10. States of Matter : Gaseous and Liquid States

10.1 Introduction:

We have learnt that substances exist in one of the three main states of matter. The three distinct physical forms of a substance are Solid, Liquid, and Gas.

Can you recall?

Water exists in the three different forms solid ice, liquid water and gaseous vapours.

Key points of differentiation between the three states can be understood as given in Table 10.1.

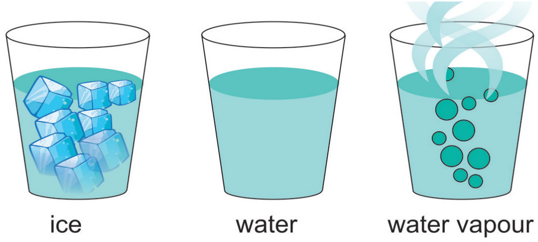
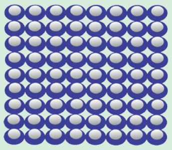
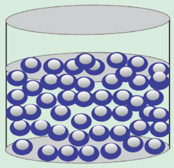
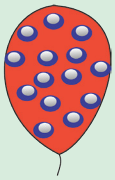


Fig. 10.1 : Different States of Water

Three states of matter are interconvertible by exchange of Heat as given below:

$$\boxed{\text{Solid}} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \boxed{\text{Liquid}} \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} \boxed{\text{Gas}}$$

Table 10.1: Distinguishing points between Solid, Liquid and Gas

Sr. No.	Points	Solid	Liquid	Gas
1	Microscopic view Mean atomic/ molecular separation	 Mean separation ≈ 3-5A^0	 Mean separation ≈ 3-10A^0	 Mean separation > 5A^0
2	Arrangement of particles (atoms/ molecules)	Particles are tightly held, and have regular arrangement of atoms/ molecules	Particles are loosely packed, irregular arragement of particles	Particles are more loosely packed, highly irregular arrangement
3	Movement of particles	Particles cannot move freely as they occupy fixed positions.	Particles can move a small distance within the liquid	Particles are in continuous random motion.
4	Shape and volume	Has definite shape and volume	Takes the shape of the container and has definite volume.	Takes the shape and the volume of its container.
5	Intermoleculer space	Very small Intermolecular space	Moderate Intermolecular space	Large Intermolecular space.
6	Effect of a small change in temperature	Volume change is small	Moderate effect on volume change	Volume change significantly high.
7	Compression or Expansion	Practically Non- compressible	Small Compressibility	Compressible

10.2 Intermolecular Forces : Intermolecular forces are the attractive forces as well as repulsive forces present between the neighbouring molecules. The attractive force decreases with the increase in distance between the molecules. The intermolecular forces are strong in solids, less strong in liquids and very weak in gases. Thus, the three physical states of matter can be determined as per the strength of intermolecular forces.

The physical properties of matter such as melting point, boiling point, vapor pressure, viscosity, evaporation, surface tension and solubility can be studied with respect to the strength of attractive forces between the molecules. During the melting process intermolecular forces are partially overcome, whereas they are overcome completely during the vapourization process.

10.2.1 Types of Intermolecular Forces:

The four types of intermolecular forces are-

i. Dipole-dipole interactions
ii. Ion-dipole interactions
iii. Dipole-Induced dipole interaction
iv. London Dispersion Forces
v. Hydrogen bonding

i. Dipole-dipole interactions : Polar molecules experience dipole-dipole forces due to electrostatic interactions between dipoles on neighboring molecules.

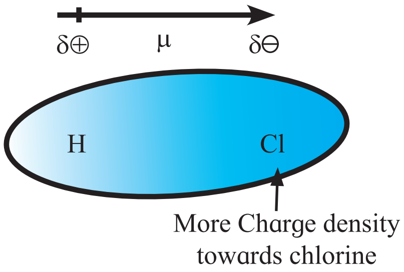
What are polar molecules or Polar covalent molecules? (Refer to Chapter 5).

Polar covalent molecule is also described as "dipole" meaning that the molecule has two 'poles'. The covalent bond becomes polar due to electronegativity difference between the bonding atoms. Hence polarity is observed in the compounds containing dissimilar atoms. For example, HCl molecule (see Fig. 10.2 (a)).

One end (pole) of the molecule has partial positive charge on hydrogen atom while at other end chlorine atom has partial negative charge (denoted by Greek letter 'δ' delta). As a result of polarisation, the molecule possesses the dipole moment.

Dipole moment (μ) is the product of the magnitude of the charge (Q) and the distance between the centres of positive and negative charge (r). It is designated by a Greek Letter (μ) (mu). Its unit is debye (D).

Dipole moment is a vector quantity and is depicted by a small arrow with tail in the positive centre and head pointing towards the negative centre.



Unequal sharing of electrons
between the bonding atoms.

Fig 10.2 (a) : Polar molecule

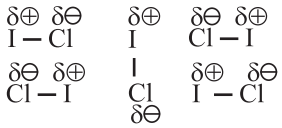


Fig 10.2 (b) : Dipole-dipole interaction

For example, the dipole moment of HF may be represented as: $\overset{+\!\!\!\longrightarrow}{\mathrm{H\text{-}\ddot{F}:}}$

The crossed arrow($+\!\!\!\longrightarrow$) above the Lewis structure represents an electron density shift.

Thus polar molecules have permanent dipole moments. When a polar molecule encounters another polar molecule, the positive end of one molecule is attracted to the negative end of another polar molecule. Many such molecules have dipoles and their interaction is termed as dipole-dipole interaction. These forces are generally weak, with energies of the order of 3-4 kJ mol^{-1} and are significant only when molecules are in close contact. i.e. in a solid or a liquid state.

For example C_4H_9Cl, (butyl chloride), $CH_3 - O - CH_3$ (dimethyl ether) ICl (iodine chloride B.P. 27 ^{0}C), are dipolar liquids. The molecular orientations due to dipole-dipole interaction in ICl liquid is shown in Fig. 10.2 (b).

In brief, more polar the substance, greater the strength of its dipole-dipole interactions. Table 10.2 enlists several substances with similar molecular masses but different dipole moments. From Table 10.2, it is clear that higher the dipole moment, stronger are the inter molecular forces, generally leading to higher boiling points.

Table 10.2 : Effect of dipole moments on boiling point (b.p.)

Substance	Molar Mass (amu)	Dipole Moment (D)	b.p. (K)
$CH_3 - CH_2 - CH_3$	44.10	0.1	231
$CH_3 - O - CH_3$	46.07	1.3	248
$CH_3 - Cl$	50.49	1.9	249
$CH_3 - CN$	41.05	3.9	355

When different substances coexist in single phase, following intermolecular interactions are present.

ii. Ion-dipole interactions : An ion-dipole force is the result of electrostatic interactions between an ion (cation or anion) and the partial charges on a polar molecule.

The strength of this interaction depends on the charge and size of an ion. It also depends on the magnitude of dipole moment and size of the molecule.

(Hydrated $Na^{\oplus}$ ion)

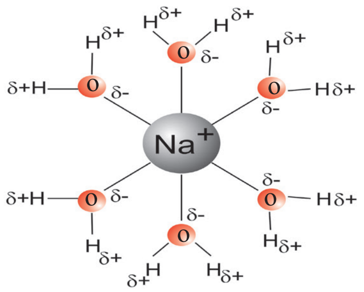


Fig. 10.2 (c) : $Na^{\oplus}$ ion(cation) - H_2O interaction

Ion-dipole forces are particularly important in aqueous solutions of ionic substances such as sodium chloride (NaCl). When an ionic compound, sodium chloride is dissolved in water, the ions get separated and surrounded by water molecules which is called **Hydration** of sodium ions.

Cations are smaller in size than the isoelectronic anions. The charge density on cation ($Na^{\oplus}$) is more concentrated than anion ($Cl^{\ominus}$). This makes the interaction between ($Na^{\oplus}$) and negative end of the polar H_2O molecule (Fig. 10.2 (c)) stronger than the corresponding interaction between ($Cl^{\ominus}$) and positive end of the polar H_2O molecule.

More the charge on cation, stronger is the ion-dipole interaction. For example, $Mg^{2\oplus}$ ion has higher charge and smaller ionic radius (78 pm) than $Na^{\oplus}$ ion (98 pm), hence $Mg^{2\oplus}$ ion is surrounded (hydrated) more strongly with water molecules and exerts strong ion-dipole interaction.

Thus the strength of interaction increases with increase in charge on cation and with decrease in ionic size or radius. Therefore, ion-dipole forces increase in the order :

$Na^{\oplus} < Mg^{2\oplus} < Al^{3\oplus}$.

iii. Dipole-Induced dipole interaction :

When polar molecules (like H_2O, NH_3) and nonpolar molecules (like benzene) approach each other, the polar molecules induce dipole in the non-polar molecules. Hence 'Temporary dipoles' are formed by shifting of electron clouds in nonpolar molecules. For example, Ammonia (NH_3) is polar and has permanent dipole moment while Benzene (C_6H_6) is non polar and has zero dipole moment. The force of attraction developed between the polar and nonpolar molecules is of the type dipole - induced dipole interaction. It can be seen in Fig 10.2(d) in the following manner:

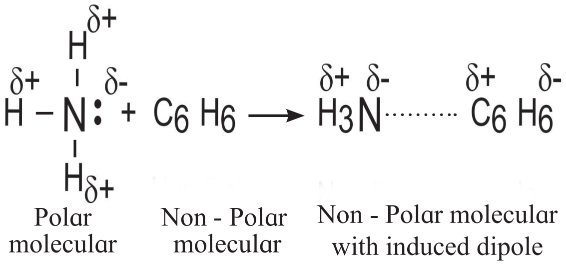


Fig. 10.2 (d) : Dipole - induced dipole interaction

iv. London Dispersion Force : The study of intermolecular forces present among nonpolar molecules or the individual atoms of a noble gas is very interesting. For example, Benzene (C_6H_6) has zero dipole moment and experiences no dipole-dipole forces, yet exists in liquid stage.

In case of nonpolar molecules and inert gases, only dipersion forces exist. Dispersion forces are also called as **London forces** due to an idea of momentary dipole which was proposed by the German Physicist, **Fritz London** in 1930. These forces are also called as **van der Waals forces**. It is the weakest intermolecular force that develops due to interaction between two nonpolar molecules. In general, all atoms and molecules experience London dispersion forces, which result from the motion of electrons. At any given instant of time, the electron distribution in an atom may be asymmetrical, giving the atom a short lived dipole moment. This momentary dipole on one atom can affect the electron distribution in the neighbouring atoms and induce momentary dipoles in them. As a result, weak attractive force develops.

