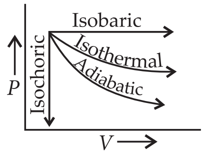
CHAPTER
2

Thermodynamics

Recap Notes

- **Thermodynamics :** It is a branch of science which deals with the study of interconversion of different forms of energies and their quantitative relationships.
- **Some basic terms :**
  - **System :** It is the part of universe under investigation where energy changes can be regulated and studied.
  - **Surroundings :** Rest part of the universe which can interact with the system or can influence the properties of the system is called *surroundings*.
  - **Boundary :** A real or imaginary surface that separates the system from the surroundings is known as *boundary*. A boundary can be rigid or non-rigid (movable), permeable or impermeable, adiabatic (non-conductor of heat) or diathermic (conductor of heat).
- **Types of system :**
  - **Open system :** A system which can exchange mass as well as energy with the surroundings.
  - **Closed system :** A system which can exchange energy but not mass with the surroundings.
  - **Isolated system :** A system which can neither exchange energy nor mass with the surroundings.
  - **State functions :** Properties which are used to define a particular thermodynamic state and are independent of the path by which the state is attained are called *state functions*. *e.g.*, pressure, mass composition, volume, temperature, internal energy, entropy, Gibbs free energy, etc.
  - **Path functions :** Variables whose values depend upon the path followed by the system in attaining that state, are known as *path functions*.
- **Types of thermodynamic processes :**
  - **Isothermal process :** Temperature of the system remains constant ($\Delta T = 0$).
  - **Isobaric process :** Pressure of the system remains constant ($\Delta P = 0$).
  - **Isochoric process :** Volume of the system remains constant ($\Delta V = 0$).
  - **Adiabatic process :** The system does not exchange heat with the surroundings (*i.e.*, $q = 0$).



  - **Reversible process :** Direction may be reversed at any stage.
  - **Irreversible process :** Proceeds only in one direction and cannot be reversed.
  - **Cyclic process :** System returns to its original state after a number of steps. For such a process, $\Delta U = 0$ and $\Delta H = 0$.
  - **Exothermic process :** Accompanied by the evolution of heat.
  - **Endothermic process :** Accompanied by the absorption of heat.
- **Internal Energy (U) :** Sum of various forms of energy such as rotational, vibrational, translational, kinetic, coulombic, nuclear, etc. is known as *internal energy*.
  - It is a state function.
  - It is extensive property and depends only on temperature.

- **Work (W) :** *Work* is a mode of energy transfer from or to the system to make some net changes in the state of the system. No work is being done when system is in equilibrium.
  Work = Force × displacement = $F \times l$
  - ▶ **Electrical work :** It is the work involved in reactions involving ions.
    Electrical work done = EMF × quantity of electricity.
  - ▶ **Pressure-volume work :** It is the work done involved in expansion or compression of the gases against external pressure.
    Work = Pressure × area × $l = P_{\text{ext}} \times \Delta V$
    where, Force = Pressure × area;
    area × l = volume and ΔV is change in volume *i.e.*, $\Delta V = (V_2 - V_1)$.
- **Heat (q) :** *Heat* is a mode of energy transfer between system and surrounding because of difference in temperature between them. It is measured in terms of calories. SI unit of heat is joule.
- **First law of thermodynamics :** This is the law of conservation of energy which states that energy can neither be created nor be destroyed, although it can be converted from one form to another.
  - ▶ The total energy of the universe remains constant.
  - ▶ ΔE or $\Delta U = q + w$ or $q = \Delta U - w$
  - ▶ q and w are not state functions but $\Delta U = (q + w)$ is a state function.
  - ▶ **Sign convention :**
    - Heat absorbed by the system = +ve
    - Heat evolved by the system = –ve
    - Work done on the system = +ve
    - Work done by the system = –ve
- **Applications :**
  - ▶ **Isothermal reversible expansion of an ideal gas :** Consider a gas enclosed in a cylinder fitted with a frictionless piston. During the expansion volume increases and pressure decreases. In the beginning external pressure P_{ext} is equal to the internal pressure of the gas therefore, the piston does not move. If the external pressure is decreased by dP, the gas expands reversibly and the piston moves through a distance dP. The work done by the gas in an infinitesimal expansion is thus given by
    $dw = -(P_{\text{ext}} - dP)dV$
    but as dP is very small thus, on ignoring $dPdV$, we get $dw = -P_{\text{ext}}\, dV = -PdV$
    - The overall work done in an isothermal reversible expansion of the ideal gas from V_1 to V_2 is as follows :

      $$w_{\text{rev}} = -\int_{V_1}^{V_2} PdV$$

      From ideal gas equation, $P = RT/V$
      Substituting the value of P in the above integral equation,

      $$w = -RT\int_{V_1}^{V_2} \frac{dV}{V} = -RT\ln\frac{V_2}{V_1}$$

      For n moles, $w = -nRT\ln\frac{V_2}{V_1}$

      $$\because \quad P_1V_1 = P_2V_2$$

      $$\therefore \quad w = -nRT\ln\frac{P_1}{P_2} = -2.303nRT\log\frac{P_1}{P_2}$$

    - The work done during an isothermal reversible compression can be given as :

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

      Thus, opposite to the first case where, work done in isothermal compression has exactly the same value with positive sign.
  - ▶ **Free expansion :** Expansion of a gas in vacuum ($P_{\text{ex}} = 0$) is called *free expansion*. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.
    i.e., $\Delta U = q - P_{\text{ex}}\,\Delta V$
    At constant V, $\Delta U = q_V$
  - ▶ **Isothermal and free expansion of an ideal gas :**
    - For isothermal expansion of an ideal gas into vacuum; $w = 0$ since, $P_{\text{ex}} = 0$
    - For isothermal irreversible change;
      $q = -w = P_{\text{ex}}(V_f - V_i)$
    - For isothermal reversible change;

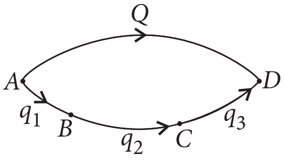
      $$q = -w = 2.303\ nRT\log\frac{V_f}{V_i}$$

    - For adiabatic change; $q = 0$, $\Delta U = w_{ad}$

- **Enthalpy (H) :** Total heat content of the system at constant pressure is known as its *enthalpy*.
    - It is an extensive property.
    - It is state function.
    - Its absolute value can not be determined.
    - Mathematically it is given as, $H = U + PV$
    - If H_2 is the enthalpy in final state and H_1 in initial state, then
      $\Delta H = (H_2 - H_1) = \Delta U + P\Delta V$
    - For exothermic reaction (*i.e.*, heat released during the reaction), ΔH is negative *i.e.*, $\Delta H < 0$. Whereas for endothermic reaction (*i.e.*, heat absorbed during the reaction), ΔH is positive *i.e.*, $\Delta H > 0$.
    - According to first law of thermodynamics, $q = \Delta U - w$; where, w is the pressure-volume work done by the system.
    - $\because \quad w = -P\Delta V$
      At constant volume ($\Delta V = 0$) then, $w = 0$
      $\therefore \quad q_v = \Delta U$
    - At constant pressure, ($\Delta P = 0$) then,
      $w = -P\Delta V$
      $q_p = \Delta U + P\Delta V$
      Comparing this equation with equation of enthalpy change, we get
      $q_p = \Delta H$
- **Relationship between ΔH and ΔU :**
    - As $P\Delta V = \Delta n_g RT$
      where, Δn_g = number of moles of gaseous products – number of moles of gaseous reactants.
      $\therefore \quad \Delta H = \Delta U + \Delta n_g RT$ or $q_p = q_v + \Delta n_g RT$
        - When $\Delta n_g = 0$, then $\Delta H = \Delta U$
        - When $\Delta n_g > 0$, then $\Delta H > \Delta U$
        - When $\Delta n_g < 0$, then $\Delta H < \Delta U$
        - For a reaction involving only solids and liquids, $\Delta n_g = 0$, thus, $\Delta H = \Delta U$.
- **Extensive and intensive properties :**
    - **Extensive properties :** The properties which depend upon the amount of matter contained in a system are called *extensive properties*. For example, mass, volume, enthalpy, entropy, free energy, heat capacity, etc.
    - **Intensive properties :** The properties which do not depend upon the amount of matter present in the system but depend only on the nature of the matter are called *intensive properties*. For example, temperature, pressure, density, refractive index, viscosity, specific heat, freezing point, boiling point, etc.
- **Enthalpy of reaction :** It is defined as the change in enthalpy, or the amount of heat evolved or absorbed when the number of moles of reactants reacts completely to give the products as given by the balanced chemical equation.
  $C_{(g)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$; $\Delta_r H = -393.5$ kJ mol^{-1}
  $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$;
  $\Delta_r H = -890.3$ kJ mol^{-1}
    - **Enthalpy of formation :** It is the change in enthalpy when one mole of a substance is formed directly from its constituent elements, *e.g.*,
      $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$; $\Delta_f H = -748$ kJ mol^{-1}
    - **Enthalpy of combustion :** It is the change in enthalpy when one mole of a substance is completely burnt in oxygen, *e.g.*,
      $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_c H = -393.5$ kJ mol^{-1}
      $\Delta_c H$ is always negative as heat is always evolved during combustion.
    - **Enthalpy of solution :** It is the change in enthalpy when one mole of a substance is dissolved in excess of water so that further dilution does not involve any heat change, *e.g.*, $NaCl_{(s)} + aq. \rightarrow NaCl_{(aq)}$;
      $\Delta_{soln} H = +5.0$ kJ mol^{-1}
    - **Enthalpy of neutralisation :** It is the change in enthalpy when one gram equivalent of an acid is completely neutralised by 1 g equivalent of a base in dilute solutions, *e.g.*,
      $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$;
      $\Delta_{neu} H = -57.1$ kJ mol^{-1}
    - **Enthalpy of fusion :** It is the change in enthalpy when one mole of a solid is completely converted into liquid state at its melting point, *e.g.*,
      $H_2O_{(s)} \rightarrow H_2O_{(l)}$ at 0 °C or 273 K;
      $\Delta_{fus} H = +6.0$ kJ mol^{-1}

