Introduction

The gas phase is noticeably different from the other two phases of matter. Here are some of the more obvious differences.

- Gases are easy to move a solid object through.
- Gases flow easily (think of the wind)
- You can squeeze a gas into a smaller volume (gases are **compressible**).
- Gases are "light" compared to solids and liquids (gases are not dense)
- You can see through most gases very easily. Many gases are invisible.
- Gases have large volume changes when they're heated or cooled.

We haven't made distinctions in the above list as to the exact gas we're talking about: oxygen gas, hydrogen gas, air, argon gas, water vapor, etc. We don't need to make the distinction because most gases have very similar properties. The chemical reactivity of different gases may be different, but their physical properties are very similar. These properties are so similar that scientists as far back as the 1600s were observing **and predicting** gas behavior. These scientists discovered that simple relationships existed between the **pressure**, **volume**, and **temperature** of gases.

The three properties: pressure, volume, and temperature

Before we discuss the relationships between the pressure, volume, and temperature of gases, we should briefly discuss the properties themselves.

1. **Pressure** is simple defined as the **force per unit area**. When you listen to the weather report, you might hear something like "Barometric pressure is 760 millimeters of mercury and falling." (*The more common unit in the U.S.A. is inches of mercury, but inches are easily related to millimeters – there are 25.4 mm for each inch.*) The weatherman is reporting the pressure of the atmosphere - literally, how hard the atmosphere pushes down on the earth - using an instrument called a **barometer**.

To make a barometer, invert a tube of a fluid into a dish of the same fluid, as shown in Illustration 1.

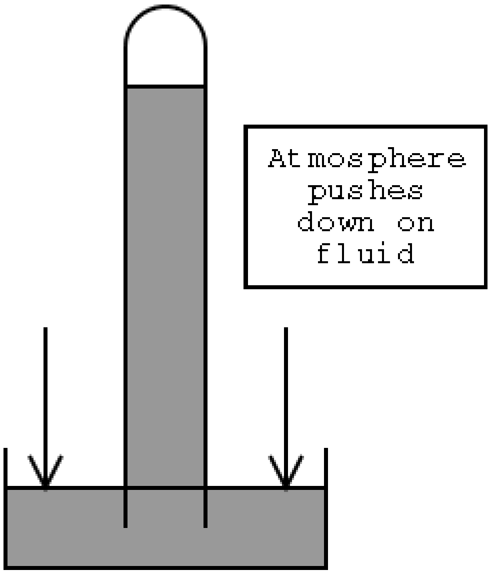

Illustration 1 - A simple barometer

- The traditional barometer contained mercury, and was invented by Torricelli in the year 1643.
- What does the empty space in the barometer contain? Nothing except a little bit of mercury vapor.
- Air pressure helps to hold the mercury in the tube against the pull of gravity.

Atmospheric pressure presses down on the open fluid and holds the column of fluid in the tube. The height of the fluid in the tube relates to the pressure of the atmosphere. The fluid inside a barometer is typically mercury, because it is very dense. You could make a water barometer, but you'd need a tube that is **34 feet high** to measure atmospheric pressure! You only need a column about two and a half feet tall with mercury.

Common units of pressure are the **mm Hg** (millimeter of mercury), the **atm** (atmosphere), and the **Pa** (Pascal, the SI unit of pressure = $kg / m \cdot s^2$). Conversion factors between these are listed below:

$$1 \text{ atm} = 760 \text{ mm Hg} = 101325 \text{ Pa}$$

You will use **atmospheres** in most of your calculations.

