Gas Law and Absolute Zero

Equipment safety goggles, Capstone, gas bulb with pressure gauge, $-10°C$ to $+110°C$ thermometer, $-100°C$ to $+50°C$ thermometer, protective gloves

Caution This experiment deals with materials that are very hot and very cold. Exercise care when handling these materials. Do not let them get in contact with your skin or clothes. Wear safety goggles to protect your eyes from splashes.

1 Purpose

To investigate how the pressure of a given quantity of gas in a fixed volume varies with the temperature. The relationship between pressure and temperature, which is approximately linear for low number densities and temperatures somewhat above liquefaction, is extrapolated to zero pressure. The temperature at which zero pressure occurs is absolute zero.

2 Description

See Fig. 1. A steel bulb is filled with air at ambient air pressure. The bulb is fitted with a pressure gauge that gives the absolute pressure inside the bulb in Kpa and lb/in^2. When the valve is opened, the pressure gauge gives the nominal outside air pressure, about $100Kpa$ or 15 lb/in^2. With the valve closed the bulb will be inserted into 4 liquids of different temperatures.

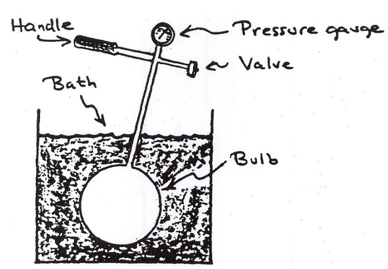


Figure 1: Fixed voloume of gas in a constant temperature bath.

For each liquid, the temperature and pressure are measured. You can obtain 5 pairs of pressure and temperature measurements. These measurements are plotted on a graph and the best straight line will be drawn. The straight line is extrapolated to zero pressure. The temperature at that point is determined and is the experimental absolute zero value.

3 Theory

In an ideal gas, the molecules are so small that they can be considered as point masses. For simplicity, we let the term molecules also include atoms. It is assumed that there are no forces between the molecules and that the energy of the gas is entirely the kinetic energy of the molecules since they are in constant motion. As they bounce off the walls of the container, they exert an outward pressure (a force per unit area). On a very short time scale the pressure fluctuates a great deal, but on a longer time scale the pressure fluctuations will average out. The average kinetic energy of the molecules increases with the temperature because the higher the temperature the faster the molecules move. The faster the molecules move, the harder they'll hit the walls, thus increasing the pressure they exert. It is found that the pressure p and Temperature (centigrade) T_C obey a linear relationship. The relationship can be written as the following, where m and b are constants

$$p = mT_C + b, \tag{1}$$

No gas is strictly ideal and there will be deviations from Eq.(1), particularly as the gas becomes more dense and/or the temperature is decreased. As the temperature decreases most gases will eventually become liquid and Eq.(1) is not valid. If data is in the range where Eq.(1) is valid, then Eq.(1) can be extrapolated to $p = 0$. The very low temperature at which this occurs is independent of the gas used and is termed **absolute zero**. According to Eq.(1) absolute zero occurs at the centigrade temperature $T_C = -\frac{b}{m} = -273.15$. There is no temperature colder than absolute zero! For a dilute gas at high enough temperatures however, Eq.(1) is a good approximation. If the kelvin temperature T is defined as $T = T_C + \frac{b}{m}$, Eq.(1) can be written as

$$p = mT. \tag{2}$$

What should the "constant" **m** be? Is it a constant for all situations? The following is a rough derivation. Let the number of gas molecules per unit volume be the number density n_N. The number of molecules striking per unit area of the container wall per unit time is $n_N v$, where v is a suitable average speed of the molecules. The momentum carried by each molecule is proportional to Mv, where M is the mass of the molecule. The momentum of the molecules carried toward the wall per unit area per unit time is proportional to $n_N M v^2$. The momentum carried away from the wall per unit area per unit time the is same value. The wall exerts a force to change v to $-v$, so $\Delta p = mv - (-mv) = 2mv$. The net momentum transferred to the wall per unit area per unit time will be proportional to $2n_N M v^2$, and according to Newton's 2nd law, is proportional to the pressure. But Mv^2 is proportional to the kinetic energy which in turn, according to kinetic theory, is proportional to the Kelvin temperature. Then we must have that the pressure is proportional to the product of the n_N and T, or

