Assoc. Prof. Cameron Kepert

Room: 456
Phone: 9351-5741
Email: c.kepert@chem.usyd.edu.au

Where are we going...?

5 main topics...

- **Gases**
  - Properties, molecular picture

- **Thermochemistry**
  - Fuels, environmental effects of fuel combustion

- **Equilibrium**
  - Gas phase, acid-base, solubility

- **Electrochemistry**
  - Galvanic and concentration cells

- **Intermolecular Forces**
  - Polymers, biomolecules

3 interleaving applications...

- **Nitrogen chemistry**
  - e.g. smog, explosives

- **Sources of chemicals**
  - e.g. ammonia, polymers

- **Batteries, Electrolysis**
  - e.g. corrosion, fuel cells
Boyle’s Law

The volume of a gas is inversely proportional to its pressure.
Bogles Law

\[ V \propto \frac{1}{P} \]

\[ V \_m^3 \]

\[ U \_m^3 \]

\[ \frac{1}{P} \text{ atm}^{-1} \]
Boyle’s Law

When the external pressure $P_{ext}$ increases, the gas pressure $P_{gas}$ also increases, keeping $T$ and $n$ fixed. This results in a decrease in volume, leading to more collisions and a balance where $P_{gas} = P_{ext}$.

Higher $P_{ext}$ causes lower $V$, which causes more collisions until $P_{gas} = P_{ext}$.
Charles’ Law

The volume of a gas is directly proportional to its Kelvin temperature.
Charles' Law

- $P_{\text{gas}} = P_{\text{atm}}$
- $T_1$ increases, fixed $n$
- Higher $T$ increases collision frequency: $P_{\text{gas}} > P_{\text{atm}}$
- $T_2$, $V$ increases
- $V$ increases until $P_{\text{gas}} = P_{\text{atm}}$
Avogadro’s Law

Equal volumes of gas at the same pressure and temperature contain equal numbers of molecules.
Empirical Gas Laws

Boyle’s Law:
- the volume of a gas is inversely proportional to its pressure
  \[ V = \frac{k_1}{P} \]

Charles’ Law:
- the volume of a gas is directly proportional to its Kelvin temperature
  \[ V = k_2 T \]

Avogadro’s Law:
- equal volumes of gas at the same pressure and temperature contain equal numbers of molecules
  \[ V = k_3 n \]
Ideal Gas Equation

\[ PV = nRT \]

**Universal gas constant** \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \)

(R has different values with different units – see later)
### Common Units of Pressure

<table>
<thead>
<tr>
<th>unit</th>
<th>atmospheric pressure</th>
<th>conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>pascal (Pa); kilopascal (kPa); hectopascal (hPa)</td>
<td>$1.01325 \times 10^5$ Pa; 101.325 kPa; 1013.25 hPa</td>
<td>SI unit</td>
</tr>
<tr>
<td>atmosphere</td>
<td>1 atm</td>
<td></td>
</tr>
<tr>
<td>mm mercury = torr</td>
<td>760 torr</td>
<td></td>
</tr>
<tr>
<td>pounds/sq inch (psi)</td>
<td>14.7 lb in$^{-2}$</td>
<td>only used by primitives</td>
</tr>
<tr>
<td>bar</td>
<td>1.01325 bar</td>
<td></td>
</tr>
</tbody>
</table>
R in Different Units

\[ R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \]

\[ = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1} \]

\[ = 8.314 \text{ kPa L mol}^{-1} \text{ K}^{-1} \]
1 atmosphere = 101.3 kPa

⇒ $R = \frac{8.314}{101.3}$ atm L mol$^{-1}$ K$^{-1}$

= 0.08206 atm L mol$^{-1}$ K$^{-1}$

See Table 5.3, Silberberg

<table>
<thead>
<tr>
<th>$R^*$</th>
<th>0.08206 atm$\cdot$L/mol$\cdot$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>62.36 torr$\cdot$L/mol$\cdot$K</td>
</tr>
<tr>
<td>$R$</td>
<td>8.314 kPa$\cdot$dm$^3$/mol$\cdot$K</td>
</tr>
<tr>
<td>$R$</td>
<td>8.314 J/mol$\cdot$K</td>
</tr>
</tbody>
</table>
Often made with sodium azide:

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

Example: Car Air Bags

Example: How many grams of NaN$_3$ are required to produce 75 L of nitrogen at 25 °C and 1.31 atm?

