Announcements

Chem 7 Final Exam
Wednesday, Oct 10 1:30-3:30AM
Schmitt Hall C-109
Chapter 1-12
70 or 75 multiple choice questions

About equal weighting of Chapter Questions---Chapter 3 heavy (% mass, balancing, stoichiometry, limiting reagent, yield).

Chapter 12: Section 12.3 only (today)

Intermolecular Forces and Liquids and Solids -12

There are attractive **intermolecular** in all solids, liquids (called condensed phases) and gases. Molecules are held together by attractive and **intramolecular** forces (bonds within a molecule).

A **phase** is a state of matter that is homogeneous, chemically uniform and has physically distinct properties (density, crystal structure, index of refraction).

Generally we recognize 4-states of matter:

1. Gas
2. Liquids
3. Solids
4. Plasma (hot ionized gas)

One can think of the phases as “different classes” of molecular motion observed at different temperatures.
You can think of the different phases as classes of possible molecular motion due to different kinetic energies (caused by temperature differences) and varying degrees of intermolecular forces.

| Phase     | ΔH  |  
|------------|-----|-----------------|
| Deposition | ΔH < 0 |  
| Sublimation | ΔH > 0 |  
| Gas        | ΔH < 0 |  
| Condensation | ΔH > 0 |  
| Evaporation | ΔH > 0 |  
| Melting    | ΔH > 0 |  
| Freezing   | ΔH < 0 |  
| Liquid     | ΔH < 0 |  

Electronegativity is an element’s inherent property to draw electrons to itself when chemically bonded to another atom in a molecule.

Lookout for bonds having: F, O, Cl, N, Br, I

Connecting Dots: large electronegativity differences in a bond => polar molecules => large dipole moments => gives rise to large IMF => decreased vapor pressure => increased boiling and melting points, higher viscosity, higher surface tension.

Identify polar bonds in a molecule, and then consider molecular geometry to gauge if there is a net dipole moment (dipole) in a molecule.

Recall your molecular and electron geometry from Chem 7.
**Intermolecular forces** are classified into four major types.

1. **Ion-dipole**: occur between neighboring an ion solution and a polar molecule (dipole) also in solution.

2. **Dipole-dipole**: occur between a neutral polar molecules (same or not the same molecules).

3. **Induced-dipoles**: occur when a ion or a dipole induces a spontaneous dipole in a neutral polarizable molecule.

4. **London Dispersion Forces** are attractive IMF’s that occur between all molecules. Spontaneous dipoles are formed randomly or induced by other charged species in neutral polarizable molecules.

---

**Summary of Intermolecular Forces (van der waals forces)**

<table>
<thead>
<tr>
<th>Type of Interaction</th>
<th>Strength</th>
<th>Interaction</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion</td>
<td>Dipole</td>
<td>Highest</td>
<td>50-600</td>
</tr>
<tr>
<td>Dipole</td>
<td>Dipole</td>
<td>--two polar molecules (dipoles) interact electrostatically.</td>
<td>5-25</td>
</tr>
<tr>
<td>Ion or Dipole</td>
<td>Dipole</td>
<td>--ion or a dipole induces a dipole in a polarizable non-polar molecule.</td>
<td>2-15</td>
</tr>
<tr>
<td>Induced Dipole</td>
<td>Induced Dipole</td>
<td>---also called London Dispersion Forces</td>
<td>0.05-40</td>
</tr>
</tbody>
</table>

---

**Flowchart for classifying intermolecular forces**

- Are polar molecules involved?  
  - NO  
  - Are hydrogen atoms bonded to N, O, or F atoms?  
    - NO  
    - Are ions involved?  
      - NO  
      - Are ions and polar molecules both present?  
        - YES  
        - London forces only (induced dipoles)  
          - Examples: Ar(g), I$_2$(s)  
        - Dipole-dipole forces  
          - Examples: H$_2$S, CH$_3$Cl  
        - Hydrogen bonding  
          - Examples: liquid and solid H$_2$O, NH$_3$, HF  
      - YES  
      - Ion dipole forces  
        - Example: KBr in H$_2$O  
    - YES  
    - Ion bonding (Section 6.2)  
      - Examples: NaCl, NH$_3$NO$_3$  

---

**Boiling point differences are explained by dipole-dipole interactions**
Hydrogen bonding is a special case of dipole-dipole intermolecular force that occurs between a hydrogen atom and an unshared pair of electrons in a polar N-H, O-H, or H-F bond.

