The Great Race: A Study of van der Waals Forces

Part A: A Study of Factors Affecting the Strength of van der Waals Forces

Background
The universe is a sticky place, fortunately. Without forces causing particles to coalesce, there would be only plasma and gases, only stars and monatomic interstellar gases. No liquids, no solids, no earth, no oceans, no us. Although all forces between atoms are ultimately electrostatic in nature, they vary widely in their strengths. They may be bonds: covalent bonds, ionic bonds or metallic bonds. Or they may be intermolecular attractive forces, IMAF’s, collectively known as van der Waals forces. These include London dispersion forces, dipole-dipole forces and the strongest of the dipole-dipole forces, hydrogen-bonds.

Let’s examine dipole-dipole forces first. Hydrogen chloride is an example of a polar molecule. That is to say that its electron cloud is permanently distorted favoring the more electronegative chlorine. The chlorine atom ends up electron rich, partially negative (δ⁻), and the hydrogen atom ends up electron poor, partially positive (δ⁺). These molecules act something like tiny magnets. But instead of having a north pole and a south pole, they have a partially positive hydrogen end and a partially negative chlorine end. And just like magnets, opposites attract.

\[
\text{N—H} \quad \text{H—Cl} \quad \text{Dipole – Dipole Force of Attraction}
\]

Hydrogen bonds represent a special class of dipole-dipole forces. They are the strongest of the dipole-dipole forces. They arise because of the extreme electronegativities of fluorine, oxygen and nitrogen. When hydrogen is bonded to one of these atoms, the electron cloud of the hydrogen is so distorted toward the highly electronegative F, O, or N that the hydrogen is virtually a naked proton. As such it is very strongly attracted to a nonbonding pair of electrons on another molecule. Consider the diagram of two ammonia molecules, NH₃, below. The middle hydrogen of the upper ammonia molecule is shown hydrogen-bonded to the lone electron pair on the lower ammonia molecule.

\[
\text{Hydrogen-Bond}
\]
London dispersion forces arise from minor instantaneous distortions in the symmetry of the electron cloud of an atom or a molecule. This is similar to the permanent dipoles of polar molecules, only these are temporary, instantaneous, and transient. For example, although a helium atom has two electrons, they are not always on exact opposite sides of the nucleus. If both electrons are shifted toward the left side of the atom, then at that instant the left side of the atom is slightly negative and the right side is slightly positive. When atoms are close to each other, as they are in liquids, the electron clouds of neighboring atoms will also be distorted to minimize repulsions and maximize attractions. This coordination sets up temporary dipole-induced temporary dipole attractions. These are London dispersion forces. Their strength depends on 1) molecular mass and 2) molecular size and shape.

Molecular mass can be used as a quick gauge of the number of protons and electrons involved. Different molecular shapes will yield different amounts of contact area between molecules. Different size molecules will have different degrees of distortion of their electron clouds, different degrees of polarizability.

All molecules, nonpolar and polar, display London dispersion forces. Dipole-dipole forces are restricted to polar molecules. Finally, hydrogen bonds are even more restricted as they only occur between molecules that have hydrogen bonded to a fluorine, oxygen or nitrogen atom as in the example of ammonia above.

You are familiar with the concept of evaporation. You know that water evaporates. You know you can smell gasoline. The odor is due to gasoline vapor - molecules of gasoline that have evaporated. You can smell fingernail polish remover (acetone). Once again you are detecting acetone molecules that have evaporated from the liquid. You know that paint dries, that the solvent in it evaporates and once again you know that you can detect the odor of those solvent vapor molecules in the air of a freshly painted room. The rate at which these liquids evaporate indicates how weak or strong the intermolecular attractive forces of the liquid are. In this lab you will use manometers to quantify the relative rates of evaporation of different liquids.

Your goal for each liquid pairing used in this lab is to determine how the molecules are different, how that difference impacts the strength of the attractive forces and to predict their relative rates of evaporation. Then you will use manometers to measure the relative rates of evaporation. From the results of these “races” you will determine the relative strength of the van der Waals forces occurring between molecules of each liquid used for each trial.

In order for a surface molecule to evaporate it must overcome, break the attractive forces holding it to other molecules of the liquid. For a liquid with strong van der Waals forces between the molecules, fewer molecules will have sufficient kinetic energy to break away.
The rate of evaporation will be low. Fewer vapor molecules will be produced. Weaker van der Waals forces mean that more surface molecules will have sufficient kinetic energy to escape, to break the forces binding them to the other liquid molecules. This results in a higher rate of evaporation. More vapor molecules will be produced.

By using manometers to measure the relative rate of change in the pressure inside the gas flask, we will be able to determine which molecules are evaporating at a faster rate and, therefore, which of the two liquids has the weaker van der Waals forces. We can then look at differences in molecular mass, molecular polarity and hydrogen bonding capability to devise some general guidelines to use to determine the relative strength of the van der Waals forces displayed by two different substances.

