

Lecture 3

Gas Laws

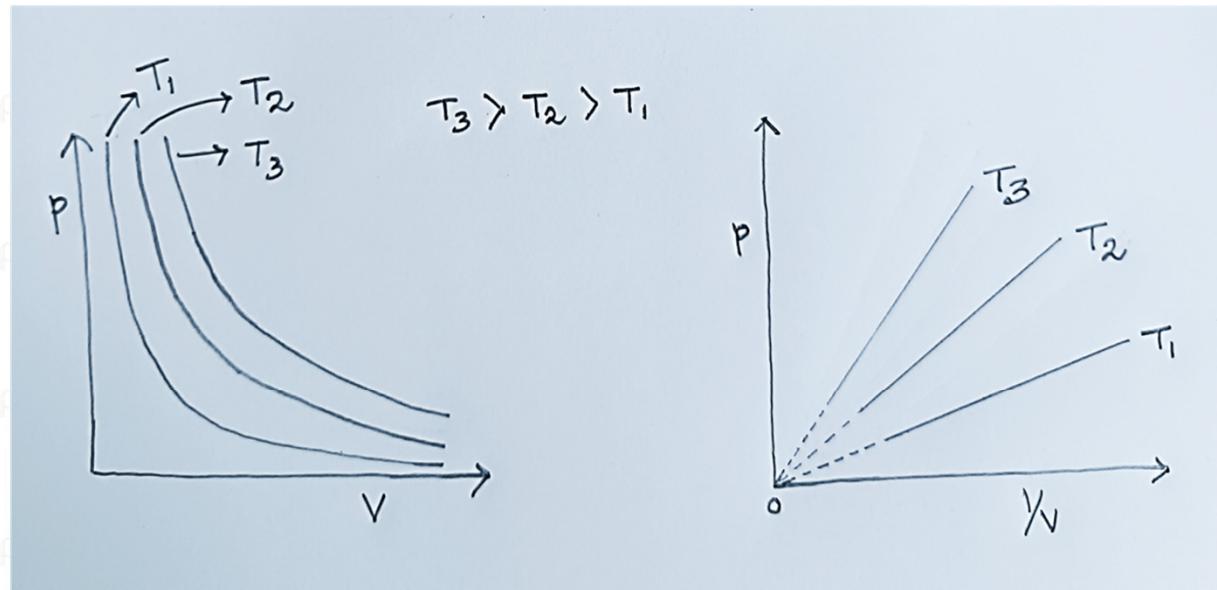
- Boyle's Law
- Charles' Law
- Avogadro's Principle
- Dalton's Law of Partial Pressure
- Graham's Law of Diffusion/Effusion

Boyle's law: At constant temperature, the pressure of a sample of gas is inversely proportional to its volume, and the volume it occupies is inversely proportional to its pressure.

$$p \propto \frac{1}{V} \quad \text{or} \quad V \propto \frac{1}{p}$$

or, $pV = \text{constant}$

This equation is of the type $xy = \text{constant}$ i.e. of a rectangular hyperbola



These curves were obtained at constant temperature, hence these are called isotherm.

Assumption:

Boyle's law is valid at low pressure (and high temp.) and real gases obey this law only at the limit of pressure tending to zero.

Thus, Boyle's law is a limiting law w.r.t $p \rightarrow 0$ and $T \rightarrow \infty$

Molecular explanation:

When a gas is compressed to half its volume, then twice as many molecules will strike the walls in a given time period. Thus, pressure exerted gets doubled. Thus, when volume is halved pressure gets doubled, i.e. $pV = \text{constant}$. At low pressure the molecules are so far apart on average, that they exert no influence on one another i.e. travel independently.

Question: How will the plot of p^{-1} vs. V look like?

Question: A fixed mass of a gas occupies 100 mL at a pressure of 3 atm. at a fixed temperature. By how much the volume would be changed if the pressure is reduced to 1.5 atm. (under the isothermal condition).

Question: A bubble (spherical radius of 1×10^{-2} cm starts its journey from a deep sea level of pressure 3.375 atm to the sea – water interface having the surrounding pressure of 1 atm. Assuming isothermal condition, calculate what would be the radius of the bubble at the sea – water interface.

