Boiling Point and Distillation
(Simple and Fractional Distillation)

Distillation is the process of heating a mixture to the point that it boils – that is, the vapor pressure of the liquid equals the atmospheric pressure, and vapor will start forming below the surface of the liquid.

If the resulting vapor is condensed, the condensed liquid will often contain more of the volatile component of the mixture than others. This allows purification by distillation.

Distillation is a technique that is used to :

- obtain a boiling point of a pure liquid.
- purify a mixture of liquids based on boiling point differences among compounds.

It has wide applications in petroleum refineries and the chemical industry.

Simple Distillation

Simple distillation allows isolation of the various components of the mixture in acceptable purity if the *difference* between the boiling points of each pure substance is greater than 40–50 is a useful method for isolating a pure liquid from other substances that are not volatile.

Fractional Distillation

The technique of **fractional distillation** is a useful method for isolating the individual pure liquid components from a mixture containing two or more volatile substances.

For mixtures of liquids having boiling points much less than 50 degrees apart, separation can be achieved only by **fractional distillation**.

To achieve complete separation, the liquid mixture may have to be vaporized and condensed many times. This is best accomplished by using a fractionating column.-Fractional distillation.

The fractionating column provides a large surface area for continuous *heat exchange between the hot ascending vapor and the cooler descending liquid*, thus resulting in a series of evaporations and condensations leading to separation of the two components.

Each step makes the vapor richer and richer in the more volatile component.

Theoretical Plates and Fractional Distillation:

- The term theoretical plates is used to express how many times the liquid is vaporized and condensed in the column.
- **HETP** refers to the height of the column equivalent to one theoretical plate.

- For example, a column 60 cm long with an efficiency of 30 plates has an HETP value of 2 cm.

- When small amounts of material are to be distilled, a column must be chosen that has an efficiency, HETP, adequate for the desired separation and also a low to moderate hold-up.

- "Holdup" refers to the condensate that remains in a column during and after distillation.

Theoretical Plates and Fractional Distillation:

The behavior of a solution of two miscible liquids, A and B, is best explained by referring to **Raoul's law** which states that

The partial pressure of liquid A (p_A) in a mixture is equal to the vapor pressure of pure liquid A (P°_A) multiplied by the mole fraction of A in the mixture (N_A).

The mole fraction is defined in the following equation:

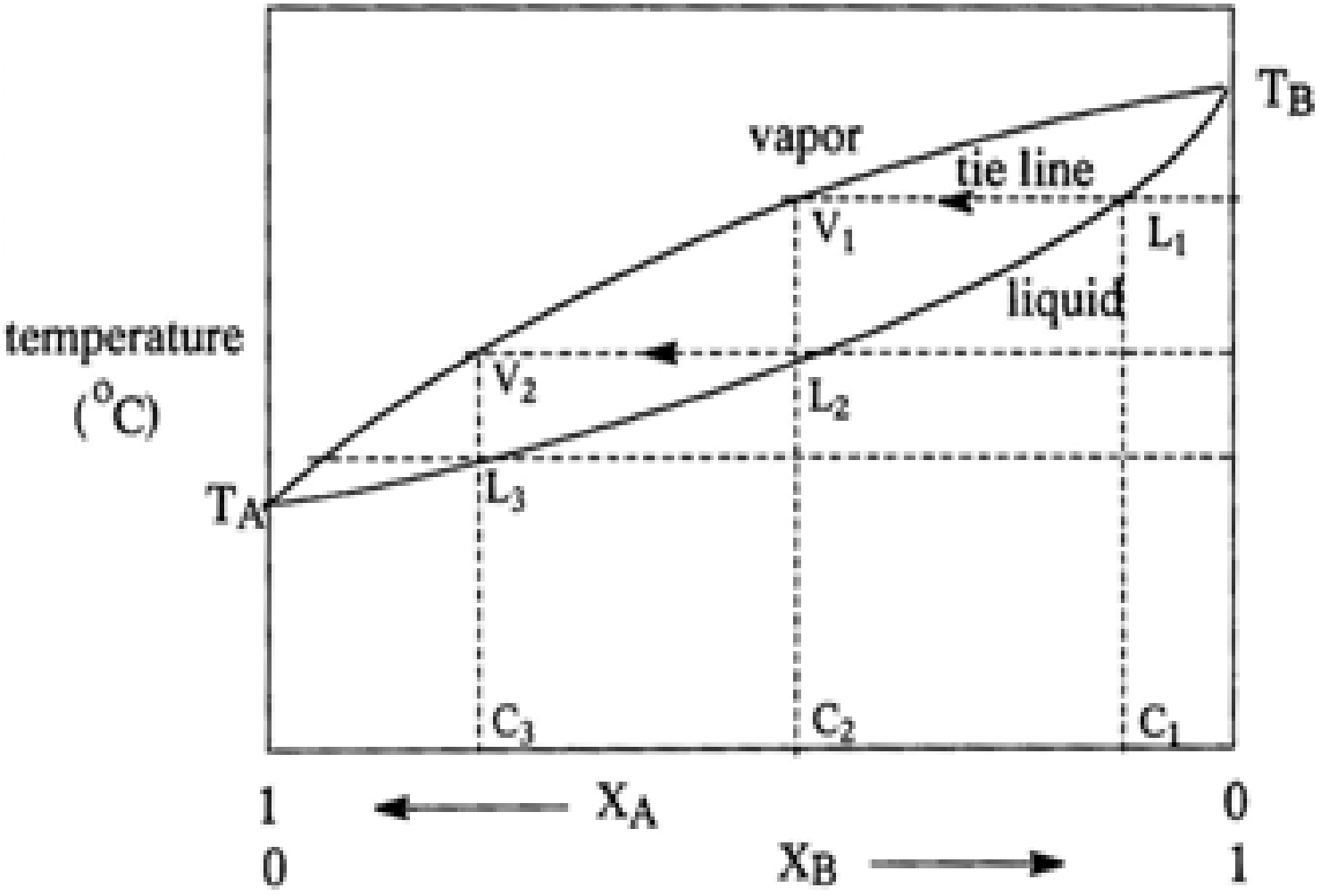
$$N_X = \frac{nX}{nX + nY + nZ + \cdots}$$

