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

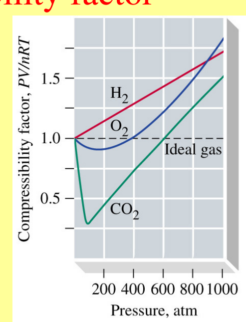
- One way to measure the deviation from ideal behaviour is to define a compressibility factor Z as:

$$Z = \frac{PV}{nRT}$$

•For an ideal gas Z=1

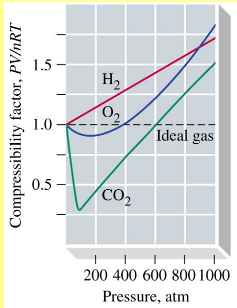
Compressibility factor

- 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

$$V_{real} = V_{measured} - nb$$

Van der Waal Equation

$$V_{real} = V_{measured} - nb$$

Substitute this into the ideal gas law

PV = nRT   becomes P(V-nb) = nRT

To get in the compressibility factor form

$$PV = nRT + Pnb$$

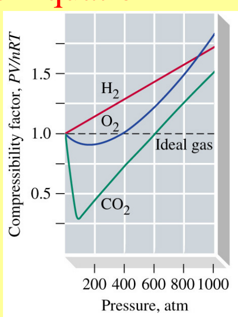
$$Z = \frac{PV}{nRT} = 1 + \frac{bP}{RT}$$

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 $(n/V)^2$, one n/V for the number of collisions and one for the force of each collision

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

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

$$Z = \frac{PV}{nRT} = \frac{V}{V - nb} - \left(\frac{an}{RTV}\right)$$

- 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

Molecule	Forces a L^2 atm mol^{-2}	Size b L mol^{-1}
He	0.034	0.0237
H_2	0.244	0.0266
Cl_2	6.49	0.0564
	Variation of a factor of 200	Variation of a factor of <3