Gases

- Gases consist of widely separated molecules in rapid motion
- Any two or more gases can be mixed to form a uniform mixture
- Gases can readily be compressed
- A gas expands to fill any container into which it is introduced

Substances that exist as gases

Noble gases (group 8 elements)

Hydrogen as H_2

Nitrogen as N_2

Oxygen as O_2

Fluorine as F_2

Chlorine as Cl_2

Pressure

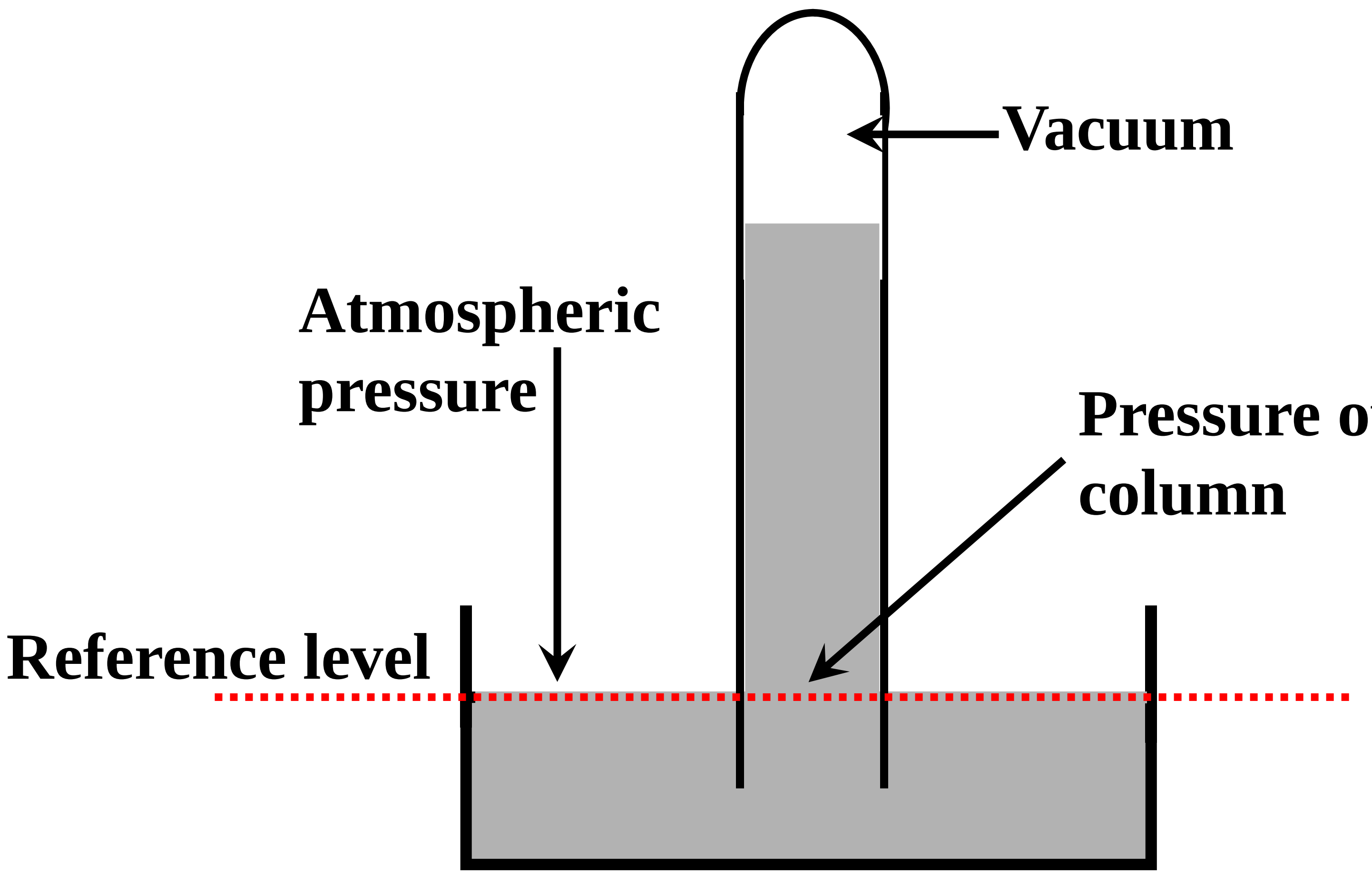
Pressure : force per unit area

$$\frac{force}{area} = \frac{kg.m.s^{-2}}{m^{2}} = kg.m^{-1}s^{-2} = pascal\,(pa)$$

