Real Gases

Sections 1.4-1.6 (Atkins 6th Ed.), 1.3-1.5 (Atkins 7-9th Eds.)

Molecular Interactions
> **Compression factor**
> **Virial coefficients**
> **Condensation**
> **Critical Constants**

Van der Waals Equation

Corresponding States

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

Last updated: Sept. 14, 2012, slight modification slide 1.
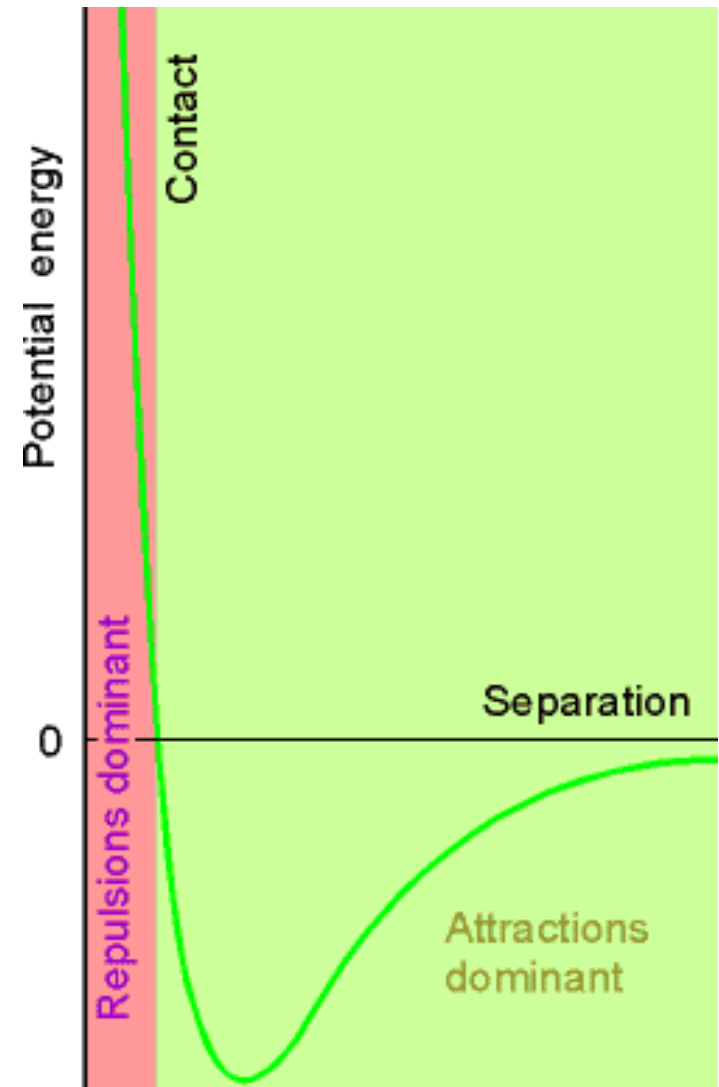
Molecular Interactions

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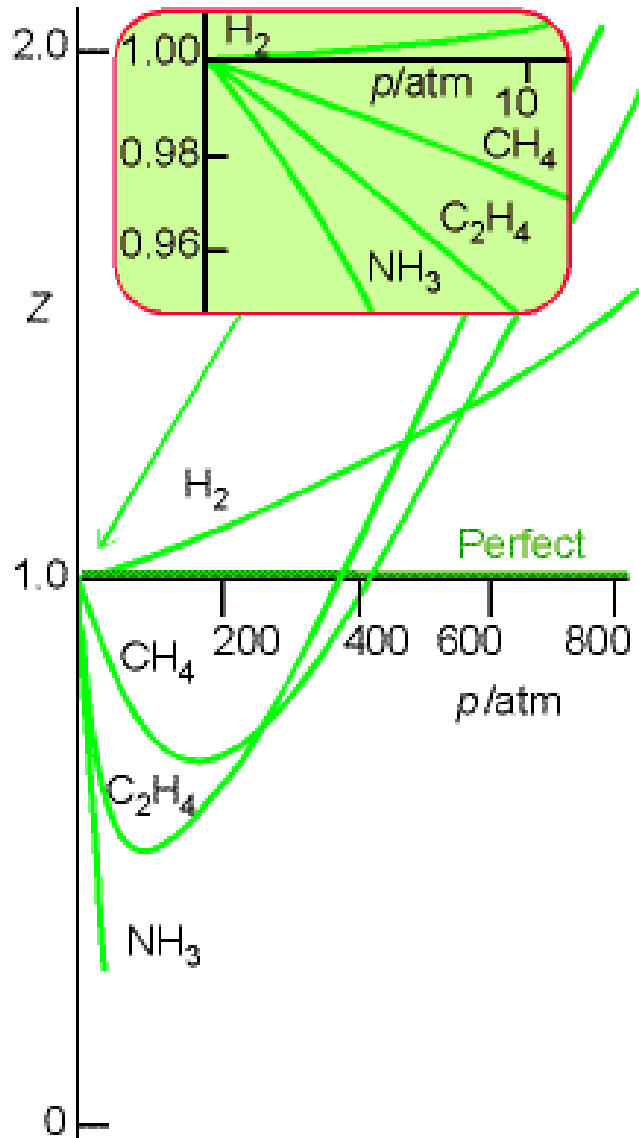- operative at high pressures, when intermolecular distances are near a single molecular diameter

