

Chapter - 5

Chemical Thermodynamics

FAST TRACK : QUICK REVISION

- ◆ **System:** Specific part of universe in which observations are made.
- ◆ **Surroundings:** Everything which surrounds the system.
- ◆ **Types of the System:**
 - Open System:** Exchange both matter and energy with the surroundings. For example – Reactant in an open test tube.
 - Closed System:** Exchange energy but not matter with the surroundings. For example – Reactants in a closed vessel.
 - Isolated System:** Neither exchange energy nor matter with the surroundings. For example – Reactants in a thermos flask.
- ◆ **Thermodynamic Processes:**
 - (i) Isothermal Process: $\Delta T = 0$
 - (ii) Adiabatic process: $\Delta q = 0$
 - (iii) Isobaric process: $\Delta P = 0$
 - (iv) Isochoric process: $\Delta V = 0$
 - (v) Cyclic process: $\Delta U = 0$
 - (vi) Reversible process: Process which proceeds infinitely slowly by a series of equilibrium steps.
 - (vii) Irreversible process: Process which proceeds rapidly and the system does not have chance to achieve equilibrium.
- ◆ **Extensive Properties:** Properties which depend upon the quantity or size of matter present in the system. For example – mass, volume, internal energy, enthalpy, heat capacity, work etc.

- ◆ **Intensive Properties:** Properties which do not depend upon the quantity or size of matter present in the system. For example – temperature, density, pressure, surface tension, viscosity, refractive index, boiling point, melting point etc.

- ◆ **State Functions:** The variables of functions whose value depend only on the state of a system or they are path independent.

For example – pressure (P), volume (V), temperature (T), enthalpy (H), free energy (G), internal energy (U), entropy (S), amount (n) etc.

- ◆ **Internal Energy:** It is the sum of all kind of energies possessed by the system.
- ◆ **First Law of Thermodynamics:** “The energy of an isolated system is constant.”

Mathematical Form: $\Delta U = q + w$

- ◆ **Sign Conventions for Heat (q) and Work (w):**

- $W = +ve$, if work is done on system
- $W = -ve$, if work is done by system
- $q = +ve$, if heat is absorbed by the system
- $q = -ve$, if heat is evolved by the system

- ◆ **Work of Expansion/ compression:** $w = -P_{\text{ext}} (V_f - V_i)$

- ◆ **Work done in Isothermal Reversible Expansion of an Ideal Gas:**

$$w_{\text{rev}} = -2.303 nRT \log V_f / V_i$$

$$\text{or } w_{\text{rev}} = -2.303 nRT \log P_i / P_f$$

- ◆ **Significance of ΔH & ΔU :** $\Delta H = q_p$ and $\Delta U = q_v$
- ◆ **Relation between ΔH & ΔU :** $\Delta H = \Delta U + (n_p - n_r)RT$ for gaseous reaction
 - $\Delta H = \Delta U$ if $(n_p - n_r)$ is zero; *e.g.* $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$
 - $\Delta H > \Delta U$ if $(n_p - n_r)$ is positive; *e.g.* $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - $\Delta H < \Delta U$ if $(n_p - n_r)$ is negative; *e.g.* $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
- ◆ **Heat Capacity (C):** Amount of heat required to raise the temperature of a substance by 1°C or 1K .

$$q = C \Delta T$$

- ◆ **Specific Heat Capacity (C_s):** Amount of heat required to raise the temperature of 1 g of a substance by 1°C or 1 K.

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

- ◆ **Molar Heat Capacity (C_m):** Amount of heat required to raise the temperature of 1 mole of a substance by 1°C or 1 K.

$$q = C_m \times n \times \Delta T$$

- ◆ **Standard State of a Substance:** The standard state of a substance at a specified temperature is its pure form at 1 bar.

- ◆ **Standard Enthalpy of Formation ($\Delta_f H^0$):** Enthalpy change accompanying the formation of one mole of a substance from its constituent elements under standard condition of temperature (normally 298 K) and pressure (1 bar).

- $\Delta_f H^0$ of an element in standard state is taken as zero.
- Compounds with -ve value of $\Delta_f H^0$ are more stable than their constituents.
- $\Delta_r H^0 = \sum a_i \Delta_f H^0$ (products) - $\sum b_i \Delta_f H^0$ (reactants); Where 'a' and 'b' are coefficients of products and reactants in balanced equation.

- ◆ **Standard Enthalpy of Combustion ($\Delta_c H^0$):** Enthalpy change accompanying the complete combustion of one mole of a substance under standard conditions (298 K, 1 bar)

- ◆ **Hess's Law of Constant Heat Summation:** The total enthalpy change of a reaction remains same whether it takes place in one step or in several steps.

- ◆ **Bond Dissociation Enthalpy:** Enthalpy change when one mole of a gaseous covalent bond is broken to form products in gas phase.

