O}(\text{l})$

[Ans. (c)]

[Hint: $\Delta n_g = 3 - 0 = 3$,

Since $\Delta n_g > 0$, there will be increase in entropy change.]

55. If an endothermic reaction occurs spontaneously at constant temperature T and pressure P , then which of the following is true? (VITEEE 2008)

- (a) $\Delta G > 0$ (b) $\Delta H < 0$ (c) $\Delta S > 0$ (d) $\Delta S < 0$

[Ans. (c)]

[Hint: $\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$\Delta S > 0$ for spontaneous process.]

56. Which is the correct expression that relates changes of entropy with the change of pressure for an ideal gas at constant temperature, among the following?

[PET (MP) 2008]

- (a) $\Delta S = nRT \ln \frac{P_2}{P_1}$ (b) $\Delta S = T (P_2 - P_1)$
 (c) $\Delta S = nR \ln \left(\frac{P_1}{P_2} \right)$ (d) $\Delta S = 2.303 nRT \ln \left(\frac{P_1}{P_2} \right)$

[Ans. (c)]

[Hint: From first law, $\Delta U = q - W$

$$0 = q - W \quad (\text{for isothermal process})$$

$$q = W = PdV$$

$$dS = \frac{q}{T} = \frac{PdV}{T}$$

$$dS = nR \frac{dV}{V}$$

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

$$\Delta S = nR \ln \left(\frac{P_1}{P_2} \right). \text{ Since } P_1 V_1 = P_2 V_2 \text{ according to Boyle's law.}]$$

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. Bond dissociation enthalpies of $H_2(g)$ and $N_2(g)$ are $436.0 \text{ kJ mol}^{-1}$ and $941.8 \text{ kJ mol}^{-1}$ and enthalpy of formation of $NH_3(g)$ is -46 kJ mol^{-1} . What is enthalpy of atomization of $NH_3(g)$? What is the average bond enthalpy of N—H bond?

Solution: $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$;

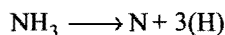
$$\Delta H = -2 \times 46 \text{ kJ/mol}$$

$$\Delta H = \Sigma(BE)_R - \Sigma(BE)_P$$

$$= (941.8 + 3 \times 436) - (6x) = -2 \times 46$$

(Here, x = BE of N—H bonds)

$$x = 390.3 \text{ kJ mol}^{-1}$$



$$\text{Heat of atomization} = 3 \times 390.3 = 1170.9 \text{ kJ mol}^{-1}$$

Example 2. Ethanol was oxidised to acetic acid in a catalyst chamber at 18°C . Calculate the rate of removal of heat to maintain the reaction chamber at 18°C with the feed rate of 30 kg per hour ethanol along with excess oxygen to the system at 18°C , given that a 42 mole per cent yield based on ethanol is obtained. Given that,

$$\Delta H_{f, H_2O(l)} = -68.4 \text{ kcal mol}^{-1}$$

$$\Delta H_{f, C_2H_5OH(l)} = -66 \text{ kcal mol}^{-1}$$

$$\Delta H_{f, CH_3COOH(l)} = -118 \text{ kcal mol}^{-1}$$

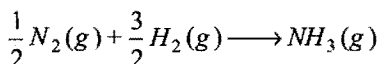
Solution: $C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O$

$$\Delta H = \Sigma(H_f)_P - \Sigma(H_f)_R = (-118 - 68.4) - (-66) = -120.4 \text{ kcal}$$

Yield is 42%. Thus, energy produced per hour will be

$$= \frac{120.4 \times 42 \times 30000}{100 \times 46} = 32979.13 \text{ kcal hour}^{-1}$$

Example 3. The standard heat of formation listed for gaseous NH_3 is -11.02 kcal/mol at 298 K . Given that at 298 K , the constant pressure heat capacities of gaseous N_2 , H_2 and NH_3 are respectively 6.96, 6.89, 8.38 cal/mol. Determine $\Delta H_{298 \text{ K}}^\circ$ and $\Delta H_{773 \text{ K}}$ for the reaction,



Solution: $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

$$\Delta H_{298 \text{ K}} = \Sigma(H_f)_P - \Sigma(H_f)_R = (-11.02 - 0)$$

$$= -11.02 \text{ kcal mol}^{-1}$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

$$\frac{\Delta H_2 - (-11.02)}{773 - 298} = (8.38 - \frac{1}{2} \times 6.96 - \frac{3}{2} \times 6.89) \times 10^{-3}$$

$$\Delta H_2 = -13.6 \text{ kcal mol}^{-1}$$

Example 4. The heat of combustion of glycogen is about 476 kJ/mol of carbon. Assume that average rate of heat loss by an adult male is 150 watt. If we were to assume that all the heat comes from oxidation of glycogen, how many units of glycogen (1 mole carbon per unit) must be oxidised per day to provide for this heat loss?

Solution: Total energy required in the day

$$= \frac{150 \times 24 \times 60 \times 60}{1000} \text{ kJ} \quad (1 \text{ watt} = 1 \text{ J sec}^{-1})$$

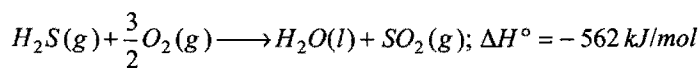
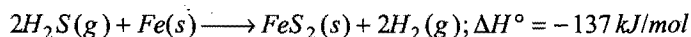
$$= 12960 \text{ kJ}$$

$$\text{Units of glycogen required} = \frac{12960}{476} = 27.22 \text{ units}$$

Example 5. At 25°C , the following heat of formations are given:

Compound	$SO_2(g)$	$H_2O(l)$
$\Delta H_f^\circ \text{ kJ/mol}$	-296.81	-285.83

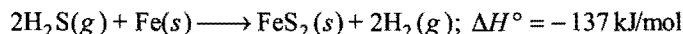
For the reactions at 25°C ,



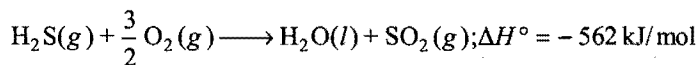
Calculate heat of formation of $H_2S(g)$ and $FeS_2(s)$ at 25°C .

Solution: Heat of formation of $H_2S = x \text{ kJ/mol}$

Heat of formation of $FeS_2 = y \text{ kJ/mol}$



$$-137 = y - 2x \quad \dots (i)$$



$$-562 = -285.83 - 296.81 - x \quad \dots (ii)$$

$$\text{From eq. (ii), } x = -20.64 \text{ kJ mol}^{-1}$$

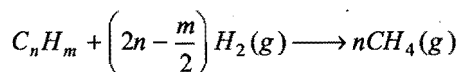
From eq. (i), we get

$$y = 2x - 137 = 2(-20.64) - 137 = -178.28 \text{ kJ mol}^{-1}$$

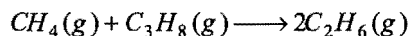
$$\Delta H_{f, H_2S} = 20.64 \text{ kJ/mol}$$

$$\Delta H_{f, FeS_2} = -178 \text{ kJ/mol}$$

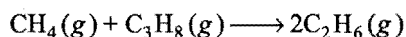
Example 6. The "heat of total cracking" of hydrocarbons ΔH_{TC} is defined as ΔH at 298.15 K and 101.325 kPa for the process below:



Given that, ΔH_{TC} is -65.2 kJ for C_2H_6 and -87.4 kJ for C_3H_8 , calculate ΔH for



Solution: ΔH_{TC} of $CH_4 = 0$



$$\begin{aligned}\Delta H &= 2\Delta H_{TC}(C_2H_6) - \Delta H_{TC}(C_3H_8) \\ &= 2(-65.2) - (-87.4) = -43 \text{ kJ}\end{aligned}$$

Example 7. A constant pressure calorimeter consists of an insulated beaker of mass 92 g made up of glass with heat capacity $0.75 \text{ J K}^{-1} \text{ g}^{-1}$. The beaker contains 100 mL of 1 M HCl at 22.6°C to which 100 mL of 1M NaOH at 23.4°C is added. The final temperature after the reaction is complete at 29.3°C . What is ΔH per mole for this neutralization reaction? Assume that the heat capacities of all solutions are equal to that of same volumes of water.

Solution: Initial average temperature of the acid and base

$$= \frac{22.6 + 23.4}{2} = 23.0^\circ\text{C}$$

Rise in temperature $= (29.3 - 23.0) = 6.3^\circ\text{C}$

Total heat produced $= (92 \times 0.75 + 200 \times 4.184) \times 6.3$

$$= (905.8) \times 6.3 = 5706.54 \text{ J}$$

Enthalpy of neutralization $= -\frac{5706.54}{100} \times 1000 \times 1$

$$= -57065.4 \text{ J} = -57 \text{ kJ}$$

Example 8. $C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$

$$\Delta H = -270.6 \text{ kJ mol}^{-1} \text{ K}^{-1}; \Delta S = -139 \text{ JK}^{-1}$$

(i) Is the reaction favoured by entropy, enthalpy both or none?

(ii) Find ΔG if $T = 300 \text{ K}$. [CBSE (Mains) 2005]

Solution: (i) Since, $\Delta H = -ve$, exothermic process and is favoured, i.e., it will be spontaneous.

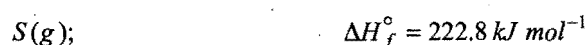
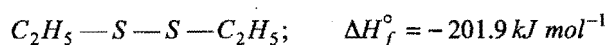
(ii) $\Delta G = \Delta H - T\Delta S$

$$= -270.6 \times 1000 - 300 \times (-139)$$

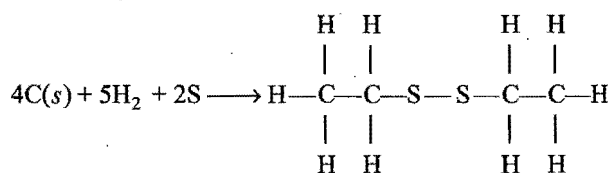
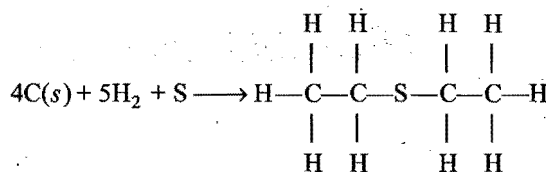
$$= -228900 \text{ J}$$

$$= -228.9 \text{ kJ}$$

Example 9. Find bond enthalpy of S—S bond from the following data:



Solution:



$$\Delta H = \Sigma(\text{BE})_R - \Sigma(\text{BE})_P$$

(i) $-147.2 =$ Heat of atomization of 4C, 10H, 1S

$$- \text{BE of } 10(\text{C}-\text{H}), 2(\text{C}-\text{S}), 2(\text{C}-\text{C})$$

(ii) $-201.9 =$ Heat of atomization of 4C, 10H, 2S

$$- \text{BE of } 10(\text{C}-\text{H}), 2(\text{C}-\text{S}), 2(\text{C}-\text{C}), (\text{S}-\text{S})$$

Subtracting (i) from (ii),

$$\begin{aligned}-201.9 + 147.2 &= \text{Heat of atomization of 1S} - \text{BE of } (\text{S}-\text{S}) \\ &= 222.8 \text{ kJ} - \text{BE of } (\text{S}-\text{S})\end{aligned}$$

$$\text{BE of } (\text{S}-\text{S}) = 277.5 \text{ kJ}$$

Example 10. A natural gas may be assumed to be a mixture of methane and ethane only. On complete combustion of 10 litre of gas at STP, the heat evolved was 474.6 kJ. Assuming $\Delta H_{\text{comb}} CH_4(g) = -894 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{comb}} C_2H_6 = -1500 \text{ kJ}$. Calculate the percentage composition of the mixture by volume.

Solution:

$$x \text{ litre} \longrightarrow CH_4; \text{ mole of } CH_4 = x/22.4$$

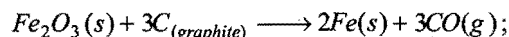
$$(10-x) \text{ litre} \longrightarrow C_2H_6; \text{ mole of } C_2H_6 = (10-x)/22.4$$

$$\text{Heat evolved} = \frac{x}{22.4} \times 894 + \frac{(10-x)}{22.4} \times 1500$$

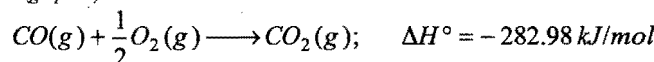
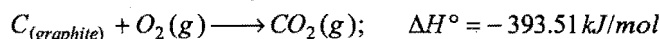
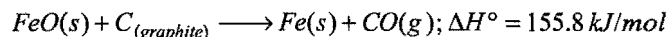
$$474.6 = \frac{x}{22.4} \times 894 + \frac{(10-x)}{22.4} \times 1500$$

$$x = 0.745, \quad \% CH_4 = 74.5\%$$

Example 11. From the data at 25°C :

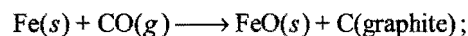


$$\Delta H^\circ = 492.6 \text{ kJ/mol}$$

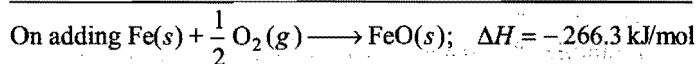
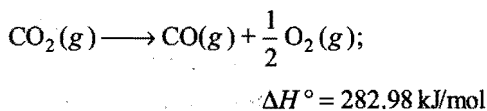
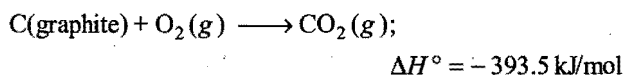


Calculate standard heat of formation of $FeO(s)$ and $Fe_2O_3(s)$.

Solution:

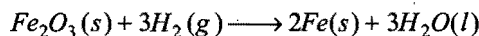


$$\Delta H^\circ = -158.88 \text{ kJ/mol}$$



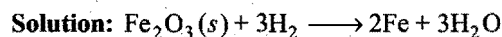
Similarly we may calculate heat of formation of Fe_2O_3 .

Example 12. Calculate, the ΔH at 85°C for the reaction:



The data are: $\Delta H_{298}^\circ = -33.29 \text{ kJ/mol}$ and

Substance	$\text{Fe}_2\text{O}_3(\text{s})$	$\text{Fe}(\text{s})$	$\text{H}_2\text{O}(\text{l})$	$\text{H}_2(\text{g})$
$C_p^\circ \text{ J/K mol}$	103.8	25.1	75.3	28.8



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

$$= (2 \times 25.1 + 3 \times 75.3) - (103.8 + 3 \times 28.8)$$

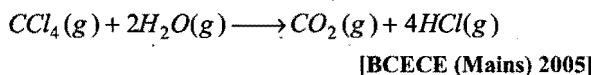
$$= 276.1 - 190.2 = 85.9 \text{ J}$$

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

$$\frac{\Delta H_{358} - (-33.29)}{358 - 298} = 85.9 \times 10^{-3}$$

$$\Delta H_{358} = -28.14 \text{ kJ/mol}$$

Example 13. The standard heats of formation at 298 K for $\text{CCl}_4(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{HCl}(\text{g})$ are -25.5 , -57.8 , -94.1 and $-22.1 \text{ kcal mol}^{-1}$ respectively, calculate ΔH_{298}° for the reaction:



Solution:

$$\Delta H_{\text{reaction}} = \Sigma \text{Heat of formation of products}$$

$$- \Sigma \text{Heat of formation of reactants}$$

$$= [\Delta H_f(\text{CO}_2) + 4\Delta H_f(\text{HCl})] - [\Delta H_f(\text{CCl}_4) + 2\Delta H_f(\text{H}_2\text{O})]$$

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

$$= -41.4 \text{ kcal}$$

Example 14. Calculate Q , W , ΔE and ΔH for the isothermal reversible expansion of 1 mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K . (IIT 2000)

Solution: In isothermal process as temperature remains constant both ΔE and ΔH are zero.

$$\Delta E = 0; \Delta H = 0$$

Applying first law of thermodynamics,

$$\Delta E = W + Q$$

$$0 = W + Q$$

or

$$Q = -W = -2.303 nRT \log \left(\frac{P_1}{P_2} \right)$$

$$= -2.303 \times 1 \times 8.314 \times 273 \log \left(\frac{1}{0.1} \right)$$

$$= 5227.169 \text{ J} = 5.227 \text{ kJ}$$

Example 15. A sample of argon at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3 . Calculate the enthalpy change in this process. $C_{v,m}$ for argon is $12.48 \text{ J K}^{-1} \text{ mol}^{-1}$. (IIT 2000)

Solution: Number of moles of argon present in the sample

$$= \frac{PV}{RT} = \frac{1.25 \times 1}{0.0821 \times 300} = 0.05075$$

For adiabatic expansion,

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

or

$$\frac{300}{T_2} = \left(\frac{2.50}{1.25} \right)^{1.66-1}$$

or

$$T_2 = 188.55 \text{ K}$$

$$C_p = C_v + R$$

$$= 12.48 + 8.314$$

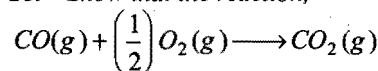
$$= 20.794 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H = n \times C_p \times \Delta T$$

$$= 0.05075 \times 20.794 \times (300 - 188.55)$$

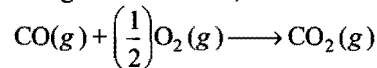
$$= 117.6 \text{ J}$$

Example 16. Show that the reaction,



at 300 K is spontaneous and exothermic, when the standard entropy change is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$ respectively. (IIT 2000)

Solution: The given reaction is,



$$\Delta G^\circ (\text{for reaction}) = G_{\text{CO}_2}^\circ - G_{\text{CO}}^\circ - \left(\frac{1}{2} \right) G_{\text{O}_2}^\circ$$

$$= -394.4 - (-137.2) - 0$$

$$= -257.2 \text{ kJ mol}^{-1}$$

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

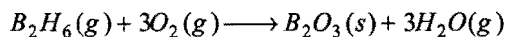
$$-257.2 = \Delta H^\circ - 298 \times (0.094)$$

or

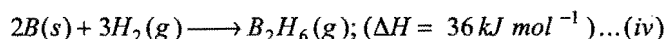
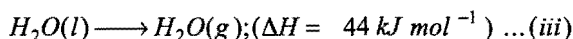
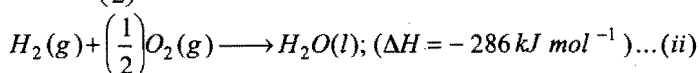
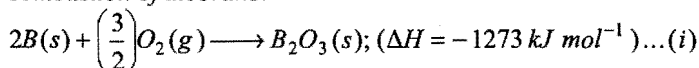
$$\Delta H^\circ = -288.2 \text{ kJ}$$

ΔG° is $-ve$, hence the process is spontaneous, and ΔH° is also $-ve$, hence the process is also exothermic.

Example 17. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

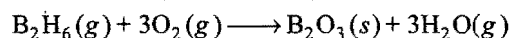


From the following data, calculate the enthalpy change for the combustion of diborane:



(IIT 2000)

Solution: The required equation,



can be obtained from

$$\text{eq. (i)} + 3\text{eq. (ii)} + 3\text{eq. (iii)} - \text{eq. (iv)}$$

$$= -1273 - 858 + 132 - 36$$

$$= -2035 \text{ kJ mol}^{-1}$$

i.e., Enthalpy of combustion of diborane is $-2035 \text{ kJ mol}^{-1}$.

Example 18. An insulated container contains 1 mole of a liquid, molar volume 100 mL at 1 bar. When liquid is steeply passed to 100 bar, volume decreases to 99 mL. Find ΔH and ΔU for the process. [IIT 2004 (Memory based)]

Solution: From first law of thermodynamics:

$$\Delta U = q + W$$

$$\Delta U = q + P \Delta U = 0 + \{-100(99 - 100)\}$$

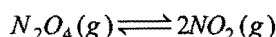
$$= 100 \text{ bar mL}$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

$$= 100 + (100 \times 99 - 1 \times 100)$$

$$= 9900 \text{ bar mL}$$

Example 19. In the following equilibrium:



when 5 mole of each are taken and temperature is kept at 298 K, the total pressure was found to be 20 bar.

$$\text{Given: } \Delta G_f^\circ N_2O_4 = 100 \text{ kJ}$$

$$\Delta G_f^\circ NO_2 = 50 \text{ kJ}$$

(i) Find ΔG of the reaction at 298 K.

(ii) Find the direction of the reaction.

(IIT 2004 (Memory based))

Solution: The reaction is:



Since, number of moles of both N_2O_4 and NO_2 are same hence their partial pressure will also be same.

$$p_{N_2O_4} = p_{NO_2} = \frac{20}{2} = 10 \text{ bar}$$

$$Q_P = \frac{[p_{NO_2}]^2}{[p_{N_2O_4}]} = \frac{10^2}{10} = 10 \text{ bar}$$

$$\Delta G_{\text{reaction}}^\circ = 2\Delta G_f^\circ NO_2 - \Delta G_f^\circ N_2O_4$$

$$= 2 \times 50 - 100 = 0$$

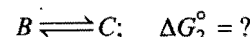
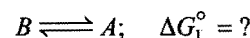
$$\text{We know that, } \Delta G = \Delta G^\circ - 2.303 RT \log Q$$

$$= 0 - 2.303 \times 8.314 \times 298 \log 10$$

$$= -5705 \text{ J}$$

Since, ΔG is negative hence reaction will be spontaneous in forward direction.

Example 20. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C , it is slowly converted into an equilibrium mixture of 1.3% of 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at 175°C . Calculate ΔG° for the following equilibria:

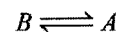


From the calculated value of ΔG_1° and ΔG_2° indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C). (IIT 2001)

Solution: Pentyne-1 $\rightleftharpoons$ Pentyne-2 + 1, 2-pentadiene

	(A)	(B)	(C)
t_{eq}	1.3	95.2	3.5

$$K_{\text{eq}} = \frac{[B][C]}{[A]} = \frac{95.2 \times 3.5}{1.3} = 256.31$$



$$K_1 = \frac{[A]}{[B]} = \frac{[C]}{K_{\text{eq}}} = \frac{3.5}{256.31} = 0.013$$

$$\Delta G_1^\circ = -2.303RT \log K_1$$

$$= -2.303 \times 8.314 \times 448 \log 0.013$$

$$= 16178 \text{ J} = 16.178 \text{ kJ}$$

for



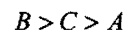
$$K_2 = \frac{[C]}{[B]} = \frac{K_{\text{eq}}[A]}{[B]^2} = \frac{256.31 \times 1.3}{(95.2)^2} = 0.037$$

$$\Delta G_2^\circ = -2.303RT \log K_2$$

$$= -2.303 \times 8.314 \times 448 \log 0.037$$

$$= 12282 \text{ J} = 12.282 \text{ kJ}$$

Stability will lie in the order



Example 21. Two moles of a perfect gas undergo the following process:

(a) A reversible isobaric expansion from (1 atm 20 L) to (1 atm 40 L).

(b) A reversible isochoric change of state from (1 atm 40 L) to (0.5 atm 40 L).

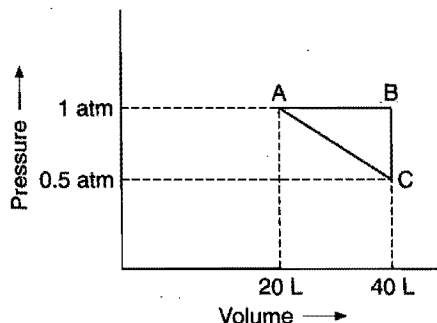
(c) A reversible isothermal compression from (0.5 atm 40 L) to (1 atm 20 L).

(i) Sketch with labels each of the process on the same P-V diagram.

(ii) Calculate the total work (W) and the total heat change (q) involved in the above process.

(iii) What will be the value of ΔU , ΔH and ΔS for the overall process? (IIT 2002)

Solution:



$AB \rightarrow$ Isobaric process

$BC \rightarrow$ Isochoric process

$CA \rightarrow$ Isothermal compression

$$\text{Total work} = W_{AB} + W_{BC} + W_{CA}$$

$$= -P \times \Delta V + 0 + 2.303 nRT \log \left(\frac{V_2}{V_1} \right)$$

$$= -1 \times 20 \times 101.3 + 0$$

$$+ 2.303 \times 2 \times 8.314 \times T \log \left(\frac{40}{20} \right) \quad \dots (1)$$

$$PV = nRT \text{ (At A)}$$

$$1 \times 20 = 2 \times 0.0821 \times T$$

$$T = \frac{20}{2 \times 0.0821} = 121.8 \text{ K}$$

From eq. (1),

$$\text{Total work} = -2026 + 2.303 \times 2 \times 8.314 \times 121.8 \log 2$$

$$= -622.06 \text{ J}$$

$$W = q = -622.06 \text{ J}$$

In cyclic process:

$$\Delta U = 0, \Delta H = 0 \text{ and } \Delta S = 0$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. **Thermodynamics:** It is the branch of science which deals with all changes in energy or transfer of energy that accompany physical and chemical processes. It is not concerned with the total energy of body but only with energy changes taking place. The laws of thermodynamics apply only to matter in bulk, i.e., to macroscopic system and not to individual atoms or molecules.

2. **Terms used in thermodynamics:**

(a) **System, surroundings and boundary:** A **system** is defined as a specified part of the universe which is under experimental investigation and the rest of the universe which can interact with the system is **surroundings**. Anything which separates system and surroundings is called **boundary**. It may be real or imaginary, conductor or non-conductor.

(b) **Types of system:** There are three types of system:

(i) **Isolated system** is one which has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surroundings. (ii) **Closed system** is one which can exchange energy but not matter with surroundings. (iii) **Open system** is one which can exchange matter as well as energy with surroundings. A system is said to be **homogeneous** if it is made of one-phase only. A system is said to be **heterogeneous** when it consists of two or more phases.

(c) **Thermodynamic properties:** These are of two types:

(i) **Intensive properties** are those which do not depend upon the quantity of matter present in the system such as pressure, temperature, specific heat, surface tension, viscosity, melting and

boiling points, etc. (ii) **Extensive properties** are those whose magnitude depends upon the quantity of matter present in the system such as volume, total energy, enthalpy, entropy, etc.

(d) **State variables:** The fundamental properties which determine the state of the system are termed **state variables**. The change in state property depends only upon the initial and final states of the system, i.e., do not depend on the path followed. Pressure, volume, temperature, internal energy, enthalpy, entropy, force, energy and number of moles are the state variables.

(e) **Thermodynamic equilibrium:** A system in which the fundamental properties do not undergo any change with time is said to be in thermodynamic equilibrium. Actually the system should be in thermal equilibrium, mechanical equilibrium and chemical equilibrium.

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

(i) **Isothermal:** Temperature remains fixed, i.e., $dT = 0$. This is achieved by placing the system in a thermostat.

(ii) **Adiabatic:** When no exchange of heat occurs between the system and surroundings, i.e., the system is thermally isolated ($dq = 0$).

(iii) **Isobaric:** Pressure remains constant throughout the change, i.e., $dP = 0$.

(iv) **Isochoric:** Volume remains constant throughout the change, i.e., $dV = 0$.

(v) **Cyclic:** When a system undergoes a number of different processes and finally returns to initial state, $dE = 0$ and $dH = 0$

(vi) **Reversible:** A process which occurs infinitesimally slowly and at every small change it is virtually in a state of equilibrium. It takes infinite time.

(vii) **Irreversible:** When the process goes from initial to final state in single step in finite time. All natural processes are irreversible.

3. Nature of work and heat: Work is a mode of transfer of energy to or from a system with reference to surroundings. If an object is displaced through a distance dx against a constant force F , then the amount of work which has to be done is equal to $F \times dx$. The mechanical work or pressure volume work is equal to $P_{\text{ext}}(V_2 - V_1)$ or $P \times dV$. The work done on the system increases its energy while work done by the system decreases its energy. On this basis, the work done has the sign convention.

Work done by the system = $-w$

Work done on the system = $+w$

The unit of work is erg. It is very small. The bigger unit is joule or kilojoule.

$$1 \text{ joule} = 10^7 \text{ ergs}; 1 \text{ kJ (kilojoule)} = 1000 \text{ J}$$

Heat is the quantity of energy which flows between system and surroundings on account of temperature difference. It is equal to $m \times s \times \Delta t$ where m is the mass, s is the specific heat and Δt is the temperature difference. The sign convention for heat is:

Heat gained by system = $+q$

Heat lost by system = $-q$

The unit of heat is calorie (cal). Since, heat and work are correlated the SI unit of heat is joule.

$$1 \text{ joule} = 0.2390 \text{ cal}$$

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

$$1 \text{ kcal} = 4.184 \text{ kJ}$$

$$1 \text{ litre-atm} = 101.3 \text{ J} = 1.013 \times 10^9 \text{ erg} = 24.206 \text{ cal}$$

4. Internal energy: Sum of all forms of energy that a system possesses is termed internal energy. It is denoted by E . It is an extensive property. It is also a state property.

