DAY SEVEN

Chemical Thermodynamics

Learning & Revision for the Day

- Thermodynamics
- First Law of Thermodynamics
- Enthalpy
- Heat Capacity and Specific Heat
- Entropy
- Second Law of Thermodynamics
- Third Law of Thermodynamics

Thermodynamics

The study of heat or any other form of energy into or out of a system, due to some physical or chemical transformations, is called **thermodynamics.**

Some basic terms used in thermodynamics are given below:

System and Surroundings

The region where the observation of transformation of heat and work are made is known as **system** and the remaining area other than system is known as **surroundings**.

On the basis of exchange of mass and energy, systems are of three types:

- The system in which neither matter nor energy can be exchanged with surroundings is known as **isolated system.**
- The system in which only energy can be exchanged with surroundings is known as **closed system**.
- The system in which energy and matter both can be exchanged with surroundings is know as **open system**.

In thermodynamics, the thermodynamic properties are classified into two types:

- Those properties, that depend on nature of matter but do not depend on quantity of the matter are called **intensive properties**. e.g. pressure, temperature, specific heat, melting point, etc.
- Those properties, that depend on quantity of the matter present in the system are called **extensive properties.** e.g. internal energy, heat, total moles, volume, enthalpy, entropy, free energy, etc.

NOTE Force is extensive property but pressure is intensive property.

State and Path Functions

The state of a system in terms of thermodynamic properties can be described by following two ways :

- The properties which does not depend upon initial and final state of system are known as **state functions**, e.g. p, V, T, U, G, S, H, etc.
- The properties which depend upon path of the system are known as **path functions.** e.g. W and q.

Thermodynamic Process

The state of a variable can be changed by means of a **thermodynamic process.** These processes are of following types:

- The process in which system does not exchange heat with its surrounding is called **adiabatic process.** i.e. $dQ = 0$.
- The process in which temperature remains constant is called **isothermal process.** i.e. $dT = 0$.
- The process in which change of state is brought about at constant pressure is called **isobaric process**. i.e. $dp = 0$.
- The process in which volume of the system remains constant is called **isochoric process** i.e. $dV = 0$.
- The process in which a system undergoes a number of different states and finally returns to its initial state is called **cyclic process**. For such a process, change in internal energy and enthalpy is zero, i.e. $dE = 0$ and $dH = 0$.
- The process, (quasistatic system), in which change taken place is infinitesimally slow and their direction at any point can be reversed by infinitesimal change in the state of the system is called **reversible process**. It is an ideal process and here, every intermediate state is in equilibrium with others, if any.
- The process, which cannot be reversed is called **irreversible process.** In this process amount of energy increases.

Concept of Work

The work is done when gas expands or contracts against the external pressure. Work done is a path function not a state function as depends upon the path followed.

$$W = p_{\text{ext}} \times \Delta V$$

(i) For expansion $\quad W = -p_{\text{ext}}(V_2 - V_1) \quad$ [Here $V_2 > V_1$]

$$\Delta V = V_2 - V_1 = +\text{ ve}, W = -\text{ ve}$$

(ii) For compression

$$W = -p_{\text{ext}}(V_2 - V_1) \qquad [\text{Here } V_2 < V_1]$$

$$\Delta V = V_2 - V_1 = -\text{ ve}, W = +\text{ ve}$$

(iii) Maximum work done for **reversible isothermal process**

$$W_{\text{rev}} = -2.303\, nRT \log \frac{V_2}{V_1}$$

where, V_2 = final volume

V_1 = initial volume

Also, $\quad W = -2.303\, nRT \log \dfrac{p_1}{p_2}$

(iv) Maximum work done for **irreversible isothermal expansion**,

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

If expansion occurs in vacuum, i.e. at zero pressure, the value of work done is zero

$$W = -p_{\text{ext}} \times \Delta V = 0 \times \Delta V = 0$$

For adiabatic change, $q = 0$

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

Heat

It is defined as the quantity of energy, which flows between system and surroundings on account of temperature difference. It is also a path function, i.e. depends upon the path followed.

$$\boxed{H = ms\,\Delta t}$$

where, m = mass of substance $\qquad s$ = specific heat

Δt = temperature difference

NOTE

(i) Heat flowing into the system is taken as positive and heat flowing out of the system is taken as negative.

(ii) Both work and heat appear only at the boundary of the system during a change in state. Both W and q are not state functions but quantity $W + q$ is a state function.

Internal Energy (E or U)

It is the sum of all the forms of kinetic and potential energy, i.e. translational, vibrational, rotational energy, etc., associated with the system. Internal energy is a state function, i.e. it depends only on the conditions of temperature, pressure and volume.

It also depends upon the quantity of the matter contained in the system. Internal energy of ideal gases is a function of temperature. Thus, for an isothermal process, $\Delta E = 0$. Internal energy changes when heat is transferred from system [i.e. absorption].

$$U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elec}} + \ldots.$$

First Law of Thermodynamics

The first law states the conservation of energy, i.e.

"Energy can neither be created nor destroyed although it may be converted from one form to another".

$$\boxed{\Delta U = q + W}$$

where, ΔU = internal energy change

q = heat $\qquad W$ = work

Sign Conventions

(i) If W is positive then work done on the system.

(ii) If W is negative then work done by the system.

(iii) If q is positive then when heat is supplied to the system.

(iv) If q is negative then when heat is lost by the system.

(v) ΔU is negative then energy transfer from system to surrounding.

(vi) ΔU is positive then energy transfer from surrounding to system.

Enthalpy

- It is the total heat content of a system at constant pressure. Indeed, it is the sum of internal energy and the product of pressure-volume work.
- It is an extensive quantity and represented by the symbol H.

$$\mathrm{H} = U + pV, \quad \Delta H = \Delta U + p\Delta V$$

Change in enthalpy at constant pressure is given by

$$\text{or } \Delta H = \Delta U + \Delta n_g RT$$

where, ΔH = enthalpy change

Δn_g = gaseous moles of products − gaseous moles of reactants.

(i) If $\Delta n_g = 0$, then $\Delta H = \Delta U$;

(ii) If $\Delta n_g > 0$ then $\Delta H > \Delta U$ and

(iii) if $\Delta n_g < 0$ then, $\Delta H < \Delta U$.

For reaction involving solids and liquids only $\Delta H = \Delta E$.

Enthalpy also changes, when a substance undergoes phase transition.

- The difference between enthalpy of products and enthalpy of reactants is known as **enthalpy change of reaction.**

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

where, ΔH_P = sum of enthalpies of products

ΔH_R = sum of enthalpies of reactants

- The measured enthalpy of a reaction at 25°C and 1 bar pressure is known as **standard enthalpy change of reaction.** ($\Delta_r H^\ominus$)

Enthalpies for Different Types of Reactions

(i) **Enthalpy of Bond Dissociation** ($\Delta_{\text{bond}}H^\ominus$) is the enthalpy change during a chemical reaction due to formation and breaking of bonds.

$$Cl_2(g) \longrightarrow 2Cl(g); \Delta_{Cl-Cl}H^\ominus = 242 \text{ kJ mol}^{-1}$$

(ii) **Standard Enthalpy of Combustion** ($\Delta_C H^\ominus$) is the amount of energy released during the complete combustion of one mole of substance in their standard state.

$$\text{e.g. } C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O; \quad \Delta_C H^\ominus = -2658 \text{kJ/mol}$$

(iii) **Enthalpy Change of Formation** ($\Delta_f H^\ominus$) is the enthalpy change during formation of a one mole of the compound from constituent element in their standard state.

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

(iv) **Enthalpy of Atomisation** ($\Delta_a H^\ominus$) is the amount of energy required to break one mole of given substance into gaseous atom.

$$\text{e.g.} \quad H_2 \longrightarrow 2H(g); \Delta_a H^\ominus = 435.0 \text{ kJ/mol}$$

(v) **Enthalpy of Sublimation** ($\Delta_{\text{sub}}H$) is the enthalpy change during sublimation of 1 mole of solid substance to gaseous substance directly.

$$\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H$$

(vi) **Enthalpy of Phase Transition** ($\Delta_t H$) is the enthalpy change during conversion of one mole of substance from one allotrope form to another allotrope form.

$$S_{(\text{rhombic})} \longrightarrow S_{(\text{monoclinic})}; \Delta_t H = -13.14 \text{ kJ}$$

(vii) **Enthalpy of Hydration** ($\Delta_{\text{hyd}}H^\ominus$) is the enthalpy change during formation of a specific hydrates due to combination of 1 mole of salt with water.

