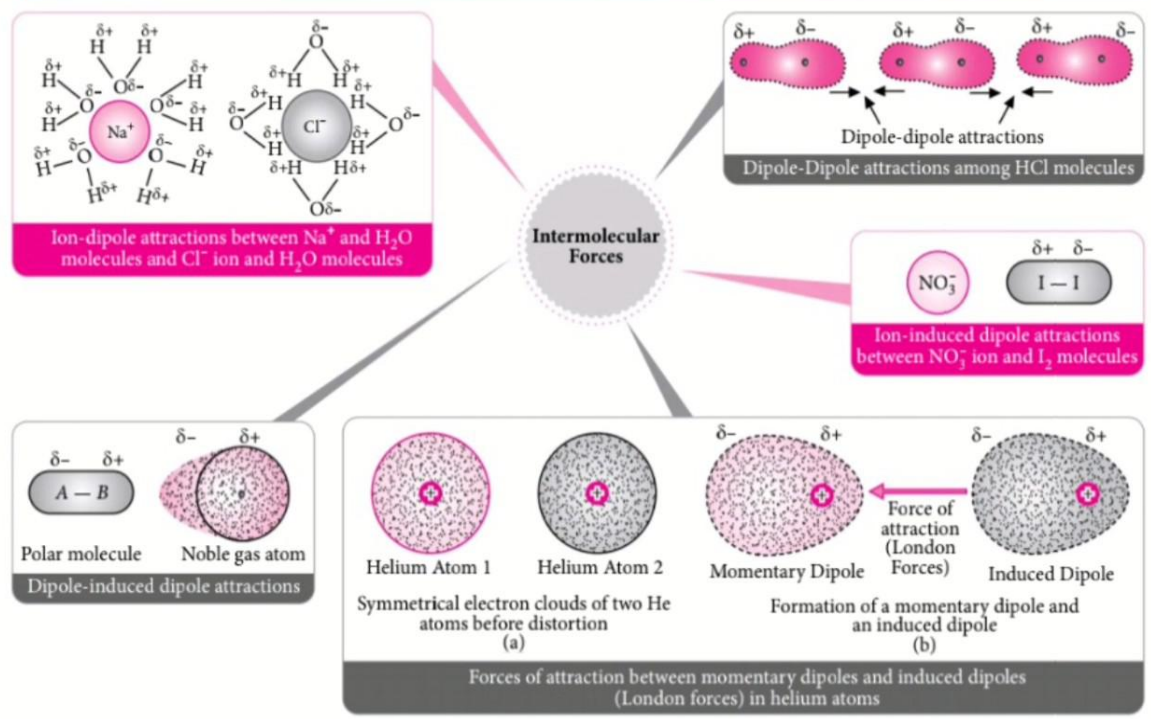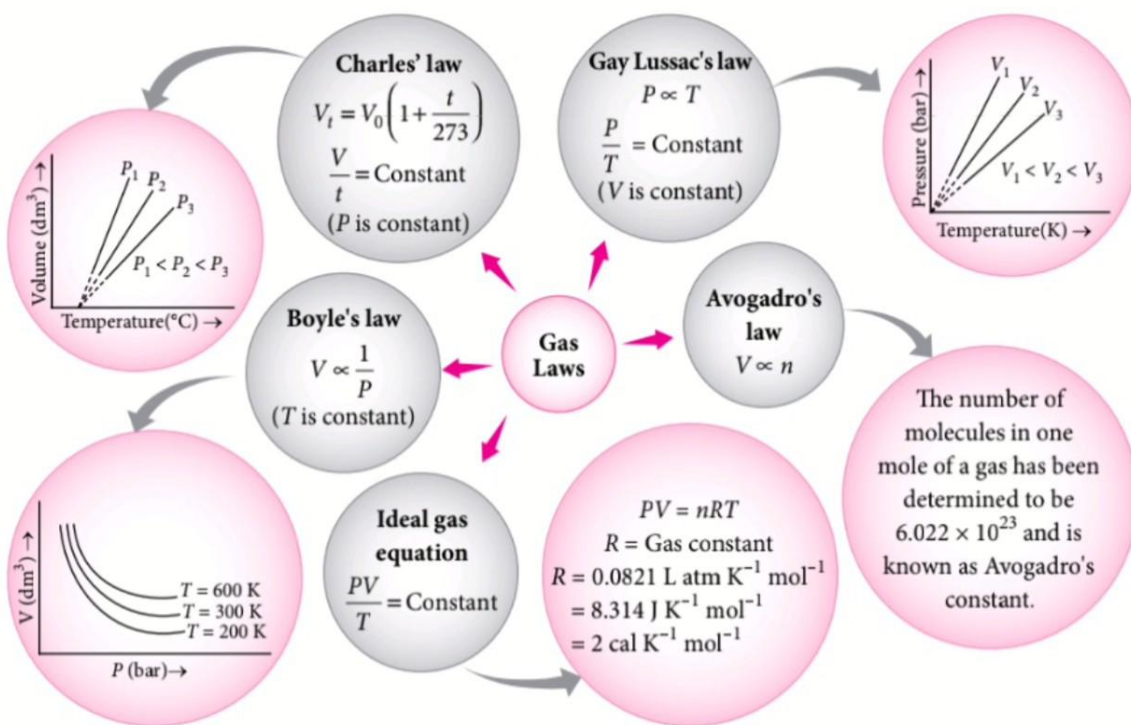**CLASS-XI**

