

# Gases

## CO<sub>2</sub>

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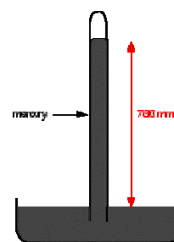
### Measurement of Gases

Gas Pressure: traditionally measured as the height to which it will raise a column of Hg in an evacuated tube

$$1 \text{ atmosphere (atm)} = 760 \text{ mm Hg} = 760 \text{ Torr}$$

In SI units  $1 \text{ atm} = 101.3 \text{ kPa}$  and  $1 \text{ bar} = 100 \text{ kPa}$

$$\therefore 1 \text{ atm} = 1.013 \text{ bar}$$



### The Ideal Gas Law

For a given quantity of gas, the volume,  $V$ , varies inversely with pressure,  $P$ , at constant temperature,  $T$

$\equiv$  Boyle's Law

that is,  $V \propto 1/P$

$$\therefore PV = \text{constant (1)}$$

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Next, at constant P, V varies linearly with T

≡ Charles' Law

that is,  $V \propto T$   $\therefore V = cT$  (where c = constant) (2)

when T is measured in degrees Kelvin (K) where  $K = ^\circ\text{C} + 273.15$

Next, at constant T and P, the volume of gas varies directly with the number of moles of gas, n

that is,  $V \propto n$   $\therefore V = Rn$  (where R = gas constant) (3)

Combining all three expressions leads to the Ideal Gas Equation:

$$PV = nRT$$

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The value of the gas constant R depends on the units of P

➤ If P is in Pascal units, and V is  $\text{m}^3$  (all proper SI units)  
use  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Note  $1 \text{ L} = 10^{-3} \text{ m}^3$

➤ If P is in atmospheres, and V is L  
use  $R = 0.0821 \text{ L-atm K}^{-1} \text{ mol}^{-1}$

➤ If P is in bar, and V is L  
use  $R = 0.0831 \text{ L-bar K}^{-1} \text{ mol}^{-1}$

T is always in Kelvin

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**Example question:**

A quantity of O<sub>2</sub> has a volume of 100.0 L at 25°C and 70.0 kPa.  
What will be the volume of this O<sub>2</sub> gas at 0°C and 1.00 bar?

For questions of this type **where the quantity of gas remains unchanged** (that is, n = constant) we recognize that for initial conditions:

$$\frac{P_1 V_1}{T_1 R} = n$$

and for the final conditions

$$\frac{P_2 V_2}{T_2 R} = n$$

Since n = n,

$$\frac{P_1 V_1}{T_1 R} = \frac{P_2 V_2}{T_2 R} \quad \therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{for constant } n$$

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We can now solve the question above.

$$P_1 = 70 \text{ kPa} = 0.7 \text{ bar}$$

$$P_2 = 1.00 \text{ bar}$$

$$T_1 = 298 \text{ K}$$

$$T_2 = 273 \text{ K}$$

$$V_1 = 100.0 \text{ L}$$

$$V_2 = ?$$

$$\therefore \frac{(0.70)(100.0)}{(298)} = \frac{(1.0)(V_2)}{(273)}$$

$$= 64.1 \text{ L}$$

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## Molar Mass and Density Calculations

The number of moles of a substance is:

$$\frac{w}{M} = \frac{(\text{mass})}{(\text{Molar mass})}$$

We can substitute this expression into the Ideal Gas Equation

$$\therefore PV = \left(\frac{w}{M}\right)RT$$

By measuring the **mass** in g, of a gas at a known P, V, and T, we can calculate its molar mass, M

≡ one of the best experimental means of **determining M for a gas**

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This equation can be rearranged to yield:

$$PM = \left(\frac{w}{V}\right)RT$$

But  $w/V = d =$  density of the gas in  $\text{g L}^{-1}$

$$\therefore \boxed{PM = dRT} \quad \text{or} \quad \boxed{\frac{PM}{RT} = d}$$

This leads to some well-known properties:

- Increasing pressure increases density (compressed He cylinders are very heavy)
- Increasing the temperature decreases density (hot air balloons rise)
- Decreasing M decreases the density

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**Example question:**

What is the density of NO<sub>2</sub> at 0°C and 740 Torr?

