The Gas Laws of Boyle and Charles

- Learn about the Gas Laws of Boyle and Charles.
- Learn about the Ideal Gas Law.
- Learn about the determination of chemical formulas.

In this laboratory exercise we will use Charles’ Law to predict how much a gas, namely Air, should contract when cooled from 100°C to Room Temperature. We will then measure how much the gas actually contracts and compare the result with the Charles’ Law prediction. We will also confirm Boyle’s Law using a Water Manometer and Air as a gas.

Modern scientific chemistry developed out of alchemy during the early 1600’s, when application of the Scientific Method began to take hold. This method, basically, dictates that Fundamental Laws and Theories must find support in direct experimental observation. The earliest chemists to apply this method to the behavior of substances were Pneumatic Chemists studying the chemistry and properties of gases. Although the gases Hydrogen and Oxygen would not be discovered and characterized for some time, considerable progress was made in studying the effects of environmental changes upon gases in general. (Hydrogen, H₂, was discovered by Henry Cavendish in 1766 and Oxygen, O₂, was discovered by Joseph Priestly in 1775.)

These environmental changes involve the variation of the pressure (P), volume (V), temperature (T) and amount (n) of the gas in a sample. The variables P, V, T, and n define the State of the gas and are referred to as State Variables. Changes in the state of the gas will influence the values of the state variables. For instance, in order to lower the pressure of a gas, we may increase its volume, decrease its temperature, or decrease the amount of gas present. Or, we may do a combination of these things. Thus, relationships between the state variables are important to understand if we wish to understand the behavior of the gas.

Robert Boyle's Experimental Apparatus
A Textbook of Physical Chemistry
Arthur W. Adamson

The first of these relationships to be established was that between volume and pressure. Robert Boyle, working with an improved design for the Air Pump developed by Otto von Guericke, studied the effect of increasing the pressure on a sample of Air. He would trap Air in the shorter leg of a bent glass tube filled with Mercury. The pressure exerted on the trapped Air would be equal to the atmospheric pressure, measured in mmHg, plus the Mercury’s height differential between the two legs of the tube. As more Mercury is added to the longer leg, a greater pressure is exerted on the Air and its volume will contract. The volume of the Air
is then proportional to the depth of the Air in the shorter leg, as measured by markings on that leg.

… because an accurate experiment of this nature would be of great importance to the doctrine of the Spring of Air, and has not yet been made (that I know) by any man; and because also it is more uneasy to be made than one would think, in regard of the difficulty as well of procuring crooked Tubes fit for the purpose, as of making a just estimate of the true place of the protuberant *Mercury's* surface; I suppose it will not be unwelcome to the reader to be informed, that after some other trials, one of which we made in a Tube whose longer leg was perpendicular, and the other, that contained the air, parallel to the horizon, we at last procured a Tube of the figure expressed in the scheme; which Tube, though of a pretty bigness, was so long, that the cylinder, whereof the shorter leg of it consisted, admitted a list of Paper, which had before been divided into 12 inches and their quarters, and the longer leg admitted another list of Paper divers foot in length, and divided after the same manner. Then Quicksilver being poured in to fill up the bended part of the Glass, that the surface of it in either leg might rest in the same Horizontal line, as we lately taught, there was more and more Quicksilver poured into the longer Tube; and notice being watchfully taken how far the *Mercury* was risen in the longer tube, when it appeared to have ascended to any of the divisions in the shorter tube, the several observations that were thus successively made, and they were made set down …

Robert Boyle
*A Defence of the Doctrine Touching the Spring and Weight of the Air*
1662

A short table of his data is as follows:

<table>
<thead>
<tr>
<th>Volume (Depth Short Leg)</th>
<th>Pressure (Atm + Height)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>29 2/16</td>
</tr>
<tr>
<td>44</td>
<td>31 15/16</td>
</tr>
<tr>
<td>40</td>
<td>35 5/16</td>
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<tr>
<td>28</td>
<td>50 5/16</td>
</tr>
<tr>
<td>16</td>
<td>87 14/16</td>
</tr>
<tr>
<td>12</td>
<td>117 9/16</td>
</tr>
</tbody>
</table>

A plot of this data reveals the inverse nature of the relationship between the Volume of a gas and its Pressure:

\[ P \sim \frac{1}{V} \]
(A plot of $P$ vs $1/V$ reveals this relationship much more evidently.)

