

LESSON 6**THERMODYNAMICS****1. BASIC TERMS**

This lesson deals with heat changes accompanying physical and chemical processes.

1.1 SYSTEM & SURROUNDINGS

Any specified portion of universe under investigation is called system and the rest of the universe is called surroundings.

1.2 TYPES OF SYSTEM**1.2.1 OPEN SYSTEM**

It is defined as a system, which can exchange matter as well as energy with the surroundings. For example, a liquid kept in an open flask.

1.2.2 CLOSED SYSTEM

It is defined as a system which can exchange only energy with the surroundings. For example, a liquid in a closed vessel.

1.2.3 ISOLATED SYSTEM

It is defined as a system which can neither exchange matter nor energy with the surroundings. For example, a thermally insulated flask.

1.3 THERMODYNAMIC PROCESS

It is an operation by which a system undergoes a change from one state to another.

1.3.1 ISOTHERMAL PROCESS

A process in which the temperature remains constant throughout its course is called isothermal process.

i.e. $\Delta T = 0$ and also $\Delta E = 0$.

1.3.2 ADIABATIC PROCESS

A process during which no heat is exchanged between the system and the surroundings is called adiabatic process.

i.e. $dq = 0$.

1.3.3 ISOCHORIC PROCESS

A process during which volume of the system remains constant is called isochoric process.

i.e. $\Delta V = 0$.

1.3.4 ISOBARIC PROCESS

A process during which pressure of the system remains constant is called isobaric process.

i.e. $\Delta P = 0$.

1.3.5 CYCLIC PROCESS

A process during which state of the system does not change is called cyclic process.

i.e. $\Delta E = 0$ and also $\Delta H = 0$.

1.3.6 REVERSIBLE PROCESS

A process in which the driving force is infinitesimally greater than the opposing force is called reversible process.

1.3.7 IRREVERSIBLE PROCESS

A process in which direction can not be altered by small changes in variables like P, V, T etc. is called irreversible process.

1.4 EXTENSIVE & INTENSIVE PROPERTIES

Properties which depend on the amount of matter are called extensive properties. e.g. mass, volume, energy, enthalpy, entropy etc.

Properties which do not depend on the amount of matter are called intensive properties. e.g. Pressure, temperature, density, specific heat, specific volume, surface tension, viscosity, electromotive force etc.

1.5 STATE FUNCTIONS OR STATE VARIABLES

Those fundamental properties which determine the state of a system are called state variables or state functions or thermodynamic parameters. The change in the state properties is dependent on the initial and final states of the system and not on the path followed.

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

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

1.6 WORK & TYPES OF WORK

Work is defined as energy transfer to or from a system with reference to the surroundings.

If an object is displaced through a distance dx against a force F , then the amount of work done is defined as

$$w = F \times dx$$

1.6.1 TYPES OF WORK

- (a) Gravitational work = mgh

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

Work is an algebraic quantity. It is +ve if the mass is lifted (h is +ve), in which case it is said that work has been produced in the surroundings and it is -ve if the mass is lowered (h is -ve), in which case the work is said to be destroyed in the surroundings or has flowed from the surroundings.

- (b) Electrical work = Charge \times potential = $q \times V$

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

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

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, $w = -ve$.

1.7 HEAT

It is defined as **the energy that flows across the boundary of a system during a change in its state by virtue of a difference in temperature between the system and its surroundings and flows from a point of higher to a point of lower temperature.**

Heat absorbed or evolved, $\Delta Q = m s \Delta t$

where m = mass of substance, s = specific heat and Δt = temperature difference.

- (i) If heat flows into the system, ΔQ or ΔH is $+ve$ and the process is referred as endothermic.
- (ii) If heat flows out of the system, ΔQ or ΔH is $-ve$, and the process is referred as exothermic.

1.8 UNITS OF HEAT AND WORK

The unit of heat is calorie. **One calorie is defined as the quantity of heat required to raise the temperature of one gram of water by $1^\circ C$.**

Since heat and work are interrelated, SI unit of heat is Joule.

$$1 \text{ cal} = 4.184 \text{ Joule}$$

$$1 \text{ litre atm} = 101.3 \text{ J} = 1.013 \times 10^9 \text{ erg} = 24.206 \text{ cal.}$$

1.9 INTERNAL ENERGY

Every substance possesses a definite amount of energy which depends upon factors such as composition of the substance, temperature and pressure. This is called intrinsic or internal energy (E).

$$E = E_T + E_R + E_V + E_B + E_E \dots\dots\dots$$

where E_T = Translational energy, E_R = Rotational energy, E_V = Vibrational energy, E_B = Bonding energy and E_E = Electronic energy.

Internal energy of a system is state function and its absolute value can not be calculated but its change can be determined. When the system undergoes a change in its state, the internal energy change is given by

$$\Delta E = E_2 - E_1$$

where E_1 = Internal energy in the initial state and E_2 = Internal energy in the final state.

In a chemical reaction, $\Delta E = E_P - E_R$

where E_P = Internal energy of products and E_R = Internal energy of reactants.

1.10 Enthalpy (H)

Heat content of a system at constant pressure is called enthalpy. It is related with internal energy by the equation,

$$H = E + PV$$

Every substance has a definite value of enthalpy in a particular state. It is also a state function like internal energy. The change in enthalpy accompanying a process can be determined as

$$\Delta H = H_2 - H_1$$

where H_1 = Enthalpy of a substance in the initial state and H_2 = Enthalpy of a substance in the final state.

In the case of a chemical reaction, $\Delta H = H_p - H_R$

where H_p = Enthalpy of products and H_R = Enthalpy of reactants.

1.11 RELATION BETWEEN ΔH AND ΔE

Let us consider a chemical reaction,



then at constant pressure (P), the enthalpy change would be given as

$$\Delta H = H_y - H_x$$

We know that, $H = E + PV$

Let E_x and V_x be the internal energy and volume of the reactants and E_y and V_y be the respective values of products. Then

$$H_x = E_x + PV_x \text{ \& } H_y = E_y + PV_y$$

$$\Delta H = (E_y + PV_y) - (E_x + PV_x)$$

$$\Delta H = (E_y - E_x) + P(V_y - V_x)$$

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

2. FIRST LAW OF THERMODYNAMICS

The philosophical argument of Mayer and the experimental work of Joule, a pupil of John Dalton led Helmholtz to state “the conservation of energy” as a principle of universal validity. The first law of thermodynamics, states that “**energy can neither be created nor destroyed although it can be converted from one form into another.**”

2.1 JUSTIFICATION OF FIRST LAW OF THERMODYNAMICS

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

- Either by allowing the heat to be absorbed by the system or to evolve out of the system.
- By doing work on the system or the work is done by the system.

If a closed system having E_1 internal energy is supplied ‘q’ amount of heat, then the internal energy of the system becomes $(E_1 + q)$.

If work (w) is done on the system, then its internal energy further increases and becomes E_2 .

Thus

$$E_2 = E_1 + q + w$$

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

$$\text{or } \Delta E = q + w. \quad \dots\dots(ii)$$

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

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

Thus, first law of thermodynamics may also be stated as “**the net energy change of a closed system is equal to the heat absorbed plus the work done on the system or minus the work done by the system.**”

2.2 CONCLUSIONS DRAWN FROM THE 1ST LAW

- (i) For an ideal gas undergoing an isothermal change, the internal energy of the system does not change. i.e. $\Delta E = 0$, then

$$0 = q + w$$

$$\text{or } q = -w$$

i.e. heat absorbed by the system is equal to the work done by the system.

$$\text{or } w = -q$$

heat evolved out of the system is equal to work done on the system.

- (ii) For an isochoric process no work is done, $w = 0$, then the first law is reduced 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 the heat lost by the system.

- (iii) For adiabatic processes involving no exchange of heat between the system and the surroundings, $q = 0$. Thus,

$$\Delta E = w$$

i.e. if work is done on the system, its internal energy increases and the work done by the system decreases its internal energy.

- (iv) If a gas expands against constant external pressure, P and the corresponding change in volume is ΔV , then work done by the system

$$w = -P\Delta V$$

Thus, equation (ii) becomes

$$\Delta E = q - P\Delta V \quad \dots\dots(iii)$$

If the process is carried out at constant volume, then $\Delta V = 0$. Thus,

$$\Delta E = q_v$$

i.e. the change in internal energy is equal to the heat absorbed or evolved at constant volume.

- (v) We have, $q = \Delta E + P\Delta V$ (from equation (iii))

$$= (E_2 - E_1) + P(V_2 - V_1) = E_2 + PV_2 - (E_1 + PV_1) = H_2 - H_1$$

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

i.e. the change in enthalpy is equal to the heat absorbed or evolved at constant pressure. This is important

as most of the chemical reactions are carried out at constant pressure and temperature.

(vi) We know that, $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_g RT$ ($\because P\Delta V = \Delta n_g RT$)

or,

$$q_p = q_v + \Delta n_g RT \quad \dots\dots(iv)$$

where Δn_g = Difference between moles of gaseous products and gaseous reactants.

2.3 HEAT CAPACITY

It is defined as the quantity of heat required to raise the temperature of the system by one degree.

$$\text{i.e. } C = \frac{dq}{dT}$$

where C = Heat capacity, dq = Amount of heat absorbed by the system and

dT = Rise in temperature.

Its unit is $J K^{-1}$ or $J / ^\circ C$.

Larger the sample, greater is its heat capacity. It is therefore, common to use specific heat capacity (specific heat) or molar heat capacity.

2.3.1 SPECIFIC HEAT

The amount of heat required to raise the temperature of 1 gm of a substance by 1 degree is called specific heat.

$$\therefore \text{Specific heat} = \frac{\text{Heat capacity}}{\text{mass (in gm)}} = \frac{\text{Heat absorbed}}{\text{Rise in temperature} \times \text{mass (in gm)}}$$

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{Molar mass}}$$

Units of specific heat & molar heat capacity are $J K^{-1} g^{-1}$ and $J K^{-1} mol^{-1}$ respectively.

Now, heat supplied = Mass \times specific heat \times rise in temperature.

$$\text{i.e. } q = m \times C_s \times \Delta T \quad \dots\dots(v)$$

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

At constant volume, $q_v = \Delta E$.

So, heat capacity at constant volume per mole,

$$C_v = \left(\frac{dE}{dT} \right)_v \quad \dots\dots(vi)$$

At constant pressure, $q_p = \Delta H$.

So, heat capacity at constant pressure per mole,

$$C_p = \left(\frac{dH}{dT} \right)_p \quad \dots\dots(vii)$$

where C_p & C_v are molar heat capacities at constant pressure & constant volume respectively. The heat capacity at constant pressure (C_p) is “generally” larger than that at constant volume (C_v) because at constant pressure, a part of heat added to the substance may be used in work of expanding whereas at constant volume all the added heat produces a rise in temperature. The term “generally” has been used because substances generally expand with increase of temperature at constant pressure, but in exceptional cases, there may be a contraction, e.g. water between 1° & 4°C .

3. PRESSURE – VOLUME WORK

3.1 ISOTHERMAL EXPANSION

No heat flows out of or into the system in an isothermal expansion, so that temperature remains constant throughout the process of expansion. Since for an ideal gas, the internal energy (ΔE), depends only on temperature, the internal energy of the gas remains constant.

i.e. $\Delta E = 0$

From 1st law of thermodynamics,

$$\Delta E = q + w$$

For isothermal process, $\Delta E = 0$, hence

$$q = -w$$

In the case of isothermal expansion, work is done by the system at the cost of heat absorbed. The magnitude of ‘q’ or ‘w’ depends on the manner in which the process of expansion is carried out i.e. reversibly or irreversibly.

ΔH can be calculated as follows

We know, $\Delta H = \Delta E + \Delta n_g RT$

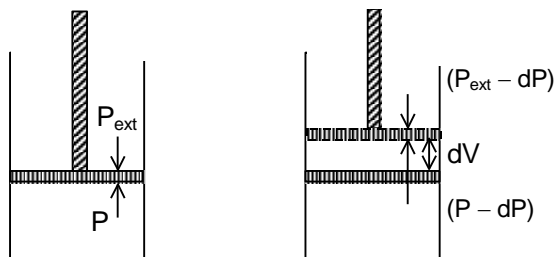
For isothermal process, $\Delta E = 0$ & $\Delta T = 0$ thus, $\Delta H = 0$.

3.1.1 Work–done in reversible isothermal expansion

Let us consider a non–insulated cylinder fitted with a weightless and frictionless piston containing an ideal gas. Let P be the pressure of the gas which equals external pressure, P_{ext} .

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

An infinitesimal expansion in volume, dV , results from an infinitesimal decrease in the external pressure, say dP . Consequently, the pressure of the gas inside the cylinder falls to $(P_{\text{ext}} - dP)$ i.e. it equals again to the external pressure and the piston come to rest again.



The workdone by the gas in each step of expansion is given as

$$dw = - (P_{\text{ext}} - dP) dV = - P_{\text{ext}} \cdot dV = - PdV$$

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

The total amount of workdone during the isothermal reversible expansion of the gas from volume V_1 to V_2 is given by

$$\int_1^2 dw = - \int_{V_1}^{V_2} PdV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV \quad (\because PV = nRT).$$

$$\int_1^2 dw = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w = -nRT \ln \frac{V_2}{V_1}$$

$$w_{\text{rev}} = -2.303 nRT \log_{10} \frac{V_2}{V_1} \quad \dots\dots(\text{viii})$$

At constant temperature,

$$P_1 V_1 = P_2 V_2$$

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

$$\therefore w_{\text{rev}} = -2.303 nRT \log_{10} \frac{P_1}{P_2} \quad \dots\dots(\text{ix})$$

For isothermal compression, work done by an ideal gas is same as isothermal expansion but with positive sign. Thus equation (viii) & (ix) is the maximum work done in an expansion, or the minimum work needed to effect a compression. This equation tells us that the work required to compress a gas from 10 atm to 100 atm is just the same as that required to compress a gas from 1 atm to 10 atm.

3.1.2 WORK DONE IN IRREVERSIBLE ISOTHERMAL EXPANSION

Irreversible isothermal expansions observed are

- (i) Free expansion
- (ii) Intermediate expansion.

Since the external pressure is zero in free expansion, the work done is zero e.g. expansion of a gas in vacuum.

The external pressure is less than gas pressure in the case of intermediate expansion. Thus, the workdone when volume changes from V_1 to V_2 is

$$w_{\text{irrev}} = - \int_{V_1}^{V_2} P_{\text{ext}} \times dV$$

$$= - P_{\text{ext}}(V_2 - V_1)$$

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

3.2 ADIABATIC EXPANSION

From first law of thermodynamics, $\Delta E = q + w$

In an adiabatic expansion, $q = 0$, $\therefore \Delta E = w$

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

$$C_v = \left(\frac{dE}{dT} \right)_v$$

or $dE = C_v \cdot dT$

and for finite changes, $\Delta E = C_v \times \Delta T = w$ (x)

The value of ΔT depends upon the nature of process (i.e. reversible or irreversible.)

3.2.1 REVERSIBLE ADIABATIC EXPANSION

If P be the external pressure and ΔV be the increase in volume, then work done by the system is

$$w = -P\Delta V$$

If ΔT is the fall in temperature, then

$$C_v \Delta T = -P\Delta V$$

For very small change in a reversible process and for one mole of a gas,

$$C_v dT = -PdV = -\frac{RT}{V} \cdot dV$$

$$\text{or, } C_v \frac{dT}{T} = -R \frac{dV}{V}$$

For a process that takes the gas from a volume V_1 at a temperature T_1 to a new volume V_2 at a temperature T_2 , we have

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

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$\log \frac{T_2}{T_1} = -\frac{R}{C_v} \log \frac{V_1}{V_2} \quad \text{.....(xi)}$$

We know that

$$C_p - C_v = R$$

Dividing it by C_v gives

$$\frac{C_p}{C_v} - 1 = \frac{R}{C_v}$$

$$\gamma - 1 = \frac{R}{C_v} \quad (\because \frac{C_p}{C_v} = \gamma)$$

Putting the value of R/C_v in equation (xi)

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

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

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

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

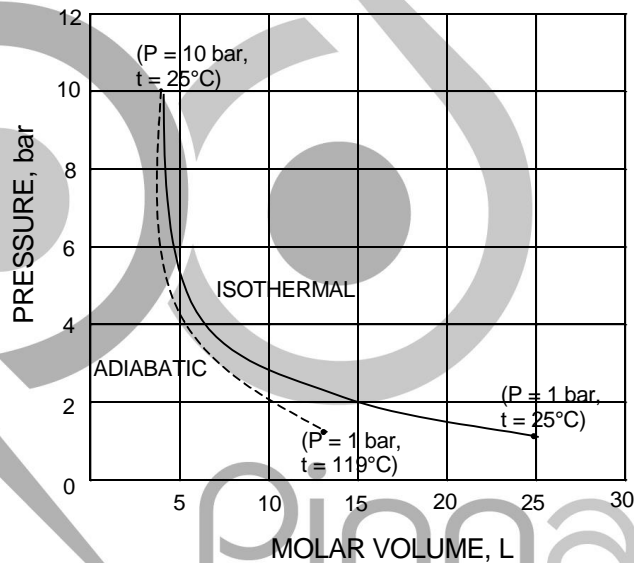
or $TV^{\gamma-1} = \text{constant}$

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

or $PV^\gamma = \text{constant}$

The above integration assumes that C_V is a constant and not a function of T . We know, for an isothermal expansion, $PV = \text{constant}$.

On plots of P versus V , curves for reversible adiabatic process are steeper than those for isothermal process as given below.



When a gas expands isothermally, thermal energy is supplied to make up for the energy delivered to the mechanical surroundings. For a balanced adiabatic expansion, work is done by the system on the surroundings ($-w$) i.e. the energy delivered to the surroundings must come from the internal of the gas. As a result, the temperature falls ($-\Delta E$) and the pressure change for a given expansion is greater than that in the corresponding isothermal expansion. From equation (xii),

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{\gamma-1} \quad (\because V_1 = \frac{RT_1}{P_1})$$

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

Now, work done $= C_V \times \Delta T = C_V (T_2 - T_1) = \frac{R}{\gamma-1} (T_2 - T_1)$

For n moles of a gas, **work done** = $\frac{nR}{\gamma - 1}(T_2 - T_1)$

3.2.2 IRREVERSIBLE ADIABATIC EXPANSION

In free expansion, the external pressure is zero, i.e. work done is zero.

$$\therefore \Delta E = w = 0$$

$$\& \Delta T = 0 \& \Delta H = 0.$$

In intermediate expansion, suppose the pressure is suddenly released to 1 atm and the gas expands adiabatically against this constant pressure. Since this is not a reversible expansion equation (xii) cannot be used.

Since, $q = 0$, $\Delta E = w$

$$w = C_V(T_2 - T_1) \quad \dots\dots(xiv)$$

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

$$w = -P_{ext}(V_2 - V_1) = -P_{ext}\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right) = -P_{ext}R\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right) \quad \dots\dots(xv)$$

Equating equations (xiv) & (xv), we get

$$w = C_V(T_2 - T_1) = -R P_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right) \quad \dots\dots(xvi) \quad (\text{For one mole})$$

Illustration 1

Question: 1 m^3 of neon gas $\left(C_V = \frac{3}{2}R\right)$ at 273.2 K and 10 atm undergoes three different expansions to a final pressure of 1 atm . Calculate the final volume and the work done in three different expansions.

- Isothermal reversible expansion
- Adiabatic reversible expansion and
- Irreversible adiabatic expansion.

Solution: (a) Final volume, $V_2 = \frac{P_1V_1}{P_2} = \frac{(1)(10)}{(1)} = 10 \text{ m}^3$

The work done by the gas in expanding equals the heat absorbed by the gas from its surroundings.

$$\therefore -w = q = nRT \ln \frac{V_2}{V_1}$$

$$n = \frac{10 \times 10^3}{0.0821 \times 273.2} = 446.1 \text{ mol}$$

$$-w = (446.1)(8.314)(273.2)(2.303) \log_{10} 10 = 232.85 \text{ kJ}$$

- For adiabatic reversible expansion,

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

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{3}{2}R + R}{\frac{3}{2}R} = \frac{5}{3}$$

$$\therefore V_2 = (10)^{3/5} (1) = \mathbf{3.981 \text{ m}^3}$$

The final temperature is obtained from

$$P_2 V_2 = nRT_2$$

$$T_2 = \frac{P_2 V_2}{nR} = \frac{(1) (3.981 \times 10^3)}{(446.1) 0.0821}$$

$$= 108.8 \text{ K}$$

For an adiabatic process, $q = 0$ & $\Delta E = w$.

Also, since C_v is constant

$$\begin{aligned} w &= nC_v (T_2 - T_1) = \left(n \frac{3}{2} R \right) (T_2 - T_1) \\ &= (446.1) \left(\frac{3}{2} R \right) (108.8 - 273.2) = \mathbf{-914.1 \text{ kJ}} \end{aligned}$$

(c) For irreversible adiabatic expansion,

From equation (xvi), we have,

$$-C_v(T_2 - T_1) = nR P_2 \left(\frac{T_2}{P_2} - \frac{T_1}{P_1} \right)$$

$$-\frac{3}{2}(T_2 - 273.2) = nR (1) \left(\frac{T_2}{1} - \frac{273.2}{10} \right)$$

$$\therefore T_2 = 174.8 \text{ K}$$

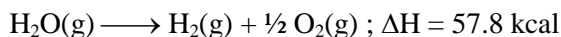
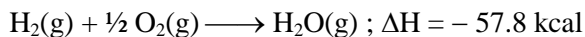
$$\therefore \Delta E = w = \frac{3}{2} nR (174.8 - 273.2) = \mathbf{-547.4 \text{ kJ}}$$

Note that there is considerably less cooling of the gas and less work is done by the gas in the irreversible adiabatic expansion than in the reversible adiabatic expansion.

4. THERMOCHEMISTRY

It is a branch of physical chemistry that deals with energy changes accompanying chemical transformations. It is also known as "Chemical Energetics". It is based on the first law of thermodynamics.

Physicochemical changes are classified as endothermic, accompanied by absorption of heat and exothermic, accompanied by the evolution of heat. For example,



For exothermic reactions ($q < 0$)

At constant pressure, $\Delta H = (H_P - H_R) = -ve$ ($\because H_P < H_R$)

At constant volume, $\Delta E = (E_P - E_R) = -ve$ ($\because E_P < E_R$)

For endothermic reaction, ($q > 0$)

At constant pressure, $\Delta H = (H_P - H_R) = +ve$ ($\because H_P > H_R$)

At constant volume, $\Delta E = (E_P - E_R) = +ve$ ($\because E_P > E_R$)

Like any other transfer of heat, the heat of a chemical reaction depends upon the conditions that hold during the process by which it is carried out.

Condition I:

If the volume of the system is kept constant, no work is done on the system and the first law of thermodynamics reduces to

$$\Delta E = q_v$$

This condition is excellently approximated when the reaction is carried out in a bomb calorimeter, where the volume remains constant.

Condition II:

During the course of an experiment under ordinary bench-top conditions, the pressure is kept constant. Many calorimeters operate at this constant atmospheric pressure. Then, we have

$$\Delta H = q_p$$

The heat of reaction measured at constant pressure is exactly equal to the change in enthalpy of the reaction system.

It is often necessary to use data obtained with bomb calorimeter which give ΔE in order to calculate ΔH .

We know that, $\Delta H = \Delta E + \Delta(PV)$

If all the reactants and products are liquids or solids, the PV values change only slightly during the reaction, provided the pressure is low (say 1 atm). In such cases, $q_P \cong q_v$.

For reactions in which gases are involved, the values of $\Delta(PV)$ depends on the change in the number of moles of gas as a result of reaction.

$$\therefore \Delta(PV) = \Delta n_g(RT)$$

$$\therefore \Delta H = \Delta E + \Delta n_g RT$$

Constant pressure processes are much common in chemistry. Therefore, usually when ever we speak of heat of reaction, it implies enthalpy change at constant pressure.

4.1 HEAT OF REACTION

It is defined as the **amount of heat evolved or absorbed when the reacting species, as represented by a balanced chemical equation have completely reacted.**

Enthalpy or heat of reaction is given by $\Delta H = \sum H_p - \sum H_R$.

4.2 STANDARD STATES

In the calculation of heat of reaction, it is a convention to assume that the heat of formation of elements in their standard state is zero. A pressure of 1 atm and a constant temperature is taken as standard state.

| State | Standard state |
|--------|--|
| Gas | Ideal gas at the given temperature & 1 atm. |
| Liquid | Pure liquid at the given temperature & 1 atm. |
| Solid | Stable crystalline form at given temperature and 1 atm pressure. |

4.3 FACTORS AFFECTING HEAT OF REACTION

(I) PHYSICAL STATE OF REACTANTS AND PRODUCTS

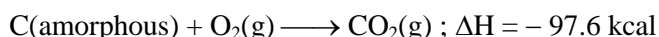
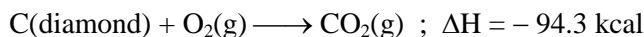
Physical state always affects the heat of reaction as heat energy is involved in changing the physical state of a substance. For example,



Difference in the value of ΔH is observed because heat is evolved when steam condenses.

(II) ALLOTROPIC FORMS OF THE ELEMENT

The value of ΔH also depends on the allotropic form used in the reaction. For example,

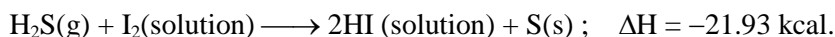


The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is called heat of transition.



(III) ENTHALPIES OF SOLUTION

Enthalpies of solution differ depending on whether the substances react together in dry state or in solution. For example,



(IV) TEMPERATURE

Enthalpy of reaction also depends on temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature.

Relation between ΔH or ΔE and temperature are given by Kirchoff's equation.

$$(\Delta\text{H}_2 - \Delta\text{H}_1) = \Delta\text{C}_\text{P} (T_2 - T_1)$$

$$(\Delta\text{E}_2 - \Delta\text{E}_1) = \Delta\text{C}_\text{V} (T_2 - T_1)$$

The above relations may be derived as follows:

For a reaction at constant pressure, $\Delta\text{H} = \text{H}_\text{P} - \text{H}_\text{R}$

Differentiating it w.r.t. T at constant P, we get

$$\left(\frac{d\Delta\text{H}}{dT}\right)_\text{P} = \left(\frac{d\text{H}_\text{P}}{dT}\right)_\text{P} - \left(\frac{d\text{H}_\text{R}}{dT}\right)_\text{P} = (\text{C}_\text{P})_\text{P} - (\text{C}_\text{P})_\text{R} = \Delta\text{C}_\text{P}$$

$$\text{or } d(\Delta\text{H}) = \Delta\text{C}_\text{P} dT$$

Integrating this equation within appropriate limits, we get

$$\int_{T_1}^{T_2} d(\Delta\text{H}) = \Delta\text{C}_\text{P} \int_{T_1}^{T_2} dT$$

$$\Delta\text{H}_{T_2} - \Delta\text{H}_{T_1} = \Delta\text{C}_\text{P} (T_2 - T_1)$$

$$\frac{\Delta\text{H}_{T_2} - \Delta\text{H}_{T_1}}{(T_2 - T_1)} = \Delta\text{C}_\text{P} \quad \dots\dots(\text{xvii})$$

This equation is used to find heat of reaction at a temperature when it is known at another temperature.

$$\text{Similarly, } \frac{\Delta\text{E}_{T_2} - \Delta\text{E}_{T_1}}{(T_2 - T_1)} = \Delta\text{C}_\text{V} \quad \dots\dots(\text{xviii})$$

In the limit as $(T_2 - T_1) \longrightarrow 0$, equation (xvii) yields the differential form

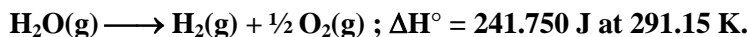
$$\frac{d(\Delta\text{H})}{dT} = \Delta\text{C}_\text{P}$$

This shows that the rate of change of the enthalpy of a reaction is equal to the difference in heat capacities of products and reactants.

