

Discussion

You used the number of electron pair domains to determine the *electronic geometry* of a given molecule. By examining the number of lone pairs of electrons present, you were subsequently able to determine the *molecular geometry* of the molecule. You found that the shapes of species in which there are lone pairs of valence electrons are related to the shapes of species in which all pairs of valence electrons are involved in bond formation.

For example, consider species with five EPDs around the central atom. These all have trigonal bipyramidal *electronic geometry*. The number of lone pairs, however, determines the actual or *molecular geometry* (trigonal bipyramidal, see-saw, T-shaped, linear). These molecular geometries are all related to trigonal bipyramidal geometry. The see-saw shape, for example, is simply the trigonal bipyramid with a lone pair of electrons replacing an atom in the equatorial plane.

Why do species with trigonal bipyramidal electronic geometry that have one (or more) lone pair(s) of electrons always have the lone pair(s) situated in the equatorial plane rather than in an axial position?

figure 2. See-saw molecular geometry (i.e. trigonal bipyramidal electronic geometry)

Because lone pairs have larger spatial requirements than do bonded pairs of electrons, a bonding electron pair is simultaneously attracted to two nuclei, while a non-bonding pair of electrons is attracted to only one nucleus. Hence, non-bonding, or lone, electron pairs on the central atom are more space-demanding than bonding pairs. This is why the lone pair in figure 2 occupies the equatorial position. The 120° bond angle gives it more room than the 90° axial bond angle. But that's not all. Read on.

Lone pairs have larger spatial requirements than bonding electron pairs. This means that all molecules with lone pairs in the valence shell of the central atom have shapes that are *distorted* from the ideal shapes corresponding to equivalent EPDs and have bond angles that are smaller than the ideal angle.

Further Questions. Answer on a separate sheet.

1. For each of the following species:
draw the Lewis structure
state the electronic geometry
state the molecular geometry
for molecules (not ions) state whether polar or non-polar
 - a) PCl_4F
 - b) ICl_4^-
 - c) IO_3^-
 - d) SO_4^{2-}
 - e) SO_3^{2-}
 - f) IF_5
 - g) AsH_3
2. Consider a fictitious molecule with formula AB_7 (No lone pairs on the central atom.).
 - a) What will be the electronic geom. of this molecule? (Hint: see Table 1)
 - b) What will be the molecular geometry of AB_7 ? Draw a diagram of this molecule, clearly indicating *all* bond angles-equatorial and axial.
 - c) If one bonding atom is replaced by a lone pair of electrons we have the molecule AB_6E . Draw a diagram of this fictitious molecule, clearly indicating the location of the lone pair.

references:

- E.R. Toon & G.L. Ellis, Laboratory Experiments for Foundations of Chemistry, Holt, Rinehart and Winston, Inc, Toronto, 1973.
- R.J. Gillespie, *Chem 13 News*, May 1996, p12.

4.3 Intermolecular Forces

van der Waals Forces \Rightarrow

\Rightarrow are a combination of many of intermolecular forces including

- a)
- b)
- c)

Intermolecular forces are a lot weaker than covalent bonds inside a molecule

			<u>Energy Required</u>
Evidence:	$\text{H}_2\text{O}_{(l)} \rightarrow$	$\text{H}_2\text{O}_{(g)}$	41 kJ/mol

	$\text{H}_2\text{O}_{(l)} \rightarrow$	$\text{H}_{2(g)} + \text{O}_{2(g)}$	242 kJ/mol
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\therefore

a) dipole-dipole force \Rightarrow

\Rightarrow

\Rightarrow

\Rightarrow

e.g. $\delta^+ \text{H}-\text{Cl}^{\delta-} \text{-----} \delta^+ \text{H}-\text{Cl}^{\delta-}$

b) London forces \Rightarrow

\Rightarrow

spherical vs. linear molecule

- spherical will have less dispersion forces \Rightarrow
- linear \Rightarrow
- C_5H_{12} – 2 isomers (different form of same molecular formula)

A

B

Using dipole-dipole and London forces to Predict Boiling Points

	Molecular Geometry	Number of Electrons	Boiling Point (°C)
CH _{4(g)}			
SiH _{4(g)}			
GeH _{4(g)}			
SnH _{4(g)}			

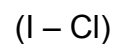
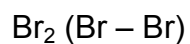
Isoelectronic molecules (same # of electrons)

Question: If you have 2 isoelectronic substances and one is polar and the other is non-polar, which should have a higher boiling point?

Answer:

Example: Br₂ and ICl are both isoelectronic with 70 e⁻ each. Br₂ has a boiling point of 59°C and ICl has a boiling point of 97°C. Explain why.

Answer:



Summary: Predicting with Dipole-Dipole and London Forces

1.

2.