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O; \quad \Delta_{\text{hyd}}H = 78.22 \text{ kJ}$$

(viii) **Enthalpy of Ionisation** ($\Delta_{\text{ion}}H^\ominus$) is the enthalpy change during complete conversion of one mole of weak acid or base into its constituent ions.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq); \quad \Delta_{\text{ion}}H^\ominus = -55.43 \text{ kJ/mol}$$

(ix) **Enthalpy of Solution** ($\Delta_{\text{sol}}H^\ominus$) is the enthalpy change during formation of solution when 1 mole of solute is added to excess of solvent.

$$\text{e.g. } NH_4Cl(s) + H_2O(l) \longrightarrow NH_4Cl(aq);$$

$$\Delta_{\text{sol}}H^\ominus = \Delta_{\text{lattice}}H^\ominus + \Delta_{\text{hyd}}H^\ominus$$

(x) **Enthalpy of Dilution** is the enthalpy change when solution containing one mole of solute is diluted from one concentration to other concentration.

$$HCl + 5H_2O \longrightarrow HCl \cdot 5H_2O, \; \Delta H_1 = X_1$$

$$HCl + 25H_2O \longrightarrow HCl \cdot 25H_2O; \Delta H_2 = X_2$$

$$HCl \cdot 5H_2O + 20H_2O \longrightarrow HCl \cdot 25H_2O; \Delta H = (X_2 - X_1)$$

Clausius-Clapeyron equation

$$-2.303 \log \frac{p_2}{p_1} = \frac{\Delta H_v}{R}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right)$$

[where, ΔH_v = molar heat of vaporisation, p_1 and p_2 are pressures at temperature T_1 and T_2].

- If S_1 and S_2 are solubilities at temperature T_1 and T_2 respectively.

$$\log \frac{S_1}{S_2} = \frac{\Delta H}{2.303 R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- The ratio of enthalpy of vaporisation and normal boiling point of a liquid approximately equals to

$$88 \text{ Jmol}^{-1}\text{K}^{-1} \left\{\frac{\Delta H_{\text{vap}}}{T_b} \approx 88 \text{ Jmol}^{-1}K^{-1}\right\}$$

Measurement of U and H

- For chemical reactions, heat absorbed at constant volume (ΔU) is measured in a bomb calorimeter. The following equation is used to measure the value of ΔU.

$$\Delta U = \frac{(W+m)(T_2 - T_1) \times S}{W_1} \times M \text{ kcal.}$$

where, $M =$ molecular mass of substance

$W_1 =$ mass of the substance, $T_1 =$ initial temperature

$T_2 =$ final temperature, $S =$ specific heat

- Measurement of heat change at constant pressure (ΔH) can be done in a water calorimeter. The following relationship is used to calculate ΔH,

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

Hess's Law of Constant Heat Summation

It states that total enthalpy change during complete course of reaction in a single step and several steps are equal. Therefore, enthalpy change during several steps conversion is equal to enthalpy change during single step conversion.

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

According to Hess's law, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

The important applications of Hess's law are given below

(i) Determination of heat of reaction.
(ii) Determination of heat of formation.
(iii) Determination of heat of transition.

Heat Capacity and Specific Heat

- The amount of heat required to raise the temperature of the system by 1°C is known as **heat capacity**.

$$C = \frac{q}{\Delta T}$$

- If the system consists of a single substance or a solution and weights 1 g, the heat capacity of the system is referred as **specific heat.**

$$q = C \times m \times \Delta T$$

where, $m =$ mass of substance,
$C =$ specific heat capacity.

If the system consists of a single substance or a solution and weighs 1 mole, the heat capacity of the system is referred as molar heat capacity.

- There are two types of molar heat capacities which are

(i) Molar heat capacity at constant pressure

$$C_p = C_p \times M$$

(ii) Molar heat capacity at constant volume $C_V = C_V \times M$

(C_p and C_V are specific heats at constant pressure and volume respectively and M is molecular weight of gas.)

- Some important relations of C_p and C_V are given below

(i) $C_p - C_V = R$ (R is the molar gas constant.)

$$C_p - C_V = \frac{R}{M}$$

(ii) The molar heat capacity at constant volume,

$$C_V = \left(\frac{3}{2}\right) R$$

(iii) Molar heat capacity at constant pressure,

$$C_p = \left(\frac{3}{2}\right) R + R = \left(\frac{5}{2}\right) R$$

(iv) Poisson's ratio, $\gamma = \dfrac{C_p}{C_V} = \left(\dfrac{5}{3}\right) = 1.66$

$\gamma = 1.66$ for monoatomic gases (like He, Ar)
$\gamma = 1.40$ for diatomic gases (like H_2, O_2, CO)
$\gamma = 1.33$ for triatomic gases (like H_2O, O_3)

Kirchhoff's Equation, $\Delta C_p = \dfrac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$

and $\Delta C_V = \dfrac{\Delta E_2 - \Delta E_1}{T_2 - T_1}$

where, $\Delta C_p = \Sigma C_p$ of products $- \Sigma C_p$ of reactants $\Delta C_V = \Sigma C_V$ of products $- \Sigma C_V$ of reactants

Entropy

- It is the measurement of randomness or disorder of the molecules. Entropy is a state function and depends only on initial and final states of the system, i.e. $\Delta S = S_{\text{final}} - S_{\text{initial}}$
- Unit of entropy is joule per Kelvin per mol. Entropy is the measure of unavailable energy.

Unavailable energy = entropy × temperature.

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

- For a reversible change at constant temperature

$$\Delta S = \frac{q_{\text{rev}}}{T} = S_{\text{final}} - S_{\text{initial}}$$

$q_{\text{rev}} =$ heat absorbed or evolved at absolute temperature, T

- If $\Delta S > 0$, heat is absorbed and if $\Delta S < 0$, heat is evolved.

The change of matter from one state to another is called **phase transition.** The entropy changes at the time of phase transition are as follows:

$$\Delta S_{\text{melting}} = \frac{\Delta H_{\text{fusion}}}{T_m}$$ ($T_m =$ melting point of substance)

$$\Delta S_{\text{vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T_b}$$

($T_b =$ boiling point of substance)

$$\Delta S_{\text{sublimation}} = \frac{\Delta H_{\text{sublimation}}}{T_{\text{sub}}}$$

($T_{\text{sub}} =$ sublimation temperature)

- Entropy change for an ideal gas
  (i) For isothermal process,

$$\Delta S = 2.303\ nR \log \frac{V_2}{V_1} = 2.303\ nR \log \frac{p_1}{p_2}$$

  (ii) For isobaric process, $\Delta S = 2.303 nC_p \log \frac{T_2}{p_1}$

  (iii) For isochoric process, $\Delta S = 2.303 nC_V \log \frac{T_2}{T_1}$

Spontaneous Process and Non-spontaneous Process

- A physical or chemical change that occurs by its own, i.e. without the help of an external source is called **spontaneous process.**
- A process which can neither take place by itself nor by initiation is called a **non-spontaneous process.**

Second Law of Thermodynamics

- It states that "entropy of the system and surrounding remains constant in a reversible equilibrium process, while it increases in an irreversible process."

