The Properties of Gases

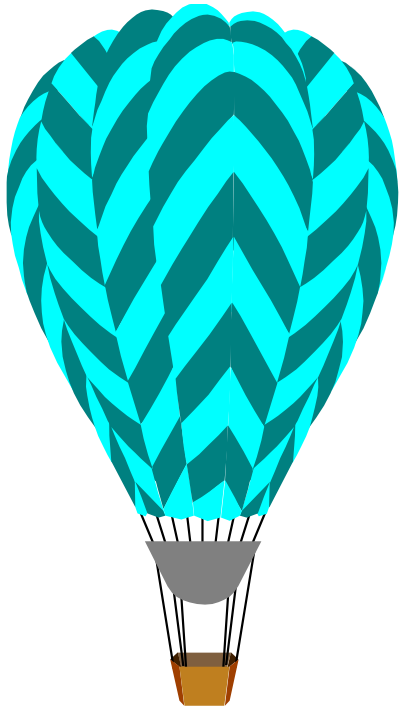
- Equations of State
- Real Gases

Bulk Variables

- V, the Volume the sample occupies (m^3)

  $m^3 = 10^6$ cc = 10^6 mL = 1000 L
- p, the Pressure of the sample (atm)

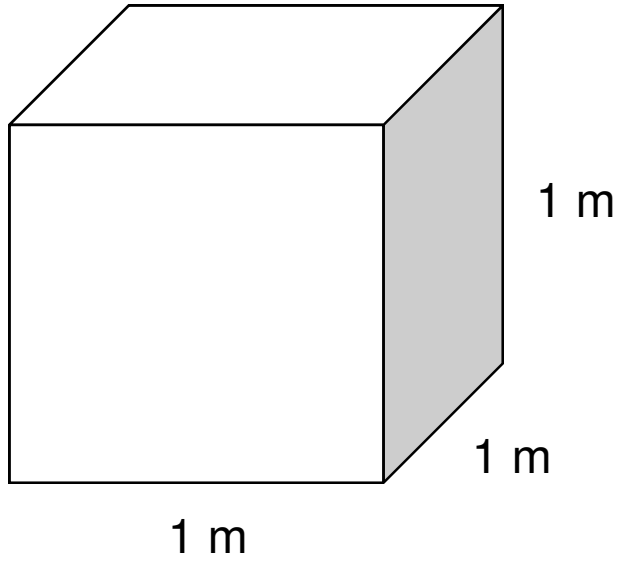
  1 atm = 101.325 kPa = 1.01 bar = 760 Torr (mmHg)
- T, the Temperature of the sample (K)
- *n*, Composition - moles



Volume

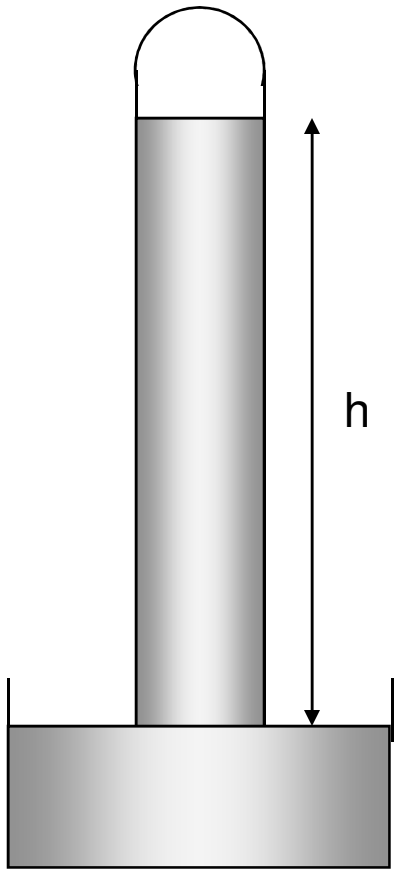
- length^3
- units
  - m^3 or cm^3
  - liter = 1000 cm^3
- molar volume