Since actually the heat capacities themselves vary with temperature, it is sufficiently accurate to use the average value of the heat capacity over the range of temperature considered.

Illustration 2

Question: Consider a reaction,



What would be ΔH° at 298.15 K? Over the small temperature range, the effectively constant C_p values per mole are

$$C_p(\text{H}_2\text{O}) = 33.56, \quad C_p(\text{H}_2) = 28.83 ; \quad C_p(\text{O}_2) = 29.12 \text{ JK}^{-1} \text{ mol}^{-1}.$$

Solution: (a) $\frac{\Delta H_{298.15}^\circ - \Delta H_{291.15}^\circ}{298.15 - 291.15} = \Delta C_p$

$$\text{Now, } \Delta C_p = C_p(\text{H}_2) + \frac{1}{2} C_p(\text{O}_2) - C_p(\text{H}_2\text{O}) = 28.83 + \frac{29.12}{2} - 33.56 = 9.83 \text{ J K}^{-1}.$$

$$\therefore \Delta H_{298}^\circ = 241.820 \text{ J}$$

Illustration 3

Question: For Ag, \bar{C}_p ($\text{JK}^{-1} \text{ mol}^{-1}$) is given by $23.43 + 0.00628 T$. Calculate ΔH if 3 mol of silver are raised from 25°C to its melting point 961°C under 1 atm pressure.

Solution: At constant P for 1 mole,

$$\Delta H = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} (23.43 + 0.00628 T) dT$$

$$\Delta H = 23.43 (T_2 - T_1) + \frac{1}{2} (0.00628 (T_2^2 - T_1^2)) \text{ Jmol}^{-1}.$$

$$\text{Since, } T_1 = 273.15 + 25 = 298.15 \text{ K and } T_2 = 273.15 + 961 = 1234.15 \text{ K.}$$

$$(T_2 - T_1) = 936 \text{ K}$$

$$\begin{aligned} \Delta H &= 23.43(936) + \frac{1}{2} (0.00628) [(1234.15)^2 - (298.15)^2] = 21930 + 4500 \\ &= 26430 \text{ J/mol.} \end{aligned}$$

$$\text{For 3 mol, } \Delta H = 3(26430) \text{ J} = 79290 \text{ J}$$

4.4 ENTHALPY or HEAT OF FORMATION

The amount of heat evolved or absorbed when one mole of a substance is formed from its constituent elements is called heat of formation.

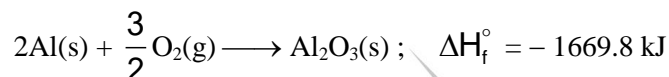
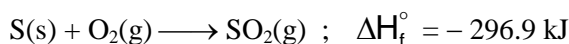


Thus, enthalpy of formation of HCl is -22 kcal .

The formation reaction of a compound has only one mole of the compound and nothing else on the product side. Only elements in their stable states of aggregation appear on the reactant side.

4.4.1 STANDARD ENTHALPY OF FORMATION (H_f°)

It is enthalpy change of a reaction by which a compound is formed from its constituent elements, the reactants and products all being in a given, standard state (i.e. at 298 K and 1 atm pressure). For example,



Let us consider a reaction, $C(s) + O_2(g) \longrightarrow CO_2(g) ; \Delta H_f^\circ = -393.5 \text{ kJ}$

$$\Delta H_f^\circ = H_P^\circ - H_R^\circ = -393.5 \text{ kJ}$$

Enthalpies of free elements in their standard states are assumed to be zero.

$$\text{so, } \Delta H_f^\circ = \Delta H_P^\circ = -393.5 \text{ kJ}$$

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

If we know the standard heats of formation of various substances, we can calculate heat of reactions under standard conditions.

Thus,

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

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

The heats of formation of all the elements in their standard states are arbitrarily taken to be zero. For example, at 1 atm and 298 K, the stable state of aggregation of bromine is the liquid state. Hence liquid bromine, gaseous hydrogen, solid zinc, solid (rhombic) sulphur and solid (graphite) carbon, all have $H_{298}^\circ = 0$.

For elementary solids that exists in more than one crystalline form, the modification that is stable at 25°C and 1 atm is assigned $H^\circ = 0$. For example, zero assignment goes to rhombic sulphur rather than to monoclinic sulphur, to graphite rather than diamond. In cases in which more than one molecular species exists (e.g. O_2 and O_3), the zero enthalpy value goes to the most stable form at 25°C and 1 atm pressure i.e. for O_2 , $H_{298}^\circ(O_2, g) = 0$.

Once, the value of the standard enthalpy of the elements at 298 K has been assigned, the value at any other temperature can be calculated using Kirchoff's equation.

$$\int_{298}^T dH^\circ = \int_{298}^T C_P^\circ dT$$

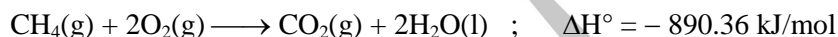
$$H_T^\circ - H_{298}^\circ = \int_{298}^T C_P^\circ dT$$

$$H_T^\circ = H_{298}^\circ + \int_{298}^T C_P^\circ dT$$

This expression holds good for both elements as well as compounds. For elements, the first term on the right hand side is zero.

4.5 ENTHALPY OR HEAT OF COMBUSTION

The amount of heat evolved or decrease in enthalpy when one mole of a substance is completely oxidised. Organic compounds containing only carbon, hydrogen and oxygen are burnt to gaseous carbon dioxide and liquid water. For example,



The measurements of the heat of combustion is used to determine the heats of formation of all organic compounds containing C, H, O, N etc.

Illustration 4

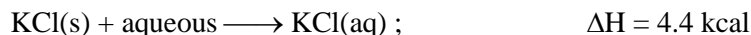
Question: $\Delta H_{\text{combustion}}^\circ (\text{CH}_4, \text{g}) = -890.36 \text{ kJ/mol}$; $H_f^\circ (\text{CO}_2, \text{g}) = -393.51 \text{ kJ/mol}$;
 $H_f^\circ (\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ/mol}$;
 $H_f^\circ (\text{CH}_4, \text{g}) = ?$

Solution: $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 $\Delta H_{\text{combustion}}^\circ = H^\circ (\text{CO}_2, \text{g}) + 2H^\circ (\text{H}_2\text{O}, \text{l}) - H^\circ (\text{CH}_4, \text{g})$
 $\therefore H^\circ (\text{CH}_4, \text{g}) = H^\circ (\text{CO}_2, \text{g}) + 2H^\circ (\text{H}_2\text{O}, \text{l}) - \Delta H_{\text{combustion}}^\circ$
 $= -393.51 + 2(-285.83) - (-890.36) = -965.17 + 890.36 = -74.81 \text{ kJ/mol}.$

Later in this lesson using Hess's law we shall find heat of reaction as given below
Heat of reaction = \sum Heat of combustion of reactants – \sum Heat of combustion of products.

4.6 ENTHALPY or HEAT OF SOLUTION

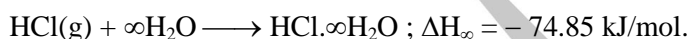
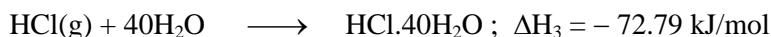
The amount of heat evolved or absorbed when one mole of solute is dissolved in excess of solvent so that further addition of solvent makes no heat change. For example,



Heat of an ideal solution is taken as zero.

4.7 HEAT OF DILUTION

The amount of heat evolved or absorbed when solution containing one mole of solute is diluted from one concentration to another. For example,



If we subtract first equation from the second in the above set, we get

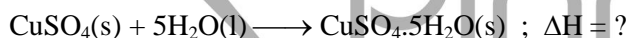
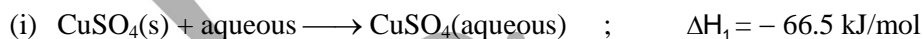


This value of ΔH is the heat of dilution. The heat of dilution of a solution is dependent on the original concentration of the solution and on the amount of the solvent added.

Illustration 5

Question: The enthalpies of solution of anhydrous CuSO_4 and hydrated $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are -66.5 and 11.7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of CuSO_4 to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Solution: Given that



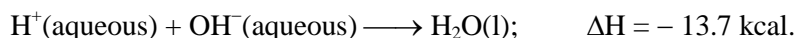
$$\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - 11.7 = -78.2 \text{ kJ}$$

4.8 ENTHALPY OR HEAT OF NEUTRALISATION

The amount of heat evolved when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base in dilute solution is called heat of neutralisation. For example,



Heat of neutralisation of a strong acid and a strong base is 13.7 kcal , or 57 kJ . The constant value is due to the fact that heat of neutralisation of strong acid and strong base is merely the heat of formation of H_2O from H^+ of an acid and OH^- of a base.



DETERMINATION OF HEAT OF NEUTRALISATION

It can be determined easily in the laboratory with the help of polythene or polystyrene bottle, fitted with a rubber cork and a stirrer as shown in the figure 1. 100 ml each of acid and alkali of equal normality are taken in separate bottles. The temperature of each solution is regularly recorded. When the 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.

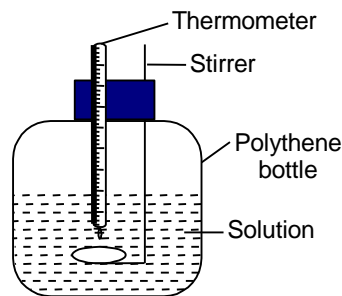


Figure 1

Let the initial temperature of acid & base be T_1K and that after mixing be T_2K .

\therefore Rise in temperature = $(T_2 - T_1)K$. Heat capacity of bottle is 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 for water.

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

where Q = Heat change in the reaction, m = mass of solution and s = specific heat of solution.

$$\text{Thus, the enthalpy of neutralisation} = \frac{Q}{100} \times 1000 \times \frac{1}{N}$$

where N = normality of the acid or base.

Illustration 6

Question: 150 ml of 0.5 N nitric acid solution at $25.35^\circ C$ was mixed with 150 ml of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be $28.77^\circ C$. Calculate the heat of neutralisation of nitric acid with sodium hydroxide.

Solution: Total mass of solution = $150 + 150 = 300$ gm

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

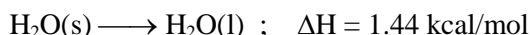
$$\therefore \text{Heat of neutralisation} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5} = \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68 \text{ kcal.}$$

Since, the enthalpy of neutralisation is always -ve, so, heat of neutralisation = **- 13.68 kcal.**

4.9 ENTHALPIES OF PHASE TRANSITION

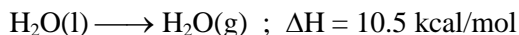
(i) ENTHALPY OF FUSION

It is the enthalpy change involved in the conversion of one mole of a substance from solid state to liquid state at its melting point. This equals latent heat of fusion per gram multiplied by the molar mass. For example,



(ii) ENTHALPY OF VAPOURISATION

It is the enthalpy change involved in converting one mole of the substance from liquid state to gaseous state at its boiling point. For example,



(iii) ENTHALPY OF SUBLIMATION

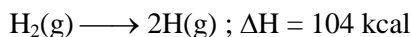
It is the enthalpy change involved in the conversion of one mole of a solid directly into its vapour at a given temperature below its melting point. For example,



$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vapourization}}$$

(IV) HEAT OF ATOMISATION

The amount of heat required for the formation of one mole of atoms in gaseous state from its elements is known as heat of atomization of that element.



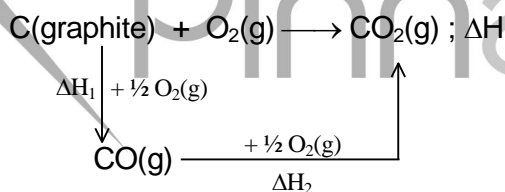
In this case, heat of atomization of hydrogen is 52 kcal/mol.

5. HESS'S LAW OF CONSTANT HEAT SUMMATION

The change in state of a system produced by a specified chemical reaction is definite. The corresponding enthalpy change is definite, since the enthalpy is a state function.

Thus, "if a specified set of reactants is transformed to a specified set of products by more than one sequence of reactions, the total enthalpy change must be the same for every sequence."

This rule, which is a consequence of the first law of thermodynamics, is known as **Hess's law**. More precisely, "the enthalpy change in a chemical or physical process is the same whether the process is carried out in one step or in several steps". For example,



$$\therefore \Delta H = \Delta H_1 + \Delta H_2$$

This property is due to the fact that the enthalpy change in a system is independent of the path followed.

5.1 APPLICATIONS OF HESS'S LAW

- (i) Using Hess's law, enthalpy changes for the reactions, which are experimentally not possible, can be calculated.

e.g. for compounds such as C_2H_6 , C_6H_6 etc. whose direct synthesis from their constituent elements is not possible, the enthalpy of formation of such compounds can be calculated.

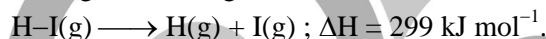
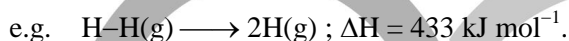
(II) CALCULATION OF HEAT OF REACTION

$$\Delta H_{\text{reaction}} = \sum \text{Heat of formation of Products} - \sum \text{Heat of formation of reactants}$$

$$\Delta H_{\text{reaction}} = \sum \text{Heat of combustion of reactants} - \sum \text{Heat of combustion of products}$$

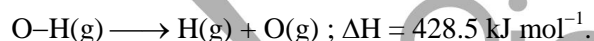
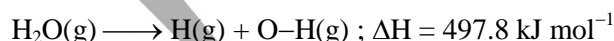
6. BOND ENERGIES

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



The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends on the nature of bonds 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 which is also the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.**

Consider the dissociation of water molecule,



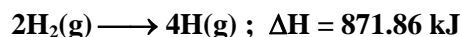
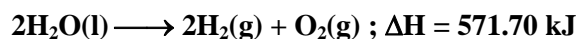
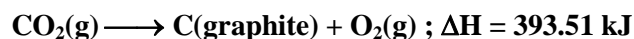
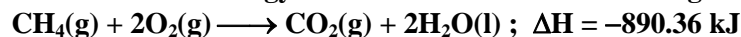
The average of these two bond dissociation energies gives the value of bond energy of O-H bond.

$$\therefore \text{B.E. of O-H bond} = \frac{497.8 + 428.5}{2} = 463.15 \text{ kJ mol}^{-1}.$$

Bond energies can be obtained from the data of heats of combustion and heats of dissociation.

Illustration 8

Question: Calculate bond energy of C-H bond from the following data.



Solution: Adding all the equations, we get



$$\therefore \text{B.E of C-H bond} = \frac{1663.39}{4} = 415.85 \text{ kJ mol}^{-1}$$

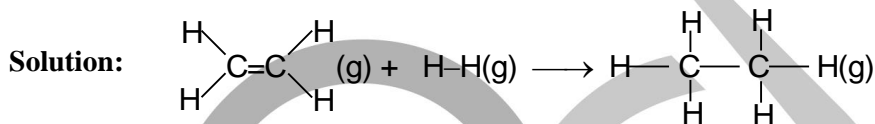
6.1 APPLICATIONS OF BOND ENERGIES

6.1.1 DETERMINATION OF HEAT OF REACTIONS

$\Delta H_{\text{reaction}} = \text{Sum of bond energies of reactants} - \text{Sum of bond energies of products.}$

Illustration 9

Question: Given that the average bond energies of C–C, C=C, C–H and H–H bonds are 80.5, 145, 98.2 and 103 kcal mol^{−1} respectively, calculate the enthalpy of the reaction per mole.



$$\Delta H_{\text{reaction}} = (\epsilon_{\text{H-H}} + \epsilon_{\text{C-H}}) - (2\epsilon_{\text{C-H}} + \epsilon_{\text{C-C}})$$

$$\Delta H_{\text{reaction}} = (103 + 145) - (196.4 + 80.5) = 248 - 276.9$$

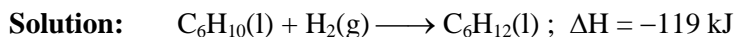
$$\Delta H_{\text{reaction}} = -28.9 \text{ kcal/mol.}$$

6.1.2 DETERMINATION OF RESONANCE ENERGY

Resonance Energy = (Experimental or actual heat of formation) – (Calculated heat of formation).

Illustration 10

Question: 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.



(This involves breaking up of one double bond and addition of one H₂ molecule).



(This involves breaking up of three double bonds and addition of three H₂ molecules).

Enthalpy change of equation (i) can be given as

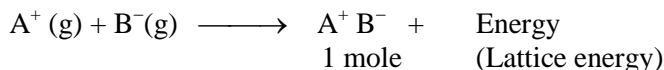
$$\Delta H = -357 = \Delta H_f(\text{C}_6\text{H}_{12}, \text{l}) - \Delta H_f(\text{C}_6\text{H}_6, \text{l})$$

$$\Delta H_f(\text{C}_6\text{H}_6, \text{l}) = -156 + 357 = 201 \text{ kJ}$$

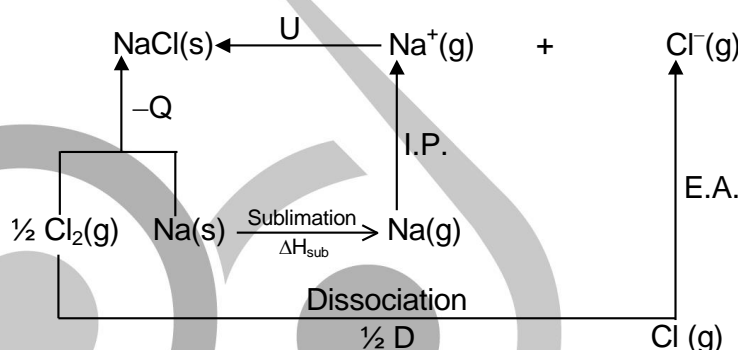
$$\begin{aligned} \therefore \text{Resonance energy} &= \text{Observed } \Delta H_f - \text{calculated } \Delta H_f \text{ of C}_6\text{H}_6 \\ &= 49 - 201 = -152 \text{ kJ} \end{aligned}$$

6.2 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 ionic compound is formed by the interaction of required number 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:



The formation of sodium chloride can occur either by direct combination of sodium(s) and molecular 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. $\text{Na(g)} + \text{I.P.} \longrightarrow \text{Na}^+(\text{g}) + e^-$ | $+\text{I.P.}$ |
| (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. $\frac{1}{2}\text{Cl}_2(\text{g}) + \frac{1}{2}\text{D} \longrightarrow \text{Cl(g)}$ | $+\frac{1}{2}\text{D}$ |
| (d) Gaseous chlorine atoms change into chlorine ions by acceptance of electrons. In this process, energy equivalent to electron affinity is released. $\text{Cl(g)} + e^- \longrightarrow \text{Cl}^-(\text{g}) + \text{E.A.}$ | $-\text{E.A.}$ |
| (e) Sodium and chlorine ions are held together by electrostatic forces to form $\text{Na}^+ \text{Cl}^-(\text{s})$. The energy equivalent to lattice energy is released. | $-U$ |

Total energies involved in the above five steps is

$$= \Delta H_{\text{sub}} + \frac{1}{2}D + \text{I.P.} - E.A - U$$

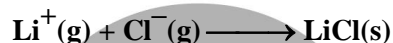
Thus, according to Hess's law

$$-Q = \Delta H_{\text{sub}} + \frac{1}{2}D + \text{I.P.} - E.A - U \quad \dots\dots\dots(\text{xix})$$

So, knowing all other quantities, U can be calculated.

Illustration 11

Question: Calculate the lattice energy for the reaction,



from the following data.

$$\Delta H_{\text{sub}}(\text{Li}) = 160.67 \text{ kJ mol}^{-1}; \quad \frac{1}{2}D(\text{Cl}_2) = 122.17 \text{ kJ mol}^{-1}; \quad \text{I.P.}(\text{Li}) = 520.07 \text{ kJ mol}^{-1};$$

$$E.A(\text{Cl}) = -365.26 \text{ kJ mol}^{-1} \text{ and } \Delta H_f^\circ(\text{LiCl}) = -401.66 \text{ kJ mol}^{-1}.$$

Solution: Applying the equation (xix),

$$-Q = \Delta H_{\text{sub}} + \frac{1}{2}D + \text{I.P.} - E.A - U$$

and substituting the respective values gives

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

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

7. 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 water in the calorimeter and s is its specific heat, T₂ is the final temperature and T₁ is the initial temperature of the system. Different types of calorimeters are used but two of the common types are

- (i) Water calorimeter and
- (ii) Bomb calorimeter

(i) Water calorimeter

It is a simple form of calorimeter which can be conveniently used in the laboratory. It is shown in Figure 2.

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 and known amount of reacting substances are taken in the boiling tube.

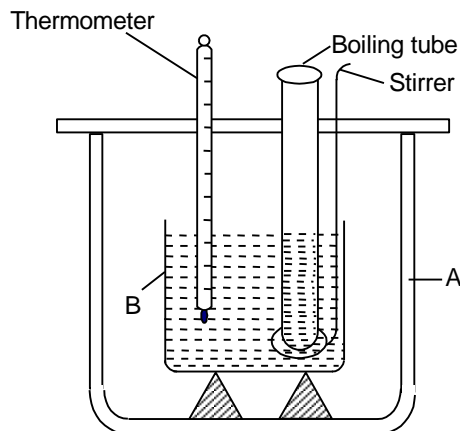


Figure 2

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 as

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

(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 figure 3.

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 .

$$\Delta E = \left(\frac{(W+m)(t_2-t_1) \times s}{w_1} \times M \right) \text{ kcal}$$

where M is the molar mass of the substance and w_1 is the mass of substance taken. ΔH can be calculated from the relation, $\Delta H = \Delta E + \Delta n_g RT$.

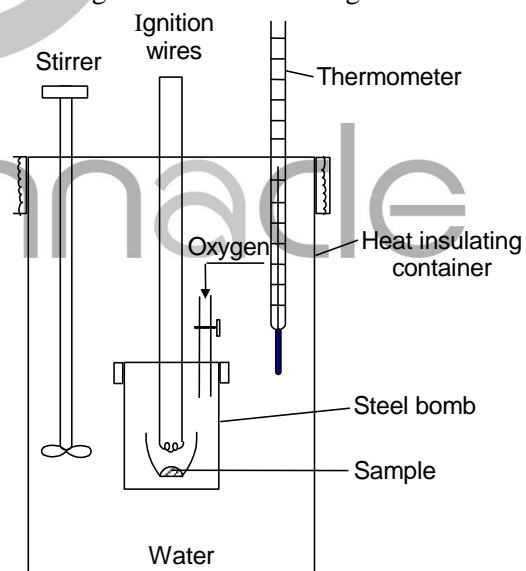


Figure 3

Illustration 12

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

Solution: Heat of combustion at constant volume, ΔE

$$= \text{Heat capacity of calorimeter} \times \text{Rise in temperature} \times \frac{\text{Molar mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

$$\text{i.e., } \Delta E = -885 \text{ kJ mol}^{-1}$$



$$\Delta n_g = 1 - 3 = -2, T = 300 \text{ K}, R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta H = \Delta E + \Delta n_g RT = -885 + (-2) \times 8.314 \times 10^{-3} \times 300$$

$$= -885 - 4.988 = -889.988 \text{ kJ mol}^{-1}$$

8. SECOND LAW OF THERMODYNAMICS

8.1 SPONTANEOUS PROCESS

In any system, a spontaneous process is one which occurs on its own without the help of external energy. The natural changes that occur around us result from such processes. For example, flow of heat from a hot body to a cold one, flow of water downhill, and the expansion of a gas from high pressure to low pressure. Besides being spontaneous, these processes are also unidirectional, i.e., they occur on their own in one direction only. A spontaneous process cannot be reversed without the aid of external work or energy. The work has to be done to move uphill or to compress a gas.

Many common chemical reactions are spontaneous and occur in one direction although finally a state of equilibrium is reached. Everything in nature has a tendency to move towards a state of lowest energy, at which point equilibrium exists. The heat energy which is given out during an exothermic reaction shows that there is a lowering in chemical energy on proceeding from the reactants to the products. From this, we may conclude that a reduction in enthalpy provides the necessary driving force for a reaction to occur. However, many endothermic reactions also proceed on their own and so it looks as though a negative enthalpy change is not a reliable criterion to judge the spontaneity of chemical reactions.

The first law of thermodynamics does not state whether a reaction is spontaneous or not and in which direction it will occur. For example, let us take a metal bar, which is heated at one end. Assuming no loss of heat from the bar, when heat passes from the hot end to the cold end, the decrease in thermal energy at the hot end is equal to the increase at the cold end. This satisfies the requirements of the I law. From experience, we know that

heat will not flow, on its own from the cold end to the hot end. However, the I law does not exclude the occurrence of such non-spontaneous processes, but only tells us that an energy decrease in one part of the system is equal to an increase in another part.

8.2 STATEMENT OF THE II LAW

Second law of thermodynamics is concerned with the direction and spontaneity of processes. There are many ways of formulating the law based on our experience of the direction or manner in which natural processes occur. Clausius stated the law as “**The transference of heat from a cold to a hot body cannot be achieved without the performance of work**’.

Because natural or spontaneous processes occur over a period of time, they must be thermodynamically irreversible. Another way of formulating the second law is ‘**Any process occurring on its own is thermodynamically irreversible**’.

The basic concept of the second law of thermodynamics is that all spontaneous processes are unidirectional and thermodynamically irreversible.

8.3 ENTROPY

To decide whether a chemical reaction can take place or not, the first factor that has to be considered is whether there is enough energy available. If the reaction is exothermic, there is no reason why it should not take place spontaneously but if the reaction is endothermic then it would not. But in nature, we come across numerous examples of endothermic reactions, which are spontaneous (for example, evaporation of water). From this, we conclude that energy alone is not the deciding factor. This is where the concept of entropy becomes important.

8.3.1 DEFINITION OF ENTROPY

If any process is carried out reversibly, so that dq_{rev} is the heat absorbed by the system in the process at constant temperature (T), then the entropy change (dS) is given by

$$dS = \frac{dq_{\text{rev}}}{T}$$

For finite changes, $\Delta S = \frac{q_{\text{rev}}}{T}$

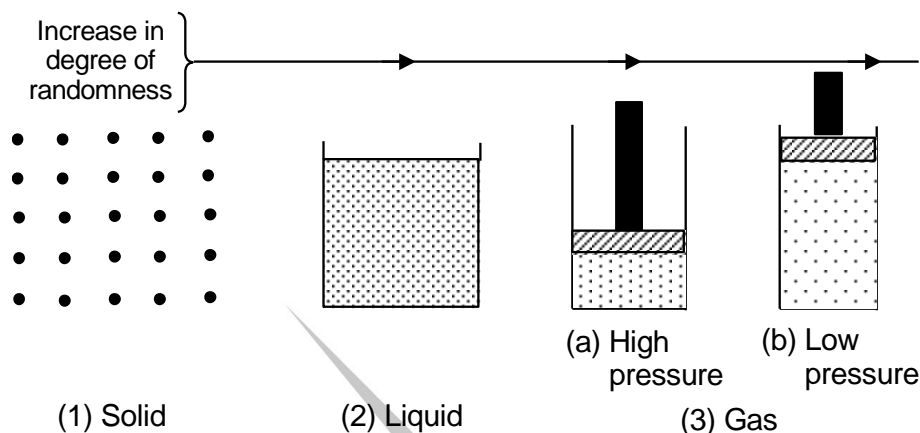
8.3.2 MEANING OF ENTROPY

Although the concept of entropy was first applied to the performance of heat engines, pictorial representations of entropy can be obtained from two sources and lead to the following conclusions,

- Entropy is the degree of disorder or randomness of a system.
- Change in entropy is the capacity for spontaneous change in a system.

Entropy is a measure of disorderness of a system.

To illustrate the meaning of disorder or randomness, consider a substance which changes state.



