Chapter 2

Ideal Gases

MANY CHEMICAL REACTIONS ARE ACCOMPANIED BY THE FORMATION OF A GAS OR OCCUR ENTIRELY IN THE GASEOUS STATE. Measuring gas parameters, such as volume and temperature, gives information about the stoichiometry of the reaction and the energy transformation that accompany the reaction. The gas parameters are: pressure, volume, temperature and density. These parameters do not change independently, but are linked together and described quantitatively by the gas laws. The idea that gases consist of a large number of tiny particles moving randomly in all possible directions provides the modern explanation for the gas laws and is the foundation of the Kinetic Molecular Theory.

2.1 The Concept of Pressure

It is interesting to note that at times gas sample can behave like a solid!. For example think of an inflatable mattress and a second mattress with coil spring. The air in the inflatable mattress serves the same function as the coils in the second mattress. In both cases when pressure is applied the mattresses deform (are compressed). When pressure is removed the mattress returns to their original shape (volume).

In the following demonstration you will see how air behaves like an elastic coil spring.

BEGIN ACTIVITY

HandsOn 4: Tire Pump and Coil Spring

You will need:

- a bicycle hand pump or a syringe without a needle
- a spring.

1. Put your thumb over the nozzle and pump the piston of either the hand pump or syringe.

Q2.1: Do you feel any resistance as you push the piston? Try to explain your observation.

2. Push the pump handle to the lowest possible position and take your hand off the handle quickly, releasing the piston.

Q2.2: What happens and how do you explain it?

3. Compress the coil spring.

Q2.3: Do you feel any resistance? Propose an explanation.

4. Put the piston of the pump to the lowest position, put your thumb over the nozzle and pull the piston.

Q2.4: Do you feel any resistance as you pull the piston? Try to explain your observation. Clue: repeat the experiment without dosing the nozzle.

5. Expand the coil spring.

Q2.5: What do you feel? Propose an explanation.

We observed in the preceding HandsOn activity that a gas behaves much like a coiled spring. If a certain force is applied to the piston, the volume of a gas under the piston is reduced. If this force is removed, the gas expands.

In the quantitative study of such elastic properties of the air, one of the greatest contributions was made in the second half of 17th century by the Irish chemist Robert Boyle (1627 - 1691). He discovered that although a force is what is acting on the piston, the amount of force applied per unit of area is the essential parameter. Boyle was talking about the concept of *pressure*. Boyle performed quantitative experiments to measure the relationship between the pressure and volume of air.

Pressure is the ratio of the force to area over which it is applied.

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

Pressure is measured in Pascals. One Pascal equals the pressure created by a force of one Newton distributed over the area of one square meter. If you are wondering how much one Pascal is, it is roughly equivalent to the pressure created by a piece of paper lying on your kitchen table.

When we applied force to solid objects, they deform. However the magnitude of the deformation depends not on the force, but rather on the pressure. To reduce the pressure on your shoulders, the straps of your backpack are made wide. Imagine how uncomfortable it would be if the straps were made of thin ropes. If the deformation is not too high, if the force is taken away, the solid returns to his original shape. The most common example of an elastic object is a coil spring. Coils springs are used in mattresses. When you sit down the coil spring shrink, when you stand up the mattress returns to its original shape.

Q2.6: Assume the pressure caused by a book balanced on your finger is P. If you were to balance the same book on your hand (with an area 50 times that of your finger), what would this new pressure be?

Q2.7: Calculate the pressure caused by a $1Kg$ book if balanced on your palm (area approximately $1.5 \times 10^{-2} m^2$) vs. the pressure created by this same book balanced on your index finger (area approximately $3 \times 10^{-4} m^2$).

We can conclude from this example that the pressure of a given force distributed over a small surface is much greater the pressure distributed over a large surface.

One of the most commonly encountered examples of pressure is that of the atmosphere. The atmosphere exerts pressure on any object on the surface of the Earth. Atmospheric pressure at sea level is $101,000$ Pascals. This means that the air presses down on 1 square meter surface with the magnitude of $101,000$ Newtons, which is approximately equivalent to the weight of $10,000$ kilograms. The following experiment will allow you to understand the relative magnitude of atmospheric pressure.

BEGIN ACTIVITY

HandsOn 6: Atmospheric Pressure

CAUTION: Do not do this without teacher supervision. Goggles and gloves are highly recommended.

You will need:

- A 12 ounce plastic bottle with screw cap
- a microwave oven
- oven mitts or winter gloves.

1. Pour two tablespoons of water into a 12 ounce plastic bottle with a screw cap.
2. With the cap **off**, place the bottle into a microwave oven and heat it until the water starts to boil.

3. Put on your oven mits or winter gloves and remove the bottle from the microwave. Immediately replace the cap.

4. Put the bottle under running cold water.

Q2.8: What do you see and how do you explain it? Clue: In this experiment the atmospheric pressure remains the same but the pressure inside the bottle drops when we cool it down.

2.2 Boyle's Law

While performing several experiments, Robert Boyle determined that at constant temperature the volume of a gas is inversely proportional to the pressure: $V \sim \frac{1}{P}$, or in other words, product of P times V remains constant when both of these variables change

$$PV = \text{const.}$$

In this equation, the constant depends on the temperature of the gas sample and the number of gas particles. The higher the pressure, the smaller the volume occupied by the gas.

BEGIN ACTIVITY

SimuLab 6: Qualitative Investigation of Boyle's Law

Gas creates pressure because its particles collide with the walls of their container. The concept of moving gas molecules is the foundation of the kinetic molecular theory.

Your objective is to:

Recognize the effect of molecular collisions with the piston on the piston's position.

You will be able to:

Predict what happens to the position of the piston when the external pressure is greater than the internal pressure of the gas.

Explain why the position of the piston fluctuates when the external and internal pressures are approximately equal.

Describe gas pressure in terms of molecular collisions.

State the relationship between frequency of collision and the volume of a given gas sample.

1. Open **SMDPlayer**, select **IntroBoyle'sLaw** in the **IdealGas** folder. PRESS **Play**. Read all the captions, and follow the instructions. Go to **File** - **Quit**

Movie gives a preliminary understanding of Boyle's law from a microscopic point of view.

2. Open **SMD**, select **Boyle-Preliminary** in the **IdealGas** folder.

You see 200 green gas molecules under a piston represented by a red bar, as shown in Figure 2.1. Note that the **Heat Bath** is on, which means that the temperature of the system is kept relatively constant throughout the experiment. The system is NOT thermally isolated.

3. Set **Iterations Between Displays** to 10. Select **Display Particles by Trajectories** and press **Start**.

The particles start to move along straight lines with various velocities. They change their trajectories when they collide with the piston or each other.

4. Click back to **Display Particles by Particle Type** and observe the **Volume versus Time** graph.

The external pressure acting on the piston accelerates it downward, reducing the volume of the gas. In the absence of collisions with the piston, a graph of volume versus time is a smooth parabola because the piston falls freely. However, when a molecule collides with the piston, the piston's velocity instantly changes and the graph as a whole changes into a set of parabolic segments. The connections of parabolic segments illustrate numerous collisions that create internal pressure which pushes the piston upward.

5. Watch the graph for approximately 4 time units (until the graph fills the screen) and then press **Pause**. To copy the graph to the "Snapshot Gallery" select **Take Snapshot :Graph.**

Determine the number of particle collisions with the piston by counting the number of parabolic segments as shown in Figure 2.2.

Q2.9: How many collisions with the piston (i.e., parabolic segments) did you count?