The same applies to liquid B. Therefore:

$$P_A = N_A . P^\circ_A \qquad \text{and} \qquad P_B = N_B . P^\circ_B$$

- From **Dalton's law**, the total vapor pressure of the solution (P_T) is the sum of the partial pressures of A and B:
- $P_T = p_A + p_B = N_A.P^\circ_A + N_B . P^\circ_B$
- $(N_A + N_B = 1)$

Vapor Liquid Composition diagram for an Ideal Mixture of Two Liquids



Vapor Liquid Composition for an Ideal Mixture of Two Liquids

A solution of A and B will boil when the total vapor pressure (P_T) equals the external pressure. This occurs at a temperature which is *intermediate* between the boiling points of the two pure liquids (lower curve in Previous Figure).

This diagram shows the temperature at which mixtures of A and B of various compositions boil (lower curve).

The composition of the vapor in equilibrium with the liquid is given by the tie line connecting the liquid and vapor curves. It is clear from the Figure that the vapor will always be richer than the liquid in the more volatile components. This makes sense, since the molecules of the more volatile component will escape more readily, and thus be in higher proportion in the vapor phase.

Azeotropes

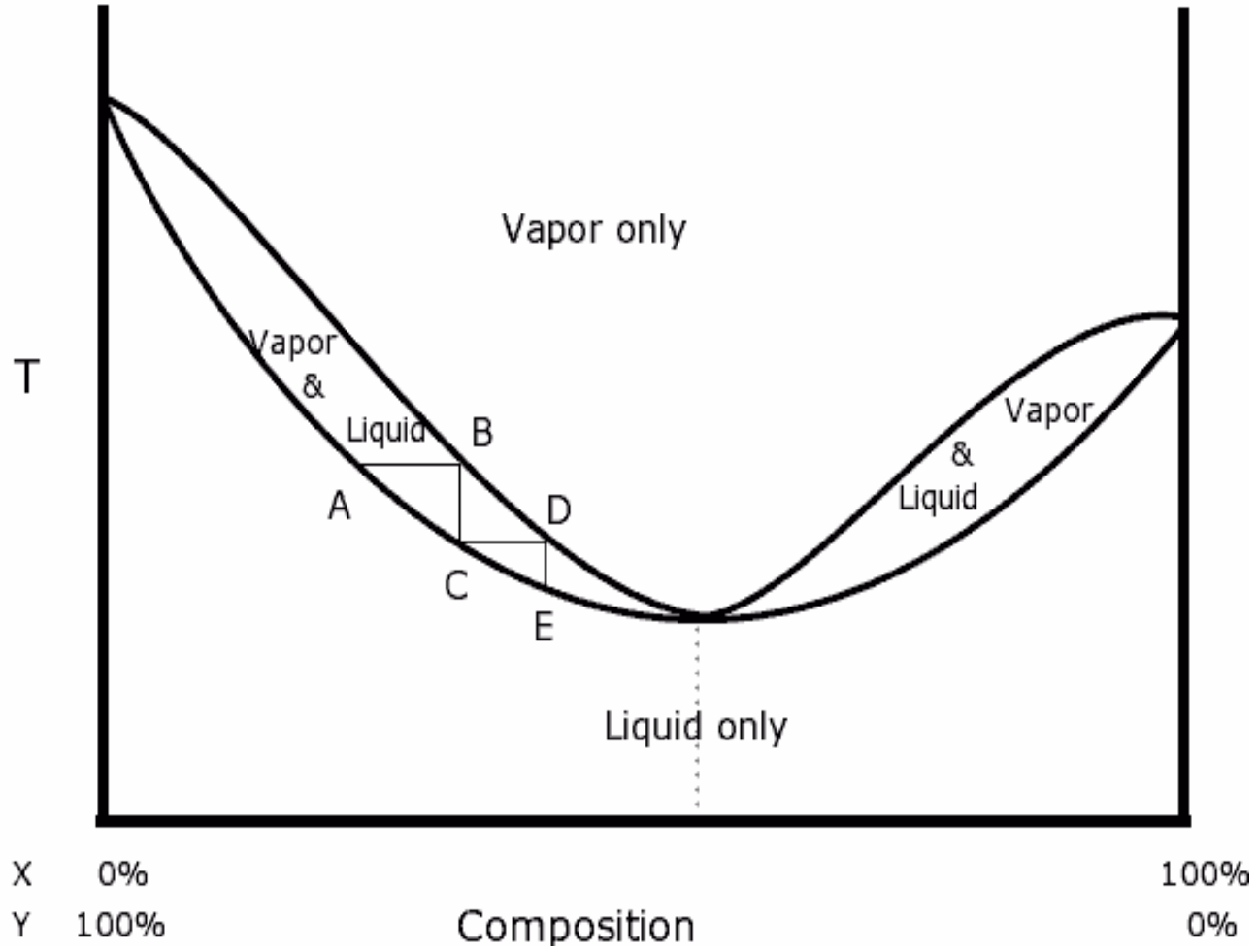
Unfortunately, distillation is not always successful for purifying organic liquids. **Some liquids form constant boiling mixtures called azeotropes.**

An azeotropic mixture has a fixed composition in the liquid phase and the same fixed composition in the vapor phase. This liquid will have a fixed boiling point and will act a pure compound.

Its proportions cannot be altered by simple distillation. This happens because, when an azeotrope is boiled, the vapor has the same proportions of constituents as the unboiled mixture.

