

NEET/JEE 2019

Focus more 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 | Thermodynamics

STATES OF MATTER (GASEOUS & LIQUIDS)

MATTER

Matter exists mainly in three states, solid, liquid and gas. The fourth, plasma state, is the ionic state of atoms existing at very high temperatures found only in the interior of stars. The fifth Bose-Einstein condensate (BEC) state, refers to supercooled solid in which atoms lose their separate identity, get condensed and behave like a single super atom.

THE GASEOUS STATE

There are few parameters which are important to understand the gaseous state *viz.* mass, volume, pressure and temperature.

Measurable Properties of Gases

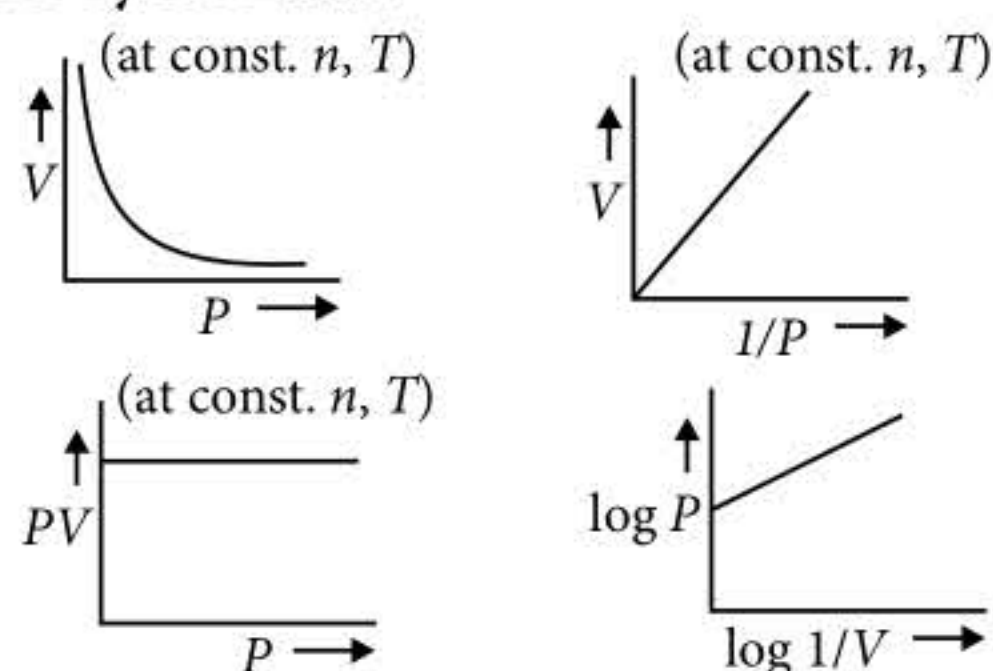
- **Mass** generally expressed in grams (SI unit is kg).
- **Volume** generally expressed in units of L, m³ or cm³ or dm³ (SI unit is m³).
- **Temperature** generally expressed in °C or K ($T(K) = t^{\circ}C + 273.15$).
- **Pressure** generally expressed in units such as atm, mm, cm, torr, bar, etc. (SI units are Pa or kPa).

Gas Laws

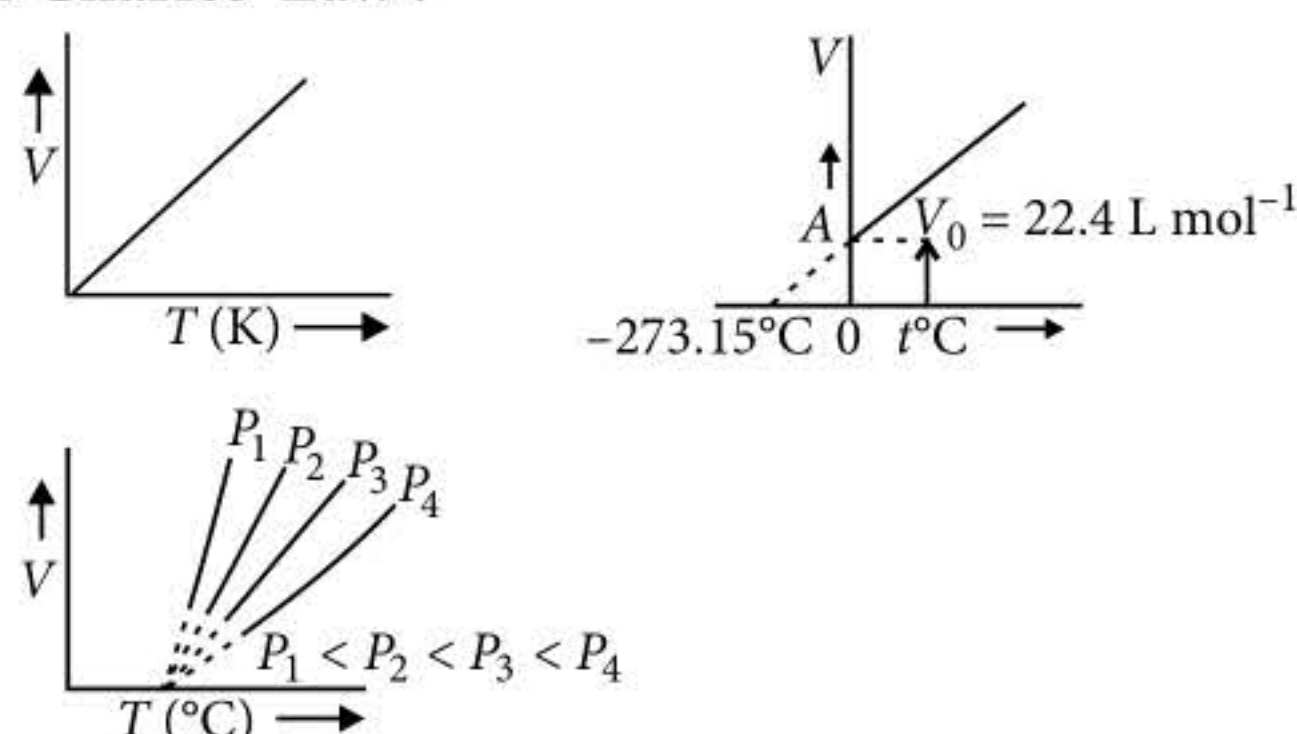
Laws	Mathematical expressions
Boyle's law (Robert Boyle)	At constant T $V \propto \frac{1}{P}$ or $PV = \text{constant}$ or $P_1V_1 = P_2V_2$
Charles' law (Jacques Charles)	At constant P $V_t = V_0 + \frac{t}{273.15} V_0$ or $V \propto T$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay-Lussac's law/ Amonton's law	At constant V $P \propto T$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Avogadro's law	At a given T and P $V \propto n$
Graham's law of diffusion	$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$
Dalton's law of partial pressures	$P_{\text{total}} = p_1 + p_2 + p_3 + \dots + p_n$ $= (n_1 + n_2 + n_3 + \dots) \frac{RT}{V}$