Another way of expressing this relationship is as:

$$P \, V = \text{constant}$$

(Eq. 2)

This, in essence, is the Law of Boyle. Note, the other state variables, temperature and amount of gas, are not allowed to vary. In other words, if either the initial (i) pressure or volume of a gas is changed, the final (f) state of the gas is given by:

$$P_i \, V_f = P_i \, V_i$$

(Eq. 3)

Much later, the French chemist Jacques Charles found that the Volume of a gas was linearly proportional to the temperature of the gas:

$$V = a \, t + b$$

(Eq. 4)

His results were later confirmed and published by Joseph Gay-Lussac in 1802. By 1848, Lord Kelvin noted the temperature scale could be based on an absolute scale $T[K]$ that we now measure in “Kelvins”. Charles’ Law recast in terms of this new temperature scale is then:

$$V \sim T[K]$$

(Eq. 5)

Thus, the Law of Charles gives us:

$$V / T[K] = \text{constant}$$

(Eq. 6)
where the pressure and amount of the gas are held fixed. In other words, if either the initial (i) temperature or volume of a gas is changed, the final (f) state of the gas is given by:

\[
\frac{V_f}{T_f} = \frac{V_i}{T_i}
\]  

(Eq. 7)

When we add the Law of Gay-Lussac (\(P \sim T[K]\)) and the Hypothesis of Avogadro (\(V \sim n\)), we arrive at the State Equation for Ideal Gases:

\[
P V = n R T
\]

(Eq. 8)

where \(R\) is an empirical constant that has the value 0.08206 L atm / K mole.
The Ideal Gas Law works well for predicting the behavior of most Real Gases under normal atmospheric conditions. However, when the pressure is extremely high or the temperature is unusually low, this Law is found to no longer be valid. Under these conditions, gases will no longer behave Ideally. Thus, in the strictest sense, the Ideal Gas Law, including all its historical antecedents, is true only in the limit of zero pressure, where the gas particles are effectively infinitely far apart and do not interact.

$$P = \lim_{P \to 0} \frac{nRT}{V}$$  \hspace{1cm} (Eq. 9)

In this laboratory, we will confirm the Law of Boyle and we will test the predictions made by the Law of Charles.

To confirm the Law of Boyle, we will construct a water manometer.

The height differential in the water levels in the two legs of the manometer will give us the pressure increase over ambient atmospheric pressure on the Air in the manometer bulb.

$$P_{\text{Air}} = P_{\text{Atm}} - P_{\text{H}_2\text{O}} + \Delta h$$  \hspace{1cm} (Eq. 10)

The atmospheric pressure measured in mmHg must be converted to cmH$_2$O. This is accomplished by multiplying the barometric pressure by the ratio in the densities of Mercury to Water:

$$P_{\text{Atm}} [\text{cmH}_2\text{O}] = P_{\text{Atm}} [\text{mmHg}] \times (13.63/1.00) \times 0.1 \text{ [cm/mm]}$$  \hspace{1cm} (Eq. 11)
\[ P_{\text{H}_2\text{O}} \] is the vapor pressure of Water, which must be subtracted from the total if we are to consider our gas simply dry Air.

The volume of the Air upon which this pressure is applied will be the sum of the volumes of the Air in the flask, in the Buret headspace and in the marked portion of the Buret:

\[ V_{\text{Air}} = V_{\text{Flask}} + V_{\text{Head}} + V_{\text{Marked}} \] (Eq. 12)

A plot of \( P_{\text{Air}} \) vs. \( 1/V_{\text{Air}} \) should, in accordance with Boyle’s Law, give us a straight line.

To test the Law of Charles, we will measure the volume occupied by a sample of Air in an Erlenmeyer Flask in a hot water bath (Boiling Water), by simply measuring the volume of the flask. We will then move the flask of Air to a cold water bath (Room Temperature). When we place the flask in the cold bath, we will do so with the flask inverted. This will allow water to flow into the flask as the Air contracts. Knowing the volume of the flask and by measuring the volume of water that flows into the flask, we can determine the volume of the Air in the cold environment. We will then predict, using the Law of Charles, the volume the Air should occupy in the cold environment based on the volume occupied in the hot environment. These two values will then be compared.
Pre-Lab Safety Questions

Another set of general safety questions.