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- In nature, all the process are irreversible (spontaneous) going to completion. Hence, entropy of the universe increases and tends to be maximum.
- **Gibbs Free Energy Change for Spontaneous and on Spontaneous Process** is a thermodynamic quantity. It is the decrease in the value of energy during the process and is equal to the useful work done by the system ($-\Delta G = -W_{\text{useful}}$). It is given by the relation

$$G = H - TS$$

- It is a state function. Hence, change in free energy (ΔG) for a process is independent of path.
- At constant temperature and pressure, the change in free energy is given by, $\Delta G = \Delta H - T\Delta S$
  This equation is also known as **Gibbs Helmholtz equation**.
  where, $\Delta G =$ Gibbs free energy (measurement of useful work)
  (i) $\Delta G > 0$, for non-spontaneous process
  (ii) $\Delta G < 0$, for spontaneous process
  (iii) $\Delta G = 0$, at equilibrium
- If $\Delta H = +\text{ve}$, $T\Delta S = +\text{ve}$, $T\Delta S > \Delta H$
  Then $\Delta G < 0$ hence, reaction becomes spontaneous
- Standard free energy change and equilibrium constant are related as $\Delta G = \Delta G^\circ + 2.303RT \log Q$
  where, $Q =$ quotient
  At equilibrium, $\Delta G = 0$
  $\therefore$ $\Delta G^\circ = -2.303RT \log K$
  $K =$ equilibrium constant

Free energy change and emf of cell are related as

$$\Delta G^\circ = -nE^\circ_{\text{cell}}F \quad \text{or} \quad \Delta G = -nFE_{\text{cell}}$$

where, $n =$ number of electrons lose or gain
$E^\circ_{\text{cell}} =$ standard electrode potential
$1\text{F} = 96500\text{C}$

Criteria for Equilibrium and Spontaneity

All spontaneous processes are quantitatively decided by temperature, enthalpy change and entropy change.

(i) **Spontaneity and Enthalpy Change** ($\Delta_r H$) The value of enthalpy change describes the spontaneity of process quantitatively as

$\Delta H = +\text{ve}$	Non-spontaneous
$\Delta H = 0$	Equilibrium state
$\Delta H = -\text{ve}$	Spontaneous

(ii) **Spontaneity and Total Entropy Change** (ΔS)

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

The value of total entropy change describes the spontaneity of process quantitatively as

$\Delta S_{\text{total}} = +\text{ve}$	Spontaneous
$\Delta S_{\text{total}} = 0$	Equilibrium
$\Delta S_{\text{total}} = -\text{ve}$	Non-spontaneous

(iii) **Effect of Temperature on Spontaneity of Process**

$\Delta_r H^-$	$\Delta_r S^-$	$\Delta_r G^-$	Reaction will be spontaneous at
–	+	–	All temperature
–	–	–	Low temperature
–	–	+	High temperature
+	+	+	Low temperature
+	+	–	High temperature
+	–	+	All temperature

NOTE Percentage efficiency of fuel % efficiency $= \frac{\Delta G}{\Delta H} \times 100$

Third Law of Thermodynamics

- According to this law, "the entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached".
- It forms the basis from which entropies at other temperatures can be measured, $\lim_{T \to 0} S = 0$

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Which of the following is an intensive property?

(a) Temperature (b) Viscosity
(c) Surface tension (d) All of these

2 Which of the following are not state functions?

I. $q + W$ II. q
III. W IV. $H - TS$

(a) I and IV (b) II, III and IV
(c) I, II and III (d) II and III

3 For the process to occur under adiabatic conditions, the correct condition is

(a) $\Delta T = 0$ (b) $\Delta p = 0$ (c) $q = 0$ (d) $W = 0$

4 Which one of the following is correct option for free expansion of an ideal gas under adiabatic condition?

→ CBSE-AIPMT 2011

(a) $q \neq 0, \Delta T = 0, W = 0$ (b) $q = 0, \Delta T = 0, W = 0$
(c) $q = 0, \Delta T < 0, W \neq 0$ (d) $q = 0, \Delta T \neq 0, W = 0$

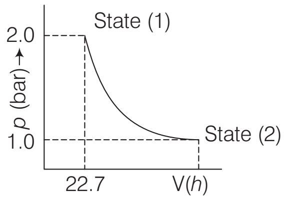
5 The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm, is

(a) – 6 J (b) – 608 J (c) + 304 J (d) – 304 J

6 The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 L to 20 L at 25°C is

(a) $2.303 \times 298 \times 0.82 \log 2$
(b) $-298 \times 10^7 \times 8.314 \times 2.303 \log 2$
(c) $2.303 \times 298 \times 0.082 \log 0.5$
(d) $2.303 \times 298 \times 2 \log 2$

7 1.0 mole of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in figure.



The work done for the expansion of gas from state (1) to state (2) at 298 K is

(a) –1717.46 J (b) –1819 J
(c) 17174 J (d) 1769.4 J

8 A piston filled with 0.04 mole of an ideal gas expands reversibly from 5.0 mL to 375 mL to at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of σ_L and W for the process will be (R = 8.314 J/mol K) (ln 7.5 = 2.01)

(a) $\sigma_L = -208$ J, $W = -208$ J (b) $\sigma_L = -208$ J, $W = +208$ J
(c) $\sigma_L = +208$ J, $W = +208$ J (d) $\sigma_L = +208$ J, $W = -208$ J

9 In a process 701 J of heat is absorbed by a system and 394 J of work is done by the system. The change in internal energy for the process will be

(a) 307 J (b) 502 J (c) 701 J (d) –394 J

10 At 27°C, one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. The value of ΔE and q are (R = 2)

(a) 0, –965.84 cal (b) –965.84 cal, –865.58 cal
(c) + 865.58 cal, –865.58 cal (d) –865.58 cal, –865.58 cal

11 One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 L to 10 L. The ΔE for this process is ($R = 2$ cal $\text{mol}^{-1}\text{K}^{-1}$)

(a) 163.7 cal (b) zero
(c) 1381.1 cal (d) 9 L atm

12 Consider the reaction;

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

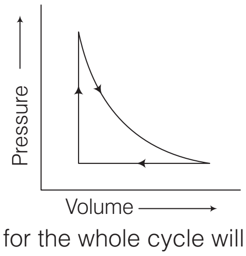
It is carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ?

(a) $\Delta H = 0$ (b) $\Delta H = \Delta U$ (c) $\Delta H < \Delta U$ (d) $\Delta H > \Delta U$

13 $\Delta E°$ of combustion of isobutylene is $-x$ kJ mol^{-1}. The value of $\Delta H°$ is

(a) $= \Delta E°$ (b) $> \Delta E°$ (c) $= 0$ (d) $< \Delta E°$

14 A sample of 1.0 mole of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in figure



The value of ΔH for the whole cycle will be

(a) 0 (b) 2 (c) 3 (d) 1

15 A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be

→ NEET 2017

(a) 1136.25 J (b) – 500 J
(c) – 505 J (d) + 505 J

16 The bond dissociation energies of X_2 Y_2 and XY are in the ratio of 1 : 0.5 : 1. ΔH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be

→ NEET 2018

(a) 800 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 200 kJ mol^{-1} (d) 400 kJ mol^{-1}

17 If enthalpies of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 250°C and 1 atm pressure is 52, –394 and –286 kJ mol^{-1} respectively. The enthalpy of combustion of $C_2H_4(g)$ will be

(a) + 1412 kJ mol^{-1} (b) –1412 kJ mol^{-1}
(c) +141.2 kJ mol^{-1} (d) –141.2 kJ mol^{-1}

18 The heat of combustion of carbon to CO_2 is –393.5kJ / mol. The heat released upon the formation of 35.2 g of CO_2 from carbon and oxygen gas is **→ CBSE-AIPMT 2015**

(a) –315 kJ mol^{-1} (b) +315 kJ mol^{-1}
(c) –630 kJ mol^{-1} (d) –3.15 kJ mol^{-1}

19 $\Delta_f U^{\ominus}$ of formation of $CH_4(g)$ at certain temperature is –393 kJ mol^{-1}.The value of $\Delta_f H^{\ominus}$ is

(a) zero (b) $< \Delta_f U^{\ominus}$
(c) $> \Delta_f U^{\ominus}$ (d) equal to $\Delta_f U^{\ominus}$

20 The heat liberated when 1.89 g of benzoic acid is burnt in a bomb calorimeter at 25°C increases the temperature of 18.94 kg of water by 0.632°C. If the specific heat of water at 25°C is 0.998 cal/g-deg, the value of the heat of combustion of benzoic acid is

(a) 881.1 kcal (b) 852.7 kcal
(c) 981.1 kcal (d) 871.2 kcal

21 Standard enthalpy of vaporisation $\Delta_{vap}H^{\circ}$ for water at 100°C is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is (assume water vapour to behave like an ideal gas).

→ CBSE-AIPMT 2012

(a) + 37.56 (b) – 43.76 (c) + 43.76 (d) + 40.66

22 On the basis of thermochemical equation (A), (B) and (C), find out which of the algebraic relationships given in option (a) to (d) is correct.

