Gases

- Petrucci, Herring Madura and Bissonnette : Chapter 6

Problem set

Chapter 6

- Questions 5, 9, 13, 26, 39, 41, 50, 57, 69, 73, 74, 78, 82

- We will be looking at Macroscopic and Microscopic properties:
  - Macroscopic
    - Properties of bulk gases
    - Observable
      - Pressure, volume, mass, temperature…
  - Microscopic
    - Properties at the molecular level
    - Not readily observable
      - Mass of molecules, molecular speed, energy, collision frequency

Macroscopic Properties

- Our aim is to look at the relationship between the macroscopic properties of a gas and end up with the gas laws

Pressure

- To contain a gas you must have a container capable of exerting a force on it (e.g. the walls of a balloon).
- This implies that the the gas is exerting a balancing force
- Normally we talk about the pressure (force/area) rather than force

Measuring Pressure

- The simplest way to measure gas pressure is to have it balance a liquid pressure.
- Therefore we need to quantify the liquid pressure

- Consider a cylinder of liquid with area A and height h
- The force exerted at the bottom of the cylinder is its weight

  $F = m.g$

- The pressure exerted is

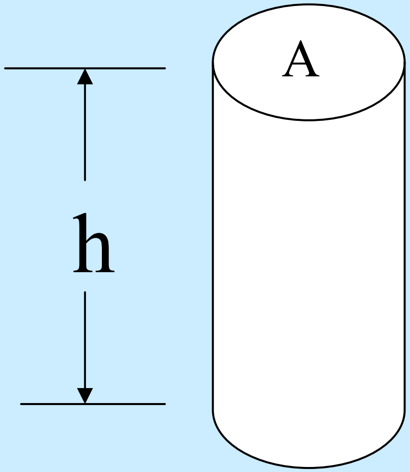
  $P = F/A = m.g/A$

- The density of the liquid is

  $d=m/V$ so $m = V.d$ but $V=A.h$

- So

  $P = m.g/A = g.V.d/A = g.A.h.d/A = g.h.d$



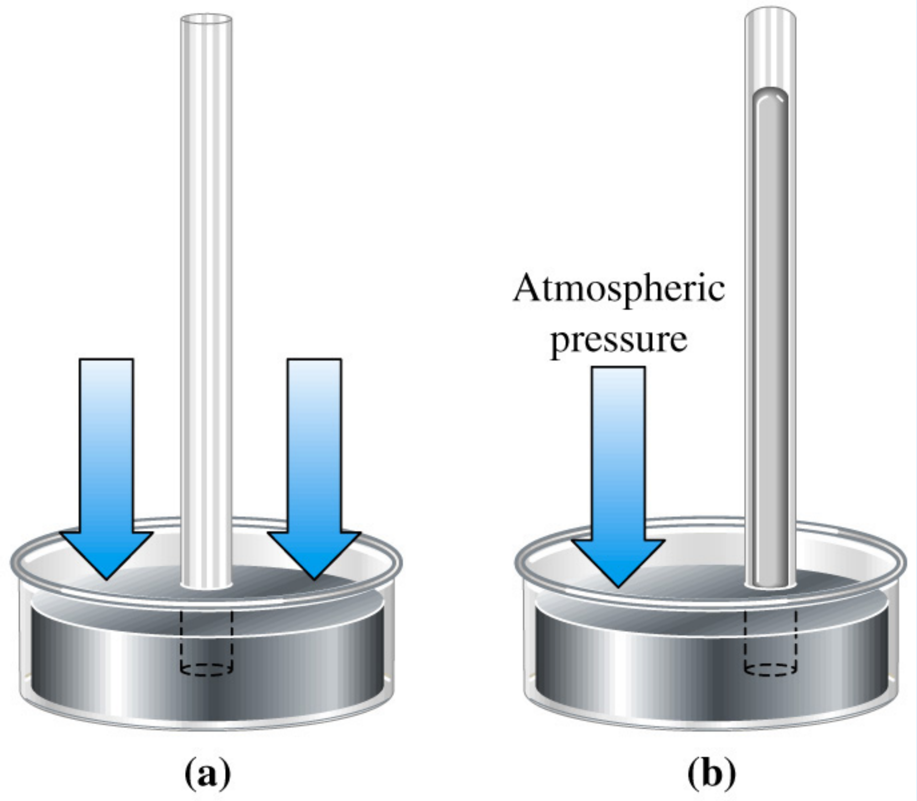
Barometer

To measure Atmospheric Pressure

On the left the tube is open

On the right the tube is closed and a liquid column is supported by the atmospheric pressure:

Air pressure equals the liquid pressure



Barometer (continued)

So for a barometer

$P = g.h.d$ P = atmospheric pressure

h = height of liquid column

d = density of the liquid

Barometer (continued)

For a barometer

$$P = g.h.d$$

Note that if we have a constant “g” and constant “d” (like with a mercury barometer on earth)

$$P \propto h$$

so we can use h as a way of describing pressure

Atmospheric Pressure

- The average pressure at sea level will support a column of 760 mm of mercury.
- This is the definition of the pressure unit of "atmospheres"

1 atm = 760 mm Hg

Also the unit mm Hg has become known as Torr (after Torricelli)

1 atm = 760 mm Hg = 760 Torr

Atmospheric Pressure

- What is 1 atm in pressure units?

$P = g.h.d$

$g = 9.81\ m.s^{-2}$, $h = 0.76\ m$,

$d_{Hg} = 13.6\ g.cm^{-3} = 13.6x10^{3}\ kg.m^{-3}$

$P = 9.81x0.76x13.6x10^{3}$

$= 1.013x10^{5}$ Pa $(N.m^{-2})$

If we made a barometer out of water, what would be the height of the water column if the pressure is 745 torr?

The problem calls for the relationship between P and h

$$P = g.h.d$$

$$P = \frac{745}{760} \times 1.013 \times 10^5 \quad \text{Pa}$$

$$d = 1.00\ \text{g cm}^{-3} = 1.00 \times 10^3\ \text{kg m}^{-3}$$

$$g = 9.81\ \text{m s}^{-2}$$

$$P = g.h.d$$

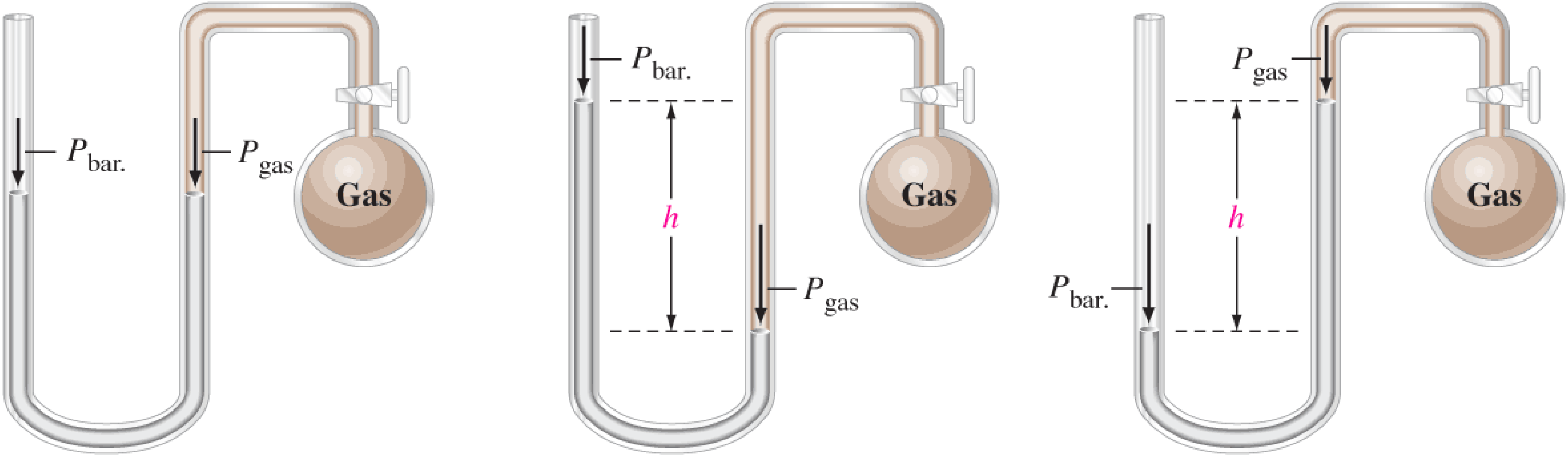
$$\frac{745}{760} \times 1.013 \times 10^5 = 9.81 \times h \times 1.00 \times 10^3$$

$h = 10.1$ m

Measuring Gas Pressures

Gas pressures can be measured with a manometer. This is similar to a barometer but measures pressure differences using a liquid.

When one side of the manometer is open to the atmosphere



$P_{gas} = P_{bar.}$

(a) The gas pressure is equal to the barometric pressure.

