

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

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Real Gases 1

Compressibility factor

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

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

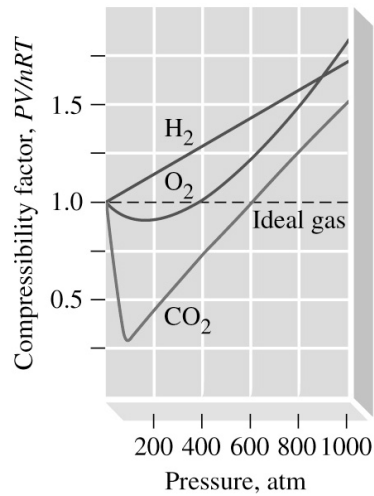
- For an ideal gas $Z=1$

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Real Gases 2

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

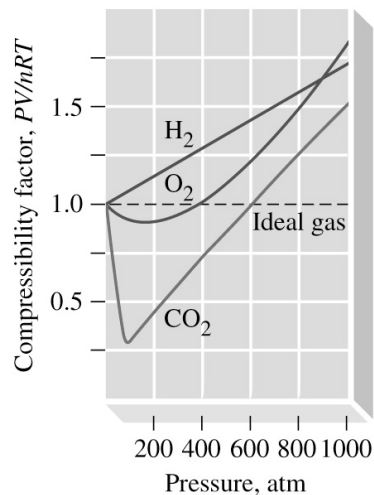


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Real Gases 3

Compressibility factor

- The compressibility factor is an empirical (experimental) prediction of real gas behaviour but doesn't tell us anything about WHY?



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Real Gases 4

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.

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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

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

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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

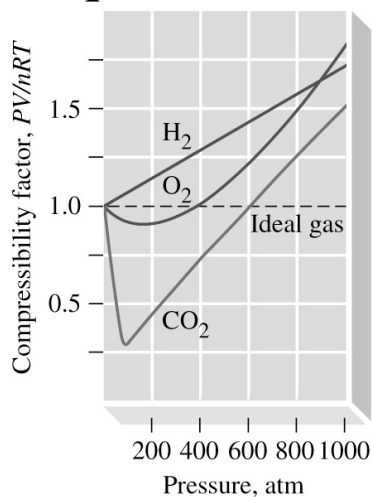
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Van der Waal Equation

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

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



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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

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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

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

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Van der Waal Equation

- Combining this pressure term into the previous equation:

$$P(V-nb) = nRT$$

we obtain van der Waal's equation

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

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Van der Waal Equation

- Expressing as compressibility:

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

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

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

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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.

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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

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Van der Waal Constants

Molecule	Forces a $\text{L}^2 \text{ atm mol}^{-2}$	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

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