The boiling points of covalent binary hydrides increase with increasing molecular mass down a Group but the hydrides of NH₃, H₂O and HF have abnormally high BP because of hydrogen bonding.

The table below shows the boiling points of various substances:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular Mass (amu)</th>
<th>Dipole Moment (D)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂H₆</td>
<td>44</td>
<td>0.1</td>
<td>231</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>46</td>
<td>1.3</td>
<td>248</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>50</td>
<td>1.9</td>
<td>249</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>44</td>
<td>2.7</td>
<td>294</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>41</td>
<td>3.9</td>
<td>355</td>
</tr>
</tbody>
</table>

As dipole moments increase in polar substances of the same mass, IMF’s increase as do boiling points (lower vapor pressure) and melting points.

Water is a highly polar molecule due to oxygen inherent ability to attract electrons more so than hydrogen.

There is more electron density near the oxygen atom and less around the hydrogen (arrows). This polarity property gives water its dissolving properties of other polar substances.
London Dispersion Forces are attractive intermolecular forces that occur when temporary dipoles are formed due to random electron motions in all polarizable molecules.

Polarizability is the ease with which an electron distribution (cloud) in the atom or molecule can be distorted by an outside ion or dipole.

2-neutral non-polar polarizable molecules

\[ E \propto \frac{1}{d^6} \]

Induced-Dipole Moment and IMF between molecules

London Dispersion Force
All molecules have at least this IMF

POLARIZABILITY
- Size and polarizability increases down a group
- Polarizability increases with molar mass (# e-) of a molecule
- Cations are less polarizable than their parent atom because they are smaller and more compact.
- Anions are more polarizable than their parent atom because they are larger.

Examples of increasing London dispersion forces with increase in size and polarizability.

1. Ion-Ion > Ion-Dipole > Dipole-Dipole > Dispersion
2. For non-polar molecules of approximately the same mass and shape and volume (i.e. polarizability the same), dipole-dipole forces dictate the difference in physical properties.
3. Hydrogen bonding occurs with polar bonds in particular H-F, H-O, H-N and an unshared pair of electrons on a nearby electronegative atom usually F, O, or N.
4. For non-polar molecules of the same molecular mass, longer less compact molecules are generally more polarizable and have greater dispersion forces and show higher boiling and melting points.
5. For non-polar molecules of widely varying molecular mass, those with more mass are typically more polarizable and experience greater London dispersion forces and exhibit higher boiling points and melting points.

Larger unbranched molecules are more polarizable than compact branched molecules.

Larger polarizability in unbranched molecules explains boiling and melting points trends in isomers.

Some Generalizations About IMF’s
1. Ion-Ion > Ion-Dipole > Dipole-Dipole > Dispersion
2. For polar molecules of approximately the same mass and shape and volume (i.e. polarizability the same), dipole-dipole forces dictate the difference in physical properties.
3. Hydrogen bonding occurs with polar bonds in particular H-F, H-O, H-N and an unshared pair of electrons on a nearby electronegative atom usually F, O, or N.
4. For non-polar molecules of the same molecular mass, longer less compact molecules are generally more polarizable and have greater dispersion forces and show higher boiling and melting points.
5. For non-polar molecules of widely varying molecular mass, those with more mass are typically more polarizable and experience greater London dispersion forces and exhibit higher boiling points and melting points.
Comparing the strengths of Intermolecular Forces

<table>
<thead>
<tr>
<th>Force</th>
<th>Strength</th>
<th>Energy-Distance</th>
<th>Interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>London Forces</td>
<td>1-10 kJ/mole</td>
<td>1/r^6</td>
<td>All-molecules</td>
</tr>
<tr>
<td>Dipole-Dipole</td>
<td>3-40 kJ/mole</td>
<td>1/r^3</td>
<td>Polar molecules</td>
</tr>
<tr>
<td>Hydrogen Bonding</td>
<td>10-40 kJ/mole</td>
<td>1/r^3</td>
<td>O-H, N-H, H-F</td>
</tr>
<tr>
<td>Ion-Dipole</td>
<td>10-50 kJ/mole</td>
<td>1/r^2</td>
<td>Ions-Polar molecules</td>
</tr>
<tr>
<td>Ion-Ion</td>
<td>&gt;&gt;200 kJ/mole</td>
<td>1/r</td>
<td>Cation-Anion</td>
</tr>
</tbody>
</table>

Arrange the following substances in order of increasing boiling points.

