

Chapter 39: Kinetic Theory of Gasses

The Kinetic Theory of Gasses

The approach we have taken thus far for describing the behavior of gases has been what is called a “macroscopic” approach, meaning that we have only dealt with the gas as a whole and only discussed the state properties, defining them properly, but not talking about their causes. There is another, different, way of discussing how and why gases behave and that is to discuss how the individual particles interact with each other and with the surroundings and how these interactions lead to the state properties. One example of this would be to talk about pressure. The previous method of discussing pressure would be to say that pressure is the force per area that the gas exerts on the sides of the container. Our new method would be to say that pressure is caused by the collisions of large numbers of particles against the container and then use that fact to relate the motion of particles as individuals to the measured force per area. This new method is called the kinetic theory of gasses. To use this new method fruitfully, there are a few assumptions that must be made regarding our sample of gas:

- 1.) All the particles of the gas are the same (i.e. we do not consider gas mixtures).
- 2.) The sample is in thermal equilibrium with the container it is in.
- 3.) The number of particles in the sample of gas is very large (on the order of moles)
- 4.) There is a lot of empty space in the gas (the particles are small compared to their separation.)
- 5.) All particles collisions are elastic.
- 6.) The forces between particles are negligible (except during collisions).

If all these assumptions are met, then the kinetic theory can apply and we can make some conclusions about the behavior of the gas in certain situations.

One of the first things that can be said is that the ideal gas law can apply. We have used this law previously, without explicitly stating the assumptions underlying it and most likely the student has used this law previously in a chemistry class. The law is a simple way to relate the properties of an ideal gas, and it is given below in two different formats:

$$PV=nRT$$

and

$$PV=NkT$$

In these equations, the variables stand for the following quantities:

n = number of mole

N = number of atoms

R = gas constant (8.31 J/mol.K)

k = Boltzmann constant (1.38×10^{-23} J/K)

The student can obviously determine that $k=R/N_A$, where N_A is Avagadro’s number.

Before we continue to move on to using the kinetic theory to calculate other relations, we should discuss one other factor about the behavior of particles in gases: gases particles don't all move at the same speed. This has been discussed briefly before, when we defined the meaning of temperature. However, we must now look a little further into this phenomena. We know that particles in a gas do not all have the same speed, there are some that are very fast and some that are very slow (compared to the others, of course). But what remains to be detailed is what is the pattern of speeds? James Maxwell (of EM fame) was the first person to determine what the speed distribution was in gases and it is now known as Maxwell's Distribution. His actual law is very complicated and was of the form:

$$P(v) = 4\pi(M/2\pi RT)^{3/2}v^2e^{-Mv^2/2RT}$$

All the variables are the same as in the ideal gas law, except for M, which is the molar mass. $P(v)$ is a strange thing called the probability distribution. It is representative of the percent of particles in a certain range when multiplied by that range. Mathematically, this means:

$P(v)\Delta v$ = fraction of particles that have speeds in the range of Δv , and where $P(v)$ is evaluated at the midpoint of the range

The above equation is actually a simplification, the real equation uses calculus and gives a more precise answer. However, for small ranges of speeds, this will work well. Some examples of how to use this will be given later.

While the above equation is intimidating and quite frankly scary, there are a few things that we can glean from it that are very useful and very simple. Most importantly, that equation tells us that particles in a gas have a distribution of differing speeds that makes a bell curve. It also tells us that the bell curve is differently shaped at different temperatures. Two different curves are shown below, illustrating this point:

EX. HIOH.) In a sample of 8 mole of oxygen gas at 300 K, how many particles have velocities

between 0 and 10 m/s? How many are between 400 and 415 m/s? Remember BOFINCH

Pressure, RMS Speed, Temperature and Mean Free Path

Our goal now is to begin to evaluate important quantities and explain their properties in relation to the kinetic theory. Since the kinetic theory deals with individual particle motion, two very important quantities are the RMS speed and the mean free path.

RMS speed stands for root mean square speed. The rms is a type of average that is often used in physics and engineering. It is a kind of average that gives more weight to higher number. It is calculated exactly as it pronounced: you find the root of the mean square. In other words, you square all of the numbers, find the average of those and find the square root. This quantity, we will find, is related to the distribution of speeds.

To begin to find other quantities, let us start with the collision of particles and see what we can learn from there:

We start with the following assumptions

- 1.) Remember that force times time equals impulse, which is the same as change in momentum.
- 2.) If N particles are in a box, $N/3$ particles will strike any one side in any time period T which is the average time it takes one particle to hit one side, bounce to the other and then return (since there are three possible directions of orientation for the motion).
- 3.) The RMS speed is the appropriate average to be used in this case.
- 4.) Collisions are treated elastically.