- **Enthalpy of vapourisation :** It is the change in enthalpy when one mole of a liquid is completely converted into its vapours at its boiling point, *e.g.*,
  $H_2O_{(l)} \rightarrow H_2O_{(g)}$ at 373 K;
  $\Delta_{vap}H = +40.6$ kJ mol^{-1}
- **Enthalpy of sublimation :** It is the change in enthalpy when one mole of a solid is directly converted into vapours, *e.g.*,
  $\Delta_{sub}H$ of iodine is +62.4 kJ mol^{-1}.
  Also, $\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$
- **Enthalpy of atomization :** It is the change in enthalpy on breaking one mole of bonds completely to obtain atoms in the gas phase, *e.g.*, $CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)}$;
  $\Delta_a H = 1665$ kJ mol^{-1}
- **Bond enthalpy :** It is the change in enthalpy associated with breaking and making of chemical bonds, *e.g.*,
  $Cl_{2(g)} \rightarrow 2Cl_{(g)}$; $\Delta_{bond}H = 242$ kJ mol^{-1}

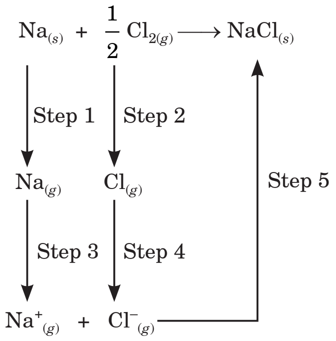
- **Hess's law of constant heat summation :** It state that the total amount of heat change in a chemical reaction is same whether the reaction takes place in one step or in number of steps.



$$Q = q_1 + q_2 + q_3$$

- **Applications of Hess's law :** The most important application of Hess's law is in the calculation of heat changes for those reactions in which experimental determination is not possible.
- The thermochemical equations can be treated as algebraic equations which can be added, subtracted, multiplied or divided.

- **Lattice enthalpy :** Hess's law can be used to determine lattice energy which may be defined as the amount of heat liberated when the requisite amounts of ions in the gaseous state combine to produce 1 mole of crystal lattice. For example, lattice energy of NaCl crystal can be determined in the following steps :



Born–Haber cycle

- **Step 1 :** Conversion of Na metal to gaseous atoms.
  $Na_{(s)} \rightarrow Na_{(g)}$; $\Delta_1 H$ = Sublimation energy
- **Step 2 :** Dissociation of Cl_2 molecules to Cl atoms.
  $Cl_{2(g)} \rightarrow 2Cl_{(g)}$; $\Delta_2 H$ = Dissociation energy
- **Step 3 :** Conversion of gaseous metal atom to metal ions by losing electron.
  $Na_{(g)} \rightarrow Na^+_{(g)} + e^-$; $\Delta_3 H$ = Ionization energy
- **Step 4 :** $Cl_{(g)}$ atoms gain an electron to form Cl^- ions.
  $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$; $\Delta_4 H$ = Electron affinity
- **Step 5 :** $Na^+_{(g)}$ and $Cl^-_{(g)}$ combine together to form the crystal lattice.
  $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$; $\Delta_5 H$ = Lattice energy
  Applying Hess's law we get,
  $\Delta_1 H + 1/2\ \Delta_2 H + \Delta_3 H + \Delta_4 H + \Delta_5 H = \Delta_f H$ (NaCl)
  On putting the various known values, we can calculate the lattice energy.

- **Spontaneity :**
  - **Spontaneous process :** The process which takes place by itself or after proper initiation under a given set of conditions is known as *spontaneous process*. All natural processes are spontaneous and cannot be reversed without the help of an external agency. Hence, spontaneous processes are irreversible. *e.g.*, flow of heat from hot reservoir to cold reservoir, flow of water down the hill, dissolution of common salt in water, diffusion of gases from high pressure to low pressure, etc.
  - **Non-spontaneous process :** The process which can neither take place by itself nor by initiation, is called *non-spontaneous process*. *e.g.*, flow of heat from cold

reservoir to hot reservoir, flow of water up the hill, dissolution of sand in water, diffusion of gas from low pressure to high pressure, etc.

- **Factors affecting spontaneity of a reaction :**
  - **Energy or enthalpy :** Every system tends to have minimum energy just in order to acquire maximum stability. Thus, the reaction which results in products of lesser energy *i.e.*, exothermic reactions must be spontaneous. *e.g.*,
    $N_2 + 3H_2 \rightarrow 2NH_3$; $\Delta H = -92.4$ kJ mol^{-1}
    $H_2O_{(l)} \rightarrow H_2O_{(g)}$; $\Delta H = +44$ kJ mol^{-1}
  - **Entropy :** Every system tends to have maximum randomness just in order to acquire maximum stability. An increase in entropy or randomness (*i.e.*, positive ΔS) favours the spontaneity of a reaction. *e.g.*, spreading of a drop of ink in a beaker filled with water is a spontaneous process, where randomness is increasing, *i.e.*, ΔS is positive.
    - For a reversible process at equilibrium, $\Delta S = 0$
    - For a process to be spontaneous in isolated system, ΔS should be positive.
    - For a process in open system, entropy of surrounding should be positive.
      $\therefore \quad \Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}}$
    - For a process to be spontaneous in such condition,
      $\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} > 0$
      (*i.e.*, positive)
    - For reversible processes,
      $\Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} = 0$
    - For irreversible process,
      $\Delta S_{\text{System}} + \Delta S_{\text{Surrounding}} > 0$

    Therefore, it can be said that for all spontaneous processes, ΔS_{Total} must be positive. Spontaneity of a process is decided by net resultant effect of energy and entropy.

    If $\Delta S_{\text{System}} = \dfrac{q_{rev}}{T}$, then, $\Delta S_{\text{Surrounding}} = -\dfrac{q_{rev}}{T}$
  - **Gibbs energy :** Gibbs energy change is given as
    $\Delta G = \Delta H - T\Delta S$
    This expression combines both factors *i.e.*, ΔH and ΔS of spontaneity.
    It means, ΔG is resultant of two factors :
    - For a reaction to be spontaneous, ΔG must be negative.
    - If $\Delta G = 0$, process is in equilibrium.
    - If ΔG = positive, process is non-spontaneous.
  - **Gibbs energy change and equilibrium:** Gibbs energy change, $\Delta_r G$ is related to the equilibrium constant of the reaction as
    $\Delta_r G = -2.303\, RT \log K$

Effect of temperature on spontaneity of reactions

$\Delta_r H^\circ$	$\Delta_r S^\circ$	$\Delta_r G^\circ$	**Description***
–	+	–	spontaneous at all temperatures
–	–	– (at low T)	spontaneous at low temperature
–	–	+ (at high T)	non-spontaneous at high temperature
+	+	+ (at low T)	non-spontaneous at low temperature
+	+	– (at high T)	spontaneous at high temperature
+	–	+ (at all T)	non-spontaneous at all temperatures

**The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.*

Practice Time

OBJECTIVE TYPE QUESTIONS

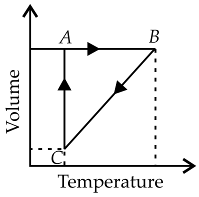
Multiple Choice Questions (MCQs)

1. System in which there is no exchange of matter, work or energy from surroundings is

(a) closed (b) adiabatic

(c) isolated (d) isothermal.

2. Five moles of a gas is put through a series of changes as shown graphically in a cyclic process. The processes $A \rightarrow B$, $B \rightarrow C$ and $C \rightarrow A$ respectively are



(a) isochoric, isobaric, isothermal

(b) isobaric, isochoric, isothermal

(c) isothermal, isobaric, isochoric

(d) isochoric, isothermal, isobaric

3. Which one of the following statements is false?

(a) Work is a state function.

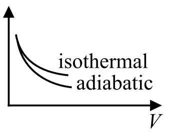
(b) Temperature is a state function.

(c) Change in the state is completely defined when the initial and final states are specified.

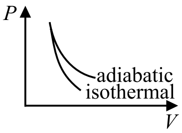
(d) Work appears at the boundary of the system.

4. The correct figure representing isothermal and adiabatic expansions of an ideal gas from a particular initial state is

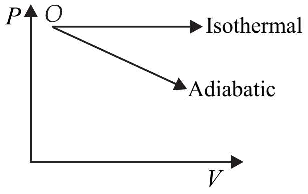
(a)



(b)



(c)



(d) none of these.