For example, $\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g}); \Delta_{\text{Cl-Cl}} H^0 = 242 \text{ kJ mol}^{-1}$

- For diatomic gaseous molecules; Bond enthalpy = Bond dissociation Enthalpy = Atomization Enthalpy

- For Polyatomic gaseous molecules; Bond Enthalpy = Average of the bond dissociation enthalpies of the bonds of the same type.

- $\Delta_r H^0 = \sum \Delta_{\text{bond}} H^0 (\text{Reactants}) - \sum \Delta_{\text{bond}} H^0 (\text{Products})$

- ♦ **Spontaneous Reaction:** A reaction which can take place either on its own or under some initiation.

- ♦ **Entropy(S):** It is a measure of the degree of randomness or disorder of a system.

- $$\Delta S_{\text{sys}} = \frac{(q_{\text{rev}})_{\text{sys}}}{\Delta T} = \frac{\Delta H_{\text{sys}}}{\Delta T}$$

- Unit of Entropy = $\text{JK}^{-1} \text{mol}^{-1}$

- ♦ **Second Law of Thermodynamics:** For all the spontaneous processes, the total entropy change must be positive.

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

- ♦ **Gibbs Helmholtz Equation for determination of Spontaneity:**

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

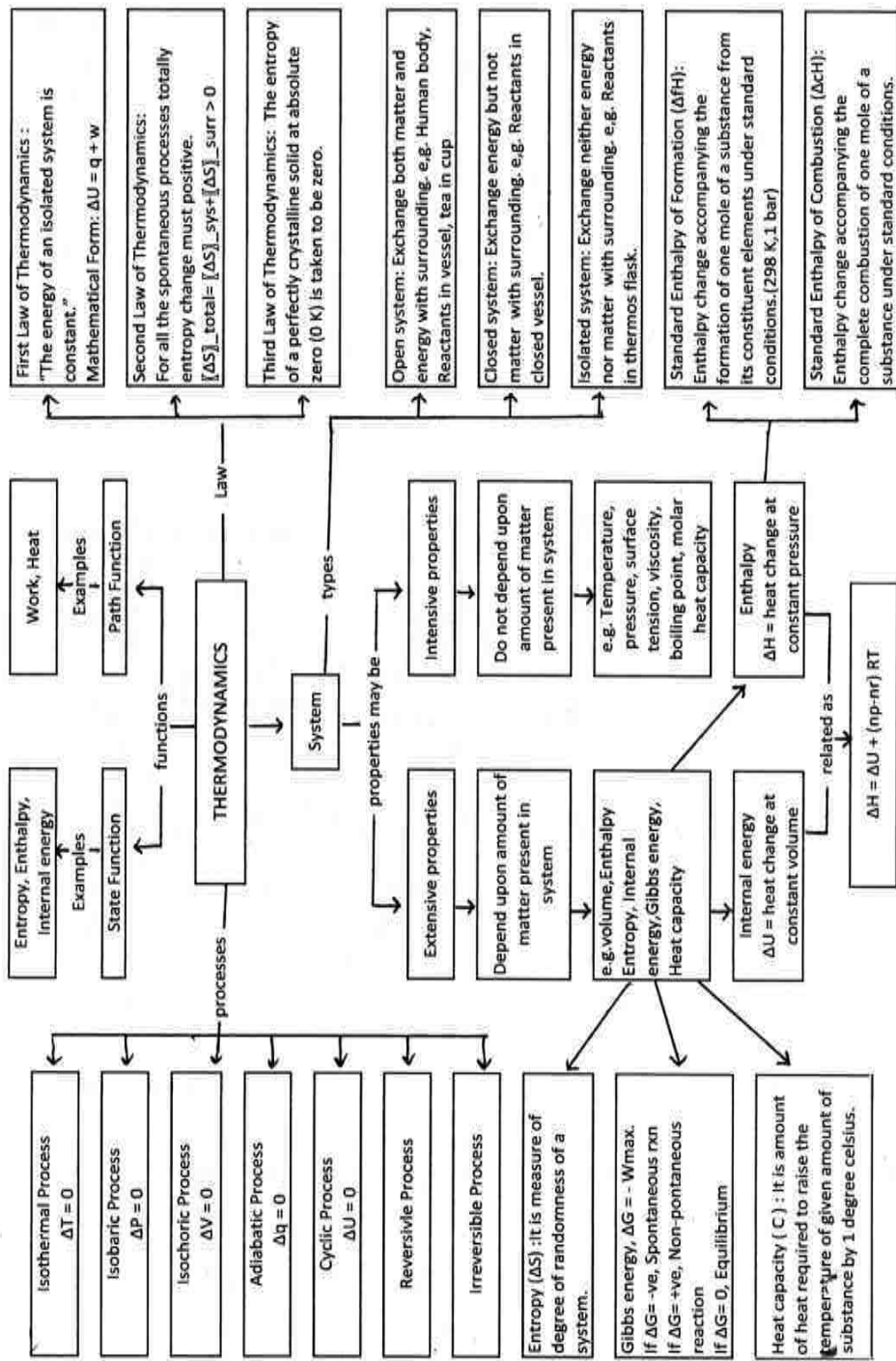
- If $\Delta G = -ve$, the process is spontaneous
- If $\Delta G = +ve$, the process is non-spontaneous
- If $\Delta G = 0$, the process is in equilibrium