  $V_m = V/n$



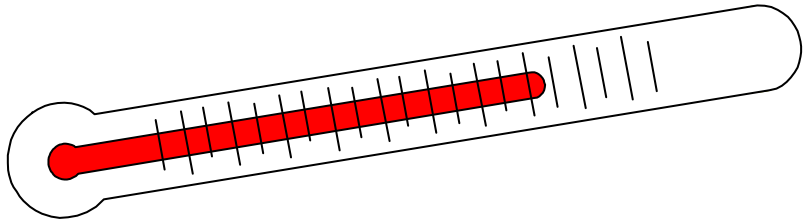
Pressure

- Force/Area
- units
  - Pascal = Newton/m^2 = Joule/m^3
  - atmosphere = 101325 Pa
  - bar = 10^0 Pa
  - mm Hg
  - Torr



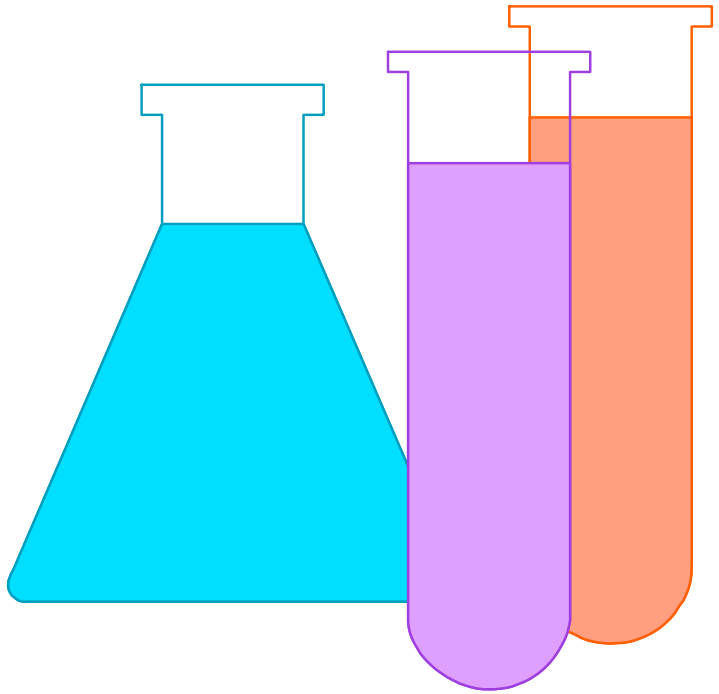
Temperature

- thermometry
  T ~ Volume
- only for an ideal gas
- or real gases in the
  low pressure limit



Composition

- moles: n_i
  $\Sigma\, n_i = n$
- mole fraction: x_i
  $\Sigma\, x_i = 1$
- partial pressure: p_i
  $\Sigma\, p_i = p$



Equations of State

- *p*,V,T, and n are not independent.
- Any three will determine the fourth.
- An equation of state is an equation that relates *p*,V,T, and n for a given substance.
- Gases have the simplest equations of state.
- The simplest equation of state is the ideal gas law, *p*V = nRT

