Gases and the Kinetic Molecular Theory

- Importance in atmospheric phenomena, gas phase reactions, combustion engines, etc.

5.1 The Physical States of Matter

- The condensed states – liquid and solid
- The gaseous state
  - Gas volume changes greatly with pressure
  - Gas volume changes greatly with temperature
  - Gases have low viscosity (flow easily)
  - Gases have low density (~1000 times lower than liquids and solids)
  - Gases are miscible in all proportions

5.2 Pressure

- Gas molecules collide with each other and the walls of the container → molecules exert force on the walls

Pressure = \( \frac{\text{Force}}{\text{Area}} \)

\( P = \frac{F}{A} \)

- Atmospheric pressure \( (P_{\text{atm}}) \) – caused by the gravitational pull of the Earth → molecules exert force on all objects
  - Barometers - measure the atmospheric pressure (Torricelli)
  - no pressure above the mercury column (vacuum)
  - the weight of the Hg column balances \( P_{\text{atm}} \)
  - the height of the Hg column is proportional to \( P_{\text{atm}} \)

\[ P_{\text{atm}} \cdot V = m_{\text{Hg}} \cdot g \]

\[ h \text{ (Hg column)} = \frac{P_{\text{atm}}}{\rho_{\text{Hg}} \cdot g} \]

\[ \rho_{\text{Hg}} = 13546 \text{ kg/m}^3 \]

\[ P_{\text{atm}} = 13546 \times 0.760 \times 9.81 = 1.01 \times 10^5 \text{ kg/m}^2 \]

- Manometers – measure the pressure of gases in containers
  - Close-end and open-end manometers
Units of Pressure

- SI unit: pascal (Pa)
  
  \[ 1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg/m} \cdot \text{s}^2 \]

  \[ P_{\text{atm}} = 1.01 \times 10^5 \text{ Pa} \quad (\text{at sea level}) \]

- Conventional units:
  
  \begin{align*}
  \text{atm} & \rightarrow 1 \text{ atm} = 101325 \text{ Pa} \quad (\text{exactly}) \\
  \text{bar} & \rightarrow 1 \text{ bar} = 100000 \text{ Pa} \quad (\text{exactly}) \\
  \text{torr} & \rightarrow 760 \text{ Torr} = 1 \text{ atm} \quad (\text{exactly}) \\
  \text{mm Hg} & \rightarrow 1 \text{ mmHg} = 1 \text{ Torr} \\
  \text{lb/in}^2 & \rightarrow 14.7 \text{ lb/in}^2 = 1 \text{ atm}
  \end{align*}

5.3 The Gas Laws

- Relate the parameters of the gaseous state – pressure, volume, temperature, and number of moles

Boyle’s Law

- At constant temperature \( T \) the pressure \( P \) of a fixed amount of gas is inversely proportional to its volume \( V \)

\[ \Rightarrow \text{At constant } T \text{ and } n: \]

\[ P = \frac{k}{V} \quad k \rightarrow \text{constant (depends on } T \text{ and } n) \]

\[ PV = k = \text{constant} \quad V \downarrow \Leftrightarrow P \uparrow \]

- Assume two states of a gas at constant \( T \)
  - state 1 \( \rightarrow P_1, V_1 \)
  - state 2 \( \rightarrow P_2, V_2 \)

\[ P_1V_1 = k \quad P_2V_2 = k \]

\[ P_1V_1 = P_2V_2 \]

**Example:** A 2.0 L sample of oxygen at 10 atm is transferred to a 15.0 L container at constant temperature. What is the new pressure?

\[ V_1 = 2.0 \text{ L} \quad P_1 = 10 \text{ atm} \quad V_2 = 15.0 \text{ L} \quad P_2 = ? \]

\[ P_2 = \frac{P_1V_1}{V_2} = \frac{10 \text{ atm} \times 2.0 \text{ L}}{15.0 \text{ L}} = 1.3 \text{ atm} \]

Charles’s Law

- At constant pressure \( P \) the volume \( V \) of a fixed amount of gas is proportional to its absolute temperature \( T \)

\[ \Rightarrow \text{At constant } P \text{ and } n:\]

\[ \frac{V}{T} = k' \quad k' \rightarrow \text{constant (depends on } P \text{ and } n) \]

\[ T \uparrow \Leftrightarrow V \uparrow \]

- Charles’s law helped devise the absolute temperature scale (Lord Kelvin)
**Variations of Charles’s law – Amontons’s law**

- At constant volume ($V$) the pressure ($P$) of a fixed amount of gas is proportional to its absolute temperature ($T$).
  
