5. Saturation pressure of water (8 points) — *Solution by Eero Uustalu.* If the pressure above a liquid is reduced below its saturated vapour pressure, the liquid starts to boil. We use this to measure p_{sat} indirectly.

Main idea. Use a sealed air bubble as a manometer. If we can trap a small air bubble somewhere in the tube, note its initial length l_0 under atmospheric pressure, and then reduce the pressure in the bubble, the bubble's length grows. Since the tube's cross-section is uniform, the bubble's pressure is determined by the ideal gas law (isothermal expansion):

$$p_{\text{bubble}} = p_{\text{atm}} \cdot \frac{l_0}{l_1}.$$

If we reduce the air bubble's pressure by pulling on the syringe plunger, dodecane carries the reduced pressure from the air bubble back through the tube to the water–dodecane interface inside the syringe. Once the pressure there drops to p_{sat}, water vapour starts forming bubbles at the interface, which grow and coalesce. At that point, pulling the syringe further no longer reduces the air bubble's pressure: any further pressure drop is immediately compensated by additional vapour evaporating at the interface. So once the air bubble stops growing in response to syringe pulling, we have $p_{\text{bubble}} = p_{\text{sat}}$ (plus a small hydrostatic correction if the tube is not laid horizontally; see below).

Why dodecane? The role of dodecane is to act as an incompressible, non-volatile piston between the syringe and the air bubble. Dodecane is hydrophobic, does not dissolve in water, and has negligible vapour pressure at room temperature (as stated in the problem). It is also lighter than water, so water stays below dodecane in any at-rest configuration.

The problem warns that water must not touch the inner surface of the tube, because traces of water get adsorbed onto the plastic wall. When the pressure in the tube is then reduced below p_{sat}, these adsorbed traces boil off, forming a series of small bubbles distributed along the tube. Each such bubble also expands during the measurement, adding uncontrolled volume to the gas column and distorting the l_0-to-l_1 ratio. By filling the tube with dodecane *before* introducing any water, the inner surface is prewetted with a hydrophobic liquid that excludes water from the wall.

Design. The tube must contain dodecane filling it from the syringe end up to a small air bubble of initial length $l_0 \approx 15\,\text{mm}$ at the far end (closed by the metal pin). Water sits in the syringe itself, not in the tube. The air bubble cannot be too small (initial length reading becomes imprecise) nor too large: during the measurement it expands by a factor of ≈ 40 (since $p_{\text{atm}}/p_{\text{sat}} \approx 101/2.6 \approx 39$ at room temperature), so an initial bubble of 15 mm expands to $\approx 0.6\,\text{m}$, comfortably fitting in a 1.5 m tube. Any additional air bubbles elsewhere in the tube or in the syringe would also expand during the measurement, distorting the result or making it impossible to reach p_{sat} within the full travel of the syringe plunger.

Note on orientation: the dodecane column has density $\approx 750\,\frac{\text{kg}}{\text{m}^3}$, so a vertical 1.5 m column of dodecane produces a hydrostatic pressure difference of $\rho g h \approx 11\,\text{kPa}$ — several times larger than the $p_{\text{sat}} \approx 2.6\,\text{kPa}$ being measured. The tube must therefore be laid horizontally, otherwise the hydrostatic correction will dominate the result.

Preparation.

- Connect the syringe to the tube.
- Dip the far end of the tube into the dodecane container and pull the syringe plunger; dodecane fills the tube.
- Lift the far end of the tube out of the dodecane and pull in a small amount of air, forming an air bubble of initial length $l_0 \approx 15\,\text{mm}$ at the far end.
- Close the far end of the tube tightly with the metal pin.

- Disconnect the syringe (keeping the plunger in place so no air enters the syringe from the open end).
- Pull a small amount of water ($\sim 1\,\mathrm{mL}$) into the syringe.
- Reconnect the syringe to the tube (a small air bubble at the Luer joint is tolerable, but minimise it).

At this point, from syringe end to far end: syringe (with water) — water–dodecane interface near the Luer joint — dodecane filling the tube — air bubble at the far end — metal pin closure.

Measurement.

- Lay the tube horizontally to avoid any hydrostatic correction in the dodecane column.
- Measure the initial bubble length l_0. Record the atmospheric pressure p_{atm} and the room temperature T_{room} from the invigilator.
- Pull the syringe plunger slowly. The bubble grows as the pressure drops. Continue until the bubble stops growing (the limit where $p_{\mathrm{bubble}} = p_{\mathrm{sat}}$). Fix the plunger at this position.
- Measure the final bubble length l_1.

Typical values: $l_0 \approx 15\,\mathrm{mm}$, $l_1 \approx 400\,\mathrm{mm}$ to $800\,\mathrm{mm}$ (depending on room temperature; at $T = 22\,^\circ\mathrm{C}$, $p_{\mathrm{sat}} \approx 2.6\,\mathrm{kPa}$ gives $l_1/l_0 \approx 101/2.6 \approx 39$, so $l_1 \approx 580\,\mathrm{mm}$).

