Critical Point Behavior of Gases

Introduction

The ideal gas law \((PV = nRT)\) predicts that the pressure is inversely proportional to the volume for any isotherm, and a graph of \(PV\) data would look like this.

![Ideal Gas Law Graph]

The ideal gas law works well for low pressures and low concentration of gas. As volume is compressed and pressure increased, the gas will begin to deviate from ideal behavior. One way to model this deviation is through the use of the van der Waal gas equation.

\[
\left( P + \frac{a}{V_m^2} \right) (V_m - b) = RT \quad \text{with } V_m = \text{molar volume} = \frac{V}{n}
\]  

(1)

or rearranged,

\[
P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}
\]

(2)

\((a/V_m^2)\) can be interpreted as an internal pressure due to intermolecular attractive forces. Those forces act to retard collisions with the wall of the container.

\(b\) is usually interpreted as the effective volume occupied by gas molecules. This co-volume reduces the free volume available for the kinetic motion of the gas.

Liquefaction and Critical Point Behavior

According to the ideal gas law, a gas can be compressed indefinitely without changing physical state irrespective of the temperature. This, of course, is false; gases liquefy when compressed if the temperature is low enough.

The liquefaction is an effect of the intermolecular forces in the gas, and the stronger the forces, the easier it is to liquefy the gas.

Liquefaction can only occur when the gas is below a particular temperature called the critical temperature. During liquefaction, the volume no longer changes with pressure as
predicted by the ideal gas law; instead, the volume remains constant once the Gas/Liquid transition is reached.

For the figure below, gases beginning at Point A can be increased in pressure (decreased in volume) at constant temperature until they hit the Gas/Liquid transition for the temperature in question. Prior to getting to the transition, one will see the normal inverse gas law behavior between pressure and volume. Once the liquid transition is reached, however, continued decrease in volume will only result in a flat pressure response as more and more gas is compressed into a liquid.

By contrast, a gas beginning at point C (above the critical temperature) will never see a liquid/gas transition since the distinction between gas and liquid is lost above the critical point.

Point B corresponds to a system at the critical transition temperature.

The critical point parameters can be related back to the van der Waal coefficients. [Atkins]

\[ V_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb} \] (3)

Using the critical point parameters for SF\(_6\) [NIST] gives the following van der Waal coefficients

\[ T_c = 318.71\text{K} \ (45.56\degree\text{C}) \quad P_c = 37.586\ \text{bar} \ (37.586 \times 10^5\ \text{Pa}) \] (4)

\[ a = 7.882\ \text{bar}\cdot\text{L}^2 \quad b = 0.08813\ \text{L} \] (5)
**Experimental**

We have a high-pressure apparatus in the lab that you will use to measure the isotherms above and below the critical temperature. The apparatus consists of a gas chamber whose volume can be adjusted and resultant pressure measured. The equipment is rated to take pressures in excess of 50bar, allowing for the observation of significant deviations from ideal gas behavior. The chamber is immersed in water and the temperature of the water is set using a thermostated bath.

*The apparatus is potentially dangerous. Do not attempt any manipulations until the instructor tells you.*

The gas we will use is SF$_6$. It is non-toxic, but has a greenhouse gas effect that is 24,000 times greater than CO$_2$, so should be treated with care.

**Set-Up**

1. Insure that thermostat water flow is turned on. (Start with temperature at 25°C.)
2. With the flush valve Open, use the large handwheel, set the piston vernier to a setting of 10mm. This setting refers to the length of the piston chamber. The volume of the chamber is obtained by multiplying the length times the area.
   \[
   \text{Volume} = 3.14 \text{cm}^2 \times \text{length in mm}
   \]
3. Close the flush valve.
4. With the SF$_6$ gas bottle in place, slowly open the regulating valve and allow enough gas into the system to reach a pressure of 5 bar.
5. Close the regulating valve.
6. Open the flush valve to allow the SF$_6$ to escape.
7. Repeat steps #2-5 two more times (for a total of 3 flushes of the system).
8. Add 5-10 bar of gas (use maximum achievable amount within this range) while the piston is set at 10mm. Close the regulating valve, then use the handwheel to set the piston to 48mm. Add more gas to reset the pressure to 5-10 bar.

**Data Collection**

9. Before proceeding, take 3 readings of the volume, pressure and temperature for the gas under these starting conditions – moving the vernier away and then resetting it to 46mm each time. Use the data and the ideal gas law to calculate the number of moles of gas present in the chamber. You will only do this at 25°C.
10. Slowly use the hand wheel to decrease the volume of the gas chamber in increments of 2mm, changing to increments of 1mm below 10mm. The pressure of the gas should begin to increase. Continue until you reach 2mm – **BUT STOP IF YOU REACH A PRESSURE $\geq$ 50bar**.
11. Measure the pressure and volume at each point, waiting to make sure the system has reached equilibrium before reading the pressure. Always be consistent about approaching the volume measurement from the same direction (e.g. from high to low).

When done with room temperature, reset the piston to 46mm and change the temperature on the bath. Once the new thermal equilibrium is reached, repeat steps #10-12. You will work at these approximate temperatures (all in °C): 25, 35, 42, and 55.
Discussion

The pressure gauge measures the difference (or “excess”) between the chamber and the ambient room air pressure. You must therefore add the current room air pressure in the room to the value of pressure on the gauge to get the total pressure inside the cylinder.

Use your initial room temperature data and the ideal gas law to calculate the number of moles of the gas.

Overlay all of your data for the 4 temperatures on a single graph showing your P vs. V results. Comment on the different behaviors of the isotherms at the different temperatures.
(a) Hand draw a line showing the liquid/vapor transition that goes across the different temperatures on the graph.
(b) Did your 55ºC data show the same plateau that you saw with your lower temperature data? If not, why not? Hint: what are the literature values for the critical point of SF\(_6\) as listed on page 2?

For your 35ºC data, make a separate graph of P vs. 1/V that overlays (a) your experimental results, (b) the ideal gas law prediction, and (c) the van der Waals prediction using equation (2) and the literature coefficients (5). [Be careful with your units!]
Unlike the previous graph, for this graph DO NOT include the data points for the volumes beyond which the sample began to form a liquid and the pressures plateau. These liquid-mixture points do not follow the gas models.
How do your experimental data compare to the two different theoretical models.

Repeat the above for your 55ºC data, make a second P v. 1/V graph showing your experimental results, the ideal gas law prediction, and the van der Waals prediction using equation (2) and the literature coefficients (5).
How do the higher temperature data compare to the lower temperature data?

Note: You will likely see differences between your experimental data and your ideal gas and van der Waals gas, but these differences should be less than a factor of 2. If they are widely different, then check your calculations.

References