PARAMETERS TO DESCRIBE A GAS

(a) **Pressure:**

The force per unit area exerted on the wall of container due to constant bombardment of gas molecules on the wall of container is called pressure.

**Units:**
1 N/m² = 1 Pa
1 atm = 1.013 × 10⁵ Pa
1 atm = 76 cm = 760 mm of Hg = 760 torr
1 torr = 1 mm Hg
1 bar = 10⁵ Pa
1 atm = 1.013 bar

**Constraints:**

\[ P = \text{constant} \]

(b) **Volume (V):**
Volume of a gas is equal to volume of container.

**Units:**
1 cc = 1 cm³ = 1 mL
1000 cc = 1000 cm³ = 1000 mL = 1 L = 1 dm³
1000 L = 1000 dm³ = 1 m³

Volume = Constant

Piston hindered from moving
(c) **Temperature:**
\[ T (K) = t^\circ (C) + 273.15 \]

(d) **no. of moles (n):**
\[ n = \text{moles} \]

**Gas Laws**

(1) Boyle's law

(2) Charle's law

(3) Gay-lussac's law (Amonton's law)

(4) Avogadro's law

(1) Boyle's law

\[ P_1 < P_2 \quad \Rightarrow \quad P \propto \frac{1}{V} \]

\[ V_1 > V_2 \]

\[ P = \frac{k}{V} \]

\[ PV = k \quad ; \quad T = \text{Constant} \]

\[ P_1 \frac{V_1}{n} = P_2 \frac{V_2}{n} = \cdots = P_n \frac{V_n}{n} \]

\[ \therefore \rho = \frac{m}{V} \quad \text{Constant} \]

\[ \rho \propto \frac{1}{V} \propto P \]

\[ \therefore \rho \propto P \]

\[ \frac{P}{P} = \frac{K}{P} \quad ; \quad T = \text{Constant} \]

\[ \frac{R_1}{P_1} = \frac{R_2}{P_2} = \cdots = \frac{P_n}{P_n} \]

"For a fixed amount of gas at constant temperature, the gas volume is inversely proportional to the gas pressure".
(2) Charles' law

\[ V = V_0 + \left( \frac{V_0}{273.15} \right) \times t \]

\( V_0 = \) volume at 0°C
\( t = \) change in temp (°C)

\[ T = t + 273.15 \]

From (1)
or, \[ \frac{V}{T} = \text{Constant} \]

\[ V \propto T ; P = \text{Constant} \]

\[ V = K T \]
\[ \gamma = Kx \]

\[ V = V_0 + V_0 \gamma \Delta t \]

\[ V = V_0 (1 + \gamma t) \rightarrow \text{(solid)} \]

\[ V = V_0 \left(1 + \frac{1}{273.15} \times t \right) \rightarrow \text{Coefficient of superficial expansion of a gas} \]

Charle's law states that, "volume of a gas increases by \( \frac{1}{273.15} \) part of that volume which the gas had at 0°C for every 1° rise in temperature is called Charle's law".

OR

"Volume of a gas is directly proportional to absolute temp keeping pressure constant".

(3) Amonton's law (Gay lussac's law)

\[ P = P_0 \left(1 + \frac{1}{273.15} \times t \right) \]

\[ \frac{P}{T} = \text{Constant} \Rightarrow V = \text{constant} \]

\[ \frac{1}{273.15} = \text{Coeff. of pressure change.} \]
(4) Avogadro’s law

\[
\frac{V_1}{n_1} = \frac{V_2}{n_2}
\]

\[
\frac{V_2}{V_1} \Rightarrow \frac{n_2}{n_1} \Rightarrow \quad T = \text{constant}
\]

\[
P = \text{constant}
\]

\[
V = kn
\]

\[
\frac{V}{n} = \text{constant}
\]

\[
\frac{V_1}{n_1} = \frac{V_2}{n_2} = \cdots = \frac{V_n}{n_n}
\]

Avogadro’s law states that, “volume of a gas is directly proportional to no. of moles keeping pressure and temp constant.”

\[
\begin{align*}
\text{(I)} & \quad V \quad T \\
\text{(II)} & \quad V \quad \frac{1}{T} \\
\text{(III)} & \quad \frac{1}{V} \quad T \\
\text{(IV)} & \quad \frac{1}{V} \quad \frac{1}{T} \\
\text{(V)} & \quad \log V \quad \log T \\
\text{(VI)} & \quad \log \frac{1}{V} \quad \log T
\end{align*}
\]

\* Ideal gas equation

\[
V \propto \frac{1}{P} \quad \text{(Boyle’s law)} \quad 1
\]

\[
V \propto T \quad \text{(Charles’ law)} \quad 2
\]
from (1) (2) (3)

\[ V = \frac{nT}{P} \Rightarrow V = \frac{knT}{P} \]

\[ PV = KnT \]

\[ K = R = \text{universal gas constant.} \]

\[ PV = nRT \]

\[ \therefore n = \frac{w}{M} \]

\[ PV = \frac{w}{M} RT \]

\[ PM = \frac{w}{V} RT \]

\[ PM = \rho RT \]

At S.T.P \( \Rightarrow P = 1 \text{ atm} \)

\[ R = 0.0821 \]

\[ T = 273 \text{ k} \]

\[ \rho = \frac{M}{\left(\frac{RT}{P}\right)} = \frac{M}{\left(\frac{0.0821 \times 273}{1}\right)} \]

\[ \rho_{S.T.P} = \frac{M}{22.4} \]

**Universal gas constant**

\[ R = \frac{PV}{nT} = \frac{F \times A \times L}{n \times T} = \frac{\text{work}}{\text{mole} \times \text{temp}} \]

Is independent of \( P, V, n, T \).