Graphical Representations

- For Boyle's Law :



- For Charles' Law :



Ideal Gas Equation

The equation which gives the simultaneous effect of pressure and temperature on the volume of a gas is known as ideal gas equation.

$$PV = nRT$$

(R is the universal gas constant or molar gas constant.)

- Value of R : $0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$
 $8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$ (C.G.S. unit)
 $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ (M.K.S. unit)
 $1.987 \approx 2 \text{ calorie K}^{-1} \text{ mol}^{-1}$

Kinetic Gas Equation

$$PV = \frac{1}{3} mnu^2$$

where, P = pressure of gas

V = volume of gas

m = mass of one molecule of gas

n = number of molecules of gas

u = root mean square speed of molecules

Relationship between Average Kinetic Energy and Absolute Temperature

$$K.E. = \frac{3}{2} kT \text{ where, } k = \frac{R}{N} = \text{Boltzmann constant}$$

Different Types of Molecular Speeds

- Most probable speed (u_{mp})

$$= \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2RT}{m \times N}}$$

- Average speed (u_{av})

$$= \frac{u_1 + u_2 + u_3 + \dots + u_n}{n} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi M}}$$

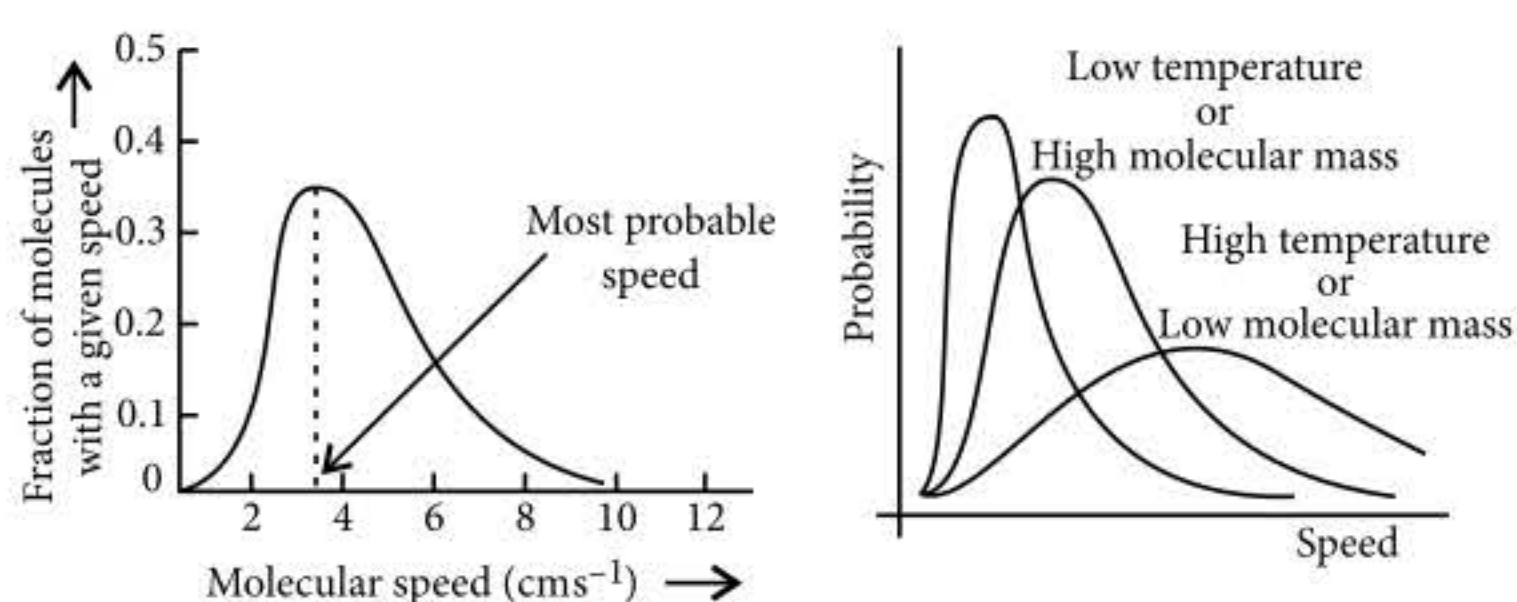
- Root mean square speed (u_{rms})

$$= \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2}{n}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

