Level-

Chapter 6

Thermodynamics

Solutions (Set-1)

Very Short Answer Type Questions :

- What type of system does the following represents? 1.
 - (a) A glass of water without lid
 - (b) A glass of water with lid
 - (c) A glass of water placed in a thermos flask
- Sol. (a) Open system
 - (b) Closed system
 - (c) Isolated system
- 2. What is an adiabatic process?
- Foundation Sol. A process during which no heat flows between the system and the surroundings is called an adiabatic process.
- Why the heat changes are generally called enthalpy changes rather than internal energy? 3.
- Sol. Because most of the processes are carried out in open vessels as constant pressure (atmospheric pressure) whereas internal energy is measured at constant volume.
- What is the significance of free energy change? 4.
- **Sol.** Free energy change signifies the useful work done by a system.
- When a system absorbs a certain amount of heat and does work, how the change in internal energy can be 5. thermodynamically related according to the first law of thermodynamics. Give the mathematical equation only.
- **Sol.** $\Delta U = q + w$, where w = negative as work is done by the system.
- Under what condition is the enthalpy change equal to the heat of reaction? 6.
- **Sol.** The enthalpy change is equal to the heat of reaction at constant pressure.

 $\Delta H = q_{p}$.

- 7. What do you understand by the reference state of a substance?
- Sol. The reference state of the substance is the state in which the substance is stable at 1 bar pressure and 298 K. It is represented by the sign \ominus in superscript.

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- 8. State Hess's law of constant heat summation.
- **Sol.** Hess's law states that the total enthalpy change of reaction is the same, regardless of whether the reaction completes in one step or in several steps.

Example :



It means the change in enthalpy from A to D *i.e.*, ΔH_4 is equal to $\Delta H_1 + \Delta H_2 + \Delta H_3$ for A \rightarrow B \rightarrow C \rightarrow D.

- 9. What is heat capacity?
- Sol. It is the quantity of heat required to raise the temperature of the system by one degree.
- 10. What is enthalpy of solution at infinite dilution?
- **Sol.** The change in enthalpy when a substance is dissolved in an infinite amount of solvent. At this point the interactions between the ions are negligible.

Short Answer Type Questions :

- 11. What factors can bring about a change in the internal energy of the system?
- Sol. The internal energy of a system changes when
 - (i) Heat is given or absorbed by the system
 - (ii) Work is done on or by the system
 - (iii) Matter enters or leave the system
- 12. Why a smooth curve is obtained when a graph is plotted for the work done by a system in the isothermal reversible expansion of an ideal gas?
- **Sol.** When reversible expansion of an ideal gas is taken into consideration, the change is brought about in number of infinite steps. The change is infinitesimally smaller such that the difference between the driving force and opposing forces are almost in equilibrium. The work done is $-\Sigma p\Delta V$. So, when the graph is plotted, they gives a smooth curve.
- 13. How the first law of thermodynamics can be justified? Give an example in support of your answer.
- **Sol.** First law of thermodynamics states that whenever a certain quantity of some form of energy is consumed, an equivalent amount of energy is produced. For example when 4.184 joules of mechanical work is done 1 calorie of heat is produced and vice-versa.
- 14. Calculate the change in internal energy of the system when it absorbs 20 kJ of heat from the surrounding and does work equivalent to 50 kJ.
- Sol. The change in internal energy is given by the expression

 $\Delta U = q + w$

Here, q = 20 kJ

w = -50 kJ (negative sign implies the work is done by the system on the surrounding)

 $\Delta U = 20 \text{ kJ} + (-50) \text{ kJ}$ = 20 - 50 kJ= -30 kJ

The internal energy of the system decreases by 30 kJ.

 One mole of carbon dioxide undergoes an isothermal and reversible expansion at 27°C from 10 L to 50 L. Calculate the work done. (R = 8.314 J)

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

 $= -2.303 \times 1 \times 8.314 \times 300 \times \log \frac{50}{10}$

= -2.303 × 8.314 × 300 × 0.699

16. State the conditions under which $q_p = q_v$ or $\Delta H = \Delta U$.

- **Sol.** (i) When the reaction is carried out in a closed vessel so that the volume remains constant, *i.e.*, $\Delta V = 0$.
 - (ii) When the reaction involves only solids or liquids or solutions but no gaseous reactants or products. This is because the volume changes of the solids and liquids during a chemical reaction are negligible.
 - (iii) When the reaction involves gaseous reactants and products but their number of moles are equal (*i.e.*, $n_p = n_r$), *e.g.*, in the reaction

 $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

17. A water storage tank placed on the top of a building contains 10³ L of water in it. It is receiving energy from the sun causing the heating effect of water. How much energy in joules would be required to raise the temperature of water from 30°C to 35°C? (Given the specific heat of water is 4.184 JK⁻¹g⁻¹)

Sol. Mass of water =
$$(10^3 \times 10^3 \text{ mL}) \times (1 \text{ gmL}^{-1})$$
 (\because D = $\frac{\text{m}}{\text{V}}$, considering density of water = 1 gmL⁻¹)

40

= 10⁶ g

 $q = m \cdot C \cdot \Delta T$ (Where $\Delta T = 35 - 30 = 5$)

$$= 10^{6} \text{ g} \times 4.184 \text{ JK}^{-1} \text{g}^{-1} \times 5$$

$$= 20.92 \times 10^{6} \text{ J}$$

- 18. What is the basic difference between enthalpy of reaction and enthalpy of formation? Illustrate with a suitable example.
- **Sol.** Enthalpy of a reaction is the amount of heat evolved or absorbed at constant temperature and at constant pressure, when number of moles of reactants represented by the chemical equation have completely reacted.

Example : CaO(s) + CO₂(g) \longrightarrow CaCO₃(s); $\Delta_r H^{\ominus} = -178.3 \text{ kJ/mol}$

Here we can see that CaCO₃(s) has not been obtained from the constituent elements C, O₂ and Ca.

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Whereas, enthalpy of formation is the amount of heat absorbed or evolved when 1 mole of compound is formed from its constituent elements under given conditions of temperature and pressure.

Example : C(s) + O₂(g) \longrightarrow CO₂(g); $\Delta_{t}H^{\ominus}$ = -393.5 kJ mol⁻¹

- 19. What do you understand by extensive and intensive properties? Give example.
- Sol. Extensive properties : Those properties which depends on the quantity of matter present in the system. Example : mass, volume, internal energy, heat capacity etc.

Intensive properties : Those properties which is independent of the quantity of matter present in the system. Example : density, melting point, boiling point, specific heat, refractive index etc.

20. Calculate ∆G° at 25°C for the reaction

$$2NO_2(g) \longrightarrow N_2O_4(g)$$

Given, $\Delta H^{\circ} = -57.20$ kJ mol⁻¹ and $\Delta S^{\circ} = -175.83$ J mol⁻¹ K⁻¹. Is the reaction spontaneous or nonspontaneous?

Sol. $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$

 $\Delta G^{\circ} = [-57.20 \times 10^3] - [298(-175.83)]$

= -57200 + 52397.34

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= -4802.66 J
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Since ΔG° is negative *i.e.*, the process is spontaneous.