$P_{gas} = P_{bar.} + \Delta P$

$(\Delta P = g \times h \times d > 0)$

(b) The gas pressure is greater than the barometric pressure.

$P_{gas} = P_{bar.} + \Delta P$

$(\Delta P = -g \times h \times d < 0)$

(c) The gas pressure is less than the barometric pressure.

▲ FIGURE 6-5
Measurement of gas pressure with an open-end manometer

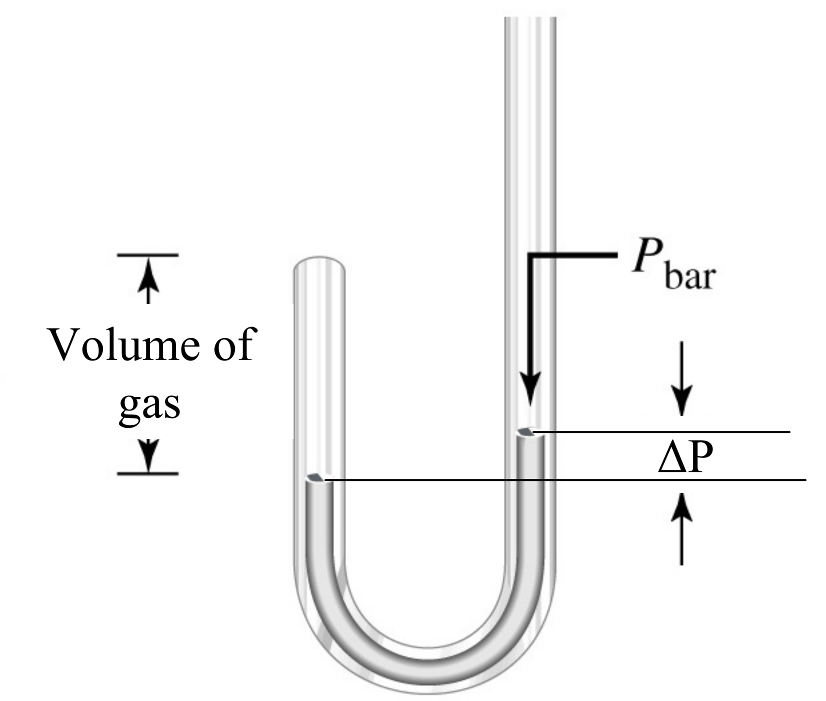
Gas Laws

- The aim is to determine the relationship between the gas observables (pressure, volume, mass, temperature).

- These were determined experimentally

Boyle's Law

- Boyle (~1622) kept the mass of gas and the temperature constant and studied the relationship between pressure and volume



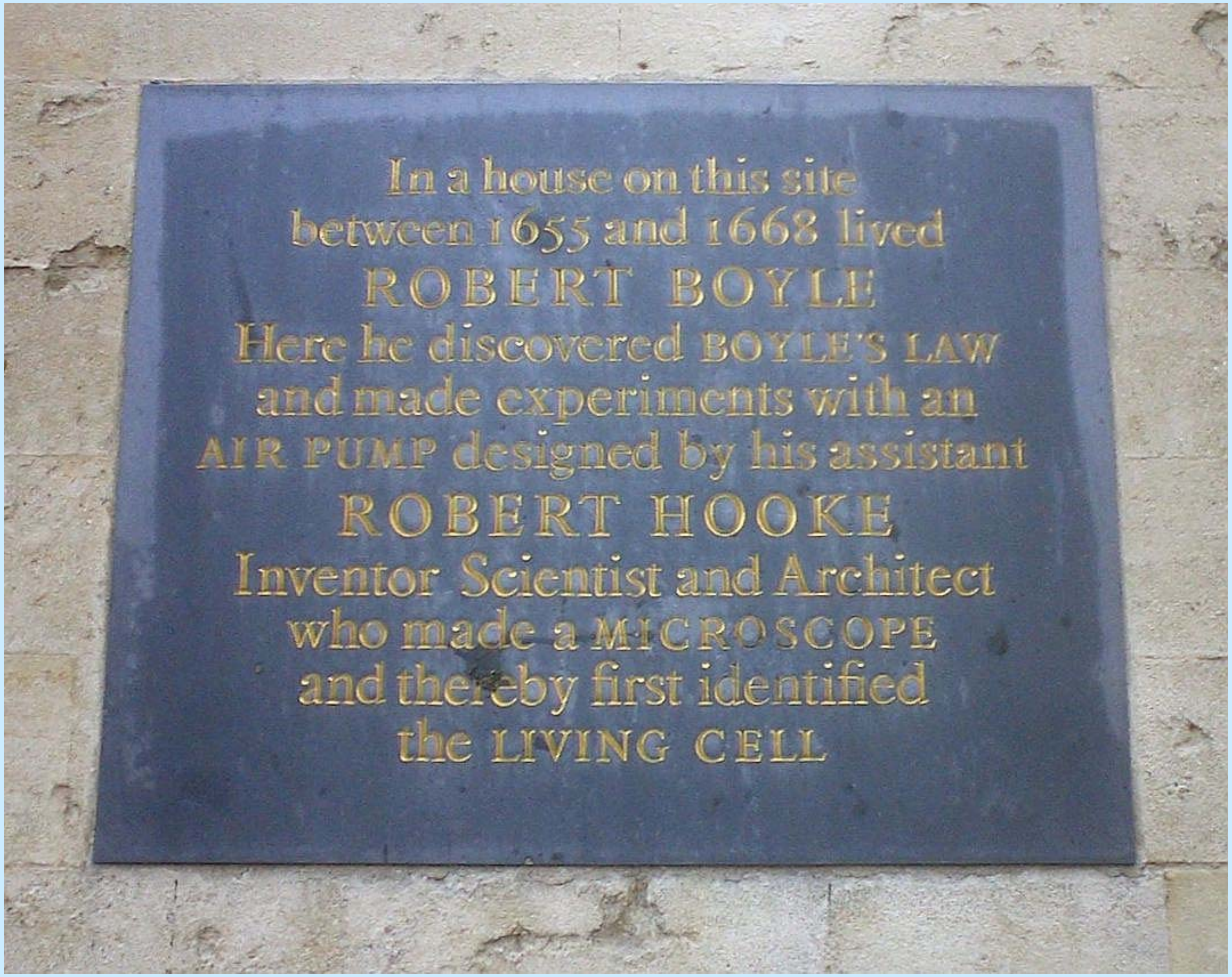
Boyle’s Law

- Boyle found that pressure and volume were inversely proportional. (double the pressure and the volume goes to one half).
- This is usually expressed as