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

The internal energy of a particular system is a definite quantity but it is impossible to determine its exact value. It is a state function. In thermodynamics, one is concerned only with energy change which occurs when the system moves from one state to another, i.e., $\Delta E = E_f - E_i$. ΔE is +ve if $E_f > E_i$ and negative if $E_f < E_i$. ΔE does not depend on the path by which final state is achieved. For a cyclic process, $\Delta E = 0$.

5. First law of thermodynamics: Energy can neither be created nor destroyed but it can be converted from one form to another.

Or

The energy of the universe is constant.

Or

Total energy of an isolated system remains constant, though it may change from one form to another.

When heat energy (q) is given to a system and work (w) is also done on it, its energy increases from E_1 to E_2 .

$$E_2 = E_1 + q + w \quad \text{or} \quad E_2 - E_1 = q + w \quad \text{or} \quad \Delta E = q + w$$

In case heat energy (q) is given to a system and work (w) is done by the system then

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

6. Enthalpy or heat content: The quantity $E + PV$ is known as enthalpy or heat content. It is denoted by H . It represents the total energy stored in a system.

$$\Delta E = q - P(V_2 - V_1) \quad \text{or} \quad E_2 - E_1 = q - PV_2 + PV_1$$

$$\text{or} \quad (E_2 + P_2V_2) - (E_1 + P_1V_1) = q \quad \text{or} \quad H_2 - H_1 = q$$

$$\text{or} \quad \Delta H = q \quad \text{or} \quad \Delta E + P \Delta V = \Delta H = q_P$$

$$\text{when } V_2 = V_1, \text{ i.e., } \Delta V = 0, \Delta E = q_V$$

$$q_V + \Delta nRT = q_P \quad \text{in the case of gases}$$

where, Δn = total number of moles of products - total number

of moles of reactants

7. Heat capacity: It is the quantity of heat required to raise the temperature of the system by one degree.

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

In the case of gases,

$$C_V \text{ (at constant volume)} = \left(\frac{\partial E}{\partial T} \right)_V$$

= Molar heat capacity at constant volume

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

= Molar heat capacity at constant pressure

$$C_P - C_V = R$$

8. Isothermal expansion of an ideal gas: The expansion in an ideal gas at constant temperature can be done reversibly or irreversibly.

w = Work done by gas in reversible expansion

$$= -2.303nRT \log \frac{V_2}{V_1} = -2.303nRT \log \frac{P_1}{P_2}$$

q = Heat absorbed from surroundings

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

w = Work done by gas in irreversible expansion

$$= -P_{\text{ext}}(V_2 - V_1)$$

Maximum work is done in reversible isothermal expansion. In isothermal process, $\Delta E = 0$ and $\Delta H = 0$.

Adiabatic expansion of an ideal gas: q in the process is zero, hence $\Delta E = w$. Work is done by the gas during expansion at the expense of internal energy. In expansion, ΔE decreases while in compression ΔE increases.

$$\Delta E = w = C_V \times \Delta T$$

The value of ΔT depends upon the process whether carried reversibly or irreversibly. The following relationships are followed by an ideal gas under adiabatic conditions:

$$PV^\gamma = \text{constant} \quad \left(\gamma = \frac{C_P}{C_V} \right)$$

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

9. Joule-Thomson effect: The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson effect. This effect is observed below the inversion temperature of a gas. The inversion temperature of a gas depends upon the van der Waals' constants of a gas. It is expressed in terms of van der Waals' constants 'a' and 'b' as:

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

10. Thermochemistry: It is concerned with heat changes accompanying physical and chemical transformations. It is also termed as chemical energetics. It is based on the first law of thermodynamics. If E_1 and E_2 represent total energies associated with reactants and products respectively, three cases may arise:

Case I: $E_1 = E_2$. Neither heat is evolved nor absorbed. Such reactions are very rare.

Case II: $E_1 > E_2$. The difference ($E_1 - E_2$) of energy will be evolved, i.e., heat is evolved.

Case III: $E_1 < E_2$. The difference ($E_2 - E_1$) of energy will be absorbed, i.e., heat is absorbed.

11. Exothermic reactions: Reactions which occur with evolution of heat

$$H_{\text{products}} < H_{\text{reactants}}, \quad \text{i.e.,} \quad \Delta H = -ve$$

Endothermic reactions: Reactions which occur with absorption of heat

$$H_{\text{products}} > H_{\text{reactants}}, \quad \text{i.e.,} \quad \Delta H = +ve$$

Sign conventions	q	ΔE	ΔH
Exothermic	(-)	(-)	(-)
Endothermic	(+)	(+)	(+)

12. Heat of reaction or enthalpy of reaction: The amount of heat evolved or absorbed when quantities of the substances indicated by chemical equation have completely reacted, it is represented as ΔH .

$$\text{Enthalpy of reaction} = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

The factors which affect the magnitude of heat of reaction are :

- Physical state of reactants and products, (ii) Allotropic forms of the elements (iii) Reaction carried at constant pressure or constant volume ($\Delta H = \Delta E + \Delta nRT$) (iv) Enthalpy of solution (v) Temperature at which the reaction is carried out.

13. Heat of formation or enthalpy of formation: It is the amount of heat evolved or absorbed when one gram mole of substance is directly obtained from its constituent elements. It is represented as ΔH_f .

If all the substances of the chemical reaction are in their standard states (i.e., at 25°C or 298 K and one atmospheric pressure), the heat of reaction or formation is called standard heat of reaction or formation respectively. These are denoted as ΔH° or ΔH_f° respectively. The enthalpies of free elements at standard conditions are taken arbitrary as zero.

The compounds which have positive enthalpies of formation are called endothermic compounds (less stable) and which have negative enthalpies of formation are called exothermic compounds (stable).

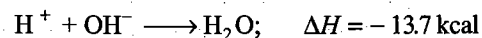
14. Heat of combustion or enthalpy of combustion: It is the amount of heat evolved when one mole of the substance is completely oxidised. It has a number of applications:

- Determination of calorific values of foods and fuels.
- Enthalpy of formation can be determined by application of Hess's law.
- Structural problems can be evaluated.

15. Enthalpy of hydrogenation: The enthalpy change associated when one mole of an unsaturated organic compound is fully hydrogenated.

16. Enthalpy of solution: The amount of heat evolved or absorbed when one mole of the substance is dissolved in excess of water so that further dilution does not bring any heat change.

17. Enthalpy or heat of neutralisation: The amount of heat evolved when one gram equivalent of an acid is neutralised by one gram equivalent of a base in dilute solution. Heat of neutralisation of a strong acid against a strong base is always constant, i.e., 13.7 kcal or 57.1 kJ . It is due to common reaction between H^+ and OH^- ions. The heat of formation of water from these ions is 13.7 kcal .



In the case of weak acids and weak bases, the heat of neutralisation is always less than 13.7 kcal because some of the evolved heat energy is utilised in bringing about complete ionisation of acid or base in solution.

18. Enthalpy of fusion: Heat absorbed in converting one mole of solid into liquid at its melting point.

19. Enthalpy of vaporisation: Heat absorbed in converting one mole of a liquid into its vapours at its boiling point.

Enthalpy of sublimation: Heat absorbed in converting one mole of solid directly into its vapour.

20. Laws of thermochemistry:

(i) **Lavoisier and Laplace law:** The heat which is required to break a compound into its elements is equal to the heat evolved during its formation from its elements.

$$\Delta H_{\text{decomposition}} = -\Delta H_f$$

(ii) **Hess's law (the law of constant heat summation):** If a chemical reaction can be made to take place in a number of ways in one or in several steps, the total change is always the same, *i.e.*, heat change depends upon the initial and final stages only and independent of intermediate steps. The thermochemical equations can be added, subtracted or multiplied by a number to obtain a desired equation.

21. Bond energy: The energy required to break one mole of bond of a particular type is termed bond dissociation energy. It depends upon the nature of bond and also the molecule in which the bond is present. The bond energies can be used for determining heats of reactions.

$$[\text{Heat of reaction} = \text{Sum of bond energies of reactants} \\ - \text{Sum of bond energies of products}]$$

The bond energies can also be used for determining resonance energy.

$$\text{Resonance energy} = \text{Observed heat of formation} \\ - \text{Calculated heat of formation}$$

22. Experimental determination of heat of reaction: The apparatus used is called calorimeter. Two of the common types of calorimeters are: (i) Water calorimeter (ii) Bomb-calorimeter. The principle of measurement is that heat given out is equal to heat taken, *i.e.*,

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

where, W = Water equivalent of the calorimeter, m = mass of the liquid, s = its sp. heat, T_2 = final temperature and T_1 = initial temperature.

23. Spontaneous process: A process which proceeds of its own accord without any outside help is termed spontaneous process. All natural processes proceed spontaneously and are thermodynamically irreversible.

Driving force: It is the force which makes the process to occur by itself. It is the resultant of two basic tendencies:

- (i) Tendency to attain a state of minimum energy.
- (ii) Tendency to attain a state of maximum randomness.

The disorder or randomness in a system is measured in terms of a thermodynamic property known as **entropy**. The absolute

value of entropy cannot be determined. The change in entropy is denoted by ΔS .

$$\Delta S = \frac{q_{\text{reversible}}}{T}$$

where, q is the heat supplied at temperature T .

$\Delta S = +$ indicates increase in randomness whereas, $\Delta S = -$ indicates the decrease in randomness.

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

24. Free energy: Free energy change, ΔG , was introduced by Gibbs. The Gibbs-Helmholtz equation is:

$$\Delta G = \Delta H - T \Delta S \quad \text{or} \quad G = H - TS$$

and

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

where, G is known as free energy. This is the maximum energy available to a system during a process which can be converted into useful work.

Negative value of ΔG indicates that the process is spontaneous. Zero value means that there is a state of equilibrium.

25. Second law of thermodynamics: It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency.

Or

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

26. Carnot cycle: It demonstrates the maximum convertibility of heat into work in a theoretical and an imaginary cycle.

$$\text{Thermodynamic efficiency} = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

The efficiency of a heat engine is always less than 1.

27. Third law of thermodynamics: The entropy of all pure crystals is zero at the absolute zero of temperature.

Questions

I. Matrix-Matching Problems (For IIT Aspirants):

[A] Match the List-I with List-II:

List-I	List-II
(a) $\Delta S_{\text{system}} > 0$ (Isolated system)	(p) Spontaneous
(b) $\Delta G < 0$	(q) Non-spontaneous photochemical reaction
(c) $\Delta S_{\text{Total}} = 0$	(r) Equilibrium
(d) $(\Delta G)_{TP} > 0$	(s) Non-spontaneous

[B] Match the Column-I with Column-II:

Column-I	Column-II
(a) Isothermal process (reversible)	(p) $W = 2.303nRT \log \left(\frac{P_1}{P_2} \right)$
(b) Adiabatic process	(q) $PV^\gamma = \text{constant}$
(c) $W = \frac{nR}{r-1} (T_2 - T_1)$	(r) $W = 2.303nRT \log \left(\frac{V_2}{V_1} \right)$
(d) Irreversible isothermal process	(s) $W = -P_{\text{ext}} (V_2 - V_1)$

[C] Match the physical properties in List-I with their relations in List-II:

List-I (Quantity)	List-II (Relation)
(a) ΔG	(p) $-nFE$ or $-nFE^\circ$
(b) ΔG°	(q) $\Delta H - T \Delta S$
(c) W or W_{max}	(r) $-RT \log_e K$
(d) ΔS°	(s) $2.303nR \log_{10} \left(\frac{V_2}{V_1} \right)$

[D] Match the Column-I with Column-II:

Column-I (Gas)	Column-II (Thermodynamic property)
(a) O_2	(p) $\gamma = 1.4$
(b) N_2	(q) $C_p = \frac{7}{2} R$
(c) CO_2, CH_4	(r) $\frac{23}{6} R$
(d) 1 mol O_2 + 2 mol O_3	(s) $\gamma = 1.33$

Here: C_p = Heat capacity at constant pressure
 $\gamma = C_p / C_v$

[E] Match the reactions in Column-I with relations of Column-II:

Column-I (Reaction)	Column-II (Relation)
(a) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	(p) $\Delta H = \Delta U + RT$
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	(q) $\Delta H = \Delta U$
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(r) $\Delta H = \Delta U - 2RT$
(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(s) Forward shift by increasing pressure

[F] Match the processes of Column-I with entropy or enthalpy changes in Column-II:

Column-I	Column-II
(a) $N_2(g) + O_2(g) \rightarrow 2NO(g)$	(p) $\Delta S = 0$
(b) $2KI(aq.) + HgI_2(aq.) \rightarrow$ $K_2[HgI_4](aq.)$	(q) $\Delta S < 0$
(c) $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$	(r) $\Delta H > 0$
(d) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$	(s) $\Delta H < 0$

[G] Match the List-I with List-II:

List-I (Reaction)	List-II (Process)
(a) $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$	(p) Combustion
(b) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$	(q) Neutralization
(c) $NaOH(aq.) + HCl(aq.) \rightarrow$ $NaCl(aq.) + H_2O$	(r) Process of formation
(d) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	(s) Reaction of apollo fuel cell

[H] Match the relations of Column-I with their names in Column-II:

Column-I	Column-II
(a) $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$	(p) Trouton equation
(b) $\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_v$	(q) Effect of temperature on the heat of reaction
(c) $\frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \Delta S_{\text{fusion}}$	(r) Kirchhoff's equation
(d) $\lim_{T \rightarrow 0 \text{ K}} S \rightarrow 0$	(s) Third law of thermodynamics

[I] Match the Column-I with Column-II:

- | Column-I | Column-II |
|---|---------------------------------------|
| (a) Amount of heat required to raise the temperature of 1 mol substance by 1°C | (p) Specific heat $\times$ molar mass |
| (b) $\frac{\Delta H}{\Delta T}$ or $\frac{\Delta U}{\Delta T}$ | (q) Heat capacity = C, C_p or C_v |
| (c) Heat evolved in the combustion of 1 g of a substance | (r) Electron gain enthalpy |
| (d) Heat evolved when an extra electron is added to valence shell of an isolated gaseous atom | (s) Calorific value |

[J] Match the Column-I with Column-II :

- | Column-I | Column-II |
|--------------------------------------|---|
| (a) $\Delta H = +ve, \Delta S = +ve$ | (p) Spontaneous at all temperature |
| (b) $\Delta H = -ve, \Delta S = +ve$ | (q) Non-spontaneous at all temperature |
| (c) $\Delta H = +ve, \Delta S = -ve$ | (r) Non-spontaneous at high temperature |
| (d) $\Delta H = -ve, \Delta S = -ve$ | (s) Spontaneous at high temperature |

Answers

1. [A] (a—p); (b—p, q); (c—r); (d—s)
 [B] (a—p, r); (b—q); (c—q); (d—s)
 [C] (a—p, q); (b—p, r); (c—p); (d—s)
 [D] (a—p, q); (b—p, q); (c—s); (d—r)
 [E] (a—q); (b—q); (c—p); (d—r, s)
 [F] (a—p, r); (b—q, s); (c—q, r); (d—q, s)

- [G] (a—p, r); (b—p); (c—q); (d—p, r, s)
 [H] (a—q, r); (b—q, r); (c—p); (d—s)
 [I] (a—p, q); (b—p, q); (c—s); (d—r)
 [J] (a—s); (b—p); (c—q); (d—r)

PRACTICE PROBLEMS

1. Write 'yes' if heat, work or matter are able to cross the boundary of the corresponding system and 'no' if passage is forbidden:

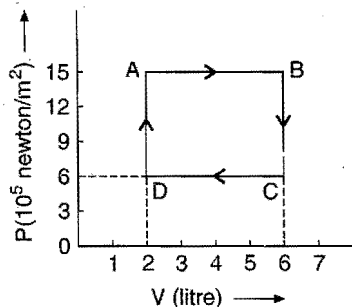
Property	Open system	Close system	Isolated system	Adiabatic system
Heat	Yes/No	Yes/No	Yes/No	Yes/No
Work	Yes/No	Yes/No	Yes/No	Yes/No
Matter	Yes/No	Yes/No	Yes/No	Yes/No

2. Which of the following are state functions?

- (i) Q (ii) W (iii) $Q + W$ (iv) $Q - W$ (v) Q_v (vi) Q_p
 (vii) $\frac{Q}{W}$ (viii) $\frac{Q}{T}$ (ix) $\frac{\Delta H}{T}$ (x) $E + PV$ (xi) $E - PV$

[Ans. (iv), (v), (vi), (viii), (ix), (x).]

3. In the adjoining diagram, the P - V graph of an ideal gas is shown. Find out from the graph (i) Work done in taking the gas



from the state $A \rightarrow B$ (ii) Work done in taking the gas from $B \rightarrow C$ (iii) Work done in a complete cycle. (1 litre = 10^{-3} m^3)

[Ans. (i) $-60 \times 10^2 \text{ J}$ (ii) zero (iii) $36 \times 10^2 \text{ J}$, i.e., net work is done by the gas]

4. A sample of a gas contracts 200 cm^3 by an average of 0.5 atmosphere while 8.5 J heat flows out into the surroundings. What is the change in energy of the system?
 (1 litre-atm = 101.3 J)

[Ans. Energy of the system increases by 1.63 J]

5. Calculate the pressure-volume work done by the system when the gas expands from 1.0 litre to 2.0 litre against a constant external pressure of 10 atmospheres. Express the answer in calorie and joule.

[Ans. -10 litre-atm, -242.2 cal, -1013.28 J]

6. A sample of a gas in a cylinder contracts by 7.5 litre at a constant pressure of 5.0 atmosphere. How much work is done on the gas by the surroundings?

[Ans. 37.5 litre-atm or 3801.75 J]

7. A sample of a gas expands from 200 cm^3 to 500 cm^3 against an average pressure of 750 torr while 1.5 J heat flows into the system. What is the change in energy of the system?
 (1 litre-atm = 101.3 J)

[Ans. Energy of the system is decreased by 28.5 J; $\Delta E = -28.5 \text{ J}$]

8. Calculate the work done when 65.38 g of zinc dissolves in hydrochloric acid in an open beaker at 300 K. (At. mass of Zn = 65.38)

- [Ans. -2494.2 J , i.e., work is done by the system]
9. 6 moles of an ideal gas expand isothermally and reversibly from a volume of 1 dm^3 to a volume of 10 dm^3 at 27°C . What is the maximum work done? Express your answer in joule.
[Ans. -34464.8 J , work is done by the system]
10. 1 mole of an ideal gas at 25°C is allowed to expand reversibly at constant temperature from a volume of 10 litre to 20 litre. Calculate the work done by the gas in joule and calorie.
[Ans. -1717.46 J or -41.1 cal , i.e., work is done by the gas]
11. Find the work done when 1 mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C .
[Ans. -3984 J]
[Hint: Use $w = -2.303 nRT \log \frac{P_1}{P_2}$]
12. How much energy is absorbed by 10 moles of an ideal gas if it expands from an initial pressure of 8 atmosphere to 4 atmosphere at a constant temperature of 27°C ? ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)
[Ans. $1.728 \times 10^4 \text{ J}$]
[Hint: In isothermal process, $\Delta E = 0$,
so q (heat absorbed) $= -w$. Thus, apply the equation
 $q = 2.303 nRT \log \frac{P_1}{P_2}$]
13. A given mass of a gas at 0°C is compressed reversibly and adiabatically to a pressure 20 times the initial value. Calculate the final temperature of the gas. $\left[\frac{C_p}{C_v} = 1.42 \right]$
[Ans. $T_2 = 662.2 \text{ K}$]
[Hint: Apply the formula $\left(\frac{T_1}{T_2} \right)^\gamma = \left(\frac{P_2}{P_1} \right)^{1-\gamma}$]
14. 3 moles of hydrogen are compressed isothermally and reversibly from 60 dm^3 to 20 dm^3 and 8.22 kJ of work is done on it. Assuming ideal behaviour, calculate the temperature of the gas.
[Ans. 300 K]
15. To what pressure must a certain ideal gas ($\gamma = 1.4$) at 373 K and 1 atmospheric pressure be compressed adiabatically in order to raise its temperature to 773 K ?
[Ans. 7.89 atm]
16. 1 mole of an ideal gas ($C_v = 12.55 \text{ J K}^{-1} \text{ mol}^{-1}$) at 300 K is compressed adiabatically and reversibly to one-fourth of its original volume. What is the final temperature of the gas?
[Ans. 752 K]
17. Calculate q , w , ΔE and ΔH for the reversible isothermal expansion of 1 mole of ideal gas at 27°C from a volume of 10 dm^3 to a volume of 20 dm^3 .
[Ans. $q = -w = 1729 \text{ J}$]
18. Calculate the internal energy change for the process in which 1.0 kcal of heat is added to 1.2 litre of O_2 gas in a cylinder at constant pressure of 1.0 atm and the volume changes to 1.5 litre .
[Ans. 0.993 kcal]
19. Calculate ΔE and ΔH when 10 dm^3 of helium at NTP is heated in a cylinder to 100°C , assuming that the gas behaves ideally. ($C_v = 3/2 R$)
[Ans. $\Delta E = 556.74 \text{ J}$
 $\Delta H = 927.9 \text{ J}$]
[Hint: $\Delta E = n \cdot C_v \cdot \Delta T$ and $\Delta H = n \cdot C_p \cdot \Delta T$
 $= \frac{10}{22.4} \times \frac{3}{2} \times 8.314 \times 100 = \frac{10}{22.4} \times \frac{5}{2} \times 8.314 \times 100$
 $= 556.74 \text{ J}$ $= 927.9 \text{ J}$]
20. For the conversion of 1 mole of $\text{SO}_2(\text{g})$ into $\text{SO}_3(\text{g})$ the enthalpy of reaction at constant volume, ΔE , at 298 K is -97.027 kJ . Calculate the enthalpy of reaction, ΔH , at constant pressure.
[Ans. $\Delta H = -98.267 \text{ kJ}$]
[Hint: Use the reaction,
 $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g}), \Delta n = 1 - \frac{3}{2} = -\frac{1}{2}$]
21. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ . This heat has been measured at constant volume and at 27°C . Calculate the heat of combustion of benzene at constant pressure. ($R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$) (IIT 1996)
[Ans. $-3273.7 \text{ kJ mol}^{-1}$]
22. 1 mole of naphthalene (C_{10}H_8) was burnt in oxygen gas at 25°C at constant volume. The heat evolved was found to be 5138.8 kJ . Calculate the heat of reaction at constant pressure. ($R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$)
[Ans. 5143.8 kJ]
[Hint: Water is present in liquid state at 25°C and naphthalene in solid state.]
23. The enthalpy of formation of methane at constant pressure and 300 K is -75.83 kJ . What will be the heat of formation at constant volume? ($R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$)
[Ans. -73.34 kJ]
24. The heat change for the reaction,
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
is -92.2 kJ . Calculate the heat of formation of ammonia.
[Ans. $-46.1 \text{ kJ mol}^{-1}$]
25. ΔH° for the reaction,
 $4\text{S}(\text{s}) + 6\text{O}_2(\text{g}) \longrightarrow 4\text{SO}_3(\text{g})$
is -1583.2 kJ . Calculate ΔH_f° of sulphur trioxide.
[Ans. -395.8 kJ]
26. Calculate the heat change in the reaction,
 $4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
at 298 K given that heats of formation at 298 K for $\text{NH}_3(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -46.0 and $-286.0 \text{ kJ mol}^{-1}$ respectively.
[Ans. $\Delta H^\circ = -1532 \text{ kJ}$]
27. Calculate the heat of combustion of 1 mole of $\text{C}_2\text{H}_4(\text{g})$ to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ at 398 K and 1 atmosphere, given that the heats of formation of $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$ and $\text{C}_2\text{H}_4(\text{g})$ are -94.1 , -57.8 and $+12.5 \text{ kcal mol}^{-1}$ respectively.
[Ans. -316.3 kcal]

28. The heats of combustion of $\text{CH}_4(g)$ and $\text{C}_2\text{H}_6(g)$ are -890.3 and $-1560 \text{ kJ mol}^{-1}$ respectively. Which has higher calorific value?

[Ans. Methane has higher calorific value.]

29. The heat of combustion of butane is 2880 kJ mol^{-1} . What is the heat liberated by burning 1 kg of butane in excess of oxygen supply?

[Ans. 49655 kJ]

30. The heat of formation of $\text{CH}_4(g)$, $\text{C}_2\text{H}_6(g)$ and $\text{C}_4\text{H}_{10}(g)$ are -74.8 , -84.7 and $-126.1 \text{ kJ mol}^{-1}$ respectively. Arrange them in order of their efficiency as fuel per gram. Heats of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -393.5 and $-285.8 \text{ kJ mol}^{-1}$ respectively.

[Ans. $\text{CH}_4 > \text{C}_2\text{H}_6 > \text{C}_4\text{H}_{10}$]

[Hint: First determine heat of combustion in each case and then find the calorific value.]

31. The heat of combustion of carbon to $\text{CO}_2(g)$ is $-393.5 \text{ kJ mol}^{-1}$. Calculate the heat released upon formation of 35.2 g of $\text{CO}_2(g)$ from carbon and oxygen gas.

[Ans. -315 kJ]

32. Calculate ΔH_f° of $\text{C}_6\text{H}_{12}\text{O}_6(s)$ from the following data:

$\Delta H_{\text{comb}}^\circ$ of $\text{C}_6\text{H}_{12}\text{O}_6(s) = -2816 \text{ kJ mol}^{-1}$, ΔH_f° of $\text{CO}_2(g) = -393.5 \text{ kJ mol}^{-1}$ and ΔH_f° of $\text{H}_2\text{O}(l) = -285.9 \text{ kJ mol}^{-1}$.

[Ans. $-1260 \text{ kJ mol}^{-1}$]

33. Calculate the amount of heat released when:

(i) 100 mL of 0.2 M HCl solution is mixed with 50 mL of 0.2 M KOH .

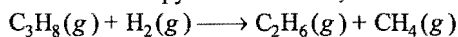
(ii) 200 mL of 0.1 M H_2SO_4 is mixed with 200 mL of 0.2 M KOH solution.

[Ans. (i) 0.57 kJ (ii) 2.18 kJ]

34. When 100 mL each of HCl and NaOH solutions are mixed, 5.71 kJ of heat was evolved. What is the molarity of two solutions? The heat of neutralisation of HCl is 57.1 kJ .

[Ans. 1 M]

35. Determine the enthalpy of the reaction,



at 25°C , using the given heat of combustion values under standard conditions.

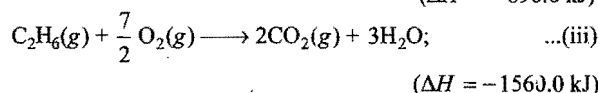
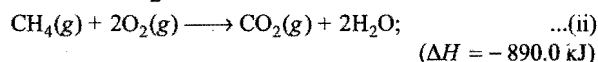
Compound	$\text{H}_2(g)$	$\text{CH}_4(g)$	$\text{C}_2\text{H}_6(g)$	$\text{C}(\text{graphite})$
ΔH° (kJ mol^{-1})	-285.8	-890.0	-1560.0	-393.5

The standard heat of formation of $\text{C}_3\text{H}_8(g)$ is $-103.8 \text{ kJ mol}^{-1}$.

(IIT 1992)

[Ans. -55.7 kJ]

[Hint: $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}; (\Delta H = -285.8 \text{ kJ}) \dots(i)$

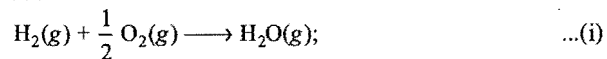


Multiplying eq. (i) by 5 and eq. (iv) by 3 and adding both the equations and subtracting eqs. (ii), (iii) and (v).]