For example, substances composed of molecules such as O_2, CO_2, N_2, halogens, methane gas, helium and other noble gases show van der Waals force of attraction.

The strength of London forces increases with increase in molecular size, molecular mass and number of electrons present in an atom or molecule.

When two nonpolar molecules approach each other, attractive and repulsive forces between their electrons and the nuclei will lead to distortions in the size of electron cloud, a property referred to as polarizability.

Polarizability is a measure of how easily an electron cloud of an atom is distorted by an applied electric field. It is the property of atom. The ability to form momentary dipoles that means the ability of another molecule to become polar by redistributing its electrons is known as **polarizability** of the atom or molecule.

More the number of electrons in a molecule, higher is its ability to become polar. Similarly more the spread out shapes, higher the dispersion forces present between the molecules. London dispersion forces are stronger in a long chain of atoms where molecules are not compact. This can affect physical property such as B.P. n-Pentane, for example boils at 309.4 K, whereas neo - pentane boils at 282.7 K. Here both the substances have the same molecular formula, C_5H_{12}, but n-pentane is longer and somewhat spread out, where as neo-pentane is more spherical and compact (see Fig. 10.3).

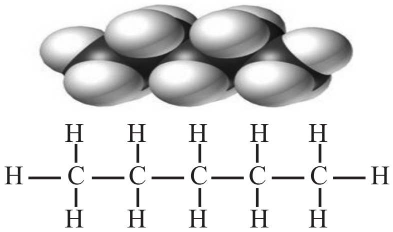


Fig 10.3 (a): Longer, less mpact molecule n-Pentane (b.p.= 309.4K)

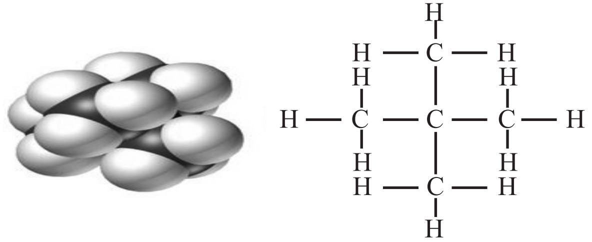


Fig 10.3 (b): More compact molecule neo - pentane (b.p.= 282.7K)

v. Hydrogen Bonding : A hydrogen bond is a special type of dipole-dipole attraction which occurs when a hydrogen atom is bonded to a strongly electronegative atom or an atom with a lone pair of electrons. Hydrogen bonds are generally stronger than usual dipole - dipole and dispersion forces, and weaker than true covalent or ionic bonds.

Definition : The electrostatic force of attraction between positively polarised hydrogen atom of one molecule and a highly electronegative atom (which may be negatively charged) of other molecule is called as **hydrogen bond**.

Strong electronegative atoms that form hydrogen bonds are nitrogen, oxygen, and fluorine. Hydrogen bond is denoted by (....) dotted line. Hydrogen bond which occurs within the same molecule represents **Intramolecular Hydrogen bond**.

A hydrogen bond present between two like or unlike molecules, represents **Intermolecular Hydrogen bond**. (See Fig. 10.4 (a) and (b)).

i. Inter molecular H-bonding

H-bonding in H–F :

$H^{\delta+}–F^{\delta-}\cdots\cdots H^{\delta+}–F^{\delta-}\cdots\cdots H^{\delta+}–F^{\delta-}\cdots\cdots H^{\delta+}–F^{\delta-}$

H-bond

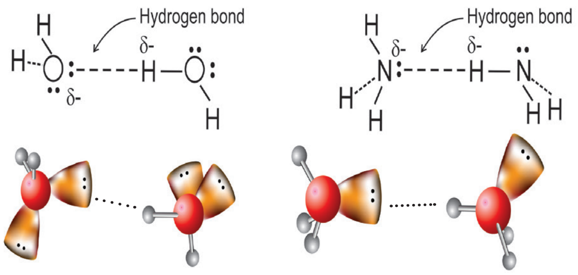
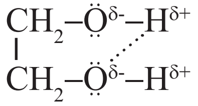


Fig. 10.4 : H-bonding in H_2O (above) and NH_3 (below) (solid line denotes covalent bond, dotted line denotes hydrogen bond)

ii. Intra molecular H-bonding :

H-bonding in ethylene glycol :



$$\begin{array}{l} CH_2–\ddot{O}^{\delta-}–H^{\delta+} \\ | \\ CH_2–\ddot{O}^{\delta-}–H^{\delta+} \end{array}$$

H - bonding and boiling point : Due to the presence of H-bonding in the compounds, more energy is required to break the bonds. Therefore, boiling point is more in case of liquid molecules containing H-bond. Hydrogen bonds can be quite strong with energies up to 40 kJ/mol.

Water in particular is able to form a vast three dimensional network of hydrogen bonds as shown in Fig. 10.5. It is because each H_2O molecule has two hydrogen atoms and two electron pairs on oxygen atom.

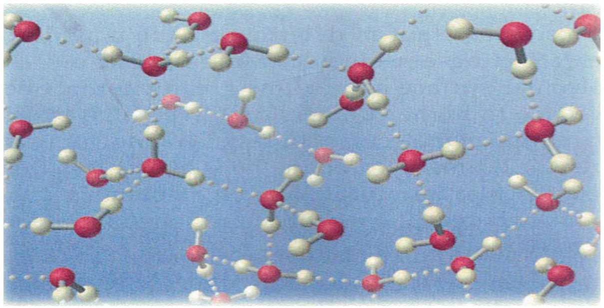


Fig. 10.5 : Liquid water contains a vast three dimensional network of hydrogen bonds

The boiling point generally increases with increase in molecular mass, but the hydrides of nitrogen (NH_3), oxygen (H_2O) and fluorine (HF) have abnormally high boiling points due to the presence of hydrogen bonding between the molecules.

Similarly due to presence of H- bond, viscosity of liquid increases. Hydrogen bonds play vital role in determining structure and properties of proteins and nucleic acid present in all living organisms. In case of gases intermolecular forces of attraction are very weak.

10.2.2 Intermolecular Forces and Thermal energy : Thermal energy is the origin of kinetic energy of the particles of matter that arises due to movement of particles (about which you must have learnt in Physics). It is directly proportional to the temperature; that means thermal energy increases with increase in temperature and vice versa.

Three states of matter are the consequence of a balance between the intermolecular forces of attraction and the thermal energy of the molecules.

If the intermolecular forces are very weak, molecules do not come together to make liquid or solid unless thermal energy is decreased by lowering the temperature.

When a substance is to be converted from its gaseous state to solid state, its thermal energy (or temperature) has to be reduced. At this stage, the intermolecular forces become more important than thermal energy of the particles.

Intermolecular Force Increases →

$\boxed{\text{Gas}} \longrightarrow \boxed{\text{Liquid}} \longrightarrow \boxed{\text{Solid}}$

Thermal energy decreases →

A comparison of various kinds of intermolecular forces discussed in this section is made in Table 10.3.

Table 10.3 : Comparison of Intermolecular Forces

Force	Strength	Characterstics
Ion-dipole	Moderate (10 - 50 kJ/mol)	Occurs between ions and polar solvents
Dipole-dipole	Weak (3 - 4 kJ/mol)	Occurs between polar molecules
London dispersion	Weak (1 - 10 kJ/mol)	Occurs between all molecules; strength depends on size, polarizability
Hydrogen bond	Moderate (10 - 40 kJ/mol)	Occurs between molecules with O-H, N-H, and H-F bonds

Can you tell?

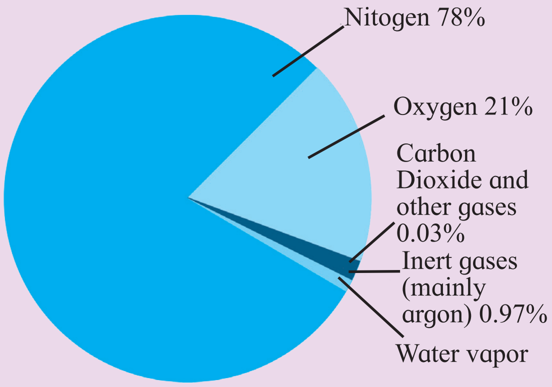
What are the various components present in the atmosphere?

Name five elements and five compounds those exist as gases at room temperature.

Just think

What is air?

It is a mixture of various gases. Air, we can not see but feel the cool breeze. The composition of air by volume is around 78 percent N_2, 21 percent O_2 and 1 percent other gases including CO_2. The chemistry of atmospheric gases is an important subject of study as it involves air pollution. O_2 in air is essential for survival of aerobic life.



Composition of air with respect to proportion of various gases

Do you know ?

Among the three compounds H_2, H_2S and H_2Se, the first one, H_2O has the smallest molecular mass. But it has the highest B.P. of 100⁰C. B.P. of H_2S is -60⁰C and of H_2Se is -41.25 ⁰C. The extraordinary high B.P. of H_2O is due to very strong hydrogen bonding even though it has the lowest molecular mass.

10.3 Characteristic properties of Gases :

Under normal conditions, out of 118 elements from the periodic table, only a few (eleven) elements exist as gases. The gaseous state is characterized by the following physical properties :

1. Gases are lighter than solids and liquids i.e. possess lower density.
2. Gases do not possess a fixed volume and shape. They occupy entire space available and take the shape of the container.
3. Gas molecules are widely seperated and are in continuous, random motion. Therefore, gases exert pressure equally in all directions due to collision of gas molecules, on the walls of the container.
4. In case of gases, intermolecular forces are weakest.
5. Gases possess the property of diffusion which is a spontaneous homogenous inter mixing of two or more gases.
6. Gases are highly compressible.

Measurable properties of Gases : (Refer to Chapter 1) : Some Important measurable properties of the gases are given below :

1. Mass: The mass, m, of a gas sample is measure of the quantity of matter it contains. It can be measured experimentally. SI unit of mass of gas is kilogram (kg). 1kg = 10^3g.

