Determination of the Molar Mass of a Volatile Liquid by Vapor Density

Background

Chemical and physical methods for determining atomic and molecular *formula weights* or molar masses have been important historically as a way of analyzing and categorizing new materials. The modern laboratory is generally equipped with 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 for determining the formula weight of a volatile liquid is a case in point. 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*. At STP this volume is 22.4 L for an ideal gas.

An understanding of the various gas laws allows for an application of this useful information to liquids and solids which are appreciably volatile, i.e., possess relatively high vapor pressures. As long as the temperature and pressure are known, a measured volume of gas can be converted to moles since:

$$n = \frac{PV}{RT}$$

Massing a sample of gas is relatively simple. These two pieces of information are the minimum required for a molar mass determination.

In the Dumas method a volatile liquid is heated 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 is then massed. If the volume of the container is known along with the high temperature, the room pressure can be used (because the system is open to the atmosphere through the orifice) to calculate moles. From there a molar mass can be determined.

This method depends on a lot of things going right. One assumption is that while the liquid is volatile enough to vaporize at the elevated temperature, it is not *so* volatile that a significant amount will be lost to evaporation through the orifice 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 intermolecular forces. Generally speaking, the larger these are, the greater the error in the determination. The situation is further complicated by the interaction of these two factors. For example, a small molecule may have significant intermolecular forces (hydrogen bonding perhaps) but a large molecule may have comparatively weak forces (like dispersion forces). Combinations run between these extreme examples making predictions of error from this source difficult.

There is another problem with the basic method which is more easily addressed. When the container is "empty", i.e., before the liquid is added or the vapor forms, there is a fixed 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. But when the liquid is present it vaporizes to some extent determined by its vapor pressure at room temperature. The presence of this vapor forces out some of the air through the orifice since the internal pressure is equalized with the room pressure and the number of gas particles remains constant if the temperature and pressure remain constant. Thus when the container is massed again there is air *missing* that should be counted in the final mass if the mass of the condensed liquid is to be determined by difference. This results in an apparent mass of liquid that is too small which in turn makes the molar mass calculation 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 that are present in the flask above the residual condensed liquid can be calculated as:

$$n_{vapor} = \frac{P_{vapor} V_{container}}{RT}$$

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 and added into the final mass of the assembly.

All of this depends, of course, on knowing the vapor pressure of the liquid, P_{vapor}. The value could be determined experimentally but for the purposes of this experiment a list of possible unknowns and their vapor pressures at 298 K will be provided.

The Experiment

The molar mass determination should be done at least twice.

The following non-locker materials will be provided:

- aluminum foil
- fine copper wire
- razor blades, pliers, wire cutters, etc.
- boiling stones
- 600 mL beaker
- hypodermic syringe

The Chemicals

The unknowns used in this experiment include the following:

acetonitrile (41.0 g/mol, $vp_{298} = 81$ mmHg, bp = 81.6°C) or ethanenitrile is a poisonous liquid with an ether-like odor. It is soluble in water and most common organic solvents. Like acetone, it forms a low-boiling azeotrope with water. 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 g/mol, $vp_{298} = 55$, bp = 78°C) or ethyl alcohol is a clear, colorless liquid with a pleasant odor and a burning taste. It absorbs water readily from the air and is miscible with water and many organic liquids. Most ethanol is used in alcoholic beverages in dilute form. It is also 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* (including the ethanol in the lab). Denaturing in this context means adding some substance which does not markedly interfere with the behavior or properties of ethanol <u>except</u> to render it unfit for drinking. Most denaturants are toxic.

ethyl acetate (88.1 g/mol, $vp_{298} = 82$ mmHg, bp = 76.5°C) has a characteristic fruity odor and a pleasant taste when diluted. 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). Prolonged breathing of vapors may cause liver and kidney damage.

isopropyl acetate (102.1 g/mol, $vp_{298} = 58$ mmHg, 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. Vapors may be irritating to mucous membranes and narcotic in high concentrations.

2-propanol (60.1 g/mol, $vp_{298} = 41$ mmHg, bp = 82.4°C) or isopropyl alcohol is a flammable liquid, miscible with water and common organic solvents. It forms a low-boiling azeotrope with water and can also be used to make low-freezing mixtures (i.e., as an antifreeze). It is a solvent in many quick-drying commercial preparations (inks, shellacs, oils, etc.) and is used as a topical antiseptic in a 70% solution (*rubbing alcohol*). Ingestion of as little as 100 mL can be fatal.