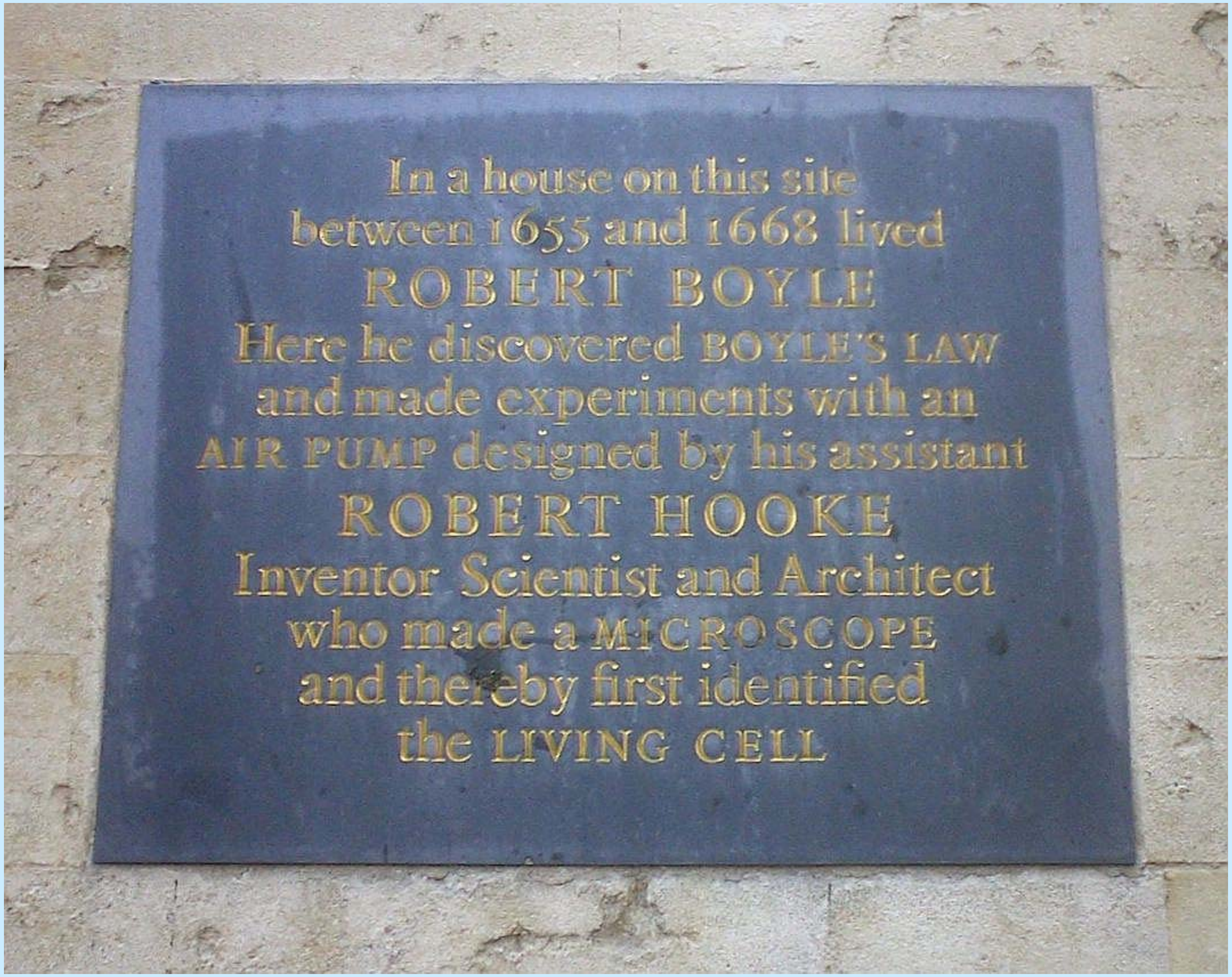
$$P.V = \text{constant}$$

or

$$P_1V_1 = P_2V_2$$



In a house on this site
between 1655 and 1668 lived
ROBERT BOYLE
Here he discovered BOYLE'S LAW
and made experiments with an
AIR PUMP designed by his assistant
ROBERT HOOKE
Inventor Scientist and Architect
who made a MICROSCOPE
and thereby first identified
the LIVING CELL



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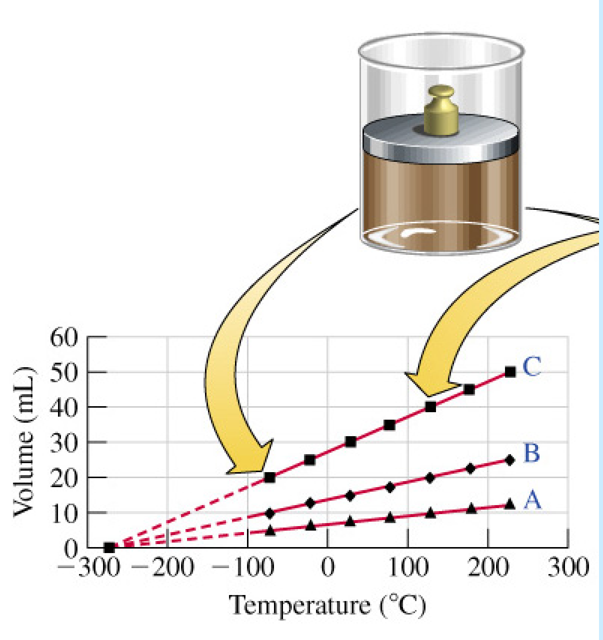
Charles's Law

- Charles (1787) and Gay-Lussac (1822) kept the mass of gas and the pressure constant and studied the relationship between temperature and volume

They found $$\frac{V_{(100^{o}C)}}{V_{(0^{o}C)}} = 1.375$$

Charles’s Law

- Further experiments showed that volume and temperature were linearly related



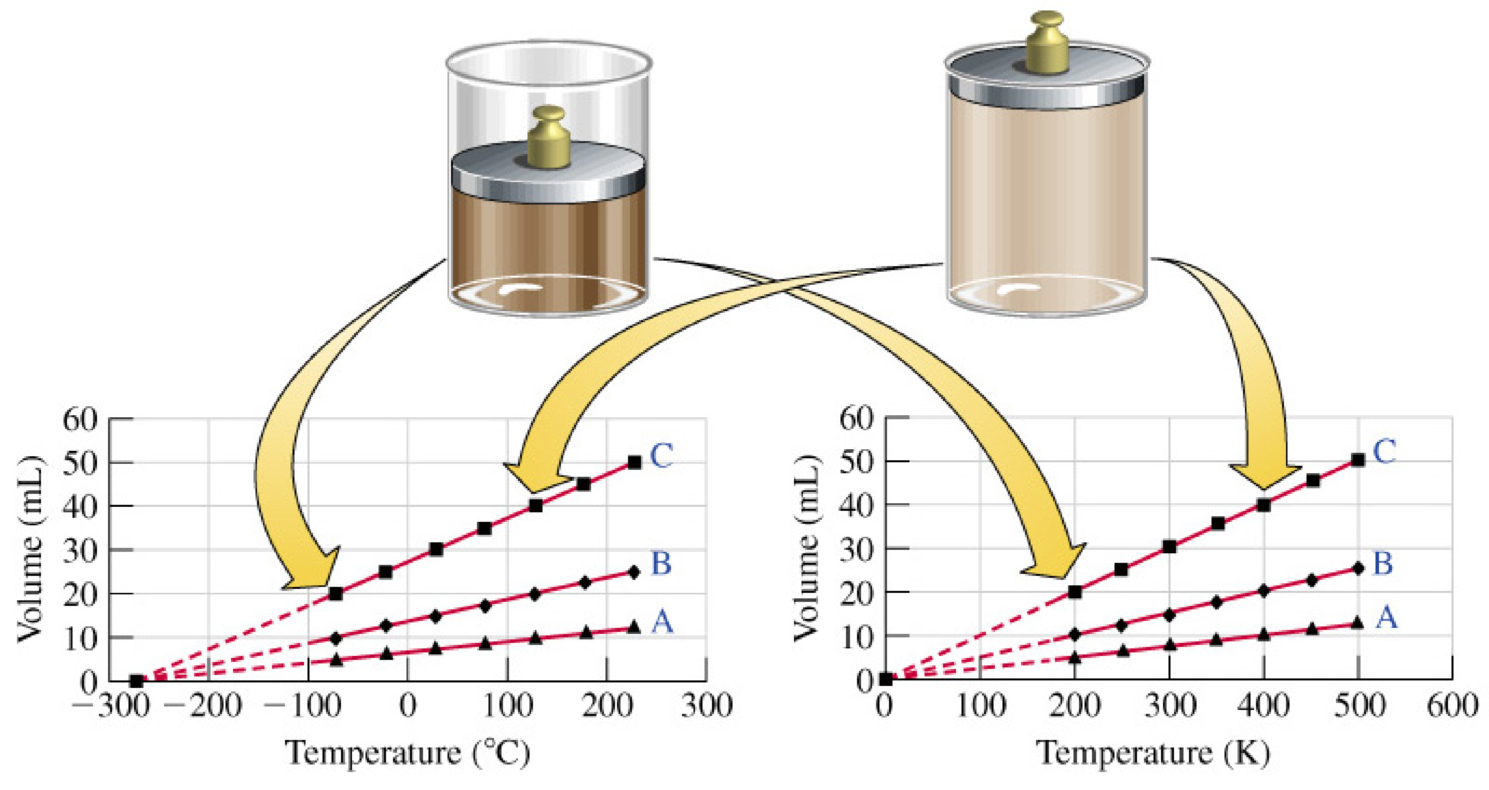
Charles's Law

- Further experiments showed that volume and temperature were linearly related and that the temperature intercept (when volume is zero) was at $-273.15^{o}C$.
- This temperature is now defined as absolute zero and the Kelvin temperature scale given by

$$T(K) = t(^{\circ}C) + 273.15$$

Charles's Law

- Graphically:



Charles's Law/Combined Gas Law

Charles's Law can be expressed as $\frac{V}{T} = \text{constant}$

Combining Boyle's Law and Charles's Law

$P.V = \text{constant and } \frac{V}{T} = \text{constant}$

gives

$$\frac{P.V}{T} = \text{constant} \quad \text{or} \quad \frac{P_1.V_1}{T_1} = \frac{P_2.V_2}{T_2}$$

Avogadro’s Law

- From Gay-Lussac’s experiment on reacting gases Avogadro concluded
  - “Equal volumes of different gases, at the same temperature and pressure, contain equal numbers of molecules”

Avogadro’s Law

- “Equal volumes of different gases, at the same temperature and pressure, contain equal numbers of molecules”
- Take 2 equal volumes of gas. They have equal numbers of molecules. Add them together, you have twice the volume and twice the number of molecules.
- Hence gas volume is proportional to number of molecules and subsequently to number of moles.

$$V \propto n \text{ or } V/n = \text{constant}$$

Gas Law

Given that :

$$P.V = \text{constant} \quad \text{(Boyle's Law)}$$

$$\frac{V}{T} = \text{constant (Charles's Law)}$$

$$\frac{V}{n} = \text{constant (Avogadro's Law)}$$

leads to

$$\frac{P.V}{n.T} = \text{constant}$$

Usually written **PV = nRT**

(Where R is a constant)

