Chapter 5: Thermodynamics

Comprehensive Study Notes

Class 11 Chemistry - NCERT Based

EXAM SPRINT - Complete Coverage for NEET and Board Examinations

Introduction

Thermodynamics is the only physical theory of universal content which Einstein believed would never be overthrown within the framework of its basic concepts. It deals with energy transformations in chemical and physical processes, studying how various forms of energy (chemical, electrical, mechanical) are interrelated and can be transformed from one form to another.

The laws of thermodynamics:

- Deal with energy changes of macroscopic systems
- Apply only when a system is in equilibrium
- Are not concerned with rate of energy transformations
- Focus on initial and final states rather than the process pathway

5.1 Thermodynamic Terms

5.1.1 The System and Surroundings

Basic Definitions:

- **System**: Part of universe where observations are made
- **Surroundings**: Everything other than the system that can interact with it
- **Universe**: System + Surroundings

- **Boundary**: Wall separating system from surroundings (real or imaginary)

Example: Reaction between substances A and B in a beaker

- System: Beaker containing reaction mixture
- Surroundings: Room where beaker is kept

5.1.2 Types of Systems

Classification based on matter and energy exchange:

1. **Open System**
    - Exchange of both energy and matter possible
    - Example: Reactants in open beaker
    - Boundary: Imaginary surface around beaker
2. **Closed System**
    - No exchange of matter, but energy exchange possible
    - Example: Reactants in closed vessel (copper/steel)
    - Energy can flow through conducting walls
3. **Isolated System**
    - No exchange of energy or matter
    - Example: Reactants in thermos flask
    - Perfect insulation from surroundings

5.1.3 The State of the System

State Variables (State Functions):

- Properties that depend only on current state, not on path taken
- Examples: Pressure (p), Volume (V), Temperature (T), Amount (n)

- Values are independent of how the state was reached
- Only minimum number of properties needed to completely define state

Key Concept: State of surroundings cannot be completely specified, but fortunately it's not necessary.

5.1.4 Internal Energy as a State Function

Internal Energy (U): Sum of all forms of energy in a system

- Chemical, electrical, mechanical, etc.
- Changes when:
  - Heat passes into/out of system
  - Work is done on/by system
  - Matter enters/leaves system

(a) Work

Adiabatic Process: No heat transfer between system and surroundings

- **Adiabatic wall**: Prevents heat transfer
- Work done on system increases internal energy

Joule's Experiment (1840-50):

- Method 1: Mechanical work (paddle churning water)
- Method 2: Electrical work (immersion rod)
- **Result**: Same amount of work produced same temperature change
- **Conclusion**: Internal energy is a state function

Mathematical Expression:

$$\Delta U = U_2 - U_1 = w_a d$$

IUPAC Sign Convention:

- Positive w: Work done ON the system
- Negative w: Work done BY the system

Other State Functions: Volume (V), Pressure (p), Temperature (T)

(b) Heat

Heat (q): Energy transfer due to temperature difference

- No work expenditure required
- Measured through temperature changes
- **Thermally conducting walls**: Allow heat transfer

IUPAC Sign Convention:

- Positive q: Heat transferred TO the system
- Negative q: Heat transferred FROM the system

(c) The General Case

First Law of Thermodynamics:

$$\Delta U = q + w$$

Key Points:

- For given state change: q and w can vary with path

- But q + w = ΔU depends only on initial and final states
- For isolated system: w = 0, q = 0, therefore ΔU = 0

Statement: "The energy of an isolated system is constant" (Law of conservation of energy)

Important Note: We can only measure changes in internal energy (ΔU), not absolute values.

5.2 Applications

5.2.1 Work

Focus: Pressure-volume work (mechanical work)

Setup: Cylinder with ideal gas and frictionless piston

- Initial: Volume V_i, Pressure p
- External pressure: p_{ex}
- Final: Volume Vf

Single-step Compression:

$$w = -p_{ex}(Vf - V_i) = -p_{ex}\Delta V$$

Multi-step Process:

$$w = -\Sigma\ p\Delta V$$

Reversible Process:

- **Definition**: Process that can be reversed by infinitesimal change
- Proceeds through series of equilibrium states

- System and surroundings always in near equilibrium

For Reversible Process:

$$w_{rev} = -\int(V_i \text{ to } Vf)\ p_{in}\ dV$$

For Ideal Gas at Constant Temperature:

$$w_{rev} = -nRT \ln(Vf/V_i) = -2.303\ nRT \log(Vf/V_i)$$

Free Expansion:

- Gas expansion in vacuum ($p_{ex} = 0$)
- No work done: $w = 0$

Special Cases:

1. **Isothermal Irreversible Change:**

   $$q = -w = p_{ex}(Vf - V_i)$$

2. **Isothermal Reversible Change:**

   $$q = -w = nRT \ln(Vf/V_i)$$

3. **Adiabatic Change:**

   $$q = 0,\ \Delta U = w_{a}d$$

5.2.2 Enthalpy (H)

(a) A Useful New State Function

Problem: Most chemical reactions occur at constant pressure, not constant volume

At Constant Pressure:

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

Enthalpy Definition:

$$H = U + pV$$

For Finite Changes at Constant Pressure:

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

Key Relationship:

$\Delta H = q_p$ (heat absorbed at constant pressure)

Important Points:

- H is a state function (depends on U, p, V - all state functions)
- ΔH is path independent
- $\Delta H < 0$: Exothermic reaction (heat evolved)
- $\Delta H > 0$: Endothermic reaction (heat absorbed)

For Gas Phase Reactions:

$$p\Delta V = \Delta n_m RT$$

where Δn_m = (moles of gaseous products) - (moles of gaseous reactants)

General Relationship:

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

(b) Extensive and Intensive Properties

Extensive Properties: Depend on quantity of matter

- Examples: Mass, volume, internal energy, enthalpy, heat capacity
- Value changes with amount of substance

Intensive Properties: Independent of quantity of matter

- Examples: Temperature, density, pressure
- Value remains same regardless of amount

Molar Properties: Extensive property per mole of substance

- Example: Molar volume (V_m), Molar heat capacity (C_m)
- Always intensive properties

(c) Heat Capacity

Definition: Heat required to raise temperature by 1°C (or 1K)

Mathematical Expression:

$$q = C\Delta T$$

Types:

- **Heat Capacity (C)**: For given amount of substance
- **Molar Heat Capacity (C_m)**: Per mole of substance
- **Specific Heat (c)**: Per unit mass of substance

Formula:

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

(d) Relationship between C_p and C_v for Ideal Gas

At Constant Volume:

$$q_v = C_v\Delta T = \Delta U$$

At Constant Pressure:

$$q_p = C_p\Delta T = \Delta H$$

For One Mole of Ideal Gas:

$$\Delta H = \Delta U + R\Delta T$$
$$C_p\Delta T = C_v\Delta T + R\Delta T$$

Therefore:

$$C_p - C_v = R$$

5.3 Measurement of ΔU and ΔH: Calorimetry

Calorimetry: Experimental technique to measure energy changes

- Process carried out in **calorimeter**
- Immersed in known volume of liquid
- Temperature changes measured

(a) ΔU Measurements

Bomb Calorimeter: Measures heat at constant volume

- **Setup**: Steel vessel (bomb) in water bath
- **Conditions**: Constant volume, no work done
- **Result**: $\Delta U = q_v$

Process:

1. Combustible substance burnt in pure oxygen
2. Heat transferred to surrounding water
3. Temperature change monitored
4. Convert to q_v using known heat capacity

(b) ΔH Measurements

Constant Pressure Calorimeter: Measures heat at atmospheric pressure

- **Result**: $\Delta H = q_p$ (heat of reaction or enthalpy of reaction)
- **Exothermic**: q_p negative, ΔH negative
- **Endothermic**: q_p positive, ΔH positive

5.4 Enthalpy Change ($\Delta_r H$) of a Reaction

Reaction Enthalpy: Enthalpy change when reactants convert to products

General Formula:

$$\Delta_r H = \Sigma a_iH(\text{products}) - \Sigma b_iH(\text{reactants})$$

Example: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$$\Delta_r H = [H(CO_2,g) + 2H(H_2O,l)] - [H(CH_4,g) + 2H(O_2,g)]$$

(a) Standard Enthalpy of Reactions

Standard State: Pure form at 1 bar pressure

- Usually data taken at 298 K
- Denoted by superscript °: ΔH°

(b) Enthalpy Changes during Phase Transformations

Standard Enthalpy of Fusion ($\Delta_{fus} H^\circ$):

- Enthalpy change for melting 1 mole of solid
- Always positive (endothermic)
- Example: $H_2O(s) \rightarrow H_2O(l)$; $\Delta_{fus} H^\circ = 6.00$ kJ mol^{-1}