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 favoured, due to dominance of attractive forces

High Pressure: Z > 1
Expansion is favoured, as repulsive forces come into play

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**:

$$pV_m = RT(1 + B'p + C'p^2 + ...) = RT(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ...)$$

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

Virial: comes from that Latin word *vis*, *viris*, meaning force - the coefficients in the **virial equation** depend on the forces of interaction between molecules of the gas

Boyle Temperature

Perfect gas: $dZ/dp = 0$ (since $Z = 1$), but in a real gas

$$\frac{dZ}{dp} = B' + 2pC' + \ldots \to B' \text{ as } p \to 0$$

$$\frac{dZ}{d(1/V_m)} \to B \text{ as } V_m \to \infty, \text{ or } p \to 0$$

At **low T**: initial $dZ/dp < 0$, B is negative
At **high T**: initial $dZ/dp > 0$, 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**)

Z

Higher temperature

Boyle temperature

Perfect gas

1

Pressure

Lower temperature
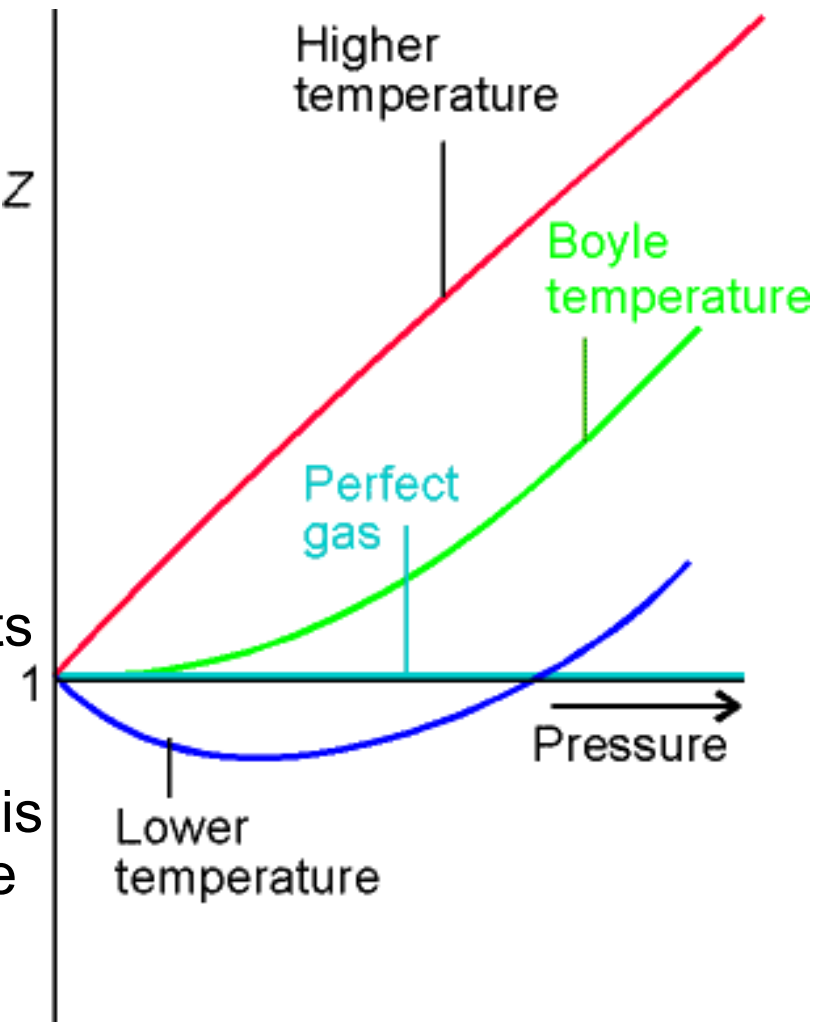
Virial Coefficients for Methane

