1. REAL GASES, GAS/LIQUID EQUILIBRIUM: Critical conditions and van der Waals constants

GOALS

● Study the macroscopic behaviour of real gases and, more specifically, their capacity to condensate, producing a liquid.

● Understand and experimentally determine the concept of temperature, pressure and critical volume of a gas.

● Using the aforementioned data, evaluate the van der Waals constants for the gas being studied.

● Simulate the behaviour of this gas in accordance with the van der Waals equation and compare it with the observed behaviour.

THEORETICAL BACKGROUND

Unlike liquids and solids, the volume occupied by a gas depends strongly on the temperature and pressure. The experimental equipment you are going to use in the lab helps to control those magnitudes, so we can analyse various properties of gases.

In some conditions, a gas may condensate. Each temperature, will have certain pressure at which the condensation will occur. This single pressure is called the **vapour pressure** at that temperature. (Moreover, using the Clausius-Clapeyron equation, the enthalpy of the process could be calculated thanks to the experimentally determined pressure/temperature pairs).

Once all the gas condensates, if the available volume expands, keeping the **temperature constant**, the resulting liquid will evaporate. Note that while liquid and vapour are in the container, the pressure does not change. If you continue expanding the volume, there comes a time when the liquid will disappear and, from there on, the pressure will drop as the volume increases, acting like a gas.

The experiment should be contrasted with the vaporisation (or boiling) process **at constant pressure** to which we are more used, as we live under constant atmospheric pressure. In this case, for example, when you heat a liquid, it reaches a temperature where the liquid starts to boil. And while the liquid is boiling, the temperature remains constant. The heat provided is only used to obtain vapour at the expense of the liquid.

When compressing a gas, there is certain temperature (characteristic for each gas) above which it cannot condensate by pressure alone. This is the **critical temperature**. Above this critical temperature, the behaviour of the gas is close to that defined by Boyle's equation (*pV=constant*), and if the pressure is also low, the ideal gas state function approximation will be reasonable. However, at high pressures, this behaviour is not as that of a ideal gas thus, a different equation of state should be employed.

Using the isotherms around the critical temperature will allow us to determine the critical conditions of a gas, i.e., the critical temperature (K), the critical molar volume (L/mol) and critical pressure (bar).

EXPERIMENTAL PROCEDURE

Equipment	Reactant
Didalab apparatus	SF_6
Thermostatic bath	
Digital thermometer with decimal accuracy	