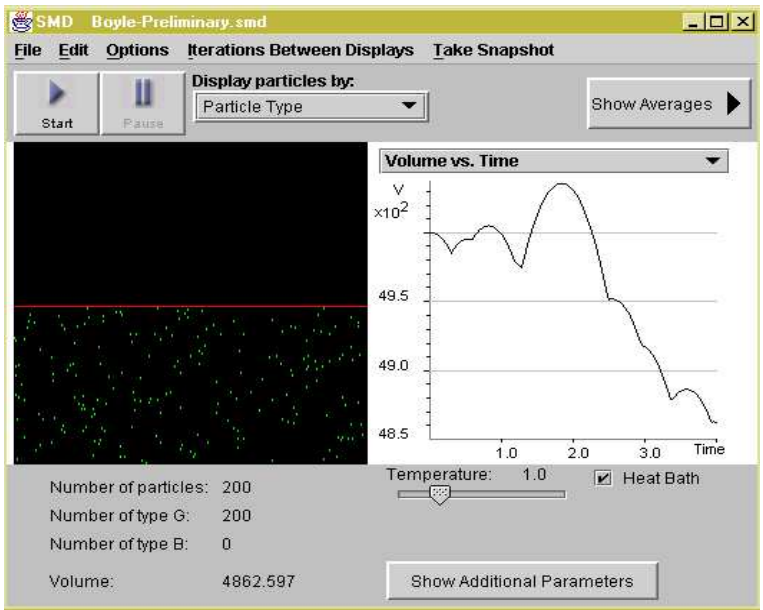

Figure 2.1: Screenshot of Boyle's Law SimuLab.

6. To speed up the program, set **Iterations Between Displays** to 1000 and press **Start**. Run the program for 200 time units (read Time from Averaging Window).

At equilibrium, the internal pressure created by the gas molecules colliding with the piston, should be equal to the external pressure, which is set at 0.04. The internal pressure value can be found in the Average Values panel. The external pressure value can be found in the Additional Parameters window by selecting **Show Additional Parameters**. Read the volume of the gas from the Average Values panel and record it. While running this simulation answer the following questions:

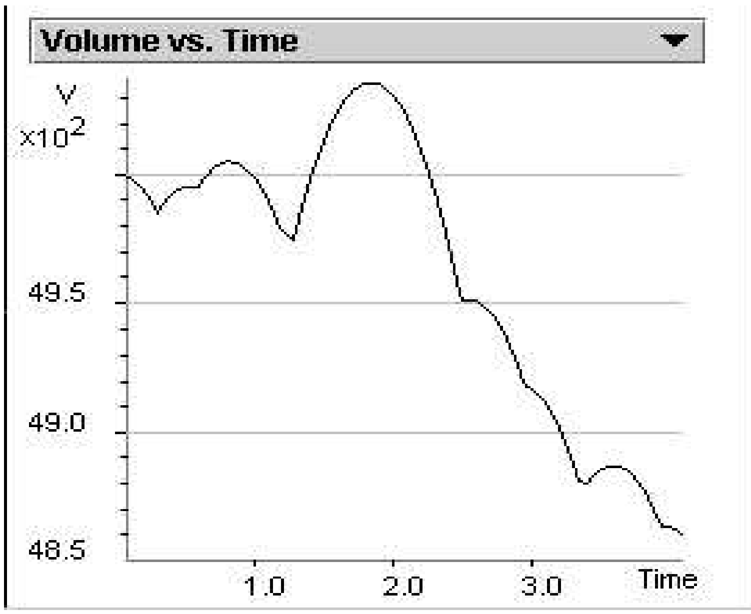

Figure 2.2: Determining the number of molecules collisions with the piston by counting the parabolic segments. The end of a parabolic segment is indicated by a jaggedness in the curve. When the number of parabolic segments is unclear-estimate. In this graph, there are 7 or 8 collisions (parabolic segments).

Q2.10: Notice that relatively few particles collide with the piston at any particular moment. Will this cause the internal pressure to (a) stay the same, (b) fluctuate a little, or (c) fluctuate greatly? Explain your reasoning.

Q2.11: If the external pressure is greater than the internal pressure, what will happen to the piston?

If the external pressure is less than the internal pressure, what will happen to the piston?

Q2.12: If the internal pressure is averaged over an extended period of time and we wait until the system comes to equilibrium, will the average internal pressure be (a) higher, (b) lower, or (c) equal to the external pressure? Explain your reasoning.

Q2.13: At equilibrium, what happens to the piston?

Q2.14: What happens to the volume of a gas at equilibrium? Does this happen in our simulation?

Q2.15: What role, if any, does the number of particles in our simulation have on the fluctuations in volume at equilibrium?

Q2.16: Describe the equilibrium state for a gas contained in a container with a piston.

7. Press **Pause**. Double the **External Pressure** to 0.08.

> Q2.17: According to Boyle's Law, predict what should happen to the average volume when we double the external pressure.

8. Select **Reset Averages** on the Average Values panel. Press **Start**.

By resetting averages you eliminate the data from the previous stage of the experiment when the pressure was 0.04.

> Q2.18: Describe what happens to the piston position and explain why. What happens to the volume of gas?

9. Select the **Pressure versus Time** graph on the Graph panel. When the internal pressure value displayed on the graph is approximately equal to the external pressure, press **Pause**. Record the volume of the gas from the main window.

You are observing the gas system approaching equilibrium where the internal and external pressure are approximately equal.

> Q2.19: How does the volume you recorded compare to your prediction? To what extent are the simulation results consistent with Boyle's Law?

10. Set **Iterations Between Displays** back to 10. Select the Volume versus Time graph on the Graph panel. Press **Start**. Watch the graph for approximately 5 time units (until graph fills the screen). Press **Pause**. Copy the graph to the "Snapshot Gallery" by selecting **Take Snapshot : Graph.**

Determine the number of particle collisions with the piston by counting the number of of parabolic segments, which represent the number of particle collisions with the piston.

Q2.20: How do the two graphs compare in terms of the number of parabolic segments? Propose an explanation for the observed 1 to 2 ratio.

Q2.21: How does the change in volume relate to the frequency of collisions with piston?

Q2.22: How does the change in frequency of collisions relate to the change in internal pressure?

BEGIN ACTIVITY

SimuLab 8: Quantitative Investigation of Boyle's Law

Your objective is to:

Test that the product PV remains constant for several positions of the piston at constant temperature.

You will be able to:

State Boyle's Law.

Construct a P versus V graph from collected data.

Construct a P versus $\frac{1}{V}$ graph.

Contrast the two curves.

Explain the significance of the slope on the P versus $\frac{1}{V}$ graph.

Predict what will happen to the PV product if the temperature is changed.

Construct a P versus number density graph.

Reformulate Boyle's Law in terms of gas density.

1. Open **SMD**, select **Boyle1000** in the **IdealGas** folder.

You will see 200 particles compressed in a container whose volume is fixed at 1000. The **Temperature** is set at 1.25 and the **Heat Bath** is on (i. e. the temperature is maintained at a relatively constant value).

2. Press **Start.**

The molecules start to move and bump into the walls of the container. The graph panel represents the internal pressure created by 200 gas particles at a given moment.

Q2.23: How do you explain the relatively large fluctuations in the pressure of the system?

3. Select **Show Averages**.

Observe the time and the other values carefully.

Q2.24: Wait for about five time units. Do you notice any change in the fluctuations of the pressure values in the Average Values panel?

4. Change **Iterations Between Displays** to 500. Let the program run for approximately 20 time units. Press **Pause**.

In order to obtain accurate value for pressure we need to average data over a longer period of time. Iteration setting of 500 speeds up the simulation.

5. Record temperature, number density, volume, and pressure data from the Average Values panel into the table. Calculate the PV value.

