

**Chapter 1 - The Properties of Gases**

I. The perfect gas.

A. The states of gases. (definition)

1. The state variables:
   - volume = V
   - amount of substance, moles = n
   - pressure = p
   - temperature = T

2. Knowledge of these defines the state of any pure gas.

3. These variables do not vary independently, but are connected by an equation of state. In general, pressure $p = f(T,V,n)$

   e.g., simplest: $pV = nRT$ (perfect or ideal gas)

4. Therefore, knowledge of any three plus the equation of state defines the state of the gas.

5. $V$ and $n$ are extensive properties, proportional to size of system. $T$ and $p$ are intensive properties, independent of size of system.

6. Pressure $p = force$ per unit area that a system exerts on its surroundings.

   Two major sources of pressure: i) downward gravitational force, and ii) impacts of molecules on surroundings.

   Pressure exerted by a gas is a manifestation of incessant impact of particles on their surroundings.

   Above system is in mechanical equilibrium with its surroundings when the force per unit area of system particles pushing the piston out equals force per unit area pushing in.

   $$p_{\text{system}} = p_{\text{surroundings}}$$

   Piston stops moving when this is achieved.
7. Units of pressure:

SI unit of force = N (Newton) = kg m/s²
area = m² (meters²)
so SI unit of pressure = N/m²
1 Pascal (Pa) = 1 N/m²

8. Other more familiar and useful units of pressure:

1 atmosphere (atm) = the pressure required to support a column of Hg 760 mm high at 0°C.
1 atm = 760. mm Hg
= 760. Torr

1 atm = 101.325 kPa (kiloPascals)
1 bar = 100 kPa
so 1 atm ~ 1 bar

9. Definition of standard pressure for reporting thermodynamic data:
= 1 bar = 750.1 Torr

10. Measurement of pressure - The Torricelli barometer:

Hg rises until the forces balance and atmospheric p = p_{grav}

This height h is 760. mm at sea level on an average day.
11. Temperature $T$:

A measure of thermal energy per unit sample of matter, and a manifestation of molecular motion, difficult to define in words.

It is the property that tells which direction heat will flow.

12. Zeroth Law of thermo = if A is in thermal equilibrium with B, and B with C, then C is also in thermal equilibrium with A.


Simplest are based on thermal expansion of a liquid in a capillary (Hg or alcohol).

Celsius scale:
- 0 mark in system where water and ice are in equilibrium
- 100 mark in system where liquid water is boiling at sea level (in equilb with steam)

Above is the typical Hg or alcohol thermometer.

Ambiguity: Hg and alcohol don't expand perfectly linearly with $T$.

Better thermometer uses expansion of an ideal gas (The ideal gas thermometer):

14. Temperature scales ($K = Kelvin$)

$$\frac{T}{K} = \theta/°C + 273.15$$ ($\theta$ is symbol used for temperature in °Celsius)
B. The gas laws.

1. The ideal gas law (or perfect gas law):
   \[ PV = nRT \]

   \( R \) = universal gas constant
   
   \[ = 8.31447 \text{ J} \text{ K}^{-1} \text{ mol}^{-1} \]
   
   \[ = 0.0820574 \text{ L} \text{ atm} \text{ K}^{-1} \text{ mol}^{-1} \]
   
   \[ = 1.98721 \text{ cal} \text{ K}^{-1} \text{ mol}^{-1} \]

   Note: 1 J = 1 Pa-m³

   Works well for most gases at room T and 1 atm.
   Works well for all gases at lower pressures or higher temperatures.

2. The response to pressure - Boyle's Law (1662):
   \[ p \propto \frac{1}{V} \text{ (at constant } n, T) \]
   
   or \[ p_1V_1 = p_2V_2 \text{ (at constant } n, T) \]
   
   or \[ pV = \text{ constant (at constant } n, T) \]

   \( p-V \) isotherms:
   lines of constant T

Figure 1-4
Figure 1-5
3. The response to temperature:

\[ V \propto T \text{ (at constant } n, p) \text{ - Charles' Law} \]

\[ \frac{V_1}{T_1} = \frac{V_2}{T_2} \]

V-T isobars (lines of constant Pressure)

Q: How would this plot look if one plotted vs Celsius temperature?