Chemists usually measure gas pressures by relating them to the pressure of the atmosphere

Barometer: used to measures the atmospheric pressure

The Barometer



The average pressure at sea level supports a column of mercury to a height of 760 mm

1 atmosphere = 760 mm Hg

1 mm Hg = 1 torr

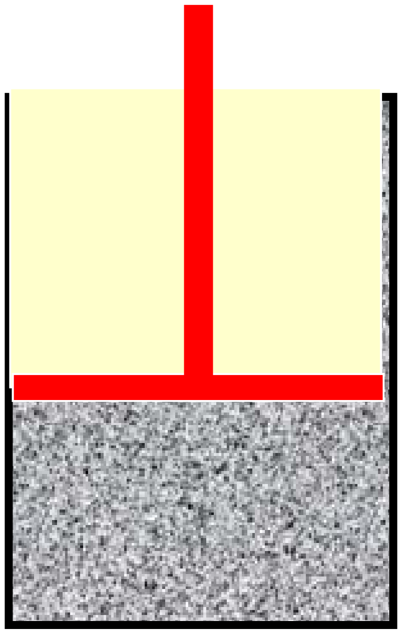
Boyle’s law

The relation between pressure, P and volume, V

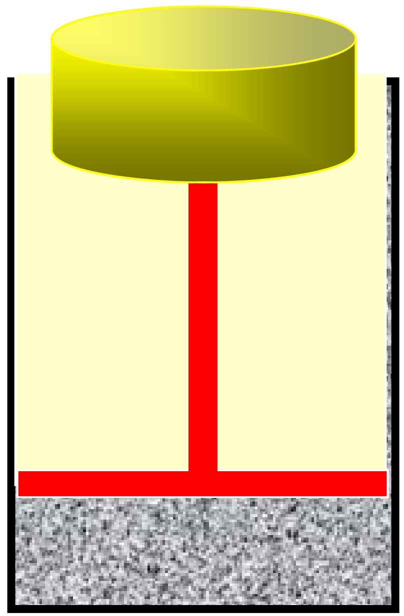
Robert Boyle 1662

At constant temperature, the volume of a sample of a gas varies inversely with the pressure

Boyle’s law



No pressure applied



Pressure applied

Boyle's law

$$V \alpha \frac{1}{P}$$

The proportionality can be changed into an equality

$$V = \frac{k}{P} \qquad \text{or} \qquad PV = k$$

This means that *PV* is always constant at constant T

$$P_1V_1 = P_2V_2 = P_3V_3 = \ldots\ldots = k$$

Example

A gas sample has a volume of 360 mL at 0.750 atm. What would be the volume if the pressure was increased to 1 atm. At constant temperature?

P_1 = 0.750 atm
V_1 = 360 mL

P_2 = 1 atm
V_2 = ?