$$PV = nRT$$

$$n = \frac{P \cdot V}{R \cdot T}$$

Ratio of moles of NaN$_3$ and N$_2$ = 6/9

\[ \therefore \text{moles of NaN}_3 = \]
\[ \therefore \text{mass NaN}_3 \text{ (mol. wt. = 65.0)} = \]
Kinetic Theory of Gases

- \( V \) increases \( \Rightarrow P \) decreases
- \( T \) increases \( \Rightarrow P \) increases
Temperature Dependence

See Silberberg - Fig 5.14, page 200
Kinetic energy $E_k = \frac{1}{2} mv^2$  
$\propto T$ 
= constant at fixed $T$

Pressure $P \propto E_k = \frac{1}{2} mv^2$  
$\propto T$ 
= same for all gases

See Silberberg - Figure 5.19, page 203
Gas Behaviour at STP

**Standard Molar Volume**

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>N₂</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1 mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P = 1 atm (760 torr)</td>
<td>P = 1 atm (760 torr)</td>
<td>P = 1 atm (760 torr)</td>
<td></td>
</tr>
<tr>
<td>T = 0°C (273 K)</td>
<td>T = 0°C (273 K)</td>
<td>T = 0°C (273 K)</td>
<td></td>
</tr>
<tr>
<td>V = 22.4 L</td>
<td>V = 22.4 L</td>
<td>V = 22.4 L</td>
<td></td>
</tr>
<tr>
<td>Number of gas particles</td>
<td>= $6.022 \times 10^{23}$</td>
<td>= $6.022 \times 10^{23}$</td>
<td>= $6.022 \times 10^{23}$</td>
</tr>
<tr>
<td>Mass = 4.003 g</td>
<td>Mass = 28.02 g</td>
<td>Mass = 32.00 g</td>
<td></td>
</tr>
<tr>
<td>$d = 0.179$ g/L</td>
<td>$d = 1.25$ g/L</td>
<td>$d = 1.43$ g/L</td>
<td></td>
</tr>
</tbody>
</table>
Gases have low densities because the molecules are far apart.

For example:

- $N_2(g)$ at 20 °C, $\rho = 1.25 \text{ g/L}$
- $N_2(l)$ at -196 °C, $\rho = 0.808 \text{ g/mL}$
- $N_2(s)$ at -210 °C, $\rho = 1.03 \text{ g/mL}$

The density of the liquid is 100-1000 times greater than the gas state.

The density of the solid is usually ~10% greater than the liquid.
Example

Find the density of oxygen gas at 25 °C and 0.85 atm

Density \( (\rho) = \frac{m}{V} = \frac{M \, n}{V} \)

\( M = \) Molar mass

So \( \rho = \frac{M \, P}{RT} \) (from \( PV = nRT \))
Implications of \( PV = nRT \)

- **Boyle’s Law**: \( PV = \text{constant for constant temperature} \)
- **Charles’ Law**: \( V/T = \text{constant for constant pressure} \)
- **Lowest temperature**: -273 °C (ie \( V = 0 \) at this temperature)
- **Gay-Lussac**: (combining volumes)
- **Avogadro’s hypothesis**: (equal volumes of gas have the same number of molecules)
- **Avogadro’s constant**: \( N_A = \# \text{molecules/mol} = 6.02 \times 10^{23} \text{ mol}^{-1} \)
- **Dalton’s law** of partial pressures (see later)

Diverse observations from single unifying theory: one of the goals of science!
Pressure arises from the force experienced on vessel wall by gas molecules bouncing off it

- momentum of gas molecule = mass \times velocity = mv
- change in momentum from bouncing off wall: \Delta p = 2mv
PV = nRT from Kinetic Theory

no. collisions/second with wall = \( \frac{1}{2} N v L^2 \)

half molecules moving towards wall

no. molecules / unit volume

area of wall

time increment \( \Delta t = 1/(\text{no. collisions/second}) \)

force = \( \frac{d(mv)}{dt} = \frac{\text{change in momentum}}{\text{time increment}} \)

= \( 2m v \times \frac{1}{2} N v L^2 \)

pressure = \( \frac{\text{force}}{\text{area}} = m v^2 N \)

\( \frac{N}{V} = \text{no. moles} \times \frac{N_A}{V} \)

no. molecules/unit volume = \( n \frac{N_A}{V} \)

Area

Momentum in change

Moment of force

Force pressure
Define temperature $T \propto$ average energy $= \frac{1}{2} mv^2$ by

$$T = N_A m v^2 / R$$

(Defines absolute temperature scale in terms of molecular energy)

Learn equation, not derivation.