Standard Enthalpy of Vaporization ($\Delta_{vap} H^\circ$):

- Enthalpy change for vaporizing 1 mole of liquid
- Always positive (endothermic)

- Example: $H_2O(l) \rightarrow H_2O(g)$; $\Delta_{vap} H° = +40.79$ kJ mol^{-1}

Standard Enthalpy of Sublimation ($\Delta_{sub} H°$):

- Direct solid to vapor conversion
- Example: $CO_2(s) \rightarrow CO_2(g)$; $\Delta_{sub} H° = 25.2$ kJ mol^{-1}

Important: Magnitude depends on strength of intermolecular interactions

(c) Standard Enthalpy of Formation

Definition: Enthalpy change for formation of 1 mole of compound from its elements in most stable states

Symbol: $\Delta_f H°$

Examples:

- $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta_f H° = -285.8$ kJ mol^{-1}
- $C(\text{graphite}) + 2H_2(g) \rightarrow CH_4(g)$; $\Delta_f H° = -74.81$ kJ mol^{-1}

Convention: $\Delta_f H° = 0$ for elements in their reference states

Calculation of Reaction Enthalpy:

$$\Delta_r H° = \Sigma\, a_i \Delta_f H°(\text{products}) - \Sigma\, b_i \Delta_f H°(\text{reactants})$$

(d) Thermochemical Equations

Definition: Balanced chemical equation with $\Delta_r H$ value

Example: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta_r H° = -1367$ kJ mol^{-1}

Important Conventions:

1. Coefficients refer to moles, not molecules
2. $\Delta_r H°$ refers to moles as specified in equation
3. When equation is reversed, sign of $\Delta_r H°$ is reversed
4. Enthalpy is extensive property

(e) Hess's Law of Constant Heat Summation

Statement: If reaction takes place in several steps, standard reaction enthalpy is sum of standard enthalpies of intermediate reactions at same temperature.

Mathematical Expression:

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \ldots$$

Application: Calculate enthalpy changes for reactions that cannot be measured directly

Example: Formation of CO(g) from C(graphite) and O_2(g)

- Cannot measure directly due to CO_2 formation
- Use combination of known reactions

5.5 Enthalpies for Different Types of Reactions

(a) Standard Enthalpy of Combustion ($\Delta c H°$)

Definition: Enthalpy change per mole when substance undergoes complete combustion in standard states

Examples:

- Butane: $C_4H_{10}(g) + 13/2\ O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$; $\Delta c H° = -2658.0\ kJ\ mol^{-1}$
- Glucose: $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$; $\Delta c H° = -2802.0\ kJ\ mol^{-1}$

Note: Body generates energy through same overall process as combustion

(b) Enthalpy of Atomization (Δa H°)

Definition: Enthalpy change for breaking 1 mole of bonds to obtain atoms in gas phase

Examples:

- $H_2(g) \rightarrow 2H(g)$; $\Delta a\ H^\circ = 435.0\ kJ\ mol^{-1}$
- $CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta a\ H^\circ = 1665\ kJ\ mol^{-1}$
- $Na(s) \rightarrow Na(g)$; $\Delta a\ H^\circ = 108.4\ kJ\ mol^{-1}$

(c) Bond Enthalpy (Δbond H°)

Two Types:

1. **Bond Dissociation Enthalpy**: Breaking 1 mole of specific bonds in gaseous molecules
   - For diatomic molecules: Same as atomization enthalpy
   - Example: $H_2(g) \rightarrow 2H(g)$; $\Delta H_{-}H = 435.0\ kJ\ mol^{-1}$
2. **Mean Bond Enthalpy**: Average energy for breaking specific bond type
   - Used for polyatomic molecules
   - Example: For $CH_{4,}$ $\Delta C_{-}H = \frac{1}{4}(\Delta a\ H^\circ) = 416\ kJ\ mol^{-1}$

Reaction Enthalpy from Bond Enthalpies:

$$\Delta_r H^\circ = \Sigma(\text{Bond enthalpies reactants}) - \Sigma(\text{Bond enthalpies products})$$

Note: Valid when all substances are in gaseous state

(d) Lattice Enthalpy

Definition: Enthalpy change when 1 mole of ionic compound dissociates into gaseous ions

Example: $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$; Δlattice H° = +788 kJ mol^{-1}

Born-Haber Cycle: Indirect method to calculate lattice enthalpy

Steps for NaCl:

1. Sublimation: $Na(s) \rightarrow Na(g)$; Δsub H° = 108.4 kJ mol^{-1}
2. Ionization: $Na(g) \rightarrow Na^+(g) + e^-$; Δi H° = 496 kJ mol^{-1}
3. Dissociation: $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$; ½Δbond H° = 121 kJ mol^{-1}
4. Electron gain: $Cl(g) + e^- \rightarrow Cl^-(g)$; Δeg H° = -348.6 kJ mol^{-1}
5. Formation: $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$; Δf H° = -411.2 kJ mol^{-1}

Using Hess's Law: Δlattice H° = +788 kJ mol^{-1}

(e) Enthalpy of Solution (Δsol H°)

Definition: Enthalpy change when 1 mole of substance dissolves in specified amount of solvent

Relationship:

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

For ionic compounds: Usually positive (endothermic dissolution)

(f) Enthalpy of Dilution

Definition: Heat change when additional solvent is added to solution

Depends on:

- Original concentration
- Amount of solvent added

Example: HCl solutions with different water amounts show varying enthalpy changes approaching limiting value in infinitely dilute solution

5.6 Spontaneity

Key Questions:

- What drives chemical reactions?
- What determines direction of spontaneous change?

Spontaneous Process: Has potential to proceed without external assistance

- Does not indicate rate of reaction
- Cannot reverse direction on its own
- Is an irreversible process

(a) Is Decrease in Enthalpy a Criterion for Spontaneity?

Initial Hypothesis: Reactions proceed to minimize energy (like water flowing downhill)

Supporting Evidence: Many exothermic reactions are spontaneous

- $\frac{1}{2}N_2(g) + 3/2H_2(g) \rightarrow NH_3(g)$; $\Delta_r H° = -46.1$ kJ mol^{-1}
- $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta_r H° = -285.8$ kJ mol^{-1}

Contradicting Evidence: Some endothermic reactions are also spontaneous

- $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$; $\Delta_r H° = +33.2$ kJ mol^{-1}
- $C(graphite) + 2S(l) \rightarrow CS_2(l)$; $\Delta_r H° = +128.5$ kJ mol^{-1}

Conclusion: Decrease in enthalpy alone cannot determine spontaneity

(b) Entropy and Spontaneity

Key Observation: Some spontaneous processes have ΔH = 0

- Example: Gas diffusion in isolated container

Entropy (S): Measure of degree of randomness or disorder

- Greater disorder → Higher entropy
- Crystalline solid: Lowest entropy (most ordered)
- Gaseous state: Highest entropy (most disordered)

Entropy as State Function:

- Independent of path
- For reversible process: $\Delta S = q_r ev/T$

Second Law of Thermodynamics:

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ΔStotal = ΔSsystem + ΔSsurroundings ≥ 0
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For spontaneous process: ΔStotal > 0 **At equilibrium**: ΔStotal = 0

(c) Gibbs Energy and Spontaneity

Problem: Most chemical systems are not isolated

- Need to consider both enthalpy and entropy changes

Gibbs Energy Definition:

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G = H - TS
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Gibbs Energy Change:

$\Delta G = \Delta H - T\Delta S$ (at constant temperature)

Relationship to Spontaneity:

- $\Delta G < 0$: Process is spontaneous
- $\Delta G > 0$: Process is non-spontaneous
- $\Delta G = 0$: System at equilibrium

Derivation: Starting from total entropy change

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

$\Delta S_{surr} = -\Delta H_{sys}/T$

Therefore: $\Delta S_{total} = \Delta S_{sys} - \Delta H_{sys}/T$

For spontaneous: $\Delta S_{total} > 0$

So: $T\Delta S_{sys} - \Delta H_{sys} > 0$

Or: $-(\Delta H_{sys} - T\Delta S_{sys}) > 0$

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

Temperature Effects on Spontaneity:

ΔH	**ΔS**	**ΔG**	**Spontaneity**
-	+	-	Always spontaneous
-	-	- (low T)	Spontaneous at low T
+	+	- (high T)	Spontaneous at high T
+	-	+	Never spontaneous

(d) Entropy and Second Law of Thermodynamics

Second Law: Natural direction of spontaneous change is increase in entropy for isolated systems

Applications:

- Explains prevalence of exothermic reactions
- Heat release increases surroundings disorder
- Overall entropy change positive

(e) Absolute Entropy and Third Law of Thermodynamics

Third Law: Entropy of pure crystalline substance approaches zero as temperature approaches absolute zero