Because their composition is unchanged by distillation, **azeotropes** are also called (especially in older texts) **constant boiling mixtures**.(see the Figure below)

Azeotropes

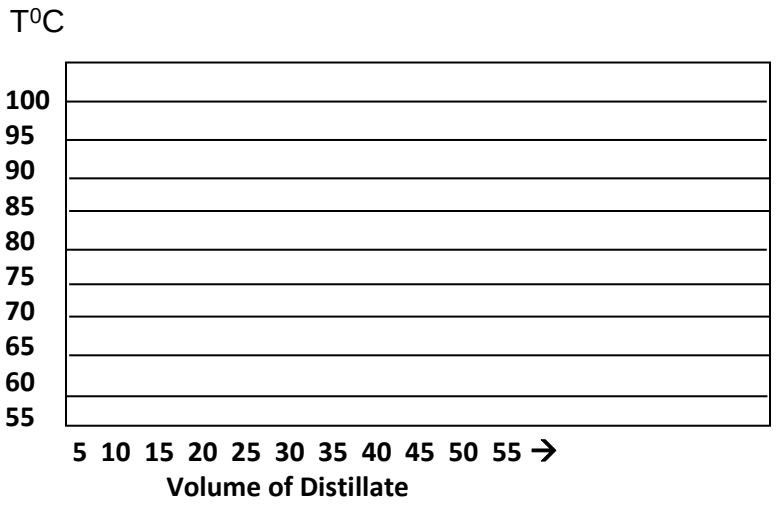

Vapor only
Vapor
&
Liquid
B
A
D
C
E
Vapor
&
Liquid
T
Liquid only
X 0%
Y 100%
Composition
100%
0%

Procedure: Simple Distillation

- Make a mixture of the two liquids (acetone-water) 50 mL each and pour it into a 250 mL round bottomed flask.
- Add 2-3 boiling chips to prevent the liquid from bumping due to superheating.
- Begin the distillation so that one drop per second is collected in the graduated cylinder (receiver) .
- Record the temperature at each 5-mL interval. Do not distill to dryness(Stop distillation when 85 mL of distillate were collected).

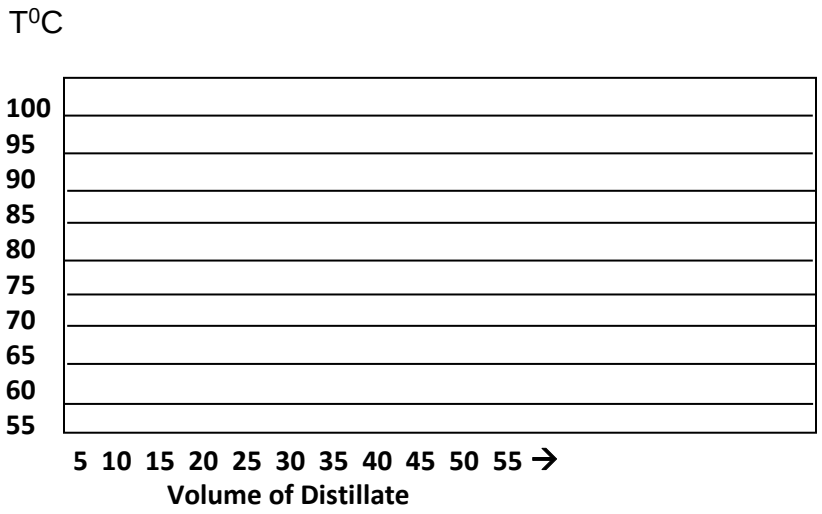
{ At 760 mm Hg, pure acetone boils at 56^0C and pure water at 100^oC}.

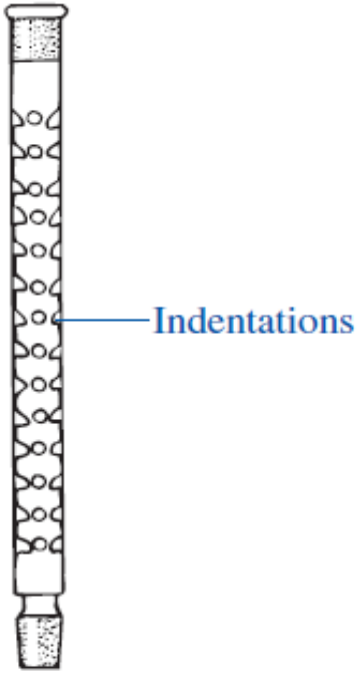
- Plot the data in the graph below.



Procedure: Fractional Distillation

- Combine the fractions that were previously collected in the graduated cylinder.
- Pour the fractions into the same 250 ml round-bottomed flask.
- Add 2-3 boiling chips, attach the fractionating column between the round – bottomed flask and the still head and proceed as for simple distillation.
- Record the temperature at each 5 mL interval. Do not distill to dryness(Stop distillation when 85 mL of distillate were collected).
- Plot the data in the graph below.