Ideal Gas Law

- The ideal gas law can be written in terms of moles or molecules

$PV = nRT$

n = number of moles R = gas constant

$PV = NkT$

N = number of molecules k = Boltzmann’s constant

Ideal Gas Law

- Values of the constants
  - R = 8.314 J K^{-1} mol^{-1} (Pa m^3 K^{-1} mol^{-1}, *kPa L K^{-1} mol^{-1}*)
    R = 0.0821 L atm K^{-1} mol^{-1}
  - k = 1.38×10^{-23} J K^{-1} (really J K^{-1} $molecule^{-1}$ but molecule is just a number)

Other useful forms of the ideal gas law

$$PV = \frac{m}{M}RT$$

m = mass of gas

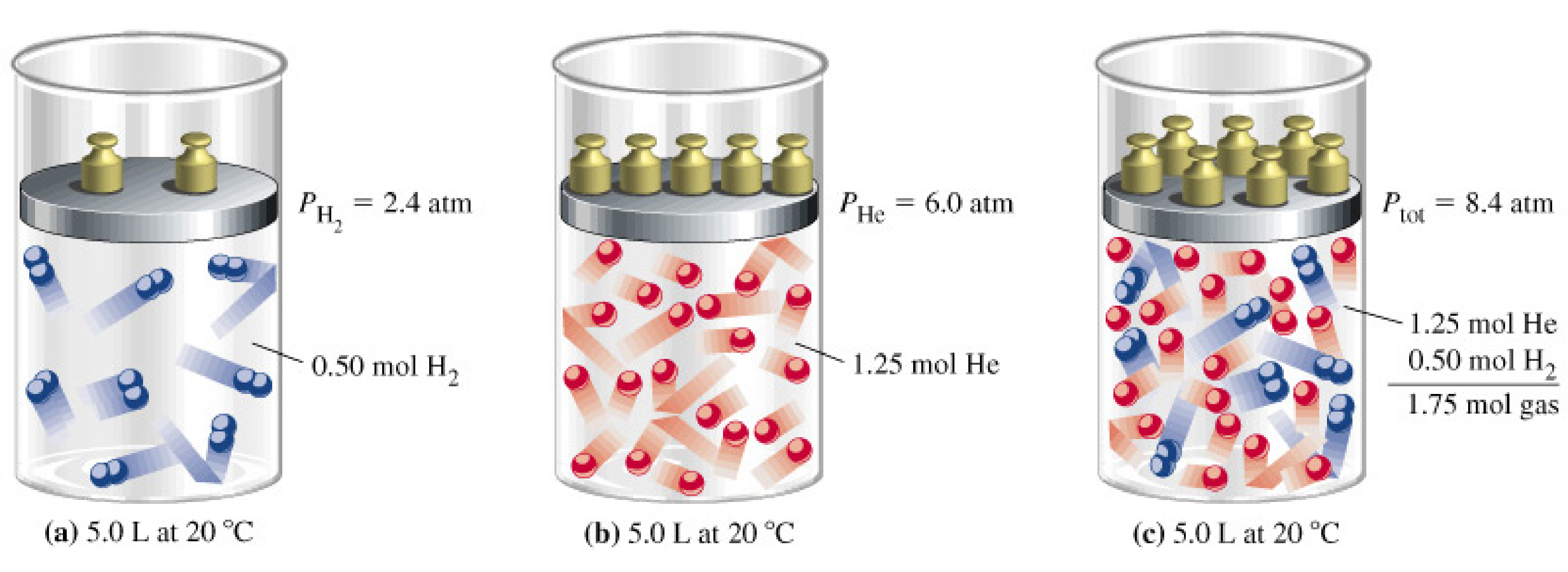
M = molar mass (molecular weight)

$$d_{gas} = \frac{m}{V} = \frac{PM}{RT}$$

Dalton’s Law

- In a gas mixture each component fills the container and exerts the pressure it would if the other gases were not present.
- Alternatively, each component acts as if it were alone in the container

Dalton's Law


P_{H_2} = 2.4 atm
0.50 mol H_2
P_{He} = 6.0 atm
1.25 mol He
P_{tot} = 8.4 atm
1.25 mol He
0.50 mol H_2
1.75 mol gas
(a) 5.0 L at 20 °C
(b) 5.0 L at 20 °C
(c) 5.0 L at 20 °C