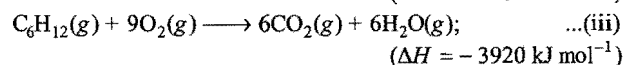
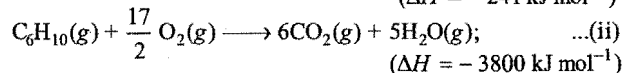
36. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are -241 , -3800 and $-3920 \text{ kJ mol}^{-1}$ respectively. Calculate the heat of hydrogenation of cyclohexene. [ISM (Dhanbad) 1992]

[Ans. -121 kJ mol^{-1}]

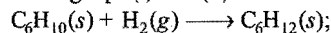
[Hint:



($\Delta H = -241 \text{ kJ mol}^{-1}$)

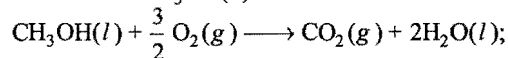


Adding eqs. (i) and (ii) and subtracting eq. (iii),

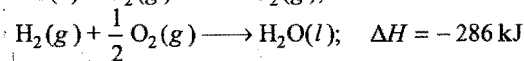
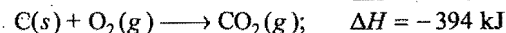


$$\Delta H = -241 - 3800 - (-3920) = -121 \text{ kJ mol}^{-1}]$$

37. From the following data of heats of combustion, find the heat of formation of $\text{CH}_3\text{OH}(l)$:



$\Delta H = -726 \text{ kJ}$



[BIT (Ranchi) 1991]

[Ans. -240 kJ mol^{-1}]

38. Calculate the heat of formation of methane, given that

heat of formation of water $= -286 \text{ kJ mol}^{-1}$

heat of combustion of methane $= -890 \text{ kJ mol}^{-1}$

heat of combustion of carbon $= -393.5 \text{ kJ mol}^{-1}$

[ISM (Dhanbad) 1993]

[Ans. $-75.5 \text{ kJ mol}^{-1}$]

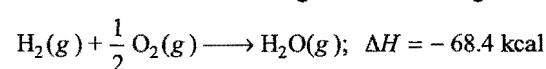
39. Calculate the standard heat of formation of C_{10}H_8 (naphthalene) if standard heat of combustion of naphthalene is -1231.0 kcal at 298 K and standard heat of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -94.0 kcal and -68.4 kcal respectively.

[Ans. 17.4 kcal]

40. The heat of combustion of liquid ethanol is -327.0 kcal . Calculate the heat of formation of ethanol, given that the heats of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -94.0 kcal and -68.4 kcal respectively.

[Ans. -66.2 kcal]

41. Calculate heat of formation of cane sugar from following data:



$\Delta H = -1350.0 \text{ kcal}$

[Ans. -535.2 kcal]

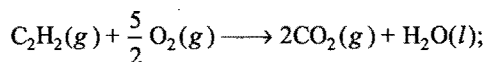
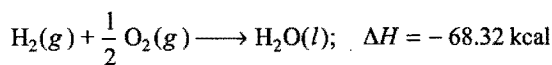
42. The heats of formation of $\text{C}_6\text{H}_6(l)$, $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ are 11.70 , -68.4 and -94.0 kcal respectively. Calculate the heat of combustion of benzene (l).

[Ans. -780.9 kcal]

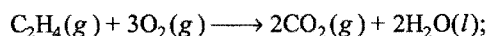
[Hint: $\text{C}_6\text{H}_6(l) + \frac{15}{2} \text{O}_2(g) \longrightarrow 6\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$; $\Delta H = ?$

$$\Delta H = 6 \times \Delta H_f(\text{CO}_2) + 3 \times \Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_6\text{H}_6)]$$

43. Calculate the heat of hydrogenation of C_2H_2 to C_2H_4 .



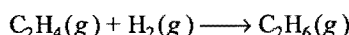
$$\Delta H = -310.61 \text{ kcal}$$



$$\Delta H = -337.32 \text{ kcal}$$

[Ans. -41.61 kcal]

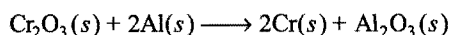
44. Calculate the heat of hydrogenation,



given that, the heat of combustion of ethylene, hydrogen and ethane are -337.0, -68.4 and -373.0 kcal respectively.

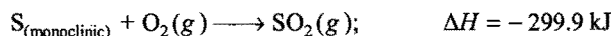
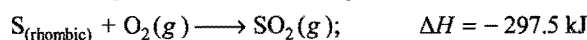
[Ans. -32.4 kcal]

45. If the heat of formation of $\text{Al}_2\text{O}_3(s)$ and $\text{Cr}_2\text{O}_3(s)$ are 1596 kJ and 1134 kJ (both exothermic) respectively. Calculate ΔH of the thermite reaction.



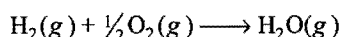
[Ans. -462 kJ]

46. Calculate the enthalpy of transition of rhombic sulphur to monoclinic sulphur from the following data:



[Ans. +2.4 kJ]

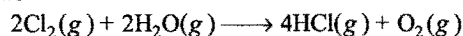
47. Calculate ΔH for the reaction,



given that bond energies of H—H and O=O bond and O—H bond are 433 kJ mol⁻¹, 492 kJ mol⁻¹ and 464 kJ mol⁻¹.

[Ans. -249 kJ]

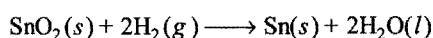
48. Using the bond enthalpy data, calculate ΔH of the following reaction:



given that, bond energies of Cl—Cl, H—Cl, O—H and O=O are 242.8, 431.8, 464 and 442 kJ mol⁻¹ respectively.

[Ans. 172.4 kJ mol⁻¹]

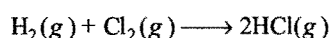
49. Calculate the enthalpy of the reaction,



given that, enthalpy of formation of $\text{SnO}_2(s)$ and $\text{H}_2\text{O}(l)$ are -580.7 kJ and -285.8 kJ respectively.

[Ans. +9.1 kJ]

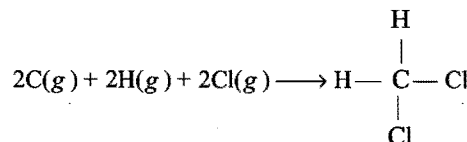
50. Calculate the enthalpy change for the reaction,



given that, bond energies of H—H, Cl—Cl and H—Cl are 436, 243 and 432 kJ mol⁻¹.

[Ans. -185 kJ mol⁻¹]

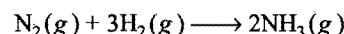
51. Use the bond energy data and calculate the enthalpy change for:



The bond energies of C—H and C—Cl are 413 and 328 kJ mol⁻¹ respectively.

[Ans. -1482 kJ mol⁻¹]

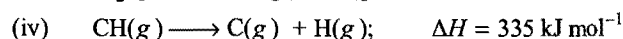
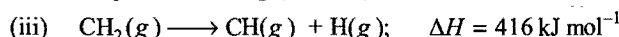
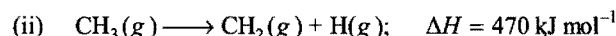
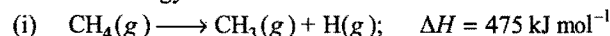
52. Calculate the heat of formation of ammonia from the following data:



The bond energies of N≡N, H—H and N—H bonds are 226, 104 and 93 kcal respectively.

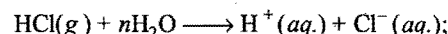
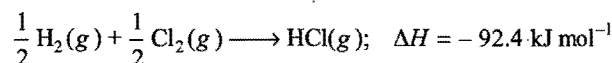
[Ans. -10 kcal]

53. Use the following bond dissociation energies to compute the C—H bond energy in methane:



[Ans. 424 kJ mol⁻¹]

54. Calculate ΔH_f° for chloride ion from the following data:

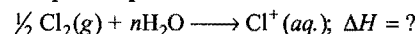


$$\Delta H = -74.8 \text{ kJ mol}^{-1}$$

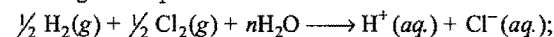
$$\Delta H_f^\circ(\text{H}^+aq.) = 0.0 \text{ kJ mol}^{-1}$$

(IIT 1992)

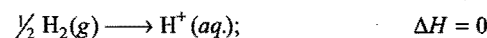
[Hint: Required equation is



Adding both equations.



$$\Delta H = -167.2$$



So, $\frac{1}{2} \text{Cl}_2(g) + n\text{H}_2\text{O} \longrightarrow \text{Cl}^-(aq.); \quad \Delta H = -167.2 \text{ kJ mol}^{-1}$]

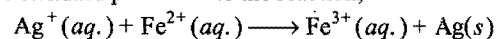
55. The heat of ionisation of formic acid is 1.5 kJ/mol. 9.2 g formic acid on reaction with 7 g ammonium hydroxide gives 10.8 kJ of heat. Calculate the heat of ionisation of ammonium hydroxide. (1 cal = 4.2 J)

[Ans. 2.04 kJ/mol]

56. Assuming that 50% of the heat of useful, how many kg of water at 15°C can be heated to 95.0°C by burning 200 litre of methane measured at NTP? The heat of combustion of methane is 211 kcal mol⁻¹.

[Ans. 11.76 kg]

57. The standard potential for the reaction,



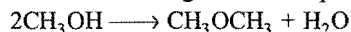
is 0.028 V. What is the standard free energy change for this reaction?

[Ans. -2.702 kJ mol⁻¹]

58. Calculate the theoretical maximum efficiency of a heat engine operating between 373 K and 173 K.

[Ans. 0.536 or 53.6%]

59. The standard free energy of formation in the gaseous state of methanol, dimethyl ether and water are -38.7 , -27.3 and -54.6 kcal respectively. Is the transformation of methanol to dimethyl ether and water in gaseous state possible?



[Hint: ΔG° for the transformation

$$= \sum \Delta G^\circ_{\text{(products)}} - \sum \Delta G^\circ_{\text{(reactants)}}$$

$= -ve$ (the transformation is possible)]

60. Ethanol boils at 78.4°C and standard enthalpy of vaporization of ethanol is 42.4 kJ mol^{-1} . Calculate the entropy of vaporization of ethanol.

[Ans. $120.9 \text{ J K}^{-1} \text{ mol}^{-1}$]

61. The following data is known about the melting of KCl:

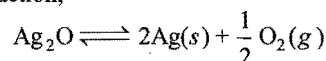
$$\Delta H = 7.25 \text{ kJ mol}^{-1} \text{ and } \Delta S = +0.007 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate its melting point.

[Ans. 1035.7 K]

[Hint: At melting point $\Delta G = 0$]

62. For the reaction,



Calculate the temperature at which free energy change is zero. At a temperature lower than this, predict whether the forward or the reverse reaction will be favoured. Give reason.

($\Delta H^\circ = +30.56 \text{ kJ}$ and $\Delta S^\circ = +0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at one atmosphere)

[Hint: Calculate T by applying the formula

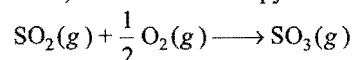
$$\Delta G = \Delta H - T \Delta S \text{ and } \Delta G = 0.$$

Then find the value of ΔG at lower temperature than T . The value of ΔG comes positive; hence, the reverse reaction will be favoured. At temperature higher than T , the reaction is spontaneous.]

63. Calculate the boiling point of the liquid if its entropy of vaporization is $110 \text{ J K}^{-1} \text{ mol}^{-1}$ and the enthalpy of vaporization is $40.85 \text{ kJ mol}^{-1}$.

[Ans. 371.36 K]

64. Using S° values, calculate the entropy of the reaction,

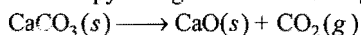


The S° values for SO_2 , O_2 and SO_3 are 248.5 , 205.0 and $256.2 \text{ J K}^{-1} \text{ mol}^{-1}$.

[Ans. $-94.2 \text{ J K}^{-1} \text{ mol}^{-1}$]

[Hint: $\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$]

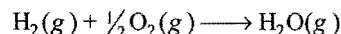
65. Calculate the entropy change for the following reaction:



$$S^\circ \quad 92.9 \quad 39.7 \quad 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

[Ans. $+166.4 \text{ J K}^{-1} \text{ mol}^{-1}$]

66. Compute the value of ΔS at 298 K for the reaction,



given that, $\Delta G^\circ = -228.6 \text{ kJ}$ and $\Delta H^\circ = -241.8 \text{ kJ}$.

[Ans. -44.3 J K^{-1}]

67. An engine operating between 150°C and 25°C takes 500 J heat from a high temperature reservoir. Assuming there is no frictional loss, calculate the work that can be done by the engine.

[Ans. 148 J]

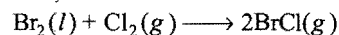
68. At 300 K , the standard enthalpies of formation of $\text{C}_6\text{H}_5\text{COOH}(s)$, $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -408 , -393 and -286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume. ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)

(IIT 1995)

[Ans. (i) $\Delta H = -3201 \text{ kJ mol}^{-1}$;

(ii) $\Delta E = -3199.75 \text{ kJ mol}^{-1}$]

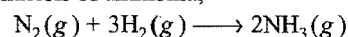
69. For the reaction,



$\Delta H = 29.37 \text{ kJ mol}^{-1}$ and $\Delta S = 104 \text{ J K}^{-1} \text{ mol}^{-1}$. Find the temperature above which the reaction would become spontaneous.

[Ans. Above 282.4 K]

70. For the synthesis of ammonia,



Calculate ΔH° , ΔS° and ΔG° at 300 K using the following data:

Species	N_2	H_2	NH_3
$\Delta H^\circ_f / (\text{kJ mol}^{-1})$	0	0	-46.2
$S^\circ / (\text{J K}^{-1} \text{ mol}^{-1})$	191.5	130.6	192.5

[Ans. $\Delta H^\circ = -92.4 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -198.3 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta G^\circ = -32.91 \text{ kJ mol}^{-1}$]

71. How much heat is required to change 15.6 g of benzene from liquid into vapour at its boiling point of 80°C ? Entropy of vaporization of benzene is $87 \text{ J K}^{-1} \text{ mol}^{-1}$.

[Ans. 6142.2 J]

72. Calculate the standard free energy change for the combustion of glucose at 298 K , using the given data.



$$\Delta H^\circ = -2820 \text{ kJ mol}^{-1}, \Delta S^\circ = 210 \text{ J K}^{-1} \text{ mol}^{-1}$$

[Ans. $\Delta G^\circ = -2882.58 \text{ kJ mol}^{-1}$]

73. The specific heat at constant volume for a gas is 0.075 cal/g and at constant pressure it is 0.125 cal/g . Calculate:

(i) the molecular weight of gas,

(ii) atomicity of gas.

[Hint: (i) $C_p - C_v = \frac{R}{M}$ where, M = molecular weight of gas

$$0.125 - 0.075 = \frac{1.987}{M}$$

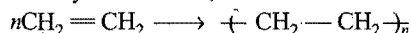
$$M = 39.74 \approx 40$$

(ii) $\frac{C_p}{C_v} = \gamma$

$$\therefore \gamma = \frac{0.125}{0.075} = 1.66$$

$\therefore 1.66$ value of γ shows that the gas is monoatomic.]

74. The polymerisation of ethylene to linear polyethylene is represented by the reaction,



where, n has a large integral value. Given that the average enthalpies of bond dissociation for $\text{C}=\text{C}$ and $\text{C}-\text{C}$ at 298 K are $+590$ and $+331 \text{ kJ mol}^{-1}$ respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

(IIT 1994)



There are equal number of $\text{C}-\text{H}$ bonds on both sides but on reactant side there are $n\text{C}=\text{C}$ bonds and on product side $(2n+1)\text{C}-\text{C}$ bonds.

Enthalpy of polymerisation

$$\begin{aligned} &= n\Delta H_{(\text{C}=\text{C})} - (2n+1)\Delta H_{(\text{C}-\text{C})} \\ &= 590n - (2n+1)(331) \\ &= 590n - 662n \quad [2n+1 \rightarrow 2n \text{ as } n \text{ is very large}] \\ &= -72n \text{ kJ} \end{aligned}$$

Enthalpy of polymerisation per mole

$$= \frac{\Delta H}{n} = -\frac{72n}{n} = -72 \text{ kJ mol}^{-1}$$

75. An athlete is given 100 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) of energy equivalent to 1560 kJ. He utilises 50% of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ mol^{-1} .

[Hint: Unused energy = $\frac{1560}{2} = 780 \text{ kJ}$

Mass of water needed for perspiration = $18 \times \frac{780}{44} = 318.96 \text{ g}$

76. Calculate the entropy of ideal mixing when 2 moles of N_2 , 3 moles of H_2 and 2 moles of NH_3 are mixed at constant temperature, assuming no chemical reaction is occurring.

[Ans. 62.80 J K^{-1}]

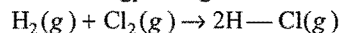
[Hint: Use the relation,

$$\Delta S = -R \sum n_i \log_e x_i$$

when n_i = no. of moles of component

x_i = mole fraction of the component]

77. Calculate free energy change for the reaction:



by using the bond energy and entropy data.

Bond energies of $\text{H}-\text{H}$, $\text{Cl}-\text{Cl}$ and $\text{H}-\text{Cl}$ bonds are 435 kJ mol^{-1} , 240 kJ mol^{-1} and 430 kJ mol^{-1} respectively. Standard entropies of H_2 , Cl_2 and HCl are 130.59 , 222.95 and $186.68 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively.

[Ans. 190.9 kJ]

[Hint: ΔG° can be calculated by using:

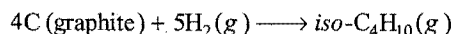
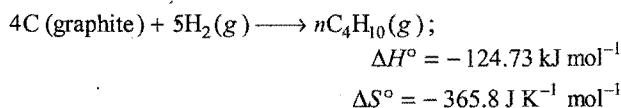
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned} \Delta H^\circ &= \sum (\text{BE})_{\text{reactants}} - \sum (\text{BE})_{\text{products}} \\ &= 435 + 240 - 2 \times 430 = -185 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= 2 \times 186.68 - 130.59 - 222.95 \\ &= 19.82 \text{ J K}^{-1} = 19.82 \times 10^{-3} \text{ kJ K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -185 - 298 \times 19.82 \times 10^{-3} = -190.9 \text{ kJ} \end{aligned}$$

78. For the reaction,



$$\Delta H^\circ = -131.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -381.079 \text{ J K}^{-1} \text{ mol}^{-1}$$

Indicate whether *normal butane* can be spontaneously converted to *iso-butane* or not.

[Ans. Yes, $\Delta G^\circ = -2.32 \text{ kJ}$]

[Hint: For $n\text{C}_4\text{H}_{10}$,

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -124.73 - 298(-365.8 \times 10^{-3}) = -15.72 \text{ kJ} \end{aligned}$$

For *iso-butane* ($\text{iso-C}_4\text{H}_{10}$),

$$\begin{aligned} \Delta G^\circ &= -131.6 - 298(-381.079 \times 10^{-3}) \\ &= -18.04 \text{ kJ} \end{aligned}$$

For conversion of $n\text{C}_4\text{H}_{10} \longrightarrow \text{iso-C}_4\text{H}_{10}$,

$$\Delta G^\circ = -18.04 - (-15.72) = -2.32 \text{ kJ}$$

Negative value shows that the process is spontaneous.]

79. The temperature of a bomb calorimeter was found to rise by 1.617 K , when a current of 3.20 amp was passed for 27 sec from a 12 V source. Calculate the calorimeter constant.

[Hint: Energy absorbed by the calorimeter

$$= I \times t \times V = 3.2 \times 27 \times 12 = 1036.8 \text{ J}$$

Calorimeter constant (ms) can be calculated as,

$$q = ms \Delta t$$

$$1036.8 = ms \times 1.617$$

$$ms = 641.187 \text{ kJ}$$

80. 1 mole of an ideal gas is allowed to expand isothermally at 27°C until its volume is tripled. Calculate ΔS_{sys} and ΔS_{univ} under the following conditions:

(a) the expansion is carried out reversibly.

(b) the expansion is a free expansion.

[Ans. (a) $\Delta S_{\text{sys}} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\Delta S_{\text{surr}} = -9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

$$(b) \Delta S_{\text{univ}} = \Delta S_{\text{sys}} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}]$$

[Hint: (a) In isothermal reversible process:

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

$$q = -W = 2.303RT \log \frac{V_2}{V_1}$$

$$= 2.303 \times 8.314 \times 300 \log 3 = 2740.6 \text{ J mol}^{-1}$$

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} = \frac{2740.6}{300} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{system}} = -9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

(b) In case of free expansion:

$$\Delta S = 2.303nR \log \left(\frac{V_2}{V_1} \right) = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{surr}} = 0]$$

81. One kilogram water at 0°C is brought into contact with a heat reservoir at 100°C . Find:

- (a) change in entropy when temperature reaches to 100°C .
 (b) what is the change in entropy of reservoir?
 (c) change in entropy of universe.
 (d) the nature of process.

[Ans. (a) 312 cal K^{-1} , (b) $-268.1 \text{ cal K}^{-1}$, (c) 43.9 cal K^{-1}
 (d) spontaneous]

[Hint: (a) $\Delta S = 2.303nC_p \log \left(\frac{T_2}{T_1} \right)$
 $= 2.303 \times \frac{1000}{18} \times 18 \log \left(\frac{373}{273} \right) = 312 \text{ cal K}^{-1}$

(b) $\Delta S_{\text{reservoir}} = -\frac{\Delta Q}{T}$

$$\Delta Q = ms \Delta t = 1000 \times 1 \times 100 = 10^5 \text{ cal}$$

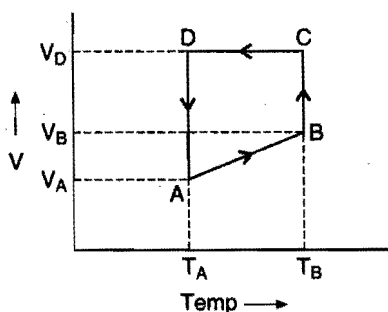
$$\Delta S = \frac{-10^5}{373} = -268.1 \text{ cal K}^{-1}$$

(c) $\Delta S_{\text{universe}} = 312 - 268.1 = 43.9 \text{ cal K}^{-1}$

(d) $\Delta S > 0$, the process will be spontaneous.]

82. A monoatomic ideal gas of two moles is taken through a cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C .

Calculate:



- (a) the temperature of gas at B.
 (b) heat absorbed or evolved in each process.
 (c) total work done in cyclic process.

[Hint: A $\rightarrow$ B: (It is isobaric process)]

$$\frac{V_A}{T_A} = \frac{V_B}{T_B}$$

$$\therefore T_B = \frac{V_B}{V_A} \times T_A = 2 \times 300 = 600 \text{ K}$$

$$q_{AB} = nC_p \Delta T = 2 \times \frac{5}{2} R \Delta T$$

$$= 2 \times \frac{5}{2} \times 2 \times 300 = 3000 \text{ cal}$$

B $\rightarrow$ C (Isothermal process)

$$\Delta U = 0$$

$$\therefore q_{BC} = W = 2.303 nRT \log \left(\frac{V_C}{V_B} \right)$$

$$= 2.303 \times 2 \times 2 \times 600 \log \frac{4}{2}$$

$$= 1.663 \times 10^3 \text{ cal}$$

C $\rightarrow$ D: (Isochoric process)

$$q_{CD} = nC_v \Delta T = 2 \times \frac{3}{2} \times 2 \times (-300) = -1800 \text{ cal}$$

D $\rightarrow$ A: (Isothermal process)

$$q_{DA} = 2.303 nRT_A \log \frac{V_A}{V_D}$$

$$= 2.303 \times 2 \times 2 \times 300 \log \frac{1}{4}$$

$$= -1.663 \times 10^3 \text{ cal}$$

$$\text{Total heat change} = 3000 + 1.663 \times 10^3 - 1800 - 1.663 \times 10^3$$

$$= 1200 \text{ cal}$$

$$\text{Work done} = -1200 \text{ cal}]$$

83. The reaction, $\text{SOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{SO}_2 + 2\text{HCl}$ is endothermic by 49.4 kJ and exoergonic by 50.8 kJ . What is the factor that makes the reaction to be spontaneous? Calculate the entropy change at 298 K .

[Ans. $\Delta S^\circ = 0.3362 \text{ kJ K}^{-1}$]

[Hint: Exoergonic means $\Delta G^\circ = -$ ve.]

$$\Delta G^\circ = -50.8 \text{ kJ},$$

$$\Delta H^\circ = 49.4 \text{ kJ}$$

Substitute these values in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to calculate entropy.

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{49.4 - (-50.8)}{298}$$

$$= 0.3362 \text{ kJ K}^{-1}]$$

84. What amount of ice will remain when 52 g ice is added to 100 g of water at 40°C ?
 Specific heat of water is 1 cal/g and latent heat of fusion of ice is 80 cal/g .

[Ans. 2 g ice]

[Hint: At the stage of thermal equilibrium at 0°C ,

Heat lost by water = Heat absorbed by ice to melt.

$$ms \Delta T = mL$$

$$100 \times 1 \times 40 = m \times 80$$

$$m = 50 \text{ g}$$

$$\text{Remaining ice} = 52 - 50 = 2 \text{ g}]$$

85. Calculate the ΔH_f° of $\text{C}_6\text{H}_{12}\text{O}_6(s)$ from the following data:

$$\Delta H_{\text{comb}} [\text{C}_6\text{H}_{12}\text{O}_6(s)] = -2816 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of } \text{CO}_2(g) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ of } \text{H}_2\text{O}(l) = -285.9 \text{ kJ/mol [BCECE 2006]}$$

[Ans. -1260 kJ/mol]

86. A liquid freezes into solid ($\Delta H = -500 \text{ J mol}^{-1}$) at 100 K and 1 atm . Find the values of:

(i) Gibbs free energy change

(ii) entropy change.

