Molecular Weight by the Dumas Method

One of the early methods for the determination of the molar mass of volatile substances was through the measurement of the density of the vapor of the substance. The method is reliable and convenient and is still employed in some situations.

In this approach, the sample is added to a small flask, the flask is heated and as the sample evaporates, the air is swept out of the container. Then flask is cooled again, and the mass of liquid which condenses must be equal to the mass of vapor that filled the flask in the previous step. A little skill is required to judge the point at which the flask is just filled with sample vapor.

The combined gas law is given by the equation;

$$p V = n R T, \qquad [1]$$

where p is the pressure of the gas in atmospheres, V is the volume of the gas sample in liters, n is the number of moles of gas present, T is the temperature of the sample in Kelvin, and R is the empirically determined quantity known as the gas law constant which has the value of 0.0821 L atm $mole^{-1}$ deg^{-1}. This relationship describes very well the behavior of gases at ordinary pressures and moderate temperatures.

In this experiment we rearrange the original combined gas law into a form more convenient for our calculations. Recall that the number of moles of a substance is equal to the mass of the substance divided by the mass of a mole of that substance:

$$n = wt / M, \qquad [2]$$

Where wt represent the mass of the sample and M is the molar mass of the substance. Substituting this relationship inot the combined gas law:

$$pV = (wt/M) RT \qquad [3]$$

And rearranging to isolate the molar mass yields

$$M = (wt R T) / (p V) \qquad [4]$$

You will recall that the ratio of mass to volume (wt/V) is commonly known as density. Thus equation 4 may be rearranged to:

$$M = (wt/ V) (R T / p) \qquad [5]$$

This is sometimes called the vapor density form of the combined gas law.

The basic outline of this experiment is to add a small amount of a liquid sample to a small pre-weighed flask. The flask is then submerged into a boiling water bath. As the sample evaporates, the air is swept out of the flask, and we finally have a flask containing only the vapor of the unknown substance. If at that point the flask is cooled, the vapors will condensed and their mass may be determined by reweighing the flask. One may repeat the process and obtain an average of replicate measurements. Subsequent measurements are the made to determine the volume of the flask, the temperature of the boiling water bath, and the prevailing atmospheric pressure. Those values and equation 5 are used to calculate the molar mass of the unknown liquid.

Procedure

1. Determine the mass of the DRY flask to the nearest milligram.

2. Add about 5 mL of your unknown to the flask. Cut a small square of aluminum foil and wrap over the top to the flask. Make a small hole in the foil with a needle.

3. Immerse the flask in the boiling distilled water bath using a clamp and ring stand. Be sue the flask is submerged at least to the neck.

4. Heat the flask until you no longer see a Schlieren pattern emerging form the hole in the foil. Schlieren patterns are like the watery lines seen rising from a heated surface. Remove the flask when the pattern disappears. The flask should contain no liquid at this point. (Some people find that holding a paper towel or shiny surface over the hole can be helpful. When vapor no longer condenses on the towel or shiny surface, vapor is no longer emerging and no liquid should remain in the flask.)

5. Cool the flask to room temperature and the vapors will condense into a small amount of liquid.

6. Dry the exterior of the flask with a paper towel and weigh the flask and contents to the nearest milligram. Remove the foil just immediately before weighing.

7. Repeat the vaporization and condensation steps (2-6) twice more so that you have three values for the mass of the condensed vapor.

8. Obtain the atmospheric pressure from the barometer in the laboratory.

9. Determine the volume of the flask by filling it completely with water and then measuring the volume of water contained in the flask with a large graduated cylinder.

10. The temperature of the boiling water bath can be interpolated from the following table (taken from the CRC Handbook of Chemistry and Physics, 41st Ed.).

Pressure (mmHg)	735	740	745	750	755	760
Boiling Point (^{o}C)	99.07	99.26	99.94	99.63	99.82	100.00

11. From the average mass of condensed liquid and the temperature, volume and pressure data, calculate the molar mass of your unknown liquid. Students are reminded to handle significant figures properly.

12. Obtain the accepted value of molecular weight of your unknown from the instructor and calculate the absolute and relative error of your result.