**Part A: The Great Race Manometer Trials**  
**Y-Quartets: Trials 4-6**

**Objective**  
Van der Waals forces arise from several different structural features of molecules. Your goal is to determine what key structural difference between the paired molecules of each set is responsible for the relative rates of evaporation of the two paired substances.

**Materials**  
- Table of Electronegativities and a Periodic Table  
- One molecular model kit or one 3x4 note card with a structural diagram for each assigned liquid  
- One manometer per lab pair: flask, one-hole stopper, 90° glass elbow, 1 pair of manometer arms, two short pieces of rubber tubing  
- 1 transparency pen or Sharpie to mark the atmospheric arm of the manometer  
- Dropper bottles of the assigned substances

**Safety**  
- There should be no open flames in this lab – no burners, no matches, and no strikers. All liquids used in this lab are flammable.  
- Always wear safety goggles when handling chemicals in the lab.  
- When inserting glass tubing into a rubber stopper  
  1. Wet the tubing and the hole of the stopper.  
  2. Hold the tubing with a paper towel that is folded over several times so that multiple layers of towel are between your fingers and the tubing.  
  3. Hold the elbow of the tubing so that you are pushing in line with the stopper. Do not hold the tubing at the end.  
  4. Push on the tubing gently with a twisting motion until the glass just protrudes from the smaller end of the stopper.  
- Follow the teacher’s instructions for cleanup of materials and disposal of chemicals. Any remaining drops of liquid should be poured into the appropriately labeled flask in the hood at the completion of each procedure.  
- Wash your hands thoroughly before leaving the lab.

**Molecular Model Procedure**  
1. Working with one other lab pair, build two (2) molecules of 1-butanol and use them to illustrate/discuss the relevant van der Waals forces and their relative strengths. Complete entries 1-4 in Data Table 4 on the Lab Report for 1-butanol. Take the models to your instructor and use them to demonstrate the van der
Waals forces involved.
2. Have your instructor check entries 1-4 in Data Table 4.
3. Now build two molecules of pentane and use them to illustrate/discuss the relevant van der Waals forces and their relative strengths. Complete entries 1-4 in Data Table 4 on the Lab Report for isopropanol. Take the models to your instructor and use them to demonstrate the van der Waals forces involved.
4. Have your instructor check entries 1-4 in Data Table for pentane.

**Manometer Procedure**
1. Each lab pair needs to assemble one manometer using Figure 1 as a guide.
   a. Securely attach the flask to a ring stand using a clamp.
   b. Check the rubber tubing for cracks. (Gases are sneaky & will leak out of the tiniest of holes.)
   c. Using the 10 cm piece of rubber tubing, connect the two arms of the manometer at the bottom – the ends opposite the tape connecting them.
   d. Attach the 8 cm piece of rubber tubing to one of the manometer arms. This will be the gas arm.
   e. Fill the U-tube half full with water.
   f. Carefully insert the short 90° elbow into the rubber stopper.
   g. Wet the tubing, hold it at the bend with a dry paper towel folded over several times, and push it into the stopper with a gentle twisting motion.
   h. Do not connect the rubber tubing to the 90° glass elbow.
   i. Do not place the stopper in the flask.
   j. Rubber tubing should overlap the glass tubing by 0.5 – 1.0 cm.

*Make this the last connection immediately after adding liquid to the flask.*

Note: A Florence flask is shown but you may be using an Erlenmeyer flask as the gas bulb.

**Experimentation**

**Trial 4:**
1. Read steps 1-6 and then practice steps 2-5 using a pencil as a pretend dropper. It is important to count the drops so that you are working simultaneously. Practice several times until both teams are able to do this process to completion quickly and simultaneously.
2. One partner of each pair should place 15 drops of 1-butanol in one manometer flask while one partner from the other pair places 15 drops of pentane in their manometer flask. Do this quickly and simultaneously.
3. Once the drops are placed in the manometer flask, quickly stopper the flask - hold the flask at the bottom with one hand while pushing the stopper in TIGHTLY with a twisting motion - then attach the rubber tubing to the 90° elbow.
4. Quickly re-push and re-twist the rubber stopper to make certain it is still on tight.
5. The other partner should be holding the U-tube, so that they can mark the initial level of the water in the gas arm using a Sharpie or a transparency pen once the rubber tubing is secured. Mark the initial water level in the atmospheric arm.

6. Decide which partner is performing which task so that you can assemble the manometer quickly once the drops are in it. Both teams need to be proficient at completing this step. It must be performed quickly and simultaneously in order to obtain reliable evaporation rate data.

