CHAPTER 6

GASES

→ Properties of gases:

1) Gases expand to fill their containers and assume the shapes of their containers.
2) They diffuse into one another and mix in all proportions.
3) We can see a gase if it has a color.

→ Four properties determine the physical behaviour of a gas

1) Amount of the gas (mol)
2) Volume
3) Temperature
4) Pressure

→ The concept of Pressure: Pressure is defined as a force per unit.

$$P\,(Pa) = \frac{F\,(N)}{A\,(m^2)}$$

N = Newton
A = m^2

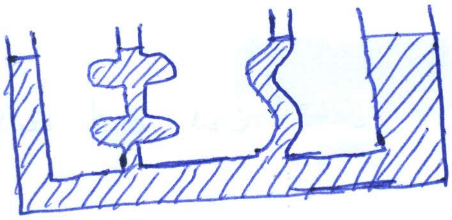
* In SI, the unit of force is a Newton and the unit of area is a m^2.

* $1\,N = 1\,kg\,m\,s^{-2}$ 1 Pascal $= 1\,N/m^2$

$$F = m \times g$$

→ Gases exert a pressure on any surface. The gases in an inflated baloon, for example, exerts a pressure on the inside surface of the baloon.

Liquid Pressure: The pressure of a gas is usually measured indirectly, by comparing it with a liquid pressure.



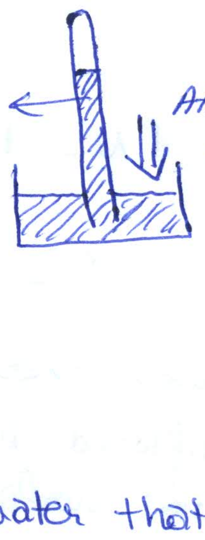
* If we fill all the containers to the same level you will determine the liquid pressures of each containers are the same. despite the different shapes and volumes.

Because the pressure of the liquid depends only on the height and the density of the liquid filling the shapes.

$$P = g \times h \times d$$

force of gravity — height — density

Barometric Pressure : Barometric pressure is the height of mercury in a barometer. The standard atmosphere (atm) is the pressure exerted by a mercury column of 760 mm in height ($d = 13.5951$ g/cm^3)



$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$$

$$1 \text{ torr} = 1 \text{ mm Hg}$$

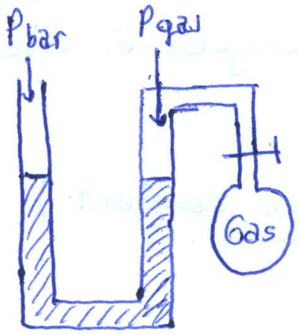
Example: What is the height of a column of water that exerts the same pressure as a column of mercury 76.00 cm height?

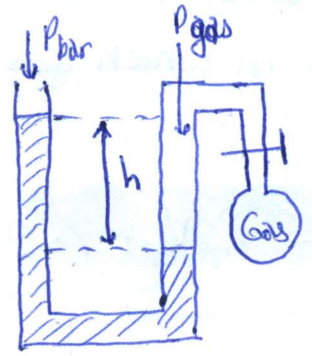
Pressure of Hg column $= g \cdot h_{Hg} \cdot d_{Hg} = g \times 76 \text{ cm} \times 13.6 \text{ g/cm}^3$

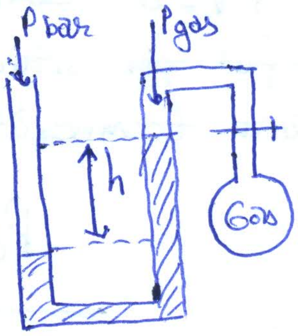
" " H_2O " $= g \cdot h_{H_2O} \cdot d_{H_2O} = g \times h_{H_2O} \times 1 \text{ g/cm}^3$

$$h_{H_2O} = 76 \text{ cm} \times \frac{13.6 \text{ g/cm}^3}{1 \text{ g/cm}^3} = 1.03 \times 10^3 = 10.3 \text{ m}$$

Manometers:







$P_{gas} = P_{bar}$

$\Delta P = 0$

$P_{gas} > P_{bar}$

$P_{gas} = P_{bar} + \Delta P$

$\Delta P = g \times h \times d > 0$

$P_{gas} < P_{bar}$

$P_{gas} = P_{bar} + \Delta P$

$\Delta P = -g \times h \times d < 0$

$$\boxed{\Delta P = P_{gas} - P_{bar}}$$

Some common pressure units:

$P = g \times h \times d$

for Hg ; $P = (1.35951 \times 10^4\ kg\,m^{-3}) \times (9.80665\,m\,s^{-2}) \times (0.760\,m)$

