❖ Introduction-

Solid ⇌ Liquid ⇌ Water
Ice   water   vapour

Energy
Changes

❖ Thermodynamics
It is phenomenon, which is concerned with the energy changes in physical and chemical transformations.

❖ System
A part of universe thermodynamics investigation is called as the System.

❖ Surroundings
The all other parts of the universe, outside the system, are called as Surroundings.

Functions

State Function

The property which depends on the state of a system and independent of a bath followed to attain it, is called as State function

Ex. S E H V A G

S:- Entropy

E:- Internal energy

H:- Enthalpy

V:- Volume

A:- Helmholtz free energy

G :- Gibbs free energy

Path function

The property which depend on the path are called as Path function

Ex. Work (W) and heat (Q)

Equilibrium

Thermodynamics Equilibrium

A system is said to be in thermodynamics equilibrium if state function do not vary with time

Non –thermodynamic equilibrium

A system is said to be in non-thermodynamics equilibrium, it state function vary with time

Types of system

↓ (On the basis of exchange of energy and matter)

Open System

A system which exchanges both energy and matter with surroundings is called as open system

Ex. Hot coffee placed in cup in a room

Closed System

A system that exchanges energy and not the matter with the surroundings, is called as a closed system

Ex. A cup container hot coffee is covered with saucer

Isolated system

A system that does not exchange energy as well as matter is called as isolated system

Ex. A hot coffee is placed in thermos flask

Properties of System

↓ (On the basis of dependence on amount of matter)

Extensive Property

A property which depends on the amount of matter, present in a system is called as Extensive Property

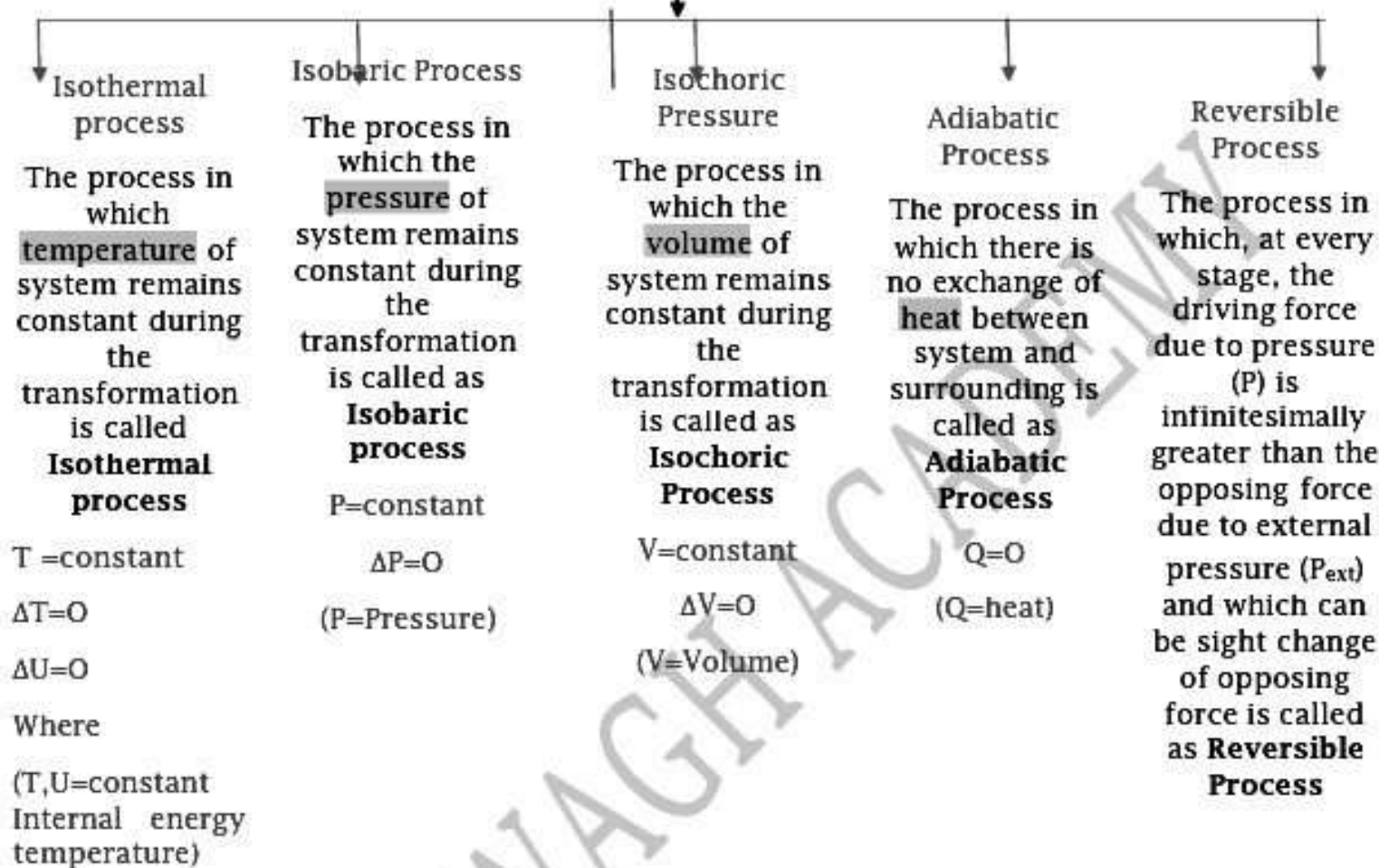Ex. Mass, volume, Internal energy, heat capacity, number of moles.