for NEET/JEE 2021

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 3

States of Matter : Gases & Liquids | Thermodynamics

States of Matter : Gases & Liquids

GASEOUS STATE OF MATTER

Ion-dipole attractions between Na^+ and H_2O molecules and Cl^- ion and H_2O molecules

Intermolecular Forces

Dipole-dipole attractions
Dipole-Dipole attractions among HCl molecules

Ion-induced dipole attractions between NO_3^- ion and I_2 molecules

Polar molecule   Noble gas atom
Dipole-induced dipole attractions

Helium Atom 1   Helium Atom 2
Symmetrical electron clouds of two He atoms before distortion
(a)

Momentary Dipole   Force of attraction (London Forces)   Induced Dipole
Formation of a momentary dipole and an induced dipole
(b)

Forces of attraction between momentary dipoles and induced dipoles (London forces) in helium atoms

The diagram shows Gas Laws with the following connected concepts:

Charles' law
$$V_t = V_0\left(1 + \frac{t}{273}\right)$$
$$\frac{V}{t} = \text{Constant}$$
(P is constant)

Volume (dm³) vs Temperature(°C) graph with $P_1 < P_2 < P_3$

Gay Lussac's law
$$P \propto T$$
$$\frac{P}{T} = \text{Constant}$$
(V is constant)

Pressure (bar) vs Temperature(K) graph with $V_1 < V_2 < V_3$

Boyle's law
$$V \propto \frac{1}{P}$$
(T is constant)

V (dm³) vs P (bar) graph with $T = 600\,K$, $T = 300\,K$, $T = 200\,K$

Gas Laws (center)

Avogadro's law
$$V \propto n$$

The number of molecules in one mole of a gas has been determined to be 6.022×10^{23} and is known as Avogadro's constant.

Ideal gas equation
$$\frac{PV}{T} = \text{Constant}$$

$$PV = nRT$$
R = Gas constant
$R = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$
$= 8.314\ J\ K^{-1}\ mol^{-1}$
$= 2\ cal\ K^{-1}\ mol^{-1}$

DALTON'S LAW OF PARTIAL PRESSURES

- The total pressure exerted by a mixture of two or more non-reacting gases enclosed in a vessel is equal to the sum of the individual partial pressures which each gas would exert when present alone in the same vessel at the same temperature.