→

→

3. You can explain and predict the relative boiling points of two substances if:

→

→

→

4. **You cannot explain and predict with any certainty the relative boiling points of the two chemical if:**

→ one of the substances has a stronger dipole-dipole and the other substance has a stronger London force

Hydrogen Bonding

→

→

→

4.3 Bonding in Solids

crystal lattice →

Classifying Solids

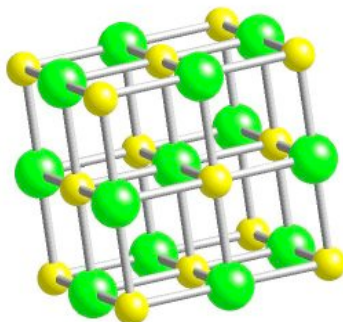
Class of Substance	Elements Combined	Examples
ionic		
metallic		
molecular		
Covalent network		

A) Ionic Crystals

Property	Interpretation
	bonds are strong
conduct electricity in liquid state but <u>NOT</u> in the solid state	
	lattice is composed of ions
high melting points	

*

The properties of ionic crystals are explained by a 3-D arrangement of positive and negative ions held together by strong, directional ionic bonds.



B) Metallic Crystals

■

→

→

→

Bonding is a result of fixed positive nuclei and loosely held mobile valence electrons. This model is called the **electron sea model**.

Electron sea model explains:

①

②

③

Explaining the Properties of Metals

Property	Explanation
	valence electrons absorb and re-emit the energy from all wavelengths of visible light
	Non-directional bonding means that planes of atoms can slide over one another while remaining bonded (see diagram below)
	Valence electrons can freely move throughout the metal (so electrons can easily enter one end and leave the other end)
	electron sea surrounding positive centers produces strong bonding

C) Molecular Crystals

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Property	Explanation
low melting point	
not very hard	
non-conductors of electricity in pure form or in a liquid	

D) Covalent Network Crystals (carbon based)

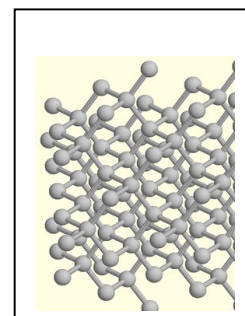
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Properties:

allotrope →

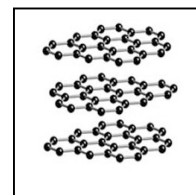
i) diamond →

→

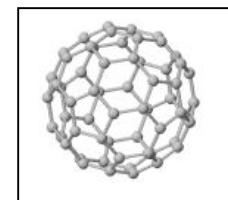


ii) graphite →

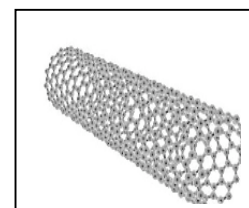
→



iii) fullerenes →



iv) carbon nanotubes →



Qualitative (Microscale) Extraction of Caffeine from Wake-Up Tablets

Purpose

The purpose of this experiment is to isolate caffeine from wake-up tablets and using a technique called solvent extraction. The experiment will be carried out on a microscale to minimize cost and chemical waste.

Introduction

Covalent (or molecular) compounds can be roughly divided into two categories: Polar and non-polar. Polar compounds have an overall dipole, owing to polar bonds whose dipole vectors do not cancel. By contrast, non-polar compounds have no net dipole. This can arise for one of two reasons: either all of the bonds in a compound are non polar, or any polar bonds present cancel, resulting in an overall dipole of zero (or close to it).

In this experiment you will be separating caffeine from the starch "filler" in a wake-up tablet. The starch filler is a polymer of glucose. It is virtually insoluble in hot water. Caffeine is a somewhat non-polar compound with significant solubility in hot water and in the non-polar solvent dichloromethane, CH_2Cl_2 (aka methylene chloride). Caffeine has very low solubility in cold water.

You will use the solubility properties of caffeine and starch to isolate caffeine from the mixture.

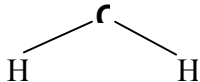
Each student (or each pair of students) requires:

- CH_2Cl_2 10 mL
- mortar and pestle (may be shared between two students)
- 2 - 50 mL beakers
- beaker tongs to handle a hot 50 mL beaker
- scoopula
- stirring rod
- hot plate
- 10 mL graduated cylinder
- centrifuge tube with stopper
- disposable glass pasteur pipet with removable rubber pipet bulb
- funnel
- filter paper
- retort stand
- ring clamp to support funnel

Pre-lab Questions:

Some advice: Read these questions carefully. Then read the entire handout.
Then answer the questions.

