

# Estimation of Absolute Zero

**Objective:** To determine the difference between the absolute (Kelvin) temperature scale and the Celsius scale, and obtain an estimate of absolute zero

**Equipment:** 125-mL Erlenmeyer flask assembly with stopper and pinch clamp; 600-mL beaker; Bunsen burner; ring stand with iron ring and clamp; wire-gauze pad; pan or trough filled with water; thermometer

**Safety:** Wear safety goggles at all times when working at the lab bench.

**Waste:** None

## INTRODUCTION

The measurement of temperature uses scales that are based on arbitrary, empirical reference points. The Fahrenheit scale, created in 1724, established the reference point of  $0.0^{\circ}\text{F}$  as the temperature of a brine solution consisting of water, ice, and ammonium chloride. The second reference point was the freezing point of pure water, which was determined to be  $32^{\circ}\text{F}$ . After additional refinements by other scientists, the boiling point of water was determined to be about  $180^{\circ}$  higher than the freezing point, or  $212^{\circ}\text{F}$ .

The Celsius (or centigrade) scale was developed by the Swedish astronomer Anders Celsius in 1744. The first reference point was the freezing point of water, which was set as  $0.0^{\circ}\text{C}$ ; the second reference point of  $100^{\circ}\text{C}$  coincided with the boiling point of pure water. The advantage of this scale is that the reference points are conveniently set exactly 100 degrees apart.

The need for an absolute temperature scale was recognized by William Thomson (also known as Lord Kelvin), who established the Kelvin scale in 1848 using an “air-thermometer” based on the thermal expansion of atmospheric gases. Lord Kelvin determined that absolute zero coincide with  $0.273^{\circ}\text{C}$ , and proposed that a temperature change of  $1.0^{\circ}\text{C}$  was equal to a change of 1.0 degree on the Kelvin scale (or 1.0 Kelvin—the term *degree* is not applied to temperatures on the Kelvin scale). The relationship between these two temperature scales is shown in Equation (1).

$$\text{K} = ^{\circ}\text{C} + 273 \quad (1)$$

The concept of absolute temperature is critical in many areas of chemistry. The **third law of thermodynamics**, for example, states that the entropy of a pure, crystalline solid at 0 Kelvin is equal to zero. The gas laws also relate the properties of gases to absolute temperature. Charles’s Law, for example, states that the volume of a gas is directly proportional to absolute temperature.

The behavior of ideal gases is explained by the following postulates of the **kinetic molecular theory**:

1. Most of the volume occupied by a sample of gas is empty space; the volume occupied by the atoms or molecules is essentially negligible.
2. Atoms or molecules in the gas phase do not interact with each other due to the large distances between them.
3. The kinetic energy of a gas sample is directly proportional to absolute temperature. One consequence of this is that the volume occupied by a gas sample will decrease as temperature decreases at constant pressure.

Postulates 1 and 3 provide a basis for estimating the value of absolute zero. Combining these two postulates, the volume occupied by the gas should approach a value of zero as the temperature approaches absolute zero. At absolute zero the kinetic energy of the atoms or molecules is zero and they occupy no volume. For an ideal gas, a plot of volume vs. temperature should allow us to extrapolate to zero volume to estimate absolute zero. Air, which consists primarily of  $N_2$  and  $O_2$ , behaves as an ideal gas under most conditions. Some gases, such as water vapor, do not behave ideally. Significant interactions between the molecules in the gas phase result in non-linear behavior, and a volume slightly less than that of an ideal gas under similar conditions.

In this lab, we will use the concept of an air-thermometer to verify the relationship between the Celsius and Kelvin scales illustrated in Eq. (1). Starting with the ideal gas law, we can rearrange to obtain a relationship between volume and temperature as:

$$V = \frac{nRT}{P} = \left(\frac{nR}{P}\right) T \quad (2)$$

Assuming a constant number of moles at constant pressure, Eq. (2) reduces to

$$V = k T \quad (3)$$

where  $k$  is a constant and  $T$  is the temperature in Kelvin. If we can measure the volume occupied by the gas at two different temperatures, then we can set up a ratio between the two measurements as indicated in Equation (4).

