I. OBJECTIVE OF THE EXPERIMENT

We will study the temperature-pressure diagram of nitrogen, in particular the triple point.

II. BACKGROUND THEORY

States of matter

Matter is made of different particle: atoms, molecules, ions, etc. These particles are subject to thermal agitation, and their speed depend on temperature. These particles interact with one another, and the forces determine the macroscopic aspect of matter: we call these different aspect phases (solid, liquid, gaseous). We also call phase any homogeneous part of a material that has the same physical and chemical properties. Examples:

- A homogeneous mixture of O₂ and N₂ represents a single gaseous phase
- a mixture of water and ice, i.e. the mixture of two chemically identical but physically distinct bodies represents two phases.

The interaction forces between particles depend on the temperature, the pressure and the volume that represent the thermodynamic variables of matter.

Phase changes

FUSION-SOLIDIFICATION

Bodies of crystalline form switch from the solid phase to the liquid phase or conversely in very specific conditions. If we supply heat to the body, it's temperature rises until it starts switching to the liquid phase. We call this the fusion process. At that point, the temperature remains constant and the energy supplied in the form of heat is consumed by the work necessary to beat the cohesion forces of the solid (Fig. 1). The amount of work required to melt a unit of mass of a pure body at the fusion temperature, is called latent heat. The solidification of a liquid generally includes a volume change. For most liquids, the volume decreases when solidifying. Therefore, an increased pressure increases the fusion temperature. However, certain liquids (water, bismuth) and certain alloys expand in volume when solidifying (ice floats in water). Therefore, an increase in pressure reduces their fusion point.
EVAPORATION-CONDENSATION

If we place a liquid in a vase, it reaches an equilibrium state. The molecules continually leave the surface to become vapor molecules. This is called evaporation. On the other hand, the vapor molecules constantly hit the surface of the liquid and penetrate it. When the amount of particles exiting the water is equal to the amount entering it, we call the vapor saturated. The pressure of the saturated vapor is called saturation pressure. It is defined by the substance and the temperature. Evaporation is a cooling process. Since the more energetic molecules leave the liquid.

![Figure 1](image)

**Figure 1**: Amount of heat required to transform 1 g of ice at $-10^\circ C$ into vapor at $100^\circ C$.

The energy supplied to the system in the form of heat produces, on the one had the work required to beat the intermolecular forces of part of the liquid, and on the other hand the work due to the volume increase. The latent heat of vaporization for a liquid at a given temperature is the amount of heat required to vaporize a unit mass of the liquid at that temperature and at the equilibrium pressure. The latent heat of vaporization depends on the temperature: it decreases temperature increases. At a certain critical point (see below), the latent heat of vaporization vanishes.

When heating a liquid-vapor mixture in a closed body, we can see that the liquid-vapor limit disappears at a given time. The temperature at which this phenomenon appears is called the critical point. While the gas is being heated, the density of the liquid decrease, and the density of the gas increases, until they are both equal. Above this temperature, the liquid can’t exist, under any pressure. To liquefy a gas, it is necessary to increase the pressure, but simultaneously reduce the temperature. A phase under the critical temperature is called vapor, above, it is called gas.

HUMIDITY

At any given time, water is present in the atmosphere under one or several different phases (solid, liquid, vapor). Invisible vapors are always present in large or small quantities. The quantity of vapor required for the saturation depends on the temperature. If the air isn’t saturated, we can saturate it either by adding vapor or reducing the temperature. The temperature at which the air must be cooled to produce this saturation is called the dew point. The condensation of water will only occur if there are impurities on which the condensation can form. These can be small salt crystals, smoke particles, etc.
The absolute humidity represents the mass of water vapor per unit volume in the air. Relative humidity is defined by the ratio of the vapor pressure to the saturating vapor pressure at that pressure (Fig. 2). It's generally expressed as a percentage. It's one of the most important parameters of meteorology. When the dew point is over the freezing point, small water droplets form. When it is under the freezing point, ice crystals form instead. Frost, clouds and fog are examples of this. Physicists use the phase change to visualize certain nuclear phenomena. The device that is used is called Wilson chamber, or fog chamber. A cylinder containing saturated vapors is closed by a piston or by a diaphragm. When increasing the volume by pulling the piston, the gas cools, and the saturated vapors condense on the ions formed by ionizing particles.

![Figure 2](image)

**Figure 2:**

- AB Vapor pressure at temperature A
- AC Saturating vapor pressure at temperature A
- AB/AC relative humidity. A

**SUBLIMATION**

Sublimation is the direct transformation from the solid state to the gaseous state, without going through the liquid state. This is through which laundry that is hung to dry in the winter can freeze and still dry. Solid CO₂ sublimates into gas, without humidifying the walls of its container. The smell of camphor or naphthalene at room temperature proves that they sublime.