7. When you are confident that both teams are able to perform this process quickly and simultaneously, perform Trial 4 using the droppers of 1-butanol and pentane.

8. Observe the relative rate of the water movement in the atmospheric arm of the two manometers. Complete Data Table 4 on the Lab Report.

9. **Clean-up:**
   a. Pour any remaining liquid in the manometer flask into the appropriately labeled “Discard Flask” in the hood.
   b. Fill the manometer flask with water and discard the water down the sink.
   c. Dry the manometer flask thoroughly using a brush wrapped with a paper towel.
   d. Obtain a fresh paper towel and dry the manometer flask again.
   e. Any water remaining in the manometer flask will also evaporate and will interfere with the results.
   f. Refill the U-Tube to the half-way point if necessary.

**Trial 5: The impact of molecular mass**
1. Repeat the Molecular Model Procedure for pentane and hexane.
2. Record your answers in Data Table 5.
3. Get instructor approval before moving on to the Manometer Procedure.
4. Refill the U-Tube to the half-way point if necessary.
5. Repeat the Manometer Procedure this time using pentane and hexane.
6. Complete Data Table 5 in the Lab Report.
7. Repeat the clean-up, properly discarding any remaining liquid, rinsing, and drying the manometer flask before moving on to Trial 6.

**Trial 6: Molecular Shape**
1. Repeat the Molecular Model Procedure for 1-butanol and t-butanol.
2. Record your answers in Data Table 6.
3. Be sure to get instructor approval before moving on to the Manometer Procedure.
4. Refill the U-Tube to the half-way point if necessary.
5. Repeat the Manometer Procedure this time using 1-butanol and t-butanol.
6. Complete Data Table 6 in the Lab Report.
7. Repeat the clean-up, properly discarding any remaining liquid, rinsing, and drying the manometer flask.

**Final Clean-up**
1. Pour any remaining liquid in the manometer flask into the appropriately labeled “Discard Flask” in the hood.
2. Fill the manometer flask with water and discard the water down the sink.
3. Flush the manometer flask with water again.
4. Dry the flask thoroughly using a brush wrapped with a paper towel.
5. Obtain a fresh paper towel and dry the flask again.
6. Dismantle the manometer and place the components in the location indicated by the instructor.

**Part B: Practical Applications of van der Waals Forces**

**Background**
Paints, nail polish and all other coatings must adhere to the surface of the material they are covering, the substrate, in order to protect it and/or make it more attractive. Automotive paint, for example, not only makes the car visually appealing, it is also absolutely essential to keep the metal from rusting and thus preserve the car. Wooden siding on houses must be painted or it will rot. Homeowners agonize over the colors they select for the exterior of their houses and for individual rooms. Fingernail polish does not serve to protect the fingernail but the myriad colors available in polish or acrylic nails can enhance any outfit from jeans to gowns. But how do coatings stick to the substrate, be it metal, wood or fingernail?

Let’s focus on nail polish. Fingernails, and of course toenails, are made of dead cells in which filamentous protein called alpha-keratin, α-keratin, has replaced most of the cytoplasm and organelles. Within each cells these filaments are cross-linked and between cells they bond end to end. Alpha keratin is a long coil of a series of amino acids. Picture a long string of pop-beads, perhaps 400 – 600 beads (the amino acids) coiled like a spring or a Slinky. Two of these coils coiled around each other and held together mainly by van der Waals forces form a dimer. Two dimers form a tetramer, two tetramers form an octamer. Parallel octamers form bundles that are held together by disulfide bridges (between cysteine amino acids), ionic bonds between glutamic acid and arginine groups (two other amino acids), and van der Waals forces. One of the challenges faced by the manufacturers of nail polish is to get it to stick to the nail.

In order to stick (to adhere) to the nail, the polish must have certain characteristics. First it has to wet the nail. It has to flow along the nail’s surface and into any nooks and crannies that may be present. The polish has to “map” or wet the surface, to make intimate physical contact at the molecular level. The solvent makes this possible. Binders, plasticizers, and pigments are the primary ingredients suspended in the solvent. The solvent allows the polish to map the surface. Only then can the polish chemically bond with the nail. Van der Waals forces are a bit more forgiving than the formation of chemical bonds. Slightly greater distances between substrate and coating are permissible for these ubiquitous attractive interactions.

The ability of any coating to wet a substrate, the surface being coated, depends on the surface tension of the coating and the surface energy of the substrate. Surface tension is the measure of force needed to deform or break the intermolecular forces on the surface of the liquid. Surface energy is the amount of attractive force that the substrate surface will exert on another material (or coating). For best wetting, the substrate should have high surface energy and the coating should have low surface tension.