$$p = n_N kT, \tag{3}$$

where k is the proportionality constant and is called Boltzmann's constant. The Boltzmann's constant is equal to universal gas constant divided by Avogadro's number ($k = R/N_A$). For Eq.(3) to be written in this simple form without an additive constant on the right hand side, the temperature must be in kelvin. Note that one degree kelvin is equal to one degree centigrade. Let the volume of the gas be V and Avogadro's number be N_A. If both the numerator and denominator of the right hand side of Eq.(3) are multiplied by V and N_A, this equation can be written

$$PV = nRT, \tag{4}$$

where n is the number of moles of the gas and $N_A k = R = 8.31\ J/mole/K$ is the universal gas constant. It is customary to write K for degrees kelvin rather than $°K$ or $deg\ K$. Will equation (4) work well for gases that have densities? Explain.

4 Experiment

Wear safety goggles to protect your eyes from splashes.

1. Begin by depressing the pin inside the end of the valve attached to the bulb. This connects the bulb to the room air and sets the bulb pressure at one atmosphere. Do not open the valve again. Record the value indicated by the pressure gauge in units of $Kpaorlb/in^2$, tapping the gauge gently with a fingernail to be sure that the needle is not sticking (a good procedure with any mechanical gauge). Record also the temperature in the room using the $-10°C$ to $+110°C$ thermometer. Be careful that your hand does not warm the bulb above room temperature.

2. First immerse the bulb in boiling water. Use the $-10°C$ to $+110°C$ thermometer to measure the temperature of the water. Do not let the thermometer touch the bottom or sides of the boiling water container, where the temperature may differ from that of the water. When equilibrium in the bulb is reached (the pressure reading becomes constant), record the pressure and the temperature. Remove the bulb from the steam bath and allow it to reach room temperature. Check to see that the pressure reading is the same as it was before subjecting the gas to the boiling water. If it is significantly different you may have a leak.

3. Immerse the bulb in a water-ice mixture. Using the same procedures as before, measure the pressure and temperature using the same thermometer.

4. **Note: In this part of the experiment, *do not use the same thermometer. You will break it!*** Use the $-100°C$ to $+50°C$ thermometer. Immerse the bulb and a suitable thermometer in alcohol. At first cool the alcohol by adding small chips of solid carbon dioxide. Do not touch the chips with unprotected fingers! As the temperature drops and the boiling alcohol becomes less violent add larger pieces of the carbon dioxide. It should be possible to lower the temperature to about $-72°C$. Record the pressure and temperature as before.

5. For the last part of the experiment, ***do not insert any thermometer as it will break.*** Immerse the bulb in liquid nitrogen. Do this slowly to minimize violent boiling. Take care not to touch the liquid nitrogen or to be splashed by it. Assume the temperature is $-196°C$. Allow the gas in the bulb to reach equilibrium and record the pressure.

6. When the bulb returns to room temperature check to see if it returns to about its original pressure.

7. Repeat the previous steps in reverse order.

5 Data Analysis

Analyze your data by plotting it on a Capstone graph display and fitting a straight line to the data points. This is a least squares fit. As the horizontal axis of the graph display will not accept negative numbers, it is necessary to rewrite Eq.(1) as

