Gases, Liquids and Solids

Silberberg 2nd Ed, Chapter 5

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Speeds of Different Molecules

- Kinetic energy $E_k = \frac{1}{2}mv^2 = \text{constant at fixed } T$
- Pressure $P = \frac{1}{2}mv^2 = \text{same for all molecules}$

Relative number of molecules with given speed

Molecular Speed

- $O_2 (32)$
- $N_2 (28)$
- $H_2O (18)$
- $He (4)$
- $H_2 (2)$

Effusion and Diffusion

- EFFUSION
- DIFFUSION

Distribution of Molecular Speeds

- See Silberberg - Fig 5.14, page 200

Graham’s Law

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

Reason: diffusion is at constant energy $= \frac{1}{2}mv^2$
If $\frac{1}{2}mv^2$ is constant, then velocity $v \propto \sqrt{\frac{1}{m}}$
Diffusion time $\propto 1/velocity \propto \sqrt{\text{molar mass}}$

Deviation from the Ideal Gas Law

$PV = nRT$ 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 $\rightarrow$ gases cannot be condensed
ideal gas model $\rightarrow$ $V = 0$ 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 liquify):
  - 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)

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:
  $PV = nN_A \frac{m}{3} v^2 = \frac{n}{N_A} m \frac{v^2}{R}$

- Better derivation, allowing molecules to travel in all three directions:
  $PV = nN_A \frac{m}{3} v^2 / 3 = \frac{2N_A}{3} E_k / 3R$
  ($E_k = \frac{1}{2}m v^2 = \text{kinetic energy}$)

ideal gas thermometer: use gas that behaves ideally to measure $T$ from observed volume and pressure using $PV = nRT$.

To Monitor the Deviation...

Look at compression ratio of pressure $\frac{pv}{nRT}$ as a function
**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 CO₂ have larger ones
- **temperature** (high T → molecules move so fast they do not “see” intermolecular forces)
- **pressure** (all gases are ideal at sufficiently low pressures)

**Correcting for Attractive Forces**

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**

\[ V = V_{\text{ideal}} + nb \]

**Experimentally-Derived Parameters**

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>a [atm \cdot L^2 mol^{-2}]</th>
<th>b [L mol]</th>
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<td>Ne</td>
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</table>

**Example**

- Find the ideal and real (van der Waals) pressure of 1.00 mol of CO₂ occupying 1.32 L at 48.0 °C.

**Virial Equation of State**

The van der Waals Equation has problems:
- e.g., value of b for He > b for Ne, wrong way round (Ne bigger than He!)

\[ \frac{PV}{nRT} = 1 + \frac{nB}{V} + \frac{n^2C}{V^2} \]

- Better: “Virial” (= “force”) equation
- B, C are T-dependent
- Can be calculated from knowledge of intermolecular forces
- first to do this: an Australian, John Barker (1969)