$$P_1V_1 = P_2V_2 \Rightarrow V_2 = \frac{P_1V_1}{P_2}$$

$$V_2 = \frac{0.750\ atm \times 360\ mL}{1 atm} = 270\ mL$$

Charles law

The relation between temperature, T and volume, V

Jacques Charles, 1787

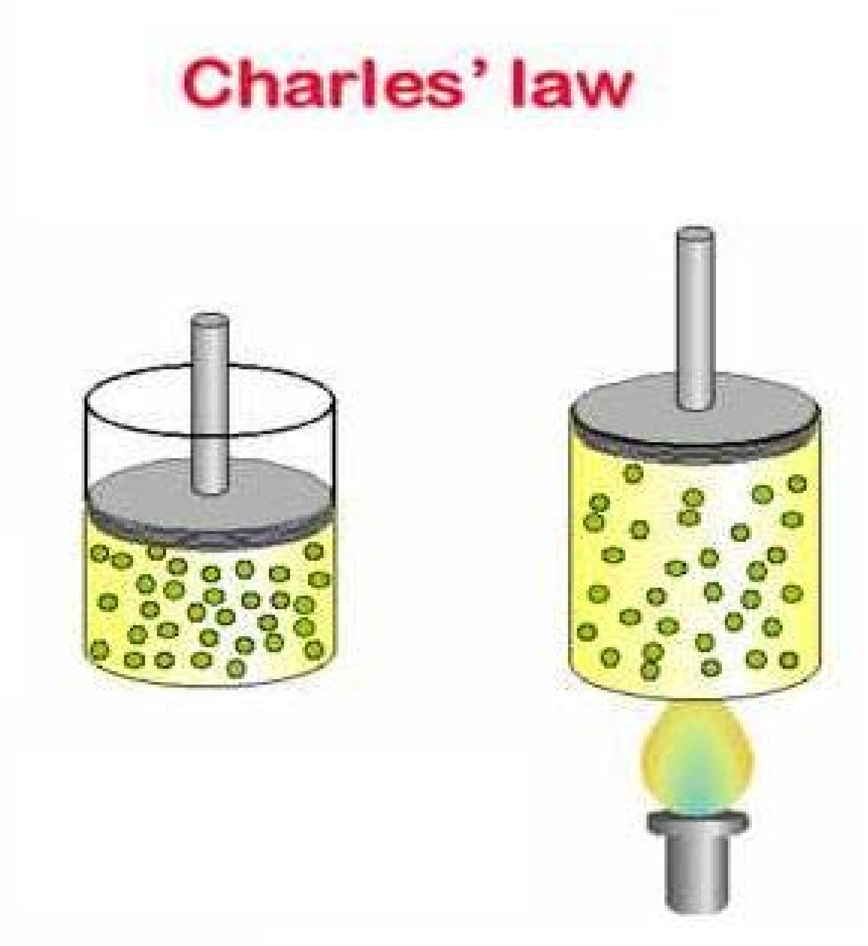
A gas expands when it is heated at constant pressure

The volume increase is not directly proportional to the Celsius temperature.

In an absolute temperature scale, with temperatures measured in Kelvin,
Volume is directly proportional to temperature