[CBSE (Mains) 2006]

[Hint: Liquid $\rightleftharpoons$ Solid]

(i) $\Delta G = 0$, at equilibrium

(ii) $\Delta S = \frac{\Delta H}{T} = \frac{-500}{100} = -5 \text{ J K}^{-1} \text{ mol}^{-1}]$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

- Thermodynamics is concerned with:
 - total energy of a system
 - energy changes in a system
 - rate of a chemical change
 - mass changes in nuclear reactions
- An isolated system is that system in which: [PET (MP) 1993]
 - there is no exchange of energy with the surroundings
 - there is exchange of mass and energy with the surroundings
 - there is no exchange of energy and mass with the surroundings
 - there is exchange of mass with the surroundings
- Identify the intensive property from the following:
 - volume
 - mass
 - enthalpy
 - temperature
- Which one of the following is an extensive property? [Comed (Karnataka) 2008]
 - Enthalpy
 - Concentration
 - Density
 - Viscosity
- For an adiabatic process, which of the following relations is correct? (CPMT 1990)
 - $\Delta E = 0$
 - $P \Delta V = 0$
 - $q = 0$
 - $q = +w$
- Which one is true from the following for isobaric process? [CET (Gujarat) 2008]
 - $\Delta P = 0$
 - $\Delta q = 0$
 - $\Delta H = 0$
 - $\Delta E = 0$
- For an ideal gas, the value of $\left(\frac{dE}{dV}\right)_T$ is: [PET (MP) 1993]
 - positive
 - zero
 - negative
 - interchangeable
- A process, in which pressure remains constant, is called:
 - isochoric process
 - isothermal process
 - adiabatic process
 - isobaric process
- A process in which volume remains constant, is called:
 - isochoric process
 - isothermal process
 - adiabatic process
 - isobaric process
- For a cyclic process, the condition is:
 - $\Delta E = 0$
 - $\Delta H = 0$
 - $\Delta E > 0$ and $\Delta H > 0$
 - both $\Delta E = 0$ and $\Delta H = 0$
- Which one of the following is a state property?
 - Heat
 - Work
 - Internal energy
 - Potential energy
- Internal energy of a system of molecules is determined by taking into consideration its:
 - kinetic energy
 - vibrational energy
 - rotational energy
 - all kinds of energies present in the molecules
- A thermodynamic quantity is that:
 - which is used in thermochemistry
 - which obeys all laws of thermodynamics
 - quantity whose value depends only upon the state of the system
 - quantity which is used in measuring thermal change
- Thermodynamic equilibrium involves: [CET (Pb.) 1991]
 - chemical equilibrium
 - thermal equilibrium
 - mechanical equilibrium
 - all the three
- For the reaction of one mole zinc dust with one mole sulphuric acid in a bomb calorimeter, ΔU and w correspond to: (AIIMS 2005)
 - $\Delta U < 0, w = 0$
 - $\Delta U < 0, w < 0$
 - $\Delta U > 0, w = 0$
 - $\Delta U > 0, w > 0$

[Hint: In bomb calorimeter, $w = 0, \Delta U = q(-ve)$]
- A system is provided with 50 joules of heat and the work done on the system is 10 joules. What is the change in internal energy of the system in joules? [EAMCET (Engg.) 2010]
 - 60
 - 40
 - 50
 - 10
- During an isothermal expansion of an ideal gas, its: (CBSE 1991)
 - internal energy increases
 - enthalpy decreases
 - enthalpy remains unaffected
 - enthalpy reduces to zero
- The work done in ergs for a reversible expansion of one mole of an ideal gas from a volume of 10 litre to 20 litre at 25°C is: [CMC (Vellore) 1991]
 - $2.303 \times 8.31 \times 10^7 \times 298 \log 2$
 - $2.303 \times 0.0821 \times 298 \log 2$
 - $2.303 \times 0.0821 \times 298 \log 0.5$
 - $2.303 \times 2 \times 298 \log 2$
- When an ideal gas is compressed adiabatically and reversibly, the final temperature is:
 - higher than the initial temperature
 - lower than the initial temperature
 - the same as initial temperature
 - dependent upon the rate of compression
- Adiabatic reversible expansion of a gas is represented by:
 - $\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$
 - $\left(\frac{T_1}{T_2}\right) = \left(\frac{P_1}{P_2}\right)^{1-\gamma}$
 - $\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$
 - all are correct
- Total energy change for a reversible isothermal cycle is:
 - always positive
 - zero
 - always negative
 - always 100 kJ per degree
- "Heat energy cannot be completely transformed into work without producing some change somewhere", is the statement of:

- (a) Hess's law
(b) first law of thermodynamics
(c) Kirchhoff's law
(d) second law of thermodynamics
23. The heat content of the system is called:
(a) internal energy (b) enthalpy
(c) free energy (d) entropy
24. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then : (KCET 2008)
(a) $\Delta H < \Delta U$
(b) $\Delta H > \Delta U$
(c) $\Delta H = \Delta U$
(d) there is no relationship between ΔH and ΔU
25. An exothermic reaction is one in which the reacting substances:
(a) have same energy as products
(b) have less energy than the products
(c) have more energy than the products
(d) are at higher temperature than the products
26. In endothermic reactions, the reactants:
(a) have more energy than products
(b) have as much energy as the products
(c) are at lower temperature than products
(d) have less energy than the products
27. Identify the reaction in which the heat liberated corresponds to the heat of formation (ΔH): (EAMCET 2006)
(a) $\text{C (diamond)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{heat}$
(b) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{heat}$
(c) $\text{C (diamond)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{heat}$
(d) $\text{S (rhombic)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{heat}$
28. In an exothermic reaction, ΔH is:
(a) positive (b) negative
(c) zero (d) may be positive or negative
29. Evaporation of water is:
(a) a process in which neither heat is evolved nor absorbed
(b) a process accompanied by chemical reaction
(c) an exothermic change
(d) an endothermic change
30. An endothermic reaction is one in which:
(a) heat is converted into electricity
(b) heat is absorbed
(c) heat is evolved
(d) heat changes to mechanical work
31. If total enthalpy of reactants and products is H_R and H_P respectively, then for exothermic reaction:
(a) $H_R = H_P$ (b) $H_R < H_P$
(c) $H_R > H_P$ (d) $H_R - H_P = 0$
32. Calculate the work done when 1 mol of an ideal gas is compressed reversibly from 1 bar to 4 bar at a constant temperature of 300 K : (DPMT 2009)
(a) 4.01 kJ (b) -8.02 kJ
(c) 18.02 kJ (d) -14.01 kJ
33. Under which of the following conditions is the relation, $\Delta H = \Delta E + P \Delta V$ valid for a closed system?
(a) Constant pressure
(b) Constant temperature
(c) Constant temperature and pressure
(d) Constant temperature, pressure and composition
34. Which of the following is an endothermic reaction?
(a) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$
(b) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
(c) $\text{NaOH}(\text{aq.}) + \text{HCl}(\text{aq.}) \rightarrow \text{NaCl}(\text{aq.}) + \text{H}_2\text{O}(\text{l})$
(d) $\text{C}_2\text{H}_5\text{OH}(\text{aq.}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$
35. Which of the following reactions is endothermic?
(a) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
(b) $\text{Fe}(\text{s}) + \text{S}(\text{s}) \rightarrow \text{FeS}(\text{s})$
(c) $\text{NaOH}(\text{aq.}) + \text{HCl}(\text{aq.}) \rightarrow \text{NaCl}(\text{aq.}) + \text{H}_2\text{O}(\text{l})$
(d) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
36. The formation of water from $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is an exothermic process because:
(a) the chemical energy of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is more than that of water
(b) the chemical energy of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is less than that of water
(c) the temperature of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is higher than that of water
(d) the temperature of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is lower than that of water
37. Which one of the following reactions is an exothermic reaction?
(a) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
(b) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
(c) $2\text{HgO}(\text{s}) \rightarrow 2\text{Hg}(\text{s}) + \text{O}_2(\text{g})$
(d) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
38. Which one of the following is not applicable for a thermochemical equation?
(a) It tells about physical state of reactants and products
(b) It tells whether the reaction is spontaneous
(c) It tells whether the reaction is exothermic or endothermic
(d) It tells about the allotropic form (if any) of the reactants
39. The enthalpies of all elements in their standard state at 25°C and one atmospheric pressure are:
(a) same (b) always positive
(c) always negative (d) zero
40. The heat of reaction does not depend upon:
(a) physical state of the reactants and products
(b) whether the reaction has been carried at constant pressure or constant volume
(c) the manner by which the reaction has been carried
(d) the temperature at which the reaction has been carried
41. The value of $\Delta H - \Delta U$ for the following reaction at 27°C will be:
$$2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$$

[AMU (Medical) 2007]

- (a) $8.314 \times 273 \times (-2)$ (b) $8.314 \times 300 \times (-2)$
(c) $8.314 \times 273 \times 2$ (d) $8.314 \times 300 \times 2$

$$[\text{Hint : } w = 2.303 nRT \log \left(\frac{P_2}{P_1} \right)]$$

$$= 2.303 \times 1 \times 8.314 \times 300 \log \frac{4}{1}$$

$$= 3458.3 \text{ J} = 3.458 \text{ kJ}$$

42. Since, the enthalpy of the elements in their standard states is taken to be zero, the heat of formation (ΔH_f) of compounds:
- is always negative
 - is always positive
 - is zero
 - may be positive or negative
43. The difference between heats of reaction at constant pressure and constant volume for the reaction,
 $2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$ at $25^\circ C$ in kJ is: (IIT 1991)
- +7.43
 - +3.72
 - 7.43
 - 3.72
44. For a gaseous reaction, $A(g) + 3B(g) \rightarrow 3C(g) + 3D(g)$, ΔE is 17 kcal at $27^\circ C$. Assuming $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$, the value of ΔH for the above reaction is:
- 15.8 kcal
 - 18.2 kcal
 - 20.0 kcal
 - 16.4 kcal
45. Which of the following statements is correct for the reaction,
 $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ at constant temperature and pressure?
- $\Delta H = \Delta E$
 - $\Delta H < \Delta E$
 - $\Delta H > \Delta E$
 - None of these
46. For the reaction, $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2} O_2(g)$ which one of the following is true?
- $\Delta H = \Delta E$
 - $\Delta H < \Delta E$
 - $\Delta H > \Delta E$
 - $\Delta H = \frac{1}{2} \Delta E$
47. Thermochemistry is the study of relationship between heat energy and:
- chemical energy
 - activation energy
 - friction energy
 - none of these
48. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta U$? [CBSE (Med.) 2006]
- $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
 - $C(s) + 2H_2O(g) \longrightarrow 2H_2(g) + CO_2(g)$
 - $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$
 - $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$
49. The enthalpy change in the reaction, $2CO + O_2 \longrightarrow 2CO_2$ is termed as:
- enthalpy of reaction
 - enthalpy of fusion
 - enthalpy of formation
 - enthalpy of combustion
50. Reaction, $H_2(g) + I_2(g) \longrightarrow 2HI$; $\Delta H = 12.40 \text{ kcal}$
 According to this, heat of formation of HI will be: [PET (MP) 1990]
- 12.40 kcal
 - 12.4 kcal
 - 6.20 kcal
 - 6.20 kcal
51. For the reactions,
 (i) $H_2(g) + Cl_2(g) = 2HCl(g) + x \text{ kJ}$
 (ii) $H_2(g) + Cl_2(g) = 2HCl(l) + y \text{ kJ}$
 which one of the following statements is correct?
 [PET (MP) 2007]
- $x > y$
 - $x < y$
 - $x - y = 0$
 - $x = y$
52. For the reactions,
 (i) $H_2(g) + Cl_2(g) = 2HCl(g) + x \text{ kJ}$
 (ii) $2HCl(g) = H_2(g) + Cl_2(g) - y \text{ kJ}$
 which one of the following statements is correct?
- $x - y > 0$
 - $x - y < 0$
 - $x - y = 0$
 - None of these
53. According to the equation,
 $C_6H_6(l) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$;
 $\Delta H = -3264.4 \text{ kJ mol}^{-1}$
 the energy evolved when 7.8 g benzene is burnt in air will be: [PET (MP) 1990]
- 163.22 kJ
 - 32.64 kJ
 - 3.264 kJ
 - 326.4 kJ
54. $\Delta H_{f(x)}$, $\Delta H_{f(y)}$, $\Delta H_{f(R)}$ and $\Delta H_{f(S)}$ denote the enthalpies of formation of x , y , R and S respectively. The enthalpy of the reaction, $x + y \longrightarrow R + S$ is given by:
- $\Delta H_{f(x)} + \Delta H_{f(y)}$
 - $\Delta H_{f(R)} + \Delta H_{f(S)}$
 - $\Delta H_{f(x)} + \Delta H_{f(y)} - \Delta H_{f(R)} - \Delta H_{f(S)}$
 - $\Delta H_{f(R)} + \Delta H_{f(S)} - \Delta H_{f(x)} - \Delta H_{f(y)}$
55. The enthalpy change for the reaction,
 $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$ is called:
- enthalpy of formation
 - enthalpy of combustion
 - enthalpy of vaporisation
 - enthalpy of sublimation
56. The heat of combustion of methane is -880 kJ mol^{-1} . If 3.2 g of methane is burnt of heat is evolved.
- 88 kJ
 - 264 kJ
 - 176 kJ
 - 440 kJ
57. The enthalpy change for the reaction,
 $2C_{(\text{graphite})} + 3H_2(g) \longrightarrow C_2H_6(g)$
 is called:
- enthalpy of formation
 - enthalpy of combustion
 - enthalpy of hydrogenation
 - enthalpy of vaporisation
58. The enthalpy of formation of water from hydrogen and oxygen is $-286.0 \text{ kJ mol}^{-1}$. The enthalpy of decomposition of water into hydrogen and oxygen is kJ mol^{-1} :
- 286.0
 - 143.0
 - 286.0
 - 143.0
59. The heat of combustion of $C_{(\text{graphite})}$ is $-393.5 \text{ kJ mol}^{-1}$. The heat of formation of CO_2 from graphite is kJ mol^{-1} :
- 393.5
 - 393.5
 - 787.0
 - 787.0
60. The enthalpies of formation of organic compounds are conveniently determined from their:
- boiling points
 - melting points
 - enthalpies of neutralization
 - enthalpies of combustion
61. ΔH combustion of a compound is always:
- positive
 - negative
 - zero
 - uncertain
62. The apparatus used for measuring the heat changes of a reaction is called:
- a thermometer
 - a calorimeter
 - a calorimeter
 - none of these
63. The heat of neutralization of any strong acid and strong base is always constant and $\Delta H = -57.3 \text{ kJ}$. This is because: [Comed (Karnataka) 2008]
- both the acid and base undergo complete ionization.
 - during neutralization, salt and water are formed.
 - 1 mole of water is formed from H^+ and OH^- ions.
 - the reaction is exothermic.

64. The enthalpy of neutralization of oxalic acid by a strong base is $-25.4 \text{ kcal mol}^{-1}$. The enthalpy of neutralization of strong acid and strong base is $-13.7 \text{ kcal eq}^{-1}$. The enthalpy of dissociation of oxalic acid is: (DPMT 2009)

(a) 1 kcal mol^{-1} (b) 2 kcal mol^{-1}
(c) $18.55 \text{ kcal mol}^{-1}$ (d) $11.7 \text{ kcal mol}^{-1}$

[Hint : Oxalic acid is dibasic acid hence expected heat of neutralization will be $(2 \times -13.7 \text{ kcal})$.

The dissociation energy of oxalic acid $= 2 \times 13.7 - 25.4$
 $= 2 \text{ kcal mol}^{-1}$]

65. The amount of heat liberated when one mole of NH_4OH reacts with one mole of HCl is: (IIT 1990)

(a) 13.7 kcal (b) more than 13.7 kcal
(c) less than 13.67 kcal (d) cannot be predicted

66. Heat of neutralisation for the reaction,



is 57.1 kJ mol^{-1} . The heat released when 0.25 mole of NaOH is titrated against 0.25 mole of HCl will be:

(a) 22.5 kJ (b) 57.1 kJ
(c) 28.6 kJ (d) 14.3 kJ

67. If $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O} + 13.7 \text{ kcal}$, then heat of complete neutralisation of one gram mole of H_2SO_4 with strong base will be: [PMT (MP) 1990]

(a) 13.7 kcal (b) 27.4 kcal
(c) 6.85 kcal (d) 3.425 kcal

68. In which of the following neutralization reactions, the heat of neutralization will be highest?

(a) HCl and NaOH (b) CH_3COOH and NaOH
(c) CH_3COOH and NH_4OH (d) HCl and NH_4OH

69. "The enthalpy of formation of a compound is equal in magnitude but of opposite sign to the enthalpy of decomposition of that compound under the same conditions." This law was presented by:

(a) Hess (b) Le Chatelier
(c) Kirchhoff (d) Lavoisier and Laplace

70. "The change of enthalpy of a chemical reaction is the same whether the reaction takes place in one step or in several steps". This law was presented by:

(a) Hess (b) Le Chatelier
(c) van't Hoff (d) Kirchhoff

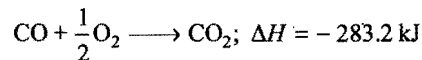
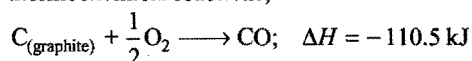
71. The enthalpy change in a reaction does not depend on the:

(a) conditions under which the reaction is carried out
(b) initial and final enthalpies of the reactants and products
(c) state of reactants and products
(d) number of intermediate steps to convert reactants to products

72. Hess's law deals with:

(a) changes in heat of reaction
(b) rate of reaction
(c) equilibrium constant
(d) influence of pressure on volume of a gas

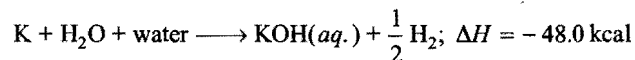
73. From the thermochemical reactions,



the heat of reaction of $\text{C}_{(\text{graphite})} + \text{O}_2 \longrightarrow \text{CO}_2$ is:

(a) $+393.7 \text{ kJ}$ (b) -393.7 kJ (c) -172.7 kJ (d) $+172.7 \text{ kJ}$

74. If $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}; \Delta H = -68.09 \text{ kcal}$



$\text{KOH} + \text{water} \longrightarrow \text{KOH}(\text{aq.}); \Delta H = -14.0 \text{ kcal}$
the heat of formation of KOH is:

(a) $-68.39 + 48 - 14.0$ (b) $-68.39 - 48.0 + 14.0$
(c) $+68.39 - 48.0 + 14.0$ (d) $+68.39 + 48.0 - 14.0$

75. The enthalpies of combustion of $\text{C}_{(\text{graphite})}$ and $\text{C}_{(\text{diamond})}$ are -393.5 and -395.4 kJ/mol respectively. The enthalpy of conversion of $\text{C}_{(\text{graphite})}$ to $\text{C}_{(\text{diamond})}$ in kJ/mol is:

(a) -1.9 (b) -788.9
(c) 1.9 (d) 788.9

76. The heat of combustion of yellow phosphorus and red phosphorus are -9.91 kJ and -8.78 kJ respectively. The heat of transition of yellow phosphorus to red phosphorus is:

[CEE (Bihar) 1992]

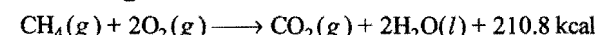
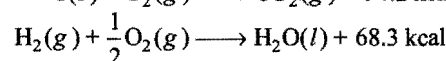
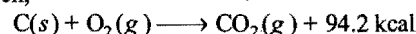
(a) -18.69 kJ (b) $+1.13 \text{ kJ}$
(c) $+18.69 \text{ kJ}$ (d) -1.13 kJ

77. What will be the heat of formation of methane, if the heat of combustion of carbon is ' x ' kJ , heat of formation of water is ' y ' kJ and heat of combustion of methane is ' z ' kJ ?

(AHMS 2008)

(a) $(-x - y + z) \text{ kJ}$ (b) $(-z - x + 2y) \text{ kJ}$
(c) $(-x - 2y - z) \text{ kJ}$ (d) $(-x - 2y + z) \text{ kJ}$

78. Given,



The heat of formation of methane in kcal will be:

[PET (MP) 1990]

(a) 45.9 (b) 47.8 (c) 20.0 (d) 47.3

79. On combustion carbon forms two oxides CO and CO_2 , heat of formation of CO_2 is -94.3 kcal and that of CO is -26.0 kcal . Heat of combustion of carbon is: [EAMCET (Med.) 2010]

(a) -26.0 kcal (b) -68.3 kcal
(c) -94.3 kcal (d) -120.3 kcal

80. The heat of combustion of ethanol determined in a bomb calorimeter is $-670.48 \text{ kcal mol}^{-1}$ at 298 K . What is ΔE at 298 K for the reaction?

(a) $-760 \text{ kcal mol}^{-1}$ (b) $-670.48 \text{ kcal mol}^{-1}$
(c) $+760 \text{ kcal mol}^{-1}$ (d) $+670.48 \text{ kcal mol}^{-1}$

81. 1 calorie is equivalent to:

(a) 4.184 J (b) 41.84 J (c) 418.4 J (d) 0.4184 J

82. For an endothermic reaction, where ΔH represents the enthalpy of reaction, the minimum value for the energy of activation will be: [IIT 1991; PMT (MP) 1993]

(a) less than ΔH (b) zero
(c) equal to ΔH (d) more than ΔH

83. If $S + O_2 \longrightarrow SO_2$; $\Delta H = -298.2 \text{ kJ}$
 $SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3$; $\Delta H = -98.7 \text{ kJ}$
 $SO_3 + H_2O \longrightarrow H_2SO_4$; $\Delta H = -130.2 \text{ kJ}$
 $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$; $\Delta H = -227.3 \text{ kJ}$

the heat of formation of H_2SO_4 will be:

- (a) -754.4 kJ (b) $+320.5 \text{ kJ}$ (c) -650.3 kJ (d) -433.7 kJ
84. Which of the following units represents the largest amount of energy?
 (a) Electron-volt (b) Erg
 (c) Joule (d) Calorie
85. If ΔH_f° for $H_2O_2(l)$ and $H_2O(l)$ are -188 kJ mol^{-1} and -286 kJ mol^{-1} , what will be the enthalpy change of the reaction $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$? [PMT (MP) 1992]
 (a) 146 kJ mol^{-1} (b) -196 kJ mol^{-1}
 (c) -494 kJ mol^{-1} (d) -98 kJ mol^{-1}
86. The bond dissociation energies for Cl_2 , I_2 and ICl are 242.3, 151 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ/mol . What is the standard enthalpy of formation of $ICl(g)$?
 (a) -211.3 kJ/mol (b) -14.6 kJ/mol
 (c) 16.8 kJ/mol (d) 33.5 kJ/mol

[Hint: $Cl_2(g) \longrightarrow 2Cl(g)$; $\Delta H_1 = 242.3 \text{ kJ/mol}$
 $I_2(g) \longrightarrow 2I(g)$; $\Delta H_2 = 151 \text{ kJ/mol}$
 $ICl(g) \longrightarrow I(g) + Cl(g)$; $\Delta H_3 = 211.3 \text{ kJ/mol}$
 $I_2(s) \longrightarrow I_2(g)$; $\Delta H_4 = 62.8 \text{ kJ/mol}$

Required equation:

$$\frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \longrightarrow ICl(g); \Delta H = ?$$

$$\Delta H = \frac{62.8 + 151 + 242.3}{2} - 211.3$$

$$= 16.75 \text{ kJ/mol}$$

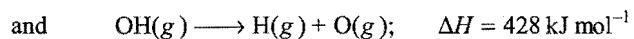
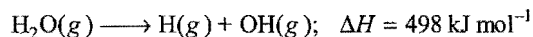
87. Standard heat of formation for CCl_4 , H_2O , CO_2 and HCl at 298K are -25.5 , -57.8 , -94.1 and -22.1 kJ/mol respectively. For the reaction,
 $CCl_4 + 2H_2O \longrightarrow CO_2 + 4HCl$
 what will be ΔH ? (SCRA 2007)
 (a) 36.4 kJ (b) 20.7 kJ (c) -20.7 kJ (d) -414 kJ
88. Heat of combustion of CH_4 , C_2H_6 , C_2H_4 and C_2H_2 are -212.8 , -373.0 , -337.0 and -310.5 kcal respectively at the same temperature. The best fuel among these gases is:
 (a) CH_4 (b) C_2H_6
 (c) C_2H_4 (d) C_2H_2
89. Given, $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -395 \text{ kJ}$
 $S(s) + O_2(g) \longrightarrow SO_2(g)$; $\Delta H = -295 \text{ kJ}$
 $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$; $\Delta H = -1110 \text{ kJ}$
 The heat of formation of $CS_2(l)$ is: [CEE (Bihar) 1992]
 (a) 250 kJ (b) 62.5 kJ (c) 31.25 kJ (d) 125 kJ
90. The heats of combustion of rhombic and monoclinic sulphur are -70960 and -71030 cal respectively. What will be the heat of conversion of rhombic sulphur to monoclinic sulphur?
 (a) -70960 cal (b) -71030 cal
 (c) 70 cal (d) -70 cal

91. The bond dissociation energy of C—H in CH_4 from the equation
 $C(g) + 4H(g) \longrightarrow CH_4(g)$; $\Delta H = -397.8 \text{ kcal}$
 is:
 (a) $+99.45 \text{ kcal}$ (b) -99.45 kcal
 (c) $+397.8 \text{ kcal}$ (d) $+198.9 \text{ kcal}$
92. The dissociation energy of CH_4 is $400 \text{ kcal mol}^{-1}$ and that of ethane is $670 \text{ kcal mol}^{-1}$. The C—C bond energy is:
 (a) 270 kcal (b) 70 kcal (c) 200 kcal (d) 240 kcal
93. Heat of reaction at constant volume is measured in the apparatus:
 (a) bomb calorimeter (b) calorimeter
 (c) pyknometer (d) pyrometer
94. When 10 mL of a strong acid is added to 10 mL of an alkali, the temperature rises by 5°C . If 100 mL of the same acid is mixed with 100 mL of the same base, the temperature rise would be:
 (a) 5°C (b) 50°C
 (c) 20°C (d) cannot be predicted
95. Energy required to dissociate 4 g of gaseous hydrogen into free gaseous atoms is 208 kcal at 25°C . The bond energy of H—H bond will be:
 (a) 1.04 cal (b) 10.4 kcal
 (c) 104 kcal (d) 1040 kcal
96. The heat of neutralisation of strong base and strong acid is 57.0 kJ . The heat released when 0.5 mole of HNO_3 solution is added to 0.20 mole of $NaOH$ solution is: (KCET 1993)
 (a) 57.0 kJ (b) 28.5 kJ
 (c) 11.40 kJ (d) 34.9 kJ
97. The enthalpy of combustion of cyclohexane, cyclohexene and H_2 are respectively -3920 , -3800 and -241 kJ mol^{-1} . The heat of hydrogenation of cyclohexene is: (AIIMS 2007)
 (a) -121 kJ mol^{-1} (b) 121 kJ mol^{-1}
 (c) -242 kJ mol^{-1} (d) 242 kJ mol^{-1}
98. If $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = r$
 and $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$; $\Delta H = s$
 then the heat of formation of CO is:
 (a) $r + s$ (b) $r - s$ (c) $s - r$ (d) $r \times s$
99. Given that, heat of neutralisation of strong acid and strong base is 57.1 kJ . Calculate the heat produced when 0.25 mole of HCl is neutralised with 0.25 mole of $NaOH$ in aqueous solution: (CPMT 1990)
 (a) 22.5 kJ (b) 57 kJ
 (c) 14.275 kJ (d) 28.55 kJ
100. Which one of the following values of ΔH° represents that the product is least stable?
 (a) $-94.0 \text{ kcal mol}^{-1}$ (b) $-231.6 \text{ kcal mol}^{-1}$
 (c) $+21.4 \text{ kcal mol}^{-1}$ (d) $+64.8 \text{ kcal mol}^{-1}$
101. The value of ΔH_{O-H} is $109 \text{ kcal mol}^{-1}$. The formation of one mole of water in gaseous state from $H(g)$ and $O(g)$ is accompanied by: (CBSE 1990)
 (a) 218 kcal (b) -109 kcal
 (c) -218 kcal (d) unpredictable

102. Heat of neutralisation of a strong dibasic acid in dilute solution by NaOH is nearly:

(a) -27.4 kcal/eq (b) -13.7 kcal/eq
(c) +13.7 kcal/eq (d) -13.7 kcal/mol

103. The enthalpy changes at 298 K in successive breaking of O—H bonds of water are



The bond enthalpy of O—H bond is:

(a) 498 kJ mol⁻¹ (b) 428 kJ mol⁻¹
(c) 70 kJ mol⁻¹ (d) 463 kJ mol⁻¹

104. ΔH and ΔE for the reaction, $\text{S}(s) + \frac{3}{2} \text{O}_2(g) \longrightarrow \text{SO}_3(g)$ are related as:

(a) $\Delta H = \Delta E - 0.5RT$ (b) $\Delta H = \Delta E - 1.5RT$
(c) $\Delta H = \Delta E + RT$ (d) $\Delta H = \Delta E + 1.5RT$

105. A spontaneous change is one in which the system suffers:

(VITEEE 2008)

(a) an increase in internal energy
(b) lowering in entropy
(c) lowering in free energy
(d) no energy change

106. The free energy change for a reversible reaction at equilibrium is:

(a) zero (b) positive
(c) negative (d) none of these

107. In the evaporation of water, the entropy:

(a) decreases (b) increases
(c) does not change
(d) sometimes increases, sometimes decreases

108. In which of the following change entropy decreases?

(a) Crystallisation of sucrose from solution
(b) Dissolving sucrose in water
(c) Melting of ice
(d) Vaporisation of camphor

109. For the precipitation reaction of Ag^+ ions with NaCl which of the following statements is true?

(a) ΔH is zero for the reaction
(b) ΔG is zero for the reaction
(c) ΔG is negative for the reaction
(d) ΔG should be equal to ΔH

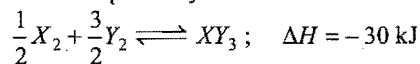
110. If enthalpy of vaporisation of water is 186.5 kJ/mol, the entropy of its vaporisation will be:

(a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0

111. A reaction is non-spontaneous when: [AMU (Medical) 2006]

(a) ΔH is +ve, ΔS is -ve
(b) both ΔH and ΔS are -ve
(c) ΔH is -ve and ΔS is +ve
(d) none of the above

112. Standard entropies of X_2 , Y_2 and XY_3 are 60, 40 and 50 $\text{JK}^{-1}\text{mol}^{-1}$ respectively. For the reaction:



to be at equilibrium, the temperature should be :

[CBSE (PMT) 2010]

(a) 750 K (b) 1000 K
(c) 1250 K (d) 500 K

[Hint : $\Delta S = \sum S_{\text{Products}} - \sum S_{\text{Reactants}}$]

$$= 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40 \right]$$

$$= 50 - (30 + 60) = -40 \text{ JK}^{-1} \text{ mol}^{-1}$$

At equilibrium, $\Delta G = \Delta H - T\Delta S = 0$

i.e., $\Delta H = T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{-40} = 750 \text{ K}$$

113. 'At absolute zero the entropy of a perfect crystal is zero.' This statement corresponds to which law of thermodynamics?