Value of ‘\( R \)’ depends on unit

<table>
<thead>
<tr>
<th>( P )</th>
<th>( V )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pa, N/m}^2 )</td>
<td>m³</td>
<td>8.31 J K⁻¹ mol⁻¹</td>
</tr>
<tr>
<td>atm</td>
<td>L</td>
<td>0.0821 Latm K⁻¹ mol⁻¹</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>1.97 cal K⁻¹ mol⁻¹</td>
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<tr>
<td>---</td>
<td>---</td>
<td>8.31 x 10⁻³ ergs K⁻¹ mol⁻¹</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>5.189 x 10⁻⁶ eV K⁻¹ mol⁻¹</td>
</tr>
</tbody>
</table>

**Note:** \( 1 \text{ atm L} = 101.3 \text{ J} \)
Dalton’s law of partial pressure

\[
\begin{array}{c|c|c}
& A & B \\
\hline
n_A & P_A & n_B \\
T,V & P_B & T,V \\
\end{array} \Rightarrow \begin{array}{c|c|c}
& n_A & n_B \\
\hline
P_T & P_A + P_B & T,V \\
\end{array}
\]

Dalton’s law of partial pressure states that “in a mixture of two non-reacting gases taken in a closed volume & a constant temp behaves as if they are present alone in the container”

Generalisation

\[
\begin{align*}
& A, B, C, D, \\
& \begin{array}{c|c|c|c|c|c}
& n_A & n_B & n_C & n_D \\
\hline
P_A & P_B & P_C & P_D & P_T \\
& V & \\
\end{array} \\
\end{align*}
\]

\[P_A V = n_A RT\]

\[P_A = n_A \frac{RT}{V} \quad (1)\]

\[P_B = n_B \frac{RT}{V} \quad (2)\]

\[P_C = n_C \frac{RT}{V} \quad (3)\]

\[P_T \cdot V = (n_A + n_B + n_C + \ldots) RT\]

\[P_T = \frac{(n_A + n_B + n_C + \ldots) \frac{RT}{V}}{V} \quad (n)\]

from (1) & (n)

\[\frac{P_A}{P_T} = \frac{n_A \frac{RT}{V}}{(n_A + n_B + \ldots) \frac{RT}{V}}\]

\[P_A = \left[\frac{n_A}{n_A + n_B + \ldots}\right] P_T\]

\[P_A = X_A P_T\]

\[P_B = X_B P_T\]

\[P_C = X_C P_T\]

\[X_A = \frac{n_A}{n_A + n_B + n_C + \ldots}\]
Amagat’s law of Partial Volume

\[
X_A = \frac{W_A}{M_A} = \frac{W_A}{M_A} + \frac{W_B}{M_B} + \frac{W_C}{M_C} + \cdots
\]

\[\begin{align*}
A + B + C + & \quad - - - - \\
n_A + n_B + n_C + & \quad - - - - \\
P_A + P_B + P_C + & \quad - - - - \\
P_T, V_T & \quad - - - - \\
\end{align*}\]

\[
P_T \cdot V_A = n_A RT \quad (1)
\]

\[
P_T \cdot V_T = (n_A + n_B + n_C + \cdots) RT \quad (2)
\]

From (1) & (2),

\[
\frac{V_A}{V_T} = X_A
\]

or \[
[ V_A = X_A \cdot V_T ]
\]

\[
[ P_A = X_A \cdot P_T ]
\]

Amagat’s law of partial volume states that, “partial volume of any gas is equal to its mole fraction times its total volume.”

\[
P_{\text{wet gas}} = P_{\text{dry gas}} + P_{\text{H}_2\text{O}}
\]

\[
P_T = P_{\text{N}_2} + P_{\text{H}_2\text{O}}
\]
1 atm = P_{N_2} + P_{H_2O}

P_{N_2} = (1 atm - P_{H_2O})

Whenever we apply ideal gas equation for a gas which is collected over water, take care that the pressure substituted is that of a dry gas.

(2) Relative humidity:

\[ P \propto W \]

\[ RH = \frac{W_{H_2O \text{ (present)}}}{W_{\text{max} H_2O \text{ vapour}}} = \frac{\text{Partial vapour pressure of } H_2O}{\text{maximum partial pressure of } H_2O \text{ (Aqueoustension)}} \]

\[ R.H\% = R.H \times 100 \]

Effusion & Diffusion

**EFFUSION**

The process of leakage of a gas through a very fine hole is called effusion.

\[ V = \text{constant} \quad P = \text{constant} \]

**DIFFUSION**

\[ \Rightarrow \text{The movement of molecules from a region of high conc. to low conc. is called diffusion.} \]
Definition of rates of Effusion & Diffusion

Effusion

\[ \frac{\Delta n}{\Delta t} \]

Diffusion

\[ \frac{\text{distance}}{\text{time}} \]

\[ V = \text{Constant} \]

\[ PV = nRT \]

\[ \frac{\Delta P}{\Delta t} \propto \frac{\Delta n}{\Delta t} \]

\[ \frac{\Delta V}{\Delta t} \propto \frac{\Delta n}{\Delta t} \]

rate = \frac{\Delta n}{\Delta t} = \frac{\Delta P}{\Delta t} \]

rate of effusion = \frac{\Delta n}{\Delta t} = \frac{\Delta V}{\Delta t} \]

