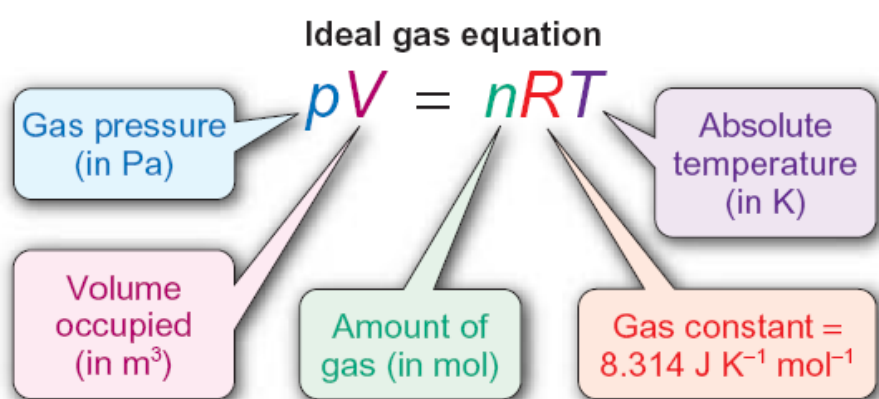


Gases

7.1 The gas laws: an empirical approach

- The three experimentally observed laws of gas behaviour can be combined to give the *ideal gas equation*.

Boyle's law $V \propto \frac{1}{p}$ constant T, n	Charles's law $V \propto T$ constant p, n	Avogadro's law $V \propto n$ constant T, p
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7.2 Using the ideal gas equation

- If any three of n, p, V , and T are known, the fourth can be calculated using the ideal gas equation $pV = nRT$.
- For a fixed amount of gas, the effect of changing the conditions can be calculated using

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

- Standard conditions for a gas at SATP (standard ambient temperature and pressure) are defined as 298.15 K (25 °C) and 1 bar.
- The molar volume, V_m , of an ideal gas at SATP is $0.0245 \text{ m}^3 \text{ mol}^{-1}$ ($24.5 \text{ dm}^3 \text{ mol}^{-1}$), although the molecules take up only a small fraction ($< 0.1\%$) of this volume.

7.3 Mixtures of gases

- Dalton's law states that the total pressure exerted by a mixture of gases is the sum of the partial pressures of each individual gas

$$p_{\text{total}} = p_A + p_B + p_C + \dots = \sum_i p_i$$

- Mole fraction of gas A in a mixture = $\frac{\text{number of moles of A}}{\text{total number of moles present}} = \frac{n_A}{n_{\text{total}}}$
- Partial pressure of gas A = $p_A = x_A p_{\text{total}}$

7.4 Kinetic molecular theory and the gas laws

- The ideal gas equation can be derived using the kinetic model of gases, making the assumptions:
 - the gas molecules have negligible size;
 - collisions are *elastic* so there is no energy loss;
 - the molecules do not interact with each other.
- Using the kinetic model of gases and these assumptions, the pressure of a gas, p , can be calculated by finding the rate of change of momentum of molecules colliding with the walls of the container

$$p = \frac{1}{3} \left(\frac{nN_A}{V} \right) mc^2$$

where m is the mass of a molecule and c is the root mean square (rms) speed. V is the volume of gas, n is the number of moles, and N_A is Avogadro's constant.

7.5 The speeds of molecules in a gas

- Gas molecules move at high speeds that depend on the temperature and their molar mass. For example, N_2 molecules at 298 K have an average speed about 500 m s^{-1} .

- The distribution of molecular speeds is described by the Maxwell–Boltzmann distribution. The maximum value in the curve represents the most probable value of the speed.
- The rate of effusion of a gas is proportional to $1/M^{1/2}$.
- Characteristic properties of molecules in a gas include:
 - the *collision cross-section*, σ , the target area presented for another molecule to collide with;
 - the *collision frequency*, Z , the number of collisions per second;
 - the *mean free path*, λ , the average distance travelled between collisions.
- Gas molecules at atmospheric pressure undergo collisions at a rate of about $1 \times 10^{10} \text{ s}^{-1}$ and have mean free paths many times larger than the size of the molecules.
- There are two different ways of representing the average speed of a molecule. (The numerical values are quite similar.)
 - The expressions for the mean kinetic energy ($\bar{E}_{\text{KE}} = \frac{1}{2} mc^2$) and for pV ($pV = \frac{1}{3} nMc^2$) depend on the average square of the molecular speeds

$$c = \left(\frac{s_1^2 + s_2^2 + \dots s_N^2}{N} \right)^{1/2} = \text{root mean square speed}$$
 - Effusion, collision frequency, and mean free path depend on the mean speed, \bar{c}

$$\bar{c} = \frac{s_1 + s_2 + \dots s_N}{N}$$

7.6 Real gases

- For many gases, the ideal gas equation describes experimental behaviour well at low pressures and high temperatures but deviations occur at high pressure and low temperatures.
- A more realistic description of gas behaviour is given by the van der Waals equation.
- The van der Waals equation is derived by introducing into the ideal gas equation terms to account for the intermolecular attractions, $a(n/V)^2$, and the finite molecular size, nb

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

Learning outcomes

By the end of this chapter you should be able to do the following.

- Describe the experimental evidence for the relation between n , p , V , and T , in the ideal gas equation.
- Use the ideal gas equation to calculate the molar volume of an ideal gas and to solve problems relating to changing the conditions of gases.
- Apply Dalton's law of partial pressures to mixtures of gases.
- Describe the assumptions underlying the kinetic theory of gases.
- Calculate the average (root mean square) speed of molecules in a gas and account for its dependence on the temperature and the molar mass of the gas.
- Explain the difference between the root mean square speed, c , and the mean speed, \bar{c} .
- Describe the Maxwell–Boltzmann distribution of molecular speeds and its dependence on the temperature and the molar mass of the gas.
- Explain what is meant by effusion and apply Graham's law.
- Calculate the frequency of collisions and mean free path between molecules in a gas.
- Account for deviations of real gases from ideal behaviour.
- Use the van der Waals equation to describe the behaviour of real gases.
- Understand the role of models in explaining the behaviour of chemical systems and the difference between an empirical approach and a theoretical approach.