$= 1.01325 \times 10^5\ kg\,m^{-1}s^{-2}$

Atmosphere	atm	
mm of Hg	mmHg	1 atm = 760 mmHg
Torr	Torr	= 760 torr
Pascal	Pa	= 101.325 Pa
Kilopascal	kPa	= 101.325 kPa
Bar	bar	= 1.01325 bar
Milibar	mbar	= 1013.25 mbar

The simple gas laws:

→ Boyle's Law: For a fixed amunt of gas at a constant temp., the gas volume is inversly proportional to the gas pressure

$n, T = \text{constant} \qquad P \propto \frac{1}{V} \quad \text{or} \quad PV = a\ (\text{constant})$

$PV = a$ can be used to derive another equation that is useful for situations in which gas undergoes a change at contstant temperature

$$\underbrace{P_i V_i = P_f V_f}_{\text{Often used to relate pressure and volume changes.}} \quad (n, T \text{ are constant})$$

Charle's Law : The volume of a fixed amount of gas at constant pressure is directly proportional to the Kelvin (absolute) temperature.

$\boxed{T(K) = t(°C) + 273.15}$

$$V \propto T \quad \text{or} \quad V = bT \quad (\text{where } b \text{ is a constant})$$

The following equation can be derived by using Charle's law.

$$\left.\frac{V_i}{T_i} = \frac{V_f}{T_f}\right\} \text{Often used to relate volume and temp. changes.}$$

Example : A baloon is inflated to a volume of 2.50 L inside a house that kept a 24°C. Then it is taken outside in a very cold winter. If the temp. outside is −25°C, what will be the volume of the baloon at outside.

$$\frac{V_i}{T_i} = b = \frac{V_f}{T_f} \qquad V_f = V_i \times \frac{T_f}{T_i} = 2.5\,L \; \frac{248\,K}{297\,K} = 2.09\,L$$

* Standard Conditions of Temp. and Pressure (STP) for gases

Standard temp $0\,°C = 273.15\,K$

" pressure $1\,atm = 760\,mmHg$

at STP $\Rightarrow$ 1 mol gas $= 6.02 \times 10^{23}$ molecules

1 mol gas $= 22.4\,L$

Avogadro's Law :

1) Equal volume of different gases compared at the same temp. and pressure contain equal number of molecules.
2) Equal number of molecules of different gases compared at the same temp. and pressure occupy equal volumes.

At fixed temperature ad pressure, the volume of gas is directly proportional to the amount of gas.

$$V \propto n \quad \text{and} \quad V = c \times n \quad (T, P \text{ constant})$$

Combining the Gas Laws

Boyle	$V \propto 1/P$	These three laws can be combined in to a single equation.
Charles	$V \propto T$	
Avogadro	$V \propto n$	

The Ideal Gas Equation

: From above three laws.

$$\boxed{PV = nRT}$$

← A gas whose behaviour conforms to the ideal gas equation is called an ideal gas.

* Gas constant (R)

$$R = \frac{PV}{RT} = \frac{1\,\text{atm} \times 22.414\,\text{L}}{1\,\text{mol} \times 273.15\,\text{K}} = 0.082057 \frac{\text{L.atm}}{\text{Kmol}}$$

$$R = 8.314\ \text{J/Kmol} = 8.314\ \text{m}^3\text{Pa/Kmol} = 62.364 \frac{\text{Torr.L}}{\text{Kmol}}$$

Example: What is the volume occupied by 13.7 g $Cl_2(g)$ at 45°C and 745 mm Hg?

$$P = 745\ mmHg \times \frac{1\ atm}{760\ mmHg} = 0.98\ atm$$

$V = ?$

$$n = 13.7 g\ Cl_2 \times \frac{1\ mol\ Cl_2}{70.91\ g\ Cl_2} = 0.193\ mol\ Cl_2$$

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

$T = 45°C + 273 = 318\ K$

$$V = \frac{nRT}{P} = \frac{0.193\ \cancel{mol} \times 0.08206\ \cancel{atm}\ L\ \cancel{mol^{-1}}\ \cancel{K^{-1}} \times 318\ \cancel{K}}{0.98\ \cancel{atm}}$$

$$= 5.14\ L$$

<u>The General Gas Equation</u>: If a gas is described under two-different set of conditions, the ideal gas equation must be applied twice to an initial and final condition.