Graham's law of diffusion or effusion

rate \propto P (\text{Pressure of gas}) \]

rate \propto A (\text{Area of hole}) \]

rate \propto \frac{1}{\sqrt{P}} \left( \rho = \text{density of gas} \right) \]

rate \propto \frac{\text{KPA}}{\sqrt{P}} \]

PM = \rho RT

M \propto \rho
\[
\text{rate} = \frac{\text{KPA}}{\sqrt{P}} = \frac{\text{KPA}}{\sqrt{M}}
\]

\[
\text{rate} = \frac{K}{\sqrt{P}} = \frac{K}{\sqrt{M}}
\]

\(\text{Graham's law states that the rate of diffusion or effusion of gas is directly proportional to the product of pressure & area of orifice and is inversely proportional to the density of gas.}\)

\(\star\)

Variations in Graham's law

\(\text{Case - I} \quad \text{(leaking alone)}\)

\[\text{A} \leftarrow \Delta n_1 \quad \text{B} \leftarrow \Delta n_2 \quad \Delta t_1 \quad \Delta t_2\]

\(\frac{\Delta n_1}{\Delta t_1} = \frac{k}{\sqrt{M_1}}, \quad \frac{\Delta n_2}{\Delta t_2} = \frac{k}{\sqrt{M_2}}\)

\[
\frac{\Delta n_1}{\Delta t_1} \times \frac{\Delta t_2}{\Delta n_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad \Rightarrow \quad \frac{\Delta n_1}{\Delta t_1} = \frac{\sqrt{M_2}}{\sqrt{M_1}}\]

\[
\Rightarrow \left[\begin{array}{l}
\frac{\Delta t_2}{\Delta t_1} = \frac{M_2}{M_1} \\
\frac{\Delta n_1}{\Delta t_1} = \frac{M_2}{M_1}
\end{array}\right]
\]

as \(\Delta n \propto \Delta P\)

\[
\frac{\Delta P_1}{\Delta t_1} \times \frac{\Delta t_2}{\Delta P_2} = \frac{M_2}{M_1}\]

\[
\Rightarrow \left[\begin{array}{l}
\frac{\Delta t_2}{\Delta t_1} = \frac{M_2}{M_1} \\
\frac{\Delta P_1}{\Delta t_1} = \frac{M_2}{M_1}
\end{array}\right]
\]
\[ \frac{\Delta P_1}{\Delta P_2} = \sqrt{\frac{M_2}{M_1}} \]

**Case I - B: (P = Constant)**

\[ \frac{\Delta n_1}{\Delta t_1} = \frac{k}{\sqrt{M_1}} \quad ; \quad \frac{\Delta n_2}{\Delta t_2} = \frac{k}{\sqrt{M_2}} \]

\[ \frac{\Delta n_1}{\Delta t_1} \times \frac{\Delta t_2}{\Delta n_2} = \sqrt{\frac{M_2}{M_1}} \quad \rightarrow \quad \frac{\Delta n_1}{\Delta n_2} = \sqrt{\frac{M_2}{M_1}} \]

\[ \frac{\Delta t_2}{\Delta t_1} = \sqrt{\frac{M_2}{M_1}} \]

as \( \Delta n \propto \Delta V \)

\[ \frac{\Delta V_1}{\Delta t_1} \times \frac{\Delta t_2}{\Delta V_2} = \sqrt{\frac{M_2}{M_1}} \quad \rightarrow \quad \frac{\Delta V_1}{\Delta V_2} = \sqrt{\frac{M_2}{M_1}} \]

\[ \frac{\Delta t_2}{\Delta t_1} = \sqrt{\frac{M_2}{M_1}} \]

**Kinetic theory of gases**

**Postulates of Kinetic Theory of gases:**

1. **Vol. of free space**
   \( V_{fs} = V - V_{molecules} = V \)

The gases are composed of very small particles with their volume almost negligible as compared to the volume of the container.

2. Gas molecules are in constant random motion.

3. All the collisions in the gas molecules are assumed to be perfectly elastic.

4. There is intermolecular attraction or repulsion between the gas molecules.

5. The pressure exerted by the gas on the wall of the container is due to constt. bombardment of molecules on the wall of container.

6. It was assumed that the K.E. of the gas molecule is directly proportional to the absolute temperature.
   \[ \text{K.E.} \propto T \]

7. There is no effect of gravity on the gas molecules.
\[ V = \text{constant} \quad Q = n \, C_v \, \Delta T \]
\[ P = \text{constant} \quad Q = n \, C_p \, \Delta T \]

Molar heat capacity at constant volume
\[ C_p - C_v = R \]
\[ \frac{C_p}{C_v} = \gamma \]

Molar heat capacity at constant pressure.

Degree of freedom

1. The number of terms in the expression of energy of a gas is known as "degree of freedom" symbol \( \gamma \).

2. Monoatomic gas molecules possess only translational motion while diatomic & polyatomic molecules possess translational as well as rotational and vibrational energy.