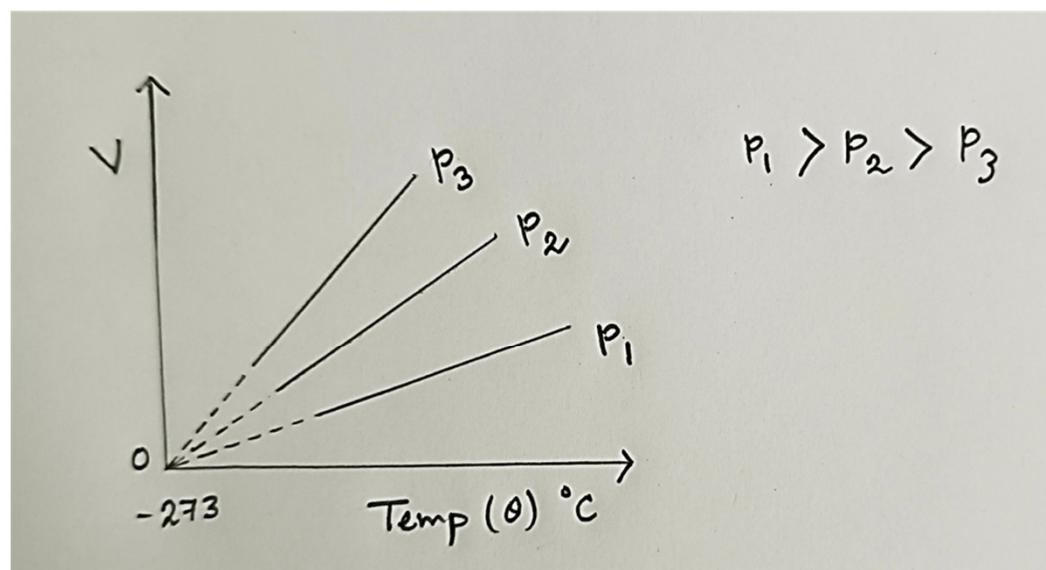
Charles' law:

Jacques Charles observed that at constant pressure, volume of a sample of gas increases linearly with temperature.

Assumption: Pressure is low (limiting law w.r.t. $p \rightarrow 0$)

Thus, $V = \text{constant} (\theta + 273.15 \text{ }^{\circ}\text{C})$ (at constant pressure) [linear equation passing through zero, $y = mx$]

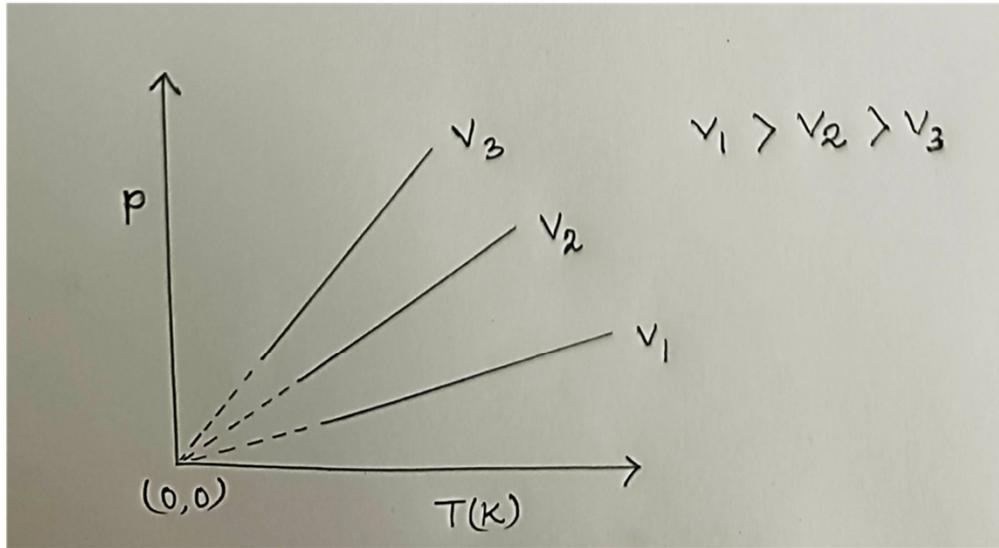
Or, $V = \text{constant} \times T$ (at constant pressure) [T in absolute temperature or T K]



Since these curves are obtained at constant pressure, so these are known as isobars.

Alternative statement:

At constant volume, pressure of a sample of gas increases linearly with temperature.