21. Calculate the standard enthalpy of formation of n-butane, given that the standard enthalpies of combustion of and n-butane, C(graphite) and H₂(g) are -2878.5 kJ mol⁻¹, -393.5 kJ mol⁻¹ and -285.8 kJ mol⁻¹ respectively.

Sol. 4C(graphite) +
$$5H_2(g) \longrightarrow C_4H_{10}(g)$$

$$\Delta_{\rm f} {\rm H}^{\ominus} = \Sigma \Delta_{\rm r} {\rm H}^{\ominus}_{\rm Products} - \Sigma \Delta_{\rm r} {\rm H}^{\ominus}_{\rm Reactants}$$

= [C₄H₁₀] - [4(C) + 5(H₂)]
= [-2878.5] - [4(-393.5) + 5(-285.8)]
= [-2878.5] - [-1574 - 1429]
= -2878.5 + 3003

- $= -124.5 \text{ kJ mol}^{-1}$
- 22. (a) Predict the direction of the given reaction

$$Ag_2O(s) \implies 2Ag(s) + \frac{1}{2}O_2(g)$$

 Δ H, Δ S and T are 40.63 kJ mol⁻¹, 108.8 JK⁻¹ mol⁻¹ and 373.4 K respectively.

(b) Define bond enthalpy.

Sol. (a) $\Delta G = \Delta H - T \Delta S$

= 40.63 - 373.4 × 108.8 × 10⁻³

 $= 40.63 \times 40.63$

= 0

Since $\Delta G = 0$, system remains at equilibrium.

(b) Bond enthalpy is the amount of energy necessary to break bonds in one mole of gaseous covalent substance to form products in the gaseous state.

23. The enthalpy change (ΔH) for the reaction,

 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ is -92.38 kJ at 298 K. What is ΔU at 298 K?

Sol. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

∆H = –92.38 kJ

$$\Delta n_{a} = 2 - 4 = -2$$

R = 8.314 × 10^{-3} kJ mol⁻¹ K⁻¹

We know that

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

$$\therefore \quad \Delta U = \Delta H - \Delta n_{g} RT$$

$$= [-92.38 \text{ kJ}] - [(-2) \times 8.314 \times 10^{-3} \times 298 \text{ kJ}]$$

$$= -92.38 + 4.955$$

$$= -87.42 \text{ kJ}$$

- 24. What do you understand by the following terms?
 - (a) Heat
 - (b) Work
- **Sol.** (a) Heat is a form of energy that is transferred between the system and its surroundings as a result of temperature difference. Its symbol is q.
 - (b) By work we mean the energy is spent during the act of moving an object against an opposing forces such as gas inside the cylinder acting against the piston.
- 25. When does entropy increase in the reaction?
- Sol. Entropy increases when
 - (i) Number of molecules of products are more than the number of molecules of reactants.
 - (ii) When solid state changes to liquid state.
 - (iii) When liquid state changes to gaseous state.
 - (iv) When the substance undergo sublimation.
- 26. What does the term state variable means?
- **Sol.** The fundamental properties which determine the state of the system are termed state variables. The change in state property depends only upon the initial and final states of the system *i.e.*, independent of the path followed. Example pressure, volume, temperature, entropy, force, etc.
- 27. Calculate the work done during isothermal reversible expansion of one mole of an ideal gas from 10 atm to 1 atm at 300 K.
- Sol. Number of moles of ideal gas (n) = 1

Initial pressure $(P_1) = 10$ atm

Final pressure $(P_2) = 1$ atm

Temperature, T = 300 K

Gas constant R = $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$

:. Work done for isothermal reversible expansion of an ideal gas.

W = -2.303 nRT log
$$\frac{P_1}{P_2}$$

= -2.303 × 1 × 8.314 × 10⁻³ kJ mol⁻¹ K⁻¹ × 300 K
= -5744.14 × 10⁻³ kJ mol⁻¹

- 28. What is meant by enthalpy of formation? Given its significance.
- **Sol.** Enthalpy of formation is defined as the enthalpy accompanying the formation of one mole of a compound from its constituent elements. It is denoted by $\Delta_t H^{\ominus}$.

The knowledge of standard enthalpies of various substances can help us to calculate standard enthalpy change of any reaction. Where standard enthalpy change of a reaction is equal to the difference of the standard enthalpies of all the products and standard enthalpies of reactants.

$$\Delta_{\rm r} {\rm H}^{\ominus} = \left[\Sigma \Delta_{\rm f} {\rm H}^{\ominus}_{\rm products} \right] - \left[\Sigma \Delta_{\rm f} {\rm H}^{\ominus}_{\rm reactants} \right]$$

The heat of atomization of PH₃(g) is 228 kcal mol⁻¹ and that of P₂H₄ is 355 kcal mol⁻¹. Calculate the average bond energy of P–P bond.

Sol. $PH_3(g) \longrightarrow P(g) + 3H(g); \Delta H_1 = 228 \text{ kcal mol}^{-1}$

$$PH_2 - PH_2 \longrightarrow 2P(g) + 4H(g); \Delta H_2 = 355 \text{ kcal mol}^{-1}$$

... On the basis of the given data

 $\Delta H_2 = \Delta H_{P-P} + 4\Delta H_{P-H}$

- or $355 = \Delta H_{P-P} + 4 \times \frac{228}{3}$
- $\therefore \Delta H_{P-P} = 51 \text{ kcal mol}^{-1}$
- 30. When an ideal gas expands into vaccum, there is neither absorption nor evolution of heat. Why?
- Sol. 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 (because p_{ext} = 0). Hence, internal energy of the system does not change *i.e.*, there is no absorption or evolution of heat.

Long Answer Type Questions :

- 31. What is meant by average bond energy? In what way is it different from bond energy of a diatomic molecule? Give a suitable example.
- Sol. Average bond energy is used in the case of polyatomic molecules because even though the molecule may be containing identical bonds with the identical bond length and energy, the energy required to break the individual bonds differ in each successive step. So in such cases average bond energy is used. For example in CH₄ molecule, all the four C-H bonds are equal in bond length and energy but differs in terms of energy required to break the bonds.

$$CH_{4}(g) \longrightarrow C(g) + 4H(g); \Delta_{2}H^{\ominus} = 1665 \text{ kJ mol}^{-1}$$

 $CH_4(g) \longrightarrow CH_3(g) + H(g); \Delta_{bond}H^{\ominus} = +427 \text{ kJ mol}^{-1}$

$$\begin{array}{l} \mathsf{CH}_3(\mathsf{g}) \longrightarrow \mathsf{CH}_2(\mathsf{g}) + \mathsf{H}(\mathsf{g}); \ \Delta_{\mathsf{bond}}\mathsf{H}^{\ominus} = +439 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \\ \mathsf{CH}_2(\mathsf{g}) \longrightarrow \mathsf{CH}(\mathsf{g}) + \mathsf{H}(\mathsf{g}); \ \Delta_{\mathsf{bond}}\mathsf{H}^{\ominus} = +452 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \\ \mathsf{CH}(\mathsf{g}) \longrightarrow \mathsf{C}(\mathsf{g}) + \mathsf{H}(\mathsf{g}); \ \Delta_{\mathsf{bond}}\mathsf{H}^{\ominus} = +347 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \end{array}$$

$$\begin{array}{l} \mathsf{Therefore}, \ \Delta_{\mathsf{a}}\mathsf{H}^{\ominus} = \frac{427 + 439 + 452 + 347}{4} \\ = 416.25 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \end{array}$$

It is different from bond energy of a diatomic molecule because the energy required in diatomic molecules is to completely dissociate the molecules into atoms by breaking the covalent bonds of a gaseous covalent compound to form the products in the gaseous phase.