3. At ordinary temp. the vibrational mode is neglected.

4. Monoatomic \( \quad \text{Ne} \quad \rightarrow \quad f = 3 \)
   Diatomic \( \quad \text{Cl} \quad \text{Cl} \quad \rightarrow \quad f = 5 \)
   Polyatomic \( \quad \text{O} \quad \text{C} \quad \text{O} \quad \rightarrow \quad f = 6 \)

\[ C_v = \frac{f}{2} \, R \]
\[ C_p = \left( \frac{f+1}{2} \right) R = \left( \frac{f+2}{2} \right) R \]
\[ \gamma = \left[ \frac{C_p}{C_v} \right] = \frac{\left( \frac{f+2}{2} \right) R}{\left( \frac{f}{2} \right) R} = 1 + \frac{2}{f} \]
\[ \gamma = 1 + \frac{2}{f} \]

Energy of a molecule at \( T \) kelvin is \( \frac{1}{2} kT \) per degree of freedom
   where \( K \) = Boltzmann's constant.
\[ \frac{R}{N_A} = \frac{8.31}{6.023 \times 10^{23}} = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ mol}^{-1} \]
K.E. of one gas molecule is equal to \( \frac{1}{2} K T \)

\[ K.E = \frac{1}{2} K T \]

Total energy of 1 mole of molecule is \( \frac{1}{2} R T \)

1 molecule \( \rightarrow \) \( \frac{1}{2} \frac{R}{N_A} T \)

1 mole \( \rightarrow \) \( \left( \frac{1}{2} \times \frac{R}{N_A} \times T \right) \times N_A = \frac{1}{2} R T \)

Total energy = \( \frac{1}{2} R T \)

**Boltzmann Velocity Distribution Curve**

The value of most probable velocity increases with temp.

The fraction of molecules possessing the most probable velocity also increases with temperature.

**Velocities of gases**

- (a) Most probable velocity \( V_{mp} \)
- (b) Average velocity \( V_{av} \)
- (c) Root mean square velocity \( V_{rms} \)

\[ (a) \text{ Most probable velocity } : (V_{mp}) : \]

Possessed by maximum number of molecules.
\[ V_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2PV}{nm}} = \sqrt{\frac{2PV_m}{M}} \]

\[ PV = nRT \rightarrow RT = \frac{PV}{n} \]

\[ PM = \rho RT \rightarrow \frac{P}{\rho} = \frac{RT}{M} \]

\[ n \rightarrow V \]
\[ 1 \rightarrow \left[ \frac{V}{n} = V_m \right]. \]

\( \star \)

(b) **Average velocity**:

\[ V_{av} = \frac{V_1 + V_2 + V_3 + \cdots + V_n}{n} \]

\[ V_{av} = \frac{8RT}{\pi M} = \sqrt{\frac{8P}{\pi \rho}} = \sqrt{\frac{8PV}{\pi nM}} = \sqrt{\frac{8PV_m}{\pi M}} \]

\( \star \)

(c) **Root mean square velocity** \((V_{rms})\):

\[ V_{rms} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + \cdots + V_n^2}{n}} \]

was defined for K.E. of gas

\[ V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3PV_m}{M}} \]

\[ V_{mp} < V_{av} < V_{rms} \]

\[ \frac{V_{mp} : V_{av} : V_{rms}}{\sqrt{2} : \sqrt{\pi} : \sqrt{3}} \]

\[ = 1:1.128 :1.224 \]

\( \star \)

**Kinetic energy**

\[ \text{Total K.E of gas molecules} \]

\[ \text{Average K.E per molecules} \]

\[ KE = \frac{3}{2} \frac{nRT}{2} = \frac{3W}{2M} \frac{RT}{n} \]

\[ n \text{ moles} \rightarrow \frac{3}{2} \text{n RT} \]

\[ n = n \text{ moles} \]

\[ 1 \text{ mole} \rightarrow \frac{3}{2} \text{ RT} \]
K.E possessed by n moles of any gas

\[ \text{N}_A \text{ particle } \rightarrow \frac{3}{2} \frac{RT}{N_A} \]

\[ \text{1 particle } \rightarrow \frac{3}{2} \frac{RT}{N_A} \times \frac{N_A}{T} = \frac{3}{2} K T \]

Boltzmann constant

\[ = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ K E (av) = \frac{3}{2} K T \]

(per molecule)

Compressibility factor (Z)

\[ Z = \frac{PV}{nRT} = \frac{PV_A}{RT} \]

\[ Z = 1 \rightarrow \text{Ideal gas} \]

\[ Z \neq 1 \rightarrow \text{Real gas} \]

\[ Z > 1 \]

- Real gas
- Positive deviation from ideal behaviour
- Intermolecular repulsion
- Can’t be liquefied

\[ Z < 1 \]

- Real gas
- Negative deviation from ideal behaviour
- Intermolecular attraction
- Can be easily liquefied

**Question**: Why H and He have Z always greater than 1?

**Answer**: 

...
Vander Waals equation

\[ P_v V_n = n RT \]

\[ V - V_{molar} = V_n \Rightarrow V_n = V \]

assumed no intermolecular forces.