In the gaseous state and at low pressures, the molecules are free to move about unrestricted. If the pressure is increased, the same number of molecules now occupy a smaller volume. The chances of finding a molecule within a given volume are greater under these conditions than when it was at lower pressure. Hence, the molecules are more ordered (or less randomly distributed) at higher pressure. Added to this, the force of intermolecular attraction increases as the pressure increases and this too has a restricting effect on the molecules.

In the liquid state, the molecules are much closer together than in the gaseous state, because the volume containing the same number of molecules is much smaller. The molecules in the liquid state are more highly ordered than a gas at high pressure. Also in the liquid state, the forces of intermolecular attraction are greater, causing a still more highly ordered state.

In the solid state, the atoms, molecules or ions that form the crystal are usually held in fixed crystal lattices, which can only vibrate and rotate. Hence in a solid, the atoms, molecules or ions have little or no choice as to where they shall be i.e., they are highly ordered or have a very small freedom.

This gradual decrease in the measure of disorder of the molecules is identified with entropy changes, being high for a gas and low for a solid.

8.3.3 ENTROPY AS THE CAPACITY FOR SPONTANEOUS CHANGE

Let us consider the following examples of spontaneous change.

(i) Expansion of a gas from a region of high pressure to a region of low pressure

Suppose, there are two bulbs filled with a gas at different pressures. If the two bulbs are connected, the gas from the bulb at high pressure will flow into the bulb at low pressure till the pressures in the two bulbs become equal. The greater the pressure difference, the greater the flow of gas, the greater is the capacity of the system for spontaneous change and the greater is the entropy change.

(ii) Solute spreading from a region of high concentration to a region of low concentration.

If the concentration difference between two solutions is considerable, there is obviously a much greater flow of solute from the high concentration to the lower concentration region.

8.3.4 DEGREE OF RANDOMNESS AND SPONTANEOUS CHANGE

The two approaches are two ways of looking at the same problem and we inevitably come to the conclusion that **a system undergoing a spontaneous change is moving to a state of greater randomness.**

This is understood well by considering the two spontaneous processes cited above.

- (i) As a gas expands from a region of high pressure to a region of low pressure, the molecules move farther apart, so that the intermolecular attraction becomes less and the molecules are given a larger volume to

move about in. Both these effects give the molecules more freedom and the system has moved to a **state of greater randomness during spontaneous expansion**.

- (ii) When a solute spreads from a region of high concentration to a region of low concentration, the molecules move farther apart. Each molecule has more space to move about in and is therefore less restricted in position. Hence, the solute molecules are more randomly distributed throughout the solvent.

8.3.5 ENTROPY AND STRUCTURE

The standard molar entropies of n-octane, 2, 2-dimethyl hexane and 2, 2, 3, 3-tetramethyl butane (all of them are isomers) are 463.6, 431.4 and 394.6 J/l respectively. As the chain becomes more branched the top-like rotation of one carbon atom with respect to another becomes more hindered. Hence, we should expect n-octane to have a greater entropy than the branched chain isomers, The above values show this relationship between entropy and structure that helps in understanding why entropy changes are important in chemical reactions.

Entropy changes in chemical reactions can be easily identified. Larger complex molecules are more ordered and have less entropy. For example, in the formation of water from its elements



a more complex molecule is produced, the number of molecules decreases, and the system becomes more ordered.

The decomposition of phosphorus pentachloride



is an endothermic process, which leads to the formation of twice as many molecules. This leads to increase in the distribution of matter and consequently results in increase in entropy of the system.

Now, let us consider the following reaction,



Normally, we would have expected no increase in the entropy of the system as the number of molecules of reactants and products are equal. However, we find that the entropy increases. The reason is heteronuclear diatomic molecules have higher entropy than homonuclear diatomic molecules because they possess a more random distribution of matter, i.e., they are more disordered.

Illustration 13

Question: For the reactions given below, predict the sign of ΔS as positive or negative?

- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$
- $\text{Ni}(\text{s}) + 4\text{CO}(\text{g}) \longrightarrow \text{Ni}(\text{CO})_4(\text{g})$
- $2\text{Ca}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CaO}(\text{s})$
- $\text{H}_2(\text{g}) + \text{S}(\text{s}) \longrightarrow \text{H}_2\text{S}(\text{g})$

- Solution:**
- Three gas molecules give rise to two gas molecules. Hence, disorderness decreases i.e., $\Delta S < 0$ (negative).
 - Four gas molecules are converted into a single gas molecule and hence, the disorderness decreases i.e., ΔS is < 0 (negative).
 - Three reacting units, of which two are solid and one gas are changed to two solid units. Disorderness decreases i.e. $\Delta S < 0$ (negative).
 - Two reacting units, one of which is a solid, forms a gaseous molecule. Since a heteronuclear gas results, disorderness increases and ΔS is positive ($\Delta S > 0$).

8.3.6 CALCULATION OF ENTROPY CHANGE

The entropy change for a given process is given by

$$\Delta S = \int dS = \int \frac{dq_{\text{rev}}}{T}$$

If we replace dq by an expression for the heat absorbed for a particular process, we can calculate the entropy change.

(a) Heating of a solid

When only heat change is involved, as in the heating of a solid, the heat change is given by the expression

Quantity of heat (q) = $m \times s \times \Delta t$ (m = mass; s = specific heat; Δt = temperature rise) or quantity of heat (q) = number of moles \times molar heat \times temperature rise

For one mole,

$$dq = C_s \cdot dT$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_s \cdot dT}{T}$$

$$\Delta S = C_s \ln \frac{T_2}{T_1}$$

(b) Change of state

There are changes taking place at constant temperatures (i.e. isothermal) during which the two states are at equilibrium with one another provided the process is carried out reversibly. The heat absorbed will be **latent heat** (L) and the temperature will be melting or boiling point.

$$\Delta S = \frac{L}{T}$$

Illustration 14

Question: The latent heat of fusion of water is 6016.6 J/mole at 0°C and 1 atm. Calculate the entropy change.

Solution: $\Delta S = \frac{L}{T} = \frac{6016.6}{273} = 22.0 \text{ J/mole/deg}$

(c) Entropy change in ideal gas

For an ideal gas changing its state from (P_1, V_1, T_1) to (P_2, V_2, T_2)

$$\Delta S = n C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= n C_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

1. For an isothermal process ($T_2 = T_1$)

$$\Delta S = nR \ln \frac{V_2}{V_1} = -nR \ln \frac{P_2}{P_1}$$

2. For an isobaric process

$$\Delta S = n C_P \ln \frac{T_2}{T_1}$$

3. For an isochoric process

$$\Delta S = n C_V \ln \frac{T_2}{T_1}$$

4. For an adiabatic process

Since $dq = 0$, $\Delta S = 0$

Such a process is called isoentropic process.

Illustration 15

Question: Calculate the entropy change per mole of substance in each of the following cases.

- The freezing of isobutane at -160°C . ΔH (solid \longrightarrow liquid) = 4540 J mol^{-1} .
- The vaporization of water at its boiling point, 100°C . ΔH (liquid \longrightarrow vapour) = 407 kJ mol^{-1} .
- Expansion reversibly and isothermally of an ideal gas from a volume of 2 dm^3 to 10 dm^3 at 27°C . Also calculate entropy change of surroundings due to the process.
- Expansion irreversibly and isothermally of an ideal gas from volume 2 dm^3 to 10 dm^3 against a constant pressure of 1 atm , at 27°C . Also calculate entropy change of surroundings due to the process.

Solution: (i) Freezing temperature of isobutane $= -160^\circ\text{C} = (-160 + 273) \text{ K} = 113 \text{ K}$

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

Here $q_{\text{rev}} = -4540 \text{ J mol}^{-1}$

$$\therefore \Delta S = \frac{-4540}{113} = -40.2 \text{ JK}^{-1} \text{ mol}^{-1}$$

Note that in freezing, the substance becomes more ordered. Hence, entropy is lost by the substance (ΔS is -ve).

- (ii) For the reversible vaporisation of water at 100°C ,

$$\begin{aligned} \Delta S &= \frac{q_{\text{rev}}}{T} = \frac{L}{T} = \frac{\Delta H_{\text{vap}}}{T} \\ &= \frac{407000}{373} = 1091.2 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

- (iii) For an isothermal process,

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

At constant temperature, $P_1 V_1 = P_2 V_2$

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

$$\therefore \Delta S = R \ln \frac{V_2}{V_1} = 8.314 \times 2.303 \log \frac{10}{2} = 13.4 \text{ J K}^{-1} \text{ mol}$$

If we treat system and surroundings as an isolated system, entropy change of surrounding = $-\Delta S$ = $-13.4 \text{ J K}^{-1} \text{ mol}$. \therefore For a reversible process entropy of universe remains constant. Total entropy change for isolated system = $\Delta S - \Delta S = 0$.

(iv) Total entropy change of the system, has to be calculated assuming a reversible path,

$$\Delta S_{\text{system}} = \int \frac{dq_{\text{rev}}}{T} = R \ln \frac{V_2}{V_1} = 13.4 \text{ J K}^{-1} \text{ mol}^{-1}. \quad [\text{same as in (iii)}]$$

If we consider system & surroundings as an isolated system, entropy change of surrounding,

$$\Delta S_{\text{surrounding}} = \frac{\text{Heat exchanged by surrounding}}{T} = \frac{q}{T}.$$

For the system,

$$\Delta E' = 0 = q + w \Rightarrow q = -w = P(V_2 - V_1). \text{ For surrounding, } q = -P(V_2 - V_1).$$

$$\Rightarrow S_{\text{surrounding}} = \frac{-1(10-2) \text{ L atm}}{300 \text{ K}} = -\frac{8}{300} \times \frac{8.314}{0.0821} = -2.7 \text{ J/mol}^{-1} \text{ K}.$$

$$\text{Entropy change of isolated system} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 13.4 - 2.7 = 10.7 \text{ J/mol}^{-1} \text{ K}.$$

For an irreversible process, entropy of universe increases.

Illustration 16

Question: The enthalpy change for the transition of liquid water to steam is 41 kJ mol^{-1} at 100°C . Calculate the entropy change for the process.

Solution: $\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(vap.)}$

The equation for entropy change is

$$\begin{aligned} \Delta S &= \frac{L}{T} = \frac{\Delta H_{\text{vap}}}{T} \\ &= \frac{41 \times 1000}{(273 + 100)} = \frac{41000}{373} = 110 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

Note that ΔS is greater than zero as there is an increase in the disorder (randomness) in the system.

Illustration 17

Question: 3 moles of $N_2(g)$ originally at 1 atm pressure are mixed isothermally with 5 moles of $H_2(g)$ also at 1 atm pressure to yield a mixture whose total pressure is 1 atm. Assuming ideal behaviour, calculate entropy of mixing.

Solution: Total pressure of mixture = 1 atm

$$\text{Final pressure of } N_2 = \frac{3}{5+3}(1) = 0.375 \text{ atm}$$

$$\text{Final pressure of } H_2 = 1 - 0.375 = 0.625 \text{ atm}$$

For N_2 , entropy change

$$\Delta S_{N_2} = -nR \ln \frac{P_2}{P_1} = -2.303 \times 3 \times 8.314 \times \log \left(\frac{0.375}{1} \right) = 28.03 \text{ J/K}$$

For H_2 , entropy change

$$\Delta S_{H_2} = -nR \ln \frac{P_2}{P_1} = -5 \times 8.314 \times 2.303 \log \frac{0.625}{1} = 16.34 \text{ J/K.}$$

$$\text{Total entropy change due to mixing} = \Delta S_{N_2} + \Delta S_{H_2} = 44.37 \text{ J/K.}$$

8.3.7 STANDARD MOLAR ENTROPIES OF ELEMENTS AND COMPOUNDS

Entropy can be defined very precisely and measured accurately. These are entropies per mole, at 1 atm in the units of Joules per Kelvin (J/K).

- Standard molar entropies of substances are always positive quantities ($S^\circ > 0$).
- Elements as well as compounds are assigned standard entropies. This is in contrast to the heats of formation, when $H_f = 0$ for elements.
- Solids in general have lower entropies than liquids and in turn liquids have lower entropies than gases. For example,

| | $S^\circ (\text{J/K})$ |
|-----------|------------------------|
| C(s) | 5.7 |
| $H_2O(l)$ | 69.9 |
| $CO_2(g)$ | 213.6 |

Illustration 18

Question: Calculate the standard entropy change for the reaction,



The standard entropy change $\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$

The entropies are $CaO(s) = 39.7 \text{ J/K}$, $CO_2(g) = 213.6 \text{ J/K}$ and $CaCO_3(s) = 92.9 \text{ J/K}$.

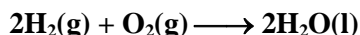
Solution: $\Delta S^\circ = S^\circ_{CaO(s)} + S^\circ_{CO_2(g)} - S^\circ_{CaCO_3(s)} = (39.7 + 213.6 - 92.9) \text{ J/K} = +160.4 \text{ J/K}$

Note that ΔS° for the decomposition of calcium carbonate is a positive quantity. This is to be expected as the gas formed CO_2 , has a much higher molar entropy than either of the solids, CaO or



Illustration 19

Question: Calculate the standard entropy change for the reaction,



Standard entropies are

$$\text{H}_2\text{O}(\text{l}) = 69.9 \text{ J/K}, \text{O}_2(\text{g}) = 205.0 \text{ J/K and } \text{H}_2(\text{g}) = 130.6 \text{ J/K}.$$

Solution: $\Delta S^\circ = 2S^\circ_{\text{H}_2\text{O}(\text{l})} - 2S^\circ_{\text{H}_2(\text{g})} - S^\circ_{\text{O}_2(\text{g})} = (139.8 - 261.2 - 205.0) \text{ J/K} = -326.4 \text{ J/K}$

Note that the entropy for the formation of water is a negative quantity.

Summarizing, we can say that a reaction, which results in the increase in the number of moles of gas, is accompanied by an increase in entropy. Conversely, if the number of moles of gas decreases, ΔS can be expected to be a negative quantity.

8.4 FREE ENERGY CHANGE (ΔG)

The two thermodynamic quantities, which affect the spontaneity of a reaction, are **enthalpy (H)** and **entropy (S)**. The next problem is how to arrange two quantities in such a way as to arrive at a single function, which can be used to determine whether a reaction is spontaneous, or not. J. Willard Gibbs introduced a new quantity called the Gibbs free energy and gave it the symbol G. The free energy of a substance, like its enthalpy or entropy is a characteristic property of the substance. In any reaction, the change in free energy, ΔG is the difference in free energies of products and reactants.

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

Gibbs showed that the sign of ΔG can be used to determine whether a reaction is spontaneous or not. For a reaction carried out at constant temperature and pressure,

- (1) If ΔG is negative, the forward reaction is spontaneous.
- (2) If ΔG is positive, the forward reaction is non-spontaneous. Instead, the reverse reaction will be spontaneous.
- (3) If ΔG is zero, the system is at equilibrium. There is no tendency for the net reaction to take place in either direction.

It can be inferred that ΔG is a measure of the driving force of a reaction. Reactions (at constant temperature and pressure) go in the direction in which there is a decrease of free energy. This implies that the direction in which a reaction takes place is determined by the relative free energies of products and reactants. If the products have a lower free energy than the reactants ($G_{\text{products}} < G_{\text{reactants}}$), the forward reaction will take place. If the reactants have a lower free energy than the products ($G_{\text{reactants}} < G_{\text{products}}$), the reverse reaction will take place. If $G_{\text{products}} = G_{\text{reactants}}$, the system is at equilibrium and there is no driving force to make the reaction go in either direction.

8.4.1 RELATIONSHIP BETWEEN ΔG , ΔH AND ΔS

ΔG is made up of two terms; an energy term and an entropy term.

$$\Delta G = \underset{\substack{\text{energy} \\ \text{term}}}{\Delta H} - T \underset{\substack{\text{entropy} \\ \text{term}}}{\Delta S}$$

where T is the temperature in Kelvin. This equation tells us that the driving force for a reaction, ΔG , represents two quantities. One of these is the enthalpy change due to the making and breaking of bonds, ΔH . The other is the product of the change in randomness, ΔS times the absolute temperature T .

Why does a reaction take place? The answer is that the reactants are unstable in the presence of each other and can exchange energy, so as to acquire a more stable state as products. In fact, all systems react so as to acquire a minimum energy irrespective of the fact that whether it is a mechanical, chemical or any other type of system.

The two factors which tend to make ΔG negative and hence gives rise to a spontaneous reaction are

(1) A negative value of ΔH

Exothermic reactions ($\Delta H < 0$) tend to be spontaneous because they contribute to a negative value of ΔG . Chemically, it means that there will be a tendency to form “strong” bonds at the expense of “weak” bonds.

(2) A positive value of ΔS

If the entropy change is positive, ($\Delta S > 0$) the term $-T\Delta S$ will make a negative contribution to ΔG . Hence, there will be a tendency for the reaction to be spontaneous provided the products are less ordered than the reactants.

In many physical processes, the increase in entropy is the major driving force. An example is the formation of a solution. When oxygen diffuses into nitrogen, or benzene is dissolved in toluene, the enthalpy change is practically zero, but ΔS is a positive quantity as the solution becomes less ordered than the pure substance. Another example is the spontaneous evaporation of water, although it is an endothermic reaction but liquid water, which is a more ordered arrangement, passes into water vapour, which is less ordered (ΔS increases).

In certain reactions, ΔS is nearly zero and ΔH is the chief and only component of the driving force of spontaneity. An example is the synthesis of hydrogen fluoride from its constituent elements,



In this reaction, ΔH has a large negative value. This is due to the fact that the bonds in HF are stronger than the bonds in H_2 and F_2 molecules.

In most cases, both ΔH and ΔS make significant contributions to ΔG . To determine the sign of ΔG , the values of ΔH and ΔS must be taken into consideration as well as the temperature.

8.4.2 STANDARD FREE ENERGY CHANGE

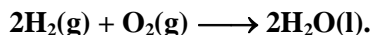
Using the equation,

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

it is possible to calculate the standard free energy change for the reaction, ΔG° . This is defined as the **free energy change when all the species involved in the reaction are at unit concentrations (for gases 1 atm and 1 M for ions or molecules in aqueous solution).**

Illustration 20

Question: Calculate the standard free energy change for the reaction at 25°C,



Given: ΔH° for the reaction is -571.0 kJ and ΔS° is -326.0 J/K .

Solution: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= -571 - 298 \left(\frac{-326}{1000} \right)$$

$$= -571 + 97.2 \text{ kJ} = -473.8 \text{ kJ}$$

This implies that the formation of $\text{H}_2\text{O}(\text{l})$ from $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ at 25°C is spontaneous.

Illustration 21

Question: For the following reaction,



$$\Delta H_{298}^\circ = 89.96 \text{ kJ}.$$

Standard molar entropies for $\text{NO}(\text{g})$, $\text{O}_2(\text{g})$ and $\text{N}_2(\text{g})$ are 210.67, 205.10 and 192.34 J/K respectively. Calculate ΔG° for the reaction.

Solution: $\Delta S^\circ = S_{\text{NO}}^\circ - \frac{1}{2} S_{\text{N}_2}^\circ - \frac{1}{2} S_{\text{O}_2}^\circ = 210.67 - 96.17 - 102.55 = 11.95 \text{ J/K}$

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

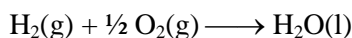
$$= 89.96 - 298 \left(\frac{11.95}{1000} \right) = 89.96 - 3.56 = 86.4 \text{ kJ/mole}$$

Thus at 25°C, the reaction does not occur spontaneously.

Illustration 22

Question: The heats of formation of $\text{H}_2\text{O}(\text{l})$ is -285.8 kJ and standard molar entropies are $S_{\text{H}_2\text{O}(\text{l})}^\circ = 69.9$, $S_{\text{H}_2(\text{g})}^\circ = 130.6$, $S_{\text{O}_2(\text{g})}^\circ = 205 \text{ J/K}$. Calculate the standard free energy of formation of liquid water at 25°C.

Solution: ΔG_f° for H_2O is ΔG° for the reaction,



$$\Delta S^\circ = S_{\text{H}_2\text{O}(\text{l})}^\circ - S_{\text{H}_2(\text{g})}^\circ - \frac{1}{2} S_{\text{O}_2(\text{g})}^\circ = 69.9 - 130.6 - 102.5 = -163.2 \text{ J/K}$$

$$\therefore \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -285.8 - \left(298 \times \frac{-163.2}{1000} \right) = -285.8 + 48.6 = -237.2 \text{ kJ/mol}$$

8.5 EFFECT OF TEMPERATURE UPON SPONTANEITY OF a REACTION

When the temperature of a system is increased, the direction in which the reaction proceeds spontaneously may or may not change. Whether it changes or not depends upon the relative signs of ΔH and ΔS° . The four possibilities are given in table.

Table: Effect of temperature on the spontaneity of a reaction at a given pressure

| Case | ΔH | ΔS° | $\Delta G^\circ = \Delta H - T\Delta S^\circ$ | Remarks |
|------|------------|------------------|--|--|
| I | – | + | Always negative. For example, $C(s) + O_2(g) \longrightarrow CO_2(g)$ | Spontaneous at all temperatures; Reverse reaction always non-spontaneous. |
| II | + | – | Always positive. For example, $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$ | Non-spontaneous at all temperatures; Reverse reaction takes place. |
| III | + | + | + at low temperatures, – at high temperatures. For example, $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$ | Non-spontaneous at low temperatures but becomes spontaneous at higher temperatures. |
| IV | – | – | – at low temperatures, + at high temperatures. For example, $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$ | Spontaneous at low temperatures but at high temperatures reverse reaction becomes spontaneous. |

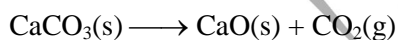
Note: (i) If ΔH and ΔS° have opposite sign (Case I and II), it is impossible to reverse the direction of spontaneity by temperature change alone. The two terms ΔH and $-T\Delta S$ strengthen one another. Therefore, ΔG° has the same sign at all temperatures. For the reaction,



ΔG° is positive at all temperatures. Hence the reaction cannot take place spontaneously at 1 atm whatever be the temperature.

(ii) When ΔH and ΔS° have the same sign (Case III and IV,) the enthalpy and entropy factors oppose each other. ΔG° changes sign as temperature increases and the direction of spontaneity reverses. At low temperatures, ΔH predominates and the exothermic reaction is favoured. With increasing temperature, the factor $T\Delta S^\circ$ increases in magnitude and at a certain stage exceeds ΔH . At high temperatures, the reaction leading to an increase in entropy occurs. This explains why exothermic reactions are spontaneous at room temperature.

In the decomposition of calcium carbonate, it is found that ΔH and ΔS° have the same sign.



On calculation,

$$\Delta G = 178.0 \text{ kJ} - T (0.1604 \text{ kJ/K})$$

- Below 1100 K, ΔH predominates, i.e., ΔG° is positive and the reaction is not spontaneous at 1 atmosphere pressure.
- Above 1100 K, $T\Delta S$ predominates and the reaction becomes spontaneous at 1 atmosphere pressure.
- At about 1100 K, $\Delta H = T\Delta S^\circ$. Hence, $\Delta G^\circ = 0$ i.e. the system is at equilibrium at 1 atmosphere, which means if we put some solid $CaCO_3$ in a vessel and heat it to 1100 K, the pressure developed by CO_2 will be 1 atmosphere.

Illustration 23

Question: At what temperature will the reaction,



become spontaneous ($\Delta H^\circ = + 131.3 \text{ kJ/mole}$ and $\Delta S^\circ = + 0.1335 \text{ kJ/K}$)?

Solution: A reaction becomes spontaneous when its ΔG value becomes negative. Since ΔS is positive for this reaction, we should calculate the minimum temperature, i.e. the temperature at which $\Delta G = 0$, assuming that the value of ΔH and ΔS are constant over the range of temperature.

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

Substituting,

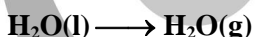
$$0 = 131.3 - T(0.1335)$$

$$T = \frac{131.3}{0.1335} = 983.5 \text{ K}$$

The reaction will be spontaneous at any temperature above 983.5 K.

Illustration 24

Question: For the vaporisation of water at 1 atmospheric pressure,



$\Delta H = + 44.3 \text{ kJ}$ and $\Delta S^\circ = + 118.8 \text{ J/K}$. Calculate the temperature at which liquid and vapour are at equilibrium at 1 atmosphere.

Solution: At equilibrium, $\Delta G^\circ = 0$

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

$$0 = \Delta H - T\Delta S^\circ$$

$$T\Delta S^\circ = \Delta H$$

$$T = \frac{\Delta H}{\Delta S^\circ} = \frac{44.3}{0.1188} = 373 \text{ K}$$

8.6 STANDARD FREE ENERGY OF FORMATION, G_f°

The standard free energy of formation, G_f° is defined as the **free energy change per mole when a compound is formed from the elements in their standard states**. Like the standard enthalpy of formation of an element, the standard free energy of formation of an element in its standard state is zero.

$$\Delta G^\circ = \Sigma G_f^\circ (\text{products}) - \Sigma G_f^\circ (\text{reactants})$$

(sum of the standard free energy of formation of products)
(sum of the standard free energy of formation of reactants)

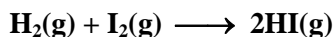
8.7 STANDARD FREE ENERGY CHANGE (ΔG°) AND EQUILIBRIUM CONSTANT (K_{eq})

The standard free energy change can be defined as the free energy change for a process at 298 K in which the reactants in their standard states are converted to the products in their standard states. It is denoted by the symbol ΔG° . Standard free energy change (ΔG°) is related to the equilibrium constant (K_{eq}) by the relation

$$\Delta G^\circ = -2.303 RT \log K_{eq}$$

Illustration 25

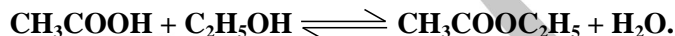
Question: Using $G_f^\circ(\text{HI}) = 1.3 \text{ kJ/mole}$, calculate the standard free energy change for the following reaction,



Solution: $\Delta G^\circ = \Sigma G_f^\circ(\text{products}) - \Sigma G_f^\circ(\text{reactants}) = 2 \times (1.3) - (0 + 0)$
 $= 2.6 - 0 = 2.6 \text{ kJ/mol}$

Illustration 26

Question: Calculate free energy change for the esterification reaction,



The equilibrium constant for the reaction at 25°C is 4.

Solution: $\Delta G^\circ = -2.303 RT \log K = -2.303 \times 8.314 \times 298 \log 4$
 $= -(2.303 \times 8.314 \times 298 \times 0.6021) = -3435.49 \text{ J/mol}$

Illustration 27

Question: Calculate the value of K_p at 25°C for an equilibrium reaction, if $\Delta G^\circ = -20 \text{ kJ/mole}$.

Solution: $\Delta G_p^\circ = -2.303 RT \log K_p$
 $-20 \times 1000 = -2.303 \times 8.314 \times 298 \log K_p$
 $\log K_p = \frac{20 \times 1000}{2.303 \times 8.314 \times 298} = 3.464$
 $K_p = \text{antilog}(3.505) = 2.91 \times 10^3$

SOLVED OBJECTIVE EXAMPLES

Example 1:

When a poly atomic gas undergoes an adiabatic process, its temperature and volume are related by the equation $TV^n = \text{constant}$, the value of n will be

- (a) 1.33 (b) 0.33
(c) 2.33 (d) 1

Solution:

For adiabatic process

$$TV^{\gamma-1} = \text{constant}$$

for poly atomic gas

$$\gamma = \frac{4}{3} = 1.33$$

$$n = 1.33 - 1 = 0.33$$

\therefore (b)

Example 2:

The difference between the heats of reaction at constant pressure and a 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

- (a) -7.43 (b) +3.72
(c) -3.72 (d) +7.43

Solution:

$$\Delta H = \Delta E + \Delta n_g RT. \text{ Here } \Delta n_g = 12 - 15 = -3. \text{ Thus, } \Delta H - \Delta E = -3 \times 8.314 \times 298 = -7.43 \text{ kJ.}$$

\therefore (a)

Example 3:

A mono atomic gas X and a diatomic gas Y, both initially at the same temperature and pressure are compressed adiabatically from a volume V to $V/2$, which gas will be at higher temperature

- (a) X (b) Y
(c) both the same (d) can't say

Solution:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

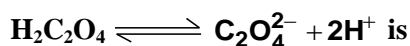
$$\therefore \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 2^{\gamma-1}$$

Since γ is more for the gas X, the temperature will also be more for it.

