

## Boiling interface: a guided discovery teaching activity

*Interfase en ebullición. Una actividad de enseñanza mediante descubrimiento guiado*

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### Resumen

En el presente trabajo se propone una actividad experimental sencilla y guiada para descubrir el mecanismo de formación de burbujas en una mezcla líquida binaria heterogénea en ebullición.

**Palabras clave:** Química general, prácticas químicas, enseñanza, burbujeo, ebullición, mezcla líquida heterogénea.

### Abstract

In the present work a simple guided experimental activity is proposed to discover the process of bubble formation during boiling of a binary heterogeneous liquid mixture.

**Keywords :** General Chemistry, chemical practices, teaching, bubbling, boiling, liquid heterogeneous mixture.

### CÓMO CITAR:

Andrade-Gamboa, J. J., Fernández-Albanesi, L., & Donati, E. R. (2025, abril-junio). Boiling interface: A guided discovery teaching activity. *Educación Química*, 36(2). <https://doi.org/10.22201/fq.18708404e.2025.2.88616>

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## Introduction

In basic chemistry courses, it is common to introduce students to the concepts of vapor pressure and boiling temperature for a liquid substance in its pure state at the initial stages of course development. These macroscopic characteristics of substances are intimately related to molecular properties that govern the interactions between molecules (Tro, 2014).

The boiling point is defined as the temperature at which the vapor pressure of the substance equals the external pressure. This point correlates with the boiling phenomenon, which involves the formation of bubbles within the bulk of the liquid.

The existence of bubbles and their release into the gas phase strictly requires a vapor pressure inside the bubble that is slightly higher than the external pressure. In this way, the vapor pressure mechanically balances the opposite effects of external pressure, the interfacial (vapor-liquid) tension, and the hydrostatic pressure produced by the liquid above the bubble. Moreover, the bubbles are formed at nucleation sites (cavities in the liquid, foreign material), essentially in the zone where the liquid is superheated—normally the bottom near the heating source in the case of pool boiling (Çengel & Ghajar, 2015).

The process of bubble formation through homogeneous nucleation involves higher overheating temperatures and occurs in the absence of heterogeneous nucleation sites. After growing, the bubbles migrate through the liquid to the vapor phase. Therefore, at a given external pressure, the liquid boils at a temperature higher than that of vapor-liquid equilibrium,  $T_{L-V}$  (Donati y Andrade-Gamboa, 2023), which is conventionally named the “boiling point” according to the definition provided above.<sup>1</sup>

When students begin studying binary liquid mixtures and their vaporization, two additional concepts are needed (Chang, 2008): the total vapor pressure over the free liquid surface is the sum of the vapor pressures of both components (Dalton’s law). Each vapor pressure depends on the mixture composition through Raoult’s law (for the  $i$ -th component, the vapor pressure in the mixture is  $p_v(i) = x_i p_v^\circ$ , where  $x_i$  is its molar fraction in the liquid and  $p_v^\circ$  is the vapor pressure of the component in its pure state).<sup>2</sup>

The boiling process in heterogeneous liquid mixtures is not usually explained in detail in basic literature.

In this paper, we present a simple experimental activity to guide students in constructing answers to the question and to form the basis for discussing the vaporization and boiling phenomena of a heterogeneous mixture of two components. Under the guided discovery teaching approach, the teacher coordinates activities that can be summarized in the following sequence (de Jong, 2006; Pozo Muncio & Gómez Crespo, 2009):

- Presentation of a problematic situation,
- Generation of hypotheses,
- Experimentation/observation,
- Drawing conclusions,
- Making an evaluation.

<sup>1</sup> Measurement of such temperature during boiling is best performed at vapor phase, as in any distillation experiment, and approximately corresponds to a vapor–liquid equilibrium in thermometer bulb by vapor condensation. Such temperature is known as vapor temperature and in the following it will be considered as a measure of the  $T_{L-V}$ .

<sup>2</sup> Assuming ideal behavior for vapor and liquid solution.

In the following, this process will be exemplified. In this method, observation is not carried out to verify statements but to stimulate reflection based on previously learned knowledge. In the present case, students must have knowledge of the topics of vapor pressure and boiling of pure liquids or homogeneous liquid mixtures, which have been briefly described in the introduction.

### Problematic situation presentation

The teacher presents a test tube containing a mixture of water and cyclohexane and asks the students what they expect regarding the boiling phenomenon in this mixture. If two-layer liquid heterogeneous mixtures have not been previously discussed, the teacher can initiate a brief discussion on immiscibility due to molecular properties and the criterion for identifying each phase based on the knowledge of their respective densities (cyclohexane—density =  $0.774 \text{ g/cm}^3$ —forms the top layer).

