

Dalton's Law of Partial Pressures

John Dalton was the first to form a hypothesis about the pressure one gas exerts on another in a mixture. When a gas is one of a mixture, its pressure is called a partial pressure. After experimenting with gases, he concluded that: *each gas exerts the same pressure it would if it alone were present at the same temperature.* Or in other words, the total pressure in a container is the sum of the partial pressures of the gases in the container. This statement is called Dalton's law of partial pressure.

Example: A metal tank contains three gases: oxygen, helium, and nitrogen. If the partial pressures of the three gases in the tank are 35 atm of O₂, 5 atm of N₂, and 25 atm of He, what is the total pressure inside of the tank?

Reasoning: The pressure inside the vessel consists of the partial pressure of each gas present, such that:

$$P_{total} = P_{Oxygen} + P_{nitrogen} + P_{He}.$$

This is true if **gas pressure** is the force exerted on container walls when gas particles collide with them. The force exerted on the wall is dependent on the number of collisions with the wall, such that the more particles of any type of gas will result in a greater pressure. Thus the mass of the gas particles do not matter (here's Kinetic theory again!). Rather we need to know the pressure exerted by each gas present in the container and can add these together to determine the total pressure exerted on the container.

$$P_{total} = 35 \text{ atm} + 5 \text{ atm} + 25 \text{ atm} = 65 \text{ atm}.$$

Problems(Dalton's)

- 1) Air contains oxygen, nitrogen, carbon dioxide, and trace amounts of other gases. What is the partial pressure of oxygen (P_{O_2}) at 101.30 kPa of total pressure if the partial pressures of nitrogen, carbon dioxide, and other gases are 79.10 kPa, 0.040 kPa, and 0.94 kPa, respectively?

$$P_{total} = P_{O_2} + P_{N_2} + P_{CO_2} + P_{other}$$

$$101.3 \text{ kPa} = P_{O_2} + 79.10 \text{ kPa} + 0.040 \text{ kPa} + 0.94 \text{ kPa}$$

$$\therefore \boxed{P_{O_2} = 21.22 \text{ kPa}}$$

- 2) A tank used by scuba divers has a P_{total} of 2.21×10^4 kPa. If P_{N_2} is 1.72×10^4 kPa and P_{O_2} is 4.641×10^3 kPa, what is the partial pressure of any other gases in the scuba tank (P_{other})?

$$\textcircled{1} P_{total} = P_{N_2} + P_{O_2} + P_{other}$$

$$\textcircled{2} \text{Rearrange: } P_{other} = P_{total} - P_{O_2} - P_{N_2}$$

$$= 2.21 \times 10^4 \text{ kPa} - 1.72 \times 10^4 \text{ kPa} - 4.641 \times 10^3 \text{ kPa}$$

$$\boxed{P_{other} = 2.59 \times 10^3 \text{ kPa}}$$

- 3) Determine the total pressure of a gas mixture that contains oxygen, nitrogen, and helium. The partial pressures are $P_{O_2} = 20.0 \text{ kPa}$, $P_{N_2} = 46.7 \text{ kPa}$ and $P_{He} = 26.7 \text{ kPa}$? (ans 93.4 kPa)

$$P_{\text{total}} = P_{O_2} + P_{N_2} + P_{He} = (20.0 + 46.7 + 26.7) \text{ kPa}$$

$$P_{\text{total}} = 93.4 \text{ kPa}$$

- 4) Will the partial pressure of oxygen in air on the top of Mount Everest be different from the partial pressure of oxygen in air at sea level (i.e. Will the composition of air differ depending on the altitude)? Explain.

No - the partial pressure (i.e. the pressure exerted by O_2 gas in the air) will not change with altitude. What will change will be the total pressure (P_{total}). Partial pressure really is the fraction of the total that is due to a particular gas - we'll hit this idea again in chapter 16 when we talk about mole fractions. ;

Graham's Law of Diffusion

Gas molecules travel and collide with other gases. These random collisions distribute the gas evenly throughout the room. Diffusion is the random scattering of gas molecules. All gases do not diffuse at the same rate. Fast moving molecules diffuse faster than slow moving molecules. At the same temperature molecules of large mass diffuse more slowly than molecules of small mass because they travel slower. This relationship can be shown by the following equation. If two substances are at the same temperature then their kinetic energies must be equal.

$$KE_1 = KE_2$$

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

From this equation we can see that the relative rates of diffusion of two gases under identical conditions vary inversely as the square roots of their molecular masses. This principle was formulated by Thomas Graham and is known as Graham's law.

Questions:

$$\text{slowest} \quad \text{fastest}$$

$$Cl_2 < CO_2 < N_2 < H_2O$$

1. Which of the following molecules would be travelling faster at $35^\circ C$? CO_2 N_2 H_2O Cl_2

The ones with the highest molar mass will move the ~~slowest~~! slowest ← ;

$$MM_{CO_2} = 44 \text{ g/mol} \quad MM_{Cl_2} = 70 \text{ g/mol}$$

$$MM_{N_2} = 28 \text{ g/mol}$$

$$MM_{H_2O} = 18 \text{ g/mol}$$

2. If the $KE = \frac{1}{2}mv^2$, explain why H₂O molecules with a KE = 300 kJ travel faster than SO₂ molecules with a KE = 300 kJ.

Because $KE_{H_2O} = KE_{SO_2}$, these molecules have the same KE (i.e. will hit the wall with the same force).

In order for this to occur, the lighter molecule, H₂O, will need to move faster than SO₂ due to its lower molar mass.

Problems:

3. What is the ratio of the speed of hydrogen molecules to that of oxygen molecules when both gases are at the same temperature? Remember that both elements are diatomic. (ans. ≈ 3.98)

H₂ lighter than O₂

$$\frac{\text{rate}_{H_2}}{\text{rate}_{O_2}} = \sqrt{\frac{MM_{O_2}}{MM_{H_2}}} = \sqrt{\frac{32 \text{ g/mol}}{2 \text{ g/mol}}} = \sqrt{16} = 4$$

\therefore H₂ moves 4x faster than O₂ at the same temperature

4. What is the ratio of the speed of helium atoms to the speed of radon atoms when both gases are at the same temperature? (ans. 7.45)

$MM_{He} = 4 \text{ g/mol}$ ← lighter: this rate goes on top!

$MM_{Rn} = 222 \text{ g/mol}$

$$\frac{\text{rate}_{He}}{\text{rate}_{Rn}} = \sqrt{\frac{MM_{Rn}}{MM_{He}}} = \sqrt{\frac{222 \text{ g/mol}}{4 \text{ g/mol}}} = 7.45$$

\therefore He moves 7.45x faster than Rn gas particles when at the same temperature.