1. What determines whether a given covalent molecule is polar or non-polar? Use water, and methane, CH_4 , and sulfur hexafluoride, SF_6 , to illustrate your answer.
2. State the intermolecular force(s) present in each of the following. Provide a diagram in each case.
 - a) water (a polar molecule)
 - b) liquid hydrogen chloride, HCl
 - c) liquid methane, CH_4 .
3. The Merck Index (we have a copy) will be useful in answering parts of this question.
 - a) Illustrate the structure of caffeine. Remember: the structural formula of a compound is not the same as its molecular formula. For example, water has a molecular formula H_2O , but its structural formula is


 - b) Is pure caffeine a liquid or a solid?
 - c) What colour is pure caffeine?
 - d) What is the solubility of caffeine in hot water, cold water, and in dichloromethane, CH_2Cl_2 , or in chloroform, CHCl_3 ? Be as quantitative as possible. (Both CH_2Cl_2 and CH_3Cl are non-polar solvents. For simplicity, we will assume that both have the same degree of non-polarity. CH_2Cl_2 is also known as methylene chloride.)
 - e) Based on the above data, do you think that caffeine is a polar or non-polar substance? Explain briefly.
 - f)
 - (i) Upon what rule of thumb is solvent extraction based?
 - (ii) Briefly explain *how* this principle is used to separate caffeine from the other ingredients in the wake-up tablet. Be specific; refer to both caffeine *and* any water-insoluble impurity.
4. What are the two main ingredients of the pill?
5. Why is the pill crushed before putting it into water?
6.
 - a) Why do you think that it is necessary to boil the crushed wake up pills in water rather than simply mixing the crushed tablets with room temperature water
 - b)
 - i) Why is it necessary to filter this aqueous solution of caffeine?
 - ii) Why must this aqueous solution of caffeine be filtered while it is still hot?
 - c) After filtering, why must the aqueous solution of caffeine be cooled before extracting into dichloromethane?

- d) When extracting the caffeine into dichloromethane, why are you asked to gently swirl the separatory funnel, rather than vigorously shake it?
 - e) Why do you think that three successive 2 mL extractions with dichloromethane are used rather than one 6 mL extraction? (Note: The answer has nothing to do with the centrifuge tube overflowing.)
7. Prepare a flow chart of the procedure for this experiment. You will refer to this flow chart during the laboratory.

Procedure:

1. Two students (or two groups, depending on whether students are working alone or in pairs) will perform this step together.
Crush a wake-up tablet using a mortar and pestle. Divide the powder approximately in half. Each student (or group) should put his or her powdered tablet in a 50 mL beaker.
2. Add ca. 10 mL of water; heat the solution, using a hot plate as the source of heat. Monitor the solution carefully. When the solution boils, remove the beaker from the heat with a pair of tongs. Unplug the hot plate right away. Make sure that the electrical cord from the hot plate is not dangling over the edge of the lab bench.
3. Immediately filter the hot solution by gravity through a fluted filter paper.
4. Cool the aqueous caffeine (i.e. the filtrate) in an ice bath. Dispose of the filter paper as indicated by your teacher.
5. Pour the cooled filtrate into a test tube. Do not be concerned if the volume of this solution is less than the original 10 mL. (This is only a qualitative separation.)
6. This step will extract the caffeine from the aqueous solution into the dichloromethane. Add 2 - 3 mL of CH_2Cl_2 to the test tube containing the aqueous caffeine. Put the lid securely on the test tube and invert it 10 times to allow the CH_2Cl_2 to thoroughly come in contact with the aqueous caffeine solution. Do not shake vigorously; the organic and aqueous layers may form an emulsion and not separate cleanly.
7. When the CH_2Cl_2 has separated from the water, it must be carefully removed from the test tube with a glass pipet. Squeeze the pipet bulb and insert it to the bottom of the test tube. Carefully release the bulb to draw the caffeine-containing CH_2Cl_2 solution into the pipet. Be careful not to draw any water into the pipet. Don't worry if you can't get all the CH_2Cl_2 layer. Put this caffeine-containing CH_2Cl_2 solution into a clean, dry beaker.
8. Repeat step 7 with two more 2 mL portions of CH_2Cl_2 , remembering not to draw any water into the pipet. Pour the combined caffeine-containing CH_2Cl_2 layers into the labelled erlenmeyer flask in the fumehood. The teacher will carefully distill (and recover!) the CH_2Cl_2 . You will see the relatively pure caffeine next class. Dispose of any chemical waste in the labelled beaker indicated by your teacher.

Post-Lab Questions

1. Caffeine belongs to a class of nitrogen-containing organic compounds called alkaloids. Briefly state some of the physiological effects of alkaloids. State at least one other common alkaloid along with its structural formula.
2.
 - a) What colour was our extracted caffeine after removal of the dichloromethane solvent?
 - b) Based on this observation, was our extracted caffeine pure?
 - c) If the extracted caffeine was impure, was (were) the impurity (or impurities) polar or non-polar? Explain briefly.
3. State two reasons why we pooled our crude caffeine (in dichloromethane) solutions and distilled the dichloromethane solvent rather than simply letting the solvent evaporate.
4. In general, what criterion (criteria) is (are) required to extract a given compound from a mixture using solvent extraction?