The mass of a gas is realated to the number of moles (n) by the expression i.

i. $$n = \frac{\text{mass in grams}}{\text{molar mass in grams}} = \frac{m}{M}$$

The following expressions are also useful in calculations.

ii.
$$n = \frac{\text{Number of molecules}}{\text{Avogadro Number}} = \frac{N}{N_A} = \frac{N}{6.022 \times 10^{23}}$$

iii.
$$\text{n} = \frac{\text{Volume of a given gas in litres at STP}}{\text{22.414 litres at STP}}$$

2. Volume: Volume (*V*) of a sample of gas is the amount of space it occupies. It is expressed in terms of different units like Litres (L), mililitres(mL), cubic centimeter (cm^3), cubic meter (m^3) or decimeter cube (dm^3). SI Unit of the volume is cubic meter (m^3).

Most commonly used unit to measure the volume of the a gas is decimeter cube or litre.

$1\ L = 1000 mL = 1000\ cm^3 = 1 dm^3$

$1\ m^3 = 10^3\ dm^3 = 10^3 L = 10^6 cm^3 = 10^6\ mL$

3. Pressure: Pressure (*P*) is defined as force per unit area.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{f}}{\text{a}}$$

Pressure of gas is measured with ‘manometer’ and atmospheric pressure is measured by ‘barometer’.

SI Unit of pressure is pascal (Pa) or Newton per meter square (N m^{-2}).

$1\ Pa = 1\ Nm^{-2} = 1\ kg\ m^{-1}\ s^{-2}$

$1\ bar = 1.00 \times 10^5\ Pa$

The bar is now replacing the standard atmosphere (atm) as the most convenient unit of pressure.

1 atm = 76 cm of Hg = 760 mm of Hg = 760 torr as 1 torr = 1mm Hg

1 atm = 101.325 kPa = 101325 Pa = $1.01325 \times 10^5\ N\ m^{-2} = 1.01325$ bar.

Can you tell?

What is the unit in which car-tyre pressure is measured ?

4. Temperature : It is the property of an object that determines direction in which energy will flow when that object is in contact with other object.

In scientific measurements temperature (T) is measured either on the celsius scale (^0C) or the Kelvin scale (K). (Note that degree sign is not used in Kelvin unit).

SI Unit of Temperature of a gas is kelvin (K). The celsius and kelvin scales are related by the expression

$$T\ (\mathrm{K}) = t^0\ \mathrm{C} + 273.15$$

5. Density : It is the mass per unit volume.

$$d = \frac{m}{V}$$

∴ SI Unit of density is kg m^{-3}.

In the case of gases, relative density is measured with respect to hydrogen gas and is called vapour density.

$$\therefore \text{ Vapour density} = \frac{\text{molar mass}}{2}$$

6. Diffusion: In case of gases, Rate of diffusion of two or more gases is measured.

$$\text{Rate of diffusion} = \frac{\text{Volume of a gas diffused}}{\text{time required for diffusion}}$$

∴ SI Unit for Rate of diffusion is $dm^3\ s^{-1}$ or $cm^3\ s^{-1}$

10.4 Gas Laws : The behavior of gases can be studied by four variables namely pressure, volume,temperature and the number of moles. These variables and measurable properties of the gases are related with one another through different gas laws.

Think of a gas in a cylinder or a sealed container. We can measure number of moles (*n*) of gas inside, the pressure (*P*) of a gas, the volume (*V*) of a gas (which is equal to the volume of the container) and the temperature (*T*) of the gas. The observed relationships between *P*, *V*, *n* and *T* are summarized by five gas laws: Boyle’s law, Charles’ law, Gay Lussac law, Avogadro law and Dalton’s law.

The gas laws are based on the experimental observations made by the scientists. Further, these gas laws have played significant role in the development of chemistry.

10.4.1 Boyle's Law: (Pressure-Volume Relationship)

Do you know ?

How does the bicycle pump work ? You can feel the increased pressure of a gas on your palm by pushing in the piston of a bicycle pump. As you push, you squash the same number of particles into a smaller volume. This squashing means particles hit the walls of the pump more often, increasing the pressure.

In 1662, Robert Boyle carried out large number of experiments on various gases. He observed that at constant temperature when the pressure was increased, the volume of the gas was reduced and vice versa.

Statement of Boyle's law: *For a fixed mass (number of moles 'n') of a gas at constant temperature, the pressure (P) of a gas is inversely proportional to the volume (V) of gas.*

OR

At constant temperature, the pressure of fixed amount (number of moles) of a gas varies inversely with its volume.

The law can be illustrated diagramatically as shown in Fig. 10.6

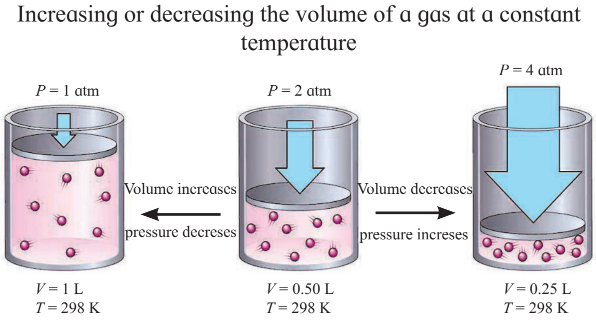


Fig. 10.6 : Schematic illustration of Boyle's Law

Mathematical Expression :

Mathematically, Boyle's law is expressed as

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

$$\therefore P = k_1 \frac{1}{V} \quad \ldots\ldots\ldots\ldots \quad (10.1)$$

(where k_1 is proportionality constant)

on rearranging, Eq. (10.1) be comes :

$$\therefore PV = k_1 \quad \ldots\ldots\ldots\ldots \quad (10.2)$$

It means that at constant temperature, product of pressure and volume of the fixed amount of a gas is constant.

Thus, when a fixed amount of a gas at constant temperature (T) occuping volume V_1 initially at pressure (P_1) undergoes expansion or compression, volume of the gas changes to V_2 and pressure to P_2.

According to Boyle's law,

$$P_1V_1 = P_2V_2 = \text{constant} \ldots\ldots(10.3)$$

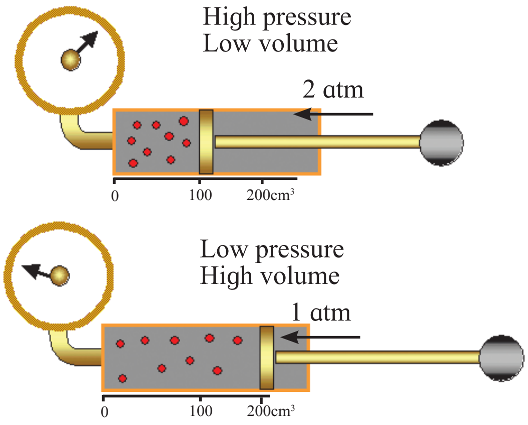
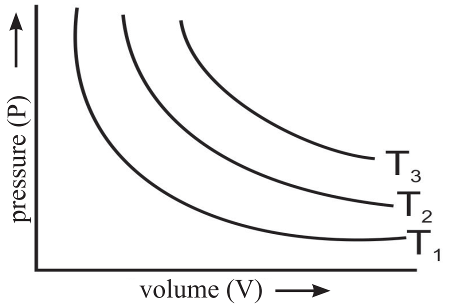


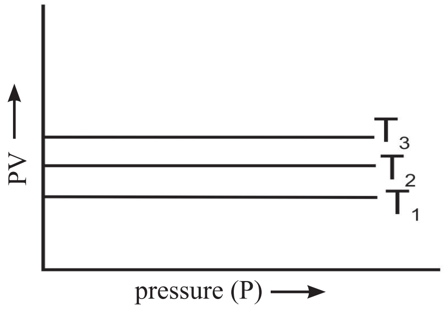
Fig. 10.7 : Schematic of the experiment Boyle's law

Figure 10.7 illustrates the Boyle's law experiment when the applied pressure increases from 1 atm to 2 atm and volume of the gas decreases from 200 cm^3 to 100 cm^3.

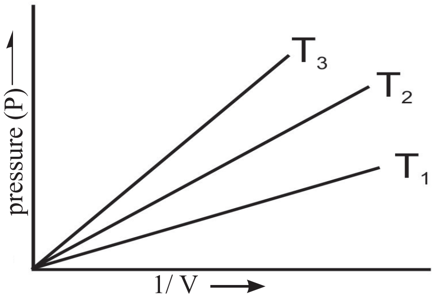
Graphical Representation : Figure 10.8 shows how the pressure-volume relationship can be expressed graphically. Figure 10.8 (a) shows a graph of the equation $PV = k$ at a given constant temperature, known as Isotherm (constant temperature plot). For a given mass of a gas, the value of k varies only with temperature.



a. Graph of pressure, P, vs volume, V, of a gas at different temperatures T_1, T_2, T_3.



b. Graph of PV vs pressure, P, of a gas at different temperatures T_1, T_2, T_3.



c. Graph of pressure, P, of a gas vs 1/V at different temperatures T_1, T_2, T_3.

Fig. 10.8 : Boyle's law : Graphical representation

If the product of pressure and volume (PV) is plotted against pressure (P), a straight line is obtained paralled to x-axis (pressure axis) as in Fig 10.8 (b).

When the pressure (P) of the gas is plotted against ($1/V$), a straight line is obtained passing through the origin as shown in Fig. 10.8 (c), provided T and n are constant.

However, at high pressure, deviation from Boyle's law is observed in the behavior of gases.

Boyle's law in terms of density of gas : With increase in pressure, gas molecules get closer and the density (d) of the gas increases. Hence, at constant temperature, pressure is directly proportional to the density of a fixed mass of gas. Therefore, from Eq. (10.2).

$$PV = k_1 \qquad \text{..........(10.2)}$$

$$\therefore \quad V = \frac{k_1}{P} \qquad \text{..........(10.4)}$$

But $d = \dfrac{m}{V}$

On Substituting V from Eq. (10.4),

$$d = \left(\frac{m}{k_1}\right) \times P$$

$$\therefore\ d = k'P, \qquad \text{.......... (10.5)}$$

where k' = New Constant.

$$\therefore\ \boldsymbol{d \propto P}$$

Above equation shows that at constant temperature, the pressure is directly proportional to the density of a fixed mass of the gas.

Internet my friend

- Watch Boyle's law experiment. www.socratica.youtube
- Find applications of Boyle's law.
- Try to study how Boyle's law helps in 'scuba-diving' i.e. Importance of Boyle's law in scuba-diving an exhilarating sport.

Problem: 10.1 : The volume occupied by a given mass of a gas at 298 K is 25 mL at 1 atmosphere pressure. Calculate the volume of the gas if pressure is increased to 1.25 atmosphere at constant temperature.