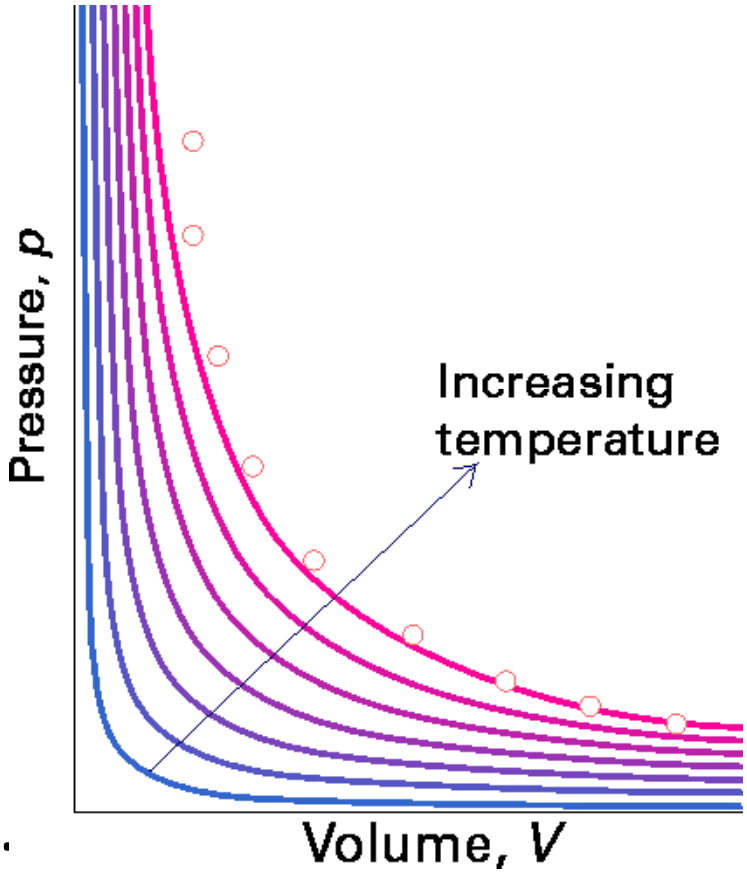
Ideal Gas Model

- Molecules may be treated as point masses relative to the volume of the system.
- Molecular collisions are elastic, i.e. kinetic energy is conserved.
- Intermolecular forces of attraction and repulsion have negligible effect on the molecular motion.

Ideal Gas Law

$$pV = nRT$$

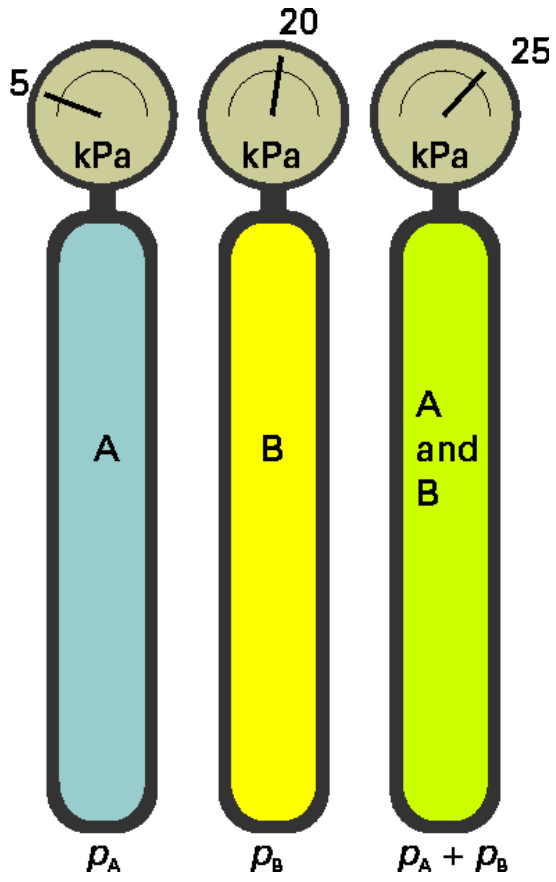
- *p* = pressure
- V = volume
- n = moles
- T = temperature
- R = universal gas contant = 0.



Partial Pressure

$$p_A V = n_A RT$$

- p_A = partial pressure of gas A
- V = total volume
- n_A = moles of gas A
- T = temperature
- R = universal gas contant = 0.08206 L-atm/mol-K

