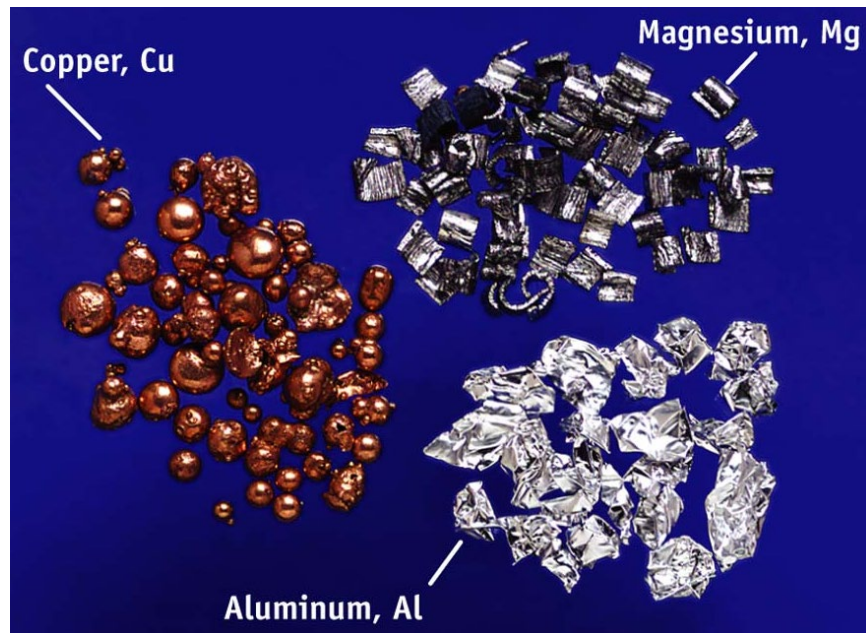




METALS



CHEMISTRY 1000

Topic #2: The Chemical Alphabet

Fall 2020

Dr. Susan Findlay

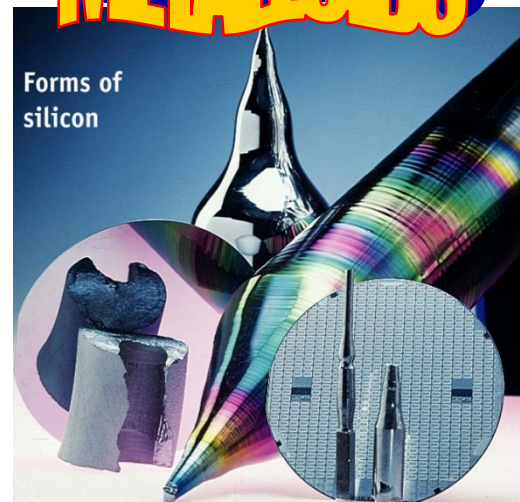
See Exercises 9.2 to 9.7

NONMETALS



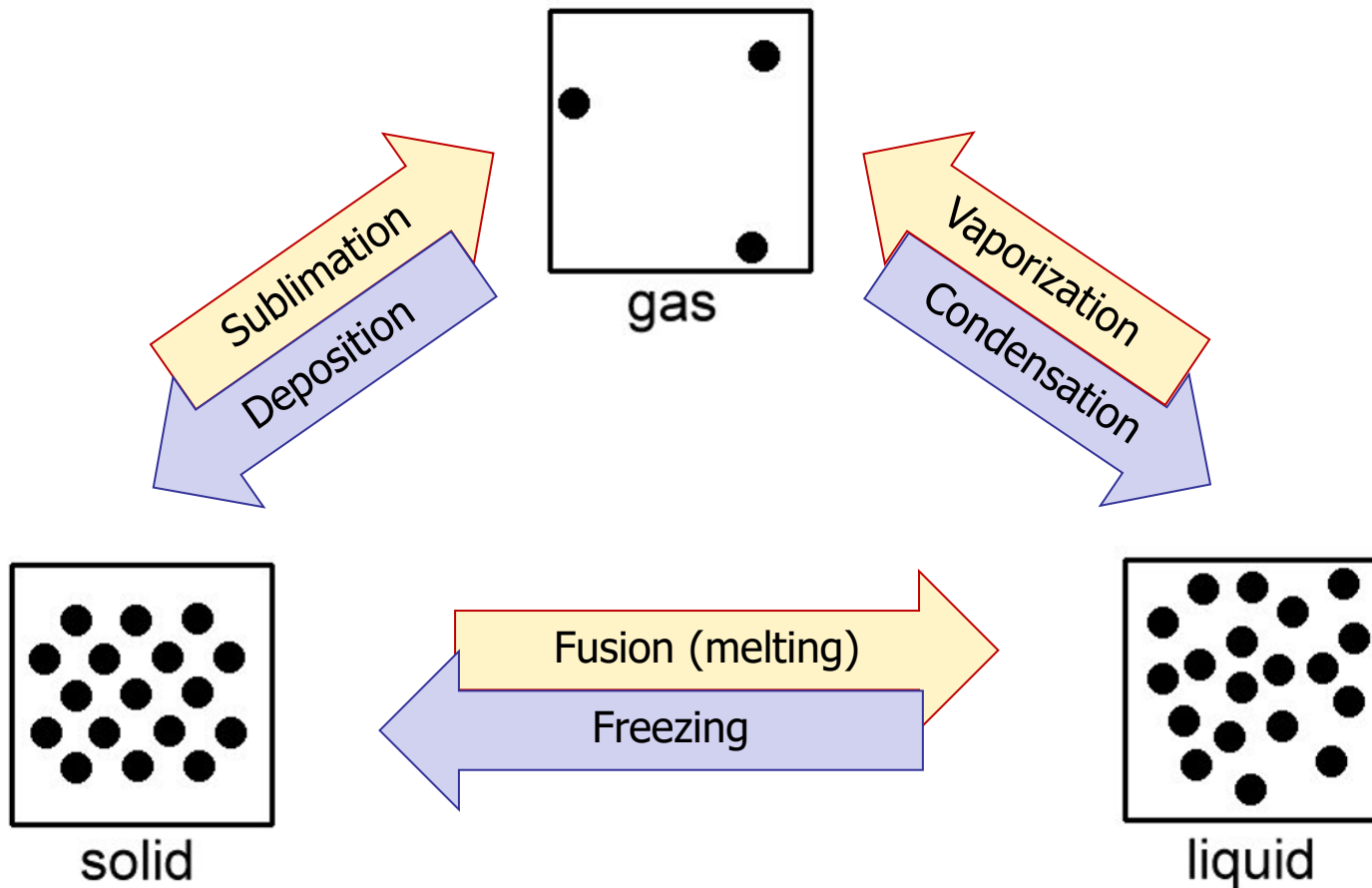
Forms of Carbon

METALLOIDS



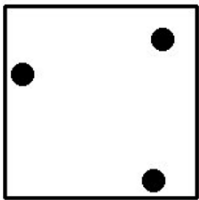
Kinetic Molecular Theory of Matter

- The three most familiar states of matter are solid, liquid and gas:



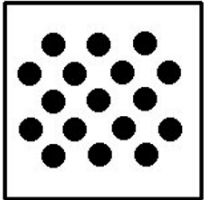
Kinetic Molecular Theory of Matter

- States of matter can be distinguished by the arrangement of particles (either molecules or atoms):



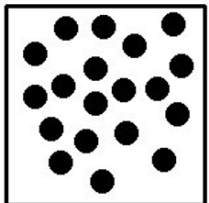
gas

- In **gases**, distances between particles are much larger than the particles themselves. As such, the most significant motion of gas particles is _____ (from one location to another).



solid

- In **solids**, particles are packed in a three-dimensional **lattice**. They cannot easily change location, so their kinetic energy is primarily due to _____ and _____ motion. This motion is averaged about the particle's location in the lattice.



liquid

- In **liquids**, particles are much closer together than in gases, but they are still able to change locations (unlike in solids). As such, particles in a liquid undergo significant amounts of **translational**, **rotational** and **vibrational** motion.



Kinetic Molecular Theory of Matter

- The kinetic-molecular theory describes the behaviour of matter:
 - Molecules are in constant motion in random directions.
 - Molecules move at different speeds, but the *average* speed is proportional to temperature. *All* substances have the same average kinetic energy at a given temperature.