Now consider a square box of side length L , containing N particles of gas. Let us try to find an equation for the average pressure exerted on a side of the box, and relate it to the kinetic energy.

$$P = F/A$$

$$F = \Delta mv(\Delta T) \quad \text{force on one particle during a collision with the wall}$$

$$\Delta T = 2L/v \quad \text{for one particle to travel across the box and back}$$

$$\Delta mv = -2mv \quad \text{for one collision}$$

$$F = -2mv/(2L/v) \quad \text{for one collision}$$

$$F = -mv^2/L \quad \text{for one collision}$$

$$F = -Nmv^2/3L \quad \text{total collisions}$$

$$F = Nmv^2/3L \quad \text{since the force on the wall is opposite to the force on the particles}$$

$$A = L^2$$

$$P = F/A = Nmv^2/3L^3$$

$$L^3 = V$$

$$P = Nmv^2/3V$$

But we need the average V , thus

$$P = Nmv_{\text{rms}}^2/3V$$

$$\text{Recalling that } KE_{\text{av}} = (1/2)mv_{\text{rms}}^2$$

$$P = (2/3)N(KE_{\text{av}})/V$$

$$PV = (2/3)N(KE_{\text{av}})$$

$$\text{Since } PV = NkT$$

$$NkT = (2/3)N(KE_{\text{av}})$$

$$KE_{\text{av}} = (3/2)kT \quad (\text{Note: this is only for the translation KE})$$

Which is our first conclusion. There are two things of importance to notice about this equation. First, we have said before that the temperature of a gas is related to the average kinetic energy of its particles, this relation tells us this. Secondly, notice that this is independent of the kind of gas or the moles of gas involved. Another thing to be aware of is that in the derivation above, the lower case m is the mass of one particle. With that understood, the student can see that:

$$KE_{\text{av}} = (3/2)kT = (1/2)mv_{\text{rms}}^2$$

EX. NRD.) What is the average kinetic energy of a sample of nitrogen gas at room temperature? What is the average speed of a nitrogen molecule at room temperature? What percentage of nitrogen particles are in a range of 20 m/s around that average speed?

As is says after the last equation, this conclusion only is related to translational kinetic energy. It turns out there is a related topic that helps explain this result. Every particle has what is called “degrees of freedom”. A degree of freedom is a unique and distinguishable way the particle can move. For example, a simple, monatomic particle can move freely and uniquely in any one of the three direction (x,y,z). Thus it has three translational degrees of freedom. A monatomic particle can also rotate, but since it is considered a sphere, its rotation is not distinguishable. If, however, we look at a diatomic particle (such as O₂), we can see that it has three translational degrees of freedom and since it can rotate in two different ways that are distinguishable (the third rotation is not distinguishable), we say that it has five degrees of freedom. A polyatomic particle, then has six degrees of freedom, since it has three translational and three rotational directions that are all different.

Particle Type	Translational degrees	Rotational degrees	Total Degrees of freedom	Example
Monatomic	3	0	3	Ne
Diatomic	3	2	5	N ₂
Polyatomic	3	3	6	NaOH

By studying gases, scientists have learned a very interesting and important fact. Many properties of gases are based almost completely on their degrees of freedom. For example,

Every molecule has exactly (on average) $(1/2)kT$ of energy for each degree of freedom.

EX. CRD.) How much energy is associated with a sample of 2 moles of a.) Monatomic, b.)

Diatomic, and c.) Polyatomic gas at room temperature?

The student may recall that in an earlier section, the rules for determining the molar specific heat for constant pressure and volume were discussed. We can now return to them and explain better how those numbers were determined. It turns out that molar specific heats are also properties that depend on degrees of freedom only. For example, if f is the number of degrees of freedom, then

$$C_v = (f/2)R = 4.16f \text{ J/mol.K}$$

$$C_p = R + C_v$$

Thus we can see that the chart below can easily be filled in:

Particle Type	C_v	C_v in J/mol.K	C_p	C_p in J/mol.K
Monatomic	$(3/2)R$	12.5	$(5/2)R$	20.8
Diatomic	$(5/2)R$	20.8	$(7/2)R$	29.2
Polyatomic	$3R$	24.9	$4R$	33.3

Sometimes students get confused about when to use $(3/2)kT$ and when to use the specific heat to solve problems regarding the energy involved in gases. Keep this guideline in mind - specific heat is used in problems involving a CHANGE of temperature, $(3/2)kT$ gives the total energy associated with the kinetic energy. Another difference is that the specific heat is a macroscopic property of the gas, while $(3/2)kT$ is a microscopic property.

