

CHEMISTRY

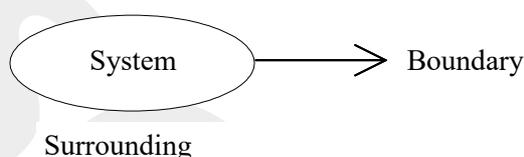
CLASS NOTES FOR CBSE

Chapter 06 Thermodynamics and Thermochemistry

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 depend 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



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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 $F = PA$

$$dW = PA \cdot dx$$

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

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

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

• **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 volume 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)

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



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- NOTE**  (i) U is a state function & is an extensive property.
(ii) $\Delta E + q_v$, 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) $\Delta U = \int C_V \cdot dT$

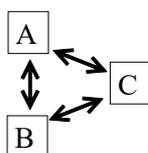
07. Degree of Freedom and Equipartition principle

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	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	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.

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



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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.
 $\Delta H = q_p =$ Heat added at constant pressure

NOTE \Rightarrow $H = f(T, P)$
 $\Delta H = \int C_p \cdot dT$
 $\Delta H = \int C_p \cdot dT$

Relationship between ΔH & ΔU :

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

Change in internal energy and enthalpy in phase transition

Fusion:

Solid ice at 273K and 1 atm pressure reversibly changes into a liquid water. Reversibly, isothermally and isobarically, absorbed heat is known as latent heat of fusion or enthalpy of fusion.

Vapourisation :

Water at 373K and 1 atm pressure changes into vapours absorbed heat is known as latent heat of vapourisation. The latent heat of vapourisation is heat exchanged isothermally, isobarically and reversibly to convert water into its vapour at boiling point.

$$\Delta H_{\text{vap.}} = \Delta U_{\text{vap.}} + RT$$

10. Calculation of Work Done in Various Process

Isothermal process : In isothermal process, work done can be calculated as

- (i) If process is reversible

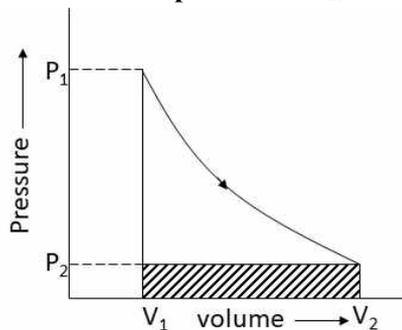
$$W = -nRT \ln \frac{V_2}{V_1}$$



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(ii) **Irreversible isothermal expansion** : $w_{\text{irr}} = -P_{\text{ext}} \Delta V - \Delta KE$.



(iii) **Free expansion of ideal gas** : when ideal gas is allowed to expand against zero external pressure, the process is called free expansion. $W = 0$ for free expansion. The temperature above which a gas gets heated up upon expansion is called **inversion temperature**.

Isobaric process

In isobaric process, pressure remains constant during the process.

$$w = - \int_{V_2}^{V_1} PdV = -P_{\text{ext}} (V_2 - V_1) = - nR\Delta T \quad \& \quad \Delta H = q_p$$

Isochoric process

Since $dV = 0 \Rightarrow W = 0$
 from 1st law $\Delta U = q$

Adiabatic process

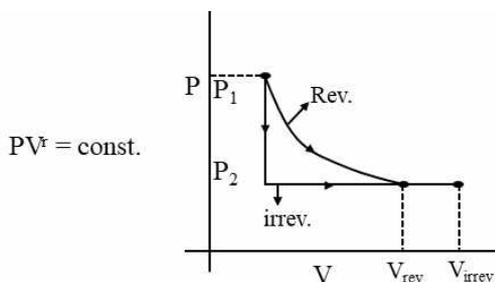
$$q = 0, W = nC_v (T_2 - T_1) = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

11. Comparison of Various Processes Under Defined Conditions

(i) **Graphical comparison between adiabatic reversible and irreversible process :**

Case-I : for same final pressure

(a) Expansion :



(b) Compression :