2. **Volume** has been discussed previously in this class. For gases, the most common volume unit you will encounter is the **liter (L)**. You should already be familiar with how to convert volumes between liters and other SI units. Just for review, the conversion factors are listed below:

$$1 \text{ mL} = 1 \text{ cm}^3$$
$$1 \text{ L} = 1 \text{ dm}^3$$
$$1 \text{ mL} = 10^{-3} \text{ L}$$

3. **Temperature** is a property you're familiar with. Although the traditional unit of temperature in the U.S.A. is Fahrenheit, in the sciences it is more common to use the **Celsius scale**. For gases in particular, it is necessary to use the **Kelvin scale**. The Kelvin scale is an **absolute** temperature scale. That is, it's zero point is set at the theoretical coldest temperature possible. All the gas laws we will present are good for

absolute temperatures only, so always convert your temperatures to Kelvin when dealing with gases! How? The conversion from Celsius to Kelvin is below:

Kelvin temperature = Celsius temperature + 273.15
Example: 25.00 ºC = 298.15 K

The empirical gas laws

The **empirical** gas laws are the observations and predictions about gas behavior mentioned in the introduction to this note pack. The word **empirical** means "based on observation", and these laws were discovered by experimentation. These laws describe the behavior of gases, but do not attempt to explain why gases behave the way they do.

Boyle's Law

The first of the empirical gas laws to be discovered was **Boyle's Law** (1661). Boyle's Law relates the pressure of a gas to its volume. A Boyle's Law experiment is rather simple, and can be performed with a syringe and some weights.

Experiment: Investigate the relationship of gas volume to pressure using a syringe and weights.

	• The syringe is plugged so that air is unable to escape while weights are being piled on. • The platform makes it easier to balance the weights on top of the syringe. • Adding weights to the syringe increases the pressure.
Illustration 2 - Boyle's Law experimental setup	

In this experiment, weights are stacked on the platform on top of the syringe and the gas volume inside the syringe is measured using the syringe's scale. The additional pressure placed on the syringe can be calculated by adding atmospheric pressure to the force per unit area the weight and platform puts on the syringe. The platform weighs 173g, and each weight weighs 500g.

The equations used to calculate the pressure come mostly from physics. First. we find out how much force is exerted by the weights on the syringe.

$$\text{Force} = \text{mass} \times \text{acceleration}$$

Since the weights and platform are being acted on by gravity, the acceleration is 9.8 m/s^2. Pressure is defined as force per unit area. The inside of the syringe is cylindrical, so the area is the area of a circle. We can find the area of the circle using

$$\text{Area} = \pi r^2$$

The diameter of the syringe used in this experiment is 2.54 cm (0.0254 m). The total pressure on the gas is found by adding the pressure from the weights to atmospheric pressure.

$$\text{Total pressure} = \frac{\text{force}}{\text{area}} + \text{Atmospheric pressure}$$

Here is a chart containing data for this experiment along with the calculations mentioned above. The pressure is reported in Pascals.

Weight on syringe (g)	**Pressure on syringe (Pa)**	**Volume of gas (mL)**
173	104431	50.0
673	114106	47.0
1173	123781	43.0
1673	133456	40.0
2173	143131	37.5

Plotting 1/volume versus pressure gives us a straight line.

