Determination of the Molecular Weight of a Volatile Liquid

- Learn about the Gas Laws.
- Learn about the Dumas Method of Molecular Weight determinations.
- Learn about the determination of chemical formulas.

In this laboratory exercise we will determine the Molecular Weight of a volatile liquid using the method of Dumas. We will then compare this determination with the Molecular Weight calculated from the chemical formula to judge the accuracy of this methodology. Although this method is no longer used for Molecular Weight determinations, this exercise provides for a nice illustration of the usefulness of the Ideal Gas Law.

Any substance can be described by four "State Variables": Pressure (P), Volume (V), Temperature (T) and Amount (n). These four variables are not independent of one another; they are related via an "Equation of State". For gases at moderate temperatures and pressures this Equation of State is rather simple and is known as the Ideal Gas Law. Known as the Ideal Gas Law, this single equation incorporates the four Historical Gas Laws:

\[ PV = nRT \]  
(Eq. 1)

R is the empirically determined Universal Gas Constant. Numerically it is equivalent to 0.08206 L\textperiodcentered atm/K\textperiodcentered mole.

In the early 1800's Stanislao Cannizzario showed that the Hypothesis of Avogadro (V \sim n), embedded in the current Ideal Gas Law, could be used to determine the molecular weights of gases. In modern terms, the number of moles of a gas can be determined from the easily measurable parameters V, T and P:

\[ n = \frac{PV}{RT} \]  
(Eq. 2)

If the mass (m) of the gas is also known, and this is also easily measurable, we can then determine its Molecular Weight:

\[ MW = \frac{m}{n} \]  
(Eq. 3)

Jean-Baptiste Andre' Dumas, in 1826, devised a method, also based on the Hypothesis of Avogadro, for determining the Molecular Weights of liquid substances that can be conveniently be turned into vapors. In this method, a liquid is placed in a container with a very small hole. The liquid is then heated in a constant temperature bath, such as a boiling Water bath, until all the liquid vaporizes. Excess vapor escapes via the hole in the container; the remainder is
sufficient to occupy entirely the container’s volume at the temperature of the bath and at the pressure of the adjoining atmosphere.

Thus,

1) The liquid is placed in a flask which is stoppered with a stopper that has a small eye-dropper pushed through it.
2) The flask is placed in a boiling Water bath.
3) The liquid vaporizes and pushes all the Air out of the flask. Vaporized gas will escape from the flask until such time as the pressure of the gas in the flask equals the pressure of the Atmosphere.

4) At this point:

\[
\text{Temperature (T) of Gas} = \text{Temp. of Water Bath}
\]
Pressure (P) of Gas = Press. of Atmosphere (as read on a Barometer)
Volume (V) of Gas = Vol. of Container

5) The flask is removed from the water bath and the re-condensed liquid is weighed:

Mass (m) of Gas = Mass of Re-condensed Liquid

Historically, the Dumas Method was one of the first techniques available for the measurement of the Molecular Weights of compounds. This was a major step towards being able to determine the Chemical Formulas of these compounds. Prior to this, the Empirical Formula of a compound could be established from mass data, however its Chemical Formula could not. Currently, the Molecular Weight of many compounds can be measured with a high degree of accuracy using Mass Spectrometry.

As an example, mass data can be used to determine the elemental composition of a compound. So, the compound Cyclohexane has the following elemental composition:

% Carbon = 85.63%
% Hydrogen = 14.37%

This mass data can be used to determine the compound's Empirical Formula:

\[
\begin{align*}
\# \text{ mole } C &= 85.63 \text{ g } / (12.011 \text{ g/mole } C) = 7.129 \text{ mole } C \\
\# \text{ mole } H &= 14.37 \text{ g } / (1.008 \text{ g/mole } H) = 14.26 \text{ mole } H \\
(# \text{ mole } H) / (# \text{ mole } C) &= (14.26 \text{ mole}) / (7.129 \text{ mole}) = 2 \\
\text{Empirical Formula} &= \text{CH}_2 \\
\text{Empirical Formula Weight} &= 1 \times (12.011) + 2 \times (1.008) = 14.027 \text{ g/mole}
\end{align*}
\]

