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Class 11 Chemistry

Chapter 5: Thermodynamics

📚 Chapter Overview

Why Thermodynamics?

Thermodynamics deals with energy changes in chemical reactions and helps us understand why reactions occur and to what extent. It's fundamental to predicting reaction spontaneity and calculating energy requirements!

Exam Importance:

- **CBSE Board:** 6-7 marks (3-4 questions including 1 long answer)
- **JEE Main:** 2-3 questions (high weightage from Hess's law and spontaneity)
- **NEET:** 2-3 questions (enthalpy calculations and Gibb's energy)

1. Introduction to Thermodynamics

1.1 What is Thermodynamics?

Thermodynamics is the branch of science that deals with the study of different forms of energy and the quantitative relationships between them.

Importance of Thermodynamics:

- Predicts whether a process is **spontaneous** or non-spontaneous
- Determines energy changes in physical and chemical processes
- Calculates **equilibrium constants** from thermodynamic data
- Essential for understanding energy efficiency in reactions

1.2 System and Surroundings

System: The part of universe under investigation

Surroundings: Everything else in universe except system

Boundary: Real or imaginary surface separating system from surroundings

1.3 Types of Systems

System Type	Mass Exchange	Energy Exchange	Example
Open System	✓ Yes	✓ Yes	Open beaker, hot water in open vessel
Closed System	✗ No	✓ Yes	Gas in closed cylinder, sealed pressure cooker
Isolated System	✗ No	✗ No	Thermos flask, perfectly insulated calorimeter

2. State Functions and Path Functions

2.1 State Functions

Properties that depend only on the **initial and final states** of the system, not on the path taken.

State Functions: P, V, T, U (Internal Energy), H (Enthalpy), S (Entropy), G (Gibbs Energy)

2.2 Path Functions

Properties that depend on the **path** taken during the process.

Path Functions: q (Heat), w (Work)

Analogy: Climbing a Mountain

State Function: Height of mountain (same whether you take steep or gentle path)

Path Function: Distance travelled (depends on which route you choose)

2.3 Intensive and Extensive Properties

Property Type	Definition	Examples
Intensive	Independent of amount of substance	Temperature, Pressure, Density, Refractive Index
Extensive	Depends on amount of substance	Mass, Volume, Energy, Enthalpy, Entropy

3. Internal Energy (U)

Internal Energy: The total energy stored within a system, including kinetic and potential energy of molecules.

$$\Delta U = U_{final} - U_{initial}$$

Important Points about Internal Energy:

- It is a **state function**
- Absolute value cannot be determined (only ΔU can be measured)
- It is an **extensive property**
- For an isolated system, $\Delta U = 0$

4. First Law of Thermodynamics

Mathematical Form:

$$\Delta U = q + w$$

q = heat absorbed by system

w = work done on system

Statement:

Energy can neither be created nor destroyed, only converted from one form to another. The total energy of universe remains constant.

Alternate form: $\Delta U_{system} + \Delta U_{surroundings} = 0$

4.1 Sign Conventions (IUPAC)

Process	Sign of q	Sign of w
Heat absorbed by system	+ (positive)	-
Heat evolved by system	- (negative)	-
Work done on system (compression)	-	+ (positive)
Work done by system (expansion)	-	- (negative)

4.2 Work Done in Different Processes

A. Work in Expansion/Compression

$$\mathbf{w = -P_{ext} \times \Delta V}$$

$$\mathbf{\Delta V = V_{final} - V_{initial}}$$

B. Isothermal Reversible Expansion (Ideal Gas)

$$\mathbf{w = -2.303\ nRT\ \log(V_f/V_i)}$$

OR

$$\mathbf{w = -2.303\ nRT\ \log(P_i/P_f)}$$

C. Free Expansion

When a gas expands into vacuum: **w = 0** ($P_{ext} = 0$)

D. Isochoric Process (Constant Volume)

$\Delta V = 0$, therefore **w = 0**

Example: Calculate work done in expansion

Problem: 1 mole of ideal gas expands from 2 L to 10 L at constant temperature of 300 K. Calculate work done.