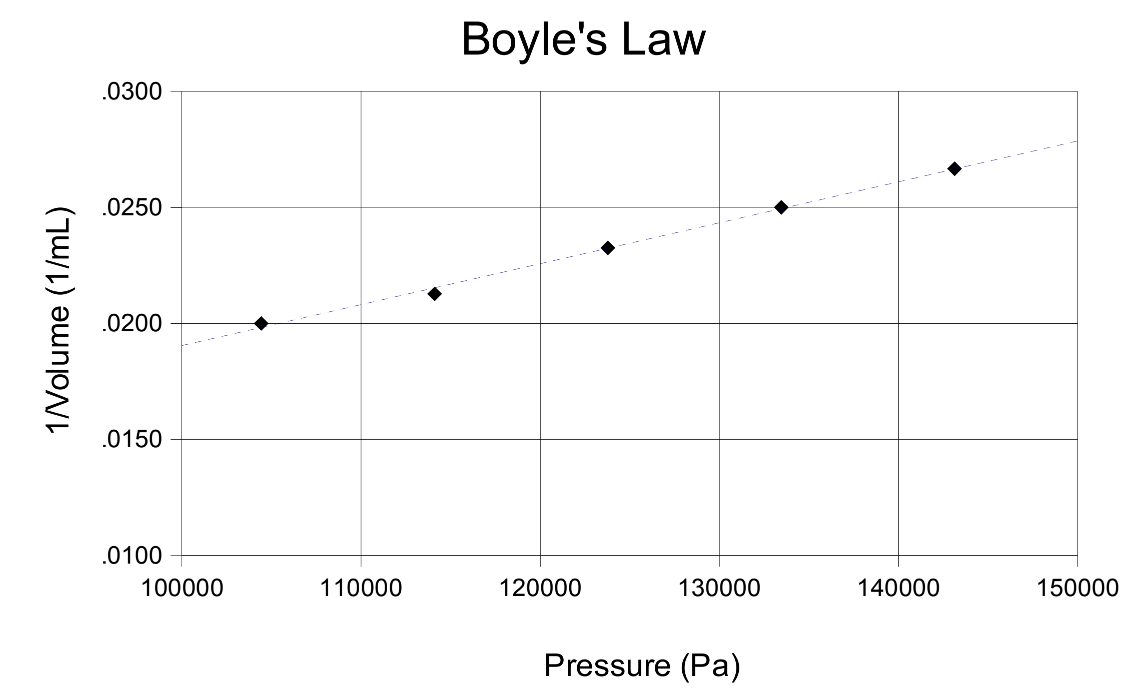

Illustration 3 - Plot of 1/volume vs. pressure

There is a linear relationship between the pressure and 1/volume. As pressure increases, 1/volume increases linearly. Multiply the pressure times the volume for each data point.

Pressure (Pa)	Volume (mL)	PV (Pa-mL)
104431	50.0	5.222×10^6
114106	47.0	5.363×10^6
123781	43.0	5.323×10^6
133456	40.0	5.338×10^6
143131	37.5	5.367×10^6

Within experimental error, we find that pressure times volume equals a constant number.

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

This is Boyle's Law.

The overall conclusion we reach is that the volume of a gas varies inversely with pressure. In plain English, if you **increase the pressure** of the gas, **the volume decreases**.

You can write Boyle's Law in a way that relates the pressure and volume of a gas at one set of conditions to the pressure and volume of a gas at another. This is the most useful form of Boyle's Law.

$$P_1V_1 = P_2V_2$$

... where "1" and "2" essentially mean "before" and "after". Let's work an example problem illustrating Boyle's Law.

How much pressure would 75 L of air at room temperature (25°C) and atmospheric pressure (1.0 atm) exert if it was put in a 4.0 L vessel? Assume the temperature remains constant.

This is a straight application of Boyle's Law. You can tell because the problem deals with a **volume change at constant temperature** and asks you for the new pressure.

$$P_1V_1 = P_2V_2$$

$P_1 = 1.0$ atm	$P_2 = ???$ (we want to find P_2)
$V_1 = 75$ L	$V_2 = 4.0$ L

Now, just plug in and solve. The units work out correctly - you will get the pressure in units of **atm**ospheres.

$$(1.0\,\text{atm}) \times (75\,\text{L}) = P_2 \times (4.0\,\text{L})$$

P_2 = 19 atm pressure exerted on the 4.0 L vessel

Boyle's Law is a simple and easy-to-apply relationship between the pressure and volume of a gas.

<u>Charles's Law</u>

The next empirical gas law to be discovered was **Charles's Law**, which was put into its modern form in the early 1800s. Charles's Law relates the volume of a gas to its temperature.

A Charles's Law experiment looks simple by modern standards (but remember, we're talking about the early 1800s) and involves heating or cooling a gas uniformly and observing the volume change at constant pressure.

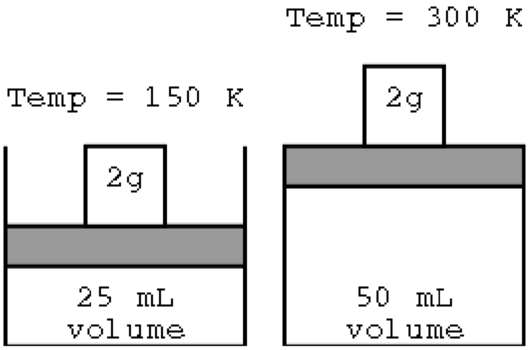

Illustration 2 - A Charles's Law experiment

- Charles's Law was discovered over a period of time - the experiments got better and better over a number of years.
- This relationship is hard to see if you don't use an absolute temperature scale.