(A) $C_{(graphite)} + O_2(g) \longrightarrow CO_2(g); \Delta_C H = x \text{ kJ mol}^{-1}$

(B) $C_{(graphite)} + \frac{1}{2}O_2(g) \longrightarrow CO(g); \Delta_C H = y \text{ kJ mol}^{-1}$

(C) $CO(g) + 1/2\,O_2(g) \longrightarrow CO_2(g); \Delta_C H = z \text{ kJ mol}^{-1}$

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

23 Consider the following liquid-vapour equilibrium

→ NEET 2016, Phase I

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

Which of the following relations is correct?

(a) $\dfrac{d\ln p}{dT} = \dfrac{-\Delta H_V}{RT}$ (b) $\dfrac{d\ln p}{dT^2} = \dfrac{-\Delta H_V}{T^2}$

(c) $\dfrac{d\ln p}{dT} = \dfrac{-\Delta H_V}{RT^2}$ (d) $\dfrac{d\ln G}{dT^2} = \dfrac{-\Delta H_V}{RT^2}$

24 The volume of gas is reduced to half from its original volume. The specific heat will be

(a) reduced to half (b) doubled
(c) remains constant (d) increases 4 times

25 The average molar heat capacities of ice and water are 37.8 and 75.6 J mol^{-1} respectively and the enthalpy of fusion of ice is 6.012 kJ mol^{-1}. The amount of heat required to change 10 g of ice at –10°C to water at 10°C would be

(a) 2376 J (b) 4752 J
(c) 3970 J (d) 1128 J

26 What are the signs of the entropy change (+ or –) in the following?

I. A liquid crystallises into a solid.
II. Temperature of a crystalline solid is raised from 0 K to 115 K.
III. $2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
IV. $H_2(g) \longrightarrow 2H(g)$

	I	II	III	IV		I	II	III	IV
(a)	–	+	+	+	(b)	–	–	–	+
(c)	–	–	+	+	(d)	+	–	–	–

27 Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 J K^{-1} mol^{-1} respectively. For the reaction

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3;\ \Delta H = -30 \text{ kJ},$$

to be at equilibrium, the temperature should be

→ CBSE-AIPMT 2010

(a) 750 K (b) 1000 K (c) 1250 K (d) 500 K

28 The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is

→ CBSE-AIPMT 2012

(a) 10.52 cal/mol K (b) 21.04 cal/mol K
(c) 5.260 cal/mol K (d) 0.526 cal/mol K

29 The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to volume of 100 dm^3 at 27°C is

(a) 38.3 J mol^{-1}K^{-1} (b) 35.8 J mol^{-1}K^{-1}
(c) 32.3 J mol^{-1}K^{-1} (d) 42.3 J mol^{-1}K^{-1}

30 For the reaction, $X_2\,O_4(l) \longrightarrow 2XO_2(g)$,
$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K.
Hence, ΔG is **→ CBSE-AIPMT 2014**

(a) 2.7 kcal (b) – 2.7 kcal
(c) 9.3 kcal (d) – 9.3 kcal

31 For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by

→ NEET 2016, Phase II

(a) $\Delta S = nR \ln\left(\dfrac{p_f}{p_i}\right)$ (b) $\Delta S = nR \ln\left(\dfrac{p_i}{p_f}\right)$

(c) $\Delta S = nRT \ln\left(\dfrac{p_f}{p_i}\right)$ (d) $\Delta S = RT \ln\left(\dfrac{p_i}{p_f}\right)$

32 The correct thermodynamic conditions for the spontaneous reaction at all temperatures is

→ **NEET-2016, Phase I**

(a) $\Delta H > 0$ and $\Delta S < 0$ (b) $\Delta H < 0$ and $\Delta S > 0$
(c) $\Delta H < 0$ and $\Delta S < 0$ (d) $\Delta H < 0$ and $\Delta S = 0$

33 Which of the following statements is correct for a reversible process in a state of equilibrium?

→ **CBSE-AIPMT 2015**

(a) $\Delta G = -2.30RT \log K$ (b) $\Delta G = 2.30RT \log K$
(c) $\Delta G° = -2.30RT \log K$ (d) $\Delta G° = 2.30RT \log K$

34 Which of the following statements is correct for the spontaneous absorption of a gas?

→ **CBSE-AIPMT 2014**

(a) ΔS is negative and therefore, ΔH should be highly positive
(b) ΔS is negative and therefore, ΔH should be highly negative
(c) ΔS is positive and therefore, ΔH should be negative
(d) ΔS is positive and therefore, ΔH should also be highly positive

35 For a given reaction, $\Delta H = 35.5$ kJ mol^{-1} and $\Delta S = 83.6$JK^{-1} mol^{-1}. The reaction is spontaneous at : (Assume that ΔH and ΔS do not vary with temperature)

→ **NEET 2017**

(a) $T < 425$ K (b) $T > 425$ K
(c) all temperatures (d) $T > 298$ K

36 Standard enthalpy and standard entropy changes for the oxidation of NH_3 at 298 K are –382.64 kJ mol^{-1} and –145.6 JK^{-1} mol^{-1} respectively standard Gibbs energy change for the same reaction at 298 K is

(a) –2221.1 kJ mol^{-1}
(b) –339.3 kJ mol^{-1}
(c) –439.3 kJ mol^{-1}
(d) –523.2 kJ mol^{-1}

37 The values of ΔH and ΔS for the reaction,

$C_{(graphite)} + CO_2(g) \longrightarrow 2CO(g)$ are 170 kJ and 170 JK^{-1}, respectively. This reaction will be spontaneous at

→ **CBSE-AIPMT 2009**

(a) 710 K
(b) 910 K
(c) 1110 K
(d) 510 K

38 The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is

(Given : $\Delta_r H°_{298\text{ K}} = -54.07$ kJ mol^{-1},
$\Delta_r S°_{298\text{ K}} = 10$ JK^{-1} mol^{-1}
and $R = 8.314$ JK^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$)

(a) 5 (b) 10
(c) 95 (d) 100

39 Identify the correct statement regarding entropy.

(a) At 0°C, the entropy of a perfectly crystalline substance is taken to be zero
(b) At absolute zero of the temperature, the entropy of all perfectly crystalline substance is positive
(c) At absolute zero of the temperature, the entropy of all crystalline substance is taken to be zero
(d) At absolute zero of the temperature, the entropy of a perfectly crystalline substance is taken to be zero

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 For an isomerisation reaction $A \rightleftharpoons B$, the temperature dependence of equilibrium constant is given by

$$\log_e K = 4.0 - \frac{2000}{T}$$

The value of $\Delta S°$ at 300 K is therefore,

(a) $4R$ (b) $5R$ (c) $400R$ (d) $2000R$

2 Quantity of 0.50 mole of an ideal gas at 20°C expands isothermally against a constant pressure of 2.0 atm from 1.0 L to 5.0 L. Entropy change of the surrounding is

(a) 6.7 JK^{-1} (b) –2.8 JK^{-1} (c) 3.9 JK^{-1} (d) –6.7 JK^{-1}

3 Consider water vapour to be a perfect gas having molar enthalpy change for vaporisation of 1 mole of water at 1 bar and 100° C is 41 kJ mol^{-1}. Find the internal energy, when 1 mol of water is vaporised at one bar pressure and 100°C.

(a) +37.9kJ mol^{-1} (b) +44.1kJ mol^{-1}
(c) –37.9kJ mol^{-1} (d) –44.1kJ mol^{-1}

4 For a reaction, $\Delta H = (+3\text{ kJ})$, $\Delta S = (+10\text{ J/K})$, beyond which temperature, this reaction will be spontaneous?