Kelvin, $T = {}^{o}C + 273$

Charles law



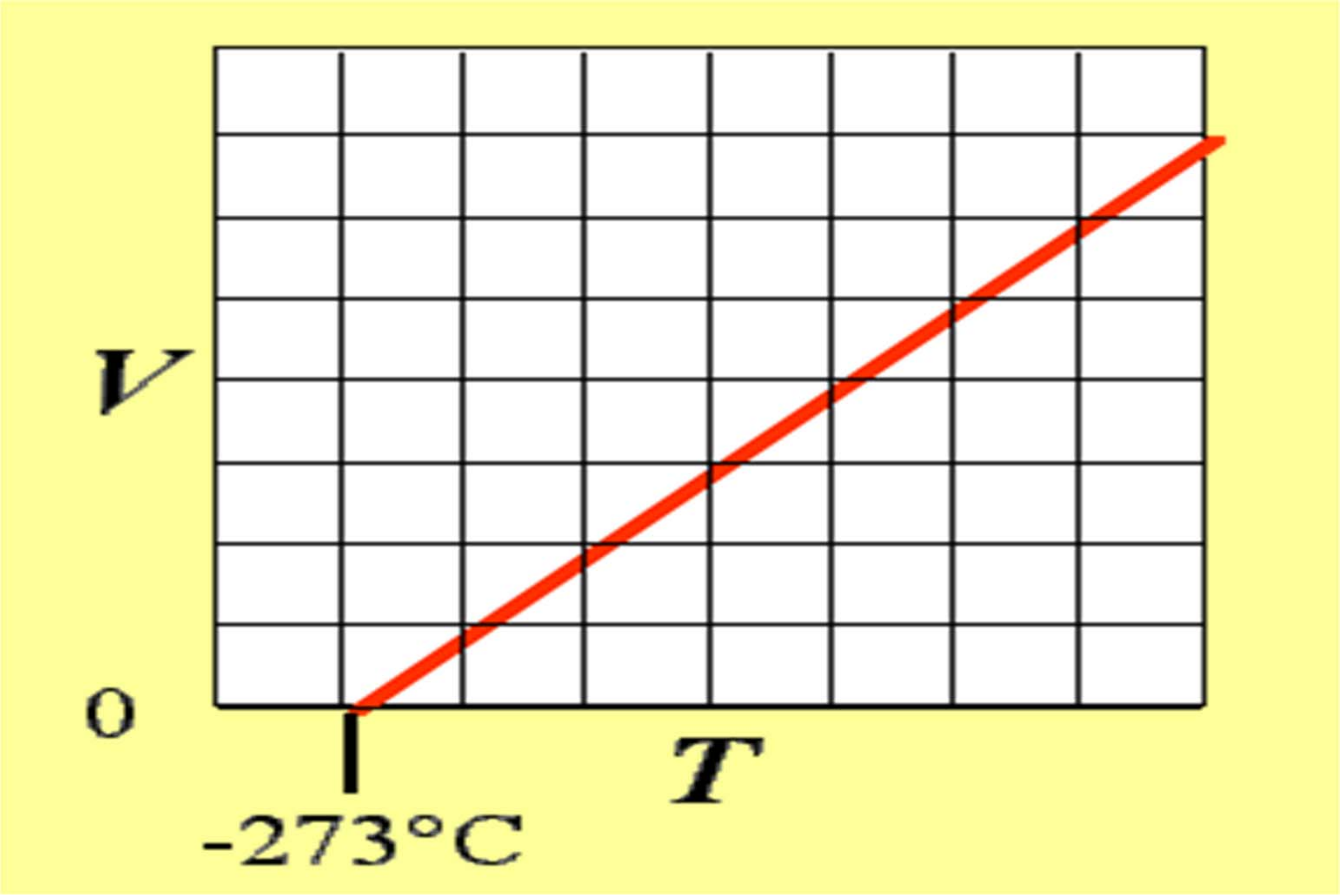
$$V \alpha T$$

The proportionality can be changed into an equality

$$V = kT \quad \text{or} \quad \frac{V}{T} = k$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \ldots. = k$$

Charles law



Charles law

Example:

A sample of gas has a volume of 2.58L at 15 ºC. What volume will the sample occupy at 38 ºC when the pressure is held constant?

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow V_2 = \frac{T_2 V_1}{T_1}$$

$$V_1 = 2.58\ L \qquad V_2 = ?$$

$$T_1 = (15 + 273)K \qquad T_2 = (38 + 273)K$$

$$V_2 = \frac{(38 + 273)2.58}{(15 + 273)} = 2.79\ L$$

Avogadro’s Law

The volume of a gas, at fixed temperature and pressure, varies directly with the number of moles of the gas considered

$$V \alpha \ n$$

The proportionality can be changed into an equality

$$V = kn \quad \text{or} \quad \frac{V}{n} = k$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = \frac{V_3}{n_3} = ... = k$$

Example:

0.50 mol of O_2 occupying 12.2L was transformed to O_3 what volume will O_3 occupy if pressure and temperature remain constant?

First write down a balanced equation

$$3O_2\ (g) \rightarrow 2O_3\ (g)$$

$$3\ mol\ O_2 = 2mol\ O_3$$

$$0.50mol\ O_2 = x\ mol\ O_3$$

$$x = \frac{0.50 \times 2}{3} = 0.33\ mol$$

Avogadro's Law

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \Rightarrow V_2 = \frac{n_2 V_1}{n_1}$$

$$V_1 = 12.2\,L \qquad V_2 = ?$$

$$n_1 = 0.5\,mol \qquad n_2 = 0.33\,mol$$

$$V_2 = \frac{0.33 \times 12.2}{0.50} = 8.1L$$

General gas law

We can combine Boyle's law with Charles law to get the relation between pressure , volume and temperature for a certain amount of a gas

$$V \alpha \frac{1}{P} \qquad\qquad V \alpha T$$

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

The proportionality can be changed into an equality

$$V = k\frac{T}{P} \Rightarrow \frac{PV}{T} = k$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = k$$

Example:

A gas sample occupies a volume of 500mL at 7.0 ^{o}C & 0.20atm. Determine the pressure when the volume is 1.0L at 107 ^{o}C.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{0.20 \times 500}{(7 + 273)} = \frac{P_2 \times 1000}{(107 + 273)} = 0.14\ atm$$

The ideal gas law

To get the relation between n, T, P, and V combine

$$V \alpha \frac{1}{P} \quad \boxed{\&} \quad V \alpha T \quad \boxed{\&} \quad V \alpha \; n$$

$$V \alpha \frac{nT}{P} \Rightarrow V = constatnt \times \frac{nT}{P}$$

$$V = \frac{nRT}{P}$$

Rearrange:

$$\boxed{PV = nRT}$$

The ideal gas law

Under normal conditions of temperature and pressure, most gases conform well with the behavior described by the equation.