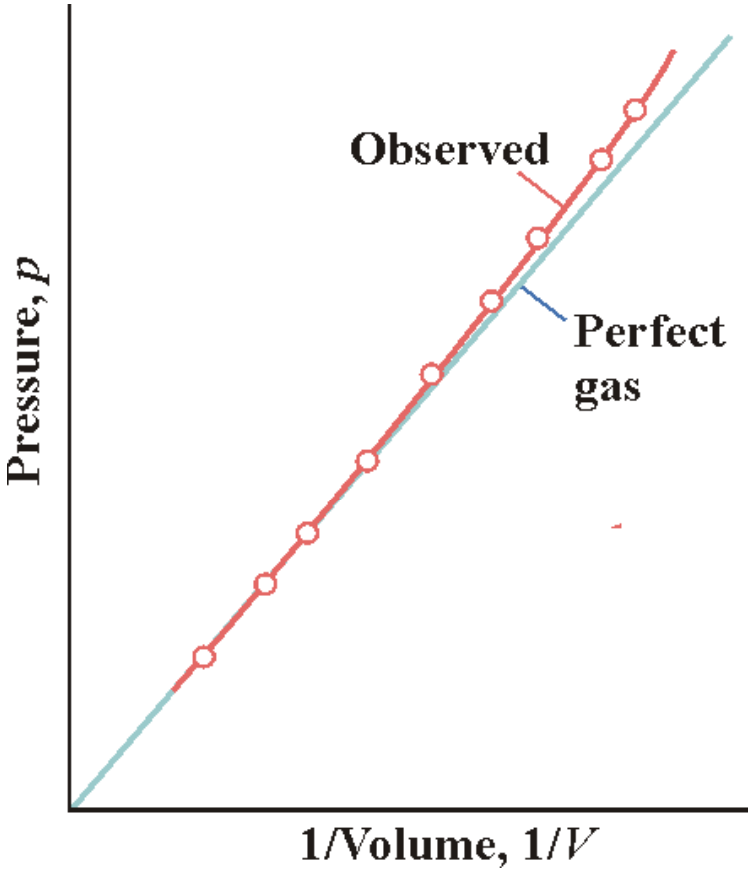


Dalton's Law

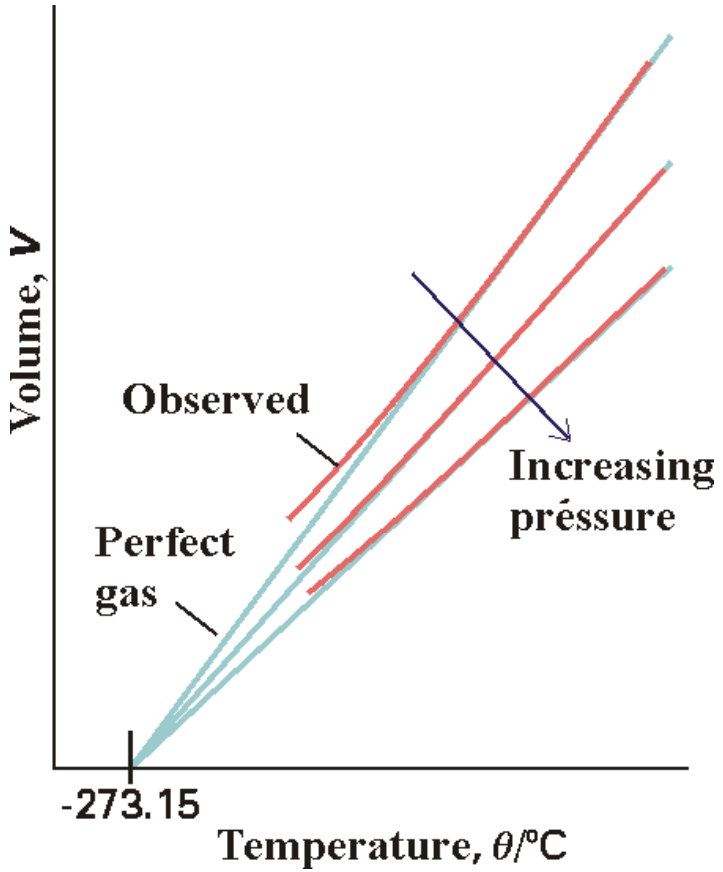
- The total pressure is the sum of all the partial pressure.

$$\sum_J p_J = \sum_J \frac{n_J RT}{V} = \frac{RT}{V} \sum_J n_J$$

$$= \frac{nRT}{V} = p$$



Deviation at high pressure



Deviation at low temperature

Real Gases

- Real gases behave like ideal gases in the limits of low P and High T.
- They deviate significantly at high P and low T.
- This is due to intermolecular forces:

- Attractive: dipole-dipole forces, H-bonds, dispersion forces
- Repulsive: repulsion of electrons

Known Facts for gases at room temperature

- **At Low Pressure < 10 atm:**
- gas behaves ideally since particles are far apart.