(a) First law (b) Second law
(c) Third law (d) None of these

114. Unit of entropy is: [PMT (Punjab) 2007]

(a) $\text{JK}^{-1} \text{ mol}^{-1}$ (b) J mol^{-1}
(c) $\text{J}^{-1} \text{ K}^{-1} \text{ mol}^{-1}$ (d) JK mol^{-1}

115. Given that $\Delta H_f(H) = 218 \text{ kJ/mol}$, express the H—H bond energy in kcal/mol: (EAMCET 2009)

(a) 52.15 (b) 911
(c) 109 (d) 5.2153

116. For which reaction from the following, ΔS will be maximum?

(a) $\text{Ca}(s) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{CaO}(s)$
(b) $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
(c) $\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$
(d) $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$

117. A particular reaction at 27°C for which $\Delta H > 0$ and $\Delta S > 0$ is found to be non-spontaneous. The reaction may proceed spontaneously if:

(a) the temperature is decreased
(b) the temperature is kept constant
(c) the temperature is increased
(d) it is carried in open vessel at 27°C

118. The least random state of water system is:

(a) ice (b) liquid water
(c) steam (d) randomness is same in all

119. Although the dissolution of ammonium chloride in water is an endothermic reaction, even then it is spontaneous because:

(a) ΔH is positive, ΔS is -ve
(b) ΔH is +ve, ΔS is zero
(c) ΔH is positive, $T\Delta S < \Delta H$
(d) ΔH is +ve, ΔS is positive and $\Delta H < T\Delta S$

120. For an exothermic reaction to be spontaneous:

(a) temperature must be high
(b) temperature must be zero
(c) temperature may have any magnitude
(d) temperature must be low

121. For the reversible process, the value of ΔS is given by the expression:

(a) $\frac{q_{\text{rev}}}{T}$ (b) $T - q_{\text{rev}}$
(c) $q_{\text{rev}} \times T$ (d) $q_{\text{rev}} - T$

122. In an electrochemical cell, if E° is the emf of the cell involving n mole of electrons, then ΔG° is:

(a) $\Delta G^\circ = nFE^\circ$ (b) $\Delta G^\circ = -nFE^\circ$
(c) $E^\circ = nF \Delta G^\circ$ (d) $\Delta G^\circ = nF/E^\circ$

123. The correct relation between equilibrium constant (K), standard free energy (ΔG°) and temperature (T) is:

[CET (J&K) 2006]

(a) $\Delta G^\circ = RT \ln K$ (b) $K = e^{-\Delta G^\circ/2.303 RT}$
(c) $\Delta G^\circ = -RT \log K$ (d) $K = 10^{-\Delta G^\circ/2.303 RT}$
(e) $\Delta G^\circ = R \ln K$

124. The value of entropy in the universe is:

(a) constant (b) decreasing
(c) increasing (d) zero

125. Which of the following thermodynamic relation is correct?

[JEE (WB) 2010]

(a) $dG = VdP - SdT$ (b) $dU = PdV + TdS$
(c) $dH = -VdP + TdS$ (d) $dG = VdP + SdT$

[Hint: $dG = dH - TdS - SdT$

$$(G = H - TS)$$

$$dH = dU + PdV + VdP$$

$$(H = U + PV)$$

and $dU = TdS - PdV$

$$\therefore dG = (TdS - PdV) + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT]$$

126. If enthalpies of formation for $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at $25^\circ C$ and 1 atm pressure be 52, -394 and -286 kJ mol^{-1} respectively, enthalpy of combustion of $C_2H_4(g)$ will be:

[CBSE 1995]

(a) +141.2 kJ mol^{-1} (b) +1412 kJ mol^{-1}
(c) -141.2 kJ mol^{-1} (d) -1412 kJ mol^{-1}

127. Identify the correct statement regarding entropy: [CBSE 1998]

(a) at absolute zero, the entropy of a perfectly crystalline substance is +ve.
(b) at absolute zero, the entropy of a perfectly crystalline substance is zero.
(c) at $0^\circ C$ the entropy of a perfectly crystalline substance is taken to be zero.
(d) at absolute zero of temperature the entropy of all crystalline substances is taken to be zero.

128. The enthalpy and entropy change for a chemical reaction are -2.5×10^{-3} cal and 7.4 cal deg^{-1} respectively. Predict whether the nature of reaction at 298 K is: [AFMC 1998]

(a) spontaneous (b) reversible
(c) irreversible (d) non-spontaneous

129. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The ΔE for this process is: ($R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) [CBSE 1998]

(a) 163.7 cal (b) 1381.1 cal
(c) 9 litre-atm (d) zero

130. The latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10 kcal/mol. What will be the change in internal energy (ΔE) of 3 moles of liquid at the same temperature?

[CBSE 1998]

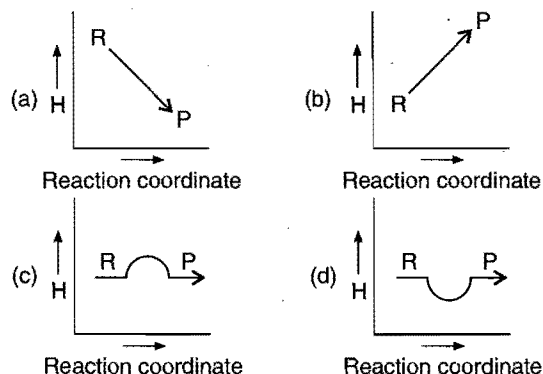
(a) 13.0 kcal (b) -13.0 kcal
(c) 27.0 kcal (d) -27.0 kcal

131. The enthalpy change of a reaction does not depend on:

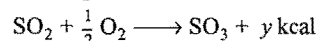
[AIIMS 1997]

(a) state of reactants and products
(b) nature of reactants and products
(c) different intermediate reactions
(d) initial and final enthalpy change of reaction

132. Which plot represents an exothermic reaction?



133. $S + \frac{3}{2} O_2 \longrightarrow SO_3 + 2x \text{ kcal};$

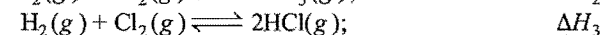
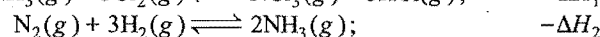
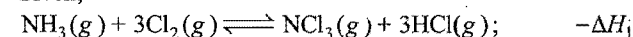


The heat of formation of SO_2 is:

[AIIMS 1997; PET (Kerala) 2008]

(a) $y - 2x$ (b) $2x + y$ (c) $x + y$ (d) $2x / y$

134. Given,



The heat of formation of $NCl_3(g)$ in terms of ΔH_1 , ΔH_2 and ΔH_3 is: [EAMCET 1998]

(a) $\Delta H_f = -\Delta H_1 + \frac{1}{2} \Delta H_2 - \frac{3}{2} \Delta H_3$

(b) $\Delta H_f = \Delta H_1 + \frac{1}{2} \Delta H_2 - \frac{3}{2} \Delta H_3$

(c) $\Delta H_f = \Delta H_1 - \frac{1}{2} \Delta H_2 - \frac{3}{2} \Delta H_3$

(d) none of the above

135. The word 'standard' in standard molar enthalpy change implies:

(a) temperature 298 K
(b) pressure 1 atm
(c) temperature 298 K and pressure 1 atm
(d) all temperatures and all pressures

136. The heat of formation (ΔH_f°) of $H_2O(l)$ is equal to:

(a) zero
(b) molar heat of combustion of $H_2(l)$
(c) molar heat of combustion of $H_2(g)$
(d) sum of heat of formation of $H_2O(g)$ and $O_2(g)$

137. An example of extensive property is:

(a) temperature (b) internal energy
(c) viscosity (d) molar heat capacity

138. For a diatomic molecule AB , the electronegativity difference between A and $B = 0.2028 \sqrt{\Delta}$ [where, Δ = bond energy of

- AB – geometric mean of the bond energies of A_2 and B_2]. The electronegativities of fluorine and chlorine are 4.0 and 3.0 respectively and the bond energies are of $F-F$: 38 kcal mol^{-1} and of $Cl-Cl$: 58 kcal mol^{-1} . The bond energy of $Cl-F$ is:
- (a) $\sim 71 \text{ kcal/mol}$ (b) $\sim 61 \text{ kcal/mol}$
(c) $\sim 48 \text{ kcal/mol}$ (d) $\sim 75 \text{ kcal/mol}$
139. The value of ΔH° for the reaction $Cu^+(g) + I^-(g) \rightarrow CuI(g)$ is -446 kJ mol^{-1} . If the ionisation energy of $Cu(g)$ is 745 kJ mol^{-1} and the electron affinity of $I(g)$ is -295 kJ mol^{-1} , then the value of ΔH° for the formation of one mole of $CuI(g)$ from $Cu(g)$ and $I(g)$ is:
- (a) -446 kJ (b) 450 kJ (c) 594 kJ (d) 4 kJ
140. If the enthalpy change for the reaction, $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$; $\Delta H = -25 \text{ kcal}$, Bond energy of $C-H$ is 20 kcal mol^{-1} greater than the bond energy of $C-Cl$ and bond energies of $H-H$ and $H-Cl$ are same in magnitude, then for the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$, $\Delta H = ?$
- (a) -22.5 kcal/mol (b) -20.5 kcal/mol
(c) -32.5 kcal/mol (d) -12.5 kcal/mol
141. The standard heat of formation of sodium ions in aqueous solution from the following data:
- Heat of formation of $NaOH(aq)$ at $25^\circ C = -470.7 \text{ kJ}$
Heat of formation of $OH^-(aq)$ at $25^\circ C = -228.8 \text{ kJ}$
- is:
- (a) -251.9 kJ (b) 241.9 kJ (c) -241.9 kJ (d) 251.9 kJ
142. AB , A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2 , AB and B_2 are in the ratio $1:1:0.5$ and the enthalpy of formation of AB from A_2 and B_2 is -100 kJ mol^{-1} , what is the bond enthalpy of A_2 ?
- (a) 400 kJ mol^{-1} (b) 200 kJ mol^{-1}
(c) 100 kJ mol^{-1} (d) 300 kJ mol^{-1}
143. The lattice energy of solid $NaCl$ is 180 kcal per mol . The dissolution of the solid in water in the form of ions is endothermic to the extent of 1 kcal per mol . If the solvation energies of Na^+ and Cl^- ions are in the ratio $6:5$, what is the enthalpy of hydration of sodium ion?
- (a) -85.6 kcal/mol (b) -97.5 kcal/mol
(c) 82.6 kcal/mol (d) $+100 \text{ kcal/mol}$
144. Which one of the following statements is false?
- [IIT (Screening) 2000, 01]
- (a) Work is a state function
(b) Temperature is a state function
(c) Work appears at the boundary of the system
(d) Change in the state is completely defined when the initial and final states are specified.
145. ΔG° for the reaction $x + y \rightleftharpoons z$ is -4.606 kcal . The value of equilibrium constant of the reaction at $227^\circ C$ is:
- (IIT 1999)
- (a) 100 (b) 10 (c) 2 (d) 0.01
($R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$)
- [Hint: $\Delta G^\circ = -RT \times 2.303 \times \log K$]
146. The enthalpy of solution of $BaCl_2(s)$ and $BaCl_2 \cdot 2H_2O(s)$ are -20.6 and 8.8 kJ mol^{-1} , respectively. The enthalpy change for the reaction is:
- (IIT 1998)
- (a) 29.8 kJ (b) -11.8 kJ
(c) -20.6 kJ (d) -29.4 kJ
147. For the reaction,
- $$A(g) + 2B(g) \longrightarrow 2C(g) + 3D(g)$$
- the value of ΔH at $27^\circ C$ is 19.0 kcal . The value of ΔE for the reaction would be: (Given, $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$): (IIT 1998)
- (a) 20.8 kcal (b) 19.8 kcal (c) 18.8 kcal (d) 17.8 kcal
148. In thermodynamics, a process is called reversible when:
- [IIT (Screening) 2000, 01]
- (a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously
149. The heat liberated when 1.89 g of benzoic acid is burnt in a bomb calorimeter at $25^\circ C$ increases the temperature of 18.94 kg of water by $0.632^\circ C$. If the specific heat of water at $25^\circ C$ is $0.998 \text{ cal g}^{-1} \text{ deg}^{-1}$, the value of heat of combustion of benzoic acid is:
- (AFMC 2010)
- (a) 881.1 kcal (b) 771.4 kcal
(c) 981.1 kcal (d) 871.2 kcal
- [Hint: Heat liberated by 1.89 g of benzoic acid,
- $$q = ms\Delta T$$
- $$= 18940 \times 0.998 \times 0.632$$
- $$= 11946.14 \text{ cal}$$
- Heat liberated by the combustion of
 1 mol benzoic acid, i.e.,
 122 g benzoic acid
- $$= \frac{11946.14}{1.89} \times 122 = 771126.5 \text{ cal}$$
- $$= 771.12 \text{ kcal mol}^{-1}]$$
150. One mole of a non-ideal gas undergoes a change state (2 atm , 3 L , 95 K) to (4 atm , 5 L , 245 K) with a change of internal energy, $\Delta U = 30 \text{ L atm}$. The change in enthalpy (ΔH) of the process in L atm :
- [IIT (S) 2002]
- (a) 40.0 (b) 42.3
(c) 44.0 (d) not defined, because pressure is not constant
151. Which of the following reactions defines ΔH_f° ?
- [IIT (S) 2003]
- (a) $C_{(\text{diamond})} + O_2(g) \longrightarrow CO_2(g)$
(b) $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \longrightarrow HF(g)$
(c) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
(d) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$
152. If the enthalpies of formation of Al_2O_3 and Cr_2O_3 are -1596 kJ and -1134 kJ respectively, then the value of ΔH for the reaction;
- $$2Al + Cr_2O_3 \longrightarrow 2Cr + Al_2O_3$$
- is: (AIIMS 2004)
- (a) -462 kJ (b) -1365 kJ
(c) -2530 kJ (d) $+2530 \text{ kJ}$
153. Which of the following is true for spontaneous process?
- [PMT (Himachal) 2006]
- (a) $\Delta G > 0$ (b) $\Delta G < 0$ (c) $\Delta G = 0$ (d) $\Delta G = T \Delta S$

154. Considering entropy(s) as a thermodynamic parameter, the criterion for the spontaneity of any process is:

[CBSE (PMT) 2004]

- (a) $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
 (b) $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$
 (c) $\Delta S_{\text{system}} > 0$ only
 (d) $\Delta S_{\text{surroundings}} > 0$ only

155. An ideal gas expands in volume from $1 \times 10^{-3} \text{ m}^3$ to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The work done is: (AIEEE 2004)

- (a) -900 J (b) -900 kJ
 (c) 270 kJ (d) +900 kJ

156. What is the value of internal energy change (ΔU) at 27°C of a gaseous reaction $2A_2(g) + 5B_2(g) \longrightarrow 2A_2B_5(g)$ (whose heat change at constant pressure is -50700 J)?

$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ (SCRA 2009)

- (a) -50700 J (b) -63171 J
 (c) -38229 J (d) +38229 J

[Hint: $\Delta H = \Delta U + \Delta n_g RT$]

$$-50700 = \Delta U + (-5) \times 8.314 \times 300$$

$$\Delta U = -38229 \text{ J}$$

157. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is: [IIT (S) 2004]

- (a) 11.4 kJ (b) -11.4 kJ (c) 0 kJ (d) 4.8 kJ

158. The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is $75 \text{ J mol}^{-1} \text{ K}^{-1}$. The boiling point of the liquid at 1 atm is: [IIT (S) 2004]

- (a) 250 K (b) 400 K (c) 450 K (d) 600 K

159. The sublimation energy of $I_2(s)$ is 57.3 kJ/mol and the enthalpy of fusion is 15.5 kJ/mol . The enthalpy of vaporisation of I_2 is: (DCE 2005)

- (a) 41.8 kJ/mol (b) -41.8 kJ/mol
 (c) 72.8 kJ/mol (d) -72.8 kJ/mol

[Hint: $\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporisation}}$]

160. ΔH and ΔS for a reaction are $+30.558 \text{ kJ mol}^{-1}$ and $0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 1 atm pressure. The temperature at which free energy change is zero and the nature of the reaction below this temperature is: [PET (Kerala) 2005]

- (a) 483 K, spontaneous (b) 443 K, non-spontaneous
 (c) 443 K, spontaneous (d) 463 K, non-spontaneous
 (e) 463 K, spontaneous

161. What would be the amount of heat released when an aqueous solution containing 0.5 mole of HNO_3 is mixed with 0.3 mole of OH^- (enthalpy of neutralisation is -57.1 kJ)?

[PET (Kerala) 2005]

- (a) 28.5 kJ (b) 17.1 kJ (c) 45.7 kJ (d) 1.7 kJ
 (e) 2.85 kJ

[Hint: 0.3 mole OH^- ion will be completely neutralised,

$$\therefore \Delta H = -57.1 \times 0.3 = -17.13 \text{ kJ}]$$

162. A process in which the system does not exchange heat with the surroundings is known as: [CET (J&K) 2005]

- (a) isothermal (b) isobaric (c) isochoric (d) adiabatic

163. The entropy of a crystalline substance at absolute zero on the basis of third law of thermodynamics should be taken as:

[CET (J&K) 2005]

- (a) 100 (b) 50
 (c) zero (d) different for different substances

164. Which of the following expressions is correct?

[JEE (Orissa) 2005]

- (a) $\Delta G^\circ = -nFE^\circ$ (b) $\Delta G^\circ = +nFE^\circ$
 (c) $\Delta G^\circ = -2.303RTnFE_{\text{cell}}^\circ$ (d) $\Delta G^\circ = -nF \log K_c$

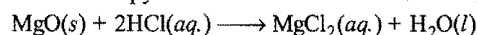
165. Consider the reaction, $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$; carried out at constant temperature and pressure. If ΔH and ΔU are enthalpy change and internal energy change respectively, which of the following expressions is true? (AIEEE 2005)

- (a) $\Delta H = 0$ (b) $\Delta H = \Delta U$
 (c) $\Delta H < \Delta U$ (d) $\Delta H > \Delta U$

[Hint: $\Delta H = \Delta U + \Delta n RT$, $\Delta n = 2 - 4 = -2$]

$$\therefore \Delta H < \Delta U]$$

166. The absolute enthalpy of neutralisation of the reaction,



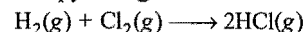
will be:

[CBSE-PMT (Pre) 2005]

- (a) $-57.33 \text{ kJ mol}^{-1}$
 (b) greater than $-57.33 \text{ kJ mol}^{-1}$
 (c) less than $-57.33 \text{ kJ mol}^{-1}$
 (d) $57.33 \text{ kJ mol}^{-1}$

[Hint: Since, MgO is an oxide of a weak base, hence its neutralisation will evolve the heat less than $57.33 \text{ kJ mol}^{-1}$]

167. The entropy values (in $\text{J K}^{-1} \text{ mol}^{-1}$) of $\text{H}_2(g) = 130.6$, $\text{Cl}_2(g) = 223$ and $\text{HCl}(g) = 186.7$ at 298 K and 1 atm pressure are given. Then entropy change for the reaction,



is:

[BHU (Pre) 2005]

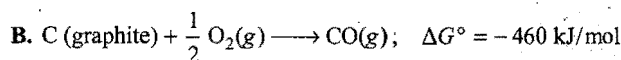
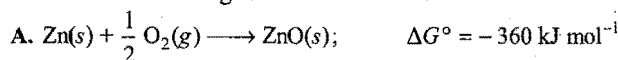
- (a) +540.3 (b) +727.3 (c) -166.9 (d) +19.8

168. A mixture of 2 mole of $\text{CO}(g)$ and one mole of O_2 , in a closed vessel, is ignited to convert the carbon monoxide to carbon dioxide. If ΔH and ΔU are enthalpy and internal energy change, then:

(KCET 2005)

- (a) $\Delta H > \Delta U$
 (b) $\Delta H < \Delta U$
 (c) $\Delta H = \Delta U$
 (d) the relationship depends on the capacity of the vessel

169. Consider the following reactions at 1000°C :



Choose the correct statement at 1000°C :

[PMT (Kerala) 2006]

- (a) zinc can be oxidised by carbon monoxide.
 (b) ZnO can be reduced by graphite.
 (c) both (a) and (b) are true.
 (d) both (a) and (b) are false.
 (e) carbon monoxide can be reduced by zinc.

170. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process?

[PET (Kerala) 2006]

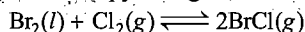
- (a) Isothermal process : $q = -w$
 (b) Cyclic process : $q = -w$
 (c) Isochoric process : $\Delta U = q$
 (d) Adiabatic process : $\Delta U = -w$
 (e) Expansion of gas into vacuum : $\Delta U = q$
 [Hint: In adiabatic process : $q = 0$

$\therefore$ From $\Delta U = q - w$

Work is done by the system,

$$\Delta U = -w \quad \text{for adiabatic process]$$

171. The enthalpy and entropy changes for the reaction:



are $30. \text{ kJ mol}^{-1}$ and $105 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The temperature at which the reaction will be in equilibrium is:

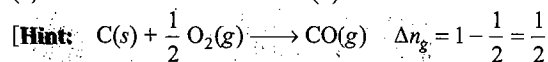
[CBSE (Med.) 2006]

- (a) 285.7 K (b) 273 K (c) 450 K (d) 300 K

172. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its element at 298 K is: ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

(AIEEE 2006)

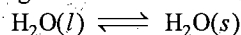
- (a) $-1238.78 \text{ J mol}^{-1}$ (b) $1238.78 \text{ J mol}^{-1}$
 (c) $-2477.57 \text{ J mol}^{-1}$ (d) $2477.57 \text{ J mol}^{-1}$



$$\Delta H - \Delta U = \Delta nRT$$

$$= \frac{1}{2} \times 8.314 \times 298 = 1238.786 \text{ J mol}^{-1}]$$

173. For a phase change:



$0^\circ \text{C}, 1 \text{ bar}$

(AIIMS 2006)

- (a) $\Delta G = 0$ (b) $\Delta S = 0$
 (c) $\Delta H = 0$ (d) $\Delta U = 0$

174. We can drive any thermodynamically forbidden reaction in the desired direction by coupling with: [PET (Kerala) 2006]

- (a) highly exothermic reaction
 (b) highly endothermic reaction
 (c) highly exergonic reaction
 (d) highly endergonic reaction
 (e) reaction with large positive ΔS values

175. Given that, bond energies of H—H and Cl—Cl are 430 kJ/mol and 240 kJ/mol respectively. ΔH_f for HCl is -90 kJ/mol . Bond enthalpy of HCl is: [CBSE (Med.) 2007]

- (a) 380 kJ mol^{-1} (b) 425 kJ mol^{-1}
 (c) 245 kJ mol^{-1} (d) 290 kJ mol^{-1}

176. The amount of heat released, when 20 mL of 0.5 M NaOH is mixed with 100 mL of 0.1 M HCl, is $x \text{ kJ}$. The heat of neutralization (in kJ mol^{-1}) is: [BHU (Mains) 2007]

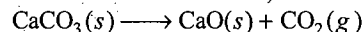
- (a) $-100x$ (b) $-50x$ (c) $+100x$ (d) $+50x$

[Hint: Number of moles of NaOH = $\frac{MV}{1000} = \frac{0.5 \times 20}{1000} = 0.01$

Number of moles of HCl = $\frac{MV}{1000} = \frac{0.1 \times 100}{1000} = 0.01$

Heat of neutralization = $\frac{-x}{0.01} = -100x]$

177. In the conversion of limestone to lime,



the values of ΔH° and ΔS° are $+179.1 \text{ kJ mol}^{-1}$ and

$160.2 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively at 298 K and 1 bar. Assuming that, ΔH° and ΔS° do not change with temperature; temperature above which conversion of limestone to lime will be spontaneous is: (AIEEE 2007)

- (a) 1118 K (b) 1008 K (c) 1200 K (d) 845 K

178. Assuming that, water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vaporised at 1 bar pressure and 100°C , (given: molar enthalpy of vaporisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$) will be:

(AIEEE 2007)

- (a) $41.00 \text{ kJ mol}^{-1}$ (b) $4.100 \text{ kJ mol}^{-1}$
 (c) $3.7904 \text{ kJ mol}^{-1}$ (d) $37.904 \text{ kJ mol}^{-1}$

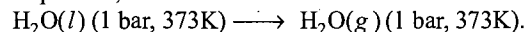
[Hint: $\Delta U = \Delta H - \Delta nRT$

$$= 41000 - 1 \times 8.314 \times 373$$

$$= 37898.878 \text{ J mol}^{-1}$$

$$= 37.9 \text{ kJ mol}^{-1}]$$

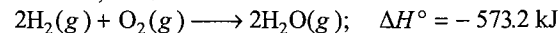
179. For the process,



The correct set of thermodynamic parameters is: (IIT 2007)

- (a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = -ve$
 (c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

180. For the reaction,



The heat of decomposition of water per mol is:

(MHT-CET 2007)

- (a) 286.6 kJ (b) 573.2 kJ (c) -286.6 kJ (d) zero

181. The free energy change $\Delta G = 0$, when: [CET (J&K) 2007]

- (a) the reactants are completely consumed
 (b) a catalyst is added
 (c) the system is at equilibrium
 (d) the reactants are initially mixed

182. In a closed container, a liquid is stirred with a paddle to increase the temperature, which of the following is true?

[PMT (Pb.) 2007]

- (a) $\Delta U = \Delta W \neq 0, q = 0$ (b) $\Delta U = W = 0, q \neq 0$
 (c) $\Delta U = 0, W = q \neq 0$ (d) $W = 0, \Delta U = q \neq 0$

183. For the gas phase reaction,



Which of the following conditions are correct?