(a) 200 K (b) 273 K
(c) 300 K (d) 373 K

5 The enthalpy of combustion of H_2, cyclohexene (C_6H_{10}) and cyclohexene (C_6H_{12}) are –241, –3800 and –3920 kJ per mol respectively. Heat of hydrogenation of cyclohexene is

(a) –121kJ mol
(b) +121kJ per mol
(c) +242 kJ per mol
(d) –242 kJ per mol

6 The molar heat capacity of water at constant pressure is 75 JK^{-1}mol^{-1}, when 10 kJ of heat is supplied to 100g of water which is free to expand, the increase in temperature of water is

(a) 4.8 K (b) 6.6 K
(c) 1.2 K (d) 2.4 K

7 The densities of graphite and diamond at 298 K are 2.25 and 3.31g cm^{-3} respectively. If the standard free energy difference (ΔG°) is equal to 1895 J mol^{-1}, the pressure at which graphite will be transformed into diamond at 298 K is

(a) 9.92×10^6 pa
(b) 9.92×10^5 pa
(c) 9.92×10^8 pa
(d) 9.92×10^7 pa

8 1 mole each of CaC_2 , Al_4C_3, Mg_2C_3 reacts with H_2O in separate open flask. Numerical value of work done by the system is in order

(a) $CaC_2 < Al_4C_3 = Mg_2C_3$
(b) $CaC_2 < Al_4C_3 < Mg_2C_3$
(c) $CaC_2 = Mg_2C_3 < Al_4C_3$
(d) $CaC_2 = Mg_2C_3 = Al_4C_3$

9 The ΔG values for the following reactions at 800°C are given as

$$S_2(s) + 2O_2(g) \longrightarrow 2SO_2(g);\ \Delta G = -544\ \text{kJ}$$
$$2Zn(s) + S_2(s) \longrightarrow 2ZnS(s);\ \Delta G = -293\ \text{kJ}$$
$$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s);\ \Delta G = -480\ \text{kJ}$$

The ΔG for the reaction

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

(a) –357 kJ
(b) –731 kJ
(c) –773 kJ
(d) –229 kJ

10 A gas is cooled and loses 50 J of heat. The gas contracts as it cools and work done on the system equal to 20 J is exchanged with the surroundings. Hence, ΔE is

(a) 70 J
(b) –30 J
(c) 30 J
(d) –70 J

11 One mole of an ideal gas ($C_V = 20\ \text{J K}^{-1}\ \text{mol}^{-1}$) initially at STP is heated at constant volume to twice the initial temperature. For the process, W and q will be

(a) $W = 0;\ q = 5.46$ kJ
(b) $W = 0;\ q = 0$
(c) $W = -5.46$ kJ; $q = 5.46$ kJ
(d) $W = 5.46$ kJ ; $q = 5.46$ kJ

12 A gas expands isothermally against a constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 20 dm^3. It absorbs 800 J of thermal energy from the surroundings. The ΔU is

(a) –312 J
(b) +123 J
(c) –213 J
(d) +231 J

13 1 mole of an ideal gas for which $C_V = 3/2R$ is reversibly at a constant pressure of 1 atm from 2 atm at 100°C. The ΔH is

(a) 3.725
(b) 37.5
(c) 375
(d) 3750

14 In conversion of limestone to lime

$$CaCO_3(s) \longrightarrow CaO\ (s) + CO_2(g)$$

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

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

15 The following data is given for the vapour phase reactions at constant pressure,

$$C_2H_6 \longrightarrow C_2H_5 + H,\ \Delta H = -420\ \text{kJ mol}^{-1}$$
$$C_2H_5 \longrightarrow C_2H_4 + H,\ \Delta H = 168\ \text{kJ mol}^{-1}$$

The enthalpy change for the reaction

$$2C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \text{ is}$$

(a) + 250 kJ mol^{-1}
(b) –588 kJ mol^{-1}
(c) +588 kJ mol^{-1}
(d) – 252 kJ mol^{-1}

16 Which of the following statement(s) is incorrect about the reaction given below,

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

at 25°C and 1 atm.

(a) Heat of formation of CO_2 = –94.3 kcal
(b) $\Delta H = \Delta U$
(c) Heat of combustion of C = –94.3 kcal
(d) Standard heat of formation of CO_2 = –94.3 kcal.

17 Which of the following statement(s) is correct for the mixing of two ideal gases at 30°C and 2 atm of pressure?

(a) $\Delta H_{\text{mixing}} = 0,\ \Delta G_{\text{mixing}} = 0,\ \Delta S_{\text{mixing}} = 0$
(b) $\Delta G_{\text{mixing}} = 0,\ \Delta S_{\text{mixing}} = 0,\ \Delta V_{\text{mixing}} = 0$
(c) $\Delta H_{\text{mixing}} = 0,\ \Delta G_{\text{mixing}} = 0,\ \Delta S_{\text{mixing}} > 0$
(d) $\Delta G_{\text{mixing}} = 0,\ \Delta H_{\text{mixing}} = 0,\ \Delta S_{\text{mixing}} = 0$

18 Heat of neutralisation of oxalic acid with NaOH is –106.7kJ mol^{-1}. The ΔH of following reaction will be equal to

$$H_2C_2O_4 \rightleftharpoons C_2O_4^{2-} + 2H^+$$

(a) 5.88 kJ mol^{-1}
(b) 7.94 kJ mol^{-1}
(c) –13.7 k cal mol^{-1}
(d) –5.88 kJ mol^{-1}

19 Exactly 100 J of heat was transferred revesibly to a block of gold at 25.00°C, from a thermal reservoir at 25.01°C and then exactly 100 J of heat was absorbed reversibled from the block of gold by a thermal reservoir at 24.99°C. Thus, entropy change of the system is

(a) 0.335 JK^{-1}
(b) –0.33 JK^{-1}
(c) 0.670 JK^{-1}
(d) 0.00 JK^{-1}

20 If the entropy change during freezing of water into ice (at 272 K) is –21.85 $\text{JK}^{-1}\text{mol}^{-1}$ for the system and +21.93 $\text{JK}^{-1}\text{mol}^{-1}$ for the surrounding then assert if the process is spontaneous or non spontaneous

(a) – 0.08 $\text{JK}^{-1}\ \text{mol}^{-1}$ spontaneous
(b) + 0.08 $\text{JK}^{-1}\ \text{mol}^{-1}$ spontaneous
(c) – 0.08 $\text{JK}^{-1}\ \text{mol}^{-1}$ non-spontaneous
(d) + 0.08 $\text{JK}^{-1}\ \text{mol}^{-1}$ non-spontaneous

ANSWERS

SESSION 1	**1** (d)	**2** (d)	**3** (c)	**4** (b)	**5** (b)	**6** (b)	**7** (a)	**8** (d)	**9** (a)	**10** (a)
	11 (b)	**12** (c)	**13** (d)	**14** (a)	**15** (c)	**16** (a)	**17** (b)	**18** (a)	**19** (b)	**20** (b)
	21 (a)	**22** (c)	**23** (c)	**24** (c)	**25** (c)	**26** (a)	**27** (a)	**28** (c)	**29** (a)	**30** (b)
	31 (b)	**32** (b,d)	**33** (c)	**34** (b)	**35** (b)	**36** (b)	**37** (c)	**38** (b)	**39** (d)	
SESSION 2	**1** (a)	**2** (a)	**3** (a)	**4** (c)	**5** (a)	**6** (d)	**7** (c)	**8** (c)	**9** (b)	**10** (b)
	11 (a)	**12** (c)	**13** (c)	**14** (d)	**15** (d)	**16** (d)	**17** (c)	**18** (b)	**19** (d)	**20** (b)

Hints and Explanations

SESSION 1

1 The properties of the system, value of which is independent of the amount of substance present in the system are called intensive properties, e.g. viscosity, surface tension, temperature, pressure, etc.

2 The thermodynamic parameters which depend only upon the initial and final states of system, are called **state functions,** such as enthalpy $(H = q + W)$, Gibbs free energy $(G = H - TS)$, etc. While, those parameters which depend on the path by which the process is performed rather than on the initial and final states are called **path functions,** such as work done, heat, etc.

3 For the process to occur under adiabatic conditions, $q = 0$, i.e. heat cannot flow from system to surrounding or *vice-versa*.

