BRUSH UP
for NEET/JEE 2020

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 (Gaseous and Liquids) | Thermodynamics

### States of Matter (Gaseous and Liquids)

- Matter is typically found in one of the three different phases or states *viz*; solid, liquid or gas.
- The major factor that is responsible for the different behaviour of solids, liquids and gases is the nature of the interactions between the particles (atoms, ions or molecules) and the effect of thermal energy on the movement of the particles.

INTERMOLECULAR FORCES OF ATTRACTION

Types of Forces	Description
Dipole-induced dipole interaction	Forces between molecules having permanent dipole moment and molecule lacking permanent dipole moment.
Dipole-dipole interaction	Forces that exist between polar molecules where the positive end of one molecule attracts the negative end of another molecule.
London-dispersion forces	Forces that exist between molecules as a result of positive nuclei of one molecule attracting the electrons of another molecule.
Hydrogen bonding	Forces that exist between molecules that have a hydrogen atom bonded to a highly electronegative atom such as oxygen, nitrogen, or fluorine.

Intermolecular Forces vs Thermal Energy

- The energy which arises by motions of atoms or molecules of a body is known as thermal energy. It is the measure of average kinetic energy of the particles of matter and it is directly proportional to the temperature of the substance.

Gas → Liquid → Solid
Intermolecular interaction becomes stronger

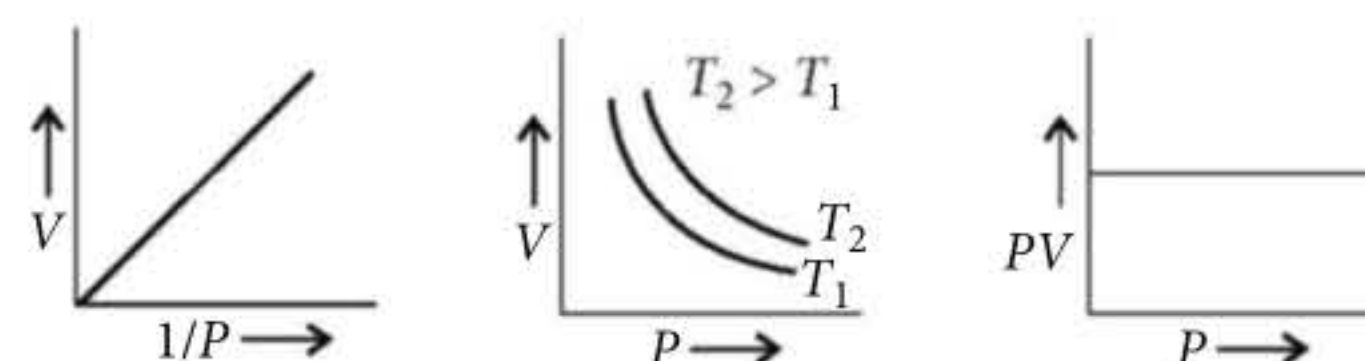Gas ← Liquid ← Solid
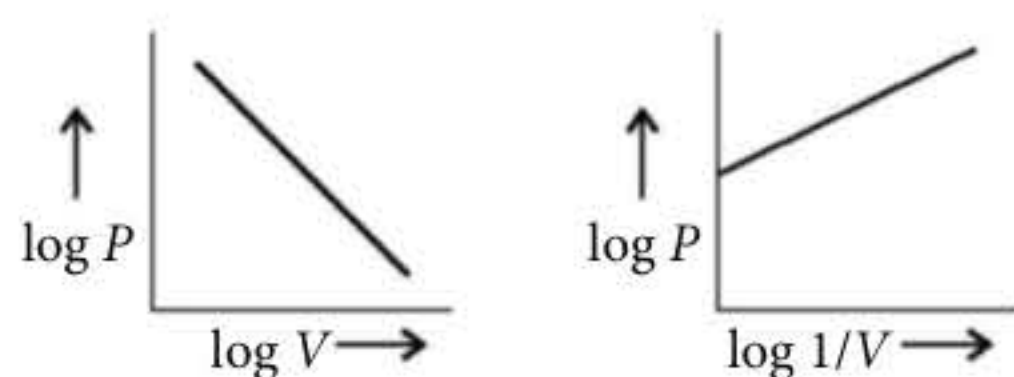Thermal energy increases
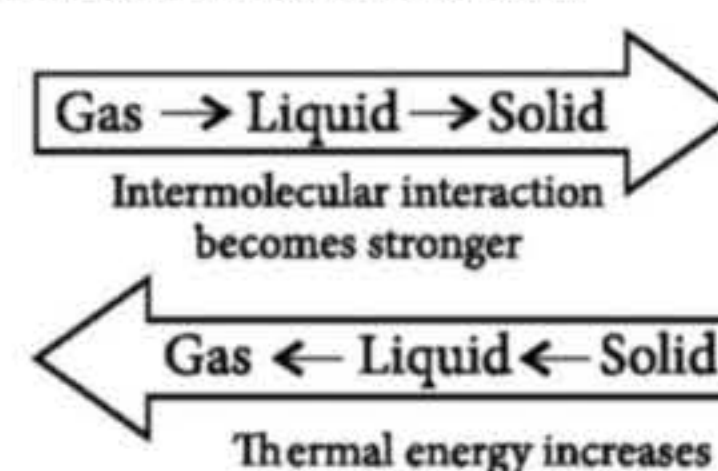
THE GAS LAWS