Another quantity that is often considered when dealing with gases is the ratio of molar specific heat at constant pressure to that at constant volume, often called γ .

$$\gamma = C_p/C_v$$

The reason this is of consequence is that it occasionally shows up in other formulae as part of an

exponent. For example, one important formula regarding gases that we skipped in our previous chapter is that for an adiabatic process,

$$pV^\gamma = \text{constant}$$

thus

$$p_1 V_1^\gamma = p_2 V_2^\gamma$$

and in the same way,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

These equations help us evaluate different quantities that we were unable to previously.

EX MNJUH.) Suppose you had the following three samples:

- 1.) Two moles of oxygen gas at room temperature
- 2.) One mole of carbon gas at room temperature
- 3.) The complete combination of the two into carbon dioxide at room temperature.

Find the following:

- a.) The molar specific heat at constant pressure and volume
- b.) γ
- c.) The total kinetic energy

for each gas.

EX BHUN.) Suppose one mole of O_2 is taken adiabatically from one atmosphere at room temperature to two atmospheres. What was its final temperature, and its initial and final volumes?

Another useful parameter to discuss when examining the microscopic properties of gases is something called the mean free path. The mean free path is simply the average (mean) distance that a particle travels between collisions. To explain, gases consist of particles always in motion, and these will naturally collide very often, depending on a number of factors. This is represented by the mean free path. The actual derivation of the mean free path is a bit complicated, so we will not present it. The equation is:

$$\lambda = V/(\text{sqr}(2)\pi d^2 N)$$

where d is the diameter of the particles, N is the number of particles and V is the volume of the gas. This equation seems to be logical, the student should take a minute and see if they understand how each variable relates to the others.

EX JNH.) What is the mean free path of oxygen at room temperature (assume a diameter of 3.0×10^{-10} m, $n = 10$ moles and a pressure of one atmosphere?)

Entropy

Once again, to summarize our purpose in this chapter, it is to take microscopic measurements of a gas and use them to derive macroscopic measurements. In other words, to see what the particles are doing individually and use that to see what the gas as whole is doing. The last thing we will examine is how to do this in regards to entropy. Entropy is related to the order or disorder of a system, as defined previously. We now need a new definition that relates entropy to the microscopic properties of a system.

Entropy is related to the number of possible similar states that exist for a system.

What this means is that when we say that the entropy increases, we mean that systems tend to move in a direction of higher probability. This is better explained through example, but two definitions must be made first. Consider a set of a number of things, such as 6 coins. If we put all six coins in a box, shook the box randomly and then opened the top and counted heads and tails, we could write a list of what we observed. Each possible outcome of what could be observed is called a microstate. Eight different microstates are listed below for this system:

HHHTTT
 THTHTH
 TTHHTH
 HTHTHT
 TTHHHH
 HTTTTT
 HHTTTT
 HHHHHH

Although each of these is a possible outcome, you will notice that the first four are all equivalent. Unless the coins were all different denominations, it would make no sense to label them coin 1,2,3,4,5,6. If different combinations are equivalent, we group them together to form what is called a configuration. There are only seven different configurations for this system:

- a.) HHHHHH
- b.) HHHHHT
- c.) HHHHTT
- d.) HHHTTT
- e.) HHTTTT
- f.) HTTTTT
- g.) TTTTTT

However, each one has differing numbers of equivalent microstates. For example, both a.) and g.) have only one microstate, while b.) and f.) both have six, c.) and e.) have 15 and d.) has 20. These are calculated using an equation of

$$W = N!/(H!T!)$$

Where N is the number of coins, H is the number of heads and T is the number of tails. W is called the multiplicity of the configuration. We can see that W is actually a measure of the number of similar states that produce the same configuration. The higher the multiplicity, the more different ways the same result can be obtained. Now think back to our last definition of entropy:

Entropy is related to the number of possible similar states that exist for a system.

Thus when we say the entropy of a system tends to increase, we mean that systems move from configurations with low multiplicity to configurations of high multiplicity. Entropy is a measure of the multiplicity of the state of a system.

The formula that relates these is:

$$S = k(\ln W)$$

Where S is the entropy of a system, k is the Boltzmann constant (Boltzmann discovered this equation) and W is the multiplicity of states of the system. It should be noted that this equation is not particularly practical for real life measurements, since the multiplicity of a system is very difficult to calculate except in the simplest of situations (for instance, try finding the multiplicity of the particles in the shell of an egg!). However, its power lies in relating the microscopic to the macroscopic. We can apply the principles to the simple situations to begin to get a better understanding of the larger situations.

EX. KIJ.) Determine the entropy of all the configurations listed above.

EX. JU.) Determine the entropy of the three most probable states of the coin experiment explained previously, carried out with 50 coins.

This previous example shows us something very important about how the multiplicity behaves as the number of objects (think gas particles) increases. We begin to get a spike at the most probable state. The more particles, the more defined this spike becomes. By the time we get to the order of moles of gas particles, the spike is so pronounced that essentially we have

everything outside of it with zero entropy and the most probable configuration with a high entropy. If the system changes, we expect it to change to that configuration.