32. A 0.150 mol sample of an ideal gas is allowed to expand at 294 K from 10.00 atm to 1.00 atm. If external pressure is kept constant at 1.00 atm. Calculate the work done.

Sol. Initial volume V₁ =
$$\frac{nRT}{p}$$

= $\frac{0.150 \times 0.0821 \times 294}{10}$
= 0.362 dm³
Final volume V₂ = $\frac{nRT}{p}$
= $\frac{0.150 \times 0.0821 \times 294}{1}$
= 3.62 dm³
∴ w = -pΔV
= -1 × (V₂ - V₁)
= -1(3.62 - 0.362)
= -1(3.26)
= -3.26 atm dm³
or -3.26 L-atm
= -3.26 × 101.3 J (1 L-atm = 101.3 J)

33. Calculate the difference in the work done when one mole of $Al_4C_3(s)$ reacts with water in a closed vessel at 27°C against atmospheric pressure and that in an open vessel under the same condition.

 $\textbf{Sol.} \ Al_4C_3(s) + 12H_2O(l) \longrightarrow 4Al(OH)_3 + 3CH_4(g)$

1 mol

When vessel is closed, volume = constant *i.e.*, $\Delta V = 0$. Hence $W = -P\Delta V = 0$.

When the vessel is open, initial volume, $V_1 = 0$ (as no gas is present).

Final volume, V_2 = Volume of 3 mole of CH_4

$$pV_2 = nRT$$

$$V_2 = \frac{nRT}{P}$$

$$w = -p(V_2 - V_1)$$

$$= -pV_2 = -p\frac{nRT}{p}$$

$$= -3 \times 8.314 \times 300$$

= -7482.6 J

The work is done by the system on the surroundings.

34. Define the relation

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

Sol. The difference between ΔH and ΔU is not usually significant for the system consisting of only solids and/or liquids.

If V_R = total volume of the gaseous reactants

 V_{P} = total volume of the gaseous products

 n_R = number of moles of gaseous reactants

 n_{P} = number of moles of gaseous products

Then at constant temperature and pressure, assuming ideal gas behaviour, we can write

$$V_R = n_R \frac{RT}{p}$$

and $V_R = n_P \frac{RT}{p}$

and $\Delta V = V_P - V_R$

$$\Delta V = (n_{P} - n_{R}) \frac{RT}{p}$$

$$\Delta V = \Delta n_g \frac{\kappa r}{p}$$

We know that

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

$$\Delta H = \Delta U + \Delta n_g \frac{RT}{p}$$

and $\Delta H = \Delta U + \Delta n_a RT$

- 35. What is the origin of energy change in a chemical reaction?
- **Sol.** Energy is released in the formation of a chemical bond between two atoms and energy is required to break the bond. Chemical reactions involve the making and breaking of chemical bonds. Energy changes in a chemical reaction is the net difference between the energy needed to break the old chemical bonds in the reactant molecules and the energy released when new bonds are formed in the products.

For example :

$$\begin{array}{l} H_{2}(g) + CI_{2}(g) \longrightarrow 2HCI(g) \\ H - H(g) \xrightarrow[\text{Energy absorbed}\\ \text{in breaking bonds} \end{array} 2H(g); \Delta H = +436 \text{ kJ} \end{array}$$

$$CI - CI(g)$$
 $\xrightarrow{\text{Energy absorbed}}$ $2CI(g); \Delta H = 242 \text{ kJ}$

2H(g) + 2CI(g)Energy released when new bonds are formed \rightarrow 2H – Cl(g); Δ H = –866 kJ (For two moles of HCl formed)

Thus, for the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

Enthalpy change,

 $\Delta H = (436 + 242) - 866$ = 678 - 866

36. For oxidation of iron

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

entropy change is -549.4 J K⁻¹ mol⁻¹ at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous? ($\Delta_r H^{\ominus}$ for this reaction is $-1648 \times 10^3 \text{ J mol}^{-1}$)

Sol. The spontaneity of a reaction can be decided by considering

 $\Delta S_{total} = \Delta S_{(svs)} + \Delta S_{surroundings}$

For calculating ΔS_{surr} , we have to consider the heat absorbed by the surroundings which is equal to $\Delta_r H^{\ominus}$. At temperature T, entropy change of the surroundings is Aedical III Add

$$\Delta S_{surr} = \frac{\Delta_r H^{\ominus}}{T}$$
 (at constant pressure)

$$=\frac{-1648\times10^3 \text{ J mol}^3}{298 \text{ K}}$$

 $= 5530 \text{ J K}^{-1} \text{ mol}^{-1}$

Thus, total entropy change for this reaction

$$\Delta_r S_{total} = 5530 \text{ J K}^{-1} \text{ mol}^{-1} + (-549.4 \text{ J K}^{-1} \text{ mol}^{-1})$$

= 4980.6 J K⁻¹ mol⁻¹

This shows that the reaction is spontaneous.

- 37. Derive an expression for pressure volume work in a irreversible process.
- Sol. Suppose an ideal gas is enclosed in a cylinder fitted with weightless and frictionless piston of area of crosssection A. If the pressure of the gas inside the cylinder is greater than the pressure outside the cylinder (external pressure) *i.e.*, $p_{int} > p_{ext}$. Piston will move outside. This will bring a change in the volume of the gas.

The process is considered to be happening at constant temperature *i.e.*, isothermal process. The change in

volume of the gas, $\Delta V = \frac{V_2 - V_1}{(\mbox{Final}) \ (\mbox{Initial})}$.



During this expansion procedure the piston moves by a certain length ' Δ I' in a single step.

The volume change = $\Delta I \times A$

 $= \Delta V = (V_2 - V_1)$

We know, $p = \frac{F}{A}$

If w = force × displacement

$$= p_{ex} \times A \times \Delta$$

$$= p_{ex}(\Delta V)$$

And w =
$$-p_{ex}(V_2 - V_1)$$

The negative sign implies that work is done by the system on the surroundings.

