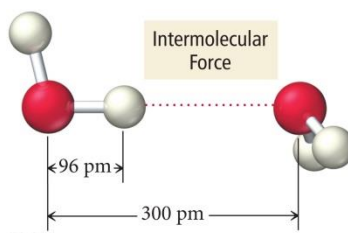


## INTERMOLECULAR FORCES

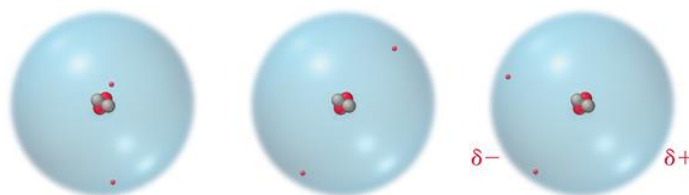
- Matter can exist in one of three forms: solid, liquid or gas. Earlier we discussed the differences in properties between these three forms of matter. In this chapter we discuss the differences in the forces between the particles of these substances, called *intermolecular forces*.
- The structure of the particles that compose a substance determine the strength of the intermolecular forces that holds the substance together, which in turn determines whether a substance is solid, liquid or gas at a given temperature.
- At room temperature, moderate to strong intermolecular forces result in liquids or solids (high melting and boiling points) and weak intermolecular forces tend to result in gases (low melting and boiling points).
- Intermolecular forces originate from interactions between charges, partial charges and temporary charges on molecules (or atoms and ions), similar to bonding forces that originate between charged particles in atoms. However, the *intermolecular forces*, even the strongest ones, are generally much *weaker than bonding forces*.
- The reason for the relative weakness of intermolecular forces compared to bonding forces is due to Coulomb's law. Bonding forces are the result of large charges (protons and electrons) interacting at small distances, whereas intermolecular forces are the result of smaller charges interacting at larger distances (see diagram below).



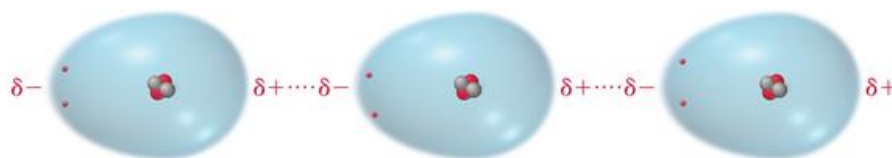
- Intermolecular forces can be divided into four types:
  1. Dispersion forces
  2. Dipole–Dipole forces
  3. Hydrogen bonding
  4. Ion–Dipole forces

## DISPERSION FORCE

- The one intermolecular force present in all atoms or molecules is the **dispersion force** (also called the **London force**). This force results from the fluctuations in the electron distribution within molecules or atoms). Since all atoms or molecules have electrons, they all exhibit dispersion forces.
- The electrons in an atom or molecule, may at any instant be unevenly distributed, causing a temporary dipole in the atom, as shown below:



- This temporary dipole on an atom can induce similar dipole in other neighboring atoms of the substance, and cause attraction between opposite dipoles on two atoms. This attraction is the dispersion force.

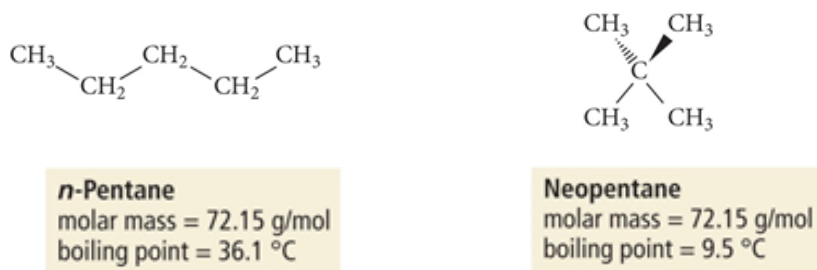


- The magnitude of the dispersion force depends on how easily the electrons in an atom or molecule can move or polarize in response to a temporary dipole, which in turn depends on the size (or volume) of the electron cloud. A large electron cloud results in a greater dispersion force because the electrons are held less tightly by the nucleus and therefore polarize more easily.
- If all other variables are constant, dispersion forces increase with increasing molar mass because atoms or molecules with greater molar mass generally have greater number of electrons dispersed over a greater volume.
- As an example, the variation in the boiling points of noble gases shown on the right is due to the larger magnitude of dispersion forces due to the larger molar mass.