Dalton’s Law

- Thus for any component i

$$P_iV = n_iRT$$

We call P_i the partial pressure of component i

- The total pressure is given by the sum of the partial pressures

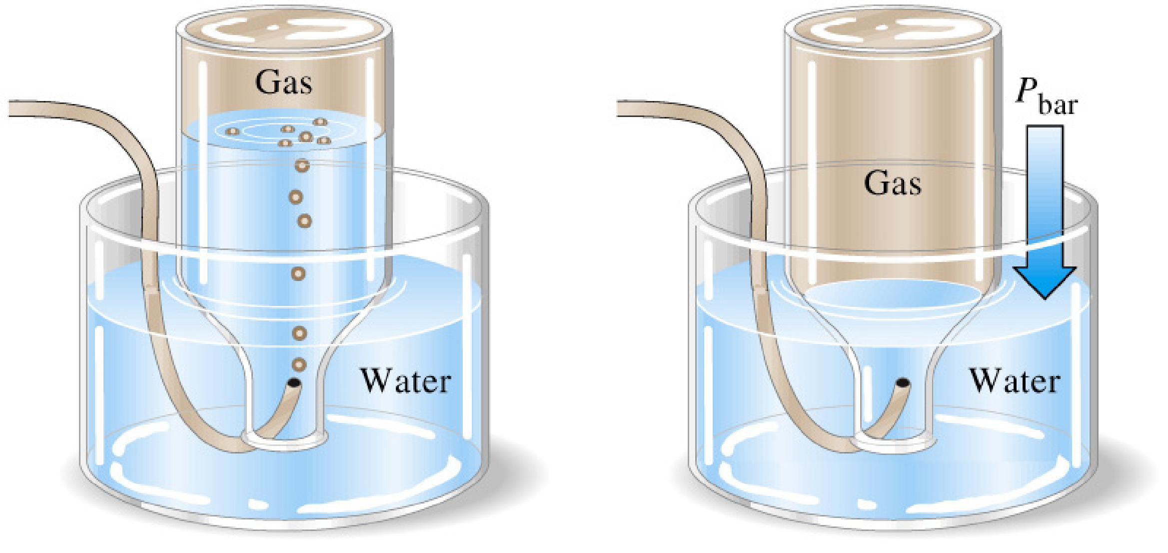
$$P = P_1 + P_2 + P_3 + \ldots.$$

- Also note that the mole fraction in the gas phase

$$\chi_i = \frac{n_i}{n} = \frac{P_i}{P}$$

Dalton's Law

- A common use of Dalton's Law is when gases are collected over water



$$P_{sample} + P_{water} = P_{bar}$$

Microscopic Properties of Gases

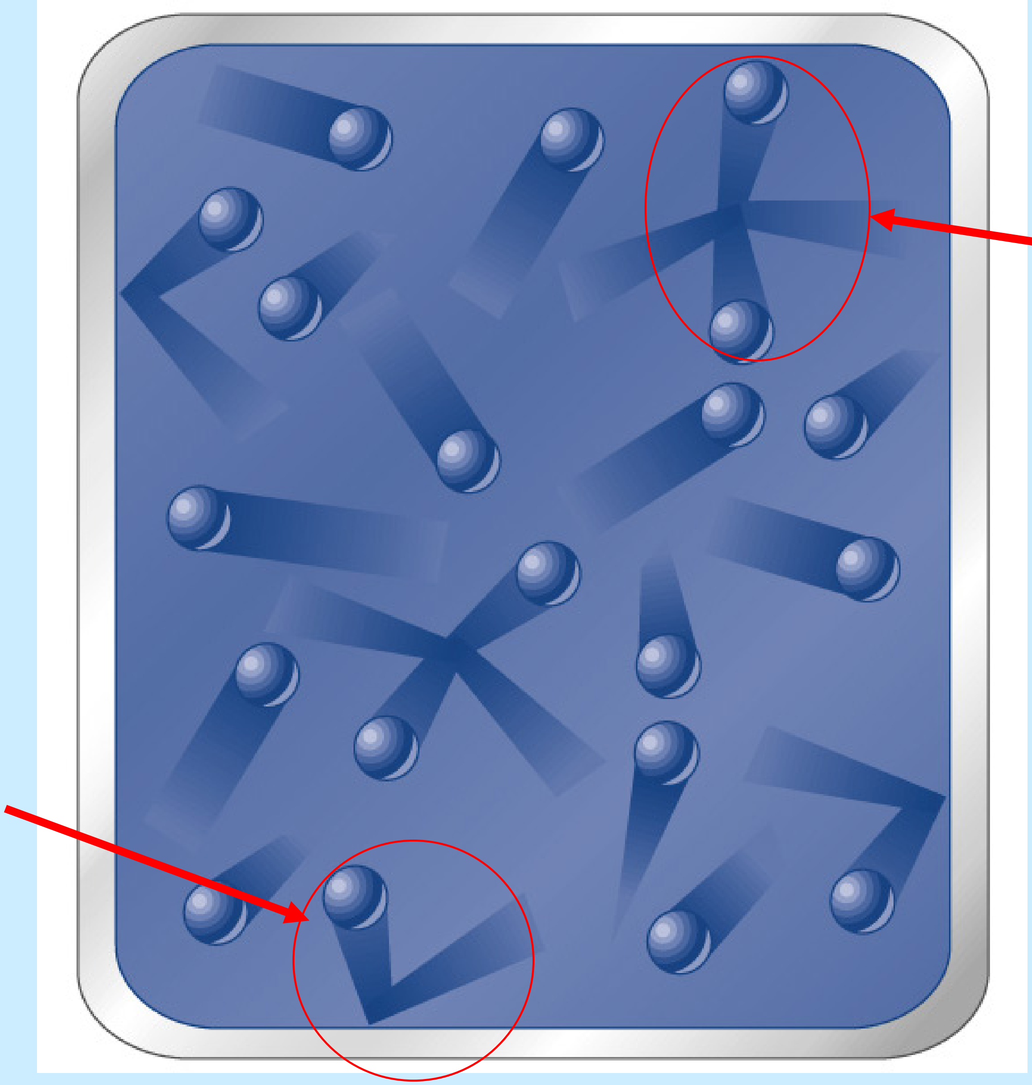
- So far we have seen the gas laws.
- These came from observations.
- In this section we want to look at a theory that explains the gas laws:

The kinetic theory of gases

or The kinetic molecular theory

Kinetic Theory of Gases: Assumptions

1. A gas is made up of a large number of extremely small particles (molecules or atoms) in constant, random, straight line motion
2. Molecules occupy very little volume (most of the container is free space)
3. Molecules collide with one another and with the walls of the container
4. There are no forces between the molecules
5. Molecules can gain or lose energy on collision but the total energy remains constant



Collision between molecules

Collision with wall

The theory will give information on the speeds of molecules, the frequency with which they collide, and the distribution of energy

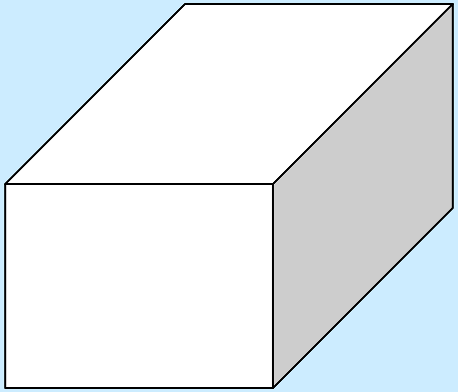
It is only useful if it can predict the gas laws

Pressure

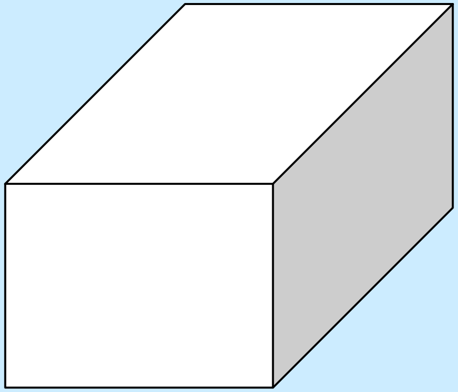
- Pressure comes from the gas molecules hitting the walls of the container
- The pressure will depend on:
  - – How many molecules hit the wall
  - – How fast they are travelling
    - (how “hard” they hit the wall)

Pressure

- Put a gas in a box of volume V.
  - N molecules each of mass m
  - each molecule has a speed u
- Think about one side of the box
  - Call that the x direction



Pressure



- When a molecule hits the wall it changes direction.
  - We assume the speed doesn’t change so the change in momentum is $2mu_x$

- The number of molecules hitting the wall depends how many molecules are in the container and how big it is N/V.
- It also depends on which way they are going ½, how fast they are moving u_x.
- i.e $\frac{1}{2}N/V\ u_x$

Pressure

- Pressure depends on $2mu_x$ AND $½N/V\ u_x$
- Hence $P \propto N/V m u_x^2$

- Not all molecules have the same speed so we should use the average of u_x and all directions are the same so $u_x = u_y = u_z = 1/3u$
- hence

$$\boxed{P = \frac{1}{3}\frac{Nm\overline{u^2}}{V}}$$

where $\overline{u^2}$ = the average of the squares of the speeds

$$P = \frac{1}{3}\frac{Nm\overline{u^2}}{V} \qquad \therefore\ PV = \frac{1}{3}Nm\overline{u^2}$$

This is looking a lot like PV = constant

If $\overline{u^2}$ is a constant at constant temperature.

This is Boyle's Law

We will not prove this but assume it is true and use the PV equations from the macroscopic and microscopic sections to learn about speed and temperature

Temperature/kinetic energy/speed

The kinetic energy of a molecule is:

$$\tfrac{1}{2}mu^2$$

The average kinetic energy of a molecule is:

$$\frac{1}{2}m\overline{u^2}$$

The kinetic energy of a mole of molecules is

$$\frac{1}{2}N_A m\overline{u^2} \qquad (N_A \text{ is Avogadro's number})$$

The kinetic energy of a mole of molecules (E) is

$$E = \frac{1}{2} N_A m\overline{u^2} \quad \therefore \quad m\overline{u^2} = \frac{2E}{N_A}$$

But

$$PV = \frac{1}{3}\frac{Nm\overline{u^2}}{} = \frac{2}{3}\frac{N.E}{N_A} = \frac{2}{3}\frac{n.E}{}$$

given that $PV = nRT$

$$nRT = \frac{2}{3}\frac{n.E}{} \quad \therefore \quad E = \frac{3}{2}RT$$

$$\boxed{E = \frac{3}{2}RT}$$

This shows that the temperature of the gas is a measure of the kinetic energy of the molecules

Molecular Speeds

Equating

$$E = \frac{1}{2} N_A m \overline{u^2} \quad \text{and} \quad E = \frac{3}{2} RT$$

Gives

$$E = \frac{1}{2} N_A m \overline{u^2} = \frac{3}{2} RT$$

$$\overline{u^2} = \frac{3RT}{N_A m} = \frac{3RT}{M}$$

The root mean square speed

$$\boxed{u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}}$$

What is the speed of a hydrogen molecule at 25°C?

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 298}{2.016 \times 10^{-3}}} = 1.92 \times 10^{3}\ \mathrm{m\,s^{-1}}$$

(7,000km/hr)

The factor of 10^{-3} in the denominator is to put the molar mass in SI units

Distribution of molecular speeds

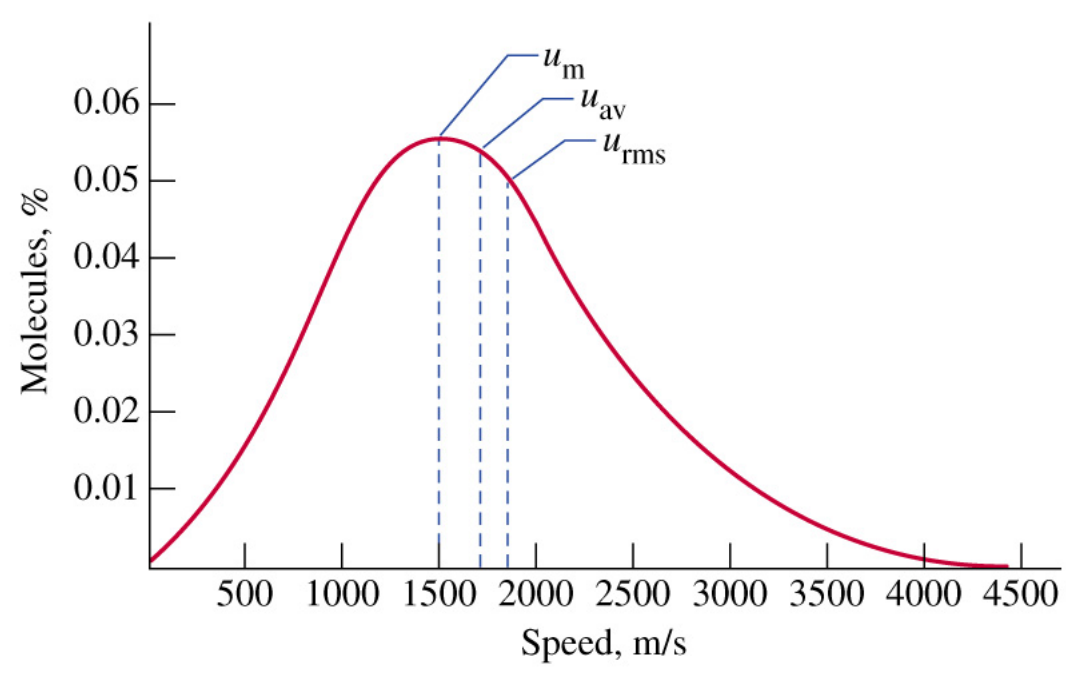
So far we have calculated the root mean square speed only

What other speeds are possible?

