Objectives

- To determine the molecular mass of an unknown volatile liquid using the Dumas method and the ideal gas law.

In the early 19th century, Jean-Baptiste Dumas, a distinguished French chemist, created a relatively simple method for determining the molecular mass of a volatile substance. In this experiment we will use a modified version of his technique to determine the molecular mass of an unknown volatile liquid.

The density of a gas is given by the ideal-gas equation as,

\[ D_{\text{gas}} = \frac{m}{V} = \frac{PM}{RT} \quad \text{(1)} \]

where \( M \) is the molecular mass of the gas. Solving for molecular mass, we obtain:

\[ M = \frac{mRT}{PV} \quad \text{(2)} \]

Thus, the molecular mass of a gas can be determined by measuring the temperature, pressure, mass, and the volume of a substance in its gaseous phase.

In this experiment we shall use a 125-mL Erlenmeyer flask in place of the glass bulb used by Dumas. A small sample of an unknown volatile liquid will be placed in the flask and the liquid vaporized by immersing the flask in a hot water bath. A piece of aluminum foil will be used to seal the flask and a tiny pinhole made in the foil to allow excess vapor to escape. The temperature of the gas will be determined by measuring the temperature of the water bath surrounding the flask and assuming that the gas and the water bath are in thermal equilibrium. Because an excess initial quantity of liquid is used, the volume of vapor produced from the liquid is greater than the volume of the flask. Upon heating, the vapor that is created initially pushes the air out of the flask and then the vapor begins exiting the flask through the pinhole until the pressure inside the flask is equal to the atmospheric pressure. Thus, the pressure of the gas can be determined by measuring the air pressure in the laboratory using a barometer. After the last of the liquid is vaporized the flask is removed from the hot water bath and the vapor inside the flask is allowed to cool and recondense. The mass of the vapor is measured by weighing the condensate remaining in the flask. The volume of the vapor is equal to the volume of the flask. To determine the volume of the flask we will weigh the flask after filling it to the brim with deionized water and then measure the temperature of the water. From the measured mass of the water and the known density of water at a given temperature, we can determine its volume, and thus the volume of the flask and the vapor. Three trials will be performed to determine the average molecular mass of the unknown liquid. A Table of densities of water at various temperatures is given below:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (g/mL)</th>
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<tbody>
<tr>
<td>15</td>
<td>0.9991</td>
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<tr>
<td>Temperature (°C)</td>
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<td>16</td>
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</tr>
<tr>
<td>30</td>
<td>0.9957</td>
</tr>
</tbody>
</table>

Information from the CRC *Handbook of Chemistry and Physics*, 64th ed., 1983-4

**Procedure**

**Materials and Equipment**

You will need the following additional items for this experiment: second utility clamp split stopper, ring stand, hot plate,
aluminum foil, rubber band, 1 small dithizone dye crystal, 2-3 boiling chips

SAFETY

Students should wear goggles. All heating should be done in the fume hood.

WASTE DISPOSAL: All chemicals used must go in the proper waste container for disposal.

Experimental Set-up and Procedure

1. Using a hot plate, a ring stand, two utility clamps, your 600-mL beaker, a 125-mL Erlenmeyer flask, a split stopper and your thermometer, assemble the apparatus shown in the Figure below inside one of the laboratory fume hoods. Use the split stopper to help clamp the thermometer. Be certain there is sufficient water in the 600-mL beaker to surround the bottom and neck of the 125-mL Erlenmeyer flask, but no so much that it overflows upon immersion of the flask. You do not need the foil and rubber band attached at this time. To assist in observation of the unknown liquid it is a good idea to mount the flask at a slight angle, as shown. Take special care that none of the water enters the flask when placing it in the beaker.
2. Again note that the level of the water in the hot water bath should be almost to the brim of the beaker when the flask is inserted, so that it covers as much of the neck of the clamped Erlenmeyer flask as possible. When you have the basic set-up accomplished, remove the flask. Place several boiling chips in the water bath and begin heating the bath. You may want to keep a squirt bottle of water handy to help maintain the level of water in the bath between trials.

3. Fill the 125-mL Erlenmeyer flask to the brim with deionized water and weigh the flask being careful not to spill any of the water out. Be sure the outside of the flask is completely dry. Record this mass. Using your thermometer measure the temperature of the water in the flask. Record this temperature.

4. Dry the 125-mL Erlenmeyer flask thoroughly inside and out using either an acetone rinse or by heating the flask over a Bunsen burner and then allowing it to cool to room temperature (your instructor will tell you which procedure to use). If you use acetone be certain that none of the waste acetone goes down the sink; all chemical waste should be placed in the proper waste container. Place the dry empty flask on the digital balance and record its mass.

5. Subtract the mass of the dry empty flask from the mass of the flask filled with water to determine the mass of water in the flask. Using Table 1 in the background section of this experiment determine the density of the water at the temperature recorded. Using these values determine the volume of your flask. Record these values.

6. If there is a barometer in your laboratory room, use it to measure the atmospheric pressure and record this value on your report form. Otherwise your instructor should provide this value. Using your forceps (tweezers), add a single crystal – just a single speck about the size of a grain of pepper – of the dry dithizone dye to the flask. Cover the flask mouth with a small piece of aluminum foil and secure in place with a rubber band. (Keep the aluminum foil cap as short as possible, so that it does not extend down more than a few centimeters below the position of the rubber band; this will help keep water from getting trapped between the foil and the flask.) Using a push-pin, make a tiny pinhole in the foil cap. Measure and record the mass of the dry flask containing the dithizone crystal with the foil and rubber band in place using the digital balances.