Virial coefficients for methane up to about 400 Bar, 350°C
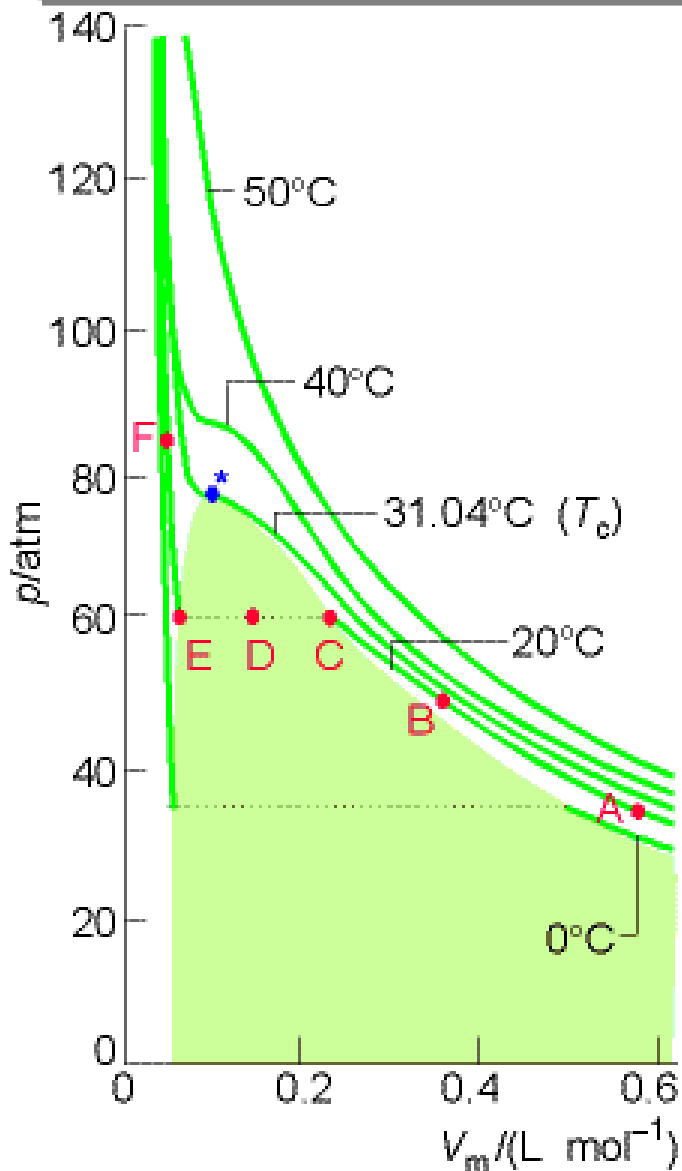
$$pV_m \;=\; RT\,(1 + B'p + C'p^2 + D'p^3)$$

T (°C)	B' (x 10⁻³ bar⁻¹)	C' (x 10⁻⁶ bar⁻²)	D' (x 10⁻⁹ bar⁻³)
0	-2.349	-0.877	29
25	-1.727	+0.438	17
50	-1.274	+1.353	7.9
100	-0.677	+1.447	4.1
150	-0.324	+1.219	2.0
200	-0.106	+0.967	0.99
250	+0.0345	+0.749	0.56
300	+0.125	+0.583	0.31
350	+0.186	+0.461	0.16

