EXPERIMENT 1

"HOW DO I LOVE THEE

LET ME COUNT THE WAYS..."

DETERMINATION OF AVOGADRO'S CONSTANT

Techniques

- Calibration
- drop counting

MSDS available for

- stearic acid, $CH_3(CH_2)_{16}COOH$
- cyclohexane, C_6H_{12}

Principles

- molar volume
- molecular structures
- surface areas and volumes
- Avogadro's constant
- percent error

Recommended Advanced Reading

- **Chapter 3 in Petrucci, Herring, Madura, & Bissonnette's General Chemistry, 10th Ed.**

INTRODUCTION

The beginning

When you begin this experiment, you should have a lab work area, a TA (or demonstrator) and a partner. In today's session you will work with your partner to:

- Calibrate a dropper and determine the number of drops of a stearic acid in cyclohexane solution required to create a monolayer of the solution on a water surface
- Calculate the mass of stearic acid required to form the monolayer, use it to estimate the thickness of the monolayer (which is related to the length of the stearic acid molecule), and then use the number of carbon atoms in stearic acid to approximate the diameter and then the volume of a carbon atom
- calculate a value for the Avogadro constant
- compare your calculated value for the Avogadro constant with a known value and determine the percent error in your value

This is a general overview of what you will be accomplishing in this experiment.

EXPERIMENT 1: *Determination of the Avogadro Constant*

Introduction

"*In a diamond shaped like a cube of 15 mm per side, there are between 500 and 1000 times more carbon atoms than there are stars in the entire visible Universe!*"

The Avogadro constant is one of the most important constants used in chemistry. It allows chemists to relate a directly measurable quantity, such as the mass of a substance in grams, to a quantity that cannot be measured directly, such as the number of atoms in the mass of a substance. For instance, the Avogadro constant could be used to determine how many atoms are present in 1 g of carbon.

Since atoms are very small compared to the things we normally measure, the units we normally use to measure quantities are very awkward to use. We would have a hard time determining the mass of a dozen atoms, since their collective mass is still too small to measure, even on an analytical balance. For this reason, a unit called the ***mole*** is very important. It is a counting unit. Just as we can say that one dozen indicates that we have 12 of a particular item, one mole indicates that we have 6.023×10^{23} of that particular item. While a mole is not very convenient for measuring doughnuts (it would be a HUGE pile!), it is very convenient for measuring small things like atoms.

The Avogadro constant has a value of 6.022×10^{23} and is given the symbol N_A. It is defined as the number of atoms contained in exactly 12 g of the ${}^{12}_{6}C$ isotope. Since atomic weights are based on this carbon isotope, and since the Avogadro constant is also based on this carbon isotope, the mass of one mole of any ion or molecule is equal to the sum of the atomic weights of all the atoms in the ion or molecule. The three equations written below are equivalent. The first gives the stoichiometry in terms of moles, the second in terms of mass, and the third in terms of molecules. This example illustrates how we can relate measurable or ***macroscopic*** quantities, such as mass, to the stoichiometry which occurs at a molecular level.

$$\textbf{2 moles } H_2 + \textbf{1 mole } O_2 \rightarrow \textbf{2 moles } H_2O \qquad [1]$$

$$\textbf{2 (2 x 1.0080) g } H_2 + \textbf{(2 x 15.999) g } O_2 \rightarrow \textbf{2 (18.015) g } H_2O \qquad [2]$$

$$2\ (6.022\text{x}10^{23})\ \text{molecules}\ H_2 + 6.022\text{x}10^{23}\ \text{molecules}\ O_2 \rightarrow 2\ (6.022\text{x}10^{23}\ \text{molecules})\ H_2O \quad [3]$$

While many sophisticated experimental methods, including electrochemical and x-ray diffraction methods, have been used to determine the Avogadro constant quite accurately, the simple technique you will be using in this laboratory experiment demonstrates that a reasonable value of the Avogadro constant may be obtained using the basic equipment available in the laboratory.

Concept of the Experiment

There are two parts to this experiment. The first part will be experimental - you will find the molar volume of stearic acid. The second part is theoretical - you will find the volume of one molecule of stearic acid using two different approximations.

In the first part of the experiment, you will add a solution of stearic acid in cyclohexane to a clean water surface in a drop wise fashion.

