### 3.1 Intermolecular Forces

Essential knowledge statements from the AP Chemistry CED:

- London dispersion forces are a result of the Coulombic interactions between temporary, fluctuating dipoles. London dispersion forces are often the strongest net intermolecular force between large molecules.
    - Dispersion forces increase with increasing contact area between molecules and with increasing polarizability of the molecules.
    - The polarizability of a molecule increases with an increasing number of electrons in the molecule, and the size of the electron cloud. It is enhanced by the presence of pi bonding.
- The dipole moment of a polar molecule leads to additional interactions with other chemical species.
    - Dipole–induced dipole interactions are present between a polar and nonpolar molecule. These forces are always attractive. The strength of these forces increases with the magnitude of the dipole of the polar molecule and with the polarizability of the nonpolar molecule.
    - Dipole–dipole interactions are present between polar molecules. The interaction strength depends on the magnitudes of the dipoles and their relative orientation. Interactions between polar molecules are typically greater than those between nonpolar molecules of comparable size because these interactions act in addition to London dispersion forces.
    - Ion–dipole forces of attraction are present between ions and polar molecules. These tend to be stronger than dipole–dipole forces.
- The relative strength and orientation dependence of dipole-dipole and ion-dipole forces can be understood qualitatively by considering the sign of the partial charges responsible for the molecular dipole moment, and how these partial charges interact with an ion or with an adjacent dipole.
- Hydrogen bonding is a strong type of intermolecular interaction that exists when hydrogen atoms covalently bonded to the highly electronegative atoms (N, O, and F) are attracted to the negative end of a dipole formed by the electronegative atom (N, O, and F) in a different molecule, or a different part of the same molecule.
- In large biomolecules, noncovalent interactions may occur between different molecules or between different regions of the same large biomolecule.

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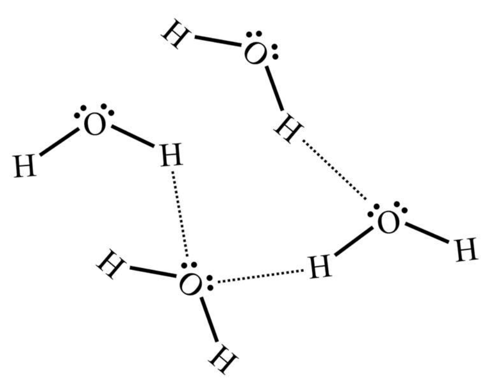
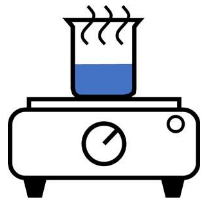
1. In chemistry, it is important to differentiate between an **intramolecular** attractive force and an **intermolecular** attractive force. In the diagram below, four water molecules are shown.

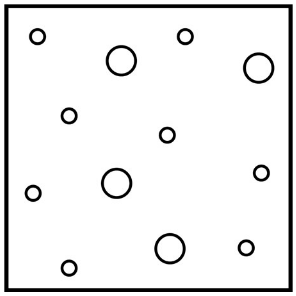


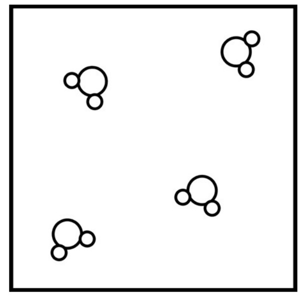
(a) Draw a circle around one example of an **intramolecular** attractive force.

(b) Draw an arrow that points to one example of an **intermolecular** attractive force.



2. Consider an experiment in which a pure sample of $H_2O$ is heated to its boiling point.





(a) Circle the particulate diagram that best represents the gas particles that are formed above the surface of $H_2O$ in this experiment.

(b) Based on your choice in part (a), when a pure sample of $H_2O$ undergoes evaporation,

( intramolecular intermolecular ) attractive forces are broken.