  $P = k'' T$

  $k'' \rightarrow$ constant (depends on $V$ and $n$)

  $\frac{P}{T} = k'' \quad T \uparrow \Leftrightarrow P \uparrow$

- Assume two states of a gas at constant $V$
  
  - state 1 $\rightarrow V_1, n_1$
  - state 2 $\rightarrow V_2, n_2$

  $V_1 = k'' n_1 \quad k'' \rightarrow$ constant (depends on $T, P$)

  $\frac{V_1}{n_1} = k'' \quad \frac{V_2}{n_2} = k'' \Rightarrow \frac{V_1}{n_1} = \frac{V_2}{n_2}$

  **Example: A balloon is filled with 5.0 L He gas at 15ºC. The temperature is changed to 35ºC. What is the new volume of the balloon?**

  $T_1 = 15ºC = 288 \text{ K} \quad V_1 = 5.0 \text{ L}$

  $T_2 = 35ºC = 308 \text{ K} \quad V_2 = ?$

  $V_2 = \frac{V_1 T_2}{T_1} = \frac{5.0 \text{ L} \times 308 \text{ K}}{288 \text{ K}} = 5.3 \text{ L}$

- Assume two states of a gas at constant $P$
  
  - state 1 $\rightarrow T_1, V_1$
  - state 2 $\rightarrow T_2, V_2$

  $V_1 = k' \quad V_2 = k' \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$

  **Example: A cylinder containing N$_2$ gas at 15ºC and 50 atm is moved to a new location at 35ºC. What is the new pressure in the cylinder?**

  $T_1 = 15ºC = 288 \text{ K} \quad P_1 = 50 \text{ atm}$

  $T_2 = 35ºC = 308 \text{ K} \quad P_2 = ?$

  $P_2 = \frac{P_1 T_2}{T_1} = \frac{50 \text{ atm} \times 308 \text{ K}}{288 \text{ K}} = 53 \text{ atm}$

**Avogadro’s Law**

- At constant temperature ($T$) and pressure ($P$) the volume ($V$) of a gas is proportional to its amount ($n$)

  - At constant $T$ and $P$:
    
    $V = k''' n \quad k''' \rightarrow$ constant (depends on $T, P$)

    $\frac{V}{n} = k''' \quad n \uparrow \Leftrightarrow V \uparrow$

  - Molar volume ($V_m$) – the volume of one mole of a substance
    
    $V_m = V/n$

- Assume two states of a gas at constant $T$ and $P$
  
  - state 1 $\rightarrow V_1, n_1$
  - state 2 $\rightarrow V_2, n_2$

  $V_1 = k''' n_1 \quad k''' \rightarrow$ constant (depends on $V/n$)

  $\frac{V_1}{n_1} = k''' \quad \frac{V_2}{n_2} = k''' \Rightarrow \frac{V_1}{n_1} = \frac{V_2}{n_2}$

- Avogadro’s principle
  
  - At constant $T$ and $P$ equal number of moles of different gases occupy equal volumes
  
  - Molar volumes of gases are very similar ($V/n = \text{constant}$)

- Molar volume ($V_m$) – the volume of one mole of a substance
  
  $V_m = V/n$
The Ideal Gas Law

\[ V = k \frac{1}{P} \]  
Boyle's Law

\[ V = k'T \]  
Charles's Law

\[ V = k''n \]  
Avogadro's Law

• Combination of the three laws:

\[ V = R \frac{nT}{P} \quad R \text{– proportionality constant} \]

\[ PV = nRT \rightarrow \text{ideal gas law} \]

\[ R \rightarrow \text{universal gas constant} \]