\[ p \propto T \text{ (at constant } n, V) \text{ - Gay-Lussac's Law} \]

\[ \frac{p_1}{T_1} = \frac{p_2}{T_2} \]

p-T isochores (lines of constant volume)
4. Avogadro's principle:

\[ V \propto n \text{ (at constant } p, T) \]

molar volume = \( V_m = \) volume occupied per mole of molecules = \( \frac{V}{n} \). Is independent of type of molecule.

\[ P V_m = RT \]

\[ V_m = \frac{RT}{P} \]

**Problem**: Calculate \( V_m \) in liters (L) for an ideal gas at 0° C and 1.00 atm pressure.

\[ V_m = R(0°C + 273.15)/1.00 \text{ atm} \text{ [must use Kelvin!]} \]

What \( R \) to use? L atm K\(^{-1}\)mol\(^{-1}\)

\[ V_m = 0.08206 \times 273.15 \text{ K}/1.00 \text{ atm} \]

\[ V_m = 22.415 \text{ L} \]

5. Standard conditions for reporting data.

STP - old definition, standard temp. and pressure: 0° C, 1 atm

SATP - standard ambient temp. & pressure: 298.15K (25° C), 1 bar


Let \( \rho \) = mass density = \( \frac{m}{V} \) = mass/Volume

moles \( n = \frac{m}{M} = \) mass/Molar_mass

\[ pV = nRT \]

\[ pV = (m/M) \text{ RT} \]

\[ m/V = M \rho/RT \]

\[ \rho = M \rho/RT \]

Therefore \( \rho \propto M \)
7. Combined plot of equation of state at fixed n:

![Combined plot of equation of state at fixed n]

Combined gas laws for fixed number of moles $n$

\[
\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}
\]

Combined gas laws for variable number of moles

\[
\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2}
\]

8. Variation of atmospheric pressure with altitude $h$ given by the *barometric formula*:

\[p = p_0 e^{-h/H}\]

where $H = RT/Mg$

Here:

- $M =$ average molar mass of air
- $g =$ acceleration of gravity
- $T$ is varying with altitude

The pressure exerted by a mixture of perfect gases is the sum of partial pressures exerted by the individual gases.

total pressure \( p = nRT/V = (n_A + n_B + ...)RT/V \)

\[
p = n_A RT/V + n_B RT/V + ...
\]

\[
p = p_A + p_B + ...
\]

\( p_A \) and \( p_B \)... are partial pressures, \( n = n_A + n_B + ... \)

10. Mole fractions and partial pressures.

mole fraction of component J defined as:

\[
x_J = n_J/n
\]

so \( x_A + x_B + ... = 1 \);

therefore: \( p_J = x_J p \)

proof: \( p_J = n_J RT/V \)

\[
= (n_J/n) (n RT/V) = (n_J/n) P
\]

so \( p_J = x_J p \)
II. Kinetic Theory of Gases.

Molecular (microscopic & classical) theory of gases which predicts:

a) equilibrium thermodynamic properties - Pressure
b) dynamical properties - rates of processes: effusion through openings, viscosity of gases, collision frequencies (used in collision theory of chemical reactions)

A. Model of Perfect Gas.

1. Elementary kinetic theory assumptions.

   a. Gas sample is mostly empty space (molecules themselves occupy small volume).
   
   b. No attractions or repulsions between molecules in free flight (i.e. travel in straight lines)
   
   c. Perfectly elastic collisions between molecules (no energy transferred into internal degrees of freedom: rot, vib, elec)
   
   d. Pressure exerted by gas = time-averaged force per unit area exerted by many individual impacts of molecules on a surface.
   
   e. Classical variables describe gas.
      
      - position \( \vec{x} \) of molecule
      - velocity \( \vec{v} \) of molecule
      - \( v_x, v_y, v_z \) are Cartesian components of velocity

2. Molecular Speed.

molecular speed \( v = |\vec{v}| \) = scalar quantity, not vector

\[
v = \sqrt{v_x^2 + v_y^2 + v_z^2}
\]
3. Root-mean-square (rms) speed of sample = \( c = \langle v^2 \rangle^{1/2} \)

\[ \langle v^2 \rangle = \frac{\sum_{i=1}^{N} v_i^2}{N} \]