- ♦ **Relation between Gibbs Energy Change and Equilibrium Constant:**

$$\Delta G^0 = -2.303 RT \log K_c$$

- ♦ **Third Law of Thermodynamics:** The entropy of a perfectly crystalline solid at absolute zero (0 K) is taken to be zero.

MIND MAP : CHEMICAL THERMODYNAMICS



CASE BASED STUDIES - QUESTIONS

PASSAGE -1

Heat of neutralization is defined as amount of heat released when one gram equivalent of a strong base reacts with one gram equivalent of strong acid. The heat of neutralization comes out to be as follows



Since the basic reaction for neutralization reaction is same for all acids and bases, hence enthalpy of neutralization for strong acid and base is always same i.e., -57.1 kJ. However, if any of the acid or base or both are weak then heat released will be less. It is because some of heat released is utilized to ionize weak acid or base or both. In case of HF (weak acid), enthalpy of neutralization is more than that of strong acid and strong base due to high enthalpy of hydration of small size of ion.

Answer the following question

1. Enthalpy of neutralization of HCN against NaOH is -51.4 kJ. What is enthalpy of ionization of HCN?
2. If heat of neutralization of HA, HB, HC, HD acids follows the order $\text{HA} > \text{HB} > \text{HC} > \text{HD}$ then arrange them in increasing order of acidic strength.
3. What will be heat change for complete neutralization of strong acid $\text{R}(\text{OH})_2$ by HCl.
4. What will heat released when equal volume of an aqueous solution of 0.5M HNO_3 is mixed with $0.3\text{M NaOH}(\text{aq})$

OR

What will be heat released when 100ml of 0.2M HCl is mixed 200ml of 0.2M KOH .

Ans: 1. 5.7KJ 2. $\text{HA} > \text{HB} > \text{HC} > \text{HD}$ 3. -114.2KJ or 1.142KJ

PASSAGE -2

According to first law of thermodynamics, the mathematical expression is as follows :

$$\Delta U = Q + W$$

Where ΔU is the change in internal energy observed when a 'Q' amount of heat is involved and 'W' amount of work is associated when the system moves from state 'A' to state 'B'. The sign of 'Q' and 'W' is taken such that ΔU is measured accurately .

Answer the following question:

1. What will be work done for isochoric process?
2. What is relationship between internal energy change and work done for an adiabatic process?
3. Define internal energy change?
4. A sample of gas present in a cylinder fitted with a frictionless piston, expands against a constant pressure of 1 atm from volume of 5L to 15L. During the process it absorbs 500J energy from surrounding. Calculate change in internal energy.

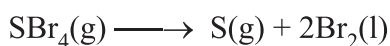
Or

60 KJ heat is supplied to a system at constant volume and temperature rises from 20°C to 24°C. Calculate the change in internal energy, work done and q.

ANS: 1. 0 2. $\Delta E = w$ 3. Definition 4. -513 J or $\Delta E = 60$ J, $w = 0$, $q = 60$ J

MULTIPLE CHOICE QUESTIONS (MCQ)

- Which one of the following thermodynamic quantities is not a state function?
 - Gibbs free energy
 - Enthalpy
 - Entropy
 - Work
- All of the following have a standard heat of formation value of zero at 25°C and 1.0 atm except:
 - N₂(g)
 - Fe(s)
 - Ne(g)
 - H(g)
- For the following reaction at 25°C, $\Delta H^\circ = +115 \text{ kJ}$ and $\Delta S^\circ = +125 \text{ J/K}$. Calculate ΔG° for the reaction at 25°C :

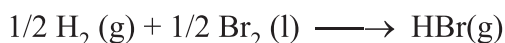


- +152 kJ
 - 56.7 kJ
 - +77.8 kJ.
 - +37.1 kJ
- Calculate $\Delta_r H^\circ$ for the following reaction at 25°C :

$$\text{Fe}_3\text{O}_4(\text{s}) + \text{CO}(\text{g}) \longrightarrow 3\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$$

ΔH_f° (kJ/mol)	-1118	-110.5	-272	-393.5
-----------------------------	-------	--------	------	--------

 - 263 kJ
 - 54 kJ
 - 19 kJ.
 - 50 kJ
 - A system suffers an increase in internal energy of 80 J and at the same time has 50 J of work done on it. What is the heat change of the system?
 - +130 J
 - +30 J
 - 130 J
 - 30 J
 - The ΔH° for the following reaction at 298 K is -36.4 kJ.