While there are no *special* problems associated with the use of these compounds in this experiment, all should be treated with caution. Inhalation of the vapors for long periods of time should be avoided. Skin contact should likewise be limited. Many of the liquids will attack plastics and finishes. Spills should be dispersed on paper toweling immediately and the toweling removed at once to the fume hood for evaporation of the liquid. The liquids will be dispensed by hypodermic syringe and most will interact with the rubber plunger, causing it to swell. For that reason, once the liquid has been injected the plunger should be pulled out of the syringe body to dry.

Technique Discussion

In essence the experiment consists of creating a container with a reproducible volume and a pin-hole orifice from which the volatile liquid will be vaporized at the boiling point of water and room pressure. After cooling, the mass of the container is greater by the amount of liquid that remains (representing the amount of vapor which filled the volume at the boiling point of water and room pressure). [a mass correction must also be made for the air displaced by the vapor as discussed previously]

A clean, dry 125 mL Erlenmeyer flask serves as a suitable container. It is small enough to mass on the analytical balance and large enough to contain a sufficient mass of vapor. The mass of the flask on the rough balance is required for the volume determination since when it is full of water it will be too heavy for the analytical balance.

A cap may be fashioned for the flask from a square of aluminum foil and secured with fine copper wire twisted tightly around the neck just below the rim. Excess foil should be removed with a razor blade as it provides a place for condensed water (from the boiling process) to "hide". The assembly should be prepared carefully so that it can be used several times. Once prepared it should be massed "empty" (analytical balance).

The unknown is introduced with a syringe. The needle is used to make a tiny hole in the foil cap and 3-4 mL of the liquid is injected. Enlarging the hole at this point with an unsteady hand will introduce serious errors into the determination.

The flask should be immersed in a 600 mL beaker of water (with a few boiling stones 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. The beaker can be suspended on a tripod over a Bunsen burner. A watch glass secured by the ring from a ring stand can be used to keep the flask from bobbing up in the water.

The water bath should be brought quickly to a boil but then the heat should be reduced to achieve a gentle boil for about 10 minutes or until all of the liquid is evaporated. The boiling point of water at room pressure and the pressure itself should be recorded.

The flask is removed from the water and allowed to cool. Water must be removed 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. When the flask has returned to room temperature and is completely dry on the outside it should be remassed.

Additional trials may be done simply by adding more liquid *through the same hole* and repeating the procedure described above.

After the final trial the cap assembly is removed and the flask rinsed thoroughly and then filled almost completely with room temperature water (record). After the outside has been carefully dried the flask can be placed on the rough balance and additional water added to fill it completely. The mass is then recorded. This last measurement, together with the first one and the density of water at room temperature, allows the volume of the flask to be determined.
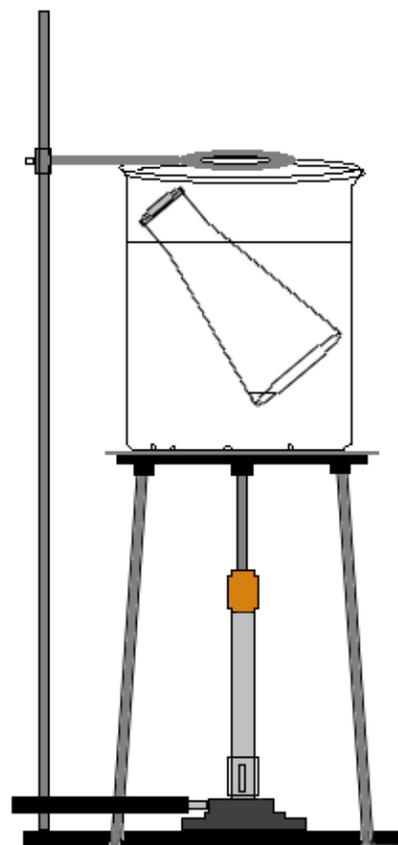
The Report

Your initial calculations should include:

[repeat the calculation sequence for your separate trials; you must then decide on the treatment of the two molar masses]

1. The apparent mass of vapor that occupied the flask at the boiling water temperature

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

3. Moles of gas occupying the flask at the temperature of the boiling water

4. Estimated molar mass of the unknown and tentative ID of the unknown

5. The moles of air displaced by the volatile liquid vapor (at RT)

6. The molar mass of air (calculated)

7. Mass of air displaced by the volatile liquid vapor

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

9. The corrected molar mass of the vapor [relative error]

Your conclusion to this experiment should include some judgment as to the validity of your two trials. To that end, you should compare your results with the list of unknowns supplied by the instructor. Be sure to consider factors such as intermolecular forces and consequent deviations from ideality to support your results. As usual, don't forget to constructively criticize your technique if your results were poor and/or inconsistent. Pay particular attention to the contribution that stray water drops might have on your results. One small drop of water (such as from an eyedropper) is about 0.05 mL.