$p \rightarrow$ Isochore

Molecular explanation:

On raising the temperature, the average speed of gas molecules increases. Thus, the molecules collide with the walls more frequently and do so with a greater impact. Therefore it exerts greater pressure on the walls of the container.

New Scale of Temperature:

From the Charles' law a new temperature scale can be created and that is known as absolute scale of temperature.

$$\text{Thus, } T \text{ (K)} = \theta \text{ } (\text{°C}) + 273.15 \text{ } (\text{°C})$$

(Symbol K as absolute temperature to honour Lord Kelvin (William Thomson))

It may be noted that according to Charles' law volume of a gas should be zero at the absolute zero temperature. Most gases will be liquefied at low temperature, specially close to absolute zero temperature all gases will be liquefied. However, the volume won't be zero. Thus, Charles' law fails to represent the true physical picture at low temperature specially close to absolute zero temperature.

From Boyle's law and Charles' law we know that

$(P_1 V_1 / T_1) = (P_2 V_2 / T_2) = \text{Constant}$, which says that for a given mass of a gas any change in pressure and temperature will be manifested by the adjustment of volume so that the value of the quotient (PV/T) remains constant.

The value of this constant depends on the mass and nature of the gas.

Avogadro Principle:

At a given temperature and pressure, the molar volume $V_m = \frac{V}{n}$, the volume per mole (of molecules) of a gas is approximately same regardless of the identity of the gas. This means volume of a sample of gas is proportional to the amount (moles) of molecules of the gas and the proportionality is independent of the gas.

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

In other words equal volume of gases at constant temperature and pressure contain equal number of molecules.

Molar volume of a perfect gas under SATP (Standard Ambient Temperature & Pressure) i.e. 298.15 K and 1 bar ($= 10^5 \text{ Pa}$) is $24.790 \text{ L mol}^{-1}$. Earlier definition was at STP (i.e. 0°C and 1 atm) molar volume of a perfect gas is $22.414 \text{ L mol}^{-1}$.

Equal number of moles of all gases will occupy the same volume at a given temperature and pressure. This is a remarkable simplification, made in 1811.

Combined gas law:

The physical state of a sample of substance is defined by its physical properties, i.e. pressure (p), temperature (T), volume (V) and no. of moles (n) for a pure gas.

It has been experimentally established that it is sufficient to specify only three of these physical properties, the fourth one gets fixed automatically, i.e. for example,

$$p = f(V, T, n)$$

This kind of equation relating four physical properties is known as equation of state.

This is valid for a homogeneous system. For a heterogeneous system, each phase will have its own equation of state.

Boyle's law: $pV = \text{constant}$ (when T and n are constant)

Charles's law: $p \propto T$ or $V \propto T$ (when n and either V or p are constant)

Avogadro's principle: $V \propto n$ (when p and T are constant)

Combining these three equations, we get

$$pV = \text{constant} \times nT$$

or, $pV = nRT$

where R is a constant, known as (universal) gas constant $[R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.206 \times 10^{-2} \text{ L atm. K}^{-1} \text{ mol}^{-1}]$

This equation is known as perfect gas equation. Any gas that obeys perfect gas equation is known as perfect gas.

A real/actual gas behave like a perfect gas only when the pressure is low i.e. $p \rightarrow 0$ limit.

Question: Suppose you are starting from Mohanpur (27 °C) with an inflated balloon of 1 L and going to Darjeeling (- 5 °C). What would be the volume of the balloon when you reach Darjeeling? On the way back from Darjeeling (- 5 °C) you inflate the bike/car tyre to a recommended value of 3×10^5 Pa. Once you reach Mohanpur you notice that the temperature has risen to 40 °C. Assume that the volume of the tyres have increased 3%, what would be the tyre pressure when you reach Mohanpur? Is it within the recommended pressure value of $\pm 5\%$?

From the combined gas law: $PV = nRT = (W/M) \times RT$

$$P = (W/M) \times (RT/V) = \rho \times (RT/M)$$

(Where, W is the mass of the gas with molar mass M and density ρ)

Thus, $\rho = (PM/RT)$

This equation is important because for a known gas, by measuring the pressure and temperature it is possible to measure the density of the gas.

Alternatively, if I can measure the density, then by measuring the P and T it is possible to know M, i.e. identity of the pure gas.

Alternatively, by measuring the density of the gas and temperature, it is possible to determine the pressure at high altitudes.