$P_{total} = p_1 + p_2 + p_3 + \dots + p_n$

$p_1 = x_1\, P_{total}$

x_1 = Mole fraction of the gas 1.

GRAHAM'S LAW OF DIFFUSION / EFFUSION

- Under similar conditions of temperature and pressure, the rates of diffusion/effusion of different gases are inversely proportional to the square root of their densities.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

where d_1, d_2 are densities of two gases.

$$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{T_1\, d_2}{T_2\, d_1}} = \sqrt{\frac{T_1\, M_2}{T_2\, M_1}}$$

KINETIC MOLECULAR THEORY OF GASES

- The molecules are separated from one another by large distances.

- Molecular collisions are perfectly elastic.

- There are no forces of interactions between the molecules.

- Kinetic gas equation, $PV = \dfrac{1}{3}mn\bar{u}^2$

  where, P = Pressure exerted by the gas,
  m = Mass of each molecule of gas,
  n = Total number of molecules of the gas present in volume V,
  $\bar{u}$ = Root mean square speed of the gas

  K.E., $E_k = \dfrac{3}{2}nRT$

  Average kinetic energy, $\bar{E}_k = \dfrac{1}{2}m\bar{u}^2 = \dfrac{3}{2}\dfrac{RT}{N_A}$

  where, N_A = Avogadro's constant

- The average kinetic energy of gas molecules is directly proportional to the absolute temperature of the gas.

- All gases are made up of a very large number of molecules.

MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

- The plot between the fraction of molecules ($\Delta N/N$) possessing particular speeds against their corresponding speeds at a particular temperature is known as Maxwell's distribution curve.
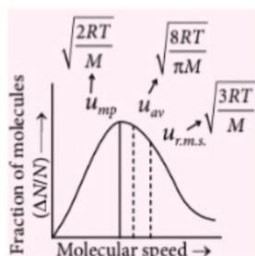
$u_{mp} : u_{av} : u_{rms} = 1 : 1.128 : 1.224$

DEVIATION FROM IDEAL GAS BEHAVIOUR

- Real gases do not follow ideal gas equation perfectly at all conditions of temperatures and pressures.

- $\dfrac{PV}{nRT} = Z$ = Compressibility factor
  - ⤷ For an ideal gas, $Z = 1$
  - ⤷ For a real gas :
    $Z > 1$ (Positive deviation)
    $Z < 1$ (Negative deviation)

- **Equation of state for real gases (van der Waals' equation) :**

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where, a and b are van der Waals' constants.

LIQUEFACTION OF GASES

- Gases can be liquefied by decreasing temperature or increasing pressure.

- **Critical pressure :** The minimum pressure required to liquefy a gas at its critical temperature.

$$P_c = \frac{a}{27b^2}$$

- **Critical volume :** Volume occupied by one mole of a gas at its critical temperature and pressure.

$$V_c = 3b$$

- **Critical temperature :** A temperature above which a gas cannot be liquefied however high pressure may be applied on the gas.

$$T_c = \frac{8a}{27Rb}$$

LIQUID STATE OF MATTER

- Liquids have definite volumes but not definite shapes.

Properties of Liquid State

- **Boiling point :** Temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.

- **Surface tension :** Force per unit length acting perpendicular to the tangential line drawn at the surface of liquid is known as surface tension.

- **Viscosity :** Internal resistance to the flow in liquids.

$F = \eta A \dfrac{dv}{dx}$, where, A = Area,

$\dfrac{dv}{dx}$ = Velocity gradient,

η = Coefficient of viscosity,

iNF SHOTS

New state of matter !

A new form of matter, a supersolid, which combines the properties of solids with those of superfluids. By using lasers to manipulate a superfluid gas known as Bose-Einstein condensate was coaxed into a quantum phase of matter that has a rigid structure-like a solid and can flow without viscosity (like superfluids).