Calculate ΔU° at 298 K. The universal gas constant, R, is 8.314 J/mol K.

- 35.2 kJ
 - +35.2 kJ
 - 36.4 kJ
 - 37.6 kJ.
- For which of the following reactions would the ΔH° for the reaction be labeled ΔH_f° ?
 - $\text{Al}(\text{s}) + 3/2 \text{H}_2(\text{g}) + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{Al}(\text{OH})_3(\text{s})$
 - $\text{PCl}_3(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{POCl}_3(\text{g})$

- (c) $1/2 \text{N}_2\text{O}(\text{g}) + 1/4 \text{O}_2(\text{g}) \longrightarrow \text{NO}(\text{g})$
 (d) $\text{CaO}(\text{s}) + \text{SO}_2(\text{g}) \longrightarrow \text{CaSO}_3(\text{s})$
8. Which statement is true for reaction? $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g})$
 (a) $\Delta S = +ve$ (b) $\Delta H > \Delta U$
 (c) $\Delta H < \Delta U$ (d) $\Delta H = \Delta U$
9. The heat of combustion of yellow phosphorous is -9.91 KJ and the red phosphorous is -8.78 KJ . The heat of transition of yellow phosphorous to red phosphorous is :
 (a) -9.91 kJ (b) -8.78 kJ
 (c) -9.34 kJ (d) -1.13 kJ
10. Entropy of universe is :
 (a) Increasing (b) decreasing
 (c) Constant (d) None of these
11. Which is state function?
 (a) q (b) w
 (c) $q + w$ (d) None of these
12. According to second law of thermodynamics
 (a) $\Delta S_{\text{total}} = +ve$ (b) $\Delta S_{\text{total}} = -ve$
 (c) $\Delta S_{\text{system}} = +ve$ (d) $\Delta S_{\text{system}} = -ve$
- Ans:** 1.(d), 2.(d), 3.(c), 4.(c), 5.(b), 6.(d), 7.(a),
 8. (c), 9.(a), 10.(c), 11.(c), 12.(a)

FILL IN THE BLANKS

- (i) is a measure of the degree of randomness or disorder of a system.
 (ii) A process which can take place either on its own or under some initiation is known as
- (iii) For evaporation of water the sign of ΔH is..... and sign of ΔS is.....
 (iv) The entropy of a perfectly crystalline solid is zero at
- (v) The heat energy exchanged between the system and surroundings at constant temperature and pressure is known as.....
- (vi) is the quantity of heat needed to raise the temperature of one mole of a substance by 1°C
 (vii) $C_p - C_v = \dots\dots\dots$
 (viii) $\dots\dots\dots = \Delta H - T\Delta S$.

- (ix) According to law of thermodynamics, $\Delta S_{\text{total}} = +ve$.
 (x) If $\Delta H = +ve$ and $\Delta S = +ve$, the reaction is spontaneous at temperature

Ans: (i) Entropy (ii) spontaneous (iii) +ve, +ve (iv) -273°C
 (v) Enthalpy (vi) molar heat capacity (vii) R (viii) ΔG
 (ix) second (x) high

TRUE AND FALSE TYPE QUESTIONS

Write true or false for following statements:

- (i) For every chemical reaction at equilibrium ΔG^0 is zero.
 (ii) Entropy is not a state function because its value depends upon the condition of temperature and pressure.
 (iii) During isothermal expansion of an ideal gas, there is no change in internal energy.
 (iv) q and w are not state function but $q+w$ is a state function.
 (v) The enthalpy of neutralization of a strong acid by a strong base is always constant.
 (v) For a spontaneous process $\Delta S_{\text{system}} = +ve$.
 (vi) ΔH is not a state function.
 (vii) The energy of universe is conserved while its entropy is increasing.
 (viii) Volume is extensive property while temperature is intensive property.
 (ix) At 0°C the entropy of a perfectly crystalline solid is zero.
 (x) Hess' law is a corollary of the first law of thermodynamics.

Ans: (i) False (ii) False (iii) True (iv) True (v) True
 (vi) False (vii) True (viii) True (ix) False (x) True

MATCH THE COLUMNS

I. Match the sign of ΔH in Column I with the sign of ΔS Column II and sign of ΔG in Column III for a Spontaneous & Non spontaneous reaction.