Equation of state for a gas mixture: Dalton's law of Partial pressure

Equation of state: $pV = nRT$

For a mixture of gases Dalton's law states that:

The pressure exerted by a mixture of perfect gases is the sum of partial pressure of the gases.

$$\text{i.e. } p = p_a + p_b + \dots$$

For example, assume certain amount of H_2 exerts 50 kPa when present alone in a container. Also, assume certain amount of N_2 exerts 160 kPa when present alone in the same container at the same temperature. When these two gases are present then the total pressure will be equal to the sum of partial pressure of these two gases i.e. 210 kPa.

$$p_1 = n_1 \frac{RT}{V}, \quad p_2 = n_2 \frac{RT}{V}, \quad \dots$$

$$p_1 + p_2 + \dots = (n_1 + n_2 + \dots) \frac{RT}{V}$$

$$\text{Now } p_1 = n_1 \frac{RT}{V}, \quad \text{so,} \quad \frac{p_1}{p} = \frac{n_1}{n} \times \frac{RT}{V}$$

$$\text{But we know, } p = n \frac{RT}{V}$$

$$\Rightarrow \frac{p_1}{p} = \frac{n_1}{n} = x_1 \text{ (say)} \quad [n = n_1 + n_2 + \dots] \quad \text{where } x_1 \text{ is the mole fraction}$$

$$\Rightarrow \boxed{p_1 = x_1 \cdot p} \quad [p_1 \text{ is the partial pressure of gas 1 having a mole fraction of } x_1]$$

Caution: The above equation is valid for mole fraction only and not for molar concentration.

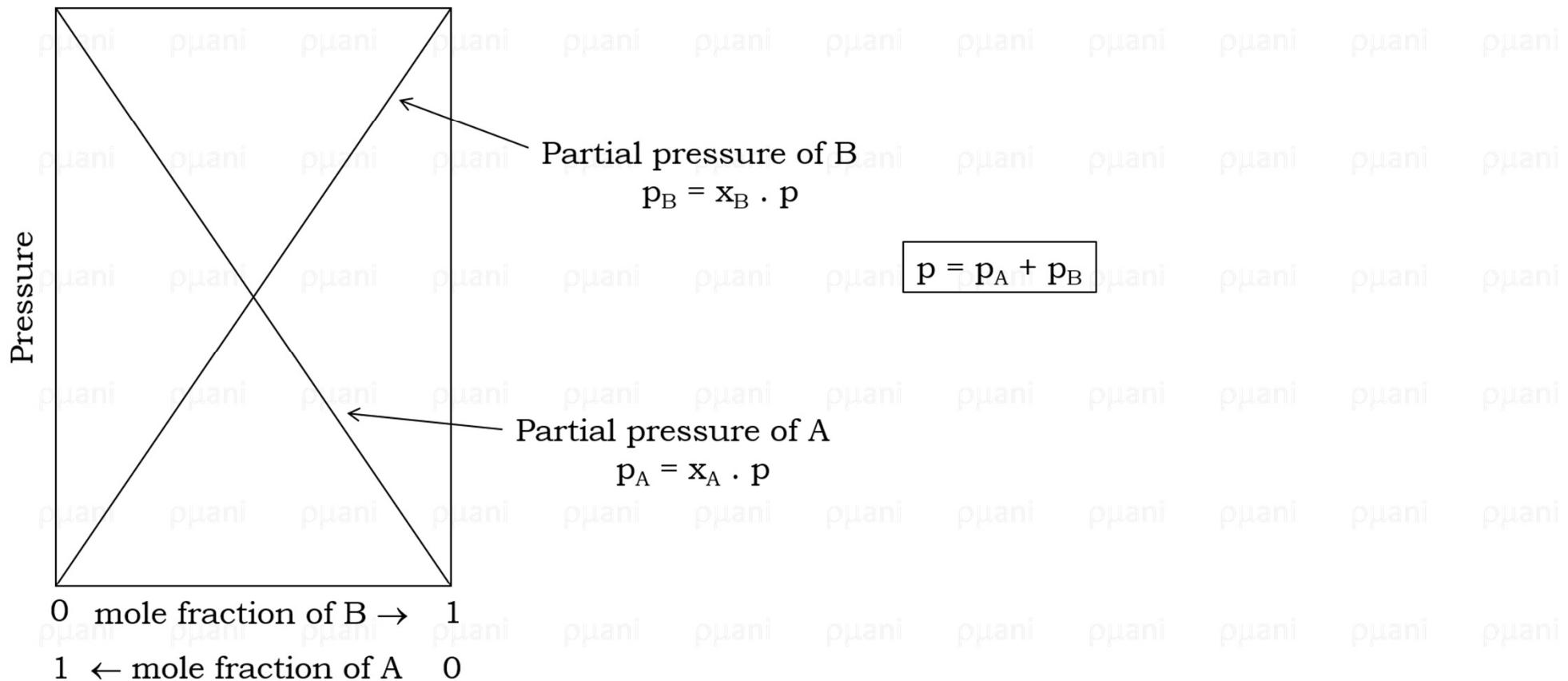
Question:(a) How will the plot of pV vs. p look like for a perfect gas at constant temperature?
(b) How the plot will change at a higher constant temperature?