[CBSE-PMT (Pre) 2008]

- (a) $\Delta H < 0, \Delta S < 0$ (b) $\Delta H > 0$ and $\Delta S < 0$
 (c) $\Delta H = 0, \Delta S < 0$ (d) $\Delta H > 0$ and $\Delta S > 0$

184. Which of the following is correct? [BHU (Screening) 2008]

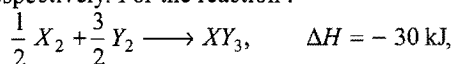
- (a) $C_V = \left(\frac{\partial U}{\partial T} \right)_P$ (b) $C_P = \left(\frac{\partial H}{\partial T} \right)_V$
 (c) $C_P - C_V = R$ (d) $\left(\frac{\partial U}{\partial V} \right)_T = \frac{-a}{V^2}$

(Internal pressure in van der Waals' equation)

185. Which of the following represents total kinetic energy of one mole of gas? [JEE (Orissa) 2008]

- (a) $\frac{1}{2} RT$ (b) $\frac{3}{2} RT$ (c) $(C_P - C_V) RT$ (d) $\frac{2}{3} RT$

186. Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and $50 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. For the reaction :



to be at equilibrium, the temperature will be : (AIEEE 2008)

- (a) 1000K (b) 1250K (c) 500K (d) 750K

[Hint : $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3$

$$\begin{aligned} \Delta S^\circ_{\text{Reaction}} &= \Delta S^\circ_{XY_3} - \frac{1}{2} \Delta S^\circ_{X_2} - \frac{3}{2} \Delta S^\circ_{Y_2} \\ &= 50 - \frac{1}{2} \times 60 - \frac{3}{2} \times 40 = -40 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\Delta G = \Delta H - T \Delta S = 0 \text{ at equilibrium.}$$

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{-40} = 750 \text{ K}$$

187. 4.48 L of an ideal gas at S.T.P requires 12 calories to raise its temperature by 15°C at constant volume. The C_p of the gas is :

[PMT (Kerala) 2009]

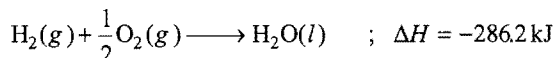
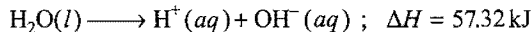
- (a) 3 cal (b) 4 cal (c) 7 cal (d) 6 cal
(e) 9 cal

$$\begin{aligned} \text{[Hint : } C_V &= \frac{\Delta U}{n \Delta T}, \quad n = \frac{4.48}{22.4} = 0.2 \\ &= \frac{12}{0.2 \times 15} = 4 \text{ cal} \end{aligned}$$

$$C_p = C_V + R = 4 + 2 = 6 \text{ cal}$$

188. On the basis of following thermochemical data :

$$[\Delta_f G^\circ \text{H}^+(aq) = 0]$$

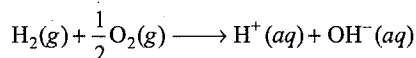


The value of enthalpy of formation of OH^- ion at 25°C is:

(AIEEE 2009)

- (a) -22.88 kJ (b) -228.88 kJ
(c) +228.88 kJ (d) -343.52 kJ

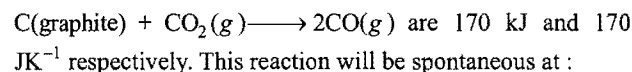
[Hint : The equation for the formation of $\text{OH}^-(aq)$ is:



It is obtained by adding the two given equations :

$$\Delta H = 57.32 + (-286.2) = -228.88 \text{ kJ}$$

189. The values of ΔH and ΔS for the reaction,



[CBSE (PMT) Pre 2009]

- (a) 510 K (b) 710 K (c) 910 K (d) 1110 K

[Hint : $\Delta G = \Delta H - T\Delta S$, ΔG should be negative for spontaneous process.

$$\therefore \Delta H - T\Delta S < 0$$

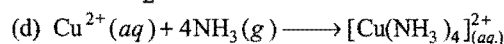
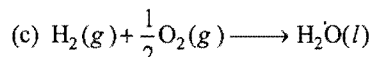
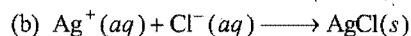
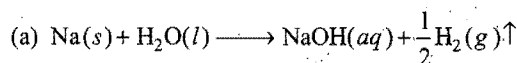
$$\Delta H < T\Delta S$$

$$\text{or } T > \frac{\Delta H}{\Delta S}, \quad T > \frac{170 \times 1000}{170}$$

$$T > 1000 \text{ K}$$

190. In which reaction, there will be increase in entropy?

(DCE 2009)

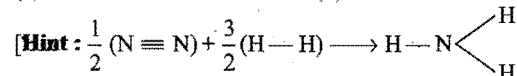


191. The species which by definition has zero standard molar enthalpy of formation at 298 K is: (IIT 2010)

- (a) $\text{Br}_2(g)$ (b) $\text{Cl}_2(g)$
(c) $\text{H}_2\text{O}(g)$ (d) $\text{CH}_4(g)$

192. The standard enthalpy of formation of NH_3 is -46 kJ mol^{-1} . If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1} , the average bond enthalpy of N—H bond in NH_3 is: (AIEEE 2010)

- (a) $+1056 \text{ kJ mol}^{-1}$ (b) $-1102 \text{ kJ mol}^{-1}$
(c) -964 kJ mol^{-1} (d) $+352 \text{ kJ mol}^{-1}$



$$\Delta H = -46 \text{ kJ mol}^{-1}$$

$$\text{BE} (\text{N} \equiv \text{N}) = -712 \text{ kJ mol}^{-1}$$

$$\text{BE} (\text{H} - \text{H}) = -436 \text{ kJ mol}^{-1}$$

$$\text{Let B.E. of } (\text{N} - \text{H}) = x \text{ kJ mol}^{-1}$$

$$\Delta H = \sum (\text{B.E.})_{\text{Reactants}} - \sum (\text{B.E.})_{\text{Products}}$$

$$-46 = \left[\frac{1}{2} (712) + \frac{3}{2} (436) \right] - 3x$$

$$x = 352 \text{ kJ mol}^{-1}$$

193. A 1 g sample of substance A at 100°C is added to 100 mL of H_2O at 25°C . Using separate 100 mL portion of H_2O , the procedure is repeated with substance B and then with substance C. How will the final temperatures of the water compare?

Substance Specific heat

A $0.6 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$

B $0.4 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$

C $0.2 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$

(DUMET 2010)

$$(a) T_C > T_B > T_A$$

$$(b) T_B > T_A > T_C$$

$$(c) T_A > T_B > T_C$$

$$(d) T_A = T_B = T_C$$

[Hint : $q = ms\Delta T$

$$s \propto \frac{1}{\Delta T}$$

Higher is the temperature of given solution, lesser is the temperature difference, so higher is the specific heat. Order of specific heat is $A > B > C$. Hence order of temperature will be :

$$T_A > T_B > T_C$$

194. For vaporisation of water at 1 atmospheric pressure, the values of ΔH and ΔS are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The temperature when Gibbs free energy change (ΔG) for transformation will be zero, is: [CBSE (PMT) 2010]

- (a) 273.4 K (b) 393.4 K
(c) 373.4 K (d) 293.4 K

[Hint : $\Delta G = \Delta H - T\Delta S$

$$0 = 40.63 \times 1000 - T \times 108.8$$

$$T = 373.4 \text{ K}$$

Set-2: The questions given below may have more than one correct answers

- Which is intensive property?
 - Mass
 - Mass/volume
 - Volume
 - Volume/mass
- Which is an irreversible process?
 - Mixing of two gases by diffusion
 - Evaporation of water at 373 K and 1 atm pressure
 - Dissolution of NaCl in water
 - All of the above
- One mole of anhydrous MgCl_2 dissolves in water and liberates 25 cal/mol of heat. $\Delta H_{\text{hydration}}$ of $\text{MgCl}_2 = -30$ cal/mol. Heat of dissolution of $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ is:
 - +5 cal/mol
 - 5 cal/mol
 - 55 cal/mol
 - 55 cal/mol
- Following enthalpy changes are given:

$\alpha\text{-D glucose}(s) \longrightarrow \alpha\text{-D glucose}(aq.);$	$\Delta H = 10.72 \text{ kJ}$
$\beta\text{-D glucose}(s) \longrightarrow \beta\text{-D glucose}(aq.);$	$\Delta H = 4.68 \text{ kJ}$
$\alpha\text{-D glucose}(s) \longrightarrow \beta\text{-D glucose}(aq.);$	$\Delta H = 1.16 \text{ kJ}$

 Calculate the enthalpy change in, $\alpha\text{-D glucose}(s) \longrightarrow \beta\text{-D glucose}(s)$
 - 14.24 kJ
 - 16.56 kJ
 - 7.2 kJ
 - 4.88 kJ
- If x and y are arbitrary extensive variables, then:
 - $(x + y)$ is an extensive variable
 - x/y is an intensive variable
 - dx/dy is an intensive variable
 - both (b) and (c)
- If x and y are arbitrary intensive variables, then:
 - xy is an intensive variable
 - x/y is an intensive variable
 - $(x + y)$ is an extensive property
 - dx/dy is an intensive property
- $$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(g); \quad \Delta H = x$$

$$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l); \quad \Delta H = y$$
 Heat of vaporization of water is:
 - $x + y$
 - $x - y$
 - $y - x$
 - $-(x + y)$
- Which is correct about ΔG ?
 - $\Delta G = \Delta H - T \Delta S$
 - At equilibrium, $\Delta G^\circ = 0$
 - At eq. $\Delta G = -RT \log K$
 - $\Delta G = \Delta G^\circ + RT \log K$
- Dissociation of sodium azide is given by,

$$\text{NaN}_3 \longrightarrow \text{Na} + 3/2 \text{N}_2;$$
 ΔH for this is:
 - $\frac{3}{2} \Delta H_f^\circ(\text{N}_2) - \Delta H_f^\circ(\text{NaN}_3)$
 - $-\Delta H_f^\circ(\text{NaN}_3)$
 - $\Delta H_f^\circ(\text{NaN}_3) - [\Delta H_f^\circ(\text{Na}) + \frac{3}{2} \Delta H_f^\circ(\text{N}_2)]$
 - $\Delta H_f^\circ(\text{Na}) + \frac{3}{2} \Delta H_f^\circ(\text{N}_2) - \Delta H_f^\circ(\text{NaN}_3)$
- The lattice energy of KCl is 202 kcal/mol. When KCl is dissolved in water 2 kcal/mol is absorbed. If the sol energies of K^+ and Cl^- are in the ratio 2 : 3; then $\Delta H_{\text{hydration}}$ of K^+ is:
 - 80 kJ/mol
 - 120 kJ/mol
 - 150 kJ/mol
 - 133.3 kJ/mol
- Which is a correct relationship?
 - $\left[\frac{dH}{dT} \right]_p - \left[\frac{dE}{dT} \right]_T = (+ve)$
 - $\left[\frac{dE}{dV} \right]_T = 0$ (for ideal gas)
 - $\left[\frac{dV}{dT} \right]_p = \frac{nR}{P}$ (for ideal gas)
 - All of the above
- The standard Gibbs free energy ΔG° is related to equilibrium constant K_p as:
 - $K_p = -RT \log \Delta G^\circ$
 - $K_p = [e/RT]^{\Delta G^\circ}$
 - $K_p = -\Delta G^\circ/RT$
 - $K_p = e^{-\Delta G^\circ/RT}$
- For the two equations given below:

$$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l) + x_1 \text{ kJ}$$

$$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(g) + x_2 \text{ kJ}$$
 Select the correct answer:
 - $x_1 > x_2$
 - $x_2 > x_1$
 - $x_1 = x_2$
 - $x_1 + x_2 = 0$
- $\Delta E = 0$, for which process?
 - Cyclic process
 - Isothermal expansion
 - Isochoric process
 - Adiabatic process
- For a reaction to be spontaneous in neither direction, which of the following is/are correct regarding the closed system?

[BHU (Mains) 2007]

 - $(\Delta G)_{T,P} = 0$
 - $(\Delta G)_{T,P} < 0$
 - $(\Delta S)_{U,V} = 0$
 - $(\Delta S)_{U,V} > 0$

Codes:

 - 1, 2 and 3 are correct
 - 1 and 2 are correct
 - 2 and 4 are correct
 - 1 and 3 are correct

Assertion-Reason TYPE QUESTIONS**Set-1**

The questions given below consist of an 'Assertion' (A) and the 'Reason' (R). Use the following keys to choose the appropriate answer:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
 (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 (c) If (A) is correct but (R) is incorrect.
 (d) If (A) is incorrect but (R) is correct.
- (A) The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.
 (R) When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of the change.
 - (A) $C_p - C_v = R$ for an ideal gas.
 (R) $\left[\frac{\partial E}{\partial V} \right]_T = 0$ for an ideal gas.
 - (A) When hydrogen gas at high pressure and room temperature expands adiabatically into a region of low pressure, there is a decrease in temperature.
 (R) Hydrogen gas at room temperature is above its inversion temperature.
 - (A) The thermodynamic factor which determines the spontaneity of a process is the free energy. For a process to be spontaneous the free energy must be -ve.
 (R) The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must always be positive if it is spontaneous.
 - (A) The Joules-Thomson coefficient for an ideal gas is zero.
 (R) There are no intermolecular attractive forces in an ideal gas.
 - (A) As temperature increases, heat of reaction also increases for exothermic as well as endothermic reactions.
 (R) $\Delta H_{\text{reaction}}$ varies according to the relation:

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$
 - (A) All exothermic reactions are spontaneous at room temperature.
 (R) $\Delta G = -ve$ for above reactions and for spontaneous reactions $\Delta G = -ve$.
 - (A) Efficiency of a reversible engine is 100% (maximum) when the temperature of sink is -273°C .
 (R) Efficiency of engine, $\eta = \frac{T_2 - T_1}{T_2}$.

Set-2

The questions given below consist of statements 'Assertion' (A) and 'Reason' (R).

- (a) If both (A) and (R) are correct and (R) is the correct reason for (A).
 (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
 (c) If (A) is true but (R) is false.
 (d) If both (A) and (R) are false.
- (A) Enthalpy of graphite is lower than that of diamond.
 (R) Entropy of graphite is lower than that of diamond.
 (AIIMS 1994)
 - (A) The enthalpy of formation of gaseous oxygen molecules at 298 K and under a pressure of one atm is zero.
 (R) The entropy of formation of gaseous oxygen molecules under the same condition is zero.
 (AIIMS 1996)
 - (A) Heat of neutralization for both HNO_3 and HCl with NaOH is 53.7 kJ per mol.
 (R) NaOH is a strong electrolyte/base.
 (AIIMS 1997)
 - (A) Decrease in free energy causes spontaneous reaction.
 (R) Spontaneous reactions are invariably exothermic.
 (AIIMS 1997)
 - (A) Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
 (R) Entropy of the system increases with increase in temperature.
 (AIIMS 1998)
 - (A) The enthalpy of formation of $\text{H}_2\text{O}(l)$ is greater than that of $\text{H}_2\text{O}(g)$.
 (R) Enthalpy change is negative for the condensation reaction

$$\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l)$$
 - (A) For a particular reaction, heat of combustion at constant pressure (q_p) is always greater than that at constant volume (q_v).
 (R) Combustion reactions are invariably accomplished by increase in number of moles.
 (AIIMS 1998)
 - (A) The enthalpy of both graphite and diamond is taken to be zero, being elementary substances.
 (R) The enthalpy of formation of an elementary substance in any state is taken as zero.
 - (A) Heat of neutralization of perchloric acid, HClO_4 , with NaOH is same as that of HCl with NaOH .
 (R) Both HCl and HClO_4 are strong acids.
 - (A) Heat of ionization of water is equal to the heat of neutralization of a strong acid with a strong base.
 (R) Water ionizes to a very small extent while H^+ ions from acid combine very rapidly with OH^- from base to form H_2O .

11. (A) Enthalpy of formation of HCl is equal to the bond energy of HCl.
 (R) Enthalpy of formation and bond energy both involve formation of one mole of HCl from the elements.
12. (A) Pressure, volume and temperature are all extensive properties.
 (R) Extensive properties depend upon the amount and nature of the substance.
13. (A) When a gas at high pressure expands against vacuum, the work done is maximum.
 (R) Work done in expansion depends upon the pressure inside the gas and increase in volume.
14. (A) When a real gas is allowed to expand adiabatically through a fine hole from a region of high pressure to a region of low pressure, the temperature of the gas falls.
 (R) Work is done at the cost of internal energy of the gas.
15. (A) Internal energy change in a cyclic process is zero.
 (R) Internal energy is a state function.
16. (A) An exothermic process, non-spontaneous at high temperature, may become spontaneous at low temperature.
 (R) With decrease in temperature, randomness (entropy) decrease.
17. (A) There is no reaction known for which ΔG is positive, yet it is spontaneous.
 (R) For photochemical reaction, ΔG is negative.
18. (A) A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.
 (R) All exothermic reactions are accompanied by decrease of randomness.
19. (A) Molar entropy of vaporization of water is different from ethanol.
 (R) Water is more polar than methanol.
20. (A) Heat of neutralization for both HNO_3 and HCl with NaOH is 53.7 kJ/mol.
 (R) NaOH is a strong electrolyte/base.
21. (A) In the following reaction:

$$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g); \quad \Delta H = \Delta U - RT$$
 (R) ΔH is related to ΔU by the equation,

$$\Delta H = \Delta U - \Delta n_g RT$$
22. (A) Enthalpy of graphite is lower than that of diamond.
 (R) Entropy of graphite is greater than that of diamond.
23. (A) For a reaction

$$2\text{NH}_3(g) \longrightarrow \text{N}_2(g) + 3\text{H}_2(g); \quad \Delta H > \Delta E$$
 (R) Enthalpy change is always greater than internal energy change.
 (AIIMS 2008)

Answers OBJECTIVE QUESTIONS

Set-1

- | | | | | | | | |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (b) | 2. (c) | 3. (d) | 4. (a) | 5. (c) | 6. (a) | 7. (b) | 8. (d) |
| 9. (a) | 10. (d) | 11. (c) | 12. (d) | 13. (c) | 14. (d) | 15. (a) | 16. (a) |
| 17. (c) | 18. (a) | 19. (a) | 20. (a) | 21. (b) | 22. (d) | 23. (b) | 24. (a) |
| 25. (c) | 26. (d) | 27. (d) | 28. (b) | 29. (d) | 30. (b) | 31. (c) | 32. (a) |
| 33. (c) | 34. (b) | 35. (a) | 36. (a) | 37. (d) | 38. (b) | 39. (d) | 40. (c) |
| 41. (d) | 42. (d) | 43. (c) | 44. (b) | 45. (b) | 46. (c) | 47. (a) | 48. (a) |
| 49. (a) | 50. (d) | 51. (b) | 52. (c) | 53. (d) | 54. (d) | 55. (b) | 56. (c) |
| 57. (a) | 58. (c) | 59. (b) | 60. (d) | 61. (b) | 62. (c) | 63. (a) | 64. (b) |
| 65. (c) | 66. (d) | 67. (b) | 68. (a) | 69. (d) | 70. (a) | 71. (d) | 72. (a) |
| 73. (b) | 74. (b) | 75. (c) | 76. (d) | 77. (d) | 78. (c) | 79. (c) | 80. (b) |
| 81. (a) | 82. (c) | 83. (a) | 84. (d) | 85. (b) | 86. (c) | 87. (d) | 88. (a) |
| 89. (d) | 90. (c) | 91. (a) | 92. (b) | 93. (a) | 94. (a) | 95. (c) | 96. (c) |
| 97. (a) | 98. (b) | 99. (c) | 100. (d) | 101. (c) | 102. (b) | 103. (d) | 104. (a) |
| 105. (c) | 106. (a) | 107. (b) | 108. (a) | 109. (c) | 110. (a) | 111. (a) | 112. (a) |
| 113. (c) | 114. (a) | 115. (c) | 116. (b) | 117. (c) | 118. (a) | 119. (d) | 120. (d) |
| 121. (a) | 122. (b) | 123. (d) | 124. (c) | 125. (a) | 126. (d) | 127. (b) | 128. (a) |
| 129. (d) | 130. (c) | 131. (c) | 132. (a) | 133. (a) | 134. (a) | 135. (b) | 136. (c) |
| 137. (b) | 138. (a) | 139. (d) | 140. (a) | 141. (c) | 142. (a) | 143. (b) | 144. (a) |
| 145. (a) | 146. (a) | 147. (d) | 148. (c) | 149. (b) | 150. (c) | 151. (b) | 152. (a) |
| 153. (b) | 154. (a) | 155. (a) | 156. (c) | 157. (b) | 158. (b) | 159. (a) | 160. (d) |
| 161. (b) | 162. (d) | 163. (c) | 164. (a) | 165. (c) | 166. (c) | 167. (d) | 168. (b) |
| 169. (b) | 170. (d) | 171. (a) | 172. (b) | 173. (a) | 174. (c) | 175. (b) | 176. (a) |
| 177. (a) | 178. (d) | 179. (a) | 180. (a) | 181. (c) | 182. (a) | 183. (d) | 184. (c) |
| 185. (b) | 186. (d) | 187. (d) | 188. (b) | 189. (d) | 190. (a) | 191. (b) | 192. (d) |
| 193. (c) | 194. (c) | | | | | | |

Set-2

- | | | | | | | | |
|-----------|-----------|---------|---------|--------------|--------------|---------|-----------|
| 1. (b, d) | 2. (a, c) | 3. (a) | 4. (d) | 5. (a, b, c) | 6. (a, b, d) | 7. (b) | 8. (a, d) |
| 9. (b) | 10. (a) | 11. (d) | 12. (d) | 13. (a) | 14. (a, b) | 15. (d) | |

Answers ASSERTION-REASON TYPE QUESTIONS

Set-1

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1. (d) | 2. (b) | 3. (d) | 4. (c) | 5. (a) | 6. (d) | 7. (a) | 8. (a) |
|--------|--------|--------|--------|--------|--------|--------|--------|

Set-2

- | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (b) | 4. (c) | 5. (b) | 6. (a) | 7. (d) | 8. (d) |
| 9. (a) | 10. (b) | 11. (d) | 12. (d) | 13. (d) | 14. (a) | 15. (a) | 16. (b) |
| 17. (d) | 18. (c) | 19. (b) | 20. (a) | 21. (d) | 22. (b) | 23. (c) | |

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions contain single correct option :

1. In which of the following pairs, both properties are intensive?
 (a) Pressure, temperature (b) Density, volume
 (c) Temperature, density (d) Pressure, volume

2. Although the dissolution of ammonium chloride (NH_4Cl) in water is an endothermic reaction, even then it is spontaneous because:

- (a) $\Delta S = -ve$ (b) $\Delta S = \text{zero}$
 (c) $T \Delta S < \Delta H$ (d) $\Delta S = +ve$ and $\Delta H < T \Delta S$

3. The S—S bond energy is if $\Delta H_f^\circ(E_t - S - E_t) = -147 \text{ kJ/mol}$;
 $\Delta H_f^\circ(E_t - S - S - E_t) = -202 \text{ kJ/mol}$ and $\Delta H_f^\circ S(g) = +223 \text{ kJ/mol}$:

- (a) 168 kJ (b) 126 kJ (c) 278 kJ (d) 572 kJ

[Hint:



$$\Delta H_{\text{reaction}} = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants})$$

$$= (-202) - (-147) = -55 \text{ kJ}$$

$$\Delta H_{\text{reaction}} = \Sigma (\text{BE})_{\text{reactants}} - \Sigma (\text{BE})_{\text{products}}$$

$$-55 = \text{Heat of sublimation and enthalpy of atomisation of sulphur} - \text{BE}(\text{S} - \text{S})$$

$$-55 = 223 - \text{BE}(\text{S} - \text{S})$$

$$\text{BE}(\text{S} - \text{S}) = 223 + 55 = 278 \text{ kJ}$$

(Common bonds of reactants and products are rejected.)]

4. Standard enthalpies of formation of O_3 , CO_2 , NH_3 and HI are 142.2, -393.2, -46.2 and +25.9 kJ mol^{-1} respectively. The order of their increasing stabilities will be:

- (a) O_3 , CO_2 , NH_3 , HI (b) CO_2 , NH_3 , HI , O_3
 (c) O_3 , HI , NH_3 , CO_2 (d) NH_3 , HI , CO_2 , O_3

[Hint: (i) Exothermic compounds are more stable than endothermic compounds.

(ii) Greater is the amount of heat evolved in the formation of a compound, more will be its stability.]

5. Combustion of octane takes place in an automobile engine. The homogeneous equation of combustion is:



The signs of ΔH , ΔS and ΔG for the reaction will be:

- (a) +ve, -ve, +ve (b) -ve, +ve, -ve
 (c) -ve, +ve, +ve (d) +ve, +ve, -ve

6. Which among the following represents the reaction of formation of the product?

- (a) $\text{C}_{(\text{diamond})} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$
 (b) $\text{S}_{(\text{monoclinic})} + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$
 (c) $2\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{N}_2\text{O}(g)$
 (d) None of the above

7. How much energy must be supplied to change 36 g of ice at 0°C to water at room temperature 25°C ?

Data for water

$\Delta H_{\text{fusion}}^\circ$	6.01 kJ/mol
$C_p \text{ liquid}$	$4.18 \text{ J K}^{-1} \text{ g}^{-1}$

- (a) 12 kJ (b) 16 kJ (c) 19 kJ (d) 22 kJ

[Hint: $\Delta H = \Delta H_{\text{fusion}}$ of two moles + $m_s \Delta T$

$$= 6.01 \times 2 + 36 \times 4.18 \times 25 \times 10^{-3}$$

$$\approx 16 \text{ kJ}]$$

8. A large positive value of ΔG° corresponds to which of these?

- (a) Small positive K (b) Small negative K
 (c) Large positive K (d) Large negative K

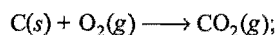
9. Consider the values for ΔH° (in kJ mol^{-1}) and for ΔS° (in $\text{J mol}^{-1} \text{ K}^{-1}$) given for four different reactions. For which reaction will ΔG° increase the most (becoming more positive) when the temperature is increased from 0°C to 25°C ?

- (a) $\Delta H^\circ = 50$, $\Delta S^\circ = 50$ (b) $\Delta H^\circ = 90$, $\Delta S^\circ = 20$
 (c) $\Delta H^\circ = -20$, $\Delta S^\circ = -50$ (d) $\Delta H^\circ = -90$, $\Delta S^\circ = -20$

[Hint: Use the relation, $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$]

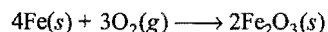
10. $\text{Fe}_2\text{O}_3(s) + \frac{3}{2} \text{C}(s) \longrightarrow \frac{3}{2} \text{CO}_2(g) + 2\text{Fe}(s)$;

$$\Delta H^\circ = +234.1 \text{ kJ}$$



$$\Delta H^\circ = -393.5 \text{ kJ}$$

Use these equations and ΔH° values to calculate ΔH° for this reaction:

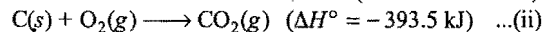


- (a) -1648.7 kJ (b) -1255.3 kJ

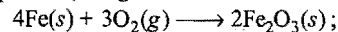
- (c) -1021.2 kJ (d) -129.4 kJ

[Hint: $2\text{Fe}(s) + \frac{3}{2} \text{CO}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s) + \frac{3}{2} \text{C}(s)$... (i)

$$(\Delta H^\circ = -234.1 \text{ kJ})$$



Multiplying eq. (i) by 2 and eq. (ii) by 3 and on adding both equations, we get:



$$\Delta H^\circ = (-234.1 \times 2) + (-3 \times 393.5)$$

$$= -1648.7 \text{ kJ}]$$

11. Consider this equation and the associated value for ΔH° :



Which statement about this information is incorrect?

- (a) If the equation is reversed, the ΔH° value equals +92.3 kJ
 (b) The four HCl bonds are stronger than four bonds in H_2 and Cl_2
 (c) The ΔH° value will be -92.3 kJ if HCl is produced as a liquid
 (d) 23.1 kJ of heat will be evolved when 1 mole of $\text{HCl}(g)$ is produced

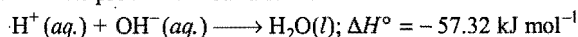
12. If the internal energy of an ideal gas decreases by the same amount as the work done by the system, the process is:

- (a) cyclic (b) isothermal (c) adiabatic (d) isolated

13. The enthalpy of neutralization of a strong acid by a strong base is $-57.32 \text{ kJ mol}^{-1}$. The enthalpy of formation of water is $-285.84 \text{ kJ mol}^{-1}$. The enthalpy of formation of hydroxyl ion is:

- (a) +228.52 kJ mol^{-1} (b) -114.26 kJ mol^{-1}
 (c) -228.52 kJ mol^{-1} (d) +114.2 kJ mol^{-1}

[Hint: The process of neutralization is:



$$\Delta H_{\text{reaction}} = \Sigma \text{ Heat of formation of products} \\ - \Sigma \text{ Heat of formation of reactants}$$

$$= \Delta H_{f, \text{H}_2\text{O}(\text{l})}^\circ - [\Delta H_{f, \text{H}^+(\text{aq.})}^\circ + \Delta H_{f, \text{OH}^-(\text{aq.})}^\circ]$$

$$-57.32 = -285.84 - (0 + x)$$

$$x = -285.84 + 57.32$$

$$= -228.52 \text{ kJ}]$$

14. For which process will ΔH° and ΔG° be expected to be most similar?

- (a) $2\text{Al}(\text{s}) + \text{Fe}_2\text{O}_3(\text{s}) \longrightarrow 2\text{Fe}(\text{s}) + \text{Al}_2\text{O}_3(\text{s})$
 (b) $2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{NaOH}(\text{aq.}) + \text{H}_2(\text{g})$
 (c) $2\text{NO}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g})$
 (d) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g})$

[Hint: (a) In this reaction, $\Delta S^\circ = 0$

$$\therefore \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta G^\circ = \Delta H^\circ]$$

15. For a particular reaction, $\Delta H^\circ = -38.3 \text{ kJ}$ and $\Delta S^\circ = -113 \text{ J K}^{-1} \text{ mol}^{-1}$. This reaction is:

- (a) spontaneous at all temperatures
 (b) non-spontaneous at all temperatures
 (c) spontaneous at temperatures below 66°C
 (d) spontaneous at temperatures above 66°C

[Hint: $\Delta G = \Delta H - T \Delta S$

For spontaneous process, $\Delta G < 0$.

$$\therefore \Delta H - T \Delta S < 0$$

$$\frac{\Delta H}{\Delta S} < T$$

$$\frac{-38.3 \times 1000}{-113} < T$$

$$\text{i.e., } T > 338.93 \text{ K, i.e., } 66^\circ\text{C}]$$

16. Which halogen in its standard state has the greatest absolute entropy per mole?

- (a) $\text{F}_2(\text{g})$ (b) $\text{Cl}_2(\text{g})$ (c) $\text{Br}_2(\text{l})$ (d) $\text{I}_2(\text{s})$

17. For which of these processes is the value of ΔS negative?

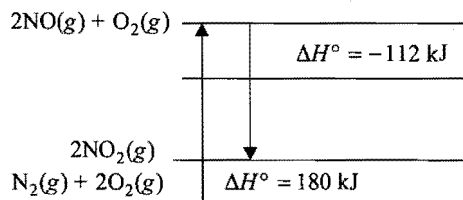
- I. Sugar is dissolved in water.
 II. Steam condenses on a surface.
 III. CaCO_3 is decomposed into CaO and CO_2 .