You will need these data for further analysis.

Table I

Volume	1000	2000	4000	8000	$10,000$
Temperature					
Number Density					
Pressure					
PV					
Deviation from average					
% deviation					

Calculate $(PV)_{ave}$ value $= \sum_{i=1}^{5} P_i V_i$:________

Deviation from average $= |(PV)_i - (PV)_{avg}|$

% deviation $= \frac{|(PV)_{ave} - P_i V_i|}{(PV)_{ave}}$ x 100

Calculate average % deviation $= \sum_{i=1}^{5} \frac{|(PV)_{ave} - P_i V_i|}{(PV)_{ave}}$ x 100 value:________

6. Select **File : Open Preset Experiment** and open **Boyle2000**. Press **Start**. After approximately 20 time units press **Pause**. Record the values and calculate the PV value as described in Step 5.

In order to test Boyle's law, we will measure the pressure of the same amount of gas at the same temperature and different volumes.

7. Repeat STEPS 6 for **Boyle4000**, **Boyle8000**, and **Boyle10000**.

Q2.25: Compare the values of PV for various volumes. Find the average value of these products and calculate the deviation of each PV value from the average. Calculate the percent deviation of each $(PV)_i$ value from the average $(PV)_{ave}$ by using this formula:

$$\%_{deviation} = \left(\frac{|(PV)_i - (PV)_{ave}|}{(PV)_{ave}} \times 100 \right)$$

Find the largest percent deviation.

To what extent are your results consistent with Boyle's Law? Hint: Refer to your percent deviation and range of values of pressure.

Q2.26: Construct a Pressure vs. Volume graph. This plot represents the dependence of pressure on volume at constant temperature. According to Boyle's law, when the temperature is constant, the graph should be a hyperbola.

If your graph varies significantly from a hyperbola, do you have any idea why this may have been so?

Q2.27: Construct a Pressure vs. $\frac{1}{Volume}$ graph. Draw the line of best fit through the data points. Determine the slope of this line and compare it to the average PV product in the above chart.

What is the relationship between the slope and the average PV product?

What is the difference between the graph of P vs. $\frac{1}{V}$ and the graphs of P vs. V graph?

Q2.28: Construct a Pressure vs. Number Density graph. Number Density is defined as Number of particles over volume: $n = \frac{N}{V}$. The distribution of data points should fall as a straight line.

What is the relationship between pressure and number density?

Compare this graph to the Pressure vs. $\frac{1}{Volume}$ graph. We should now be able to state an alternative form of Boyle's law: *at constant temperature, the gas pressure is directly proportional to the gas number density.*

Q2.29: Find the slope of the Pressure vs. Number Density graph and comment on the relationship between the slope and temperature of the system.

Q2.30: Graph the PV product vs. Pressure.

What slope do you expect? What do you find? Explain the deviation from your prediction (Hint: consider that ideal gas behavior is followed at low pressures and high temperatures).

2.3 Temperature

BEGIN ACTIVITY

HandsOn 8: The Subjective Sensation of Temperature

1. Label three bowls each half-filled with hot (roughly 50^0C) water as 1, 2, and 3.
2. Fill the bowl 1 with hot water (roughly 40^0 C) and bowl 3 with cold water (roughly 20^0 C). Pour 1/3 of water from bowl 1 and 1/3 from bowl 3 into bowl 2 and stir.
3. Immerse your left hand into bowl 1 and your right hand into bowl 3. Let your hands stay there for a minute. After you've done that, take them out and immerse both of your hands into bowl 2.

Q2.31: Is water in the middle bowl hot or cold? Explain.

From this simple experiment, you have hopefully discovered that the hand is not an accurate thermometer. Galileo observed that almost all substances expand when they are heated. This insight led to the construction of the first thermometer.

BEGIN ACTIVITY

HandsOn 10: HandsOn: Galileo's Thermometer

We can try to duplicate Galileo's thermometer with the aid of everyday household items.

You will need (as shown in Figure 2.3):

- a small glass or plastic bottle
- a cork that fits the bottle
- a thin glass tube about 10 inches long (you can use a transparent plastic straw if you do not have a glass tube)
- a drill with drill bit slightly smaller than the diameter of the tube

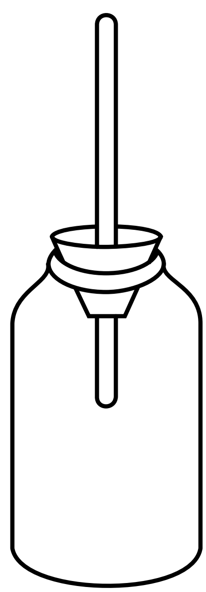

Figure 2.3: Schematic of Galileo's Thermometer experiment.

1. Drill a hole in the cork and slide the tube through until 0.5 inch. of the tube appears on the other side of the cork, ensuring that there is a tight fit. If the fit is not so tight, remove the tube and wrap some plastic wrap or Parafilm around the tube and reinsert.

2. Remove the straw and cork from the bottle. Carefully dip 0.5 inch of the tube below the cork into a cup of coffee or cooking oil and cover the upper end of the straw using your finger so that 0.5 inch of liquid stays in the straw when you take it out.

3. Insert the end of the cork into the bottle so that the top of the 0.5 inch of liquid is even with the top of the cork. Hold the bottle tightly in your hand.

Q2.32: What happened to the plug of liquid?

4. Mark your straw every 0.5 inch. You have invented your own temperature scale, where room temperature corresponds to zero and the temperature of your hands to, for example, ten. You can assign your own values to your thermometer since you invented it! Notice that your thermometer does not have a wide temperature range.

Q2.33: How would you increase the temperature range of your thermometer?

BEGIN ACTIVITY

SimuLab 10: Galileo's Thermometer – Movie

Due to the small number of particles in our system it would take a very long time for a liquid droplet in a tube to reach thermal equilibrium. To reduce the time of this activity, we will explore a movie of the simulation.

Your objective is to:

Understand the principle of how a thermometer works in terms of molecular motion.

You will be able to:

Explain how a thermometer works in terms of molecular motion.

Explain why the column of liquid goes down as temperature is decreased.

1. Open **SMDPlayer**, select **Galileo-Thermometer** in the **IdealGas** folder. Press **Play**.

The movie pauses at the opening frame and displays the first explanatory caption. In order to better visualize the particles, you can select **Edit : Background White**. The narrow column on the screen represents our thermometer tube, blue particles represent air molecules, and the green layer represents a liquid droplet.

2. Press **Play** to resume the movie. The movie pauses at each explanatory caption. Repeat this step until the end of the movie is reached.

At a given temperature, the droplet fluctuates around a certain equilibrium position. Each time the temperature drops in our simulation, the equilibrium position of the green layer also drops. Near the end of the movie, we simulate the effect of the thermometer inserted into an extremely hot environment: everything is thrown out of the tube and your thermometer breaks!

Q2.34: Describe the relationship between the height of the gas sample and the temperature. Explain how the thermometer works in terms of molecular motion.

2.4 Charles Law

A century after Boyle derived his law, the French scientist Jacques Charles (1746 - 1823) discovered a linear relationship between gas temperature and gas volume when pressure is kept constant. Using a temperature versus volume graph, he discovered that the volume of any gas at constant pressure would approach zero at -273^{0}C. He did not publish these results. Twenty years later, another French chemist, Joseph Gay-Lussac, repeated Charles' experiments, got the same results, and published them. At that time, however, no one could even get close to -273^{0}C in a laboratory, so Gay-Lussac could only determine his law by extrapolating the volume line on his graph until it crossed the temperature-axis. Later, this temperature was called absolute zero. The name for the new temperature scale, which has the origin at absolute zero, is the Kelvin scale. Zero degrees in Kelvin corresponds to -273^{0}C and is the temperature at which all molecular motion ceases.

