

## 2. GAS/LIQUID EQUILIBRIUM. Vapour pressure, coexistence curves, Clausius-Clapeyron equation.

### GOALS

- Study the macroscopic behaviour of real gases and, more specifically, their capacity to condensate, producing a liquid.
- Understand the **vapour pressure** of a liquid concept, at a determined temperature.
- Use experimental data to represent the vapour/liquid coexistence curve for a substance.
- Check the applicability of what is known as the Clausius-Clapeyron equation and its capacity to determine the vaporisation molar enthalpy of a liquid.
- Determine the normal boiling point for a substance that, in laboratory conditions, clearly behaves as a gas.
- Check, for the substance being used, whether *Trouton's Rule* (1884) can be applied.

### 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. For each temperature, there will be a certain pressure at which the condensation will occur. This 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 an ideal gas thus, a different equation of state should be employed.

The series of  $p/T$  pairs at which condensation occurs, phenomena that you are going to look at in the experiment, represent the liquid/vapour equilibria or the **vapour-liquid coexistence curve** and both magnitudes are related by the **Clausius-Clapeyron equation**:

$$\frac{d \ln p}{d\left(\frac{1}{T}\right)} = -\frac{\Delta_{\text{vap}}.H_m}{R}$$

Appropriate use of experimental data and the aforementioned equation are used to calculate the **vaporisation molar enthalpy**. Besides, the **normal boiling point** of the substance could also be calculated.

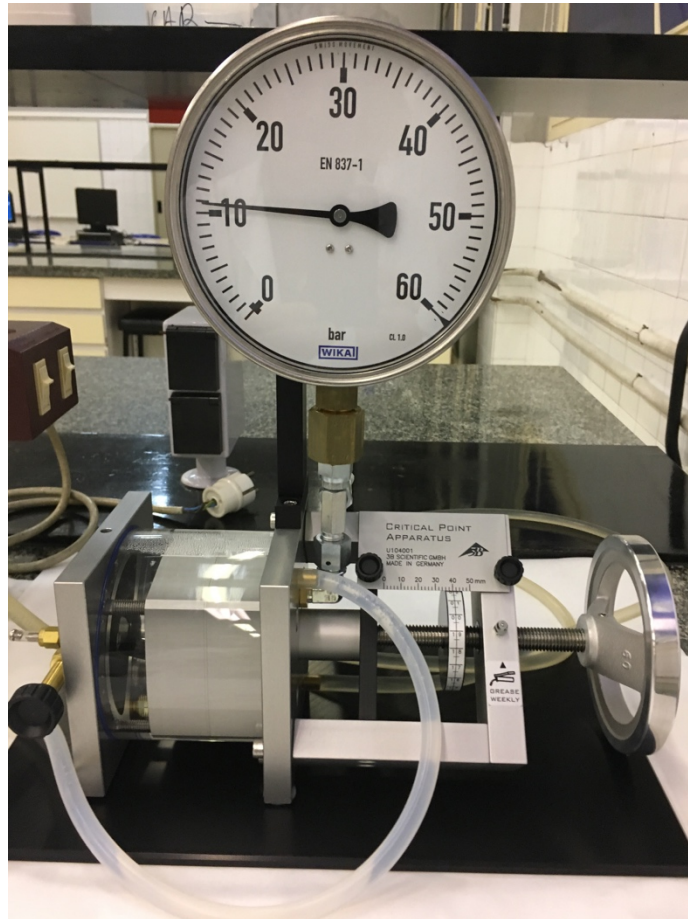
These pressure/temperature pairs at which condensation (or boiling) occurs, determine a **thermodynamic equilibrium** situation where Gibb's free energy change will equal to zero. Therefore, once the vaporisation enthalpy has been obtained using the Clausius-Clapeyron equation, at the equilibrium condition  $\Delta G = 0$ , also allows you to calculate the **vaporisation entropy**, although certain approximations (that the student is expected to be able to explain) are required for it.

At the normal boiling point for a liquid, this entropy is very close to a value between 20-22 cal/mol K (according to a rule stated by Trouton in the late 19th century), which you will try to verify.