38. At 60°, dinitrogen tetroxide is 50% dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Foundation Foundation

Sol. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

If N_2O_4 is 50% dissociated, the given equilibrium is

	$N_2O_4(g) \equiv$	$\implies 2NO_2(g)$			
Initial moles	1.0	0			
Equilibrium moles	0.5	2 × 0.5			
Total mole = 1 + 0.5					
Pressure = 1 atm					
Mole fraction of N ₂ O ₄ , $x_{N_2O_4} = \frac{0.5}{1.5}$					

Mole fraction of NO₂, $x_{NO_2} = \frac{1}{1.5}$

$$p_{N_2O_4} = \frac{0.5}{1.5} \times 1 \text{ atm}, \ p_{NO_2} = \frac{1}{1.5} \times 1 \text{ atm}$$

The equilibrium constant K_p is given by

$$K_{p} = \frac{(p_{NO_{2}})^{2}}{(p_{N_{2}O_{4}})} = \frac{\left[\frac{1}{1.5}\right]^{2}}{\left[\frac{0.5}{1.5}\right]} = 1.33 \text{ atm}$$

Since,

$$\Delta_r G^{\ominus} = -RT \ln K_p$$

= (-8.314 J K⁻¹ mol⁻¹) × (333 K) × (2.303) × (0.1239)
= -763.8 kJ mol⁻¹

The reaction $CH_3COOH(I) + C_2H_5OH(I) \implies CH_3COOC_2H_5(I) + H_2O(I)$ was carried out at 300 K by taking 39. 1 mol each of reactants. The reaction reached equilibrium when $\frac{2}{3}$ rd of reactants were consumed. Calculate Gibb's energy change for the reaction.

0

 $\frac{2}{3}$

Sol.

 $CH_3COOH(I) + C_2H_5OH(I) \implies CH_3COOC_2H_5(I) + H_2O(I)$ 1 mol

3

At equilibrium

Initial mole

The equilibrium constant,

$$K_{\rm C} = \frac{[\rm CH_3\rm COOC_2\rm H_5][\rm H_2\rm O]}{[\rm CH_3\rm COO\rm H][\rm C_2\rm H_5\rm O\rm H]}$$
$$= \frac{\left[\frac{2}{3}\right]\left[\frac{2}{3}\right]}{\left[\frac{1}{3}\right]\left[\frac{1}{3}\right]} = 4$$

1 mol

1

3

Since,

 $\Delta_r G^{\ominus} = -2.303 \text{ RT logK}$ $= -2.303 \times 8.314 \times 300 \times \log 4$ = -2.303 × 8.314 × 300 × 0.6020 = -3457.97 J mol⁻¹ = -3.458 kJ mol⁻¹

40. List differences between reversible and irreversible process.

Sol.		Reversible process		Irreversible process
	1.	It is a process which follows reversible path.	1.	It is a process which follows irreversible path.
	2.	It is an ideal process and takes infinite time.	2.	It is a spontaneous process and takes finite time.
	3.	In this process, the opposing force and driving force differ only by infinitesimally small magnitude.	3.	There is large difference between driving and opposing force.
	4.	Work obtained is maximum.	4.	Work obtained is not maximum.
	5.	It is only an imaginary process and cannot be realised in actual practice.	5.	It is a natural process and occurs in a particular directions under given set of conditions.
	6.	It occurs through infinite number of steps under equilibrium conditions at each step.	6.	Equilibrium exist only in the beginning and at the completion stage.

41. What are the conditions for ΔG to be negative by considering Gibb's Helmholtz equation?

Sol. Gibb's Helmholtz equation is

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

The conditions for ΔG to be negative are :

- (i) Both the energy factor as well as entropy factor are favourable *i.e.*, ΔH is negative and ΔS is positive. Under these conditions ΔG would be certainly negative and the process will be spontaneous.
- (ii) Energy factor favours but entropy factor opposes *i.e.*, ΔH is negative and ΔS is also negative. Under these conditions ΔG would be negative if ΔH is greater than T ΔS in magnitude and that would be possible at low temperature.
- (iii) Energy factor opposes but entropy factor favours *i.e.*, ΔH is positive and ΔS is also positive. Under these conditions ΔG would be negative if T ΔS is greater than ΔH in magnitude and that would be possible at high temperature.
- 42. Standard enthalpies of combustion of C₂H₄(g), C₂H₆(g) and H₂(g) are -1410.8, -1559.8 and -285.9 kJ mol⁻¹ at constant pressure and 298 K respectively. What is the enthalpy of hydrogenation of C₂H₄(g) at constant volume and at 298 K?

Sol. (i)
$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O; \Delta_cH^{\ominus} = -1410.8 \text{ kJ mol}^{-1}$$

(ii)
$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O; \Delta_cH^{\ominus} = -1559.8 \text{ kJ mol}^{-1}$$

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(I); \Delta_c H^{\ominus} = -285.9 \text{ kJ mol}^{-1}$

Our aim is :

 $(\text{iv}) \quad C_2H_4(g) + 3H_2(g) \longrightarrow C_2H_6(g); \ \Delta_cH^{\ominus} = ?$

 $-136.9 = \Delta U - 2.48$ $\Delta U = -136.9 + 2.48$

43. Calculate standard heat of formation of CS₂. Given that standard heat of combustion of C, S and CS₂ are -393.3, -293.72 and -1108.76 kJ mol⁻¹.

Sol. Our aim :

(i)
$$C(s) + 2S(s) \longrightarrow CS_2(I); \Delta H = ?$$

The data provided is :

(ii)
$$C(s) + O_2(g) \longrightarrow CO_2(g); \Delta H = -393.3 \text{ kJ mol}^{-1}$$

- (iii) $S(s) + O_2(g) \longrightarrow SO_2(g); \Delta H = -293.72 \text{ kJ mol}^{-1}$
- (iv) $CS_2(I) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g); \Delta H = -1108.76 \text{ kJ mol}^{-1}$

Multiply equation (iii) by 2, we get

(v)
$$2S(s) + 2O_2(g) \longrightarrow 2SO_2(g); \Delta H = -587.44 \text{ kJ}$$

Add equation (ii) with equation (v), we get

(vi)
$$C(s) + 2S(s) + 3O_2(g) \longrightarrow 2SO_2(g) + CO_2(g); \Delta H = -980.74 \text{ kJ}$$

Subtract equation (iv) from equation (vi), we get

 $C(s) + 2S(s) \longrightarrow CS_2(I); \Delta H = +128.02 \text{ kJ mol}^{-1}$

$$\Delta_{f}H_{CS_{2}}^{\ominus}$$
 = +128.02 kJ

- Give the appropriate reasons for the following
 - (a) Is it preferable to determine a change in enthalpy than change in internal energy?
 - (b) Is it necessary to define the 'standard state'?
 - (c) Is it necessary to specify the phases of the reactants and products in the thermochemical equation?
- **Sol**. (a) Normally the changes takes place at constant pressure (atmospheric pressure) and thus it is preferable to measure enthalpy changes.
 - (b) Yes, it is necessary to define 'standard state' because it holds significance for being at constant pressure of 1 bar and a temperature of 298 K. This state represents the most stable state of the substances.
 - (c) Yes, it is necessary to specify the phases of the reactants and products in the thermochemical equation because heat changes during the course of reaction depends on the physical states of reactants and products.
- 45. (a) Hess's law is just an extension of the law of conservation of energy. Justify the statement.
 - Bond formation is always exothermic, comment. (b)
- **Sol**. (a) The first law of thermodynamics states that energy can neither be created nor destroyed but it changes its forms. This holds true for the law of conservation of mass. Hess's law also predicts the similar fact that total energy change during the same course of reaction is independent of the path by which reaction is made.
 - (b) Formation of a bond involves decrease in the potential energy of atoms forming the bond and thus energy is released when a bond is formed. This decrease in potential energy is evolved as heat in the reaction and brings about stability of the atoms.

