

Gases

Pressure is formally defined as the force exerted on a surface per unit area:

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{A}$$

Force is measure in Newtons

Area is measured in m^2 and it refers to the Area the particle/object is touching (From the equation we can see that the lower area means larger the force)

Atmospheric Pressure- atmospheric pressure is the pressure that results from particles in the atmosphere (i.e. oxygen, nitrogen, argon, carbon dioxide) continuously colliding with surrounding objects (e.g. the wall of the container). The pressure is greatest at the surface of the earth because gravity is pulling majority of the molecules down (i.e. pressure increases with an increase in altitude). The variables that affect the pressure of GASES are:

- Volume of the container (increase in volume corresponds to a decrease in pressure)
- Amount (moles) (increase in moles corresponds to an increase in pressure)
- Temperature (in Kelvin) (increase in temperature corresponds to increase in pressure)

Since air completely surrounds everything, air pressure acts on all objects. The place of the air does not matter i.e. air trapped in a container will still exert the same pressure as it would have outside. The standard measurement of pressure is in Pascals (Pa) where 1 pascal = $1\text{N}/\text{m}^2$ (the formula for pressure above). The value of atmospheric pressure MUST be memorized:

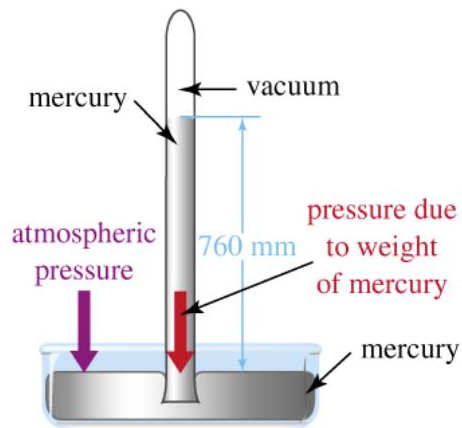
1 atm	=	760 mm Hg
	=	760 Torr
	=	14.7 psi
	=	101,325 Pa
	=	1.01325 bar

(1 bar= 100 000 pascals)

Barometer

A barometer is an instrument that is able to measure air pressure. Its use as a device to measure air pressure (initially used simply to make a vacuum, was first discovered by Torricelli). His following experiment proves the existence of air pressure:

Torricelli filled a tube with mercury. He then inverted the tube quickly in an open dish of mercury. He found that the mercury did not fall completely from the tube to the dish (what would be logically predicted- i.e. pouring a glass of water), but instead remained at a height of 760 mm above the dish:

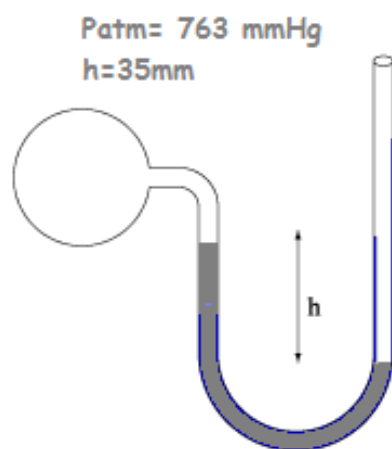


The pressure from the atmosphere is pushing down the mercury in the dish. However the downward pressure of the mercury (due to its weight) is pushing upwards i.e. the level of mercury wants to rise. Once the two pressures are equal (i.e. at a height of 760mm), the level of mercury can no longer rise. This gives a relative indication of the pressure that exists in the atmosphere (atmospheric pressure)

Manometer

- does not measure specifically the atmospheric pressure but instead can measure the pressure of any gas

Example



The right hand side is open whereas the left-hand bulb contains the unknown gas (exerting an unknown pressure)

1. We know the right hand side is experiencing 1 atmospheric pressure (i.e. 760 torr)
2. Draw a horizontal line in the other side of the u-tube
3. From this, we know the left hand side pressure + the x mm of mercury = to the atmospheric pressure
4. i.e. $P_{\text{atm}} = P_{\text{(unknown)}} + x \text{ mm}$
5. Rearranging the equation, we can find the unknown pressure in torr (use torr because it already relies on the height of movement of mercury)