- **At Moderate Pressure 10 – 50 atm:**
- Particles come closer together, attraction dominates and gas is easier to compress than ideal gas.

$$p_{real} < p_{ideal}$$

- **At High Pressure > 50 atm:**
- molecules very close together, repulsion dominates and gas harder to compress than ideal gas.

$$p_{real} > p_{ideal}$$

- **keep in mind two opposing factors that determine how close gas particles will be:**

- high temperature means high kinetic energy which keeps particles apart and promotes ideal behaviour.

- high pressure means high concentration so that particles will be closer together which favours non ideal behaviour.

- At “low” temperature molecules do not have enough kinetic energy to overcome the attractive forces between molecules and so the lower the temperature the less ideal the gas behaviour. Thus at the boiling point, the attractive forces are so strong compared to the disruptive kinetic energy effects that gases condense.

How to determine whether a gas is behaving ideally?

- Suppose we measure the pressure, volume and temperature of a known amount of a gas, n.
- If the gas is behaving ideally then the value of

$$\frac{pV}{nRT} = \frac{pV_m}{RT} = 1$$

- It then seems sensible to use this ratio called the **compression factor (Z).**

Compressibility factor

- The compressibility of a gas is defined by:

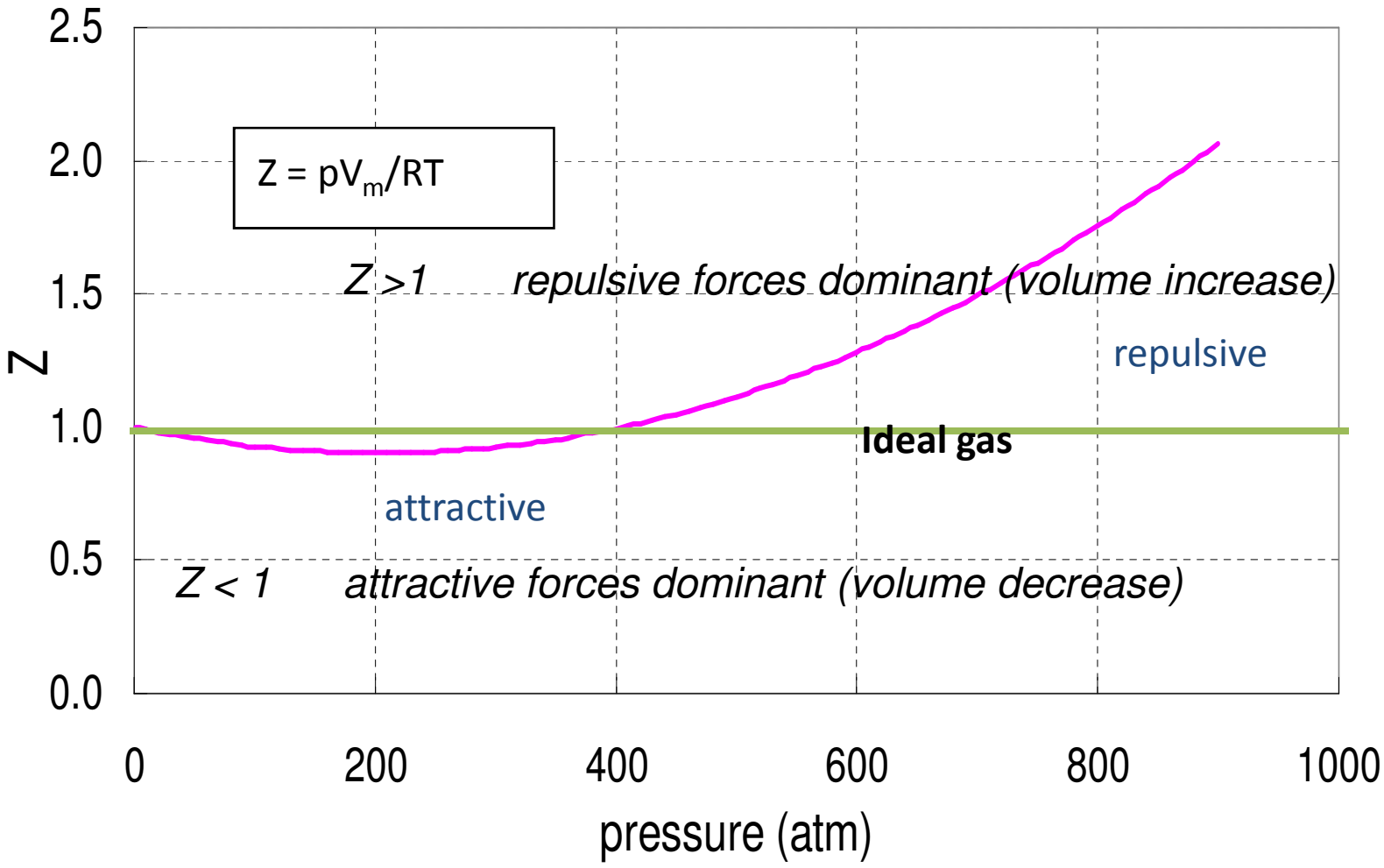
$$Z = \frac{pV_m}{RT}$$

- It is convenient measure of the deviation from ideal gas behavior.
- If the gas behaves ideally, then Z=1 at all pressures and temperatures.
- For real gases, however, Z varies with pressure, and deviates from its ideal value

Z = 1 ideal gas behaviour
Z < 1 real gas behavior, $p < p_{ideal}$, attraction dominates
Z > 1 real gas behavior, $p > p_{ideal}$, repulsion dominates

Argon Compressibility

273 K

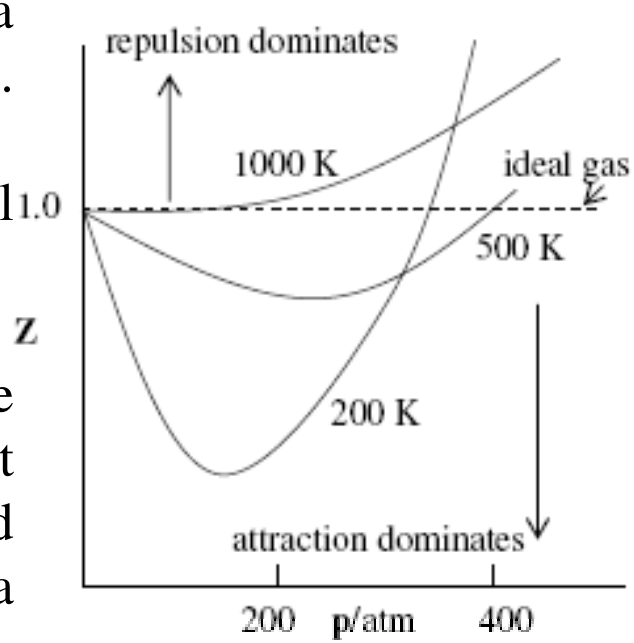


- **At very high pressure the Z factor is always greater than 1 (high deviation).**
- **In this case the volume of the gas is larger than expected from ideal gas.**
- **due to intermolecular repulsion forces, the volume occupied by the gas is larger.**
- **At low and moderate pressure the Z factor is always less than 1 (low deviation).**
- **In this case the volume of the gas is smaller than expected from ideal gas.**
- **due to intermolecular attraction forces, the volume occupied by the gas is smaller.**

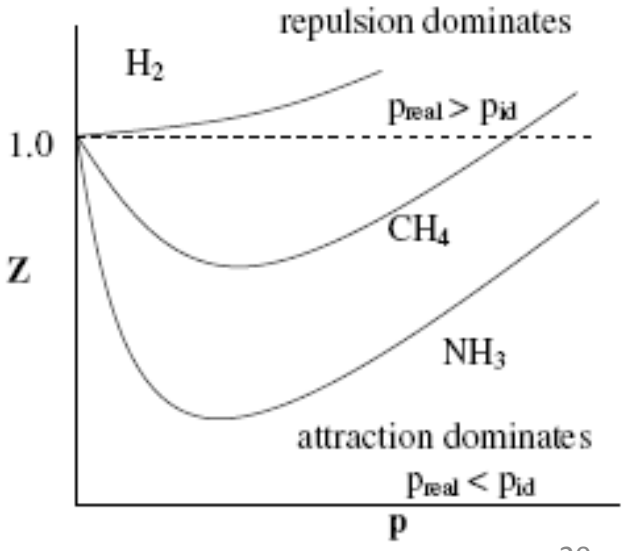
Typical gas behaviour as a function of pressure at a constant temperature is seen from a plot of Z vs p.