7. Obtain an unknown sample from your instructor and record the unknown number on your report form (your instructor may also require you to attach the label from the unknown to your report).

Trials 1 – 3

1. Bring the water in the bath to a gentle boil. Careful remove the foil cap so as not to tear it and add approximately 2 mL of your unknown liquid to the flask. Swirl to dissolve the dithizone dye in the unknown liquid. Secure the cap to the flask and carefully immerse the flask in the boiling water bath. Clamp the neck of the flask to the support at a slight angle as shown on the previous page using your utility clamp and lower it so that as much of the neck of the flask as possible is submerged in the boiling water bath. It is extremely important that no water gets inside the flask and that the water in the bath is already boiling when you immerse the flask. Mount the thermometer in the bath, so it is as close to the unknown as possible.

2. The unknown is a volatile liquid that boils at a temperature below that of water. Consequently, the liquid inside the 125-mL Erlenmeyer flask will begin to boil when immersed in the boiling water bath. Watch the liquid carefully. After driving out all of the air in the flask the vapor from the unknown liquid should begin to exit the pinhole in the foil. The unknown liquid should vaporize completely (as evidenced by the disappearance of the color of the dissolved dithizone dye and the dye precipitating out on the wall of the flask). Keep the flask in the boiling water for three minutes after the last of the unknown liquid vaporizes to ensure that the vapor is in complete thermal equilibrium with the boiling water in the bath. Record the temperature of the boiling water indicated on your thermometer.

3. Carefully remove the 125-mL flask from the boiling water bath, being certain not to get any water or water vapor into the flask. (The vapor inside the flask will recondense as it cools and so you should observe some liquid form at the bottom of the flask after removing it from the water bath.) Dry the outside of the flask thoroughly using a paper towel and allow it to stand away from any heat source until it reaches room temperature. Make sure there are no water droplets on the outside of the aluminum cap. Reweigh the flask (with the condensed unknown liquid inside
and the aluminum cap and rubber band in place) and record this mass.

4. Remove the cap, add another 2 mL or so of your unknown liquid. Repeat the steps above twice more for a total of three trials beginning at the step following the heading, “Trials 1 – 3” above. (There is no need to rinse and dry the flask or add more dithizone dye between trials.)

5. Finally, discard the aluminum foil, return the rubber band and equipment your borrowed, and pour the liquid in the flask into the chemical waste container. You may need to use a small amount of your remaining unknown solution or acetone to rinse out all of the dithizone dye.

6. Using the data you collected and the equations presented in the background section of this experiment determine the average molecular mass of your unknown liquid and then answer the questions on the report form.

Pre-laboratory Assignment: Determination of Molar Mass via the Dumas Method

A student performs the Dumas bulb experiments and collects the following data:

- Mass of empty flask: 31.022 g
- Mass of flask filled with water: 161.175 g
- Temperature of water in flask: 22.7°C
- Atmospheric pressure: 759.1 mmHg

She then performs the experiment with her unknown liquid and records the following data:

- Temperature of boiling water bath: 100.1°C
- Mass of condensate after boiling: 0.306 g

Use these data to find the molecular mass of her unknown liquid. Show all work below.

Lab Report: Determination of Molar Mass via the Dumas Method

Data

Unknown Number:

Mass of the flask filled to the brim with water:

Temperature of the water inside the flask:

Mass of dry empty flask:
Mass of water in flask \((\text{difference of flask + water and empty flask})\):

Density of water at the recorded temperature (from Table 1):

Volume of flask:
\((\text{determined from your measured mass of water and its density})\)

Atmospheric Pressure (from barometer):

Mass of the dry flask, dithizone crystal, foil, and rubber band:

Data:

Trial One:

Temperature of boiling water bath:

Mass of flask, dithizone, foil, rubber band, and condensate:

Mass of condensate (subtract mass of flask, foil, etc. from above):

Trial Two:

Temperature of boiling water bath:

Mass of flask, dithizone, foil, rubber band, and condensate:

Mass of condensate (subtract mass of flask, foil, etc. from above):

Trial Three:

Temperature of boiling water bath:
Mass of flask, dithizone, foil, rubber band, and condensate:

Mass of condensate (subtract mass of flask, foil, etc. from above):

Results

Determine the molecular mass of your unknown liquid for each of your three trials. Show all of your calculations below. Record the average molecular mass of your unknown liquid below.

Record the average molecular mass of your unknown liquid: __________________ Unknown number: _____________

Questions

Indicate how each of the following possible sources of error would be expected to affect your calculated molecular mass. (Indicate both the directions and, when possible, the approximate magnitude of the errors.) Justify each of your answers with supporting rationale or equations.

1. Air was not completely swept out of the flask by the unknown liquid after it had completely vaporized, so that the gas in the flask was a mixture of air and unknown.

2. The volume of the flask at 100°C was greater than that at room temperature because of expansion of the glass. (The expansion of the glass is \(1.4 \times 10^{-5}\)\ deg\(^{-1}\). That is, the volume of the flask increases by \(1.4 \times 10^{-3}\)\ percent per degree rise in temperature.)

3. The vapor was not an ideal gas. (Hint: Remember that the temperature of the vapor was not far above the boiling point of the unknown liquid. This fact should tell you the direction of the deviation from ideality.)

4. Although the unknown liquid completely vaporized, the gas in the bulb never reached the temperature of the boiling water.