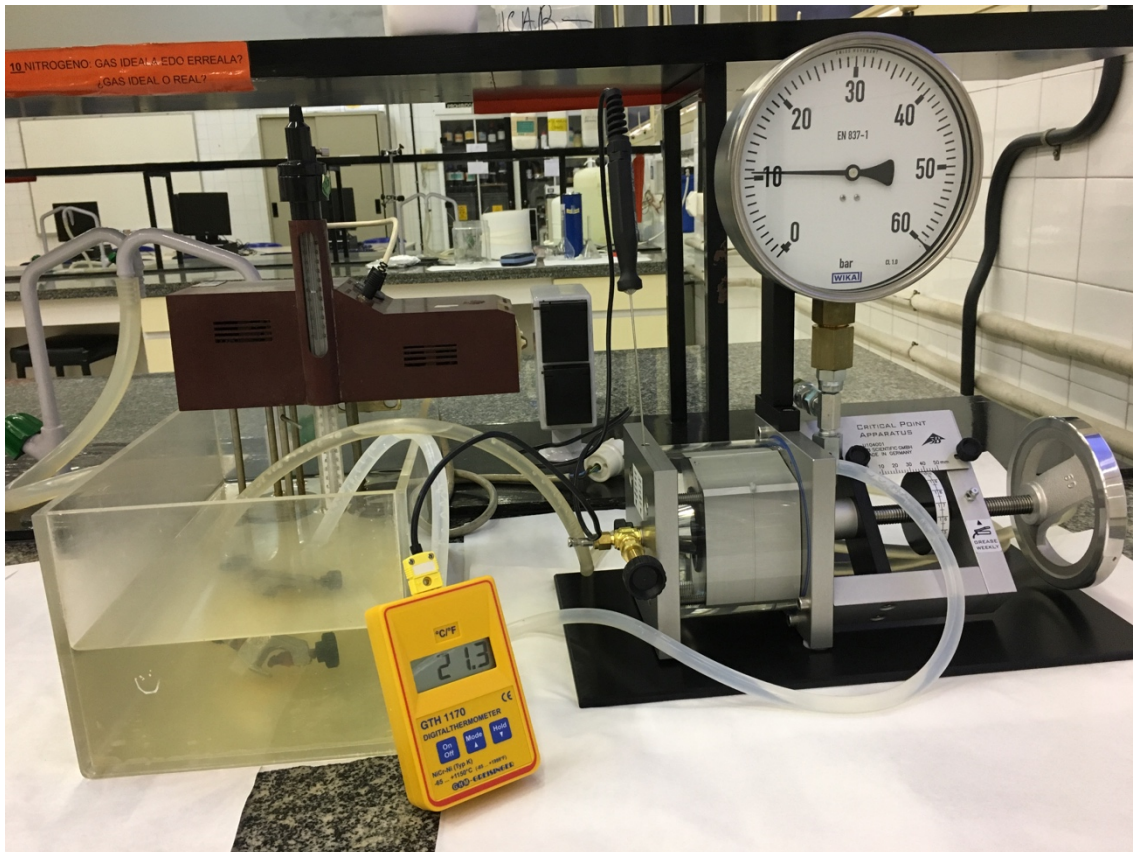
## EXPERIMENTAL PROCEDURE

Equipment	Reactant
Didalab apparatus	SF <sub>6</sub>
Thermostatic bath	
Digital thermometer with decimal accuracy	

A small quantity of a reasonably inert and not particularly dangerous gas such as **sulphur hexafluoride** (SF<sub>6</sub>) is 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.

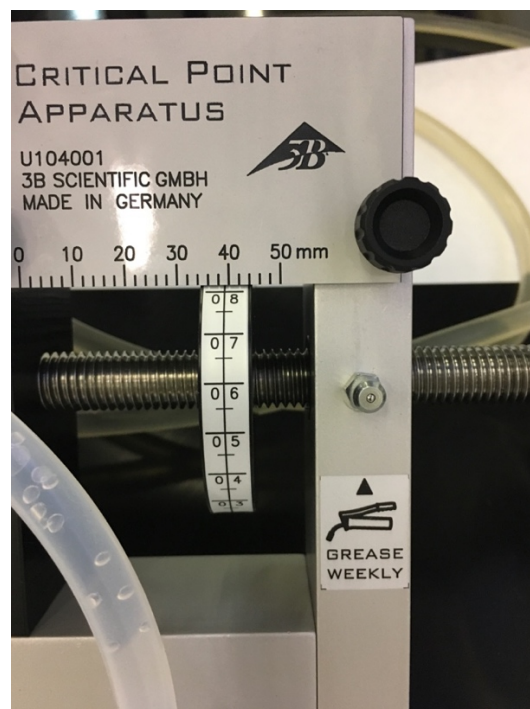


The figure also shows the flywheel used to move the piston that encloses the gas from the right. Moving the piston will change the pressure on our gas, which will be measured by a manometer (in bar) connected to the system. (1Bar = 0.1 MPa =  $10^5$  Pa = 1/1.01325 atmospheres).