Given : $P_1 = 1$ atm, $V_1 = 25$ mL

$P_2 = 1.25$ atm, $V_2 = ?$

Solution :

According to Boyle's law,

$$P_1V_1 = P_2V_2$$

Substituting the values of P_1V_1 and P_2 in the above expression we get

$$V_2 = \frac{P_1V_1}{P_2} = \frac{1 \times 25}{1.25} = 20 \text{ ml}$$

Volume occupied by the gas is 20 mL

10.4.2 Charles' law : (Temperature -Volume Relationship)

Just think

1. Why does bicycle tyre burst during summer?
2. Why do the hot air balloons fly high?

J. Charles (1746-1823) and Gay Lussac (1778-1850) worked independently on influence of temperature on volume of a gas. Their experiments showed that for a given mass of a gas at constant pressure its volume increases with an increase in temperature. It was found that for an increase of every degree of temperature, volume of the gas increases by $\frac{1}{273.15}$ of its original volume at 0 ⁰C. This observation is expressed mathematically as follows :

$$V_t = V_0 + \frac{t}{273.15} V_0 \qquad \text{........ (10.6)}$$

Where V_t and V_0 are the volumes of the given mass of gas at the temperatures t ⁰C and 0 ⁰C.

Rearranging the Eq. (10.6) gives

$$V_t = V_0 \left(1+\frac{t}{273.15}\right)$$

$$\therefore V_t = V_0 \left(\frac{t + 273.15}{273.15}\right) \qquad \text{........ (10.7)}$$

At this stage, a new scale of temperature was introduced, namely, the **absolute temperature scale**. This absolute temperature (T K) was defined as

T K = t ⁰C + 273.15

This also called **thermodynamic scale of temperature**. The units of this absolute temperature scale is called (K) in the honour of **Lord Kelvin** who determined the accurate value of absolute zero as -273.15 ⁰C in 1854. The Eq. (10.7) is now rewritten by replacing the celcius temperatures by absolute temperaturs as follows :

$$V_t = V_0 \left(\frac{T_t}{T_0}\right) \qquad \text{........ (10.8)}$$

where $T_t = t + 273.15$ and $T_0 = 273.15$

The Eq. (10.8) on rearrangement takes the following form :

$$\frac{V_t}{T_t} = \frac{V_0}{T_0}$$

From this, a general equation can be written as follows :

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \text{........ (10.9)}$$

$$\therefore \frac{V}{T} = \text{constant} = k_2$$

$$\therefore V = k_2T \qquad \text{........ (10.10)}$$

The Eq. (10.10) is the mathematical expression of Charles law, which is stated as follows :

'At constant pressure, the volume of a fixed mass of a gas is directly proportional to its temperature in kelvin.'

The law can be illustrated diagramatically as shown in Fig. 10.9.

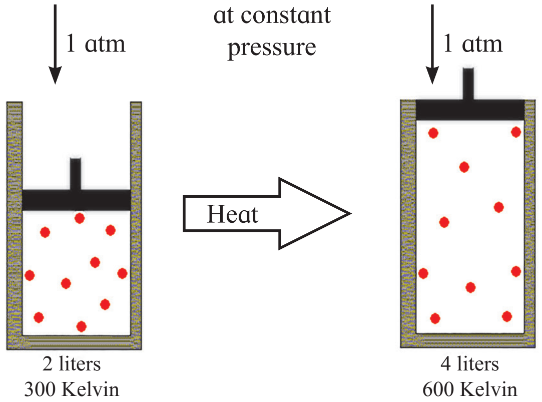


Fig. 10.9 : At constant pressure, volume changes with temperature

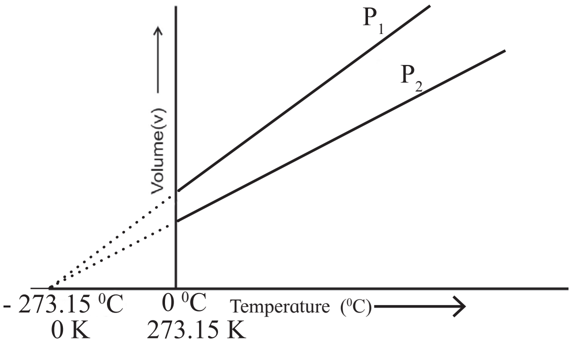


Fig. 10.10 : Graph of volume against temperature

Absolute zero temperature and Charles law

According to Charles law, Eq. (10.10), the graph of volume of a gas (at given constant pressure, say P_1) plotted versus its temperature in celsius, is a straight line with a positive slope. (See Fig. 10.10). On extending the line to zero volume, the line intercepts the temperature axis at -273.15 ^{0}C. At any other value of pressure, say P_2, a different straight line for the volume temperature plot is obtained, but we get the same zero - volume temperature intercept at - 273.15 ^{0}C. The straight line of the volume versus temperature graph at constant pressure is called **isobar**. Zero volume for a gas sample is a hypothetical state. In practice all the gases get liquified at a temperature higher than - 273.15 ^{0}C. This temperature is the lowest temperature that can be imagined but practically cannot be attained. It is the **absolute zero** temperature on the kelvin scale (0 K).

Isobars: A graph of volume (V) vs absolute temperature (T) at a constant pressure is known as Isobar.

Remember

On the kelvin scale, water freezes at at nearly 273 K and boils at about 373 K. (Note that we write kelvin temperatures in K without a ^{0}(degree) sign)

In short, Charles' law explains that at constant pressure, gases expand on heating and contract on cooling. Thus hot air is less dense than cold air.

10.4.3 Gay-Lussac's Law: (Pressure-Temperature Relationship) :

Just think

1. List out various real life examples of Charles law.
2. Refer and watch Charles law experiments.

Problem 10.2 : At 300 K a certain mass of a gas ocupies 1 × 10^{-4} dm^3 volume. Calculate its volume at 450 K and at the same pressure.

Given : T_1 = 300 K,

$V_1 = 1 \times 10^{-4}$ dm^3, T_2 = 450 K,

V_2 = ?

Solution : According to Charles' law, at constant pressure.

$$\frac{V_1}{T_1}=\frac{V_2}{T_2} \qquad \therefore V_2=\frac{V_1\times T_2}{T_1}$$

$$=\frac{450\times1\times10^{-4}}{300}$$

$\therefore$ $V_2 = 1.5 \times 10^{-4}$ dm^3

It relates the pressure and absolute temperature of a fixed mass of a gas at constant volume.

Statement: *At constant volume, pressure (P) of a fixed amount of a gas is directly proportional to its absolute temperature (T).*

Mathematical Expression:

Mathematically, the law can be expressed as :

$P \propto T$

$\therefore P = k_3 T$ ....(10.11)

$$\therefore \frac{P}{T} = \text{constant} \quad (\text{at constant } V \text{ and } m)$$

Graphical Representation : When a graph is plotted between pressure (P) in atm and Temperature (T) in kelvin, a straight line is obtained as shown in Fig. 10.11. It is known as **isochore**. With the help of this law, one can unterstand relation between pressure and temperature in day to day life.

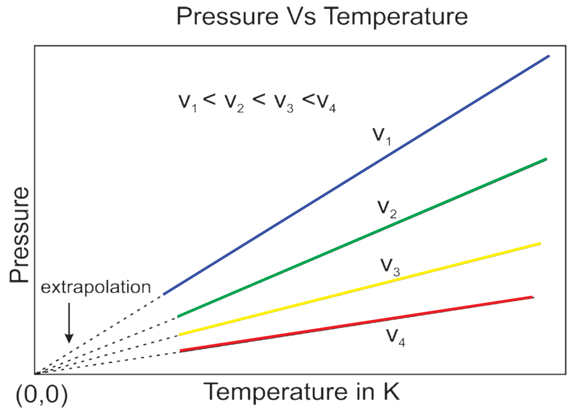


Fig. 10.11 : Pressure Vs Temperature graph of a gas

10.4.4 Avogadro Law: (Volume-Amount Relationship) :

Use your brain power

Why the pressure in the automobile tyres changes during hot summer or winter season?

In 1811 Italian scientist Amedeo Avogadro combined Dalton's atomic theory with Gay Lussac's Law of combining volumes (Chapter 1) to put forth what is known as **Avogadro law**. It states that **equal volumes of all gases at the same temperature and pressure contain equal number of molecules**. This means that at a fixed temperature and pressure, the volume of a gas depends upon the number of molecules of the gas, that is, the amount of the gas.

Avogadro law can be expressed mathematically as : $V \propto n$ (where 'n' is the number of moles of the gas in volume 'V')

On converting the proportionality into equation we get

$$V = k_4 n \qquad \text{........ (10.12)}$$

$$\text{or } \frac{V}{n} = \text{constant (at constant temperature and pressure)}$$

Avogadro Law can be well represented from Fig. 10.12 as follows :

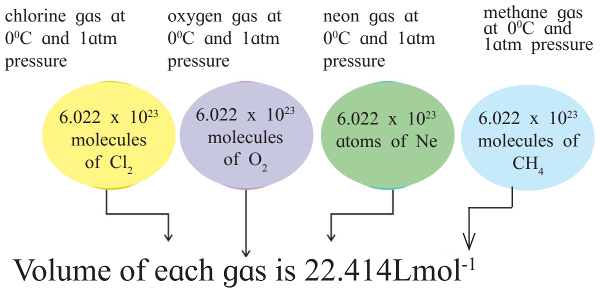


Fig. 10.12 : Avogadro Law

Can you recall?

1 mole of a gas contains Avogadro number of molecules = 6.022×10^{23}.

As the volume of a gas is directly proportional to number of moles, one mole of any gas at STP occupies 22.414 L mol^{-1} volume. This volume is known as **molar volume**.

Remember

What are STP conditions?

STP means Standard Temperature and Pressure.

IUPAC has set STP as

standard Pressure = **1 bar** = **10^5 Pa**

standard temperature = **273.15 K** = **0^0C**

Under these STP conditions molar volume of an ideal gas or mixture of two or more gases = **22.71 L mol^{-1}**

The old STP conditions are also in use, where

standard pressure = **1 atm** = **1.013 bar**

standard temperature = **273.15 K** = **0^0C**

Under the old STP conditions molar volume of an ideal gas or mixture of two or more gases = **22.414 L mol^{-1}**

Relation between molar mass and density (d) of a gas : We have learnt how to find number of moles of a gas. (Refer to Chapter 1.)