### Hypothesis Generation

Student predictions may include that both components will boil individually or that only the component with the lower boiling point will boil. If the teacher deems it necessary, this stage can be supported by proposing key questions to help students formulate their hypotheses.

### Experimental Activity

Students will recognize that the way to verify or refute the proposed hypothesis is by heating the mixture and observing its behavior. The teacher then proposes to carry out the experiment.

The materials required are distilled water, cyclohexane (CAS number 110-82-7), a small test tube (10-15 mL capacity), and a thermometer (optional).

**Caution:** Cyclohexane is flammable and potentially irritating to the skin and respiratory system (Young, 2007). Gloves and safety goggles must be worn, and the procedure must be performed in a fume hood.

**Procedure:** Water and cyclohexane are added to the test tube to form a two-layer system, each layer being approximately 2 cm high. The tube is placed on a hot plate, using a clamp and support, and heated slowly from room temperature. The temperature should be increased gradually.

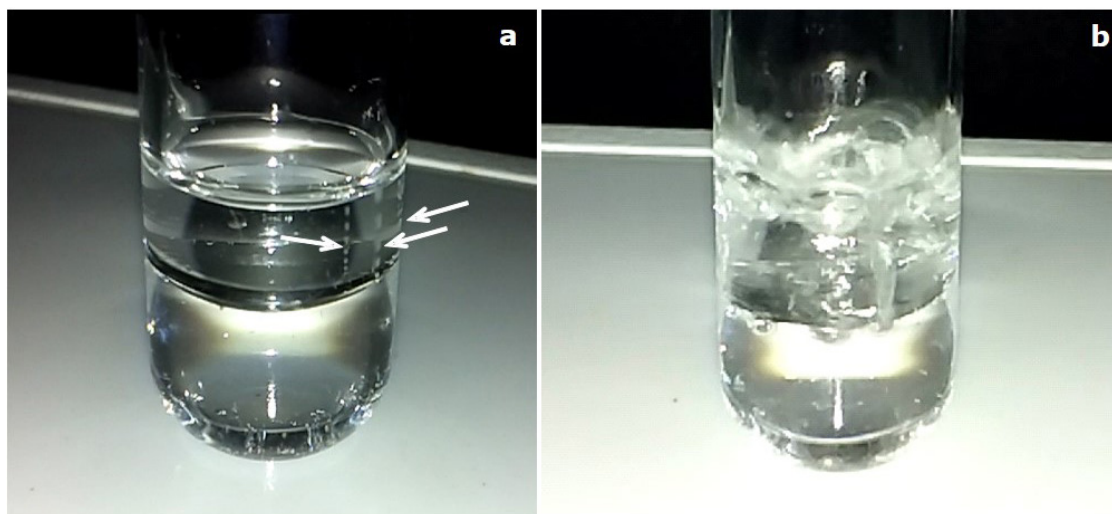
At a certain point, bubbling begins, as shown in Figure 1a, and the teacher encourages students to carefully observe the phenomenon to determine where the bubbles form. As the heating continues, the bubbling may become more tumultuous, as shown in Figure 1b. The observation reveals that bubbling occurs at the interface between the liquid phases, while bubble generation is not observed in the bulk of either the water or the cyclohexane.

Temperature measurements can optionally be taken. Using a digital thermometer<sup>3</sup>, temperatures at both phases and at the interface can be recorded. The obtained values depend on the heating time, as the hot plate provides continuous power. For instance, once bubbling has started, the temperatures measured ( $P_{\text{ext}} = 690 \text{ torr}$ )<sup>4</sup> 89 °C and 75 °C in the middle of the water and cyclohexane phases, respectively, and 77 °C at the interface.

<sup>3</sup> Digital Thermometer TTX 200 Type T.

<sup>4</sup> The experiment was carried out in a place located 693 m above sea level.

**FIGURE 1.** Two-layer water-cyclohexane liquid system under heating (upper layer is cyclohexane). Interface bubbling begins (a), as indicated by the arrows, and more energetic bubbling (b).



### Drawing a conclusion

After conducting the experimental activity, the teacher can coordinate a discussion with the students to conceptualize the most important physicochemical aspects of the subject. Some aspects that could form the core of this discussion are presented below.