Calculation. From the ideal gas law at constant temperature,

$$p_{\mathrm{sat}} = p_{\mathrm{atm}} \cdot \frac{l_0}{l_1}.$$

With $l_0 = 14.5\,\mathrm{mm}$, $l_1 = 660\,\mathrm{mm}$, $p_{\mathrm{atm}} = 101\,\mathrm{kPa}$:

$$p_{\mathrm{sat}} = 101 \cdot \frac{14.5}{660} \approx 2.2\,\mathrm{kPa}.$$

Dominant source of systematic error. Incomplete saturation: it takes time for water to evaporate at the interface inside the syringe, and if the plunger is pulled too fast, the pressure temporarily falls below p_{sat} (supersaturated vapour). The measured l_1 is then larger than its true equilibrium value, giving an underestimate of p_{sat}. Mitigation: pull slowly and wait for the bubble to stabilise before recording l_1.

A secondary source is residual air: from the Luer joint, from air dissolved in the dodecane, or from water traces adsorbed on the tube wall (if dodecane pre-wetting was imperfect). These behave as additional gas in the air bubble and artificially reduce the apparent p_{sat}. Careful preparation — filling the tube with dodecane before any water enters, keeping the water–dodecane interface inside the syringe, and avoiding air at the Luer joint — minimises this.

Grading for methods similar to official solution, that don't need to know the partial water pressure of the ambient room air. (8 points total)

For methods that require knowing the partial water pressure of the ambient room air, look at alternate scheme.

Part (i) — description of procedure and principle (2 points).

- Main idea: using the air bubble as a manometer **0.5 pts**
- Recognising that $p_{\mathrm{bubble}} = p_{\mathrm{sat}}$ when the bubble stops growing under syringe pulling **0.5 pts**

- Correct role of dodecane: serves as piston; negligible vapour pressure; prevents water from wetting tube walls **0.6 pts**
- Application of the ideal gas law (or equivalent isothermal pressure–volume relation) to relate initial and final bubble lengths to pressures **0.4 pts**

Part (ii) — performing the measurements (4 points).

- Correct tube preparation: dodecane fills the entire tube, small air bubble at the far end, water in the syringe **1.0 pts**
- Correct choice of initial bubble length (approximately 10 mm to 20 mm) **0.5 pts**
- Documentation of preparation steps with a clear sequence **0.5 pts**
- Tabulation of the measured quantities l_0 and l_1 **0.8 pts**
- Recording atmospheric pressure p_{atm} and room temperature T_{room} **0.2 pts**
- Slow pulling of the syringe / waiting for stabilisation **0.6 pts**
- Tube laid horizontally (or a correction applied if vertical) **0.4 pts**

Part (iii) — determination of p_{sat} and systematic error (2 points).

- Correct computation of p_{sat} from l_0, l_1, p_{atm} **0.4 pts**
- Result within a factor of 1.5 of the expected value for the measured T_{room} **1.2 pts**
- *Otherwise*, within a factor of 2 of the expected value **0.6 pts**
- *Otherwise*, within a factor of 3 of the expected value **0.3 pts**
- Identification of incomplete saturation (or a comparable dominant systematic source) **0.4 pts**

(The three tolerance bands are mutually exclusive: award only the highest band the result falls in.)

Grading (methods that depend on knowing the partial pressure of ambient water moisture in the room air). (Maximally 5.6 points of 8 points total.)

The summary of these solutions is that they had a "dry" end of the long tube, with some dodecane in the middle to act as a piston, and the other end of the tube having the syringe on it, with some water in it. Over enough time, the water in the syringe will evaporate (raising the partial pressure of water, from the room's ambient water vapor pressure, to the saturated vapor pressure), moving the dodecane piston towards the dry end.

If the dry end of the long tube was sealed, additional assumptions have to be made, which have to be explicitly justified.

Part (i) — description of procedure and principle (2 points).

- Explicitly stating, that the result comes to be lower than the real saturated vapor pressure of water, due to the ambient room air (and as such, the near end of the syringe where the water evaporates) also having water vapor already in it **1.6 pts**
- Application of the ideal gas law **0.4 pts**

Part (ii) — performing the measurements and calculating the expressions (max 3.2 out of 4 points).

For the sake of clarity, let's say that the room air pressure is p, length from the end of the dodecane until the (dry) end of the tube is x, and the volume of the entire half of the system from the dodecane of the syringe side to be V_{TOT}. Likewise, the respective new pressure, length, and volume, after the water vapor pressure has reached saturation on the syringe side, to be p_{new}, x_{new}, and $V_{\mathrm{TOT,new}}$.

- Expressing $p_{\mathrm{sat}} = p\left(\frac{x}{x_{\mathrm{new}}} - 1\right)$ if the dry end is sealed (or $p_{\mathrm{sat}} = p\left(\frac{V_{\mathrm{TOT,new}}}{V_{\mathrm{TOT}}} - 1\right)$ if dry end is left open) **1 pts**
- If it's **explicitly** stated how/why $p_{\mathrm{new}} \approx p + p_{\mathrm{sat}}$, due to $\frac{x}{x_{\mathrm{new}}} \gg \frac{V_{\mathrm{TOT,new}}}{V_{\mathrm{TOT}}}$ or something similar. (give automatically if dry end was left unsealed) **1 pts**
- Documentation of preparation steps with a clear sequence **0.3 pts**
- Recording atmospheric pressure p_{atm} and room temperature T_{room} **0.2 pts**
- Waiting for stabilisation **0.3 pts**
- Tube laid horizontally (or a correction applied if vertical) **0.4 pts**

Part (iii) — determination of systematic error, sourcing from other than that of the ambient room's water vapor pressure (max 0.4 points out of 2 points).

- Identification of incomplete saturation (or a comparable dominant systematic source) **0.4 pts**