fractionating column

Simple Distillation

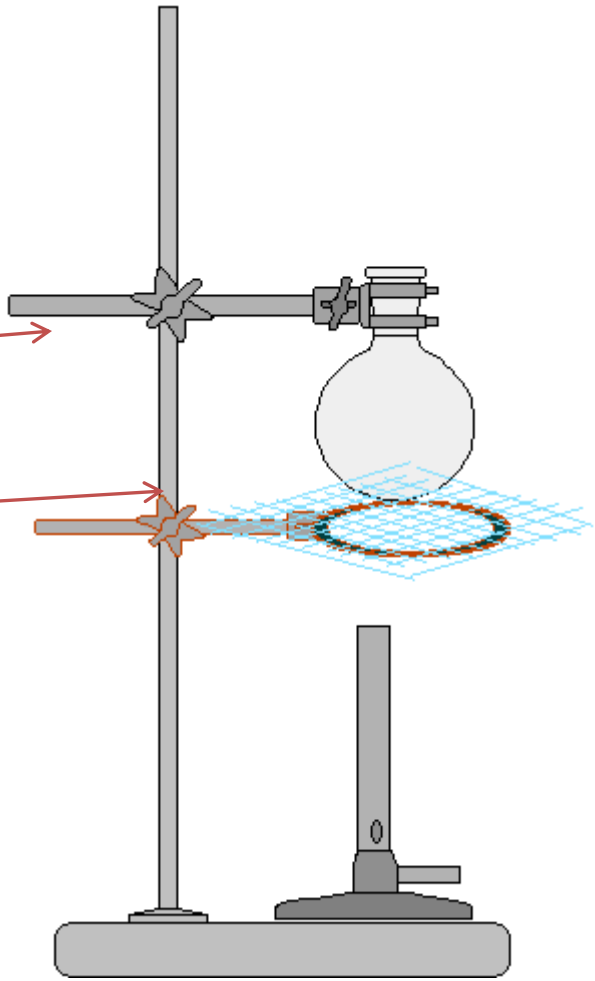
This is a step by step representation of the simple distillation set-up:

Hold your round bottomed flask (stillpot) by the clamp.

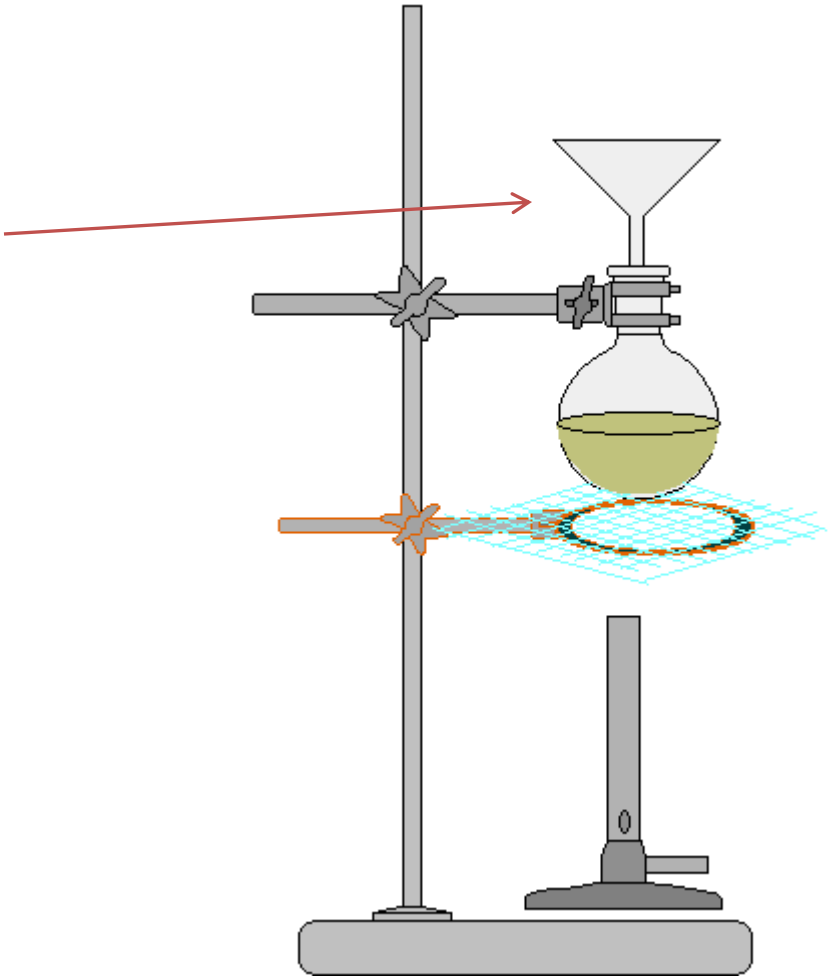
Let the flask sit on the wire gauze (on the ring).

The Bunsen burner should be placed in a proper position, just below the flask.

Do not light the Bunsen burner yet.