The energy released (or change in enthalpy) when a bond is formed from isolated gaseous atoms is known Redications of Raliash Educational as bond enthalpy.

Chapter 6

Thermodynamics

Solutions (Set-2)

First Law of Thermodynamics

- 1. Select the correct statement about heat change at constant pressure.
 - (1) Path function and extensive property
 - (3) State function and extensive property
- (2) State function and intensive property
- (4) Path function and intensive property

Sol. Answer (3)

Heat at constant pressure = ΔH

2. What is the work done in cyclic process as shown in given P-V diagram?

$$(2) -12 P_0 V_0 \qquad (3) 9 P_0 V_0 \qquad (4) - P_0 V_0$$

(1) -6 P₀V₀

Sol. Answer (1)

Magnitude of work = |Area of rectangle|

$$= (3P_0 - P_0) (4V_0 - V_0)$$
$$= (2P_0) (3V_0)$$
$$= 6P_0V_0$$

3. A gas is expanded isothermally from 2 L to 5 L volume at constant pressure of 1.5 atm. What is the change in internal energy of system? (in atm L)

(1) -3 (2) +3 (3) -6 (4) Zero

Sol. Answer (4)

 $\Delta U = nC_{\sqrt{\Delta}}T$ $\Delta T = 0 \implies \Delta U = 0$

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4. 2 moles of ideal gas is expanded reversibly from 4 atm to 3 atm at constant temperature of 300 K. Calculate the work done (approx.). [log4 = 0.6, log3 = 0.48]

(1) - 273 cal (2) - 332 cal (3) - 402 cal (4) - 315 cal

Sol. Answer (2)

W = $-2.303 \text{ nRT} \log \frac{V_2}{V_1} = -2.303 \text{ nRT} \log \frac{P_1}{P_2}$

- 5. What is the change in internal energy of 1 mole of monoatomic gas when temperature is increased by 200°C adiabatically and reversibly?
 - (1) 2.50 kJ (2) 5.9 kJ (3) 1.93 kJ (4) 3.10 kJ

Sol. Answer (1)

$$W_{rev} = \frac{nR}{y-1} [T_2 - T_1]$$
$$= \frac{1 \times 8.314 \times 200}{\frac{5}{3} - 1} = 2.5 \text{ kJ}$$

[Thermochemistry]

6. The heat of reaction for P_4 (white, s) + $6Cl_2(g) \rightarrow 4PCl_3(I)$ is - 1280 kJ. What is the heat of formation of $PCl_3(I)$ (in kJ/mol)?

$$(1) - 640 (2) - 540 (3) - 320 (4) - 290$$

Sol. Answer (3)

$$\frac{1}{4}P_4$$
 (white, s)+ $\frac{3}{2}Cl_2(g) \rightarrow PCl_3, \Delta H_f^\circ$

7. Calculate standard heat of combustion of ethanol ($C_2H_5OH(I)$). Given that Δ_fH° (C_2H_5OH , I) = - 278 kJ/mol, Δ_fH° (C_2 , g) = - 394 kJ and Δ_fH° (H_2O , I) = - 286 kJ/mol.

Sol. Answer (2)

$$\begin{split} & C_2H_5OH(I) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(I) \\ & \Delta_CH^\circ = 2\Delta_fH^\circ(CO_2) + 3\Delta_fH^\circ(H_2O) - \Delta_fH^\circ(H_2O) \\ & = 2(-394) + 3(-286) - (-278) \\ & = -1,368 \text{ kJ/mol} \end{split}$$

- 8. Among following standard enthalpy of formation is non-zero for
 - (1) C (graphite) (2) $Br_2(I)$ (3) $H_2(g)$ (4) $I_2(g)$

Sol. Answer (4)

For $I_2(s)$, $\Delta_f H^\circ = 0$

What is the heat of reaction of following reaction? 9. $3C(g) + 4H_2(g) \rightarrow H_3C \longrightarrow CH_3(g)$ Given that BE of H-H = x, H-C = y and C-C = z. (1) 4x - 2z - 8y (2) x - y - z (3) 4x - 2y - 2z (4) 4y + 5x - zSol. Answer (1) $\Delta H_r = 4(BE \text{ of } H_2) - 2BE(C - C) - 8 BE(C - H)$ 10. The heat of formation of CO₂ is -407 kJ/mol. The energy required for the process $3CO_2(g) \rightarrow 3C(g) + 2O_3(g)$ is (1) Less than 1221 kJ (2) More than 1221 kJ (3) Is equal to 1221 kJ (4) Cannot be predicted Sol. Answer (2) $\Delta H_{f(CO_2)}$ for 3 moles will be = 3 × 407 = 1221 kJ :. With O₂ it should be greater than 1221 kJ 11. The heat of combustion of sucrose $C_{12}H_{22}O_{11}$ (s) at constant volume is -1348.9 kcal mol⁻¹ at 25°C, then the heat of reaction at constant pressure, is (1) - 1348.9 kcal (2) – 1342.344 kcal 1250 kcal – 1250 kcal (3)**Sol.** Answer (1) $\begin{array}{ccc} C_{12}H_{22}O_{11} & + & 12O_2 \\ (s) & & (g) \end{array} \xrightarrow{(g)} & 12CO_2 & + & 11H_2O \\ \end{array}$ 12. For the reaction, $C_7H_8(I) + 9O_2(g) \longrightarrow 7CO_2(g) + 4H_2O(I),$ the calculated heat of reaction is 232 kJ mol⁻¹ and observed heat of reaction is 50.4 kJ mol⁻¹, then the resonance energy is (1) – 181.6 kJ mol⁻¹ (2) + 181.6 kJ mol⁻¹ (3) 172 kJ mol⁻¹ (4) -172 kJ mol^{-1} Sol. Answer (1) Resonance Energy = $-232 - (-50.4) = -182.2 \text{ kJ mol}^{-1}$ 13. Given that $A(s) \longrightarrow A(I)$ $\Delta H = x$ $A(I) \longrightarrow A(g)$ $\Delta H = y$ The heat of sublimation of A will be

(1) x - y (2) x + y (3) x or y (4) -x + y

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Sol. Answer (2)

According to Hess's law $\Delta H_{sub} = x + y$

- 14. AB, A₂ and B₂ are diatomic molecules. If the bond enthalpies of A₂, AB and B₂ are in the ratio 1 : 1 : 0.5 and enthalpy of formation of AB from A_2 and B_2 is -100 kJ mol⁻¹. What is the bond enthalpy of A_2 ?
 - (3) 300 kJ mol⁻¹ (1) 400 kJ mol⁻¹ (2) 200 kJ mol⁻¹ (4) 100 kJ mol⁻¹
- **Sol.** Answer (1)