Solution:

Given: n = 1 mol, V_i = 2 L, V_f = 10 L, T = 300 K, R = 8.314 J K^{-1} mol^{-1}

For isothermal reversible expansion:

$w = -2.303\ nRT \log(V_f/V_i)$

$w = -2.303 \times 1 \times 8.314 \times 300 \times \log(10/2)$

$w = -2.303 \times 8.314 \times 300 \times \log(5)$

$w = -2.303 \times 8.314 \times 300 \times 0.699$

w = -4009 J = -4.01 kJ

Answer: Work done = -4.01 kJ (negative sign indicates work done by system)

5. Enthalpy (H)

Enthalpy: Heat content of a system at constant pressure

$$\boxed{H = U + PV}$$

For a change at constant pressure:

$$\boxed{\Delta H = \Delta U + P\Delta V}$$

5.1 Relationship between ΔH and ΔU

For gases:

$PV = nRT$

$P\Delta V = \Delta n_g RT$

where Δn_g = (number of moles of gaseous products) - (number of moles of gaseous reactants)

Therefore:

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

Key Points:

- At constant pressure: $\Delta H = q_p$ (heat at constant pressure)
- At constant volume: $\Delta U = q_v$ (heat at constant volume)
- For reactions involving only solids/liquids: $\Delta H \approx \Delta U$ ($\Delta ng \approx 0$)

Example: Relation between ΔH and ΔU

Problem: For the reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ at 298 K, $\Delta H° = -572$ kJ. Calculate $\Delta U°$.

Solution:

Δng = (moles of gaseous products) - (moles of gaseous reactants)

$\Delta ng = 0 - (2 + 1) = -3$

$\Delta H = \Delta U + \Delta ngRT$

$-572 = \Delta U + (-3) \times 8.314 \times 10^{-3} \times 298$

$-572 = \Delta U - 7.43$

$\Delta U = -572 + 7.43$

$\Delta U° = -564.57$ kJ

6. Heat Capacity

6.1 Molar Heat Capacities

A. Heat Capacity at Constant Volume (C_v)

$$C_v = (\partial U/\partial T)_V$$

B. Heat Capacity at Constant Pressure (C_p)

$$C_p = (\partial H/\partial T)_P$$

6.2 Relationship between C_p and C_v

$$C_p - C_v = R$$

(For ideal gases only)

Important Relations:

- $C_p > C_v$ always
- γ (gamma) = C_p/C_v
- For monoatomic gases: γ = 1.67
- For diatomic gases: γ = 1.40
- For polyatomic gases: γ = 1.33

7. Types of Enthalpy Changes

7.1 Standard Enthalpy of Formation ($\Delta H°_f$)

Enthalpy change when 1 mole of compound is formed from its elements in their standard states.

Examples:

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ $\Delta H°_f = -286$ kJ/mol

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$ $\Delta H°_f = -393.5$ kJ/mol

Note: $\Delta H°_f$ of elements in standard state = 0

7.2 Standard Enthalpy of Combustion ($\Delta H°_c$)

Enthalpy change when 1 mole of substance is completely burnt in excess oxygen.

Examples:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H°_c = -890$ kJ/mol

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H°_c = -1368$ kJ/mol

7.3 Enthalpy of Atomization ($\Delta H°_a$)

Enthalpy change when 1 mole of bonds are broken to form gaseous atoms.

Examples:

$CH_4(g) \rightarrow C(g) + 4H(g) \quad \Delta H^\circ_a = 1660$ kJ/mol

$H_2(g) \rightarrow 2H(g) \quad \Delta H^\circ_a = 436$ kJ/mol

7.4 Bond Enthalpy (ΔH°_{bond})

Energy required to break one mole of particular bonds in gaseous state.

$$\Delta H^\circ_{reaction} = \Sigma(\text{Bond enthalpies of bonds broken}) - \Sigma(\text{Bond enthalpies of bonds formed})$$

7.5 Enthalpy of Phase Transitions

Process	Enthalpy Change	Example
Fusion (melting)	ΔH°_{fus}	$H_2O(s) \rightarrow H_2O(l) = +6.01$ kJ/mol
Vaporization	ΔH°_{vap}	$H_2O(l) \rightarrow H_2O(g) = +40.66$ kJ/mol
Sublimation	ΔH°_{sub}	$I_2(s) \rightarrow I_2(g) = +62.4$ kJ/mol

Important Relation:

$\Delta H^\circ_{sub} = \Delta H^\circ_{fus} + \Delta H^\circ_{vap}$

7.6 Lattice Enthalpy

Energy released when gaseous ions combine to form one mole of ionic solid.