Intensive property

A property which is independent of the amount of matter, present in a system, is called as intensive property

Ex. Pressure, temperature surface tension, Viscosity Melting point, Boiling point, specific heat

Process

A transition from one equilibrium state to another is called as Process

Isothermal process	Isobaric Process	Isochoric Pressure	Adiabatic Process	Reversible Process
The process in which **temperature** of system remains constant during the transformation is called **Isothermal process**	The process in which the **pressure** of system remains constant during the transformation is called as **Isobaric process**	The process in which the **volume** of system remains constant during the transformation is called as **Isochoric Process**	The process in which there is no exchange of **heat** between system and surrounding is called as **Adiabatic Process**	The process in which, at every stage, the driving force due to pressure (P) is infinitesimally greater than the opposing force due to external pressure (P_{ext}) and which can be sight change of opposing force is called as **Reversible Process**
T =constant	P=constant	V=constant	Q=0	
ΔT=0	ΔP=0	ΔV=0	(Q=heat)	
ΔU=0	(P=Pressure)	(V=Volume)		
Where				
(T,U=constant Internal energy temperature)				

❖ Features of Reversible Process:-
a. The driving force and opposing force differ by an infinitesimal amount
b. The process can be reversed by an infinitesimal change in condition
c. A reversible process infinity slowly and takes place in infinite number of steps
d. At the end of every step of the process, the system attains mechanical equilibrium with surroundings

❖ <u>Expression for pressure – volume (pv) work</u>

Consider a certain amount of gas at constant pressure P, which is enclosed in a cylinder fitted with frictionless, rigid, movable piston of Area A, as shown in fig. It is allowed to undergo expansion as...

Let
Force $= f = - P_{ext} \times A$ .....(1)
$W = f \times d$ ......(2)

So, substituting value of f in eq^n (2)
We get, $W = - P_{ext} \times A \times d$ ....(3)

$A \times d = \Delta V$ = change in volume ....(4)
Put eq^n (4) in eq^n (3)

$W = - P_{ext} \times \Delta V$
$W = - P_{ext} \times (V_2 - V_1)$

Where
  f = force
  W = work done
  P_{ext} = external pressure
  V_1 = Initial volume
  V_2 = Final volume
  A = Area
  d = displacement
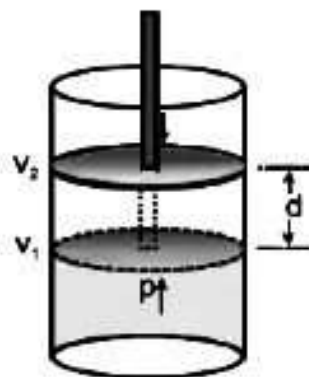
$$W = - P_{ext} (V_2 - V_1)$$

During expansion	During compression
Volume increase	volume decrease
So $V_2 > V_1$	So $V_1 > V_2$
$W = -ve$	$W = +ve$

Nature of

Work

W=Force x displacement

$W = f \times d$ ....(1)

It is also realized that

$W = P \times V$ ....(2)

So now, P = pressure $= \frac{force}{Area} = \frac{f}{A}$

$A = Area = d^2$

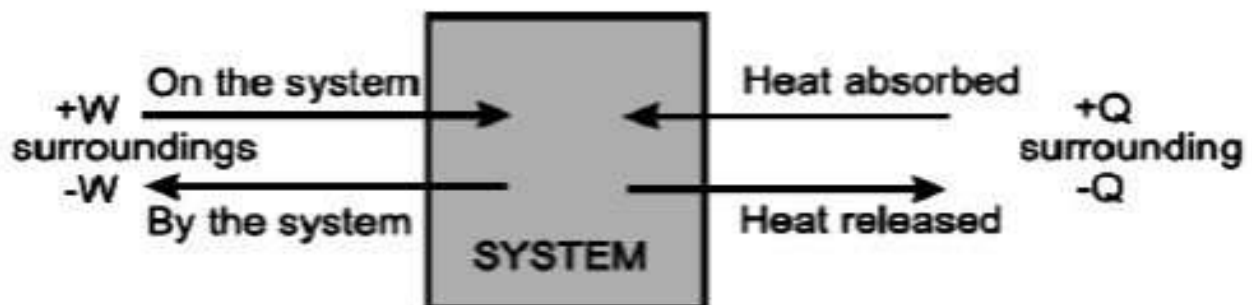d = displacement

$V = Volume = d^3$

So,

$P \times V = \frac{f}{A} \times V = \frac{f}{d2} \times d^3 = f \times d = W$

So, $\underline{W = P \times V}$

Heat

The form of energy, by which the system exchanges energy with its surroundings is called as **heat**

❖ Sign convention of work and heat:-

-W → Work done by the system
+W → Work done on the system
+Q → Heat is absorbed by the system
-Q → Heat is released by the system

❖ **Free expansion:-**
1. The expansion against zero opposing force, is called as **free expansion**
2. Free expansion, occur in vaccum

> Pext = 0
> So, W = - Pext * ΔV
> **W = 0**

❖ **Work unit conversion**

> $1\ dm^3 \cdot bar = 100\ J$

❖ **Expression for the maximum work:-**

Consider n moles of an ideal gas enclosed in a cylinder fitted with frictionless movable rigid piston.