 $\frac{1}{2}A_2 + \frac{1}{2}B_2 \longrightarrow \frac{1}{2}AB$ $\Delta H = \frac{1}{2}$ B.E. of H₂ + $\frac{1}{2}$ B.E. of B₂ - B.E. of A-B

[Second Law of Thermodynamics]

(4)

- 15. For the reaction $2HgO(s) \rightarrow 2Hg(l) + O_2(g)$
 - (1) $\Delta H > 0$ and $\Delta S < 0$
 - (3) $\Delta H < 0$ and $\Delta S < 0$

 $\Delta H > 0$ and $\Delta S > 0$ (2)

 $\Delta H < 0$ and $\Delta S > 0$

Sol. Answer (2)

 $2HgO(s) \rightarrow 2Hg(l) + O_2(g)$

It is endothermic [:: $\Delta n_g > 0$]

- $\therefore \Delta H > 0 \text{ and } \Delta S > 0$
- Foundation 16. If the entropy of vaporisation of a liquid is 110 JK⁻¹ mol⁻¹ and its enthalpy of vaporisation is 50 kJmol⁻¹. The boiling point of the liquid is

(1) 354.5 K	(2) 454.5 K	(3) 554.5 K	(4)	445.5 K
Answer (2)		A ANDS		
ΔS_{vap} = 110 J/K/mol		Consol.		
$\Delta H_{vap} = 50 \times 10^3 \text{ J/mol}$	There	Divisio		

Sol. Answer (2)

$$\Delta S = \frac{\Delta H}{T_{B,P}}$$

$$T_{B.P.} = \frac{50 \times 10^3}{110} = 454.54 \text{ K}$$

17. 1 mole of an ideal gas is expanded from an initial pressure of 1 bar to final pressure of 0.1 bar at constant temperature of 273 K. Predict which of the following is not true.

(1) $\Delta E = 0$ (2) $\Delta H = 0$ (3) PV is constant (4) ∆S < 0

Sol. Answer (4)

For an isothermal process, $\Delta E = 0$, PV = constant, $\Delta H = 0$ and $\Delta S > 0$.

18. Which of the following conditions should be satisfied for the given reaction to be spontaneous at 0°C and 1 atm?

 $H_2O(s) \longrightarrow H_2O(l)$

(1)
$$\Delta H = \Delta G$$
 (2) $\Delta H < T\Delta S$ (3) $\Delta H > T\Delta S$ (4) $\Delta H = T\Delta S$

Sol. Answer (2)

If $\Delta H < T \Delta S$

The $\Delta G < 0$ (–ve) and reaction will be spontaneous

- 19. The free energy change due to a reaction is zero when
 - (1) The reactants are initially mixed

(2) A catalyst is added

(3) The system is at equilibrium

(4) The reactants are completely consumed

Sol. Answer (3)

At equilibrium $\Delta G = 0$

20. From the given graph



Which of the following statement is correct?

- (1) The point B represents the state of equilibrium
- (2) The equilibrium composition strongly favours the reactant
- (3) From the point B formation of product is equally spontaneous as of reactant
- (4) From the point B formation of reactant is more spontaneous than that of product

Sol. Answer (1)

At equilibrium $\Delta G = 0$

- 21. For which of the following reaction, entropy change is positive?
 - (1) $H_2(g) + O_2(g) \rightarrow H_2O_2(I)$ (2) $CH_3OH(I) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(I)$

$$(3) \quad 2NO_2(g) \rightarrow N_2O_4(g)$$

(4)
$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

Sol. Answer (4)

 $\Delta ng > 0 \implies$ Entropy change is positive.

22. What is the value of $\Delta S_{universe}$ for a spontaneous reaction?

(1) Greater than zero (2) Less than zero (3) Zero (4) Always negative

Sol. Answer (1)

If $\Delta S_{universe}$ = Positive

23. The reaction $4AI(s) + 3O_2(g) \rightarrow 2AI_2O_3(s)$ is exothermic in nature. The reaction would be

- (1) Spontaneous at all temperature
- (3) Spontaneous at high temperature

(2) Spontaneous at low temperature

Foundation

(4) Non-spontaneous always

Sol. Answer (2)

 $\Delta H = -ve, \Delta S = -ve$

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

Reaction would be spontaneous only at low temperature.

- 24. The value of ΔG° is -1.2 kcal/mol at 600 K for a reaction at equilibrium. The value of its equilibrium constant is
 - (1) e^{-1} (2) e^2 (3) e (4) e^{-2}
- Sol. Answer (3)

 $\Delta G^{\circ} = - RT ln K$

$$-1.2 = -\frac{2 \times 600}{1000}$$
 ln K

- \Rightarrow In K = 1
 - K_{eq} = e
- 25. Select the correct statement.
 - (1) Exothermic reaction is always spontaneous
 - (2) Endothermic reaction is always Non-spontaneous
 - (3) Exothermic reaction is always spontaneous if entropy change of reaction is positive
 - (4) Endothermic reaction is always non-spontaneous if entropy change of reaction is positive

Sol. Answer (3)

For spontaneous process

 $\Delta G = \Delta H - T \Delta S < 0$

 ΔH = -ve for exothermic process

- 26. 1 mol of diatomic ideal gas expands from 1 L to 10 L in reversible isothermal process. The entropy change ∆S of surrounding for this process
 - (1) + 1.9 J/mol K (2) 8.3 J/mol K (3) 19.15 J/mol K (4) + 14.2 J/mol K
- Sol. Answer (3)

 $\Delta S_{System} = n Rln(v_2/v_1)$ (Isothermal process)

 $\Delta S_{Surr} = -n Rln (v_2/v_1)$

 $= -1 \times 8.31 \times \ln(10)$

27. According to second law of thermodynamics,

- (1) Heat can't flow spontaneously from a reservoir at lower temperature to a reservoir at higher temperature
- (2) All spontaneous process leads to increase in entropy of universe
- (3) Melting a solid increases entropy, therefore a spontaneous process
- (4) All of these

Sol. Answer (4)

All statements are representing second law of thermodynamics.