Thermodynamics

- A specified part of the universe which is under thermodynamic consideration is called the system.
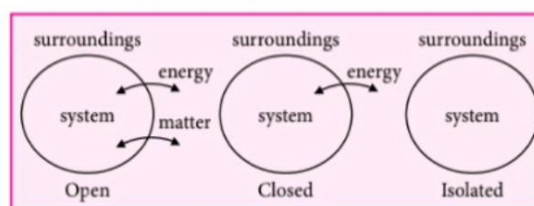
THERMODYNAMICS TERMS

- **Extensive properties :** Properties of the system whose value depends upon the amount or size of the substance present in the system e.g., Gibbs free energy, enthalpy, entropy, internal energy, etc.
- **Intensive properties :** Properties of the system whose value is independent of the amount or size of the substance present in the system but depends only upon the nature of the substance e.g., temperature, pressure, viscosity, etc.
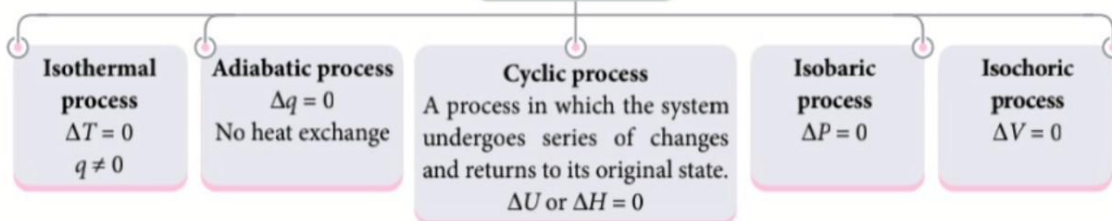- **State function :** A physical quantity is said to be a state function if its value depends only upon the state of the system and is independent of the path by which the state is reached e.g., volume, temperature, internal energy, enthalpy.
- **Path function :** A physical quantity is a path function if it depends upon the path by which the change is brought about e.g., work and heat.

Different Types of Systems

Types of Processes

Isothermal process $\Delta T = 0$ $q \neq 0$	Adiabatic process $\Delta q = 0$ No heat exchange	Cyclic process A process in which the system undergoes series of changes and returns to its original state. ΔU or $\Delta H = 0$	Isobaric process $\Delta P = 0$	Isochoric process $\Delta V = 0$

FIRST LAW OF THERMODYNAMICS

Energy can neither be created nor destroyed, although it can be converted to one form to another form. The total energy of the universe remains constant.

$$\Delta U = q + w$$

where, ΔU = Change in internal energy; q = heat change; w = work done

Sign Conventions
q = +ve (when heat is absorbed by the system)
q = –ve (heat is evolved by the system)
w = +ve (work is done on the system)
w = –ve (work is done by the system)

Work
- For isothermal reversible expansion,
$$q = -w = p_{ext}(V_f - V_i)$$
$$= nRT \ln \frac{V_f}{V_i}$$
$$= 2.303 \, nRT \log \frac{V_f}{V_i}$$
$$= 2.303 nRT \log \frac{P_i}{P_f}$$

- For adiabatic reversible process, $q = 0$
$$\Delta U = w_{ad} = nC_v\Delta T = \frac{nR}{\gamma - 1}\Delta T$$

Enthalpy change (ΔH)	Internal energy change (ΔU)
Heat absorbed or evolved (ΔH) during a reaction at constant pressure.	The change in internal energy (ΔU) is the heat absorbed or evolved at constant volume.