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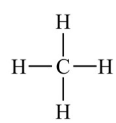
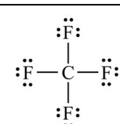
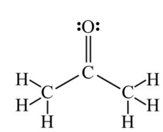
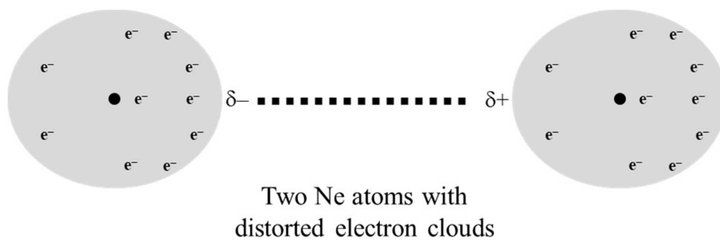
| Substance | Structural Formula | Boiling Point (K) |
|---|---|---|
| methane |  | 112 |
| carbon tetrafluoride |  | 145 |
| acetone |  | 329 |

3. Each substance listed in the table above is classified as a covalent (molecular) substance. Based on the data in the table, which substance experiences the strongest intermolecular attractive forces in the liquid phase? Justify your answer by making a connection between the data in the table and what happens to the molecules in a molecular substance during evaporation.

**London dispersion forces** (named in honor of German-American physicist Fritz London) are a result of the Coulombic interactions between temporary, fluctuating dipoles. What does a temporary dipole look like? Consider the following example, involving two atoms of neon (Ne).


In the diagram above, two atoms of Ne are relatively far apart from each other. When these atoms get closer together, the nucleus of one atom can become attracted to the electrons of the other atom, and vice versa. In addition, repulsions can occur between the electrons of different atoms. The electron clouds of each atom can become distorted, resulting in the formation of temporary dipoles, as shown in the following diagram.




**polarizability**: the ease with which the electron cloud in an atom or molecule can be distorted

**London dispersion forces (LDFs)**: attractions between atoms or molecules that are caused by temporary dipoles

The strength of the London dispersion forces increases as the number of electrons in an atom or molecule increases.

The larger the electron cloud is, the more likely it is that the electron cloud can be distorted or polarized.

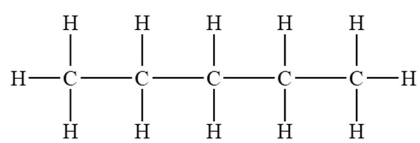
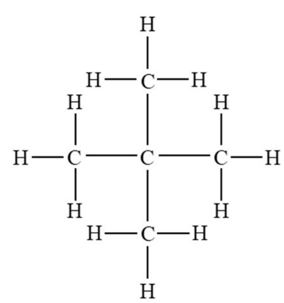
In other words, the larger the electron cloud is, the more polarizable it is and the stronger the London dispersion forces between the particles.

Comparing the relative strength of the attractive forces between the particles helps us to make predictions about boiling points. The boiling point of a substance is related to the relative strength of the attractive forces between the particles.

| Substance | Boiling Point (K) |
|---|---|
| Ne | 27 |
| Ar | 87 |
| Kr | 120 |
| Xe | 165 |

| Substance | Boiling Point (K) |
|---|---|
| $F_2$ | 85 |
| $Cl_2$ | 239 |
| $Br_2$ | 332 |
| $I_2$ | 457 |

4. Explain the trend in boiling point shown in each data table above in terms of London dispersion forces and the polarizability of atoms and molecules.

| Substance | Formula | Structural Formula | Boiling Point (K) |
|---|---|---|---|
| pentane | $C_5H_{12}$ |  | 309 |
| 2,2-dimethylpropane | $C_5H_{12}$ |  | 283 |

5. Molecular shape, surface area, and contact area between molecules can affect the relative strength of the London dispersion forces between molecules. Give an explanation for the difference in boiling point shown in the table above.

**Topic 3.1 is “Intermolecular Forces.” However, a better title might be “Interparticle Forces.”**

- **London dispersion forces in noble gases occur between atoms, not molecules.**
- **Ion-dipole forces occur between ions and molecules.**

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6. Review the information in the data table shown with Question #3. Explain why $CF_4$ has a higher boiling point than $CH_4$.

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Unlike London dispersion forces (which are a result of temporary, fluctuating dipoles), **dipole–dipole forces** are a result of the attractions between molecules that have permanent dipoles. The relative strength of dipole-dipole forces depends on the magnitudes of the dipoles and their relative orientation.