Robert Boyles Law

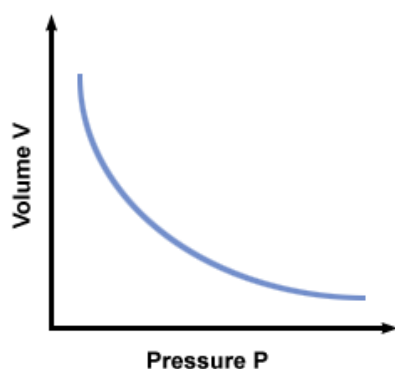
At a constant temperature for a fixed mass (moles of gas), the pressure and the volume of gas are inversely proportional i.e. as pressure increases volume decreases and as pressure decreases, volume increases.

$$V \propto \frac{1}{P}$$

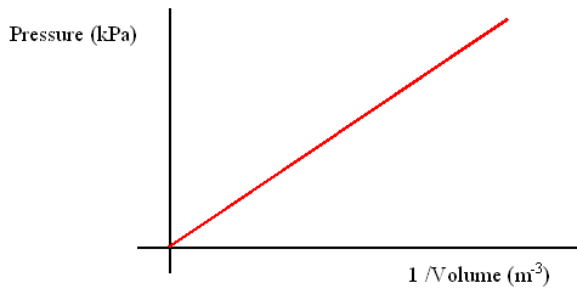
The alpha symbol means “proportional to” i.e. the volume is equal to the inverse of pressure times some random constant.

How Robert Boyle came up with this

He used a closed end monometer and filled it with mercury. Initially the level of the mercury was equal on both sides of the tube. He then added 760mm of mercury to one side (i.e. doubled the pressure = 2atm) and found that the volume of gas halved. He plotted these two values on a graph with pressure on the x axis and volume on the y axis and found that a hyperbolic relationship existed.



However when he took the inverse of pressure (i.e., he let $1/P = y$), he found there was a linear relationship.



We can therefore use the following formula ONLY if the moles and the temperature of the gas is CONSTANT (i.e. not changed)

$$P_1V_1 = P_2V_2$$

Where P_1 = one of the pressures

V_1 = the volume at that pressure

P_2 = the second pressure of the same system (i.e. moles and temperature the same)

V_2 = the second volume corresponding to the second pressure

NOTE: the identity of the gas DOES NOT MATTER (i.e. it can change from P_1 to P_2)

Looking at the molecular level, a lower volume means a smaller distance the particles must travel to collide with the wall. For example, if we have a large classroom full of children randomly running around, the children are much more likely to bump into the walls if we make the classroom, smaller

Charles Law

For constant moles of gas and at a constant pressure, the volume is directly proportional to KELVIN temperature.

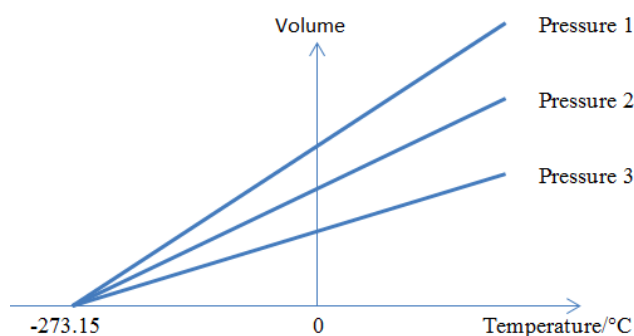
$$V \propto T$$

V = volume
 T = absolute temperature
 (assumes pressure constant and closed system)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Note: we will no longer use degrees Celsius because of the it is an arbitrary value entirely based on water(has no mathematical significance) Kelvin is the measure of the average kinetic energy in the

system therefore if we double the temperature in kelvin, than we also double the kinetic energy of the molecule. The whole of the gas laws relies on this correlation between kinetic energy and temperature (on the other hand 2 degrees C does not have double the energy than something at 1 degree C). 0 Kelvin is -273.15 degrees C; therefore to convert Celsius into Kelvin we simply add 273.15.



