Formula Weight from Gas Density

Chemical and physical methods for determining 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 gram-atomic weight of a gaseous element or compound under fixed conditions, what we know today as the 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:

\[ \text{FW} = \frac{g}{PV}RT \]  

(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 fill a container, expelling air and excess compound through a tiny orifice. Once the liquid has vaporized, the container is cooled to room temperature. Gradually the vapor which filled the container at the higher temperature condenses to a liquid and can be weighed. The mass can then be used, along with the volume of the container, the water bath temperature, and the atmospheric pressure (because the system is open to the atmosphere through the orifice) to determined the formula weight 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 unknowns used in this experiment are:

**acetonitrile** (41.0 g/mole, bp = 81.6 °C) has an ether-like odor. It is soluble in water and most common organic solvents. Avoid breathing vapors and skin contact.

**ethanol** (46.0 g/mole, bp = 78 °C) is a clear, colorless liquid with a sweet odor. It is soluble in water and many organic liquids. Nearly all ethanol sold as "alcohol" (not for drinking) has been denatured. Denaturing means adding a substance which renders the ethanol unfit to drink.
**ethyl acetate** (88.1 g/mole, bp = 76.5 °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, 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 plastics, oils and fats.

**2-propanol** (60.1 g/mole, bp = 82.4 °C) is a flammable liquid, miscible with water and common organic solvents. It 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 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 until all of the liquid in the flask evaporates. After removing the flask, record the water bath temperature and the barometric pressure.

6. Allow the flask 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 under the edge. 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 1), allows the volume of the flask to be determined.

Questions

1. What is the **density** of dry acetone (C$_3$H$_6$O) vapor at 95 °C and a pressure of 735 torr?

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

**Data Treatment:** Include the following in your calculations and discussion:

Tabulate the data obtained: mass of vapor occupying flask, temperature of the water bath (in Kelvin), atmospheric pressure, and volume of the flask (based on water density – show calculation).

Calculate the formula weight (molar mass) of the organic liquid from each trial and the average.

Use your formula weight to identify the unknown liquid.

Using the elemental analysis for your compound (below), determine the correct **molecular formula**.

- **Acetonitrile**: 58.5% C, 7.4% H, 34.1% N
- **Ethanol**: 52.1% C, 13.1% H, 34.8% O
- **Ethyl acetate**: 54.5% C, 9.2% H, 36.3% O
- **Isopropyl acetate**: 58.8% C, 9.9% H, 31.3% O
- **2-Propanol**: 60.0% C, 13.4% H, 31.3% O

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