

Ideal Gas Laws and the Absolute Zero of Temperature (approx. 2 h 15 min.)(6/20/12)

Introduction

The ideal gas law, $PV = nRT$, is a useful formula that was discovered by experimental observation. In SI units P stands for pressure in N/m^2 (i.e. Pascals); V is for volume in cubic meters; n is the number of moles; $R = 8.314 \text{ J/mol-K}$ is the universal gas constant; and T is the absolute temperature in Kelvins. This law has been tested on numerous gases and shows remarkable agreement with experiment over a large range of pressures, volumes and temperatures when the number of moles per unit volume is not too high.

Equipment

One each for each of six constant-temperature stations:

- Boyle's Law unit
- 2000 ml beaker
- metal sphere
- thermometer
- pitcher for water

For specific temperature stations: a bucket of crushed ice; 1 liter room temp. water; 4 large hotplates

For Whole Class: eye protection; rulers; grid paper; gloves; stopcock lubricant (one tube for class)

Setup: Six teams should fill six 2000 ml beakers halfway with water and maintain their respective temperatures at: 0°C (mixture of ice and water in equilibrium); room temperature; 40°C ; 58°C ; 77°C ; and 95°C . (*Note for instructor: Crushed ice is available in room 207 (door combination: 0812).*) Consult your instructor or the other lab groups before selecting your temperature. Begin heating as soon as possible, since reaching the higher temperatures may be time consuming.

Some Historical Background

In 1643 the Italian physicist Evangelista Torricelli developed a barometer which enabled him to determine that the pressure exerted by Earth's atmosphere was equal to the pressure at the bottom of a column of mercury 76 cm high (with near vacuum above it). Pressure measurements referenced to vacuum pressure as zero are called absolute pressures, as it is not possible to attain lower pressure than that of a perfect vacuum.

Boyle's Law

In 1662 Robert Boyle experimentally confirmed and published what is known as Boyle's Law: For a fixed amount of gas, kept at a fixed temperature, absolute pressure and volume are inversely proportional (i.e. doubling one halves the other).

Amontons' Law

Although Galileo and others are credited with inventing the first air thermometers around 1592, it was not until 1702 that Guillaume Amontons devised a method to measure temperature in terms of proportional change in the absolute pressure of an enclosed fixed volume of air. In effect, Amontons proposed that temperature, for a fixed amount of air in a fixed volume, was directly proportional to absolute pressure (Amontons' law). This suggested that Boyle's law could be generalized to state that, for a fixed amount of gas, pressure is inversely proportional to volume and directly proportional to temperature, or: $PV = (\text{a constant})T$. But no standard temperature scale had yet been generally accepted, and Amontons' work remained obscure. (Note that this was long before Charles's Law was discovered in 1787.) It wasn't until 1742 that Celsius proposed a temperature scale based on dividing the temperature difference between the freezing and boiling temperatures of pure water into 100 equal intervals called *degrees* that the basis for today's universally accepted Celsius temperature scale was established.

Avogadro's Law

In 1811 Amedeo Avogadro hypothesized that two given samples of an ideal gas, of the same volume and at the same temperature and pressure, contain the same number of molecules. In other words, for a fixed temperature and pressure, the number of molecules is directly proportional to the volume. This along with the later development of the kinetic theory of gases set the stage for the acceptance of the equation of state of an ideal gas in its present day form: $PV = nRT$.

Notes on the operation of the Boyle's Law unit:

The pressure gauge employs a Bourdon tube, a circular, sealed-end tube having an oval cross section that tends to "uncurl" when the internal pressure exceeds the external pressure. To operate the "quick disconnect" fitting, slide the brass sleeve at the base of the pressure gauge about 3 mm toward the body of the gauge. Connect the tubing from the syringe by inserting the male fitting and releasing the sleeve. Vary the pressure by moving the plunger in the syringe. Observe the movement of the tube, linkage and pointer thru the transparent casing.

The gauge graduations are in pounds per square inch (psi) $1 \text{ psi} = 6895 \text{ Pa}$. The absolute pressure of the atmosphere at sea level is normally about 14.7 psia (= 76 cm Hg). (Absolute pressure is sometimes expressed in "psia", as opposed to pressure measured by a gauge set to read zero when at atmospheric pressure, such as the gauge on a tire pump, which measures "gauge pressure" in "psig".) If your gauge does not read 14.7 when open to atmospheric pressure, you must correct all of your readings by either adding or subtracting the difference between your reading for atmospheric pressure and 14.7. (If your gauge is grossly in error, bring it to the attention of your instructor. It may be preferable to replace it with a more accurate one.)

When making measurements, wait about 30 seconds after setting the desired volume before reading the pressure. Usually a slight drop in pressure will be noted after a compression. This results from the gas returning to room temperature after the slight temperature increase due to the compression. (Likewise, an expansion will cause a slight temperature decrease.)

Before making each reading, tap the fitting at the base of the gauge with a pencil to overcome static friction effects in the gauge gear and linkage system. Make sure the pressure has stabilized.