$$\frac{V_1}{V_2} = \frac{(kT_1)}{(kT_2)} \quad (4)$$

The constants will cancel. If we let  $Y$  equal the constant in Eq. (1), we can rewrite Eq. (1) as

$$T \text{ (K)} = t \text{ (}^\circ\text{C)} + Y \quad (5)$$

and we can rewrite Eq. (4) as:

$$\frac{V_1}{V_2} = \frac{(t_1 + Y)}{(t_2 + Y)} \quad (6)$$

If  $V_1$ ,  $V_2$ ,  $t_1$ , and  $t_2$  are all known by experimental measurement, this equation can be solved algebraically to determine the value of  $Y$ . Using our air-thermometer, we can measure the volume of air accurately by replacing it with an equal volume of water and measuring the mass of water. From the mass and density of water we can determine volume. The volume occupied by the gas will be determined at two different temperatures:  $T_{\text{high}}$ , which equals the boiling point of water ( $100^\circ\text{C}$ ), and  $T_{\text{low}}$ , which is approximately room temperature ( $\sim 20^\circ$ ). Using the volume-temperature relationship in Eq. (6) we can estimate the value of  $Y$ .

Alternatively, we can perform a graphical analysis in which we plot volumes vs. temperature (in  $^\circ\text{C}$ ) and extrapolate to zero volume. The point at which the line intersects the x-axis represents the difference between  $0.0^\circ\text{C}$  and absolute zero on the Kelvin scale.

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## Pre-Lab Questions

1. List two assumptions of the kinetic molecular theory cited in this lab exercise, and how they are relevant to the estimation of absolute zero.

2. A student performed this experiment and collected the following data:

$$V_{\text{high}} \text{ at } T_{\text{high}} (100.0 \text{ }^{\circ}\text{C}) = 262 \text{ mL}$$

$$V_{\text{low}} \text{ at } T_{\text{low}} (22.4 \text{ }^{\circ}\text{C}) = 201 \text{ mL}$$

- a) Plot volume on the ordinate (y-axis) vs. temperature on the abscissa (x-axis). Draw a line connecting the points, and extrapolate this line to where it intersects the x-axis.

$$Y = \text{_____ } ^{\circ}\text{C}$$

- b) Calculate the percent error between the experimentally determined value of Y and the accepted value of absolute zero,  $-273 \text{ }^{\circ}\text{C}$ .

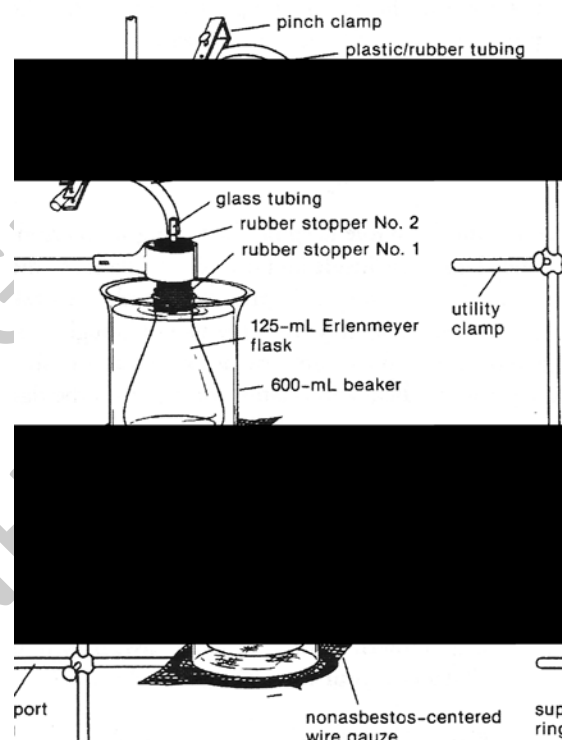
$$\% \text{ error} = \text{_____}\%$$

3. Extrapolation using more than two data points can decrease the error in the estimated value. How could you modify the procedure to obtain a reliable third data point, e.g., volume at a third temperature?