Example:

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ $\Delta H^\circ_{lattice} = -788$ kJ/mol

8. Hess's Law of Constant Heat Summation

Statement:

The total enthalpy change in a reaction is the same whether it occurs in one step or several steps.

Reason: Enthalpy is a state function

Example: Formation of CO_2

Direct path:

$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = -393.5$ kJ/mol

Two-step path:

Step 1: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H^\circ_1 = -110.5$ kJ/mol

Step 2: $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ_2 = -283.0$ kJ/mol

$\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 = -110.5 + (-283.0) = -393.5$ kJ/mol ✓

8.1 Applications of Hess's Law

- Calculate enthalpy changes that cannot be measured directly
- Determine enthalpies of formation

- Calculate lattice energies using Born-Haber cycle
- Find bond energies

Example: Calculate ΔH°_f of CH_4

Given:

ΔH°_c(C, graphite) = -393.5 kJ/mol

$\Delta H^\circ_c(H_2)$ = -286 kJ/mol

$\Delta H^\circ_c(CH_4)$ = -890 kJ/mol

Solution:

Target equation: $C(s) + 2H_2(g) \rightarrow CH_4(g)$ $\Delta H^\circ_f = ?$

Given equations:

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ = -393.5$ kJ

(2) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H^\circ = -286$ kJ

(3) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^\circ = -890$ kJ

Rearranging: (1) + 2×(2) - (3):

$\Delta H^\circ_f = -393.5 + 2(-286) - (-890)$

$\Delta H^\circ_f = -393.5 - 572 + 890$

$\Delta H^\circ_f = -75.5$ kJ/mol

9. Born-Haber Cycle

Application of Hess's Law to calculate lattice enthalpy of ionic compounds.

Example: Lattice Enthalpy of NaCl

Target reaction: $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ U = ?

Given data:

$\Delta H°_f(NaCl) = -411$ kJ/mol

$\Delta H°_{sub}(Na) = +108$ kJ/mol

IE(Na) = +496 kJ/mol

$½\Delta H°_{diss}(Cl_2) = +121$ kJ/mol

EA(Cl) = -349 kJ/mol

Born-Haber Cycle:

$Na(s) \rightarrow Na(g)$ $\Delta H°_{sub} = +108$ kJ/mol

$Na(g) \rightarrow Na^+(g) + e^-$ IE = +496 kJ/mol

$½Cl_2(g) \rightarrow Cl(g)$ $½\Delta H°_{diss} = +121$ kJ/mol

$Cl(g) + e^- \rightarrow Cl^-(g)$ EA = -349 kJ/mol

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ U = ?

By Hess's Law:

$\Delta H°_f = \Delta H°_{sub} + IE + ½\Delta H°_{diss} + EA + U$

$-411 = 108 + 496 + 121 - 349 + U$

$-411 = 376 + U$

U = -787 kJ/mol

10. Second Law of Thermodynamics

Statement:

The entropy of the universe always increases in a spontaneous process.

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$ (for spontaneous process)

10.1 Entropy (S)

Entropy: A measure of randomness or disorder of a system.

$$\Delta S = q_{rev}/T$$

(For reversible process at constant temperature)

Key Points about Entropy:

- It is a **state function**
- It is an **extensive property**
- $S_{gas} > S_{liquid} > S_{solid}$
- Entropy increases with increase in temperature
- Entropy increases with increase in volume

10.2 Standard Entropy of Reaction

$$\Delta S^\circ = \Sigma\, S^\circ(\text{products}) - \Sigma\, S^\circ(\text{reactants})$$

Predicting Sign of ΔS:

- Gas → Liquid or Liquid → Solid: $\Delta S < 0$ (negative)
- Solid → Liquid or Liquid → Gas: $\Delta S > 0$ (positive)
- Increase in number of gaseous molecules: $\Delta S > 0$
- Decrease in number of gaseous molecules: $\Delta S < 0$

10.3 Third Law of Thermodynamics

Statement:

The entropy of a perfect crystalline substance at absolute zero (0 K) is zero.

$S = 0$ **at** $T = 0$ **K**

This provides a reference point for calculating absolute entropies.