But \( v_i^2 = v_{x_i}^2 + v_{y_i}^2 + v_{z_i}^2 \) \((v_i \text{ veloc in x-dir for molecule } i)\)

\[ \langle v^2 \rangle = \frac{\sum_{i} \left( v_{x_i}^2 + v_{y_i}^2 + v_{z_i}^2 \right)}{N} \]
\[ = \frac{\sum_{i} v_{x_i}^2}{N} + \frac{\sum_{i} v_{y_i}^2}{N} + \frac{\sum_{i} v_{z_i}^2}{N} \]
\[ = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \]

\[ \uparrow \text{ mean-square speed in } x\text{-direction} \]

But since motion is random:

\[ \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \]

So: \( \langle v^2 \rangle = 3 \langle v_x^2 \rangle \)

root-mean-square speed:

\[ \sqrt{\langle v^2 \rangle} \text{ or } \langle v^2 \rangle^{1/2} \text{ has units speed or velocity} \]
3. **Pressure** exerted by N molecules.

Container volume $V = a \times b \times c$

follow 1 typical molecule and its motion in $x$-direction

time interval between collisions with face A = $\Delta t$

$\Delta t = \text{time required to travel distance } 2a$

velocity $\times$ time = distance

$v_x \Delta t = 2a$

$\Delta t = \frac{2a}{v_x}$

To calculate pressure $P$, need force per unit area

1st, find time-averaged force $F$ exerted by 1 molecule

avg force in time $\Delta t$ (during which we have 1 collision)

$F = \text{force of 1 collision}$

$F = \frac{\text{momentum change in 1 collision}}{\Delta t}$

$F = \frac{2mv_x}{\Delta t} = \frac{mv_x^2}{a}$

$P_1 = \text{pressure due to 1 molecule} = \frac{\text{Force}}{\text{Area}}$

$P_1 = \left( \frac{mv_x^2}{a} \right) \frac{1}{bc}$ \hspace{1cm} \text{where area of face A} = bc

$P_1 = \left( \frac{mv_x^2}{abc} \right) = \frac{mv_x^2}{V}$ \hspace{1cm} \text{where V is container volume}$

Now the pressure due to N molecules in volume V:

$P = \frac{Nm\left<v_x^2\right>}{V}$
But we already showed that \( \langle v^2 \rangle = 3 \langle v_x^2 \rangle \)

So:

\[
P = \frac{Nm\langle v^2 \rangle}{3V}
\]

key result

Recognize \( \frac{N}{V} = \mathcal{N} \) = number density (not mass density)

\[
P = \mathcal{N} \frac{m\langle v^2 \rangle}{3}
\]

Could also write: \( PV = \frac{1}{3} Nmc^2 \)

Now, avg translational (kinetic) energy \( E_t \) of a single molecule of mass \( m \) is:

\[
E_t = \langle \frac{1}{2} mv^2 \rangle = \frac{1}{2} m\langle v^2 \rangle
\]

So:

\[
PV = \frac{2}{3} NE_t
\]

But we also know that:

\[
PV = nRT
\]

or

\[
PV = Nk_B T
\]

(where \( n = \) moles and \( N = \) molecules)

So:

\[
\frac{2}{3} NE_t = Nk_B T
\]

\[
E_t = \frac{3}{2} k_B T
\]

Equipartition theorem result for translational energy

So avg k.e. of a molecule depends only on \( T \), not on mass of particle
Problem:

Calculate \( \langle v^2 \rangle \) and \( \langle v^2 \rangle^{1/2} \) of He atoms and Cl\(_2\) molecules at 300 K.

\[
P V = \frac{N m \langle v^2 \rangle}{3} = N k_B T
\]

So:

\[
\frac{m \langle v^2 \rangle}{3} = k_B T
\]

\[
\langle v^2 \rangle = \frac{3 k_B T}{m}
\]

\[
c = \langle v^2 \rangle^{1/2} = \left( \frac{3 k_B T}{m} \right)^{1/2}
\]

\[
\langle v^2 \rangle_{\text{He}} = \frac{3 \times 1.38 \times 10^{-23} \text{JK}^{-1} \times 300 \text{K}}{4.002 \frac{\text{g/mol}}{\text{mol}} \times 10^{-3} \frac{\text{kg}}{\text{g}} \times \frac{1 \text{mol}}{6.022 \times 10^{23}}} = 1.869 \times 10^6 \text{m}^2/\text{s}^2
\]

\[
c_{\text{He}} = \langle v^2 \rangle_{\text{He}}^{1/2} = 1,367 \text{m/s}
\]

\[
\langle v^2 \rangle_{\text{Cl}_2} = \langle v^2 \rangle_{\text{He}} \times \frac{4.002}{70.90} = 1.055 \times 10^5 \text{m}^2/\text{s}^2
\]

\[
c_{\text{Cl}_2} = \langle v^2 \rangle_{\text{Cl}_2}^{1/2} = 325 \text{m/s}
\]
B. Distribution of Molecular Velocities.