To be vander waal equation

(a) Pressure Correction  (b) Volume Correction

(a) Pressure Correction

\[ P_c \propto \frac{n}{V} \Rightarrow \text{Conc. of gas molecules colliding per unit time within the wall of container.} \]

\[ P_c \propto \frac{n}{V} \Rightarrow \text{Conc. of gas molecules behind every colliding molecule.} \]

\[ P_c \propto \frac{n^2}{V^2} \]

\[ \text{or, } P_c = \frac{a n^2}{V^2} \quad [a= \text{Vander Waal's constant}] \]

Unit of \(a = \text{atm} L^2 \text{ mol}^{-2}\)

(b) Volume Correction

- 2 molecules \(\frac{4}{3} \pi (2r)^3\)
- 2 molecules \(8 \times \frac{4}{3} \pi r^3\)
- 1 molecules \(4 \times \frac{4}{3} \pi r^3\)
- 1 mole molecules \(4 \times \frac{4}{3} \pi r^3 \times N_A\)

Let the volume occupied by 1 mole molecule
\[ b = 4N_A \times \frac{4}{3} \pi r^3 \quad r = \frac{\sqrt[3]{3b}}{16N_A\pi} \]
\[ b = 4N_A \times V \]

Unit of \( b \) = L mole\(^{-1} \)
\[ V_{\text{molecules}} (n \text{ moles}) = n \times b \]
\[ V_s = V_{\text{container}} - V_{\text{molecules}} \]
\[ V_s = V - nb \]
\[ V_s = V + V_c \]
\[ V_c = nb \]

**Vander Waal’s equation can be written as:**
\[ P_s V_n = nRT \]

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

**Variations in Vander Waals equation**

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

\*(a) Low pressure :-*
\[ \text{neglected} \quad P \downarrow \Rightarrow V \downarrow \Rightarrow V - nb \approx V \]
\[ V \downarrow \Rightarrow \frac{an^2}{V^2} \downarrow \]

\[ P \downarrow \Rightarrow \text{hence, } \frac{an^2}{V^2} \text{ is net negligible} \]

**Vander Waal’s equation changes to**

\[ \left( P + \frac{an^2}{V^2} \right) (V) = nRT \]

\[ PV + \frac{an^2}{V} = nRT \]

\[ \frac{PV}{nRT} + \frac{an^2}{V \times nRT} = 1 \]

\[ Z + \frac{an}{VRT} = 1 \]
\[
\left[ Z = 1 - \frac{a}{V R T} \right]
\]

for \( n = 1 \)

\[
Z = 1 - \frac{a}{V R T} \implies Z < 1
\]

**At low pressure:**

1. Intermolecular attraction
2. Can be liquify
3. Negative deviation from ideal behaviour

**High pressure:**

\[
\left( P + \frac{a V^2}{R T} \right) (V - n b) = n R T
\]

\[
P \implies V \downarrow = V - n b \implies \text{remain as it is}
\]

\[
V \downarrow = \frac{a V^2}{R T} \implies \text{but very less as compared to } P \implies \text{hence } \frac{a V^2}{R T} \text{ can be neglected.}
\]

Now, Vander Waal’s equation changes:

\[
P (V - n b) = n R T
\]

\[
PV - nP b = n R T
\]

\[
\frac{PV}{n R T} - \frac{nP b}{n R T} = 1
\]

\[
Z - \frac{P b}{R T} = 1
\]

\[
Z = 1 + \frac{P b}{R T} \implies Z > 1
\]

**Rx**

\[
\rightarrow \text{Pressure} \uparrow \implies \text{Real gas}
\]

(a) Intermolecular repulsion

(b) Cannot liquify

(c) Positive deviation from ideal behaviour

**Isotherm:** A plot between pressure and volume keeping temperature constant called isotherm.
**Critical temp (T_c):** The temp above which a gas can never be liquify is called critical temp.

\[ T_c = \frac{8a}{27R_b} \]

\( a, b = \text{Vander waal constant.} \)

**Critical Pressure (P_c):**

\[ P_c = \frac{a}{27b^2} \]

**Critical Volume (V_c):** Volume of one mole of gas at critical point is called critical volume.

\[ V_c = 3b \]

**Calculation of Critical Constants**

\[
\left[ P + \frac{a}{V^2} \right] (V - b) = RT
\]

\[ (V^2P + a) (V - b) = V^2RT \]

\[ PV^3 - PbV^2 + aV - ab = V^2RT \]

\[
V^3 - \left( \frac{b + RT}{P} \right) V^2 + \frac{a}{P} V - \frac{ab}{P} = 0 \quad \text{(I)}
\]

At critical point

\[
V^3 - \left( \frac{b + RT}{P_c} \right) V^2 + \frac{a}{P_c} V - \frac{ab}{P_c} = 0
\]

At Critical Point:

\[ (V - V_c)^3 = 0 \]

\[ V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \quad \text{.... (II)} \]

By (i) and (ii)

\[ 3V_c = b + \frac{RT_c}{P_c} \]
\[ 3 V_c^2 = \frac{a}{P_c} \]
\[ V_c^2 = \frac{a b}{P_c} \]
\[ \frac{V_c^2}{3 V_c^2} = \frac{a b / P_b}{a / P_c} \]

\[ V_c = 3 b \]
\[ P_c = \frac{a}{27 b^2} \]
\[ T_c = \frac{8 a}{27 R b} \]

**Virial equation**

Whenever compressibility factor of a gas is expanded in the terms of \( 1/V_m \) or \( P \), the expansion is called **Virial equation**

\[ Z = \frac{P V_m}{R T} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \cdots \quad \infty \]
\[ Z = \frac{P V_m}{R T} = 1 + B \left( \frac{P}{R T} \right) + C \left( \frac{P}{R T} \right)^2 + D \left( \frac{P}{R T} \right)^3 + \cdots \quad \infty \]

**Boyle’s temperature \( (T_b) \)**

![Boyle's temperature graph]

\[ T_b = \frac{a}{R b} \]

The temperature at which a real gas behaves like an ideal gas is called “Boyle’s temperature.”