For example, if we had 10,000 coins in our box, and they all started out as heads (low entropy) and then we shook the box, we would expect about 5,000 heads and 5,000 tails (the highest entropy). Thus the entropy increased. If we shook again, we would expect again about 5,000 of each, but probably not the same ones in the same states (same configuration, different states). If we kept on shaking it, we would continue to expect its entropy to stay the same. We would indeed be surprised if we got all heads (entropy decreasing).

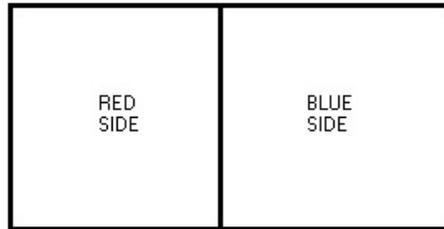
Getting all heads is possible, just not very probable. This means that it is possible for a system to temporarily decrease entropy, but on the whole, entropy tends to increase.

The important thing about this section is that you can notice how the microscopic property of states leads to the macroscopic property of entropy. Systems tend to end up in a situation that is the most probable of all the possible situations. Entropy has to do with probability.

Assignment #**&*&&

- 1.) Determine the number of atoms in a sample of an ideal gas with a volume of 2 L, a pressure of 2 atm. and a temperature of 100° C.
- 2.) If a sample of N₂ gas is at 1 atm, room temperature and has a volume of 100 m³ (a typical room filled with air), a.) How many particles have speeds between 350 m/s and 360 m/s? b.) How many are between 3000 and 3010 m/s?
- 3.) If a balloon is filled with helium at 2 atm and is at room temperature (volume = 0.10 m³), what is the number of particles with speeds in a range of 10 m/s around the root mean square speed?
- 4.) A.) What is the average translational kinetic energy of an oxygen molecule at room temperature? B.) What is the rms speed?
- 5.) Consider a sample of gas made up of only 15 particles, with speeds listed below in m/s.
200, 210, 280, 280, 300, 300, 315, 315, 315, 315, 360, 360, 400, 470, 500
A.) Calculate the average speed, the most probable speed and the rms speed.
B.) If these were O₂ molecules, what is the temperature of the gas?
C.) If each speed represented one mole of particles, instead of single particles, what would be the volume of the gas at 2 atmospheres?
- 6.) If CO₂ gas is at 20° C, how much energy is associated with 3 moles? What is the rms speed?
- 7.) If neon is in a closed container and heated to 800° C, what is the rms speed of the particles?
- 8.) If a gas with a molar mass of 100 g/mol has an rms speed of 200 m/s, what is its temperature?
- 9.) If 8 moles of CO are held at a constant pressure of 10 atm and heated with 500 J of energy, by how much (%) would it expand if it began at 60° C?
- 10.) Suppose 3 moles of He was taken from 10° C to 200° C, what would be its final pressure if it remained at a volume of 2 L?
- 11.) Imagine an experiment where 4 moles of an ideal gas went from 10° C, 2 atmospheres to 6 atm at the same volume. How many degrees of freedom did it have if 47058 J of energy was used? Notes: this is an imaginary (non-possible) gas, and some error is to be expected from the experiment.

- 12.) If 3 moles of argon are taken from 2 atm at 80° C to 160° C adiabatically, what is the percent change in volume and what is its final pressure?
- 13.) What is the mean free path in the following situations?
- A.) Oxygen while exhaling? (Assume mass = 0.1 g, $V = 0.001 \text{ m}^3$)
- B.) Steam in a pressure cooker? ($V = 0.001 \text{ m}^3$, $T = 300 \text{ K}$, Pressure = 2.5 atm, assume diameter of water particles to be about $1 \times 10^{-9} \text{ m}$)
- C.) Helium in a balloon ($V = 0.1 \text{ m}^3$, room temperature, pressure of 3 atmospheres, diameter = $1 \times 10^{-10} \text{ m}$)
- 14.) Consider the following situation:
Ten balls are placed into the red side of a box divided as shown below:



- The divider is removed and box is shaken vigorously. The balls are tallied as either being on the red or the blue side.
- A.) Determine all the different configurations possible.
- B.) Determine the entropy associated with each one.
- C.) Make a bar graph of entropy versus states.
- 15.) Consider an experiment similar to the one above. This time use four balls and three compartments (red, blue, yellow).
- A.) Determine the possible configurations.
- B.) Determine the entropy associated with each one.
- 16.) Imagine the coin experiment as described in the chapter, carried out with 30 coins. Determine the entropy of the 9 most probable and the 10 least probable states. Make a bar graph of these outcomes.