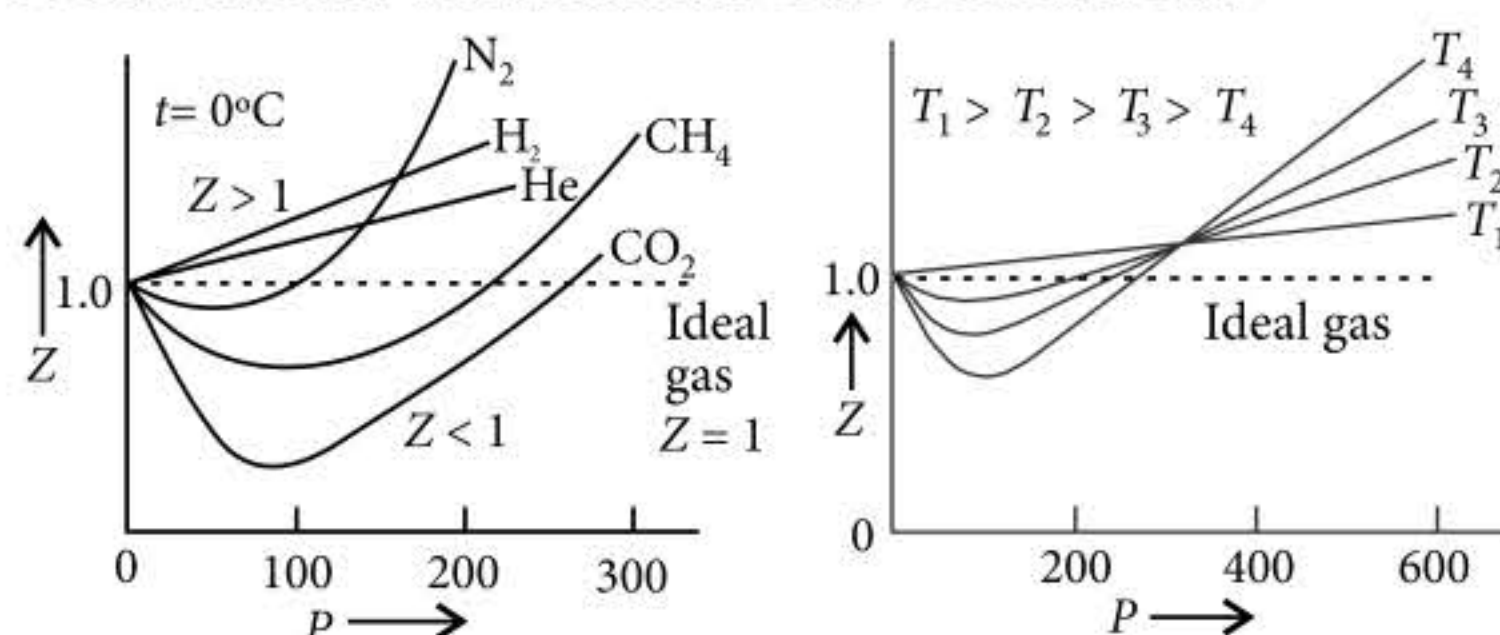
Relation Between Different Types of Speed

$$u_{mp} : u_{av} : u_{rms} : 1 : 1.128 : 1.224$$

Maxwell - Boltzmann Distribution Curve



Deviation From Ideal Gas Behaviour



- The extent to which a real gas departs from the ideal behaviour may be expressed in terms of compressibility factor (Z), where

$$Z = \frac{V_m}{V_{m(\text{ideal})}} = \frac{PV_m}{RT} \quad [V_m = \text{molar volume}]$$

- For an ideal gas : $Z = 1$
- For a real gas : $Z \neq 1$
- For negative deviation $Z < 1$ and for positive deviation $Z > 1$.

Solution Senders of Chemistry Musing

Set - 60

- Samaroha Nandi, West Bengal
- Sujit Roy, West Bengal

Solution Senders of Chemdoku

- Mitali Sharma, Haryana
- Anitha Pagadala, Andhra Pradesh

• **van der Waals' Equation of State for Real Gases :**

To explain the behaviour of real gases, van der Waals modified the ideal gas equation by taking into account :

- (i) the volume of the gas molecules and
- (ii) the forces of attraction between the gas molecules.