The piston is allowed to expand isothermally and reversibly from initial volume V_1 to final volume V_2 at temperature T.

At every step, the P_{ext} is made infinitesimally smaller than pressure (P) of gas.

dw = Pext x dv
dw = -P x dv
Integrating both sides

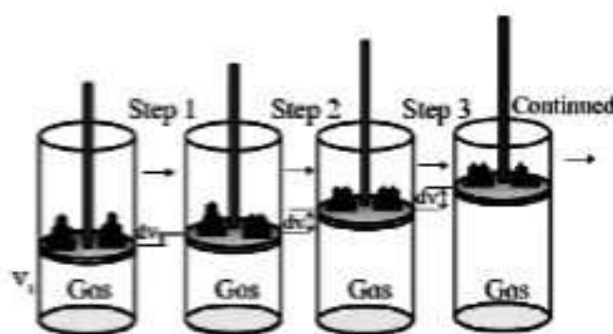$$\int_{W1}^{W2} dw = - \int_{V1}^{V2} P.dv \qquad (1)$$

As PV = nRT

$$So\ P = \frac{nRt}{V} \qquad (2)$$

• Substituting the value of P from eqⁿ (2) into eqⁿ (1)

$$W_{max} = - \int_{V1}^{V2} \frac{nRT}{V} . dv$$

$$= -nRT \cdot \int_{V1}^{V2} \frac{1}{V} \cdot dv$$

$$= -nRT \ln[V]_{V1}^{V2}$$

$$= -nRT(\ln[V_2]-\ln[V_1])$$

$$W_{max}= -nRT \ln \left(\frac{V2}{V1}\right) \qquad (a)$$

$$\frac{1}{x}dx = \ln x$$

$$\ln x = 2.303 \times \log x$$

$$\ln m - \ln n = \ln \left(\frac{m}{n}\right)$$

So

$$W_{max} = -2.303nRT \log_{10} \left(\frac{V2}{V1}\right) \qquad ....(b)$$

According to Boyle's Law,

$$\frac{V2}{V1} = \frac{P1}{P2}$$

so

$$W_{max} = -2.303nRT \log_{10} \left(\frac{P1}{P2}\right) \qquad .... (c)$$

❖ Internal Energy :-

The definite amount of energy stored in a substance is called as **internal energy**

Change in
Internal energy = ΔU = ($U_2 - U_1$) of a system

Where U_2 = Internal energy of final state
$\quad\quad$ U_1 = Internal energy of Initial state

❖ First law of thermodynamics:-
Statement:-

1. Energy of the universe remains constant
2. The total internal energy of an isolated system is constant
3. Energy can be neither be created nor be destroyed, but can be converted from one from to another.
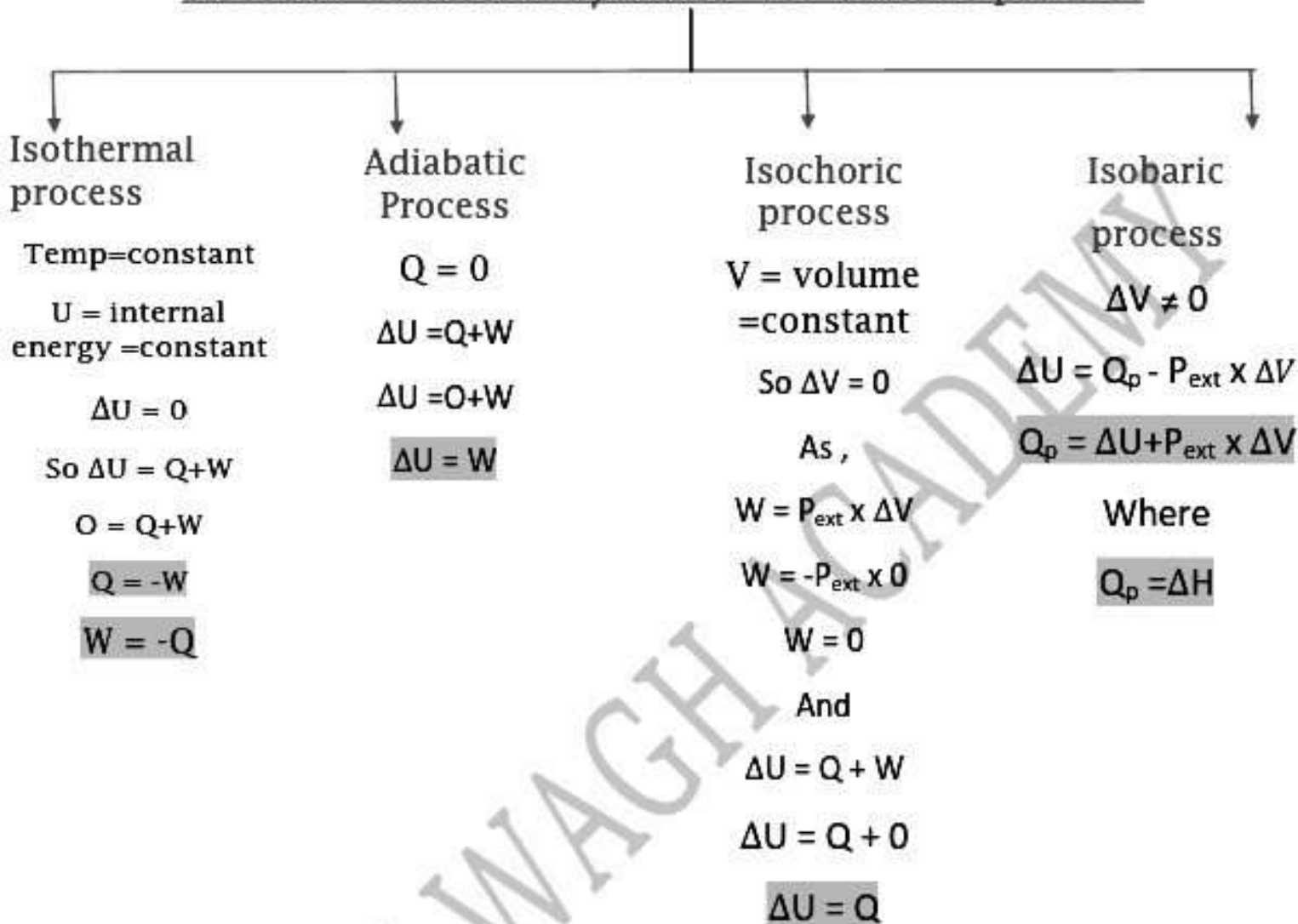
❖ Formation of 1st Law of thermodynamics