C_2H_6, NH_3, Ar, NaCl, AsH_3

Flowchart for classifying intermolecular forces

 Arrange the following substances in order of increasing boiling points.

C_2H_6, NH_3, Ar, NaCl

Ar < C_2H_6 < NH_3 < NaCl

nonpolar  nonpolar  polar  ionic

London  London  dipole-dipole H-bonding ion-ion

Arrange the following non-polar molecules in order of increasing melting point.

SiF_4, CS_2, Cl_4, GeCl_4

Solution. None of these molecules poses a net dipole moment. Only dispersion forces exist and these are expected to increase with increasing molecular mass (more polarizable as a molecule gets larger). The molar masses of these substances follow:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molar Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS_2</td>
<td>76.131</td>
</tr>
<tr>
<td>SiF_4</td>
<td>104.077</td>
</tr>
<tr>
<td>Cl_4</td>
<td>519.631</td>
</tr>
<tr>
<td>GeCl_4</td>
<td>214.402</td>
</tr>
</tbody>
</table>

The intermolecular forces, and the melting points, should increase in the following order: CS_2 < SiF_4 < GeCl_4 < Cl_4. The experimentally determined melting points are -110.8, -90.4, 49.5, and 171 °C, respectively.

For each pair of substances, identify the dominant intermolecular forces in each substance, and select the substance with the higher boiling point.

(a) MgCl_2 or PCl_3
(b) CH_3NH_2 or CH_3F
(c) CH_3OH or CH_3CH_2OH
(d) Hexane (CH_3CH_2CH_2CH_2CH_3) or 2,2-dimethylbutane

PLAN: • Bonding forces are stronger than nonbonding (intermolecular) forces.
• Hydrogen bonding is a strong type of dipole-dipole force.
• Dispersion forces are decisive when the difference is molar mass or molecular shape.
For each pair of substances, identify the dominant intermolecular forces in each substance, and select the substance with the higher boiling point.

**SOLUTION:**

(a) Mg²⁺ and Cl⁻ are held together by ionic bonds while PCl₃ is covalently bonded and the molecules are held together by dipole-dipole interactions. Ionic bonds are stronger than dipole interactions and so MgCl₂ has the higher boiling point.

(b) CH₃NH₂ and CH₃F are both covalent compounds and have bonds which are polar. The dipole in CH₃NH₂ can H bond while that in CH₃F cannot. Therefore CH₃NH₂ has the stronger interactions and the higher boiling point.

(c) Both CH₃OH and CH₃CH₂OH can H bond but CH₃CH₂OH has more CH for more dispersion force interaction. Therefore CH₃CH₂OH has the higher boiling point.

(d) Hexane and 2,2-dimethylbutane are both nonpolar with only dispersion forces to hold the molecules together. Hexane has the larger surface area, thereby the greater dispersion forces and the higher boiling point.

---

**In which substances would hydrogen bonding forces occur between molecules?**

C₂H₆, HCHCl₂, CH₃CH₂OH, HNO₃, PH₃

**Solution.** Hydrogen is bonded to one of the very electronegative atoms in CH₃CH₂OH and HNO₃. Hydrogen bonding should occur in both of these substances.

---

**What type of intermolecular forces can you recognize in the following ionic and covalent compounds.**

HBr(g)  HBr is a polar molecule: dipole-dipole forces. There are also dispersion forces between HBr molecules.

CH₄  CH₄ is non-polar: London dispersion forces.

SO₂  SO₂ is a polar molecule: dipole-dipole forces. There are also dispersion forces between SO₂ molecules.

---

**Which of the following statements is incorrect?**

(A) CH₃CH₂OH should have a viscosity and boiling point greater than HOCH₂CH₂OH

(B) The large specific heat capacity and the large heat of vaporization, ΔH_vap, of water are both a result of strong hydrogen-bonding forces.

(C) The surface tension of a liquid is a result of strong and imbalanced intermolecular attractive forces acting at the surface of the liquid relative to its interior.

(D) The observation that water forms a U-shaped meniscus climbing up the side of glassware is a result of cohesive forces being greater than adhesive forces.

(E) Polar molecules is a result of moderate electronegativity differences between bonded atoms in molecules, but molecular geometry must be considered to determine if a molecule is polar overall.