$$PM = dRT$$

Molar mass of NO<sub>2</sub> = 14.0 + 2x(16.0) = 46.0 g mol<sup>-1</sup>

$$\therefore \left(\frac{740}{760}\right)(46.0) = d(0.0821)(273)$$

$$d = 2.00 \text{ g L}^{-1}$$

**Example question:**

1.40 L of a gas at 27°C and 1.17 bar weighs 2.273g.  
What is its molar mass?

$$PV = \left(\frac{w}{M}\right)RT = \frac{2.27}{M}(0.0821)(300)$$

$$\therefore M = 34.5 \text{ g mol}^{-1}$$

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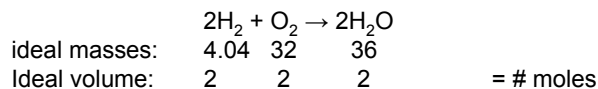
## Gases and Stoichiometry

Volume measurements can be converted to mass measurements for chemical reactions

**Example:**

What mass of H<sub>2</sub>O can be produced by the complete reaction of 1.68 L O<sub>2</sub> and 2.90 L H<sub>2</sub>, all at 25°C and 1 bar?

Begin with a balanced equation:



**Why?**  $V = n\left(\frac{RT}{P}\right) = nk$  at fixed T, P k = constant

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Determine the limiting reagent L.R.

$$\text{Ideal volume ratio: } \frac{\text{H}_2}{\text{O}_2} = \frac{2}{1} \quad \text{Actual: } \frac{\text{H}_2}{\text{O}_2} = \frac{2.90}{1.68} = \frac{1.73}{1}$$

• • L. R. = H<sub>2</sub>

$$\begin{aligned} \bullet \bullet \quad \text{mass of H}_2 \text{ consumed: } w &= \frac{\text{MPV}}{\text{RT}} = \frac{(2.02)(1)(2.90)}{(0.0821)(298)} \\ &= 0.237 \text{ g H}_2 \end{aligned}$$

Now calculate the mass of H<sub>2</sub>O produced:

$$\text{mass } \frac{\text{H}_2}{\text{H}_2\text{O}} \quad \text{Ideal: } \frac{4.04}{36.0} \quad \text{Actual: } \frac{0.237}{x}$$

$$x = 2.11 \text{ g H}_2\text{O}$$

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## Partial Pressures

Each gas in a mixture is unaffected by other gases  
(that is, each gas acts as if it were in a vacuum)

Therefore, the ideal gas applies to each single gas in a mixture as well as their total, and the **total gas pressure** is a **sum of the individual gas pressures**

$$\text{that is: } P_{\text{TOT}} = P_1 + P_2 + \dots + P_n = \sum_{i=1}^n P_i \quad = \text{Dalton's Law of Partial Pressures}$$

The **individual** pressure  $P_i$  of gas  $i$  in a **mixture of gases** is termed the **partial pressure of gas  $i$**

$$\text{For a mixture of gases, the number of moles of gas } i \text{ is } n_i = \frac{P_i V}{RT}$$

$$\text{and the total number of moles of gas is } n_{\text{TOT}} = \frac{P_{\text{TOT}} V}{RT}$$

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The **mole fraction** of gas i is  $X_i$

$$X_i = \frac{n_i}{n_{\text{TOT}}} = \frac{P_i V}{RT} \div \frac{P_{\text{TOT}} V}{RT} = \frac{P_i V}{RT} \cdot \frac{RT}{P_{\text{TOT}} V} = \frac{P_i}{P_{\text{TOT}}}$$

$$\therefore \frac{n_i}{n_{\text{TOT}}} = \frac{P_i}{P_{\text{TOT}}} = X_i \quad \text{where } X_i = \text{mole fraction of } i \text{ in a mixture}$$

Therefore, for any gas in a mixture its mole fraction ( $n_i/n_{\text{TOT}}$ ) is the same as its pressure fraction ( $P_i/P_{\text{TOT}}$ )

Note:  $\sum_i X_i = 1$

Also since  $P_i = \frac{n_i}{n_{\text{TOT}}} \cdot P_{\text{TOT}}$

$$\therefore P_i = X_i P_{\text{TOT}}$$

i.e., the partial pressure of any gas i in a mixture is equal to its mole fraction x the total pressure

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**Example:**

What is the partial pressure of  $O_2$  in 2.00 g of air in a 1 L container at  $20^\circ\text{C}$ ?