Question: Assume a perfect gas is heated to 500 K in a vessel of constant volume. If it enters the vessel at a pressure of 300 atm. and a temperature of 300 K, what pressure would it exert at the working temperature?

Question: A container of volume 8.206 L holds 1 mole of perfect gas A and 3 moles of perfect gas B at 300 K. What is the total pressure in 'atm' unit?

Question: The mass percentage composition of dry air is approximately N₂: 75, O₂: 24, Ar: 1. What would be the partial pressure of each gas when the total pressure is 1 atm? (Assume all the gases behave perfectly) (M of N₂, O₂, Ar = 28, 32, 40)

Total pressure in a system of a binary mixture of two pure gases can be understood using the following diagram:



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Concept of Partial Pressure: Only Mathematical or it has a physical significance?

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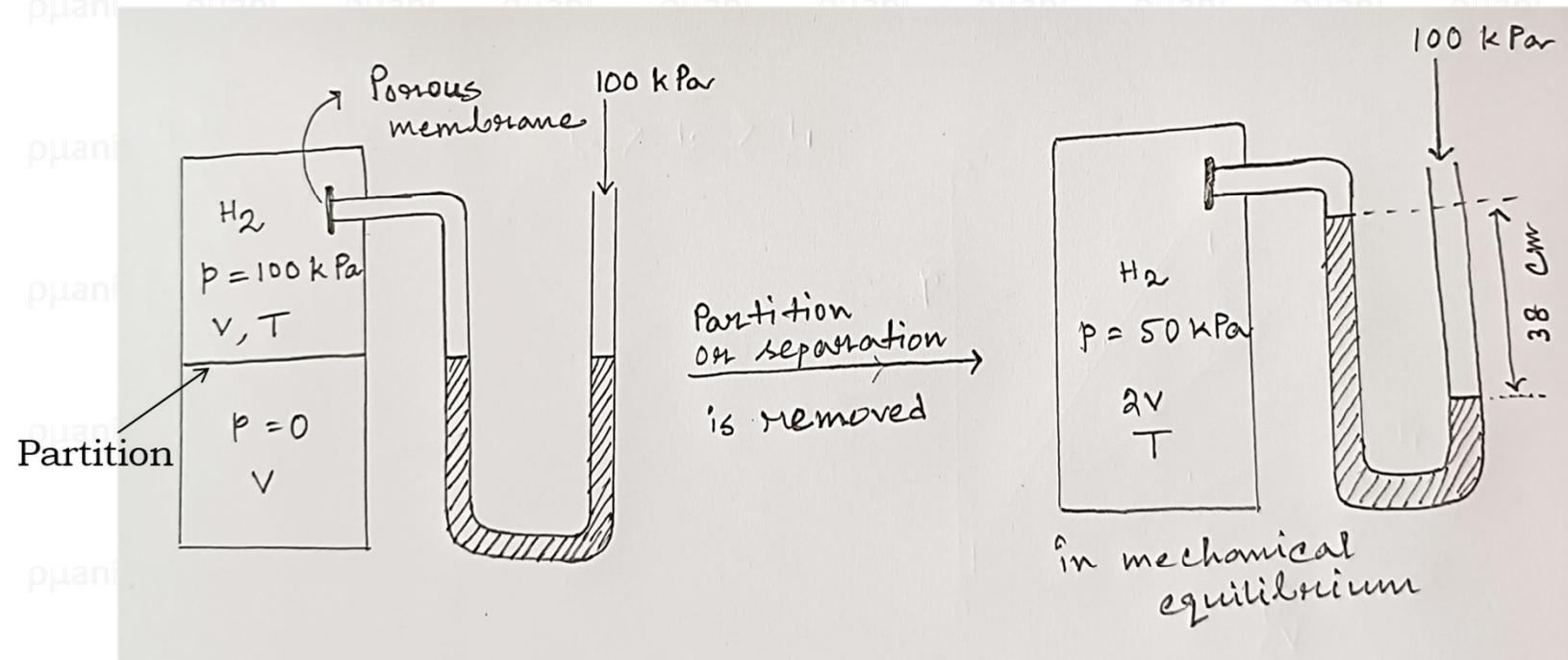
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Example of partial pressure:

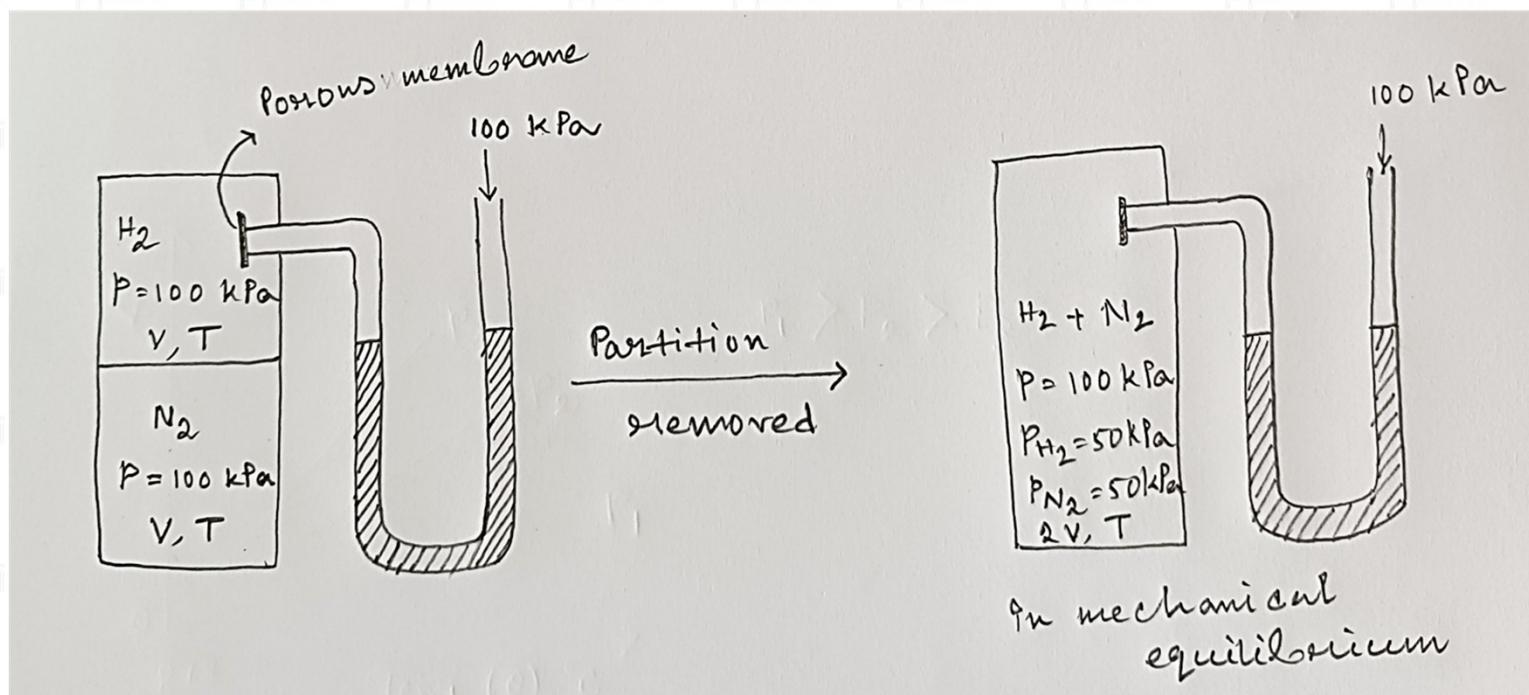
Case – I:



Courtesy: Castellan's book of Physical Chemistry

Example of partial pressure:

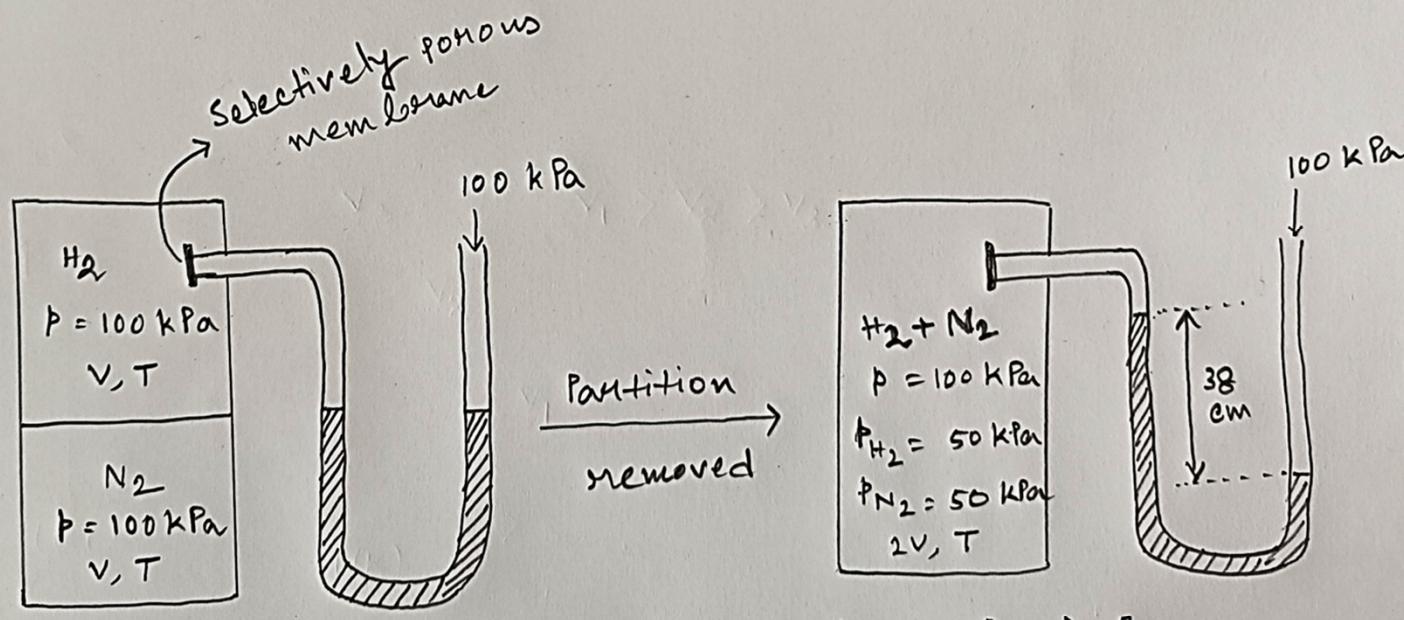
Case – II:



Courtesy: Castellan's book of Physical Chemistry

Example of partial pressure:

Case – III:



in mechanical
equilibrium

Assumption: Volume of left hand tube (above Hg level) is negligibly small

Courtesy: Castellan's book of Physical Chemistry

Amagot's law of partial volume:

The total volume of a mixture of non-interacting gases is the sum of partial volume of the constituents of the mixture, at a particular temperature.

$$V = v_1 + v_2 + v_3 + \dots$$

From the ideal gas equation,

$$v_1 = n_1 * (RT/P), \quad v_2 = n_2 * (RT/P), \quad v_3 = n_3 * (RT/P) \dots \dots \dots \text{(where, } n_1, n_2, n_3 \text{ are the number of moles of components 1, 2, 3, respectively.....)}$$

Thus,

$$(v_1 + v_2 + v_3 + \dots) = (n_1 + n_2 + n_3 \dots) * (RT/P) = n * (RT/P) = V$$

$$\text{Thus, } v_1 = n_1 * (RT/P) = (n_1/n) * V = x_1 * V$$

Or, \$v_i = n_i * (RT/P) = x_i * V\$

This (Amagot's law of partial volume) equation is identical to the Dalton's equation of partial pressure.