In the next simulation we will demonstrate Charles' Law from a microscopic point of view. We will put a gas in a cylinder under a piston and keep the external pressure constant. Imagine that this pressure is created by a constant weight resting on top of the piston. At any given temperature, the particles have a certain average velocity. They collide with the piston and the walls of the cylinder, thus, causing pressure. If the temperature is lowered, the average velocity of the particles decreases, and the particles collide with the piston and cylinder walls less frequently and with less force and thus the internal pressure drops. Since the weight resting on top of the piston remains constant, the piston descends until the pressure inside the cylinder becomes equal to the external pressure, therefore reaching equilibrium again. As the volume of the gas decreases the number of collisions with the walls increase and thus the internal pressure increases. Since we only have 200 particles in this simulation, there are relatively few collisions with the piston, and the piston constantly moves up and down. In a real experiment, with 10^{23} or more molecules in a sample, the drumming on the piston produced by such a great number of molecules is constant and would not lead to macroscopic oscillations, and the piston, after a few initial initial oscilations stays almost constant.

BEGIN ACTIVITY

SimuLab 12: Charles' Law – Movie

Your objective is to:

Recognize the microscopic origin of the volume variations with temperature at constant external pressure.

You will be able to:

State Charles' Law.

Construct a volume versus temperature graph from collected data.

State the relationship between volume and temperature.

Determine the temperature at which the volume would be zero and explain the significance of this point.

Propose reasons as to why the $\frac{V}{T}$ value deviates from predictions of Charles' Law.

State the relationship between number density and temperature.

1. Open **SMDPlayer**, select **Charles** in the **IdealGas** folder. Select **Show Averages**. Press **Play** to resume the movie. The movie pauses at each explanatory caption. Follow the instructions in each caption, making sure to **Reset Averages** in the Average Values panel. Repeat this step until the end of the movie is reached. If you wish to see the temperature in Kelvin scale press **Real Units** button.

Notice that the average pressure stays approximately the same throughout the entire movie. Note that the temperature throughout the movie decreased by a factor of 2.5. In our simulation, the temperature of the gas sample is equal to the average kinetic energy of the molecules. The average kinetic energy is proportional to the average velocity squared $\left(E_k = \left(\frac{mv^2}{2}\right)_{avg}\right)$. Therefore, the average velocity is decreased by $\sqrt{2.5} \approx 1.6$. Did you notice that the particles move slower at the end of the movie than at the beginning? To compare, you can watch the movie again.

	T_1	T_2	T_3	T_4	T_5
$Temperature$					
$Pressure$					
$NumberDensity\ (N/V)$					
$Volume$					
V/T					
Deviation from average					
% Deviation					

Calculate average $\left(\frac{V}{T}\right)_{avg}$ value $= \sum_i^5 \frac{V_i}{T_i}$: ______________

Deviation from average $= \left|(\frac{V}{T})_i - (\frac{V}{T})_{ave}\right|$

% Deviation $= \frac{\left|(\frac{V}{T})_i - (\frac{V}{T})_{ave}\right|}{(\frac{V}{T})_{avg}} \times 100$

Q2.35: Plot Volume vs. Temperature on a graph. Draw a line of best fit through the points.

Q2.36: What is the relationship between volume and temperature?

Q2.37: On a Volume vs. Temperature graph, for an ideal gas the line intersects the temperature axis at the origin. Comment on the extent to which your graph is consistent with Charles' Law.

Q2.38: Compare the values of $\frac{V}{T}$ for various temperatures. Find the average value of these ratios and calculate the deviation of each $\frac{V}{T}$ value from the average. Calculate the percent deviation of each $\left(\frac{V}{T}\right)_i$ value: and calculate the average percent deviation.

Q2.39: Plot the *Number density vs. Temperature* graph.

Q2.40: How does number density vary with temperature?

2.5 Gay-Lussac Law

Joseph Gay-Lussac (1778-1850) continued investigating gases and performed an experiment in which he changed the temperature and kept the volume constant. He found that at constant volume the pressure increases linearly with temperature. The graph of pressure vs. temperature is a straight line. The slope of this line depends on the volume of the gas sample and on the number of gas particles. For various volumes the lines, when extrapolated, cross approximately at the point $P = 0$, $T =$ -273^{0}C on the graph. This point corresponds to the same temperature as in the Charles' Law graphs where pressure was held constant. At this temperature the gas exerts no pressure at all. Later this temperature was called absolute zero, and a new temperature scale called Kelvin was established. Zero degrees Kelvin, corresponds to -273^{0}C. Gas pressure is created by collisions of particles with the walls, therefore at absolute zero the particles of gas should completely stop moving. In terms of the Kelvin temperature scale, the Gay-Lussac law can be written as

$$\frac{P}{T} = const,$$

where the constant depends on the volume and the number of gas particles.

BEGIN ACTIVITY

SimuLab 14: Gay-Lussac Law

Your objective is to:

Recognize the microscopic origin of the internal pressure variations with temperature at constant volume.

You will be able to:

State Gay-Lussac's Law.

Construct a *Pressure vs Temperature* graph.

Extrapolate the slope on the graph to $P = 0$ and explain the significance of this point.

Determine the temperature range at which data is consistent with Gay-Lussac Law.

Suggest reasons why deviations from Gay-Lussac Law occur.

Copy the table below.

	$T = 4$	$T = 3$	$T = 2$	$T = 1.25$	$T = 1$
Pressure					
P/T					
Deviation from ave.					
% deviation					

Average $\frac{P}{T}$ value: _____________

1. Open **SMD**, select **Gay-Lussac** in the **IdealGas** folder.

You see 200 gas molecules in a fixed volume, the temperature is $T = 4.0$ and the Number Density $\left(\frac{N}{V}\right) = 0.02$ (number of particles divided by volume).

2. Select **Show Averages**. Press **Start**. Watch the Pressure vs. Time graph for approximately 5.0 time units.

You can see that the fluctuations of pressure are rather significant and the values on the Average Values panel are constantly changing. In order to obtain accurate measurements, you need to average data for significantly longer times, such as 20 time units.

3. Change **Iterations Between Displays** to 500. Let the program run for approximately 20 computer time units as shown in figure 2.4. Press **Pause**.

Setting Iterations Between Displays at 500 speeds up the simulation.

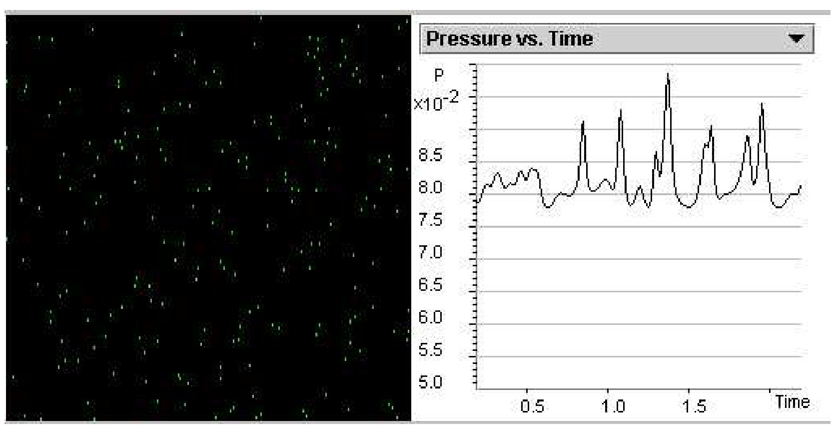

Figure 2.4: Screenshot of Gay-Lussac's Law SimuLab.