What is the real average speed?

Distribution of molecular speeds

All speeds are possible but are not equally likely



u_m is the "most probable speed" (mode)

u_{av} is the average speed (mean)

u_{rms} is the root mean square speed

Average speeds

The three average speeds can be obtained from the distribution

$$u_m = \sqrt{\frac{2RT}{M}} \qquad u_{av} = \sqrt{\frac{8RT}{\pi M}} \qquad u_{rms} = \sqrt{\frac{3RT}{M}}$$

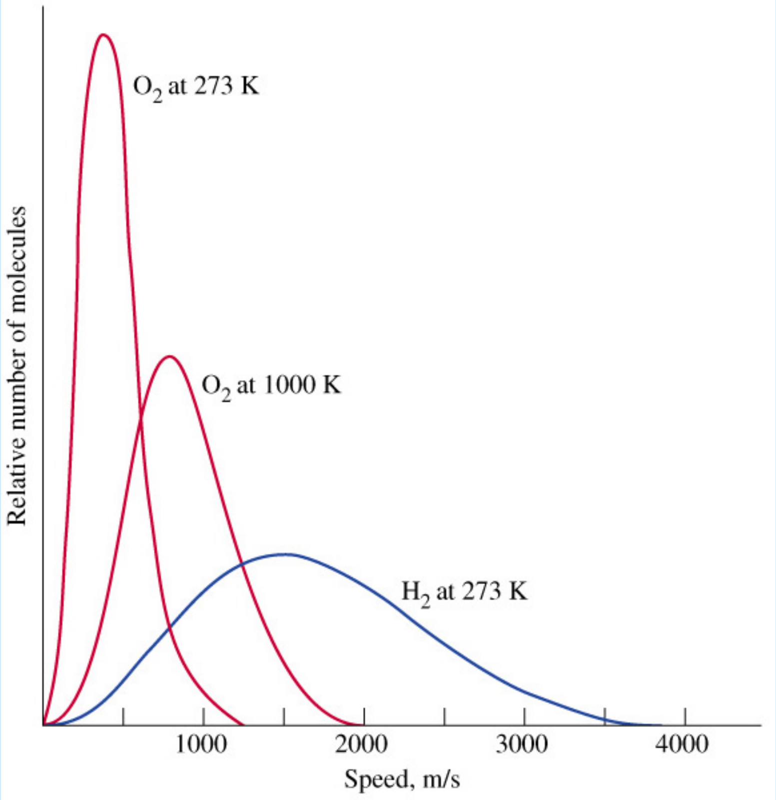
$$\frac{u_{av}}{u_m} = \frac{\sqrt{\frac{8RT}{\pi M}}}{\sqrt{\frac{2RT}{M}}} = \sqrt{\frac{8}{2\pi}} = 1.13 \qquad \frac{u_{rms}}{u_m} = \frac{\sqrt{\frac{3RT}{M}}}{\sqrt{\frac{2RT}{M}}} = \sqrt{\frac{3}{2}} = 1.22$$

Variation in speed with temperature and molar mass

The average speeds vary with $\sqrt{T}$ and $1/\sqrt{M}$

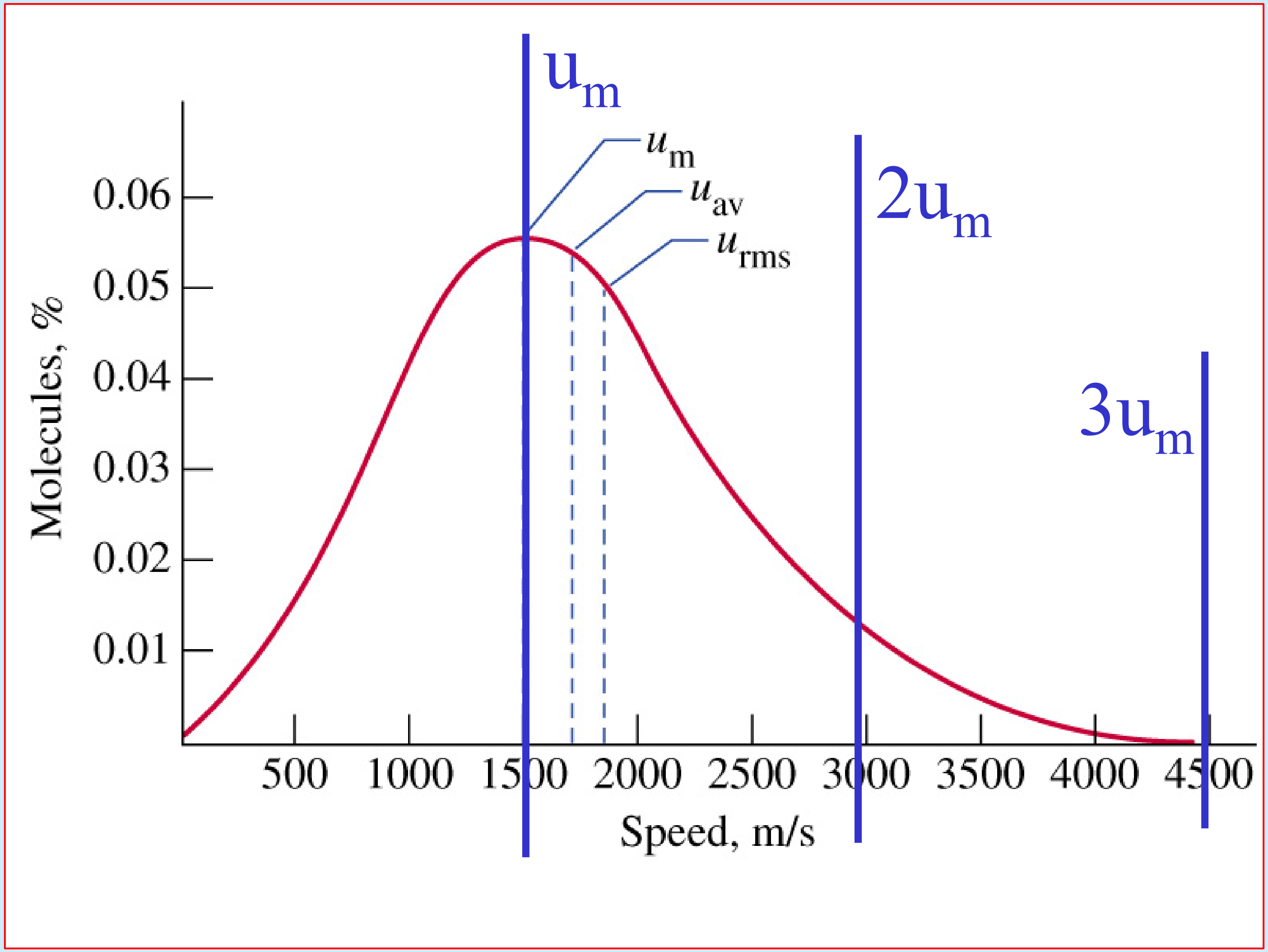
The red curves are for O_2 at two temperatures.

The left O_2 curve and the blue H_2 curve are at the same temperature.



How broad is the speed distribution

We know the average speeds. Do most molecules have speeds similar to the average? Do a lot go faster?