11. Gibbs Free Energy (G)

Gibbs Free Energy: The part of total energy of a system that can be converted into useful work.

$$G = H - TS$$

For a process at constant temperature and pressure:

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

11.1 Spontaneity Criteria

Condition	Nature of Process
$\Delta G < 0$ (negative)	**Spontaneous** - Process occurs naturally
$\Delta G = 0$	**Equilibrium** - No net change
$\Delta G > 0$ (positive)	**Non-spontaneous** - Process doesn't occur naturally

11.2 Effect of Temperature on Spontaneity

ΔH	ΔS	ΔG = ΔH - TΔS	Spontaneity
- (Exothermic)	+ (Increase)	Always negative	Spontaneous at all temperatures
+ (Endothermic)	- (Decrease)	Always positive	Non-spontaneous at all temperatures
- (Exothermic)	- (Decrease)	Negative at low T	Spontaneous at low temperature only
+ (Endothermic)	+ (Increase)	Negative at high T	Spontaneous at high temperature only

Example: Calculate ΔG and predict spontaneity

Problem: For a reaction at 300 K, $\Delta H° = -120$ kJ and $\Delta S° = -200$ J/K. Is the reaction spontaneous?

Solution:

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = -120 - 300 \times (-200 \times 10^{-3})$

$\Delta G° = -120 - 300 \times (-0.2)$

$\Delta G° = -120 + 60$

$\Delta G° = -60$ kJ

Answer: Since $\Delta G° < 0$, the reaction is spontaneous at 300 K.

11.3 Relationship between ΔG° and Equilibrium Constant

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

OR

$$\Delta G° = -RT \ln K_{eq}$$

K_{eq} value	ΔG°	Implication
K > 1	Negative	Products favored
K = 1	Zero	Equilibrium
K < 1	Positive	Reactants favored

12. Solved Numerical Examples

Example 1: Calculate ΔH for a reaction

Problem: Calculate ΔH for: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Given bond energies: N≡N = 946 kJ/mol, H-H = 436 kJ/mol, N-H = 391 kJ/mol

Solution:

ΔH = Σ(Bond energies broken) - Σ(Bond energies formed)

Bonds broken: 1(N≡N) + 3(H-H)

Bonds formed: 6(N-H) [2 NH_3 molecules × 3 bonds each]

ΔH = [946 + 3(436)] - [6(391)]

ΔH = [946 + 1308] - [2346]

ΔH = 2254 - 2346

ΔH = -92 kJ/mol

Example 2: Isothermal work calculation

Problem: 2 moles of ideal gas at 300 K expands isothermally and reversibly from 10 L to 20 L. Calculate work done.

Solution:

For isothermal reversible expansion:

$w = -2.303\ nRT \log(V_f/V_i)$

$w = -2.303 \times 2 \times 8.314 \times 300 \times \log(20/10)$

$w = -2.303 \times 2 \times 8.314 \times 300 \times \log(2)$

$w = -2.303 \times 2 \times 8.314 \times 300 \times 0.301$

$w = -3455$ J $= -3.46$ kJ

Example 3: Calculate ΔG at different temperature

Problem: A reaction has $\Delta H° = 50$ kJ and $\Delta S° = 100$ J/K. At what temperature will it become spontaneous?

Solution:

For spontaneity: $\Delta G < 0$

At equilibrium: $\Delta G = 0$

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

$T = \Delta H/\Delta S$

$T = 50 \times 10^3 / 100$

$T = 500$ K

Answer: Reaction becomes spontaneous above 500 K

Example 4: Calculate standard enthalpy of formation

Problem: Calculate ΔH°_f of $C_2H_5OH(l)$

Given: $\Delta H^\circ_c(C) = -393.5$ kJ/mol, $\Delta H^\circ_c(H_2) = -286$ kJ/mol, $\Delta H^\circ_c(C_2H_5OH) = -1368$ kJ/mol

Solution:

Target: $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$

$2C(s) + 2O_2(g) \rightarrow 2CO_2(g) \quad \Delta H^\circ = 2(-393.5) = -787$ kJ

$3H_2(g) + 1.5O_2(g) \rightarrow 3H_2O(l) \quad \Delta H^\circ = 3(-286) = -858$ kJ

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H^\circ = -1368$ kJ

$\Delta H^\circ_f = (-787) + (-858) - (-1368)$

$\Delta H^\circ_f = -277$ kJ/mol

Example 5: Entropy calculation

Problem: Calculate ΔS when 1 mole of ice melts at 0°C. $\Delta H_{fus} = 6.01$ kJ/mol.