⇒ There is no need to memorize the mathematical expression for the individual gas laws since they can all be derived from the ideal gas law

• Ideal gas – obeys the ideal gas law

• \( R \) is determined experimentally

\[ R = 0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \]

\[ R = 8.314 \text{ J/mol} \cdot \text{K} \]

• Assume two states of a gas

– state 1 \( \rightarrow P_1, V_1, n_1, T_1 \)

– state 2 \( \rightarrow P_2, V_2, n_2, T_2 \)

\[ \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} = R \quad \Rightarrow \quad \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \]

Note: \( T \) must always be in Kelvin

Example: A 5.0 L gas sample at 1.0 atm and 10ºC is moved to a 2.0 L container and heated to 300ºC. What is the new pressure?

\[ P_1 = 1.0 \text{ atm} \quad V_1 = 5.0 \text{ L} \quad T_1 = 10^\circ \text{C} = 283 \text{ K} \]

\[ P_2 = ? \quad V_2 = 2.0 \text{ L} \quad T_2 = 300^\circ \text{C} = 573 \text{ K} \]

\[ n_1 = n_2 \]

\[ \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \quad \Rightarrow \quad P_2 = \frac{P_1V_1 	imes n_2T_2}{n_1T_1 V_2} \]

\[ P_2 = \frac{P_1V_1 T_2}{V_2} = \frac{1.0 \text{ atm} \times 5.0 \text{ L} \times 573 \text{ K}}{283 \text{ K} \times 2.0 \text{ L}} = 5.1 \text{ atm} \]

Example: A 3.0 g sample of methane, CH₄, is placed in a 2.0 L container at 22ºC. What is the pressure in the container?

\[ PV = nRT \]

\[ V = 2.0 \text{ L} \quad T = 22^\circ \text{C} = 295 \text{ K} \]

moles of CH₄ (n):

\[ n = 3.0 \text{ g CH}_4 \times \left( \frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \right) = 0.19 \text{ mol CH}_4 \]

\[ P = \frac{nRT}{V} = \frac{0.19 \text{ mol} \times 0.08206 \text{ L atm/mol.K} \times 295 \text{ K}}{2.0 \text{ L}} = 2.3 \text{ atm} \]

Standard conditions

• Standard temperature and pressure (STP)

\[ P = 1 \text{ atm}; \quad T = 0^\circ \text{C} = 273.15 \text{ K} \]

• The molar volume of the ideal gas at STP

\[ V_m = \frac{V}{n} = \frac{nRT}{P} = \frac{RT}{P} \]

\[ V_m = \frac{RT}{P} = \frac{0.08206 \text{ L atm/mol.K} \times 273.15 \text{ K}}{1 \text{ atm}} = 22.41 \text{ L/mol} \]
5.4 Applications of the Ideal Gas Law

The molar mass and density of gasses

\[ \text{density} = \frac{\text{mass}}{\text{volume}} \quad \rightarrow \quad d = \frac{m}{V} \]

\[ \text{molar mass} = \frac{\text{mass}}{\text{moles}} \quad \rightarrow \quad M = \frac{m}{n} \quad \rightarrow \quad m = nM \]

\[ PV = nRT \quad \rightarrow \quad n = \frac{PV}{RT} \]

\[ d = \frac{m}{V} = \frac{nM}{RT} \quad \rightarrow \quad d = \frac{MP}{RT} \quad \rightarrow \quad M = \frac{dRT}{P} \]

- The density of a gas is proportional to its molar mass and pressure and inversely proportional to its temperature

**Example:** Calculate the density of O\(_2\) at STP.

\[ M = 32.00 \text{ g/mol} \]

\[ P = 1 \text{ atm} \quad T = 0^\circ\text{C} = 273.15 \text{ K} \quad (\text{STP}) \]

\[ d = \frac{MP}{RT} = \frac{32.00 \text{ g/mol} \times 1 \text{ atm}}{0.08206 \text{ L·atm/mol·K} \times 273.15 \text{ K}} = 1.428 \frac{\text{g}}{\text{L}} \]

