Real Gases

• The gas laws we obtained from experiments performed under normal conditions of temperature and pressure
  – Therefore we can usually use the ideal gas law
• Under more extreme conditions we get deviations from the ideal gas law

Compressibility factor

• One way to measure the deviation from ideal behaviour is to define a compressibility factor $Z$ as:
  \[ Z = \frac{PV}{nRT} \]

• For an ideal gas $Z=1$

Compressibility factor

• Different gases deviate from ideal behaviour in different ways
• Deviation can be positive ($Z>1$) or negative ($Z<1$)
• Deviation always positive at sufficiently high pressure
Compressibility factor
• The compressibility factor is an empirical (experimental) predictor of real gas behaviour but doesn’t tell us anything about WHY?

Van der Waal Equation
• This is an attempt to correct the assumptions of the kinetic theory of gases for real gas behaviour, and to modify the ideal gas equation to account for it.
• We will judge its success by its ability to explain the shapes of the compressibility factor curves.

Van der Waal Equation
• Assumption 2 of the kinetic theory:
  - Molecules occupy very little volume (most of the container is free space)
  - What if we allow them to have a volume (say $b \text{ L mol}^{-1}$)
  - The molecules then have less volume in which to move so
    $$V_{\text{real}} = V_{\text{measured}} - nb$$
Van der Waal Equation

\[ V_{\text{real}} = V_{\text{measured}} - nb \]

Substitute this into the ideal gas law

\[ PV = nRT \quad \rightarrow \quad P(V-nb) = nRT \]

To get in the compressibility factor form

\[ Z = \frac{PV}{nRT} = 1 + \frac{bP}{RT} \]

A plot of \( Z \) against \( P \) would be a straight line of intercept 1

This equation fits \( H_2 \) and the high pressure end well but not all gases at all pressures

Van der Waal Equation

\[ Z = \frac{PV}{nRT} = 1 + \frac{bP}{RT} \]

Assumption 4 of the kinetic theory:

- There are no forces between the molecules
- What if we allow for van der Waal forces to exist between molecules.
- These have two effects
  1. The number of collisions with the walls goes down
  2. The force that each collision makes with the wall goes down
Van der Waal Equation

Thus the observed pressure will be less than expected for an ideal gas.

This decrease will depend on \((n/V)^2\), one \(n/V\) for the number of collisions and one for the force of each collision.

\[
P_{\text{measured}} = P_{\text{ideal}} - a \left(\frac{n}{V}\right)^2 \quad \text{so} \quad P_{\text{ideal}} = P_{\text{measured}} + a \left(\frac{n}{V}\right)^2
\]

Van der Waal Equation

Combining this pressure term into the previous equation:

\[
P(V-nb) = nRT
\]

we obtain van der Waal’s equation

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

Van der Waal Equation

Expressing as compressibility:

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

\[
Z = \frac{PV}{nRT} - \frac{V}{V-nb} \left(\frac{an}{RTV}\right)
\]
Van der Waal Equation

\[ Z = \frac{PV}{nRT} = \frac{V}{V - nb} \left( \frac{a}{RTV} \right) \]

- If “a” and “b” are zero, Z=1
- Neglecting “a” for a minute, if b is non-zero the first term and Z is greater than 1
- Neglecting “b”, if a is non-zero Z is less than 1
- The first term is responsible for positive deviations, the second for negative deviations from ideal behaviour.

Van der Waal Equation

• Summary
  - Positive deviations are due to the molecules having finite size and is quantified by the “b” factor
  - Negative deviations are due to the molecules having intermolecular forces and is quantified by the “a” factor

Van der Waal Constants

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Forces a L^2 atm mol^{-2}</th>
<th>Size b L mol^{-1}</th>
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</thead>
<tbody>
<tr>
<td>He</td>
<td>0.034</td>
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<td>H₂</td>
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<td>0.0266</td>
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<td>Cl₂</td>
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<td>0.0564</td>
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<tr>
<td></td>
<td>Variation of a factor of 200</td>
<td>Variation of a factor of &lt;3</td>
</tr>
</tbody>
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