- For a short video showing the movement of gas particles at increasing temperatures, please see <http://www.kcvs.ca/details.html?key=gases>

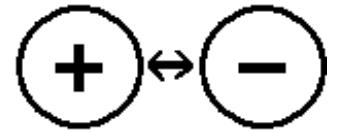


Intermolecular Forces

- Intermolecular forces are attractive forces that operate **between different** molecules (and/or ions). They are not bonds!
- There are six general kinds of intermolecular forces, each of which is based on **electrostatic attraction**. The strength of an intermolecular force is determined by the strength and permanence of the charges/dipoles involved and by the distance between the charges/dipoles.
 - ion – ion forces
 - ion – dipole forces
 - ion – induced dipole forces
 - dipole – dipole forces
 - dipole – induced dipole forces
 - induced dipole – induced dipole forces
- Hydrogen bonding is a particularly important intermolecular force that will be discussed with the dipole-dipole forces.



Ion-Ion Forces

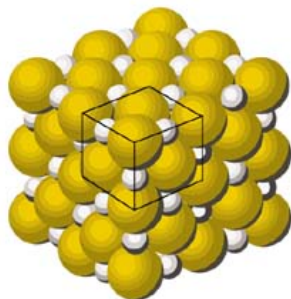
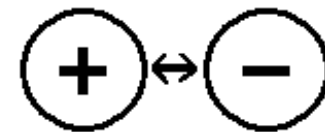


- The force of attraction between positively charged and negatively charged ions depends on both the magnitude of the charges and the distance between the ions:

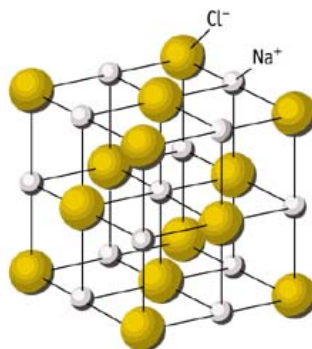
$$F = \frac{1}{4\pi\epsilon} \frac{(Z^+e)(Z^-e)}{d^2}$$

- This **Coulomb force** is the strongest force outside of those operating at subatomic levels. Because this force is so strong between ions, ionic compounds tend to form strong solid lattices. The vast majority of ionic compounds are solid under normal laboratory conditions because the solid state maximizes the attractive forces between the cations and anions (*as shown on the next page*).