- Finding the molar mass of a volatile liquid

  - Weigh a flask with a known volume
  - Fill the flask with the vapors of the volatile liquid at a known temperature and pressure
  - Cool the flask and let the vapors condense
  - Reweigh the flask to get the mass of the vapors

**Example:** Calculate the molar mass of a liquid if 0.955 g of its vapors occupy 2.50 L at 200°C and 45.0 Torr.

\[ d = \frac{m}{V} = \frac{0.955 \text{ g}}{2.50 \text{ L}} = 0.382 \text{ g/L} \]

\[ T = 200^\circ\text{C} = 473 \text{ K} \]

\[ P = 45.0 \text{ Torr} \times \frac{1 \text{ atm}}{760 \text{ Torr}} = 0.0592 \text{ atm} \]

\[ M = \frac{dRT}{P} = \frac{0.382 \text{ g/L} \times 0.08206 \text{ L·atm/mol·K} \times 473 \text{ K}}{0.0592 \text{ atm}} = 250 \frac{\text{g}}{\text{mol}} \]

Mixtures of Gasses

- Mixtures are treated just like pure gases – same gas laws apply

- **Partial pressure** of a gas in a mixture – the pressure the gas would exert if it occupied the container alone

- Dalton’s **law of partial pressures** – the total pressure \((P)\) of a gaseous mixture is the sum of the partial pressures \((P_i)\) of its components

\[ P = P_A + P_B + \ldots \quad \text{or} \quad P = \sum P_i \]

- Mole fraction \((\chi_i)\) of a gas in a mixture – a fraction of the total number of moles that belongs to that gas

\[ \chi_i = \frac{n_i}{n} = \frac{n_i}{\sum n_i} \quad \sum n_i = n \quad \sum \chi_i = 1 \]

- The sum of all mol fractions is equal to one

- The ideal gas law can be written for each gas in a mixture in terms of partial pressures

\[ P_iV = n_iRT \quad \text{or} \quad PV = nRT \]
The partial pressure of a gas is proportional to its mol fraction.

\[ P_i = \chi_i P \]

\[ \Rightarrow \text{The partial pressure of a gas is proportional to its mol fraction} \]

\[ \frac{PV}{nRT} = \frac{P}{n} = \chi \]

\[ P = \frac{nRT}{V} \]

\[ P = \frac{nRT}{V} \]

Example: Calculate the total pressure and the partial pressures of He and Ne in a 2.0 L mixture containing 1.0 g He and 2.0 g Ne at 20ºC.

grams of He and Ne → moles of He and Ne → mole fractions of He and Ne

total pressure → partial pressures

\[ 1.0 \text{ g He} \times \frac{1 \text{ mol He}}{4.00 \text{ g He}} = 0.25 \text{ mol He} \]

\[ 2.0 \text{ g Ne} \times \frac{1 \text{ mol Ne}}{20.18 \text{ g Ne}} = 0.099 \text{ mol Ne} \]

\[ \chi_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{He}} + n_{\text{Ne}}} = \frac{0.25}{0.25 + 0.099} = 0.72 \]

\[ \chi_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{He}} + n_{\text{Ne}}} = \frac{0.099}{0.25 + 0.099} = 0.28 \]

\[ n = 0.25 + 0.099 = 0.35 \text{ mol} \]

\[ PV = nRT \rightarrow P = \frac{nRT}{V} \]

\[ P_{\text{He}} = \chi_{\text{He}} P = 0.72 \times 4.2 \text{ atm} = 3.0 \text{ atm} \]

\[ P_{\text{Ne}} = \chi_{\text{Ne}} P = 0.28 \times 4.2 \text{ atm} = 1.2 \text{ atm} \]

Example: A 2.5 L sample of O₂ gas was collected over water at 26ºC and 745 torr atmospheric pressure. What is the mass of O₂ in the sample? (The vapor pressure of water at 26ºC is 25 torr.)