Note that as $p \rightarrow 0$ the gas must approach ideal behaviour and so Z must $\rightarrow 1$

The initial decrease in the plot is expected since attraction dominates at low to moderate pressures. But at high temperatures molecules move faster and overcome attractive forces sot that they only show a small dip which is hardly noticeable.



The same plot is shown for different gases all at the same temperature.
You can make a reasonable guess as to the relative extent of deviation for a compound from the magnitude of its boiling point and heat of evaporation. The larger these are the greater the deviation from the value of 1.0



Real gas equation of state
"The Virial equation of state"

$$Z = \frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots\ldots\ldots\ldots$$

- Coefficient B and C are second and third virial coefficients, respectively.
- It is more convenient to use p as an independent variable:

$$\boldsymbol{Z = \frac{pV_m}{RT} = 1 + B^{\backslash}p + C^{\backslash}p^2 + \ldots\ldots\ldots\ldots} \quad Z = 1 + \frac{\mathrm{Bp}}{\mathrm{RT}}$$

- A real gas may behave like an ideal gas over an extended range in pressure when B=0.0.
- The temperature at which this occurs is called the Boyle temperature ($\boldsymbol{T_B}$).

Example:

What is the molar volume of nitrogen gas (N_2) at 500 K and 600 bar according to:

(a) the ideal gas low

(b) the virial equation (B = 0.0169 L mol-1 for N_2 at 500 K)

(a) the ideal gas low

$$V_m = \frac{RT}{p} = \frac{(8.314 X 10^{-2}\, L bar K^{-1} mol^{-1})(500 K)}{600 bar}$$

$= 6.93 \times 10^{-2}$ L mol^{-1}

(b) the virial equation (B = 0.0169 L mol-1 for N_2 at 500 K)

Do it your self? (Z then V_m)

$$Z = 1 + \frac{Bp}{RT} \qquad Z = \frac{pV_m}{RT}$$

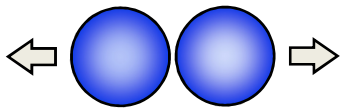
The Van der Waals equation

- **Why the real gas does not follow the ideal gas low?**
- The gas molecules are not point particles
- Repulsion between gas molecules.

V_m is replaced by $V_m - b$

b is the volume per mole that occupied by the molecules.

$$p(V_m - b) = RT$$



repulsion

$$p\left(V_m - b\right) = RT$$

$$p\left(\frac{V_m - b}{RT}\right) = 1$$

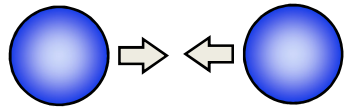
$$\frac{PV_m}{RT} - \frac{pb}{RT} = 1$$

$$\frac{PV_m}{RT} = 1 + \frac{pb}{RT} = Z = 1 + B^{\backslash} p$$

$$\frac{b}{RT} = B^{\backslash}$$

- Gas molecules attracted each other
- Real gases are more compressible than ideal gases
- Pressure in real gases is less than ideal gases
- Correction for the pressure by adding $\frac{a}{V_m^2}$

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$



$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- When V_m is large V_m >>b and p>> $\frac{a}{V_m^2}$
- So that the equation is reduced to the ideal gas low

What is the molar volume of ethane at 350 K and 70 bar according to:
(a) the ideal gas law
(b) the Van der Waal equation
(a=5.562 $L^2 mol^{-1} bar$) and (b= 0.0638 $L\ mol^{-1}$)

- (a) the ideal gas law

  Do you it yourself

- (b) the Van der Waal equation