Useful information: mole % air = 21.0%  $O_2$ , 78.0%  $N_2$ , 1.00% Ar; average molar mass of air =  $29.0 \text{ g mol}^{-1}$

Total air pressure calculated from:  $P_{\text{TOT}} = \frac{n_{\text{TOT}} RT}{V}$

$$\therefore P_{\text{TOT}} = (2.00/29.0)(0.0831)(293)/(1.00) = 1.68 \text{ bar}$$

Since  $P_{O_2} = X_{O_2} P_{\text{TOT}}$  and  $X_{O_2} = \frac{21.0}{100}$

$$P_{O_2} = \left(\frac{21}{100}\right)(1.68) = 0.353 \text{ bar} = 35.3 \text{ kPa}$$

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**Example:**

The density of a mixture of  $N_2$  gas and  $Cl_2$  gas is  $1.58 \text{ g L}^{-1}$  at  $25^\circ\text{C}$  and 1 bar total pressure. What is the partial pressure of  $N_2$ ?

In this problem the correct form of  $PV = nRT$  to use is:  $P(\bar{M}) = dRT$

where  $\bar{M} = X_{N_2}M_{N_2} + X_{Cl_2}M_{Cl_2}$

In a mixture with  $n$  components:  $\bar{M} = X_1M_1 + X_2M_2 + \dots + X_nM_n$

$$\therefore \bar{M} = \frac{dRT}{P} = (1.58)(0.0831)(298)/(1.0) = 39.1 \text{ g mol}^{-1}$$

In this problem, since  $X_{N_2} + X_{Cl_2} = 1$   $\therefore X_{Cl_2} = 1 - X_{N_2}$

$$\therefore \bar{M} = X_{N_2}M_{N_2} + (1 - X_{N_2})M_{Cl_2}$$

$$\begin{aligned} \therefore 39.1 &= X_{N_2}(28.0) + (1 - X_{N_2})(70.8) \\ &= 70.8 - 42.8X_{N_2} \end{aligned}$$

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Solve for  $X_{N_2} = 0.74$

$$\therefore P_{N_2} = X_{N_2}P_{TOT} = (0.74)(1.0 \text{ bar}) = 0.74 \text{ bar}$$

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### Vapour-Liquid Equilibrium

Consider the arrangement shown to the right, filled with a liquid and say  $N_2$



Any liquid in a closed container will reach an equilibrium state where the molecules enter the liquid (condense) and leave the liquid (evaporate) at the same rate

The total pressure of the gas phase will be equal to the pressure of  $N_2$  plus the pressure caused by the gas molecules that originated from the liquid (say water)

$$P_{\text{TOT}} = P_{\text{Nitrogen}} + P_{\text{Water}}$$

The partial pressure of the water vapour is referred to as the **vapour pressure** of water.

Its value is fixed at any given temperature, and is independent of the amount of liquid or the presence of any other gases

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At higher temperatures the vapour pressure increases because more energy is given to liquid molecules, allowing them to escape into the gas phase (See Table in lab manual)

Solvents that are more volatile (lower boiling points) have higher vapour pressures

Interesting and proper definition of boiling point: the temperature at which the vapour pressure of a solvent is equal to atmospheric pressure.

Water boils at a lower temperature at higher altitudes. It is really hard to have a hot cup of tea on top of Mt. Everest!

#### Example:

Some nitrogen is collected over water at 293 K. If 500 mL of gas is collected at 101.3 kPa, what mass of  $N_2$  is present?

$P_{\text{Water}}$  at 293 K = 2.34 kPa (from data tables)

$$\begin{aligned} n_{\text{TOT}} &= \frac{P_{\text{TOT}} V}{RT} = (1.013 \text{ bar})(0.5\text{L}) / (0.0831 \text{ L}\cdot\text{bar K}^{-1} \text{ mol}^{-1})(293) \\ &= 2.08 \times 10^{-2} \text{ mol} \end{aligned}$$

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Similarly:  $n_{\text{Water}} = \frac{P_{\text{Water}} V}{RT} = (2.34 \times 10^{-2})(0.5)/(0.0831)(293) = 4.81 \times 10^{-4} \text{ mol}$

$\therefore n_{\text{N}_2} = n_{\text{TOT}} - n_{\text{Water}} = 2.08 \times 10^{-2} - 4.81 \times 10^{-4} = 2.03 \times 10^{-2} \text{ mol}$

• • #g  $\text{N}_2 = 2.03 \times 10^{-2} \text{ mol} \times 28 \text{ g mol}^{-1} = 0.57 \text{ g}$