5. The temperature of the system increases during an

(a) isothermal expansion

(b) adiabatic compression

(c) adiabatic expansion

(d) isothermal compression.

6. For which of the following reactions will ΔH be equal to ΔU?

(a) $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$

(b) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$

(c) $2SO_{3(g)} \rightarrow 2SO_{2(g)} + O_{2(g)}$

(d) $2NO_{2(g)} \rightarrow N_2O_{4(g)}$

7. In thermodynamics, which one of the following properties is not an intensive property?

(a) Pressure (b) Temperature

(c) Volume (d) Density

8. Which of the following reactions corresponds to the definition of enthalpy of formation ?

(a) $C_{(g)} + O_{2(g)} \longrightarrow CO_{2(g)}$

(b) $C_{(s)} + O_{2(l)} \longrightarrow CO_{2(g)}$

(c) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

(d) $C_{(l)} + O_{2(s)} \longrightarrow CO_{2(g)}$

9. 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 surroundings in a closed 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 closed system.

10. Enthalpy of combustion of carbon to CO_2 is -393.5 kJ mol^{-1}. What amount of heat will be released upon formation of 35.2 g of CO_2 from carbon and oxygen gas?

(a) 214.8 kJ (b) 314.8 kJ
(c) 414.8 kJ (d) 514.8 kJ

11. Work done in reversible isothermal process is given by

(a) $-2.303\ nRT \log \frac{V_2}{V_1}$ (b) $\frac{nR}{(\gamma - 1)}(T_2 - T_1)$
(c) $-2.303\ nRT \log \frac{V_1}{V_2}$ (d) $+2.303\ nRT \log \frac{V_2}{V_1}$

12. The standard heat of formation at 298 K for $CCl_{4(g)}$, $H_2O_{(g)}$, $CO_{2(g)}$ and $HCl_{(g)}$ are –25.5, –57.8, –94.1 and –22.1 kcal per mole respectively. Then ΔH at 298 K for the reaction

$CCl_{4(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 4HCl_{(g)}$ is

(a) – 32.9 kcal (b) – 41.4 kcal
(c) – 99.2 kcal (d) – 323.6 kcal

13. In endothermic reactions,

(a) reactants have more energy than products
(b) reactants have less energy than products
(c) reactants and products have same energy
(d) reactants have lower temperature than products.

14. When 1 M H_2SO_4 is completely neutralised by sodium hydroxide, the heat liberated is 114.64 kJ. What is the enthalpy of neutralisation?

(a) +114.64 kJ (b) –114.64 kJ
(c) –57.32 kJ (d) +57.32 kJ

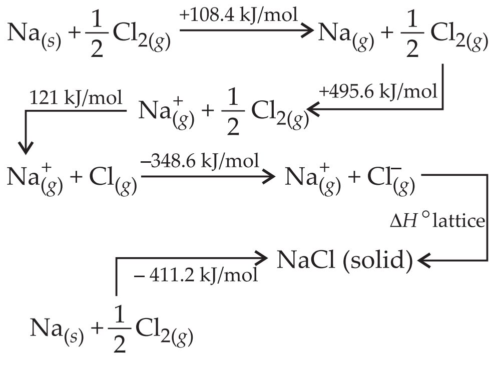
15. In the reaction, $S + \frac{3}{2}O_2 \longrightarrow SO_3 + 2x$ kJ

and $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3 + y$ kJ.

Heat of formation of SO_2 is

(a) $x + y$ (b) $x - y$
(c) $2x - y$ (d) $2x + y$

16. For one mole of $NaCl_{(s)}$ the lattice enthalpy is



(a) –788 kJ/mol (b) +878 kJ/mol
(c) +788 kJ/mol (d) –878 kJ/mol

17. The heat of neutralization is maximum when

(a) sodium hydroxide is neutralized by acetic acid
(b) ammonium hydroxide is neutralized by hydrochloric acid
(c) sodium hydroxide is neutralized by formic acid
(d) sodium hydroxide is neutralized by hydrochloric acid.

18. Which of the following processes is a non-spontaneous process?

(a) Dissolution of salt or sugar in water
(b) Mixing of different gases through diffusion
(c) Precipitation of copper when zinc rod is dipped in aqueous solution of copper sulphate
(d) Flow of heat from a cold body to a hot body in contact

19.

Bond	**Bond enthalpy**
$N \equiv N$	945 kJ mol^{-1}
$H - H$	436 kJ mol^{-1}
$N - H$	391 kJ mol^{-1}

Calculate the enthalpy change of the reaction,
$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

(a) –89 kJ mol^{-1} (b) –93 kJ mol^{-1}
(c) –105 kJ mol^{-1} (d) 105 kJ mol^{-1}

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. Calculate the resonance energy of N_2O from the following data: ΔH_f of N_2O = 82 kJ mol^{-1}. Bond energies of $N \equiv N$, $N = N$, $O = O$ and $N = O$ bonds are 946, 418, 498 and 607 kJ mol^{-1} respectively.

(a) – 88 kJ mol^{-1} (b) –170 kJ mol^{-1}
(c) – 82 kJ mol^{-1} (d) –258 kJ mol^{-1}

22. The second law of thermodynamics states that

(a) entropy of the universe is decreasing continuously.
(b) energy can neither be created nor destroyed.
(c) all spontaneous processes are thermodynamically irreversible.
(d) at absolute zero free energy is zero.

23. The heats of neutralization of CH_3COOH, $HCOOH$, HCN and H_2S are –13.2, –13.4, –2.9 and –3.8 kcal per equivalent respectively. The correct increasing order of acid strength is

(a) $HCOOH < CH_3COOH < H_2S < HCN$
(b) $HCN < H_2S < CH_3COOH < HCOOH$
(c) $HCOOH < CH_3COOH < HCN < H_2S$
(d) $CH_3COOH < H_2S < HCN < HCOOH$

24. One word answer is given for the following definitions. Mark the one which is incorrect.

(a) The process in which temperature remains constant : Isobaric
(b) The process in which volume remains constant : Isochoric
(c) The relation between ΔH and ΔU when all the reactants and products are solid : $\Delta H = \Delta U$
(d) The relation between ΔG, ΔH and ΔS : $\Delta G = \Delta H - T\Delta S$

25. Choose the reaction with negative ΔS value.

(a) $2NaHCO_{3(s)} \longrightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$
(b) $Cl_{2(g)} \longrightarrow 2Cl_{(g)}$
(c) $2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$
(d) $2KClO_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$

26. The enthalpies of the elements in their standard states are assumed to be

(a) zero at 298 K
(b) unity at 298 K
(c) zero at all temperatures
(d) zero at 273 K.

27. According to the 3rd law of thermodynamics, the entropy at 0 K is zero for

(a) elements in their stable form
(b) perfectly crystalline solid
(c) substances at 1 atm and 25 °C
(d) gaseous substances only.

28. Which of the following condition is not favourable for the feasibility of a reaction?

(a) ΔH = +ve, $T\Delta S$ = +ve and $T\Delta S > \Delta H$
(b) ΔH = –ve, $T\Delta S$ = +ve
(c) ΔH = –ve, $T\Delta S$ = –ve and $T\Delta S < \Delta H$
(d) ΔH = +ve, $T\Delta S$ = +ve and $T\Delta S < \Delta H$

29. Match the column I with column II and mark the appropriate choice.

	Column I		**Column II**
(A)	$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O$	(i)	$\Delta_{sol}H$
(B)	$H_{2(g)} \rightarrow 2H_{(g)}$	(ii)	$\Delta_{lattice}H$
(C)	$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$	(iii)	$\Delta_{comb}H$
(D)	$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$	(iv)	$\Delta_{disso}H$

(a) (A) → (iv), (B) → (iii), (C) → (i), (D) → (ii)
(b) (A) → (ii), (B) → (i), (C) → (iv), (D) → (iii)
(c) (A) → (i), (B) → (ii), (C) → (iii), (D) → (iv)
(d) (A) → (iii), (B) → (iv), (C) → (ii), (D) → (i)

30. In conversion of limestone to lime,

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

the values of ΔH and ΔS are +179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH and ΔS do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is

(a) 1118 K (b) 1008 K
(c) 1200 K (d) 845 K

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 31 to 35.

Hess's Law of Constant Heat Summation
This law was presented by Hess in 1840. According to the law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change is always the same.
Thus, the total enthalpy change of a chemical reaction depends on the initial and final stages only.

$$\begin{tikzcd} A \arrow[r, "\Delta H_1"] & B \arrow[d, "\Delta H_2"] \\ D \arrow[u, "\Delta H_{\text{direct}}"] & C \arrow[l, "\Delta H_3"] \end{tikzcd}$$

Total enthalpy change from A to D,
$\Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3$
$\Delta H_{\text{total}} + \Delta H_{\text{direct}} = 0$
i.e., $\Delta H_{\text{total}} = -\Delta H_{\text{direct}}$
For example, formation of CO_2 from C in two

different manners involves a total heat change of –393.5 kJ/ mol

Single step process :

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -393.5$ kJ/mol

Two step process :

(i) $C(s) + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$; $\Delta H = -110.5$ kJ/mol

(ii) $CO(g) + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -283.0$ kJ/mol

$\Delta H_{\text{Total}} = -110.5 + (-283.0) = -393.5$ kJ/mol

31. For the given reactions,

$H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$; $\Delta H = -124$ kcal
$H_{2(g)} \rightarrow 2H_{(g)}$; $\Delta H = 104$ kcal
$F_{2(g)} \rightarrow 2F_{(g)}$; $\Delta H = 37.8$ kcal

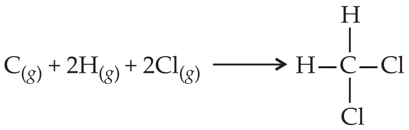
then the value of ΔH for $H_{(g)} + F_{(g)} \rightarrow HF_{(g)}$ is

(a) 142 kcal (b) – 132.9 kcal
(c) 132 kcal (d) 134 kcal.