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

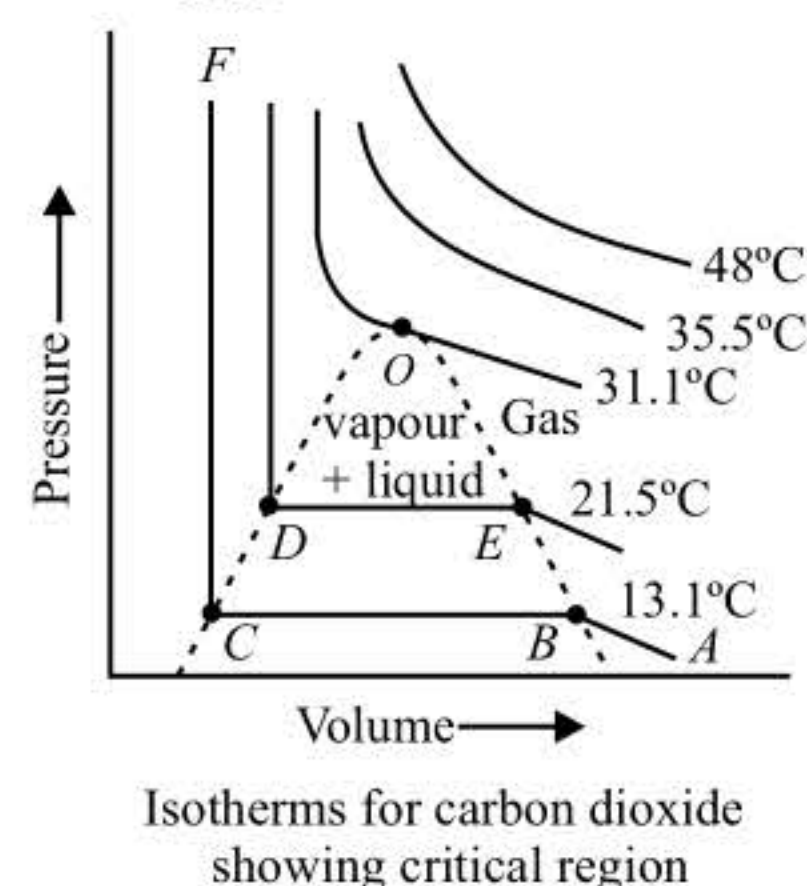
where, a and b are van der Waals' constants and their values depend on the nature of the gas.

van der Waals' constant	Significance	Units
a	Measure of magnitude of attractive forces	atm L ² mol ⁻² or bar dm ⁶ mol ⁻²
b	Measure of effective size of the gas molecules	L mol ⁻¹ or dm ³ mol ⁻¹

Liquefaction of Gases and Critical Constants

- A gas can be liquefied by cooling the gas or applying pressure on the gas or the combined effect of both. However, for every gas, there is a particular temperature above which a gas cannot be liquefied howsoever high pressure we may apply on the gas. This temperature is called critical temperature (T_c). The corresponding pressure and volume are called critical pressure (P_c) and critical volume (V_c).

$$T_c = \frac{8a}{27Rb}, P_c = \frac{a}{27b^2}, V_c = 3b$$



THE LIQUID STATE

Property	Mathematical expression	Effect of temperature
Vapour pressure		
The pressure exerted by the vapour of the liquid in equilibrium with its surface at a particular temperature.	$\log \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ (Clausius-Clapeyron equation)	Increases with increase in temperature due to decrease in the magnitude of interparticle forces.
Surface tension		
The force acting on the surface of liquid at right angle to any line of one centimetre length.	$\frac{\gamma_1}{\gamma_2} = \frac{n_1 d_2}{n_2 d_1}$ (γ_1 and d_1 are the surface tension and density of water and γ_2 and d_2 are the surface tension and density of liquid whose surface tension is to be determined.)	Decreases with increase in temperature.
Viscosity		
The internal resistance, to flow in liquids, which one layer offers to another layer trying to pass over it.	Force of friction between two adjacent layers of liquid having area A cm ² , separated by distance x and having a velocity difference of V cm s ⁻¹ is given as $f = \eta \frac{AV}{x}$ where, η is coefficient of viscosity.	$\eta = Ae^{-Ea/RT}$, Decreases with increase in temperature (about 2% decrease per degree rise in temperature).

THERMODYNAMICS

Thermodynamics includes the study of all energy correlations and energy transformation, most commonly heat into work and vice-versa.