Solution:

$T = 0°C = 273$ K

$\Delta S = q_{rev}/T = \Delta H_{fus}/T$

$\Delta S = 6.01 \times 10^3 / 273$

$\Delta S = 22.0$ J/K

Note: Positive ΔS indicates increase in disorder (solid → liquid)

13. Practice Questions

13.1 Multiple Choice Questions (MCQs)

Q1. Which of the following is a state function?

(a) Work

(b) Heat

(c) Internal energy

(d) Both work and heat

Q2. For an adiabatic process, which is true?

(a) $q = 0$

(b) $w = 0$

(c) $\Delta U = 0$

(d) $\Delta H = 0$

Q3. Standard enthalpy of formation of $H_2O(l)$ is:

(a) ΔH for $H_2(g) + O_2(g) \rightarrow H_2O(l)$

(b) ΔH for $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

(c) ΔH for $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(d) None of these

Q4. For the reaction: $2A(g) + B(g) \rightarrow 2C(g)$, $\Delta H = \Delta U$ when:

(a) $\Delta ng = 0$

(b) $\Delta ng = 1$

(c) Temperature is constant

(d) Pressure is constant

Q5. Enthalpy of combustion is always:

(a) Positive

(b) Negative

(c) Zero

(d) Can be positive or negative

Q6. Which of the following has maximum entropy?

(a) Ice at 0°C

(b) Water at 0°C

(c) Water at 100°C

(d) Steam at 100°C

Q7. For a reversible isothermal expansion of ideal gas:

(a) $\Delta U = 0$

(b) $\Delta H = 0$

(c) $q = -w$

(d) All of the above

Q8. Reaction is spontaneous when:

(a) $\Delta G > 0$

(b) $\Delta G < 0$

(c) $\Delta G = 0$

(d) $\Delta H < 0$

Q9. The relation $C_p - C_v = R$ is valid for:

(a) Ideal gases only

(b) Real gases only

(c) All gases

(d) Liquids and gases

Q10. Which law is called law of conservation of energy?

(a) Zeroth law

(b) First law

(c) Second law

(d) Third law

Q11. Hess's law is based on:

(a) Enthalpy is a state function

(b) Entropy is a state function

(c) Heat is a state function

(d) Work is a state function

Q12. At equilibrium, ΔG is:

(a) Positive
(b) Negative
(c) Zero
(d) Maximum

Q13. Entropy of vaporization is:

(a) Greater than entropy of fusion
(b) Less than entropy of fusion
(c) Equal to entropy of fusion
(d) Zero

Q14. Hess's law is used to determine:

(a) Enthalpy changes that cannot be measured directly
(b) Entropy changes
(c) Free energy changes
(d) Work done

Q15. Dissolution of NH_4Cl in water is:

(a) Exothermic
(b) Endothermic
(c) Neither exothermic nor endothermic
(d) Depends on temperature

Q16. Which combination makes a process always spontaneous?

(a) $\Delta H < 0, \Delta S > 0$

(b) $\Delta H > 0, \Delta S < 0$

(c) $\Delta H < 0, \Delta S < 0$

(d) $\Delta H > 0, \Delta S > 0$

Q17. Standard state of an element is:

(a) Most stable form at 1 bar and 298 K

(b) Gaseous state

(c) Liquid state

(d) Solid state

Q18. Bond enthalpy of Cl-Cl is 242 kJ/mol. ΔH for $Cl_2(g) \rightarrow 2Cl(g)$ is:

(a) 121 kJ/mol

(b) 242 kJ/mol

(c) 484 kJ/mol

(d) -242 kJ/mol

Q19. In an isolated system:

(a) $\Delta U = 0$

(b) $\Delta H = 0$

(c) $\Delta S > 0$

(d) Both (a) and (c)

Q20. An exothermic reaction is always spontaneous when:

(a) ΔS is positive

(b) ΔS is negative

(c) Temperature is high

(d) Temperature is low

Answer Key:

1.(c) 2.(a) 3.(b) 4.(a) 5.(b) 6.(d) 7.(d) 8.(b) 9.(a) 10.(b)

11.(a) 12.(c) 13.(a) 14.(a) 15.(b) 16.(a) 17.(a) 18.(b) 19.(d) 20.(a)

13.2 Case-Based Questions

Case Study 1: Haber Process

The Haber process is used for industrial synthesis of ammonia: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. At 298 K, ΔH° = -92.4 kJ/mol and ΔS° = -198.3 J/K·mol. The reaction is exothermic but involves decrease in entropy due to decrease in number of gaseous molecules.