4 In adiabatic process, heat exchange is constant, so $q = 0$ and for free enpansion,

$$W = 0, \therefore \Delta T = 0.$$

5 Work done $(W) = -p_{\text{ext}}(V_2 - V_1)$

$$= -3 \times (6-4) = -6 \text{ L atm}$$

$$= -6 \times 101.32 \text{ J}$$

$$(\because 1 \text{ L atm} = 101.32 \text{ J})$$

$$= -607.92 \approx -608 \text{ J}$$

6 $W = -2.303 nRT \log \dfrac{V_2}{V_1}$

$$= -2.303 \times 1 \times 8.314 \times 10^7 \times 298 \log \frac{20}{10}$$

$$= -298 \times 10^7 \times 8.314 \times 2.303 \log 2$$

7 The given diagram represents that the process is carried out in infinite steps. Hence, it is isothermal reversible expansion of the ideal gas from pressure 2.0 atm to 1.0 atm at 298 K.

$$W = -2.303 nRT \log \frac{p_1}{p_2}$$

$$W = -2.303 \times 1 \times 8.314 \times 298 \times 0.3010 \text{ J}$$

$$W = -1717.46 \text{ J}$$

8 In isothermal reversible expansion, $\Delta U = 0$, thus, $\sigma_L = -W$

Therefore, $W = -208$ J

9 Internal energy change,

$$\Delta U = q + W$$

$$= 701 \text{ J} + (-394 \text{ J})$$

$$= +307 \text{ J}$$

10 $W = 2.303\, nRT \log \dfrac{p_2}{p_1}$

$$= 2.303 \times 2 \times 300 \log \frac{10}{2} = 965.84$$

At constant temperature, $\Delta E = 0$

$$\Delta E = q + W$$

$$\therefore \quad q = -W = -965.84 \text{ cal}$$

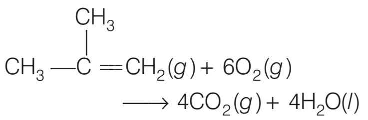
11 Isothermal process means temperature remains constant. At constant temperature, internal energy (ΔE) also remains constant. So, $\Delta E = 0$

12 At constant p or T,

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

Here, $\Delta n = n_P - n_R = 2 - 4 = -2$

$$\Delta H < \Delta U$$

13 

$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2(\mathit{g}) + 6O_2(\mathit{g}) \longrightarrow 4CO_2(\mathit{g}) + 4H_2O(\mathit{l})}$$

Here $\Delta n_g = 4 - 7 = -3$

$$\because \quad \Delta H^\circ = \Delta E^\circ + \Delta n_g RT$$

$$\therefore \quad \Delta H^\circ = \Delta E^\circ - 3RT$$

$$\Delta H^\circ < \Delta E^\circ$$

14 The net enthalpy change, ΔH for a cyclic process is zero as enthalpy change is a state function.

15 According to first law of thermodynamics,

$$\Delta U = q + W$$

where, ΔU = internal energy

q = heat absorbed or evolved, W = work done.

Also, work done against constant external pressure (irreversible process).

$$W = -p_{\text{ext}}\, \Delta V.$$

Work done in irreversible process,

$$W = -p_{\text{ext}}\, \Delta V = -p_{\text{ext}}(V_2 - V_1)$$

$$= -2.5 \text{ atm } (4.5 \text{ L} - 2.5 \text{ L})$$

$$= -5 \text{ L atm} = -5 \times 101.3 \text{ J}$$

$$= -505 \text{ J}$$

Since, the system is well insulated, $q = 0$

$\therefore \quad \Delta U = W = -505$ J

Hence, change in internal energy, ΔU of the gas is -505 J.

16 Relation between heat of reaction $(\Delta_r H)$ and bond energies (BE) of reactants and products is given by

$$\Delta_r H = \Sigma \text{BE}_{\text{Reactants}} - \Sigma \text{BE}_{\text{Products}}$$

The reaction of formation for XY is

$$\frac{1}{2} X_2(g) + \frac{1}{2} Y_2(g) \longrightarrow XY(g);\ \Delta H$$

$$= -200 \text{ kJ mol}^{-1}$$

Given the bond dissociation energies of X_2, Y_2 and XY are in the ratio 1 : 0.5 : 1. Let the bond dissociation energies of X_2, Y_2 and XY are a kJ mol^{-1}, $0.5a$ kJ mol^{-1}, respectively.

$$\therefore \quad \Delta_r H = \sum \text{BE}_{\text{Reactants}} - \Delta\text{BE}_{\text{Products}}$$
$$= \left[\frac{1}{2}\times a + \frac{1}{2}\times 0.5a\right] - [1\times a]$$
$$-200 = \frac{a}{2} + \frac{a}{4} - a$$
$$-200 = \frac{2a + a - 4a}{4} = \frac{-a}{4}$$
$$a = 800 \text{ kJ mol}^{-1}$$

$\therefore$ The bond dissociation energy of
$$X_2 = a \text{ kJ mol}^{-1}$$
$$= 800 \text{ kJ mol}^{-1}$$

17 $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$
$$\Delta H_{\text{reaction}} = [2\times \Delta H_f^\circ (CO_2) + 2\times \Delta H_f^\circ (H_2O)] - [\Delta H_f^\circ (C_2H_4) + 3\times \Delta H_f^\circ (O_2)]$$
$$= [2(-394) + 2(-286)] - [52 + 0]$$
$$= -1412 \text{ kJ mol}^{-1}$$

18 Given, $C(s) + O_2(g) \longrightarrow CO_2(g)$;
$$\Delta_f H = -393.5 \text{ kJ mol}^{-1}$$

$\because$ Heat released on formation of 44 g or 1 mole
$$CO_2 = -395.5 \text{ kJ mol}$$

$\because$ Heat released on formation of 35.2 g of CO_2
$$= \frac{-393.5 \text{ kJ mol}^{-1}}{44\text{g}} \times 35.2 \text{ g}$$
$$= -315 \text{ kJ mol}^{-1}$$

19 The reaction is
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta n_g = (n_P - n_R)_g = 1 - 3 = -2$$
$$\Delta_f H^\ominus = \Delta_f U^\ominus + \Delta n_g RT$$
As $\quad \Delta n_g = -2$
$$\therefore \quad \Delta_f H^\ominus < \Delta_f U^\ominus$$

20 Heat capacity,
$$C_V = 18.94 \times 0.998 \times 10^3$$
$$= 18.902 \times 10^3 \text{ cal/deg}$$
$$\text{Moles of benzoic acid} = \frac{1.89}{122}$$
$$C_p = C_V + R = 18.902 \times 10^3 + 2$$
$$= 20.902 \times 10^3 \text{ cal}$$
$$\text{Heat of combustion} = \frac{C_p \times \Delta t}{\text{moles}}$$
$$= \frac{20.902 \times 10^3 \times 0.632 \times 122}{1.89}$$
$$= 852.7 \times 10^3 \text{ cal}$$
$$= 852.7 \text{ kcal}$$

21 $H_2O(l) \xrightarrow{100^\circ\text{ C}} H_2O(g)$
$$\Delta_{\text{vap}} H^\circ = \Delta_{\text{vap}} E^\circ + \Delta n_g RT$$
$$\Delta_{\text{vap}} H^\circ = \text{enthalpy of vaporisation}$$
$$= 40.66 \text{ kJ mol}^{-1}$$

For the above reaction,
$$\Delta n_g = n_p - n_r = 1 - 0 = 1$$
$$R = 8.314$$
$$T = 100^\circ\text{C}$$
$$= 273 + 100$$
$$= 373 \text{ K}$$
$$\therefore \; 40.66 \text{ kJ mol}^{-1} = \Delta_{\text{vap}} E^\circ + 1 \times 8.314 \times 10^{-3} \times 373$$
$$\Delta_{\text{vap}} E^\circ = 40.66 \text{ kJ mol}^{-1} - 3.1 \text{ kJ mol}^{-1}$$
$$= +\ 37.56 \text{ kJ mol}^{-1}$$

22 $C + O_2 \longrightarrow CO_2(g)$;
$$\Delta_c H = x \text{ kJ mol}^{-1}$$
$$C_{\text{(graphite)}} + \frac{1}{2}O_2(g) \longrightarrow CO(g);$$
$$\Delta_c H = y \text{ kJ mol}^{-1}$$
$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g);$$
$$\Delta_c H = z \text{kJ mol}^{-1}$$

(i) = (ii) + (iii)

$\Rightarrow \quad x = y + z$

23 The given phase equilibria is

Liquid $\rightleftharpoons$ Vapour

This equilibrium states that, when liquid is heated, it converts into vapour but on cooling, it further converts into liquid, which is derived by Clausius Clapeyron and the relationship is written as,
$$\frac{d\ln p}{dT} = -\frac{\Delta H_V}{RT^2}$$
where, ΔH_V = Heat of vaporisation

24 Specific heat does not depend upon the volume of a substance. It is an intensive property depending only on the nature of the gas.