1. Identify one OSHA recommended source for information concerning Chemical Protective Clothing.

2. Provide at least four examples of Chemical Resistant gloves. What type of glove is best when using liquid Benzene?

3. What type of footwear should be used while cleaning up a moderate spill of typical laboratory solvents?
Procedure

Boyle’s Law

1. Construct the water manometer as pictured below.

2. Without the flask in place, add Water to the burets until they are filled to between the 40 and 50 mL mark. Attach the Flask to stopper. The upper part of the stopper should touch the upper lip of the buret. The position of the two Water levels will move slightly. Mark the position of bottom of the stopper on the flask with a wax pencil.

3. Measure the height of the Water in the buret connected to the flask. This will give you $V_{Marked}$.

4. Using a meter stick, measure the height from the top of the lab bench to the Water level in both burets in centimeters. The difference in these heights will give you $\Delta h$.

5. Now add Water to the open buret until the height differential is about 10cm. Repeat the measurements of Steps #3 and #4.

6. Repeat this process until the height differential is about 50 cm.
7. To measure $V_{\text{Head}}$, remove the flask and drain the Water from the apparatus. Measure the height of the headspace with a ruler. Use this height measurement to determine the headspace volume by measuring out this same height from the 0.0 mL mark on the buret and reading the corresponding volume.

8. To measure $V_{\text{Flask}}$, fill the empty flask to the wax pencil mark with Water. Using a graduated cylinder, measure this volume.

9. Measure the atmospheric pressure using the lab’s barometer. Also measure the ambient temperature in the Air.

Charles’ Law

1. Obtain an Erlenmeyer Flask with a one-holed stopper and glass tube through it. Place the flask in a hot water bath according to the figure below. The flask must be completely dry. Mark the lower level of the stopper with a wax pencil.

2. Heat the water in the beaker to boiling and continue heating it for about 10 minutes. Assume that the air in the flask is now at the same temperature as the water. Record this temperature.

3. Place your finger over the end of the tube, remove the flask from the boiling water bath and invert it in a pan of cold water run from the tap. Remove your finger from the tube after the flask is submerged, and keep it submerged for at least 10 minutes.

4. Assume that the air in the flask is now at the same temperature as the water. Record the temperature of the cold water used to cool the flask.
5. Equalize the pressure within the flask with the atmospheric pressure by raising the flask until the water levels inside and outside the flask are the same. **Assume that the air pressure inside the flask is the same as the air pressure in the room.**

6. Place your finger over the tube, remove the flask from the cool water, and set it upright on the desk top.

7. Remove the stopper assembly and, using your graduated cylinder, carefully measure the volume of water in the flask. Record this as the volume change on cooling.

8. Measure the total volume of water in the flask. Record this value, which represents the original volume of hot air.

9. The difference between these volume measurements is the volume of the cooled air.
Data Analysis

Boyle’s Law

1. For each trial, determine $P_{\text{Air}}$ and $V_{\text{Air}}$. A value for $P_{\text{H2O}}$ can be found in the Appendix. Tabulate your results.

2. Plot $P_{\text{Air}}$ vs. $V_{\text{Air}}$. Is the result reasonably linear?

Charles’ Law

1. Calc. the Temp. of Hot Air in Degrees Kelvin:

2. Calc. the Temp. of Cold Air in Degrees Kelvin:

3. Calc. the Vol. of Hot Air:

4. Determine Vol. of Cold Air using:
   
   i) The Measured Data
   
   ii) The Law of Charles:

5. Calculate the Percentage Difference Between the Prediction of the Law of Charles and the Measured Results:

   Hint: Take the Law of Charles results as "True."
Post Lab Questions

1. A 2.90 mL air bubble forms in a deep lake at a depth where the temperature is 8°C at a total pressure of 1.98 atm. The bubble rises to a depth where the temperature and pressure are 15°C and 1.50 atm. Calculate its new volume.

2. One of the following substances is a liquid at Room Temperature and Pressure, whereas all the others are gases. Which is the liquid? Explain your reasoning. Of the gases, which will behave the least ideally? Again, explain your reasoning.

   CH₃OH (Methanol)
   C₃H₈ (Propane)
   N₂
   He
### Appendix - Some Physical Properties of Water

<table>
<thead>
<tr>
<th>Temp [°C]</th>
<th>Vapor Press [mmHg]</th>
<th>Density [g/mL]</th>
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