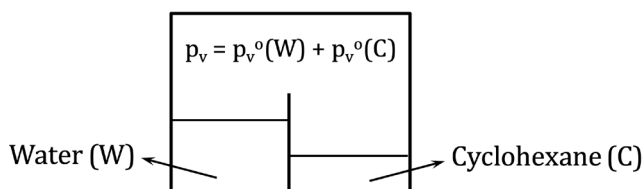
From the main experimental observation, it can be concluded that the boiling phenomenon in a liquid heterogeneous mixture can occur, and that boiling happens at the interface, while no boiling is observed in the individual liquids.

The interpretation of this behavior involves a sequence of reasoning that can be depicted as follows:

The formation of bubbles at the interface contributes to the vapor formation of both components of the mixture. The gas pressure in these bubbles can be conceptualized through a thought experiment (Figure 2), in which both liquids, at a given temperature, are contained in separate vessels, exposing their free surfaces to a closed empty space. Regardless of the quantities of the liquids, the total gas pressure is the sum of the vapor pressures of each pure component at the same temperature. Thus, the pressure of a bubble formed at the interface,  $p_v$ , is

$$p_v = p_v^\circ(W) + p_v^\circ(C) \quad (1)$$

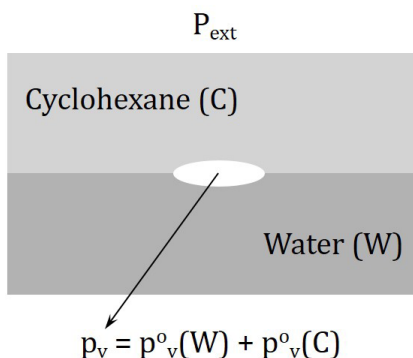
**FIGURE 2.** Experimental design to account for the contributions to the vapor pressure in a bubble at the interface.



where  $p_v^\circ(W)$  is the vapor pressure of pure water and  $p_v^\circ(C)$  is the vapor pressure of pure cyclohexane, both at the temperature of the interface. The bubble formation is schematized in Figure 3. Above a certain temperature, the vapor pressure at the interface will be sufficient to form bubbles. This is consistent with what was discussed in the

introduction regarding homogeneous systems: the vapor pressure inside the bubble must be significantly greater than the external pressure for bubble formation. Therefore, the interface temperature must be higher than the equilibrium liquid-vapor temperature at the interface.

**FIGURE 3.** Bubble formation at the interface. The vapor pressure inside the bubble ( $p_v$ ), as indicated above for the general case, is the sum of the vapor pressures of pure water  $p_v^o(W)$  and cyclohexane  $p_v^o(C)$ .



To calculate the vapor pressure at the interface using equation (1), the teacher can remind students that vapor pressure versus temperature data for pure substances are tabulated. Analytical fittings of these data are also available with the Antoine equation (Yaws, 2015):

$$\text{Log}_{10}[p_v^o(\text{torr})] = A - B/[T(^{\circ}\text{C}) + C] \quad (2)$$

where A, B, and C are constants (Antoine coefficients) tabulated for several liquids (Yaws, 2015). Table 1 contains such constants for water and cyclohexane.

**TABLE 1.** Antoine coefficients for temperature ranges between minimum ( $T_{min}$ ) and maximum ( $T_{max}$ ) temperatures (Yaws, 2015).

Substance	A	B	C	$T_{min}-T_{max}$ ( $^{\circ}\text{C}$ )
Water	8.05573	1723.6425	233.08	0.01-373.98
Cyclohexane	6.88938	1200.8256	218.815	-14.92-105.07

As an example, the vapor pressures of cyclohexane, water, and a mixture of both are calculated for  $T = 50^{\circ}\text{C}$  as follows. Using equation (2) and the coefficients from Table 1, we obtain:

#### Vapor pressure of water:

$$\log_{10} p_v^o(W) = 8.05573 - 1723.6425/[50 + 233.08] = 1.96684 \Rightarrow p_v^o(W) = 10^{1.96684} \text{ torr} = 92.65 \text{ torr.}$$

#### Vapor pressure of cyclohexane:

$$\log_{10} p_v^o(C) = 6.88938 - 1200.8256/[50 + 218.815] = 2.42227 \Rightarrow p_v^o(C) = 10^{2.42227} \text{ torr} = 264.41 \text{ torr.}$$

Finally, the vapor pressure of a mixture of water and cyclohexane is calculated (equation 1) as:

$$p_v = p_v^o(W) + p_v^o(C) = 92.65 \text{ torr} + 264.41 \text{ torr} = 357.06 \text{ torr}$$

In addition, the teacher can encourage students to plot the vapor pressure curves for the two components (using equation 2) and the sum of them. The sum represents the temperature dependence of  $p$  as described in equation (1). Such a graph is shown in Figure 4, which provides a more direct method for calculating the vapor pressures than the analytical procedure and allows a direct relationship between numerical values and the phenomenon being described.