150 Kelvin is about -123 °C, and 300 Kelvin is about 27 °C. The gas in each case is being pressed down by a 2 g weight (so the pressure is constant) . As the absolute temperature is doubled, the volume of the gas doubles. Other experiments have produced similar results.

The conclusion we can draw in this case is that volume relates directly to temperature. In plain English, if you **increase the temperature** of a gas, the **volume increases proportionally**.

Mathematically, you can write this as:

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

... where "1" and "2" are defined as before. Let's work an example problem illustrating Charles's Law.

How much would a 1.00 L balloon shrink if cooled from 25.0 °C to -72.0 °C at constant pressure?

This is a straight application of Charles's Law. You can tell because the problem deals with a **temperature change at constant pressure** and asks you for the new volume.

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

V_1 = 1.00 L
T_1 = 298.2 K

V_2 = ??? (we want to find V_2)
T_2 = 201.2 K

Now, just plug in and solve. The units work out correctly - you will get the volume in units of **liters**.

$$\frac{(1.00\,\mathrm{L})}{(298.2\,\mathrm{K})}=\frac{V_2}{(201.2\,\mathrm{K})}$$

V_2 = **0.675 L**

So the balloon shrinks from 1.00L to 0.675 L (it's only 2/3 as big)! We used Kelvins for temperature in the calculation. Charles's Law is based on **absolute temperatures only** and to use it you must **convert the temperature to an absolute scale**.

Aside from the wrinkle that you must convert your temperatures to Kelvin units, Charles's law is as simple to use to predict gas properties as Boyle's Law!

<u>The combined gas law</u>

You can think of Charles's Law and Boyle's Law as peanut butter and chocolate - two great tastes that go great together. In fact, we can combine these two laws and get the Reese's Peanut Butter Cup of gas laws - the combined gas law.

$$\frac{P_1 \times V_1}{T_1}=\frac{P_2 \times V_2}{T_2}$$

So if we know the **initial state** of the gas (pressure, volume, temperature), we can find out what happens to the gas if we change any two of the variables. As an example, let's modify the problem we used as our Boyle's Law example. We know that we might make it easier to stuff 75 L of air into a 4 L space if we lower the temperature. Let's find out how much easier.

75.0 L of air at 25.0 ^{o}C and 1.00 atm is put into a cooled 4.00 L vessel at -10.0 ^{o}C. Find the pressure inside the vessel.

Use the combined gas law. We're varying both volume **and** temperature!

$$\frac{P_1 \times V_1}{T_1}=\frac{P_2 \times V_2}{T_2}$$

P_1 = 1.00 atm	P_2 = ??? (we want to find P_2)
T_1 = 298.2 K	T_2 = 263.2 K
V_1 = 75.0 L	V_2 = 4.00 L

Plug in and solve.

$$\frac{(1.00\,\text{atm})\times(75.0\,\text{L})}{(298.2\,\text{K})}=\frac{P_2\times(4.00\,\text{L})}{(263.2\,\text{K})}$$

P_2 = 16.5 atm pressure inside the vessel. Compare to 19 atm at room temperature!

Helpful hint: You don't have to remember three equations. Just remember the combined gas law! To get Boyle's Law out of the combined gas law, drop the temperatures out. To get Charles's Law out of the combined gas law, drop the pressures.

At this point, we're state-of-the-art as of the 1800s. We can relate three important properties of any gas using simple relations. Next, we will discuss more modern observations and give a theoretical explanation of the gas laws.

Summary

In this note pack, we have discussed several important gas properties - pressure, volume, and temperature. We have seen how each of these are measured. We have also talked about experiments that show relationships between these properties. Taken together, these relationships are called the empirical gas laws and can relate a gas at any one set of conditions to the same gas at a different set of conditions. You should be able to use the combined gas law to calculate what happens to one property of a gas when one or more of its other properties changes.