32. In which of the enlisted cases, Hess's law is not applicable?

(a) Determination of lattice energy
(b) Determination of resonance energy
(c) Determination of enthalpy of transformation of one allotropic form to another
(d) Determination of entropy

33. Use the bond energy data and calculate the enthalpy change for



$$C_{(g)} + 2H_{(g)} + 2Cl_{(g)} \longrightarrow CH_2Cl_2$$

The bond energies of C — H and C — Cl are 413 and 328 kJ mol^{-1} respectively.

(a) –1465 kJ/mol (b) 1465 kJ/mol
(c) –1482 kJ/mol (d) 1482 kJ/mol

34. A hypothetical reaction, $A \longrightarrow 2B$, proceeds through following sequence of steps :

$A \longrightarrow C$; $\Delta H = q_1$
$C \longrightarrow D$; $\Delta H = q_2$
$\frac{1}{2}D \longrightarrow B$; $\Delta H = q_3$

The heat of reaction is

(a) $q_1 - q_2 + 2q_3$ (b) $q_1 + q_2 - 2q_3$
(c) $q_1 + q_2 + 2q_3$ (d) $q_1 + 2q_2 - 2q_3$

35. Given :

$NH_{3(g)} + 3Cl_{2(g)} \rightarrow NCl_{3(g)} + 3HCl_{(g)}$; $-\Delta H_1$ ...(i)
$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$; $-\Delta H_2$ ...(ii)
$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$; ΔH_3 ...(iii)

The heat of formation of $NCl_{3(g)}$ in the terms of ΔH_1, ΔH_2 and ΔH_3 is

(a) $\Delta H_f = -\Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(b) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
(c) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} + \frac{3}{2}\Delta H_3$
(d) none of these.

Case II : Read the passage given below and answer the following questions from 36 to 40.

A thermodynamically irreversible process is always accompanied by an increase in the entropy of the system and its surroundings taken together while in a thermodynamically reversible process, the entropy of the system and its surrounding taken together remain unchanged i.e. for reversible process

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

and for irreversible process

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

combining the two we have

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad 0$$

where 'equal' to sign refers to a reversible process while the 'greater than' sign refers to an irreversible process.

Change in entropy for an ideal gas under different conditions may be calculated as

$$\Delta S = 2.303\, nR \log_{10}\frac{V_2}{V_1} = 2.303\, nR \log_{10}\frac{P_1}{P_2}$$

(for isothermal process)

$$\Delta S = 2.303\, nC_P \log_{10}\frac{T_2}{T_1} = 2.303\, nC_P \log_{10}\frac{V_2}{V_1}$$

(for isobaric process)

$$\Delta S = 2.303\, nC_V \log_{10}\frac{T_2}{T_1} = 2.303\, nC_V \log_{10}\frac{P_2}{P_1}$$

36. Calculate entropy change when 5 moles of an ideal gas expands reversibly and isothermally from an initial volume of 5 litre to 50 litre at 27°C.

(a) 190.15 JK^{-1} (b) 95.74 JK^{-1}
(c) 87.25 JK^{-1} (d) 90.13 JK^{-1}.

37. The entropy of the universe

(a) increasing and tending towards maximum value
(b) decreasing and tending to be zero
(c) remains constant
(d) decreasing and increasing with a periodic rate.

38. The total entropy change for a system and its surroundings increases, if the process is

(a) reversible (b) irreversible

(c) exothermic (d) endothermic.

39. ΔS is positive for the change

(a) mixing of two gases (b) boiling of liquid

(c) melting of solid (d) all of these.

40. Entropy changes for the process,

$H_2O_{(l)} \longrightarrow H_2O_{(s)}$,

at normal pressure and 274 K are given below

$\Delta S_{\text{system}} = -22.13$, $\Delta S_{\text{surr}} = +22.05$,

the process is non-spontaneous because

('surr' stands for surrounding and 'u' stands for universe)

(a) ΔS_{system} is – ve (b) ΔS_{surr} is +ve

(c) ΔS_{u} is – ve (d) $\Delta S_{\text{system}} \neq \Delta S_{\text{surr}}$

Case III : Read the passage given below and answer the following questions from 41 to 45.

The enthalpy of a system is defined as the sum of the internal energy of the system and the energy that arises due to its pressure and volume. Mathematically, the enthalpy is defined by the equation,

$H = U + PV$

Enthalpy change (ΔH) of a system is the heat absorbed or evolved by the system at constant pressure.

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

41. Which of the following is not correct about enthalpy?

(a) It is an extensive property.

(b) It is not a state function.

(c) Its absolute value cannot be determined.

(d) Enthalpy of a compound is equal to enthalpy of formation of that compound.

42. In which of the following reactions will ΔU be equal to ΔH?

(a) $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$

(b) $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$

(c) $N_2O_{4(g)} \longrightarrow 2NO_{2(g)}$

(d) $2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$

43. Lattice enthalpies are determined by

(a) Born-Haber cycle (b) Hess's law

(c) lattice cycle (d) none of these.

44. In which of the following thermochemical changes ΔH is always negative?

(a) Enthalpy of solution

(b) Enthalpy of hydrogenation

(c) Enthalpy of reaction

(d) Enthalpy of transition

45. The heat of a chemical reaction is given by the following expression

(a) $\Delta H = \Sigma H_R - \Sigma H_P$ (b) $\Delta H = \Sigma H_R$

(c) $\Delta H = \Sigma H_P - \Sigma H_R$ (d) $\Delta H = \Sigma H_P$

Case IV : Read the passage given below and answer the following questions from 46 to 50.

In chemical thermodynamics, the type of work involved is mostly pressure-volume work that is the work done when a system (gas) expands or contracts against an external opposing pressure. Hence, work is also defined as the transfer of energy that can be used to change the height of a mass in the surroundings.

Pressure-volume work : The work W, that is done due to the expansion or compression of a gas against an external opposing pressure P is called pressure-volume work.

$$PV = \frac{f}{A} \times V = \frac{f}{d^2} \times d^3 = f \cdot d = W$$

46. Which of the following statement is correct?

(a) $\Delta U = W_{\text{adiabatic}}$

(b) W_{ad} = + ve, when work is done on the system

(c) W_{ad} = – ve, when work is done by the system

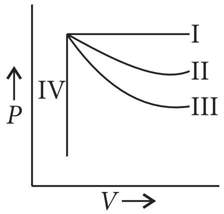
(d) All of the above.

47. A process in which the system does not exchange heat with the surroundings is known as

(a) isothermal (b) isobaric

(c) isochoric (d) adiabatic.

48. Which of the following is correct match as far as the thermodynamic processes are involved?



Curve	Thermodynamic Process
1. I	i. Adiabatic
2. II	ii. Isochoric
3. III	iii. Isobaric
4. IV	iv. Isothermal

The correct match is

	1	**2**	**3**	**4**
(a)	i	ii	iii	iv
(b)	iii	iv	i	ii
(c)	ii	i	iv	iii
(d)	iii	iv	ii	i

49. 3 moles of an ideal gas are expanded isothermally and reversibly from 10 m^3 to 20 m^3 at 300 K. The work done is (R = 8.314 J K^{-1} mol^{-1}).

(a) +5.187 kJ
(b) –5.187 kJ
(c) –2.175 kJ
(d) +3.750 kJ

50. A gas expands in vacuum. The work done by the gas is

(a) zero
(b) minimum
(c) maximum
(d) cannot be predicted.

Assertion & Reasoning Based MCQs

For question numbers 51-60, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

51. Assertion : The heat absorbed during the isothermal expansion of an ideal gas against vaccum is zero.
Reason : The volume occupied by the molecules of an ideal gas is zero.

52. Assertion : U is a state function.
Reason : T is an intensive property.

53. Assertion : Sublimation of the solid is non-spontaneous.
Reason : Sublimation is endothermic process.

54. Assertion : The sum of $q + w$ is a state function.
R**eason :** Work and heat are state functions.

55. Assertion : Enthalpy of formation of graphite is zero but of diamond it is not zero.
Reason : Enthalpy of formation of the most stable allotrope is taken as zero.

56. Assertion : Decrease in free energy causes spontaneous reaction.
Reason : Spontaneous reactions are invariable exothermic reactions.

57. Assertion : Heat of neutralisation for both H_2SO_4 and HCl with NaOH is 53.7 kJ mol^{-1}.
Reason : Both HCl and H_2SO_4 are strong acids.

58. Assertion : Some salts are sparingly soluble in water at room temperature.
Reason : The entropy increases on dissolving the salts.