If the Molecular Weight of the compound is also known, it can be used in conjunction with the above results to obtain the correct Chemical Formula for the compound. For Cyclohexane, the Molecular Weight can be experimentally measured using a method such as that of Dumas and is found to have a current value of 84.2 g/mole. Thus:

\[
\begin{align*}
\text{Empirical Formula Weight} &= 14.027 \text{ g/mole} \\
\text{Molecular Weight} &= 84.2 \text{ g/mole} \\
\text{MW} / \text{EFW} &= (84.2 \text{ g/mole}) / (14.027 \text{ g/mole}) = 6 \\
\text{The Molecule contains 6 Empirical Formula Units, or:} \\
\text{Chemical Formula} &= \text{C}_6\text{H}_{12}
\end{align*}
\]

In this laboratory, we will determine the molecular weight of a volatile liquid using the Dumas Method. This result will be compared with the known Molecular Weight of the compound in order to evaluate the accuracy of this method.
Pre-Lab Questions

1. The Molecular Weight of an unknown liquid is determined using the Dumas Method. The following data has been obtained:

   Atmospheric Pressure = 754.6 Torr
   Vol. Flask = 213 mL
   Temp. of Water Bath = 100°C
   Mass of Re-Condensed Liquid = 0.582g

   What is the Molecular Weight of the liquid?
Procedure

Perform this experiment in the Fume Hood.

1. Pour approximately 700mL of water into a 1000mL beaker. Add a few boiling chips to the water.

2. Assemble the Dumas apparatus as shown above. Mark the position of the stopper with a wax pencil.

3. Weigh the empty 250mL Erlenmeyer flask with vent assembly. The flask and vent assembly must be dry.

4. Remove the glass stopper and add approximately 5mL of liquid sample to the flask. Replace the stopper. (Note which liquid you are using.)

5. Submerge the flask in the beaker of water. Use a clamp above the stopper of the flask to hold it in place. Adjust the water level so that water will come to the neck of the flask, but will not splash out of the beaker when boiling. The bottom of the flask should be 1 cm above the bottom of the beaker.

6. As directed, suspend a thermometer in the water with a suitable clamp. Do not let the thermometer touch the beaker or the flask.

7. Heat the water to boiling.

8. Note when the liquid begins to boil. Continue heating for 5 minutes after the liquid has completely vaporized and record the temperature of the boiling water.

9. Remove the flask from the boiling water and immerse the flask under cold running water. Keep the water away from the vent assembly.

10. After the flask has cooled to room temperature, carefully dry the outside of the flask and vent assembly. Weight the flask, vent assembly and condensed sample.

11. Remove the stopper and and rinse the flask with water. Drain dry and fill the flask with deionized water. Insert the stopper so that it is in the same position as before. Be sure the water fills the eye dropper.

12. Carefully dry the outside of the flask, vent assembly and stopper. Weigh the filled flask.

13. Measure the atmospheric pressure using the barometer in the lab.

14. Clean and return all equipment. (Unless you will be completing the experiment in the Addendum.)
Data Analysis

1. Determine the Pressure of the Gas in Atmospheres.

2. Determine the Temperature of the Gas in degrees Kelvin.


5. Determine the Molecular Weight of the Gas.

6. Use a CRC Handbook of Chemistry and Physics or other reference source to determine the Chemical Formula of the Liquid used. Use this to determine the accepted Molecular Weight of the liquid.

7. Calculate the Percentage Error for your Experimental Result.

8. Identify possible Sources of Error in your experiment. Which Source of Error is likely the greatest contributor to the Error in your experiment? Explain.
Post Lab Questions

1. Cyclopropane is a hydrocarbon that when mixed in the proper ratio with Oxygen can be used and an anesthetic. At 755 Torr and 25°C, 1.523 g of the gas occupies 890.6 mL. Combustion data for the gas show it has an elemental composition of 85.7% Carbon and 14.3% Hydrogen.

   i) Determine the Molecular Weight of this compound.
   
   ii) Determine the Empirical Formula of the compound.
   
   iii) Determine the Chemical Formula of the compound.

2. Hydrides of Boron are frequently used in forming detonators, because of their inherent instability. When 1.00 g of a particular hydride of boron is injected into a piston at 25°C and 754.7 Torr, it is found to occupy a volume of 390 mL. This hydride has been shown to have a composition of 85.63% Boron and 14.37% Hydrogen.

   i) Determine the Molecular Weight of this Hydride of Boron.
   
   ii) Determine the Empirical Formula of this compound. (Hint: 1.8 = 9/5)
   
   iii) Determine the Chemical Formula of this compound.

3. The Ideal Gas Law is a limiting law; it is only valid in the limit of zero Pressure where intermolecular interactions are minimal.

   \[ PV = nRT \quad \text{limit P \sim 0} \]  

   (Eq. 4)

   What is the error in your Molecular Weight determination if the Ideal Gas Law is in error by 10%?