TYPES OF SYSTEMS

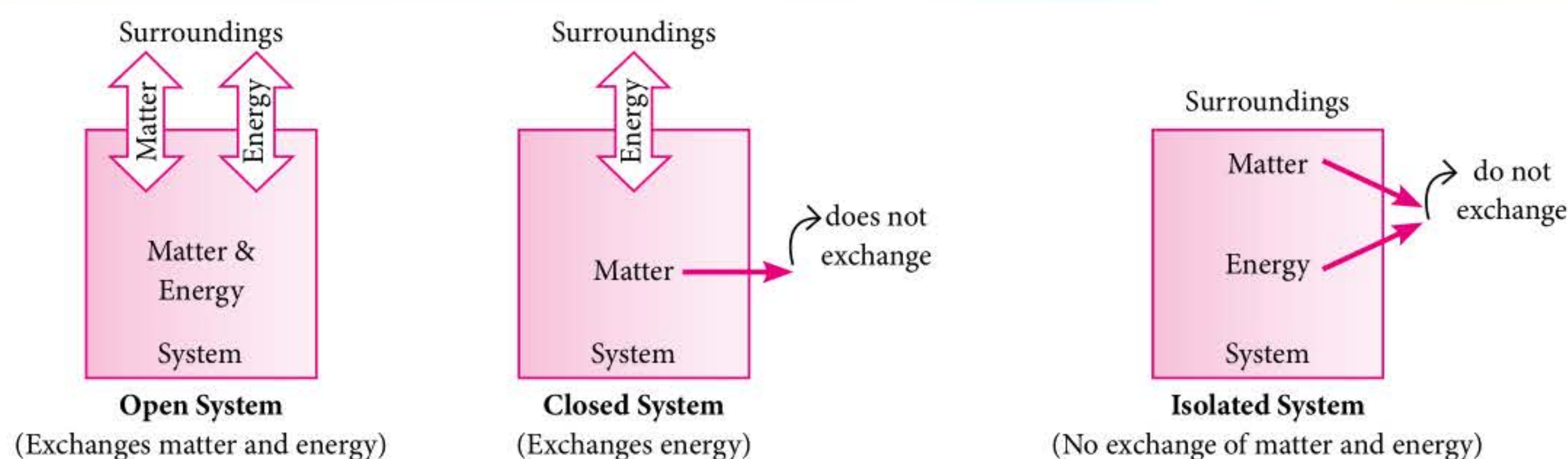
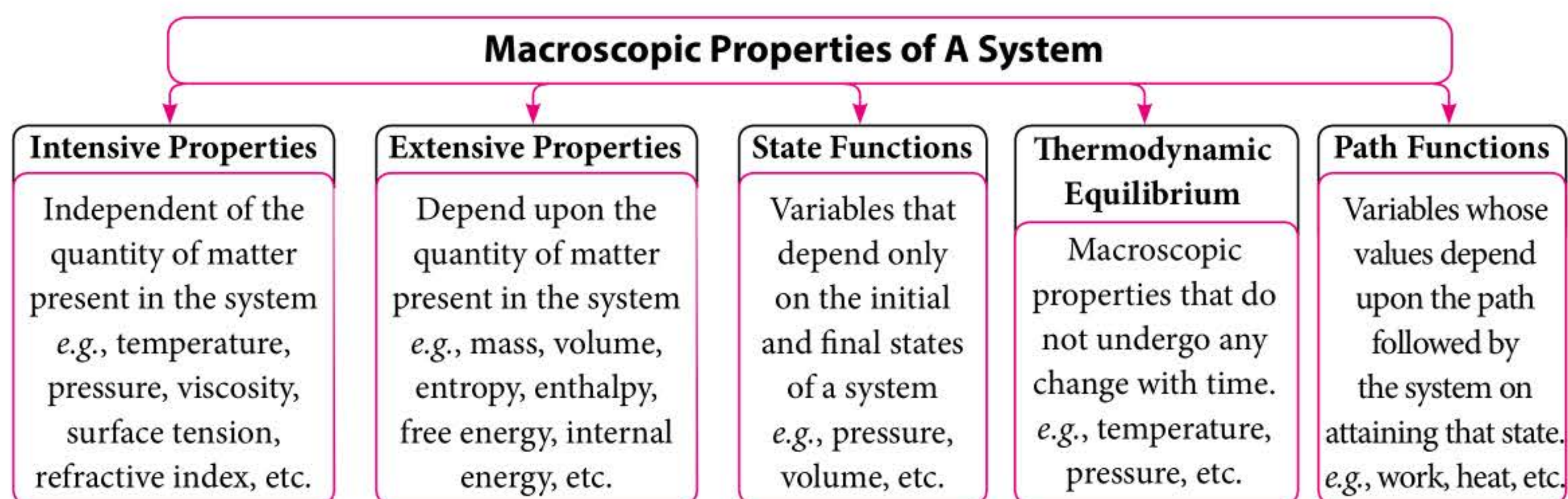
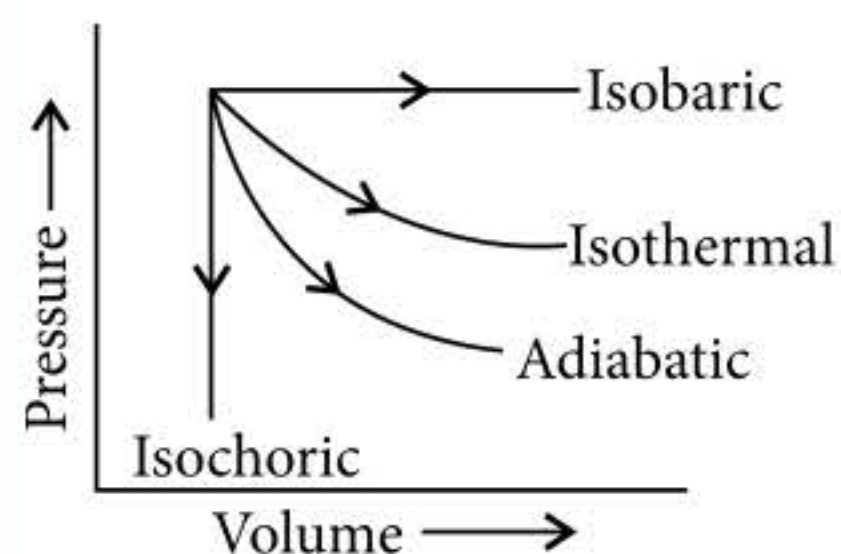


Illustration of exchange of matter and energy with surroundings in open, closed and isolated systems



THERMODYNAMIC PROCESSES

- (i) If $dq = 0$, process is adiabatic.
- (ii) If $dT = 0$, the process is isothermal.
- (iii) If $dV = 0$, process is isochoric.
- (iv) If $dP = 0$, process is isobaric.