Although every identical gas molecule in a sample may have same average speeds and average Cartesian velocity components (averaged over period of time), at any instant of t there is a wide range of velocities possible.

Let \( f(v_x) \, dv_x \) = fraction of molecules having x-component of velocity in range \( v_x \) to \( v_x + dv_x \).

Also = prob that a single given molecule has x-comp of velocity in range \( v_x \) to \( v_x + dv_x \).

\( f(v_x) \) = probability density that a single given molecule has x-comp of velocity in range \( v_x \) to \( v_x + dv_x \).

This distribution is the Maxwell-Boltzmann distribution, which can be derived from the Boltzmann equation

\[
f(v_x) = \left( \frac{2\pi k_B T}{m} \right)^{1/2} e^{-mv_x^2/2k_BT}
\]

Have similar probability densities in y and z directions

So: \( F(v_x, v_y, v_z) \) = prob density that a given molecule has \( v_x, v_y, v_z \) components
Max-Boltz in 3D

\[
F(v_x, v_y, v_z) = \left( \frac{2\pi k_B T}{m} \right)^{-3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2k_B T}
\]

where \(v_x^2 + v_y^2 + v_z^2 = v^2\)

distribution of molecular velocities

\[F(v_x, v_y, v_z)dv_x, dv_y, dv_z = \text{a probability or fraction, is normalized}\]

Meaning that

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} F(v_x, v_y, v_z) dv_x dv_y dv_z = 1
\]

\[
\int_{-\infty}^{\infty} e^{-mv_x^2/2k_B T} \left( \frac{2\pi kT}{m} \right)^{1/2} \int_{-\infty}^{\infty} e^{-mv_y^2/2k_B T} \left( \frac{2\pi kT}{m} \right)^{1/2} \int_{-\infty}^{\infty} e^{-mv_z^2/2k_B T} \left( \frac{2\pi kT}{m} \right)^{1/2} = 1
\]

Calculation of averages using M-B distribution

\[
\langle v_x^2 \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_x^2 F(v_x, v_y, v_z) dv_x dv_y dv_z
\]

\[
= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_x^2 e^{-mv_x^2/2k_B T} \left( \frac{2\pi kT}{m} \right)^{1/2} \int_{-\infty}^{\infty} e^{-mv_y^2/2k_B T} \left( \frac{2\pi kT}{m} \right)^{1/2} \int_{-\infty}^{\infty} e^{-mv_z^2/2k_B T} \left( \frac{2\pi kT}{m} \right)^{1/2} = 1
\]

\[
\neq 1 = 1 = 1
\]

integral over \(v_x\) is integral of type

\[
\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{\sqrt{\pi}}{2a^{3/2}}
\]

where

\[
\alpha = \frac{m}{2k_B T}
\]
So:  \( \langle v_x^2 \rangle = \frac{\sqrt{\pi}}{2 \left( \frac{m}{2k_B T} \right)^{3/2}} \cdot \left( \frac{2\pi k_B T}{m} \right)^{1/2} \cdot (1) \cdot (1) \)

\[ \langle v_x^2 \rangle = \frac{k_B T}{m} \]

\[ \langle v^2 \rangle = 3 \langle v_x^2 \rangle = \frac{3k_B T}{m} = \frac{3RT}{M} \]

\[ c^2 = \langle v^2 \rangle \]

\[ c^2 = \left( \frac{3k_B T}{m} \right) = \left( \frac{3RT}{M} \right) \]

C. Maxwell Distribution of Speeds.

Let \( f(v)dv \) = fraction of molecules having speed in range \( v \) to \( v+dv \)
or = prob that a given molecule has speed in range \( v \) to \( v+dv \)
\( (v= \text{length of the velocity vector}) \)

\[ f(v)dv = F(v_x, v_y, v_z) \quad 4\pi v^2 \quad dv \]

Maxwell Boltzmann distribution of speeds

\[ f(v)dv = \left( \frac{2\pi k_B T}{m} \right)^{-3/2} e^{-mv^2/2k_BT} \quad 4\pi v^2 \quad dv \approx v^2 e^{-\alpha v^2} \]