A small quantity of a reasonably inert and not particularly dangerous gas such as **sulphur hexafluoride** (SF_6) is put into put into the apparatus shown below. The gas is placed in the transparent tube on the left part, where it can be compressed by a piston.
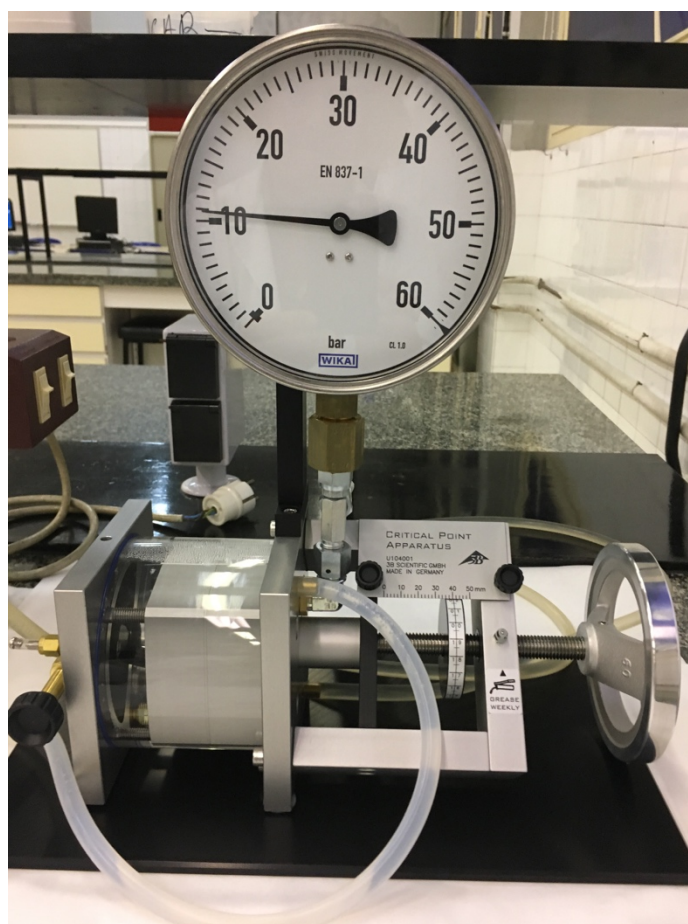
The tube is contained in a water jacket that keeps it at the **desired temperature**, as seen in the following figure on the left. Water circulates around this jacket, thanks to the motor impulse of a thermostatic bath, connected to the jacket by silicon tubes.
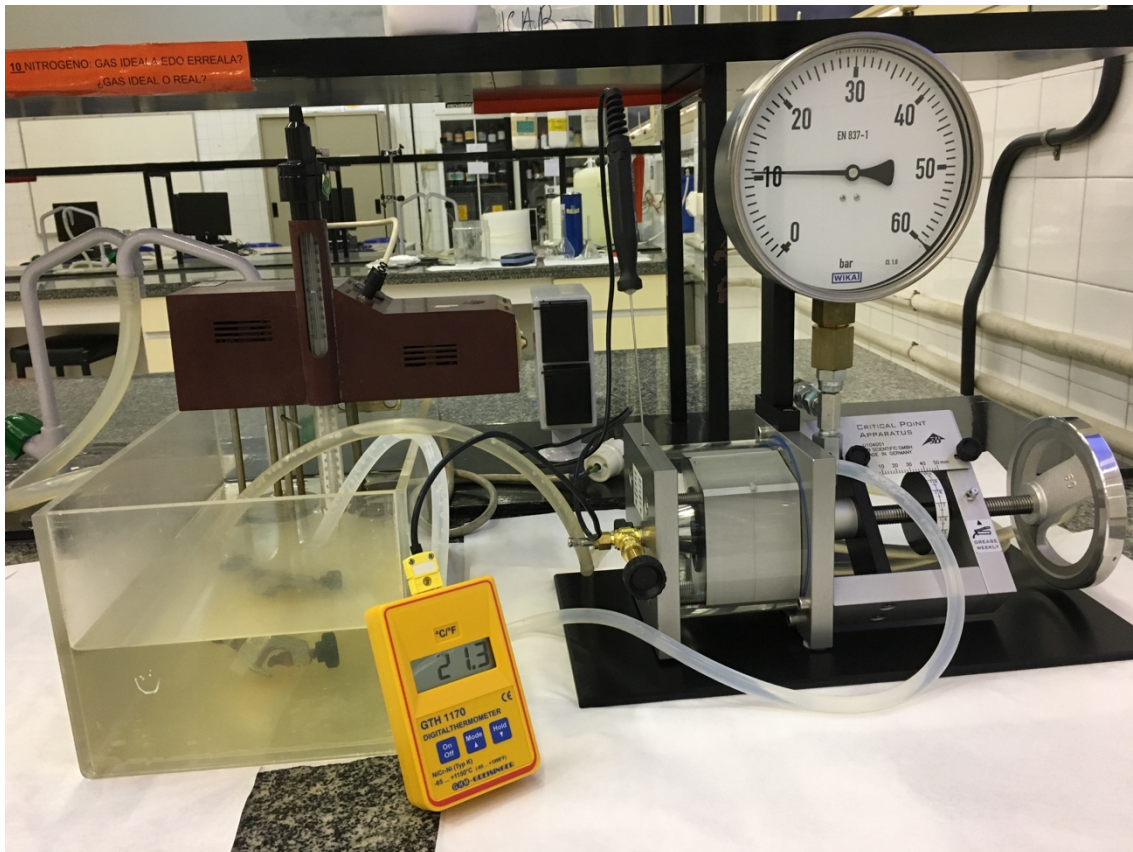
The figure also shows the flywheel used to move the piston that encloses the gas from the right. Moving the piston will change the pressure on our gas, which will be measured by a manometer (in bar) connected to the system. (1Bar = 0.1 MPa = 10^5 Pa = 1/1.01325 atmospheres).

The aim is to determine the P-V isotherms for sulphur hexafluoride at five different temperatures in an interval ranging from 33 to 49ºC, varying approximately four degrees between one temperature and the next. The first temperature will be close to 33, and once we reach the temperature in question using the thermostatic bath, we will determine the exact temperature of water using a digital thermometer (with decimal precision) and note it down on the laboratory notebook. Then, the pressure on the apparatus will be positioned at 10 bar.
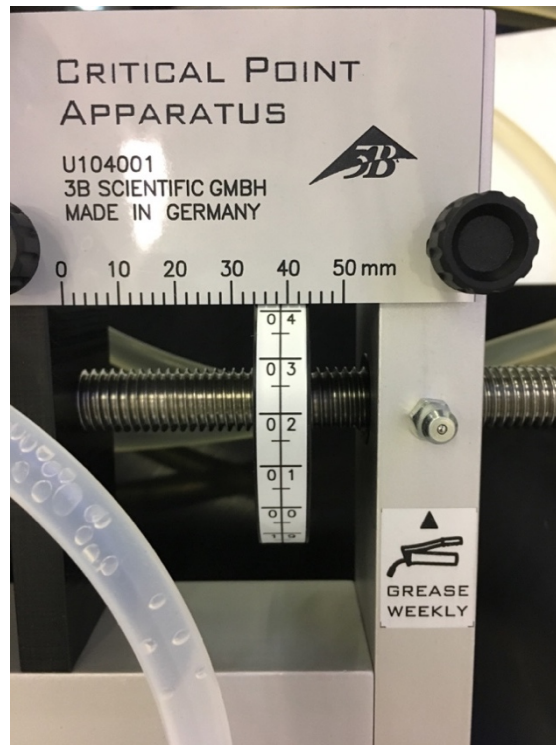
We will measure the volume the gas occupies under these conditions reading the 0-50mm scale at the right of the apparatus. For doing so, we will adjust the 0-19 scale (the wheel) so as to be in line with the scale above. Here you can see some examples:

The distance measured in this picture is 40 mm + 0,0 mm= 40mm
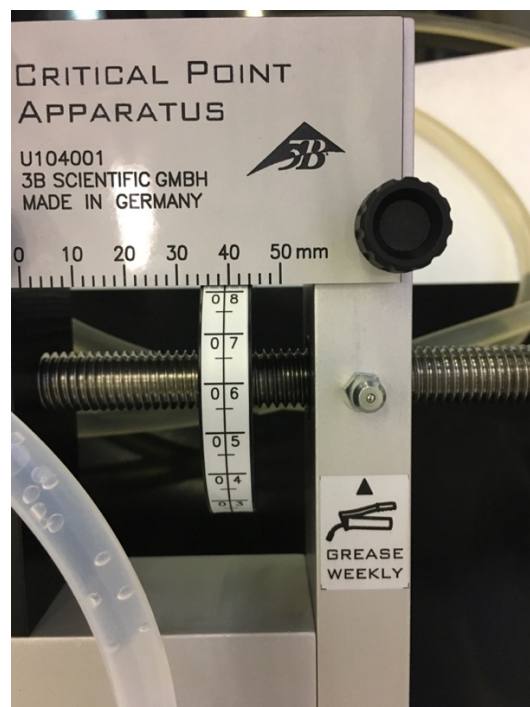
In this case, the distance measured is 38 mm + 0,8 mm= 38,8mm

The distance measured is 38 mm + 0,4 mm= 38,4 mm

After measuring the volume at 10 bar, we will move the flywheel to 11 bar, and we will measure the volume again. Continue using the same method with other pressures, until you observe that the pressure is starting to be constant. At that point, continue compressing the gas moving the piston 2 mm until the pressure increases up to 45 bar, and the isotherm is complete. The value measured in the scale at the right is the distance the piston has moved in mm; if we multiply it by its surface (3,14 cm^2), we will have the volume the gas occupies.

When the gas turns into liquid, you will see that the pressure has to increase a lot to change the volume, since the liquids cannot be compressed.

To start a new experiment at the next temperature, first bring down the pressure to 10 bar turning the flywheel. Change the bath temperature and wait until it reaches the chosen temperature (around 10 minutes), repeating the measurements as before.

The following details should be considered when carrying out the experiment:

- ⇨ The flywheel should always be turned slowly.
- ⇨ Each time the volume is reduced, the pressure might take a few seconds to stabilise, more so at small volumes.
- ⇨ During the experiment, a liquid might appear at a specific pressure (equilibrium vapour pressure). This is the pressure at which the gas vaporises (or the liquid boils), at this particular temperature. It is not easy to see this in the experiment; we will observe how the pressure remains constant, even if the volume changes.
- ⇨ At other temperatures, liquid might not appear as the pressure is increased, due to exceeding the gas's critical temperature.

⇨ In certain conditions, all the gas disappears. Remember that, in this particular case, you will be compressing a liquid, so a small variation in volume will require the pressure to increase excessively.

After performing the experiment at that temperature, close to 33ºC, repeat it at the other four temperatures, between 33ºC and 49ºC.

Questions to be resolved

1. Plot the data from the Tables for the five temperatures on a single graph representing pressure (in Bar) over volume (in mL). Analysing the plotted curves, what behaviour would you mention?

2. You will see in the diagram that, at the lowest temperatures, there is a horizontal zone where the pressure does not change with the volume. What process is taking place? Why does this region not appear at higher temperatures?

3. Using this diagram, estimate the values corresponding to the Critical Temperature (in K) and the Critical Pressure (in Bar) of the SF_6.

4. Also estimate the Critical Volume (in L/mol) explaining any suppositions you have made.

5. With data from sections 3 and 4, calculate the van der Waals constants for SF_6, and compare with literature data.

6. Using constants from section 5, simulate the behaviour of the SF_6 at lower and higher temperatures used in the experiments. Complete the simulated results with the experimental data. Discuss the comparison.