\therefore (a)

Example 4:

Heat of neutralization of oxalic acid is $-53.35 \text{ kJ mol}^{-1}$ using NaOH. Hence ΔH of



(a) 5.88 kJ

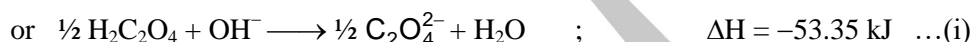
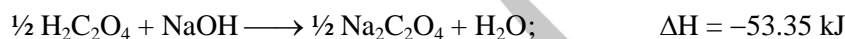
(b) -5.88 kJ

(c) -13.7 kcal

(d) 7.9 kJ

Solution:

By the definition of heat of neutralization, we have



Subtracting equation (ii) from (i) we get



\therefore (d)

Example 5:

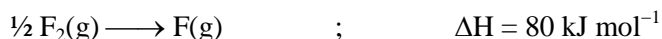
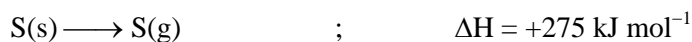
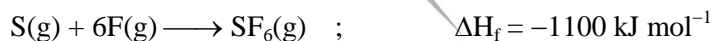
The standard heat of formation values of $\text{SF}_6(\text{g})$, $\text{S}(\text{g})$ and $\text{F}(\text{g})$ are: -1100 , 275 and 80 kJ mol^{-1} respectively. Then the average S – F bond energy in SF_6

(a) 301 kJ mol^{-1}

(b) 320 kJ mol^{-1}

(c) 309 kJ mol^{-1}

(d) 280 kJ mol^{-1}

Solution:


Therefore heat of formation = Bond energy of reaction – Bond energy of product

$$-1100 = [275 + 6 \times 80] - [6 \times \text{S} - \text{F}]$$

Thus bond energy of S – F = 309 kJ mol^{-1}

Example 6:

At a particular temperature $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$; $\Delta H = -57.1 \text{ kJ}$

The approximate heat evolved when 400 ml of 0.2 M H_2SO_4 is mixed with 600 ml of 0.1 M KOH solution will be

(a) 3.426 kJ

(b) 13.7 kJ

(c) 5.2 kJ

(d) 55 kJ

Solution:

$$\text{Number of equivalent of H}_2\text{SO}_4 \text{ taken} = \frac{0.2 \times 2 \times 400}{1000} = 0.16$$

$$\text{Number of equivalent of KOH added} = \frac{600 \times 0.1}{1000} = 0.06$$

Number of equivalents of acid and bases which neutralized each other = 0.06

$$\therefore \text{Heat evolved} = 0.06 \times 57.1 \text{ kJ} = 3.426 \text{ kJ}$$

 \therefore (a)

Example 7:

A sample of oxygen gas expands its volume from 3 litre to 5 litre against a constant pressure of 3 atm. If the work done during expansion be used to heat 10 mole of water initially present at 290 K, its final temperature will be

(Specific heat capacity of water = $4.18 \text{ J K}^{-1} \text{ g}^{-1}$)

(a) 292.0 k

(b) 290.8 k

(c) 298.0 k

(d) 293.7 k

Solution:

Work done in expansion

$$= P \times V$$

$$= 3 \times (5 - 3) \text{ 6 lit-atm}$$

we have 1 litre atm = 101.3 J

$$\text{work done} = 6 \times 1.013 \text{ J} = 607.8 \text{ J}$$

Let ΔT be the change in temperature of water.

$$\therefore P\Delta V = m \times s \times \Delta T$$

$$607.8 = 180 \times 4.184 \times \Delta T$$

$$\Delta T = 0.81 \text{ K}$$

$$T_f = T_i + \Delta T = 290.9 \text{ K}$$

 \therefore (b)

Example 8:

The molar heat capacity of water in equilibrium with ice at constant pressure is

(a) zero

(b) infinity (∞)

(c) $40.45 \text{ kJ K}^{-1} \text{ mol}^{-1}$

(d) $75.48 \text{ J K}^{-1} \text{ mol}^{-1}$
Solution:

We know that heat capacity at constant pressure is given by

$$C_p = \left(\frac{\Delta H}{\Delta T} \right)_p$$

Since the phase transformation i.e., ice \rightleftharpoons water, takes place at a fixed temperature so $\Delta T = 0$.

$$\therefore C_p = \frac{\Delta H}{0} = \infty$$

\therefore (b)

Example 9:

One mole of ice is converted into water at 273 K. The entropies of $H_2O(s)$ and $H_2O(l)$ are 38.20 and 60.01 J mole⁻¹ K⁻¹ respectively. The enthalpy change for the conversion is

- (a) 59.54 J mole⁻¹ (b) 5954 J mole⁻¹
(c) 594.5 J mole⁻¹ (d) 320.6 J mole⁻¹

Solution:

$\Delta G = \Delta H - T\Delta S$. At equilibrium $\Delta G = 0$, so $\Delta H = T\Delta S$. $\Delta H = 273 \times (60.01 - 38.20) = 5954.13$ J mole⁻¹.

\therefore (b)

Example 10:

The ΔH_f° for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are -393.5, -110.5 and -241.8 kJ. mole⁻¹ respectively. The standard enthalpy change in kJ for the reaction.

$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ is

- (a) + 524.1 (b) + 41.2
(c) - 262.5 (d) - 41.2

Solution:

(a) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5$ kJ mole⁻¹

(b) $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$; $\Delta H = -110.5$ kJ mole⁻¹

(c) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$; $\Delta H = -241.8$ kJ mole⁻¹

For getting $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$, add (b) and (c) and subtract (a).
Thus $-110.5 - 241.8 + 393.5 = 395.5 - 352.3 = 41.2$ kJ mole⁻¹.

\therefore (b)

SOLVED SUBJECTIVE EXAMPLES

Example 1:

A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm³ to 2.50 dm³. Calculate the enthalpy change in process?

Solution:

$$n = \frac{PV}{RT} = \frac{1.25 \times 1}{0.0821 \times 300} = 0.05$$

$TV^{\gamma-1} = \text{constant}$ for adiabatic process

$$\therefore T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

On solving, $T_2 = 188.55 \text{ K}$

$$\Delta H = nC_p \Delta T = -0.05 \times 20.794 \times 111.45 = -115.87 \text{ J}$$

Example 2:

An ideal gas having initial pressure P , volume V and temperature T is allowed to expand adiabatically until its volume becomes $5.66 V$ while its temperature falls to $T/2$.

- (i) How many degrees of freedom do the gas molecules have?
- (ii) Obtain an expression for the work done by the gas during the expansion as a function of the initial pressure P and volume V .

Solution:

For an adiabatic process,

$$TV^{\gamma-1} = \text{constant}$$

$$\therefore T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} = \frac{T_1}{2} (5.66 V_1)^{\gamma-1}$$

$$\text{Hence, } 2 = (5.66)^{\gamma-1}$$

$$\text{or } \log 2 = (\gamma - 1) \log 5.66$$

$$\therefore \gamma = 1.4$$

The gas is, therefore a diatomic gas and have five degrees of freedom.

The work done by a gas during an adiabatic process is

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

$$\text{Since } P_1 V_1^\gamma = P_2 V_2^\gamma = P_2 (5.66 V_1)^\gamma$$

$$P_2 = \frac{P_1}{(5.66)^\gamma}$$

$$\therefore W = \left[\frac{P_1 (5.66 V_1)^\gamma}{(5.66)^\gamma} - P_1 V_1 \right] \frac{1}{0.4} = 1.25 P_1 V_1$$

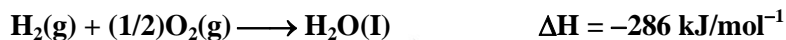
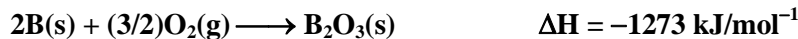
$$\text{or } W = 1.25 PV$$

Example 3:

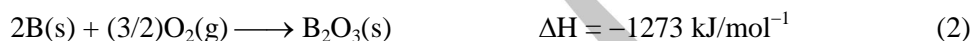
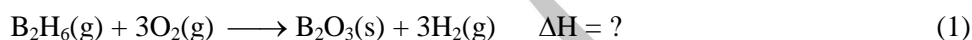
Diborane is a potential rocket fuel which undergoes combustion according to the reaction,



From the following data, calculate the enthalpy change for the combustion of diborane.



Solution:



$$\Delta H_f(\text{B}_2\text{O}_3) = -1273 \text{ kJ/mol}$$

$$\Delta H_f(\text{H}_2\text{O}(\text{g})) = -286 + 44 = -242 \text{ kJ/mol}$$

$$\Delta H_f(\text{B}_2\text{H}_6(\text{g})) = 36 \text{ kJ/mol}$$

$$\Delta H(\text{for reaction(1)}) = -1273 - [(3 \times 242) + 36] = -2035 \text{ kJ/mol}$$

Example 4:

A sample of solid naphthalene C_{10}H_8 , weighing 0.6 g is burnt to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ in a constant volume calorimeter at 298 K. In this experiment the observed temperature rise of the calorimeter and its contents is 2.27°C . In a separate experiment, the total heat capacity of the calorimeter was found to be 2556 cal/deg. What is ΔE for the combustion of one mole of naphthalene? What is ΔH for this reaction. Also calculate the enthalpy of formation of naphthalene.

$$\Delta H_f^\circ (\text{H}_2\text{O}, \text{l}) = -68.32 \text{ kcal/mol}$$

$$\Delta H_f^\circ (\text{CO}_2, \text{g}) = -94.05 \text{ kcal/mol}$$

Solution:

$$\text{Heat released} = 2.27 \times 2556 = 5.802 \text{ kcal}$$

$$\Delta E = -\frac{5.802 \times 128}{0.6} = -1237.76 \text{ kcal/mol}$$

$$\text{Also, } \Delta H = \Delta E + \Delta nRT$$

For the reaction:



$$\Delta n = 10 - 12 = -2$$

$$\therefore \Delta H = -1237.76 - (2 \times 2 \times 10^{-3}) \times 298 = -1238.952 \text{ kcal/mol}$$

$$\text{Also } -1238.952 = 10 \Delta H_f^\circ \text{CO}_2(\text{g}) + 4 \Delta H_f^\circ \text{H}_2\text{O}(\text{l}) - \Delta H_f^\circ \text{C}_{10}\text{H}_8(\text{s})$$

$$-1238.952 = 10 \times (-94.05) + 4(-68.32) - \Delta H_f^0(\text{C}_{10}\text{H}_8)$$

$$\therefore \Delta H_f^0(\text{C}_{10}\text{H}_8) = 25.172 \text{ kcal/mol}$$

Example 5:

Find standard heat of formation of $\text{OH}^- (\text{aq})$. It is given



Solution:

By convention the heat of formation of $\text{H}^+(\text{aq})$ is arbitrarily taken as zero at 25°C and at unit concentration i.e.,

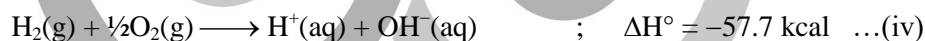


With this convention, the heat of formation of other ions can be evaluated.

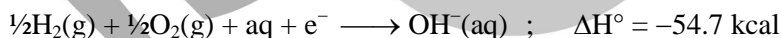
Thus, the heat of formation of $\text{OH}^- (\text{aq})$ can be calculated from the following reactions:



On adding equation (i) and (ii), we get



Now, on subtracting equation (i) from equation (iv), we have



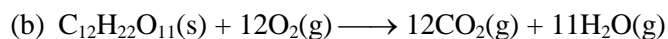
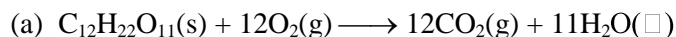
That is, standard heat of formation of $\text{OH}^- (\text{aq})$ is **-54.7 kcal**.

Example 6:

When maltose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$ burns in a calorimetric bomb at 298 K yielding water and carbondioxide, the heat of combustion is **-1350 kcal/mol**. Calculate the heat of combustion of maltose of constant pressure if the water vapour resulting from the combustion is (a) condensed and (b) not condensed.

Solution:

The combustion reaction of maltose can be shown for (a) and (b) as follows:



Case (a): When water is condensed

It is given that,

$$\Delta H_v = -1350 \text{ kcal/mol}$$

$$\Delta n = 0 ; R = 1.987 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1}$$

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

On inserting these values in the expression

$$\Delta H_p = \Delta H_v + \Delta nRT$$

$$\Delta H_p = -1350 + 0 \times RT = -1350 \text{ kcal/mol}$$

Case (b) : When water is not condensed



It is given that,

$$\Delta H_v = -1350 \text{ k cal/mol}$$

$$\Delta n = (12 + 11 - 12) = 11 ;$$

$$R = 1.987 \times 10^{-3} \text{ kcal/mol}$$

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

On inserting these values in the expression

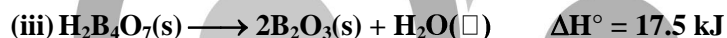
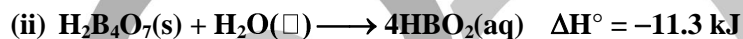
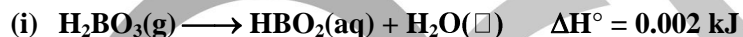
$$\Delta H_p = \Delta H_v + \Delta nRT$$

$$\Delta H_p = [-1350 + (11 \times 1.987 \times 10^{-3} \times 298)] = \text{kcal}$$

$$\Delta H_p = -1343 \text{ kcal/mol}$$

Example 7:

Given the following information



Calculate ΔH° for the reaction



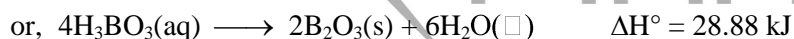
Solution:

equation (i) $\times 4$ – equation (ii) + equation (iii)

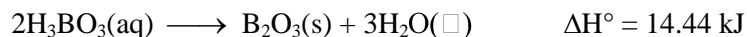
On doing so,



$$\Delta H^\circ = (0.02 \times 4 + 11.3 + 17.5) \text{ kJ}$$



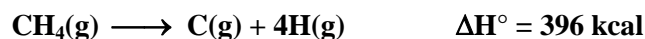
or, On dividing throughout by 2 we get



This problem can be solved using intrinsic energy method as well.

Example 8:

The enthalpy change for the following processes at 25°C and under constant pressure of one atmosphere are as follows:



Calculate C – C bond energy in the molecule of C_2H_6 .

If molar heat of sublimation of carbon, $\text{C}(\text{s})$ and molar heat of dissociation of $\text{H}_2(\text{g})$ are 171.8 and 104.1 kcal respectively. Calculate the standard heat of formation of ethane, $\text{C}_2\text{H}_6(\text{g})$.

Solution:

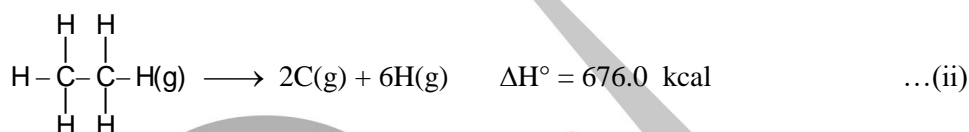
It is given that



That is, $4 \times \text{B.E. of C-H} = 396 \text{ kcal}$

$$\therefore \text{B.E. of C-H} = \frac{396}{4} \text{ kcal} = 99.0 \text{ kcal}$$

Again,



It means that

$$6 \times \text{B.E. of C-H} + \text{B.E. of C-C} = 676.0 \text{ kcal}$$

$$\text{or, } 6 \times 99.0 + \text{B.E. of C-C} = 676.0$$

$$\therefore \text{B.E. of C-C} = (676.0 - 594) \text{ kcal} = 82.0 \text{ kcal}$$

That is B.E. of C-C = 82.0 kcal

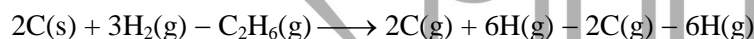


ΔH° for the following reaction is to be found:



Equation (iii) $\times 2$ + equation (iv) $\times 3$ - equation (ii)

On doing so,



$$\Delta H^\circ = [(2 \times 171.8) + 3 \times 104.1 - 676] \text{ kcal}$$

$$\text{or, } 2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}), \quad \Delta H^\circ = -20.1 \text{ kcal}$$

That is, heat of formation of $\text{C}_2\text{H}_6(\text{g})$, $\Delta H^\circ = -20.1 \text{ kcal}$

Example 9:

One mole of an ideal monoatomic gas undergoes an isoergic reversible change from 25°C and 1 atm. to twice the original volume. Calculate q , W and ΔH .

Solution:

An isoergic change is a change where $\Delta U = 0$, which means process is isothermal if the gas is ideal. Hence the process is isothermal reversible.

$$\text{Hence } q = RT \ln \frac{V_2}{V_1}; \quad \text{Here } \frac{V_2}{V_1} = 2$$

So $q = 8.313 \times 298 \log_e 2 \text{ Joule} = 1717.2 \text{ Joule}$

In isothermal process $q = W = 1717.2 \text{ Joule}$ and $\Delta H = 0$

Example 10:

A mole of steam is condensed at 100°C , the water is cooled to 0°C and frozen to ice. What is the difference in entropies of the steam and ice? The heats of vaporization and fusion are 540 cal gm^{-1} and 80 cal gm^{-1} respectively. Use the average heat capacity of liquid water as $1 \text{ cal gm}^{-1} \text{ degree}^{-1}$.

Solution:

Entropy change during condensation of steam

$$\Delta S_1 = \frac{18 \times 540}{373} \text{ cal/}^\circ = -26.06 \text{ cal/}^\circ$$

Entropy change during cooling of water from 100°C to 0°C

$$\Delta S_2 = 18 \times 1 \ln \frac{273}{373} \text{ cal/}^\circ = -5.62 \text{ cal/}^\circ$$

Entropy change during freezing of water at 0°C

$$\Delta S_3 = -\frac{18 \times 80}{273} \text{ cal/}^\circ = -5.27 \text{ cal/}^\circ$$

So total entropy change $= -26.06 - 5.62 - 5.27 = -36.95 \text{ cal/}^\circ$

Hence difference in entropy between steam and ice $= 36.95 \text{ cal/}^\circ$

Example 11:

Calculate the resonance energy of acetic acid from the following data:

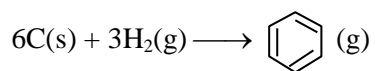
- (i) Enthalpy of formation of water (\square) $= -286 \text{ kJ mol}^{-1}$
- (ii) Enthalpy of formation of $\text{CO}_2(\text{g}) = -393.5 \text{ kJ mol}^{-1}$
- (iii) Enthalpy of formation of $\text{CH}_3\text{CO}_2(\text{g}) = -384.5 \text{ kJ mol}^{-1}$
- (iv) Enthalpy of vapourization of $\text{H}_2\text{O}(\square) = 168 \text{ kJ mol}^{-1}$
- (v) Enthalpy of dissociation of $\text{CH}_4(\text{g}) = 1652 \text{ kJ mol}^{-1}$
- (vi) Enthalpy of formation of $\text{C}_6\text{H}_6(\text{g}) = 90 \text{ kJ mol}^{-1}$
- (vii) Resonance energy of $\text{C}_6\text{H}_6(\text{g}) = 150 \text{ kJ mol}^{-1}$
- (viii) Bond enthalpy of $\text{C} = \text{C}$ bond $= 617 \text{ kJ mol}^{-1}$
- (ix) Bond enthalpy of $\text{C} - \text{O}$ bond $= 420 \text{ kJ mol}^{-1}$
- (x) Heat of atomization of carbon $= 718.5 \text{ kJ mol}^{-1}$
- (xi) Heat of atomization of gaseous oxygen $= 248 \text{ kJ mol}^{-1}$
- (xii) Heat of atomization of gaseous hydrogen $= 217 \text{ kJ mol}^{-1}$

Solution:

R.E. of benzene $= \Delta H_f(\text{observed}) - \Delta H_f(\text{theoretical})$

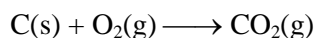
$$-150 = 90 - \Delta H_f(\text{theoretical})$$

$$\Delta H_f(\text{theoretical}) = 240 \text{ kJ mol}^{-1}$$



$$\therefore \Delta H_f(\text{theoretical}) = 6 \times \Delta H_{\text{atomiz C(g)}} + 6\Delta H_{\text{atomiz H(g)}} - 3\epsilon_{\text{C-C}} - 3\epsilon_{\text{C-C}} - 6\epsilon_{\text{C-C}}$$

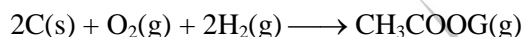
$$\therefore \epsilon_{\text{C-C}} = 348 \text{ kJ mol}^{-1}$$



$$\Delta H_f(\text{CO}_2) = \Delta H_{\text{atomiz C(g)}} + 2\Delta H_{\text{atomiz O(g)}} - 2\epsilon_{\text{C=O}}$$

$$-393.5 = 718.5 + 496 - 2\epsilon_{\text{C=O}}$$

$$\therefore \epsilon_{\text{C=O}} = 804 \text{ kJ mol}^{-1}$$



$$\Delta H_f(\text{theoretical}) = (2 \times 718.5) + 868 - 1239 - 348 - 804 - 420 - 400$$

$$= -410 \text{ kJ mol}^{-1}$$

$$\text{R.E. of CH}_3\text{CO}_2\text{H} = \Delta H_f(\text{observed}) - \Delta H_f(\text{theoretical}) = -384.5 - (-410)$$

$$= 25.5 \text{ kJ mol}^{-1}$$

Example 12:

In the 'Benson group' method for evaluating standard enthalpies of formation of hydrocarbons, each group $-\text{CH}_3$, $-\text{CH}_2$ etc. are assigned separate enthalpies of formation, and Δf_f^0 for the hydrocarbon is additively calculated. On this basis Δf_f^0 for normal pentane, isopentane and normal butane are -147.3 kJ/mole , -156.6 kJ/mol and -126.6 kJ/mole respectively. Calculate Δf_f^0 isobutene.

Solution:

For n-pentane $= \text{CH}_3 - (\text{CH}_2)_3 - \text{CH}_3$ with two $-\text{CH}_3$ and three $-\text{CH}_2$ groups ; $\Delta f_f^0 = 2x + 3y$ where x and y are the Δf_f^0 values for $-\text{CH}_3$ and, similarly

$$\Delta f_f^0 = 2x + 3y$$

$$\therefore 2x + 3y = -147.3 \text{ kJ/mol}$$

$$2x + 2y = -126.6 \text{ kJ/mol}$$

On solving we will get

$$x = -42.6 \text{ kJ/mol}$$

$$y = -20.7 \text{ kJ/mol}$$

In isopentane $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CH}_3$, we have three CH_3 , one $-\text{CH}_2-$ and

one $-\text{CH}-$ groups.

Thus $3x + y + z = -156.6 \text{ kJ/mol}$ where, $z = \Delta f_f^0$ for $-\text{CH}-$ group

$$\therefore z = -8.1 \text{ kJ/mol.}$$

For isobutene $\text{CH}_3 - \text{CH} = \text{CH}_2$ we have three $\Delta f_f^0 = 3x + z$

$$\text{i.e., } [3(-42.6) + (-8.1) \text{ kJ/mol}] = -135.9 \text{ kJ/mol}$$

MIND MAP

**CHEMICAL
THERMODYNAMICS
& ENERGETICS**

1. Mathematical form of 1st law is

$$q = \Delta E - W$$

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

Since heat given to the system and work done on the system raise the internal energy of the system, these two operations are given +ve value. The converse of the two operations is assigned -ve values.

2. a. Workdone in reversible isothermal expansion:

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

b. Irreversible isothermal expansion:

$$W = -P_{\text{ext}} (V_2 - V_1)$$

c. Reversible adiabatic expansion

$$W = \frac{R}{\gamma - 1} (T_2 - T_1)$$

d. Irreversible adiabatic expansion.

$$W = -RP_{\text{ext}} \frac{(T_2 P_1 - T_1 P_2)}{P_1 P_2}$$

9. $\Delta H_{\text{reaction}} = \sum \text{Bond energies of reactants} - \sum \text{Bond energies of products}$.

Resonance energy = [Experimental heat of formation] - [Theoretical heat of formation].

3. Work done in reversible isothermal expansion of an ideal gas is more than that in irreversible isothermal expansion similar is the case with adiabatic expansion.

8. (a) Heat of neutralisation and combustion is always exothermic.

(b) $Q = m \times s \times (T_2 - T_1)$ where q = Heat change, m = Mass of solution, s = Specific heat of solution.