Deviations occur under extreme conditions (low temperature and high pressure)

By convention:
Standard temperature and pressure STP are defined as 0 ºC (273K) and exactly 1atm pressure

The volume of 1mol of an ideal gas, from experimental measures is 22.4L

This data can be used to determine the value of R

$$P\,V = n\,R\,T \rightarrow R = PV/nT$$

P = 1atm **n = 1 mol** **T = 273 K** **V = 22.4L**

$$R = \frac{1atm \times 22.4\,L}{1mol \times 273\,K} = 0.082\ L.atm.mol^{-1}K^{-1}$$

$$R = 8.314\ \ J.K^{-1}.mol^{-1}$$

$$\boxed{PV = nRT}$$

n: number of moles = weight/molecular weight (g / M.wt)

$$PV = \frac{g}{M.wt} RT$$

Example:

A gas sample occupies a volume of 462mL at 35 ºC & 1.15atm. Determine the volume at S.T.P.

P_1= 1.15 atm	**P_2= 1 atm**
V_1= 462 mL	**V_2=?**
T_1= (35+273)K	**T_2= 273 K**

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{1.15\ atm \times 462\ mL}{308\ K} = \frac{1 atm \times V_2}{273\ K}$$

$$\boldsymbol{V_2 = 471 mL}$$

Example:

0.250 mol of nitrogen gas occupies a volume of 10.0L at 100°C. what is the pressure of nitrogen?

$\boxed{P = ?}$ $\boxed{V = 10.0L}$ $\boxed{n = 0.250 \text{ mol}}$ $\boxed{T = 373 \text{ K}}$

$$\boxed{PV = nRT}$$

$$P = \frac{0.250\ mol \times 0.082\ L.atm.mol^{-1}K^{-1} \times 373\ K}{10.0L}$$

$$P = 0.766\ atm$$

Example

What is the volume of 10.0 g of CO_2 gas at 27ºC & 2.00 atm.

$$PV = \frac{g}{M.wt} RT$$

M. Wt (CO_2) = 44.0 g/mol

$$2.00\ atm \times V = \frac{10.0\ g}{44.0\ g\ /\ mol} 0.082\ L.atm.mol^{-1}K^{-1}\ 300\ K$$

$$V = 2.80\ L$$

Example

What is the density of NH_3 gas at 100 °C & 1.15 atm?

$$density = \frac{mass}{volume} = \frac{g}{L}$$

To get the density set the volume = 1.00 L and solve for g

M.wt for NH_3 = 17.0 g/mol

$$1.15\,atm \times 1.00\,L =$$

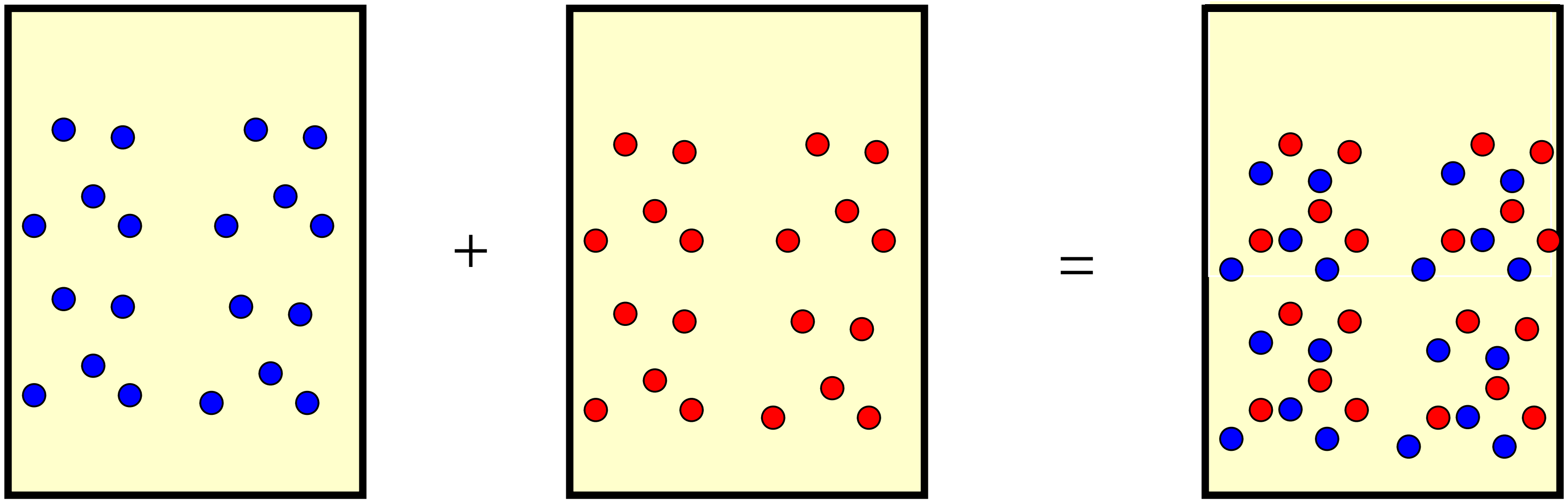
$$\frac{g}{17.0\,g\,/\,mol} \times 0.082\,\frac{L.atm}{mol.K} \times 373\,K$$