Interestingly, Jacques Charles found that for all the pressures he tested, the relationship converged at a point at -273.15 degrees C. He concluded that this must be the point where the gas has no energy and therefore no volume.

Molecules- if we increase the temperature, we are increasing the kinetic energy in which the gas are hitting the wall. If the wall is allowed to move, the greater force/ pressure is able to push the wall outwards and thus increase the volume.

Gay-Lussac's Law

At a constant volume, the pressure is directly proportional to the absolute temperature (kelvin)

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Gay-Lussac also formulated his law on combining volumes. He observed that when gases react, the ratio between the volumes of the gases is always SIMPLE whole numbers. Using Avogadro's Law, this seems logical. If double the moles are formed in reaction, the volume will also double.

Molecule- As temperature increases, so does the kinetic energy in which the molecule is hitting the wall (this means a greater force and more frequently). Since pressure is simply the force acting on an area, this corresponds to an increase in pressure

Avogadro's law

At equal temperature and pressure, equal volumes of gas contain equal number of molecules (moles) i.e. volume is directly proportional to moles

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Molecule- If we add more moles, there are more molecules bouncing about, and thus hitting the wall. This increases the pressure and thus moves the wall outwards, consequently increasing volume

Empirical Gas Law

Arriving at the combined empirical gas law

Recall that **Boyle's Law** states that: $P \propto \frac{1}{V}$; $PV = k_1$

And that **Charles' Law** is: $V \propto T$; $\frac{V}{T} = k_2$

Now if we divide the expression for Boyle's Law by T , we need to bear in mind that the constant k_1 will be different at different values of T - it can thus be written as $k_1(T)$, meaning that it is a function of T .

$$\frac{PV}{T} = \frac{k_1(T)}{T}$$

Similarly, if we multiply Charles' Law by pressure, P , we obtain: $\frac{PV}{T} = k_2(P)P$

Therefore: $\frac{k_1(T)}{T} = k_2(P)P$

and so $\frac{PV}{T} = \text{constant}$

Ideal Gas Law

The ideal gas law is:

$$PV = nRT$$

P is pressure (typically in Pascals but depends on ideal gas constant), V is volume (typically in m^3 but depends on ideal gas constant), R is the ideal gas constant (SEE BELOW) and T is temperature (in kelvin)

- if the temperature and the moles are constant, then PV will just equal a random constant (THIS IS BOYLES LAW)
- If moles and pressure is kept constant, then Volume is proportional to Temperature (CHARLES LAW). This equation shows this as $V (\text{random constant}) = \text{Random constant} \times R \times T$ i.e. V/T is a constant
- If the pressure and temperature is kept constant, the Volume is proportional to the number of moles (AVOGADRO'S LAW).

R in the equation is the universal gas constant. It can be found through rearranging the ideal gas law to make R the subject, then entering known values. THE VALUE MUST be selected correctly corresponding to the UNITS used for the other parts (i.e. pressure in pascals, volume in m^3 etc.):

$$\begin{aligned} R &= 0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1} \\ &= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 8.3145 \text{ kg m}^2 \text{ s}^{-1} \text{ K}^{-1} \text{ mol}^{-1} \\ &= 8.3145 \text{ dm}^3 \text{ kPa K}^{-1} \text{ mol}^{-1} \end{aligned}$$

The ideal gas law only is applicable to an ideal gas. An ideal gas is one in which:

1. The different gas molecules DO NOT REACT
2. The volume of the particles are negligent (i.e., if the volume is extremely small, then the volume of the molecules will no longer be negligible)
3. The molecules movement is completely random in straight lines (if the temperature is extremely low, temporary dipoles will form, preventing random movement)
4. The collisions are perfectly elastic (i.e. no kinetic energy is lost during collisions)

NOTE: An ideal gas does not technically exist, however, at 1 atm most gases are close to being ideal

Circumstances where the ideal gas law is not applicable:

Small volume/High pressures- small volume means that the volume of the molecules relative to the container is no longer negligent.