4. (a) $\Delta H = \Delta E + \Delta n_g RT$

(b) The changes in internal energy & enthalpy of a system caused by change in temperature are given by

$$\Delta E = n\bar{C}_V(\Delta T) \quad \& \quad \Delta H = n\bar{C}_P(\Delta T)$$

7. Hess's Law

The enthalpy change in a physical or chemical process is same, whether the process is carried out in one step or several steps.

$$\Delta H_{\text{reactions}} = \sum \text{Heat of combustion of reactants} - \sum \text{Heat of combustion of products}$$

$$\Delta H_{\text{reactions}} = \sum \text{Heat of formation of products} - \sum \text{Heat of formation of reactants}$$

6. (a) For a reaction to be spontaneous, the change in free energy (ΔG) is always -ve.

$$(b) \Delta G = \Delta H - T\Delta S$$

$$(c) \Delta G^\circ = -2.303 RT \log_{10} K$$

5. (a) For a reaction in which $\Delta n_g = 0$, ΔS is not always zero.

$$(b) \Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

$$(c) \Delta S = \frac{\Delta H_{\text{rev}}}{T} \quad (\text{where } T \text{ is transition temperature.})$$

EXERCISE – I (BUILDING A FOUNDATION)**BASIC DEFINITION****SINGLE CORRECT ANSWER TYPE****Section – A**

1. Out of molar entropy (I), specific volume (II), heat capacity (III), volume (IV), extensive properties are
 - (a) I, II
 - (b) I, II, IV
 - (c) II, III
 - (d) III, IV
2. Thermodynamic equilibrium involves
 - (a) Chemical equilibrium
 - (b) Mechanical equilibrium
 - (c) Thermal equilibrium
 - (d) All of above simultaneously
3. A well stoppered thermos flask contains some ice cubes. This is an example of:-
 - (a) Closed system
 - (b) Open system
 - (c) Isolated system
 - (d) Non-thermodynamic system
4. Which of the following is a closed system?
 - (a) Jet engine
 - (b) Tea placed in a steel kettle
 - (c) Open kettle
 - (d) Rocket engine during propulsion
5. Select the correct order in the following:
 - (a) $1 \text{ erg} > 1 \text{ joule} > 1 \text{ cal}$
 - (b) $1 \text{ cal} > 1 \text{ joule} > 1 \text{ erg}$
 - (c) $1 \text{ erg} > 1 \text{ cal} > 1 \text{ joule}$
 - (d) $1 \text{ joule} > 1 \text{ cal} > 1 \text{ erg}$
6. Which of the following is state function?
 - (a) Temperature
 - (b) Potential energy
 - (c) Internal energy
 - (d) All of these
7. Thermodynamics is not concerned about.....
 - (a) Energy changes involved in a chemical reaction
 - (b) The extent to which a chemical reaction proceeds
 - (c) The rate at which a reaction proceeds
 - (d) The feasibility of a chemical reaction

MULTIPLE CORRECT ANSWER TYPE

8. Which of the following statements is correct?
- (a) The presence of reacting species in a covered beaker is an example of open system
 - (b) There is an exchange of energy as well as matter between the system and the surrounding in a close system
 - (c) The presence of reactants in a closed vessel made up of copper is an example of a closed system
 - (d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a isolated system
9. Which of the following is an extensive property?
- (a) Kinetic energy
 - (b) Potential energy
 - (c) Internal energy
 - (d) Temperature

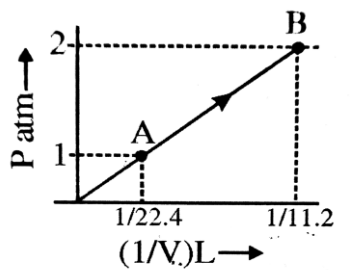
FLOT, ΔU & W CALCULATION**SINGLE CORRECT ANSWER TYPE****Section – B**

1. In a closed insulated container a liquid is stirred with a paddle to increase the temperature only. Which of the following is true?
- (a) $\Delta E = W \neq 0, q = 0$
 - (b) $\Delta E = W = q \neq 0$
 - (c) $\Delta E = 0, W = q \neq 0$
 - (d) $W = 0, \Delta E = q \neq 0$
2. The change in the internal energy for an isolated system at constant volume is
- (a) $\Delta U \neq 0$
 - (b) $\Delta U = \Delta q + \Delta W$
 - (c) $\Delta U = 0$
 - (d) None of these
3. A system is provided 50 J of heat and work done on the system is 10 J. The change in internal energy during the process is:-
- (a) 40 J
 - (b) 60 J
 - (c) 80 J
 - (d) 50 J
4. An ideal gas expands against a constant external pressure of 2.0 atmosphere from 20 litre to 40 litre and absorb 10 kJ of heat from surrounding. What is the change in internal energy of the system? (Given: 1 atm – litre = 101.3 J)
- (a) 4052 J
 - (b) 5948 J
 - (c) 14052 J
 - (d) 9940 J
5. A system undergoes a process in which $\Delta E = + 300$ J while absorbing 400 J of heat energy and undergoing an

- expansion against 0.5 bar. What is the change in the volume (in L)?
- 4
 - 5
 - 2
 - 3
6. One mole of an ideal gas at 25°C expands in volume from 1.0 L to 4.0 L at constant temperature. What work (in J) is done if the gas expands against vacuum ($P_{\text{external}} = 0$)?
- -4.0×10^2
 - -3.0×10^2
 - -1.0×10^2
 - Zero
7. At 25°C , a 0.01 mole sample of a gas is compressed from 4.0 L to 1.0 L at constant temperature. What is the work done for this process if the external pressure is 4.0 bar?
- $1.6 \times 10^3 \text{ J}$
 - $8.0 \times 10^2 \text{ J}$
 - $4.0 \times 10^2 \text{ J}$
 - $1.2 \times 10^3 \text{ J}$
8. What is the change in internal energy when a gas contracts from 377 mL to 177 mL under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat?
- 40.52 J
 - 83.48 J
 - 248 J
 - None of these
9. A gas absorbs 200 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 L to 1.0 L. Calculate the change in internal energy.
- 120.025 J
 - 115.025 J
 - 135.025 J
 - 124.025 J
10. The temperature of 1 mole of an ideal gas is increased by 1°C at constant pressure. The work done is
- $-R$
 - $-2R$
 - $-R/2$
 - $-3R$
11. When freezing of a liquid takes place in a system
- May have $q > 0$ or $q < 0$ depending on the liquid
 - Is represented by $q > 0$
 - Is represented by $q < 0$
 - Has $q = 0$
12. Mechanical work is specially important in systems that contain
- Gas-liquid
 - Liquid-liquid

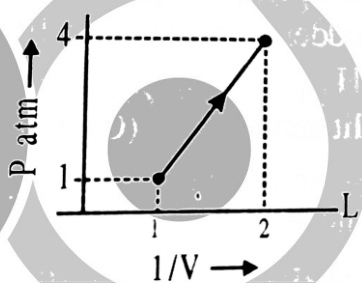
- (c) Solid-solid
- (d) Amalgam

13. Calculate work done for an ideal gas in going from state A to state B ($\ln 2 = 0.7$)



- (a) 15.68 L – atm
- (b) 25.68 L – atm
- (c) 30.68 L – atm
- (d) 35.68 L – atm

14. Calculate $w = ?$ ($\ln 2 = 0.7$)



- (a) 2.1 L – atm
- (b) 3.1 L – atm
- (c) 1.1 L – atm
- (d) 4.1 L – atm

15. A gas expands against a variable pressure given by $P = \frac{20}{V}$ (where P in atm and V in L). During expansion from volume of 1 litre to 10 litre, the gas undergoes a change in internal energy of 400 J. How much heat is absorbed by the gas during expansion?

- (a) 46 J
- (b) 4660 J
- (c) 5065.8 J
- (d) 4260 J

16. A sample of an ideal gas is expanded 1 m^3 to 3 m^3 in a reversible process for which $P = KV^2$, with $K = 6 \text{ bar/m}^6$. Work done by the gas is

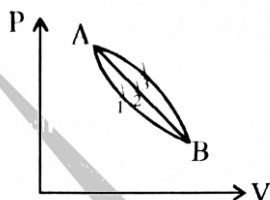
- (a) 5200 kJ
- (b) 15600 kJ
- (c) 52 kJ
- (d) 5267.6 kJ

CALCULATION OF ΔH , ΔU , Q & W

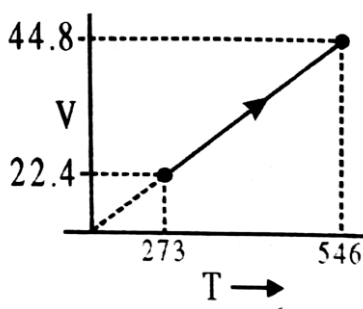
SINGLE CORRECT ANSWER TYPE

Section – C

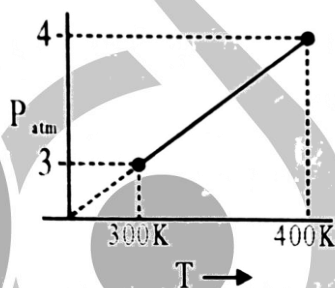
1. A given mass of gas expands reversible from the state A to the state B by three paths 1, 2 and 3 as shown in the figure. If w_1 , w_2 and w_3 respectively be the work done by the gas along three paths then



- (a) $w_1 > w_2 > w_3$
 - (b) $w_1 < w_2 < w_3$
 - (c) $w_1 = w_2 = w_3$
 - (d) $w_2 < w_3 < w_1$
2. Which of the following expressions is true for an ideal gas?
 - (a) $\left(\frac{\partial V}{\partial T}\right)_P = 0$
 - (b) $\left(\frac{\partial P}{\partial T}\right)_V = 0$
 - (c) $\left(\frac{\partial U}{\partial V}\right)_T = 0$
 - (d) $\left(\frac{\partial U}{\partial T}\right)_V = 0$
 3. Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 to 1 atm at a constant temperature of 273 K. The gas behaves ideally.
 - (a) 6180 calories.
 - (b) 8180 calories.
 - (c) 7180 calories
 - (d) 9180 calories
 4. A liquid of volume of 100 L and at the external pressure of 10 atm is confined inside an adiabatic bath. External pressure of the liquid is suddenly increased to 100 atm and the liquid gets compressed by 1 L against this pressure then find ΔH
 - (a) 6000 lit atm.
 - (b) 2000 lit atm.
 - (c) 9000 lit atm.
 - (d) 1200 lit atm.
 5. For 1 mole of ideal gas. Calculate $w = ?$



- (a) -283 R
 - (b) -253 R
 - (c) -263 R
 - (d) -273 R
6. For 1 mole of monoatomic gas. Calculate ΔH .

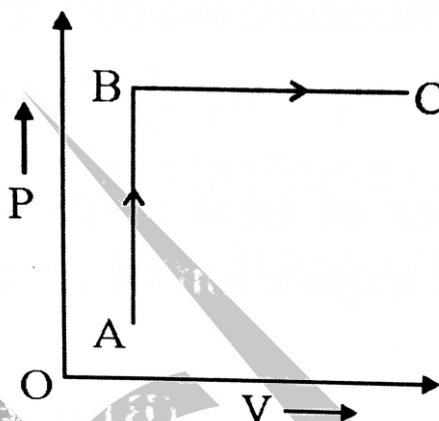


- (a) 250 R
 - (b) 240 R
 - (c) 230 R
 - (d) 220 R
7. 2 mole of an ideal gas at 27°C expands isothermally and reversibly from a volume of 4 litre to 40 litre. The work done (in kJ) by the gas is
- (a) $w = -28.72 \text{ kJ}$
 - (b) $w = -11.488 \text{ kJ}$
 - (c) $w = -5.736 \text{ kJ}$
 - (d) -4.988 kJ
8. For two mole of an ideal gas
- (a) $C_V - C_P = R$
 - (b) $C_P - C_V = 2R$
 - (c) $C_P - C_V = R$
 - (d) $C_V - C_P = 2R$
9. A balloon is 1 m in diameter & contains air at 25°C & 1 bar pressure. If it is filled with air isothermally & reversibly until the pressure reaches 5 bar. Assume pressure is proportional to diameter of balloon. Calculate work done by air (bar m^3)
- (a) 78π
 - (b) 156π
 - (c) 624π

(d) 625π

10. A thermodynamic process is shown in the following figure. In the process AB, 600 J of heat is added to the system and in BC, 200 J of heat is added to the system. The change in internal energy of the system in the process AC would be given

$$P_A = 3 \times 10^4 \text{ Pa}, V_A = 2 \times 10^{-3} \text{ m}^3, P_B = 8 \times 10^4 \text{ Pa}, V_C = 5 \times 10^{-3} \text{ m}^3$$



- (a) 560 J
(b) 800 J
(c) 600 J
(d) 640 J
11. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 15 to 50 litres.
(a) – 1236 calories
(b) – 1436 calories
(c) – 1036 calories
(d) – 1536 calories
12. 5 mole of an ideal gas expand isothermally and irreversibly from a pressure of 10 atm to 1 atm against a constant external pressure of 1 atm. W_{irr} at 300 K is:
(a) – 15.921 kJ
(b) – 11.224 kJ
(c) – 110.83 kJ
(d) None of these
13. With what minimum pressure (in kPa), a given volume of an ideal gas ($C_{p,m} = 7/2 R$), originally at 400 K and 100 kPa pressure can be compressed irreversibly adiabatically in order to raise its temperature to 600 K:
(a) 362.5 kPa
(b) 275 kPa
(c) 437.5 kPa
(d) 550 kPa
14. During an expansion of ideal gas the work done by gas is 100 J and the heat capacity of process is found to be $+2 \text{ J}/^\circ\text{C}$ find ΔE of gas if the final temperature of gas is 25°C higher than its initial temperature.
(a) – 40 J
(b) – 50 J

- (c) -70 J
 (d) -35 J
15. Calculate ΔE for the conversion of 1 mole of water into 1 mole of steam at a temperature of 100°C and at a pressure of 1 atmosphere. Latent heat of vaporization of water is 9720 cal/mole .
 (a) 7979 calories
 (b) 6979 calories
 (c) 5979 calories
 (d) 8979 calories
16. One mole of an ideal gas ($C_{v,m} = \frac{5}{2}R$) at 300 K and 5 atm is expanded adiabatically to a final external pressure of 2 atm against a constant pressure of 2 atm . Final temperature of the gas is
 (a) 270 K
 (b) 273 K
 (c) 248.5 K
 (d) 200 K
17. During an adiabatic process, the pressure of gas is found to be proportional to the cube of its absolute temperature. The ratio of $(C_{p,m}/C_{v,m})$ for gas is
 (a) $\frac{3}{2}$
 (b) $\frac{5}{3}$
 (c) $\frac{7}{2}$
 (d) $\frac{4}{3}$
18. If a gas at a pressure of 10 atm at 300 K expands against a constant external pressure of 2 atm from a vol. of 10 litres to 20 litres find work done? [Isothermal process]
 (a) -10 L atm
 (b) -20 L atm
 (c) -30 L atm
 (d) -40 L atm
19. If w_1 , w_2 , w_3 and w_4 for an ideal gas are magnitude of work done in isothermal, adiabatic, isobaric and isochoric reversible expansion processes, the correct order will 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) $w_3 > w_1 > w_2 > w_4$
20. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following:
 (a) $q = 0, \Delta T \neq 0, W = 0$
 (b) $q \neq 0, \Delta T = 0, W = 0$
 (c) $q = 0, \Delta T = 0, W = 0$
 (d) $q = 0, \Delta T < 0, W \neq 0$
21. 10 litre of a non linear polyatomic gas at 127°C and 2 atm pressure is suddenly released to 1 atm pressure and the gas expanded adiabatically against constant external pressure, the final temperature and volume of the

gas respectively are.

- (a) $T = 350 \text{ K}$; $V = 17.5 \text{ L}$
 - (b) $T = 300 \text{ K}$; $V = 15 \text{ L}$
 - (c) $T = 250 \text{ K}$; $V = 12.5 \text{ L}$
 - (d) None of these
22. One mole of an ideal gas undergoes a change of state (2.0 atm, 3.0 L) to (2.0 atm, 7.0 L) with a change in internal energy (ΔU) = 30 L – atm. The change in enthalpy (ΔH) of the process in L – atm
- (a) 22
 - (b) 38
 - (c) 25
 - (d) None of these
23. The work done by the gas in reversible adiabatic expansion process is
- (a) $\frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$
 - (b) $\frac{nR (T_1 - T_2)}{\gamma - 1}$
 - (c) $\frac{P_2 V_2 - P_1 V_1}{\gamma}$
 - (d) None of these
24. One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Calculate work done under the following conditions.
- (i) Expansion is carried out reversibly.
 - (a) – 595.9 R
 - (b) – 795.9 R
 - (c) – 690.9 R
 - (d) – 395.9 R
 - (ii) Expansion is carried out irreversibly.
 - (a) – 370 R
 - (b) – 770 R
 - (c) – 270 R
 - (d) – 570 R
25. One mole of a non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm.
- (i) Find the final temperature if expansion is carried out reversibly.
 - (a) 140 K
 - (b) 150 K
 - (c) 160 K
 - (d) 120 K
 - (ii) Calculate work done if expansion is carried out irreversibly.
 - (a) – 220.93 R
 - (b) – 360.93 R
 - (c) – 450.93 R
 - (d) – 210.93 R
26. A gas expands adiabatically & reversibly such that $T \propto V^{-1/2}$.

The value of γ ($C_{p,m}/C_{v,m}$) of the gas will be

- (a) 1.30
- (b) 1.50
- (c) 1.70
- (d) 2

MULTIPLE CORRECT ANSWER TYPE

27. Assume ideal gas behavior for all the gases considered and neglect vibrational degree of freedom. Separate equimolar samples of Ne, O₂, CO₂ and SO₂ were subjected to a twostep process as mentioned. Initially all are at same state of temperature and pressure.

Step I → All undergo reversible adiabatic expansion to attain same final volume, which is double the original volume thereby causing the decreases in their temperature.

Step → After step I all are given appropriate amount of heat isochorically to restore the original temperature.

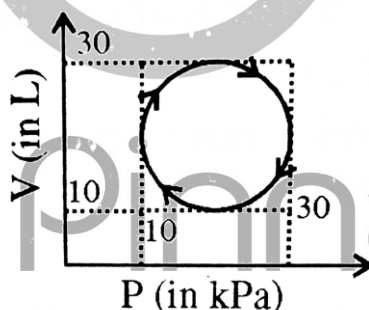
Mark the correct option (s):

- (a) Due to step I only, the decrease in temperature will be maximum for Ne
- (b) During step II, heat given will be minimum for SO₂
- (c) There will be no change in internal energy for any of the gas after both the steps of process are completed
- (d) The P – V graph of O₂ and CO₂ will be same

CYCLIC PROCESS & POLYTROPIC PROCESS

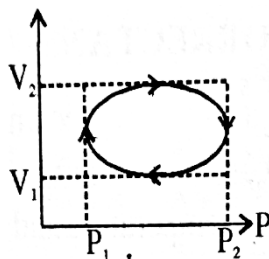
Section – E

1. Heat absorbed by a system in going through a cyclic process shown in figure is



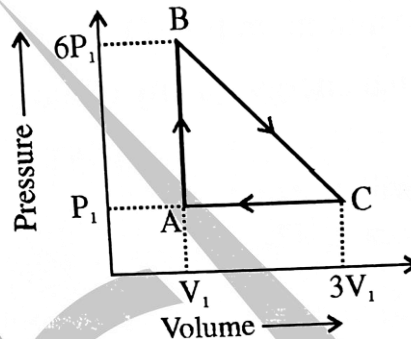
- (a) $10^7 \pi \text{ J}$
- (b) $10^6 \pi \text{ J}$
- (c) $10^2 \pi \text{ J}$
- (d) $10^4 \pi \text{ J}$

2. In the cyclic process shown in P – V diagram, the magnitude of the work done is

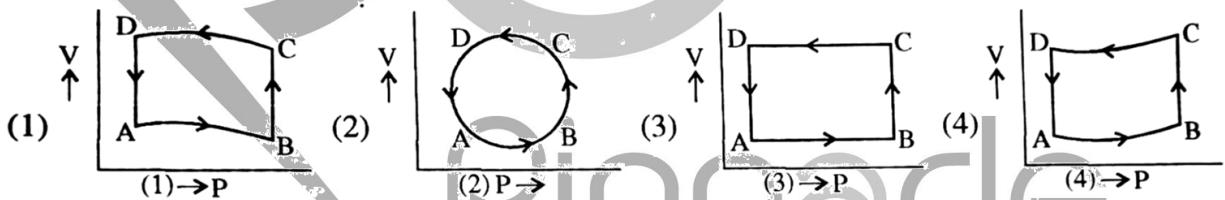


- (a) $\pi \left(\frac{P_2 - P_1}{2} \right)^2$
 (b) $\pi \left(\frac{V_2 - V_1}{2} \right)^2$
 (c) $\frac{\pi}{4} (P_2 - P_1)(V_2 - V_1)$
 (d) $\pi (V_2 - V_1)^2$

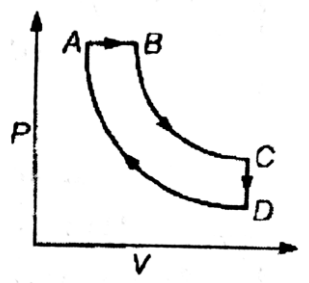
3. An ideal gas is taken around the cycle ABCA as shown in P – V diagram. The net work done during the cycle is equal to

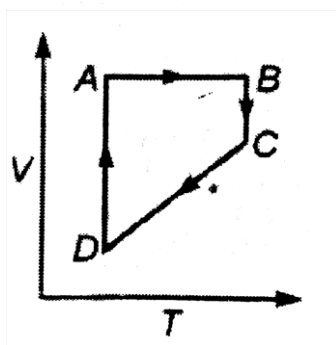


- (a) $12 P_1 V_1$
 (b) $6 P_1 V_1$
 (c) $5 P_1 V_1$
 (d) $P_1 V_1$
4. In diagram (1 to 4), variation of volume with changing pressure is shown. A gas is taken along the path ABCDA. The change in internal energy of the gas will be

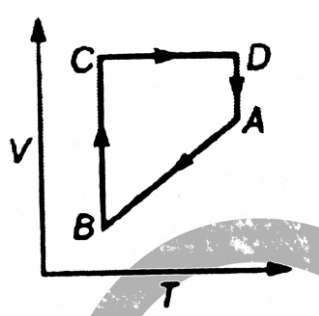


- (a) Positive in all the cases (1) to (4)
 (b) Positive in cases (1), (2), (3) but zero in case (4)
 (c) Negative in cases (1), (2), (3) but zero in case (4)
 (d) Zero in all the cases
5. A cyclic process ABCD is shown in P – V diagram for an ideal gas. Which of the following diagram represents the same process?

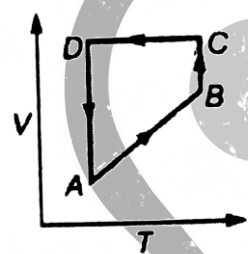




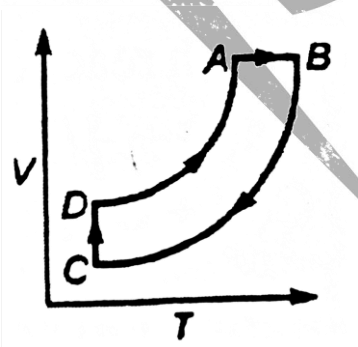
(a)



(b)



(c)



(d)

6. For 1 mole of ideal monoatomic gas if $\frac{P}{V^2} = \text{constant}$ and initial temperature is 100 K. If gas is expanded from 1 L to 2 L then:

(Assume $R = 0.0821 \frac{\text{L-atm}}{\text{mole-K}}$, $1 \text{ L-atm} = 24 \text{ cal}$)

(i) Heat capacity (in cal) is

- (a) $\frac{11}{3}$
(b) $\frac{11}{6}$
(c) $\frac{22}{3}$
(d) $\frac{44}{3}$

- (ii) The total heat absorbed (in cal) is
- 1966.66
 - 2566.66
 - 566.66
 - 4566.66
- (iii) Approximate value of work done (in cal) is
- 460
 - 650
 - 378
 - 540
7. $\frac{1}{22.4}$ mol of an ideal monatomic gas undergoes a reversible process for which $PV^2 = C$. The gas is expanded from initial volume of 1 L to final volume of 2 L starting from initial temperature of 273 K. Find the heat exchanged during the process (in L atm).
- $$R = \frac{22.4}{273} \text{ L atm mole}^{-1}\text{K}^{-1}$$
- 0.50
 - 0.75
 - 0.10
 - 0.25

SLOT
SINGLE CORRECT ANSWER TYPE
Section – F

- ΔS for the reaction; $\text{MgCO}_3 (\text{s}) \rightarrow \text{MgO} (\text{s}) + \text{CO}_2 (\text{g})$ will be:
 - 0
 - ve
 - + ve
 - ∞
- Change in entropy is negative for:-
 - Bromine (ℓ) \rightarrow Bromine (g)
 - $\text{C} (\text{s}) + \text{H}_2 \text{O} (\text{g}) \rightarrow \text{CO} (\text{g}) + \text{H}_2 (\text{g})$
 - $\text{N}_2 (\text{g}, 1 \text{ atm}) \rightarrow \text{N}_2 (\text{g}, 0.1 \text{ atm})$
 - $\text{Fe} (\text{at } 400 \text{ K}) \rightarrow \text{Fe} (\text{at } 300 \text{ K})$
- For which reaction from the following, ΔS will be maximum?
 - $\text{Ca} (\text{s}) + 1/2 \text{O}_2 (\text{g}) \rightarrow \text{CaO} (\text{s})$
 - $\text{CaCO}_3 (\text{s}) \rightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$
 - $\text{C} (\text{s}) + \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g})$
 - $\text{N}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{NO} (\text{g})$
- In which reaction ΔS is positive
 - $\text{H}_2\text{O} (\ell) \rightarrow \text{H}_2\text{O} (\text{s})$
 - $3\text{O}_2 (\text{g}) \rightarrow 2\text{O}_3 (\text{g})$
 - $\text{H}_2\text{O} (\ell) \rightarrow \text{H}_2\text{O} (\text{g})$

- (d) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
5. When two gases are mixed the entropy:-
- Remains constant
 - Decreases
 - Increases
 - Becomes zero
6. Unit of molar entropy is:-
- $\text{JK}^{-1} \text{mol}^{-1}$
 - J mol^{-1}
 - $\text{J}^{-1} \text{K}^{-1} \text{mol}^{-1}$
 - JK mol^{-1}
7. When you make ice cubes, the entropy of water
- Does not change
 - Increases
 - Decreases
 - May either increase or decrease depending on the process used
8. When two mole of an ideal gas $\left(C_{p,m} \frac{5}{2}R\right)$ heated from 300 K to 600 K at constant pressure. The change in entropy of gas (ΔS) is
- $\frac{3}{2}R \ln 2$
 - $-\frac{3}{2}R \ln 2$
 - $5R \ln 2$
 - $\frac{5}{2}R \ln 2$
9. The entropy change for a phase transformation is:
- $\frac{\Delta U}{\gamma + dT}$
 - $\frac{\Delta T}{\Delta H}$
 - $\frac{\Delta H}{T}$
 - $\frac{\Delta H + \Delta G}{T}$
10. What is the melting point of benzene if $\Delta H_{\text{fusion}} = 9.95 \text{ kJ/mol}$ and $\Delta S_{\text{fusion}} = 35.7 \text{ J/K - mol}$?
- 278.7°C
 - 278.7 K
 - 300 K
 - 298 K
11. When one mole of an ideal gas is compressed to half of its initial volume and simultaneously heated to twice its initial temperature, the change in entropy of gas (ΔS) is:
- $C_{p,m} \ln 2$
 - $C_{v,m} \ln 2$
 - $R \ln 2$
 - $(C_{v,m} - R) \ln 2$
12. What is the change in entropy when 2.5 mole of water is heated from 27°C to 87°C ?