4. Record the pressure from the Average Values panel for this trial in your Table for $T = 4$. Calculate the $\frac{P}{T}$ value. Press **Reset Averages** on the Average Values panel.

You are preparing data for the future analysis.

5. Set the **Temperature** to $T = 3$. Press **Start**. Let the program run for 20 time units. Press **Pause**. Record *Pressure* and calculate P/T ratio. Select **Reset Averages** on the Average Values panel.

Ressetting Averages allows you to delete the data values from the previous experiment.

6. Repeat Step 5 for Temperatures $T = 2$, $T = 1.25$,and $T = 1$.

Q2.41: Compare the values of P/T obtained for various temperatures with the average value of P/T from the table. $\left|\left(\frac{P}{T}\right)_i - \left(\frac{P}{T}\right)_{avg}\right|$. Express the differences in percents

$$\frac{\left|\left(\frac{P}{T}\right)_i - \left(\frac{P}{T}\right)_{avg}\right|}{\left(\frac{P}{T}\right)_{avg}} \times 100$$

and record them into the table.

Q2.42: What conclusions can you draw about the consistency of the $\frac{P}{T}$ constant in relation to temperature?

Q2.43: Plot a Pressure vs. Temperature graph. Approximate it by a straight line. Determine the slope of the graph. Extrapolate the line to $P = 0$.

Q2.44: What is the temperature when $P = 0$? Explain your result.

2.6 Avogadro's Law

In 1809, Gay-Lussac performed several experiments with reacting gases showing that under constant conditions of pressure and temperature, volume was not necessarily a conserved quantity. In other words, if you start out with three volumes of gas, you won't necessarily end up with three volumes at the end of a chemical reaction; mass *is* conserved in a chemical reaction, volume is *not*. For example, if two volume units of hydrogen gas are mixed with one volume unit of oxygen gas at constant pressure, the water vapor produced by the reaction occupies two volume units

$$2H_{2(gas)} + O_{2(gas)} \rightarrow 2H_2O_{(gas)}.$$

In this example, the number of atoms (i.e., mass) is conserved on each side of the equation but the volume of gas is not conserved.

Two years later Italian scientist Amadeo Avogadro (1776-1856) explained these results by stating that *in equal volumes of any gas at the same temperature and pressure there are equal numbers of particles.* The name of the unit that represents a certain fixed number of particles is a *mole.* One mole contains the Avogadro number N_A of molecules, $N_A = 6.02 \cdot 10^{23}$. Then we can reformulate the Avogadro law: *at constant temperature and pressure the volume of gas is proportional to the number of moles of gas particles:*

$$\frac{V}{n} = const$$

Remembering that molecular collisions with the sides of a container cause pressure, then for a chemical reaction performed in a container of constant volume the Avogadro law gives: *at constant temperature and volume the pressure is proportional to the number of moles of gas.*

$$\frac{P}{n} = const$$

BEGIN ACTIVITY

SimuLab 16: Avogadro's Principle

Your objective is to:

Recognize the role of the number of moles (here the number of particles) in the determination of the internal pressure of a gas.

You will be able to:

State the relationship between the number of particles and the volume they occupy if pressure and temperature remain constant.

Calculate the volume when temperature and pressure remain constant.

State Avogadro's hypothesis.

Contrast number density to mass density.

Predict what happens to each parameter if the number of particles is doubled.

Copy the table below.

	T	P	V	N (*# of particles*)	*mass*
Avogadro40					
Avogadro200					
Avogadro100					
Avogadro100					

1. Open **SMDPlayer**, select **IntroAvogadro'sLaw** from the **Ideal Gas** folder. PRESS **Play**. Read all the captions and follow the instructions. Go to **File - Quit**

Movie gives a preliminary understanding of Avogadro's Principle from a microscopic point of view.

2. Open **SMD**, select **Avogadro40** in the **IdealGas** folder. In order to better visualize the particles, you can select **Edit : Background White**. To speed up the simulation, change the **Iterations Between Displays** to 1000. Select **Show Averages**.

   In this experiment you are visualizing 40 particles (displayed as a B particle type), each of which has a mass of 1.0 unit.

3. Press **Start**. Observe the **Pressure versus Time** graph for approximately 40 time units as shown in figure 2.5. Press **Pause**.

   The gas is approaching equilibrium. The pressure fluctuates around an average value.

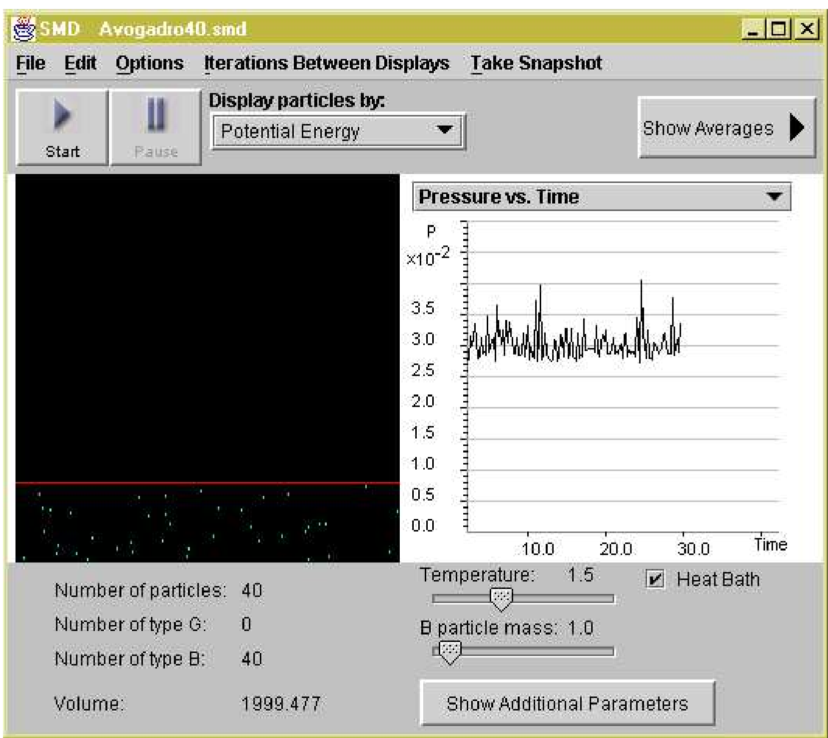

Figure 2.5: Screenshot of Avogadro's SimuLab.

4. Record the temperature T, pressure P, volume V, number of type B particles N, and the B particle mass m.

You are collecting data for future analysis and recording it in the first row of the data table.

5. Open **Avogadro200** by selecting **File – Open Preset Experiment**.

In this experiment you are visualizing 200 particles of mass 1.0. Note that the piston is now above the screen and you can not see it.

6. Repeat Steps 3 and 4.

You are collecting data for future analysis and recording it in the second row of the data table.

Q2.45: Are there any changes in parameters other than the number of particles? If so, what are they?

Q2.46: What is the relationship between the number of particles and the volume they occupy if pressure and temperature remain the same?

Q2.47: What do you predict the volume to be if you have 100 particles, each with a mass of 1.0?

7. Open **Avogadro100** by selecting **File – Open Preset Experiment**.

This simulation contains 100 particles of mass 1.0.

8. Repeat Steps 3 and 4.

You are collecting data for future analysis and recording it in the third row of the data table.

Q2.48: Speculate: What do you think will happen if we increase the mass of the particles? Why? To test your speculation, move onto the next steps.

9. Select **File – Reset Experiment**. Set **B particle mass** to $m = 10$.

Now this simulation contains 100 particles of mass 10.0.

