Name: Chandra Shekhar
College: IIT Gandhinagar
Subject: Chemistry
Weightage: High
Title: Thermodynamics

Thermodynamics

Introduction to Thermodynamics

Thermodynamics explores the interconversion of energy forms and their impact on physical and chemical systems. Its foundational laws are derived from empirical observations.

Key Concepts

1. **System and Surroundings:**
   - **System:** The portion of the universe under study.
   - **Surroundings:** Everything outside the system.
   - **Boundary:** The interface that separates the system from its surroundings.
2. **Classification of Systems:**
   - **Isolated:** No matter or energy exchange. (e.g., Thermos flask)
   - **Closed:** Exchanges energy but not matter. (e.g., Sealed container)
   - **Open:** Exchanges both matter and energy. (e.g., Open vessel)
3. **State of a System:** Defined by properties like pressure (P), volume (V), and temperature (T).
4. **State vs Path Functions:**
   - **State functions:** Depend only on initial and final states (e.g., U, H, S).
   - **Path functions:** Depend on the route taken (e.g., q, w).
5. **Extensive vs Intensive Properties:**
   - **Extensive:** Vary with the quantity of matter (e.g., mass, enthalpy).
   - **Intensive:** Independent of quantity (e.g., temperature, pressure).
6. **Thermodynamic Processes:**
   - **Isothermal:** Constant temperature
   - **Adiabatic:** No heat exchange
   - **Isobaric:** Constant pressure
   - **Isochoric:** Constant volume
   - **Cyclic:** System returns to original state
   - **Reversible:** Infinitely slow and reversible process
   - **Irreversible:** Fast, spontaneous and non-reversible
7. **Internal Energy (U):** Total energy within a system; a state function.
8. **Heat and Work:**
   - **Heat (q):** Energy transfer due to temperature difference

- **Work (w):** Energy transfer through non-thermal means
- **P-V Work:** $w = -P_{ext}\Delta V$
- **Reversible expansion:** $w = -nRT\ln(\frac{V_2}{V_1})$

First Law of Thermodynamics

"Energy can neither be created nor destroyed."

$$\Delta U = q + w$$

Special cases:

- **Isothermal:** $\Delta U = 0 \Rightarrow q = -w$

- **Adiabatic:** $q = 0 \Rightarrow \Delta U = w$
- **Isochoric:** $w = 0 \Rightarrow \Delta U = q_V$
- **Isobaric:** $\Delta U = q_P - P\Delta V$

Enthalpy (H)

$$H = U + PV, \quad \Delta H = \Delta U + P\Delta V$$

At constant pressure: $\Delta H = q_P$

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

Thermochemistry

Study of heat flow in chemical reactions.

Reaction Types

- **Exothermic:** $\Delta H < 0$ (e.g., combustion)
- **Endothermic:** $\Delta H > 0$ (e.g., decomposition of $CaCO_3$)

Standard Enthalpies

- **Formation (ΔH_f°):** 1 mole compound from elements
- **Combustion (ΔH_c°):** 1 mole substance completely burns
- **Neutralization (ΔH_{neut}°):** 1 eq. acid + 1 eq. base, typically -57.3 kJ/mol for strong acid-base

Hess's Law

Enthalpy is a state function:

> "Total enthalpy change is the same, whether reaction occurs in one step or many."

Bond Enthalpy

$$\Delta H_{rxn} = \sum \text{Bond energies of reactants} - \sum \text{Bond energies of products}$$

Second Law of Thermodynamics

"In spontaneous processes, total entropy increases."

Entropy (S)

- $\Delta S = \frac{q_{rev}}{T}$
- **Spontaneous:** $\Delta S_{total} > 0$
- **Reversible:** $\Delta S_{total} = 0$
- **Standard entropy change:** $\Delta S = \sum S_{products} - \sum S_{reactants}$

Entropy increases with:

- Temperature
- Phase change: solid $\rightarrow$ liquid $\rightarrow$ gas
- Increase in gas moles

Gibbs Free Energy (G)

$$G = H - TS, \quad \Delta G = \Delta H - T\Delta S$$

Spontaneity criteria:

- $\Delta G < 0$: Spontaneous
- $\Delta G > 0$: Non-spontaneous
- $\Delta G = 0$: Equilibrium

Third Law of Thermodynamics

"Entropy of a perfect crystal at absolute zero is zero."

Key Constants and Values

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- 1 cal = 4.184 J
- Enthalpy of fusion (ice): 6.01 kJ/mol
- Vaporization (water): 10.5 kcal/mol
- Halogen bond energy order: $Cl_2 > Br_2 > F_2 > I_2$
- Heat of reaction is path-independent