- (a) 16.6 J/K
 (b) 9 J/K
 (c) 34.02 J/K
 (d) 1.89 J/K
13. The entropy of vaporization of benzene is $85 \text{ JK}^{-1} \text{ mol}^{-1}$. When 117 g benzene vaporize at its normal boiling point, the entropy change of surrounding is:
 (a) -85 JK^{-1}
 (b) $-85 \times 1.5 \text{ JK}^{-1}$
 (c) $85 \times 1.5 \text{ JK}^{-1}$
 (d) None of these
14. One mole of an ideal gas expands isothermally and reversibly at 25°C from a volume of 10 litres to a volume of 20 litres.
 (i) What is the change in entropy of the gas?
 (a) 2.76 J/K.
 (b) 3.76 J/K.
 (c) 4.76 J/K.
 (d) 5.76 J/K.
 (ii) How much work is done by the gas?
 (a) 1851 J.
 (b) 1718 J.
 (c) 2.78 J.
 (d) 1518 J.
 (iii) What is q ?
 (a) 1318 J.
 (b) 1418 J.
 (c) 1718 J.
 (d) 1518 J.
 (iv) What is the change in the entropy of the surroundings?
 (a) -7.76 J/K
 (b) -5.76 J/K
 (c) -3.76 J/K
 (d) -2.76 J/K

GIBB'S FREE ENERGY

SINGLE CORRECT ANSWER TYPE

Section – G

- Identify the correct statement regarding entropy
 - At absolute zero temperature, the entropy of perfectly crystalline substances is +ve
 - At absolute zero temperature entropy of perfectly crystalline substance is taken to be zero
 - At 0°C the entropy of a perfectly crystalline substance is taken to be zero
 - At absolute zero temperature, the entropy of all crystalline substances is taken to be zero
- For a process to be spontaneous at constant T and P:

- (a) $(\Delta G)_{\text{system}}$, must be negative
 - (b) $(\Delta G)_{\text{system}}$, must be positive
 - (c) $(\Delta S)_{\text{system}}$, must be positive
 - (d) $(\Delta S)_{\text{system}}$, must be negative
3. For a reaction to occur spontaneously –
- (a) ΔG must be negative
 - (b) $(\Delta H - T\Delta S)$ must be negative
 - (c) $(\Delta H + T\Delta S)$ must be negative
 - (d) ΔH must be negative
4. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?
- (a) Endothermic and decreasing disorder
 - (b) Exothermic and increasing disorder
 - (c) Endothermic and increasing disorder
 - (d) Exothermic and decreasing disorder
5. What is the sign of ΔG for the process of ice melting at 283 K?
- (a) $\Delta G > 0$
 - (b) $\Delta G = 0$
 - (c) $\Delta G < 0$
 - (d) None of these
6. Which of the following reaction is expected never to be spontaneous:-
- (a) $2\text{O}_3 \rightarrow 3\text{O}_2$ $\Delta H = -\text{ve}, \Delta S = +\text{ve}$
 - (b) $\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$ $\Delta H = -\text{ve}, \Delta S = -\text{ve}$
 - (c) $\text{Br}_2(\ell) \rightarrow \text{Br}_2(\text{g})$ $\Delta H = +\text{ve}, \Delta S = +\text{ve}$
 - (d) $2\text{Ag} + 3\text{N}_2 \rightarrow 2\text{AgN}_3$ $\Delta H = +\text{ve}, \Delta S = -\text{ve}$
7. Which of the following is true for the reaction $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ at 100°C and 1 atmosphere
- (a) $\Delta S = 0$
 - (b) $\Delta H = 0$
 - (c) $\Delta H = \Delta U$
 - (d) $\Delta H = T\Delta S$
8. For a perfectly crystalline solid $C_{p,m} = aT^3$, where a is constant. If $C_{p,m}$ is $0.42 \text{ J/K} - \text{mol}$ at 10 K , molar entropy at 20 K is:
- (a) 0.42 J/K mol
 - (b) 0.14 J/K mol
 - (c) 1.12 J/K mol
 - (d) zero
9. Consider the following spontaneous reaction $3\text{X}_2(\text{g}) \rightarrow 2\text{X}_3(\text{g})$. What are the sign of ΔH , ΔS and ΔG for the reaction?
- (a) $+\text{ve}, +\text{ve}, +\text{ve}$
 - (b) $+\text{ve}, -\text{ve}, -\text{ve}$
 - (c) $-\text{ve}, +\text{ve}, -\text{ve}$
 - (d) $-\text{ve}, -\text{ve}, -\text{ve}$

10. For the reaction $2\text{H (g)} \rightarrow \text{H}_2 \text{ (g)}$, the sign of ΔH and ΔS respectively are:
- +, -
 - +, +
 - , +
 - , -
11. For a reaction to occur spontaneously:
- ΔS must be negative
 - $(-\Delta H + T \Delta S)$ must be positive
 - $\Delta H + T \Delta S$ must be negative
 - ΔH must be negative
12. The free energy change $\Delta G = 0$, when
- The system is at equilibrium
 - Catalyst is added
 - Reactants are initially mixed thoroughly
 - The reactants are completely consumed
13. Suppose that a reaction has $\Delta H = -40 \text{ kJ}$ and $\Delta S = -50 \text{ J/K}$. At what temperature range will it change from spontaneous to non-spontaneous?
- 0.8 K to 1 K
 - 799 K to 800 K
 - 800 K to 801 K
 - 799 K to 801 K
14. 18 gm of ice is converted into water at 0°C and 1 atm. The entropies of $\text{H}_2\text{O (s)}$ and $\text{H}_2\text{O (l)}$ are 38.2 and 60 J/mol - K respectively. The enthalpy change for this conversion is
- 5951.4 J/mol
 - 595.14 J/mol
 - 5951.4 J/mol
 - None of these
15. At what temperature, will the following process would not be spontaneous?
- $\text{A (g)} \rightarrow \text{A (l)}$
 $\Delta H = -20 \text{ kJ}$ $\Delta S = -50 \text{ J/K}$
- > 200 K
 - > 300 K
 - 350 K
 - > 400 K
16. Calculate standard entropy change in the reaction
- $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow 2 \text{Fe (s)} + 3\text{H}_2\text{O(l)}$
- Given: $S_m^\circ(\text{Fe}_2\text{O}_3, \text{S}) = 87.4$ $S_m^\circ(\text{Fe, S}) = 27.3$
 $S_m^\circ(\text{H}_2, \text{g}) = 130.7$, $S_m^\circ(\text{H}_2\text{O, l}) = 69.9 \text{ JK}^{-1}\text{mol}^{-1}$
- 212.5 $\text{JK}^{-1} \text{mol}^{-1}$
 - 215.2 $\text{JK}^{-1} \text{mol}^{-1}$
 - 120.9 $\text{JK}^{-1} \text{mol}^{-1}$
 - None of these

17. Calculate ΔG° (kJ/mol) at 127°C for a reaction with $K_{\text{equilibrium}} = 10^5$:

- (a) -38.294
- (b) -16.628
- (c) -9.16
- (d) None of these

18. When reaction is carried out at standard states then at the equilibrium:

- (a) $\Delta H^\circ = 0$
- (b) $\Delta S^\circ = 0$
- (c) Equilibrium constant $K = 0$
- (d) Equilibrium constant $K = 1$

MISCELLANEOUS

SINGLE CORRECT ANSWER TYPE

Section – H

1. For the auto-ionization of water at 25°C , $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$ equilibrium constant is 10^{-14} . What is ΔG° for the process?
 - (a) $\simeq 8 \times 10^4 \text{ J}$
 - (b) $\simeq 3.5 \times 10^4 \text{ J}$
 - (c) $\simeq 10^4 \text{ J}$
 - (d) None of these
2. Read following statement (s) carefully and select the right option:
 - (I) The enthalpy of solution of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in a large volume of water is endothermic to the extent of 3.5 kcal/mol . If $\Delta H = -23.2 \text{ kcal mol}^{-1}$ for the reaction,

$$\text{CaCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$$
 Then heat of solution of CaCl_2 (anhydrous) in a large volume of water is -19.7 kcal/mol
 - (II) For the reaction $2\text{Cl}(\text{g}) \rightarrow \text{Cl}_2(\text{g})$; the sign of ΔH and ΔS are negative,
 - (a) Statement I and II both are wrong
 - (b) Both are correct
 - (c) Only I is correct
 - (d) Only II is correct
3. The internal energy of the fluid is $U = 34 + 3PV$ (S.I. units). Find ΔU for change in state from $(100 \text{ Pa}, 3\text{m}^3)$ to $(400 \text{ Pa}, 6\text{m}^3)$
 - (a) 6300
 - (b) 5300
 - (c) 7300
 - (d) 8300
4. One mole of non-linear triatomic ideal gas is compressed adiabatically at 300 K from 1 atm to 16 atm . Calculate work done under the following conditions.
 - (I) Compression is carried out reversibly.
 - (a) 500 R
 - (b) 600 R
 - (c) 900 R

- (d) 800 R
- (II) Compression is carried out irreversibly.
- (a) 3370 R
(b) 2525 R
(c) 3058 R
(d) 3375 R
5. Calculate change in internal energy for Vander Waal gas under going from state – I (300 K, $2 \times 10^{-2} \text{ m}^3$) to state – II (400 K, $4 \times 10^{-2} \text{ m}^3$) for one mol. of vanderwaal gas.

Given:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

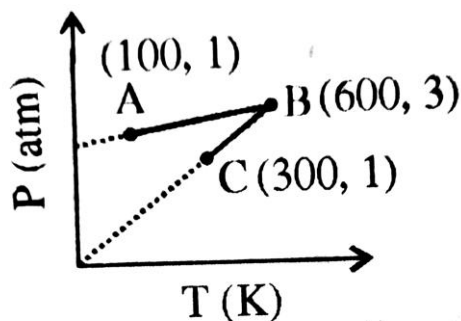
$$C_V = 12 \text{ J/Kmol}$$

$$a = 2 \text{ J} \cdot \text{m}^3/\text{mol}^2$$

- (a) 1250
(b) 1350
(c) 1450
(d) 1550

MULTIPLE CORRECT ANSWER TYPE

6. Assume ideal gas behavior for all the gases considered & vibrational degrees of freedom to be active. Separate equimolar sample of Ne, SO_2 & CH_4 were subjected to a two-step process as mentioned. Initially all are at same state of temperature & pressure.
- Step – I** → All undergo reversible adiabatic expansion to attain same final volume, which is double the original volume thereby causing the decreases in their temperature.
- Step – II** → After step I all are given appropriate amount of heat isochorically to restore the original temperature.
- Mark the correct option (s)
- (a) Due to step I only, the decrease in temperature will be maximum for Ne.
(b) During step II, heat given will be minimum for CH_4
(c) There will be no net change in internal energy for any of the gas after both the steps of process are completed.
(d) The P – V graph of CH_4 & SO_2 will be same for overall process.
7. One mole of an ideal gas is subjected to a two step



- reversible process (A – B and B – C). The pressure at A and C is same. Mark the correct statement (s):
- Work involved in the path AB is zero
 - In the path AB work will be done on the gas by the surrounding
 - Volume of gas at C = 3 × volume of gas at A
 - Volume of gas at B is 16.42 litres
8. The value of $\Delta H_{\text{transition}}$ of C (graphite) \rightarrow C (diamond) is 1.9 kJ/mol at 25°C entropy of graphite is higher than entropy of diamond. This implies that:
- C (diamond) is more thermodynamically stable than C (graphite) at 25°C
 - C (graphite) is more thermodynamically stable than C (diamond) at 25°C
 - Diamond will provide more heat on complete combustion at 25°C
 - $\Delta G_{\text{transition}}$ of C (diamond) \rightarrow C (graphite) is – ve
9. Which of the following statement (s) is/are true?
- $\Delta E = 0$ for combustion of C_2H_6 (g) in a sealed rigid adiabatic container
 - $\Delta_f H^\circ$ (S, monoclinic) $\neq 0$
 - If dissociation energy of CH_4 (g) is 1656 kJ/mol and C_2H_6 (g) is 2812 kJ/mol, then value of C – C bond energy will be 328 kJ/mol
 - If ΔH_f (H_2O , g) = - 242 kJ/mol; ΔH_{vap} (H_2O , l) = 44 kJ/mol then, $\Delta_f H^\circ$ (OH^- , aq.) will be 142 kJ/mol
10. Which of the following statement is/are correct as per IUPAC sign convention?
- The work done by the system on the surrounding is negative
 - The work done by the surrounding on the system is positive
 - The heat absorbed by the system from the surrounding is positive
 - The heat absorbed by the surrounding from the system is positive
11. Calculate the entropy change (J/mol K) of the given reaction. The molar entropies [J/K – mol] are given in brackets after each substance.
- $$2\text{PbS (s)} [91.2] + 3\text{O}_2 \text{ (g)} [205.1] \rightarrow 2\text{PbO (s)} [66.5] + 2\text{SO}_2 \text{ (g)} [248.2]$$
- 113.5
 - 168.3
 - + 72.5
 - 149.2
12. Consider the following reaction at temperature T:
- $$\text{CH}_2 = \text{CH}_2 \text{ (g)} + \text{Cl}_2 \text{ (g)} \rightarrow \text{ClCH}_2\text{CH}_2\text{Cl (g)}$$
- $$\Delta_r H^\circ = - 217.5 \text{ kJ/mol}, \Delta_r S^\circ = - 233.9 \text{ J/K – mol}$$
- Reaction is supported by:
- Entropy
 - Enthalpy
 - Both (a) & (b)
 - Neither
13. Using the listed [ΔG°_f values] calculate ΔG° for the reaction
- $$3\text{H}_2\text{S (g)} [- 33.6] + 2\text{HNO}_3 \text{ (l)} [- 80.6] \rightarrow 2\text{NO (g)} [+86.6] + 4\text{H}_2\text{O (l)} [- 237.1] + 3\text{S (s)} [0]$$
- 513.0
 - 1037.0
 - + 433.4

(d) + 225.0

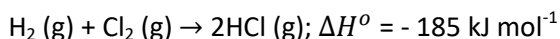
PROBLEMS RELATED WITH ΔU & ΔH SINGLE CORRECT ANSWER TYPE

Section – I

- Enthalpy change during a reaction does not depend upon:
 - Allotropic form of the element
 - Temperature
 - Physical state of reactants and products
 - Number of steps in the reaction
- ΔH for transition of carbon in the diamond form to carbon in the graphite form is -453.5 cal. This suggests that:
 - Graphite is chemically different from
 - Graphite is as stable as diamond
 - Graphite is more stable than diamond
 - Diamond is more stable than graphite
- The magnitude of heat of solution on addition of solvent to solution
 - Decreases
 - Increases
 - Remains constant
 - Increases or decreases
- For the reactions,
 - $H_2(g) + Cl_2(g) \rightarrow 2HCl(g) + xKJ$
 - $H_2(g) + Cl_2(g) \rightarrow 2HCl(l) + yKJ$
 Which one of the following statement is correct:
 - $x > y$
 - $x < y$
 - $x = y$
 - more data required
- 1150 kcal heat is released when following reaction is carried out at constant volume $27^\circ C$
 $C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(l)$
 Find the heat change at const. pressure:

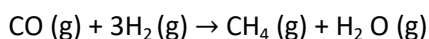
$$\Delta H = \Delta U + \Delta nRT$$
 - -1052.4 KCal
 - -1232.4 KCal
 - -1062.4 KCal
 - -1152.4 KCal
- For the reaction: $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$:
 - $\Delta H = \Delta E$
 - $\Delta H > \Delta E$
 - $\Delta H < \Delta E$
 - None of the above

7. Consider the reaction at 300 K

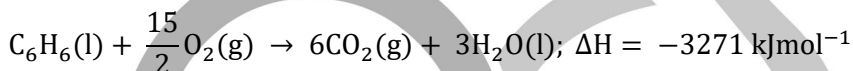


If 2 mole of H_2 completely react with 2 mole of Cl_2 to form HCl. What is ΔU° for this reaction?

- (a) 0
(b) -185 J
(c) 370 kJ
(d) None of these
8. Which of the indicated relationship is correct for the following exothermic reaction carried out at constant pressure?



- (a) $\Delta E = \Delta H$
(b) $\Delta E > \Delta H$
(c) $w < 0$
(d) $q > 0$
9. consider the reaction at 300 K



What is ΔU for the combustion of 1.5 mole of benzene at 27°C ?

- (a) -3267.25 kJ
(b) -4900.88 kJ
(c) -4906.5 kJ
(d) -3274.75 kJ
10. At 5×10^5 bar pressure density of diamond and graphite are 3 g/cc and 2 g/cc respectively, at certain temperature ' T '. find the value of $\Delta U - \Delta H$ for the conversion of 1 mole of graphite to 1 mole of diamond at temperature ' T ':
- (a) 100 kJ/mol
(b) 50 kJ/mol
(c) -100 kJ/mol
(d) None of these

ENTHALPY OF FORMATION & COMBUSTION

SINGLE CORRECT ANSWER TYPE

Section – J

1. Which of the following value of ΔH_f° represent 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) $+64.8 \text{ kcal mol}^{-1}$
2. Given
- $\text{C}(\text{diamond}) \text{O}_2 \rightarrow \text{CO}_2; \Delta H = -395 \text{ kJmol}^{-1}$
 $\text{C}(\text{graphite}) \text{O}_2 \rightarrow \text{CO}_2; \Delta H = -393 \text{ kJmol}^{-1}$

The enthalpy of formation of diamond from graphite is

- + 2.0 kJ
 - 1.5 kJ
 - 788 kJ
 - 788 kJ
3. Which of the following equations represents a reaction that provides the enthalpy of formation of CH_3Cl ?
- $\text{C (s)} + \text{HCl (g)} + \text{H}_2 \text{ (g)} \rightarrow \text{CH}_3\text{Cl (g)}$
 - $\text{C (s)} + 3\text{H (g)} + \text{Cl (g)} \rightarrow \text{CH}_3\text{Cl (g)}$
 - $\text{C (s)} + 3/2 \text{ H}_2 \text{ (g)} + 1/2 \text{ Cl}_2 \text{ (g)} \rightarrow \text{CH}_3\text{Cl (g)}$
 - $\text{CH}_4 \text{ (g)} + \text{Cl}_2 \text{ (g)} \rightarrow \text{CH}_3\text{Cl (g)} + \text{HCl (g)}$
4. Use the given standard enthalpies of formation (in kJ/mol) to determine the enthalpy of reaction of the following reaction:
- $$\text{NH}_3 \text{ (g)} + 3 \text{ F}_2 \text{ (g)} \rightarrow \text{NF}_3 \text{ (g)} + 3\text{HF (g)}$$
- $\Delta H_f^\circ (\text{NH}_3, \text{g}) = -46.2 \text{ kJ mol}^{-1}$; $\Delta H_f^\circ (\text{NF}_3, \text{g}) = -113.0 \text{ kJ mol}^{-1}$
 $\Delta H_f^\circ (\text{HF, g}) = -269.0 \text{ kJ mol}^{-1}$
- 335.8 kJ/mol
 - 873.8 kJ/mol
 - 697.2 kJ/mol
 - 890.4 kJ/mol
5. The standard enthalpy of formation of octane (C_8H_{18}) is - 250 kJ/mol. Calculate the enthalpy of combustion of C_8H_{18} . The enthalpy of formation of $\text{CO}_2 \text{ (g)}$ and $\text{H}_2 \text{O (l)}$ are - 394 kJ/mol and - 286 kJ/mol respectively:
- 5200 kJ/mol
 - 5726 kJ/mol
 - 5476 kJ/mol
 - 5310 kJ/mol
6. Determine the enthalpy of formation of $\text{B}_2\text{H}_6 \text{ (g)}$ in kJ/mol of the following reaction:
- $$\text{B}_2\text{H}_6 \text{ (g)} + 3\text{O}_2 \text{ (g)} \rightarrow \text{B}_2\text{O}_3 \text{ (s)} + 3\text{H}_2\text{O (g)}$$
- Given: $\Delta_r H^\circ = -1941 \text{ kJ/mol}$; $\Delta H_f^\circ (\text{B}_2\text{O}_3, \text{s}) = -1273 \text{ kJ/mol}$;
 $\Delta H_f^\circ (\text{H}_2\text{O, g}) = -241.8 \text{ kJ/mol}$
- 75.6
 - + 75.6
 - 57.4
 - 28.4
7. Consider the following reactions:
- $$\text{C (s)} + \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)} + x \text{ kJ}$$
- $$\text{C (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow \text{CO (g)} + y \text{ kJ}$$
- The heat of formation of CO (g) is:
- (x + y) kJ/mol
 - (x - y) kJ/mol
 - (y - x) kJ/mol
 - None of these

8. What amount of energy (kJ) is released in the combustion of 5.8 g of C_4H_{10} (g)?
 $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$; $\Delta H^\circ = -756 \text{ kJ mol}^{-1}$
 (a) 575.6
 (b) 37.8
 (c) 182
 (d) 57.56
9. Calculate heat of the following reaction at constant pressure,
 $F_2O(g) + H_2O(g) \rightarrow O_2(g) + 2HF(g)$
 The heats of formation of $F_2O(g)$, $H_2O(g)$ and $HF(g)$ are $5.5 \text{ kcal mol}^{-1}$, $-57 \text{ kcal mol}^{-1}$ and $-64 \text{ kcal mol}^{-1}$ respectively.
 (a) $-76.5 \text{ kcal mol}^{-1}$
 (b) $-78.5 \text{ kcal mol}^{-1}$
 (c) $-86.5 \text{ kcal mol}^{-1}$
 (d) $-77.9 \text{ kcal mol}^{-1}$
10. Calculate the enthalpy change of the following reaction
 $3C_2H_2(g) \rightarrow C_6H_6(g)$
 Given Enthalpy of combustion of $C_2H_2(g) = -1.30 \text{ KJ mol}^{-1}$ and that of $C_6H_6(g) = -3.30 \text{ KJ mol}^{-1}$
 (a) -0.60 KJ/mol
 (b) -0.70 KJ/mol
 (c) -0.80 KJ/mol
 (d) -0.90 KJ/mol
11. A gas mixture of 3.67 litres (at 1 atm) of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2 (at 1 atm). Find out the amount of heat evolved on burning this gas mixture. The heats of combustion of ethylene and methane are -1423 and -891 kJ mol^{-1} at 25°C .
 (a) 182.85 KJ
 (b) 186.85 KJ
 (c) 196.85 KJ
 (d) 166.80 KJ

BOND ENTHALPY

SINGLE CORRECT ANSWER TYPE

Section – K

1. The entropies of $H_2(g)$ and $H(g)$ are 130.6 and $114.6 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively at 298 K . Using the data given below calculate the bond energy of H_2 (in kJ/mol):
 $H_2(g) \rightarrow 2H(g)$; $\Delta G^\circ = 406.6 \text{ kJ mol}^{-1}$
 (a) 377.2
 (b) 436.0
 (c) 425.5
 (d) 430.5
2. The enthalpy change for the following reaction is 368 kJ . Calculate the average O – F bond energy.
 $OF_2(g) \rightarrow O(g) + 2F(g)$
 (a) 184 kJ/mol

- (b) 368 kJ/mol
 (c) 536 KJ/mol
 (d) 736 KJ/mol
3. The enthalpy change for the reaction, $C_2H_6(g) \rightarrow 2C(g) + 6H(g)$ is X kJ. The bond energy of C – H bond is
- (a) $\frac{X}{2}$
 (b) $\frac{X}{2}$
 (c) $\frac{X}{2}$
 (d) Data insufficient
4. Calculate P – Cl bond enthalpy
 Given $\Delta_f H^\circ (PCl_3, g) = 306 \text{ kJ/mol}$; $\Delta H_{atomization} (P, s) = 314 \text{ kJ/mol}$;
 $\Delta_f H^\circ (Cl, g) = 121 \text{ kJ/mol}$
- (a) 123.66 kJ/mol
 (b) 371 kJ/mol
 (c) 19 kJ/mol
 (d) None of these
5. Calculate the enthalpy for the following reaction using the given bond energies (kJ/mol)
 (C – H = 414; H – O = 463; H – Cl = 431, C – Cl = 326; C – O = 335)
 $CH_3 - OH(g) + HCl(g) \rightarrow CH_3 - Cl(g) + H_2O(g)$
- (a) – 23 kJ/mol
 (b) – 42 kJ/mol
 (c) – 59 kJ/mol
 (d) – 511 kJ/mol
6. Based on the values of B.E. given, $\Delta_f H^\circ$ of $N_2H_4(g)$ is:
 Given: N – N = 159 kJ mol⁻¹; H – H = 436 kJ mol⁻¹
 $N \equiv N = 941 \text{ kJ mol}^{-1}$; N – H = 398 kJ mol⁻¹
- (a) 711 kJ mol⁻¹
 (b) 62 kJ mol⁻¹
 (c) – 98 kJ mol⁻¹
 (d) – 711 kJ mol⁻¹
7. Find the bond enthalpy of S – S bond from the following data:
 $\Delta_f H^\circ$ of $C_2H_5 - S - C_2H_5(g) = -147.23 \text{ kJ mol}^{-1}$
 $\Delta_f H^\circ$ of $C_2H_5 - S - S - C_2H_5(g) = -201.92 \text{ kJ mol}^{-1}$
 $\Delta_f H^\circ$ of S (g) = 222.80 kJ mol⁻¹
- (a) 277.49 kJ mol⁻¹
 (b) 288.49 kJ mol⁻¹
 (c) 299.49 kJ mol⁻¹
 (d) 177.49 kJ mol⁻¹
8. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction
 $C_4H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
- Data:**

| Bond | Bond enthalpy |
|-----------------------------------|----------------------------|
| C – C | 336.81 kJmol ⁻¹ |
| C = C | 606.68 kJmol ⁻¹ |
| C – H | 410.87 kJmol ⁻¹ |
| H – H | 431.79 kJmol ⁻¹ |
| (a) – 120.08 kJ mol ⁻¹ | |
| (b) – 130.08 kJmol ⁻¹ | |
| (c) – 150.08 kJmol ⁻¹ | |
| (d) – 160.08 kJmol ⁻¹ | |

OTHER TYPE OF ENTHALPY REACTION SINGLE CORRECT ANSWER TYPE

Section – L

- Hess's law states that:
 - The standard enthalpy of an overall reaction is the sum of the enthalpy changes in individual reactions.
 - Enthalpy of formation of a compound is same as the enthalpy of decomposition of the compound into constituent elements, but with opposite sign.
 - At constant temperature the pressure of a gas is inversely proportional to its volume
 - The mass of a gas dissolved per litre of a solvent is proportional to the pressure of the gas in equilibrium with the solution
- An imaginary reaction $X \rightarrow Y$ takes place in three steps
 $X \rightarrow A, \Delta H = -q_1$; $B \rightarrow A, \Delta H = -q_2$; $B \rightarrow Y, \Delta H = -q_3$
 If Hess's law is applicable, then the heat of the reaction ($X \rightarrow Y$) is:
 - $q_1 - q_2 + q_3$
 - $q_2 - q_3 - q_1$
 - $q_1 - q_2 - q_3$
 - $q_3 - q_2 - q_1$
- The enthalpy change for a reaction does not depend upon:
 - The physical states of reactants and products
 - Use of different reactants for the same product
 - The number of intermediate reaction steps
 - The differences in initial or final temperatures of involved substances
- Calculate the standard enthalpy of reaction for the following reaction using the listed enthalpies of reaction:
 $3\text{Co(s)} + 2\text{O}_2\text{(g)} \rightarrow \text{Co}_3\text{O}_4\text{(s)}$
 $2\text{Co(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CoO(s)}; \Delta H_1^0 = -475.8 \text{ kJ mol}^{-1}$
 $6\text{CoO(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Co}_3\text{O}_4\text{(s)}; \Delta H_2^0 = 355.0 \text{ kJmol}^{-1}$
 - 891.2 kJ
 - 120.8 kJ
 - + 891.2 kJ
 - 830.8 kJ
- From given following equations and ΔH^0 values, determine the enthalpy of reaction at 298 K for the reaction:

- $\text{C}_2\text{H}_4(\text{g}) + 6\text{F}_2(\text{g}) \rightarrow 2\text{CF}_4(\text{g}) + 4\text{HF}(\text{g})$
 $\text{H}_2(\text{s}) + \text{F}_2(\text{g}) \rightarrow 2\text{HF}(\text{g}); \Delta H_1^0 = -537 \text{ kJ mol}^{-1}$
 $\text{C}(\text{s}) + 2\text{F}_2(\text{g}) \rightarrow \text{CF}_4(\text{g}); \Delta H_2^0 = -680 \text{ kJ mol}^{-1}$
 $2\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}); \Delta H_3^0 = 52 \text{ kJ mol}^{-1}$
 (a) -1165
 (b) -2486
 (c) +1165
 (d) +2486
6. If $\Delta_f H^0(\text{C}_2\text{H}_4)$ and $\Delta_f H^0(\text{C}_2\text{H}_6)$ are x_1 and $x_2 \text{ kcal mol}^{-1}$, the heat of hydrogenation of C_2H_4 is
 (a) $x_1 + x_2$
 (b) $x_1 - x_2$
 (c) $x_2 - x_1$
 (d) $x_1 + 2x_2$
7. Heat of combustion of ethanol at constant pressure and at temperature $T \text{ K}$ is found to be $-q \text{ J mol}^{-1}$. Hence, heat of combustion (in J mol^{-1}) of ethanol at the same temperature at constant volume will be:
 (a) $RT - q$
 (b) $-(q + RT)$
 (c) $q - RT$
 (d) $q + RT$
8. If the enthalpy of formation and enthalpy of solution of $\text{HCl}(\text{g})$ are -92.3 kJ mol and -75.14 kJ/mol respectively then find enthalpy of formation of $\text{Cl}^-(\text{aq})$:
 (a) -17.16 kJ/mol
 (b) -167.44 kJ/mol
 (c) 17.16 kJ/mol
 (d) None of these
9. At 25°C , 1 mole of MgSO_4 was dissolved in water, the heat evolved was found to be 91.2 kJ . One mole of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ on dissolution gives a solution of the same composition accompanied by an absorption of 13.8 kJ . The enthalpy of hydration, i.e., ΔH for the reaction $\text{MgSO}_4(\text{s}) + 7\text{H}_2\text{O}(\text{l}) \rightarrow \text{MgSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$ is:
 (a) -105 kJ/mol
 (b) -77.4 kJ/mol
 (c) 105 kJ/mol
 (d) None of these
10. The magnitude of enthalpy change for neutralization of the reaction;
 $\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ (Given $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}); -57 \text{ kJ/mol}$) will be:
 (a) Less than 57 kJ mol^{-1}
 (b) -57 kJ mol^{-1}
 (c) Greater than 57 kJ mol^{-1}
 (d) 57 kJ mol^{-1}
11. Enthalpy of neutralization of HCl by NaOH is -57.1 kJ/mol and by NH_4OH is -51.1 kJ/mol . Calculate the enthalpy of dissociation of NH_4OH .
 (a) 6.0 kJ/mol

- (b) 7.0 kJ/mol
 (c) 8.0 kJ/mol
 (d) 9.0 kJ/mol
12. The enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ is $-285.83 \text{ kJ mol}^{-1}$ and enthalpy of neutralization of a strong acid and a strong base is $-55.84 \text{ kJ mol}^{-1}$. What is the enthalpy of formation of OH^- ions?
- (a) $-229.99 \text{ kJ mol}^{-1}$
 (b) $-339.99 \text{ kJ mol}^{-1}$
 (c) $-449.99 \text{ kJ mol}^{-1}$
 (d) $-338.99 \text{ kJ mol}^{-1}$
13. Calculate ΔH° for the reaction
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 at 25°C . Given $\Delta_f H^\circ(\text{Ag}^+, \text{aq}) = 105.58 \text{ kJ mol}^{-1}$, $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167.16 \text{ kJ mol}^{-1}$
 and $\Delta_f H^\circ(\text{AgCl}, \text{s}) = -127.07 \text{ kJ mol}^{-1}$
- (a) $-65.49 \text{ kJ mol}^{-1}$
 (b) $-60.49 \text{ kJ mol}^{-1}$
 (c) $-50.49 \text{ kJ mol}^{-1}$
 (d) $-70.49 \text{ kJ mol}^{-1}$
14. Calculate the enthalpy change when one mole of $\text{HCl}(\text{g})$ is dissolved in a very large amount of water at 25°C .
 The change in state is $\text{HCl}(\text{g}) + \text{aq} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 Given: $\Delta_f H^\circ(\text{HCl}, \text{g}) = -92.31 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167.16 \text{ kJ mol}^{-1}$
- (a) $-74.85 \text{ kJ mol}^{-1}$
 (b) $-80.85 \text{ kJ mol}^{-1}$
 (c) $-70.85 \text{ kJ mol}^{-1}$
 (d) $-66.85 \text{ kJ mol}^{-1}$
15. Calculate the resonance energy of N_2O from the following data:
 $\Delta_f H^\circ$ of $\text{N}_2\text{O} = 82 \text{ kJ mol}^{-1}$. Bond energy of $\text{N} \equiv \text{N}$, $\text{N} = \text{N}$, $\text{O} = \text{O}$ & $\text{N} = \text{O}$ bonds is 946, 418, 498 & 607 kJ mol^{-1} respectively.
- (a) -88 kJ mol^{-1}
 (b) -78 kJ mol^{-1}
 (c) 98 kJ mol^{-1}
 (d) -108 kJ mol^{-1}
16. The standard molar enthalpies of formation of cyclohexane (l) & benzene (l) at 25°C are -156 & $+49 \text{ kJ mol}^{-1}$ respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25° is -119 kJ mol^{-1} . Use these data to estimate the magnitude of the resonance energy of benzene.
- (a) 200 kJ mol^{-1}
 (b) 152 kJ mol^{-1}
 (c) 100 kJ mol^{-1}
 (d) 211 kJ mol^{-1}
17. The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are -2839.2 , -2275.2 and $-5506 \text{ kJ mol}^{-1}$ respectively. Calculate the resonance energy of benzene. The bond enthalpy of $\text{C}-\text{H}$ bond is given as equal to $+410.87 \text{ kJ/mol}$.
- (a) -80.68 kJ/mol

- (b) -23.68 kJ/mol
 (c) -96.68 kJ/mol
 (d) -46.68 kJ/mol

18. Calculate the enthalpy of combustion of methyl alcohol at 298 K from the following data

| Bond | C – H | C – O | O – H | O = O | C = O |
|--|-------|-------|-------|-------|-------|
| Bond Enthalpy (kJ mol^{-1}) | 414 | 351.5 | 464.5 | 494 | 711 |

Resonance energy of $\text{CO}_2 = -143 \text{ kJ mol}^{-1}$

Latent heat of vaporization of methyl alcohol = 35.5 kJ mol^{-1} .