$$T = \frac{1}{m}p - \frac{b}{m}. \tag{5}$$

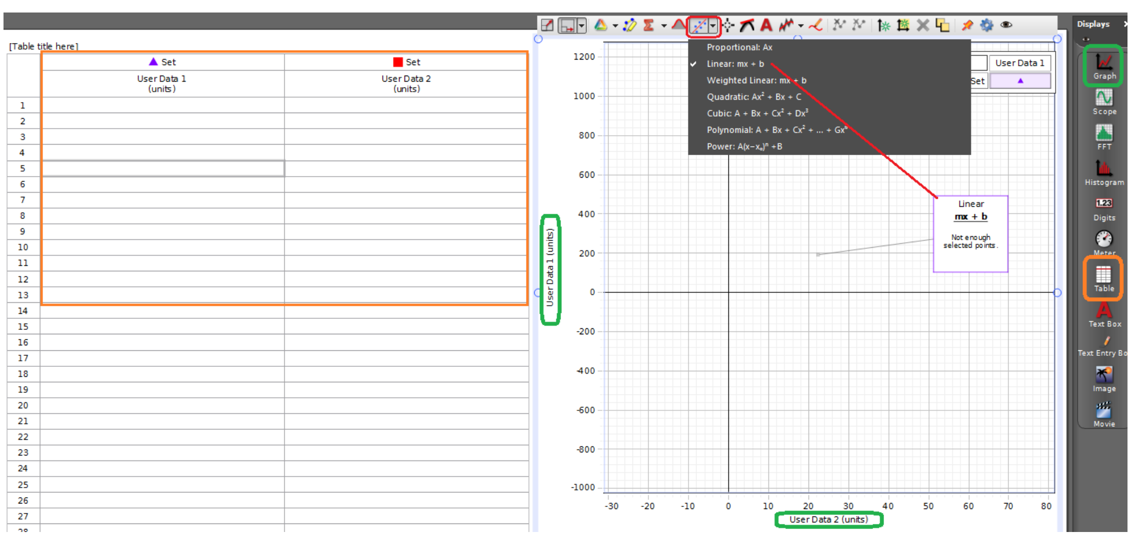
The temperature T will be plotted on the vertical axis and the pressure p on the horizontal axis. The slope of the line is $\frac{1}{m}$ and the vertical axis intercept (when $p = 0$) is $-\frac{b}{m}$, which is the value of absolute zero. To plot your data and find the slope and vertical axis intercept You're required to.

1. Open New Empty Data Table by selecting it from the Displays column on the right side of Capstone.

2. Enter your 5 pairs of data points in the table columns.

3. Drag the Graph icon from the Displays column to the Capstone white screen. Click on select measurements of both axis of the graph and select user data that corresponds to temperature for the vertical axis. Next, select user data that corresponds to pressure for the horizontal axis.

4. Use the illustration below as a guidance to setup the software.



5. At the top of the graph window there is a Curve Fit button, click it and then choose linear. The least squares straight line fit will appear through your data points. Print out the required number of graphs.

6. Obtain values for m and b. In doing so, give units. Consider the following questions.
   - What are the dimensions of temperature?
   - List all the units of temperature.
   - What are the dimensions of m and b?
   - What units of m and b are you using? Hint: They are not the same.
   - What does the slope corresponds to in the graph?

6 Results

Discuss your results. Suggestions.

- Does your data fit a straight line? Explain.
- What is your value for absolute zero in degrees centigrade ($-\frac{b}{m}$)? Do the units make sense?
- Since Boltzmann's constant $k = 1.38 \times 10^{-23}\ J/K$, what is n_N for your experiment? Hint: k is given in S.I. units. Express m in S.I. units, and calculate the density in molecules per cubic meter.
- The diameter of the bulb is about 10 cm. Neglecting the wall thickness of the bulb, and the volume of the connecting tubing and pressure gauge, about how many moles of air are you working with?
- One of the assumptions in your data analysis is that the density of the air in the bulb stays constant. How many reasons can you think of for this not to be so? What errors can occur if the air in the bulb is not constant?

Exercise. Work out and obtain Eq.(4) from Eq.(3).

7 Comment

You might think that at zero degrees Kelvin, atomic and molecular motion will cease. This is not the case. There is still a little bit of motion to these particles at absolute zero which is called zero point energy.

8 Finishing Up

Wipe off any spills. Be considerate for your fellow mates. Leave your bench as your found it. Take care.