59. Assertion : Spontaneous process is an irreversible process and may be reversed by some external agency.
Reason : Decrease in enthalpy is a contributory factor for spontaneity.

60. Assertion : Entropy of system increases for a spontaneous reaction.
Reason : Enthalpy of reaction always decreases for spontaneous reaction.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. State the difference between adiabatic and isothermal processes.

2. State first law of thermodynamics.

3. Define enthalpy of formation.

4. When is bond energy equal to bond dissociation energy?

5. Under what conditions will a reaction be spontaneous if both ΔH and ΔS are negative?

6. Give an example of a spontaneous process which is endothermic.

7. State the second law of thermodynamics.

8. State two ways by which the internal energy of a system may be changed.

9. Give one point of difference : Extensive and intensive properties.

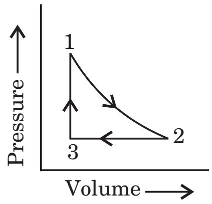
10. What will be the sign of ΔS for the following reaction?

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

Short Answer Type Questions (SA-I)

11. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol^{-1}. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vaporisation for water?

12. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in figure. What will be the value of ΔH for the cycle as a whole?



13. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also.

14. The enthalpy of reaction for the reaction :
$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ is $\Delta_r H = -572$ kJ mol^{-1}.
What will be standard enthalpy of formation of $H_2O_{(l)}$?

15. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27 °C from 10 litre to 5 litre. Calculates q, w and ΔU for this process.
(R = 2.0 cal K^{-1} mol^{-1}, atomic weight of Argon = 40)

16. Calculate the entropy change in surrounding when 1.00 mol of $H_2O_{(l)}$ is formed under standard conditions.

$\Delta_f H = -286$ kJ mol^{-1}.

17. Justify the following statements :

(a) Many thermodynamically feasible reactions do not occur under ordinary conditions.

(b) At low temperature, enthalpy change dominates the value of ΔG and at high temperature it is the entropy which dominates the value of ΔG.

18. (a) What is a thermochemical equation?

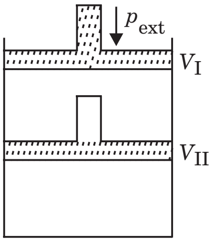
(b) Write one application of Hess's law.

19. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

20. Derive the relationship, $\Delta H = \Delta U + \Delta n_g RT$.

Short Answer Type Questions (SA-II)

21. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Figure. Explain graphically.



22. Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

23. Comment on the spontaneity of a reaction at constant temperature and pressure in the following cases :

(i) $\Delta H < 0$ and $\Delta S > 0$

(ii) $\Delta H > 0$ and $\Delta S < 0$

(iii) $\Delta H > 0$ and $\Delta S > 0$

24. (i) Classify the following processes as reversible or irreversible :

(a) Dissolution of sodium chloride.

(b) Evaporation of water at 373 K and 1 atm pressure.

(c) Mixing of two gases by diffusion.

(d) Melting of ice without rise in temperature.

(ii) When an ideal gas expands in vacuum, there is neither absorption nor evolution of heat. Why?

25. (i) Explain why the enthalpy changes for the given reactions are not enthalpies of formation of $CaCO_3$ and HBr.

(a) $CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$; $\Delta_r H = -178.3 \text{ kJ mol}^{-1}$

(b) $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$; $\Delta_r H = -72.8 \text{ kJ mol}^{-1}$

26. Benzene burns in O_2 according to the equation:

$$C_6H_{6(l)} + \frac{15}{2} O_{2(g)} \longrightarrow 3H_2O_{(g)} + 6CO_{2(g)}$$

If enthalpy of formation of $C_6H_{6(l)}$, $H_2O_{(g)}$ and $CO_{2(g)}$ are 11.7, – 68.3, and –94 k cal respectively, calculate the amount of heat liberated by burning 1 kg benzene.

27. The heat of solution of anhydrous $CuSO_4$ is –15.9 kcal and that of $CuSO_4 . 5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.

28. The molar heat of formation of $NH_4NO_{3(s)}$ is – 367.54 kJ and those of $N_2O_{(g)}$ and $H_2O_{(l)}$ are +81.46 kJ and –285.78 kJ respectively at 25 °C and 1.0 atmospheric pressure. Calculate ΔH and ΔU for the reaction,

$NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)}$

29. A heated copper block at 130 °C loses 340 J of heat to the surroundings which are at room temperature of 32 °C. Calculate

(i) the entropy change of the system (copper block)

(ii) the entropy change in the surroundings

(iii) the total entropy change in the universe due to this process.

Assume that the temperature of the block and the surroundings remains constant.

30. Assume ΔH° and ΔS° to be independent of temperature, at what temperature will the reaction given below become spontaneous?

	$N_{2(g)}$	+	$O_{2(g)}$	$\rightleftharpoons$	$2NO_{(g)}$
Given S° in $JK^{-1} mol^{-1}$	191.4		204.9		210.5

and $\Delta H^\circ = 180.8 \text{ kJ mol}^{-1}$

31. The following data is known about $ZnSO_4$: $\Delta H = 7.25 \text{ kJ mol}^{-1}$ and $\Delta S = 7.0 \text{ JK}^{-1} \text{ mol}^{-1}$. Calculate its melting point.

32. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 298 K. Given:

(a) Lattice energy of NaCl = 778 kJ mol^{-1}

(b) Hydration energy of NaCl = –774.3 kJ mol^{-1}

(c) Entropy change at 298 K = 43 J mol^{-1}

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

$$B_2H_{6(g)} + 3O_{2(g)} \longrightarrow B_2O_{3(s)} + 3H_2O_{(g)}$$

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

$2B_{(s)} + 3/2\, O_{2(g)} \longrightarrow B_2O_{3(s)}$

$\Delta H = -1273 \text{ kJ mol}^{-1}$

$H_{2(g)} + 1/2\, O_{2(g)} \longrightarrow H_2O_{(l)}$

$\Delta H = -286 \text{ kJ mol}^{-1}$

$H_2O_{(l)} \longrightarrow H_2O_{(g)}$

$\Delta H = 44 \text{ kJ mol}^{-1}$

$2B_{(s)} + 3H_{2(g)} \longrightarrow B_2H_{6(g)}$

$\Delta H = 36 \text{ kJ mol}^{-1}$

34. The enthalpy change involved in the oxidation of glucose is –2880 kJ/mol. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after consuming 125 g of glucose?

35. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L. Calculate the value of q, w, ΔU and ΔH.

($R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, at. wt. of Ar = 40)

Long Answer Type Questions (LA)

36. Answer the following :

(i) Why does entropy of a solid increases on fusion?

(ii) State the thermodynamic conditions of spontaneous occurrence of a process.

(iii) Why a non-spontaneous reaction becomes spontaneous when coupled with a suitable spontaneous reaction?

(iv) For an isolated system, $\Delta U = 0$, what will be ΔS?

37. (a) The melting point of ice is 273 K. At this temperature the enthalpy of fusion of ice is 6.025 kJ mol–1. Calculate the entropy change for melting of 1 mole of ice. State giving reason whether the entropy change for vaporization of one mole of water will be more or less than entropy change per mole for fusion of ice.

(b) Calculate the entropy change involved in the conversion of one mole of liquid water at 373 K to vapour at the same temperature (Latent heat of vaporization, $\Delta H_{vap} = 2.257$ kJ/g).

38. Calculate the standard Gibbs energy change for the combustion of α-*D* glucose at 298 K

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$

Given that standard enthalpies of formation (kJ mol^{-1})

$C_6H_{12}O_6 = -1274.5$, $CO_2 = -393.5$, $H_2O = -285.8$.

Entropies (J K^{-1} mol^{-1})

$C_6H_{12}O_6 = 212.1$, $O_2 = 205.0$, $CO_2 = 213.6$, $H_2O = 69.9$

39. A gas absorbs 120 J of heat and expands against the external pressure of 1.10 atm from a volume of 0.5 L to 2.0 L. What is the change in internal energy? (1 L atm = 101.3 J)

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

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)};\ \Delta H = -57.1 \text{ kJ}$$

Calculate the heat evolved for the following experiments:

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

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

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

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

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. (c) : In isolated system, work, energy or heat are not exchanged with the surroundings.

2. (a) : Process $A \rightarrow B$ is isochoric, *i.e.*, volume remains constant.

Process $B \rightarrow C$ is isobaric, *i.e.*, pressure remains constant.

Process $C \rightarrow A$ is isothermal, *i.e.*, temperature remains constant.

3. (a) : Work is not a state function.

4. (a) : Slope of adiabatic curve is steeper than isothermal curve.

5. (b) : $\Delta U = q + w$ if $q = 0$ for adiabatic process, then $\Delta U = w$, *i.e.*, work done on the system or work of compression brings in an increase in temperature.

6. (a) : $\Delta H = \Delta U + \Delta n_gRT \Rightarrow \Delta H = \Delta U$ if $\Delta n_g = 0$

For $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)};\ \Delta n_g = 0$

7. (c) : Volume is an extensive property.

8. (a) : Enthalpy of formation is the heat change when 1 mole of a substance is formed from its constituent elements in gaseous state.

9. (c) : In a closed system there is no exchange of matter but exchange of energy is possible. A closed vessel made of copper can exchange heat with the surroundings.