**dipole-dipole forces**: attractions between polar molecules in which the partial negative charge of one polar molecule is attracted to the partial positive charge on another nearby polar molecule

If we compare two different molecules that have comparable size electron clouds, the attractions between polar molecules tends to be greater than the attraction between nonpolar molecules. This can be explained because the dipole-dipole attractive forces act in addition to the London dispersion forces.

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7. Review the information in the data table shown with Question #3. Explain why acetone, $(CH_3)_2CO$, has a higher boiling point than $CF_4$.

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| $CH_3CH_3$ | $CH_3F$ |
| --- | --- |
| ethane | fluoromethane |

8. Which of the substances shown above do you predict should have a higher boiling point? Justify your answer in terms of the following.
   - the polarity of the molecules
   - the type of intermolecular forces experienced by each substance
   - the relative strength of the intermolecular forces

9. A mixture of $CCl_4(g)$ and $HCl(g)$ is at a temperature of 600 K. This mixture is cooled to 340 K. At this temperature, $CCl_4$ condenses, changing from a gas into a liquid, while the HCl remains in the gaseous state. Answer the following questions based on this observation.

(a) Identify all types of intermolecular forces present in each substance.

$CCl_4$ ______________________________________________

HCl ______________________________________________

(b) Which substance, $CCl_4$ or HCl, has the higher boiling point?

(c) Which substance, $CCl_4$ or HCl, experiences stronger intermolecular attractive forces?

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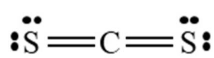
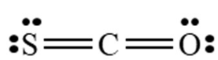
| Substance | Structure | Boiling Point |
|---|---|---|
| Carbon disulfide ($CS_2$) |  | 319 K |
| Carbonyl sulfide (COS) |  | 223 K |

10. The table above gives the molecular structures and boiling points for the compounds $CS_2$ and COS. Answer the following question based on the information in the data table.

(a) Identify all types of intermolecular forces present in each substance.

$CS_2$ ______________________________________________

COS ______________________________________________

(b) Which substance, $CS_2$ or COS, experiences stronger intermolecular attractive forces?

Questions like #9 and #10 can be challenging for AP Chemistry students. Here are some helpful guidelines.

- It is important to pay attention to the data you are given. This is especially true when the data seems to contradict the predictions that you might have made on your own, based on the molecular structure, polarity, and the types of intermolecular forces present in each substance.
- It is possible that a nonpolar molecule with a large electron cloud can have a higher boiling point than a polar molecule with a small electron cloud. For example, octane, $C_8H_{18}$, is a nonpolar substance that boils at 125°C, and water, $H_2O$, is a polar substance that boils at 100°C.
- Suppose that you compare two different molecules that are both nonpolar. Suppose that one molecule has a larger electron cloud than the other molecule. The molecule with the larger electron cloud should be more polarizable, experience stronger London dispersion forces, and have a higher boiling point.
- Suppose that you compare two different molecules *whose electron clouds are approximately the same size.* Suppose that one molecule is nonpolar and the other molecule is polar. The polar molecule should experience stronger intermolecular attractive forces (i.e., a combination of LDFs and dipole-dipole forces). The polar substance should have a higher boiling point.
- Suppose that you compare two different substances. One substance is a nonpolar molecule with a larger electron cloud. The other substance is a polar molecule with a smaller electron cloud. In this situation, *you cannot make a prediction about which substance will have stronger intermolecular attractive forces.* However, if you are given a table of experimental data, pay attention to the data.

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| Substance | Boiling Point | Types of Intermolecular Forces Present in This Substance |
|---|---|---|
| $Br_2$ | 332 K | |
| BrCl | 278 K | |

11. Identify all of the intermolecular forces present between molecules in each substance in the table above. Explain the difference in boiling points by comparing the relative strength of the attractive forces between molecules.