Polarity and Miscibility

In some molecules, the bond strengths are not all equal. This often causes the formation of ***polar*** molecules, meaning that there is a slight separation of charge in the molecule. This makes one part of the molecule slightly negative and the other part slightly positive. Because of this charge separation within the molecule, polar molecules are attracted to one another. The negative part of one molecule attracts the positive part of another molecule. One example of a polar molecule is water, with the oxygen being slightly negative and the hydrogens being slightly positive. Due to its polarity, water forms hydrogen bonds with itself, as shown in Figure 1.

In general, polar molecules **"like"** other polar molecules (following the rule "like dissolves like"). Water, which is polar, will dissolve acetic acid, which is also polar. (The solution of acetic acid in water is commonly referred to as ***vinegar***). Water will not, however, dissolve butane, which is ***non-polar***, as no significant charge separation occurs in the butane molecule. Some large molecules are neither polar nor non-polar, but have two parts that are different, one part being polar and the other part being non-polar. The question then arises as to what happens when a polar solvent like water comes into contact with a molecule which has a polar part and a non-polar part?

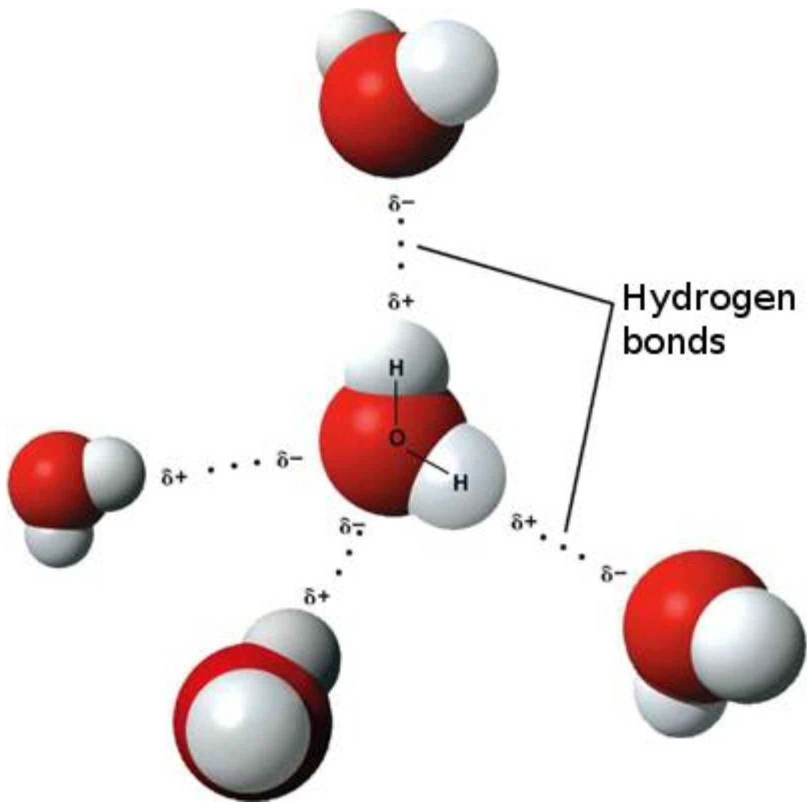


Figure 1. Hydrogen bonding in water (courtesy of Wikipedia)

In this experiment, you will be using such a molecule. ***Stearic acid***, shown in Figure 2, is a long chain hydrocarbon with a carboxyl or –COOH functional group at one end. The long chain hydrocarbon consists of sixteen methylene or $-CH_2-$ groups linked in a chain with a methyl, or $-CH_3$ group at one end. This hydrocarbon chain is the non-polar part of stearic acid. On the other hand, the –COOH group is polar.