$\Delta U = Q+W \quad\quad$ or $\quad\quad du = dQ + dW$

Where ΔU = change in internal energy of the system
$\quad\quad$ Q $\quad$ = Heat supplied to the system
$\quad\quad$ W $\quad$ = Amount of work done

First law of thermodynamics for various process

Isothermal process

Temp=constant

U = internal energy =constant

$\Delta U = 0$

So $\Delta U = Q+W$

$0 = Q+W$

$Q = -W$

$W = -Q$

Adiabatic Process

$Q = 0$

$\Delta U = Q+W$

$\Delta U = 0+W$

$\Delta U = W$

Isochoric process

V = volume =constant

So $\Delta V = 0$

As,

$W = P_{ext} \times \Delta V$

$W = -P_{ext} \times 0$

$W = 0$

And

$\Delta U = Q + W$

$\Delta U = Q + 0$

$\Delta U = Q$

Isobaric process

$\Delta V \neq 0$

$\Delta U = Q_p - P_{ext} \times \Delta V$

$Q_p = \Delta U + P_{ext} \times \Delta V$

Where

$Q_p = \Delta H$

❖ Enthalpy

Enthalpy of a system is the sum of internal energy of a system and pv work

$H = U + PV$

$H = U_1 + P_1 V$ and $H_2 = U_2 + P_2 V_2$

$\Delta H = H_2 - H_1$

$\Delta H = (U_2 - P_2 V_2) - (U_1 + P_1 V_1)$ as p = constant

$\quad = (U_2 - U_1) + (P_2 V_2 - P_1 V_1)$ so $P_1 = P_2 = P$

$\quad = (U_2 - U_1) + (PV_2 - PV_1)$

$\quad = (U_2 - U_1) + P(V_2 - V_1)$ as $(U_2 - U_1) = \Delta U$

$\Delta H = \Delta U + P \Delta V$ ....(1) $(V_2 - V_1) = \Delta V$

As $Q_p = \Delta U + P\Delta V$ ....(2)

So from (1) & (2)

$\Delta H = Q_p$

The change in enthalpy of a system is equal to heat transferred from is at constant pressure.