**TRIPLE POINT**

The three phases of a body can coexist at a temperature and pressure that are the coordinates of the triple point on a (\(T, p\)) diagram. At this point, the three curves join (vaporization, fusion and sublimation). The vaporization curve can be extended under the triple point, which indicates a supercooled state. These points of the curve represent metastable equilibrium states. The vaporization curve of the supercooled liquid is always above the sublimation curve. For instance, water and ice have the same vapor tension (4.58 Torr) at the triple point (\(T_f = 0.0096^\circ\text{C}\)), but at \(-10^\circ\text{C}\) the vapor tension is 2.15 Torr for supercooled water and 1.95 Torr for ice.
LIQUID HELIUM

At low temperature, helium has a very specific behavior. It has no triple point in the general sense of the term. At very low temperatures and pressures, the liquid phase is more stable than the gaseous phase. There exist two liquid phases $^1\text{He}$ stable at rather high temperatures, and $^2\text{He}$ stable at very low temperatures. There is an equilibrium curve between both liquids (Fig. 3).

At the triple point $\lambda$ ($T = 2.2 \, \text{K}; \, p = 3.9 \, \text{Torr}$) the two liquids and the vapor coexist. At the point $\lambda'$ ($T = 1.75 \, \text{K}; \, p = 30 \, \text{atm}$) the two liquids and the solid coexist.

The liquid $^1\text{He}$ is very mobile and volatile. Its vaporization heat is only of 5 calories. The $^2\text{He}$ liquid has very strange properties: it’s extremely mobile and 200 more heat conductive than copper. The transformation of $^1\text{He}$ into $^2\text{He}$ occurs with no volume change or latent heat exchange. The internal energy doesn’t change. However, under constant pressure, we observe a discontinuous specific heat.

All the processes caused by the variation of the three thermodynamic variables, i.e. $T$, $V$ and $p$, can be illustrated in the three dimensional space and its projection on the planes $(p,V), \, (p,T), \, (V,T)$.

La figure 4 represents the $(V,T,p)$ space as well as the projections on the aforementioned spaces.

The curves contained in the $T,p$ plane correspond to the isochoric processes (at constant volume), those of the $V,T$ plane are isochoric (at constant pressure) and those of the $V,p$ are isothermal (constant temperature). The separation surfaces in the $(V,T,p)$ space are intersected by the planes $V = \text{cst}, \, T = \text{cst}, \, p = \text{cst}$ according to the corresponding projection lines.

The slope $\frac{dp}{dt}$ at any boundary between two phases $i$ and $j$ is given by the Clausius-Clapeyron equation and is connected to the latent heat $L_{i,j}$:

$$\frac{dp}{dt} = \frac{L_{i,j}}{TV_{i,j}}$$  (1)
where \( \Delta V_{i,j} = V_j - V_i \) represents the volume difference of the considered body in both phases I and j.

The latent heat \( L_{i,j} \) is defined as the heat required to transform one unit of phase \( i \) into the phase \( j \) at equilibrium (i.e. slowly) and constant temperature. If \( V \) is indicated in \( \text{m}^3/\text{mole} \), \( L_{i,j} \) will be in J/mole.

\[
\Delta V = V_j - V_i
\]

\[
L_{i,j} = \frac{\Delta U}{\Delta T}
\]

\[
V = V_j + V_i = \text{cst}
\]

The released or absorbed heat of a body is therefore not only used for temperature variations, but also for separating particle when the body transforms from one phase to another. Let’s mention water, as an example

- in order to increase the temperature of 1g of ice from \(-1 \degree C\) to \(0 \degree C\), we need 1 calorie.
- the fusion of one gram of ice requires 80 calories, though the temperature doesn’t change during the whole process.

The three curves of sublimation, vaporization and fusion have one single intersection: the \textit{triple point} for which the three phases coexist in equilibrium (Fig. 5).

The determination of the triple point can be achieved from the knowledge of at least two of these three curves of phase change. For most materials, the triple point is located at low temperatures and pressures. To determine this, it is then necessary to reduce the pressure and temperature in a sealed container, which can be done simultaneously by means of a vacuum pump. The fundamental question that arises is to know starting what pressure is it possible to have temperatures lower than the triple point. We are therefore faced with the problem of obtaining a pressure \( p_{\text{min}} \) low enough to lower the temperature below the triple point.
PUMPING ON A LIQUID PHASE

When immersed in a thermally isolated Dewar, a liquid keeps its own temperature $T$. However, if the isolation isn’t perfect, there will be a heat exchange of $Q'$ Joules/s with the outside. If, by using a vacuum pump, we reduce the pressure vaporization pressure of the liquid, we will generate an excess of vaporization, which will require a latent heat $Q''$ every second. The difference $Q'' - Q'$ must come from the liquid, therefore, it is cooled, solidified, and continues to be cooled. The vacuum however, is limited to a minimum pressure $p_{\text{min}}$, that depends on the characteristics of the pump. The amount of moles of vapor exchanged with is outside is equal to the number of moles $\mu$ of substance sublimated every second by the incoming heat $Q$:

$$\mu = \frac{Q}{L_s} \quad (2)$$

where $L_s$ is the sublimation heat of the solid. The ideal gas equation can be applied here, and allow us to calculate the corresponding vapor volume $V_s$:

$$V_s = \mu \frac{RT}{p_{\text{min}}} \quad (3)$$

i.e.: $$p_{\text{min}} = \mu R \frac{T_s}{V_s} \quad (4)$$

In order to calculate the solid’s minimal temperature $T_{\text{min}}$ when in equilibrium with the vapor pressure $p_{\text{min}}$, we start from the Clausius-Clapeyron equation. The volume of the solid being negligible with respect to the vapor, we can replace: $\Delta V_{i,j}$ with $\frac{RT_{\text{min}}}{p_{\text{min}}}$ whence:
\[ \frac{dp}{p} = \frac{L_s}{R T^2} \, dT, \quad L_s \text{ is supposed independent of temperature}. \]  

(5)

After integration:

\[ \log p + \log C = -\frac{L_s}{RT} \]

(6)

In order to determine the integration constant \( C \), let’s write equation (6) for two different equilibrium conditions, e.g. \( T_0 \) (triple point with pressure \( p_0 \)) and \( T_{\text{min}} \) (sublimation temperature at minimum pressure \( p_{\text{min}} \)):

\[ -\frac{R}{L_s} (\log p_0 + \log C) = \frac{1}{T_0} \]

\[ -\frac{R}{L_s} (\log p_{\text{min}} + \log C) = \frac{1}{T_{\text{min}}} \]

(7)

Subtracting the first equation from the second yields:

\[ -\frac{R}{L_s} (\log p_{\text{min}} + \log p_0) = \frac{1}{T_{\text{min}}} - \frac{1}{T_0} \]

which leads to:

\[ T_{\text{min}} = \left( \frac{1}{T_0} - \frac{R}{L_s} \log \frac{p_{\text{min}}}{p_0} \right)^{-1} \]

(8)

III. EXPERIMENTAL SETUP

Figure 6 shows a diagram of the setup

Before doing anything, make sure you have gone through all of the tips below:

- Liquid nitrogen under 1 atm boils at \(-195.8^\circ\text{C}\). Any contact will cause severe burns.
- Try to avoid gas exchange between the Dewar and the atmosphere, to avoid the formation of frost in the Dewar.
- The optimal fill level of the main Dewar is indicated by the red line.
- Avoid letting the vane pump work on the atmosphere, i.e. with an open valve. The pump heats up.
- When turning off the pump, immediately introduce atmospheric pressure into it, by opening the valve 2 (lever pointing right) without letting oil reach the valve.
- Never let the agitator run when the nitrogen is solid.
- When in presence of small crystals in the liquid, reduce the speed of the agitator.
- When in presence of liquid only, the maximal speed of the joint should be the graduation “4” on the potentiometer.
IV. MEASURING TEMPERATURE AND PRESSURE

In order to determine the three curves (sublimation, fusion and vaporization), and their intersection on a \((T, p)\) diagram, we need two main conditions:

1) The indicated values must be instantaneous (no measurement inertia)

2) The two indications must be simultaneous (we need values of \(T, p\) at the same moment)

We will use an electronic pressure gauge to measure the and a platinum probe to measure the temperature.

For the values of temperature to be exact, we need a good thermal contact between the probe and the measured body, which isn’t the case for solid nitrogen, since it’s porous. The probe has been perfected to best satisfy this condition.
V. SPOTTING THE TRIPPLE POINT

The method consists in performing manipulations that maintain the presence of several phases simultaneously, after a cooling process. By using this method, we will eventually reach the triple point, and stay there long enough to verify that the temperature $T_j$ and corresponding pressure $p_j$ remain constant.

VI. SUGGESTED EXPERIMENTS

1) Pump the liquid nitrogen until reaching a partial evaporation, which will cool the rest of the liquid. After a few minutes, we notice that a solid phase appears. Keep pumping until reaching approx. 10 Torr.

2) Close valve (3) (lever pointing up). Stop pumping, and write down the measurements for $(T, p)$, as the nitrogen gets warmer.

3) Using these measurements, plot $p = p(T)$ at constant volume, you should get three branches ($P_J, F_J, J_C$). We should notice four different stages during this process:
   - simultaneous increase of $T$ and $p$ (sublimation curve)
   - constant $T$ and $p$ (triple point)
   - approximate constant value of $T$ and increase in $p$ (fusion curve)
   To obtain the vaporization curve, stop pumping just before formation of a solid phase and trace the increase of $T$ and $p$.

4) Repeat steps 1 through 3 at least once.

5) Solidify the nitrogen (down to approx. 10 Torr), and close the valve (3). After having filled the Dewar (10) with liquid nitrogen, let nitrogen into the system using the valve (4). What phenomenon can you observe? How can you explain this?

6) Knowing the parameter of the pump, use equation (8) to calculate the minimal temperature that can be reached.

Fig. 7: Image of the experimental setup.