

Gases and The Gas Laws

Why Do We Care about this Stuff?

Fundamentals. The kinetic theory underlying the gas laws is one of the great successes of the development of our molecular view of the world, with a myriad of practical applications in everyday life (e.g., hot air balloons, compressed air balloons, explosions, internal combustion engine, ...).

Measuring “amount of reaction”. We have done this using:

(i) # moles of reagent, (ii) mass of reagents, (iii) volume of a pure liquid or solid component whose density is known, (iv) volume of a solution whose concentration is known, and to that list we now want to add:

(v) volume of a gaseous component of known temperature and (partial) pressure

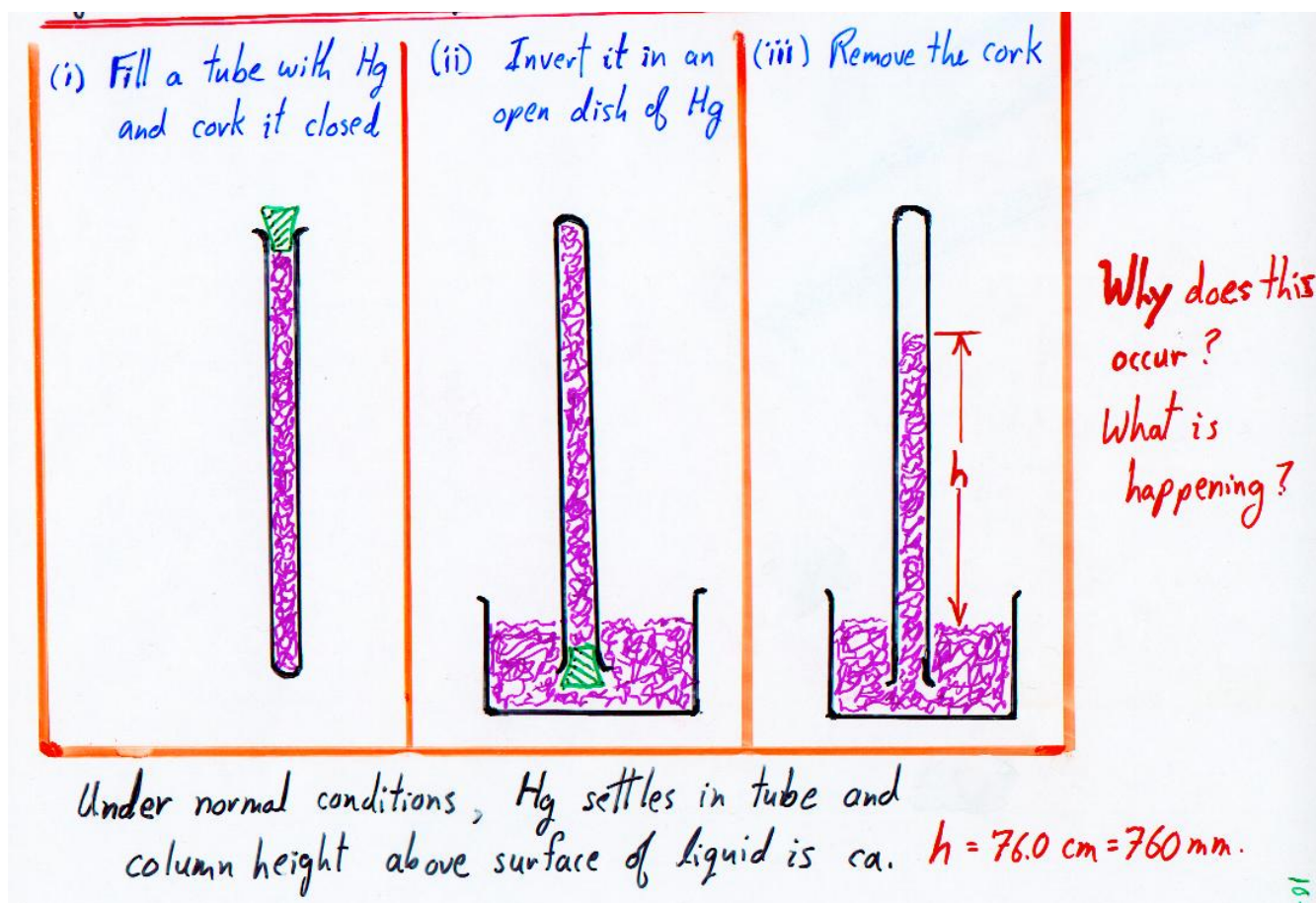
What is Pressure?

Pressure is macroscopically defined as the amount of *force per unit area*,

- in SI units the amount of pressure is specified in terms of N/m^2 (newtons per square meter) or Pa (pascal)
- but more commonly we use the units atm (atmospheres), bar, torr (or mm Hg), and in a few backward countries, lb/in^2

How do these units arise? How are they related? How is pressure measured?

How do we construct a mercury (Hg) barometer?



What pressure, in SI units, will support a column of Hg 760 mm high ?

Assume that the mercury is in a tube of cross-section area of A [cm²]

Volume of liquid Hg in column (above surface) =

Since the density of liquid Hg is 13.595 08 g/cm³,

mass of Hg supported in column =

Force downward exerted by column (recall $F = m a$; $a = g = 9.806 65$ m/s²)

= upward force supporting column

Area over which this Force is exerted =

$$\therefore \text{Pressure} = \frac{\text{Force}}{\text{Area}} =$$

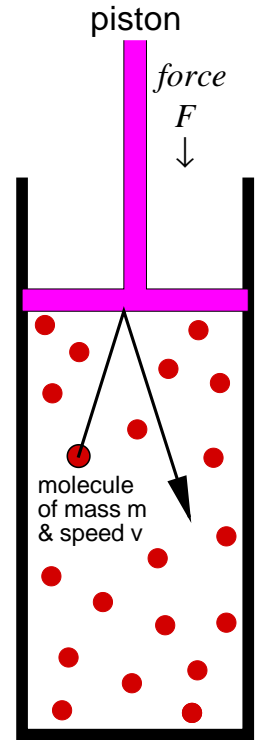
Define: 1 standard atmosphere of pressure:

TABLE 6.1 Some Common Pressure Units

Atmosphere (atm)	
Millimeter of mercury (mmHg)	1 atm = 760 mmHg
Torr (Torr)	= 760 Torr
Newton per square meter (N/m ²)	= 101,325 N/m ²
Pascal (Pa)	= 101,325 Pa
Kilopascal (kPa)	= 101.325 kPa
Bar (bar)	= 1.01325 bar
Millibar (mb)	= 1013.25 mb

What is the “microscopic” (or molecular) nature of pressure ?

A gas is a medium in which the distances between molecules are much greater than the sizes of the molecules, and except when undergoing a collision with one another or the wall of the container, they travel in straight lines. Consider the trajectory of one of the molecules in a cylinder of gas with a piston pushing down with a force \vec{F} . When an upward-moving molecule of mass m and vertical speed u collides with the piston and rebounds downward:



Change in molecule's momentum is

∴ momentum gained by piston is

But:

$$\begin{aligned} \text{Force} &= \text{mass} \times \text{acceleration} = m \frac{du}{dt} = \frac{d(mu)}{dt} \\ &= \{ \text{rate of change of momentum with time} \} \end{aligned}$$

∴ Net force of gas on piston

$$= (\text{momentum change per collision}) \times (\text{no. collisions/sec})$$

What is the “microscopic” nature of temperature ?

Temperature is the vulgar common for the sophisticated scientific concept called (by me) “*degree of hotness*”, which is more quantitatively specified as the *average translational kinetic energy per (free) molecule*.

But compare: (a) a pot of boiling water @ 100°C
 (b) an oven heated to 100°C

The “degree of hotness” is the same for both, but *which* would you rather put your hand in? Why?

For a fixed amount of gas in a fixed volume of gas, how does increasing temperature affect the pressure?

The Gas Laws

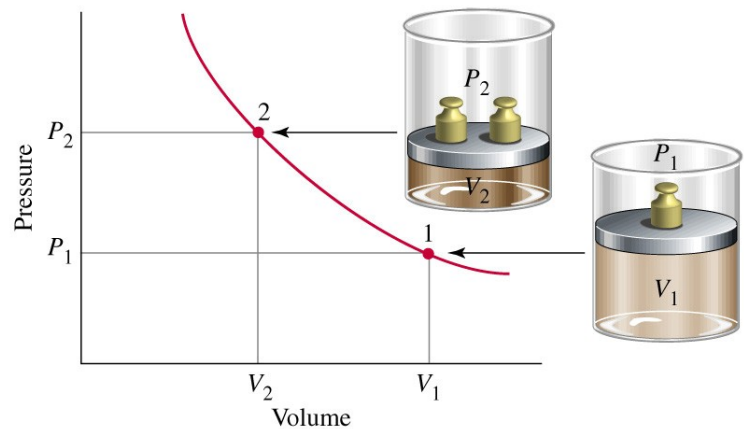
1. Boyle's Law

Our everyday experience (e.g., a bicycle pump) tells us that if we force a given amount of gas to occupy a smaller volume, its pressure increases.

Careful experimental measurement shows that the relationship between the two (for a fixed amount of gas at a fixed temperature!) is precisely reciprocal

$$P \propto \frac{1}{V} \quad \text{or}$$

$$PV = \text{const.}(T)$$

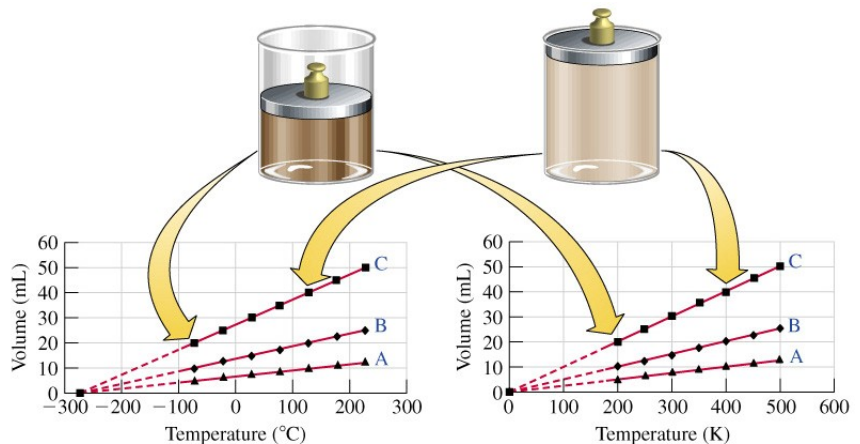


2. Charles' Law

Empirically find that for a fixed amount of gas at a fixed pressure, its volume varies linearly with temperature; i.e., where T_0 is some chosen initial temperature

$$V(T) = V(T_0) + b(T - T_0) = V(T_0) [1 + \alpha(T - T_0)]$$

and also empirically find that when T is in $^{\circ}\text{C}$, for all gases $\alpha = 1/273.15$



If we let our reference temperature $T_0 = 0^\circ\text{C}$, the above equation becomes

$$V(T) = V(0^\circ\text{C}) [1 + \alpha(T - 0)] =$$

Comparing volumes at two arbitrary temperatures T_1 and T_2 , we obtain

$$\frac{V(T_2)}{V(T_1)} =$$

This suggested a more convenient temperature scale (proposed by Lord Kelvin)

This in turn suggested the existence of some *absolute zero of temperature*!

It also means that Charles' Law provides the basis for a gas thermometer for measuring temperature!

3. Avogadro's Hypothesis

“At a fixed temperature and pressure, the volume of a gas is directly proportional to the amount (no. moles) of gas.”

A more modern interpretation gives us an alternate statement:

“Equal volumes of different gases at the same temperature and pressure contain equal numbers of molecules.”

This tells us that we can use the volume of a gaseous component species to as a measure of the “**{amount of reaction}**” in a chemical process!

Careful modern experiments tell us that the volume of exactly 1.0 moles of any (ideal) gas at “standard temperature and pressure” (STP) is 22.414 L
[where STP corresponds to $P = 1.0$ atm pressure (= 101.325 kPa)
and temperature = $0^\circ\text{C} = 273.15\text{ K}$]

The Ideal Gas Law

- Boyle's law says that for fixed n & T : $V \propto \frac{1}{P}$ or $V = k_b(n, T) \times \frac{1}{P}$
- Charles' law says that for fixed n & P : $V \propto T$.

For Boyle's law to remain valid, necessarily $k_b(n, T) \propto T$ which means that:

$$V = k_A(n) \times \frac{T}{P}$$

- But Avogadro's hypothesis (law) say that for fixed T & P : $V \propto n$

For Boyle's & Charles' laws to remain valid, necessarily $k_a(n) \propto n$ or

$$k_a(n) = R \times n \quad \text{where } R \text{ is a pure numerical constant!}$$

This then means that $V = R \times \frac{nT}{P}$ or $PV = nRT$

What is the value of R ?

Recall ... the volume of 1.0 mole of *any* (ideal) gas at STP (1.0 atm & 0°C) is 22.4141 L = $22.4141 \times 10^{-3} \text{ m}^3$

$$\therefore R = \frac{PV}{nT} =$$

Exercise 1: What is the numerical value of R if

- a) pressure is in bar and volume in L?
- b) pressure is in torr and volume in L?

Gas law problems are of 2 types:

1. Use the overall Ideal Gas equation $PV = nRT$ directly: given values of 3 variables, determine the fourth (and perhaps use it for something)

N.B. (i) *Essential* to ensure that units for the value of R match those used for P & V !

(ii) *Essential* to specify T in the Kelvin scale.

Exercise 2: What is the volume of 44.6 g of $\text{N}_2(\text{g})$ at 100°C and a pressure of 227.5 kPa?

2. Use proportionality relations!

Rearranging the ideal gas equation gives

$$\frac{PV}{nT} = R = \{\text{a constant}\} = \frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

for *any* two samples of *any* two (ideal) gases

Exercise 3: If a given sample of gas at 23°C and 720 torr occupies 3.72 L, *what is* its volume at -22°C and 830 torr?

Consider some more general problems.

Exercise 4: If 0.896 g of a compound of N and O occupies 524 mL at $P = 730$ torr and $T = 28^\circ\text{C}$, *what are* its molecular weight and its molecular formula?

Exercise 5: Consider the reaction $2 \text{NaN}_3(\text{s}) \xrightarrow{\text{heat}} 2 \text{Na}(\text{l}) + 3 \text{N}_2(\text{g})$
 How many grams of $\text{NaN}_3(\text{g})$ are required to produce 20.0 L of $\text{N}_2(\text{g})$ at 30.0°C and 786 mm Hg?

Gaseous Mixtures & Partial Pressures

From the Ideal Gas Law, we see that $P = nRT/V$.

Given a mixture of gases consisting of n_1 moles of species 1, n_2 moles of species 2, n_3 moles of species 3, and n_4 moles of species 4 all in the same rigid container at the same temperature, each component exerts a pressure against the walls, *completely oblivious to the presence of the others!*

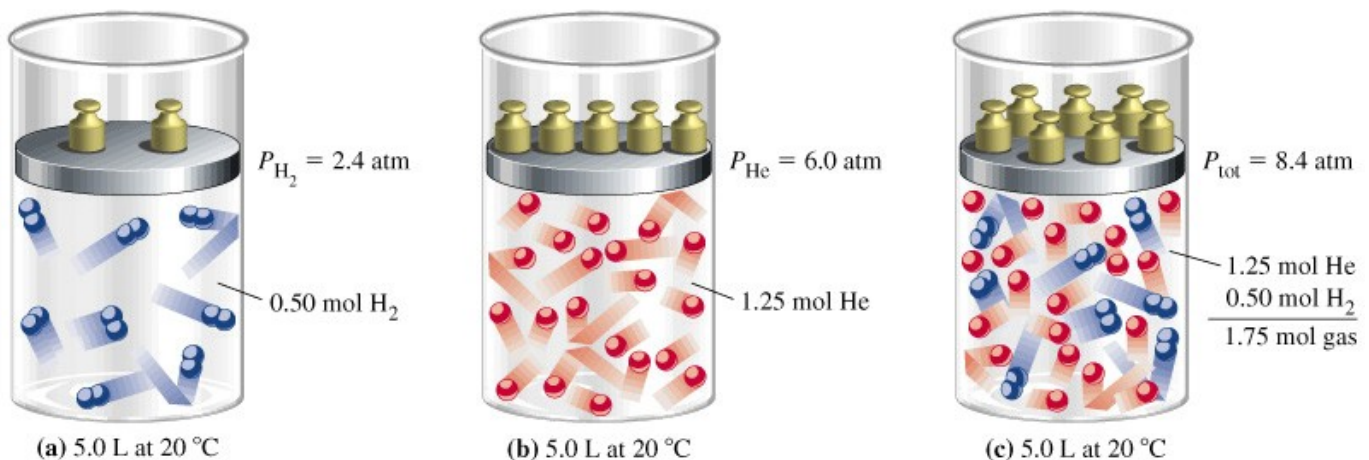
$$P_1 = \frac{n_1 RT}{V} \quad P_2 = \frac{n_2 RT}{V} \quad P_3 = \frac{n_3 RT}{V} \quad P_4 = \frac{n_4 RT}{V}$$

Dalton's law of partial pressures then tells us that

$$\text{and} \quad P_{\text{tot}} = P_1 + P_2 + P_3 + P_4 = \frac{(n_1 + n_2 + n_3 + n_4) RT}{V} = \frac{n_{\text{tot}} RT}{V}$$

P_i is called the *partial pressure* of species i : $\frac{P_i}{P_{\text{tot}}} = \frac{n_i}{n_{\text{tot}}} =$

Exercise 6: If a rigid 5.0 L container at 20°C contains 0.50 moles of H₂ and 1.25 moles of He, what are the partial pressures of the two components and the total pressure in the container?

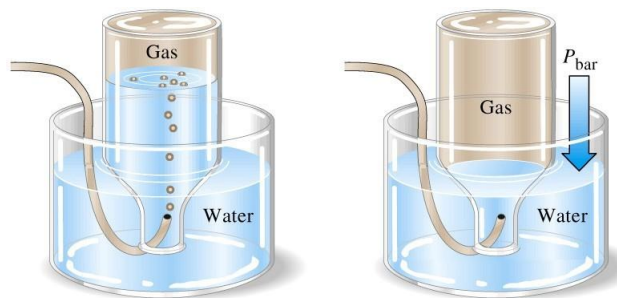


How can we measure amount of gas produced in a reaction?

Ans. collect the gas “over water”.

Perform the reaction in a sealed container and collect the gas produced as shown in the diagram below in a bottle which initially was completely filled with water. After the reaction stops, adjusting the height of the bottle to make the level of water inside and outside the bottle exactly the same makes the pressure of gas in the bottle exactly equal to the (assumed known) atmospheric pressure. The volume of gas in the bottle is then the volume of gaseous product.

But ... while the total pressure of gas in the bottle equals the (assumed known) external atmospheric pressure ...



Exercise 7: If solid calcium carbide CaC_2 is heated gently in water it will produce acetylene gas C_2H_2 (g) and calcium hydroxide $\text{Ca}(\text{OH})_2$ (aq). If a 2.00 g sample of CaC_2 reacts in this way to produce 524 mL of gas which is collected “over water” at 23°C and 1.050 atm, what was the % yield for the experiment?

► Vapor Pressure of Water at Various Temperatures

Temperature (°C)	Vapor Pressure (mmHg)
15.0	12.79
17.0	14.53
19.0	16.48
21.0	18.65
23.0	21.07
25.0	23.76
30.0	31.82
50.0	92.51

The Kinetic-Molecular Theory of Gases

The assumptions underlying the Kinetic-Molecular Theory of Gases are:

1. Gases consist of large numbers of tiny particles (atoms or molecules) moving in straight-line random trajectories.
2. Gas molecules (or atoms) are very small compared to the distance between them, so most of the space they move about in is completely empty; in the “ideal” limit, we think of them as “point masses” occupying no space.
3. The duration of collisions of molecules with each other or with the walls of their container is very much shorter than the time between collisions; in the idea limit, the collisions are assumed to be instantaneous.
4. The forces between molecules are negligible, except at the instant of collision.
5. While individual molecules may gain or lose energy in a collision, the total energy of the system (ensemble of molecules) remains constant.

A simplified Kinetic Theory Derivation of Boyle’s Law

Consider a cubic box of volume V containing N molecules of gas, and assume

- all molecules have the same speed u
- all molecules move parallel to one of the three orthogonal axes x , y , & z .

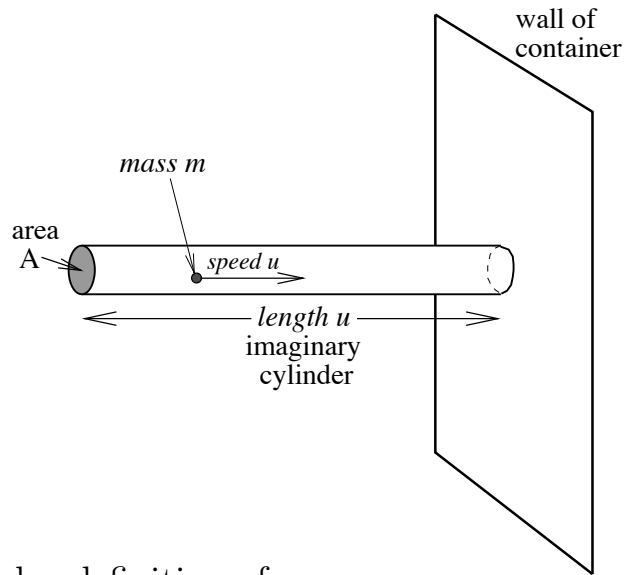
This means that on average:

- $1/6$ of the molecules move with speed u in the $+x$ direction
- $1/6$ of the molecules move with speed u in the $-x$ direction
- $1/6$ of the molecules move with speed u in the $+y$ direction
- $1/6$ of the molecules move with speed u in the $-y$ direction
- $1/6$ of the molecules move with speed u in the $+z$ direction
- $1/6$ of the molecules move with speed u in the $-z$ direction

Consider molecules moving in the $+y$ direction. Since each molecule moves a distance u in 1 second:

no. molecules which hit a circle of area A on the right hand wall in 1 second

$$\begin{aligned}
 &= [\text{no. molecules in a cylinder of length } u \text{ to left of the circle of area } A] / 6 \\
 &= [\text{molecular concentration}] \times [\text{volume of cylinder of length } u \text{ and area } A] / 6 \\
 &=
 \end{aligned}$$



Recalling our earlier discussion of the molecular definition of *pressure*

The force on wall segment of area A due to colliding gas molecules
 = [momentum transfer to wall per collision] \times [no. collision/sec with area A]

Therefore

$$P = \frac{\text{force}}{\text{area}} =$$

and hence $PV =$

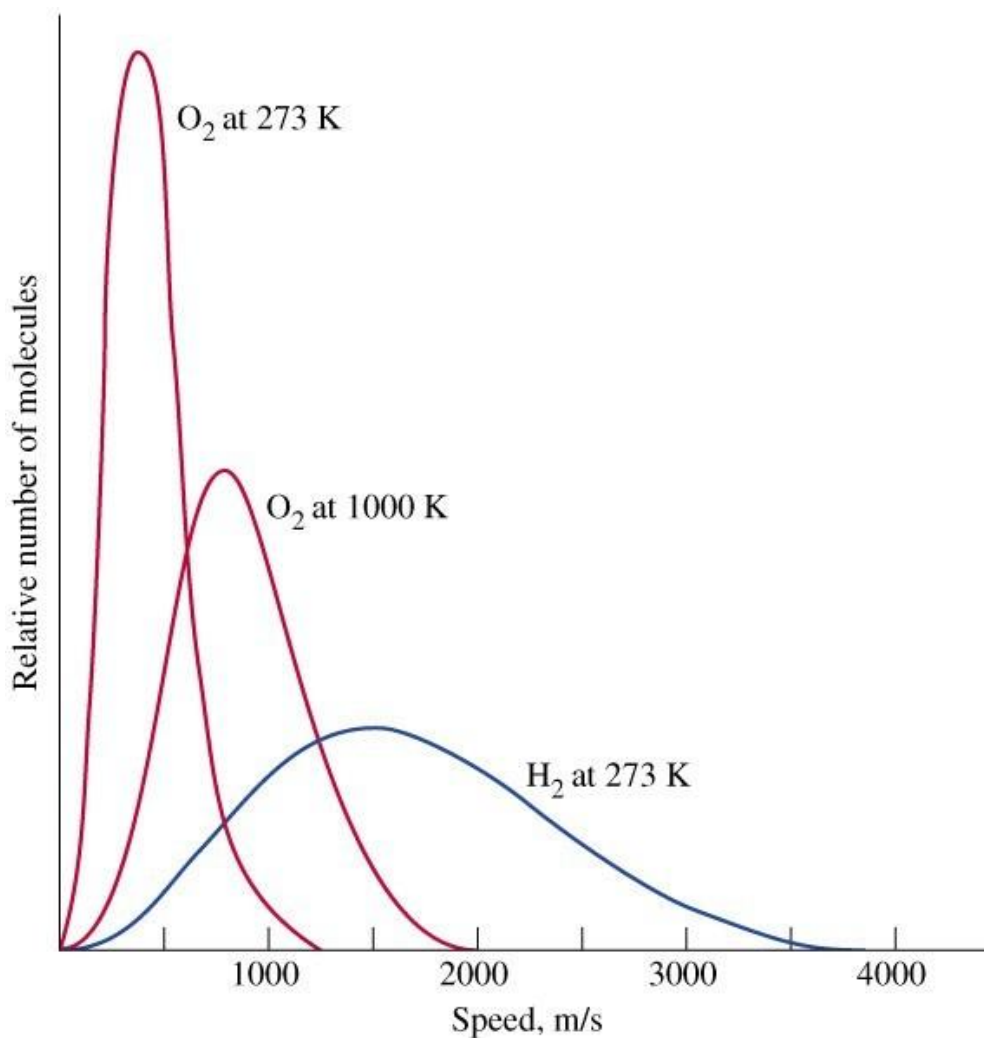
Aside! We know that

- molecules actually travel randomly in all directions
- molecules actually have a distribution of molecular speeds, which turns out to have the mathematical form $f(u) \propto u^2 \times \exp\{-\frac{1}{2} m u^2 / k_B T\}$

Doing all the math using the 3-D speed distribution get *exactly* the same result, except that we replace $\frac{1}{2} m u^2$ by $\frac{1}{2} m \overline{u^2}$

We will use that average-speed expression from here on.

But ... we know that $PV = nRT =$



Exercise 8: In air at 500°C, what is the r.m.s. speed: (a) of an O₂ molecule? (b) of an N₂ molecule? (c) What are these molecular speeds at a temperature of 1000°C?

Effusion is the escape of gases from a container through a tiny hole.

The number of “collisions/sec” with the (empty!) patch of wall corresponding to the hole will be proportional to the product of

- the area of the hole
- the number density (concentration) of molecules in the container
- the (average) molecular speed

Thus, for effusive leakage from a container containing a mixture of gases, the escaping gas may have a different % composition than the original mixture.

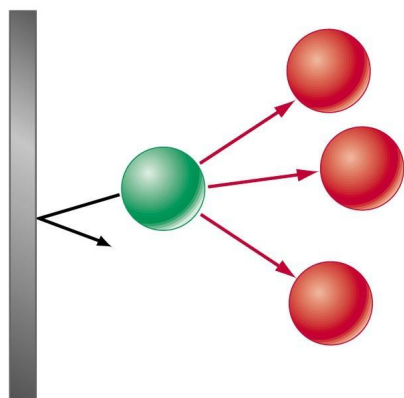
Exercise 9: If a space capsule in which the air is 0.40 atm of O_2 , 0.54 atm of N_2 , 0.02 atm of H_2 and 0.04 atm of CH_4 has a tiny hole caused by a meteorite hit, what is the % composition of the escaping air? (Compare this to the % composition of the capsule’s air.)

Non-Ideal Gases

According to the ideal gas law, $PV = nRT$ or $\frac{PV}{nRT} = 1$

but this is not exact! Because molecules have finite size, and because there are *intermolecular forces*, there are deviations from ideality. A simple non-ideal *equation of state* is the *Van der Waals equation*

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



This is an “empirical” equation; the constant a and b are determined by doing careful fits to experimental PV/nRT values.

Exercise 10: From fits to data, it has been determined that for $\text{CO}_2(\text{g})$ the Van der Waals constants are $a = 3.59 \text{ atm (L/mol)}^2$ and $b = 0.0427 \text{ L/mol}$.

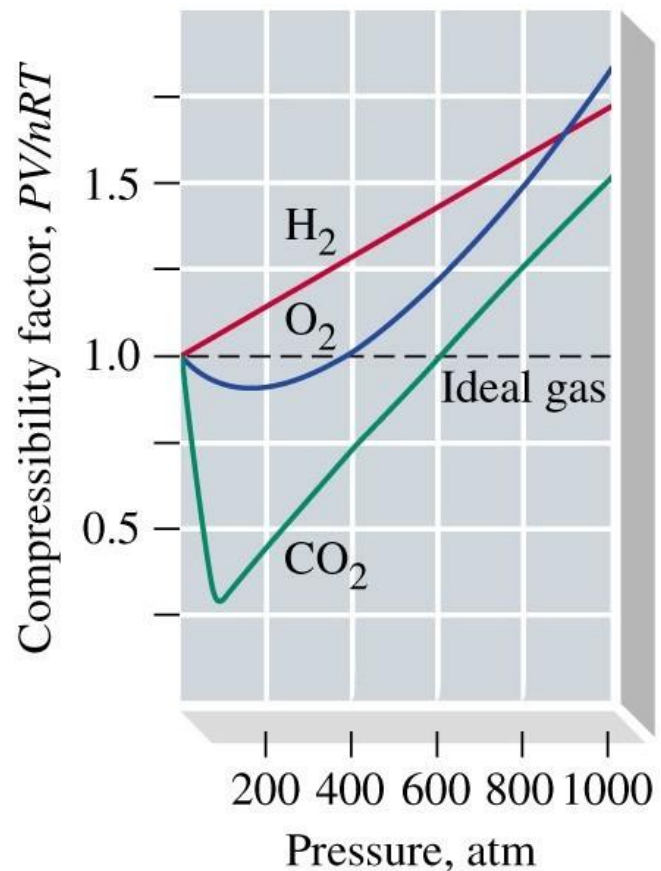
- What is the apparent volume of a CO_2 molecule?
- What is the deviation from ideality (i.e., how much does PV/nRT differ from 1.0?) for CO_2 gas at a pressure of 2.0 atm and temperature of 100°C ?

Alternately, using the theory of “statistical mechanics” and a knowledge of the intermolecular forces between molecules, physical chemists have derived the “*Virial Equation of State*”

$$\frac{PV}{nRT} = 1 + B(T) \left(\frac{n}{V}\right) + C(T) \left(\frac{n}{V}\right)^2 + \dots$$

in which the “*virial coefficients*” $B(T)$, $C(T)$, ... etc., can be calculated from a knowledge of the forces between the interacting molecules!

$$B(T) = 2\pi N_A \int_0^\infty \left[1 - e^{-V(r)/k_B T}\right] r^2 dr$$



How much of this kinetic theory stuff do you really need to know ?