RMS speed \( \langle v^2 \rangle^{1/2} \) which = \( c \)

\[ \langle v^2 \rangle = \int_0^\infty dv \cdot f(v) \cdot v^2 \]

\[ \langle v^2 \rangle = \left( \frac{3RT}{M} \right) \]
\[ \langle v^2 \rangle^{1/2} = \left( \frac{3RT}{M} \right)^{1/2} = c \]

\[ \langle v^2 \rangle^{1/2} = \langle v \rangle = c^* \]

\[ \left( \frac{3RT}{M} \right)^{1/2} \left( \frac{8RT}{\pi M} \right)^{1/2} \left( \frac{2RT}{M} \right)^{1/2} \]

**Speed of sound \sim \text{average speed in gas}**

**D. Types of Average Speeds.**

1. **Most probable speed** \( c^* \)
   
   maximum of \( \mathcal{F}(v) \)
   
   occurs at \( d\mathcal{F}(v)/dv = 0 \)
   
   Solve for \( v \)
   
   \[ c^* = \left( \frac{2RT}{M} \right)^{1/2} \]

2. **Mean speed** \( \langle v \rangle \) or \( \bar{c} \)
   
   \[ \langle v \rangle = \int_0^\infty dv \mathcal{F}(v)v \]
   
   \[ \langle v \rangle = \left( \frac{2\pi kT}{m} \right)^{-3/2} \int_0^\infty dv \frac{e^{-mv^2/2kT}}{4\pi v^2} \times v \]
   
   is integral of type \( \int dx x^3 e^{-\alpha x^2} \)
   
   \[ \langle v \rangle = \left( \frac{8RT}{\pi M} \right)^{1/2} = \left( \frac{2.546 RT}{M} \right)^{1/2} \]

3. **Mean relative speed** = \( \bar{c}_{\text{rel}} \)

The mean speed at which a molecule approaches another molecule. Collision rates between molecules depends on mean relative speed

\[ \bar{c}_{\text{rel}} = 2^{1/2}\bar{c} \]
and for the case of two dissimilar molecules:

\[ \bar{c}_{rel} = \left( \frac{8RT}{\pi \mu} \right)^{1/2} \] where \( \mu \) is reduced mass

**Proof:**

mean relative speed \( = \bar{c}_{rel} = \left( \langle v_1 \rangle^2 + \langle v_2 \rangle^2 \right)^{1/2} \)

\[ \frac{\text{mean speed of 1}}{\text{mean speed of 2}} \]

Now since \( \langle v_i \rangle = \left( \frac{8k_B T}{\pi m_i} \right)^{1/2} \)

We have:

\[ \bar{c}_{rel} = \left( \frac{8k_B T}{\pi m_1} + \frac{8k_B T}{\pi m_2} \right)^{1/2} = \left( \frac{8k_B T}{\pi} \right)^{1/2} \left( \frac{1 + 1}{m_1 + m_2} \right)^{1/2} = \frac{1}{\mu_{12}} \]

\[ \mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \]

Note: if \( m_1 = m_2 \) \( \bar{c}_{rel} = \sqrt{2} \left( \frac{8k_B T}{\pi m_1} \right)^{1/2} = \sqrt{2}\bar{c} \)

**E. Kinetic Energy Distribution.**

\[ \mathcal{E}_E(E)dE = \text{fraction of molecules with K.E. value in interval } E \text{ to } E+dE \]

Given \( E = \frac{1}{2} m v^2 = \frac{1}{2} m \left( v_x^2 + v_y^2 + v_z^2 \right) \)

\[ \mathcal{E}_E(E)dE = \frac{e^{-E/k_B T} 2\pi \sqrt{E}}{\left( \pi k_B T \right)^{3/2}} dE \]
Problem: Gas phase reaction has activation energy = $E_a$. What fraction $f$ of gas sample has kinetic energy greater than some required activation energy $E_a$ for chemical reaction?

$$\text{fraction } f = \int_{E_a}^{\infty} \frac{2\pi\sqrt{E} \, e^{-E/k_B T}}{(\pi k_B T)^{3/2}} \, dE$$

F. Collision rates with a wall or opening in a wall.

Use: calculation of pressure, escape rate (effusion)