Boyle's Law

- At constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.

$$P \propto \frac{1}{V} \text{ (at constant } T \text{ and } n)$$

or $P_1V_1 = P_2V_2 = $ constant

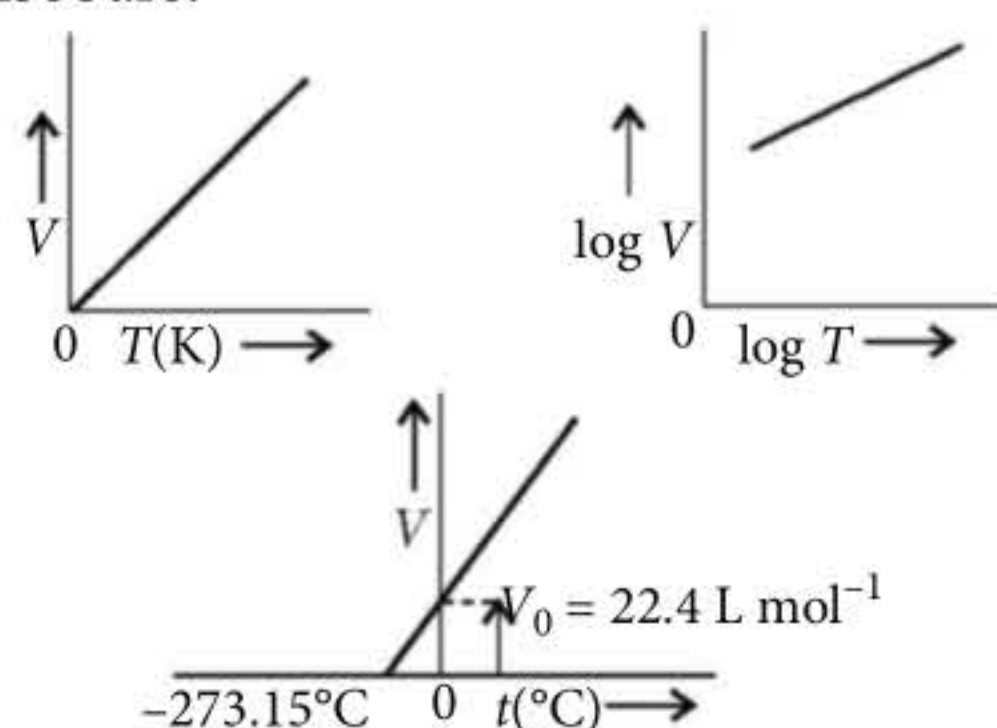- The plots drawn at constant temperature for a gas are called isotherms.