Stearic Acid

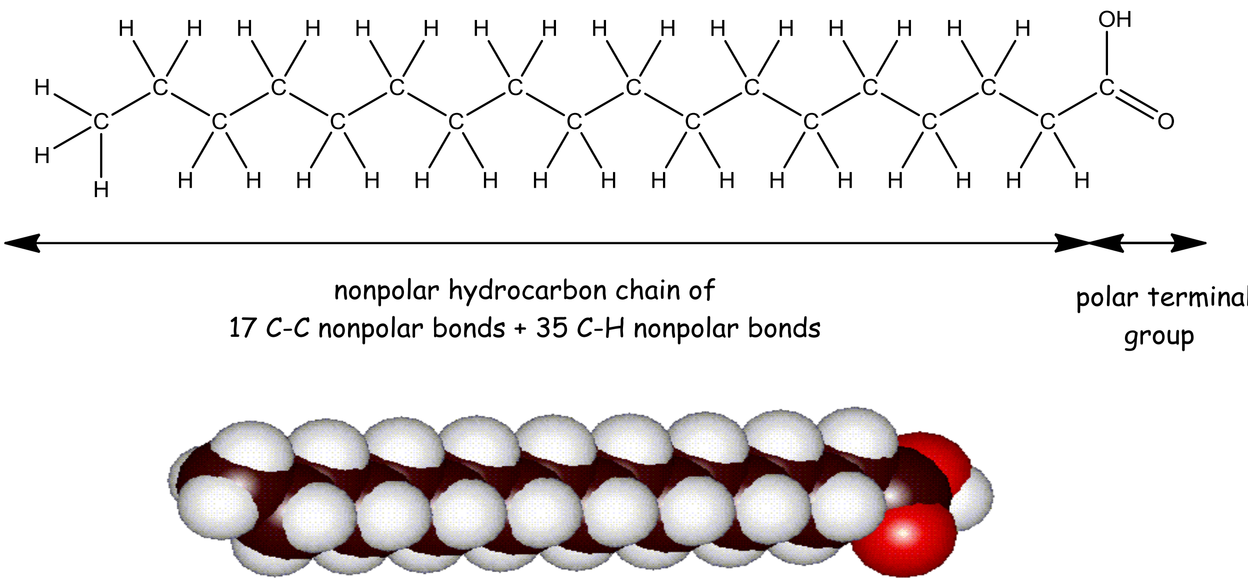


Figure 2. Structural and space-filling models of Stearic Acid

What happens when we put stearic acid in water? As Figure 3 shows, the polar –COOH groups all dissolve in the water, but the non-polar hydrocarbon tails, which "dislike" water, try to remain as far as possible from the water surface and, as a result, they are projected above the water surface.

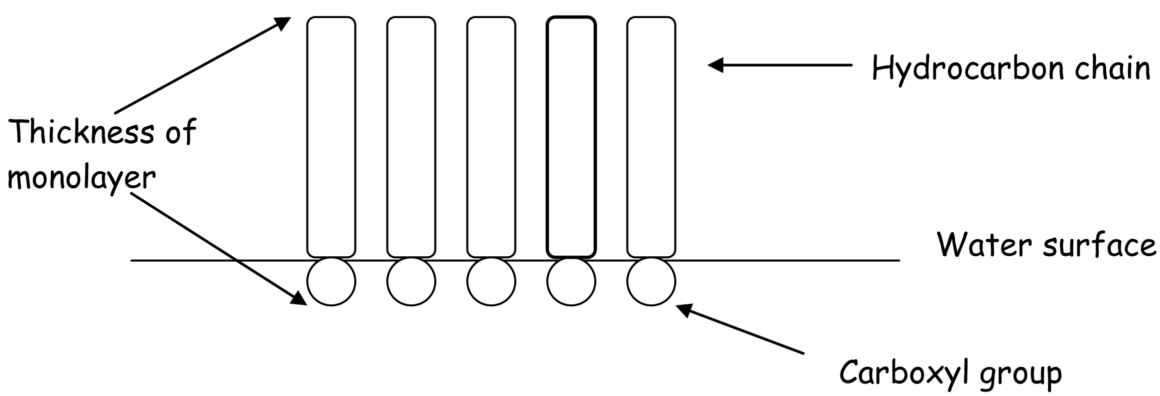


Figure 3. Stearic acid in water

We can go on adding stearic acid molecules to the water surface until we form a ***monolayer***. This means that we cannot add another molecule to the water because there is no space on the water surface where it will fit.

In this experiment, you will add a stearic acid solution drop wise to a clean water surface until a monolayer is formed. Once the number of drops required to form a monolayer is known, you can calculate the mass of stearic acid required to form a monolayer. From this measurement, you will estimate the thickness of the monolayer, which can be related to the length of the stearic acid molecule. Since the number of carbon atoms in stearic acid is known, you will be able to approximate the diameter of a carbon atom in two different ways. You can then use the diameter to determine the volume of a single carbon atom. This volume will allow you to calculate Avogadro's number.

Errors in the Measurement

What kind of accuracy can be expected from this experiment? How close might your value be to the accepted value for Avogadro's number? The measurement is based on the assumption that a monolayer of stearic acid forms on the surface and that the molecules are packed closely in the arrangement illustrated in Figure 3. The thickness of this monolayer is the direct measurement of the experiment and from this measurement, the diameter of the carbon atom is obtained. This value is then cubed to obtain the volume, so the error is multiplied three times in this calculation.