We know,

$$n = \frac{m}{M} ,$$

where m = mass of a gas,

M = molar mass of a gas.

Substituting in equation (10.12) we get,

$$V = k_4 \text{ x } \frac{m}{M}$$

$$\therefore M = k_4 \frac{m}{V} \qquad \text{..... (10.13)}$$

But $\frac{m}{V} = d$

substituting this in Eq. (10.13) we get

$$\boldsymbol{M = k_4 d} \qquad \text{...... (10.14)}$$

Where d = density of a gas.

M = Molar mass

m = mass of gas

$\therefore d \alpha M$

From Eq. (10.14), we can conclude that the density of a gas is directly proportional to its molar volume.

10.5 Ideal Gas Equation : A gas that follows strictly all the three laws; Boyle's law, Charles' law and Avogadro law is an **ideal gas**. Practically an ideal gas does not exist. Real gases show ideal behaviour under certain specific condition, when intermolecular interactions are practically absent. Yet these three gas laws and the ideal gas equation obtained by treating them mathematically are found to be very valuable in Chemistry.

10.5.1 Derivation of Ideal Gas Equation :

The three gas laws, namely, Boyle's law, Charles law and Avogadro law, are combined mathematically to obtained what is called ideal gas equation.

Let us write the propotionalities of the three gas laws :

1. At constant T and n, $V \alpha \frac{1}{P}$ (Boyle's law)
2. At constant P and n, $V \alpha T$ (Charles' law)
3. At constant P and T, $V \alpha n$ (Avogadro law)

Combining all the above three mathematical propornalities we get,

$$V \alpha \frac{nT}{P}$$

Converting this proportionality into an equation by introducing a constant of proportionality we get,

$$\therefore V = R\left(\frac{nT}{P}\right)$$

On rearraninging above equation, we obtain,

$$\therefore \boldsymbol{PV = nRT} \qquad \text{............. (10.15)}$$

This equation is known as the **Ideal Gas Equation**. In the ideal gas equation, if three variables are known, fourth can be calculated. It describes the state of an ideal gas, therefore, it is also called as equation of state. Here **R** is called **Gas constant**, The value of R is the same for all the gases. Therefore it is called Universal gas constant.

10.5.2 Values of 'R' in different Units :

The value of R depends upon the units used to express P, V and T. Hence we recall STP conditions for determining values of 'R'.

i. R in SI Unit (in Joules) : Value of R can be calculated by using the SI units of P,V and T. Pressure P is measured in N m^{-2} or Pa, volume V in meter cube (m^3) and Temperature T in kelvin (K),

$$R = \frac{PV}{nT}$$

$$\therefore R = \frac{10^5\text{Pa x } 22.71 \text{ x } 10^{-3}\text{ m}^3}{1 \text{ mol x } 273.15 \text{ K}}$$

$$\therefore R = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{mol}^{-1}$$

then $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

ii. R in litre atmosphere : If pressure (P) is expressed in atmosphere (atm) and volume in litre (L) or decimeter cube (dm^3) and Temperature in kelvin (K), (that is, **old STP conditions**), then value of R is :

$$R = \frac{1\text{atm x } 22.414 \text{ L}}{1 \text{ mol x } 273.15 \text{ K}}$$

$$\therefore R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

OR

$$R = 0.08206 \text{ dm}^3 \text{ atm K}^{-1}\text{mol}^{-1}$$

Note : Often Pressure (P) is measured in atmosphere (atm). The conversion between the units is done by noting that 1 atm = 1.013×10^5 Nm^{-2} or 1 atm = 101.3 kPa

Table 10.4 Unit of R

Pressere (P)	Volume (V)	Number of moles (n)	Temperture (T)	Gas consant (R)
Pa (pascals)	m^3	mol	K	8.314 J K^{-1} mol^{-1}
atm	dm^3	mol	K	0.0821 atm dm^3 K^{-1} mol^{-1}
atm	L	mol	K	0.0821 L atm K^{-1} mol^{-1}

iii. R in calories:

We know, 1 calorie = 4.184 Joules

$$\therefore R = \frac{8.314}{4.184} = 1.987 \cong 2 \text{ cal } K^{-1} \text{ mol}^{-1}$$

While using ideal gas equation one should use consistent units. The most common units are shown in Table 10.4.

10.5.3 Expression for Molar mass :

Ideal gas equation can be used to determine the Molar mass (M) of a compound. Rearranging the equation (10.15)

$$n = \frac{PV}{RT} \quad \text{.............} \quad (10.16)$$

But for a known mass of a gas 'm', the number of moles,

$$n = \frac{m}{M}$$

On substituting this in equation (10.16) we get

$$\frac{m}{M} = \frac{PV}{RT}$$

$$\therefore M = \frac{mRT}{PV} \quad \text{.......} \quad (10.17)$$

10.5.4 Combined Gas law :

The ideal gas equation is written as

$$PV = nRT \quad \text{......} \quad (10.15)$$

On rearranging Eq. (10.15) we get

$$\therefore \frac{PV}{T} = nR = \text{constant}$$

$$\therefore \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{......} \quad (10.18)$$

The ideal gas equation used in this form is called **combined gas law**. We have to assume a gas under two different sets of conditions where pressure, volume and temperatures are written for one state as P_1, V_1, T_1 and the other state as P_2, V_2, T_2, respectively.

Problem 10.3 : A sample of N_2 gas was placed in a flexible 9.0 L container at 300K at a pressure of 1.5 atm. The gas was compressed to a volume of 3.0L and heat was added until the temperature reached 600K. What is the new pressure inside the container?

Given Data : V_1 = 9 L V_2 = 3L

P_1 = 1.5 atm T_2 = 600K

T_1 = 300 k P_2 = ?

Solution : According to combined gas law equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \therefore \frac{1.5 \times 9}{300} = \frac{P_2 \times 3}{600}$$

$\therefore$ P_2 = 9 atm

Problem 10.4 : Find the temperature in ^0C at which volume and pressure of 1 mol of nitrogen gas becomes 10 dm^3 and 2.46 atmosphere respectively.

Given : P = 2.46 atm, V = 10 dm^3, n = 1mol, R = 0.0821 dm^3-atm$k^{-1}$$mol^{-1}$ T = ?

Solution : Ideal gas equation is

$$PV = nRT$$

$$\therefore T = \frac{PV}{nR} = \frac{2.46 \times 10}{1 \times 0.0821}$$

T = 299.63K

Temp. in ^0C = 299.63 - 273.15

= 26.48 ^0C

10.5.4 Relation between density, molar mass and pressure :

Ideal gas equation can be expressed in terms of density as follows :

$$PV = nRT \quad \text{.......} \quad (10.5)$$

On rearranging it gives

$$\frac{n}{V} = \frac{P}{RT}$$

But we know $n = \frac{m}{M}$

On substituting value of 'n', rearranged equation becomes-

$$\therefore \frac{m}{MV} = \frac{P}{\mathrm{R}T} \qquad \text{(at constant temperature)}$$

$$\therefore \frac{d}{M} = \frac{P}{\mathrm{R}T} \qquad \text{....... (10.19)}$$

where $\frac{m}{V} = d =$ density of a gas

On rearranging equation (10.19) we get expression to calculate molar mass of a gas in terms of its density.

$$M = \frac{dRT}{P} \qquad \text{.......(10.20)}$$

From equation (10.19) ***Boyle's law*** *can be stated in terms of density as : at constant temperature, pressure of a given mass of gas is directly proportional to its density.*

10.5.6 Dalton's law of Partial Pressure :

John Dalton not only put forth the atomic theory, but also made several contributions to understanding of the behaviour of gases. He formulated the law of partial pressure in 1801. This law is applicable for those gases which do not react chemically on mixing. The pressure exerted by an individual gas in a mixture of two or more gases is called **partial pressure**. It is also the pressure that each gas would exert if it were present alone. Daltons law of partial pressure is stated as :

The total pressure of a mixture of two or more non reactive gases is the sum of the partial pressures of the individual gases in the mixture.

Mathematically, Dalton's law may be expressed as,

$$P_{Total} = P_1 + P_2 + P_3 + \text{.... (at constant } V \text{ and } T\text{)}$$

Where P_{Total} is the total pressure of the mixture and P_1, P_2, P_3, ... are the partial pressures of the individual gases 1, 2, 3, ... in the mixture.

Partial pressure and mol fraction : We know that the pressure of a pure gas is given by the ideal gas equation

$$P = \frac{n\mathrm{R}T}{\mathrm{V}} \qquad \text{.... (10.21)} \quad (V \text{ and } T \text{ are constant})$$

$$\therefore P \propto \mathrm{n}.$$

Consequently, the pressure of an individual gas in a mixture of gases is proportional to its amount in that mixture. This implies that the total pressure (P_T) of a mixture of gases at constant volume (V) and Temperature (T) is equal to the sum of the pressure that individual gas exerts in the mixture. This is Dalton's law of partial pressures. It is shown in Fig. 10.13.

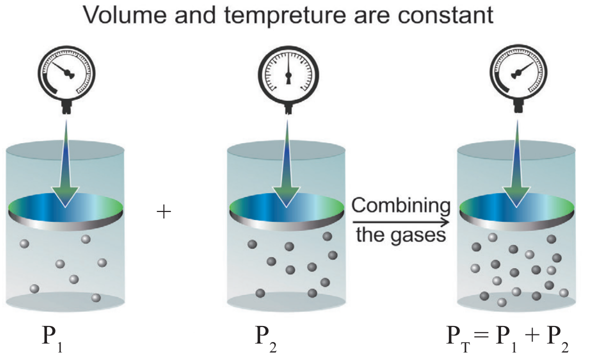


Fig. 10.13 : Schematic illustration of Dalton's law of partial pressures

Just think

Do all pure gases obey all the gas laws? Do the mixtures of gases obey the gas laws ? Yes, the gas laws are also applicable to the mixtures of gases. As we have learnt in section 10.5.3 that the measurable properties of mixture of the gases such as pressure, temperature, volume and amount of gaseous mixture are all related by an ideal gas law.