**calculate** $z_w = \frac{\text{# of collisions}}{\text{unit Area} \times \text{unit time}} = \text{"collision frequency"}$

consider small time interval = $dt$ patch of area = $A$

# of collisions due to molecules with $z$-veloc will be number of molecules within distance = $v_z dt$ of patch (only those will strike)

That will = number in cylinder of volume $Av_z dt$

Which will = $\mathcal{N} Av_z dt$ where $\mathcal{N}$ is number density of molecules (# per unit vol)

# of collisions due to molecules with $v_z$ velocity = $\mathcal{N} Av_z dt f(v_z) f(v_x) f(v_y) dv_x dv_y$

Total # = $\mathcal{N} Adt \int_0^\infty v_z f(v_z) dv_z \int dv_x f(v_x) \int dv_y f(v_y)$

$$\begin{align*}
  \int \frac{dv_x f(v_x)}{v_x} & = 1 \\
  \int \frac{dv_y f(v_y)}{v_y} & = 1 \\
\end{align*}$$

$$z_w = \frac{\text{total # coll}}{Adt}$$

$$z_w = \mathcal{N} \int dv_z v_z f(v_z)$$

$$= \mathcal{N} \int dv_z \left( \frac{2\pi k_B T}{m} \right)^{-1/2} v_z e^{-mv_z^2/2kT}$$

$$z_w = \mathcal{N} \sqrt{\frac{RT}{2\pi M}}$$
or using $\bar{c} = \langle v \rangle = \left( \frac{8RT}{\pi M} \right)^{1/2}$

$z_w = \mathcal{N} \frac{\bar{c}}{4}$

G. Collisions between molecules.

Need to consider this in order to determine:
- mean free path
- diffusion coefficient
- heat conductivity
- viscosity

1. Collision cross section $\sigma$ and effective target

\[
\sigma = \text{area the molecule sweeps out as it travels, } \sigma = \pi d^2, \text{ where } d = \text{hard sphere diameter, no long-range attractive forces}
\]

2. Collision frequency $z$ of one molecule

\[
z = \sigma \bar{c} \mathcal{N} = \frac{\sigma \bar{c} \mathcal{N}}{k_B T}
\]

Collision cross-sections

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma$/nm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_6$</td>
<td>0.88</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.52</td>
</tr>
<tr>
<td>He</td>
<td>0.21</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.43</td>
</tr>
</tbody>
</table>

* More values are given in the Data section."
3. Mean free path $\lambda = \text{avg distance traveled by a molecule between collisions}$

$$\lambda = \frac{c_{\text{rel}}}{Z} = \frac{k_B T}{\sigma P}$$

note $\lambda \propto \frac{1}{P}$

**Problem**

A requirement for effusive flow through an opening is that radius of opening must be small compared to $\lambda$.

$O_2$ has effective spherical diameter $d = 3.61\,\text{Å}$. At 25°C at what pressure will the mean free path be equal to a hole of radius = 1 mm?

require $\lambda = 1 \text{ mm} = 10^{-3} \text{ m}$

$$\lambda = \frac{k_B T}{\sigma P} \quad P = \frac{k_B T}{\sigma \lambda} \quad \sigma = \pi d^2$$

$$P = \frac{1.38 \times 10^{-23} \text{ J} \cdot \text{K} \times 298 \text{ K}}{\pi \left(3.61 \times 10^{-10} \text{ m}\right)^2 10^{-3} \text{ m}} = 10.0 \text{ pascals}$$

$$x \frac{1 \text{ atm}}{101325 \text{ Pa}} = 9.91 \times 10^{-5} \text{ atm}$$

4. **Graham’s Law of Effusion**

already have $z_w = \text{collisions per unit time per unit area with wall or opening}$

$A = \text{area of opening}$

Effusion rate $R = z_w A = A \left(\frac{k_B T}{2 \pi m}\right)^{1/2}$
Compare 2 gases

\[
\frac{\mathcal{R}_1}{\mathcal{R}_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{molec weights}
\]

\[
\mathcal{R} \propto \frac{1}{\sqrt{M}}
\]

Requirement for effusion: \( \lambda > \text{diameter of opening} \)

Then, molecules pass independently through the opening rather than creating a hydrodynamic flow.