Ion-Ion Forces

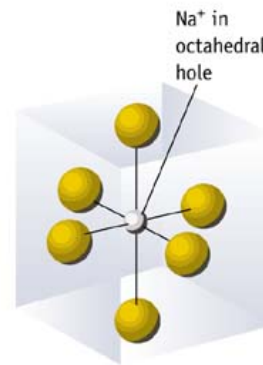


(a)



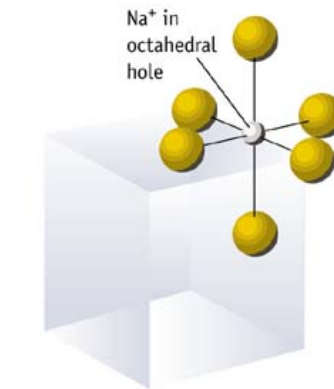
NaCl unit cell (expanded)

(b)



1 hole of this kind
in the center of the
unit cell

Octahedral holes in a face-centered lattice



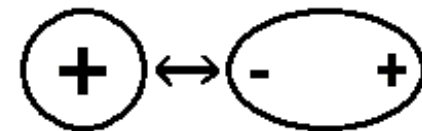
12 holes of this kind in the 12
edges of the unit cell
(a net of 3 holes)

(c)

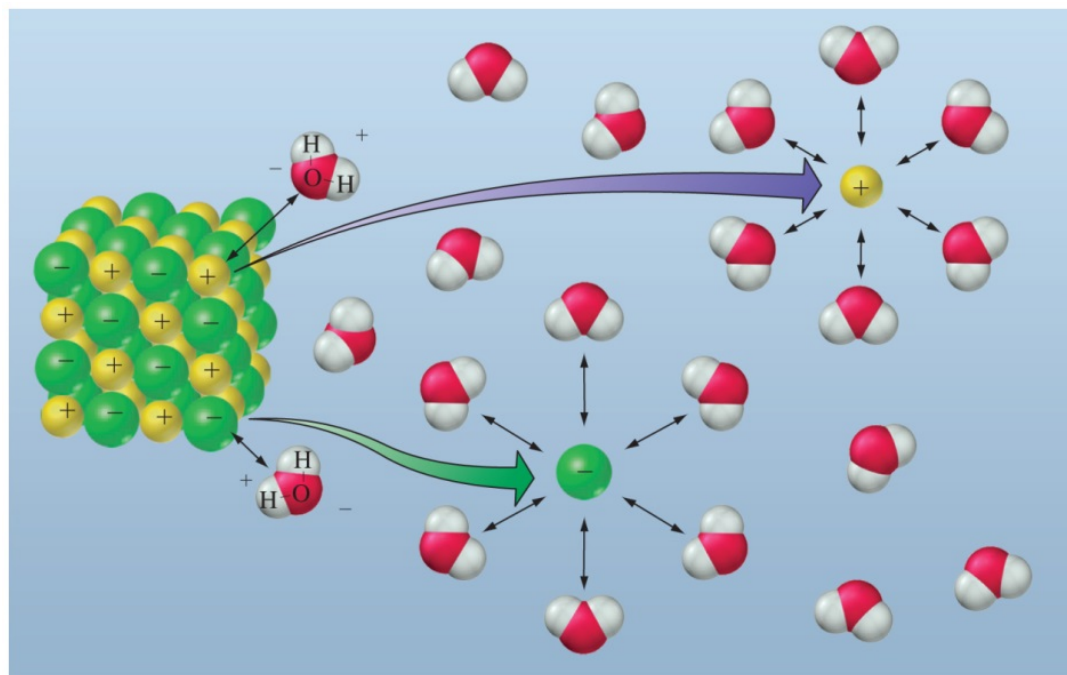
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- As a result, ionic compounds have very high boiling points, requiring large amounts of heat to overcome the strong attractive forces holding the lattice together.
- Even when an ionic compound is dissolved in a solvent, these strong ion-ion forces lead the cations and anions to arrange themselves such that each cation is closer to anions than to other cations (*and vice versa*).

Ion-Dipole Forces

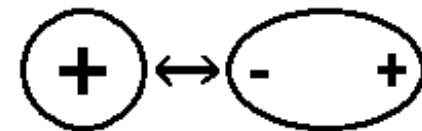


- The attractive forces between ions and polar molecules are also strong. When an ionic solid (such as the NaCl shown below) is dissolved in polar solvent such as water, many of the solvent molecules are organized around each ion to maximize the ion-dipole attractions:



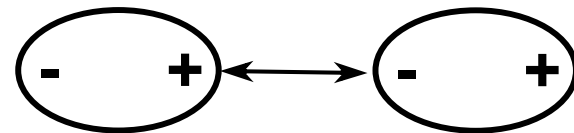


Ion-Dipole Forces

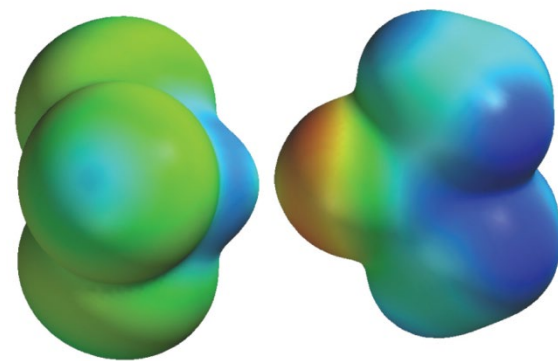
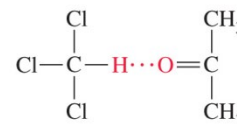
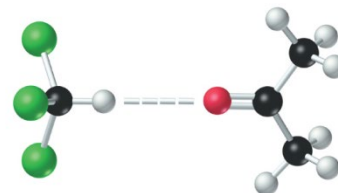


- Because the strength of electrostatic attractions are strongly distance-dependent, ion-dipole forces tend to be the strongest intermolecular forces in aqueous solutions of ionic compounds. Why?