**Inversion temperature \( (T_i) \)**

- Gas expands ⇒ warms up
  - \( (T_i) \)
- Gas expands ⇒ cools down
  - \( T_i = \frac{2 a}{R b} = 2 T_b \)

A temp below which a gas is expanded, it cools down and vice versa happens above that temperature, is called “**inversion temperature**”
**SOLVED EXAMPLES**

**Ex. 1** When 2 gm of a gaseous substance A is introduced into an initially evacuated flask at 25°C, the pressure is found to be 1 atm. 3 gm another gaseous substance B is then added to it at the same temperature and pressure. The final pressure is found to be 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights of A and B.

**Sol.** Let $M_A$ and $M_B$ be the molecular weights of A and B.

Using $PV = nRT$ for A, we get:

$$\frac{2}{M_A}RT = \frac{1}{V}$$

...(i)

and using Dalton’s Law: $P_{\text{total}} = \frac{(n_A + n_B)RT}{V} \Rightarrow 1.5 = \frac{2}{(M_A + \frac{3}{M_B})}RT$ ...(ii)

Solving (i) and (ii), we get $\frac{M_A}{M_B} = \frac{1}{3}$

**Ex. 2** Which of the two gases, ammonia and hydrogen chloride, will diffuse faster and by what factor?

**Sol.** By Graham’s Law:

$$\frac{f_{\text{NH}_3}}{f_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} = \sqrt{\frac{36.5}{17}} = 1.46 \Rightarrow f_{\text{NH}_3} = 1.46f_{\text{HCl}}$$

Thus, ammonia will diffuse 1.46 times faster than hydrogen chloride gas.

**Ex. 3** The ratio of rate of diffusion of gases A and B is 1 : 4 and their molar mass ratio is 2 : 3. Calculate the composition of the gas mixture initially effusing out.

**Sol.** By Graham’s Law:

$$\frac{f_A}{f_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \Rightarrow \frac{1}{4} = \frac{P_A}{P_B} \sqrt{\frac{3}{2}} \Rightarrow \frac{P_A}{P_B} = \frac{1}{4} \sqrt{\frac{2}{3}}$$

$$\Rightarrow$$ Mole ratio of gas A and B effusing out = $\frac{1}{4} \sqrt{\frac{2}{3}}$ [moles $\propto$ pressure]

**Ex. 4** At 30°C and 720 mm of Hg, the density of a gas is 1.5 g/l. Calculate molecular mass of the gas. Also find the number of molecules in 1 cc of the gas at the same temperature.

**Sol.** Assuming ideal behaviour and applying ideal gas equation:

$$PV = nRT$$

Another form of gas equation is $PM_0 = dRT$

$$\Rightarrow M_0 = \frac{dRT}{T} = \frac{1.5 \times 0.0821 \times 303}{720/760}$$

(T = 30 + 273 K)

$$\Rightarrow M_0 = 39.38$$

Now number of molecules = $n \times N_0$

$$= \frac{PV \times N_0}{RT} = \frac{720/760 \times 1 \times 10^{-3}}{0.0821 \times 303} \times 6.023 \times 10^{23}$$

$$= 2.29 \times 10^{19}$$
Ex. 5 The pressure exerted by 12 gm of an ideal gas at temperature \( t^\circ C \) in a vessel of volume \( V \) litre is one atm. When the temperature is increased by 10\(^\circ\) at the same volume, the pressure rises by 10\% calculate the temperature \( t \) and volume \( V \). (molecular mass of the gas = 120 gm/mole)

Sol. Using Gas equation : \( PV = nRT \)
We have, \( P \times V = 0.1 \times R \times t \) ...(1)
and \( 1.1 \times P \times V = 0.1 \times R \times (t + 10) \) ...(2)

Using (i) and (ii), we have: \( \frac{t}{t+10} = \frac{1}{1.1} \)
\( \Rightarrow t = 100 \) k or \( t = -173^\circ C \)

Putting the value of \( t \) in (i), we get:
\( \Rightarrow 1 \times V = 0.1 \times 0.0821 \times 100 \Rightarrow V = 0.821 \) L

Ex. 6 Assuming that the air is essentially a mixture of nitrogen and oxygen in mole ratio of 4 : 1 by volume. Calculate the partial pressures of \( N_2 \) and \( O_2 \), on a day when the atmospheric pressure is 750 mm of Hg. Neglect the pressure of other gases.

Sol. From Dalton's Law of partial pressure, we have
Partial pressure of nitrogen = \( p_{N_2} = \chi_{N_2} \times P \) and Partial pressure of oxygen = \( p_{O_2} = \chi_{O_2} \times P \)

Now, \( \chi_{N_2} = 4/5 \), and \( \chi_{O_2} = 1/5 \)

\( \Rightarrow p_{N_2} = \frac{4}{5} \times 750 = 600 \text{ mm of Hg} \) and \( p_{O_2} = \frac{1}{5} \times 750 = 150 \text{ mm of Hg} \)

Ex. 7 An open vessel at \( 27^\circ C \) is heated until three fifth of the air has been expelled, Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated.