(i) Calculate ΔG° for the reaction at 298 K:

(a) -33.3 kJ/mol (b) -151.5 kJ/mol (c) +151.5 kJ/mol (d) +33.3 kJ/mol

(ii) Why is high temperature used despite exothermic nature?

(a) To increase yield (b) To increase rate of reaction
(c) To decrease activation energy (d) To make ΔG negative

(iii) Calculate equilibrium constant K_p at 298 K: (Given: ΔG° = -33.3 kJ/mol)

(a) 6.8×10^5 (b) 6.8×10^3 (c) 1.5×10^{-6} (d) 1.5×10^{-4}

(iv) High pressure is used in Haber process because:

(a) Δng is negative (b) Δng is positive
(c) To increase temperature (d) To decrease entropy

Answers: (i) a, (ii) b, (iii) a, (iv) a

Case Study 2: Dissolution Energy Changes

When ionic solids dissolve in water, the process involves breaking of ionic bonds (lattice enthalpy) and formation of ion-water interactions (hydration enthalpy). $CuSO_4$ dissolves with evolution of heat (exothermic), while NH_4Cl dissolves with absorption of heat (endothermic).

(i) For $CuSO_4$, dissolution is exothermic. This means:

(a) Lattice energy > Hydration energy (b) Lattice energy < Hydration energy
(c) Lattice energy = Hydration energy (d) Cannot be determined

(ii) If lattice enthalpy of $CuSO_4$ is +775 kJ/mol and enthalpy of solution is -66 kJ/mol, calculate hydration enthalpy:

(a) +709 kJ/mol (b) -709 kJ/mol (c) +841 kJ/mol (d) -841 kJ/mol

(iii) NH_4Cl dissolution is endothermic, yet it dissolves spontaneously because:

(a) ΔH is negative (b) ΔS is positive and $T\Delta S > \Delta H$
(c) ΔG is positive (d) Temperature is high

(iv) Which factor favors solubility when dissolution is endothermic?

(a) Decrease in entropy (b) Increase in entropy
(c) Decrease in temperature (d) Increase in pressure

Answers: (i) b, (ii) d, (iii) b, (iv) b

Case Study 3: Bomb Calorimetry

A bomb calorimeter is used to measure heat of combustion. In an experiment, 0.5 g of a fuel with empirical formula CH_2 was burnt in bomb calorimeter. The heat capacity of calorimeter is 8.93 kJ/K and temperature increased by 1.45 K. The molecular formula is C_8H_{16}.

(i) Calculate heat released by combustion of 0.5 g fuel:

(a) 6.15 kJ (b) 12.95 kJ (c) 14.41 kJ (d) 10.32 kJ

(ii) Calculate calorific value (kJ/g) of the fuel:

(a) 12.95 kJ/g (b) 20.5 kJ/g (c) 25.9 kJ/g (d) 30.2 kJ/g

(iii) Why is $\Delta U \neq \Delta H$ in combustion reactions?

(a) Temperature changes (b) Pressure changes
(c) $\Delta ng \neq 0$ (d) Volume is constant

(iv) Advantage of bomb calorimeter:

(a) Measures ΔH directly (b) Measures ΔU accurately
(c) Can measure for liquids only (d) Works at variable pressure

Answers: (i) b, (ii) c, (iii) c, (iv) b

14. Memory Tricks & Tips

🎯 State Functions vs Path Functions:

"PUSH-TV" for State Functions

- **P**ressure
- **U** (Internal Energy)
- **S** (Entropy)
- **H** (Enthalpy)
- **T**emperature
- **V**olume

"QW" for Path Functions: **Q**uiet **W**alk (Heat and Work)

🎯 Spontaneity Memory:

"ENIS"