Dipole-Dipole Forces

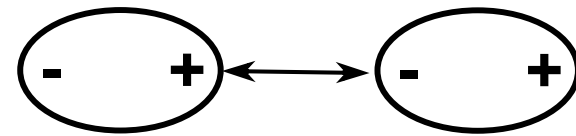


- Molecules with permanent dipoles (i.e. polar molecules) also experience attractive forces. They will align themselves to maximize the attractions between the positive ends of the dipoles and the negative ends of the dipoles:





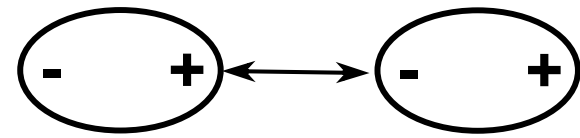
Dipole-Dipole Forces



- **Hydrogen bonding** is a special case of dipole-dipole attraction. This is due to the very large dipole moment that occurs when a hydrogen atom is bonded to a very small, very electronegative atom (i.e. F, O or N). The large dipole moment combined with the small size of the atoms involved (H and either F, O or N) results in a particularly strong dipole-dipole attraction.
- **In hydrogen bonding, both the atom bonded to H and the atom attracted to H must be either F, O or N.** They do not, however, have to be the same element.
e.g.



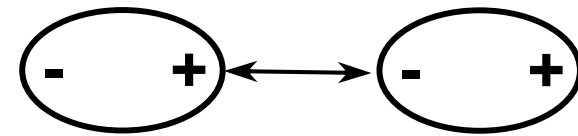
Dipole-Dipole Forces



- Unlike most intermolecular forces, hydrogen bonds require a specific pair of atoms to be in close proximity. Hydrogen bonds are **directional**:



Dipole-Dipole Forces



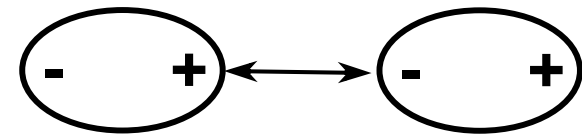
- Hydrogen bonds are longer than covalent bonds but shorter than the usual distance between unbonded atoms (even of the same elements):

Despite the name, “hydrogen bonds” are not really bonds at all! They are simply strong intermolecular attractions.

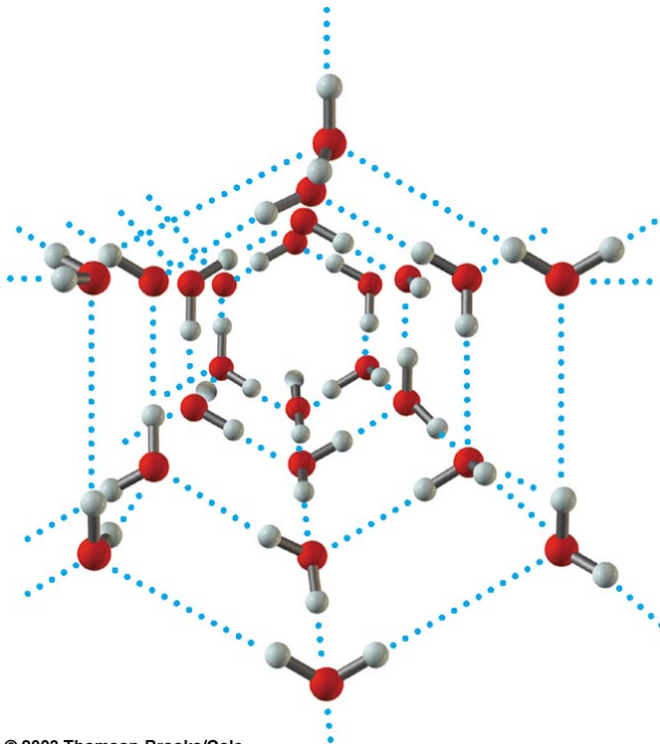
Hydrogen bonding is intermolecular (not intramolecular).

When you boil water, you will break hydrogen bonds attracting water molecules to each other, but every water molecule is still H₂O!!!

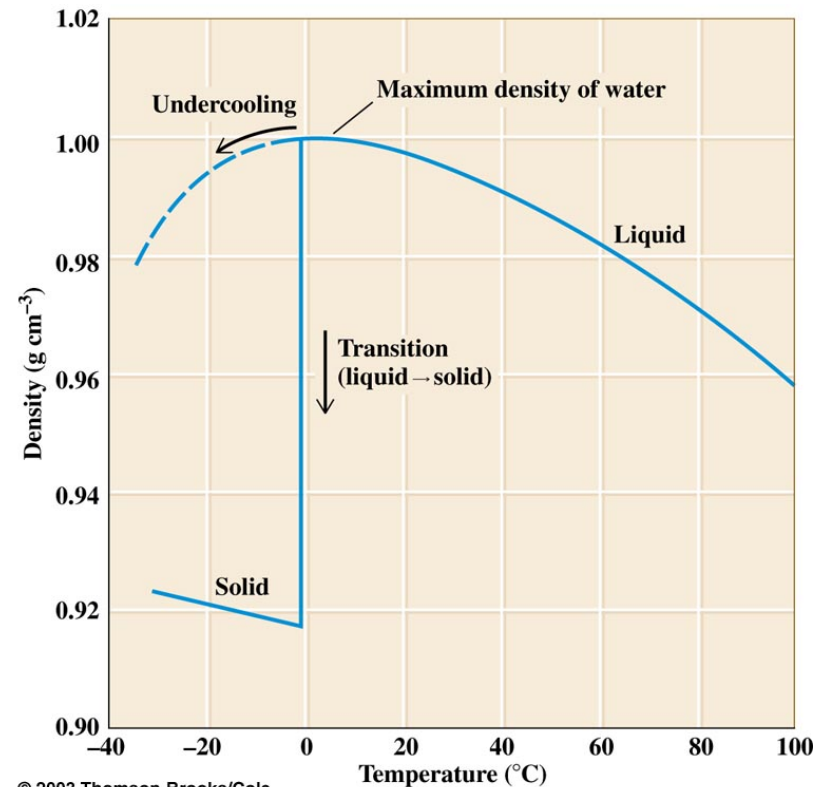
Dipole-Dipole Forces



- Hydrogen bonding is responsible for the open cage structure of ice along with the unusual relationship between temperature and density of water/ice:

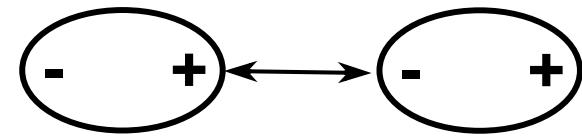


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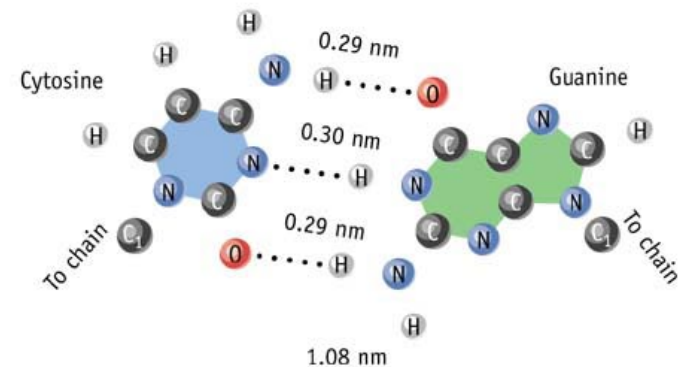
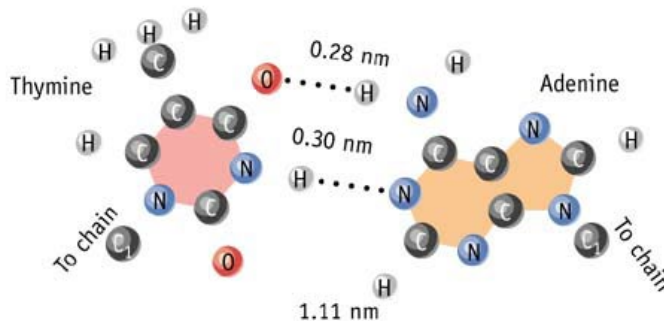
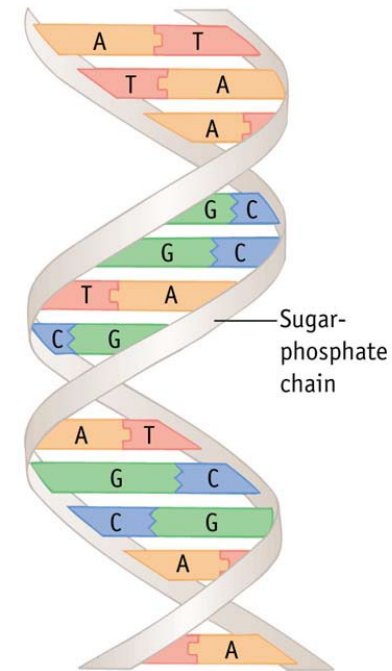
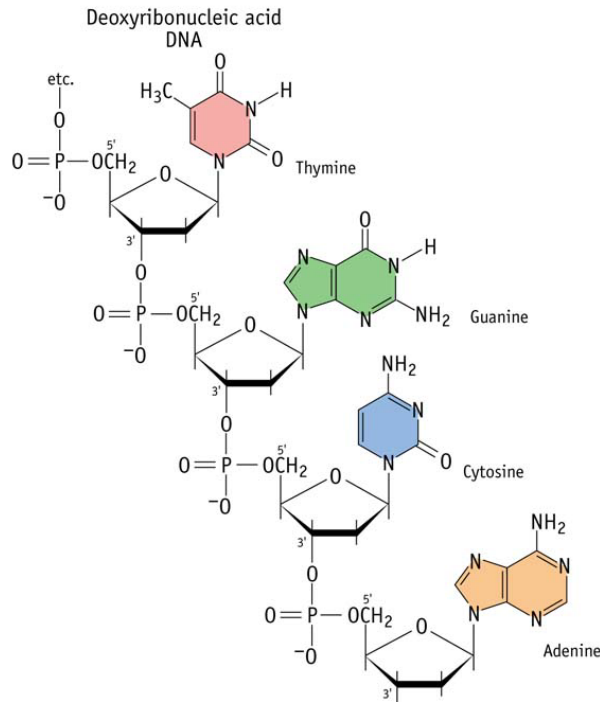


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Dipole-Dipole Forces

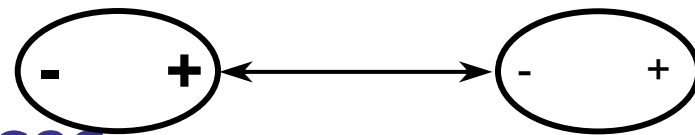


- Hydrogen bonding is also a factor in the double helix of DNA:





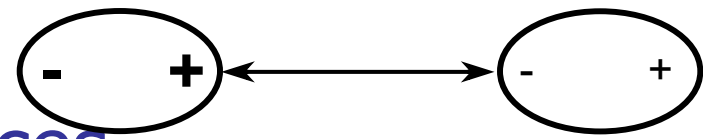
Dipole-Induced Dipole Forces



- **Induced dipoles** can occur when a polar molecule and a nonpolar molecule approach closely enough that the dipole of the polar molecule exerts a force on the valence electrons of the nonpolar molecule, setting up a temporary dipole:
- As a general rule, atoms whose valence electrons are less strongly attracted to their nucleus are more susceptible to induced dipoles (taking on larger induced dipoles). This is referred to as **polarizability**, and larger atoms are more **polarizable** than smaller atoms in the same group.