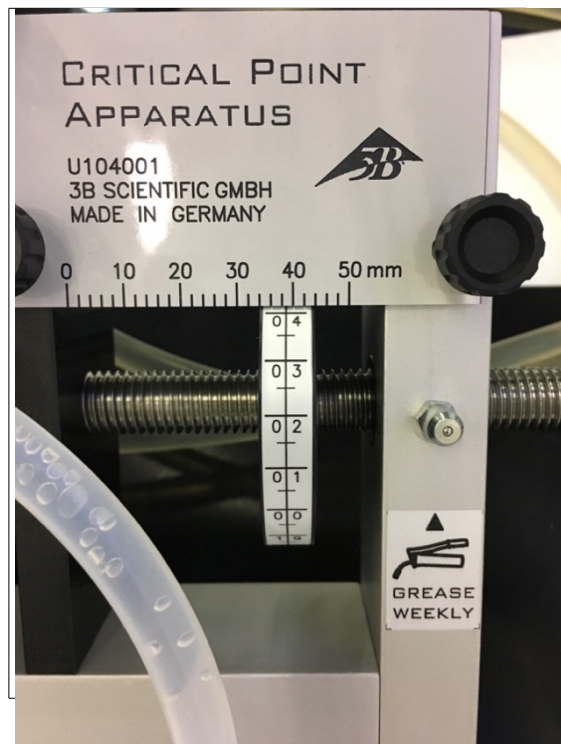
Vapour pressures are going to be determined for the sulphur hexafluoride at five different temperatures in an **interval between approximately 25 and 41°C**. Having obtained the temperature in question using the thermostatic bath, the flywheel has to be positioned so as to put a pressure of 10 bar upon the gas. Our first temperature will be one close to 25°C, which you will measure with the thermometer and write down on your notebook. 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  $40 \text{ mm} + 0,0 \text{ mm} = 40 \text{ mm}$



In this case, the distance measured is  $38 \text{ mm} + 0,8 \text{ mm} = 38,8 \text{ mm}$



The distance measured is  $38 \text{ mm} + 0,4 \text{ mm} = 38,4 \text{ mm}$

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 ( $3,14 \text{ cm}^2$ ), 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.

**After doing the experiment at a temperature, close to  $25^\circ\text{C}$ , repeat it at four other temperatures between  $25^\circ\text{C}$  and  $41^\circ\text{C}$ .** To start a new experiment, first bring down the pressure to 10 bar turning the flywheel. During this descent, the liquid boils as it is quickly transformed into gas. While liquid and gas are both present, pressure remains constant, as seen when compressing the gas. In the end, all the liquid will disappear and leaving just the gas.

Change the bath temperature and wait until it reaches the chosen temperature (around 10 minutes), repeating the measurements as before.

Finally, measurements will also be taken **at  $50^\circ\text{C}$** , where it should be emphasised that **the gas will not condensate** because we are over the critical temperature of the  $\text{SF}_6$ .

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: once vaporisation begins, while liquid and gas are both present, reducing the volume only causes more liquid to vaporise even though the pressure remains practically constant.
- ⇒ 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.

### Questions to be resolved

1. Plot the data obtained for the six temperatures on a single graph that represents pressure (in Bar) over volume (in mL). Considering the curves you are plotting, 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 on the curve obtained at the highest temperature?
3. Using the Clausius-Clapeyron equation described in the *Physical Chemistry I* Course, perform the appropriate representation in Excel to calculate the vaporisation molar enthalpy  $\Delta_{\text{vap}}H_m$  or heat required to vaporise or boil one mol of our substance. Express the vaporisation enthalpy in S.I. units of  $\text{J mol}^{-1}$ .
4. Appropriate use of the Clausius-Clapeyron equation will also allow you to determine the **normal boiling temperature** of the  $\text{SF}_6$ . Calculate it and explain your reasoning.
5. With data from questions 3 and 4, you determine the molar vaporisation entropy  $\Delta_{\text{vap}}S_m$  of  $\text{SF}_6$  in  $\text{J mol}^{-1} \text{K}^{-1}$  and check whether it reasonably meets **Trouton's rule**.
6. Additionally, calculate the temperature at which the  $\text{SF}_6$  will boil under a pressure of 5 and 10 Bar.
- 7.-Compare the obtained results with the ones reported on the literature.