Clearly the distribution is narrow

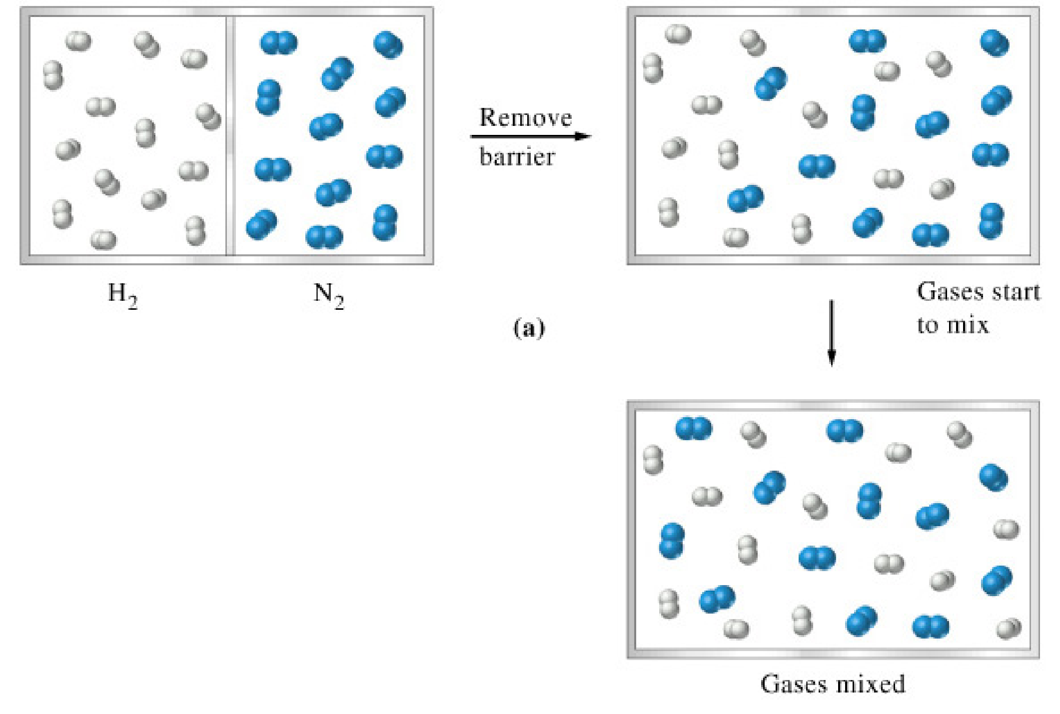
It is possible to calculate the fraction of molecules that have a speed greater than u

Speed u	Fraction of molecules with speeds greater than u
0	1 (all molecules go faster than 0)
$3u_m$	$4.5x10^{-4}$
$5u_m$	$4x10^{-10}$
$10u_m$	$4x10^{-43}$

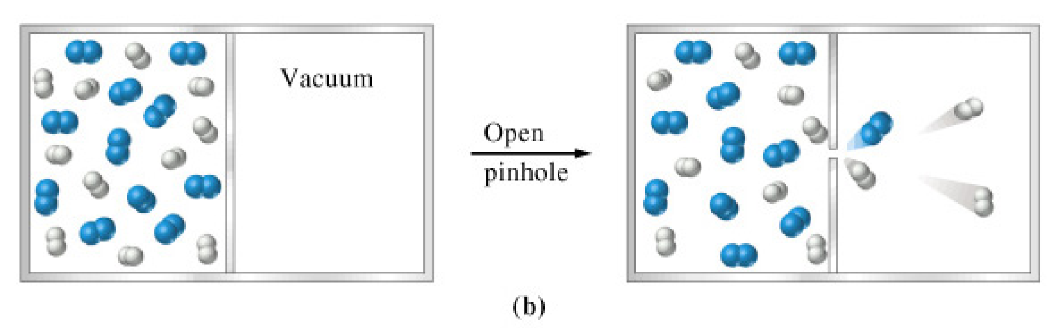
Most molecules have speeds close to u_m

Diffusion and Effusion

Diffusion



Effusion



Collisions with the Wall

The number of collisions that molecules make with the wall depend on how many molecules there are (per unit volume) and how fast they are moving. Z_{wall} will have units of $m^{-2}\ s^{-1}$

$$Z_{wall} \propto \frac{N}{V}.u_{av}$$ actually $$Z_{wall} = \frac{1}{4}\frac{N}{V}.u_{av}$$

Effusion

We can obtain a quantitative understanding of effusion by recognizing that effusion is the loss of a molecule that would normally hit the wall.

$$Z_{\text{wall}} = \frac{1}{4}\frac{N}{V}.u_{\text{av}}$$

The rate at which molecules leave the container is the wall collision rate times the area of the hole

$$\text{Rate of effusion} = Z_{\text{wall}}.A = \frac{1}{4}\frac{N}{V}.u_{\text{av}}.A$$

$\therefore$ for 2 gases (A and B) in the same container

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{Z_{\text{wall}}(\text{A}).\text{A}}{Z_{\text{wall}}(\text{B}).\text{A}} = \frac{\frac{1}{4}\frac{N_A}{V}.u(\text{A})_{av}.\text{A}}{\frac{1}{4}\frac{N_B}{V}.u(\text{B})_{av}.\text{A}}$$

$$= \frac{N_A}{N_B}\frac{u(\text{A})_{av}}{u(\text{B})_{av}} = \frac{N_A}{N_B}\frac{\sqrt{8RT/\pi M_A}}{\sqrt{8RT/\pi M_B}} = \frac{N_A}{N_B}\frac{\sqrt{M_B}}{\sqrt{M_A}}$$

Note that the ratio of the number of molecules is the ratio of the partial pressures

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{P_A}{P_B}\frac{\sqrt{M_B}}{\sqrt{M_A}}$$

and for EQUAL pressures

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$ Graham's Law

Aside

Students often have problems with questions involving rates and or time, because they are inverses

Always remember that $\text{Rate} = \frac{\text{molecules}}{\text{time}}$

So the faster the rate the smaller the time

Collisions between molecules

When studying interactions between gas molecules you need to know how often the molecules actually collide

The collision frequency is the number of collisions a particular molecule makes in one second. This will depend on how many molecules there are (per unit volume), how fast they are moving, and how big they are.

Collisions between molecules

For a gas where all the molecules are the same, and have a diameter d, the collision frequency is Z_A

$$Z_A = \sqrt{2}\pi d^2 u_{av} \frac{N}{V} = \sqrt{2}\pi d^2 u_{av} \frac{P}{kT}$$

Z_A will have units of s^{-1}

Collisions between molecules

To calculate the total number of collisions for all molecules we must multiply Z_A by N/V to count all the molecules, and by ½ so we don't count them twice.

$$Z_{AA} = \frac{1}{2}\frac{N}{V}\sqrt{2}\pi d^2 u_{av}\frac{N}{V} = \frac{1}{\sqrt{2}}\pi d^2 u_{av}\left(\frac{N}{V}\right)^2$$

Z_{AA} will have units of $s^{-1}m^{-3}$

Mean free path

A related parameter is the average distance a molecule travels between collisions. This is the mean free path

The collision frequency is Z_A s^{-1}

The time between collisions is $1/Z_A$ s

The average speed of the molecules is u_{av}

Since distance is speed times time

$$\lambda = \frac{u_{av}}{Z_A} = \frac{1}{\sqrt{2}\pi d^2}\frac{V}{N}$$

So how big are these numbers??

Nitrogen at 298K and 1 atm

$$u_{av} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\times 8.314\times 298}{\pi\times 28.01\times 10^{-3}}} = 475\ \mathrm{m\ s^{-1}}$$

$$d \approx 4.0\times 10^{-10}\ \mathrm{m}$$

$$\frac{N}{V} = \frac{P}{kT} = \frac{1.013\times 10^{5}}{1.38\times 10^{-23}\times 298} = 2.46\times 10^{25}\ \mathrm{m^{-3}}$$

$$Z_{wall} = \frac{1}{4}u_{av}\frac{N}{V} = \frac{1}{4}\times 475\times 2.46\times 10^{25} = 2.92\times 10^{27}\ \ \mathrm{m^{-2}s^{-1}}$$

$$Z_{A} = \sqrt{2}\pi d^{2}u_{av}\frac{N}{V} = \sqrt{2}\times\pi\times\left(4.0\times 10^{-10}\right)^{2}\times 475\times 2.46\times 10^{25} = 8.3\times 10^{9}\ \ \mathrm{s^{-1}}$$

$$\lambda = \frac{u_{av}}{Z_{A}} = \frac{475}{8.3\times 10^{9}} = 5.6\times 10^{-8} = 56\ \mathrm{nm}$$

