Classical Mechanics
&
Properties of Gases

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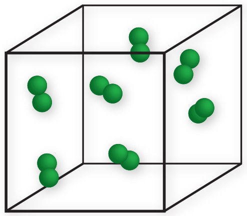
Properties of gases

- The gas phase differs from the other phases in that there are only weak interactions between particles
- Relatively simple models can be used to describe the gas phase

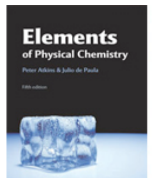
Properties of gases

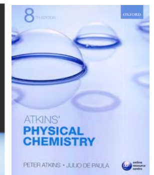
- Ideal & real gases
- Kinetic theory of gases
- Maxwell-Boltzmann distribution
- Applications of kinetic theory



Learning Resources

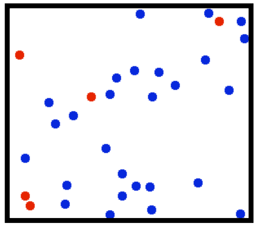
- Handout, Slides, Questions
- wallace.chem.ox.ac.uk





- Physical Chemistry *Atkins*
- Elements of Physical Chemistry *Atkins & de Paula*

Defining a gas

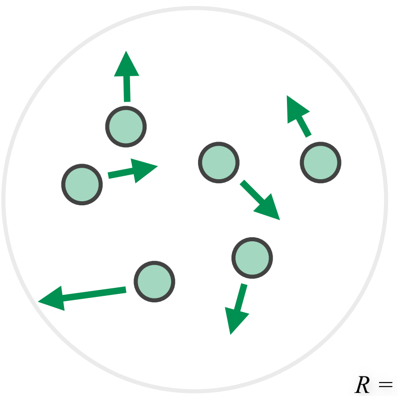


- A collection of particles in constant, rapid, random (Brownian) motion
- A gas fills any container it occupies
- The effects of intermolecular forces are generally very small, and may often be ignored

Characteristics of a gas

- The physical state of a pure gas may be defined by four physical properties
  - Pressure, P
  - Amount of substance, n
  - Volume, V
  - Temperature, T
- If we know any three variables, we can use an equation of state to determine the fourth.

Ideal gases



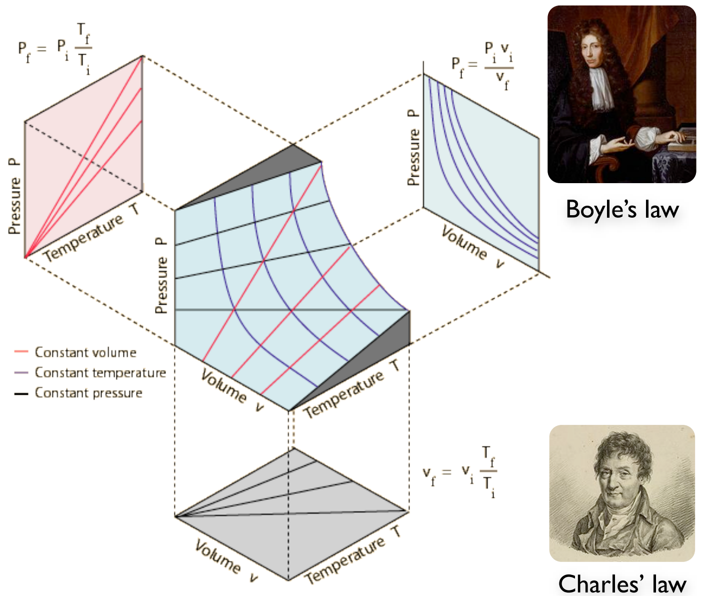
$p \propto T \quad p \propto N \quad p \propto 1/V$

$$p \propto \frac{NT}{V}$$

$$pV = Nk_BT$$

$$pV = nRT$$

$R = 8.314\ JK^{-1}mol^{-1}$ = Molar gas constant
$k_B = 1.38 \times 10^{-23}\ JK^{-1}$ = Boltzmann constant
$(N_A k_B = R)$



Ideal gas assumptions

$$pV = nRT$$

- The molecules obey Newton's law of motion
- There are no attractive or repulsive interactions between molecules
- The molecules undergo perfectly elastic collisions
- The volume occupied by the molecules is negligibly small in comparison to the size of the container

Pressure

- Force exerted by the gas per unit area
- SI units of Newtons per square metre (Nm^{-2}), or Pascals (Pa)
  - *1 Torr = 1 mmHg = 133.3 Pa*
  - *1 bar = 1000 mbar = 100 000 Pa*
- Pressure can be measured due to the force arising from collisions of gas particles with a surface

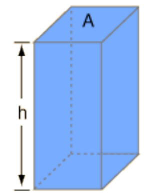
Partial pressures

- Partial pressure is the pressure that a gas would exert if it alone occupied the container
- Dalton's law
  - The total pressure p exerted by a mixture of gases is simply the sum of the partial pressures p_i of the component pressures

$$p = \sum_i p_i$$

An example

Barometric pressure



$$\Delta p = -\rho g \Delta h$$

$$V = hA$$

$\rho = M/V$

$$p = \frac{F}{A} = \frac{-Mg}{A} = \frac{-(\rho V)g}{A} = -\rho g h$$

$$\Delta p = -\rho g \Delta h$$

An example

Barometric pressure

$$\Delta p = -\rho g \Delta h$$

$$\rho = \frac{M}{V} = \frac{Nm}{V}$$

$pV = Nk_BT$

$$\frac{\Delta p}{\Delta h} = -\frac{mpg}{k_BT}$$

$$\frac{\mathrm{d}p}{\mathrm{d}h} = -\frac{mpg}{k_BT}$$

$$\frac{1}{p}\mathrm{d}p = -\frac{mg}{k_BT}\mathrm{d}h$$

$$\int_{p_0}^{p} \frac{1}{p}\mathrm{d}p = -\frac{mg}{k_BT}\int_0^h \mathrm{d}h$$

$$\ln\left[\frac{p}{p_0}\right] = -\frac{mgh}{k_BT} \qquad p = p_0 e^{-\frac{mgh}{k_BT}}$$