The polish must also form a continuous film over the nail. Van der Waals forces, in addition to chemical bonds, also play a role in the formation of this plasticized film that forms as the polish dries. Pigments are embedded in this film and give the polish color. As the solvent evaporates from the polish, the polymer, with its resident pigments, links and cross links forming a hard, continuous plastic film over the nail. At the molecular level it
would appear like a thick layer of inter-twined cooked spaghetti noodles. They chemically bond to each other in some spots but van der Waals forces exist everywhere throughout the film. Although individually much weaker than covalent bonds, the sheer number of van der Waals interactions that a polymer, a *macromolecule*, can form makes them a considerable attractive force.

In Part A, molecular mass, size and shape were all mentioned as impacting the strength of London dispersion forces. The largest molecule used in this lab, heptane, C\textsubscript{7}H\textsubscript{16}, is a chain of seven carbons with a molecular mass of 100.23 amu. Imagine the London dispersion force strength available in a polymer such as nitrocellulose. Each monomer unit has a molecular mass of 297 amu. A single polymer of nitrocellulose is comprised of tens of thousands of these monomers giving rise to a molecular mass of perhaps 3,000,000 amu. Intertwined these polymer molecules will be very strongly attracted to each other. As a result, nail polish forms a hard cohesive film. By wetting and mapping the surface of the nail, the polish is also strongly attracted to the keratin of the fingernail. Also as the polish moves into micro-imperfections in the nail and hardens there, it becomes mechanically bound to the nail.

Think about the process of coloring nails. You may first sand or file the nail to rough up the surface. You shake the bottle of polish vigorously to evenly disperse the various components throughout the solvent. You apply the polish with a brush and the solvent carries the components into the valleys and micro-pockets on the nail where bonds and van der Waals forces form between the nail and the binder and plasticizer. As the solvent evaporates, the plasticizer, with associated pigments, forms a solid colored layer of intertwined macromolecules that sticks to the nail.

**Part B: Practical Applications of van der Waals Forces**

**Materials**
- 3x4 notecard
- Pencil
- Pen
- Sharpie
- 2 droppers: 1 for tap water & 1 for detergent water
- 5 cm x 10 cm piece of wax paper
- 5 cm x 5 cm piece of wax paper

**Procedure**
**Mapping & Wetting:**
1. On a 3 x 4 notecard, draw and label the following lines approximately 1 cm apart.
2. Go to one of the microscopes, turn on the light, and slide the card onto the stage.
3. Rotate the objective lenses to the 10/0.25 N.A. lens, then rotate the objective lenses to the 40/0.65 N.A. lens.
4. Decide which view you prefer to use to describe the appearance of:
   a. the note card
   b. each line
5. Describe the appearance of each on the lab report and answer the questions.

<table>
<thead>
<tr>
<th>Light Pencil</th>
<th>Heavy Pencil</th>
<th>Light Pen</th>
<th>Heavy Pen</th>
<th>Sharpie</th>
</tr>
</thead>
</table>

American Association of Chemistry Teachers
Wetting: Can water be made “wetter?”

1. Obtain a 5 cm x 20 cm piece of wax paper and lay it on the bench. It is important that the paper lay flat on the bench. Lay two rulers on the long sides if it does not appear to be laying flat.

2. Using a clean dropper, slowly place 12 drops of tap water onto a single spot 5 cm in from the short edge of the wax paper. The drops should only fall 0.5 cm from the dropper tip to the growing bead on the wax paper. You should have a single bead of water on the paper. Measure and record the diameter of the bead.

3. Repeat using a dropper full of detergent water. Place these drops on a single spot 5 cm in from the opposite side of the wax paper. Measure and record the diameter of this “bead” and describe it on the lab report.

4. Look at each bead of water from the side. Draw what you see on your lab report.

Surface area:

1. We often sand or file substrates before applying a new coating. This is strongly recommended for all glossy or shiny surfaces. Ever wonder why? One reason is certainly to clean off any residues which may be adhering to the surface. But the other is to increase the contact area between the substrate and the coating. A sanded surface offers much more contact area for the paint to adhere to – provided the coating maps the surface well. That is flows into all of the valleys and interstices offered by the surface. This process provides for mechanical as well as chemical bonding between the substrate and the coating.

2. Measure Figures A & B on the lab report and answer the questions. Answer the questions on the lab report.

Surface Energy:

1. This is a property of the substrate that measures how strongly it attracts other substances to its surface. Let’s pit surface energy for different substances acting as the substrate against the pull due to gravity on drops of water.
   a. Hold your hand out palm up and place drops of water on the pads (where your fingerprints are) of three fingers, one small drop, one slightly larger drop and one even larger drop. Now turn your hand over so that the palm and your fingers are facing down. Results?
   b. Repeat this process with three drops on a 5 cm x 5 cm piece of wax paper. Results?
   c. Try it on your fingernails, on a glass plate, on a piece of wood, a piece of metal, a piece of plastic, etc.