\[ P_{\text{oxygen}} = P_{\text{total}} - P_{\text{water}} = 745 - 25 = 720 \text{ torr} \]

\[ T = 26 + 273.15 = 299 \text{ K} \]

\[ n_{\text{O}_2} = \frac{P_{\text{O}_2}V}{RT} = \frac{720 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times 2.5 \text{ L}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}} = 0.097 \text{ mol} \]

\[ 0.097 \text{ mol O}_2 \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 3.1 \text{ g O}_2 \]
Stoichiometry and the Ideal Gas Law

• The volume ratios of gases in reactions are the same as their mole ratios (follows from Avogadro’s principle)

\[ 3 \text{H}_2(g) + \text{N}_2(g) \rightarrow 2\text{NH}_3(g) \]

⇒ 3 mol H₂ react with 1 mol N₂
⇒ 3 L H₂ react with 1 L N₂

**Example:** How many liters of N₂ are needed to react completely with 5.0 L H₂?

\[ 5.0 \text{ L H}_2 \times \left( \frac{1 \text{ L N}_2}{3 \text{ L H}_2} \right) = 1.7 \text{ L N}_2 \]

• The ideal gas law can be used to convert between the number of moles of gaseous reactants (or products) and their volumes at certain T and P

Example: Calculate the volume of CO₂ produced by the decomposition of 2.0 g CaCO₃ at 25°C and 1.0 atm.

\[ \text{CaCO}_3(s) \rightarrow \text{CaO(s)} + \text{CO}_2(g) \]

\[ 2.0 \text{ g CaCO}_3 \times \left( \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g CaCO}_3} \right) \times \left( \frac{1 \text{ mol CO}_2}{1 \text{ mol CaCO}_3} \right) = 0.020 \text{ mol CO}_2 \]

\[ V = \frac{nRT}{P} = \frac{0.020 \text{ mol} \times 0.08206 \text{ L·atm/mol·K} \times 298 \text{ K}}{1.0 \text{ atm}} = 0.49 \text{ L} \]

Example: Calculate the mass of NaN₃ needed to produce 10 L of N₂ in an air bag at 25°C and 1.0 atm by the reaction:

\[ 6\text{NaN}_3(s) + 2\text{Fe}_2\text{O}_3(s) \rightarrow 3\text{Na}_2\text{O}_2(s) + 4\text{Fe(s)} + 9\text{N}_2(g) \]

\[ T = 298 \text{ K} \quad P = 1 \text{ atm} \quad V = 10 \text{ L} \quad n = ? \]

\[ n = \frac{PV}{RT} = \frac{1 \text{ atm} \times 10 \text{ L}}{0.08206 \text{ L·atm/mol·K} \times 298 \text{ K}} = 0.41 \text{ mol} \]

\[ 0.41 \text{ mol N}_2 \left( \frac{6 \text{ mol NaN}_3}{9 \text{ mol N}_2} \right) \left( \frac{65.02 \text{ g NaN}_3}{1 \text{ mol NaN}_3} \right) = 18 \text{ g NaN}_3 \]

5.5 The Kinetic Molecular Theory

• Postulates of the Kinetic Molecular Theory
  – The gas particles are negligibly small (their volume can be neglected)
  – The gas particles are in constant, random motion and move in straight lines until they collide
  – The gas particles do not interact except during collisions. The collisions are elastic so there is no loss of energy due to friction
  – The average kinetic energy of gas particles, \( \bar{E}_k \), is proportional to the absolute temperature, T

• A molecular view of the gas laws
  – Boyle’s law \( (V \propto 1/P) \)
• A molecular view of the gas laws
  – Charles’s law ($V \propto T$)

• A molecular view of the gas laws
  – Avogadro’s law ($V \propto n$)

• Average kinetic energy of the gas particles
  $$E_k \propto T \quad \Rightarrow \quad \bar{u}^2 \propto T \quad \Rightarrow \quad \sqrt{u^2} \propto \sqrt{T}$$

  $m$ – mass of particles
  $\bar{u}^2$ – average square speed

• Root-mean-square speed of the gas particles
  $$u_{rms} = \sqrt{\bar{u}^2} \quad u_{rms} \propto \sqrt{T}$$

  $$u_{rms} = \sqrt{\frac{3RT}{M}}$$

Example: Calculate the root-mean-square speed of N$_2$ at 25°C.