10. Repeat Steps 2 and 3.

You are collecting data for future analysis and recording it in the fourth row of the data table.

Q2.49: What happened to the parameters of temperature, pressure, and volume when you changed the mass of the particle?

Q2.50: In our simulations, "density" always refers to number density $\frac{N}{V}$. The density which you are probably most familiar with is mass density $\frac{M}{V} = \frac{mN}{V}$; where M is mass, V is volume, m is mass of a single particle and N is the number of particles.

What happens to the number density when the B particle is set to a mass of $m = 10$ in Step 7?

Q2.51: What happens to the mass density when the B particle is set to mass $m = 10$? Contrast this to the Number Density above and explain.

Q2.52: What do you predict the volume would be for 175 particles of Mass=5?

Q2.53: Consider two 1-liter balloons at room temperature. One balloon is filled with one mole of He gas and the other with one mole of Ne gas. How do their pressures, mass densities, and number densities compare?

BEGIN ACTIVITY

SimuLab 18: Avogadro's Principle Movie

Your objective is to:

Investigate the relationship between the number of gas particles and the volume they occupy if temperature and pressure are kept constant.

You will be able to:

State the relationship between the number of particles and the volume they occupy if pressure and temperature remains constant.

State Avogadro's hypothesis.

Contrast mass density with number density.

Explain the relationship between volume, number density and mass density in terms of Avogadro's Principle.

1. Open **SMDPlayer**, select **Avogadro** in the **IdealGas** folder.

2. Press **Play**. The movie pauses at the opening frame and displays the first explanatory caption. Select **Show Averages**. The movie pauses at each explanatory caption.

3. Press **Play** to resume the movie after each caption. Be sure to reset **Averages** when instructed to do so thus eliminating data from previous setting.

You see a mixture of gases under a piston. Follow the instructions in the captions.

The Averages panel displays **average** (not instantaneous) values of the parameters as the experiment proceeds.

Q2.54: What has happened to the total number of particles as the product molecules are formed?

Q2.55: If the temperature and the pressure of the system are kept constant, what will happen to the volume as the number of gas particles decreases?

Q2.56: What happened to the mass density of the gas? Explain.

Q2.57: What happened to the number density? Explain.

Q2.58: Explain the changes in volume, number density, and mass density in terms of Avogadro's Principle.

2.7 Ideal Gas Law

We arrive at the gas state equation by combining Boyle's Law, Charles' Law, Gay-Lussac's Law, and Avogadro's Principle:

$$\frac{PV}{NT} = k.$$

where $k = 1.38 \cdot 10^{-23} J/K$ is the Boltzmann constant and N is the number of particles in the gas. Usually we use moles instead of number of particles, because the number of particles is huge in typical laboratory gas samples while the numbers of moles have reasonable values. In a mole there is the Avogadro number N_A of molecules. If the number of moles in the gas sample is n, then $N = N_A n$ is the number of particles. If we define $R = kN_A$ we can rewrite the gas equation as:

$$PV = nN_A kT$$

or

$$PV = nRT$$

where $R = 8.31 J/(K \cdot mole)$ is the so called *universal gas constant* and n is the number of moles of gas. The above equation is called the **ideal gas law**. It is valid only if the gas possess "ideal" properties:

- Gas particles have no volume.
- Gas particles do not interact with each other.

An Ideal gas is *not* real, but rather a hypothetical substance. *Real* gas molecules, however, *do* have a tiny volume and *do* interact with each other. Therefore there are always deviations from the Ideal Gas Law. When conditions are close to "ideal" (i.e., at low pressures and high temperatures) the deviations are very small. Often, though, conditions are "less than ideal". This occurs when any of the ideal gas properties above fails to be true. For example, at low temperatures we can not neglect the interaction between the molecules which lead to phase transitions.

Q2.59: What kind of virtual experiment would you perform to determine if you are modeling a real or ideal gas?

BEGIN ACTIVITY

SimuLab 20: Ideal Gas Law

Your objective is to:

Test the ideal gas law by obtaining V, T and P measurements and evaluating the consistency of the $\frac{PV}{NT}$ ratio at various conditions.

You will be able to:

Test the validity of the ideal gas law at low densities and high temperatures.

Define the Boltzmann constant.

Test that the ideal gas law is valid for various molecular masses.

Find the limits of the ideal gas law in terms of gas density and temperature.

1. Open **SMD**, select **IdealGasLaw** in the **IdealGas** folder. To better visualize the particles, select **Edit**: Background Gray.

   You are visualizing a gas mixture that consists of 100 green and 100 blue particles as shown in figure 2.6. You will perform three experiments (set ups A, B and C).

2. Set **Iterations Between Displays** to 1000. Select **Show Averages**.

   Higher number of Iterations Between Displays speeds up the program.

3. Press **Start** and wait for approximately 20 time units. Press **Pause**. Record temperature T, pressure P, volume V, number of particles N (set-up A in your table). Calculate number density $\frac{N}{V}$ and $\frac{PV}{NT}$.

   The system has reached the equilibrium and you are collecting data for further analysis.

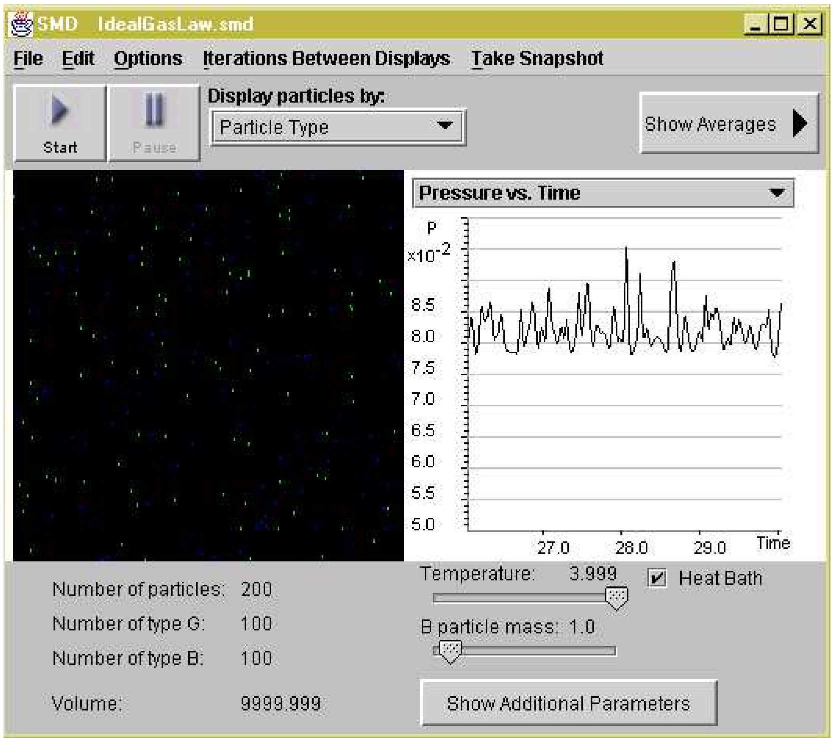

Figure 2.6: Screenshot of the Ideal Gas Law SimuLab.

Table I

	T	P	V	N	$\frac{N}{V}$	$\frac{PV}{NT}$
A						
B						
C						

Set-up A: 100 green particles, 100 blue, mass = 1

Set-up B: 100 green particles, mass = 1

Set-up C: 100 blue particles, mass = 10

4. Select **File – Reset Experiment**. Select **Edit – Particles** and choose **Remove all B particles** (blue particles) and click on the display window to take this action. Select **Reset Averages** in the Average Values panel. Repeat Step 3, using set-up B in your table.

