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CHEMISTRY

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CLASS 11 & 12th



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CLASS 11th

**Thermodynamics and
Thermochemistry**

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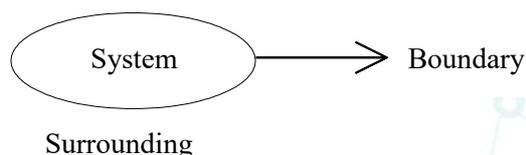


Thermodynamics

01. Introduction

The study of energy transformations is the subject matter of thermodynamics.

Some Basics Terms



Types of system

- (I) **Based on exchange of mass and energy**
 - (i) **Isolated system** : It cannot exchange matter and energy with the surrounding.
 - (ii) **Closed system** : It can exchange energy but not matter.
 - (iii) **Open system** : It can exchange matter.
- (II) **Based on system composition**
 - (i) **Homogeneous system** : Made up of one phase only
 - (ii) **Heterogeneous system** : More than one phase.

02. Properties of a System

Particular set of its measurable quantities.

Intensive property : value does not depend on the size (or mass) of the system.

Extensive property : value depends on the size (or mass) of the system.

Variables like P, V, T are *State Functions* or *State Variables* because their values depends only on initial and final state.

Path function

Function which depends on the path .

State functions : Pressure, volume, temperature, Gibb's free energy, internal energy, entropy

Path function : Work, heat, Loss of energy due to friction

03. Reversible and Irreversible Process

S.No.	Reversible process	Irreversible process
1.	Driving force is infinitesimally small.	Driving force is large and finite. PV
2.	A reversible heat transfer take place across temperature difference dT	Irreversible heat transfer take place across difference ΔT
3.	It is an ideal process.	It is a real process
4.	It take infinite time for completion of process.	It take finite time for completion of process.

Cyclic Process $\Delta E = 0$ and $\Delta H = 0$

Isochoric Process $\Delta V = 0$

Isobaric Process $\Delta P = 0$

04. Work

PV- Work analysis :

For small displacement dx due to force F , work done on the system.

$$dw = F \cdot dx$$

Also $F = PA$

$$dW = PA \cdot dx$$

$$V = (\ell - x)A$$

$$\Rightarrow dV = -A \cdot dx \quad \Rightarrow dW = -P_{\text{ext}} \cdot dV$$

$$\Rightarrow W_{PV} = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

• **Isothermal Process** $dT = 0$

• **Adiabatic process** $q = 0$

05. Heat

Heat is defined as the energy that flows into or out of a system.

(i) $q_V = nC_V dT$ (for constant volume process)

(ii) $q_P = nC_P dT$ (for constant pressure process)

(iii) $C_{p,m} - C_{v,m} = R$

(iv) C_V & C_P depends on temperature even for an ideal gas. ($C = a + bT + cT^2 \dots$)

06. Internal Energy (E & U)

$$U = U_{\text{Kinetic}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

- NOTE**  (i) U is a state function & is an extensive property.
 (ii) $\Delta U = q_V$, heat supplied to a gas constant volume, since all the heat supplied goes to increase the internal energy of the gas.
 (iii) $U = f(T, V)$
 (iv) $dU = C_V dT$
 (v) $\Delta U = \int C_V \cdot dT$

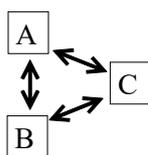
07. Degree of Freedom and Equipartition principle

The **degree of freedom** in a molecule are given by the number of coordinates required to locate all the mass points (atoms) in a molecule. it has three degree of freedom corresponding to translation motion in the three independent spatial directions X, Y and Z. If a molecule contain N atoms, each atom contributes these three degree of freedom, so the molecule has a total of 3N degree of freedom.

Atomicity	n_u	n_{R_0}	n_{vib}	C_V		C_P		γ	
				Excl.Vib	Incl.Vib	Excl.Vib	Incl.Vib	Excl.Vib	Incl.Vib
Mono	3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di	3	2	2	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri	Linear	3	2	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	3R	6R	4R	7R	$\frac{4}{3}$	$\frac{7}{6}$

08. Laws of Thermodynamics

Zeroth law of thermodynamics : It is based on thermal equation, two systems in thermal equilibrium with a 3rd system are also in thermal equilibrium with each other.



First Law:

“Total energy of universe remain constant”. It is law of conservation of energy.

$$\Delta U = q + W,$$

09. Enthalpy

Enthalpy is a measure of the total energy of a thermodynamics system.

$$H = U + PV$$

$$dH = dU + d(PV)$$

Property of Enthalpy parameter

- (i) Enthalpy is a thermodynamic potential. It is a state function and an extensive quantity.
- (ii) The change ΔH is positive endothermic reaction, and negative in exothermic process.
- (iii) $\Delta H = \Delta U + P \Delta V$
combining with first law.

$$\Delta H = q_p = \text{Heat added at constant pressure}$$