From Figure 4, it is straightforward to calculate, for an external pressure ( $P_{\text{ext}} = 690$  torr), the equilibrium temperatures,  $T_{\text{L-V}}$ , for the individual components and the mixture. The results are:

$$T_{\text{L-V}}(\text{W}) = 97.3\text{ }^{\circ}\text{C},$$

$$T_{\text{L-V}}(\text{C}) = 77.6\text{ }^{\circ}\text{C}$$

$$T_{\text{L-V}}(\text{mixture}) = 66.9\text{ }^{\circ}\text{C}$$

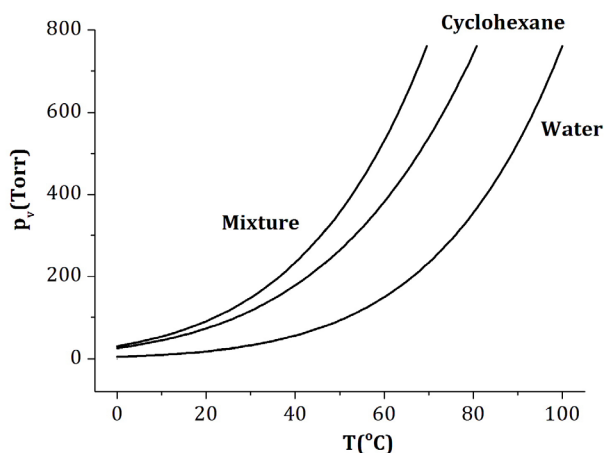


FIGURE 4. Vapor pressures of water, cyclohexane, and the mixture as a function of temperature. All curves are plotted up to the value of normal pressure (760 torr).

Comparing these values with the measured liquid temperatures (89 °C, 75 °C for water and cyclohexane, respectively), it can be concluded that while bubbling at the interface occurs, the temperatures of each layer are lower than their respective boiling points, and bubbling cannot be produced in each phase (it should also be considered that liquid superheating is necessary for boiling). Conversely, the temperature of the liquid-vapor equilibrium at the interface is lower than the measured value (77 °C). This suggests that bubble formation requires a temperature increase of approximately 10 °C. As observed in the experiment (Figure 1a), the best locations for nucleation are on the inner surface of the test tube in contact with the interface (see also supplementary material).

In the absence of temperature measurements, a qualitative interpretation of the phenomenon can also be made from Figure 4. Since, at any external pressure,  $T_{\text{L-V}}(\text{mixture})$  is lower than  $T_{\text{L-V}}(\text{W})$  and  $T_{\text{L-V}}(\text{C})$ , it can be concluded that a mixture of immiscible liquids will boil at a temperature lower than the boiling point of any of the individual components in their pure form (Pavia, Lampman, Kriz, and Engel, 2002).

## Making an evaluation

The teacher can introduce applications related to the phenomenon discussed. The final statement of the previous section provides the conceptual foundation for one of the most popular applications: steam distillation. This process is used to extract high-boiling natural products that are immiscible with water (such as essential oils) at temperatures below the boiling point of water (Pavia, Lampman, Kriz, & Engel, 2002; Doyle & Mungall, 1980). Steam distillation avoids the decomposition of natural products. In this process, the vapor, composed of both components, is subsequently condensed. It is important to calculate the vapor composition, which can be done using Dalton's law: the partial pressure of each component is the product of its molar fraction and the total pressure. In this case, for cyclohexane:

$$p^{\circ}(C) = y(C)P_{\text{ext}} \quad (3)$$

where  $y(C)$  is the molar fraction of cyclohexane at vapor. From Figure 4, at  $T_{L-V} = 66.9^{\circ}\text{C}$ ,  $p^{\circ}(C) = 485.9$  torr and from equation (3), we can calculate:

$$y(C) = 485.9 \text{ torr} / 690 \text{ torr} = 0.70.$$

This shows that the vapor is richer in the more volatile component. In the case of steam distillation used to extract high-boiling point substances, water is the most volatile component, and the calculation of the steam composition helps estimate the amount of water needed to carry out the procedure (Pavia, Lampman, Kriz, & Engel, 2002; Doyle & Mungall, 1980).

A measurement of the vapor temperature under the theoretical value of  $T_{L-V}$  requires enough interfaces within the heterogeneous mixture distributed throughout the volume. This is achieved, for example, by forming an emulsion between both liquids. In steam distillation of plant products, a similar situation occurs due to the presence of multiple water-vegetal material contacts.

Other applications of this phenomenon include:

- The use of fuel-water emulsions to promote atomization (spraying) in combustion chambers, induced by micro-explosions due to the violent vapor formation in the liquid-liquid emulsion (Avedisian & Andres, 1978; Kadoka & Yamasaki, 2002).
- The use of mixtures of immiscible liquids with water (e.g., n-hexane-water) to increase the efficiency of energy transfer through interface boiling in heat exchangers (Sump & Westwater, 1970).

## Some Topics for Further Discussion

To stimulate students' understanding, several situations can be proposed for discussion. The following questionnaire could serve as a guide:

- Regarding all aspects discussed, what would you expect if the total external pressure is:
  1. Lower than atmospheric pressure?
  2. Higher than atmospheric pressure?

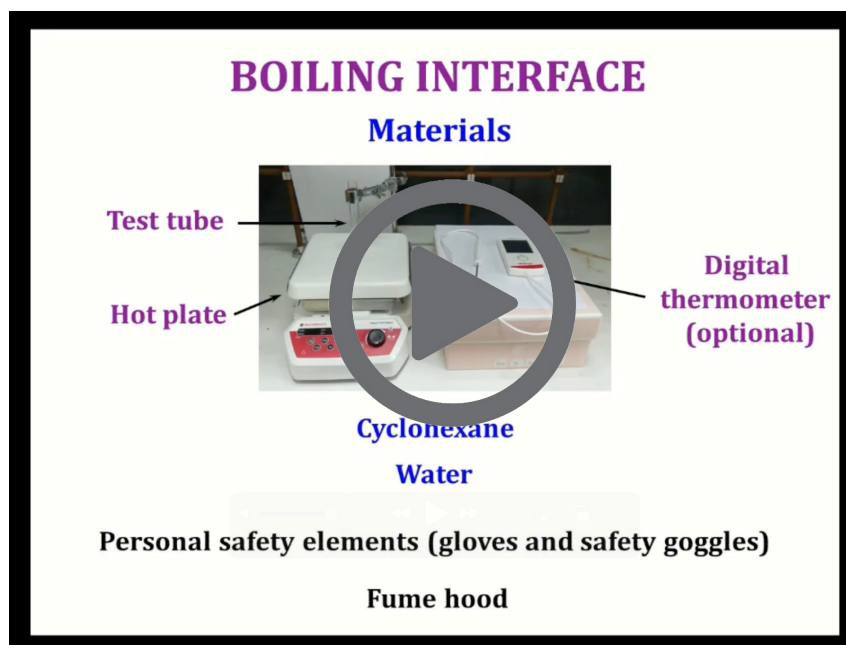
- What would the graph in Figure 4 look like for a natural product with a high boiling point? Explain why it can be steam distilled at temperatures below its boiling point to avoid decomposition.
- Imagine the behavior of a system formed by three layers of pure liquids. Propose different characteristics for each liquid and discuss each case.
- Could a solid be steam distilled? Explain.
- If an experimental setup like that depicted in Figure 2, but open to the external atmosphere, is heated as in the performed experiment, what behavior would you expect?
- If the liquid mixed with water were water-miscible, what alternative formulations should be considered, and how would the graph in Figure 4 change?

### Final Considerations

A simple laboratory experiment demonstrates that boiling in a heterogeneous liquid mixture occurs at the liquid-liquid interface at a temperature lower than the boiling point required for each substance individually, at each vapor pressure of the mixture. Under a guided discovery approach, students conduct an experiment that allows them to make observations like those that generate knowledge in scientific fields. Regardless of the topic, such activities generate more enthusiasm and motivation than traditional laboratory work, in which a concept learned theoretically is tested. In particular, the proposed experiment clearly visualizes the essence of the behavior of a heterogeneous liquid mixture when heated, complementing the descriptions in basic literature for a deeper understanding.

### Supplementary Material

To complement the images in Figure 1, a video showing different bubble formation scenarios at the interface is available as supplementary material.



### Acknowledgment

The authors would like to acknowledge the suggestions of the anonymous reviewers, which greatly improved the clarity of the manuscript.

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