S.N.	Column I- $[\Delta H]$	Column II- $[\Delta S]$	Column III- $[\Delta G]$
1.	-Ve	(a) +Ve	(p) +Ve at low temperature
2.	+Ve	(b) +Ve	(q) -Ve at High Temperature
3.	+Ve	(c) +Ve	(r) -Ve at all temperature
4.	+Ve	(d) -Ve	(s) +Ve at all Temperature

II. Match the Process in Column I with the parameters in Column II and parameters in Column III

S.N.	Column I	Column II	Column III
1.	Isochoric Process	(a) Temperature constant	(p) w is not zero
2.	Isothermal Process	(b) Volume Constant	(q) T not constant
3.	Adiabatic Process	(c) Pressure Constant	(r) $\Delta U=0$
4.	Isobaric Process	(d) Heat Constant	(s) Work is zero

ANS :

MATCH-I : 1. b, r 2. a, q 3. d, s 4. c, p

MATCH-II : 1. b, s 2. a, r 3. d, q 4. c, p

ASSERTION AND REASON TYPE QUESTIONS

In the following questions a statement of assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below for each question.

- A and R both are correct, and R is correct explanation of A.
 - A and R both are correct, but R is not the correct explanation of A.
 - A is true but R is false.
 - A and R both are false.
- Assertion (A): Enthalpy of graphite is lower than that of diamond.
Reason (R): Entropy of graphite is greater than that of diamond.
 - Assertion (A): Enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ is greater than that of $\text{H}_2\text{O}(\text{g})$.
Reason (R): Enthalpy change is negative for condensation reaction, $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
 - Assertion (A): ΔH and ΔU are same for the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$
Reason (R): All the reactants and products are gases.
 - Assertion (A): if both ΔH^0 and ΔS^0 are positive then the reaction will be spontaneous at high temperature
Reason (R): All processes with positive entropy change are spontaneous.
 - Assertion (A): Enthalpy of formation of HCl is equal to bond energy of HCl.
Reason (R): Enthalpy of formation and bond energy both involve the formation of one mole of HCl from the elements.

6. **ASSERTION :** The standard free energy change for all the spontaneously occurring reaction are negative
REASON: The standard free energies of the elements in their standard states at 1 bar and 298 K are taken as zero
7. **ASSERTION:** Enthalpy and Entropy of any elementary substances in the standard state are taken as zero.
REASON: At absolute zero, particles of perfectly crystalline substances become completely motionless.
8. **ASSERTION :** Enthalpy of Neutralization of CH_3COOH by NaOH is less than that of HCl by NaOH
REASON : CH_3COOH is a weak acid hence need energy to ionize completely.
9. **ASSERTION :** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero
REASON: Internal energy of a gas depends upon Pressure of the gas.
10. **ASSERTION :** A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic
REASON : All exothermic reactions are accompanied by decrease of randomness.

Ans: 1. (ii) 2. (i) 3. (ii) 4. (iii) 5. (i) 6. (ii) 7. (iv) 8. (i) 9. (iii) 10. (iii)

ONE WORD ANSWER TYPE QUESTIONS

1. 'w' amount of work is done by the system and 'q' amount of heat is supplied to the system. What type of system would it be?
2. What is the work done in free expansion of an ideal gas?
3. What is the sign of ΔG^0 for spontaneous reaction?
4. Write the relation between ΔH and ΔU for $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$.
5. Write the SI unit of entropy.
6. Name the calorimeter used to measure ΔU .
7. What is the standard enthalpy of formation of graphite?
8. What is the sign of ΔH for $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g})$?
9. If $K_c = 1$, what will be the value of ΔG ?
10. An exothermic reaction is spontaneous at all temperature. What is the sign of ΔS ?

Ans: 1. Closed system 2. $W = 0$ 3. $\Delta G = -ve$ 4. $\Delta H = \Delta U$ 5. $\text{J K}^{-1} \text{mol}^{-1}$
 6. Bomb calorimeter 7. Zero 8. $\Delta H = +ve$ 9. Zero 10. $\Delta S = +ve$

1-MARK QUESTIONS

- Name the thermodynamic system to which following belong:
(i) Human body (ii) Milk in Thermos flask (iii) Tea in steel kettle
- Identify State functions out of the following: Enthalpy, Entropy, Heat, Temperature, Work, Gibb's free energy.
- Give two examples of state function.
- Write the mathematical statement of first law of thermodynamics.
- Predict the internal energy change for an isolated system?

[Ans. Zero]

- Why ΔH is more significant than ΔU ?
- Write one example each of extensive and intensive properties.
- Write a chemical equation in which ΔH and ΔU are equal.
- Write the relationship between ΔH and ΔU for the reaction:
$$\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$$
- Define standard enthalpy of formation.
- Why is the standard enthalpy of formation of diamond not zero although it is an element?
- The enthalpy of atomization of CH_4 is 1665 kJ mol^{-1} . What is the bond enthalpy of C – H bond?