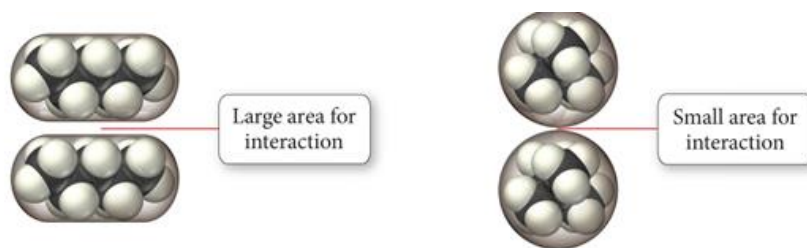
Noble Gas	Molar Mass (g/mol)	Boiling Point (K)
He	4.00	4.2
Ne	20.18	27
Ar	39.95	87
Kr	83.80	120
Xe	131.30	165

## DISPERSION FORCE

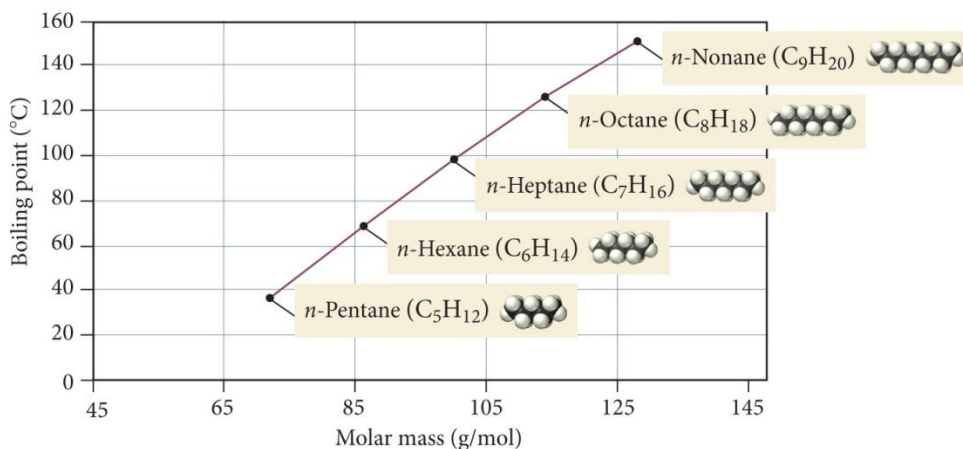
- Molar mass alone, however, does not determine the magnitude of the dispersion force. For example, even though *n*-pentane and neopentane have the same molar mass, they do not have the same much different dispersion forces indicated by the difference in their boiling points.



- The difference in boiling point of these two compounds is attributed to the difference in their shapes (long for *n*-pentane and bulky for neopentane), which provides greater opportunity of interaction between neighboring molecules.

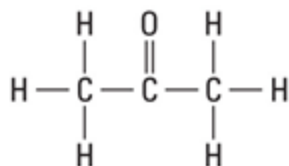


- Although molecular shapes and other factors must always be considered to determine the magnitude of the dispersion forces, molar mass can act as a guide when comparing the dispersion forces within a family of similar elements or compounds as shown below:

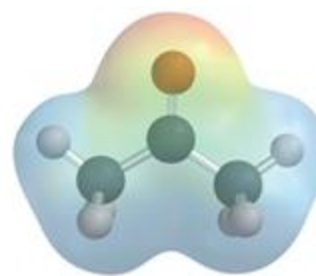


## DIPOLE-DIPOLE FORCE

- The *dipole-dipole force* exists in all molecules that are polar. Polar molecules have electron-rich regions (with  $\delta^-$ ) and electron deficient regions (with  $\delta^+$ ). For example, acetone, shown below, has an electron-rich region around the oxygen atom (since it is more electronegative than the rest of the molecule) and an electron deficient region surrounding the carbon and hydrogen atoms.