❖ **Relationship between ΔH and ΔU for chemical reactions**

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

$\Delta H = \Delta U + P(V_2 - V_1)$ .... $(PV_1 = n_1RT)$

$\Delta H = \Delta U + PV_2 - PV_1$

$\Delta H = \Delta U + (n_2RT - n_1RT)$ .... $(PV_1 = n_1RT)$

$\Delta H = \Delta U + (n_2 - n_1) RT$

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

❖ **Work done in a chemical Reaction :-**

The work done by system at constant temp and pressure is given below as

$W = P_{ext} \times \Delta V$ where, $P_{ext} = -P$

$W = -P \times \Delta V$

$\quad = -P(V_2 - V_1)$ Ideal Gas Equation

$W = -PV_2 + PV_1$ $PV_1 = n_1RT$

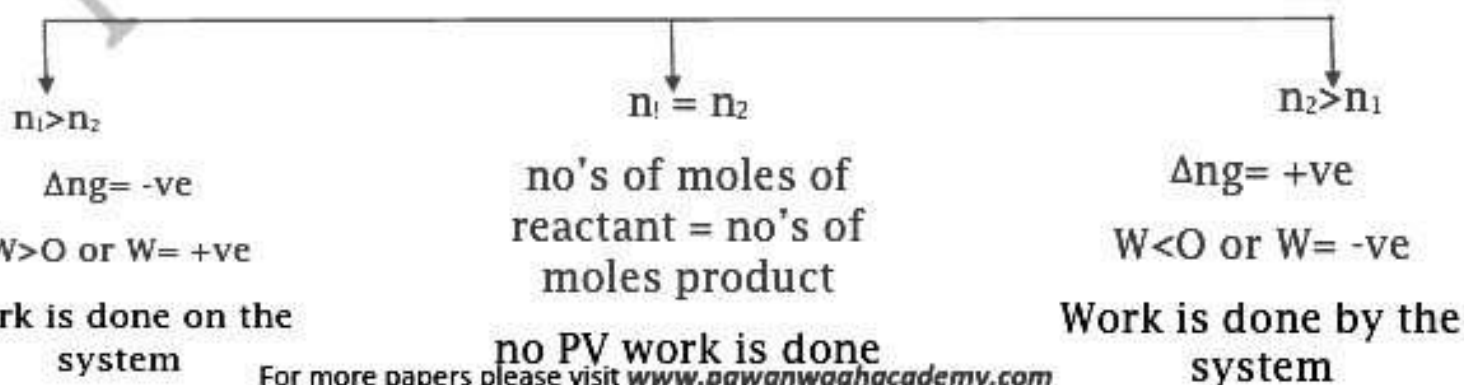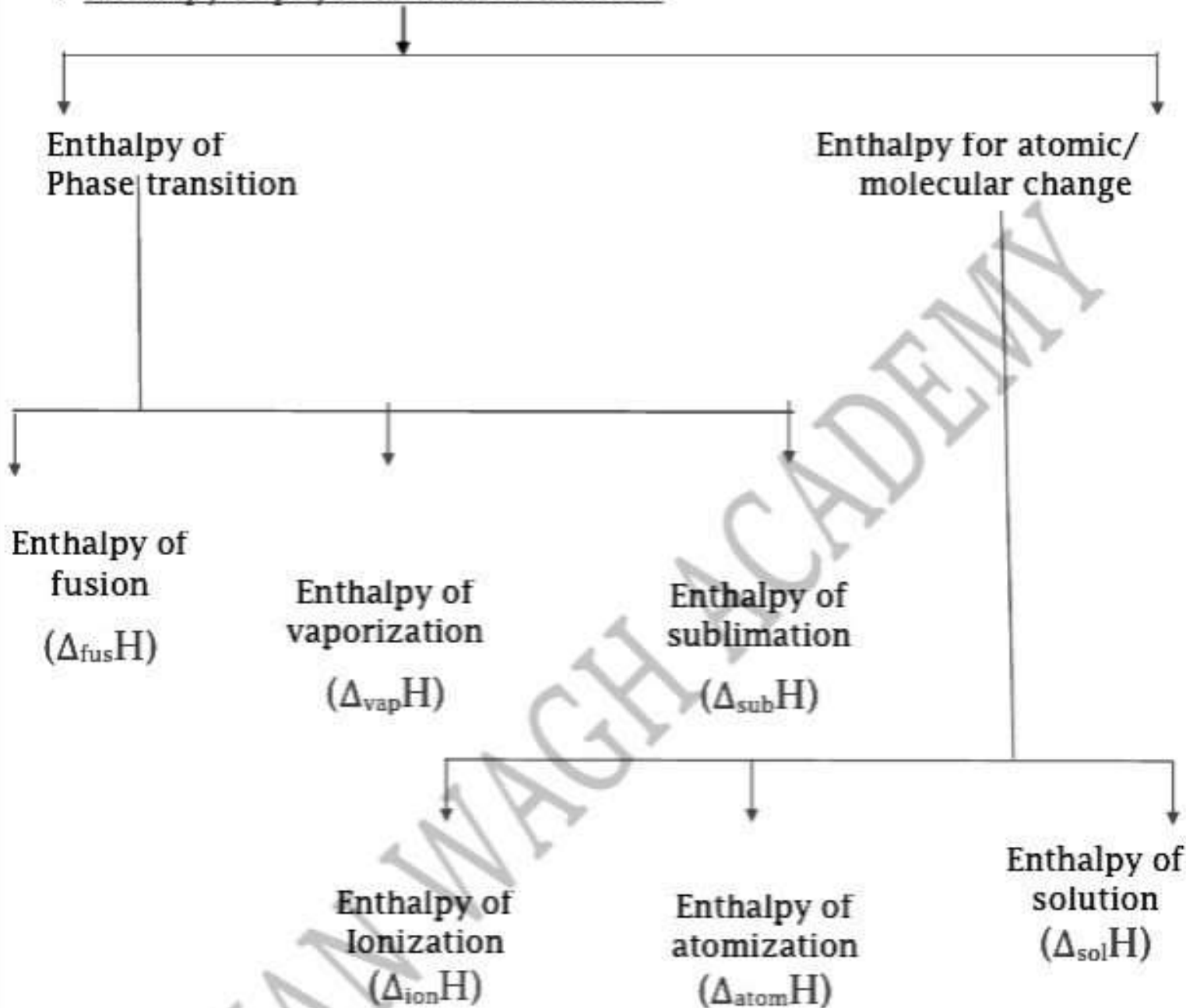$W = -n_2RT + n_1RT$ $PV_2 = n_2RT$

$W = -(n_2 - n_2)RT$ $\Delta n_g = n_2 - n_1$

So $W = -\Delta n_g RT$

$n_1 > n_2$	$n_1 = n_2$	$n_2 > n_1$
Δn_g = -ve	no's of moles of reactant = no's of moles product	Δn_g = +ve
W > O or W = +ve		W < O or W = -ve
Work is done on the system	no PV work is done	Work is done by the system

