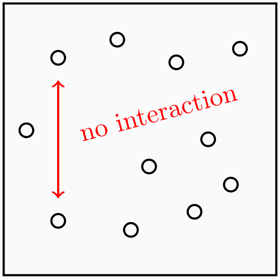
Lecture 10: Real Gases

Compressibility Diagram, van der Waals

Ideal Gases

- Particles in an ideal gas do not interact with eachother
- Ideal Gas Law ($PV = nRT$) is an Equation of State: Equation that describes the relationship between state variables
- State Variable - depend only on the current state of the system, not the path to get there
  - Examples: Pressure (P), Volume (V), Temperature (T), mols of gas (n)
- Ideal Gas law is very accurate, $< 1\%$ error at STP



Intensive vs Extensive Variables

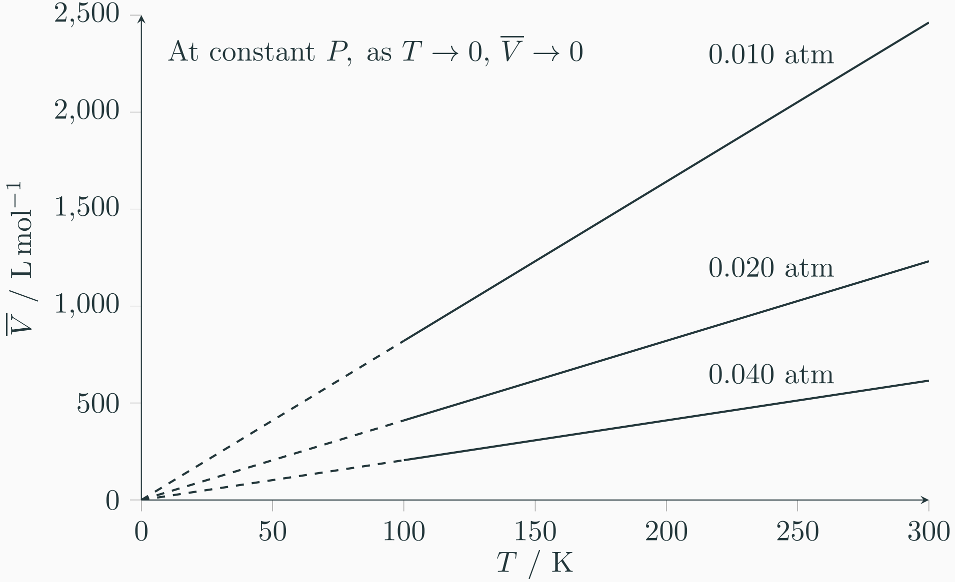
Extensive

- $P{\color{red}V} = nRT$
- Proportional to size/amount of material in the system
- Examples: Volume, mass, energy

Intensive

- $P{\color{red}\overline{V}} = RT$
- Does not depend on size/amount of material in system
- Examples: Pressure, temperature, density

Considering some limits of $P\overline{V} = RT$



Considering some limits of $P\overline{V} = RT$

At constant T, $P\overline{V} = \text{constant}$

$$P\overline{V} = RT \implies R = \frac{P\overline{V}}{T}$$

Using standard values:

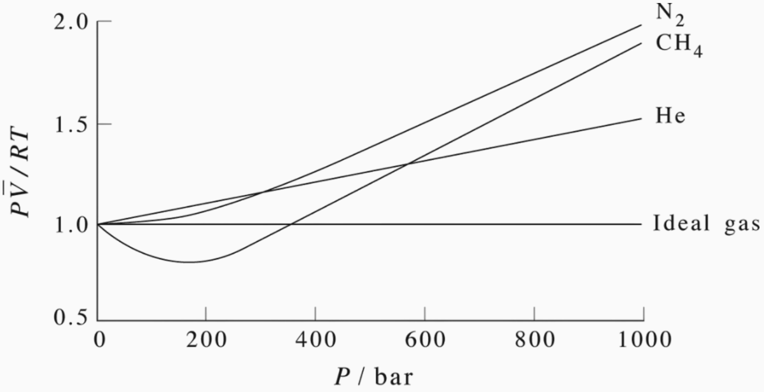
$$P = 1 \text{ atm} \qquad \boxed{\overline{V} = 22.4 \text{ L/mol}} \qquad T = 273.15 \text{ K}$$

$$\begin{aligned} R &= \frac{(1 \text{ atm})(22.4 \text{ L/mol})}{273.15 \text{ K}} \\ &= \boxed{0.0821 \ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}} \\ &= \boxed{8.314 \ \frac{\text{J}}{\text{mol} \cdot \text{K}}} \end{aligned}$$