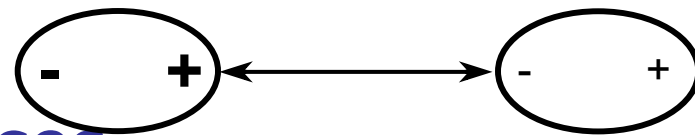
Dipole-Induced Dipole Forces



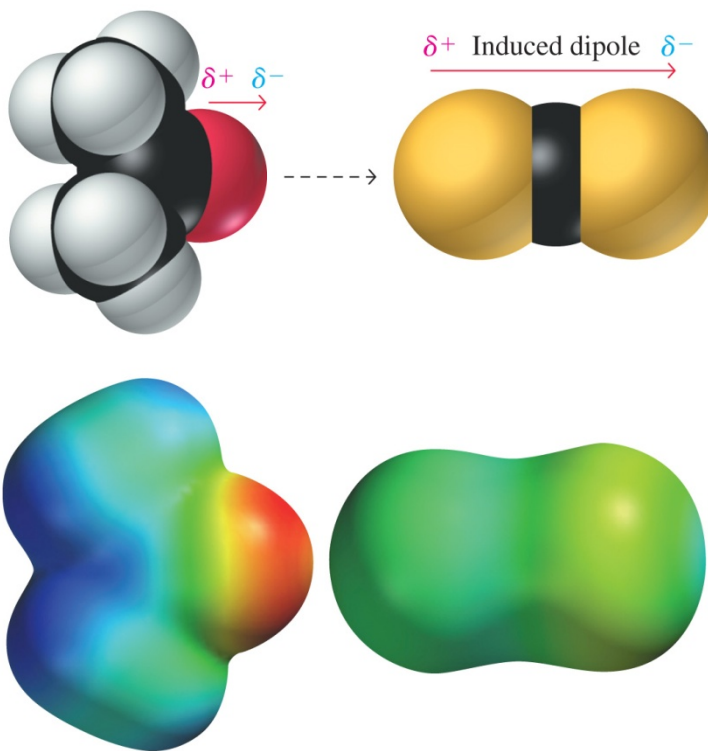
- The polarizability of molecules also increases with the size of the molecule. This is why large molecules tend to be more viscous and have higher boiling points than smaller molecules of similar polarity.

e.g.

Dipole-Induced Dipole Forces



- The diagram below shows the induction of a dipole in carbon disulfide, CS_2 , by the polar solvent acetone, $(\text{CH}_3)_2\text{C}=\text{O}$.



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Induced Dipole-Induced Dipole Forces

- The previous four intermolecular forces all required at least one of the two species to have a permanent dipole; however, even completely nonpolar species exist as solids and/or liquids at low enough temperatures (or high enough pressures).
e.g. liquid N₂ and liquid He are used routinely in labs.
- So, why would nonpolar substances be attracted to each other?
How can one nonpolar particle induce a dipole in another?

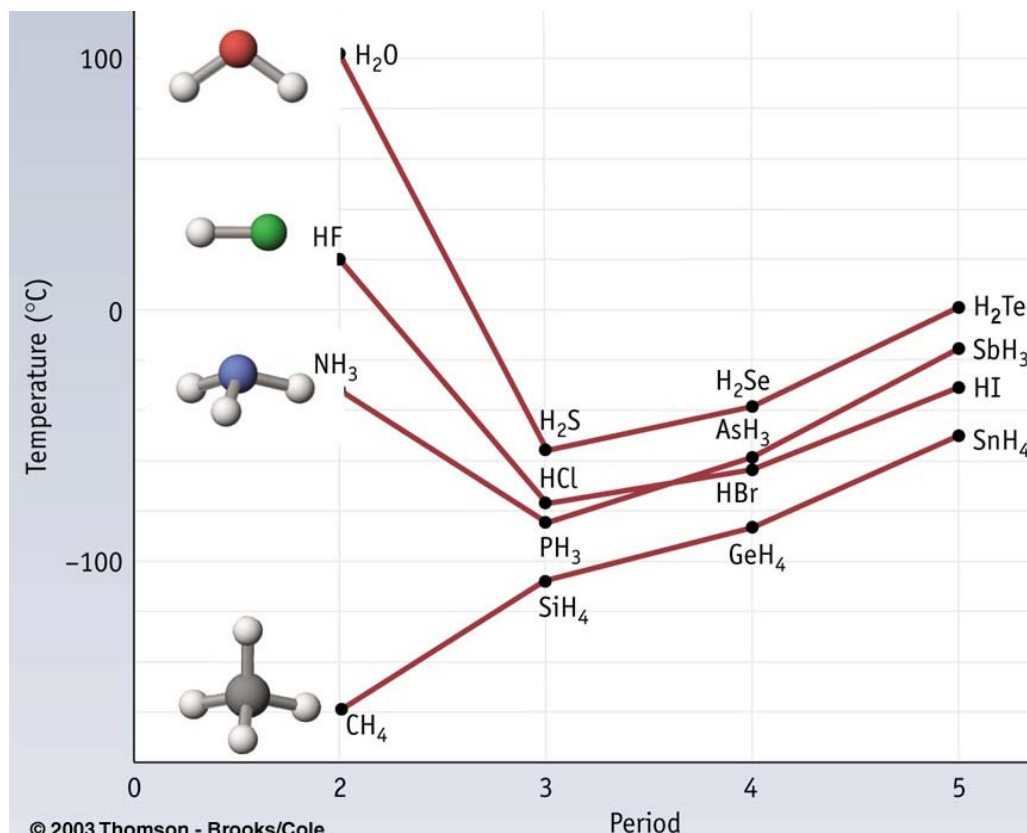


Induced Dipole-Induced Dipole Forces

- Motion of electrons is random. As such, there will be times where more electrons in a nonpolar molecule happen to be on one side than the other. This results in a temporary dipole on that molecule – and this temporary dipole will induce temporary dipoles on the surrounding molecules. This is a cascade effect.
- The attractions between these **fluctuation-induced dipoles** are also called **London dispersion forces**. Their strength depends on the polarizability of the atoms/molecules in question.
e.g. Cl_2 vs. Br_2 vs. I_2

Intermolecular Forces Exercise

- Discuss how intermolecular forces affect the following:
 - General trend for boiling points of the Group 14 hydrides?
 - Boiling points of Group 14 hydrides compared to other groups?
 - Anomously high boiling points of H_2O , HF and NH_3 ?