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## PROCEDURE

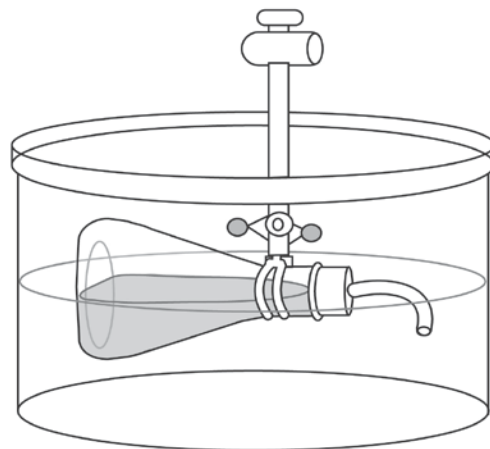
1. Obtain the necessary stopper/tubing assembly from the lab cart and assemble the Erlenmeyer flask apparatus as illustrated in Figure 1. Ensure that the tubing connections are tight and will not leak. Have your TA check the apparatus before continuing.
2. Weigh the flask assembly (Erlenmeyer+stopper+tubing+pinch clamp) to the nearest 0.1 g, and record this mass on line 4 on your Data Sheet.
3. Fill the 600-mL beaker with about 300 mL of tap water, and place it on the wire gauze pad/ring stand as indicated in Figure 1. Lower the flask assembly into the beaker until the water level in the beaker is even with the bottom of the stopper in the neck of the flask. Make sure that the flask is not making contact with the bottom or sides of the beaker. Clamp the flask securely in this position as indicated in Figure 1.



**Figure 1. Air-Thermometer apparatus**

4. Open the pinch clamp on the tubing so that the tubing is open, but the pinch clamp is still securely attached to the tubing. Heat the water in the beaker until it boils, and continue boiling for 5 minutes.
5. Measure the temperature of the boiling water in your beaker, and record this temperature as  $T_{\text{high}}$  on line 1 on your Data Sheet.
6. Keep the water boiling while you close the pinch clamp on the tubing. Tighten the extension clamp holding the rubber stopper assembly, and use this clamp as a handle to move the flask assembly. Remove the flask assembly from the beaker and submerge it in the pan or trough containing cold tap water.
7. With the flask neck and tubing submerged under the surface of the water, carefully open the pinch clamp. Water will flow into the flask as the air in the flask contracts as it cools. Be sure to keep the flask and tubing submerged during this entire process!

8. While holding the flask and tubing under water, allow the flask to cool for 10 minutes. You can also run cold tap water over the flask to cool it more quickly, but be sure to keep the flask and tubing submerged under water.
9. While keeping the flask submerged, adjust the level of the flask in the trough so that the water level inside the flask matches the water level outside the flask (i.e., in the trough), as illustrated in Figure 2. This step ensures that the pressure inside and outside the flask are equal. When the water levels are equal, close the pinch clamp tightly and remove the flask assembly from the trough. Measure the temperature of the water in the trough, and record this value on line 2 on your Data Sheet as  $T_{\text{low}}$ .



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**Figure 2. Procedure to equalize pressure in the air thermometer apparatus**

10. With the flask assembly upright on the bench top, remove any water in the plastic tubing above the pinch clamp using a paper towel or cotton swab. Then open the pinch clamp and allow any water in the tubing to drain into the flask. Remove the extension clamp, dry the flask assembly with a towel, and reweigh the assembly. Record the mass on line 6 on your Data Sheet. Calculate the mass of water that was sucked into the flask assembly by difference, and record this mass on line 7 on your Data Sheet.
11. Using a piece of tape or a marker, mark the level of the bottom of the stopper on the neck of the flask assembly. Remove the stoppers and fill the flask to the brim with tap water. Open the pinch clamp slightly and re-insert the stoppers, pushing them down until the bottom of the stopper assembly aligns with the marker or tape on the neck of the flask. This process will cause some water to fill the tubing in the stopper assembly. If the level of water in the tubing is below the position of the pinch clamp, add water to the tubing. Once the level of water in the tubing is above the level of the pinch clamp, tighten the clamp and remove any excess water. The volume of water in the flask assembly is now the same as the volume of air in the original sample. Reweigh the water-filled flask assembly and record your mass on line 3 on the Data Sheet. Again, calculate the mass of water in the filled flask by difference. Record this mass on line 5 on your Data Sheet. (Note: the volume of water in the flask will not be the same as the nominal volume printed on the flask.)
12. Perform the required calculations for Trial #1. Record your results and plot your data as instructed. Report your results to your TA before continuing.