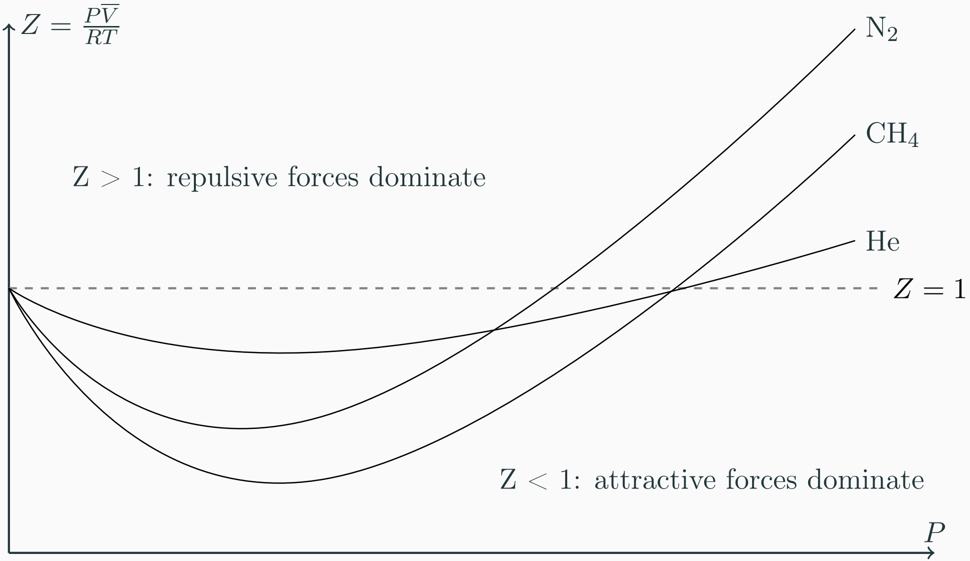
Compressibility Factor

Ideal gas works great at low/moderate pressures

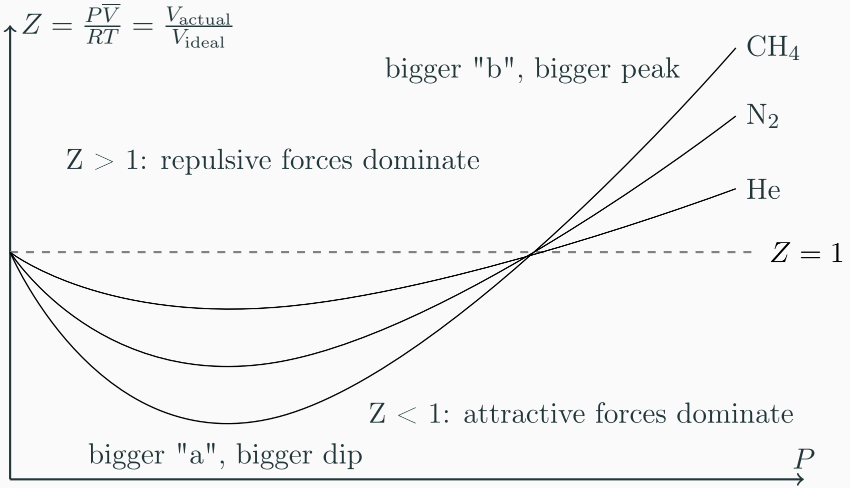
Deviations occur as pressure increases, visualize by plotting compressibility $Z = \frac{P\overline{V}}{RT}$



Compressibility Factor



Compressibility Factor



Low Pressure: $Z < 1, V_{\text{actual}} < V_{\text{ideal}}$ since attraction reduces volume

High Pressure: $Z > 1, V_{\text{actual}} > V_{\text{ideal}}$ since repulsive forces particles apart

Van der Waals Equation

$$\left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT$$

vdw Parameters

- a: correction for intermolecular forces (attractive)
  - Relative strength of IMFs:
    - Hydrogen bonding: H bonded to F, O, N, more bonding = stronger
    - Dipole–Dipole: has net dipole, more EN difference = stronger
    - London Dispersion: always present, more polarizability = stronger
  - $a \uparrow \quad \text{IMF} \uparrow \quad V_{\text{actual}} \downarrow \quad Z \downarrow$
- b: correction for molecular size (repulsion)
  - Molecular size: more atoms = larger molecule size
  - Atomic radius: increases down and left
  - $b \uparrow \quad \text{size} \uparrow \quad V_{\text{actual}} \uparrow \quad Z \uparrow$

Compressibility Factor Z for van der Waals Gas

Recall our definitions:

$$Z = \frac{P\overline{V}}{RT} \qquad P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

Substitute in:

$$Z = \frac{\left(\frac{RT}{\overline{V}-b} - \frac{a}{\overline{V}^2}\right)\overline{V}}{RT} = \boxed{\frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}}}$$

Cubic Form of van der Waals Equation

$$\left(P + \frac{a}{\overline{V}^2}\right)(\overline{V} - b) = RT$$

Expand out:

$$P\overline{V} - Pb + \frac{a}{\overline{V}} - \frac{ab}{\overline{V}^2} = RT$$

Multiply through by $\overline{V}^2$:

$$P\overline{V}^3 - (Pb + RT)\overline{V}^2 + a\overline{V} - ab = 0$$

This cubic form is important for analyzing phase diagrams!

Other Equations of State

- **van der Waals:**

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

- **Redlich-Kwong:**

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}(\overline{V} + b)T^{1/2}}$$

- **Peng-Robinson:**

$$P = \frac{RT}{\overline{V} - \beta} - \frac{\alpha}{\overline{V}(\overline{V} + \beta) + \beta(\overline{V} - \beta)}$$

Other Equations of State