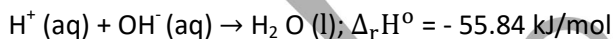
Latent heat of vaporization of water = 40.6 kJ mol^{-1} .

- (a) $-669.7 \text{ kJ mol}^{-1}$
 (b) $-329.7 \text{ kJ mol}^{-1}$
 (c) $-69.7 \text{ kJ mol}^{-1}$
 (d) $-889.7 \text{ kJ mol}^{-1}$
19. Set up a Born – Haber cycle to find the lattice energy of NaCl crystal. Given $\Delta H_f^\circ (\text{NaCl}) = -410 \text{ kJ mol}^{-1}$.
 Ionization enthalpy of Na = 495 kJ mol^{-1} , electron affinity of chlorine = 365 kJ mol^{-1} , sublimation enthalpy of Na = 315 kJ mol^{-1} and dissociation enthalpy of $\text{Cl}_2 (\text{g}) = 240 \text{ kJ mol}^{-1}$.
- (a) -975 kJ/mol
 (b) -860 kJ/mol
 (c) -750 kJ/mol
 (d) -675 kJ/mol

PARAGRAPH FOR QUESTION NO 20 TO 22

Enthalpy of neutralization is defined as the enthalpy change when 1 mole of acid/base is completely neutralized by base/acid in dilute solution.

For strong acid and strong base neutralization net chemical change is



$\Delta H_{\text{ionization}}^\circ$ of aqueous solution of strong acid and strong base is zero.

When a dilute solution of a weak acid or base is neutralized, the enthalpy of neutralization is somewhat less because of the absorption of heat in the ionization of the weak acid or base, for weak acid/base

$$\Delta H_{\text{neutralization}}^\circ = \Delta H_{\text{ionization}}^\circ + \Delta_r H^\circ (\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O})$$

20. If enthalpy of neutralization of CH_3COOH by NaOH is -49.86 kJ/mol then enthalpy of ionization of CH_3COOH is:
- (a) 5.98 kJ/mol
 (b) -5.98 kJ/mol
 (c) 105.7 kJ/mol
 (d) None of these
21. What is ΔH° for complete neutralization of strong diacidic base $\text{A}(\text{OH})_2$ by HNO_3 ?
- (a) -55.84 kJ
 (b) -111.68 kJ
 (c) 55.84 kJ
 (d) None of these

22. Under the same conditions how many mL of 0.1 M NaOH and 0.05 M H_2A (strong diprotic acid) solution should

be mixed for a total volume of 100 mL produce the highest rise in temperature:

- (a) 25 : 75
- (b) 50 : 50
- (c) 75 : 25
- (d) 66.66 : 33.33

CALORIMETRY

SINGLE CORRECT ANSWER TYPE

Section – M

- Stearic acid $[\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}]$ is a fatty acid, the part of fat that stores most of the energy. 1.0 g of stearic acid was burned in a bomb calorimeter. The bomb had a heat capacity of $652 \text{ J/}^\circ\text{C}$. If the temperature of 500 g water ($c = 4.18 \text{ J/g }^\circ\text{C}$) rose from 25.0 to 39.3 $^\circ\text{C}$, how much heat was released when the stearic acid was burned? [Given $C_p(\text{H}_2\text{O}) = 4.18 \text{ J/g }^\circ\text{C}$]
 - (a) 39.21 kJ
 - (b) 29.91 kJ
 - (c) 108 kJ
 - (d) 9.32 kJ
- Gasoline has an enthalpy of combustion 24000 kJ/gallon . When gasoline burns in an automobile engine, approximately 30% of the energy released is used to produce mechanical work. The remainder is lost as heat transfer to the engine's cooling system. As a start on estimating how much heat transfer is required, calculate what mass of water could be heated from 25°C to 75°C by the combustion of 1.0 gallon of gasoline in an automobile?
 - (a) 34.45 kg
 - (b) 80.383 kg
 - (c) 22 kg
 - (d) 224 kg
- A 0.05 L, sample of 0.2 M aqueous hydrochloric acid is added to 0.05 L of 0.2 M aqueous ammonia in a calorimeter. Heat capacity of entire calorimeter system is 480 J/K . The temperature increase is 1.09 K . Calculate $\Delta_r H^\circ$ in kJ/mol for the following reaction:
 $\text{HCl (aq.)} + \text{NH}_3 \text{ (aq.)} \rightarrow \text{NH}_4\text{Cl (aq.)}$
 - (a) -52.32
 - (b) -61.1
 - (c) -55.8
 - (d) -58.2
- A coffee cup calorimeter initially contains 125 g of water, at a temperature of 24.2°C . 8 g ammonium nitrate (NH_4NO_3), also at 24.2°C , is added to the water and the final temperature is 18.2°C . What is the heat of solution of ammonium nitrate in kJ/mol ? The specific capacity of the solution is $4.2 \text{ J/}^\circ\text{C g}$.
 - (a) 33.51 kJ/mol
 - (b) 39.5 kJ/mol
 - (c) 32.2 kJ/mol
 - (d) 37.3 kJ/mol
- Enthalpy of neutralization of HCl by NaOH is -55.84 kJ/mol and by NH_4OH is -51.34 kJ/mol . The enthalpy of

ionization of NH_4OH is:

- (a) 107.18 kJ/mol
- (b) 4.5 kJ/mol
- (c) -4.5 kJ/mol
- (d) None of these

EXERCISE – II (READY FOR CHALLENGES)

LEVEL-II

SINGLE CHOICE CORRECT

- The difference between heats of reaction at constant pressure and constant volume of the following reaction, would be

$$2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \quad \text{at } 25^\circ\text{C in kJ mol}^{-1} \text{ is}$$
 - (a) -7.43
 - (b) +3.72
 - (c) -3.72
 - (d) +7.43
- The product of combustion of an aliphatic thiol (RSH) at 298 K are
 - (a) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$ and $\text{SO}_2(\text{g})$
 - (b) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and $\text{SO}_2(\text{g})$
 - (c) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$ and $\text{SO}_2(\text{l})$
 - (d) $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and $\text{SO}_2(\text{l})$
- For the combustion reaction at 298 K

$$2\text{Ag}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow 2\text{Ag}_2\text{O}(\text{s})$$
 Which of the following relation will be true?
 - (a) $\Delta H = \Delta U$
 - (b) $\Delta H > \Delta U$
 - (c) $\Delta H < \Delta U$
 - (d) ΔH and ΔU bear no relation with each other
- For which of the following equations, will ΔH be equal to ΔU ?
 - (a) $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$
 - (b) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$
 - (c) $2\text{NO}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g})$
 - (d) $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{N}_2\text{O}_5(\text{g})$
- The bond enthalpies of H-H, Cl-Cl and H-Cl are 435, 243 and 431 kJ mol⁻¹, respectively. The enthalpy of formation of HCl(g) will be
 - (a) 92 kJ mol⁻¹
 - (b) -92 kJ mol⁻¹
 - (c) 247 kJ mol⁻¹
 - (d) 770 kJ mol⁻¹
- The molar enthalpies of combustion of $\text{C}_2\text{H}_2(\text{g})$, C(graphite) and $\text{H}_2(\text{g})$ are -1300, -394 and -286 kJ mol⁻¹, respectively. The standard enthalpy of formation of $\text{C}_2\text{H}_2(\text{g})$ would be
 - (a) -226 kJ mol⁻¹
 - (b) -626 kJ mol⁻¹
 - (c) 226 kJ mol⁻¹
 - (d) 626 kJ mol⁻¹
- The ΔH_f° for $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -393.5, -110.5 and -241.8 kJ mol⁻¹ respectively. The standard enthalpy change (in kJ mol⁻¹) for the reaction

$$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \quad \text{would be}$$

- (a) 524.1 (b) 41.2
(c) -262.5 (d) -41.2
8. Equal volumes of 1 M HCl and 1 M H₂SO₄ are neutralised completely by dil NaOH solution and x kcal and y kcal heat are liberated respectively. Which of the following relationship between x and y will be true?
 (a) $x = y$ (b) $x = \frac{y}{2}$
 (c) $x = 2y$ (d) $x = \frac{1}{2y}$
9. Heat capacity of H₂ at constant P and T is
 (a) 3 cal mol⁻¹ K⁻¹ (b) 5 cal mol⁻¹ K⁻¹
 (c) 7 cal mol⁻¹ K⁻¹ (d) ∞
10. The heats of neutralisation of four acids A, B, C, D are -13.7, -9.4, -11.2 and -12.4 kcal respectively when they are neutralised by a common base. The acidic character obeys the order
 (a) $A > B > C > D$ (b) $A > D > C > B$
 (c) $D > C > B > A$ (d) $D > B > C > A$
11. The dissociation energy of CH₄ and C₂H₆ are respectively 360 and 620 kcal/mol. The bond energy of C-C bond would be
 (a) 260 kcal/mol (b) 180 kcal/mol
 (c) 130 kcal/mol (d) 80 kcal/mol
12. A system is provided 50 J of heat and work done on the system is 10 J. The change in internal energy during the process is
 (a) 40 J (b) 60 J
 (c) 80 J (d) 50 J
13. The ΔG in the process of melting of ice at -15°C would be
 (a) ΔG is -ve (b) ΔG is +ve
 (c) $\Delta G = 0$ (d) All of these
14. Temperature of 1 mole of a gas is increased by 1° at constant pressure. The work done is
 (a) R (b) 2R
 (c) R/2 (d) 3R
15. Heat of neutralisation of NaOH and HCl is 57.46 kJ/equivalent. The heat of ionisation of water (kJ/mol) will be
 (a) -57.46 (b) +57.46
 (c) -114.92 (d) +114.92
16. On standard conditions ΔH and ΔS for a particular reaction are -1.17×10^3 J/mole and -105 J/mol K respectively. This reaction will be
 (a) exothermic and spontaneous. (b) exothermic and non-spontaneous.
 (c) spontaneous and reversible. (d) spontaneous and non-reversible.
17. At 0°C $\Delta_{\text{fus}}H^\circ = 6$ kJ mole⁻¹, change of entropy for freezing 1 mole ice will be
 (a) ∞ (b) 0

- (c) $21.98 \text{ J mole}^{-1} \text{ K}$ (d) 13.6 J
18. $\Delta_c H^\circ_{\text{C}_2\text{H}_6}$ and $\Delta_c H^\circ_{\text{C}_2\text{H}_2}$ are $-341.1 \text{ kcal mole}^{-1}$ and $-310.0 \text{ kcal mole}^{-1}$ respectively then
 (a) ethane is better welding gas having more magnitude of $\Delta_c H^\circ$.
 (b) ethyne is better welding gas having more value of $\Delta_c H^\circ$.
 (c) ethyne is better welding gas having more magnitude of $\Delta_c H^\circ/\text{unit weight}$.
 (d) ethane is better welding gas as here oxidation state of C is -3 .
19. For $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g}) + 44 \text{ kcal}$; $\Delta_r H^\circ$ and $\Delta_f H^\circ_{\text{HCl}(\text{g})}$ are
 (a) $-44 \text{ kcal mole}^{-1}$; $-22 \text{ kcal mole}^{-1}$ (b) $-44 \text{ kcal mole}^{-1}$; $-44 \text{ kcal mole}^{-1}$
 (c) $-22 \text{ kcal mole}^{-1}$; $-22 \text{ kcal mole}^{-1}$ (d) $-22 \text{ kcal mole}^{-1}$; $+22 \text{ kcal mole}^{-1}$
20. Heats of combustion of $\text{CH}_4(\text{g})$, $\text{C}_2\text{H}_4(\text{g})$ and $\text{C}_2\text{H}_6(\text{g})$ are -890 , -1411 and -1560 kJ/mole ; most favourable fuel gas combination will be as
 (a) $1 : 3 : 6$ (b) $3 : 1 : 6$
 (c) $6 : 3 : 1$ (d) $8 : 1 : 1$
21. On adding 0.5 L each of NaOH and HCl rise in temperature has found as 4°C , on adding 1 L of each rise in temperature must be
 (a) 1°C (b) 2°C
 (c) 3°C (d) 4°C
22. All spontaneous changes in the universe result into
 (a) increase in entropy of the system.
 (b) decrease in entropy of the system.
 (c) increase in entropy of the surroundings
 (d) increase in entropy of universe.
23. Universal gas constant 'R' can be defined as ; at constant pressure
 (a) mechanical work associated with 1 mole gas in order to increase temperature by 1°C .
 (b) mechanical work associated with 1 mole gas when expands by 1 L at 278 K .
 (c) mechanical work associated with 1 L gas at STP when it expands by 1 L .
 (d) mechanical work done by 1 mole gas when it expands by 22.4 L at STP.
24. $\text{C}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g})$; $\Delta_r H^\circ = -110 \text{ kJ}$
 $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$; $\Delta_r H^\circ = 132 \text{ kJ}$.
 Composition of steam and O_2 when it passed over coke keeping temperature 1273 K will be
 (a) $1 : 2$ (b) $5 : 3$
 (c) $4 : 5$ (d) $1 : 1$
25. For the reaction $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$; $\Delta H^\circ = -67650 \text{ cal}$ at 25°C . Calculate ΔH° at 100°C , given that the required molar heat capacities are as follows
 $C_p(\text{CO}, \text{g}) = 6.97 \text{ cal } ^\circ\text{C}^{-1}$
 $C_p(\text{CO}_2, \text{g}) = 8.97 \text{ cal } ^\circ\text{C}^{-1}$
 $C_p(\text{O}_2, \text{g}) = 7.00 \text{ cal } ^\circ\text{C}^{-1}$

- (a) -54.6 cal (b) -67650.4 cal
(c) -67684.4 cal (d) -67762.5 cal
26. An intensive property is that property which depends upon
(a) the nature of the substance
(b) the amount of the substance
(c) both the amount and nature of the substance
(d) neither the nature nor the amount of the substance
27. ΔH_f° of $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$, $\text{N}_2\text{O}(\text{g})$ and $\text{NO}_2(\text{g})$ in KJ/mol are respectively -393 , -110 , 81 and 34 . Calculate ΔH in KJ of the following reaction.
 $2\text{NO}_2(\text{g}) + 2\text{CO}(\text{g}) \longrightarrow \text{N}_2\text{O}(\text{g}) + 3\text{CO}_2(\text{g})$
(a) 836 (b) 1460
(c) -836 (d) -1460
28. Temperature of 1 mole of a gas is increased by 1° at constant pressure work done is
(a) R (b) $2R$
(c) $R/2$ (d) $3R$
29. Which of the following thermodynamic quantities is an outcome of the second law of thermodynamics?
(a) enthalpy (b) internal energy
(c) work (d) entropy
30. The difference between heats of reaction at constant pressure and constant volume for the reaction
 $2\text{C}_6\text{H}_6(\ell) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\ell)$ at 25°C in KJ mol^{-1} is
(a) -7.43 KJmol^{-1} (b) 7.43 KJmol^{-1}
(c) 2.477 KJmol^{-1} (d) $-2.477 \text{ KJmol}^{-1}$
31. For a reaction at equilibrium
(a) $\Delta G = \Delta G^\circ \neq 0$ (b) $\Delta G^\circ = 0$
(c) $\Delta G = \Delta G^\circ = 0$ (d) $\Delta G = 0, \Delta G^\circ \neq 0$
32. When 1 mole gas is heated at constant volume, temperature is raised from 298 to 309 K . Heat supplied to the gas is 500 J . Then which statement is correct?
(a) $q = w = 500 \text{ J}, \Delta u = 0$ (b) $q = \Delta u = 500 \text{ J}, w = 0$
(c) $q = w = 500 \text{ J}, \Delta u = 0$ (d) $\Delta u = 0, q = w = -500 \text{ J}$
33. In thermodynamics a process is called reversible when
(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
34. What is true for the reaction?
 $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
(a) $\Delta H = \Delta E$ (b) $\Delta H > \Delta E$
(c) $\Delta H < \Delta E$ (d) none

35. Calculate the work done when 1 mol of an ideal gas is compressed reversibly from 1.00 bar to 5.0 bar at a constant temperature of 300 K
- (a) -14.01 KJ (b) 16.02 KJ
 (c) 4.01 KJ (d) -8.02 KJ
36. The factor that does not influence the heat of reaction is
- (a) the physical state of reactants and products
 (b) the temperature
 (c) the pressure or volume
 (d) the method by which the final products are obtained
37. $(\Delta H - \Delta E)$ for the formation of NH_3 from N_2 and H_2 is
- (a) RT (b) $2RT$
 (c) $-RT$ (d) $-2RT$
38. $\text{A(l)} \rightleftharpoons \text{A(g)}$, $\Delta H_{\text{vap.}} = 460.6 \text{ cal/mol}$ boiling point = 50 K, what is boiling point at 10 atm?
- (a) 150 K (b) 75 K
 (c) 100 K (d) none
39. Heat of neutralization of $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) is -26 Kcal/mole. The dissociation energy of $\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons 2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$ is
- (a) 12.3 Kcal/mole (b) 1.4 Kcal/mole
 (c) -13.7 Kcal/mole (d) -1.4 Kcal/mole
40. The heats of combustion of yellow phosphorus and red phosphorous are -9.19 kJ and - 8.78 kJ respectively, then heat of transition of yellow phosphorus to red phosphorous is
- (a) - 18.69 kJ (b) +1.13 kJ
 (c) +18.69 kJ (d) 0.41 kJ
41. The enthalpies of formation of organic compounds are conveniently determined from their
- (a) boiling points (b) melting points
 (c) enthalpies of neutralization (d) enthalpies of combustion
42. Thermodynamic equilibrium involves
- (a) chemical equilibrium (b) thermal equation
 (c) mechanical equation (d) all the three
43. 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
44. The heat content of the system is called
- (a) internal energy (b) enthalpy
 (c) free energy (d) entropy

45. The apparatus used for measuring the heat changes of a reaction is called
- thermometer
 - a colorimeter
 - a calorimeter
 - none of these

The questions given below consist of statements 'Assertion' (A) and 'Reason' (R).

- If both 'A' and 'R' are correct and 'R' is correct reason for 'A'.
 - If both 'A' and 'R' are correct but 'R' is not the correct explanation for 'A'.
 - If 'A' is true but 'R' is false.
 - If both 'A' and 'R' are false.
46. (A) Enthalpy of graphite is lower than that of diamond.
(R) Entropy of graphites lower than that of diamond.
47. (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 & increase in volume.
48. (A) Molar entropy of vaporization of water is different form ethanol.
(R) Water is more polar than methanol
49. (A) A reaction which is spontaneous & accompanied by decrease of randomness must be exothermic.
(R) All exothermic reaction are accompanied by decrease of randomness.
50. (A) The enthalpy of formation of $\text{H}_2\text{O}(\ell)$ is greater than that of $\text{H}_2\text{O}(\text{g})$.
(R) Enthalpy change is negative for the condensation reaction.
 $\text{H}_2\text{O}(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell)$

LEVEL-II

SINGLE CHOICE CORRECT

- The standard enthalpies of formation at 300 K for $\text{CCl}_4(\text{l})$, $\text{H}_2\text{O}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{HCl}(\text{g})$ are -107 , -242 , -394 and -93 kJ mol^{-1} , respectively. The value of $\Delta U_{300\text{K}}$ for the following reaction, would be

$$\text{CCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 4\text{HCl}(\text{g})$$
 - -170 kJ mol^{-1}
 - -175 kJ mol^{-1}
 - $-182.5 \text{ kJ mol}^{-1}$
 - $-282.5 \text{ kJ mol}^{-1}$
- Which of the following option is true?
 If $\Delta H^\circ_{\text{ioniz}}(\text{HCN}) = 45.2 \text{ kJ mol}^{-1}$ and $\Delta H^\circ_{\text{ioniz}}(\text{CH}_3\text{COOH}) = 2.1 \text{ kJ mol}^{-1}$.
 - $\text{pK}_a(\text{HCN}) = \text{pK}_a(\text{CH}_3\text{COOH})$
 - $\text{pK}_a(\text{HCN}) > \text{pK}_a(\text{CH}_3\text{COOH})$
 - $\text{pK}_a(\text{HCN}) < \text{pK}_a(\text{CH}_3\text{COOH})$
 - $\text{pK}_a(\text{HCN}) = (45.17/2.07) \text{pK}_a(\text{CH}_3\text{COOH})$
- Which of the following expression is true?
 - $\Delta H^\circ_f(\text{CO}, \text{g}) = \frac{1}{2} \Delta H^\circ_f(\text{CO}_2, \text{g})$
 - $\Delta H^\circ_f(\text{CO}, \text{g}) = \Delta H^\circ_f(\text{C}, \text{graphite}) + \frac{1}{2} \Delta H^\circ_f(\text{O}_2, \text{g})$
 - $\Delta H^\circ_f(\text{CO}, \text{g}) = \Delta H^\circ_f(\text{CO}_2, \text{g}) - \frac{1}{2} \Delta H^\circ_f(\text{O}_2, \text{g})$

$$(d) \Delta H_f^\circ(\text{CO}, g) = \Delta H_f^\circ(\text{C, graphite}) + \Delta H_f^\circ(\text{CO}, g)$$

4. The enthalpy of combustion of $\text{H}_2(g)$ at 298 K to give $\text{H}_2\text{O}(g)$ is -249 kJ mol^{-1} and bond enthalpies of H-H and O=O are 433 kJ mol^{-1} and 492 kJ mol^{-1} , respectively. The bond enthalpy of O-H would be
 - (a) 464 kJ mol^{-1}
 - (b) -464 kJ mol^{-1}
 - (c) 232 kJ mol^{-1}
 - (d) -232 kJ mol^{-1}
5. For a monatomic gas, the value of the ratio of $C_{p,m}$ and $C_{v,m}$ is
 - (a) $5/3$
 - (b) $7/5$
 - (c) $9/7$
 - (d) $9/11$
6. In a flask colourless N_2O_4 is in equilibrium with brown coloured NO_2 . At equilibrium when the flask is heated at 100°C , the brown colour deepens and on cooling it becomes less coloured. The change in enthalpy, ΔH for this system will be
 - (a) Negative
 - (b) Positive
 - (c) Zero
 - (d) Undefined
7. In which case of mixing of a strong acid and a strong base each of 1N concentration, temperature increase will be highest
 - (a) 15 mL acid – 20 mL base
 - (b) 110 mL acid – 40 mL base
 - (c) 25 mL acid – 25 mL base
 - (d) 35 mL acid – 15 mL base
8. How many ml of 1M KOH and 0.5 M H_2SO_4 solutions, respectively when mixed for a total volume of 100 ml produce the highest rise in temperature?
 - (a) 67 : 33
 - (b) 33 : 67
 - (c) 40 : 60
 - (d) 50 : 50
9. If heat of neutralisation is -13.7 kcal and $\Delta_f H^\circ(\text{H}_2\text{O}) = -68 \text{ kcal}$ then enthalpy of OH^- would be
 - (a) 54.3 kcal
 - (b) -54.3 kcal
 - (c) 71.3 kcal
 - (d) -71.3 kcal
10. Which of the following statement will be true?
 - (a) $\left(\frac{\delta H}{\delta T}\right)_P - \left(\frac{\delta E}{\delta T}\right)_V = R$
 - (b) $\left(\frac{\delta H}{\delta T}\right)_P > \left(\frac{\delta E}{\delta T}\right)_V$
 - (c) $\left(\frac{\delta E}{\delta V}\right)_T$ for ideal gas is zero
 - (d) All of these
11. Latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is $10.0 \text{ kcal mol}^{-1}$. What will be the change in internal energy of 3 mole of liquid at same temperature?
 - (a) 13.0 kcal
 - (b) -13.0 kcal
 - (c) 27.0 kcal
 - (d) -27.0 kcal
12. 16 g oxygen gas expands at STP to occupy double of its original volume. The work done during the process will be
 - (a) 260 kcal
 - (b) 180 kcal
 - (c) 130 kcal
 - (d) 272.84 kcal
13. One mole of ice is converted into water at 273 K. The entropies of $\text{H}_2\text{O}(s)$ and $\text{H}_2\text{O}(l)$ are 38.20 and 60.01 J

$\text{mol}^{-1} \text{K}^{-1}$ respectively. The enthalpy change for the conversion will be

- (a) 59.54 J mol^{-1} (b) 5954 J mol^{-1}
(c) 595.4 J mol^{-1} (d) 320.6 J mol^{-1}

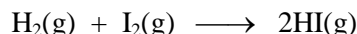
14. Which of the following represents $\Delta_f H^\circ_{\text{CO(g)}}$

- (a) $\text{C}_{(\text{diamond})} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g})$ (b) $\text{C}_{(\text{graphite})} + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g})$
(c) $\text{CO}_2(\text{g}) + \text{C}(\text{g}) \longrightarrow 2\text{CO}(\text{g})$ (d) $\text{C}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g})$

15. One mole non-ideal gas undergoes change of state (1 atm, 2 L, 90 K) \longrightarrow (2 atm, 3L, 300 K) with a change in internal energy 35 L atm. ΔH for the change will be

- (a) 35 L atm (b) 31 L atm
(c) 39 L atm (d) -31 L atm

16. Using $G_f^\circ(\text{HI}) = 1.3 \text{ kJ/mole}$, calculate the standard free energy change for the following reaction



- (a) 3.6 kJ/mole (b) 4.0 kJ/mole
(c) 2.6 kJ/mole (d) 1.5 kJ/mole

17. Heat capacity and molar heat capacity of "water $\xrightleftharpoons{0^\circ\text{C}}$ ice" system will be

- (a) ∞ , $40.6 \text{ kJ mol}^{-1} \text{K}$ (b) ∞ , 0
(c) 0, $40.6 \text{ kJ mol}^{-1} \text{K}$ (d) ∞ , ∞

18. For $\text{C}_3\text{H}_8(\text{g}) + \frac{9}{2}\text{O}_2(\text{g}) \longrightarrow 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$ at 298 K, the difference of heats of reaction at constant pressure and at constant volume is

- (a) 7.43 kJ (b) -6.194 kJ
(c) 6.194 kJ (d) -7.43 kJ

19. For $\text{X}_2\text{O}_4(\text{l}) \longrightarrow 2\text{XO}_2(\text{g})$

$\Delta U = 2.1 \text{ kcal}$, $\Delta S = 20 \text{ kcal/K}$ at 300 K. $\Delta_r G^\circ$ will be

- (a) 2.7 kcal (b) -2.7 kcal
(c) 4.081 kcal (d) -4.081 kcal

20. $\Delta_f H^\circ$ for products A, B, C and D are $-94 \text{ kcal mol}^{-1}$, $-231 \text{ kcal mol}^{-1}$, $21.4 \text{ kcal mol}^{-1}$ and $64.8 \text{ kcal mol}^{-1}$ respectively. Most stable product will be

- (a) A (b) B
(c) C (d) D

ONE OR MORE THAN ONE CHOICE CORRECT

1. Which of the following statement(s) is/are correct?

- (a) Absolute value of enthalpy cannot be determined.
(b) Absolute value of internal energy cannot be determined.
(c) Absolute value of entropy can be determined.
(d) Internal energy, enthalpy and entropy are intensive properties.