$P_iV_i = n_iRT_i \qquad P_fV_f = n_fRT_f$

$R = \frac{P_i V_i}{n_iT_i} \qquad R = \frac{P_fV_f}{n_fT_f} \Rightarrow \boxed{\frac{P_iV_i}{n_iT_i} = \frac{P_fT_f}{n_fT_f}}$

$R = R$

General Gas Equation

Applications of the Ideal Gas Equation

→ <u>Molar Mass Determination</u>:

$$PV = nRT \quad \text{and} \quad n = \frac{m}{M} \Rightarrow PV = \frac{mRT}{M} \Rightarrow \boxed{M = \frac{mRT}{PV}}$$

<u>Example</u>: A glass vessel weighs 40.1305 g when empty, it weighs 138.2410 g when filled with water at 25°C, ($d_{H_2O} = 0.9970\ g/mL$) and 40.2959 g when filled with propylene gas at 740.3 mmHg and 24.0 °C. What is the molar mass of propylene.

Mass of water $= 138.2410 g - 40.1305 g = 98.1105\ g$

Volume of " $= 98.1105\ g\ H_2O \times \frac{1\ mL\ H_2O}{0.9970\ g\ H_2O} = 98.41\ mL = 0.09841\ L$

Mass of gas $= 40.2959 g - 40.1305 g = 0.1654\ g$

$T = 24\,°C + 273.15 = 297.2\ K$

$$P = 740.3\ mmHg \times \frac{1\ atm}{760\ mmHg} = 0.9741\ atm$$

$$PV = \frac{mRT}{M} \Rightarrow M = \frac{mRT}{PV}$$

$$M = \frac{0.1654\ g \times 0.08206\ \cancel{atm}\,\cancel{L}\,mol^{-1}\cancel{K^{-1}} \times 297.2\ \cancel{K}}{0.9741\ \cancel{atm} \times 0.09841\ \cancel{L}}$$

$$= 42.08\ g\ mol^{-1}$$

→ Gas Densities

$$PV = nRT = \frac{mRT}{M} \Rightarrow \boxed{d = \frac{m}{V} = \frac{MP}{RT}}$$

* Gas density depends on the pressure and temperature.

$d_{gas} \uparrow \quad P \uparrow$

$d_{gas} \downarrow \quad T \uparrow$

* The density of a gas is directly proportional to its molar mass (M).

Example: What is the density of oxygen gas (O_2) at 298 K and 0.987 atm?

$M_{O_2} = 32.0\ g\ mol^{-1}$

$$d = \frac{m}{V} = \frac{MP}{RT} = \frac{32.00\ g\,\cancel{mol^{-1}} \times 0.987\ \cancel{atm}}{0.08206\ \cancel{atm}\ L\ \cancel{mol^{-1}}\cancel{K^{-1}} \times 298\ \cancel{K}} = 1.29\ g/L$$

Example: $2NaN_3(s) \xrightarrow{\Delta} 2Na(s) + 3N_2(g)$

If an airbag has a volume of 36 L and its to be filled with N_2 gas at a pressure of 1.15 atm at 26°C. How many grams of NaN_3 must be decomposed?

$$n = \frac{PV}{RT} = \frac{1.15\ \cancel{atm} \times 36\ \cancel{L}}{0.08206\ \cancel{L}\ \cancel{atm}\ mol^{-1}\cancel{K^{-1}} \times 293\ \cancel{K}} = 1.72\ mol\ N_2$$

$$g\ NaN_3 = 1.72\ \cancel{mol\ N_2} \times \frac{2\ \cancel{mol\ NaN_3}}{3\ \cancel{mol\ N_2}} \times \frac{65.01\ g\ NaN_3}{1\ \cancel{mol\ NaN_3}} = 74.5\ g\ NaN_3$$

Example: Zinc blend is the most importan zinc ore. Roasting of ZnS is the first step in the commercial production of Zn.

$$2ZnS(s) + 3O_2(g) \xrightarrow{\Delta} 2ZnO(s) + 3SO_2(g)$$

What volume of SO_2 forms per liter of O_2 consumed?

$T = 25\,°C$, $P = 745$ mmHg.

$$?\,L\ SO_2 = 1.00\,L\ O_2(g) \times \frac{2\,L\ SO_2(g)}{3\,L\ O_2(g)} = 0.667\,L\ SO_2(g)$$

Mixtures of Gases:

Dalton's law of partial pressures states that the total pressure of a mixture of gases is the sum of the partial pressures of the components of the mixture. For a mixture of gases, A, B, and so on,

$$P_{tot} = P_A + P_B + \cdots$$

In a gasous mixture of n_A moles of A, n_B moles of B, and so on, the volume of each gas would individually occupy at a pressure equal to P_{tot}.