Mathematically : ΔE or $\Delta U = q + W$

- **Sign Convention for q and w :**
 - Work is done on the system = W (+ve)
 - Work is done by the system = W (-ve)
 - Heat is absorbed by the system = q (+ve)
 - Heat is given out by the system = q (-ve)

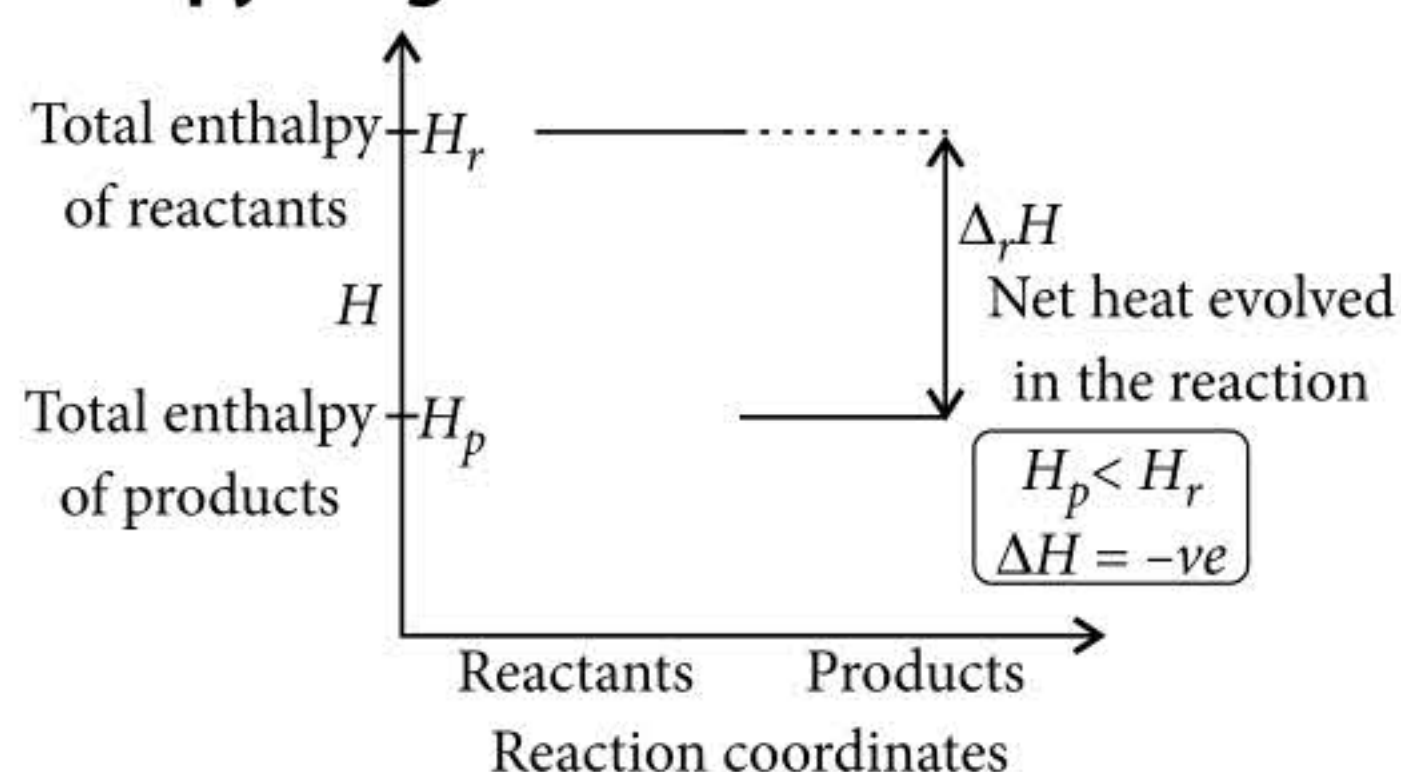
ENTHALPY (H)

- Total heat content of the system at constant pressure is known as its enthalpy.
 - Its absolute value can not be determined.
 - Mathematically, it is given as $\Delta H = \Delta U + P\Delta V$