Virial Coefficients for Methane, 2

Here are the coefficients B, C and D plotted as functions of temperature:
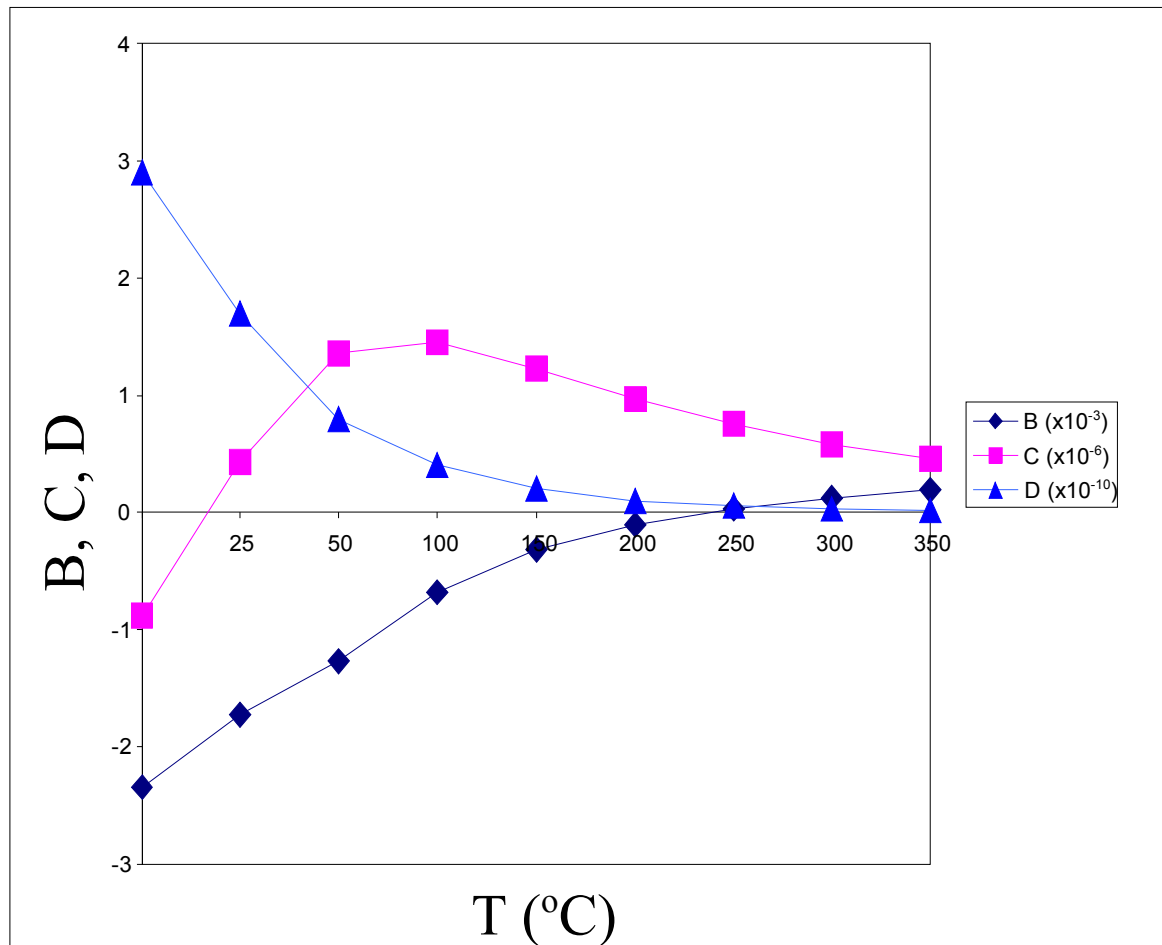
Condensation

CO$_2$ gas compressed by a piston at 20°C:
A: p rises, in accordance with Boyle's law
B: deviations from ideal gas behaviour
CDE: piston moves without any pressure increase at all - non-ideal behaviour
This line: **vapour pressure (*liq-gas eqb*)**