$$V_A = \frac{n_A RT}{P_{tot}} \qquad V_B = \frac{n_B RT}{P_{tot}}$$

$$V_{tot} = V_A + V_B + \cdots$$

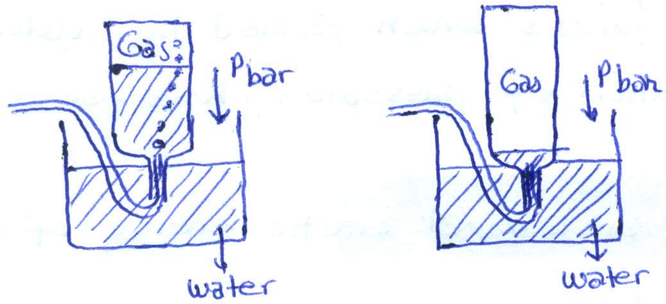
$$\text{Volume \% A} = \frac{V_A}{V_{tot}} \times 100\%, \quad \text{Volume \% B} = \frac{V_B}{V_{tot}} \times 100\%$$

$$\frac{P_A}{P_{tot}} = \frac{n_A(\cancel{RT/V_{tot}})}{n_{tot}(\cancel{RT/V_{tot}})} = \frac{n_A}{n_{tot}} \quad \text{and} \quad \frac{V_A}{V_{tot}} = \frac{n_A(\cancel{RT/P_{tot}})}{n_{tot}(\cancel{RT/P_{tot}})} = \frac{n_A}{n_{tot}}$$

$$\Downarrow$$

$$\boxed{\frac{n_A}{n_{tot}} = \frac{P_A}{P_{tot}} = \frac{V_A}{V_{tot}} = \chi_A} \rightarrow \text{Mole fraction of A gas}$$

Collecting Gas Over a Liquid:



The bottle is filled with water and its open end is hold below the water level in the container. Gas is directed in to the bottle with a gas-generating aparatus. The volume of gas collected is measured by raising or lowering the bottle until the water levels inside and outside are the same.

The total pressure inside is the sum of the pressure of gas collected an the pressure of water vapor.

$$P_{total} = P_{bar} = P_{gas} + P_{H_2O}$$

or

$$P_{gas} = P_{bar} - P_{H_2O}$$

Example: In the following rxn 81.2 mL of O_2 is collected over water at 23°C and barometric pressure is 751 mmHg. What mass of Ag_2O decomposed? (P_{H_2O} at 23°C = 21.1 mmHg)

$$2\,Ag_2O\,(s) \longrightarrow 4\,Ag\,(s) + O_2\,(g)$$

$$P_{bar} = P_{O_2} + P_{H_2O}$$

$$P_{O_2} = 751 \text{ mmHg} - 21.1 \text{ mmHg} = 730 \text{ mmHg}$$

$$P_{O_2} = 730 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.961 \text{ atm}$$

$V = 81.2 \text{ mL} = 0.0812 \text{ L}$, $T = 23°C + 273 = 296 \text{ K}$

$n = ?$

$$n = \frac{PV}{RT} = \frac{0.961 \cancel{\text{atm}} \times 0.0812 \cancel{\text{L}}}{0.08206 \cancel{\text{atm}}\,\cancel{\text{L}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}} \times 296 \cancel{\text{K}}} = 0.00321 \text{ mol}$$

$$?\text{g } Ag_2O = 0.00321 \text{ mol } O_2 \times \frac{2 \text{ mol } Ag_2O}{1 \text{ mol } O_2} \times \frac{231.7 \text{ g } Ag_2O}{1 \text{ mol } Ag_2O}$$

$$= 1.49 \text{ g } Ag_2O$$

Kinetic-Molecular Theory of Gases

In this theory, the forces which formed by molecular collisions, are important for calculation of pressure. These forces depend on several factors.

1) The amount of translational kinetic energy of molecules

$$e_k = \frac{1}{2} m u^2$$

u → speed of molecule

m → mass of molecule

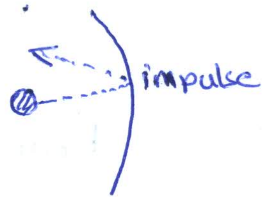
2) The frequency of molecular collisions, the number of collisions per second

collision frequency $\propto$ molecular speed $\times$ molecules per unit volume

collision frequency $\propto (u_x) \times (N/V)$

3) The momentum transfer, or impulse. Impulse is defined as the transfer of momentum when a molecule hits the wall of a vessel (as the molecule reverses its direction)

impulse $\propto$ (mass of particle) $\times$ (molecular speed)



impulse $\propto (m u_x)$

* The pressure of a gas (P) is the product of impulse and collision frequency.

$$P \propto (m u_x) \times (u_x) \times (N/V) \propto (N/V)\, m u_x^2$$

* We have to use average value of u_x^2 which is donated by $\overline{u_x^2}$ since the molecules in a gas sample travels at different speeds.

$$P \propto \frac{N}{V} m \overline{u_x^2}$$

* $\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3} \overline{u^2}$

$$P = \frac{1}{3} \frac{N}{V} m \overline{u^2}$$