Sol. In the given questions, volume is constant. Also, as the vessel is open to atmosphere, the pressure is constant. This means that the gas equation is simply reduced to the following form:
\( nT = \text{constant} \) (Use \( PV = nRT \))
or \( n_1 T_1 = n_2 T_2 \)

Now let \( n_1 = \) initial moles and \( n_2 = \) final moles
\( \Rightarrow n_2 = 2/5 \times n_1 \) (as 3/5th of the air has been expelled)

\( \Rightarrow T_2 = \frac{n_1 T_1}{n_2} = \frac{n_1 T_1}{2/5n_1} = \frac{5}{2} T_1 \)

\( \Rightarrow T_2 = \frac{5}{2} (300) = 750 \text{ K} = 477^\circ C \)

Ex. 8 When 3.2 gm of sulphur is vaporized at 450\(^\circ\) C and 723 mm pressure, the vapour occupies a volume of 780 m, what is the formula for the sulphur under these conditions?

Sol. The molecular weight = no. of atoms \( \times \) atomic mass
So let us find the molecular weight of S from the data given.

\( M_0 = \frac{gRT}{PV} = \frac{3.2 \times 0.082 \times 723}{(723 \times 760) \times (780/1000)} = 256 \)

\( \Rightarrow \text{Number of atoms} = \frac{256}{32} = 8 \)

Hence, molecular formula of sulphur = \( S_8 \)
**Ex.9** A spherical balloon of 21 cm diameter is to be filled with \( H_2 \) at NTP from a cylinder containing the gas at 20 atm at 27°C. If the cylinder can hold 2.80L of water, calculate the number of balloons that can be filled.

**Sol.**

The capacity of cylinder = 2.80 L

Let \( n \) = moles of hydrogen contained in cylinder and \( n_0 \) = moles of hydrogen required to fill one balloon.

\[
n = \frac{PV}{RT} = \frac{20 \times 280}{0.0821 \times 300} = 2.273
\]

\[
n_0 = \frac{\text{volume of balloon}}{22400} \quad \text{(Note : the balloons are being filled at S.T.P.)}
\]

\[
= \frac{4/3 \pi r^2}{22400} = \frac{4/3 \times 3.14 \times (10.5)^3}{22400} = 0.2164
\]

\( \Rightarrow \) Number of balloons that can be filled = \( \frac{n}{n_0} = 10.50 \approx 10 \)

**Ex.10** A mixture containing 1.12L of \( H_2 \) and 1.12L of \( D_2 \) (deuterium) at S.T.P. is taken inside a bulb connected to another bulb by a stop-cock with a small opening. The second bulb is fully evacuated; the stop-cock is opened for a certain time and then closed. The first bulb is found to contain 0.05 gm of \( H_2 \). Determine the % age composition by weight of the gases in the second bulb.

**Sol.**

In the first bulb :

Initial moles of \( H_2 \) = 1.12 / 22.4 = 1/20

Initial moles of \( D_2 \) = 1.12/22.4 = 1/20

Now after opening of stop-cock, mass of \( H_2 \) left in the first bulb = 0.05

\( \Rightarrow \) Moles of \( H_2 \) = 0.05/2 = 1/40

\( \Rightarrow \) Moles of \( H_2 \) effused into second bulb = 1/20 - 1/40 = 1/40

Let \( n \) be number of moles of \( D_2 \) effused.

From Graham’s Law :

\[
\text{\( \frac{n}{1/40} = \sqrt{\frac{2}{4}} \)}
\]

\( \Rightarrow \) \( n = \frac{\sqrt{2}}{80} \) = moles of \( D_2 \) in second bulb.

In the second bulb :

The mass of \( H_2 \) gas = 1/40 \times 2 = 0.05 gm

The mass of \( D_2 \) gas = \( \sqrt{2}/80 \times 4 \) = 0.07 gm

\( \Rightarrow \) Total mass = 0.05 + 0.07 = 0.12 gm

\( \Rightarrow \) % of \( H_2 \) = 0.05/1.12 \times 100 = 41.67 %

\( \Rightarrow \) % of \( D_2 \) = 0.07/1.12 \times 100 = 58.13 %

**Ex.11** The pressure in a bulb dropped from 2000 mm to 1500 mm of Hg in 47 min when the contained \( O_2 \) leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas (B) of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of Hg was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 min.

**Sol.**

Now as \( P \propto n \) (moles), we define the rate of diffusion as the drop in the pressure per second. First we try to find the rate of diffusion of the gas B.
The rate of diffusion of $O_2 = R_o = (2000 - 1500)/47 = 10.638$ mm/min.
Assuming that gas B was present alone in the bulb. Let the rate of diffusion of $B = R_b$.
From Graham's Law of diffusion, we have:

\[
\frac{R_b}{R_o} = \sqrt{\frac{M_o}{M_b}} = \sqrt{\frac{32}{79}} = 0.636
\]

\[\Rightarrow \quad R_b = 10.638 \times 0.636 = 6.77 \text{ mm/min}
\]
Now the bulb contains mixture of $O_2$ and B in the mole ratio of 1 : 1 at total pressure of 4000 mm Hg.
\[\Rightarrow \quad P_{O_2} = P_B = 2000 \text{ mm of Hg}
\]
As the pressure and temperature conditions are same for both gases in the second case (same bulb), so the rate of diffusion will remain same in the second case also.
Let $X_o$ and $X_b$ be the final pressure in the bulb after leakage for 74 minutes.
\[R_o = \frac{2000 - X_b}{74} = 10.638
\]
\[\Rightarrow \quad X_o = 1212.78
\]
\[R_b = \frac{2000 - X_b}{74} = 6.77 \quad \Rightarrow \quad X_b = 1498.96
\]
As $P \propto n$
\[\Rightarrow \quad \text{Ratio of moles is given as: } X_o : X_b = 1 : 1235
\]