$T = 25^\circ C = 298 \text{ K}$

$M = 28.02 \text{ g/mol} = 0.02802 \text{ kg/mol}$

$R = 8.314 \text{ J/mol·K}$

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{0.02802 \text{ kg mol}^{-1}}} \approx 515 \text{ m/s}$$

The Maxwell Distribution of Speeds

• Gives the fraction of particles moving at each particle speed

• Gas molecules travel with a wide range of speeds with a bell-shaped distribution

• The most probable speed, the average speed and the root-mean-square speed are very close in magnitude

• The range of speeds widens and $u_{rms}$ increases with increasing the temperature
• The range of speeds widens and $u_{rms}$ increases with decreasing the molar mass of the gas
  – Lighter gases have higher molecular speeds

$E_k = \frac{1}{2} m u^2 = \frac{1}{2} m u_{rms}^2 = \frac{1}{2} m \left( \frac{3RT}{M} \right) = \frac{m3RT}{2mN_A}$

$u_{rms} = \sqrt{\frac{3RT}{M}}$

⇒ $u_{rms}$ depends on $T$ and $M$
⇒ $E_k$ depends only on $T$
⇒ $T$ is a measure of the average kinetic energy of the molecular motion

- The meaning of temperature
- Diffusion and Effusion

**Diffusion** – gradual dispersal of one substance through another
- gases diffuse from places with high to places with low concentration

**Effusion** – escape of a substance through a small hole into vacuum
- effusion through porous materials, pin holes, cracks, etc.

**Graham’s Law** – the effusion rate ($ER$) of a gas is inversely proportional to the square root of its molar mass (same relation is valid in general for the diffusion rate)

$ER \propto \sqrt{\frac{1}{M}}$

– Can be explained with $u_{rms} = \sqrt{3RT/M}$

- The time of effusion ($t_{eff}$) is inversely proportional to $ER$

$t_{eff} \propto \frac{1}{ER} \Rightarrow t_{eff} \propto \sqrt{M}$

For two gases, A and B:

$\frac{ER(A)}{ER(B)} = \frac{M_B}{M_A}$

$t_{eff}(A) = \sqrt{\frac{M_A}{M_B}}$

$t_{eff}(B) = \sqrt{\frac{M_A}{M_B}}$

t_{eff}(O_2) = \frac{32.00 \text{ g/mol}}{2.02 \text{ g/mol}} \times 15 \text{ s} = 60 \text{ s}$

5.6 Real Gases

- Real gases deviate from ideal behavior
- Compression factor ($Z$)

$Z = PV/nRT$

- For ideal gases:

$PV = nRT \Rightarrow Z = PV/nRT = 1$

- A plot of $Z$ versus $P$ gives a straight line for ideal gases, but not for real gases
• **Negative deviations** – important at moderately high pressures \((PV/nRT < 1)\)
  – Due to attractive forces between the molecules
  – The molecules attract each other and impact the walls with a weaker force \((P\) and \(Z\) decrease)

• **Positive deviations** – important at very high pressures \((PV/nRT > 1)\)
  – Due to the actual volume of the molecules
  – The physical volume of the molecules reduces the free volume in the container, but we still use the volume of the entire container, \(V\), which is larger than the free volume \((Z\) increases)

**Van der Waals equation:**

\[
(P + \frac{an^2}{V^2})(V - nb) = nRT
\]

- \(a, b\) - van der Waals constants (zero for ideal gases)
- \(an^2/V^2\) - pressure correction \((a\) depends on the attractive forces between molecules)
- \(nb\) - volume correction \((b\) is a measure for the actual volume of the gas molecules)

• Real gases approach ideal behavior at low pressures and high temperatures (away from conditions of condensation)