Kinetic Molecular Theory of Gases/Ideal Gases

- In an 'ideal gas':
 - The distance between gas particles (atoms or molecules) is much larger than the size of the particles. The gas particles therefore occupy a negligible fraction of the volume.
 - Gas particles are in constant motion.
 - Gas particles do not interact except when they collide.
 - When gas particles collide with each other (or the walls of their container), collisions are elastic. No energy is lost.
 - Gas particles in a sample move at different speeds, but the average speed is proportional to temperature. All gases have the same average kinetic energy at a given temperature.

Law of Large Numbers (*as applied here*)

The behaviour of a system containing many molecules is unlikely to deviate significantly from the behaviour predicted from the statistical average of the properties of the individual molecules.

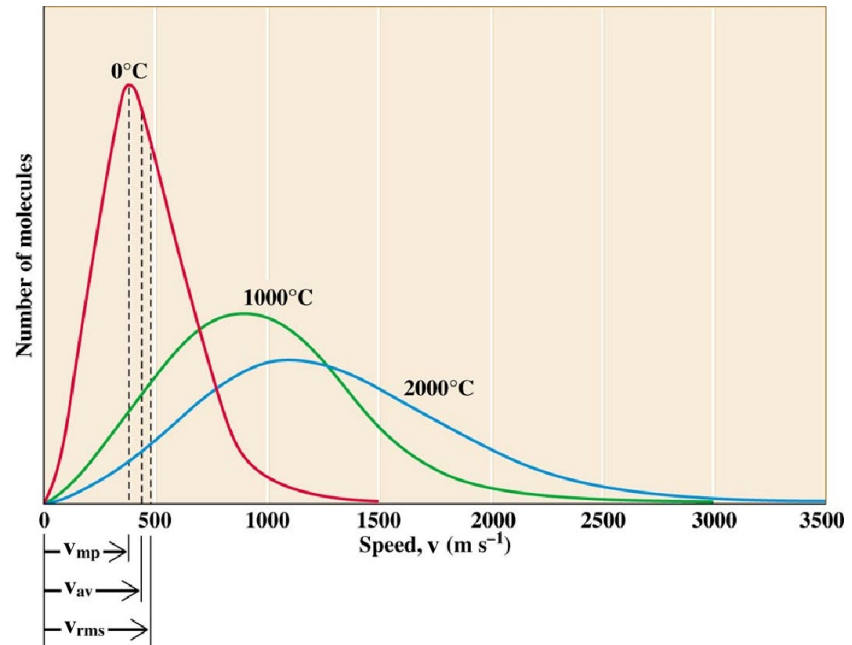
Kinetic Molecular Theory of Gases/Ideal Gases

- The kinetic energy of a particle depends on its mass and speed:

$$E_k = \frac{1}{2}mv^2$$

where E_k is kinetic energy, m is mass and v is speed.

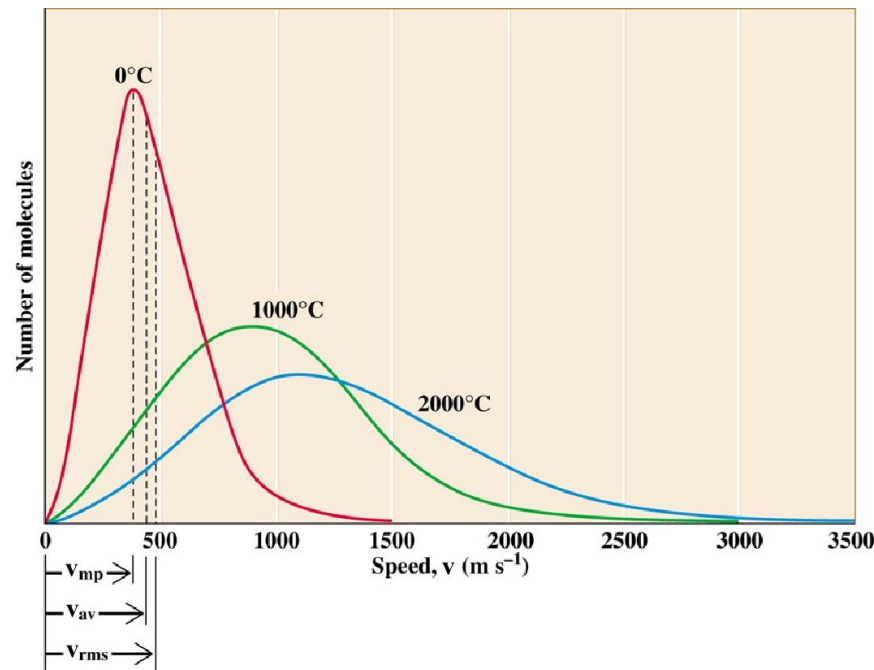
- Speeds of molecules are distributed statistically in a Maxwell-Boltzmann distribution:



- When the temperature increases, the average speed of the gas particles increases and the distribution of speeds spreads out.