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 Constants
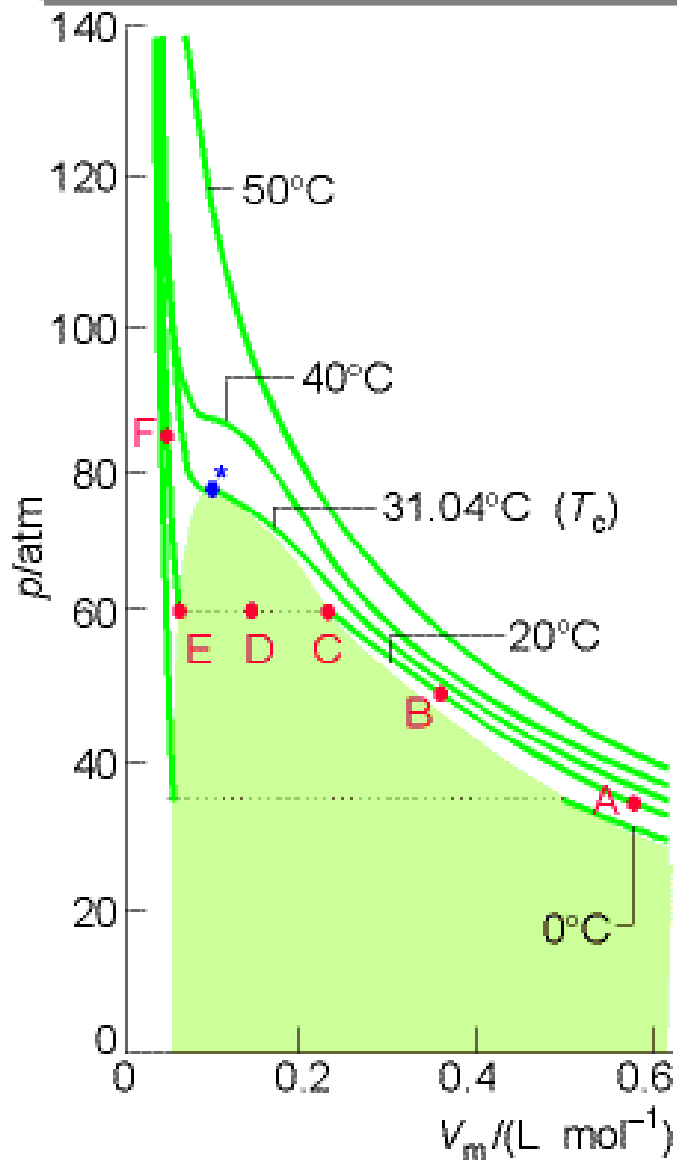
The 31.04ºC isotherm for CO_2:

If compression takes place at the so-called **critical temperature**, T_c, the surface separating the gas and liquid phases does not appear, and horizontal parts of the isotherm merge at the **critical point** - 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**

van der Waals Equation

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. This is an **semiempirical** theory, which means it is based upon **experimental observations**, combined with a rigourous thermodynamic treatment.
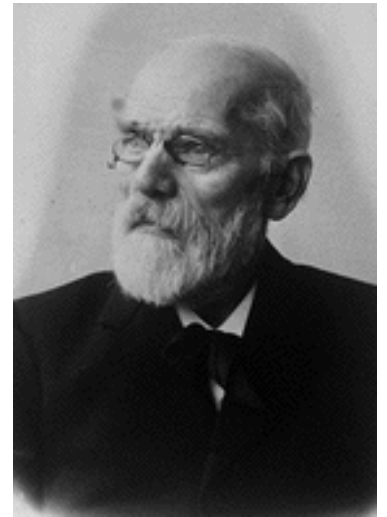
The **van der Waals equation** is written as

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

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 behaviour, 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

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

$-a(n/V)^2$: *a* is a positive proportionality constant

a and *b* should not be assigned specific molecular properties, but rather, serve as coefficients which help to accurately model gas behaviour, 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.
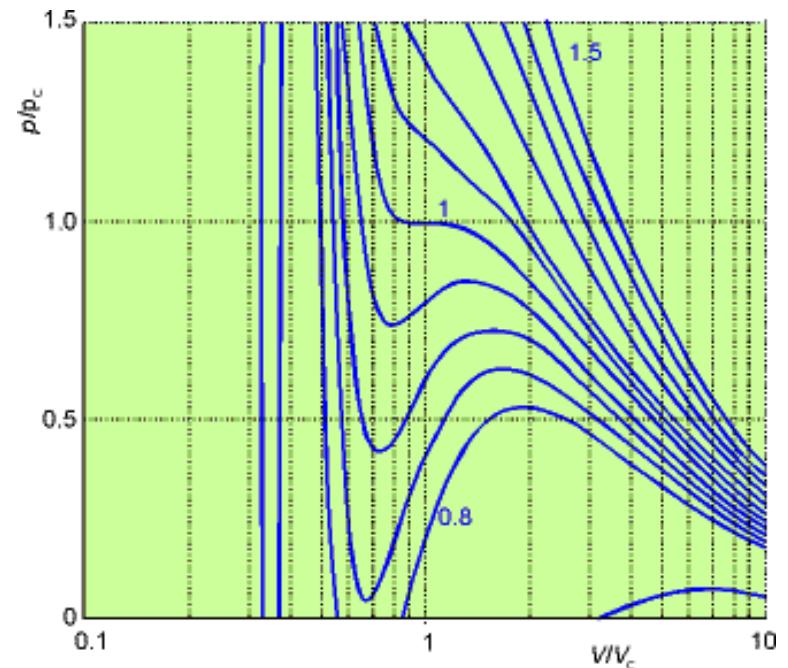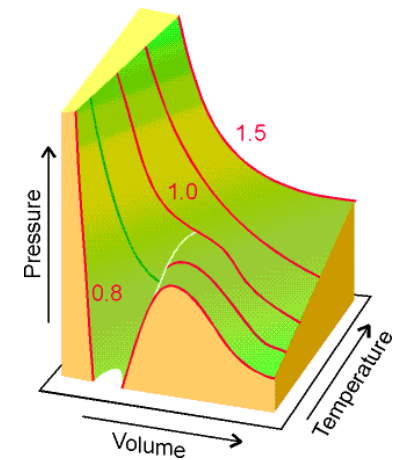
- *van der Waals equation:*
analytical expression, allows for some general observations on real gases (see table, next page)
- *virial equation:*
many accurate measurements at many temperatures, and **numerical analysis**