[Ans. 416.25 kJ]

- Identify the species for which $\Delta_f H^\circ = 0$, at 298 K; $\text{O}_3(\text{g})$, $\text{Br}_2(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{CH}_4(\text{g})$.
- For the reaction $2\text{Cl}(\text{g}) \longrightarrow \text{Cl}_2(\text{g})$; what are the sign of ΔH and ΔS ?
- Out of Diamond and Graphite which has higher entropy?
- Write an example of endothermic spontaneous reaction.
- State second law of thermodynamics.
- State third law of thermodynamics.
- Which has more entropy? 1 mol $\text{H}_2\text{O}(\text{l})$ at 25°C or 1 mol $\text{H}_2\text{O}(\text{l})$ at 35°C .
- At what temperature the entropy of a perfectly crystalline solid is zero?

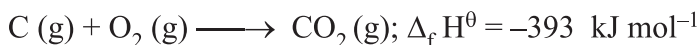
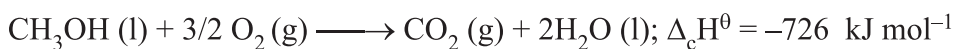
21. For a certain reaction $\Delta G^0 = 0$, what is the value of K_c ?
22. For a reaction both ΔH and ΔS are negative. Under what conditions does the reaction occur.

2-MARKS QUESTIONS

1. In a process 701 J of heat is absorbed by a system and 394 J work is done by the system. What is the change in internal energy for the process?
[Ans. 307 J]
2. Neither 'q' nor 'w' is state functions but $q + w$ is a state function. Explain.
3. Classify the following as extensive or intensive properties :-
Heat capacity, Density, Temperature, Molar heat capacity.
4. Derive the relationship between ΔH and ΔU .
5. Derive the relationship $C_p - C_v = R$.
6. State and explain Hess's Law of Constant Heat Summation with a suitable example.
7. Derive the relationship between ΔH and ΔU .
Given, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta_r H^\theta = -92.4 \text{ kJ mol}^{-1}$;
What is the standard enthalpy of formation of NH_3 gas?
[Ans. $-46.2 \text{ kJ mol}^{-1}$]
8. Calculate the enthalpy change for the reaction:
 $H_2(g) + Br_2(g) \longrightarrow 2 HBr(g)$.
Given the bond enthalpies H_2 , Br_2 and HBr are 435 kJ mol^{-1} , 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively.
[Ans. -109 kJ mol^{-1}]
9. Is the bond dissociation enthalpy of all the four C – H bonds in CH_4 same? Give reason in support of your answer.
10. Define the term entropy. Write its unit. How does entropy of a system change on increasing temperature?
11. The equilibrium constant for a reaction is 10. What will be the value of ΔG^θ ? $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$.
[Ans. $-5.744 \text{ kJ mol}^{-1}$]
12. The ΔH and ΔS for $2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$ are given $+61.17 \text{ kJ mol}^{-1}$ and $+132 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Above what temperature will the reaction be spontaneous?
[Ans. $>463.4 \text{ K}$]

3-MARKS QUESTIONS

- Differentiate between the following (with examples)
 - Open and Closed System.
 - Adiabatic and Isothermal process.
 - State function and path function
- Calculate the maximum work obtained when 0.75 mole of an ideal gas expands isothermally and reversibly at 27°C from a volume of 15L to 25L. [Ans. -955.7 J]
- Calculate the number of kJ necessary to raise the temperature of 60 g of aluminium from 35 to 55°C. Molar heat capacity of Al is 24 J mol⁻¹ K⁻¹. [Ans. 1.067 kJ]
- The reaction of cyanamide, NH₂CN (s), with Dioxygen was carried out in a bomb calorimeter, and ΔU was found to be -742.7 kJ mol⁻¹ at 298K. Calculate Enthalpy change for the reaction at 298K,
$$\text{NH}_2\text{CN (s)} + 3/2 \text{O}_2\text{(g)} \longrightarrow \text{N}_2\text{(g)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O (l)}$$
[Ans. -741.5 kJ mol⁻¹]
- The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are -890.3 kJ mol⁻¹, -393.5 kJ mol⁻¹ and -285.8 kJ mol⁻¹ respectively. Calculate enthalpy of formation of methane gas. [Ans. -74.8 kJ mol⁻¹]
- Explain the Born Haber Cycle to determine the lattice enthalpy of NaCl.
- Enthalpies of formation of CO(g), CO₂(g), N₂O(g) and N₂O₄ (g) are -110, -393, 81 and 9.7 kJ mol⁻¹ respectively. Find the value of Δ_rH for the reaction; N₂O₄(g) + 3 CO (g) → N₂O (g) + 3CO₂ (g)
[Ans. -777.7 kJ mol⁻¹]
- The combustion of 1 mol of benzene takes place at 298K. After combustion CO₂ and H₂O are formed and 3267 kJ mol⁻¹ of heat is liberated. Calculate Δ_fH⁰ (C₆H₆).
Given: Δ_fH⁰ (H₂O) = -286 kJ mol⁻¹, Δ_fH⁰(CO₂) = -393 kJ mol⁻¹
[Ans. 48.51 kJ mol⁻¹]
- Calculate the standard enthalpy of formation of CH₃OH(l) from the following data:



[Ans. -239 kJ mol^{-1}]

10. Give reasons:

- (i) Evaporation of water is endothermic process but it is spontaneous.
- (ii) A real crystal has more entropy than an ideal crystal.
- (iii) Entropy of universe is increasing.