2. Which of the following are endothermic processes?

- (a) Combustion of glucose.
 (b) Decomposition of water.
 (c) Dehydrogenation of ethane to ethene.
 (d) Conversion of graphite to diamond.
3. For an ideal gas undergoing isothermal irreversible expansion
 (a) $\Delta U = 0$ (b) $\Delta H = 0$
 (c) $\Delta S = 0$ (d) $w = 0$
4. Under which of the conditions the process will be spontaneous?
 (a) $\Delta G = -ve$ (b) $\Delta S_{\text{Total}} = +ve$
 (c) $\Delta S_{\text{Total}} = -ve$ (d) $\Delta S_{\text{Total}} = 0$
5. The correct expressions for an adiabatic process are
 (a) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$ (b) $\frac{P_2}{P_1} = \left(\frac{T_1}{T_2}\right)^{\frac{\gamma-1}{\gamma}}$
 (c) $P_1 V_1^\gamma = P_2 V_2^\gamma$ (d) $P_1 V_1^{\gamma-1} = P_2 V_2^{\gamma-1}$
6. Which of the following are irreversible processes?
 (a) Mixing of two gases.
 (b) Evaporation of water at 373K and 1 atm in a closed system.
 (c) Dissolution of NaCl in water.
 (d) $H_2O(s)$ at $-4^\circ C$.
7. Which of the options given below are correct?
- | ΔH | ΔS | Nature of reaction |
|------------|------------|--|
| (a) $(-)$ | $(+)$ | Spontaneous at all temperatures |
| (b) $(+)$ | $(-)$ | Nonspontaneous regardless of temperature |
| (c) $(+)$ | $(+)$ | Spontaneous only at high temperature |
| (d) $(-)$ | $(-)$ | Spontaneous only at low temperature |
8. Which of the following affect the heat of reaction?
 (a) Physical states of reactants and products.
 (b) Allotropic forms of elements.
 (c) Temperature.
 (d) Reaction carried out at constant pressure or constant volume.
9. Which of the following type of energies are involved in Born Haber's cycle?
 (a) $\Delta H_{\text{sublimation}}$ (b) I.E.
 (c) Bond dissociation energy (d) Lattice energy
10. Which of the following are true about resonance energy?
 (a) Resonance energy = Experimental heat of formation – Calculated heat of formation.
 (b) Resonance energy = Calculated heat of formation – Experimental heat of formation.
 (c) Greater the resonance energy, more the compound will be stable.
 (d) Lesser the resonance energy, more the compound will be stable.

MATCH THE FOLLOWING

| Column I | Column II |
|---|--|
| I. The amount of energy which must be invested in a reaction to get it started. | (A) Chemical equilibrium |
| II. A state in which the rate of forward reaction is exactly equal to the rate of the reverse reaction | (B) Activation energy |
| III. A process or reaction which consumes heat. | (C) Endothermic |
| IV. A process or reaction that releases heat. | (D) Exothermic |
| | (E) Is not affected by addition of catalyst. |

REASONING TYPE

Directions: Read the following questions and choose

- (A) If both the statements are true and statement-2 is the correct explanation of statement-1.
 (B) If both the statements are true but statement-2 is not the correct explanation of statement-1.
 (C) If statement-1 is True and statement-2 is False.
 (D) If statement-1 is False and statement-2 is True.

- Statement-1:** The thermodynamic function which determines the spontaneity of a process is the free energy. For a process to be spontaneous, the change in free energy must be negative.

Statement-2: The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must be always positive if it is spontaneous.

(a) (A) (b) (B) (c) (C) (d) (D)
- Statement-1:** All exothermic reactions are spontaneous at room temperature.

Statement-2: In the relation $\Delta G = \Delta H - T\Delta S$, if ΔG becomes negative for a reaction, the negative sign of ΔG indicates spontaneous reaction.

(a) (A) (b) (B) (c) (C) (d) (D)
- Statement-1:** As solid changes to liquid and then to vapour state, entropy increases.

Statement-2: On going from solid to liquid and then to vapour state, randomness increases.

(a) (A)

(b) (B)

(c) (C)

(d) (D)

4. **Statement-1:** Efficiency of a reversible engine is maximum (100%) when temperature of the sink is -273°C (T_1)

Statement-2: η (efficiency) = $\frac{T_2 - T_1}{T_2}$

(a) (A)

(b) (B)

(c) (C)

(d) (D)

5. **Statement-1:** Endothermic reaction is spontaneous at all temperatures.

Statement-2: ΔG is negative when $T\Delta S > \Delta H$

(a) (A)

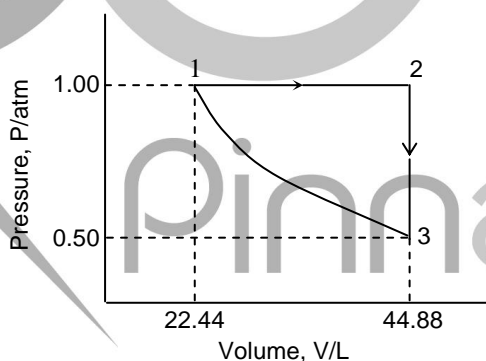
(b) (B)

(c) (C)

(d) (D)

LINKED COMPREHENSION TYPE

A sample consisting of 1 mol of a monoatomic perfect gas ($C_v = \frac{3}{2}R$) is taken through the cycle as shown.



- Temperature at points (1), (2) and (3) are respectively.
 (a) 273 K, 546 K, 273 K
 (b) 546 K, 273 K, 273 K
 (c) 273 K, 273 K, 273 K
 (d) 546 K, 546 K, 273 K
- ΔH for the overall cycle is:
 (a) $+5.67 \times 10^3 \text{ J}$
 (b) $-5.67 \times 10^3 \text{ J}$
 (c) $-11.34 \times 10^3 \text{ J}$
 (d) Zero
- ΔE for the process (1 \rightarrow 2) is:
 (a) 0.00 J
 (b) $+3.40 \times 10^3 \text{ J}$

(c) -3.40 J

(d) $-3.40 \times 10^3 \text{ J}$

EXERCISE – III (CROSSING THE HURDLES)

SUBJECTIVE PROBLEMS

1. Using the data given below, calculate the bond enthalpy of C–C and C–H bonds.

$$\Delta H_c^\circ (\text{ethane}) = -1556.5 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\circ (\text{propane}) = -2217.5 \text{ kJ mol}^{-1}$$

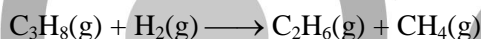
$$\text{C}(\text{graphite}) \longrightarrow \text{C}(\text{g}) \quad \Delta H = 719.7 \text{ kJ mol}^{-1}$$

$$\text{Bond enthalpy of H–H} = 435.1 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ (\text{H}_2\text{O}, \text{l}) = -284 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ (\text{CO}_2, \text{g}) = -393.3 \text{ kJ mol}^{-1}$$

2. Determine the enthalpy of the following reaction at 25°C

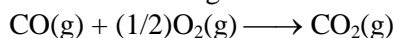


| | | | | |
|---------------------------------|------------------------|-------------------------|----------------------------------|-----------------------------|
| Given Compound: | $\text{H}_2(\text{g})$ | $\text{CH}_4(\text{g})$ | $\text{C}_2\text{H}_6(\text{g})$ | $\text{C}(\text{graphite})$ |
| $\Delta H/\text{kJ mol}^{-1}$: | -285.8 | -890.0 | -1560.0 | -393.5 |

The standard enthalpy of formation of $\text{C}_3\text{H}_8(\text{g})$ is $-103.8 \text{ kJ mol}^{-1}$.

3. For a reaction $\text{M}_2\text{O}(\text{s}) \longrightarrow 2\text{M}(\text{s}) + \frac{1}{2} \text{O}_2$; $\Delta H = 30 \text{ kJ mole}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mole}^{-1}$ at (1 atm). Calculate upto which temperature, the reaction would not be spontaneous.
4. The polymerization of ethylene to linear polyethylene is represented by the following reaction

$$n\text{CH}_2 = \text{CH}_2 \longrightarrow (-\text{CH}_2 - \text{CH}_2 -)_n \quad (n = \text{large integer value}).$$
 Calculate the enthalpy of polymerization per mol of ethylene 298 K if average enthalpies of bond dissociation for C = C and C – C are 590 and 331 kJ mol^{-1} respectively.
5. When 12.0 g of carbon (graphite) reacted with oxygen to form CO and CO_2 at 25°C and constant pressure, 313.8 kJ of heat released and no carbon remained. Calculate the mass of oxygen consumed.
 If $\Delta H_f^\circ (\text{CO}, \text{g}) = -110.5 \text{ kJ mol}^{-1}$ and $\Delta H_f^\circ (\text{CO}_2, \text{g}) = -393.5 \text{ kJ mol}^{-1}$.
6. A gas mixture consisting of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2 . Find out the amount of heat evolved on burning one litre of the gas mixture if heats of combustion of ethylene and methane are – 1423 and – 891 kJ mol^{-1} at 25°C .
7. Show that the following reaction



at 300 K is spontaneous and exothermic, when the standard entropy change is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$, ΔG_f°

$(\text{CO}_2, \text{g}) = -394.4$ and $\Delta G_f^\circ (\text{CO}, \text{g}) = -137.2$



8. Calculate the equilibrium constant for the following reaction at 400 K.
 If $\Delta H^\circ = 77.2 \text{ kJ mole}^{-1}$ and $\Delta S^\circ = 122 \text{ JK}^{-1} \text{ mole}^{-1}$.
- $$\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$
9. Calculate the heat of dissociation for acetic acid from the following data
- $$\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} ; \quad \Delta H = -13.2 \text{ kcal}$$
- $$\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} ; \quad \Delta H = -13.7 \text{ kcal}$$
- Also calculate heat of dissociation for NH_4OH if
- $$\text{HCl} + \text{NH}_4\text{OH} \longrightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O} ; \quad \Delta H = -12.27 \text{ kcal}$$
10. Calculate the resonance energy of N_2O from the following data
 If ΔH_f° of N_2O is 82 kJ mole^{-1} , $\epsilon_{\text{N} \equiv \text{N}} = 946 \text{ kJ mole}^{-1}$, $\epsilon_{\text{N} = \text{N}} = 418 \text{ kJ mole}^{-1}$,
 $\epsilon_{\text{O} = \text{O}} = 498 \text{ kJ mole}^{-1}$ and $\epsilon_{\text{N} = \text{O}} = 607 \text{ kJ mole}^{-1}$
11. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L.
 Calculate q, w, ΔE and ΔH for this process.
12. Determine the resonance energy of gaseous benzene from the following data.
 If $\Delta H_{\text{diss}}^\circ (\text{H}, \text{g}) = 435.9 \text{ kJ mole}^{-1}$, $\Delta H_{\text{sub}}^\circ (\text{C}, \text{graphite}) = 718.4 \text{ kJ mole}^{-1}$,
 $\Delta H_f^\circ (\text{Benzene}, \text{g}) = 82.9 \text{ kJ mole}^{-1}$, $\epsilon_{\text{C}-\text{H}} = 416.3 \text{ kJ mole}^{-1}$, $\epsilon_{\text{C}-\text{C}} = 331.4 \text{ kJ mole}^{-1}$ and
 $\epsilon_{\text{C}=\text{C}} = 591.3 \text{ kJ mole}^{-1}$
13. Calculate the lattice energy of $\text{KF}(\text{s})$.
 if $\Delta H_f^\circ (\text{KF}, \text{s}) = -563 \text{ kJ mole}^{-1}$, $\Delta H_{\text{ioniz}}^\circ = 419 \text{ kJ mole}^{-1}$, $\Delta H_{\text{sub}}^\circ = 88 \text{ kJ mole}^{-1}$,
 $\Delta H_{\text{EA}}^\circ = -322 \text{ kJ mole}^{-1}$ and $\Delta H_{\text{diss}}^\circ = 158 \text{ kJ mole}^{-1}$.
14. Two moles of a perfect gas undergo the following processes:
 (a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L).
 (b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L)
 (c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L)
 (i) Sketch with labels each of the processes on the same P-V diagram.
 (ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.
 (iii) What will be the values of ΔU , ΔH and ΔS for the overall process?
15. The heat evolved on combustion of 1 g starch ($\text{C}_6\text{H}_{10}\text{O}_5$) into CO_2 and $\text{H}_2\text{O}(\text{l})$ is 17.49 kJ g^{-1} . Compute the enthalpy of formation of 1 g starch. Given: ΔH_f° of $\text{H}_2\text{O}(\text{l}) = -285.85 \text{ kJ mole}^{-1}$, ΔH_f° of $\text{CO}_2 = -293.7 \text{ kJ mole}^{-1}$.

ANSWERS
EXERCISE – I
ANSWER KEY
BASIC DEFINITION

| | | | | | | | | |
|------|------|------|------|------|------|------|--------|----------|
| 1. D | 2. D | 3. C | 4. B | 5. B | 6. D | 7. C | 8. C,D | 9. A,B,C |
|------|------|------|------|------|------|------|--------|----------|

FLOT, ΔU & W CALCULATION

| | | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|------|------|
| 1. A | 2. C | 3. B | 4. B | 5. C | 6. D | 7. D | 8. B | 9. D |
| 10. A | 11. C | 12. A | 13. A | 14. C | 15. C | 16. A | | |

CALCULATION OF ΔH , ΔU , Q & W

| | | | | | | | | |
|-------|-------|-------|-------|-------|----------------------|----------------------|-------|-----------|
| 1. B | 2. C | 3. B | 4. C | 5. D | 6. A | 7. B | 8. B | 9. A |
| 10. A | 11. B | 12. B | 13. B | 14. B | 15. D | 16. C | 17. A | 18. B |
| 19. D | 20. C | 21. A | 22. B | 23. A | 24. (I)-C, (II)-C | 25. (I)-B, (II)-D | 26. B | 27. A,C,D |

CYCLIC PROCESS & POLYTROPIC PROCESS

| | | | | | | |
|------|------|------|------|------|-------------------------------|------|
| 1. C | 2. C | 3. C | 4. D | 5. C | 6. (I)-A, (II)- B, (III)-A | 7. D |
|------|------|------|------|------|-------------------------------|------|

SLOT

| | | | | | | | | |
|-------|-------|-------|-------|---------------------------------------|------|------|------|------|
| 1. C | 2. D | 3. B | 4. C | 5. C | 6. A | 7. C | 8. C | 9. C |
| 10. B | 11. D | 12. D | 13. B | 14. (I)-D, (II)-B, (III)-C, (IV)-B | | | | |

GIBB'S FREE ENERGY

| | | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. B | 2. A | 3. B | 4. B | 5. C | 6. D | 7. D | 8. C | 9. D |
| 10. D | 11. B | 12. A | 13. D | 14. A | 15. D | 16. B | 17. A | 18. D |

MISCELLANEOUS

| | | | | | | | | |
|----------------|-------|-------|---------------------|------|---------|---------|---------------|---------------|
| 1. A | 2. B | 3. A | 4. (I)-C, (II)-D | 5. A | 6. A, C | 7. C, D | 8. B, C, D | 9. A, B, C |
| 10. A, B, C | 11. B | 12. B | 13. A | | | | | |

PROBLEMS RELATED WITH ΔU & ΔH

| | | | | | | | | | |
|------|------|------|------|------|------|------|------|------|-------|
| 1. D | 2. C | 3. C | 4. B | 5. D | 6. B | 7. D | 8. B | 9. B | 10. A |
|------|------|------|------|------|------|------|------|------|-------|

ENTHALPY OF FORMATION & COMBUSTION

| | | | | | | | | | |
|-------|------|------|------|------|------|------|------|------|-------|
| 1. D | 2. A | 3. C | 4. B | 5. C | 6. C | 7. C | 8. B | 9. A | 10. A |
| 11. B | | | | | | | | | |

BOND ENTHALPY

| | | | | | | | |
|------|------|------|------|------|------|------|------|
| 1. B | 2. A | 3. D | 4. A | 5. A | 6. B | 7. A | 8. A |
|------|------|------|------|------|------|------|------|

OTHER TYPE OF ENTHALPY REACTION

| | | | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. A | 2. B | 3. C | 4. A | 5. B | 6. C | 7. A | 8. B | 9. A | 10. C |
| 11. A | 12. A | 13. A | 14. A | 15. A | 16. B | 17. B | 18. A | 19. A | 20. A |
| 21. B | 22. B | | | | | | | | |

CALORIMETRY

| | | | | |
|------|------|------|------|------|
| 1. A | 2. B | 3. A | 4. A | 5. B |
|------|------|------|------|------|

EXERCISE – II
SINGLE CHOICE CORRECT

| | | | | |
|---------|---------|---------|---------|---------|
| 1. (a) | 2. (b) | 3. (c) | 4. (b) | 5. (b) |
| 6. (c) | 7. (a) | 8. (b) | 9. (d) | 10. (b) |
| 11. (d) | 12. (b) | 13. (b) | 14. (a) | 15. (b) |
| 16. (b) | 17. (c) | 18. (c) | 19. (a) | 20. (d) |
| 21. (d) | 22. (d) | 23. (a) | 24. (b) | 25. (d) |
| 26. (d) | 27. (c) | 28. (a) | 29. (d) | 30. (a) |
| 31. (d) | 32. (b) | 33. (c) | 34. (b) | 35. (c) |
| 36. (d) | 37. (d) | 38. (c) | 39. (d) | 40. (d) |

| | | | | |
|---------|---------|---------|---------|---------|
| 41. (d) | 42. (d) | 43. (d) | 44. (b) | 45. (c) |
| 46. (b) | 47. (d) | 48. (b) | 49. (c) | 50. (a) |

SINGLE CHOICE CORRECT

| | | | | |
|---------|---------|---------|---------|---------|
| 1. (c) | 2. (b) | 3. (d) | 4. (a) | 5. (a) |
| 6. (b) | 7. (c) | 8. (d) | 9. (b) | 10. (d) |
| 11. (c) | 12. (d) | 13. (b) | 14. (b) | 15. (c) |
| 16. (c) | 17. (d) | 18. (b) | 19. (d) | 20. (b) |

ONE OR MORE THAN ONE CHOICE CORRECT

| | | | | |
|--------------|--------------|--------------|--------------|------------|
| 1. (a, b, c) | 2. (b, c, d) | 3. (a, b) | 4. (a, b) | 5. (a, c) |
| 6. (a, c, d) | 7. (a,b,c,d) | 8. (a,b,c,d) | 9. (a,b,c,d) | 10. (a, c) |

MATCH THE FOLLOWING

I – (B) ; II – (A), (E) ; III – (C), (E) ; IV – (D), (E)

REASONING TYPE

| | | | | |
|--------|--------|--------|--------|--------|
| 1. (c) | 2. (d) | 3. (a) | 4. (a) | 5. (d) |
|--------|--------|--------|--------|--------|

LINKED COMPREHENSION TYPE

| | | |
|--------|--------|--------|
| 1. (a) | 2. (d) | 3. (b) |
|--------|--------|--------|

EXERCISE – III

SUBJECTIVE PROBLEMS

1. $\epsilon_{C-C} = 343.25 \text{ kJ mol}^{-1}$, $\epsilon_{C-H} = 413.925 \text{ kJ mole}^{-1}$

2. $-55.7 \text{ kJ mole}^{-1}$

3. $T < 428.57 \text{ K}$

4. -72 kJ mole^{-1}

5. 27.5 g

6. 50.88 kJ

8. 1.958×10^{-4}

9. $0.5 \text{ kcal}, 1.43 \text{ kcal}$

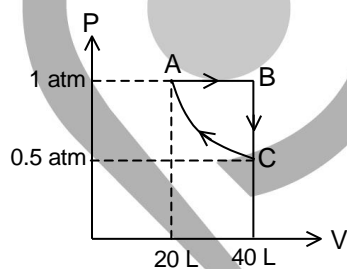
10. -88 kJ mole^{-1}

11. $\Delta H = W = -q = 103.635 \text{ cal}, \Delta E = 0$

12. $269.7 \text{ kJ mole}^{-1}$

13. $-827 \text{ kJ mole}^{-1}$

14. (a)



(b) $-620.77 \text{ J}, +620.77 \text{ J}$

(c) $\Delta U = \Delta H = \Delta S = 0$

15. -2.21 kJ

PROFICIENCY TEST– I

The following 10 questions deal with the basic concepts of this section. Answer the following briefly. Go to the next section only if your score is greater than or equal to 8. Do not consult the study material while attempting the questions.

1. In the relation,
$$\Delta H = \Delta E + \Delta n_g RT.$$
 Δn_g refers to _____.
2. For a reaction involving condensed phase, ΔH and ΔE are _____.
3. Enthalpy and internal energy are related by the relation _____.
4. The amount of heat absorbed/evolved at constant volume is equal to _____.
5. The heat capacity at constant pressure is generally _____ than that at constant volume.
6. The work-done during isothermal reversible expansion of an ideal gas is _____ than that during irreversible isothermal expansion.
7. The work-done during isothermal reversible expansion of an ideal gas is given by the relation _____.
8. Work done during adiabatic reversible expansion of an ideal gas is _____ than that during adiabatic irreversible expansion.
9. For a monoatomic and a diatomic ideal gas, molar heat capacity at constant volume is _____ and _____ respectively.
10. Temperature and heat are _____ and _____ properties respectively.

ANSWERS TO PROFICIENCY TEST– I

1. Difference in the number of moles of gaseous products and gaseous reactants.
2. same
3. $H = E + PV$
4. Change in internal energy.
5. Greater
6. More
7. $w = -2.303nRT \log \frac{V_2}{V_1}$
8. More
9. $\frac{3}{2}R$ and $\frac{5}{2}R$.
10. Intensive and extensive


Pinnacle

PROFICIENCY TEST– II

The following 10 questions deal with the basic concepts of this section. Answer the following briefly. Go to the next section only if your score is greater than or equal to 8. Do not consult the study material while attempting the questions.

1. In exothermic and endothermic reactions, the total enthalpy of reactants is respectively _____ than and _____ than that of products.
2. The standard molar enthalpy of an element in its stable state of aggregation at 298 K is taken to be _____.
3. The products of combustion of a hydrocarbon at 398 K are _____ and _____.
4. The enthalpy of neutralization of a weak acid is _____ than that of a strong acid. The difference of the latter from the former is known as enthalpy of _____ of the weak acid.
5. The amount of heat evolved when one mole of crystalline solid is formed from its constituent gaseous ions is called _____.
6. When 1 mol of graphite is converted into diamond, the enthalpy change is known as _____.
7. At 1 atm and 298 K, the stable state of aggregation of carbon is _____.
8. True/False. The terms, bond enthalpy and bond dissociation energy stand for the one and same thing.
9. True/False. At 298 K, the enthalpy of combustion of CH_4 corresponds to the reaction,
$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}).$$
10. True/False. The heat change accompanying combustion of diamond and enthalpy of formation of carbon dioxide has the same value.

ANSWERS TO PROFICIENCY TEST– II

1. Less, more
2. Zero
3. $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$
4. Less, ionisation
5. Lattice energy
6. Enthalpy of transition
7. Graphite
8. False. Bond dissociation energy refers to a particular bond in a polyatomic molecule whereas bond enthalpy refers to the average of bond dissociation enthalpies required to break bond of the same kind in a molecule.
9. False. At 298 K, $\text{H}_2\text{O}(\text{l})$ is stable species and not $\text{H}_2\text{O}(\text{g})$.
10. False. Enthalpy of combustion of graphite and enthalpy of formation of carbon dioxide refer to one and the same chemical equation.



Pinnacle

PROFICIENCY TEST– III

The following 10 questions deal with the basic concepts of this section. Answer the following briefly. Go to the next section only if your score is greater than or equal to 8. Do not consult the study material while attempting the questions.

1. Entropy of a substance in gaseous, liquid and solid states follows the order _____.
2. Free energy, enthalpy and entropy are related to each other by the equation _____.
3. For a process occurring at constant T and P, the change in free energy is given by _____.
4. For a reaction at equilibrium, the value of ΔG is _____ zero.
5. The reaction, $I_2(g) + Cl_2(g) \longrightarrow 2ICl(g)$ involves _____ in entropy.
6. True/False. $\Delta H_{\text{sub}} = \Delta H_{\text{Fusion}} + \Delta H_{\text{vapo.}}$
7. True/False. A spontaneous reaction always leads to increase in entropy.
8. True/False. All endothermic reactions are non-spontaneous.
9. True/False. The standard free energy of formation of elements in its stable state of aggregation at 298 K is taken to be zero.
10. True/False. Entropy change of phase transition is given by $\Delta S = \frac{L}{T}$, where L is latent heat of phase change and T is the temperature at which change in phase takes place.

ANSWERS TO PROFICIENCY TEST– III

1. $S(\text{gaseous state}) \gg S(\text{liquid state}) > S(\text{solid})$
2. $G = H - TS$
3. $\Delta G = \Delta H - T\Delta S$
4. Equal to
5. Increase
6. True
7. False
8. False
9. True
10. True