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

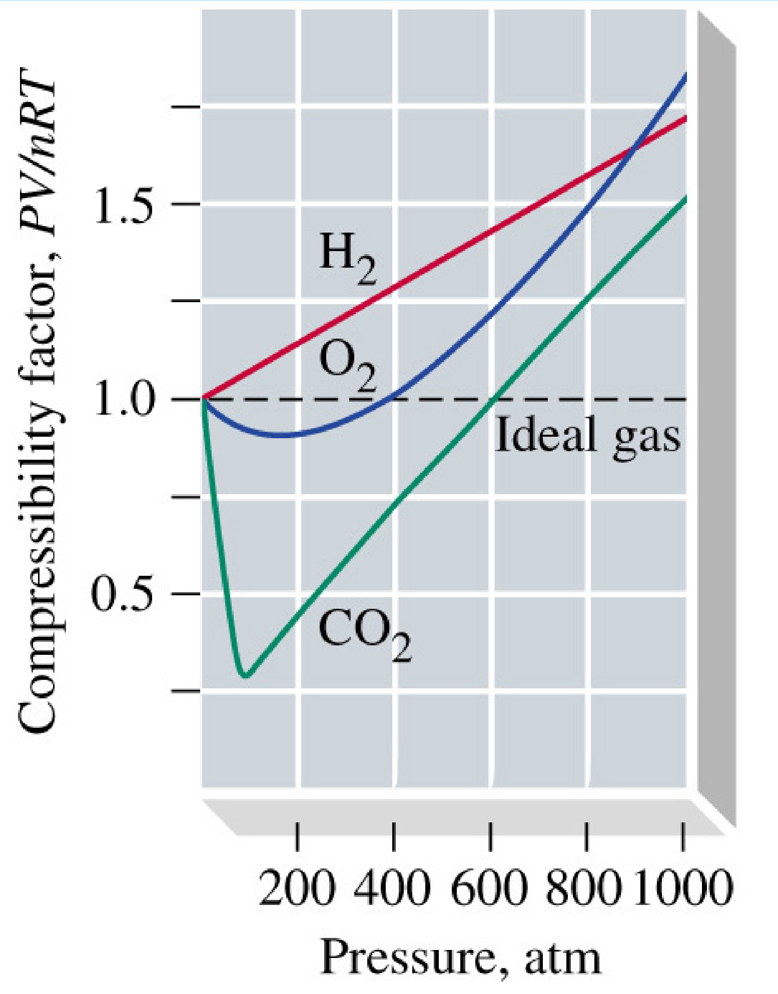
- One way to measure the deviation from ideal behaviour is to define a compressibility factor Z as:

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

- For an ideal gas Z=1

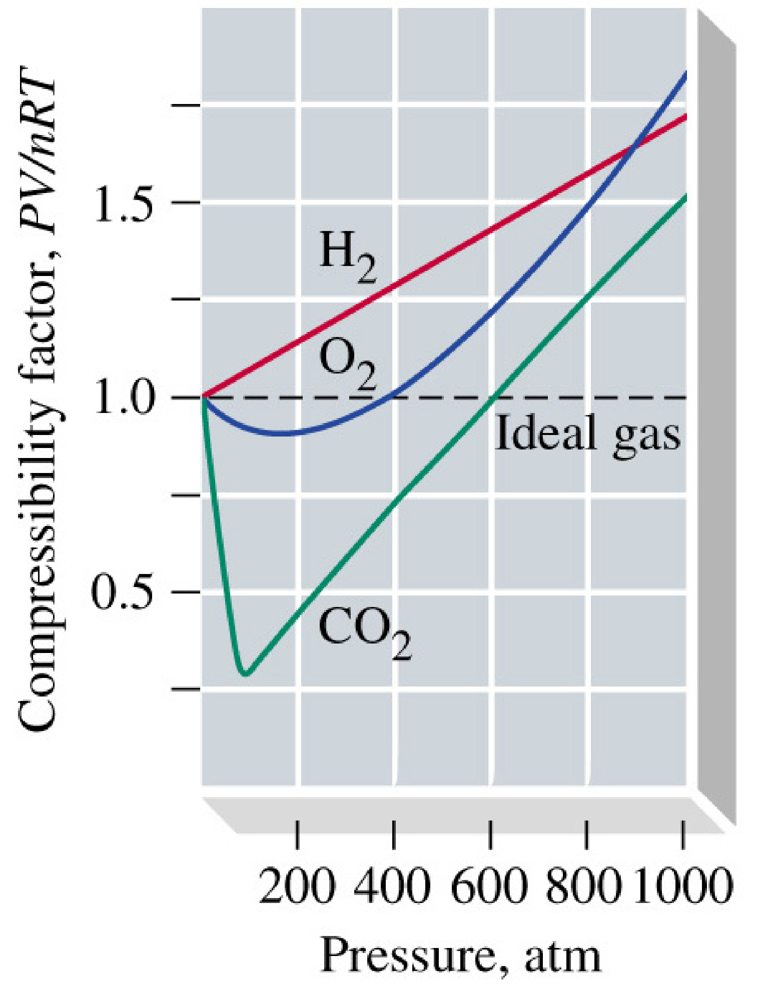
Compressibility factor

- 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

$$PV = nRT + Pnb$$

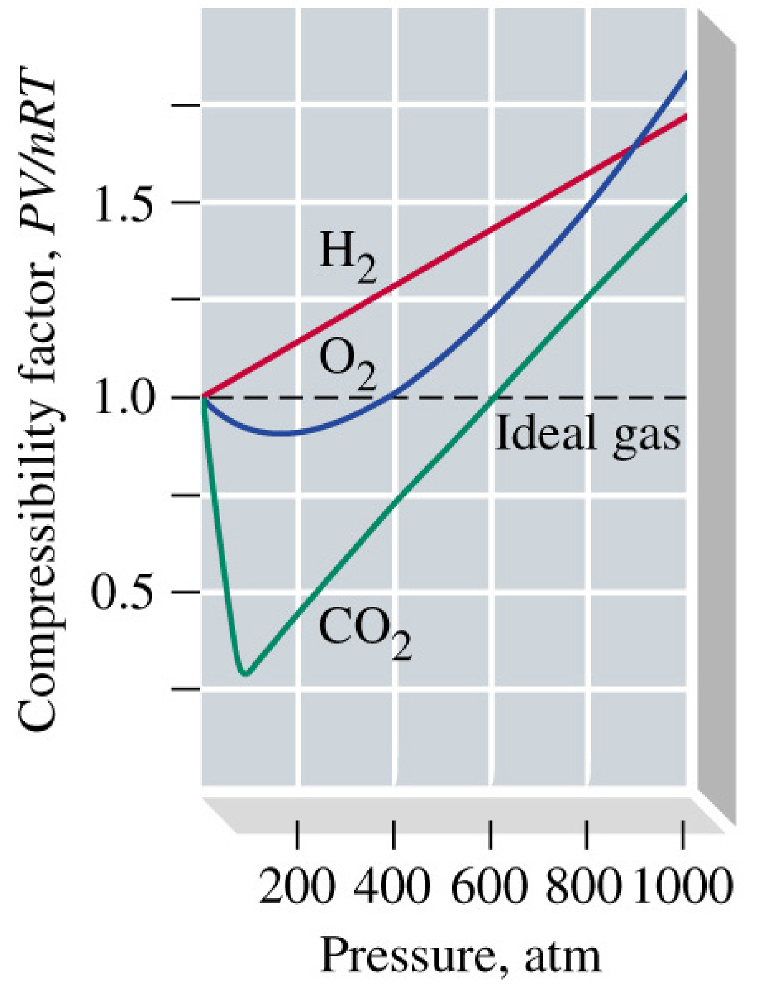
$$Z = \frac{PV}{nRT} = 1 + \frac{bP}{RT}$$

A plot of Z against P would be a straight line of intercept 1

van der Waal Equation

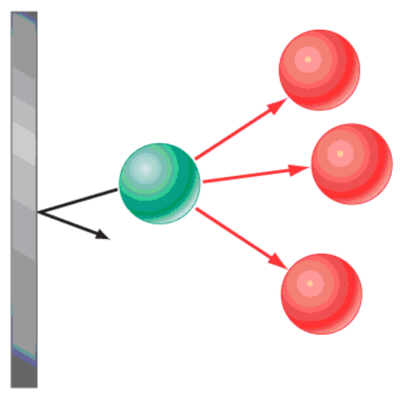
$$Z = \frac{PV}{nRT} = 1 + \frac{bP}{RT}$$

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



▲ FIGURE 6-22
Intermolecular forces of attraction

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

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

van der Waal Equation

– Combining this pressure term into the previous equation:

$$P(V\text{-}nb) = nRT$$

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.

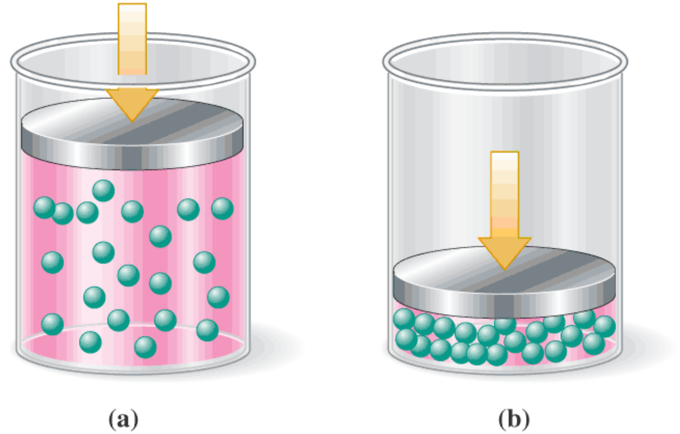
van der Waal Equation

- 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 “b”

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

- We defined “b” as the volume of the molecules. This can be estimated from the volume of one mole of the pure liquid.



▲ FIGURE 6-21
The effect of finite molecular size

van der Waal “a”

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

- “a” is a measure of the intermolecular forces. We will see more about this later in the course.

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
Compare Cl_2 to He	variation of a factor of 200	variation of a factor of <3