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 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

\[ PV = nRT \quad \text{becomes} \quad P(V-nb) = nRT \]

To get in the compressibility factor form

\[ PV = nRT + Pnb \]

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

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

Van der Waal Equation

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

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

• 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 \( \frac{n}{V} \)^2, one \( \frac{n}{V} \) 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:

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

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

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

\[ Z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{an}{RTV} \]

- 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.

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>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.034</td>
<td>0.0237</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.244</td>
<td>0.0266</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>6.49</td>
<td>0.0564</td>
</tr>
</tbody>
</table>

Variation of $a$ factor of 200

Variation of $b$ factor of <3