The results generally give a value of Avogadro's number which is too large, sometimes by a factor of 100. A large value is the result of adding too few drops of solution in the formation of the monolayer. Any dirt in the plastic dish or impurities in the water may hinder the formation of the monolayer. Even a trace of grease from fingers or hair can give a serious error. The solvent evaporates quickly and if evaporation occurs while the drop is being formed, the solution will be effectively more concentrated and fewer drops will be required. Also, the dropper should be held vertically since the size of the drop depends on the angle at which it emerges. As much as possible, the angle, if not exactly vertical, should be the same to ensure all the drops are of the same size. These and other factors are serious enough to cause large errors in the final value. Nevertheless, the fact that such a large number can be measured at all by such a simple method is the remarkable feature of this experiment.

(TTD) Things to Do

- View the video and complete the prelab exercises before coming to the laboratory.
- Calibrate a dropper and determine the volume per drop of pure cyclohexane.
- Determine the number of drops of stearic acid in cyclohexane required to form a monolayer of stearic acid on a pure water surface.
- Determine the thickness of the monolayer, the diameter of a carbon atom and the volume of a carbon atom. Use this volume to calculate the Avogadro constant.
- Compare the calculated and actual values of the Avogadro constant and calculate the percent error.
- Use safe laboratory procedures at all times.

Safety Precautions

1. **Wear approved eye protection at all times**.
2. Do not inhale the cyclohexane vapours!

PROCEDURE

Equipment and chemicals needed

Chemicals	*Equipment*
Stearic acid in cyclohexane	2 plastic petri dishes
cyclohexane	10 mL graduated cylinder
	50 mL beaker
	Plastic pipette

Determination of the Avogadro Constant

Starting the experiment

1. In a 50 mL beaker, obtain approximately 10 mL of cyclohexane.

2. Transfer approximately 5.00 mL of cyclohexane to a 10 mL graduated cylinder. It is not important WHAT volume you transfer, but you should be able to read it EXACTLY. It is PREFERABLE if it is at a whole gradation (5.00 mL, 6.00 mL, etc.).

3. Obtain a plastic pipette that has had its end pulled to a fine tip.

4. Carefully, squeeze the bulb and draw up as much pure cyclohexane as you can into the bulb.

5. Holding the plastic pipette vertically over the graduated cylinder, squeeze the bulb gently and add the cyclohexane to the graduated cylinder. COUNT the number of drops of cyclohexane required to increase the volume of cyclohexane in the graduated cylinder by EXACTLY 1.00 mL.

6. Repeat Step 5 at least once or until your number of drops required to add 1.00 mL of cyclohexane agrees to ± 2 drops. Empty the pipette when you are done.

7. Calculate the volume/drop by dividing the volume of cyclohexane ADDED by the number of drops added.

8. Calculate the AVERAGE volume/drop by averaging your results from Step 7.

Moving on!

Measurement of the Volume of Stearic Acid Solution Required To Cover the Water Surface

9. Obtain a stoppered bottle containing the stearic acid solution. Note down the concentration of the solution written on the bottle.

10. Open the bottle. Quickly, draw some of the solution into your empty pipette. Shake the solution in the pipette bulb and then discard it.

11. Carefully draw as much stearic acid solution as you can into the bulb.

12. Obtain a clean plastic dish and lid.

13. Add distilled water to the plastic dish until it is about half full.

14. CAREFULLY, add one drop of the solution to the surface of the water. Watch the surface at an angle. If the drop dissolves, it will disappear quickly.

15. Repeat Step 14, until ONE drop which is added DOES NOT DISSOLVE, but remains as a dropon the surface of the water for AT LEAST 30 SECONDS!

REMEMBER....this last drop is ONE MORE than the number needed to form a monolayer!!!

Almost there!

16. Record the number of drops required to form a monolayer.

17. Measure the diameter of the dish using a ruler and record this value.

Finishing the experiment

18. Repeat Steps 12-17, PREFERABLY with a dish of different diameter.

Cleaning Up!

19. Discard the water in the plastic dishes in the sink and rinse the dishes well. Return the plastic dishes and lids to the appropriate place.

20. Dispose of any remaining stearic acid solution in the pipette and any cyclohexane solution remaining in the beaker in the waste container in the fumehood labelled Waste Solvent Only.