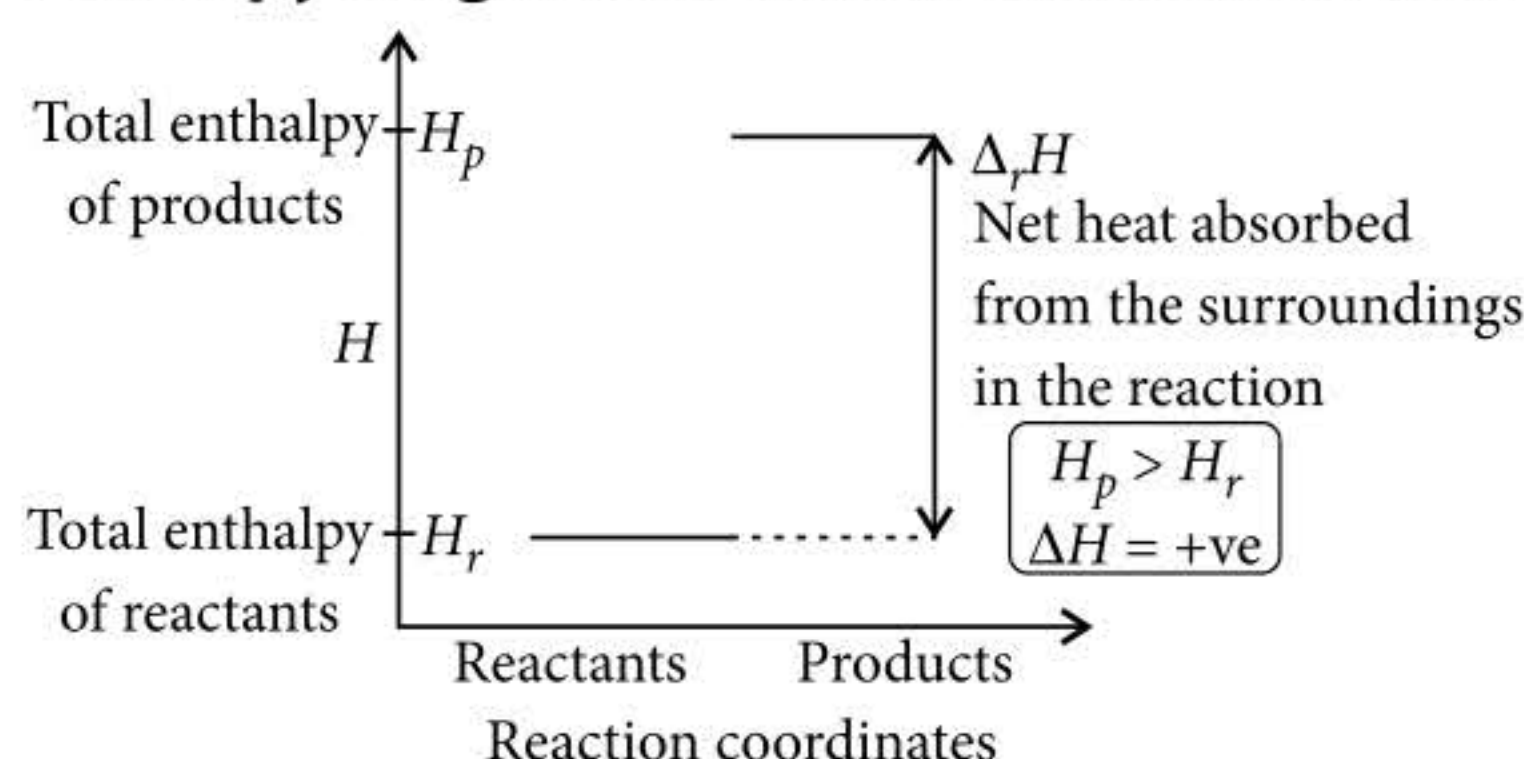
FIRST LAW OF THERMODYNAMICS

- It states that energy can neither be created nor destroyed, although it can be converted from one form to another.

Enthalpy Diagram for Exothermic Reactions

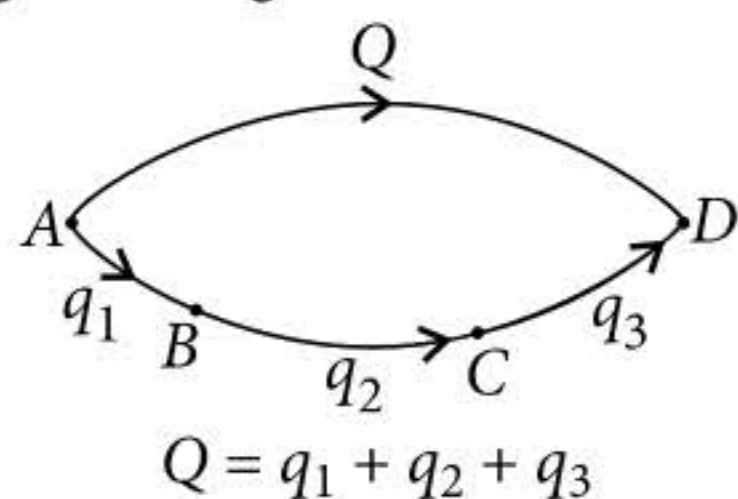


Enthalpy Diagram for Endothermic Reactions



HESS'S LAW OF CONSTANT HEAT SUMMATION

- The total amount of heat change in a chemical reaction is same whether the reaction takes place in one step or in number of steps. It depends only upon the nature of the initial reactants and final products and is independent of the path by which this change is brought about.



Applications of Hess's law

- To calculate the heat changes for those reactions for which experimental determination is not possible.
 - The thermochemical equations can be treated as algebraic equations which can be added, subtracted, multiplied or divided.
- Kirchhoff's Equation**: Variation of heat of reaction with temperature.
 - At constant pressure,

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_{p(\text{products})} - C_{p(\text{reactants})}$$

- At constant volume,

$$\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = C_{v(\text{products})} - C_{v(\text{reactants})}$$

SECOND LAW OF THERMODYNAMICS

- This law states that, 'it is impossible to convert heat into equal amount of work without compensation.'

