Chemical and physical methods for determining \textit{formula weights} (or molar masses) have been important historically as a way of identifying new materials. The modern laboratory has a large variety of instrumentation which makes many of these methods obsolete. However the principles upon which the older methods were based are not insignificant and many form the foundation for the prediction of physical and chemical properties and behaviors of substances.

The classic Dumas method (Jean Baptiste André Dumas (1800-1884), French Chemist) for determining the formula weight of a volatile liquid is a case in point. Amedeo Avogadro proposed as early as the mid-1800's that equal volumes of gases measured under identical conditions would contain equal numbers of gas particles. With an established relative atomic mass scale it was possible to describe a constant volume which would contain a \textit{gram-atomic weight} of a gaseous element or compound under fixed conditions, what we know today as the \textit{molar volume}.

The ideal gas law that resulted from this knowledge can be used to determine the formula weight of liquids and solids which are appreciably volatile (vaporize at a relatively low temperature). Measuring the weight of a sample of gas that occupies a container of known volume at a given temperature and pressure enables a determination of its formula weight using a form of the ideal gas law derived from $PV = nRT$ by substituting for $n$ ($n = g/FW$) and rearranging:

$$FW = \frac{g}{PV}RT \quad (1)$$

In the Dumas method a volatile liquid is heated in a water bath to a known temperature (above its boiling point) and allowed to escape from a container through a tiny orifice. Once the liquid has vaporized, the container is cooled to room temperature. Gradually the vapor which remained in the container at the higher temperature condenses to a liquid and can be weighed. If the volume of the container is known along with the water bath temperature, the atmospheric pressure can be used (because the system is open to the atmosphere through the orifice). The formula weight can be determined from equation 1.

This method depends on a lot of things going right. One necessity is that the liquid must be volatile enough to vaporize at a high temperature, but not so volatile that a significant amount is lost to evaporation as the container cools. The vapor is also assumed to behave ideally at the temperature and pressure at which it occupies the container. The amount of error implicit in this approximation varies from compound to compound and is tied to the variables which create deviations from ideal behavior: molecular volume and the forces that allow condensation. Generally speaking, the larger these are, the greater the error in the determination.

There is another problem with the basic method which is more easily addressed. The "empty" container is really filled with an amount of air determined by the volume,
temperature and pressure in the container. This air has mass and contributes to the overall mass of the container assembly. At the end of the experiment, some of the liquid vaporizes, depending on its vapor pressure at room temperature. The presence of this vapor forces out some of the air through the orifice since the internal pressure will be equalized with the room pressure. The number of gas particles remains constant if the temperature and pressure remain constant. Thus when the container is weighed again there is air missing that needs to be counted in the final mass when the mass of the condensed liquid is determined by difference. This results in an apparent mass of liquid that is too small, which in turn makes the formula weight too small.

The moles of air forced out by the vapor are equal to the moles of vapor that forms. This is determined by the vapor pressure of the liquid at room temperature. If this value is known, the moles of vapor present in the flask above the condensed liquid can be calculated as:

\[ n_{\text{vapor}} = \frac{P_{\text{vapor}} V_{\text{container}}}{RT} \]  

(2)

Avogadro's Law tells us that these moles of vapor must equal the moles of air displaced since the conditions are the same for both. These "missing" moles of air can be converted to grams using the weighted average molar mass of air (29.0 g/mole) and added into the final mass of the assembly. The vapor pressure at 298 K for each compound is provided below.

The unknowns used in this experiment include the following:

**acetonitrile** (41.0 g/mole, \( P_{\text{acetonitrile}} = 81 \) torr, \( bp = 81.6 {^\circ}\text{C} \)) is a poisonous liquid with an ether-like odor. It is soluble in water and most common organic solvents. It is used in many organic syntheses and wherever a polar solvent with high dielectric constant is required. Breathing the vapors should be avoided. Skin contact may cause irritation.