- **E**xothermic ($\Delta H < 0$) and Entropy increase ($\Delta S > 0$) → Spontaneous
- **N**ever spontaneous: Endothermic ($\Delta H > 0$) and Entropy decrease ($\Delta S < 0$)
- **I**t depends on temperature for other combinations
- **S**pontaneous when $\Delta G < 0$

🎯 Enthalpy Types Memory:

"FCAVLBS" (Fickle CBS)

- **F**ormation
- **C**ombustion
- **A**tomization
- **V**aporization
- **L**attice
- **B**ond
- **S**ublimation

🎯 Sign Conventions:

"Heat IN is Positive, Work ON is Positive"

- Heat absorbed by system: q = +ve
- Work done on system (compression): w = +ve
- Heat released by system: q = -ve
- Work done by system (expansion): w = -ve

15. Common Mistakes to Avoid

❌ Mistake 1: Confusing ΔH and ΔU

Wrong: "$\Delta H = \Delta U$ always"

Right: "$\Delta H = \Delta U + P\Delta V$ or $\Delta H = \Delta U + \Delta n_g RT$"

Remember: They are equal only when $\Delta n_g = 0$ or for solids/liquids

❌ Mistake 2: Sign Convention Errors

Wrong: "Work done by system is positive"

Right: "Work done by system (expansion) is negative (IUPAC convention)"

Remember: Always use IUPAC sign conventions in CBSE exams

❌ Mistake 3: Standard Enthalpy of Formation

Wrong: "ΔH°_f for $O_2(g)$ is -393 kJ/mol"

Right: "ΔH°_f for all elements in standard state is ZERO"

Remember: Standard state = most stable form at 1 bar, 298 K

❌ Mistake 4: Spontaneity Prediction

Wrong: "Exothermic reactions are always spontaneous"

Right: "Spontaneity depends on $\Delta G = \Delta H - T\Delta S$, not just ΔH"

Remember: Both enthalpy and entropy determine spontaneity

❌ Mistake 5: Entropy Trend

Wrong: "Entropy decreases when ice melts"

Right: "Entropy increases: solid → liquid → gas"

Remember: Entropy is measure of disorder/randomness

16. Exam Strategy & Preparation

📝 Topic-wise Priority for Board Exams:

Topic	Priority	Marks Weightage
First Law & ΔH vs ΔU	⭐⭐⭐ HIGH	2-3 marks
Hess's Law & Calculations	⭐⭐⭐ HIGH	3 marks
Gibbs Energy & Spontaneity	⭐⭐⭐ HIGH	2-3 marks
Entropy & Second Law	⭐⭐ MEDIUM	2 marks
Born-Haber Cycle	⭐⭐ MEDIUM	3 marks
System Types & Definitions	⭐ LOW	1 mark

⏰ Last Minute Revision Checklist:

- ✅ First Law: $\Delta U = q + w$
- ✅ $\Delta H = \Delta U + \Delta n_gRT$ relationship
- ✅ $C_p - C_v = R$
- ✅ $\Delta G = \Delta H - T\Delta S$ and spontaneity criteria
- ✅ Hess's Law applications
- ✅ Born-Haber cycle for NaCl
- ✅ Sign conventions (IUPAC)
- ✅ Types of enthalpy changes

✍️ Writing Tips for Long Answers:

- **For Hess's Law:** Write all given equations → Manipulate to get target → Add/subtract with signs
- **For Born-Haber:** Write all steps clearly → Show cycle diagram if possible → Apply Hess's Law
- **For Spontaneity:** Calculate $\Delta G = \Delta H - T\Delta S$ → Check sign → State conclusion clearly
- **For Calculations:** Always write formula first → Substitute values with units → Show steps → Box final answer

⚡ Quick Revision Table:

Concept	Key Formula/Rule
First Law	$\Delta U = q + w$
Enthalpy-Internal Energy	$\Delta H = \Delta U + \Delta n_g RT$
Work (Isothermal)	$w = -2.303nRT \log(V_f/V_i)$
Heat Capacity Relation	$C_p - C_v = R$
Gibbs Energy	$\Delta G = \Delta H - T\Delta S$
Spontaneity	$\Delta G < 0$
Equilibrium	$\Delta G° = -2.303RT \log K$
Entropy Change	$\Delta S = q_{rev}/T$

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