Compare these calculated isotherms with the experimental isotherms of CO_2: the most notable anomaly are the so-called **van der Waal's loops**, where the isotherms drop suddenly below T_c (**they suggest increase p results in increased V**) - they can be fixed by a **Maxwell construction** (loops replaced by horizontal lines). The vdW coefficients are found by comparison of experimental and theoretical curves

Selected Equations of State

A variety of equations of state similar to van der Waals equation have been developed and applied to differeny types of gases.

	Equation	Reduced form*	Critical constants		
			p_c	V_c	T_c
Perfect gas	$p = \dfrac{RT}{V_m}$				
Van der Waals	$p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$	$p_r = \dfrac{8T_r}{3V_r - 1} - \dfrac{3}{V_r^2}$	$\dfrac{a}{27b^2}$	$3b$	$\dfrac{8a}{27bR}$
Berthelot	$p = \dfrac{RT}{V_m - b} - \dfrac{a}{TV_m^2}$	$p_r = \dfrac{8T_r}{3V_r - 1} - \dfrac{3}{T_r V_r^2}$	$\dfrac{1}{12}\left(\dfrac{2aR}{3b^3}\right)^{1/2}$	$3b$	$\dfrac{2}{3}\left(\dfrac{2a}{3bR}\right)^{1/2}$
Dieterici	$p = \dfrac{RTe^{-a/RTV_m}}{V_m - b}$	$p_r = \dfrac{e^2 T_r e^{-2/T_r V_r}}{2V_r - 1}$	$\dfrac{a}{4e^2 b^2}$	$2b$	$\dfrac{a}{4Rb}$
Virial (Kammerlingh Onnes)	$p = \dfrac{RT}{V_m}\left\{1 + \dfrac{B(T)}{V_m} + \dfrac{C(T)}{V_m^2} + \cdots\right\}$				

* Reduced variables are defined in Section 1.5.

Note the different critical constants that can be calculated "exactly" from the coefficients *a* and *b*

Summary of the vdW 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 V_m is high, then $V_m - b \approx V_m$, $p = RT/V_m$

(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 $T < T_c$ calculated isotherms oscillate, passing through a minimum followed by a maximum, converging as $T \rightarrow T_c$
  - at the flat **inflection**, the 1st and 2nd derivatives are zero:
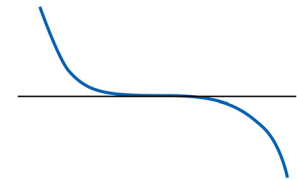
$$\frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0$$

$$\frac{d^2p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0$$

Solve the two equations in two unknowns: V_m and T, then find p with the equation of state! This gives:

$$V_c = 3b \,, \quad p_c = \frac{a}{27b^2} \,, \quad T_c = \frac{8a}{27Rb}$$

At this point, the **critical compression factor**, $Z_c = p_c V_c/RT_c = 3/8$

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**:

$$p_r = \frac{p}{p_c}, \quad V_r = \frac{V_m}{V_c}, \quad T_r = \frac{T}{T_c}$$

Van der Waal "hoped" that gases in the same reduced volume at the same reduced temperature would exert the same pressure: he was correct - these gases behave the same - **principle of corresponding states**.

Rewrite vdW with reduced constants

$$p_r p_c = \frac{RT_r T_c}{V_r V_c - b} - \frac{a}{V_r^2 V_c^2}$$

Replace constants with critical point values

$$\frac{a p_r}{27b} = \frac{8aT_r}{27b(3bV_r - b)} - \frac{a}{9b^2 V_r^2}$$

Rearrange for p_r: *a* and *b* are gone!

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$