Use a glass funnel to transfer the impure liquid into the round bottomed flask

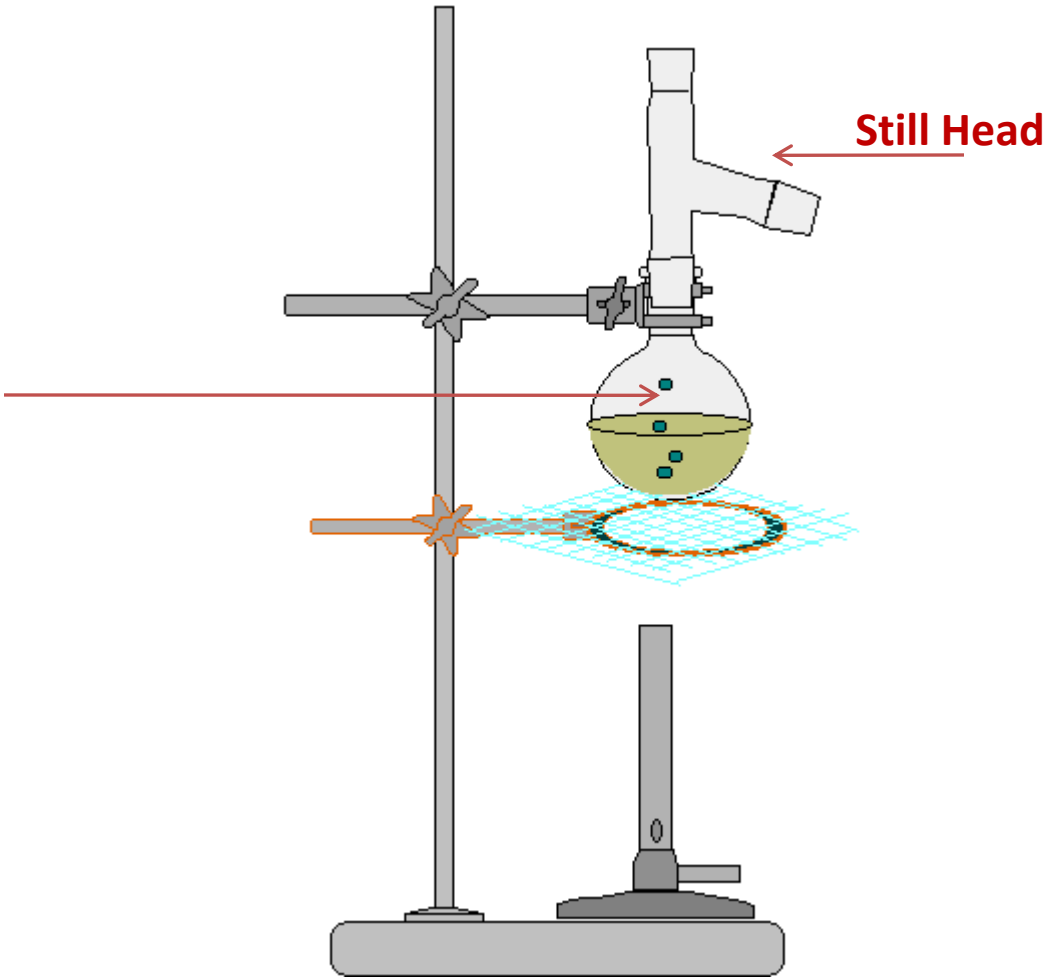


After delivering the liquid, remove the funnel.

Add few boiling chips to prevent bumping.

Apply a thin layer of grease on ground glass parts of the still head.

Attach the still head by inserting within the neck of the round bottomed flask.



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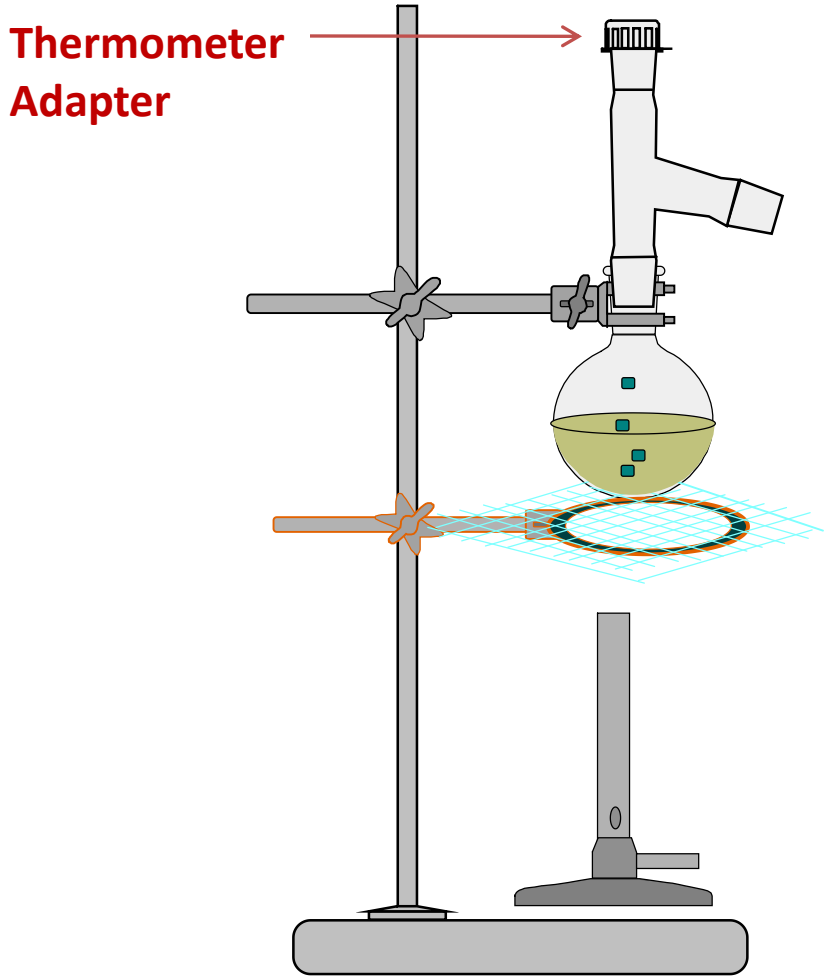
Attach the thermometer adapter.

Fix it on the top of the still head.



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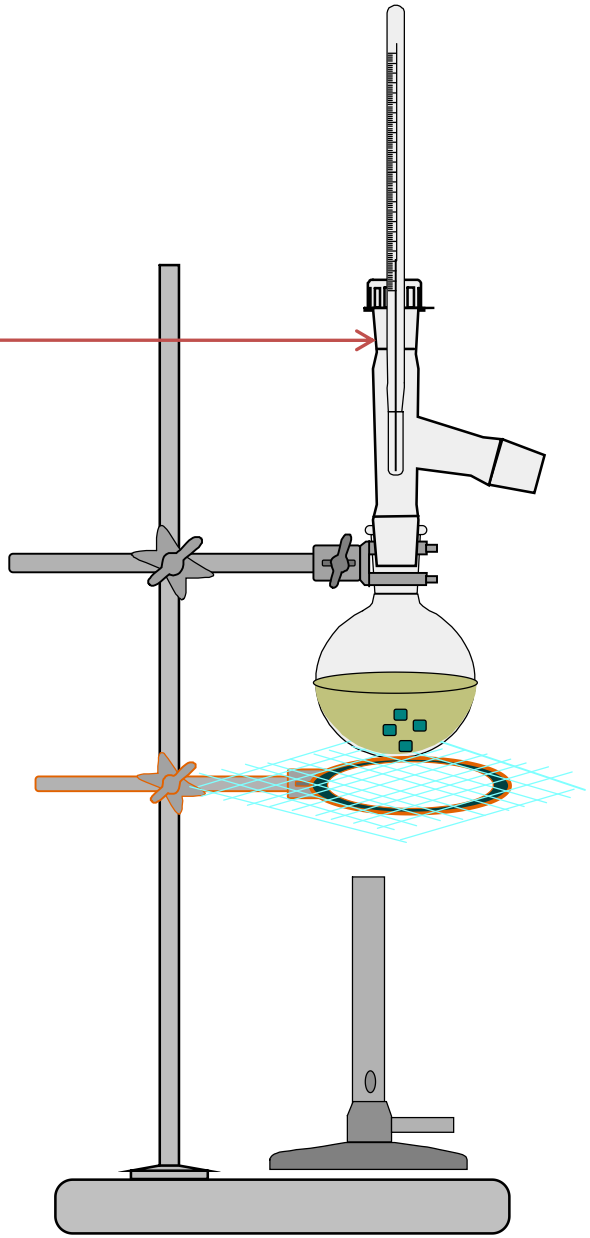
Insert the thermometer through the adapter.