- (a) I only (b) II only
 (c) I and III only (d) II and III only

18. When solid NH_4NO_3 is dissolved in water at 25°C , the temperature of the solution decreases. What is true about the signs of ΔH and ΔS for this process?

	ΔH	ΔS
(a)	-	+
(b)	-	-
(c)	+	+
(d)	+	-

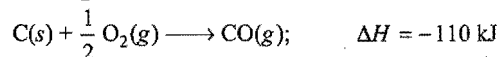
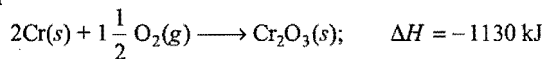
19. The diagram below shows the heat of reaction between N_2 , O_2 , NO and NO_2 :



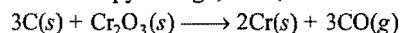
Which of the following statements pertaining to the formation of NO and NO_2 are correct?

- The standard heat of formation of NO_2 is 68 kJ mol^{-1} .
 - NO_2 is formed faster than NO at higher temperature.
 - The oxidation reaction of nitrogen to NO_2 is endothermic.
 - These two reactions often take place in troposphere and causes green house effect.
 - These two reactions often take place and are responsible for city smog.
- (a) 1 and 2 (b) 1 and 3 (c) 1 and 4 (d) 3 and 4
 (e) 3 and 5

20. The enthalpy changes for two reactions are given by the equations:

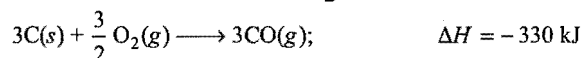
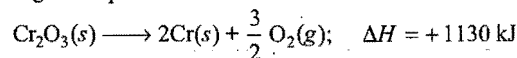


What is the enthalpy change, in kJ, for the reaction?

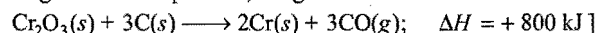


- (a) -1460 kJ (b) -800 kJ (c) $+800 \text{ kJ}$ (d) $+1020 \text{ kJ}$
 (e) $+1460 \text{ kJ}$

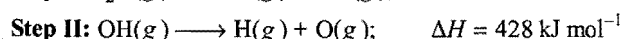
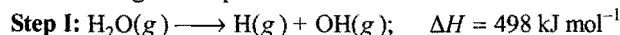
[Hint: The given equations can be written as:



Adding the above equations, we get:



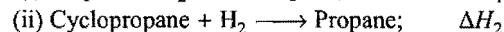
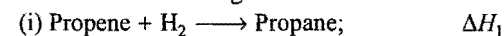
21. The enthalpy change at 298 K for decomposition is given in the following two steps:



The bond enthalpy of the $\text{O}-\text{H}$ bond is:

- (a) 498 kJ mol^{-1} (b) 463 kJ mol^{-1}
 (c) 428 kJ mol^{-1} (d) 70 kJ mol^{-1}

22. Consider the following two reactions:

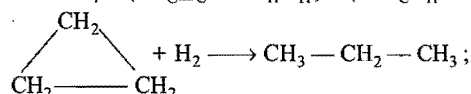


Then, $\Delta H_2 - \Delta H_1$ will be:

- (a) 0 (b) $2\text{BE}_{\text{C}-\text{C}} - \text{BE}_{\text{C}=\text{C}}$
 (c) $\text{BE}_{\text{C}=\text{C}}$ (d) $2\text{BE}_{\text{C}=\text{C}} - \text{BE}_{\text{C}-\text{C}}$

[Hint: $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{H}_2 \longrightarrow \text{CH}_3-\text{CH}_2-\text{CH}_3$;

$$\Delta H_1 = (\text{BE}_{\text{C}=\text{C}} + \text{BE}_{\text{H}-\text{H}}) - (2\text{BE}_{\text{C}-\text{H}} + \text{BE}_{\text{C}-\text{C}})$$



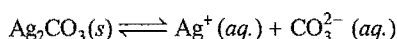
$$\Delta H_2 = (\text{BE}_{\text{C}-\text{C}} + \text{BE}_{\text{H}-\text{H}}) - (2 \times \text{BE}_{\text{C}-\text{H}})$$

$$\Delta H_2 - \Delta H_1 = 2\text{BE}_{\text{C}-\text{C}} - \text{BE}_{\text{C}=\text{C}}]$$

23. Under which circumstances would the free energy change for a reaction be relatively temperature independent?

(a) ΔH° is negative
 (b) ΔH° is positive
 (c) ΔS° has a large positive value
 (d) ΔS° has a small magnitude

24. Use the free energy change, $\Delta G^\circ = +63.3 \text{ kJ}$, for this reaction, to calculate the K_{sp} of $\text{Ag}_2\text{CO}_3(s)$ in water at 25°C :



(a) 3.2×10^{-26} (b) 8×10^{-12} (c) 2.9×10^{-3} (d) 7.9×10^{-2}

25. Which statement(s) is/are true?

1. S° values for all elements in their states are positive.
 2. S° values for all aqueous ions are positive.
 3. ΔS° values for all spontaneous reactions are positive.
 (a) 1 only (b) 1 and 2 only
 (c) 2 and 3 only (d) All of these

26. The enthalpy of a reaction does not depend upon:

(a) the intermediate reaction steps
 (b) the temperature of initial and final state of the reaction
 (c) the physical states of reactants and products
 (d) use of different reactants for the formation of the same product

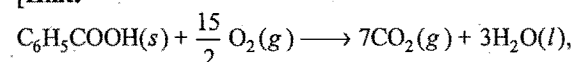
27. When a solution of 500 mL of 2 M KOH is added to 500 mL of 2 M HCl, then the rise in temperature T_1 is noted. When the same experiment is repeated by mixing 250 mL of each solution, the rise in temperature T_2 is noted:

(a) $T_1 = T_2$ (b) $T_1 = 2T_2$ (c) $T_2 = 2T_1$ (d) $T_1 = 4T_2$

28. The heat of combustion of solid benzoic acid at constant volume is -321.30 kJ at 27°C . The heat of combustion at constant pressure is:

(a) $-321.30 - 300R$ (b) $-321.30 + 300R$
 (c) $-321.30 - 150R$ (d) $-321.30 + 900R$

[Hint:



$$\Delta n = 7 - \frac{15}{2} = -\frac{1}{2}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$= -321.30 - \frac{1}{2} \times R \times 300 = -321.30 - 150R]$$

29. $A \longrightarrow B$; $\Delta U = 40 \text{ kJ mol}^{-1}$

If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy?

(a) More than 40 kJ (b) Zero
 (c) Less than 40 kJ (d) 40 kJ

30. For the process, $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$:

(a) $\Delta H = +ve$, $\Delta S = +ve$ (b) $\Delta H = -ve$, $\Delta S = +ve$
 (c) $\Delta H = +ve$, $\Delta U = -ve$ (d) $\Delta H = -ve$, $\Delta S = -ve$

31. Match the thermodynamic properties (List-I) with their relation (List-II):

List-I

List-II

A. Free energy change (ΔG°) (i) $RT \log_e K$
 B. Entropy change ΔS° (ii) $-nFE$

C. ΔH° enthalpy change of a reaction in standard state (iii) $RT^2 \left(\frac{d \ln K}{dT} \right)_P$

D. Standard free energy change (ΔG°) (iv) $-\left\{ \frac{d \Delta G}{dT} \right\}_P$

Select the correct answer:

Codes:	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(ii)	(iv)	(iii)	(i)
(c)	(iv)	(ii)	(iii)	(i)
(d)	(i)	(ii)	(iv)	(iii)

32. An ideal gas is allowed to expand under adiabatic conditions. The zero value is of:

(a) ΔT (b) ΔS
 (c) ΔG (d) none of these

33. Match the physical changes in List-I with their relations given in List-II:

List-I

List-II

A. ΔG	(i) $\Delta U + P\Delta V$
B. ΔH	(ii) $-nFE$
C. ΔS°	(iii) $-RT \log_e K$
D. ΔG°	(iv) $nR \log_e \left(\frac{V_2}{V_1} \right)$

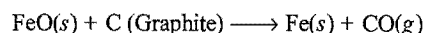
Select the correct answer from the given codes:

Codes:	A	B	C	D
(a)	(ii)	(i)	(iv)	(iii)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iv)	(iii)	(ii)	(i)
(d)	(i)	(ii)	(iv)	(iii)

34. Given the following data:

Substance	$\Delta H^\circ(\text{kJ/mol})$	$S^\circ(\text{J/mol K})$	$\Delta G^\circ(\text{kJ/mol})$
$\text{FeO}(s)$	-266.3	57.49	-245.12
C (Graphite)	0	5.74	0
$\text{Fe}(s)$	0	27.28	0
$\text{CO}(g)$	-110.5	197.6	-137.15

Determine at what temperature the following reaction is spontaneous?



- (a) 298 K
 (b) 668 K
 (c) 966 K
 (d) ΔG° is +ve, hence the reaction will never be spontaneous.

[Hint: $\Delta H_{\text{reaction}} = \Sigma \{ \Delta H_f^\circ \text{Fe}(s) + \Delta H_f^\circ \text{CO}(g) \}$

$$- \{ \Delta H_f^\circ \text{FeO}(s) + \Delta H_f^\circ \text{C(graphite)} \}$$

$$= (0 - 110.5) - (-266.3 + 0) = 155.8 \text{ kJ mol}^{-1}$$

$$\Delta S_{\text{reaction}} = \Sigma [S_{\text{Fe}(s)}^\circ + S_{\text{CO}(g)}^\circ] - [S_{\text{FeO}(s)}^\circ + S_{\text{C(graphite)}}^\circ]$$

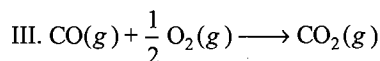
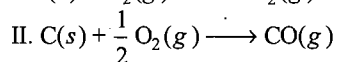
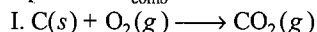
$$= (27.28 + 197.6) - (57.49 + 5.74)$$

$$= 161.65 \text{ JK}^{-1} \text{ mol}^{-1}$$

For spontaneous reaction, $T > \frac{\Delta H}{\Delta S}$; $T > \frac{155.8 \times 1000}{161.65}$

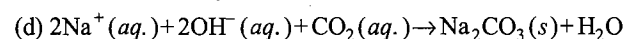
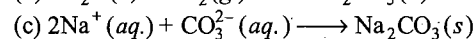
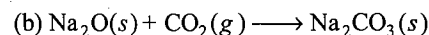
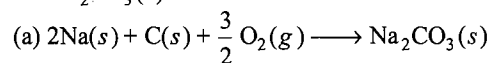
$\therefore T > 966 \text{ K}$

35. Which of the following equations has/have enthalpy changes equal to $\Delta H_{\text{comb}} \text{ C?}$



- (a) I and II (b) I, II and III
(c) I and III (d) I only

36. The enthalpy change of which reaction corresponds to ΔH_f° for $\text{Na}_2\text{CO}_3(s)$ at 298 K?



37. Enthalpy is equal to: (VITEEE 2007)

(a) $T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_P$ (b) $-T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_P$

(c) $T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_V$ (d) $-T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_V$

[Hint: $G = H - TS$... (i)]

$$G = U + PV - TS$$

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

From the first and second laws,

$$T\Delta S = \Delta U + P\Delta V$$

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

At constant pressure, $\Delta P = 0$

$$\frac{\Delta G}{\Delta T} = -S \quad \dots (ii)$$

From eqs. (i) and (ii),

$$G = H + T \frac{\Delta G}{\Delta T}$$

OR

$$G = H + T \left(\frac{\partial G}{\partial T} \right)_P$$

$$-\frac{H}{T^2} = -\frac{G}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P$$

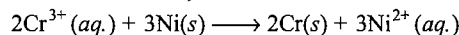
$$= \left[\frac{\partial(G/T)}{\partial T} \right]_P$$

$$H = -T^2 \left[\frac{\partial(G/T)}{\partial T} \right]_P$$

38. When a bomb calorimeter is used to determine the heat of reaction, which property of the system under investigation is most likely to remain constant?

- (a) Number of molecules (b) Pressure
(c) Temperature (d) Volume

39. For the reaction shown, which is closest to the value of ΔH°



$$\Delta H_f^\circ \quad (\text{kJ mol}^{-1})$$

$$\text{Cr}^{3+}(aq.) \quad -143$$

$$\text{Ni}^{2+}(aq.) \quad -54$$

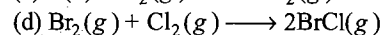
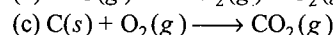
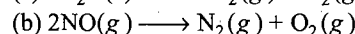
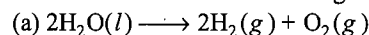
- (a) 124 kJ (b) 89 kJ
(c) -89 kJ (d) -124 kJ

40. An ice cube at 0.00°C is placed in 200 g of distilled water at 25°C . The final temperature after the ice is completely melted is 5°C . What is the mass of the ice cube?

$$(\Delta H_{\text{fus}} = 340 \text{ J g}^{-1}, C_p = 4.18 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1})$$

- (a) 23.6 g (b) 46.3 g
(c) 50.0 g (d) 800 g

41. Which reaction occurs with the greatest increase in entropy?



42. The bond dissociation energies for single covalent bonds formed between carbon and A, B, C, D and E atoms are:

Bond Bond energy (kcal mol^{-1})

(i) C—A 240

(ii) C—B 382

(iii) C—D 276

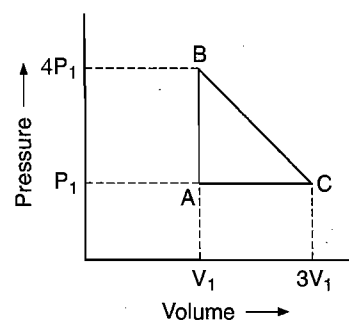
(iv) C—E 486

This indicates that the smallest atom is:

- (a) A (b) B (c) C (d) E

[Hint: C—E bond has highest bond energy; it means that the covalent bond C—E will be strongest. Smaller is the size of atom, stronger is the covalent bond.]

43. An ideal gas is taken around the cycle ABCA as:



- (a) $12P_1V_1$ (b) $6P_1V_1$ (c) $3P_1V_1$ (d) P_1V_1

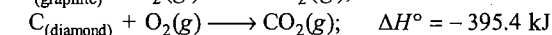
[Hint: Work done in the cyclic process

$$= \text{Area bounded (ABCA)}$$

$$= \frac{1}{2} \times AC \times AB$$

$$= \frac{1}{2} \times 2V_1 \times 3P_1 = 3P_1V_1]$$

44. One gram mole of graphite and diamond were burnt to form CO_2 gas.



- (a) graphite is more stable than diamond
 (b) diamond is more stable than graphite
 (c) graphite has greater affinity with oxygen
 (d) diamond has greater affinity with oxygen

[Hint: Thermal stability of one isotope is directly proportional to the heat of combustion.]

45. Which among the following is not an exact differential?

- (a) Q (dQ = heat absorbed)
 (b) U (dU = change in internal energy)
 (c) S (dS = entropy change)
 (d) G (dG = Gibbs free energy change)

[Hint: Heat ' Q ' is a path dependent function, hence its exact differentiation is not possible; however, internal energy, entropy and Gibbs free energy are state functions, hence can be differentiated exactly.]

46. A gas expands adiabatically at constant pressure such that:

$$T \propto \frac{1}{\sqrt{V}}$$

The value of γ , i.e., (C_p / C_v) of the gas will be:

- (a) 1.30 (b) 1.50 (c) 1.70 (d) 2

[Hint: $T \propto \frac{1}{\sqrt{V}}$

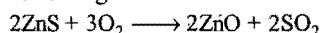
$$TV^{1/2} = \text{constant}$$

For adiabatic process, $TV^{\gamma-1} = TV^{\gamma-1} = \text{constant}$

$$\therefore \gamma - 1 = \frac{1}{2}, \gamma = \frac{3}{2}$$

47. $2\text{Zn} + \text{O}_2 \longrightarrow 2\text{ZnO}; \quad \Delta G^\circ = -616 \text{ J} \quad \dots \text{(i)}$
 $2\text{Zn} + \text{S} \longrightarrow 2\text{ZnS}; \quad \Delta G^\circ = -293 \text{ J} \quad \dots \text{(ii)}$
 $2\text{S} + 2\text{O}_2 \longrightarrow 2\text{SO}_2(\text{g}); \quad \Delta G^\circ = -408 \text{ J} \quad \dots \text{(iii)}$

ΔG° for the following reaction:



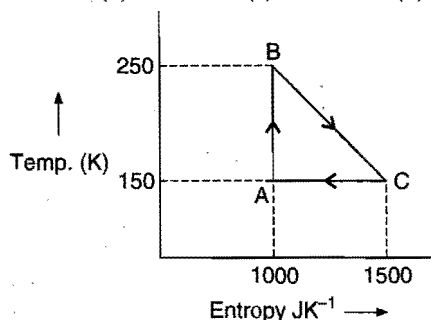
would be:

- (a) -731 J (b) -1317 J (c) +731 J (d) +1317 J

[Hint: $\Delta G^\circ = 2\Delta G^\circ_{\text{ZnO}} + 2\Delta G^\circ_{\text{SO}_2} - 2\Delta G^\circ_{\text{ZnS}}$
 $= [-616 - 408] - [-293]$
 $= -1024 + 293$
 $= -731 \text{ J}]$

48. The efficiency of the reversible cycle shown in the figure will be:

- (a) 33.33% (b) 56% (c) 66% (d) 25%



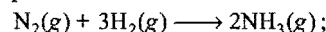
[Hint: Efficiency of cycle = $\frac{\text{Area of closed cycle}}{\text{Area under the curve}} \times 100$

$$= \frac{\frac{1}{2} \times (1500 - 1000) \times (250 - 150)}{\frac{1}{2} \times (1500 - 1000) \times (250 - 150) + (1500 - 1000) \times (150 - 0)} \times 100$$

$$= \frac{\frac{1}{2} \times 500 \times 100}{\frac{1}{2} \times 500 \times 100 + 500 \times 150} \times 100$$

$$= \frac{500 \times 50 \times 100}{500 \times 50 + 500 \times 150} = 25\%$$

49. In Haber's process of ammonia manufacture:



$$\Delta H_{25^\circ\text{C}}^\circ = -92.2 \text{ kJ}$$

Molecules	$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$
$C_p \text{ J K}^{-1} \text{ mol}^{-1}$	29.1	28.8	35.1

If C_p is independent of temperature, then reaction at 100°C as compared to that of 25°C will be:

- (a) more endothermic (b) less endothermic
 (c) more exothermic (d) less exothermic

[Hint: Use: $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$]

50. Consider the following statements:

- I. Change in enthalpy is always smaller than change in internal energy.
 II. The variation in enthalpy of a reaction with temperature is given by Kirchhoff's equation.
 III. The entropy change in reversible adiabatic process is equal to zero.

Select the correct answer:

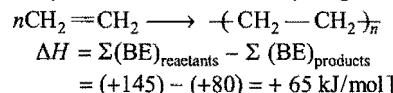
- (a) I and II (b) II and III
 (c) III and I (d) all are correct

51. In C_2H_4 , energy of formation of $(\text{C}=\text{C})$ and $(\text{C}-\text{C})$ are -145 kJ/mol and -80 kJ/mol respectively. What is the enthalpy change when ethylene polymerises to form polythene?

[JEE (Orissa) 2006]

- (a) +650 kJ/mol (b) +65 kJ/mol
 (c) -650 kJ mol⁻¹ (d) -65 kJ mol⁻¹

[Hint: Polymerisation of ethene may be given as:



[Note: C-H bonds are common in both reactants and products.]

52. If 150 kJ of energy is needed for muscular work to walk a distance of 1 km, then how much of glucose one has to consume to walk a distance of 5 km, provided only 30% of energy is available for muscular work. The enthalpy of combustion of glucose is 3000 kJ mol⁻¹:

[PMT (Kerala) 2007]

- (a) 75 g (b) 30 g (c) 180 g (d) 150 g
 (e) 45 g

53. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is:

(Given, $\Delta_r H_{298\text{K}}^\circ = -54.07 \text{ kJ mol}^{-1}$,
 $\Delta_r S_{298\text{K}}^\circ = 10 \text{ J K}^{-1} \text{ mol}^{-1}$ and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$;
 $2.303 \times 8.314 \times 298 = 5705$) (IIT 2007)

- (a) 5 (b) 10 (c) 95 (d) 100

[Hint: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= -54.07 \times 1000 - 298 \times 10$$

$$= -57050 \text{ J}$$

$$\Delta G^\circ = -2.303 RT \log_{10} K$$

$$-57050 = -5705 \log_{10} K$$

$$\log_{10} K = 10]$$

54. The lattice enthalpy and hydration enthalpy of four compounds are given below :

Compound	Lattice enthalpy (kJ/mol)	Hydration enthalpy (kJ/mol)
P	+ 780	- 920
Q	+ 1012	- 812
R	+ 828	- 878
S	+ 632	- 600

The pair of compounds which is soluble in water is :

[PET (Kerala) 2008]

- (a) P and Q (b) Q and R (c) R and S (d) Q and S
(e) P and R

[Hint : For solubility of ionic compounds, hydration energy must be greater than lattice energy.]

Following questions may have more than one correct options :

1. Which of the following are correct about irreversible isothermal expansion of ideal gas ?

(a) $W = -q$

(b) $\Delta U = 0$

(c) $\Delta T = 0$

(d) $W = -nRT \ln \frac{P_1}{P_2}$

2. The work done during adiabatic expansion or compression of an ideal gas is given by :

(a) $n C_V \Delta T$

(b) $\frac{nR}{(\gamma - 1)} (T_2 - T_1)$

(c) $-nR P_{\text{ext}} \left[\frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right]$

(d) $-2.303 RT \log \frac{V_2}{V_1}$

3. For an ideal gas $\left(\frac{C_{Pm}}{C_{Vm}} = \gamma \right)$; of molar mass M , its specific heat capacity at constant volume is :

(a) $\frac{\gamma R}{(\gamma - 1)M}$ (b) $\frac{\gamma}{M(\gamma - 1)}$ (c) $\frac{M}{R(\gamma - 1)}$ (d) $\frac{\gamma RM}{\gamma - 1}$

[Hint : $\frac{C_{Pm}}{C_{Vm}} = \gamma$, $C_{Pm} - C_{Vm} = R$

$$C_{Vm} = \frac{R}{\gamma - 1} \text{ and } C_{Pm} = \frac{R\gamma}{\gamma - 1}$$

$$\frac{\gamma}{\gamma - 1} = C_{Vm} \times M$$

$$C_{Vm} = \frac{x}{M(\gamma - 1)}]$$

Answers

● Single correct option

- | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (d) | 3. (c) | 4. (c) | 5. (b) | 6. (d) | 7. (b) | 8. (a) |
| 9. (c) | 10. (a) | 11. (c) | 12. (c) | 13. (c) | 14. (a) | 15. (d) | 16. (b) |
| 17. (b) | 18. (c) | 19. (e) | 20. (c) | 21. (b) | 22. (b) | 23. (d) | 24. (b) |
| 25. (a) | 26. (a) | 27. (a) | 28. (c) | 29. (b) | 30. (d) | 31. (b) | 32. (d) |
| 33. (a) | 34. (c) | 35. (d) | 36. (a) | 37. (b) | 38. (d) | 39. (a) | 40. (b) |
| 41. (a) | 42. (d) | 43. (c) | 44. (a) | 45. (a) | 46. (b) | 47. (a) | 48. (d) |
| 49. (d) | 50. (b) | 51. (b) | 52. (d) | 53. (b) | 54. (e) | | |

● One or more than one correct options

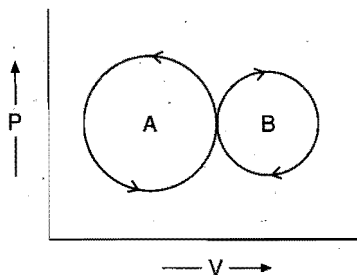
1. (a,b,c,d) 2. (a,b,c) 3. (b)

Integer Answer TYPE QUESTIONS

This section contains 11 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :

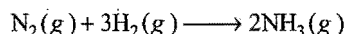
X	Y	Z	W
0	0	0	0
1	1	1	1
2	2	2	2
3	3	3	3
4	4	4	4
5	5	5	5
6	6	6	6
7	7	7	7
8	8	8	8
9	9	9	9

- A bubble of 8 moles of helium is submerged at certain depth in water. The temperature of water increases by 30°C . How much heat is added approximately to helium (in kJ) during expansion?
- For a liquid, enthalpy of fusion is $1.435 \text{ kcal mol}^{-1}$ and molar entropy change is $5.26 \text{ cal mol}^{-1} \text{ K}^{-1}$. The freezing point of liquid in celcius will be :
- For the reaction, $\text{Ag}_2\text{O}(s) \rightleftharpoons 2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g)$
 ΔH , ΔS and T are $40.63 \text{ kJ mol}^{-1}$, $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and 373.4 K respectively. Free energy change ΔG of the reaction will be:
 4. Standard Gibbs Free energy change ΔG° for a reaction is zero. The value of equilibrium constant of the reaction will be:
 5. ΔG° for the reaction $x + y \rightleftharpoons z$ is -4.606 kcal . The value of equilibrium constant of the reaction at 227°C is $(x \times 10^2)$. The value of 'x' is :
 6. 4.48 L of an ideal gas at STP requires 12 cal to raise the temperature by 15°C at constant volume. The C_p of the gas is cal.
 7.



In the present graph, the area of circle A and B are 25 unit and 20 unit respectively. Work done will be unit.