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| Substance | Boiling Point |
|---|---|
| $CH_4$ | 112 K |
| $SiH_4$ | 161 K |
| $GeH_4$ | 185 K |
| $SnH_4$ | 221 K |

12. Explain the trend in boiling point shown in the data table above in terms of London dispersion forces and the polarizability of the molecules.

| Set #1 | |
|---|---|
| Substance | Boiling Point |
| $NH_3$ | 240 K |
| $PH_3$ | 186 K |
| $AsH_3$ | 211 K |
| $SbH_3$ | 256 K |

| Set #2 | |
|---|---|
| Substance | Boiling Point |
| $H_2O$ | 373 K |
| $H_2S$ | 213 K |
| $H_2Se$ | 232 K |
| $H_2Te$ | 271 K |

| Set #3 | |
|---|---|
| Substance | Boiling Point |
| HF | 293 K |
| HCl | 188 K |
| HBr | 206 K |
| HI | 238 K |

London dispersion forces tend to increase with the size of the electron cloud and the polarizability of the molecules. In each of the sets shown above, there is a trend in which a larger electron cloud results in more polarizability and a higher boiling point.

13. Circle three substances shown in the tables above that have the following properties.
    - The molecule has a relatively small electron cloud
    - The substance has a relatively high boiling point compared to other substances in the same set

| | B | C | **N** | **O** | **F** |
|---|---|---|---|---|---|
| atomic radius (pm) | 88 | 77 | **75** | **73** | **71** |
| electronegativity | 2.04 | 2.55 | **3.04** | **3.50** | **3.98** |

**Hydrogen bonding** is an important type of attractive force that involves the following details.
One substance behaves as a **hydrogen bond donor**. The other substance behaves as a **hydrogen bond acceptor**.

| Requirements for a substance to be a **hydrogen bond donor** |
|---|
| The substance contains a hydrogen atom that is covalently bonded to a highly electronegative atom (N, O, or F). |
| Requirements for a substance to be a **hydrogen bond acceptor** |
| The substance contains a highly electronegative atom (N, O, or F) with a lone pair of electrons on it. This atom (N, O, or F) has a partial negative charge on it because it is part of a polar bond (dipole). |

14. Both HF and $CH_3F$ contain one fluorine atom and at least one hydrogen atom.

(a) Draw a diagram to show how a HF molecule can form a hydrogen bonding attractive force with another HF molecule.

(b) Explain why $CH_3F$ cannot form a hydrogen bonding attractive force with another $CH_3F$ molecule.

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| Compound | Molecular Formula | Boiling Point |
|---|---|---|
| 1 | $C_2H_6O$ | 249 K |
| 2 | $C_2H_6O$ | 351 K |

15. Use the information in the data table above to draw the correct Lewis electron-dot diagram for compound 1 and compound 2 in the boxes below. Include all bonding pairs and nonbonding pairs. Each atom in each diagram should have a formal charge of zero.

Compound 1 (BP = 249 K)
(cannot form hydrogen bonds with itself)

Compound 2 (BP = 351 K)
(can form hydrogen bonds with itself)