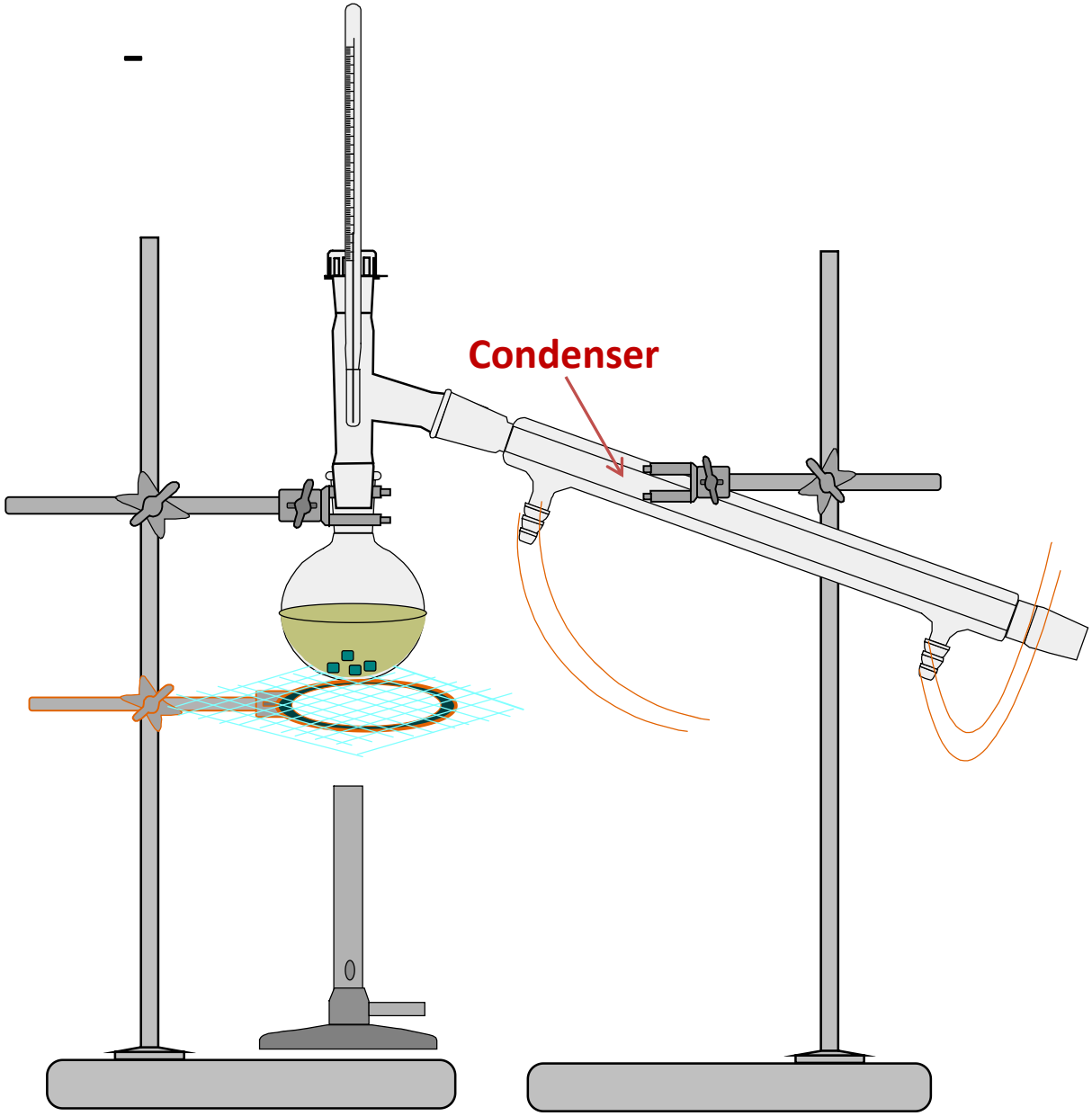
Make sure that the thermometer bulb is just below the lower end of the still head side arm.



Bring a stand and a clamp near your set-up.

Hold the condenser by the clamp and adjust the height of the condenser.

Carefully move the stand (and the condenser) so that the side arm of the still head slips into the condenser.



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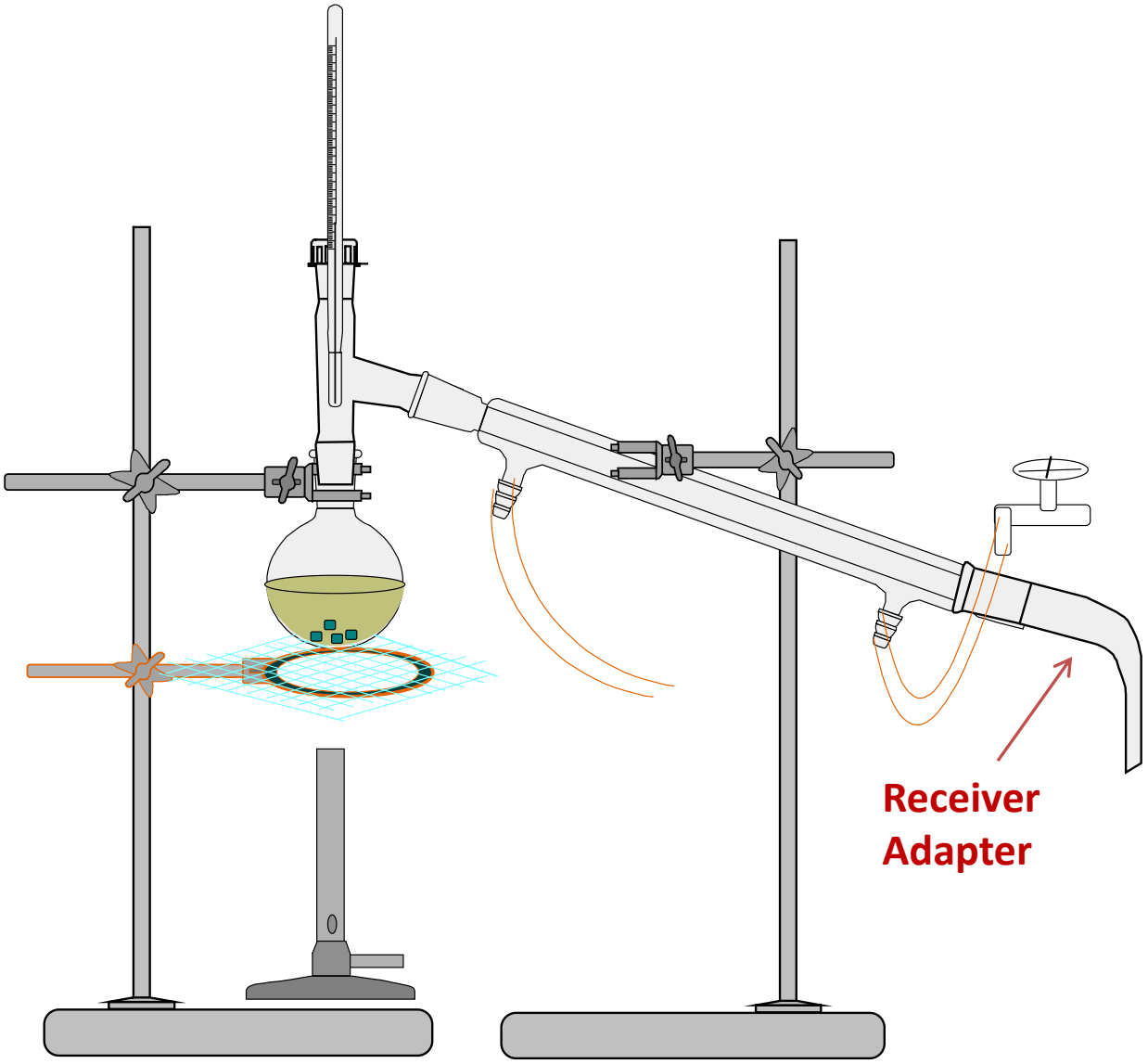
Apply a thin layer of grease to the male joint of the condenser.

Attach a receiver adapter to that end of the condenser. Use a plastic clamp.

Attach the lower rubber tube to the water tap.



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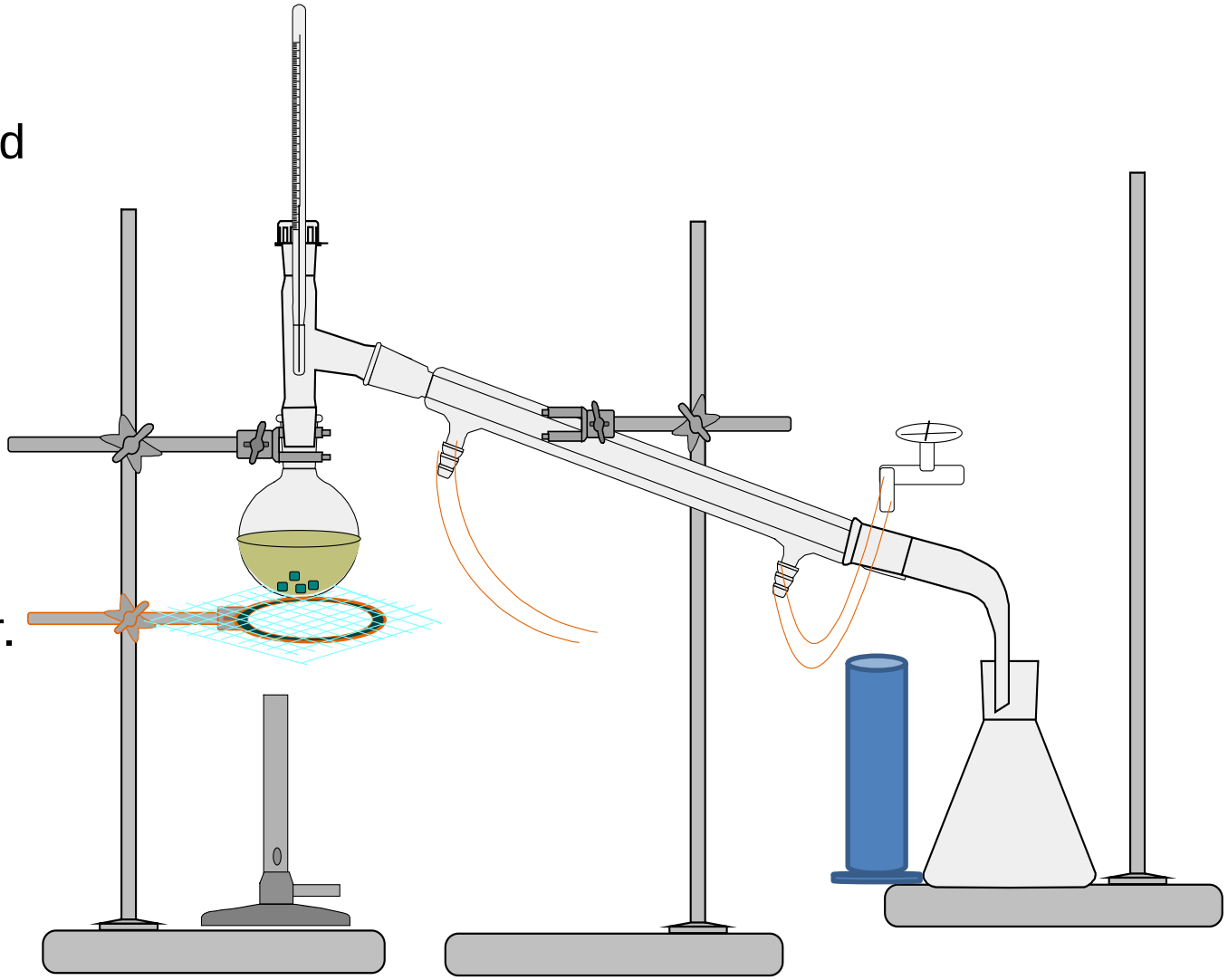
Bring a third stand near your set-up.

Place a conical flask (or a graduated Cylinder) under the tip of the receiving adapter.



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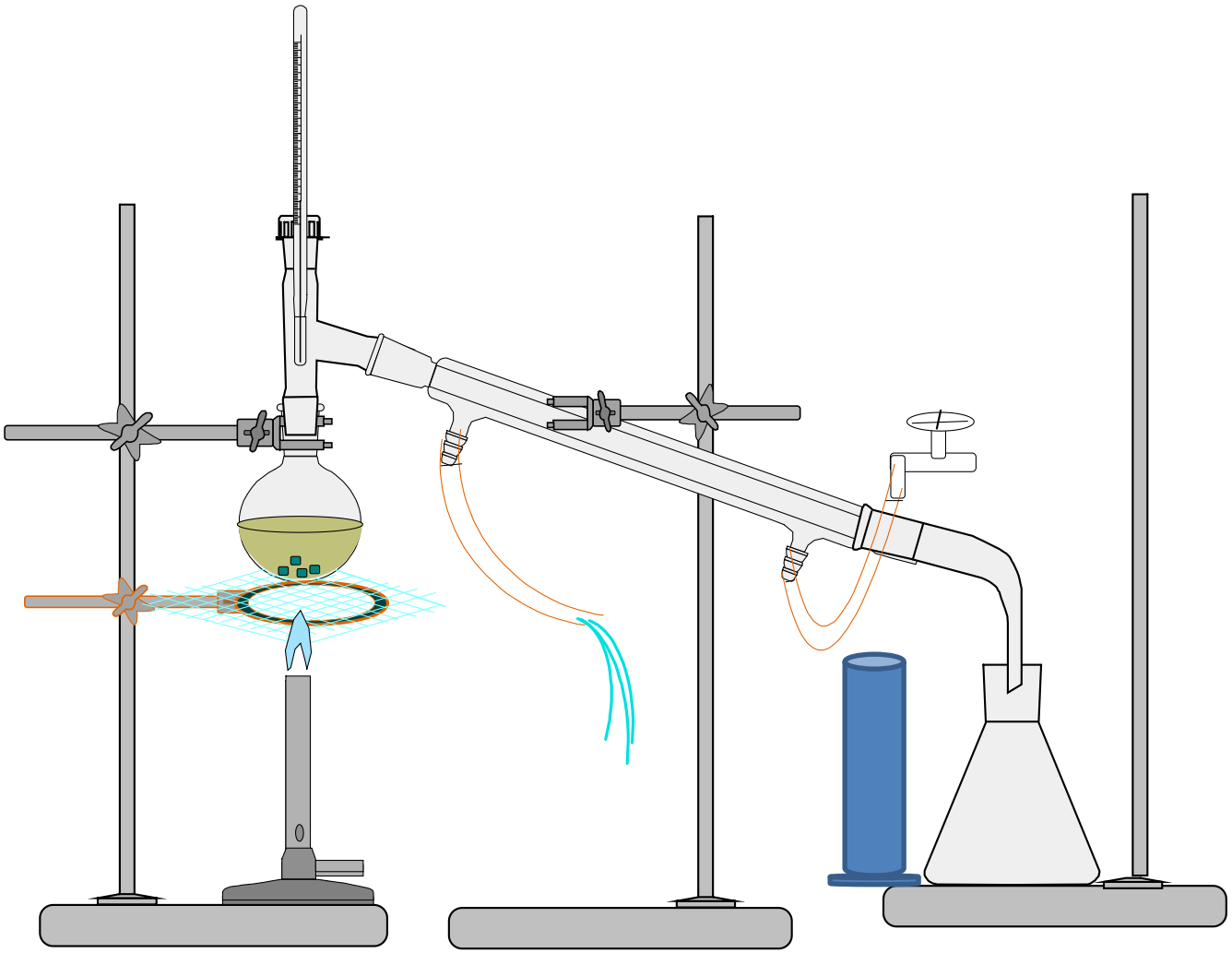
Open the water tap allowing the water to run through the condenser from below.

Check your set-up(**Instructor**).

Light the Bunsen burner to start your distillation.



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Make sure that the boiling is smooth-

No bumping.

Adjust the flame if necessary.

Record the temperature and volume of distillate.