11. For the reaction at 298 K, $2\text{A} + \text{B} \longrightarrow \text{C}$; $\Delta H = 400 \text{ kJ mol}^{-1}$, $\Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$. At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

[Ans. $T > 2000 \text{ K}$]

12. Reaction $\text{X(s)} \rightarrow \text{Y(g)}$ $\Delta H = +ve$ is spontaneous at temperature 'T'. Determine

- (i) Sign of ΔS for this reaction.
- (ii) Sign of ΔG for $\text{Y} \longrightarrow \text{X}$
- (iii) Sign of ΔG at a temperature $< T$

5-MARKS QUESTIONS

1. (a) What is reversible process in Thermodynamics?
(b) Name the thermodynamic processes for which : (i) $\Delta q = 0$ (ii) $\Delta U = 0$
(iii) $\Delta V = 0$ (iv) $\Delta P = 0$
(c) Water decomposes by absorbing 286.2 kJ of electrical energy per mole. When H_2 and O_2 combine to form one mole of H_2O , 286.2 kJ of heat is produced. Which thermodynamic law is proved? Write its statement.
2. (a) Why work done in isothermal reversible process is always maximum?
[Hint: $q_v = \Delta U$ and $q_p = \Delta H$]
(b) It has been found that 221.4 J is needed to heat 30g of ethanol from 15°C to 18°C . Calculate (a) specific heat capacity, and (b) molar heat capacity of ethanol.

[Ans. (a) $2.46 \text{ Jg}^{-1} \text{ }^\circ\text{C}^{-1}$, (b) $113.2 \text{ J mol}^{-1} \text{ }^\circ\text{C}^{-1}$]

3. (a) Differentiate the terms Bond dissociation enthalpy & Bond Enthalpy.
 (b) Calculate enthalpy change for the process $\text{CCl}_4(\text{g}) \longrightarrow \text{C}(\text{g}) + 4\text{Cl}(\text{g})$ and calculate Bond enthalpy of C–Cl bond in CCl_4 .

Given: $\Delta_{\text{vap}}H^\theta = 30.5 \text{ kJ mol}^{-1}$; $\Delta_f H^\theta(\text{CCl}_4) = -135.5 \text{ kJ mol}^{-1}$;

$\Delta_a H^\theta(\text{C}) = 715 \text{ kJ mol}^{-1}$ and $\Delta_a H^\theta(\text{Cl}_2) = 242 \text{ kJ mol}^{-1}$

[Ans. 1304 kJ mol^{-1} , 326 kJ mol^{-1}]

4. Predict the sign of ΔS for the following changes:

(i) Freezing of water.

(ii) $\text{C}(\text{graphite}) \longrightarrow \text{C}(\text{diamond})$

(iii) $\text{H}_2(\text{g})$ at 298 k and 1 bar $\longrightarrow \text{H}_2(\text{g})$ at 298 k and 10 bar

(iv) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$

(v) $2\text{NaHCO}_3(\text{s}) \longrightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$

5. (i) Define Gibbs Energy. Give its mathematical expression. What is Gibb's energy criteria of Spontaneity.

(ii) For the reaction:

$2\text{A}(\text{g}) + \text{B}(\text{g}) \longrightarrow 2\text{D}(\text{g})$, $\Delta U^\theta = -10.5 \text{ kJ}$ and $\Delta S^\theta = -44.1 \text{ J K}^{-1}$.

Calculate $\Delta_r G^\theta$ for the reaction, and predict whether the reaction will occur spontaneously.

[Ans. $\Delta_r G^\theta = +0.16 \text{ kJ}$, Non-spontaneous]

HOTS QUESTIONS

1. Does entropy increase or decrease when egg is boiled?

Ans.: On boiling egg, entropy decreases as due to denaturation, the helical structure of protein become more complicated and random coiled structure.

2. 10 g of argon is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L. Calculate q , w , ΔU and ΔH .

Solution: $q = -2.303 nRT \log V_2 / V_1 = -2.303 \times 10/40 \text{ mol} \times 2 \text{ Cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log 5/10 = -103.635 \text{ Cal}$

For isothermal compression $\Delta U = 0$

$W = \Delta U - q = 0 - (-103.635) = +103.635 \text{ Cal}$

Also when temperature is constant,

$$PV = \text{constant}, \Delta H = \Delta U + \Delta(PV) = 0 + 0 = 0$$

3. 1 mole of an ideal gas expand isothermally and reversibly from a pressure of 10 atm to 1 atm at 300 K. Calculate the height to which an object of 50 kg can be lifted by this expansion.