Structural formula





Electrostatic potential map

- The result is that acetone has a permanent dipole that can interact with other acetone molecules as shown below.



The positive end of a polar molecule is attracted to the negative end of its neighbor.

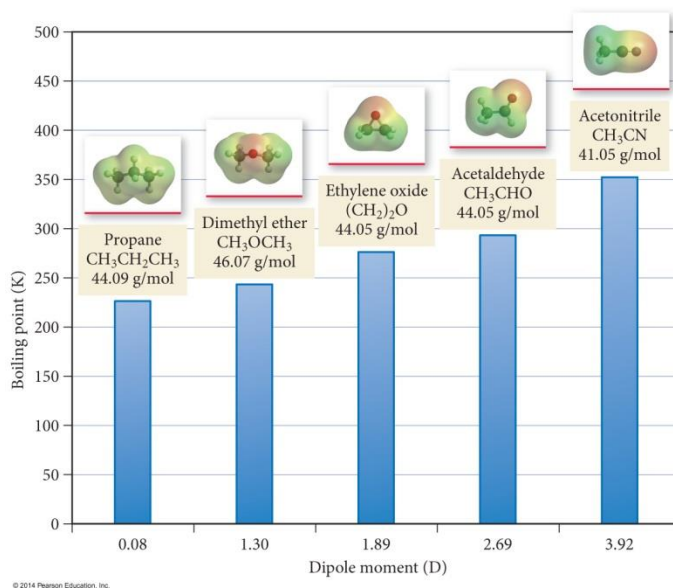
- Polar molecules, therefore, have higher boiling and melting points than nonpolar molecules. Recall that all molecules (polar and nonpolar) have dispersion forces. Polar molecules have, in addition, dipole-dipole forces, which raises their boiling and melting points relative to nonpolar molecules of similar molar mass. For example, compare formaldehyde and ethane:

Name	Formula	Molar Mass (amu)	Structure	bp ( $^{\circ}\text{C}$ )	mp ( $^{\circ}\text{C}$ )
Formaldehyde	$\text{CH}_2\text{O}$	30.03	$  \begin{array}{c}  \text{O} \\     \\  \text{H}-\text{C}-\text{H}  \end{array}  $ 	-19.5	-92
Ethane	$\text{C}_2\text{H}_6$	30.07	$  \begin{array}{c}  \text{H} \quad \text{H} \\    \quad   \\  \text{H}-\text{C}-\text{C}-\text{H} \\    \quad   \\  \text{H} \quad \text{H}  \end{array}  $ 	-88	-172

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## DIPOLE-DIPOLE FORCE

- When comparing molecules with similar molar masses, the magnitude of their dipole moment (an indication of their polarity) can be correlated with the magnitude of their dipole-dipole forces and its effect on the boiling point of the molecule.



### Examples:

1. Which of these molecules have dipole–dipole forces?

a)  $\text{CO}_2$

+

b)  $\text{CH}_2\text{Cl}_2$

c)  $\text{CH}_4$

2. Which molecule below has the highest boiling point?

a)  $\text{Cl}_2$

b)  $\text{Br}_2$

c)  $\text{I}_2$

## HYDROGEN BONDING

- Polar molecules containing hydrogen atoms bonded directly to small electronegative atoms—most importantly fluorine, oxygen and nitrogen—exhibit an intermolecular force called **hydrogen bonding**. HF, NH<sub>3</sub> and H<sub>2</sub>O, for example, all undergo hydrogen bonding.
- The large electronegativity difference between hydrogen and these very electronegative elements causes a large  $\delta^+$  charge on hydrogen and large  $\delta^-$  charge on the F, N and O atoms, and since these atoms are small, the hydrogen atom on one molecule can approach them in an adjacent molecule very closely. The result is a strong attraction between the H on one molecule and the F, O or N on its neighbor—an attraction called **hydrogen bond**.