Charles' Law

- Pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature i.e., $V \propto T$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{(at constant } P\text{)}$$

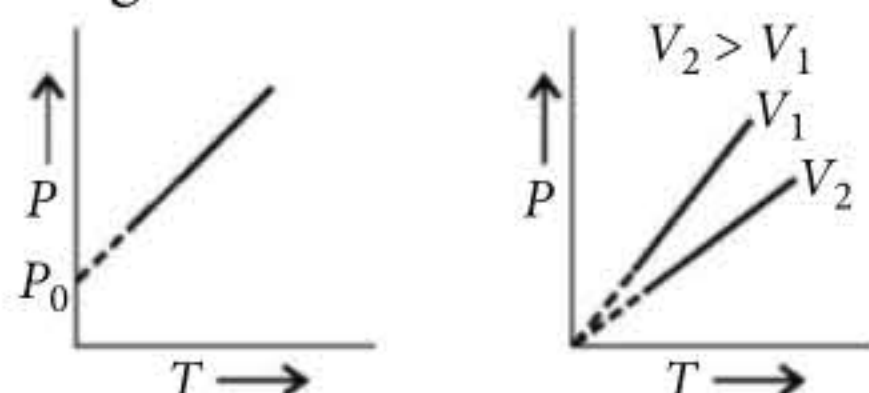- Graphs between V and T at constant pressure are called isobars.

Gay-Lussac's Law or Amonton's Law

- At constant volume, pressure of a fixed amount of a gas varies directly with the temperature i.e., $P \propto V$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{(at constant } V\text{)}$$

- The plots drawn between P and T at constant volume for a gas are called isochores.

Avogadro's Law

- At constant, P and T, $V \propto n$.
  or $n_1 V_1 = n_2 V_2$
  At a given temperature and pressure equal volumes contain equal number of moles, independent of the kind of gas.

IDEAL GAS EQUATION

- Combined gas law : $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$

- Thus, $\dfrac{PV}{T}$ = constant = K, $K \propto n$ or $K = nR$
  $PV/T = nR$ or $PV = nRT$

- The gases which obey the ideal gas equation under all conditions of temperature and pressure are called ideal gases.

Units of pressure	Units of volume	Values of gas constant (R)	Units of gas constant (R)
atm	L	0.0821	L atm K^{-1} mol^{-1}
atm	cm^3	82.1	atm cm^3 K^{-1} mol^{-1}
dynes cm^{-2}	cm^3	8.314×10^7	ergs K^{-1} mol^{-1}
dynes cm^{-2}	cm^3	1.987	cal K^{-1} mol^{-1}
Pa or N m^{-2}	m^3	8.314	J K^{-1} mol^{-1}

- **Relationship between molar mass and density :** Let m be the mass of a gas in grams and M be the molar mass of that gas.

  We know, $n = \dfrac{m}{M}$

  Now, $PV = nRT = \dfrac{m}{M} RT$

  $P = \dfrac{m}{V} \dfrac{RT}{M} = \dfrac{dRT}{M}$ or $M = \dfrac{dRT}{P}$

  $\dfrac{dT}{P} = \dfrac{M}{R}$, since M and R are constant for a gas.

  $\therefore \dfrac{dT}{P}$ = constant $\therefore \dfrac{d_1 T_1}{P_1} = \dfrac{d_2 T_2}{P_2}$

Dalton's Law of Partial Pressures

- The total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.

- $P_{\text{total}} = p_1 + p_2 + p_3 + \dots$
  $p_1 = P_{\text{total}} \times$ mole fraction of gas 1.
  i.e., partial pressure = total pressure × mole fraction

Graham's Law of Diffusion

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

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

✓ PEEP INTO PREVIOUS YEARS

1. The volume occupied by 1.8 g of water vapour at 374°C and 1 bar pressure will be
   [Use $R = 0.083$ bar L K^{-1} mol^{-1}]
   (a) 96.66 L (b) 55.87 L (c) 3.10 L (d) 5.37 L
   (Odisha NEET 2019)

2. At 300 K, the density of a certain gaseous molecule at 2 bar is double to that of dinitrogen (N_2) at 4 bar. The molar mass of gaseous molecule is
   (a) 56 g mol^{-1} (b) 112 g mol^{-1}
   (c) 224 g mol^{-1} (d) 28 g mol^{-1}
   (JEE Main 2017)

3. Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape?
   (a) 3/8   (b) 1/2
   (c) 1/8   (d) 1/4   *(NEET 2016)*

KINETIC GAS EQUATION

- $PV = \dfrac{1}{3} mnu^2$

  where, P = pressure of gas
  V = volume of gas
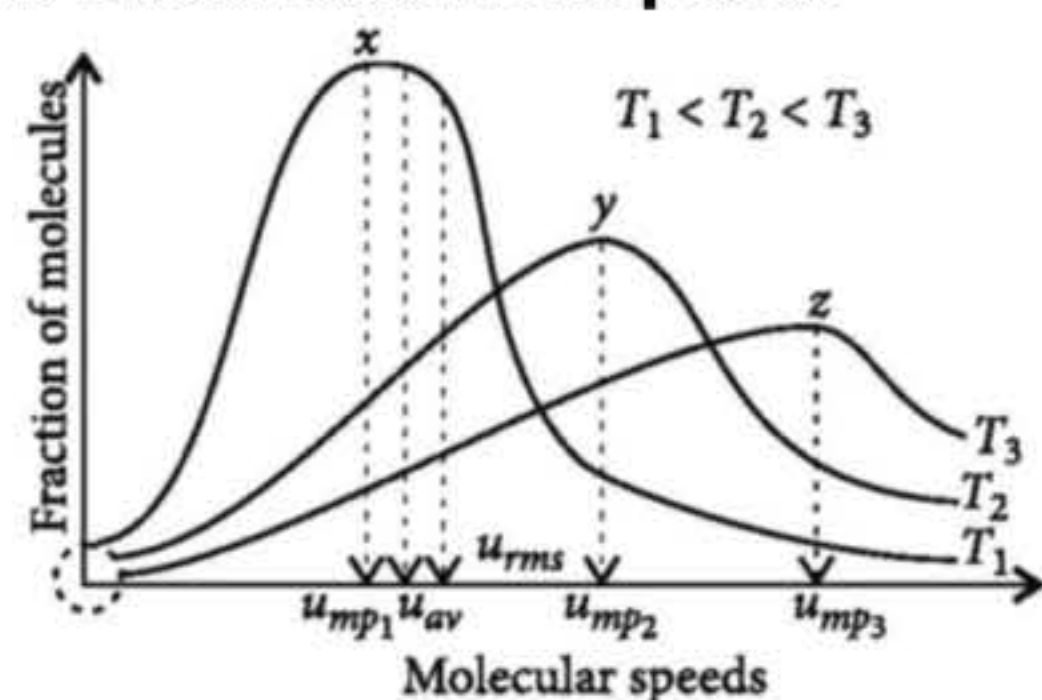 m = mass of one molecule of gas
  n = number of molecules of gas
  u = root mean square speed of molecules

Kinetic Energy and Molecular Speeds

Average speed	Root mean square speed	Most probable speed
$u_{av} = \sqrt{\dfrac{8RT}{\pi M}}$	$u_{rms} = \sqrt{\dfrac{3RT}{M}}$	$u_{mp} = \sqrt{\dfrac{2RT}{M}}$

Maxwell's Distribution of Speeds

Molecular speeds

$\because$ Signifies that speed is never zero but it tends towards zero

- Average kinetic energy per molecule

$$= \frac{3}{2} \cdot \frac{R}{N} \cdot T = \frac{3}{2} kT$$

where, k = Boltzmann constant
$$= 1.3806 \times 10^{-16} \text{ erg deg}^{-1}$$

- Total kinetic energy of n moles of a gas $= n \times \dfrac{3}{2} RT$.

- Most probable : average : r.m.s. $= \sqrt{2} : \sqrt{\dfrac{8}{\pi}} : \sqrt{3}$
  $$= 1:1.128:1.224$$

- $u_{rms} > u_{av} > u_{mp}$

Kinetic Molecular Theory of Gases

- The gas laws were based on simple experimental facts hence, a theoretical proof or derivation for the same was proposed, on the basis of kinetic molecular theory of gases, by Maxwell and Boltzmann as :
  - Gases are made up of a large number of small molecules whose size is negligible as compared to the distance of separation between them.
  - Molecules move randomly in different directions with different speeds.
  - The intermolecular forces of attraction or repulsion are almost negligible, except when molecules collide.
  - The collisions are called elastic collisions because no energy change occurs when two molecules collide, i.e., the total kinetic energy remains constant.
  - The average kinetic energy of a molecule is proportional to its absolute temperature.
  - The pressure exerted by the gas is due to bombardment of its molecules on the walls of the container per unit area.

REAL GASES

- The gases which obey the gas laws only at low pressure and high temperature are called real gases.

van der Waals' Equation of State

The deviations from ideal gas behaviour can be ascertained to the following faulty assumptions by kinetic theory of gases :

- The real volume of the gas molecules is negligible when compared to the volume of the gas.
- There are no forces of attraction or repulsion between the gas molecules. Hence, van der Waals suggested the following corrections :
  - The gas molecules possess finite volume and hence should not be neglected. It is especially true at high pressures and low temperatures and should be accounted for.
  - In case of real gases, both the forces of attraction as well as repulsion operate between gas molecules.
  - The ideal gas equation can be written after volume correction as :
    $$P(V - nb) = nRT$$

- After pressure correction :

$$P_{ideal} = P_{real} + a\left(\frac{n^2}{V^2}\right)$$

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

  a, b are van der Waals' constants; different for each gas.

  Unit of $a \rightarrow$ atm L^2 mol^{-2}; S.I. unit $\rightarrow$ Pa m^6 mol^{-2}
  Unit of $b \rightarrow$ L mol^{-1}; S.I. unit $\rightarrow$ m^3 mol^{-1}

- **Significance of van der Waals constants.** 'a' is a measure of the magnitude of attractive forces whereas 'b' is a measure of the effective size of the gas molecules. $b = 4v$ where v is actual volume of gas molecules. 'b' is called excluded volume or co-volume. Greater the value of 'a' more easily the gas is liquefiable.

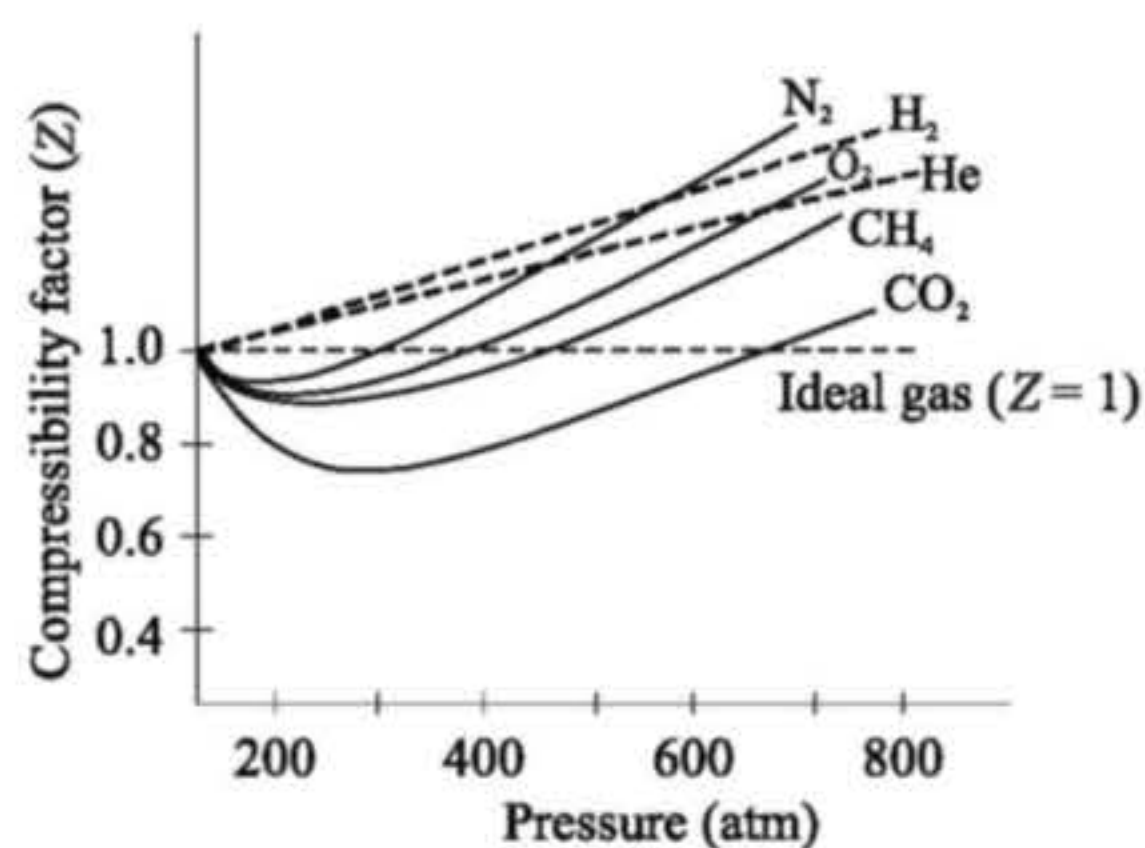- **Compressibility factor (Z) :** It measures the deviation from ideal behaviour and is given as

  $$Z = \frac{PV}{nRT}; \ Z = 1 \text{ for ideal gas, } Z \neq 1 \text{ for real gases,}$$

  $$Z = \frac{V_{real}}{V_{ideal}}$$

  $Z > 1$ for positive deviation from ideal behaviour, $Z < 1$ for negative deviation from ideal behaviour.

- The isotherms for one mole of different gases, plotted against the Z value and pressure, P at 0 °C are shown as :

- For gases like He, H$_2$ the Z value increases with increase in pressure (positive deviation). It is because, the repulsive forces become more significant and the attractive forces become less dominant. Hence, these gases are difficult to condense.

- For gases like CH$_4$, CO$_2$, NH$_3$, etc., the Z value decreases initially (negative deviation) but increases at higher pressure. It is because at low pressures, the attractive forces are more dominant over the repulsive forces, whereas at higher pressures the repulsive forces become significant as the molecules approach closer to each other.

- But for all the gases, the Z value approaches one at very low pressures, indicating the ideal behaviour.

- **Boyle temperature (or Boyle point)** is the temperature at which a real gas obeys ideal gas law over an appreciable range of pressure.

- **Critical temperature (T_c)** is the temperature above which a gas cannot be liquefied howsoever high pressure may be applied on the gas. The corresponding pressure and volume are called critical pressure (P_c) and critical volume (V_c).

Liquid State

- Liquid state is intermediate between gaseous and solid states. They possess fluidity like gases but incompressibility like solids.

Properties	Description
Surface tension	Force per unit length acting perpendicular to the tangential line on the surface. It decreases with increases in temperature. $$r = \frac{work\ (w)}{change\ in\ area\ (A)} = \frac{Force\ (F)}{length\ (l)}$$ cgs unit = dynes cm^{-1} SI unit = Nm^{-1}
Viscosity	Internal resistance of flow in liquids which one layer offers to another layer trying to pass over. coefficient of viscosity, $$\eta = \frac{f.dx}{A.dv}$$ SI unit of viscosity coefficient = N sec m^{-2} cgs unit of viscosity coefficient = poise
Vapour pressure	It is the pressure exerted by the vapours on the liquid surface. It increases with rise in temperature. $$\log\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ Increases with increase in temperature due to decrease in the magnitude of interparticle forces.

4. A gas at 350 K and 15 bar has molar volume 20 percent smaller than that for an ideal gas under the same conditions. The correct option about the gas and its compressibility factor (Z) is
   (a) $Z < 1$ and repulsive forces are dominant
   (b) $Z > 1$ and attractive forces are dominant
   (c) $Z > 1$ and repulsive forces are dominant
   (d) $Z < 1$ and attractive forces are dominant.
   (NEET 2019)

5. Which of the following statement(s) is (are) correct regarding the root mean square speed (u_{rms}) and average translational kinetic energy (E_{av}) of a molecule in a gas at equilibrium?

   (a) u_{rms} is inversely proportional to the square root of its molecular mass.
   (b) E_{av} is doubled when its temperature is increased four times.
   (c) u_{rms} is doubled when its temperature is increased four times.
   (d) E_{av} at a given temperature does not depend on its molecular mass. **(JEE Advanced 2019)**

6. A liquid can exist only
   (a) between triple point and critical point
   (b) at any temperature above melting point
   (c) between melting point and critical point
   (d) between boiling and melting points.
   (Karnataka CET 2016)

➤ Normal boiling point of a liquid is approximately 2/3 of its critical temperature.

➤ T_i (inversion temperature) $= \dfrac{2a}{R \cdot b}$

➤ Average K.E. $= \bar{E}_k = \dfrac{3}{2}kT$

➤ Critical constants : $V_c = 3b$, $T_c = \dfrac{8a}{27Rb}$,

   $P_c = \dfrac{a}{27b^2}$, $P_c V_c = \dfrac{3}{8}kT_c$

➤ Volume coefficient (α_V) $= \dfrac{V_t - V_0}{V_0 \times t}$

➤ Pressure coefficient (α_P) $= \dfrac{P_t - P_0}{P_0 \times t}$

➤ $\dfrac{\Delta H_{vap}}{T_b} = 88 \text{ J K}^{-1}\text{mol}^{-1}$ (Trouton's rule)

➤ A number of substances are known which when added to water, lower its surface tension. These substances are called surfactants or surface active agents e.g. CH_3OH, C_2H_5OH, soaps, etc.

➤ Surface tension decreases with increase in temperature and becomes zero at the critical temperature while viscosity of a liquid decreases with increase in temperature by about 2% per degree rise in temperature.

Thermodynamics

• The study of the flow of heat or any other form of energy in or out of a system as it undergoes a physical or chemical transformation is called thermodynamics.

• **System :** The specified portion of the universe under observation.

• **Surrounding :** The remaining part of the universe which is not a part of the system and is not under study.

TYPES OF SYSTEM

• **Open system :** can exchange matter as well as energy with surroundings.

• **Closed system :** can exchange energy but not matter with surroundings.

• **Isolated system :** cannot exchange matter as well as energy with surroundings.

THERMODYNAMIC PROPERTIES

• **Intensive properties :** Properties which do not depend on the amount of matter present in the system.
  Examples : Pressure, Temperature, Density, Melting point, Boiling point etc.

• **Extensive properties :** Properties which depend on the amount of matter present in the system.
  Examples : Mass, Volume, Heat capacity, Enthalpy, Entropy etc.
  Ratio of two extensive properties is always intensive,
  i.e., $\dfrac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$