Temperature

- Temperature is a measure of the average kinetic energy of the particles in a gas
  - Temperature reflects the velocity distribution of gas particles
  - The velocity of a single particle constantly changes due to collisions
  - The total number of particles with a given velocity is constant
  - The distribution of molecular speeds in an ideal gas is given by the Maxwell-Boltzmann distribution
- Temperature is a direct result of the motion of particles
  - It is only a meaningful concept when describing matter

Ideal gases

$$pV = nRT$$

- The molecules obey Newton's law of motion
- There are no attractive or repulsive interactions between molecules
- The molecules undergo perfectly elastic collisions
- The volume occupied by the molecules is negligibly small in comparison to the size of the container

Real gases

$$pV = n\cancel{R}T$$

- The molecules obey Newton's law of motion
- There are ~~no~~ attractive or repulsive interactions between molecules
- The molecules undergo ~~perfectly elastic collisions~~ elastic, inelastic and reactive collisions
- The volume occupied by the molecules is ~~negligibly small~~ in comparison to the size of the container not negligible

Real Gases

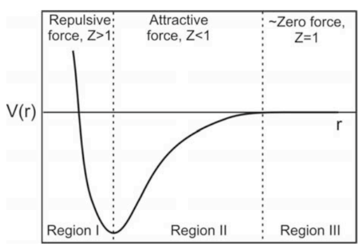
- The ideal gas equation breaks down when molecular size effects or intermolecular forces become important.
  - High P. Particles forced closer together and interact more strongly
  - Low T. Particle motion is slow, so forces have a long time to act

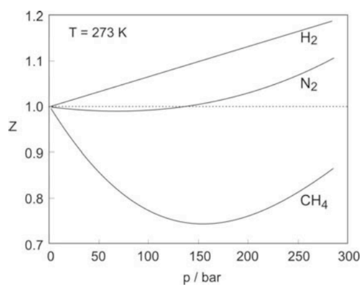
The compression factor

$$Z = \frac{V_m}{V_m^o} = \frac{pV_m}{RT}$$

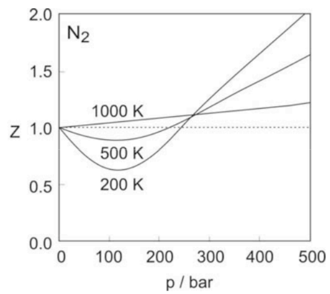
- Quantifies the deviations of a real gas from ideal gas behaviour
  - V_m = molar volume, $V_m{}^o$ = molar volume of an ideal gas
- Provides information on the dominant types of intermolecular forces
  - $Z = 1$ No intermolecular forces, ideal gas behaviour
  - $Z < 1$ Attractive forces dominate, molar volume reduced
  - $Z > 1$ Repulsive forces dominate, molar volume increased
- The behaviour of Z as a function of pressure (or temperature) reflects the intermolecular potential.

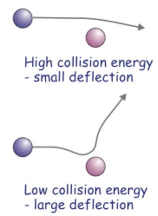
The compression factor

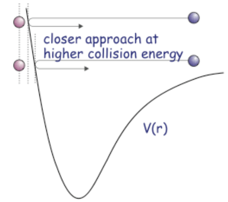




The compression factor

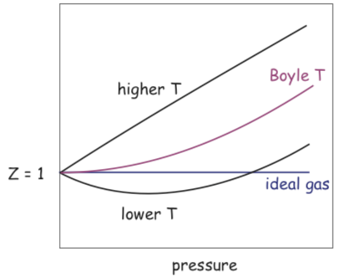






The Boyle temperature

- For an ideal gas, $Z = 1$ $dZ/dp = 0$
- For a real gas, $Z \rightarrow 1$ at low pressure, but dZ/dp does not necessarily $\rightarrow 0$
- For real gases, there is a single temperature at which $dZ/dp \rightarrow 0$ and $Z \rightarrow 1$ as $p \rightarrow 0$.
  - This is the Boyle temperature
  - Here the attractive and repulsive interactions balance and the real gas behaves ideally



Equations of state for real gases

Virial expansion

- Real gases may be treated by taking the ideal gas equation as the first term in a series expansion

$$pV_m = RT\left(1 + B'p + C'p^2 + ...\right)$$

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

- This is called a virial expansion
- B and C are virial coefficients

Equations of state for real gases

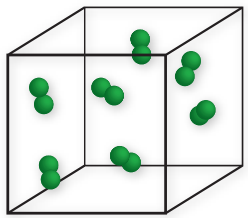
- An alternative is to use the van der Waal's equation.

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

- a and b are temperature independent constants called the van der Waal's coefficients, whose values depend on the gas species

Ideal & real gases

- pV=nRT
- Ideal Gas Assumptions
- Deviations from ideality
  - Compressibility
  - Boyle Temperature
  - Virial Expansions



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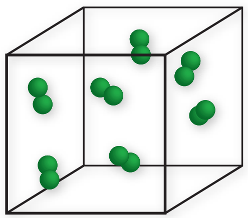

"That's amazing—I was just thinking the same thing."