Kinetic Molecular Theory of Gases/Ideal Gases

- There are three different ways to look at the speed of gas particles in a sample:
 - v_{mp} = 'most probable' speed
 - v_{av} = 'average' speed
 - v_{rms} = 'root mean square' speed (square each particle's speed then calculate the average then take the square root)





Kinetic Molecular Theory of Gases/Ideal Gases

- Because kinetic energy is proportional to v^2 , it makes most sense to use v_{rms} in kinetic energy and temperature calculations.

$$\overline{E_k} = \frac{1}{2}mv_{rms}^2 = \frac{3}{2}k_B T \qquad \overline{E_k} = \frac{3}{2}RT$$

where $\overline{E_k}$ is the average kinetic energy of gas particles, m is the mass of one particle, T is temperature (in Kelvin), and k_B is the Boltzmann constant ($R = k_B \cdot N_A$ where R is the ideal gas constant and N_A is Avogadro's number).

- At a constant temperature:
 - particles with _____ mass will have _____ v_{rms}
 - particles with _____ mass will have _____ v_{rms}



Kinetic Molecular Theory of Gases/Ideal Gases

- The Maxwell-Boltzmann equation can be derived from the kinetic-molecular theory of gases:

$$P = \frac{Nm v_{rms}^2}{3V} \quad \text{or} \quad PV = \frac{Nm v_{rms}^2}{3}$$

where P is pressure, V is volume, N is the number of gas particles, m is the mass of one particle, and v_{rms} is the root-mean-square speed.

- We can rationalize why each property belongs in the numerator or denominator of this equation by remembering that pressure is force exerted on an area:

$$P = \frac{F}{A}$$



Kinetic Molecular Theory of Gases/Ideal Gases

- Since the Maxwell-Boltzmann equation and the ideal gas law both describe ideal gases, they can be related:

$$PV = \frac{Nm v_{rms}^2}{3} \quad \text{and} \quad PV = nRT$$

$$M v_{rms}^2 = 3RT \quad \text{or} \quad v_{rms} = \sqrt{\frac{3RT}{M}}$$



Kinetic Molecular Theory of Gases/Ideal Gases

- In order to use either $Mv_{rms}^2 = 3RT$ or $v_{rms} = \sqrt{\frac{3RT}{M}}$ and have the units cancel out properly, M must be in kg/mol.
- Calculate v_{rms} for N_2 at 20 °C.



Kinetic Molecular Theory of Gases/Ideal Gases

- You have a sample of helium gas at $0.00\text{ }^{\circ}\text{C}$. To what temperature should the gas be heated in order to increase the root-mean-square speed of helium atoms by 10.0% ?



Nonideal Gases

- The ideal gas law and kinetic molecular theory are based on two simplifying assumptions:
 - The actual gas particles have negligible volume.
 - There are no forces of attraction between gas particles.These two assumptions are not always valid.
- Under what conditions would you expect these assumptions to no longer apply?



Nonideal Gases

- Under ideal conditions, the volume of a container of gas is almost 100% empty space – so the volume available for gas particles to move into is the entire volume of the container.
- Under nonideal conditions, there is less “available volume” in the same sized container. We can correct for this “excluded volume” by adding a term to the ideal gas law:

$$P(V - nb) = nRT$$

where b is an experimentally determined constant specific to the gas. This constant tends to _____ as the size of the gas particles increases.

- The effect of this “excluded volume” is to _____ the pressure of the gas.



Nonideal Gases

- Under ideal conditions, particles in a gas sample don't experience intermolecular forces.
- Under nonideal conditions, the gas particles are close enough together that they do experience intermolecular forces. We can correct for these attractive forces by adding a term to the ideal gas law:

$$\left(P + a \frac{n^2}{V^2}\right)V = nRT$$

where a is an experimentally determined constant specific to the gas. This constant tends to _____ as the strength of IMF between the gas particles increases.

- The effect of the intermolecular forces is to _____ the pressure of the gas.



Nonideal Gases

- When both corrections are applied, we get the **van der Waals equation**:

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$$

- The table below gives some sample values for a and b

		a (Pa·m ⁶ ·mol ⁻²)	b (m ³ ·mol ⁻¹)
Hydrogen	H ₂	0.0245	2.65×10^{-5}
Methane	CH ₄	0.2303	4.31×10^{-5}
Ammonia	NH ₃	0.4225	3.71×10^{-5}
Water	H ₂ O	0.5537	3.05×10^{-5}
Sulfur dioxide	SO ₂	0.6865	5.68×10^{-5}



Nonideal Gases

		a (Pa·m ⁶ ·mol ⁻²)	b (m ³ ·mol ⁻¹)
Hydrogen	H ₂	0.0245	2.65×10^{-5}
Ammonia	NH ₃	0.4225	3.71×10^{-5}

- You have two 1.00 L containers at 298 K. One contains 1.00 mol of hydrogen gas while the second contains 1.00 mol of ammonia gas.
 - (a) Calculate the pressure in each container according to the ideal gas law.
 - (b) Calculate the actual pressure in each container.



Nonideal Gases

		a (Pa·m ⁶ ·mol ⁻²)	b (m ³ ·mol ⁻¹)
Hydrogen	H ₂	0.0245	2.65×10^{-5}
Ammonia	NH ₃	0.4225	3.71×10^{-5}



Nonideal Gases

		a (Pa·m ⁶ ·mol ⁻²)	b (m ³ ·mol ⁻¹)
Hydrogen	H ₂	0.0245	2.65×10^{-5}
Ammonia	NH ₃	0.4225	3.71×10^{-5}