The partial pressures of individual gases can be written in terms of ideal gas equation as follows :

$$P_1 = n_1\left(\frac{\mathrm{R}T}{V}\right), \quad P_2 = n_2\left(\frac{\mathrm{R}T}{V}\right),$$

$$P_3 = n_3\left(\frac{\mathrm{R}T}{V}\right), \text{ ... and so on .... (10.21)}$$

$$\therefore P_{Total} = n_1\left(\frac{\mathrm{R}T}{V}\right) + n_2\left(\frac{\mathrm{R}T}{V}\right) + n_3\left(\frac{\mathrm{R}T}{V}\right) \text{......}$$

$$= \left(\frac{RT}{V}\right)(n_1 + n_2 + n_3 ...) = \frac{RT}{V} n_{Total} \qquad .... (10.22)$$

Mole fraction of any individual gas in the mixture is given by the equation

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3 ...} = \frac{n_1}{n_{Total}} \qquad .. (10.23)$$

From Eq. (10.21) and Eq. (10.23) we get

$$n_1 = P_1 \Big/ \left(\frac{RT}{V}\right) \qquad .... (10.24)$$

and

$$n_{Total} = P_{Total} \Big/ \left(\frac{RT}{V}\right) \qquad .... (10.25)$$

By combining equation Eq. (10.24) and Eq. (10.25) we get

$$\frac{n_1}{n_{Total}} = X_1 = \frac{P_1 \Big/ \left(\frac{RT}{V}\right)}{P_{Total} \Big/ \left(\frac{RT}{V}\right)} = \frac{P_1}{P_{Total}} \qquad .... (10.26)$$

Therefore it follows that

$$P_1 = X_1.P_{Total} \qquad ...... (10.27)$$

Similarly,

$P_2 = X_2.P_{Total}, P_3 = X_3.P_{Total}$ and so on.

Thus partial pressure of a gas is obtained by multiplying the total pressure of mixture by mole fraction of that gas.

Just think

Where is the Dalton's law applicable? The most important gas mixture is of course the air around us. Dalton law is useful for the study of various phenomena in air including air pollution.

Problem 10.5 : A mixture of 28g N_2, 8 g He and 40 g Ne has 20 bar pressure. What is the partial pressure of each of these gases ?

Solution : Partial pressure mole fraction x total pressure

Step 1 : Determine the number of moles (n) of each gas from its mass (m) and molar mass (M), using the formula

$$n = \frac{m}{M}$$

$$n_{N_2} = \frac{28\ g}{28\ g\ mol^{-1}} = 1\ mol$$

$$n_{He} = \frac{8\ g}{4\ gmol^{-1}} = 2\ mol$$

$$n_{Ne} = \frac{40g}{28\ g\ mol^{-1}} = 2\ mol$$

Step 2 : Determine the mole fraction of each gas using the formula

$$X_{N_2} = \frac{n}{n_{Total}}$$

$$X_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{He} + n_{Ne}} = \frac{1\ mol}{(1 + 2 + 2)\ mol} = \frac{1}{5}$$

$$X_{He} = \frac{n_{He}}{n_{Total}} = \frac{2\ mol}{5\ mol} = \frac{2}{5}$$

Similarly $X_{Ne} = \frac{2}{5}$

Step 3 : Calculate the partial pressure

$$P_{N_2} = X \times P_{Total} = \frac{1}{5} \times 20\ bar = 4\ bar$$

$$P_{He} = X_{He} \times P_{Total} = \frac{2}{5} \times 20\ bar = 8\ bar$$

$$P_{Ne} = X_{Ne} \times P_{Total} = \frac{2}{5} \times 20\ bar = 8\ bar$$

Aqueous Tension :A vapor is a gas in contact with a liquid of the same substance. For example, the 'gas' above the surface of liquid water is described as water vapour. The pressure of the water vapour is known as its **vapour pressure**.

Suppose the liquid water is placed into a container and air above is pumped away and the container is sealed. Then the liquid water evaporates and only water vapour remains in the above space. After sealing, the vapour pressure increases initially, then slows down as some water molecules condense back to form liquid water. After a few minutes, the vapour pressure reaches a maximum called the **saturated vapour pressure**. (We will learn more about in section 10.9.2) The pressure exerted by saturated water vapour is called **Aqueous Tension (P_{aq}).**

When a gas is collected over water in a closed container, it gets mixed with the saturated water vapour in that space. The measured pressure, therefore, corresponds to the pressure of the mixture of that gas and the saturated water vapour in that space.

Pressure of pure and dry gas can be calculated by using the aqueous tension. It is obtained by subtracting the aqueous tention from total pressure of moist gas.

$$\therefore P_{Dry\ gas} = P_{Total} - P_{aq}$$

i.e. $P_{Dry\ gas} = P_{Total}$ - Aqueous Tension

Table 10.5 : Aqueous Tension of Water (Vapour Pressure) as a function of Temperature

Temp. (K)	Pressure (bar)	Temp. (K)	Pressure (bar)
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

The above table reflects that Aqueous Tension increases with increase in temperature.

10.6 Kinetic Molecular Theory of Gases :

The kinetic molecular theory of gases is a theoretical model put forth to explain the behavior of gases.

Assumptions of kinetic molecular theory of gases :

1. Gases consist of tiny particles (molecules or atoms).
2. On an average, gas molecules remain far apart from each other. Therefore the actual volume of the gas particles is negligible as compared to the volume of the container. (That is why the gases are highly compressible).
3. The attractive forces between the gas molecules are negligible at ordinary temperature and pressure. (As a result gas expands to occupy entire volume of the container).
4. Gas molecules are in constant random motion and move in all possible directions in straight lines. They collide with each other and with the walls of the container.
5. Pressure of the gas is due to the collision of gas particles with the walls of container.
6. The collisions of the gas molecules are perfectly elastic in nature, which means that the total energy of the gaseous particle remains unchanged after collision.
7. The different molecules of a gas move with different velocities at any instant and hence have different kinetic energies. But average kinetic energy of the gas molecules is directly proportional to the absolute temperature.

   Average K.E. $\propto$ T

10.7 Deviation from Ideal behaviour :

An **ideal gas** is the one that exactly follows the ideal gas equation. On rearranging the ideal gas equation, n = PV/RT. If we use 1 mole of any gas then the ratio PV/RT is predicted to have numerical value of 1 at all pressures. If a gas does not obey the ideal gas law, the ratio will be either greater than 1 or less than 1, such a gas is said to be a **Real Gas**.

A. Ideal Gas:

1. A gas that obeys all the gas laws over the entire range of temperature and pressure.
2. There are no ineractive forces between the molecules.
3. The molecular volume is negligibly small compared to the volume occupied by the gas. These are point particles.

B. Real Gas :

1. Real gas does not obey Boyle's law and Charles' law under all the conditions of temperature and pressure.

A deviation from the ideal behaviour is observed a **high pressure and low temperature** It is due to two reasons.

(1) The intermolecular attractive forces are not negligible in real gases. These do not allow the molecules to collide the container wall with full impact. This results in decrease in the pressure.

(2) At high pressure, the molecular are very close to each other. The short range repulsive forces start operating and the molecules behave as small but hard spherical particles.

The volume of the molecule is not negligible. Therefore,x less volume is available for molecular motion.

At very low temperature, the molecular motion becomes slow and the molecules are attracted to each other due to the attractive force. Hence, here again the behaviour of the real gas deviates from the ideal gas behaviour.

Deviation with respect to pressure can be studied by plotting pressure (P) vs volume (V) curve at a given temperature. (See Fig. 10.14 and Table 10.6).

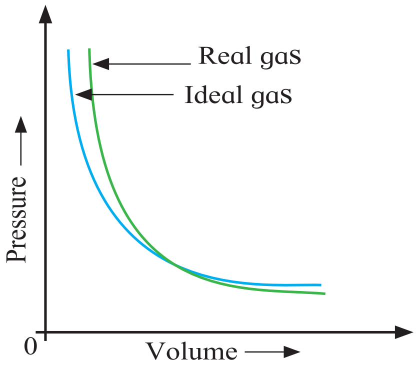


Fig. 10.14 : Plot of pressure Vs volume for real and ideal Gas

At very high pressure, the measured volume is more than theoretically calculated volume assuming ideal behaviour. But at low pressure, measured and calculated volumes approach each other.

Compressibility Factor (Z) : Real Gases show ideal behavior when pressure approaches zero. Deviation from ideal behaviour can be measured in terms of compressibility factor Z which is the ratio of product PV and nRT.

$$Z = \frac{PV}{nRT}$$

Figure 10.15 shows the graph of Z vs P. It is a straight line parallel to x - axis (pressure axis) where $Z = 1$.

For ideal gas $Z = 1$ at all the value of temperature and pressure. The significance of Z is better understood from the following derivation. we can write two equation (10.28) and (10.29) for real and ideal gas respectively.

$$Z = \frac{PV_{real}}{nRT} \qquad \text{......... (10.28)}$$

$$\text{and} \quad 1 = \frac{PV_{ideal}}{nRT} \qquad \text{......... (10.29)}$$

$$\therefore \quad \frac{P}{nRT} = \frac{I}{V_{ideal}}$$

Substituing the value of $\frac{P}{nRT}$ in Eq. (10.28), we get

$$Z = \frac{V_{real}}{V_{ideal}} \qquad \text{......... (10.30)}$$

Table 10.6 : Difference between Ideal Gas and Real Gas

Ideal gas	Real Gas
1. Strictly obeys Boyle's and Charles' law. $\frac{PV}{nRT} = 1$	1. Shows deviation from Boyle's and Charles' law at high pressure and temperature. i.e. obeys Boyle's law and Charles' law at low pressure and high temperature. $\frac{PV}{nRT} \neq 1$
2. Molecules are perfectly elastic.	2. Molecules are not perfectly elastic.
3. No attraction or repulsion between the gas molecules i.e. collision without loss of kinetic energy (K.E.)	3. Intermoleculer attraction is present, hence collision takes place with loss of kinetic energy.
4. Actual volume of the gas molecules is negligible as compared to total volume of the gas.	4. Actual volume of individual gas molecule is significant at high pressure and low temperature.
5. Can not liquify even at low temperature but continues to obey Charles' law and finally occupies zero volume at -273^{0}C.	5. Undergo liquefaction at low temperature when cooled and compressed.
6. Such a gas does not exist.	6. Gases that exist in nature like H_2, O_2, CO_2 N_2, He, etc.