Resetting Averages eliminates the data from previous experiments. You are now collecting data for this experiment.

5. Select **File – Reset experiment**. Select **Edit – Particles** and choose **Remove all G** which removes all green particles. Set the **B particle mass** to 10. Select **Reset Averages** in the Averages Values panel. Repeat Step 3 using set-up C in your table.

Q2.60: Compare the values of $\frac{PV}{NT}$ found in set-ups A, B, and C. Calculate the average value which represents the Boltzmann constant in computer units.

Theoretically, the Boltzman constant is 1.0 in our computer simulation. In set-up A the gas density is 0.02 and is too high to give the theoretical value. In set-up B and C, the gas density is 0.01 and approaches ideal behavior.

Now we will determine the range of densities for which the ideal gas law equation is valid.

6. Select **File – Reset experiment**. Select **Edit – Particles** and choose **Change all particles to G** (making all particles green).

You are preparing experimental set-up D.

7. Select **Show Additional Parameters**. Using scroll bar and / or arrow key, set **Number Density** to 0.1. Press **Start**. Wait approximately 10 time units so that equilibrium is reached.

   At this point, **Reset Averages** in the Average Values panel and wait another 20 time units. Press **Pause.** Record parameters in your table and compute $\frac{N}{V}$ and $\frac{PV}{NT}$.

You are watching the approach to equilibrium and collecting data for set-up D when equilibrium has been reached.

Table II

	T	P	V	N	$\frac{N}{V}$	$\frac{PV}{NT}$
D						
E						
F						

Set-up D: 200 green, $\frac{N}{V} = 0.1$

Set-up E: 200 green, $\frac{N}{V} = 0.2$

Set-up F: 200 green, $\frac{N}{V} = 0.5$

Q2.61: How does your ratio $\frac{PV}{NT}$ compare to the theoretical value of 1.0?

8. Repeat Step 7 for **Number Density** 0.2 and 0.5.

You are collecting data for set-ups E and F.

Q2.62: Comment on the consistency of the $\frac{PV}{NT}$ ratio as number density of the gas increases.

Now we will determine the range of temperatures for which the ideal gas law equation is valid.

9. To configure setup G : set **Number Density** to 0.02.

You are creating a very low density gas. You can choose the option "distribute particles instantaneously" to save time.

10. Set **Temperature** to 2. Press **Start**. Wait approximately 10 time units so that equilibrium is reached. At this point, **Reset Averages** in the Average Values panel and wait another 20 time units. Record parameters in your table and compute $\frac{PV}{NT}$ in the data table.

You are collecting data for set-up G. Resetting Averages eliminates data from when the system was not yet at equilibrium.

Table III

	T	P	V	N	$\frac{N}{V}$	$\frac{PV}{NT}$
G						
H						
I						

Set-up G: 200 green, $T = 2$

Set-up H: 200 green, $T = 1$

Set-up I: 200 green, $T = 0.5$

11. Repeat Step 10 for temperatures 1 and 0.5.

You are collecting data for set-up H and I.

Q2.63: How consistent is the $\frac{PV}{NT}$ ratio when the temperature is varied in set-ups G, H, and I? Comment on conditions necessary for ideal gas behavior.

Consequences of the Ideal Gas Law

- When a gas is compressed at constant temperature, the gas particles have less space to move around. They collide with the walls more frequently, and the internal pressure increases in accordance with Boyle's law: PV =const.

- When we decrease temperature at constant volume, the velocity of the particles decreases. If the volume is kept constant, they collide less frequently and exert less force on the walls of the container. This is consistent with Gay-Lussac's law: $\frac{P}{T}$ =const. At absolute zero the particles have a velocity of zero, they do not collide with the walls of the container, and the internal pressure is zero.

- If the external pressure is kept constant and the temperature is lowered, the volume of the gas decreases. At the lowered temperature, the molecules move slower, therefore collide less frequently. As a result, the internal pressure decreases. Since the external pressure is constant, the gas volume decreases until the number of collisions results in an internal pressure which is equal to the external pressure. We are assuming that gas particles have no volume and the pressure is only generated by collisions with container walls. We also assume that the volume of a gas will reach zero at absolute zero. This is consistent with Charles' law: $\frac{V}{T}$ =const.

- When we increase the number of particles and keep temperature and external pressure constant, the number of collisions increases and the gas expands. This is consistent with Avogadro principle for the case when P is constant and T is constant: $\frac{V}{n}$ =const. When V is constant and T is constant we obtain $\frac{P}{n}$ =const.

- A mole of any gas at standard temperature and pressure (STP), i.e. 0^0C temperature and pressure of 1 atm, occupies $\frac{RT}{P} = \frac{8.31 \times 273}{101{,}000} = 0.0224$ m^3 = 22.4 liters. The universal gas constant is commonly measured in the units of $R = 0.082$ liters $\times$ atm/Kelvin $\times$ mole or $8.351 J/Kmol$.

2.8 Dalton's Law

Until this point, the assumptions of the ideal gas model effectively provided the prediction of the gas behavior at low densities and high temperatures. We can try to extend the model in order to predict the pressure produced by a *mixture* of various molecules. Since we define molecules as noninteracting particles of zero volume, all of them would move in the container independently. They would collide with the walls and produce pressure. The molecules of a particular kind cause a pressure that is unaffected by the presence (or absence) of other molecules. This is called the *partial pressure* of that gas. The molecules of another kind would produce its own partial pressure, and so on. Then the total pressure in the container is the sum of all these partial pressures. This statement is known as **Dalton's Law of Partial Pressures**:

$$P = P_1 + P_2$$

where P is the total pressure, and P_1 and P_2 represent the partial pressure of Gas 1 and Gas 2.

BEGIN ACTIVITY

SimuLab 22: Dalton's Law

In our simulation it is more convenient to use number of particles instead of number of moles. Moreover, in the simulation units the Boltzmann constant $k = 1$. Hence, the partial pressures

$$P_i = \frac{N_i}{V} T,$$

where N_i is just a number of molecules of certain type.

Your objective is to:

Recognize why the total pressure of the gas mixture is equal to the sum of partial pressures of the components from the microscopic point of view.

You will be able to:

State Dalton's Law.

State the relationship between the number of particles and pressure they exert at constant temperature and volume.

Calculate the final pressure as the number of particles are varied when the initial pressure and number of particles are given.

Copy the table below.

	$\frac{N}{V}$	P	T
100 Blue and 100 Green			
100 Blue			
100 Green			

1. Open **SMDPlayer**, select **IntroDalton'sLaw** from the **IdealGas** folder. PRESS **Play**. Read all the captions and follow the instructions. Go to **File -Quit**

   Movies gives a preliminary understanding of partial pressures from a microscopic point of view.

2. Open **SMD**, select **Dalton** in the **IdealGas** folder.

   You are visualizing 100 green particles with a mass of 1.00 and 100 blue particles each with a mass of 10.0 as shown in Figure 2.7.

3. Change the **Iterations Between Displays** to 500. Select **Show Averages**.

   Increasing Iterations speeds up the simulation.