❖ Enthalpy of physical transformations

```
                    Enthalpy of physical transformations
                              │
        ┌─────────────────────┴─────────────────────┐
        ▼                                            ▼
  Enthalpy of                               Enthalpy for atomic/
  Phase transition                          molecular change
        │                                            │
  ┌─────┼──────────────────────┐                     │
  ▼     ▼                      ▼                      │
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Enthalpy of
fusion

$(\Delta_{fus}H)$

Enthalpy of
vaporization

$(\Delta_{vap}H)$

Enthalpy of
sublimation

$(\Delta_{sub}H)$

Enthalpy of
Ionization
$(\Delta_{ion}H)$

Enthalpy of
atomization
$(\Delta_{atom}H)$

Enthalpy of
solution
$(\Delta_{sol}H)$

I) Enthalpy of phase transition :-

The enthalpy change, that occurs where one phase of a substance is converted into another at constant temperature and pressure without change in chemical composition, is called as **Enthalpy of phase transition.**
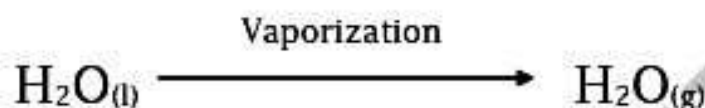
a) Enthalpy for fusion($\Delta_{fus}H$) :-

The enthalpy change that occurs, where one mole of a solid is converted into liquid, at constant temperature and pressure, is called as **Enthalpy of fusion**

$$H_2O_{(s)} \xrightarrow{\text{Fusion}} H_2O_{(l)}$$
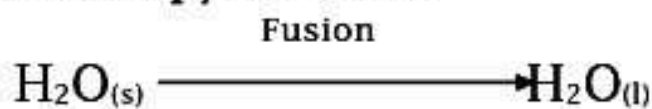
b) Enthalpy of vaporization ($\Delta_{vap}H$) :-

The enthalpy change that occurs, where one mole of a liquid is converted into gas (vapors) at constant temperature and pressure, is called as **enthalpy of vapourization**.

$$H_2O_{(l)} \xrightarrow{\text{Vaporization}} H_2O_{(g)}$$

c) Enthalpy of sublimation ($\Delta_{sub}H$) :-

The enthalpy change that occurs, when one mole of solid is directly converted into vapour at constant temperature and pressure, is called as enthalpy of sublimation
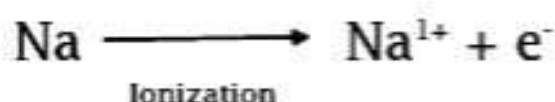
$$H_2O_{(s} \xrightarrow{\text{Sublimation}} H_2O_{(g)}$$
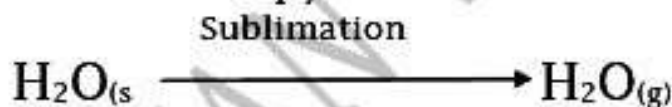
❖ Relation

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

II) Enthalpy for atomic/molecular change

1) Enthalpy of ionization ($\Delta_{ion}H$):-

The enthalpy change that occurs during the removal of an electron from one mole of gaseous atom, is called as Enthalpy of ionization

$$Na \xrightarrow{\text{Ionization}} Na^{1+} + e^-$$

2) Electron gain enthalpy ($\Delta_{eg}H$):-

The enthalpy change that occurs, when one mole of gas-phase atom of an element accept electron to form gaseous anion, is called as electron gain enthalpy

$$Cl_{(g)} + e^- \longrightarrow Cl_{(g)}^-$$

3) Enthalpy of atomization ($\Delta_{atom}H$):-

The enthalpy change that occurs, when one mole of gaseous substance undergoes dissociation into, is called as enthalpy of Atomization

$$Cl_{2(g)} \xrightarrow{\text{Atomization}} Cl_{(g)} + Cl_{(g)}$$
molecule   atom   atom
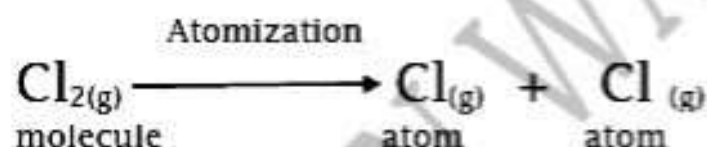
4) Enthalpy of solution ($\Delta_{Sol}H$):-

The enthalpy change, that occurs when one mole of a substance is dissolved in specified amount of solvent, is called as enthalpy of solution