Ex.12 **A 672 ml of a mixture of oxygen-ozone at N.T.P. were found to be weigh 1 gm. Calculate the volume of ozone in the mixture.**

**Sol.** Let V ml of ozone are there in the mixture

\[\Rightarrow \quad (672 - V) \text{ ml; } = \text{ vol. of oxygen}
\]

Mass of ozone at N.T.P. = \[\frac{V}{22400} \times 48\]

Mass of oxygen at N.T.P. = \[\frac{672 - V}{22400} \times 32\]

\[\Rightarrow \quad \frac{V}{22400} \times 48 + \frac{672 - V}{22400} \times 32 = 1 \quad \Rightarrow \quad \text{On solving we get: } V = 56 \text{ ml}
\]

Ex.13 **A 20 L flask contains 4.0 gm of $O_2$ & 0.6 gm of $H_2$ at 100° C. If the contents are allowed to react to form water vapors at 100° C, find the contents of flask and there partial pressures.**

**Sol.** $H_2$ reacts with $O_2$ to form water $[H_2O_{(g)}]$

\[2H_2(g) + O_2(g) \rightarrow 2H_2O(g)\]

\[\Rightarrow \quad \text{2 moles of } H_2 = 1 \text{ mole of } O_2 = 2 \text{ moles of } H_2O
\]
Here masses of $H_2$ and $O_2$ are given, so one of them can be in excess. So first check out which of the reactants is in excess.
Now, Moles of $O_2 = 4/32 = 0.125$ and Moles of $H_2 = 0.6/2 = 0.3$
Since 1 mole of $O_2 = 2$ moles of $H_2$
\[\Rightarrow \quad 0.125 \text{ moles of } O_2 = 2 \times 0.125 \text{ moles of } H_2
\]
i.e. 0.25 moles of $H_2$ are used, so $O_2$ reacts completely whereas $H_2$ is in excess.
\[\Rightarrow \quad \text{Moles of } H_2 \text{ in excess } = 0.3 - 0.25 = 0.05 \text{ moles.}
\]
Also, 2 moles of \( \text{H}_2 = 2 \text{ moles of H}_2\text{O} \\
\Rightarrow \quad 0.25 \text{ moles of H}_2 = 0.25 \text{ moles of H}_2\text{O} \text{ are produced}.
\Rightarrow \quad \text{Total moles after the reaction} = 0.05 \text{ (moles of H}_2\text{)} + 0.25 \text{ (moles of H}_2\text{O)} = 0.3
\Rightarrow \quad \text{The total pressure } P_{\text{total}} \text{ at the end of reaction is given by} :
\begin{align*}
P_{\text{Total}} &= \frac{nRT}{V} = \frac{0.3 \times 0.0821 \times 373}{20} = 0.459 \text{ atm}
\end{align*}

Now, partial pressure of \( A = \text{ mole fraction of A } \times P_{\text{total}} \\
\Rightarrow \quad P_{\text{H}_2} = \frac{0.05}{0.3} \times 0.459 = 0.076 \text{ atm}
\Rightarrow \quad P_{\text{H}_2\text{O}} = \frac{0.25}{0.3} \times 0.459 = 0.383 \text{ atm}

**Ex.19** The compressibility factor for 1 mole of a van Waals gas at 0\(^{\circ}\)C and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecular is negligible, calculate the van der Waals constant \('a'\).

Using van der Waal’s equation of state :
\begin{align*}
\left( P + \frac{a}{V^2} \right) (V - nb) &= nRT \\
\text{Now : } V - nb &= V(\text{given})
\end{align*}

\Rightarrow \quad \text{The equation is reduced to} : \left( P + \frac{a}{V^2} \right) V = RT
\begin{align*}
Z &= \frac{PV}{RT} = \frac{V}{RT} \left( \frac{RT}{V} - \frac{a}{V^2} \right) = 1 - \frac{a}{RTV}
0.5 &= \frac{100 \times V}{0.0821 \times 273} \\
\Rightarrow & \quad V = 0.112 \text{L}
\end{align*}

Also, \( 0.5 = 1 - \frac{a}{RTV} \)

Substitute the values of \( V \) and \( T \) :
\Rightarrow \quad a = 1.25 \text{ litre}^2 \text{ mol}^{-2} \text{ atm}.

**Ex.20** Calculate the pressure exerted by 5 mole of \( \text{CO}_2 \) in one litre vessel at 47\(^{\circ}\)C using van der waals equation. Also report the pressure of gas if it behaves ideally in nature.

\( a = 3.592 \text{ atm litre}^2 \text{ mol}^{-2}, b = 0.0427 \text{ litre mol}^{-1} \)

Using van der waals equation of state :
\begin{align*}
\left( P + \frac{a}{V^2} \right) (V - nb) &= nRT
\end{align*}

Substituting the given values, we get : \left( P + \frac{3.592 \times 5^2}{t^2} \right) (1 - t \times 0.0427) = 5 \times 0.0821 \times 320
\Rightarrow \quad P = 77.218 \text{ atm}

If the gas behaves ideally, then using : \( PV = nRT \)
\Rightarrow \quad P = \frac{5 \times 0.0821 \times 320}{1} \text{ atm} = 131.36 \text{ atm}