Gases, Liquids and Solids III

Silberberg 2nd Ed, Chapter 5
www.chem.usyd.edu.au/hpage3.htm (login “chem”, passwd “chem@usyd”)
Any questions or requests - email to c.kepert@chem.usyd.edu.au
Molecular Speed

Relative number of molecules with given speed

O₂ (32)
N₂ (28)
H₂O (18)
He (4)
H₂ (2)

Speeds of Different Molecules

Kinetic energy \( E_k = \frac{1}{2} m v^2 \)
\( \propto T \)
= constant at fixed T

Pressure \( P \)
\( \propto E_k = \frac{1}{2} m v^2 \)
\( \propto T \)
= same for all molecules
Effusion and Diffusion
Graham’s Law

Rate of gas effusion/diffusion $\propto \frac{1}{\sqrt{\text{molar mass}}}$

**Reason:** diffusion is at constant energy $= \frac{1}{2} m v^2$
If $\frac{1}{2} m v^2$ is constant, then velocity $v \propto \frac{1}{\sqrt{m}}$

Diffusion time $\propto 1/\text{velocity} \propto \sqrt{\text{molar mass}}$
Distribution of Molecular Speeds

See Silberberg - Fig 5.14, page 200
Definition of Temperature

The Kinetic Theory of Gases *assumes* that temperature is proportional to the average kinetic energy of the gas.

**Approximate derivation from Friday’s lecture:**

\[ PV = n N_A m v^2 \]

\[ T = N_A m v^2 / R \]

**Better derivation, allowing molecules to travel in all three directions:**

\[ PV = n N_A m v^2 / 3 \]

\[ T = N_A m v^2 / 3R = 2 N_A E_k / 3R \]

\( E_k = 1/2 m v^2 = \text{kinetic energy} \)

**Ideal gas thermometer:** use gas that behaves ideally to measure T from observed volume and pressure using \( PV = nRT \).
PV = nRT is an equation of state - it provides the relation between variables in a given state.

The Ideal Gas Law is based on the Kinetic Theory of Gases, which approximates molecules as tiny hard particles with no interaction.

ideal gas model  ➔ gases cannot be condensed
ideal gas model  ➔ V = 0 at T = 0
Real Gases – Deviations From Ideality

A breakdown of ideal gas assumptions arises because of
INTERMOLECULAR FORCES

Long-range attractive forces *(these enable gases to liquefy):*
- dipole-dipole
- hydrogen bonding
- dispersion

Short-range repulsive force *(non-zero size of molecules):*
- from Pauli Principle (cannot push molecules on top of each other, or they would have same quantum numbers)
Look at compression ratio \( \frac{pV}{nRT} \) as a function of pressure.

\[
\frac{pV}{nRT} = 1 \quad \text{for an ideal gas}
\]
compression ratio
PV/nRT

CO₂ 300 K

Ideal Gas
Size of Non-Ideal Effects

Deviation from ideality depends on the following:

- **type of molecule** (strength of intermolecular forces): He has weakest forces, more polarizable molecules such as CO$_2$ have larger ones.

- **temperature** (high T $\Rightarrow$ molecules move so fast they do not “see” intermolecular forces).

- **pressure** (all gases are ideal at sufficiently low pressures).
The Behaviour of Real (Non-Ideal) Gases

Diagram showing the relationship between PV/RT and P_ext for different gases such as H2, He, CO2, and CH4. The diagram illustrates the deviation from ideal gas behavior with increasing pressure. The key points are:

- For PV/RT > 1, the effect of molecular volume predominates.
- For PV/RT < 1, the effect of intermolecular attractions predominates.
Intermolecular forces lessen the force of impact with the wall - real pressure is *lower*

\[ P = P_{\text{ideal}} - a \left( \frac{n}{V} \right)^2 \]
Correcting for Repulsive Forces

\[ V = V_{\text{ideal}} + nb \]
Non-Ideal Gas Equations of State: 
*The van der Waals Equation*

**Ideal:**

\[ P \times V = nRT \]

**Non-Ideal:**

\[
\left( P + \frac{n^2a}{V^2} \right) \times (V - nb) = nRT
\]

- Corrects for long range attraction
- Corrects for short range repulsion (finite volume of molecules)
Experimentally-Derived Parameters

\[ \left( P + \frac{n^2a}{V^2} \right) \times (V - nb) = nRT \]

<table>
<thead>
<tr>
<th>Gas</th>
<th>( a \left( \text{atm} \cdot \text{L}^2/\text{mol}^2 \right) )</th>
<th>( b \left( \text{L}/\text{mol} \right) )</th>
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</table>

\( a \) -

\( b \) -
Example

• Find the ideal and real (van der Waals) pressure of 1.00 mol of CO$_2$ occupying 1.32 L at 48.0 °C.
The van der Waals Equation has problems:

- e.g., value of \(b\) for He > \(b\) for Ne, wrong way round (Ne bigger than He!)

### Virial Equation of State

- Better: “Virial” (= “force”) equation

\[
\frac{PV}{nRT} = 1 + B \frac{n}{V} + C \left( \frac{n}{V} \right)^2
\]

- \(B, C\) are \(T\)-dependent
- Can be calculated from knowledge of intermolecular forces
- First to do this: an Australian, John Barker (1969)