Real Gases

Molecular Interactions
- Compression factor
- Virial coefficients
- Condensation
- Critical Constants

van der Waals Equations

Corresponding States
Real gases have very different behavior from ideal gases, notably in cases of high pressure or near the condensation point - a number of additional interactions must be considered.

Molecular Interactions

Repulsive forces:
- assist expansion of gas
- significant when molecules are close to one another
- operative at high pressures, when molecules near a single molecular diameter

Attractive forces:
- assist compression of gas
- can have influence over a long distance (close but not touching)
- operative at moderate pressures

Compression Factor

The compression factor of a gas can be defined as:

\[ Z = \frac{pV_m}{RT} \]

where \( V_m \) is the molar volume, \( V/n \).

**Ideal gas: Z = 1**
Departure from \( Z = 1 \) means that a gas is not behaving as an ideal gas.

**Intermediate Pressure: Z < 1**
Compression is favored, due to dominance of attractive forces.

**High Pressure: Z > 1**
Expansion is favored, as repulsive forces come into play.

Important Question

How do we go about representing this real (i.e. non-ideal) behavior in a logical manner?

**Empirical Models**
Use parameters, set out in a logical manner, to fit experimental data

**Semi-empirical Models**
Similar to empirical, but add a "theoretical component"

**Theoretical Models**
Virial Coefficients

For a real gas with large molar volumes and higher temperatures, the isotherms are almost identical to those of an ideal gas. However, there are some small differences which suggest that the perfect gas law is only the first term in a power series:

\[ pV_m = RT \left( 1 + B' p + C' p^2 + \ldots \right) \]

These are the virial equations of state, where coefficients B and C have to be evaluated at each temperature!

- **p = 0**: Close to ideal gas law, but not exact
- **p increases**: B contributes, linear relation between Z and p
- **p higher**: C and higher order terms contribute, deviation from linearity

\[ pV_m = RT \left( 1 + B V_m + C V_m^2 + \ldots \right) \]

Virial Coefficients for Methane

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>B' (x 10⁻³ bar⁻¹)</th>
<th>C' (x 10⁻⁶ bar⁻²)</th>
<th>D' (x 10⁻⁹ bar⁻³)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>-2.349</td>
<td>-0.877</td>
<td>29</td>
</tr>
<tr>
<td>25</td>
<td>-1.727</td>
<td>+0.438</td>
<td>17</td>
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<tr>
<td>50</td>
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<tr>
<td>300</td>
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<td>+0.583</td>
<td>0.31</td>
</tr>
<tr>
<td>350</td>
<td>+0.186</td>
<td>+0.461</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Boyle Temperature

Perfect gas: \( \frac{dZ}{dp} = 0 \) (since \( Z = 1 \)), but in a real gas:

\[ \frac{dZ}{dp} = -B' + 2pC' + \ldots \rightarrow B' \text{ as } p \rightarrow 0 \]

\[ \frac{dZ}{d(V_m^{-1})} \rightarrow B \text{ as } V_m \rightarrow \infty \text{ or } p \rightarrow 0 \]

At low T: initial \( \frac{dZ}{dp} < 0 \), B is negative
At high T: initial \( \frac{dZ}{dp} > 0 \), B is positive
(Correspond to the first order B coefficients at these temperatures)

The temperature at which the initial slope is zero is the Boyle Temperature, \( T_B \), where \( B = 0 \) (real gas corresponds to an ideal gas)
A Compression/Condensation Experiment

Increase $p$

CO$_2$ Compression and Condensation

A: $p$ rises, in accordance with Boyle's law
B: deviations from ideal gas behavior
CDE: piston moves without any pressure increase at all - non-ideal behavior
This line: vapor pressure (liq-gas equilibrium)

A liquid appears, just to the left of C, amount of liquid increases moving from C to D to E
Pressure does not increase, since the gas is beginning to condense.
E: sample is almost entirely liquid

Even a small volume reduction (E to F) requires an immense increase in applied pressure from the piston
Critical Behavior: The 31.04°C Isotherm for CO₂

If compression takes place at the so-called critical temperature, \( T_c \), the surface separating the gas and liquid phase does not appear, and the horizontal parts of the isotherm merge at the critical point. A liquid phase does not form above the critical temperature.