5. Collison frequency between molecules.

Let \( z_{1(2)} = \) # of collisions per unit time of one molecule of type 1 with all molecules of type 2

\[
\text{# of collisions in time dt} = \text{vol of this cylinder} \ast \mathcal{N}_2
\]

\[
= \overline{c}_{rel} \pi \mathbf{v} (r_1 + r_2)^2 \mathcal{N}_2
\]

let \( d_{12} = r_1 + r_2 = \text{collision diameter for molec 1 \& 2 types} \)

\[
z_{1(2)} = \overline{c}_{rel} \pi d_{12}^2 \mathcal{N}_2
\]

\[
z_{1(2)} = \left( \frac{8k_BT}{\pi \mu_{12}} \right)^{1/2} \pi d_{12}^2 \mathcal{N}_2
\]

Now, total rate of collisions per unit volume between molecules of type 1 and those of type 2 is:

\[
Z_{12} = z_{1(2)} \mathcal{N}_1 = \left( \frac{8k_BT}{\pi \mu_{12}} \right)^{1/2} \pi d_{12}^2 \mathcal{N}_1 \mathcal{N}_2
\]
Collision theory of gas phase reaction rates uses this collision frequency.

\[
\text{Rate} = Z_{12} \times (\text{Probability of successful rxn upon collision})
\]

\[
\approx e^{-E_a/k_B T} f
\]

\(E_a = \text{activation energy}\)
\(f = \text{geometric factor}\)

\[
\text{Rate} = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \pi d_{12}^2 \frac{f e^{-E_a/k_B T}}{N_1 N_2}
\]

\(\sim \text{rate constant} \ \kappa \ \text{gives concentrations}\)

\[
\kappa c_1 c_2 \quad (2^{\text{nd}} \text{ order rate law})
\]

If type 1 and type 2 molecules are identical:

\[
Z_{12} \rightarrow Z_{11} = \frac{\langle v \rangle \pi d^2}{\sqrt{2}} \mathcal{N}_1^2 \quad \text{where } d \text{ is diam of } 1 \ \langle v \rangle \text{ is } \left(\frac{8k_B T}{\pi m_1}\right)^{1/2}
\]
III. Real gases.

A. Molecular Interactions.

1. In general - gases deviate from ideal behavior due to interactions between molecules.

   Repulsive forces - exist over very short range, a molecular diameter. Called *excluded volume* forces. Causes deviation from ideality only when the density is so high that the physical volume of the molecules begins to become comparable to \( V \).

   Attractive forces - exist over several molecular diameters.

2. The compression factor \( Z \) = a dimensionless quantity expressing deviation from ideality.

\[
Z = \frac{pV}{nRT}
= 1 \text{ for gas obeying ideal gas law.}
\]

Since \( \frac{V}{n} = V_m \)

\[
Z = \frac{pV_m}{RT}
\]

Also,

\[
Z = \frac{V_m}{V_m^o}
\]

where \( V_m^o \) is ideal gas molar volume = \( RT/p \)
Figure 1-14
Atkins Physical Chemistry, Eighth Edition
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3. Virial expansions:

Since ideality pertains at low $p$, this suggests that we mathematically expand $Z$ in the pressure:

$$Z = 1 + B'p + C'p^2 + ...$$

$B'$, $C'$ are called the 2nd and 3rd virial coefficients.

Virial coefficients are not just curve-fitting parameters, but can be calculated from molecular properties by statistical mechanics.

Alternately, the virial expansion can be expressed in powers of $1/V_m$

$$Z = (1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ...)$$

4. Condensation:

Decreasing the volume of a confined gas (increasing its $p$ and density) at constant $T$ below a certain $T$ called the critical temperature $T_c$ causes condensation.
5. Critical constants:

Every gas has a critical point with a critical pressure $P_c$
critical volume $V_c$
critical temperature $T_c$

$T_c$ = temperature above which a gas can not be made to undergo a condensation phase transition no matter how much it is compressed. Always one phase.

### Synoptic Table 1C.2 Critical constants of gases

<table>
<thead>
<tr>
<th></th>
<th>$P_c$/atm</th>
<th>$V_c$/($\text{cm}^3\text{mol}^{-1}$)</th>
<th>$T_c$/K</th>
<th>$Z_c$</th>
<th>$T_e$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>48.0</td>
<td>75.3</td>
<td>150.7</td>
<td>0.292</td>
<td>411.5</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>72.9</td>
<td>94.0</td>
<td>304.2</td>
<td>0.274</td>
<td>714.8</td>
</tr>
<tr>
<td>He</td>
<td>2.26</td>
<td>57.8</td>
<td>5.2</td>
<td>0.305</td>
<td>22.64</td>
</tr>
<tr>
<td>O$_2$</td>
<td>50.14</td>
<td>78.0</td>
<td>154.8</td>
<td>0.308</td>
<td>405.9</td>
</tr>
</tbody>
</table>