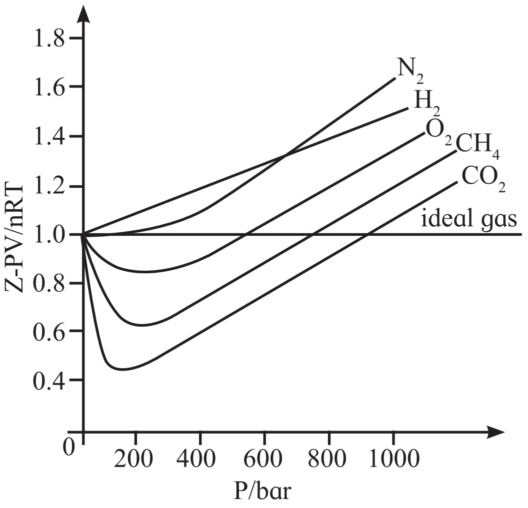


Fig. 10.15 : Graph of compressibility factor Z versus pressure for some gases

The Eq.(10.30) implies that the compressibility factor is the ratio of actual molar volume of a gas to its molar volume if it behaved ideally, at that temperature and pressure.

A positive deviation in Z, (Z > 1), means that the volume of a molecule cannot be neglected and the gas is difficult to compress. **At lower pressure**, the gases have Z = 1 or Z < 1. Under this conditon the molecular volume is negligible and the gases are compressible. Here, the gases show ideal behaviour.

10.7 Liquefaction of gases and critical constant : Most gases behave like ideal gases at high temperature. For example, the PV curve of CO_2 gas at 50^{0}C is like the ideal Boyle's law curve. As the temperature is lowered the PV curve shows a deviation from the ideal Boyle's law curve. At a particular value of low temperature the gas gets liquified at certain increased value of pressure. For example, CO_2 gas liquifies at 30.98 ^{0}C and 73 atmosphere pressure (See Fig. 10.16).

This is the highest temperature at which liquid CO_2 can exist. Above this temperature, howsoever large the pressure may be, liquid CO_2 cannot form. Other gases also show similar behaviour.

The temperature above which a substance cannot be liquified by increasing pressure is called its critical temperature (T_c).

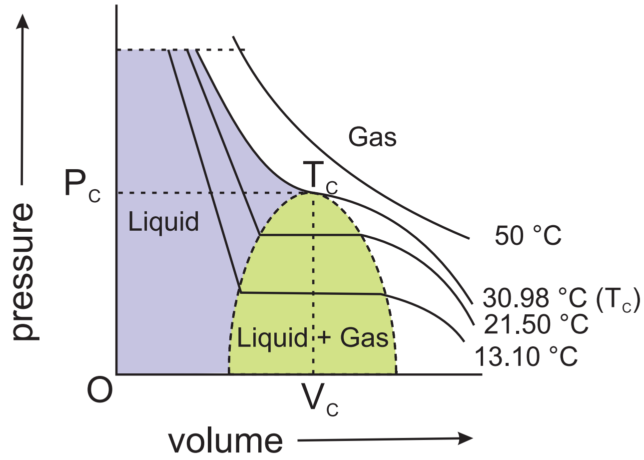


Fig. 10.16 : Liquefaction of CO_2 : Isotherms at various temperature

Above the critical temperature a substance exists only as gas. **The molar volume at critical temperature is called the critical volume (V_c)**. and **the pressure at the critical temperature is calles the critical pressure (P_c)** of that substance. The Table 10.7 gives the values of these three critical constants for some common gases.

Table 10.7 : Critical constants for common Gases

Substance	Tc / K	Pc/ bar	Vc/dm^{3}mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.0	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

From the Table 10.7 it is seen that the gases that we come across in everyday life, namely, N_2 and O_2 , have T_c values much below 0 ^{0}C and their P_c values are high. Consequently, liquefaction of O_2 and N_2 (and air) requires compression and cooling.

The T_c value of CO_2 nearly equals the room temperature, however, its P_c value is very high. Therefore CO_2 exists as gas under ordinary condition.

Problem 10.5 : Water has T_c = 647.1 K and P_c = 220.6 bar. What do these values imply about the state of water under ordinary conditions?

Solution : The T_c and P_c values of water are very high compared to the room temperature and common atmosheric pressure. Consequently water exists in liquid state under ordinary condition of temperature and pressure.

Study of PV curves of various gases at different temperatures reveals that under certain conditions the substance changes completely from gaseous to liquid state or liquid to gaseous state, without having the coexistence of two states. In other words, there is a continuity between the gaseous and liquid state. This continuity is recognized by using the term **Fluid** for either gas or liquid. Under these conditions liquid is just a very dense gas. Liquid and gas can be distingushed from each other only when the fluid is at a temperature below T_c.

Remember

When a liquid, which is exposed to atmosphere, is heated, its vapour pressure increases. Eventually it becomes equal to the atmospheric pressure. At this temperature the vaporisation takes place throughout the bulk of the liquid, and the vapour formed escapes freely, into the surroundings. We call this **boiling point** of the liquid. The boiling temperature (boiling point) depends upon the pressure to which the surface of the liquid is exposed. If the pressure is **1 atm**, the boiling temperature is called **normal boiling point**. If the pressure is **1 bar**, the boiling temperature is called **stadard boiling point**.

For water: normal b.p. = 100 ^{0}C, standard b.p. = 99.6 ^{0}C

Problem 10.6

CO_2 has T_c = 38.98^{0}C and P_c = 73 atm. How many phases of CO_2 coexist at (i) 50 ^{0}C and 73 atm, (ii) 20 ^{0}C and 50 atm.

Solution:

(i) 50 ^{0}C and 73 atm represent a condition for CO_2 above its T_c. Therefore, under this condition CO_2 exists only as single phase.

(ii) 20^0 C and 50 atm represent a condition for CO_2 below its T_c. Therefore, under this condition two phases of CO_2, namely, liquid and gas can coexist

Problem 10.7 : In which of the following cases water will have the highest and the lowest boiling point ?

Water is boiled

a. in an open vessel,

b. in a pressure cooker,

c. in a evacuated vessel.

Solution : Higher the pressure to which a liquid is exposed, higher will be its boiling point. The pressure to which water is exposed is maximum in the pressure cooker and minimum in the evacuated vessel. Therefore b.p. of water is highest in (b) and lowest in (c).

Internet my friend

1. https://chem.libretexts.org>bookshelves. Gas laws : overview
2. Collect information about State of Mater

10.8 Liquid state : Liquid state is the intermediate state between solid state and gaseous state. Molecules of liquid are held together by moderately strong intermolecular forces and can move about within the boundary of the liquid. As a result, liquid posseses properties such as fluidity, definite volume and ability to take shape of the bottom of the container in which it is placed. Different liquids are characterized by their quantitative properties such as density, boiling point, freezing point, vapour pressure, surface tension and viscosity. We will look at some of these propeties in the following sections.

10.8.1 : Vapour Pressure : Molecules of liquid have a tendency to escape from its surface to form vapour about it. This called evaporation. When a liquid is placed in a closed container.It undergoes evaporation and vapours formed undergo condensation. At equilibrium, the rate of evaporation and rate of condensation are equal. The pressure exerted by the vapour in equilibrium with the liquid is known as **saturated vapour pressure** or simply **vapour pressure**.

The vapour pressure of water is also called **Aqueous Tension**. (Refer to Table 10.5) Schematically vapour pressure is explained in Fig. 10.17.

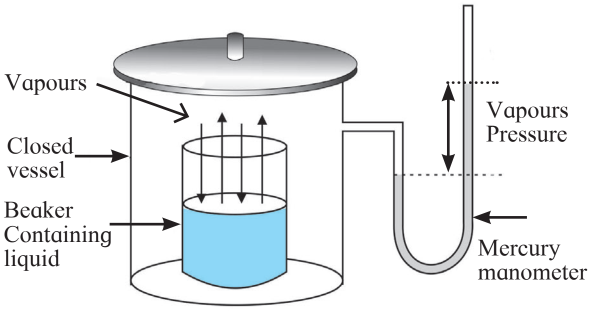


Fig. 10.17 : Vapour pressure of a liquid

Factors affecting vapour pressure :

a. Nature of liquid : Liquids having relatively weak intermolecular forces possess high vapour pressure. These are called valatile liquids. For example, petrol evaporates quickly than motor oil.

b. Temperature : When the liquid is gradually heated, its temperature rises and its vapour pressure increases.

Unit : Vapour pressure is measured by means of a manometer. The most common unit for vapour pressure is torr. 1 torr = 1 mm Hg. For example, water has a vapour pressure of apporximately 20 torr at room temperature. (Refer to section 10.5.6 and Table 10.5)

Just think

What makes the oil rise through the wick in an oil lamp ?

10.8.2 Surface Tension : Many phenomena such capillary rise of liquids, spherical shapes of liquid drops are due to the property of liquids called **surface tension**. Surface of a liquid acts as a stretched membrane. The particles in the bulk of liquid are uniformly attracted in all directions and the net force acting on the molecules present inside the bulk is zero. But the molecules at the surface experience a net attractive force towards the interior of the liquid, or the forces acting on the molecules on the surface are imbalanced (see Fig.10.18). Therefore, liquids have a tendency to minimize their surface area.

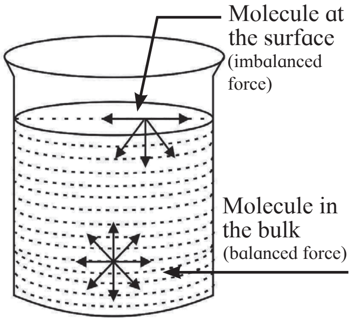


Fig. 10.18 : Imbalance of forces at the surface of a liquid

Surface tension is a temperature dependent property. When attractive forces are large, surface tension is large. Surface tension decreases as the temperature increases. With increase in temperature, kinetic energy of molecules increases. So intermolecular forces of attraction decrease, and thereby surface tension decreases.

The force acting per unit length perpendicular to the line drawn on the surface of liquid is called surface tension.

Unit : Surface tension is measured in SI Unit, Nm^{-1}, denoted by Greek letter "γ" (Gamma)

Application of surface tension :

i. Cleaning action of soap and detergent is due to the lowering of interfacial tension between water and oily substances. Due to lower surface tension, the soap solution penetrates into the fibre, surrounds the oily substance and washes it away.

ii. Efficacy of toothpastes, mouth washes and nasal drops is partly due to presence of substances having lower surface tension. This increases the efficiency of their penetrating action.

10.8.3 Viscosity : As noted earlier, liquids (fluids) have a tendency to flow. Viscosity measures the magnitude of internal friction in a liquid or fluid to flow as measured by the force per unit area resisting uniform flow, different layers of a liquid flow with different velocity. This called **laminar flow**. Here, the layers of molecules in the immediate contact of the fixed surface remains stationary. The subsequent layers slip over one another. Strong intermolecular forces obstruct the layers from slipping over one another, resulting in a friction between the layers.