The critical temperature, molar volume, and pressure, \( T_c \), \( V_c \), and \( p_c \), are called the critical constants, which are unique to each substance.

Certain substances have a very dense phase which can fill an entire volume at \( T > T_c \) and these are referred to as supercritical fluids.
Johannes Diderik van der Waals (1837-1923), a Dutch physicist, won the 1910 Nobel Prize in Physics for his work on the equation of state for gases and liquids.

His formulation is a semi-empirical model, which means it is based upon experimental observations, combined with a rigorous thermodynamic treatment.

### van der Waals Equation

The van der Waals equation is written as

\[ p = \frac{nRT}{V - nb} - \frac{an}{V^2} \]

where \( a \) and \( b \) are van der Waals coefficients, specific to each gas.

Term \( a \) is adjusted to represent the attractive forces of the molecules, without giving any specific physical origin to these forces;

\( V - nb \), not \( V \), now represents the volume in which molecules can move.

### Justifying the van der Waals Equation

The coefficients \( a \) and \( b \) are adjusted to model certain features of the gas behavior, and are dependent upon the attractive and repulsive forces between molecules in the gas.

\( V - nb \): \( nb \) is the very small approximate volume occupied by the molecules themselves.

The frequency and forces of the collisions are both reduced by attractive forces, by a strength proportional to \( n/V \) (molar concentration); thus, pressure is reduced as the square of this concentration, and this contribution is written as:

\[-a(n/V)^2: \text{\( a \) is a positive proportionality constant}\]

The parameters \( a \) and \( b \) should not be assigned specific molecular properties, but rather, serve as coefficients which help to accurately model gas behavior, and can be assigned specifically to each type of gas.
Reliability of the van der Waals Equation

It is unrealistic to expect that such a simple equation will be a perfect equation of state for all gaseous substances.

- van der Waals equation:
analytical expression, allows for some general observations on real gases

- virial equation:
many accurate measurements at many temperatures, and numerical analysis

Compare these calculated isotherms with the experimental isotherms of CO₂: the most notable anomaly are the so-called van der Waal’s loops, where the isotherms drop suddenly below Tc (they suggest increase p results in increased V) - they can be fixed by a Maxwell construction (see text) - and the vdW coefficients are found by comparison of experimental and theoretical curves.

Summary of the van der Waals Equation

(1) Perfect gas isotherms are obtained at high temperatures and large molar volumes:
- at high T, the first term may be much greater than the second
- if Vₘ is high, then Vₘ - b ≈ Vₘ and p = RT/Vₘ

(2) Liquids and gases exist when cohesive and dispersive forces are balanced:
- first term from KE and repulsion, second term from attraction

(3) Critical constants are related to the van der Waals coefficients:
- for T < Tc, calculated isotherms oscillate, passing through a minimum followed by a maximum, converging as T approaches Tc
- at the flat inflection, the 1st and 2nd derivatives are zero!

\[ p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \]

Solve using some algebra and find critical constants:

\[ V_c = \frac{3b}{p_c} \quad \frac{p_c}{RT} = \frac{3}{8} \]
Principle of Corresponding States

In many areas of science it is useful to compare a fundamental property of different objects on a relative scale for purposes of comparison.

For different gases, we use **reduced variables**:

\[
\begin{align*}
p_r &= \frac{p}{p_c} \\
V_r &= \frac{V}{V_c} \\
T_r &= \frac{T}{T_c}
\end{align*}
\]

The observation that real gases at the same reduced \(V\) and reduced \(T\) exert the same reduced pressure is the **principle of corresponding states**.