25 Molar heat capacity of ice
$$= 37.8 \text{ J mol}^{-1}$$
Molar heat capacity of water
$$= 75.6 \text{ J mol}^{-1}$$
Enthalpy of fusion of ice
$$= 6.012 \text{ kJ mol}^{-1}$$
$$= 6.012 \times 10^3 \text{ J mol}^{-1}$$

The conversion of 10 g of ice at -10°C to water at 10°C involves following steps

10 g of ice at $-10^\circ\text{C} \xrightarrow{\text{I}}$ 10 g ice at 0°C

10 g ice at $0^\circ \xrightarrow{\text{II}}$ 10 g water at 0°C

10 g water at $0^\circ\text{C} \xrightarrow{\text{III}}$ 10 g water at 10°C

Heat required for I step
$$= 37.8 \times \frac{10}{18} \times (-10)$$
$$= \frac{37.8 \times 10 \times 10}{18} = 210 \text{ J}$$
Heat required for II step
$$= \frac{6.012 \times 10^3 \times 10}{18} = 3340 \text{ J}$$
Heat required for III step
$$= 75.6 \times \frac{10}{18} \times 10 = 420 \text{ J}$$
Total heat required
$$= 210 + 3340 + 420 = 3970 \text{ J}$$

26 In I disorder decreases, while in case of II, III and IV disorder increases.
$$\Delta S(\text{I}) = -\text{ve}$$
$$\Delta S\ (\text{II, III, IV}) = +\text{ve}$$

27 For the reaction,
$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3; (\Delta H = -30 \text{ kJ})$$
$$\Delta S^\circ = S^\circ_{(XY_3)} - \left[\frac{1}{2}S^\circ_{X_2} + \frac{3}{2}S^\circ_{Y_2}\right]$$
$$= 50 - \left[\frac{1}{2}\times 60 + \frac{3}{2}\times 40\right]$$
$$= 50 - [30 + 60] = 50 - 90$$
$$= -40 \text{ JK}^{-1}\text{mol}^{-1}$$

We know that,
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
At equilibrium,
$$\Delta G^\circ = 0$$
$$\Delta H = T\Delta S^\circ$$
$$T = \frac{\Delta H}{\Delta S^\circ}$$
$$= \frac{-30 \times 10^3 \text{ J mol}^{-1}}{-40 \text{ J K}^{-1}\text{mol}^{-1}} = 750 \text{ K}$$

28 Molar entropy change for the melting of ice,
$$\Delta S_{\text{melt}} = \frac{\Delta H_{\text{fusion}}}{T} = \frac{1.435 \text{ kcal / mol}}{(0 + 273) \text{ K}}$$
$$= 5.26 \times 10^{-3} \text{ kcal/mol K}$$
$$= 5.26 \text{ cal/mol K}$$

29 Entropy change for isothermal expansion is
$$\Delta S = 2.303 nR \log \frac{V_2}{V_1}$$
$$= 2.303 \times 2 \times 8.314 \log \frac{100}{10}$$
$$= 38.294 = 38.3 \text{ J mol}^{-1}\text{K}^{-1}$$

30 The change in Gibbs free energy is given by

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

where, ΔH = change enthalpy of the reaction

ΔS = change entropy of the reaction

Thus, in order to determine ΔG, the values of ΔH must be known. The value of ΔH can be calculated by using equation

$$\Delta H = \Delta U + \Delta n_g RT \qquad \ldots(i)$$

where, ΔU = change in internal energy using

Δn_g = number of moles of gaseous products – number of moles of gaseous reactants = 2 – 0 = 2

R = gas constant = 2 cal

given, $\Delta U = 2.1$ kcal

$$= 2.1 \times 10^3 \text{ cal}$$

$$[\because 1 \text{ kcal} = 10^3 \text{ cal}]$$

By putting the values in eq. (i) we get,

$$\therefore \quad \Delta H = (2.1 \times 10^3) + (2 \times 2 \times 300)$$

$$= 3300 \text{ cal}$$

Hence, $\Delta G = \Delta H - T\Delta S$

$$\Rightarrow \quad \Delta G = (3300) - (300 \times 20)$$

$$\Delta G = -2700 \text{ cal}$$

$$\therefore \quad \Delta G = -2.7 \text{ kcal}$$

31 Entropy change is given as,

$$\Delta S = nC_p \ln \frac{T_f}{T_i} + nR \ln \frac{p_i}{p_f} \qquad \ldots(i)$$

For isothermal process, $T_i = T_f$

$$\therefore nC_p \ln \frac{T_f}{T_i} = nC_p \ln \frac{T_i}{T_i} = 0 \qquad [\ln 1 = 0]$$

From Eq. (i)

$$\Delta S = nR \ln \frac{p_i}{p_f}$$

32 We have the Gibbs Helmholtz reaction for spontaneity as

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

For reaction to be spontaneous, ΔG must be negative.

For this, ΔH should be negative and ΔS should be positive.

$$\therefore \quad \Delta H < 0 \text{ and } \Delta S > 0.$$

and also $\Delta S = 0$ shows ΔG a negative quantity.

33 Mathematical expression of the thermodynamic equilibrium is

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q$$

At equilibrium when $\Delta G = 0$ and $Q = K$ then $\Delta G = \Delta G^\circ + 2.303\, RT \log K = 0$

$$\Delta G^\circ = -2.303\, RT \log K$$

34 ΔS [change in entropy] and ΔH [change in enthalpy] are related by the equation $\Delta G = \Delta H - T\Delta S$

[Here, ΔG = change in Gibbs free energy]

For adsorption of a gas, ΔS is negative because randomness decreases. Thus, in order to make ΔG negative [for spontaneous reaction], ΔH must be highly negative. Hence, for the adsorption of a gas, if ΔS is negative, therefore, ΔH should be highly negative.

35 According to Gibbs-Helmholtz equation, Gibbs energy $(\Delta G) = \Delta H - T\Delta S$

Where, ΔH = Enthalpy change

ΔS = Entropy change

T = Temperature

For a reaction to be spontaneous

$$\Delta G < 0.$$

$\therefore$ Gibbs-Helmholtz equation becomes,

$$\Delta G = \Delta H - T\Delta S < 0 \text{ or, } \Delta H < T\Delta S$$

$$\text{or,} \quad T > \frac{\Delta H}{\Delta S} = \frac{35.5 \text{ kJ mol}^{-1}}{83.6 \text{ JK}^{-1}\text{mol}^{-1}}$$

$$= \frac{35.5 \times 1000}{83.6} = 425 \text{ K}$$

$$T > 425 \text{ K}$$

36 $\Delta G = \Delta H - T\Delta S$

$$= -382.64 - 298(-145.6 \times 10^{-3})$$

$$= -339.3 \text{ kJ mol}^{-1}$$

37 Given, $\Delta H = 170 \text{ kJ} = 170 \times 10^3$ J

$$\Delta S = 170 \text{ JK}^{-1};\ T = ?$$

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

For spontaneous reaction,

$$\Delta G < 0$$

$$\Rightarrow 0 < 170 \times 10^3 - T \times 170\ ;\ T > 1000$$

$$\therefore \quad T = 1110 \text{ K}$$

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

$$= -54.07 \times 10^{-3} - 298 \times 10$$

$$= -57.05 \times 10^{-3} \text{ J}$$

Also, $\Delta G^\circ = -2.303\, RT \log K$

$$\Rightarrow \quad \log K = \frac{-\Delta G^\circ}{2.303\, RT}$$

$$= \frac{57.05 \times 10^3}{2.303 \times 8.314 \times 298} = 10$$

39 This is the statement of third law of thermodynamics.

SESSION 2

1 Variation of K with temperature is given by

$$\log K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

Given, $\quad \log K = 4.0 - \dfrac{2000}{T}$

On comparing, $\dfrac{\Delta S^\circ}{R} = 4$

or $\quad \Delta S^\circ = 4R$

2 $\Delta S_{\text{system}} = 2.303\, nR \log \dfrac{V_2}{V_1}$

$$= 2.303 \times 0.5 \times 8.3143 \log \frac{5}{1}$$

$$\approx 6.7 \text{ JK}^{-1}$$

3 The change $H_2O(l) \longrightarrow H_2O(g)$

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

or $\quad \Delta U = \Delta H - \Delta n_g RT$

$$= 41 \text{ kJmol}^{-1} - 1$$

$$\times 8.314 \text{ Jmol}^{-1}\text{ K}^{-1} \times 373 \text{ K}$$

$$= 41 \text{ kJ mol}^{-1} - 3101 \text{ J mol}^{-1}$$

$$= 41 \text{ kJmol}^{-1} - 3.101 \text{ kJmol}^{-1}$$

$$= 37.9 \text{ kJ mol}^{-1}$$

4 $\Delta G = \Delta H - T\Delta S$

For spontaneous reaction, ΔG must be negative.