28. Consider the following sequence of reaction at 300 K

Reaction :

	$I:M\toN,$	$\Delta H^{\circ} = x kJ$		
	$II:N\toO,$	∆H° = y kJ		
	III : $O \rightarrow P$,	$\Delta H^{\circ} = z kJ$		
	x, y and z are positive inte	eger and x > y > z		
	S° : M > N > O > P	(at 300 K)		
	Select the Nonspontaneou	s reaction at 300 K.		5
	(1) $P \rightarrow N$	(2) $O \rightarrow M$	(3)	$M \to P \qquad (4) P \to O$
Sol.	Answer (3)			130
	For spontaneous process 2	∆G = –ve	7.	110 inite
	∆H = –ve			4. Out incest
	∆S = +ve			Sal Sal
	S : M > N > O > P			cation the
	ΔΗ ΔS		$\langle \cdot \rangle$	- HOU
	$P \rightarrow N = -ve +ve$		Par 2	3.
	$O \to M \texttt{=} - \texttt{ve} \texttt{+} \texttt{ve}$	i Ca	°,	
	$M \to P = \texttt{+ve} - \texttt{ve}$	1econisio		
	$P \rightarrow O = -ve +ve$	2.		
29.	In which of the following pr	ocess, the entropy decrease	es?	
	(1) $4NO_2(g) + O_2(g)$	$\rightarrow 2N_2O_5(g)$	(2)	$2HCI(g) \longrightarrow H_2(g) + CI_2(g)$
	_ , , _ , , _ , , , , , , , , , , , , ,			
	(3) $2NH_3(g) \longrightarrow N_2(g)$	$)+3H_{2}(g)$	(4)	$CH_4(g) \longrightarrow C(g) + 4H(g)$
Sol.	Answer (1)			
	In reaction 1, number of ga	aseous molecule decreases		
30.	Conversion of diamond to g	graphite is		
	(1) Spontaneous only at hi	igh temperature	(2)	Spontaneous only at low temperature
	(3) Always non-spontaneo	us	(4)	Always Spontaneous

Sol. Answer (4)

 $\text{Diamond} \rightarrow \text{Graphite}$

 $\Delta S = +ve$

 $\Delta H = -ve$

 \Rightarrow G = -ve (always)

One mole of monoatomic ideal gas at temperature T₁ K is compressed adiabatically and final temperature becomes T₂ K. Select the correct relation.

(2) $T_1 = T_2$

(4) Cannot be compared

(1) $T_1 > T_2$

(3) $T_1 < T_2$

Sol. Answer (3)

For adiabatic process

For compression w = +ve

 $\Delta U = +ve$

So $T_2 > T_1$

32. Calculate the average molar heat capacity at constant volume of a mixture containing 2 moles of monoatomic and 3 moles of diatomic ideal gas.

(1) R	(2)	2.1 R	(3)	3.2 R	In inite	(4)	4 R

Sol. Answer (2)

$$\frac{n_{1}C_{V_{1}} + n_{2}C_{V_{2}}}{n_{1} + n_{2}} = C_{V \text{ (average)}}$$

33. What is the change in entropy when 2.5 mole of water is heated from 27°C to 87°C?

Given
$$C_{P,M}(H_2O) = 4.2 \text{ J/g} [ln 1.2 = 0.18]$$

(1) 16.4 J K⁻¹ (2) 34.02 J K⁻¹ (3) 2.89 J K⁻¹ (4) 18.2 J K⁻¹

Sol. Answer (2)

$$\Delta S = nC_P \int_{T_1}^{T_2} dln T$$

34. Which amount the following is most soluble in water?

	Compound	∆H _{hydration} (kJ mol ⁻¹)	ΔH _{lattice} (K)
(1)	А	-400	+500
(2)	В	-300	+650
(3)	С	-200	+150
(4)	D	-100	+250

Sol. Answer (3)

Miscellaneous

35. A hungry man weighing 80 kg take quickly 20 g lunch, and then climbs up a mountain making it to a height of 200 m. If 60% of food energy was wasted as heat and the rest was used as climbing work. The fuel intake could have been any one of the following with given enthalpy of combustion?

(4)

- Glucose 16 kJ/g
- (3) Fructose syrup 13 kJ/g

(2)Wheat bread 20 kJ/g Olive oil 35 kJ/q

Sol. Answer (2)

Work done = $M \times a \times displacement$

= 80 × 9.8 × 200 = 156.8 kJ

40% of total energy = 156.8 kJ

100% of total energy = $\frac{156.8 \times 100}{40}$ = 392 kJ

- If an element X has three allotropes A, B and C. If heat of combustion at standard state for A, B and C are -36. 100, -150 and -110 kJ/mol respectively. The correct order of stability is
 - (2) B > C > A(3) A > C > B A = B = C(1) A > B > C(4)
- Sol. Answer (3)

[Heat of Combustion] decreases as Stability increases.

37. Considering the reaction $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) + 200 \text{ kJ}$. The signs of ΔH , ΔS and ΔG respectively are

(1) +, -, -(2) -, +, +

Sol. Answer (4)

38. For the reaction,

 $NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$

The value of ΔH at 27°C is 12 kcal, what is the value of ΔU for the reaction? [R = 2.0 cal K⁻¹mol⁻¹]

- Divisions (3) 9.8 kcal (1) 10.8 kcal (2) 11.8 kcal (4) 12.8 kcal
- Sol. Answer (1)

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

 $\Delta U = 12 - \frac{2 \times 2 \times 300}{1000} = 10.8 \text{ kcal}$

39. The heat of combustion of ethene (C_2H_4) is -1409.3 kJ/mol. Calculate the weight of ethene required to produce 470 kJ of heat on combustion.

(1) 12.5 g (2) 9.34 q (3) 23 g (4) 18.4 g

Sol. Answer (2)

1409.3 kJ heat is produced by = 28 g ethene

470 kJ heat will be produced by = $\frac{28}{1409.3} \times 470 = 9.34$ g

24 Thermodynamics

40. Two moles of an ideal gas is compressed isothermally and reversibly from a volume 2 L to 0.5 L at initial pressure of 1 atm. The work done by gas is (Given 1 L atm = 101 J)

(1) 280 J 250 J (2)150 J (3) 184 J (4) Sol. Answer (1) w = - 2.303 nRT log $\frac{V_2}{V_4}$ $= -2.303 P_1 V_1 \log \frac{V_2}{V_1}$ $= -2.303 \times 1 \times 2 \log \frac{0.5}{2}$ = 2.76 L atm ≃ 280 J 41. During an adiabatic process, a gas obey $TV^{0.4}$ = constant. The gas could be (1) He (2) SO_2 (3) N_2 (4) NH_3 Sol. Answer (3) $TV^{\gamma-1}$ = constant $\gamma - 1 = 0.4$ $\gamma = 1.4$ \Rightarrow Diatomic gas 42. In which of the following reaction, $K_p \ge K_c$ at 25°C? PCI₅(g) $\rightarrow PCl_3(g) + Cl_2(g)$ (1) $H_2(g) + I_2(g) \implies 2HI(g)$ (2) (3) $2H_2O(g) \longrightarrow 2H_2(g) + O_2(g)$ All of these (4)Sol. Answer (4) 43. A system performs 5 J of work on its surroundings and absorbs 95 J heat from surroundings. The change in internal energy of the system is +90 J (3) -100 J (4) (1) +100 J (2)-90 J Sol. Answer (2) q = +95 J, w = -5 J $\Delta U = q + w = 90 J$ 44. Average bond energy of S-F and C-H is x and y. if y is 2 times of x $SF_{6} \longrightarrow S(g) + 6F(g)$ $\Delta H_{r}^{o} = Q \ kJ$ $CH_4(g) \longrightarrow C(g) + 4H(g) \quad \Delta H_r^\circ = P \ kJ$ (1 mol) Then $\frac{Q}{P}$ is (1) 1 1.5 6 (2)(3)0.75 (4)

Sol. Answer (2)

