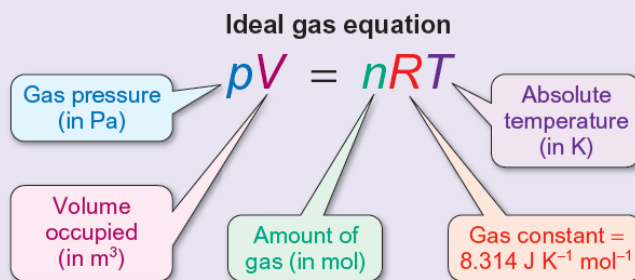# 8

Gases

8.1   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	Charles's law	Avogadro's law
$V \propto \dfrac{1}{p}$	$V \propto T$	$V \propto n$
constant T, n	constant p, n	constant T, p

Ideal gas equation

$$pV = nRT$$

Gas pressure (in Pa)

Absolute temperature (in K)

Volume occupied (in m³)

Amount of gas (in mol)

Gas constant = 8.314 J K⁻¹ mol⁻¹

8.2   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 $\dfrac{p_1 V_1}{T_1} = \dfrac{p_2 V_2}{T_2}$.

- 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 0.0248 m³ mol⁻¹ (24.8 dm³ mol⁻¹), although the molecules take up only a small fraction (<0.1%) of this volume.

? For practice questions on these topics, see questions 1, 4–9, 11 and 14 at the end of this chapter (p.378).

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8.3   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

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

- Mole fraction of gas A in a mixture $= \dfrac{\text{number of moles of A}}{\text{total number of moles present}} = \dfrac{n_A}{n_{total}}$

- Partial pressure of gas A $= p_A = x_A p_{total}$

? For practice questions on these topics, see questions 6, 7, 10 and 22 at the end of this chapter (p.378).

8.4 Kinetic molecular theory and the gas laws

- The ideal gas equation can be derived using the kinetic theory of gases, making the assumptions that:
    - 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 theory 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 amount in moles, and N_A is Avogadro's constant.

? For practice questions on these topics, see questions 25 and 26 at the end of this chapter (p.380).

8.5 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 of about $500\,ms^{-1}$.

- 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 $1/M^{1/2}$ (Graham's law).

- 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 mean number of collisions per second;
    - the *mean free path*, λ, the mean distance travelled between collisions.

- Gas molecules at atmospheric pressure undergo collisions at a rate of about $1 \times 10^{10}\,s^{-1}$ and have mean free paths many times larger than the size of the molecules.   →

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➜ • There are two different ways of representing the average speed of a molecule. (The numerical values are quite similar.)

• Root mean square (rms) speed, c. The expressions for the mean kinetic energy ($\bar{E}_{KE} = \frac{1}{2}mc^2$) and for $pV(pV = \frac{1}{3}nMc^2)$ depend on the mean square of the molecular speeds

$$c = \left(\frac{s_1^2 + s_2^2 + \cdots s_N^2}{N}\right)^{1/2} = \text{root mean square speed}$$

• Mean speed, $\bar{c}$. Effusion, collision frequency, and mean free path depend on the mean speed.

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

? For practice questions on these topics, see questions 11, 12, 15–19, 24, 25, 28–30 at the end of this chapter (p.378).

8.6 Real gases

• For many gases, the ideal gas equation describes experimental behaviour well at low pressures and high temperatures but deviations occur at high pressures 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

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

? For practice questions on this topic, see questions 21, 23, 27, 31–33 at the end of this chapter (p.378).

» Concept review

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 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.

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Key equations

The ideal gas law	$pV = nRT$	(8.5)
Partial pressures and Dalton's law	$p_{total} = p_A + p_B + p_C +$	(8.8)
	$p_A = x_A p_{total}$	(8.10)
	$x_A = \dfrac{n_A}{n_{total}}$	(8.9)
p–V relationship derived from the kinetic theory	$pV = \frac{1}{3} n N_A m c^2$	(8.13b)
Root mean square speed of gas molecules	$c = \left(\dfrac{3RT}{M}\right)^{1/2}$	(8.19)
Graham's law of effusion	Rate of effusion $\propto \dfrac{1}{M^{1/2}}$	(8.20)
Mean free path	$\lambda = \dfrac{RT}{\sqrt{2}\,N_A \sigma p}$	(8.23)
van der Waals equation	$\left(p + a\left(\dfrac{n}{2}\right)^2\right)(V - nb) = nRT$	(8.25)