- Repeat the experiment with a second clean, dry Erlenmeyer flask. It is important that you use a different flask for the second attempt, since it will be difficult to remove all the water vapor from the previous flask. The presence of water vapor would contribute to the partial pressure in the flask and affect your results.
- If time permits, perform a third trial.

## CALCULATIONS

**Perform the following calculations for each trial, and record your results on the Data Sheet in the appropriate spaces.**

- Calculate the volume of water drawn into the flask for each trial using Equation (7).

$$\text{Volume (mL)} = \text{mass H}_2\text{O (g)} \times \text{density of water (g/mL)} \quad (7)$$

The mass of water drawn into the flask was calculated by difference, and is found on line 7 on the Data Sheet. The density of water can be assumed to be 1.00 g/mL (3 significant figures.) for the water temperatures typically encountered in this exercise.

- In a similar fashion, calculate the volume of water required to completely fill the flask and stopper assembly, using the mass of water from line 5 of the Data Sheet. This volume equals the volume of air in the flask assembly at the high temperature. Record this on the Data Sheet as  $V_{\text{high}}$ .
- The volume of air in the flask at the low temperature ( $T_{\text{low}}$ ) can be found as the difference between  $V_{\text{high}}$  and the volume of water drawn into the flask at  $T_{\text{low}}$ . Record this volume on your Data Sheet as  $V_{\text{low}}$ .
- Using Eq. (6), calculate the value of Y algebraically. Record this value on line 8 on the Data Sheet.
- Prepare a plot of Volume vs. T ( $^{\circ}\text{C}$ ). To ensure that you have enough room to extrapolate your plot, rotate your graph paper  $90^{\circ}$  so that the x-axis is on the longer side of the graph. Allow enough room to the right of the origin ( $x = 0$ ) to plot volumes at both  $T_{\text{high}}$  and  $T_{\text{low}}$ , and enough room on the left of the origin to extrapolate your plot to where it intersects the x-axis.
- Plot your  $V_{\text{high}}$  and  $V_{\text{low}}$  values on the graph paper, and extrapolate the line to where it intersects the x-axis. Determine the temperature (in  $^{\circ}\text{C}$ ) at the point of intercept. Record this temperature as Y on line 10 on your Data Sheet.



# Data Sheet

	<i>Trial 1</i>	<i>Trial 2</i>	<i>Trial 3</i>
1. Temp. of boiling water ( $T_{\text{high}}$ ), °C	_____	_____	_____
2. Temp. trough water ( $T_{\text{low}}$ ), °C	_____	_____	_____
3. Mass of flask assembly (full of water), g	_____	_____	_____
4. Mass of flask assembly (empty), g	_____	_____	_____
5. Mass of water needed to fill flask, g	_____	_____	_____
Volume of air needed to fill flask assembly, $V_{\text{high}}$ , mL	_____	_____	_____
6. Mass of flask + water drawn in by cooling, g	_____	_____	_____
7. Mass of water drawn in by cooling, g	_____	_____	_____
Volume of water drawn in by cooling, mL	_____	_____	_____
Volume of air in flask at $T_{\text{low}}$ $V_{\text{low}}$ , mL	_____	_____	_____
8. Value of Y calculated algebraically, °C	_____	_____	_____
9. Value of Y obtained graphically, °C	_____	_____	_____
10. Best value for absolute zero, °C	_____	_____	_____

## Post-Lab Questions

1. A student performing this experiment used a thermometer that consistently read temperatures that were 2 degrees lower than the actual temperature. How would this affect the experimentally determined value of Y? Explain.
2. Another student forgot to completely close the pinch clamp before removing the flask from the boiling water, and did not close the clamp until he had placed the flask on the bench top. How would this affect the extrapolated value of Y? Explain.
3. Another student decided to use the same flask from trial 1 to perform a second determination without completely drying the flask. How would this affect the values of  $V_{\text{low}}$  and  $V_{\text{high}}$ ? Explain.
4. The true value of Y is  $-273^{\circ}\text{C}$ . Calculate the percent error in your experimentally determined value of Y.

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