Viscosity is the force of friction between the successive layers of a flowing liquid. It is also the resistance to the flow of a liquid.

When a liquid flows through a tube, the central layer has the highest velocity, whereas the layer along the inner wall in the tube remains stationary. This is a result of the viscosity of a liquid (see Fig. 10.19). Hence, a velocity gradient exists across the cross-section of the pipe/tube.

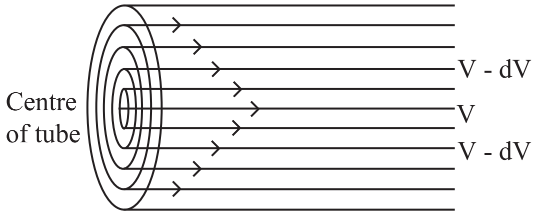


Fig. 10.19 : Laminar flow of a liquid (fluid) through a tube/pipe

Viscosity is a temperature dependent property.

$$\text{Viscosity} \propto \frac{1}{\text{Temperature}}$$

Viscosity also depends on molecular size and shape. Larger molecules have more viscosity and spherical molecules offer the least resistance to flow and therefore are less viscous. Greater the viscosity, slower is the liquid flow.

Unit : Viscosity is expressed in terms of **coefficient of viscosity, 'η' (Eta)**. It is defined as the degree to which a fluid resists flow under an applied force, measured by the tangential frictional force per unit area per unit velocity gradient when the flow is laminar.

SI unit of viscosity coefficient is **$N\ s\ m^{-2}$** (newton second per square meter). In CGS system the unit (η) is measured in poise.

$1 \text{ poise} = 1 \text{ gm cm}^{-1}\text{s}^{-1} = 10^{-1} \text{ kg m}^{-1}\text{s}^{-1}$

Illustration of viscosity :

i. Lubricating oils are viscous liquids. Gradation of lubricating oils is done on the basis of viscosity. A good quality Lubricating oil does not change its viscosity with increase or decrease in temeperature.

ii. Increase blood viscosity than the normal value is taken as an indication of cardio vascular disease.

iii. Glass panes of old buildings are found to become thicker with time near the bottom. This is one evidence which indicates that glass is not a solid but a supercooled viscous liquid.

Internet my friend

https://www.britannica.com/science/viscosity.

Exercises

1. Select and write the most appropriate alternatives from the given choices.

A. The unit of viscosity is

a. dynes b. newton

c. gram d. poise

B. Which of the following is true for 2 moles of an ideal gas ?

a. $PV = nRT$ b. $PV = RT$

c. $PV = 2RT$ d. $PV = T$

C. Intermolecular forces in liquid are -

a. greater than gases

b. less than solids

c. both a and b

d. greater than solids

D. Interactive forces are .... in ideal gas.

a. nil b. small

c. large d. same as that of real gases

E. At constant temperature the pressure of 22.4 dm^3 volume of an ideal gas was increased from 105 kPa to 210 kPa, New volume could be-

a. 44.8 dm^3 b. 11.2dm^3

c. 22.4 dm^3 d. 5.6dm^3

2. Answer in one sentence.

A. Name the term used for mixing of different gases by random molecular motion and ferquent collision.

B. The pressure that each individual gas would exert if it were alone in the container, what do we call it as ?

C. When a gas is heated the particles move more quickly. What is the change in volume of a heated gas if the pressure is kept constant ?

D. A bubble of methane gas rises from the bottom of the North sea. What will happen to the size of the bubble as it rises to the surface ?

E. Convert the following temperatures from degree celcius to kelvin.

a. -15° C b. 25° C

c. -197° C d. 273° C

F. Convert the following pressure values into Pascals.

a. 10 atmosphere c 107000 Nm^{-2}

b. 1 kPa. d. 1 atmosphere

G. Convert :

a. Exactly 1.5 atm to pascals

b. 89 kPa to newton per square metre (Nm^{-2})

c. 101.325 kPa to bar

d. -100° C to kelvin

e. 0.124 torr to standard atmosphere

H. If density of a gas is measured at constant temperature and pressure then which of the following statement is correct ?

a. Density is directly proportional to molar mass of the gas.

b. Greater the density greater is the molar mass of the gas.

c. If density, temperature and pressure is given ideal gas equation can be used to find molar mass.

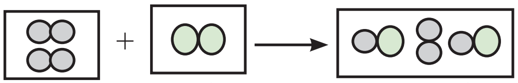
d. All the above statements are correct.

I. Observe the following conversions.

a.

$H_2 + Cl_2 \longrightarrow 2HCl$

b.



$2H_2 + Cl_2 \longrightarrow 2HCl + H_2$

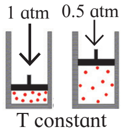
Which of the above reactions is in accordance with the priciple of stoichiometry ?

J. Hot air balloons float in air because of the low density of the air inside the balloon. Explain this with the help of an appropriate gas law.

3. Answer the following questions.

A. Identify the gas laws from the following diagrams.

Diagrams Gas laws

a.


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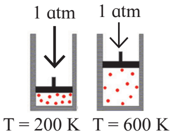
b.


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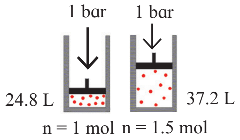
c.


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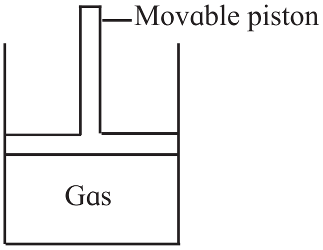
B. Consider a sample of a gas in a cylinder with a movable piston.



Show digramatically the changes in the position of piston, if -

a. Pressure is increased from 1.0 bar to 2.0 bar at constant temperature.

b. Temperature is decreased from 300 K to 150 K at constant pressure

c. Temperature is decreased from 400 K to 300 K and pressure is decreased from 4 bar to 3 bar.

D. List the characteristic physical properties of the gases.

E. Define the terms:
- a. Polarizability
- b. Hydrogen bond
- c. Aqueous tension
- d. Dipole moment

F. Would it be easier to drink water with a straw on the top of the Mount Everest or at the base ? Explain.

G. Identify type of the intermolecular forces in the following compounds.

a. $CH_3 - OH$ b. $CH_2 = CH_2$

c. $CHCl_3$ d. CH_2Cl_2

H. Name the types of intermolecular forces present in Ar, Cl_2, CCl_4 and HNO_3

I. Match the pairs of the following :

'A'	'B'
a. Boyle's law	i. at constant pressure and volume
b. Charles' law	ii. at constant temperature
	iii. at constant pressure

J. Write the statement for :

(a) Boyle's law (b) Charles' law

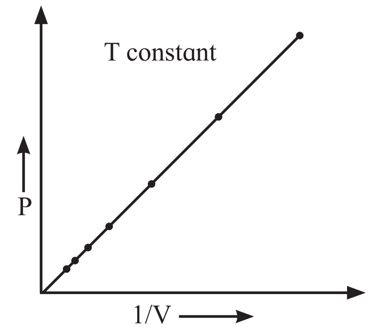
K. Differentiate between Real gas and Ideal gas.

4. Answer the following questions

A. State and write mathematical expression for Dalton's law of partial pressure and explain it with suitable example.

B. Derive an Ideal gas equation. Mention the terms involved in it. Also write how it is utilised to obtain combined gas law.

C. With the help of graph answer the following -



At constant temperature,

a. Graph shows relation between pressure and volume. Represent the relation mathematically.

b. Identify the law.

c. Write the statement of law.

D. Write Postulates of kinetic theory of gases.

E. Write a short note on -

a. Vapour pressure.

b. Surface tension

c. Viscosity.

5. Solve the following

A. A balloon is inflated with helium gas at room temperature of 25^0C and at 1 bar pressure when its initial volume is 2.27L and allowed to rise in air.

As it rises in the air external pressure decreases and the volume of the gas increases till finally it bursts when external pressure is 0.3bar. What is the limit at which volume of the balloon can stay inflated ? (Ans:7.567L)

B. A syringe has a volume of 10.0 cm^3 at pressure 1 atm. If you plug the end so that no gas can escape and push the plunger down, what must be the final volume to change the pressure to 3.5 atm?

(Ans:2.9 cm^3)

C. The volume of a given mass of a gas at 0^0C is 2 dm^3. Calculate the new volume of the gas at constant pressure when

a. The temperature is increased by 10^0C.

(Ans: 2.07 dm^3)

b.The temperature is decreased by10^0C.

(Ans:1.93 dm^3)

D. A hot air balloon has a volume of 2800 m^3 at 99^0 C. What is the volume if the air cools to 80^0 C?

(Ans:2657 m^3)

E. At 0^0C, a gas occupies 22.4 liters. How nuch hot must be the gas in celsius and in kelvin to reach volume of 25.0 literes?

(Ans:31.7 ^{0}C/304.9 K)

F. A 20 L container holds 0.650 mol of He gas at 37^0C at a pressure of 628.3 bar. What will be new pressure inside the container if the volume is reduced to 12 L. The temperature is increased to 177 ^{0}C and 1.25 mol of additional He gas was added to it?

(Ans:4443 bar/4385 atm)

G. Nitrogen gas is filled in a container of volume 2.32 L at 32^0C and 4.7 atm pressure. Calculate the number of moles of the gas.

(Ans:0.436 moles)

H. At 25 ^{0}C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at the height where temperature is 10 ^{0}C and volume of the gas 640 mL ?

(Ans : 676.6 mm Hg)

I. A neon-dioxygen mixture contains 70.6 g dioxygen and 167.5g neon.If pressure of the mixture of the gases in the cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture?

(Ans:p_{O_2}= 5.25 bar, p_{Ne}=19.75 bar)

J. Calculate the pressure in atm of 1.0 mole of helium in a 2.0 dm^3 container at 20.0^0C.

(Ans:12.02 atm)

K. Calculate the volume of 1 mole of a gas at exactly 20 ^{0}C at a pressure of 101.35 kPa.

(Ans: 24.055 dm^3)

L. Calculate the number of molecules of methane in 0.50 m^3 of the gas at a pressure of 2.0×10^2 kPa and a temperature of exactly 300 K.

(Ans: 2.4×10^{25})

Activity :

Perform different activities related to concepts mentioned in chapter.