g = 0.638 The density is 0.638 g/L

Dalton's law of partial pressures

Total pressure of a mixture of gases, that do not react, is equal to the sum of the partial pressures of all the gases present.

$$P_{total} = p_A + P_B + P_C + \ldots\ldots.$$



$P_A = 0.4$ atm

$P_B = 0.5$ atm

$P_{total} =$
$p_A + P_B = 0.9$atm

If n_A mol of gas A is mixed with n_B mol of gas B

$$\mathbf{n_T = n_A + n_B}$$

$$\frac{n_A}{n_{total}} = X_A : \text{mole fraction of A}$$

$$\frac{n_B}{n_{total}} = X_B : \text{mole fraction of B}$$

For each gas apply the ideal gas law

$$P_A = \frac{n_A RT}{V} \qquad\qquad P_B = \frac{n_B RT}{V}$$

$$P_{total} = \frac{n_A RT}{V} + \frac{n_B RT}{V} = \left(n_A + n_B\right)\frac{RT}{V}$$

$$\frac{P_A}{P_{total}} = \frac{\dfrac{n_A RT}{V}}{\dfrac{n_{total} RT}{V}} = \frac{n_A}{n_{total}} = X_A$$

$$\frac{P_A}{P_{total}} = X_A \rightarrow P_A = X_A P_{total}$$

For P_B $\quad$ $\boldsymbol{P_B = X_B \times P_{total}}$

Example:

2.43 mol of N_2 gas was mixed with 3.07mol of O_2 gas in a 5.00L container at 298K.

1. **Determine the partial pressure of each gas**
2. **Determine the total pressure**

$$P_{N_2} = \frac{n_{N_2}RT}{V} = \frac{2.43 \times 0.082 \times 298}{5.00} = 11.9atm$$

$$P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{3.07 \times 0.082 \times 298}{5.00} = 15.0atm$$

$$P_{total} = P_{N_2} + P_{O_2} = 11.9 + 15.0 = 26.9atm$$

Example:

The total pressure of a mixture of 40.0g of O_2 and 40.0g of H_2 is 0.900 atm. What is the partial pressure of O_2 gas?

$$P_{O_2} = X_{O_2} P_{total} = \frac{n_{O_2}}{n_{O_2} + n_{H_2}} = \frac{\frac{40.0}{32}}{\frac{40.0}{32} + \frac{40.0}{4}} = 0.112$$

$$P_{O_2} = 0.112 \times 0.900 = 0.101 atm$$

Real gases

Deviations from ideal behavior occur under

1. **High pressures**
2. **Low temperatures**

Two reasons for the deviation:

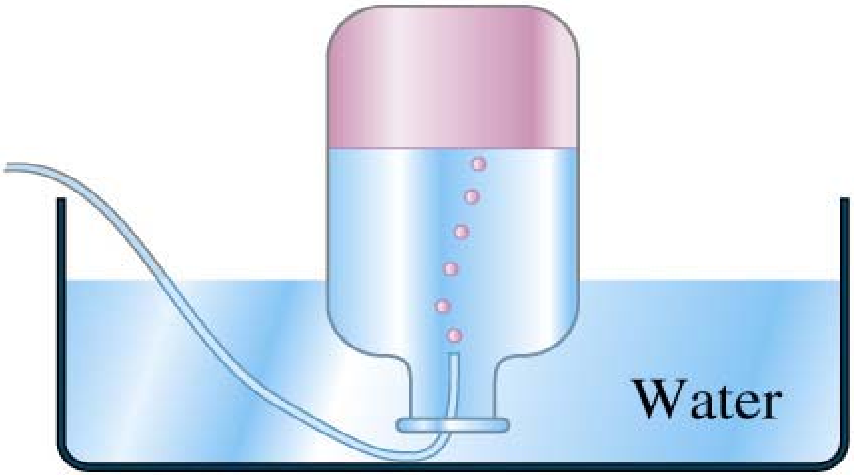
1. **Molecular volume**
2. **Intermolecular forces of attraction**

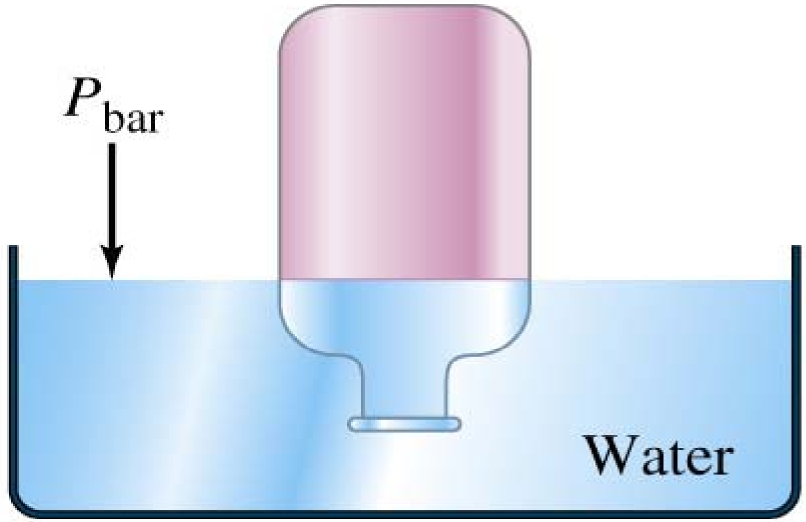
van der Waals equation

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

Solved problems

A 370 mL of O_2 gas is collected over water at 23 ºC and 0.992 atm.
what volume would this sample occupy dry and at STP?
(water vapor pressure at 23 ºC = 0.0277atm)





$$P_{total} = 0.992\,atm$$

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

$$0.992 = P_{O_2} + 0.0277 \rightarrow P_{O_2} = 0.964\,atm$$

P_1= 0.964 atm	**P_2= 1.000 atm**
V_1= 370 mL	**V_2=?**
T_1= (23+273)K	**T_2= 273 K**

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{0.964\ atm \times 370\ mL}{296\ K} = \frac{1 atm \times V_2}{273\ K}$$

$$\boldsymbol{V_2 = 329\,mL}$$

Stoichiometric problems

What is the volume of CO_2 produced from decomposition of 152g of $CaCO_3$ at 373K and 1.00 atm?

$$CaCO_3\ (s) \rightarrow CO_2\ (g) + CaO(s)$$

$$\#\text{ of moles of }CaCO_3 = \frac{152g}{100.0g/mol} = 1.52mol$$

1 mol $CaCO_3$ = 1 mol CO_2

1.52 mol $CaCO_3$ = 1.52 mol CO_2

$$\boxed{PV = nRT}$$

$$V = \frac{1.52 \times 0.0820 \times 373}{1.00} = 46.5L$$

Example

O_2(g) reacts with C_2H_6 according to the equation

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

1. What volume of O_2 is needed to react with 15.0L of C_2H_6?
2. What volume of CO_2 is produced from the reaction of 15L of C_2H_6?

2 L of C_2H_6 == 7 L O_2

15 L of C_2H_6 == X L O_2

$$X = \frac{15.0 \times 7}{2} = 52.5L$$

2 L of C_2H_6 == 4 L CO_2

15 L of C_2H_6 == X L CO_2

$$X = \frac{15.0 \times 4}{2} = 30L$$