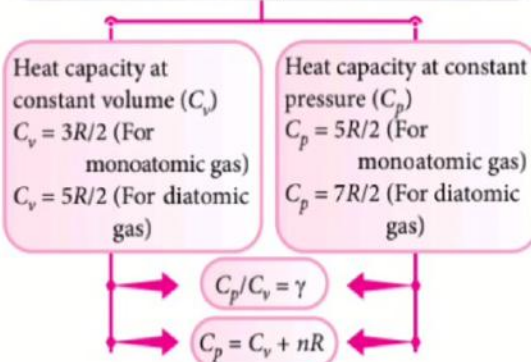$$\Delta H = \Delta U + P\Delta V$$
$$\Delta H = \Delta U + \Delta n_g RT$$
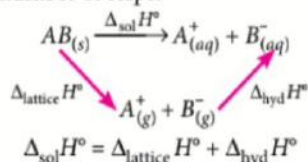Δn_g = change in number of gaseous moles

HEAT CAPACITY

It is the amount of heat required to raise the temperature of the system through 1°C
$$C = q/\Delta T$$

Heat capacity at constant volume (C_v)	Heat capacity at constant pressure (C_p)
$C_v = 3R/2$ (For monoatomic gas)	$C_p = 5R/2$ (For monoatomic gas)
$C_v = 5R/2$ (For diatomic gas)	$C_p = 7R/2$ (For diatomic gas)

$$C_p/C_v = \gamma$$
$$C_p = C_v + nR$$

HESS'S LAW

- The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.

$$AB_{(s)} \xrightarrow{\Delta_{sol}H^\circ} A^+_{(aq)} + B^-_{(aq)}$$

$\Delta_{lattice}H^\circ \searrow A^+_{(g)} + B^-_{(g)} \nearrow \Delta_{hyd}H^\circ$

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

- Enthalpy of reaction = (Sum of bond enthalpies of reactants) – (Sum of bond enthalpies of products)
- Enthalpy of reaction = (Sum of enthalpies of products) – (Sum of enthalpies of reactants)

ENTROPY

- The property of a system which measures the degree of disorder or randomness in the system.

$$\Delta S = \frac{q_{rev}}{T}$$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

- For isothermal process, $\Delta S_t = nC_v \ln \frac{V_2}{V_1} = nC_p \ln \frac{P_1}{P_2}$

- For isochoric process, $\Delta S_v = nC_v \ln \frac{T_2}{T_1}$

- For isobaric process, $\Delta S_p = nC_p \ln \frac{T_2}{T_1}$

- $\Delta_{fusion}S^\circ = \frac{\Delta_{fusion}H^\circ}{T_f}$; $\Delta_{vap}S^\circ = \frac{\Delta_{vap}H^\circ}{T_b}$

- **Second law of thermodynamics** : The entropy of the universe is continuously increasing in the course of every spontaneous change.

GIBBS FREE ENERGY

- $G = H - TS$, where, G = Gibbs free energy
- $\Delta G = \Delta H - T\Delta S$
- **Units** : kJ/mol, J/mol
- $\Delta G^\circ = \Sigma \Delta_f G^\circ_{(products)} - \Sigma \Delta_f G^\circ_{(reactants)}$
- $\Delta G^\circ = -2.303\, RT \log K_{eq}$
- $\Delta G = RT \ln \frac{V_1}{V_2} = RT \ln \frac{P_2}{P_1}$

Gibbs Free Energy

$\Delta G = -ve$	$\Delta G = 0$	$\Delta G = +ve$
Spontaneous	At equilibrium	Non-spontaneous

- If $\Delta H = +ve$; $\Delta S = +ve \Rightarrow \Delta G = -ve$ if $T\Delta S > \Delta H$ (At high temperature)
- If $\Delta H = -ve$, $\Delta S = +ve \Rightarrow \Delta G = -ve$ (at all temperatures)
- If $\Delta H = -ve$, $\Delta S = -ve \Rightarrow \Delta G = -ve$ if $\Delta H > T\Delta S$ (at low temperature)

THIRD LAW OF THERMODYNAMICS

- At absolute zero, the entropy of a perfectly crystalline substance is taken as zero. $S_0 = 0$
- The most important application of the third law of thermodynamics is that it helps in the calculation of the absolute entropies of the substances at room temperature (or at any temperature T). These determinations are based upon the heat capacity measurements.
- **Residual entropy** : The entropy possessed by a substance at absolute zero is called its residual entropy.