If the pointer in the gauge starts to drift when the volume is held constant, the gas may be leaking around the syringe plunger O-ring. You may coat it lightly with stopcock lubricant to prevent leakage. If the tubing is leaking near the connection you may need to push it on tighter.

Confirming Boyle's Law

Boyle's law was discovered long before the ideal gas law and is a special case of it. In modern terms, it states that the product of pressure and volume, PV , remains constant for a fixed number of moles of an ideal gas kept at a constant temperature.

Procedure:

In Boyle's law the volume V is the total volume occupied by the gas, thus $V = V_s + V_o$ where V_s is the volume of the syringe and V_o is the volume inside the gauge, tubing and fittings.

To obtain V_o , first disconnect the tubing at the gauge and set the plunger at the 0-cc mark on the syringe. Reconnect the tubing and record the pressure reading.

Pull the plunger in the syringe until the pressure reading is 1/2 of the original reading. According to Boyle's Law, the total volume at this pressure should be twice V_o . Therefore,

$V_s = V_o = \underline{\hspace{2cm}}$ cc. Note that this value for V_o must be added to the volume of the syringe at all pressure settings.

Disconnect the syringe from the gauge; set the plunger at 15 cc and reconnect. Move the plunger in increments of 5 cc to each value above and below 15 cc. At each value (after reaching equilibrium) record pressure and volume (below). Repeat this three times and take averages.

$V = V_S + V_O$	$1/V$	P_1	P_2	P_3	P_{AVE}

Plot P vs. 1/V and analyze the graph.

To what extent is it consistent with Boyle's law? (i.e. is the graph a straight line through the origin?)

Determining the Absolute Zero of Temperature

We can neither get to zero pressure nor to very low temperatures in this lab, but we can extrapolate our results to those values and get a decent estimate of the absolute zero of temperature.

The ideal gas law, with temperature, T_C , in degrees Celsius, is

$PV = nR(T_C + T_0)$, where T_0 is the absolute temperature, in K, at 0 °C. Thus, for a constant number of moles, n, and a constant volume, V, of gas, the temperature is linearly related to the pressure:

$T_C = m P - T_0$, where the slope of the graph is: slope $\equiv m = V / nR$.

Procedure:

Connect the tubing from the metal sphere to the pressure gauge.

IMPORTANT: Do not allow the plastic tubing to kink or to come in contact with the heat source.

The six 2000-ml beakers should each be about 1/2 full with water and at different temperatures. One should contain a mixture of ice and water in equilibrium at 0 °C. A second beaker should have water at room temperature. The remaining 4 beakers should be at nominal temperatures of 40, 58, 77 and 95 °C.

Starting from the lowest temperature beaker, completely immerse the sphere in the water/ice mixture and record the (corrected) pressure and temperature (below) once the sphere is in equilibrium with the water. ALLOW AT LEAST 3 MINUTES TO REACH THERMAL EQUILIBRIUM.

Proceed to the higher temperature beakers and record the equilibrium pressures and temperatures. USE CAUTION WHEN WORKING WITH HOT WATER. EYE PROTECTION AND GLOVES ARE AVAILABLE AND RECOMMENDED FOR YOUR PROTECTION.

T_C						
P						

Plot T_C vs. P and analyze the graph.

Using Excel or Data Studio (or grid paper, if necessary) to plot temperature vs. pressure, find the equation of the line for your data.

Linear equation of graph (show units): _____

From the equation of the line determine the absolute zero of temperature in $^{\circ}\text{C}$ (i.e. the temperature, in Celsius, at which $P = 0$). A good result would be within 5% of the accepted value of -273°C .

Absolute zero temperature on Celsius scale: $T_C = \text{_____}^{\circ}\text{C}$

Calculate the % difference between your result and the accepted value of -273°C :

_____ = _____ %.

Discuss how your graph can be used to determine an absolute temperature scale with the unit of temperature being numerically equal to a Celsius degree.

From your analysis, determine the absolute (i.e. Kelvin) temperature at 0°C .

T (on the Kelvin scale) at $0^{\circ}\text{C} = \text{_____}\text{K}$

Going Further:

Using the slope from the equation for your graph of T_C vs. P, calculate the “molar density”, n/V , of

the gas used in your metal sphere in moles per cubic meter: $n/V = \text{_____} = \text{_____} = \text{_____}$.
(Hint: You will have to convert to SI units.)

THINKING ABOUT IT:

In reality, at atmospheric pressure, all gases become liquids before reaching absolute zero temperature, and thus no longer obey the ideal gas law. What numerical value, provided near the beginning of the lab, was essential to know in order to assure that the temperature extrapolated to zero pressure from your gauge readings should be the absolute zero of the temperature used in the ideal gas equation of state? _____ Why was it necessary to know this value?

In order for a real gas to accurately follow the ideal gas law at low temperatures, interactions between its molecules must be insignificant. Assuming its molecules do not stick to its container's walls, describe a physical process that could plausibly be performed with a fixed number of moles of a real gas to bring its temperature close to the absolute zero of temperature.