16. Explain why $NH_4^+$ can behave as a hydrogen bond donor, but it cannot behave as a hydrogen bond acceptor.

17. Explain why $NCl_3$ can behave as a hydrogen bond acceptor, but it cannot behave as a hydrogen bond donor.

18. Explain why $NH_2Cl$ can behave as both a hydrogen bond donor and a hydrogen bond acceptor.

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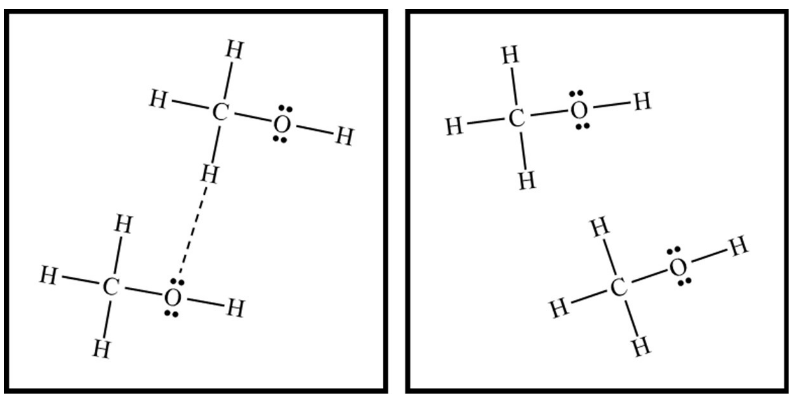
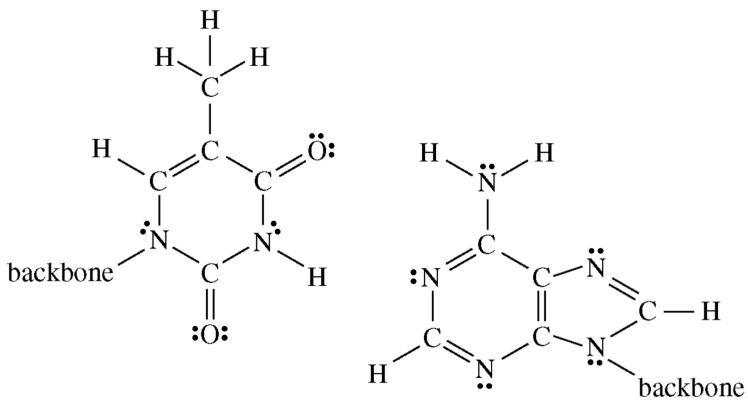


19. Explain why the diagram on the left does NOT represent a hydrogen bonding attractive force. In the box on the right, draw a hydrogen bonding attractive force as a dashed line.

In a large molecule, it is possible for a hydrogen bonding attractive force to be formed between a hydrogen atom (bonded to N, O, or F) and the negative end of a dipole formed by N, O, or F in another region of the same molecule. Examples of this situation can occur in large biomolecules such as proteins, carbohydrates, and DNA.

20. Thymine and adenine form a base pair in the DNA molecule. In the diagram below, thymine is shown at the left and adenine is shown at the right. The bases are attached to the backbone portion of the DNA strands. Draw two dashed lines to represent two hydrogen bonding attractions on the diagram below.

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**Ion-dipole forces** represent an attractive force between an ion and a polar molecule. They usually occur in a solution, when an ionic compound is dissolved in a polar solvent such as $H_2O$.

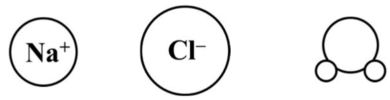
Coulomb's law can be applied when comparing the relative strength of an ion-dipole attractive force. The attractive force between an ion and a polar molecule should increase as the magnitude of charge on the ion increases and as the size of the ion decreases.

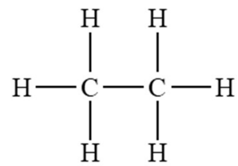
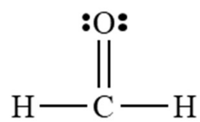
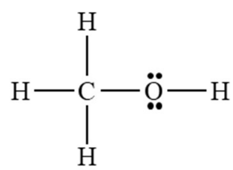
| Ion | Ionic Radius (pm) |
|---|---|
| $Cl^-$ | 167 |
| $I^-$ | 206 |
| $S^{2-}$ | 170 |
| $Te^{2-}$ | 207 |

21. Which ion in the table above is most likely to have the strongest interactions with nearby water molecules in an aqueous solution? Justify your answer in terms of Coulomb's law.

22. A small amount of NaCl(*s*) is dissolved completely into water to form a solution of NaCl(*aq*). Draw a particle diagram below to represent the attractions between the ions and the surrounding water molecules.

In your drawing, each ion should be surrounded by three water molecules with the proper orientation, based on the charge of the ion and the direction of the dipole in the water molecule. Use the following symbols in your diagram.



| Name | Structural Formula | Molar Mass (g/mol) | Polar or Nonpolar? | Boiling Point (K) |
|---|---|---|---|---|
| ethane |  | | | 185 |
| formaldehyde |  | | | 254 |
| methanol |  | | | 338 |

23. (a) Identify all types of intermolecular forces present in each substance.

ethane, $C_2H_6$ ________________________________________

formaldehyde, $CH_2O$ ________________________________________

methanol, $CH_3OH$ ________________________________________

(b) Explain the differences in boiling point shown in the data table above in terms of the relative strength of the intermolecular forces.