- Q = 12x P = 4y $\frac{Q}{P} = \frac{12x}{4y} = 3 \times \frac{1}{2} = 1.5$
- 45. The heat of neutralisation of a strong acid and strong base is 57 kJ/mol. The heat released when 0.4 moles of HCl solution reacts with 0.3 moles of NaOH is
 - (1) 57.0 kJ (2) 11.4 kJ (3) 17.1 kJ (4) 22.8 kJ

Sol. Answer (3)

Heat released = $0.3 \times 57 = 17.1 \text{ kJ}$

46. One mole of a perfect gas expands isothermally to ten times of its original volume. The change in entropy is

(1) 0.1 R (2) 10 R (3) 2 R (4) 2.303 R

Sol. Answer (4)

 $\Delta S = nRln\frac{V_2}{V_1}$

47. Bond energies of H – H bond is 80 kJ/mol, I – I bond is 100 kJ/mol and for H – I bond is 200 kJ/mol, the enthalpy of the reaction :

 $\mathrm{H_2}(g)$ + $\mathrm{I_2}(g) \rightarrow 2\mathrm{HI}(g)$ is

(1) -120 kJ (2) -220 kJ (3) +100 kJ (4) +120 kJ

Sol. Answer (2)

 $H_2(g) + I_2(g) → 2HI(g)$ ΔH = ΣB.E_r - ΣB.E_n = 80 + 100 - 2 × 200 = - 220 kJ

- 48. The enthalpy of formation of H₂O(*I*) is −280.70 kJ/mol and enthalpy of neutralisation of a strong acid and strong base is −56.70 kJ/mol. What is the enthalpy of formation of OH⁻ ions?
 - (1) –22.9 kJ/mol (2) –224 kJ/mol (3) –58.7 kJ/mol (4) –214 kJ/mol

Sol. Answer (2)

 $\Delta H_{f(OH^-)} = -280 - (56.70) = -224 \text{ kJ/mole}$

- 49. The heat of neutralisation of a strong dibasic acid in dilute solution by NaOH is nearly
 - (1) -27.4 kcal/eq (2) 13.7 kcal/mol (3) -13.7 kcal/eq (4) -13.7 kcal/mol
- **Sol.** Answer (3)
 - $H^+ + OH^- \rightarrow H_2O$ $\Delta H = -13.7 \text{ kcal/eq}$
- 50. The heat released in neutralisation of HCl and NaOH is 13.7 kcal/mol, the heat released on neutralisation of NaOH with CH_3COOH is 3.7 kcal/mol. The ΔH° of ionisation of CH_3COOH is
 - (1) 10.2 kcal (2) 10 kcal (3) 3.7 kcal (4) 9.5 kcal

26	Thermodynamics		Solutions of Assignment (Level-I) (Set-2)
Sol.	Answer (2)		
	∆H = 13.7 – 3.7 = 10 kcal		
51.	Which of the following reactions represents the entha	lpy of	formation of water?
	(1) $H^+(aq) + OH^-(aq) \rightarrow H_2O(I)$	(2)	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(I)$
	(3) $2H_2(g) + O_2(g) \rightarrow 2H_2O(I)$	(4)	$2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(I)$
Sol.	Answer (2)		
	Enthalpy associated with formation of one mole of wa	ater fro	om its constituent elements in their natural states.
52.	The energy required to break 76 g gaseous fluorine energy of $F-F$ bond will be	into fr	ree gaseous atom is 180 kcal at 25°C. The bond
	(1) 180 kcal (2) 90 kcal	(3)	45 kcal (4) 104 kcal
Sol.	Answer (2)		
	$F_2 \rightarrow 2F_{38g}$		
	∵ 76 g F ₂ needs 180 kcal energy		
	$\therefore 38 \text{ g F}_2 \text{ needs energy} = \frac{180}{76} \times 38 = 90 \text{ kcal}$		
53.	The heat of combustion of yellow phosphorus and respectively. Then the heat of transition of yellow phose	red p sphorus	ohosphorus are -9.91 kJ/mol and - 8.78 kJ/mol is to red phosphorus is
	(1) -18.69 kJ (2) +1.13 kJ	(3)	+18.69 kJ (4) –1.13 kJ
Sol.	Answer (4)		olli ssili
	$P \rightarrow P$ (yellow) P (red)		the massen
	$\Delta H_{\text{Transition}} = -9.91 - (-8.78) = -1.13 \text{ kJ}$	127	N LOAND
54.	Which of the following represents heat of formation (2	∆H _f)?	Sherry Contraction of the second seco
	(1) C(diamond) + $O_2(g) \rightarrow CO_2(g)$	(2)	$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
	(3) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \to HF(g)$	(4)	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Sol. Answer (3)

There is formation of one mole of gas from its constituent elements in their standard states.

$$\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$$

55. 10 g of each Pb, Al , Ag and Cu is given 100 kJ of heat and temperature rise is x, y, z and w kelvins respectively.

Then select the correct relation. [given heat capacity (in J/g k) is 0.9, 0.386, 0.233 and 0.128 for Al, Cu, Ag and Pb respectively]

(1) x < y (2) y < w (3) z < w (4) x < z

Sol. Answer (2)

 $\Delta T \propto \frac{1}{\text{heat capacity}}$ so x > z > w > y

56. In a process, 120 J heat is given to O₂ gas and 180 J work is done on the gas. The molar heat capacity for this process is (Assume gas is ideal and gas constant is R)

(1)
$$\frac{2R}{5}$$
 (2) $\frac{5R}{2}$ (3) R (4) $\frac{R}{5}$
Sol. Answer (3)
 $q = 120 J$
 $w = 180 J$
 $\Delta U = n \times \frac{5}{2}R \times \Delta T = 300 J \Rightarrow n\Delta T = \frac{120}{R}$
 $C_{w} = \frac{q}{n\Delta T} = \frac{120}{120/R} \Rightarrow R$
57. 1 mol of Ca(OH)₂ is completely neutralised by HCl then heat released in the reaction is (Only magnitude)
(1) More than 57.4 kJ (2) Less than 57.4 kJ
(3) Equal to 57.4 kJ (4) Cannot be determined or compared
Sol. Answer (1)
Ca(OH)₂ + 2HCl \rightarrow CaCl₂ + 2H₂O
 $\Delta H_{i} = 2 \times$ Heat of neutrialisation (kJ/mol)
58. Which of the following is(are) state function as well as intensive property?
(A) Entropy
(B) Internal energy
(C) Pressure
(I) A. B and C (2) Only A and B (3) Only B (4) Only C
Sol. Answer (4)
H, U, Pressure are state function.
H,U are extensive properties.
59. C, H₁CP(H)(1 on complete combustion produce CO₂(g) and H₂O(I) at 300 k. The difference between ΔH and ΔU
at this temperature is
(I) -2.49 kJ (2) $+2.49 \text{ kJ}$ (3) $+4.98 \text{ kJ}$ (4) -4.98 kJ
Sol. Answer (1)
C₂H₃OH(I) + 3O₂(g) \rightarrow 2CO₂(g) + 3H₂O(I)
 $\Delta H - \Delta U = \Delta ngRT$
 $\Delta ng = -1$