Low temperatures- low temperatures means that temporary dipoles form between molecules (the molecules are moving so slow that they are able to attract to one other via a positive negative charge). Thus the movement of the molecules can no longer be assumed to be random

Density Equation

$$PV = \frac{\text{mass} \times RT}{M_r}$$

and

$$\rho = \frac{P \times M_r}{RT}$$

1. In the first equation, we simply replaced moles with mass/molar mass in the ideal gas law
2. Density = mass/volume, therefore we replaced the volume with the rearranged version of (1)

THE MOLECULAR VIEW OF GASES

The kinetic energy (energy of movement) of a molecule is given by the equation:

$$KE_{avg} = \left[\frac{1}{2} mv^2 \right]$$

The speed is difficult to find, however this can be done through using a molecular beam apparatus. Molecules pass through various slits through a vacuum, allowing only the molecules that are moving in a straight line. A detector records the time in which each particle reached the end of the tube, thus calculating the speed (distance/time). The experiment found that heavier molecules had the most molecules travelling slower than the lighter molecules.

HOWEVER SINCE THE HEAVIER MOLECULES HAVE A LARGER MASS, the OVERALL KINETIC ENERGY IS THE SAME FOR ALL GAS SPECIES AT A FIXED TEMPERATURE (this can be seen from the equation above of kinetic energy. A larger m gives a lower v and lower v gives a larger m)

The average kinetic energy is the kinetic energy OF ONE MOLECULE (the energy of all the molecules added and divided by the number of molecules) and is given by the following

$$\overline{KE} = \frac{1}{2} m\overline{v}^2 \quad (1)$$

The bar on top signifies an average. This seems logical because the average kinetic energy is given when using the average velocity (the rest of the terms are fixed for all molecules). The following formula is an alternate way of representing the average kinetic energy (EXTREMELY IMPORTANT)

$$= \frac{3RT}{2N_A} \quad (2)$$

*** NA is Avogadro's number i.e. 1 mole

Therefore In one mole (just multiply by 1 mole i.e. Avogadro's number):

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

Solving equation one and two, we are able to calculate the average speed/velocity of the molecule:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M_r}}$$

**** Mr is the molar mass

RATES OF DIFFUSION and EFFUSION

Effusion- the escape of gas molecules through a small hole (molecular dimension i.e. extremely small) without collisions

Diffusion- the spreading of one molecule throughout another (can be same molecule)

le gas would effuse out of a puncture in a tyre and diffuse into the surrounding atmosphere

GRAHAM'S LAW- Graham proposed the following law relating to the effusion of gases. He stated that the rate of effusion is inversely proportional to the molar mass of the gas. What this means is, a light gas will travel faster than a heavier gas molecule.

$$\frac{\text{Rate}_A}{\text{Rate}_B} = \sqrt{\frac{\text{Molar Mass}_B}{\text{Molar Mass}_A}}$$

(Rate can also be replaced by time)

Dalton's law of partial pressures

Since the identity of the gas does not matter when calculating the pressure (this is because gases are assumed to take up no volume), Dalton identified that each must be exerting a pressure independently:

In a mixture of gases in which no chemical reaction occurs, each gas contributes to the total pressure of the amount that it would exert if the gas were in a container by itself

This means that total pressure can be found if we are given the individual pressures of the gases:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots + P_i$$

Since the identity of the gas does not matter when calculating pressure, each gas will contribute to the overall pressure based on the amount there is. This means that if a certain gas makes up half of all the gas, it will also contribute to half the pressure (if it makes up one quarter of the total gas, then it will exert one quarter of the total pressure). THE FRACTION WHICH THE GAS MAKES UP OF A MIXTURE IS CALLED THE MOLE FRACTION (just an important term):

$$\text{mole fraction of A} = x_A = \frac{n_A}{n_{\text{total}}}$$