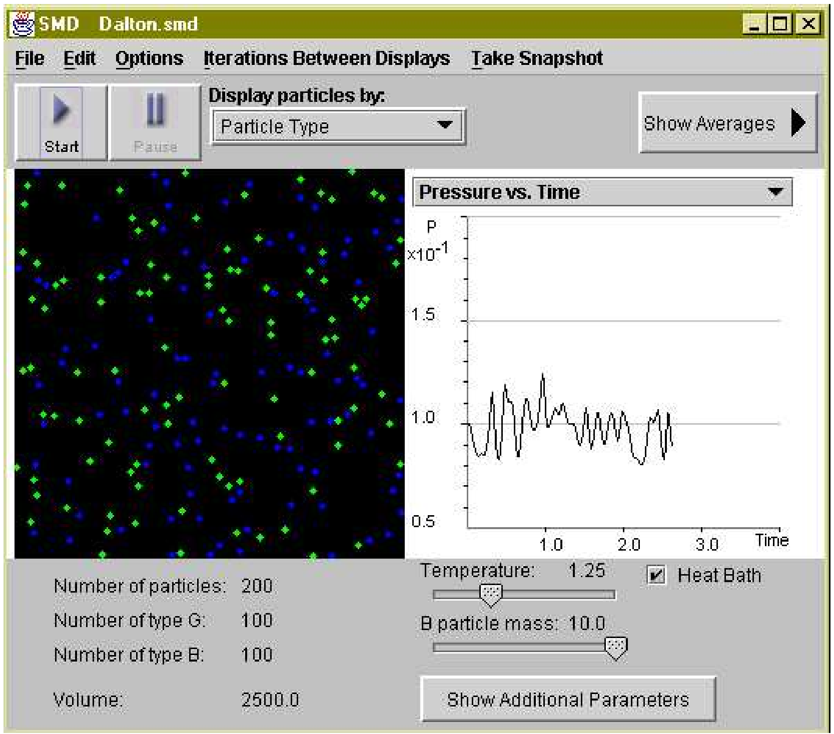

Figure 2.7: Screenshot of Dalton's Law SimuLab.

4. Press **Start** and run the simulation for approximately 40 time units. Press **Pause**. Record in your table the number density $\frac{N}{V}$, pressure P and temperature T from the averaging window.

   The system is approaching equilibrium.

5. Select **Edit : Edit Particles** and choose **Remove all G particles**. Press **Reset Averages** in the Average Values panel. Repeat Step 4. Note that the blue particles have a mass of 10.

   You are are collecting data for future analysis.

6. Select **File : Reset Experiment**. Select **Edit : Edit Particles** and choose **Remove all B particles**. Repeat Step 4. Note that the green particles have a mass of 1.
7. Using the data recorded in your table, add the pressure of the 100 blue particles to that of the 100 green particles

You are summing partial gas pressures.

Q2.64: Compare this calculated result to the total pressure of the mixture when both blue and green particles were present. Explain what you find.

Q2.65: Does the mass of a particle affect the pressure it exerts? Justify your answer.

Q2.66: What is the relationship between the number of particles present and the pressure they exert in a given container?

8. Select **File : Reset Experiment**. Select **Edit : Edit Particles** and choose **Remove particles** to remove any 20 particles on the screen.

You are lowering the density.

Q2.67: What do you predict the pressure will now be?

9. Select **Reset Averages** in the Average Values panel. Press **Start** and wait for 40 time units. Press **Pause**.

The system is approaching equilibrium.

Q2.68: Verify your pressure prediction.

2.9 Research Projects

Try one of the suggestions below or design your own. Or, feel free to write an essay using any of the questions throughout this chapter as inspiration.

BEGIN ACTIVITY

Research Project 12: Boyle's Law

See SimuLab 7 .

To further investigate the universality of Boyle's law, test it for various temperatures. Set $T = 1.25$, 1.5, 2, 4 and repeat steps 6-8 (in SimuLab 7 for each temperature value.

Q2.69: What happened to the PV product when the temperature increased? Explain.

Q2.70: At low pressures what is the temperature range in which the data is most consistent with Boyle's law?

BEGIN ACTIVITY

Research Project 14: Gay-Lussac Law

See SimuLab 13.

To extend the SimuLab, repeat Step 6 with $\frac{N}{V} = 0.10$.

	$T = 4$	$T = 3$	$T = 2$	$T = 1.25$	$T = 1$
Pressure					
P/T					
Deviation from ave.					
% Deviation					

Average $\frac{P}{T} =$

Plot a Pressure vs. Temperature graph. Determine the line of best fit and the slope. Extend the line to $P = 0$. Find the temperature corresponding to $P = 0$.

Q2.71: Contrast this graph to that obtained from the $\frac{N}{V} = 0.02$ experiment. What are the similarities and the differences you see?

Q2.72: What happens to the $\frac{P}{T}$ ratio as the number density of the gas sample is increased? Explain.

BEGIN ACTIVITY

Research Project 16: Charles' Law

See SimuLab 11 .

To see if the Volume vs. Temperature graphs for different pressures are straight lines that cross close to the origin we recommend that you perform the following investigation. Instead of using the prerecorded movie, you should repeat the Charles' Law experiment at different pressures using charles.smd files in the **IdealGas** folder.

BEGIN ACTIVITY

Research Project 18: Avogadro's Principle

See SimuLab 15 . Open one of the files: Abvogadro40, Avogadro100 or Avogadro200.

Deselect **Lock Piston Position** check box so that the piston is free to move. Set **Pressure** to the same value you obtained in the previous experiments. Remove 25 particles by selecting **Edit : Edit Particles**. Set **B particle mass** to 5 and predict what will be the volume of the gas at equilibrium. Run the simulation for 1000 time units.

Q2.73: Find the average volume and compare it with your prediction.

BEGIN ACTIVITY

Research Project 20: Ideal Gas Law

See SimuLab 19 .

To more precisely define the temperature and number density range in which the ideal gas law is obeyed, perform 20-40 additional experiments. Using the IdealGas application, run the simulations 20-40 times, changing the temperature and number density parameters as you are measuring the pressure. Draw a Temperature vs. Number Density graph using the data from these experiments. Label each data point with the $\frac{PV}{NT}$ value. The theoretical value of the $\frac{PV}{NT}$ ratio is 1.00. Draw a line connecting the points for which the deviation is less then 5% from the ideal gas value of 1.0. Using your pencils shadow the temperature region for which the ideal gas law is valid.

Q2.74: Describe the region of applicability of the ideal gas law in terms of density and temperature.

BEGIN ACTIVITY

Research Project 22: Gay-Lussac Law II

In order to be confident about the results of an experiment it must be repeated many times. Gay Lussac is remembered for his very precise as well as accurate measurements that he made of T & P as he ascended in a balloon. You can determine the precision (reproducibility) of our measurements. Run the SimuLab for 20 time units, pause the simulation, and record density, pressure, and temperature values for this trial into the first row of the table from SimuLab 13. Calculate the $\frac{P}{T}$ value for this trial and record it into the table. Select **Reset Averages** in the Average Values panel.

Make a copy of the table below:

Trials	$\frac{N}{V}$	P	T	$\frac{P}{T}$	*Deviation from average*	*% deviation*
1						
2						
3						
4						
5						
Average value						

Average $\left(\frac{P}{T}\right)_{avg}$ value:________;

Do not reset the experiment each time but continue to run the simulation for additional 20 time units from the point it has reached in the previous time interval. Reset Averages after each trial. Repeat the same simulation four (or more) times. Find the average values of density, pressure, and temperature. Determine their deviations from the average value in percents. Find the average value of the $\frac{P}{T}$ ratios and calculate the deviation of each $\frac{P}{T}$ value from the average. Calculate the percent deviation of each $\left(\frac{P}{T}\right)_i$ value from the $\left(\frac{P}{T}\right)_{avg}$ average $\left(\frac{\left|\left(\frac{P}{T}\right)_i-\left(\frac{P}{T}\right)_{avg}\right|}{\left(\frac{P}{T}\right)_{avg}} \times 100\right)$; and calculate the average percent deviation.

> Q2.75: What conclusions can you make about the precision (reproducibility) of this virtual experiment?