Significance:

- Perfect order at 0 K
- Allows calculation of absolute entropy values
- Standard entropies used in calculations

5.7 Gibbs Energy Change and Equilibrium

At Equilibrium: Free energy is minimum

- $\Delta_r G = 0$ for reversible reaction

Relationship with Equilibrium Constant:

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

Combined Equation:

$\Delta_rG° = \Delta_rH° - T\Delta_rS°$

Applications:

1. Calculate K from $\Delta_rG°$
2. Calculate $\Delta_rG°$ from measured K
3. Predict reaction feasibility

Key Relationships:

- Large negative $\Delta_rH°$: Large K (near completion)
- Large positive $\Delta_rH°$: Small K (little product formation)
- $\Delta_rS°$ also affects K value significantly

NEET-Specific Important Points

High-Yield Topics:

1. **First Law Applications**: $\Delta U = q + w$ calculations
2. **Enthalpy Calculations**: Using Hess's Law and formation enthalpies
3. **Bond Energy Problems**: Reaction enthalpy from bond enthalpies
4. **Spontaneity Predictions**: Using $\Delta G = \Delta H - T\Delta S$
5. **Equilibrium Constants**: $\Delta G°$ and K relationships

Common NEET Question Patterns:

1. **Numerical Problems**:
    - Calorimetry calculations
    - Hess's law applications

    - Bond enthalpy computations
    - Gibbs energy and equilibrium
2. **Conceptual Questions**:
    - System types identification
    - Spontaneity criteria
    - State function properties
    - Sign conventions
3. **Graph Interpretation**:
    - Enthalpy diagrams
    - Phase change processes
    - Temperature-dependent spontaneity

Memory Aids and Mnemonics

Sign Conventions (IUPAC):

- **Heat**: + (into system), - (out of system)
- **Work**: + (on system), - (by system)

Spontaneity Criteria:

- **$\Delta G < 0$**: Spontaneous (Go!)
- **$\Delta G > 0$**: Non-spontaneous (No go!)
- **$\Delta G = 0$**: Equilibrium

State Functions: "UPVTH"

- U (Internal energy), P (Pressure), V (Volume), T (Temperature), H (Enthalpy)

Practice Questions for NEET

Multiple Choice Questions:

1. Which of the following is not a state function? a) Internal energy b) Heat c) Enthalpy d) Entropy
2. For the reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H = -92.4$ kJ The enthalpy of formation of NH_3 is: a) -92.4 kJ/mol b) -46.2 kJ/mol c) +92.4 kJ/mol d) +46.2 kJ/mol
3. A process will be spontaneous if: a) $\Delta H < 0$ only b) $\Delta S > 0$ only c) $\Delta G < 0$ d) Both $\Delta H < 0$ and $\Delta S > 0$

Short Answer Questions:

1. State and explain the first law of thermodynamics.
2. What is Hess's law? Give one application.
3. Define standard enthalpy of formation with example.

Long Answer Questions:

1. Derive the relationship $\Delta H = \Delta U + \Delta n_g RT$ for gas phase reactions.
2. Explain how Gibbs energy change determines spontaneity of reactions.
3. Calculate lattice energy of NaCl using Born-Haber cycle.

Summary Tables

Enthalpy Types:

Type	Symbol	Definition	Sign
Formation	$\Delta_f H°$	1 mol compound from elements	Can be +/-
Combustion	$\Delta_c H°$	Complete burning in O_2	Always -
Fusion	$\Delta_{fus} H°$	Solid to liquid	Always +
Vaporization	$\Delta_{vap} H°$	Liquid to gas	Always +

Type	Symbol	Definition	Sign
Sublimation	Δsub H°	Solid to gas	Always +

System Types:

System	Matter Exchange	Energy Exchange	Example
Open	Yes	Yes	Open beaker
Closed	No	Yes	Sealed conducting vessel
Isolated	No	No	Thermos flask

EXAM SPRINT - Master Thermodynamics with focused study on energy calculations, spontaneity criteria, and equilibrium relationships. Regular practice with numerical problems involving enthalpy changes, Gibbs energy, and equilibrium constants is essential for NEET success.

Key Success Strategy: Focus on sign conventions, understand the relationship between different thermodynamic quantities, and practice applying Hess's law. Master the conditions for spontaneity and the connection between ΔG and equilibrium constants.

Source: NCERT Chemistry Class 11, Chapter 5 - Comprehensive coverage for NEET preparation