$$NaCl_{(s)} + \underset{\text{Solvent}}{aq} \xrightarrow{\hspace{1cm}} \underset{\text{Solution}}{NaCl_{(aq)}}$$
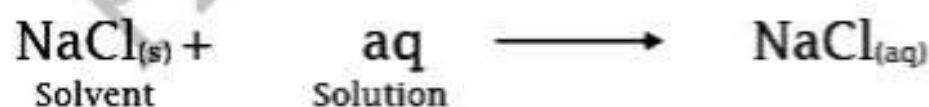
❖ Relation: $\quad \Delta_{sol}H = \Delta_{L}H + \Delta_{hyd}H$

Where

$\Delta_{sol}H$ = Enthalpy of solution

$\Delta_L H$ = Enthalpy Lattice enthalpy

$\Delta_{hyd}H$ = Enthalpy of hydration

5) Enthalpy of Chemical Reaction ($\Delta_r H$)

The difference between the sum of enthalpies of products and that of reactants in the balanced chemical equation of reaction is called as enthalpy of chemical Reaction

Consider

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

$$\Delta_Y H = \Sigma H_{Products} - \Sigma H_{Reactants}$$
$$H = (c\,H_c + dH_D) - (aH_A + bH_b)$$

Enthalpy of chemical Reaction (conditions)

1) If $\Sigma H_{Products} > \Sigma H_{Reactants}$

So $\Delta_Y H$ = +ve

Endothermic Reaction

2) If $\Sigma H_{Reactants} > \Sigma H_{Product}$

So $\Delta_Y H$ = -ve

Exdothermic Reaction

❖ **Thermodynamics standard state**

T = Temperature = 298K (25°C)

P = Pressure = 1 bar

C = concentration = 1M

❖ Standard enthalpy of reaction ($\Delta_r H$)

The enthalpy change that occurs, when the reactants and products involved in the reaction, are in standard state, is called as standard enthalpy of reaction.

❖ Standard enthalpy of formation ($\Delta_f H$)

The enthalpy change, that occurs when one mole of a pure compound in its standard state is formed from its elements in their standard state, is called as standard enthalpy of formation

$$C_{(s)} + 2H_{2\,(g)} \xrightarrow{\text{Formation}} CH_{4\,(g)}$$
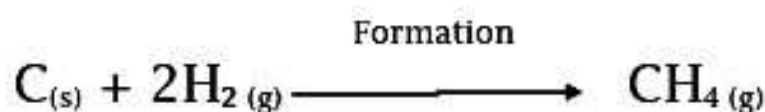
❖ <u>Some important points</u>:-

1) $\Delta_f H°(H_2) = \Delta_f H°(Cl_2) = \Delta_f H° (C) = \Delta_f H° (O_2) = 0$
2) $\Delta_f H°_{\text{(compound)}} = H°_{\text{(compound)}}$

❖ Standards enthalpy of combustion($\Delta_c H$) :-

The enthalpy change that occurs, when one mole of a substance, in standard state, is completely oxidized in a reaction, is called as standard enthalpy of combustion

❖ Bond Enthalpy:-

The enthalpy change required to break particular covalent bond in one mole of gaseous molecule to produce gaseous atoms or radicals, is called as Bond enthalpy

$$\underset{\substack{\text{Gaseous} \\ \text{molecules}}}{HCl_{(g)}} \longrightarrow \underset{\text{gaseous atom}}{H_{(g)} + Cl_{(g)}}$$
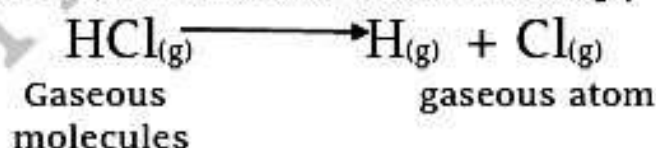
Bond Enthalpy is given by:-

Bond Enthalpy = $\Sigma \Delta H°_{\text{(Reactants)}} - \Sigma \Delta H°_{\text{(Products)}}$

❖ Hess's Law of constant heat summation

It states that "The overall enthalpy change, for a reaction is equal to the sum of enthalpy changes of individual steps in the reaction".

❖ Application of Hess's Law :-

The Hess's Law has been useful to calculate the enthalpy changes for the various reactions.

## ❖ Spontaneous (Irreversible) process

The process that do not require any external influence or force for their occurrence, is called as Spontaneous or irreversible process.

OR