Given, $\quad \Delta H = +3 \text{ kJ} = 3000$ J

$\Delta S = +10$ J/K

(a) If $T = 200$ K,

$$\Delta G = 3000 - 200 \times 10 = 1000 \text{ J}$$

(b) If $T = 273$ K,

$$\Delta G = 3000 - 273 \times 10 = 270 \text{ J}$$

(c) If $T = 300$ K,

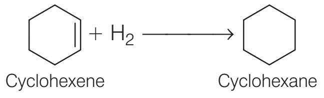
$$\Delta G = 3000 - 300 \times 10 = 0$$

(d) If $T = 373$ K,

$$\Delta G = 3000 - 373 \times 10 = -730 \text{ J}$$

Hence, beyond 300 K temperature, the reaction will be spontaneous.

5



ΔH = [ΔH of combustion of cyclohexane – ΔH of combustion of cyclohexene + ΔH of combustion of H_2)

$$= -[3920 - (-3800 - 241)]\text{kJ}$$

$$= -[-3920 + 4041]\text{kJ}$$

$$= -[121]\text{kJ} = -121 \text{ kJ}$$

6 According to heat capacity rule,

$$q = mc\Delta T, c = \frac{q}{m(T_2 - T_1)}$$

Given that, $c = 75\ \text{J K}^{-1}\ \text{mol}^{-1}$

$$q = 10\ \text{kJ} = 1000\ \text{J}$$

Mass = 100 g water

Molar mass of water = 18 g

$$75 = \frac{1000}{5.55 \times \Delta T}$$

$$\left(\text{Number of moles} = \frac{100}{18} = 5.55\right)$$

$$\Delta T = \frac{1000}{5.55 \times 75} = 2.4\ \text{K}$$

7 Volume of graphite $= \dfrac{\text{Mass}}{\text{Density}}$

$$= \frac{12}{2.25}$$

Volume of diamond $= \dfrac{12}{3.31}$

Change in volume,

$$\Delta V = \left(\frac{12}{3.31} - \frac{12}{2.25}\right) \times 10^{-3}\ \text{L}$$

$$= 1.91 \times 10^{-3}\ \text{L}$$

$$\Delta G^\circ = \text{work done} = -\ p\Delta V$$

$$p = -\frac{\Delta G^\circ}{\Delta V} = \frac{1895\ \text{J mol}^{-1}}{1.91 \times 10^{-3} \times 101.3}$$

$= 9794\ \text{atm}\ [\because 1\ \text{atm} = 10^5 \times 1.013\ \text{Pa}]$

$= 9.92 \times 10^8\ \text{Pa}$

8 $CaC_2(s) + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2(g)$

1 mol

$Al_4C_3(s) + 12\ H_2O \longrightarrow 4\ Al(OH)_3 + 3CH_4(g)$

3 mol

$Mg_2C_3(s) + 4\ H_2O \longrightarrow 2Mg(OH)_2 + C_3H_4(g)$

1 mol

Thus, $CaC_2 = Mg_2C_3 < Al_4C_3$

9 ΔG of formation of different substances are as

$2\ SO_2 = -\ 544\ \text{kJ}$, $2\ ZnS = -\ 293\ \text{kJ}$

$2\ ZnO = -\ 480\ \text{kJ}$

For the reaction,

$2ZnS + 3O_2(g) \longrightarrow 2\ ZnO(s) + 2\ SO_2(g)$

$$\Delta G = [\Delta G_{(\text{products})} - \Delta G_{(\text{reactants})}]$$

$$= [(-\ 480) + (-544) - (-\ 293)]$$

$$= -\ 1024 + 293 = -\ 731\ \text{kJ}$$

10 System loses heat, hence $q = -\ 50\ \text{J}$

Also, gas contracts due to cooling, hence $W = 20\ \text{J}$

$\therefore \Delta E = q + W = -\ 50 + 20 = -\ 30\ \text{J}$

11 $W = p\Delta V = p \times 0 = 0$

$q = C_V(\Delta T) = 20 \times 273 = 5460\ \text{J}$

12 $W = -\ p\Delta V = p^{(V_2 - V_1)} = -\ 1(20 - 10)$

$= -10\ \text{L dm}^3$

$= -10 \times 101.27\ \text{J}$

$= -\ 1012.7\ \text{J}$

$\Delta U = q + W = 800 - 1012.7 = -\ 212.7\ \text{J}$

13 $C_p - C_V = R$

$$C_p = C_V + R = \frac{5}{2}R$$

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

$$\Delta H = C_p \Delta T = \frac{5}{2}R(373 - 298)$$

$$= \frac{5}{2} \times 2 \times 75\ \text{cal} = 375\ \text{cal.}$$

14 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

For a spontaneous change, $\Delta G^\circ = -\ ve$

Thus, $T\Delta S^\circ > \Delta H^\circ$

$$\therefore T > \frac{\Delta H^\circ}{\Delta S^\circ} > \frac{179.1 \times 1000\ \text{J}}{160.2\ \text{J/K}} > 1118\ \text{K}$$

15 $C_2H_5 + H \longrightarrow C_2H_6;$

$\Delta H = -\ 420\ \text{kJ mol}^{-1}$

$\underline{C_2H_5 \longrightarrow C_2H_4 + H;}$

$\Delta H = 168\ \text{kJ mol}^{-1}$

$\therefore 2C_2H_5 \longrightarrow C_2H_6 + C_2H_4;$

$\Delta H = -\ 252\ \text{kJmol}^{-1}$

16 Standard heat of formation of a substance is defined as the enthalpy change which takes place when 1 mole of a substance is formed from its most stable allotropic form. C graphite is most stable allotropic form having $\Delta H_{\text{graphite}} = 0$

17 For mixing of two ideal gases ,

$\Delta H_{\text{mixing}} = 0\ \Delta V_{\text{mixing}} = 0$, $\Delta G_{\text{mixing}} = 0$ but entropy always increases thus

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

18 Heat of neutralisation of reaction,

$2NaOH + H_2C_2O_4 \rightleftharpoons Na_2C_2O_4 + 2H_2O;$

$\Delta H = -106.7\ \text{kJmol}^{-1}$

Since, the heat of neutralisation of strong acid and strong base $= -57.32\ \text{kJmol}^{-1}$

$$\therefore \Delta H_{\substack{\text{neutralisation of}\\ 2H^+ \text{and } OH^-}} = \Delta H_{\substack{\text{neutralisation}\\ \text{(given)}}} - \Delta H_{\text{dissociation}}$$

$$(H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-})$$

$$-57.32 \times 2 = -\ 106.7 - \Delta H_{\text{diss}}.$$

$$\Delta H_{\text{diss.}} = +\ 7.94\ \text{kJmol}^{-1}$$

19 $\Delta S_{(\text{system})} = \dfrac{q_{\text{rev}}}{T}$

$$\Delta S_{(\text{system})_1} = \frac{100\text{J}}{298\text{K}} = 0.335\ \text{JK}^{-1}$$

$$\Delta S_{(\text{system})_2} = \frac{100\text{J}}{298\text{K}} = -0.335\ \text{JK}^{-1}$$

$$\Delta S_{(\text{system})} = \Delta S_{(\text{system})_1} + \Delta S_{(\text{system})_2}$$

$$= 0.335 - 0.335 = 0.00\ \text{JK}^{-1}$$

20 $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$

$= -21.85\ \text{JK}^{-1}\ \text{mol}^{-1} + (+\ 21.93\ \text{JK}^{-1}\ \text{mol}^{-1})$

$= 0.08\ \text{JK}^{-1}\ \text{mol}^{-1}$

$\because \Delta S_{\text{process}} > 0$ at 272 K,

the freezing of ice

$H_2O(l) \longrightarrow H_2O(s)$ is a spontaneous process at 272 K.