Graham's law of diffusion of gases:

Gas molecules have the tendency to spread throughout the space available. This process is called diffusion. If two jars containing different (or same) gases are placed one above the other, connected through the mouth of the jars, then gas from one jar will flow/diffuse to the other jar, irrespective of which gas is lighter/heavier. When the flow of gas happens through porous membrane or through tiny holes, it is known as effusion.

In 1829, T. Graham put forward this law:

At constant temperature and pressure, rate of diffusion (or effusion) is inversely proportional to the square root of density of the gas or molar mass of the gas.

$$\text{Thus, } r_1/r_2 = (\rho_2/\rho_1)^{1/2} \quad \text{and} \quad r_1/r_2 = (M_2/M_1)^{1/2}$$

This means lighter gas will diffuse faster than the heavier gas.

Utility: Separation of isotopes of hydrogen or Uranium.

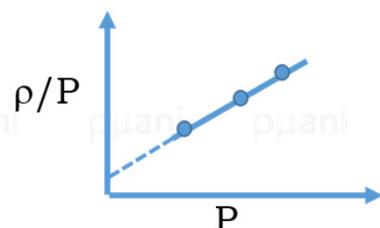
Limiting density:

We know $\rho = (PM/RT)$

or, $\rho/P = M/RT$

Thus, for a given gas (i.e. fixed M) and at a fixed temperature, (ρ/P) should be constant.

However, experimentally, ρ/P for a gas at a particular temperature varies with pressure. This is due to non-ideality of the gases and observed for almost all gases.



However, by extrapolating ρ/P vs. P plot to P tending to zero, when the gas starts behaving ideally, the value of ρ/P can be obtained.

Then, putting that value of ρ/P in the above equation, at a fixed temperature molar mass of the unknown gas can be obtained.

This method of determining the molecular weight is known as the method of limiting density.

Relative density (vapour density):

The density of gas relative to that of hydrogen at a given P and T is known as relative density (D).

As $\rho = (PM/RT)$, hence,

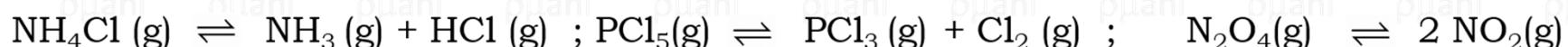
$$D = \rho/\rho_{H_2} = M/M_{H_2} = M/2$$

Note that D is a dimensionless quantity.

The density of gas is generally measured by (a) Dumas Method, (b) Victor- Meyer method.

Abnormal vapour density:

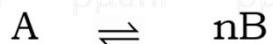
From the vapour density measurement, it is possible to calculate the molecular weight of a gaseous substance. However, in certain cases, for example,



the experimentally obtained value of molecular weight is much less than the actual one and the value decreases to a lower limit (half the actual value) as the temperature is raised.

For the above reaction, the NH_4Cl (or PCl_5 or N_2O_4) dissociates and thus the total number of molecules increases (doubles), and at a fixed P and T, this increases the volume but there is no change in the mass of the substance. This decreases the density and hence the M. As the temperature increases the dissociation increases and M decreases. At sufficiently high temperature, dissociation is complete and thus M reached its lowest value (half).

Suppose,



Initial no. of moles:



(where, α is the degree of dissociation)

Let V be the molar volume at the experimental pressure and temperature. If M_0 and M are the actual and experimental molar masses and ρ_0 and ρ are the corresponding densities, then

$$\rho_0 V = \rho [1 + (n-1) \alpha] V \quad \text{where } \rho_0 = M_0 P / RT \text{ and } \rho = MP / RT$$

$$(\rho_0 / \rho) = (M_0 / M) = 1 + (n-1) \alpha$$

$$\alpha = (M_0 - M) / (n-1) M \quad \text{or} \quad \alpha = (\rho_0 - \rho) / (n-1) \rho$$

From the above equation the degree of dissociation can be calculated.

As and when low vapour density is observed, dissociation is invoked.

If there is no change in the number of moles, e.g. for $2HI \rightleftharpoons H_2 + I_2$

The volume, density and molecular weight remains unaffected.

Molecular Association:

There are examples of reaction in which molecules in the vapour phase associate to form dimers, tetramers, octamers etc. For example, formation of S₈, dimers of formic acid, acetic acid etc.

In such cases, because of molecular association, the number of molecules in the vapour phase decreases (at a fixed T and P) and thus, the volume decreases. The experimental vapour densities are then found to be more than the theoretical value.