Entropy (S)

- Entropy is defined as a measure of randomness or disorder of the system. The order of randomness or entropy of solid, liquid and gas is, gas > liquid > solid.

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

Free Energy (G)

- Free energy of a system is defined as the maximum amount of energy available to the system during a process which can be converted into useful work.

$$\Delta G = -W_{max}$$

Mathematically, $G = H - TS$

$\Delta G = \Delta H - T\Delta S$ (Gibbs-Helmholtz equation)

For a reaction to be spontaneous ΔG must be negative.

- $\Delta G^\circ = -nFE^\circ$
 - $\Delta G^\circ = \sum G_{f(\text{products})}^\circ - \sum G_{f(\text{reactants})}^\circ$
 - $\Delta G^\circ = -2.303 RT \log K_{eq}$
- Effect of Temperature on Spontaneity of Reactions**

$\Delta_r H^\circ$	$\Delta_r S^\circ$	$\Delta_r G^\circ$	Description*
-	+	-	spontaneous at all temperatures
-	-	-(at low T)	spontaneous at low temperature
-	-	+(at high T)	non-spontaneous at high temperature
+	+	+(at low T)	non-spontaneous at low temperature
+	+	-(at high T)	spontaneous at high temperature
+	-	+(at all T)	non-spontaneous at all temperatures

* The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.

THIRD LAW OF THERMODYNAMICS

- At absolute zero temperature, the entropy of a perfectly crystalline substance is taken as zero.
- For solid at temperature, T K

$$\Delta S = S_{TK} - S_{0K} = \int_0^T \frac{C_p dT}{T} = C_p \ln T$$

From third law of thermodynamics, $S_{0K} = 0$

$$S_T = C_p \ln T = 2.303 C_p \log T$$

For liquids and gases, the absolute entropy at a given temperature T is given by the expression,

$$S = \int_0^{T_f} \frac{C_{p(s)} dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_{p(l)} dT}{T} + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^T \frac{C_{p(g)} dT}{T}$$

SPEED PRACTICE

1. Which of the following represents enthalpy of formation of water?

- (a) $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(g)}; \Delta H = -242 \text{ kJ}$
 (b) $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(l)}; \Delta H = -286 \text{ kJ}$
 (c) $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(l)}; \Delta H = 286 \text{ kJ}$
 (d) $2\text{H}_{2(g)} + \text{O}_{2(g)} \longrightarrow 2\text{H}_2\text{O}_{(l)}; \Delta H = -572 \text{ kJ}$

2. Calculate the temperature of 4.0 mole of a gas occupying 5 dm^3 at 3.32 bar.

- (a) 50 K (b) 60 K (c) 70 K (d) 75 K

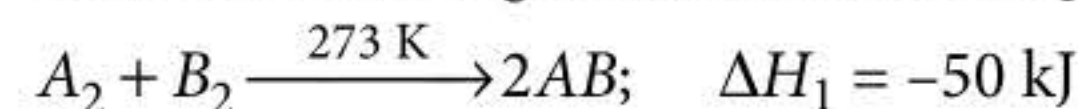
3. Two gas bulbs A and B are connected by a tube having a stopcock. Bulb A has a volume of 100 mL and contains hydrogen. After opening the gas from A to the evacuated bulb B, the pressure falls down by 40%. The volume (mL) of B must be

- (a) 75 (b) 150 (c) 125 (d) 200

4. The standard heat of formation of $\text{CH}_{4(g)}$, $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(g)}$ are -76.2 , -398.8 and $-241.6 \text{ kJ mol}^{-1}$ respectively. The amount of heat evolved (in kJ) by burning 1 m^3 of methane measured under normal conditions is

- (a) 805 (b) 35973 (c) 22.4 (d) 3121

5. From the following data, what is the ΔC_p of reaction?



- (a) -2.0 kJ K^{-1} (b) -0.75 kJ K^{-1}
 (c) -0.31 kJ K^{-1} (d) Unpredictable

6. The average molar heat capacities of ice and water are respectively 37.8 J mol^{-1} and 75.6 J mol^{-1} and

the enthalpy of fusion of ice is $6.012 \text{ kJ mol}^{-1}$. The amount of heat required to change 10 g of ice at -10°C to water at 10°C would be

- (a) 2376 J (b) 4752 J (c) 3970 J (d) 1128 J

7. 0.24 g of a volatile gas upon vaporization gives 45 mL vapour at NTP. What will be the vapour density of the substances?

- (a) 95.39 (b) 5.973 (c) 95.93 (d) 59.73

8. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula $\text{C}_n\text{H}_{2n-2}$. What is the value of n ?

- (a) 1 (b) 4 (c) 3 (d) 8

9. The lattice enthalpy and hydration enthalpy of four compounds are given below:

Compounds	Lattice enthalpy (in kJ mol^{-1})	Hydration enthalpy (in kJ mol^{-1})
P	+780	-920
Q	+1012	-812
R	+828	-878
S	+632	-600

The pair of compounds which is soluble in water is

- (a) P and Q (b) Q and R
 (c) R and S (d) P and R

10. Which of the following is the enthalpy of the following reaction?



(Given that, $\Delta H_f^\circ(\text{Fe}^{3+}) = -100 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{Zn}^{2+}) = -15 \text{ kJ mol}^{-1}$)

- (a) +85 kJ (b) -115 kJ
 (c) +155 kJ (d) -155 kJ