The process which have natural tendency to occur in a direction, which leads to equilibrium, is called as Spontaneous or irreversible process
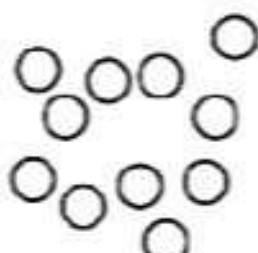
❖ Entropy :-

The molecular disorder or randomness of a system, is measured by term **entropy** (S)
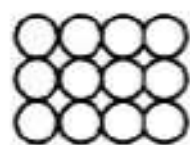
Ice highly
ordered
state

$H_2O(l)$
disordered
state

$H_2O (g)$
highly
disordered
state

Expression for entropy change (ΔS)

$$\Delta S = \frac{Qrev}{T}$$

where
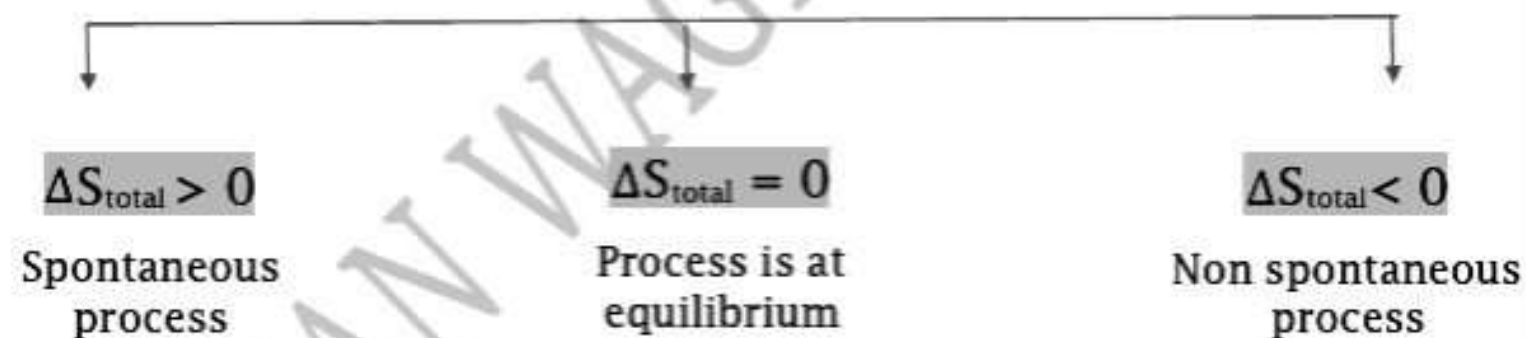Q_{rev} = amount of heat transferred in a reversible manner
T = Temperature in kelvin

❖ Second law of thermodynamics
The second law of thermodynamics states that total entropy of a system and its surroundings increases in a spontaneous process

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

❖ Three conditions for ΔS total

$\Delta S_{total} > 0$	$\Delta S_{total} = 0$	$\Delta S_{total} < 0$
Spontaneous process	Process is at equilibrium	Non spontaneous process

❖ Gibb's Energy (G)
G = H - TS

also

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

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

where
G = Gibb's energy
H = Enthalpy
T = Temperature (Kelvin)
S = Entropy
ΔG = change in Gibb's energy
ΔH = Enthalpy change
ΔS = change in entropy

❖ **Relation between ΔG and ΔS_{total} :-**

$$\Delta S_{surr} = \frac{-\Delta H}{T} \quad ....(1)$$

$$\Delta S_{system} = \Delta S \quad ....(2)$$

$$\Delta S_{total} = \Delta S_{sytem} + \Delta S_{surrounding}$$

$$\Delta S_{total} = \Delta S - \frac{\Delta H}{T} ....(3)$$

So $T \Delta S_{total} = T\Delta S - \Delta H$

Also, $-T\Delta S_{total} = \Delta H - T\Delta S ....(4)$

$\Delta G = \Delta H - T\Delta S \quad ....(5)$

Comparing eqⁿ 4 & 5

$$\boxed{\Delta G = - T \, \Delta S_{total}}$$

3 conditions

$\Delta S_{total} > 0$	$\Delta S_{total} = 0$	$\Delta S_{total} < 0$
$\Delta G < 0$	$\Delta G = 0$	$\Delta G > 0$
Spontaneous	Process is at equilibrium	Non-spontaneous process
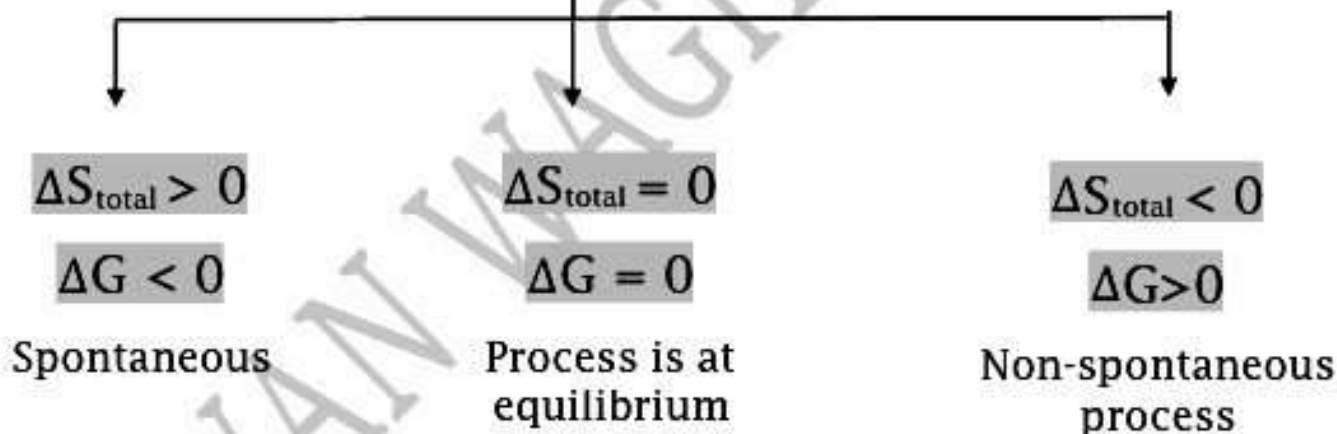
❖ <u>Temperature of Equilibrium</u>

The temperature at which, the spontaneous process changes to non-spontaneous process, is called as temperature of equilibrium

$$T_{eq} = T = \frac{\Delta H}{\Delta S}$$

Where $T_{eq} = T$ = Temperature of equilibrium in kelvin

❖ Gibb's function and equilibrium constant

$$\Delta G = \Delta G^0 + RT \ln Q \ldots\ldots\ldots\ldots (1)$$

Consider,

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

Reaction Quotient

$$Q_c = \frac{[Products]}{[Reactants]} = ([A].[B] \,/\, [C].[D])$$

When all reactants and products are gases,

$$Q_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} \qquad \ldots\ldots\ldots\ldots(3)$$

At equilibrium $Q_c = K_c$
& $Q_p = K_p$ and $\Delta G = 0$

$$\Delta G = \Delta G^0 + RT \ln K.$$

At equilibrium
$$\Delta G = 0$$

So $\quad 0 = \Delta G^0 + RT \ln k$

$$\boxed{\begin{aligned} \Delta G^0 &= -RT \ln K_p \\ \Delta G^0 &= -RT \ln K_c \end{aligned}}$$

also $\quad \ln = 2.303 \times \log_{10}$

$$\boxed{\begin{aligned} \Delta G^0 &= -2.303\ RT \log_{10} K_p \\ \Delta G^0 &= -2.303\ RT \log_{10} K_c \end{aligned}}$$