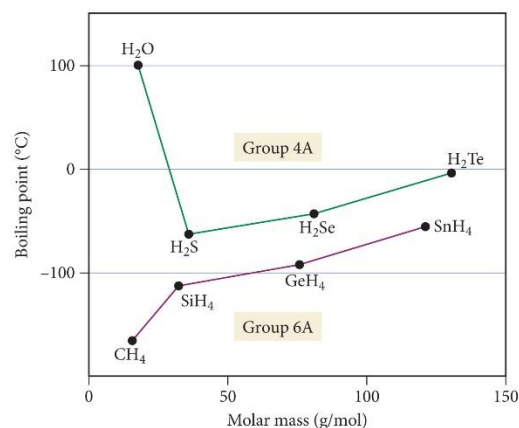


When H bonds directly to F, O, or N, the bonding atoms acquire relatively large partial charges, giving rise to strong dipole-dipole attractions between neighboring molecules.

- Hydrogen bonds should not be confused with chemical bonds. **Chemical bonds occur** between individual atoms **within a molecule**, whereas hydrogen bonds—like dispersion forces and dipole-dipole forces—are **intermolecular forces** and **occur between molecules**.
- Hydrogen bonds are only 2-5% as strong as a typical chemical bond. They are, however, the strongest intermolecular forces we have discussed so far. Substances containing molecules that form hydrogen bonds boiling and melting points compared to substances that do not contain molecules that form hydrogen bonds. The table below is a comparison between ethanol (that forms H-bonds) and dimethyl ether (that does not form H-bonds):

Name	Formula	Molar Mass (amu)	Structure	bp (°C)	mp (°C)
Ethanol	C <sub>2</sub> H <sub>6</sub> O	46.07		78.3	-114.1
Dimethyl Ether	C <sub>2</sub> H <sub>6</sub> O	46.07		-22.0	-138.5

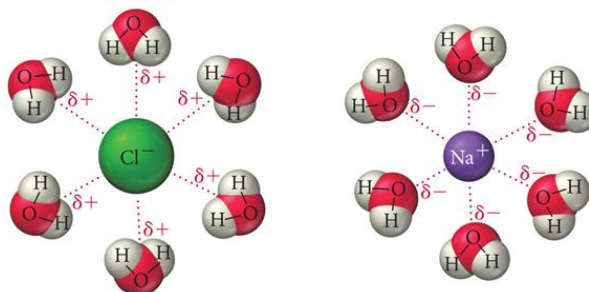
- The diagram on the right shows comparison of the boiling points of the simple hydrogen compounds from Group 4A and 6A elements. In general boiling points increase with increasing molar mass, as expected due to dispersion forces. However, because of H-bonding, the expected boiling point of water is much higher than expected.



## ION-DIPOLE FORCE

- The *ion-dipole force* occurs when an ionic compound is mixed with a polar compound and is especially important in aqueous solutions of ionic compounds. For example, when NaCl is mixed with water, the  $\text{Na}^+$  and  $\text{Cl}^-$  interact with water molecules via ion-dipole forces, as shown below:

The positively charged end of a polar molecule such as  $\text{H}_2\text{O}$  is attracted to negative ions and the negatively charged end of the molecule is attracted to positive ions.



- Ion-dipole forces are the strongest of the four types of intermolecular forces discussed and are responsible for the ability of ionic compounds to form solutions with water.
- The table below shows a comparison of the four types of intermolecular forces:

Type	Present in	Molecular perspective	Strength
Dispersion	All molecules and atoms		
Dipole-dipole	Polar molecules		
Hydrogen bonding	Molecules containing H bonded to F, O, or N		
Ion-dipole	Mixtures of ionic compounds and polar compounds		

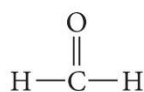
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**Examples:**

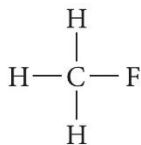
1. Which substance below has the highest boiling point?



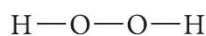
2. Identify the intermolecular forces present in each molecule below, and determine which is a liquid at room temperature?



Formaldehyde

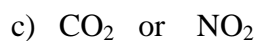
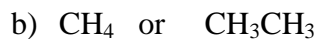
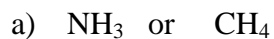
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Fluoromethane



Hydrogen peroxide

3. In each pair of compounds shown below, pick the one with the higher boiling points and explain your reasoning:



4. Predict the order of freezing point for the following:  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{KBr}$ .