**ethanol** (46.0 g/mole, \( P_{\text{ethanol}} = 55 \) torr, \( bp = 78 {^\circ}\text{C} \)) is a clear, colorless liquid with a pleasant odor and a burning taste. It is miscible with water and many organic liquids. It is used in the laboratory as a common solvent, in pharmaceuticals, and as a common topical antiseptic. Nearly all ethanol sold as "alcohol" (**not for drinking**) has been denatured. Denaturing in this context means adding some substance which does not markedly interfere with the behavior or properties of ethanol except to render it unfit for drinking.

**ethyl acetate** (88.1 g/mole, \( P_{\text{ethyl acetate}} = 82 \) torr, \( bp = 76.5 {^\circ}\text{C} \)) has a characteristic fruity odor. It is somewhat soluble (1 mL in 10 mL) in water and mostly soluble in common organic solvents. It is used in artificial fruit essences and as a solvent for lacquers and varnishes (including fingernail polish).
isopropyl acetate (102.1 g/mole, P_isopropyl acetate = 58 torr, bp = 90 °C) is a colorless liquid which is soluble in about 20 parts water but miscible with ethanol and ether. It is a solvent for cellulose derivatives, plastics, oils and fats.

2-propanol (60.1 g/mole, P_2-propanol = 41 torr, bp = 82.4 °C) is a flammable liquid, miscible with water and common organic solvents. It is a solvent in many quick drying commercial preparations (inks, shellacs, oils, etc.) and is used as a topical antiseptic as a 70% solution (rubbing alcohol).

Many of the liquids will dissolve plastics and finishes. Spills should be immediately soaked up with paper towels and the towels placed in the fume hood for evaporation of the liquid.

Procedure

1. The critical portion of this experiment lies in the preparation of the sample flask. Obtain a clean, dry 125-mL Erlenmeyer flask and record its mass on a top-loading balance.

2. Fashion a cap for the flask from a square of aluminum foil and secured it with fine copper wire twisted tightly around the neck just below the rim. Remove excess foil should with a razor blade to prevent it from collecting condensation. The assembly should be prepared carefully so that it can be used several times. Once prepared it should be weighed "empty" to 0.1 mg on an analytical balance.

3. Introduce 3-4 mL of the unknown liquid with a syringe. The needle is used to make a tiny hole in the foil cap and the liquid is injected. Avoid enlarging the hole at this point with an unsteady hand.

4. Clamp the flask into a 600 mL beaker of water (with a stir bar added). The water level should be high enough to cover most of the flask but not so high as to allow water to enter through the hole in the foil or to bubble in around and under the copper wire loop. Place the beaker on a hot-plate.

5. Bring the water bath to a gentle boil for about 10 minutes or until all of the liquid is evaporated. Record the boiling point of water at room pressure and the barometric pressure.

6. Remove the flask from the water and allow it to cool to room temperature. Dry the water completely from the outside of the flask. Be especially careful about the cap edges as steam from the boiling water can condense just under the edges and change the mass of the container significantly. Reweighed the flask when it has returned to room temperature and is completely dry on the outside.

7. Additional trials may be done simply by adding more liquid through the same hole and repeating the procedure described above.
8. After the final trial, remove the cap assembly and rinse the flask thoroughly. Dry the outside of the flask and fill the flask *almost* completely with room temperature water (record). Place on a top-loading balance and add additional water to fill it completely. Record the mass. This last measurement, together with the first one and the density of water at room temperature *(Table I)*, allows the volume of the flask to be determined.

**Questions**

1. What is the density of dry acetone vapor at 95 °C and a pressure of 735 torr?

2. Why is it important to allow the liquid to vaporize slowly?

**Data Treatment**

Determine the following:

1. The *apparent* mass of vapor occupying the flask at the boiling water temperature.

2. The volume of the flask, based on water density.

3. The formula weight of the organic liquid.

4. The moles of air displaced by the volatile liquid vapor (at room temperature).

5. The mass of air displaced by the volatile liquid vapor.

6. The *true* mass of vapor that occupied the flask at the boiling water temperature.

7. The *corrected* formula weight of the vapor and relative error.

8. Using the elemental analysis for your compound, determine the correct molecular formula.

**Table I  Density (g/mL) of Water at Various Temperatures (°C)**

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