21. Throw any paper towels that were used into the trash can.

22. Remember to get your raw data, written in PEN, signed by your TA and to attach this raw data to your report in order to receive a grade!

Calculations

Calibration of Pipette

1. Calculate the volume per drop for each calibration by dividing the total volume of cyclohexane added using the pipette by the number of drops it took to add that volume.

2. Calculate the average volume per drop by taking the average of the values calculated in Step 1 of the calculations.

Length of Stearic Acid Molecule

3. Calculate the volume of solution required to form a monolayer by multiplying the number of drops added to form a monolayer by the volume/drop.

4. Calculate the mass of stearic acid in that volume by multiplying the volume in Step 3 by the concentration of the stearic acid solution (written on the bottle).

5. Calculate the volume of stearic acid, V, by dividing the mass of stearic acid by the density of stearic acid, 0.847 g/mL.

6. Calculate the area of the monolayer, A, using $A = \pi r^2$, where r is the radius of the water surface.

7. Calculate the thickness of the monolayer, t, by dividing the volume of stearic acid, V, by the area, A.

Volume of a Carbon Atom

The main portion of the stearic acid molecule consists of 18 carbon atoms linked together. In addition, there is an extra hydrogen atom at one end and an oxygen atom and hydroxyl group at the other end. We can roughly account for the presence of these extra atoms by assuming that they are the equivalent of 2 more carbon atoms. Thus we can picture the stearic acid molecule as being 20 balls of equal diameter linked together.

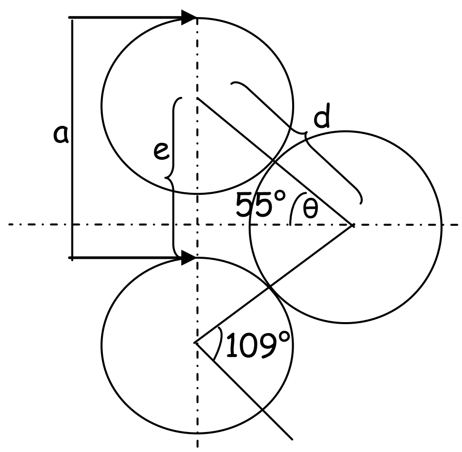
The question now is: How are they linked together? We can use two approximations.

(a) Volume of a Carbon Atom Based Upon a LINEAR Array

8. Calculate the diameter of a carbon atom, assuming that the 20 "balls" are joined in a straight line (remember: we are assuming that the thickness of the monolayer represents the length of the stearic acid molecule).

9. Calculate the volume of a carbon atom using $V = 4/3\ \pi r^3$, where r is the RADIUS of the carbon atom.

(b) Volume of a Carbon Atom Based Upon the ACTUAL Bond Angle



The actual bond angle between the carbon atoms in the chain is 109°. Thus, the chain is represented by this figure. The length occupied by two carbon atoms is "a" and the length occupied by one atom is "e". The distance "e" is therefore 1/20 of the length of the molecule, or the thickness of the monolayer. The diameter, d, of the carbon atom is therefore e/sin θ.

10. Calculate the value of "e" using the thickness of the monolayer.

11. Calculate the diameter of the carbon atom using $d = e/\sin\theta$.

12. Calculate the volume of a carbon atom using $V = 4/3\ \pi r^3$, where r is the RADIUS of the carbon atom.

Calculation of Avogadro's Number

13. Calculate Avogadro's number using the equation

$$N_A = \frac{\text{volume / mol}}{\text{volume / atom}}$$

Where the volume/mol of C atoms = atomic mass /density= 12 g/mol / 3.51 g/cm^3 = 3.42 cm^3/mol\

14. Compare the values obtained using the volume of a carbon atom obtained in Step 9 and that obtained in Step 12.

15. Calculate the percent error with respect to the known value of Avogadro's number.

Points to Ponder

- Is the error found reasonable for this type of experiment? Comment on your reasons.

- What are the sources of error inherent in the experiment? How does each source of error contribute to the result (ie. does it increase or decrease the value of the Avogadro constant?)

Lab Report

- *Refer to page iii in the FYI section.*

- Complete all the calculations, as outlined in the procedural section, and don't forget to include significant figures. **Failure to include significant figure values will result in substantial reduction of the report grade!**

- **Remember to attach your TA SIGNED raw data written in PEN to the report in order to receive a grade!**