*More values are given in the Data section.*

B. The van der Waals equation - an intuitively appealing approximate equation of state for a real gas.

1. Constructing the equation.

a) First account for repulsive forces. Replace $V$ in $pV=nRT$ by the effective available volume the molecules have to move in:

Modified equation becomes

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

Where $b = \text{excluded volume vdw parameter}$

Excluded volume effect is to **increase** the $P$ at fixed $n$, $T$. 
Derive relation between $b$ and the physical volume of a particle for the hard sphere gas case:

Answer: $b = 4V_{\text{particle}}N_{\text{avo}}$

For example: if molecule is 1.0 Å in radius

$b = 4 \times (4/3)\pi (1 \text{ Å})^3 \times 6.02 \times 10^{23} = 1.009 \times 10^{-5} \text{ m}^3/\text{mol}$

~ $1.0 \times 10^{-2} \text{ L/mol}$

b) **Second account for attractive forces.** Should be proportional to the frequency of collisions in the sample:

collision frequency $\propto (n/V)^2 = (\text{molar conc})^2$

$$(P + a n^2/V^2)(V-nb) = nRT$$

Where $a = \text{vdW attractive forces parameter.}$

Attractive term effect is to **decrease** the observed pressure $p$, everything else remaining fixed.

Every gas is characterized by parameters $a$ and $b$.

**Synoptic Table 1C.3  van der Waals coefficients**

<table>
<thead>
<tr>
<th></th>
<th>$a/(\text{atm dm}^6 \text{ mol}^{-2})$</th>
<th>$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1.337</td>
<td>3.20</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.610</td>
<td>4.29</td>
</tr>
<tr>
<td>He</td>
<td>0.0341</td>
<td>2.38</td>
</tr>
<tr>
<td>Xe</td>
<td>4.137</td>
<td>5.16</td>
</tr>
</tbody>
</table>

*More values are given in the Data section.*

So what is the effective “hard sphere” radius of an Argon atom?

$$b = 4V_{\text{Ar}} * N_{\text{avo}}$$

$$3.2 \times 10^{-2} \ell_{\text{mol}}^{-1} = 4 \left(\frac{4}{3}\pi R^3\right)N_{\text{avo}}$$

Solve for $R$.  

(Top Hat question)
2. van der Waals isotherms:

![Diagram of van der Waals isotherms]

3. Relation of a and b to critical constants:

Since vdW equation predicts the critical point, derive relationship between critical point and parameters a and b.

At critical point:

\[
\frac{dp}{dV} = 0 \quad \frac{d^2p}{dV^2} = 0
\]

Use \( n=1 \) and differentiate vdW equation:

\[
V_c = 3b
\]

\[
P_c = \frac{a}{27b^2}
\]

\[
T_c = \frac{8a}{27bR}
\]
C. The principle of corresponding states.

Define reduced variables (dimensionless variable):

\[ P_r = \frac{P}{P_c} \]
\[ V_r = \frac{V}{V_c} \]
\[ T_r = \frac{T}{T_c} \]

Observation that real gases behave virtually identically if expressed in terms of reduced (dimensionless) variables.

I.e., at same reduced V & T they exert approximately the same reduced pressure.

Works very well for spherical molecules.

Why does this work so well? To see this rewrite vdw equation in terms of reduced variables.

Start with \((P + \frac{a}{V^2})(V-nb) = nRT\)
set \( n = 1 \)

\[(P + a/V_m^2)(V_m - b) = RT\]

Make substitutions:

\[(P_rP_c + a/V_m^2)(V_rV_c - b) = RT_rT_c\]

Now sub in \( V_c = 3b \), \( P_c = a/(27b^2) \), \( T_c = 8a/(27Rb) \)

Now reorganize, noting that a's + b's disappear, leaving:

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

Since no a or b remain in the equation, the equation of state in reduced variables is identical for every type of gas (as long as vDW equation is valid).

Example: \( \text{H}_2 \) at 1 atm and 298 K behaves identically to \( \text{NH}_3 \) at 8.7 atm and 3638 K. How did we determine this? Look up the critical constants of the gases in question and use the principle of corresponding states.
Notes: