Equations of state: Ideal gas law

Select LEARNING OBJECTIVES:

- Be able to identify the characteristics of an ideal gas - what makes a gas ideal.
- Understand what a state variable is - pressure, volume, temperature, number.
- Understand what an equation of state is.
- Apply the ideal gas law to find an unknown state variable.
    - $PV=NkBT$

  where P= pressure (in Pa), V = volume (in $m3$), N = number of particles, kB = some number (Boltzmann's constant) and T= temperature (in Kelvin).
- Use proportional reasoning to understand how one given state variable may change if the others change by some amount.

TEXTBOOK CHAPTERS:

- Giancoli (Physics Principles with Applications 7th) :: 13-5, 13-6, 13-7, 13-8
- Knight (College Physics : A strategic approach 3rd) :: 12.2
- BoxSand :: Ideal Gas Law

WARM UP: When you mix cold water with warm water, when does the system reach thermodynamic equilibrium? Explain this macroscopically and microscopically.

TEMPERATURE IS CONSTANT

$\overline{KE}_{TR}$ IS CONSTANT

Consider a container filled with a gas, how can we describe this system? Before we answer that, let's revisit ph201 where we were interested in describing the motion of an object. Our system was the object and we used initial and final positions and velocities to help predict the motion. Thus at any instant of time, we could have said that our system (e.g. object) is in a state with a given position and velocity. This state could have been in mechanical equilibrium (i.e. no net force acting on it) or not in mechanical equilibrium (a net force acting on the object). If the object was not in equilibrium then the state of the system was constantly changing (i.e. it's position and velocity were changing). The important thing to take away here is that position and velocity were macroscopic quantities which defined a state of our system. Similarly our container of gas can be described by macroscopic quantities that describe it's state. In fact, we could also use the position and velocity of each individual particle of the gas to describe the state of the gas system. However, we have seen that the number of particles is such a large number that it is practically impossible to do. This is where the kinetic theory of gases comes into play. The kinetic theory of gases along with Boltzmann's postulate lead us to our current understanding of temperature as a macroscopic quantity that is a measure of the average microscopic translational kinetic energy. We also learned that pressure is a macroscopic measure of the collective microscopic forces that gas particles impart on walls of a container. Thus we now have 2 macroscopic variables with which we can describe our gas system. It turns out we will also need volume, and number of particles. Since these quantities (P, T, V, N) describe the state of our gas system they are known as state variables.

At any instant of time the pressure, volume, temperature, and number of particles in our system of gas have unique values. If the system is not in equilibrium then these state variables constantly change as the system tends towards equilibrium. Thus only at equilibrium are we able to write a nice mathematical relationship between each state variable that is not dependent on time. This mathematical description of how these state variables relate to one another in equilibrium is known as an equation of state.

Equations of state

Examples:

Ideal gas

- Point particles, non-interacting other than elastic collisions between each other and the walls.
- $\boxed{P\,V = N\,k_B\,T = n\,R\,T}$

Van der Waals

- Particles with volume, weak interactions.
- $\left(P + \frac{N^2}{V^2\,N_A^2}\,a\right)\left(V - \frac{N}{N_A}\,b\right) = N\,k_B\,T$
- "a" and "b" are fitting parameters
    - a relates to the average interaction between particles.
    - b relates to the excluded volume that arises since the particles now have finite size.

Ideal gas

In this class we will only study the idea gas equation of state, which is often referred to as the ideal gas law. The functional form is given above under the equations of state heading, however you might be curious as to why it has that form? Before we address this, we should list our assumptions for which the idea gas law is valid.

Assumptions

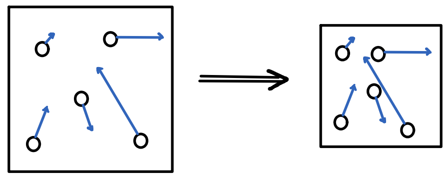
- Gas is made up of point particles with no attractive interactions between one another.
- The random motion of the particles obey Newton's laws of motion.
- The number of particles is very large. (Our state variables are macroscopic quantities which have ties to the microscopic quantities of the gas via statistics, the number must be large so that the statistics hold true).
- The volume of the container is much larger than the volume of particles. This statement is equivalent to saying that the density is low. This ensure that the particles are very far apart and are not interacting.

An ideal gas can be composed of atoms, molecules, or even fundamental particles like electrons so long as the above assumptions are valid.

Back to the leading question, why is the equation of state for an ideal gas $P\,V = N\,k_B\,T$? We will attempt to construct this equation using the ideas we learned from our microscopic model of gases in a qualitative way. With just a little bit more effort we can actually use our microscopic model of gases in a quantitative way to arrive at the ideal gas law as well, however this takes a bit more time. Our qualitative analysis will consist of 3 experimentally verifiable situations, each referred to by the names of the scientists who helped contribute to the understanding of the phenomenon.

Boyle's Law

If you decrease the volume of a container slowly so that the temperature remains roughly constant and no particles are allowed to enter or escape what happens to the pressure?

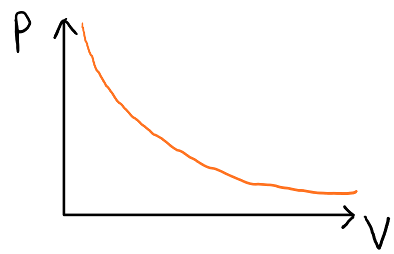


By decreasing the volume such that temperature doesn't change, more collisions occur in a given amount of time, thus the pressure will increase.

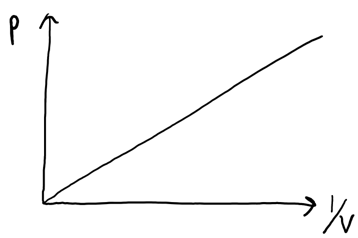
$$P \propto \frac{1}{V}$$

OR

$$PV = \text{CONSTANT}$$

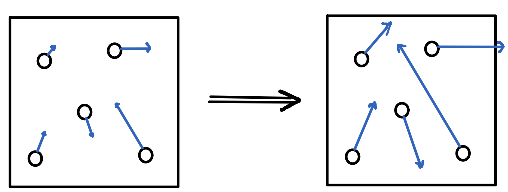


Practice: The volume of a gas was changed and measurements of the pressure were recorded while keeping the temperature and number of particles the same. How could we plot a graph that shows a linear trend?



Gay-Lussac's law

If you increase the temperature (i.e. increase the average translational kinetic energy) of the gas while holding the number of particles and volume constant, how does the pressure change?

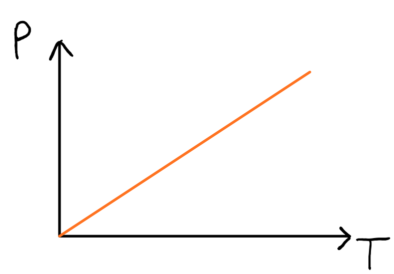


By increasing the temperature (i.e. average translational kinetic energy) while keeping the number of particles and volume the same, the pressure will increase because the particles are moving faster on average and thus the impulse imparted on the wall is larger on average.

$$P \propto T$$

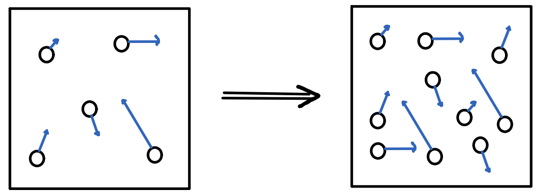
OR

$$\frac{P}{T} = \text{CONSTANT}$$



Avogadro's law

If you increase the number of particles in a container while keeping the volume and temperature (i.e. average translational kinetic energy) constant, how does the pressure change?

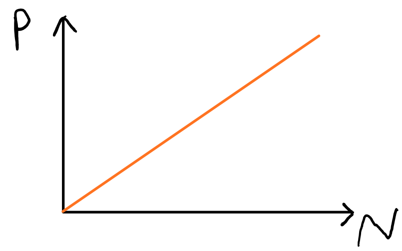


By Increasing the number of particles in the container while keeping the volume and temperature (i.e. average translational kinetic energy) constant, the pressure will increase because more particles are hitting the walls in a given amount of time thus imparting a larger impulse on the walls.

$$P \propto N$$

OR

$$\frac{P}{N} = \text{CONSTANT}$$



At this point you might be wondering, how do we know that the pressure is directly proportional to number of particles and temperature? And why is pressure inversely proportional to volume? For instance, perhaps pressure is proportional to temperature squared. After all, this proportionality still correctly predicts that pressure will increase as temperature increases. In fact, we cannot be sure of either case. To resolve this issue we must rely on experiments to confirm the proposed proportionalities or go through a bit more rigorous mathematical analysis (which is possible with the information we know thus far). For now let's rely on the experimental evidence which supports our conclusions stated above. Now we can combine all three laws together and get the following relationship…

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

As is turns out, the proportionality constant is Boltzmann's constant.

$$P = \frac{k_B N T}{V}$$

This is hopefully not too surprising; recall that Boltzmann's postulate connected the microscopic behavior of the particles of a gas to the macroscopic measurement of temperature. Thus you can view Boltzmann's constant as a sort of connection between the microscopic world and the macroscopic world. Basically, I hope that you can appreciate the role that Boltzmann's constant plays in the ideal gas law as you solve problems.

PRACTICE: An ideal gas initially has a set of state variables T_1, P_1, N_1, and V_1. If the pressure is tripled while the temperature is held constant, what is the final volume in terms of the initial?

1. 9 V_1
2. 3 V_1
3. V_1
4. $V_1/3$
5. $V_1/9$

$P_1V_1 = N_1k_BT_1$

w/ T CONSTANT & N CONSTANT $\Big\}$ $P_1V_1 = \text{CONSTANT} \rightarrow P_1 \propto \frac{1}{V_1}$

IF $P_1 \rightarrow 3P_1$

THEN $V_1 \rightarrow \frac{1}{3}V_1$

PRACTICE: An ideal gas initially has a set of state variables T_1, P_1, N_1, and V_1. If the volume is doubled while the temperature is tripled, what is the final pressure in terms of the initial?

(a) $P_1/3$
(b) $P_1/2$
(c) $2P_1/3$
(d) P_1
(e) $3P_1/2$
(f) $3P_1/4$
(g) $2P_1$
(h) $3P_1$

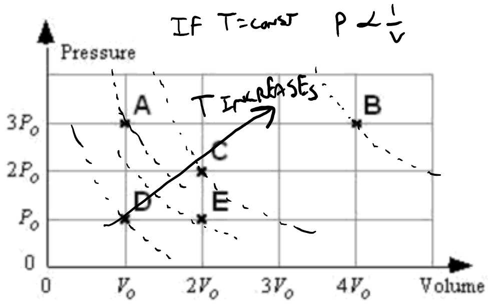
$P_1V_1 = N_1k_BT_1$

w/ N_1 = CONSTANT $\longrightarrow P_1V_1 \propto T_1 \longrightarrow P_1 \propto \frac{T_1}{V_1}$

IF $V_1 \rightarrow 2V_1$
AND $T_1 \rightarrow 3T_1$
THEN $P_1 \rightarrow \frac{3}{2}P_1$

PRACTICE: Five points representing five different states of one mole of an ideal gas are labeled on the pressure-volume graph below. Rank the temperatures of the idea gas in the labeled states.

IF T=CONST $P \propto \frac{1}{V}$



$PV = nRT$ w/ n = CONST

$PV \propto T$

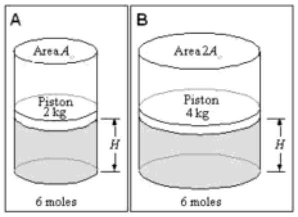
A	B	C	D	E
3PV	12PV	4PV	PV	2PV

$T_B > T_C > T_A > T_E > T_D$

PRACTICE: Two cylinders are filled to the same height H with ideal gases. The gases are different, and the cross-sectional areas of the cylinders are different. Both cylinders have pistons that are free to move without friction.

The temperature of the gas in cylinder A is ____________ the temperature of the gas in cylinder B.

1. greater than
2. less than
3. equal to



$PV = nRT$

w/ n = CONSTANT $\longrightarrow PV \propto T$

P?...

$P = \frac{F_\perp}{A}$

$$\left.\begin{aligned} F_{\perp_A} &= \tfrac{1}{2} F_{\perp_B} \\ A_A &= \tfrac{1}{2} A_B \end{aligned}\right\} P_A = P_B$$

$\therefore V \propto T$ w/ $V_A = \frac{1}{2} V_B \longrightarrow T_A = \frac{1}{2} T_B$

Questions for discussion:

(1) Consider a container of hydrogen gas. Now consider a container of neutron gas. Which container do you expect to behave closer to an ideal gas?

(2) A gas behaves more closely as an ideal gas at
   a. low pressure and low temperature.
   b. low pressure and high temperature.
   c. high pressure and low temperature.
   d. high pressure and high temperature.