Solution: $w_{(\text{exp.})} = -[2.303 nRT \log (P_i / P_f)]$
 $= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 300 \text{ K} \times \log 10/1$
 $= 5.74 \times 10^3 \text{ J}$

Now, $mgh = 5.74 \times 10^3 \text{ J}$ or $50 \text{ kg} \times 9.81 \text{ m s}^{-2} \times h = 5.744 \times 10^3 \text{ J}$

$\therefore h = 11.7 \text{ m}$

UNIT TEST-I

Time Allowed: 1 Hr.

Maximum Marks : 20

General Instructions:

- (i) All questions are compulsory.
(ii) Maximum marks carried by each question are indicated against it.
-

1. For the reaction $2\text{Cl}(\text{g}) \longrightarrow \text{Cl}_2(\text{g})$; what are the sign of ΔH and ΔS ? [1]
2. Write an example of endothermic spontaneous reaction. [1]
3. 'w' amount of work is done by the system and 'q' amount of heat is supplied to the system. What type of system would it be? [1]
4. In a process 701 J of heat is absorbed by a system and 394 J work is done by the system. What is the change in internal energy for the process? [2]
5. State and explain Hess's Law of Constant Heat Summation with a suitable example. [2]
6. Calculate the number of kJ necessary to raise the temperature of 60 g of aluminium from 35 to 55°C. Molar heat capacity of Al is $24 \text{ J mol}^{-1} \text{ K}^{-1}$. [3]
7. Calculate the standard enthalpy of formation of $\text{CH}_3\text{OH}(\text{l})$ from the following data:
 $\text{CH}_3\text{OH}(\text{l}) + 3/2 \text{ O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}); \Delta_c H^\circ = -726 \text{ kJ mol}^{-1}$
 $\text{C}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \Delta_f H^\circ = -393 \text{ kJ mol}^{-1}$
 $\text{H}_2(\text{g}) + 1/2 \text{ O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}); \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$
8. (a) For oxidation of iron, $4 \text{ Fe}(\text{s}) + 3 \text{ O}_2(\text{g}) \longrightarrow 2 \text{ Fe}_2\text{O}_3(\text{s})$ entropy change is $-549.4 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K. In spite of negative entropy change of this reaction, why is the reaction spontaneous? ($\Delta_r H^\circ$ for this reaction is $-1648 \text{ kJ mol}^{-1}$) [2]
(b) For the reaction: $2\text{A}(\text{g}) + \text{B}(\text{g}) \longrightarrow 2\text{D}(\text{g})$, $\Delta U^\circ = -10.5 \text{ kJ}$ and $\Delta S^\circ = -44.1 \text{ J K}^{-1}$. Calculate ΔG° for the reaction, and predict whether the reaction will occur spontaneously. [3]

UNIT TEST-II

Time Allowed: 1 Hr.

Maximum Marks : 20

General Instructions:

- (i) All questions are compulsory.
(ii) Maximum marks carried by each question are indicated against it.
-

- Among following, the property which is intensive is [1]
(a) Mass (b) Volume
(c) Temperature (d) Length
- Heat of formation is zero for which substance. [1]
(a) CaCO_3 (b) HCl
(c) Carbon (Diamond) (d) Carbon (Graphite)
- What is an isochoric process and what is the work value associated with isochoric process? [1]
- Name the law which is based on the statement "enthalpy is a state function." [1]
- Heat of combustion of ethane is $-1560 \text{ KJ mol}^{-1}$ while that of acetylene is $-1296 \text{ KJ mol}^{-1}$. Which is better fuel and why? [1]
- Derive the expression for work done in isothermal reversible expansion. [3]
- Define standard enthalpy of combustion and standard enthalpy of formation taking C_2H_6 (gas) molecule in both cases. [2]
- State 'Hess law of Constant heat summation'. The molar heat of combustion of $\text{C}_2\text{H}_2(\text{g})$, $\text{C}(\text{Graphite})$ and $\text{H}_2(\text{g})$ are 310.62 kcal , 94.05 kcal and 68.32 kcal respectively. Calculate the standard heat of formation of $\text{C}_2\text{H}_2(\text{g})$. [3]
- The reaction of Cyanamid, $\text{NH}_2\text{CN}(\text{s})$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be $-742.7 \text{ kJmol}^{-1}$ at 298 K . Calculate enthalpy change for the reaction at 298 K .



10. (i) State the First Law of Thermodynamics.
- (ii) Define Entropy. What is the effect of temperature on Entropy?
- (iii) Two moles of an ideal gas are held by a piston under 5 atm pressure at 300 K. The pressure is suddenly released to 0.4 atm and the gas is allowed to expand isothermally. Calculate W, q, ΔE , ΔH . [5]
