

3.1 Equations of state

The “state” of a pure substance is specified by giving

- the state of aggregation (e.g. s, l, or g)
- the amount of substance (e.g. in grams or moles)
- the temperature, pressure and volume of the sample

Make sure you are familiar with the various units for pressure, volume and temperature.

Pressure, P ↔ force per unit area

SI Units: $1 \text{ Pa} = 1 \text{ N} / \text{m}^2$

Other units: $1 \text{ kPa} = 10^3 \text{ Pa}$

$1 \text{ bar} = 100 \text{ kPa} = 10^5 \text{ Pa}$

$1 \text{ atm} = 1.01325 \text{ bar} = 101.325 \text{ kPa}$

$1 \text{ torr} = 1/760 \text{ atm} \Rightarrow 1 \text{ atm} = 760 \text{ torr}$

Volume, V ↔ provides a measure of the space occupied

SI Units:

m^3

m^3 is too large for most applications

Instead we use litres (L)

$1 \text{ m}^3 = 1000 \text{ L}$

$1 \text{ L} = 10^{-3} \text{ m}^3$

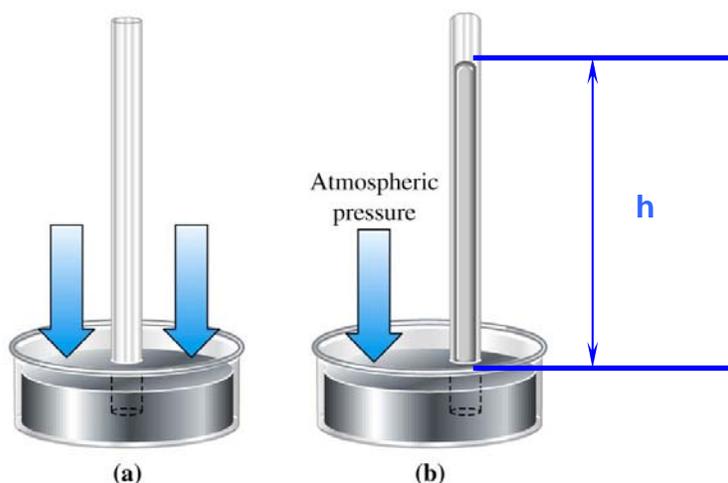
Temperature, T ↔ provides a measure of the average kinetic energy of the molecules in a sample

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

Note: $T > 0 \text{ K}$ and $t > -273.15^\circ\text{C}$

Digging Deeper: the measurement of pressure

The pressure exerted by the atmosphere can be measured using a mercury barometer.

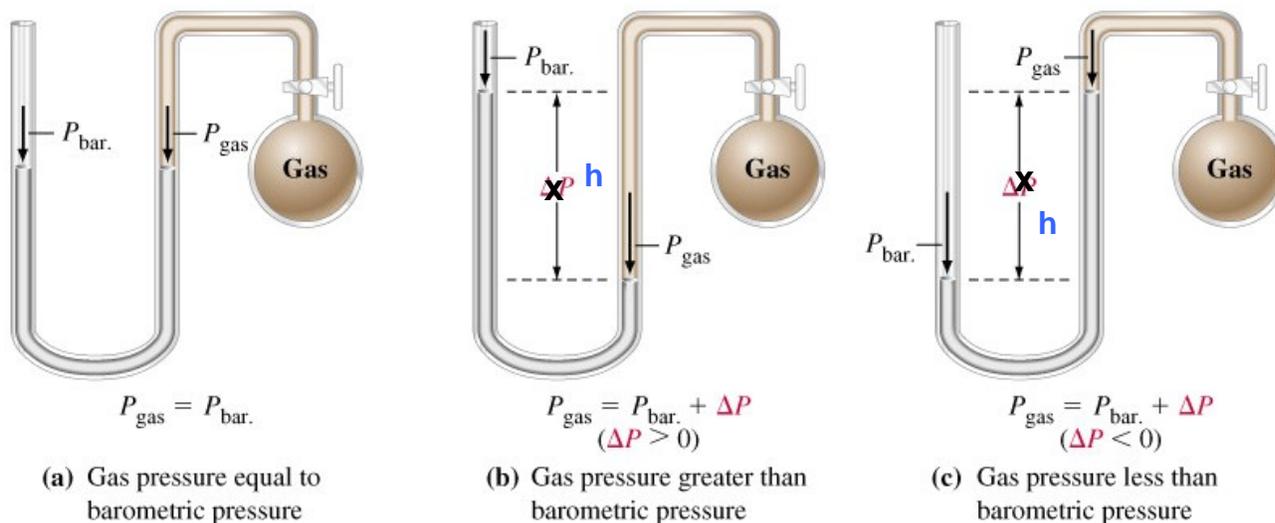


The height of the mercury column in the inverted tube provides a measure of the pressure exerted by the atmosphere.

Under normal atmospheric conditions, h is about 760 mmHg.

Note: 1 torr \equiv 1 mmHg

The pressure of exerted by a sample of gas can be measured using a mercury manometer.



$$P_{\text{gas}} = P_{\text{atm}} + h$$

$$P_{\text{atm}} = P_{\text{gas}} + h$$

or

$$P_{\text{gas}} = P_{\text{atm}} - h$$



Our own experience tells us that n , P , V and T are not independent. For example:

An equation of state tells us how P , V , T and n are inter-related. The equation of state for a given substance is sometimes determined empirically.

If we make certain assumptions about the behaviour of the molecules making up the sample, then we can use the laws of physics to derive the equation of state. In this module, we are concerned with the equation of state for an **ideal gas**.

The equation of state for an ideal gas is:

where R is a constant.

$$\begin{aligned} R &= 8.3145 \frac{\text{kPa}\cdot\text{L}}{\text{K}\cdot\text{mol}} \\ &= 8.3145 \frac{\text{Pa}\cdot\text{m}^3}{\text{K}\cdot\text{mol}} \\ &= 0.083145 \frac{\text{bar}\cdot\text{L}}{\text{K}\cdot\text{mol}} \\ &= 0.082058 \frac{\text{atm}\cdot\text{L}}{\text{K}\cdot\text{mol}} \end{aligned}$$

More specifically, the derivation of the ideal gas equation is based on the following assumptions.

- (1) The molecules of the gas move randomly but in straight lines, changing direction only when they collide with each other or with the walls of the container.
- (2) When the molecules collide, kinetic energy is conserved.
- (3) The distances between the molecules are much greater than the sizes of the molecules themselves.
- (4) The attractive and/or repulsive forces acting on a molecule are very weak except when molecules reach the same point in space or collide with the walls of the container.
- (5) Each molecule in the gas has its own kinetic energy but the average kinetic energy of the molecules is directly proportional to the kelvin temperature.

Despite its relatively simplistic form, the ideal gas equation is remarkably realistic, provided the gas is not close to its condensation point. Deviations from ideal behaviour are most significant when the pressure is high or the temperature is very low.

Note: Your textbook mentions a number of gas laws (e.g. Avogadro's law, Boyle's law, and Charles' law). The ideal gas law combines all of these laws into one. We expect you to remember and know the ideal gas law only.

3.2 Using the ideal gas equation

Example: Calculate the volume of one mole of ideal gas at 0°C and 101 kPa. What is the volume at 25°C and 101 kPa?

Example: A sample of gas occupies a volume of 2.00 L at 25°C and 101 kPa. What is the volume 35°C and 151 kPa?

Example: A 0.474-g sample of gas occupies a volume of 0.250 L at 100°C and 101 kPa. What is molar mass of this gas?

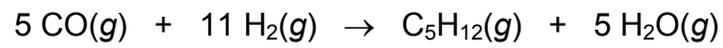
It is possible to use the ideal gas equation to derive a simple relationship showing how the density of a gas is related to its molar mass.

$$PV = nRT$$

Example: What is the mass of a $\text{NaN}_3/\text{Fe}_2\text{O}_3$ “pellet” required to inflate an automobile airbag with $\text{N}_2(g)$ at 26°C and 735 torr, if the airbag has a volume of 65.0 L? The reaction is given below.



Example: What volume of which reactant gas remains if 15.0 L CO and 25.0 L H₂ react according to the chemical equation below? What volume of C₅H₁₂ is produced. Assume that the volumes are measured at 722°C and 129 kPa.



3.3 Gas mixtures

Consider a mixture of gases containing

n_A moles of gas A

n_B moles of gas B

n_C moles of gas C

Define: $P_A =$

It is easy to show that the sum of the partial pressures is equal to the total pressure.

If it is assumed that the gases in the mixture behave “ideally”, then we can apply $PV = nRT$ to each gas separately or to the entire mixture:

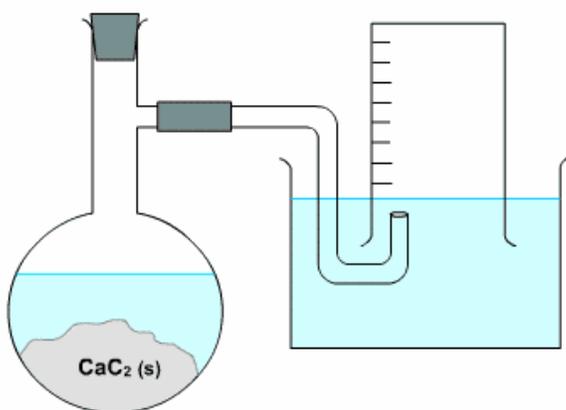
Example: (a) Calculate the total volume of gas produced when 0.200 kg of nitroglycerin, $C_3H_5N_3O_9$, decomposes at 115°C and 99.8 kPa. The decomposition reaction is given below.

(b) What is the partial pressure of CO_2 in the product mixture?



Collecting gases over water

An important application of the use of partial pressures arises when small amounts of gas, generated for laboratory use, are collected over water. For example, small amounts of acetylene gas, $C_2H_2(g)$, can be generated by heating an aqueous solution of calcium carbide. The gas can be collected over water using the following set up.



We adjust the inverted cylinder until the height of the water level is the same inside and out. (When the levels are equal, we know that the total pressure of gas inside the inverted cylinder is equal to the atmospheric pressure.)

The gas that is collected in the cylinder is “wet gas”, i.e. it is mixed with water vapour. The partial pressure of water vapour in the sample is determined by the temperature of the water. (See the table on the right.)

t (in °C)	VP of water (in torr)
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

Example: Calcium carbide, CaC_2 , is heated gently in water to produce acetylene gas, $\text{C}_2\text{H}_2(g)$, and calcium hydroxide, $\text{Ca}(\text{OH})_2$. The acetylene gas is collected over water at 23°C and 1.05 atm. If 2.00-g CaC_2 yields 524 mL of “wet” C_2H_2 gas, then what is the % yield for the experiment?

3.4 Kinetic Theory Revisited

Two of the main assumptions of kinetic theory are:

- (1) the molecules are in continuous random motion,
- (2) the average kinetic energy of the molecules is proportional to the kelvin temperature.

more specifically it is assuming that $KE_{avg} = 3/2 * RT$

The motion of the molecules must be random (or chaotic) because organized motion could not be sustained for any significant length of time. Why?

At the molecular level, the walls of the container are not perfectly flat (i.e. it is full of irregularities). Even if the molecular motion was perfectly orderly (e.g. all molecules moving in parallel paths towards the left), the molecules would soon hit the wall. Any irregularity in the wall of the container would deflect some particle out of its path. The collision of the deflected particle with another particle would deflect another one, and so on. The motion inside the container would soon become chaotic and random.

It is possible to show that for perfectly random motion, subject to the constraint that $KE_{avg} = (3/2) RT$, the distribution of molecular speeds must be:

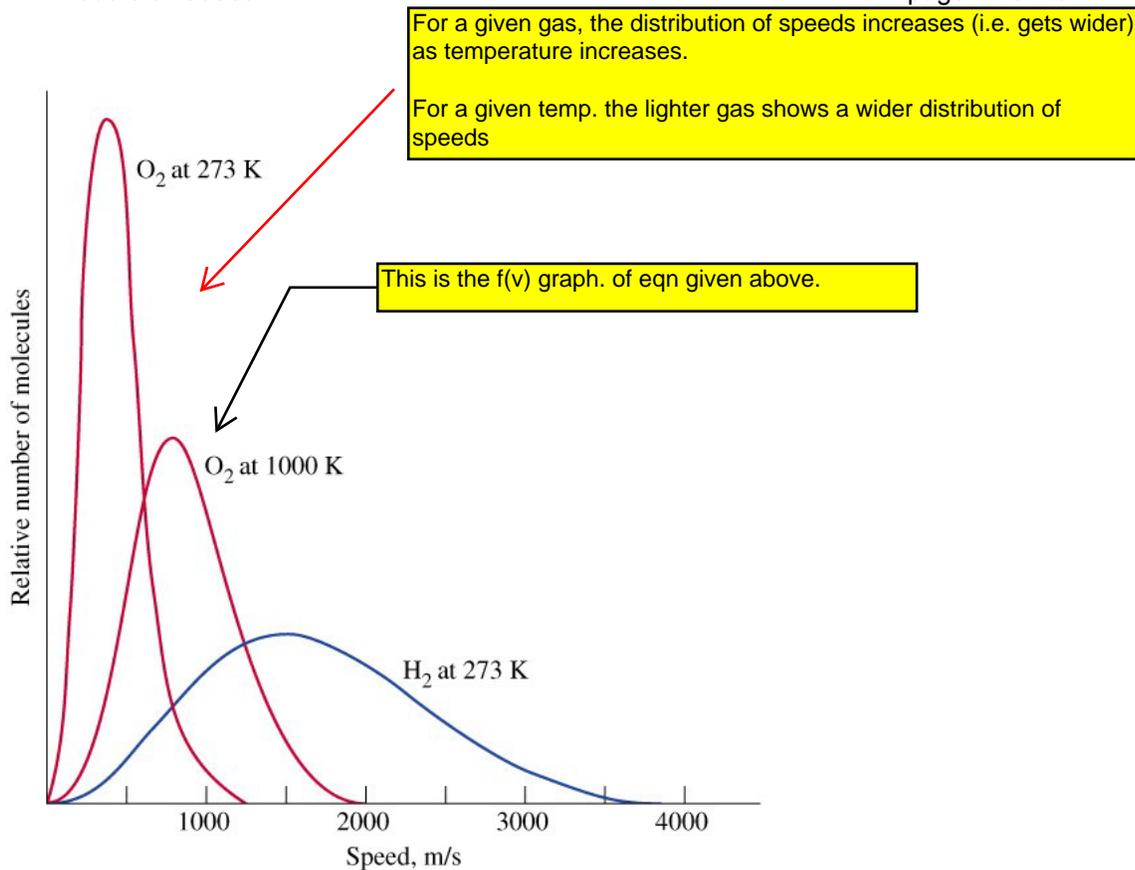
$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 e^{-\left(\frac{Mv^2}{2RT} \right)}$$

$f(v)$ is a distribution of molecular speeds. As in $f(v) =$ fraction of molecule that has velocity v .

$f(v)$ is the fraction of molecules in the sample that have speed v .

Note: You don't have to remember this equation. Just remember that there is a distribution of molecular speeds. For a given gas, the distribution is narrow if T is small and broad if T is large. Also, for a fixed temperature, the lighter the gas, the broader the distribution of speeds.

See the figures on the next page.



For a large sample, we are most concerned with the **average speed of the molecules**. There are two important “average” speeds to consider:

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \leftrightarrow \text{the average speed}$$

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \leftrightarrow \text{the root-mean-square speed}$$

Note that both averages are proportional to $(1/\sqrt{M})$, not $(1/M)$.

Thus at a given temp. H₂ molecules move 4 times faster than O₂ molecules. Any molecule with RMS speed is representative of the whole mass.

Therefore, lighter molecules travel faster, on average, than do heavier molecules.

The root-mean-square speed interests us the most: a molecule moving with speed v_{rms} has an kinetic energy equal to the average kinetic energy.

Rates of Effusion and Diffusion of gases

effusion ↔	molecules escape through an opening (example air leak from tire).
diffusion ↔	molecules of one gas mix among those of another gas.

Since we know the average speed (both v_{avg} and v_{rms}) is proportional to $(1/\sqrt{M})$, we expect that the rates of effusion and diffusion will also be proportional to $(1/\sqrt{M})$. If we compare to gases, X and Y, under the same conditions of temperature and pressure, then we expect that the rates of effusion (or diffusion) will obey the following relationship:

$$\{(rate_eff\} \text{ prop } \{ \{1\} \text{ over } \{sqrt[\text{molar mass}]\} \}$$

$$\frac{(rate)_X}{(rate)_Y} = \sqrt{\frac{M_Y}{M_X}} \quad \text{"Graham's Law"}$$

This is known as Graham's law of effusion. (Graham's law holds only approximately for diffusion processes, but we'll assume that is it valid for both effusion and diffusion processes.)

Example: A lecture theatre with 40 rows of seats is filled with professors attending a lecture on how to make a simple course really tough. A student disguised as a professor releases laughing gas (N_2O) from the front of the room at the same time that another student releases hydrogen cyanide (HCN) from the back of the room. (Note: HCN is instantly fatal when breathed in.) In what row, counting from the front, do the professors first begin to die laughing?

$$m = 27.028 \text{ g/mol}$$

let x be the dist. travelled by the N_2O gas when the two gasses meet.

$$\frac{(\text{rate})_{\text{HCN}}}{(\text{rate})_{\text{N}_2\text{O}}} = \sqrt{\frac{m_{\text{N}_2\text{O}}}{m_{\text{HCN}}}} = 1.276.$$

(rate) N_2O

Thus HCN diffuses 1.276 times faster than N_2O and travels 1.276 times the distance.

$$\text{Therefore } (40-x)/x = 1.276 \Rightarrow x = 17.57$$

3.5 Real gases

The ideal gas model is obviously not perfect. It neglects

- (1) the sizes of the molecules themselves

But molecules ARE NOT point masses.

An ideal gas could be compressed to zero volume without condensing to liquid!!!

- (2) intermolecular forces

Molecules are made of charged particles and exert forces on each other.

For real gases, we expect the volume (V) to be greater than or equal to an equivalent number of moles of liquid. We also expect that the pressure (P) will be less than the pressure predicted by the ideal gas equation.

Due to the fact that the particles attract and come closer together. So the particles are pushing against the walls less. AND that the particles are NOT 0 point. Thus cannot become 0 sized.

Van der Waals devised an equation of state that incorporated these ideas:

$$(P + \frac{a}{v^2})(v - nb) = nRT$$

In this equation, a and b are molecule-dependent constants.

a ↔ Provides a measure of a strength of the intermolecular attractions

b ↔ Provides a measure of the sizes of the molecules

The values of a and b tend to increase with the size of the molecule, as shown in the table below.

	Gas	a (in $\text{L}^2 \text{bar mol}^{-2}$)	b (in L mol^{-1})
	H_2	0.24646	0.026665
increasing Size	O_2	1.3820	0.03186
	CO	1.4734	0.039523
	CO_2	3.6551	0.048216
	C_5H_{12}	19.124	0.14510

Recall 1 BAR = 100 kPa
1 atm. = 1.031325 bar.

Example: Use the ideal gas equation and the van der Waals equation to estimate the pressure exerted by 1.00 mol of $\text{CO}(g)$ in a 0.500 L container at 300 K.

$$\text{Ideal} \Rightarrow P = \frac{(1 \text{ mol})(0.083145 \text{ bar L/K mol})(300\text{K})}{(0.5 \text{ L})}$$

= 49.9 bar.

VanderWalls $\Rightarrow P = 48.3 \text{ bar}$ (c.f above Vander Walls eqn.).

$\rightarrow P_{\text{ideal}}$ is only 3% larger than P_{real} . So its a pretty decent estimate.

There are other equations that chemists use to model the relationship between P , V and T . One of the most useful equations is the virial equation of state, which has the form

$$\frac{P\bar{V}}{RT} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \dots$$

where $\bar{V} = V/n$ is the molar volume (i.e. the volume per mole of gas). The equation above is called the virial equation of state. The second-, third- and higher-order terms in this equation account for deviations from ideal gas behaviour. These terms become increasingly important as the volume decreases (i.e. as the pressure increases).

B, C, D etc. are called "virial" coefficients. This eqn is based on the "virial" expansion. This expansion gives the needed "corrections" to the ideal gas behavior. It makes up for the deviation from the ideal gas law. The neat thing is that you can extend this eqn's RHS to how many ever terms you want to get more and more accurate.

Note: these 'virial coefficients' are molecule dependent.

For an ideal gas $\frac{PV}{RT} = 1$

Example: For $O_2(g)$, $B = -21.89 \text{ cm}^3 \text{ mol}^{-1}$ and $C = 1230 \text{ cm}^6/\text{mol}$.

What is the pressure exerted by 1.00 mol O_2 if it is confined to a 0.500 L flask at 273 K?