10. (b) : $C + O_2 \rightarrow CO_{2};\ \Delta_cH = -393.5$ kJ mol^{-1}

For the formation of 44 g of CO_2, 393.5 kJ mol^{-1} of heat is released.

So, heat released for the formation of 35.2 g of CO_2

$$= \frac{393.5}{44} \times 35.2 = 314.8 \text{ kJ}$$

11. (a)

12. (b) : $CCl_{4(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 4HCl_{(g)}$

$\Delta H^\circ_{f\,(\text{kcal})}$ $\quad -25.5 \quad 2 \times -57.8 \quad -94.1 \quad 4 \times -22.1$

$$\Delta H^\circ_{\text{Reaction}} = \Delta H^\circ_{f(\text{Products})} - \Delta H^\circ_{f(\text{Reactants})}$$
$$= -94.1 + 4(-22.1) - [-25.5 + 2(-57.8)]$$
$$= -182.5 + 141.1 = -41.4 \text{ kcal}$$

13. (b) : For endothermic reactions, $H_R < H_P$.

14. (c) : 1 M H_2SO_4 = 2 N H_2SO_4

As heat of neutralisation is heat evolved for 1 mole of H^+ ions, therefore enthalpy of neutralisation = –114.64/2 = –57.32 kJ

15. (c) : After applying Hess's law on the given reactions, we can get the value of heat of formation of SO_2. Hess's law states that the amount of heat evolved or absorbed in chemical change is same whether the process takes place in one step or multiple steps.

Given, $S + \frac{3}{2}O_2 \longrightarrow SO_3$, $\Delta H_1 = -2x$ kJ

$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$, $\Delta H_2 = -y$ kJ

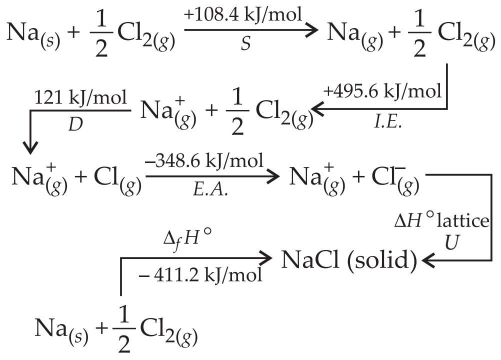
$S + O_2 \longrightarrow SO_2$, $\Delta H_3 = -z$ kJ

From Hess's law

$\Delta H_3 + \Delta H_2 = \Delta H_1 \Rightarrow -z - y = -2x$

$z = 2x - y$

16. (a) :



$\Delta_f H = S + D + I.E. + E.A. + U$

$-411.2 = 108.4 + 121 + 495.6 - 348.6 + U$

$U = -787.6$ kJ/mol ≈ – 788 kJ/mol

17. (d) : Heat of neutralization is maximum for neutralization of a strong acid with strong base.

18. (d)

19. (b) :

	N_2	+ $3H_2$	→ $2NH_3$; ΔH = ?
$B.E.$: kJ	N≡N 945	3H – H 3 × 436	6N – H 6 × 391

$$\Delta H = \Sigma B.E._{(\text{Reactants})} - \Sigma B.E._{(\text{Products})}$$
$$= 945 + 3(436) - 6(391) = -93 \text{ kJ mol}^{-1}$$

20. (c) : For free expansion $w = 0$ and for adiabatic process $q = 0$

$\Delta U = q + w = 0$ this means that internal energy remains constant.

Therefore, $\Delta T = 0$

21. (a) : $N \equiv N + 1/2\ O = O \longrightarrow N = N = O$

$\Delta H^\circ_f = \Sigma B.E.$ of reactants – $\Sigma B.E.$ of products

$= [B.E.(N \equiv N) + 1/2\ B.E.(O = O)] - [B.E.(N = N) + B.E.(N = O)]$

$= (946 + 1/2 \times 498) - (418 + 607) = 170$ kJ

Resonance energy = ΔH°_f (observed) – ΔH°_f (calculated)

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

22. (c)

23. (b) : Stronger the acid, more will be heat of neutralization. Negative sign signifies evolution of heat.

24. (a) : In isothermal process, temperature remains constant.

25. (c) : ΔS has negative value if Δn_g = –ve

i.e. number of gaseous moles decreasing during a reaction.

For (a), $\Delta n_g = 2 - 0 = 2$

For (b), $\Delta n_g = 2 - 1 = 1$

For (c), $\Delta n_g = 2 - 3 = -1$ (ΔS negative)

For (d), $\Delta n_g = 3 - 0 = 3$

26. (a) : The enthalpies of all elements in their standard state at 25° C or 298 K are zero.

27. (b)

28. (d) : For a reaction to be feasible; its free energy must be negative ;

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

In all three cases (a, b, c), ΔG is negative but in option (d), ΔG is positive which is not favourable for the feasibility of the reaction.

29. (d) : (A) : $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O$ shows combustion reaction

(B) : $H_{2(g)} \rightarrow 2H_{(g)}$ shows bond dissociation

(C) : $NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$ shows dissociation of NaCl

(D) : $NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ shows dissolution of NaCl

30. (a) : $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

For a spontaneous process, $\Delta G^\circ < 0$

i.e. $\Delta H^\circ - T\Delta S^\circ < 0$

or $\Delta H^\circ < T\Delta S^\circ$ or, $T\Delta S^\circ > \Delta H^\circ$

or $T > \frac{\Delta H}{\Delta S}$ *i.e.* $T > \frac{179.1 \times 1000}{160.2}$

or $T > 1117.9$ K ≈ 1118 K

31. (b) : For the reaction,

$H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$; $\Delta H^\circ = -124$ kcal

$\Delta H^\circ = \Sigma B.E.$ (reactants) – $\Sigma B.E.$ (products)

or $-124 = \Delta H_{H-H} + \Delta H_{F-F} - 2\Delta H_{H-F}$

$= 104 + 37.8 - 2\Delta H_{H-F}$

$\therefore \quad 2\Delta H^\circ_{H-F} = 104 + 37.8 + 124 = 265.8$ kcal

Bond energy of H–F $= \dfrac{265.8}{2} = 132.9$ kcal

$\therefore \quad \Delta H^\circ$ for the given reaction = – 132.9 kcal

32. (d) : Hess's law cannot be used for the determination of entropy.

33. (c) : $\Delta H = [-2 \times 413 + (-2 \times 328)]$

$= [-826 - 656] = -1482$ kJ/mol

34. (c) : $A \longrightarrow C, \Delta H = q_1$ ...(i)

$C \longrightarrow D, \Delta H = q_2$ ...(ii)

$D \longrightarrow 2B, \Delta H = 2q_3$ ...(iii)

Now adding (i), (ii) and (iii), we get

i.e., $q_1 + q_2 + 2q_3$, is the heat of reaction for the reaction $A \to 2B$.

35. (a) : For the reaction, $\frac{1}{2}N_2 + \frac{3}{2}Cl_2 \to NCl_3$

Applying : $\frac{1}{2}$Eqn.(ii) + Eqn(i) – $\frac{3}{2}$Eqn.(iii)

We get $\Delta H_f = \frac{1}{2}(-\Delta H_2) + (-\Delta H_1) - \frac{3}{2}\Delta H_3$

$= -\Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

36. (b) : $\Delta S = 2.303 nR \log_{10}\frac{V_2}{V_1}$

$= 2.303 \times 5 \times 8.314 \log_{10}\frac{50}{5} = 95.74 \text{ JK}^{-1}$

37. (a) : Entropy of universe is tending towards maximum.

38. (b) : $\Delta S > 0$ for irreversible process.

39. (d) : In every process randomness increases.

40. (c) : $\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$

$= -22.13 + 22.05 = -0.08$

For a spontaneous process, ΔS must be positive *i.e.*,

$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0$

41. (b) : Enthalpy is a state function.

42. (b) : $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$

$\Delta n = 2 - (1 + 1) = 0$

$\Delta H = \Delta U + \Delta nRT$

$\Delta H = \Delta U + (0)\,RT$

$\therefore \quad \Delta H = \Delta U$

43. (a) : An enthalpy diagram called Born-Haber cycle is used to determine the lattice enthalpies.

44. (b) **45. (c)**

46. (d) : For an adiabatic process, $dq = 0$

$\Delta U = W_{\text{adia}}$

The positive sign expresses that W_{ad} is positive when work is done on the system. If the work is done by the system, W_{ad} will be negative.

47. (d) : If a process is carried out under such condition that no exchange of heat takes place between the system and surroundings, the process is termed as adiabatic. The system is thermally isolated, *i.e.*, $dq = 0$ and the temperature of the system varies.

48. (b)

49. (b) : $W_{\max} = -2.303\, nRT \log\frac{V_2}{V_1}$

$n = 3$ mol, $R = 8.314$ J K^{-1} mol^{-1}, $T = 300$ K

$V_1 = 10$ m^3, $V_2 = 20$ m^3

Hence, $W_{\max} = -2.303 \times 3 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$\times\, 300 \text{ K} \times \log\frac{20\text{ m}^3}{10\text{ m}^3}$

$= -2.303 \times 3 \times 8.314 \text{ J} \times 300 \times \log 2$

$= -2.303 \times 3 \times 8.314 \text{ J} \times 300 \times 0.301$

$= -5187 \text{ J} = -5.187$ kJ

The amount of work done is –5.187 kJ.

50. (a) : $W = 0$ because $P_{ex} = 0$.

51. (b) **52. (b)**

53. (d) : Sublimation of the solid is spontaneous due to increase in entropy.

54. (c) : $\Delta E = q + w$

Internal energy is a state function, but not q or w.

55. (a) : Graphite is the most stable form.

56. (c) : Exothermic reactions are spontaneous at low temperature but becomes non-spontaneous at high temperature.

57. (a) **58. (b)**

59. (b)

60. (a) : ΔS is +ve and ΔH is –ve for a spontaneous reaction at all temperatures.

SUBJECTIVE TYPE QUESTIONS

1. In adiabatic process no heat can flow from the system to the surroundings or vice versa, whereas, in isothermal process temperature remains constant throughout the process.

2. According to first law of thermodynamics, energy can neither be created nor be destroyed although it may be changed from one form to another.

3. The enthalpy change accompanying the formation of one mole of a compound from its elements is called enthalpy of formation.

4. When bond energy is measured in isolated gaseous state, it becomes equal to bond dissociation energy.

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

Given, ΔH = –ve and ΔS = –ve

For a reaction to be spontaneous, ΔG should be negative, reaction takes place spontaneously only at lower temperature.

6. $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$

It is endothermic as well as spontaneous.

7. Whenever a spontaneous process takes place, it is always accompanied by an increase in total entropy of the universe.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

8. (i) If the work is done by or on the system.

(ii) Heat is absorbed by the system or heat is evolved from the system.

9. Extensive properties: Properties that depend on the quantity of matter contained in the system, e.g., mass, volume, etc.

Intensive properties: Properties which depend on the nature of the substance and not on the amount of substance, e.g., viscosity, etc.

10. The sign of ΔS for the reaction,

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$, is +ve as the solid changes into gaseous state

11. Enthalpy of a reaction is the energy change per mole for the process.

18 g of H_2O = 1 mole (ΔH_{vap} = 40.79 kJ mol^{-1})

For 2 moles of H_2O, enthalpy of vaporisation = 2 × 40.79
= 81.58 kJ

$\Delta H^\circ_{\text{vap}}$ = 40.79 kJ mol^{-1}

12. For a cyclic process $\Delta H = 0$

13. Molar enthalpy change for graphite (ΔH)
= enthalpy change for 1 g × molar mass of C
= – 20.7 × 12
= – 2.48 × 10^2 kJ mol^{-1}

Since the sign of ΔH = –ve, it is an exothermic reaction.

14. $2H_2 + O_2 \longrightarrow 2H_2O;\ \Delta_r H^\circ = 572$ kJ mol^{-1}

$\Delta_f H^\circ$ will be half of the enthalpy of the given equation as enthalpy of formation is the enthalpy change of the reaction when 1 mole of the compound is formed from its elements.

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O;\ \Delta_f H^\circ = \frac{-572}{2} = -286 \text{ kJ mol}^{-1}$$

15. $$W_{\text{iso, rev}} = -2.303nRT\log\frac{V_2}{V_1} = -2.303nRT\log\frac{5}{10}$$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log\frac{5}{10} = 103.9 \text{ cal}$$

For isothermal process $\Delta U = 0$

From 1st law of thermodynamics, $\Delta U = q + W$

$\therefore\ q = -W = -103.9$ cal

16. $\Delta H_f^\circ[H_2O_{(l)}] = -286$ kJ/mol

$\therefore\ q_{\text{surroundings}} = +286$ kJ/mol

$$\Delta S_{(\text{surr})} = \frac{q}{298} = \frac{286 \times 1000}{298} \text{ JK}^{-1}\text{ mol}^{-1} = 959.73 \text{ JK}^{-1}\text{ mol}^{-1}$$

17. (a) Under ordinary conditions, the average energy of the reactants may be less than the threshold energy. They require some activation energy to initiate the reaction.

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

At lower temperature, if value of ΔH is negative ΔG will be –ve and if ΔH is positive, ΔG will be positive. While at higher temperature $-T\Delta S$ will be high, thus, sign of ΔS will decide whether ΔG will be positive or negative.

18. (a) The balanced chemical equation which includes the amount of heat evolved or absorbed during the reaction is called a thermochemical equation.

(b) Hess's law is found very useful in calculating the enthalpy change for the reaction for which experimental determination is not possible.

19. Heat absorbed by the system (q) = 701 J

Work done by the system (w) = –394 J

According to first law of thermodynamics,

$\Delta U = q + w = 701 + (-394) = 701 - 394 = 307$ J

20. The enthalpy H can be written as :

$$H = U + pV \quad \text{...(i)}$$

For finite changes at constant pressure, we can write equation (i) as

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

Since p is constant, we can write

$$\Delta H = \Delta U + p\Delta V \quad \text{...(ii)}$$

Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$pV_A = n_A RT$

and $pV_B = n_B RT$

Thus, $pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$

or $p(V_B - V_A) = (n_B - n_A)RT$

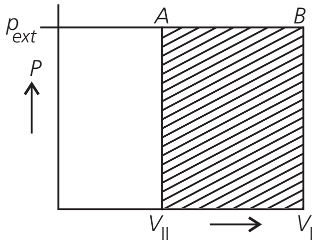
or $p\Delta V = \Delta n_g RT$ ...(iii)

where, $\Delta n_g = n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$

Substituting the value of $p\Delta V$ from equation (iii) in equation (ii), we get

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

21. Work done is equal to the shaded area ABV_IV_{II}



22. $q = \Delta U + (-w)$

$-w = p\Delta V$

$\therefore \quad q = \Delta U + p\Delta V$

At constant volumes $\Delta V = 0$

Hence, $q_V = \Delta U + 0 = \Delta U$

At constant pressure,

$q_p = \Delta U + p\Delta V$

Since $\Delta U + p\Delta V = \Delta H$

$\Rightarrow \quad q_p = \Delta H$

Hence, at constant volume and at constant pressure heat change is a state function because it is equal to ΔU and ΔH respectively which are state functions.

23. (i) Both energy factor and randomness factor favour the process. Hence, reaction will always be spontaneous.

(ii) Both factor opposes the process. Hence, reaction would always be non-spontaneous.

(iii) Energy factor opposes but randomness factor favours. For spontaneity, $T\Delta S > \Delta H$. Hence, reaction is spontaneous at high temperature and non-spontaneous at low temperature.

24. (i) (a) Reversible (b) Reversible

(c) Irreversible (d) Reversible.

(ii) In an ideal gas, there are no intermolecular forces of attraction. Hence, no energy is required to overcome these forces. Moreover, when a gas expands against vacuum, work done is zero as $P_{ext} = 0$. Hence, internal energy of the system does not change *i.e.*, there is no absorption or evolution of heat.

25. (i) (a) Given enthalpy change is not enthalpy of formation of $CaCO_3$ because it is not being formed from constituting elements.

(b) Given enthalpy change is not enthalpy of formation of HBr because 2 moles of HBr are being formed.

26. $6C + 3H_2 \longrightarrow C_6H_{6(l)}$; $\Delta H_f^\circ = 11.7$ k cal ...(i)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O_{(g)}$; $\Delta H_f^\circ = -68.3$ kcal ...(ii)

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta H_f^\circ = -94$ kcal ...(iii)

To get required equation, multiply eq. (ii) by 3 and eq. (iii) by 6 and then add; we get:

$6C + 3H_2 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$ ...(iv)

$\Delta H^\circ = -768.9$ kcal

Subtract eq. (i) from (iv), we get:

$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$

$\Delta H^\circ = -780.6$ kcal

78 g C_6H_6 gives heat = 780.6 kcal

$\therefore \quad$ 1000 g C_6H_6 will give heat = $\frac{780.6 \times 1000}{78}$

$= 10067.7$ kcal/mol

Heat liberated by burning 1 kg benzene = 10067.7 k cal/mole

27. Given:

(a) $CuSO_4 + aq \longrightarrow CuSO_4 \cdot 5H_2O_{(aq)}$; $\Delta H = -15.9$ kcal

(b) $CuSO_4 \cdot 5H_2O + aq \longrightarrow CuSO_4 \cdot 5H_2O_{(aq)}$; $\Delta H = +2.8$ kcal

subtracting eqn. (b) from (a), we get:

$CuSO_4 + 5H_2O \longrightarrow CuSO_4 \cdot 5H_2O$:

$\Delta H = -15.9 - 2.8 = -18.7$ kcal

Heat of hydration of $CuSO_4 = -18.7$ kcal

28. $NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2H_2O_{(l)}$

ΔH_f (kJ) $\quad -367.54 \quad 81.46 \quad 2 \times -285.78$

$\Delta H = \Delta H_f$ (Products) $- \Delta H_f$ (Reactants)

$= [2 \times (-285.78) + 81.46] - (-367.54)$

$= -122.56$ kJ $= -122.56 \times 10^3$ J

$\Delta n_g = n_p - n_r = 1 - 0 = 1$

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

$\Delta U = -122.56 \times 10^3 - 1 \times 8.314 \times 298$

$= -125.04 \times 10^3 J = -125.04$ kJ

29. $T_{system} = 130\,°C = 130 + 273$ K $= 403$ K,

$T_{surr} = 32\,°C = 32 + 273$ K $= 305$ K

$q_{system} = -340$ J, $q_{surr} = +340$ J

(i) $\Delta S_{system} = \frac{q_{system}}{T_{system}} = \frac{-340 \text{ J}}{403 \text{ K}} = -0.84 \text{ J K}^{-1}$

(ii) $\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{+340 \text{ J}}{305 \text{ K}} = +1.11 \text{ J K}^{-1}$

(iii) ΔS_{total} or $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$

$= -0.84 + (+1{\cdot}11)$ J K^{-1} $= 0{\cdot}27$ J K^{-1}

30. As $\Delta S^\circ = S^\circ_{Product} - S^\circ_{Reactant}$

$\Delta S^\circ = (2S^\circ_{NO}) - (S^\circ_{N_2} + S^\circ_{O_2})$

$= 2 \times 210.5 - (191.4 + 204.9)$

$= 24.7$ J K^{-1} mol^{-1} $= 24.7 \times 10^{-3}$ kJ K^{-1} mol^{-1}

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

$\Delta G^\circ = 180.8 - (T \times 24.7 \times 10^{-3})$ kJ mol^{-1}

for a spontaneous process ΔG° should be –ve which is possible if

$$T\Delta S^\circ > \Delta H^\circ;\ \ T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T > \frac{180.8\times 10^3}{24.7} = 7319\,\text{K}$$

The reaction becomes spontaneous above the temperature of 7320 K.

31. $\Delta S_{(\text{fus})} = \dfrac{\Delta H_{(\text{fus})}}{T_f}$ or $T_f = \dfrac{\Delta H_{(\text{fus})}}{\Delta S_{(\text{fus})}}$

$\Delta H_{(\text{fus})} = 7.25$ kJ mol^{-1} = $7.25 \times 1000 = 7250$ J mol^{-1}

$\Delta S_{(\text{fus})} = 7.0$ JK^{-1} mol^{-1}

$$\therefore \quad T_f = \frac{(7250\ \text{J mol}^{-1})}{(7.0\ \text{JK}^{-1}\ \text{mol}^{-1})} = 1035.7\ \text{K}$$

32. $\Delta H_{\text{dissolution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration}} = 778 - 774.3$

$= 3.7$ kJ mol^{-1} = 3700 J mol^{-1}

$\Delta S_{\text{dissolution}} = 43$ J mol^{-1}

$\therefore \quad \Delta G_{\text{dissolution}} = \Delta H - T\Delta S$

$= 3700 - 298 \times 43 = -9114$ J

or $\quad \Delta G_{\text{dissolution}} = -9.114$ kJ.

33. The given reaction can be obtained as follows:

$B_2H_{6(g)} \longrightarrow 2B_{(s)} + 3H_{2(g)}$; $\Delta H = -36$ kJ mol^{-1}

$2B_{(s)} + 3/2\ O_{2(g)} \longrightarrow B_2O_{3(s)}$; $\Delta H = -1273$ kJ mol^{-1}

$3[H_2O_{(l)} \longrightarrow H_2O_{(g)}]$; $\Delta H = 3 \times 44$ kJ mol^{-1}

$3[H_{2(g)} + 1/2\ O_{2(g)} \longrightarrow H_2O_{(l)}]$; $\Delta H = -\,3 \times 286$ kJ mol^{-1}

Adding all the above equations,

$B_2H_{6(g)} + 3O_{2(g)} \longrightarrow B_2O_{3(s)} + 3H_2O_{(g)}$;

$\Delta H = -2035$ kJ mol^{-1}

34. Energy available for muscular work from

1 mole of glucose = $\dfrac{2880\times 25}{100} = 720$ kJ/mole

Thus 180 g of glucose (mol. wt. of glucose) supplies 720 kJ energy.

125 g of glucose will supply = $\dfrac{720}{180}\times 125$ = 500 kJ

100 kJ is needed needed to walk 1 km

500 kJ is needed to walk $\dfrac{1}{100}\times 500 = 5.0$ km

35. $w = -2.303 nRT \log\dfrac{V_2}{V_1}$

$$= -2.303\times\frac{10}{40}\times 2\times 300\times\log\frac{5}{10}$$

$w = 103.991$ cal

$\Delta U = 0$, $q = \Delta U - w$

$\therefore \quad q = -w = -103.991$ cal

When temperature is constant,

$P_1V_1 = P_2V_2$ or PV = constant

$\Delta H = \Delta U + \Delta(PV) = 0 + 0 = 0.$

36. (i) In a solid, the constituent particles are fixed. On melting, they fall apart and are free to move, i.e., their randomness increases.

(ii) For spontaneous occurrence, ΔG of the process must be < 0, *i.e.*, –ve. This can be so under the following conditions :

(a) ΔH is negative and ΔS is positive (at any temperature).

(b) If ΔH and ΔS both are positive, then T should be so high that $T\Delta S < \Delta H$.

(c) If both ΔH and ΔS are negative, then T should be so low that $T\Delta S < \Delta H$.

(iii) The overall free energy change of the coupled reaction is negative.

(iv) When energy factor has no role to play, for the process to be spontaneous ΔS must be +ve *i.e.*, $\Delta S > 0$.

37. (a) $\Delta S_{(\text{fusion})} = \dfrac{\Delta H(\text{fusion})}{T} = \dfrac{6025}{273}$ = 22.07 J K^{-1} mol^{-1}.

The entropy change for the conversion of 1 mole of liquid water to steam at the boiling point will be more as compared to the value at the freezing point, because in the vaporisation randomness increases (due to the conversion of liquid into vapour) much more than in fusion.

(b) Latent heat of vaporisation per mole

$= 2.257 \times 10^3 \times 18 = 40{,}626$ J mol^{-1}

$\Delta S(\text{vap}) = \dfrac{\Delta H(\text{vap})}{T} = \dfrac{40626}{373}$ = 108.9 J K^{-1} mol^{-1}

38. As $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ_f = \Delta H^\circ_{f\,(\text{product})} - \Delta H^\circ_{f\,(\text{reactant})}$

$\therefore \quad \Delta H^\circ = [6\Delta H^\circ_f(CO_2) + 6\Delta H^\circ_f(H_2O)]$

$-\,[\Delta H^\circ_f(C_6H_{12}O_6) + 6\Delta H^\circ_f(O_2)]$

$= [6 \times (-393.5) + 6 \times (-285.8)] - [(-1274.5) + 6 \times 0]$

$[\Delta H^\circ_f(O_2) = 0]$

$= -\,2361.0 - 1714.8 + 1274.5 = -\,2801.3$ kJ mol^{-1}

Similarly $\Delta S^\circ = S^\circ_{(\text{product})} - S^\circ_{(\text{reactant})}$

$\Delta S^\circ = [6S^\circ(CO_2) + 6S^\circ(H_2O)] - [S^\circ(C_6H_{12}O_6) + S^\circ(O_2)]$

$= [6 \times (213.6) + 6 \times (69.9)] - [(212.1) + 6 \times (205.0)]$

$= [1281.6 + 419.4] - [212.1 + 1230]$

$= 258.9$ J K^{-1}mol^{-1}

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

$\Delta H^\circ = -\,2801.3$ kJ = 2801300 J mol^{-1}

$\Delta S^\circ = 258.9$ J K^{-1} mol^{-1}

$T = 298$ K

$\therefore \quad \Delta G^\circ = -\,2801300 - 298 \times (258.9)$

$= -\,2878.4$ kJ.mol^{-1}

39. Work of expansion,

$W = -P\Delta V$

$P\Delta V = -1.10 \times (2.0 - 0.5) = -1.10 \times 1.5$

$= -1.650$ L atm

$= -1.650 \times 101.3$ J (1 L atm = 101.3 J)

$= -167.1$ J

Since work is done by the system, $w = -167.1$ J

Heat absorbed by the system = 120 J or $q = +120$ J

Now, $\Delta E = q + w = 120 + (-167.1) = -47.1$ J

40. According to reaction :

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)};\ \Delta H = -57.1 \text{ kJ}$$

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

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

0.50 mole NaOH ≡ 0.50 mole OH^- ions

On mixing, 0.50 mole of water is formed.

Heat evolved for the formation of 0.50 mole of water

$= 57.1 \times 0.5 = 28.55$ kJ

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

0.30 mole KOH ≡ 0.30 mole OH^- ions

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

Heat evolved in the formation of 0.3 mole of water

$= 57.1 \times 0.3 = 17.13$ kJ

(iii) 100 mL of 0.2 M HCl will give

$100 \times \dfrac{0.2}{1000} = 0.02$ mole of H^+ ions and 100 mL of 0.3 M NaOH will give $\dfrac{0.3}{1000} \times 100 = 0.03$ mole of OH^- ions

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

Heat evolved in the formation of 0.02 mole of water

$= 0.02 \times 57.1 = 1.142$ kJ

(iv) 400 mL of 0.2M H_2SO_4 will give $\dfrac{400 \times 0.2}{1000} = 0.08$ mole of H^+ ions

and 600 mL of 0.1M KOH will give $\dfrac{600 \times 0.1}{1000} = 0.06$ mole of OH^- ions

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

Heat evolved in the formation of 0.06 mole of water

$= 0.06 \times 57.1 = 3.426$ kJ.

☺☺☺