8. For the reaction,



Heat of reaction at constant volume exceeds the heat of reaction at constant pressure by the value of xRT . The value of x is :

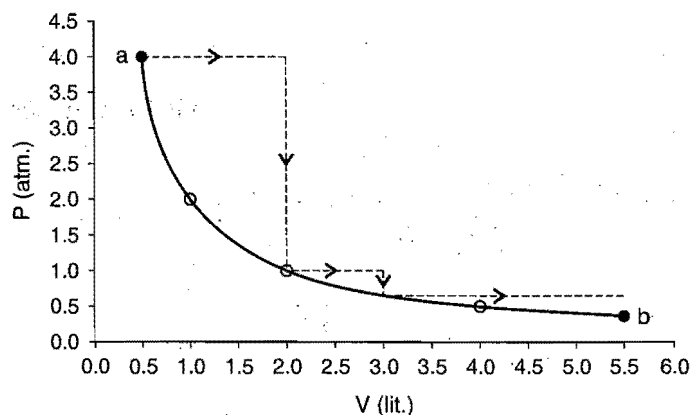
9. Gas (A_x) has the ratio of specific heat, equal to 1.66. The value of x will be :

10. For a liquid the vapour pressure is given by :

$$\log_{10} P = \frac{-400}{T} + 10$$

Vapour pressure of the liquid is 10^x mm Hg . The value of x will be :

11. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d , then the integer closest to the ratio w_d / w_s is:



(IIT 2010)

[Hint : w_d = work done along dotted line

$$= \sum P \Delta V$$

$$= 4 \times 1.5 + 1 \times 1 + 2.5 \times \frac{2}{3} = 8.65 \text{ L atm}$$

w_s = It is reversible isothermal process

$$= 2.303nRT \log \left(\frac{V_2}{V_1} \right)$$

$$= 2.303 \times (PV) \log \left(\frac{V_2}{V_1} \right)$$

$$= 2.303 \times 2 \log \frac{5.5}{0.5} = 4.79 \text{ L atm}$$

$$\frac{w_d}{w_s} = \frac{8.65}{4.79} \approx 2]$$

Answers

- | | | | | | | | |
|--------|---------|---------|--------|--------|--------|--------|--------|
| 1. (3) | 2. (0) | 3. (0) | 4. (1) | 5. (1) | 6. (6) | 7. (5) | 8. (2) |
| 9. (1) | 10. (9) | 11. (2) | | | | | |

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Chemical reactions are invariably associated with the transfer of energy either in the form of heat or light. In the laboratory, heat changes in physical and chemical processes are measured with an instrument called calorimeter. Heat change in the process is calculated as:

$$q = ms \Delta T; \quad s = \text{Specific heat} \\ = c \Delta T; \quad c = \text{Heat capacity}$$

Heat of reaction at constant volume is measured using bomb calorimeter.

$$q_v = \Delta U = \text{Internal energy change}$$

Heat of reaction at constant pressure is measured using simple or water calorimeter:

$$q_p = \Delta H \\ q_p = q_v + P \Delta V \\ \Delta H = \Delta U + \Delta nRT$$

The amount of energy released during a chemical change depends on the physical state of reactants and products, the condition of pressure, temperature and volume at which the reaction is carried out. The variation of heat of reaction with temperature and pressure is given by Kirchhoff's equation:

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p; \quad \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_v$$

(At constant pressure) (At constant volume)

Answer the following questions:

1. Match the List-I with List-II and select the answer from the given codes:

List-I

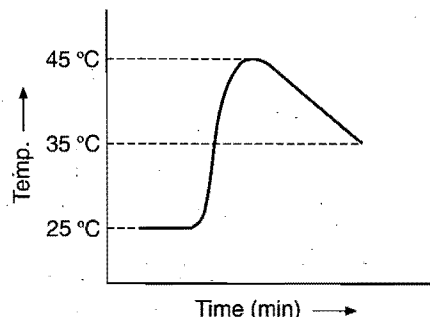
List-II

- | | |
|--|--------------------------------|
| A. $C(s) + O_2(g) \longrightarrow CO_2(g)$ | 1. $\Delta H = \Delta U + RT$ |
| B. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ | 2. $\Delta H = \Delta U$ |
| C. $NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$ | 3. $\Delta H = \Delta U - 2RT$ |
| D. $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$ | 4. $\Delta H = \Delta U + 2RT$ |
| E. $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ | 5. $\Delta H = \Delta U - RT$ |

Codes:	A	B	C	D	E
(a)	1	2	3	4	5
(b)	5	2	3	4	1
(c)	1	3	4	2	5
(d)	2	3	4	1	5

2. The heat capacity of a bomb calorimeter is 500 J/K. When 0.1 g of methane was burnt in this calorimeter, the temperature rose by 2°C. The value of ΔU per mole will be:
(a) +1 kJ (b) -1 kJ (c) +160 kJ (d) -160 kJ
3. For which reaction will $\Delta H = \Delta U$? Assume each reaction is carried out in an open container:
(a) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$
(b) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
(c) $C(s) + 2H_2O(g) \longrightarrow 2H_2(g) + CO_2(g)$
(d) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

4. What value of ΔT should be used for the calorimetry experiment that gives the following graphical results?



- (a) 10°C (b) 25°C (c) 20°C (d) 35°C

5. The enthalpy of fusion of ice is 6.02 kJ mol⁻¹. The heat capacity of water is 4.18 J g⁻¹ °C⁻¹. What is the smallest number of ice cubes at 0°C, each containing one mole of water, that are needed to cool 500 g of liquid water from 20°C to 0°C?

- (a) 1 (b) 7 (c) 14 (d) 125

[Hint: Heat released to cool 500 g water from 20°C to 0°C,

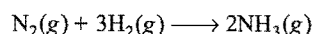
$$q = ms \Delta T \\ = 500 \times 4.18 \times 20 = 41800 \text{ J} = 41.8 \text{ kJ}$$

Number of moles of water (ice) that will melt to absorb 41.8 kJ

$$= \frac{41.8}{6.02} \approx 7$$

∴ Number of cubes of ice that will melt = 7]

6. The enthalpy change (ΔH) for the reaction,



is -92.38 kJ at 298 K. The internal energy change ΔU at 298 K is: (AIIMS 2006)

- (a) -92.38 kJ (b) -87.42 kJ (c) -97.34 kJ (d) -89.9 kJ

[Hint: $\Delta n_g = 2 - 4 = -2$

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

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

$$= -92.38 \times 1000 - (-2) \times 8.314 \times 298 \\ = -87424 \text{ J} = -87.424 \text{ kJ}]$$

7. The specific heat of I₂ in vapour and solid state are 0.031 and 0.055 cal/g respectively. The heat of sublimation of iodine at 200°C is 6.096 kcal mol⁻¹. The heat of sublimation of iodine at 250°C will be:

- (a) 3.8 kcal mol⁻¹ (b) 4.8 kcal mol⁻¹
(c) 2.28 kcal mol⁻¹ (d) 5.8 kcal mol⁻¹

[Hint: $I_2(s) \rightleftharpoons I_2(g)$

$$\Delta C_p = (0.031 - 0.055) \times 10^{-3} \times 254$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$

$$\frac{\Delta H_2 - 6.096}{50} = (0.031 - 0.055) \times 10^{-3} \times 254 \\ \Delta H_2 = 5.79 \text{ kcal mol}^{-1}]$$

● Passage 2

In a chemical reaction, the bonds of reactants are decomposed and new bonds of products are formed. The amount of energy required to break a particular bond in a gaseous molecule under standard conditions homolytically is called the standard bond dissociation enthalpy of that bond (ΔH_{A-B}°).

Bond energies can be used to obtain an approximate value for a reaction enthalpy of a gas phase reaction if the appropriate enthalpies of formation are not available.

$$\Delta H_{\text{reaction}}^\circ = \sum \text{Bond energy of bonds, broken in the reactants} - \sum \text{Bond energy of bonds, formed in the products}$$

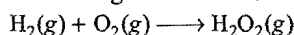
Bond energy depends on three factors:

- Greater is the bond length, lesser is the bond energy.
- Bond energy increases with the bond multiplicity.
- Bond energy increases with the electronegativity difference between the bonding atoms.

Answer the following questions:

- Arrange N—H, O—H and F—H bonds in the decreasing order of bond energy:
 - F—H > O—H > N—H
 - O—H > N—H > F—H
 - N—H > O—H > F—H
 - F—H > N—H > O—H
- X_2 represents halogen molecule. Bond energy of different halogen molecules will lie in following sequences:
 - $F_2 > Cl_2 > Br_2 > I_2$
 - $Cl_2 > Br_2 > F_2 > I_2$
 - $I_2 > Cl_2 > Br_2 > F_2$
 - $Br_2 > F_2 > I_2 > Cl_2$

[Hint: Bond energy of F_2 is surprisingly low due to strong repulsion between the lone pairs of two fluorine atoms.]
- Which among the following sequences is correct about the bond energy of C—C, C=C and C≡C bonds?
 - $C \equiv C > C = C > C - C$
 - $C \equiv C < C = C < C - C$
 - $C = C > C \equiv C > C - C$
 - $C \equiv C > C - C > C = C$
- In CH_4 molecule, which of the following statements is correct about the C—H bond energy?
 - All C—H bonds of methane have same energy
 - Average of all C—H bond energies is considered
 - Fourth C—H bond requires highest energy to break
 - None of the above
- Use the bond energies to estimate ΔH for this reaction:



Bond	Bond energy
H—H	436 kJ mol ⁻¹
O—O	142 kJ mol ⁻¹
O=O	499 kJ mol ⁻¹
H—O	460 kJ mol ⁻¹

- 127 kJ
 - 209 kJ
 - 484 kJ
 - 841 kJ
- The heat of formation of NO from its elements is +90 kJ mol⁻¹. What is the approximate bond dissociation energy of the bond in NO?

$$BE_{N \equiv N} = 941 \text{ kJ mol}^{-1} \quad BE_{O=O} = 499 \text{ kJ mol}^{-1}$$
 - 630 kJ mol⁻¹
 - 720 kJ mol⁻¹
 - 760 kJ mol⁻¹
 - 810 kJ mol⁻¹

● Passage 3

The change in Gibbs free energy (ΔG) of the system alone provides a criterion for the spontaneity of a process at constant temperature and pressure. A change in the free energy of a system at constant temperature and pressure will be:

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}}$$

At constant temperature and pressure:

$$\Delta G_{\text{system}} < 0 \text{ (spontaneous)}$$

$$\Delta G_{\text{system}} = 0 \text{ (equilibrium)}$$

$$\Delta G_{\text{system}} > 0 \text{ (non-spontaneous)}$$

Free energy is related to the equilibrium constant, as:

$$\Delta G^\circ = 2.303RT \log_{10} K_e$$

Answer the following questions:

- The free energy for a reaction having $\Delta H = 31400 \text{ cal}$, $\Delta S = 32 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 1000°C is: [JEE (Orissa) 2005]
 - 9336 cal
 - 7386 cal
 - 1936 cal
 - +9336 cal
- For a spontaneous reaction ΔG , equilibrium ' K ' and E_{cell}° will be respectively: (AIEEE 2005)
 - ve, > 1, +ve
 - +ve, > 1, -ve
 - ve, < 1, -ve
 - ve, > 1, -ve
- For a system in equilibrium, $\Delta G = 0$, under conditions of constant.....: (KCET 2005)
 - temperature and pressure
 - temperature and volume
 - pressure and volume
 - energy and volume
- If both ΔH and ΔS are negative, the reaction will be spontaneous:
 - at high temperature
 - at low temperature
 - at all temperatures
 - at absolute zero
- A reaction has positive values of ΔH and ΔS . From this you can deduce that the reaction:
 - must be spontaneous at any temperature
 - cannot be spontaneous at any temperature
 - will be spontaneous only at low temperature
 - will be spontaneous only at high temperature
- For a reaction to be spontaneous at all temperatures:
 - $\Delta G - \text{ve}, \Delta H + \text{ve}$ and $\Delta S + \text{ve}$
 - $\Delta G + \text{ve}, \Delta H - \text{ve}$ and $\Delta S + \text{ve}$
 - $\Delta G - \text{ve}, \Delta H - \text{ve}$ and $\Delta S - \text{ve}$
 - $\Delta G - \text{ve}, \Delta H - \text{ve}$ and $\Delta S + \text{ve}$

3 moles of CO_2 gas expands isothermally against external pressure of 1 bar. Volume increases from 10 L to 30 L respectively. The system is in thermal contact of surroundings at temperature 15°C . Entropy change in isothermal process is:

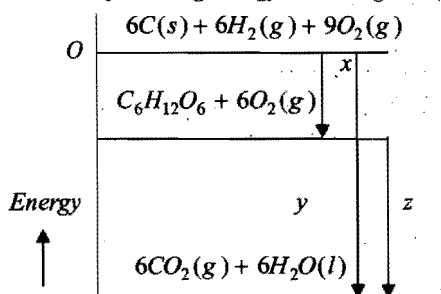
$$\Delta S = 2.303 nR \log \left(\frac{V_2}{V_1} \right)$$

Answer the following questions:

- If CO_2 behaves like an ideal gas, then entropy change of system (ΔS_{system}) will be:
 - +27.4 J K⁻¹
 - 9.1 J K⁻¹
 - 27.4 J K⁻¹
 - 9.1 J K⁻¹
- Select the correct relation:
 - $\Delta S_{\text{system}} > 0, \Delta S_{\text{surr.}} = 0$
 - $\Delta S_{\text{surr.}} < 0, \Delta S_{\text{system}} > 0$
 - $\Delta S_{\text{system}} = 0, \Delta S_{\text{surr.}} = 0$
 - $\Delta S_{\text{surr.}} > 0, \Delta S_{\text{system}} < 0$

● Passage 4

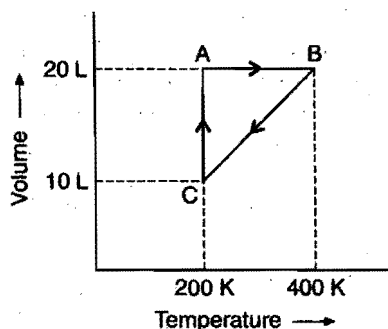
Consider the following energy level diagram:



Answer the following questions on the basis of the given diagram:

- The heat of formation of glucose is:
 - $-x$
 - $-y$
 - $x - y$
 - $-x + z$
- In the given diagram z refers to:
 - $6 \times \Delta H_f^\circ \text{CO}_2$
 - $\Delta H_f^\circ \text{C}_6\text{H}_{12}\text{O}_6$
 - $\Delta H_{\text{combustion}}^\circ \text{C}_6\text{H}_{12}\text{O}_6$
 - $\Delta H_{\text{combustion}}^\circ \text{C(s)} + \Delta H_f^\circ \text{H}_2\text{O(l)}$
- The quantity y is equal to:
 - $\Delta H_{\text{combustion}}^\circ \text{C(s)} + \Delta H_{\text{combustion}}^\circ \text{H}_2\text{(g)}$
 - $x + z$
 - $x - z$
 - $\Delta H_f^\circ \text{CO}_2 + \Delta H_{\text{H}_2\text{O}}$
- Select the incorrect statement(s):
 - combustion of glucose is exothermic process
 - standard state of glucose is $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$
 - heat of formation of glucose = Heat of combustion of glucose
 - $x + y = z$

● Passage 5



Graph for one mole of gas

Answer the following questions based on the above diagram:

- Process, $A \rightarrow B$ represents:
 - isobaric
 - isochoric
 - isothermal
 - adiabatic
- The pressure at C is:
 - 3.284 atm
 - 1.642 atm
 - 0.0821 atm
 - 0.821 atm
- Work done in the process $C \rightarrow A$ is:
 - zero
 - 8.21 L atm
 - 16.2 L atm
 - unpredictable

- The process which occurs in going from, $B \rightarrow C$ is:
 - isothermal
 - adiabatic
 - isobaric
 - isochoric
- The pressures at A and B in the atmosphere are respectively:
 - 0.821 and 1.642
 - 1.642 and 0.821
 - 1 and 2
 - 0.082 and 0.164

● Passage 6

The thermodynamic property that measures the extent of molecular disorder is called entropy. The direction of a spontaneous process for which the energy is constant is always the one that increases the molecular disorder. Entropy change of phase transformation can be calculated using Trouton's formula $\left(\Delta S = \frac{\Delta H}{T}\right)$. In the reversible adiabatic process, however, ΔS will

be zero. The rise in temperature in isobaric and isochoric conditions is found to increase the randomness or entropy of the system.

$$\Delta S = 2.303 C \log (T_1 / T_2)$$

$$C = C_p \text{ or } C_v$$

Answer the following questions:

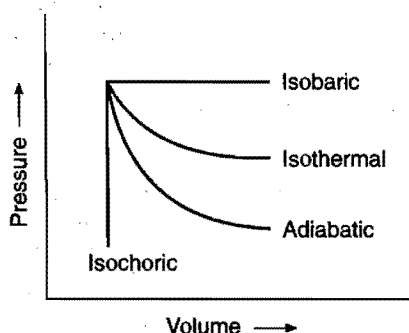
- The entropy change in an adiabatic process is:
 - zero
 - always positive
 - always negative
 - sometimes positive and sometimes negative
- If, water in an insulated vessel at -10°C , suddenly freezes, the entropy change of the system will be:
 - $+10 \text{ J K}^{-1} \text{ mol}^{-1}$
 - $-10 \text{ J K}^{-1} \text{ mol}^{-1}$
 - zero
 - equal to that of surroundings
- The melting point of a solid is 300 K and its latent heat of fusion is 600 cal mol^{-1} . The entropy change for the fusion of 1 mole of the solid (in cal K^{-1}) at the same temperature would be:
 - 200
 - 2
 - 0.2
 - 20
- For which of the following cases $\Delta S = \frac{\Delta H}{T}$?
 - A process for which $\Delta C_p = 0$ but $\Delta C_v \neq 0$
 - An adiabatic process
 - An isobaric or isothermal process
 - An isothermal reversible phase transition process
- When 1 mol of an ideal gas is compressed to half of its volume, its temperature becomes double; then the change in entropy (ΔS) would be:
 - $C_v \ln 2$
 - $C_p \ln 2$
 - $C_v R \ln 2$
 - $(C_v - R) \ln 2 \times C_p$

$$[\text{Hint: } \Delta S = 2.303 C_p \log_{10} \left(\frac{V_1}{V_2} \right)]$$

$$= C_p \ln \left(\frac{V_1}{V_2} \right) = C_p \ln_e \left(\frac{1}{1/2} \right) \\ = C_p \ln_e 2]$$

● Passage 7

The pressure-volume behaviour of various thermodynamic processes is shown in graphs:



Work is the mode of transference of energy. If the system involves gaseous substance and there is difference of pressure between system and surroundings, such a work is referred to as pressure-volume work ($w_{PV} = -P_{ext} \Delta V$). It has been observed that reversible work done by the system is the maximum obtainable work.

$$w_{rev} > w_{irr}$$

The works of isothermal and adiabatic processes are different from each other.

$$w_{\text{isothermal reversible}} = 2.303nRT \log_{10} \left(\frac{V_2}{V_1} \right) = 2.303nRT \log_{10} \left(\frac{P_1}{P_2} \right)$$

$$w_{\text{adiabatic reversible}} = C_V (T_1 - T_2)$$

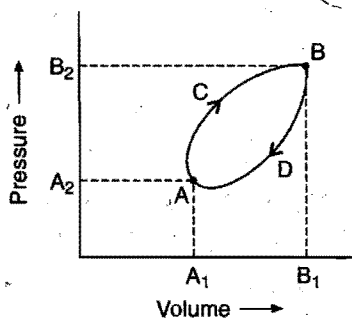
Answer the following questions:

1. If w_1, w_2, w_3 and w_4 are work done in isothermal, adiabatic, isobaric and isochoric reversible processes, then the correct sequence (for expansion) would be:

- (a) $w_1 > w_2 > w_3 > w_4$ (b) $w_3 > w_2 > w_1 > w_4$
 (c) $w_3 > w_2 > w_4 > w_1$ (d) $w_3 > w_1 > w_2 > w_4$

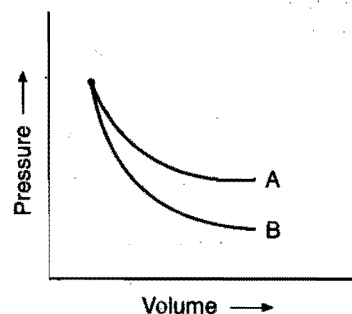
[Hint: w = Work done = Area under curve.]

2. A thermodynamic system goes in acyclic process as represented in the following P - V diagram:



The net work done during the complete cycle is given by the area:

- (a) cycle ACBDA
 (b) AA_1B_1BDA
 (c) AA_2B_2B
 (d) half of area bounded by curve
3. P - V plots for two gases during adiabatic processes are given in the given figure:



Plot A and plot B should correspond to:

- (a) He and O_2 (b) He and Ar (c) O_2 and He (d) O_2 and F_2

[Hint: Slope of the adiabatic curve $\propto \gamma$

Slope of B > Slope of A

He ($\gamma = 1.66$); O_2 ($\gamma = 1.44$)

Thus, correct answer will be (c).]

4. The q value and work done in isothermal reversible expansion of one mole of an ideal gas from initial pressure of 1 bar to final pressure of 0.1 bar at constant temperature 273 K are:

- (a) 5.22 kJ, -5.22 kJ (b) -5.22 kJ, 5.22 kJ
 (c) 5.22 kJ, 5.22 kJ (d) -5.22 kJ, -5.22 kJ

[Hint: $w = -2.303nRT \log \left(\frac{P_1}{P_2} \right)$

$$= -2.303 \times 1 \times 8.314 \times 273 \log \left(\frac{1}{0.1} \right)$$

$$= -5.227 \text{ kJ}$$

$$q = -w = +5.227 \text{ kJ for isothermal process}]$$

5. Calculate work done when 1 mole of an ideal gas is expanded reversibly from 20 L to 40 L at a constant temperature of 300 K.

- (a) 7.78 kJ (b) -1.73 kJ (c) 11.73 kJ (d) -4.78 kJ

Answers

Passage 1.	1. (d)	2. (d)	3. (b)	4. (c)	5. (b)	6. (b)	7. (d)
Passage 2.	1. (a)	2. (b)	3. (a)	4. (b)	5. (a)	6. (a)	
Passage 3.	1. (a)	2. (a)	3. (a)	4. (c)	5. (d)	6. (d)	8. (b)
Passage 4.	1. (a)	2. (c)	3. (b)	4. (c, d)			
Passage 5.	1. (b)	2. (b)	3. (b)	4. (c)	5. (a)		
Passage 6.	1. (a)	2. (c)	3. (b)	4. (d)	5. (b)		
Passage 7.	1. (d)	2. (a)	3. (c)	4. (a)	5. (b)		

SELF ASSESSMENT

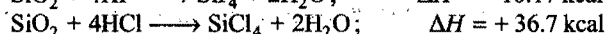
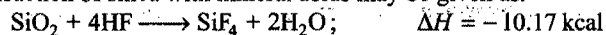
ASSIGNMENT NO. 7

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Reaction of silica with mineral acids may be given as:



which among the following is correct?

- HF and HCl both will react with silica
- Only HF will react with silica
- Only HCl will react with silica
- Neither HF nor HCl will react with silica

[Hint: Exothermic reactions are spontaneous]

2. In Mayer's relation,

$$C_P - C_V = R$$

'R' stands for:

- translational kinetic energy of 1 mol gas
- rotational kinetic energy of 1 mol gas
- vibrational kinetic energy of 1 mol gas
- work done to increase the temperature of 1 mol gas by one degree

[Hint: $PV = RT$ (For 1 mol gas) ... (i)]

$$P(V + \Delta V) = R(T + 1) \quad \dots (ii)$$

From eqs. (i) and (ii)

$$P\Delta V = R$$

i.e.,

$$W = R \text{ (work done)}$$

3. For an ideal gas, the Joule-Thomson coefficient is:

- zero
- positive
- negative
- depends on atomicity of gas

4. Entropy change in reversible adiabatic process is:

- infinite
- zero
- equal to $C_V \Delta T$
- equal to $nR \ln \left(\frac{V_2}{V_1} \right)$

5. For a process to be in equilibrium, it is necessary that:

- $\Delta S_{\text{system}} = \Delta S_{\text{surr.}}$
- $\Delta S_{\text{system}} = -\Delta S_{\text{surr.}}$
- $\Delta S_{\text{system}} = 0$
- $\Delta S_{\text{surr.}} = 0$

6. Predict the sign of ΔS for each of the following processes, which occur at constant temperature:

- The volume of 2 mol of O_2 (g) increases from 44L to 54L
- The pressure of 2 mol of O_2 (g) increases from 1 atm to 1.2 atm.

I

II

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

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

7. Which of the following statements must be true for the entropy of a pure solid to be zero?

- The temperature must be zero kelvin
- The solid must be perfectly crystalline
- The solid must be an element
- The solid must be ionic

- I
- I and II
- I, II and III
- All are correct

8. Which of the following statements is correct?

- Slope of adiabatic $P-V$ curve is smaller than that in isothermal one
- Slope of adiabatic $P-V$ curve will be same as that in isothermal one
- Slope of adiabatic $P-V$ curve will be larger than in isothermal one
- Slope of adiabatic $P-V$ curve will be zero

9. $\left(\frac{\partial H}{\partial P} \right)_T$ for an ideal gas is equal to:

- zero
- $\frac{\Delta VRT}{P}$
- $\frac{P\Delta V}{T}$
- $nR\Delta T$

10. A refrigerator is used to remove heat from enclosure at 0°C at the rate of 600 watt. If the surroundings temperature is 30°C , calculate the power needed:

(a) 303 watt (b) 11000 watt
(c) 65.9 watt (d) 110 watt

SECTION-II

Multiple Answers Type Objective Questions

11. ΔU will be zero for which processes?
(a) Cyclic process (b) Isothermal expansion
(c) Isochoric process (d) Adiabatic process
12. If x and y are two intensive variables then:
(a) xy is an intensive variable
(b) $\frac{x}{y}$ is an intensive variable
(c) $(x + y)$ is an intensive variable
(d) $\frac{dx}{dy}$ is an extensive property
13. Which of the following expressions is/are correct for an adiabatic process?
(a) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ (b) $\frac{P_2}{P_1} = \left(\frac{T_1}{T_2}\right)^{\gamma-1/\gamma}$
(c) $P_2 V_2^\gamma = P_1 V_1^\gamma$ (d) $P_1 V_1^{\gamma-1} = P_2 V_2^{\gamma-1}$
14. Select the state functions among the following:
(a) temperature (b) entropy
(c) work (d) enthalpy
15. Select the correct expressions among the following:
(a) $\frac{\Delta G - \Delta H}{T} = \left(\frac{\partial \Delta G}{\partial T}\right)_P$ (b) $\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P$
(c) $\frac{\Delta S}{nF} = \left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_P$ (d) $\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_{T/C_P}$
16. Which of the following are correct for an ideal gas?
(a) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (b) $\left(\frac{\partial H}{\partial P}\right)_T = 0$
(c) $\left(\frac{\partial T}{\partial P}\right)_H = 0$ (d) $\left(\frac{\partial P}{\partial T}\right)_V = 0$
17. The Clausius-Clapeyron equation may be given as:
(a) $\log_{10} \left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$
(b) $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$
(c) $\frac{dP}{dT} = \frac{q}{T\Delta V}$
(d) $\frac{dP}{dT} = \frac{\Delta V}{\Delta S}$
18. Which of the following is/are not state function?
(a) q (b) $q - w$
(c) $\frac{q}{w}$ (d) $q + w$

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.
19. **Statement-1:** Most of the combustion reactions are exothermic.

Because

Statement-2: Products are more stable than reactants in exothermic process.

20. **Statement-1:** There is no exchange in internal energy in a cyclic process.

Because

Statement-2: In a cyclic process, the system returns to original state in a number of steps.

21. **Statement-1:** The value of enthalpy of neutralization of weak acid and strong base is always numerically less than 57.1 kJ.

Because

Statement-2: All the OH^- ions furnished by 1 gram equivalent of strong base are not completely neutralized.

22. **Statement-1:** Heat of solution is positive when $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is dissolved in water but it is negative when anhydrous CuSO_4 is dissolved in water.

Because

Statement-2: Molar masses of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and CuSO_4 are different.

23. **Statement-1:** The extensive property of a single pure substance depends upon the number of moles of the substance present.

Because

Statement-2: Any extensive property expressed per mole becomes intensive.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4×4 matrix should be as follows:

	p	q	r	s
a	p	q	r	s
b	p	q	r	s
c	p	q	r	s
d	p	q	r	s

24. Match the List-I with List-II:

List-I	List-II
(a) $\left(\frac{\partial T}{\partial P}\right)_H$	(p) V
(b) $\left(\frac{\partial G}{\partial P}\right)_T$	(q) T
(c) $\left(\frac{\partial H}{\partial S}\right)_P$	(r) $-S$
(d) $\left(\frac{\partial G}{\partial T}\right)_P$	(s) μ_{JT}

25. Match the List-I with List-II and select the correct answer from the given codes:

List-I (Thermodynamic properties)	List-II (Expression)
(I) ΔG	(A) $-RT \log_e K$
(II) ΔH°	(B) $RT^2 \left(\frac{d \ln K}{dT}\right)_P$
(III) ΔS	(C) nFE
(IV) ΔG°	(D) $-\left[\frac{\partial \Delta G}{\partial T}\right]_P$

Codes:

- (a) I-C, II-B, III-D, IV-A
 (b) I-B, II-C, III-D, IV-A
 (c) I-A, II-B, III-C, IV-D
 (d) I-D, II-A, III-B, IV-C

26. Match the List-I with List-II:

List-I	List-II
(a) Perfectly crystalline solid	(p) $\Delta U = 0$
(b) Reversible reaction at equilibrium	(q) $T = \text{constant}$
(c) Isothermal process	(r) $\lim_{T \rightarrow 0K} S \rightarrow 0$
(d) $\left(\frac{\partial G}{\partial P}\right) = -S$	(s) $\Delta S_{\text{universe}} = 0$

Answers

- | | | | | | | | |
|-----------------------------|---------------|--------------------------------|---------------|------------|---------------|---------------|---------------|
| 1. (b) | 2. (d) | 3. (a) | 4. (b) | 5. (b) | 6. (c) | 7. (b) | 8. (c) |
| 9. (a) | 10. (c) | 11. (a, b) | 12. (a, b, d) | 13. (a, c) | 14. (a, b, d) | 15. (a, c, d) | 16. (a, b, c) |
| 17. (a, b, c) | 18. (a, b, c) | 19. (a) | 20. (a) | 21. (c) | 22. (c) | 23. (b) | |
| 24. (a-s) (b-p) (c-q) (d-r) | 25. (a) | 26. (a-r) (b-s) (c-p, q) (d-q) | | | | | |