# LIQUIDS, SOLIDS, AND INTERMOLECULAR FORCES

Chapter 12

## Intermolecular Forces

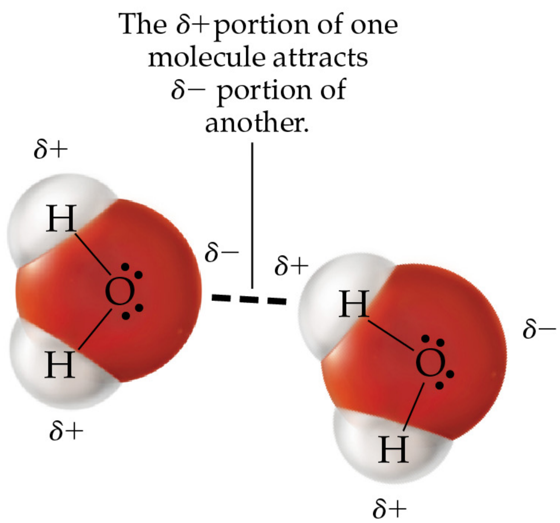
- The attractive forces which exist between different molecules are called intermolecular forces.
- There are three distinct forces we will consider, each with a range of strength
  - Hydrogen Bonding
  - Dipole-Dipole Forces
  - London Dispersion Forces

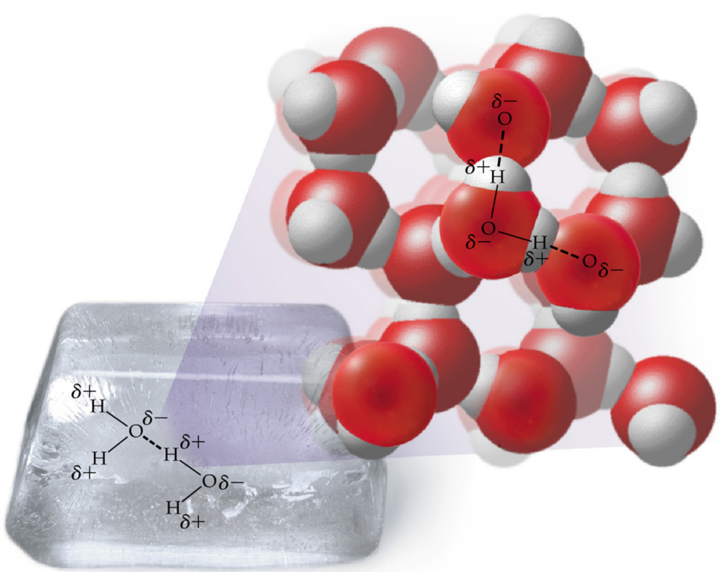
# Hydrogen Bonding

- When hydrogen atoms are bonded to very electronegative atoms, they develop a partially positive charge since the electrons are pulled away from the atom.
- The lone pairs on an electronegative atom of a *different* molecule will be attracted to this partial positive charge, making a hydrogen bond.

# Hydrogen Bonding

- Hydrogen atoms that are covalently bonded to F, O, and N atoms <u>only</u> may participate in hydrogen bonding.
- Similarly, the lone pairs on a F, O, or N atom of another molecule may participate in hydrogen bonding.
- There are no exceptions to this.
- <u>Do not confuse a covalent bond with hydrogen with a hydrogen bond! Covalent bonds share electrons between atoms in the same molecule; hydrogen bonds are attractions between different molecules (for the purpose of this course.)</u>


The δ+ portion of one molecule attracts δ− portion of another.
δ+
H
O
H
δ+
δ−
δ+
H
O
H
δ−
δ+


δ−
O
δ+
H
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δ−
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H
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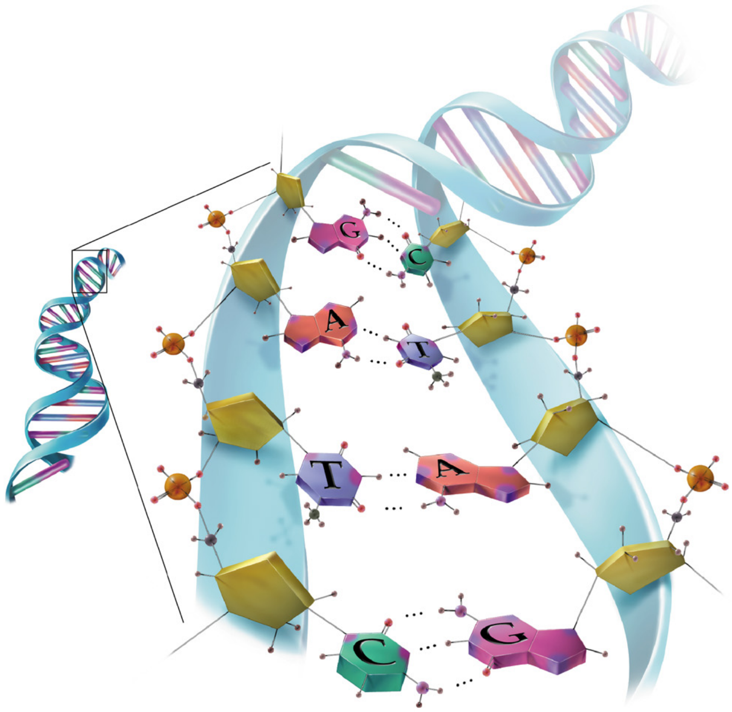
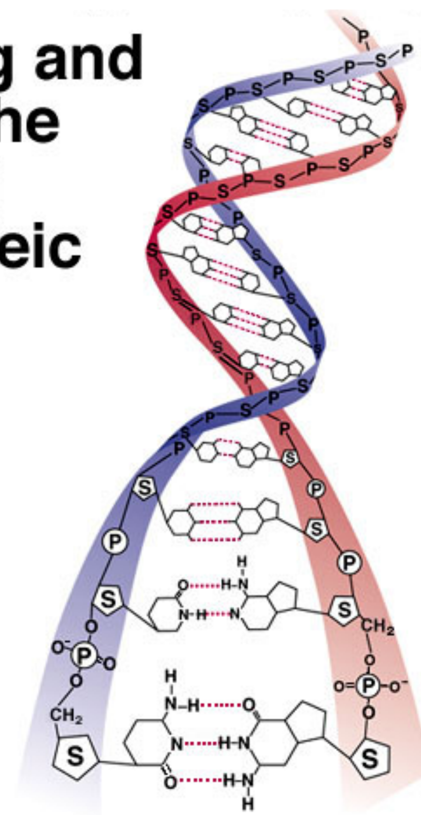
H
O
δ−
H
δ+






# Covalent Bonding and H bonding in the Structure of Deoxyribonucleic Acid (DNA)



# Examples

- Show how water molecules can hydrogen bond with each other.
- Show how water and ammonia can hydrogen bond together.
- Which of these compounds can hydrogen bond with water?

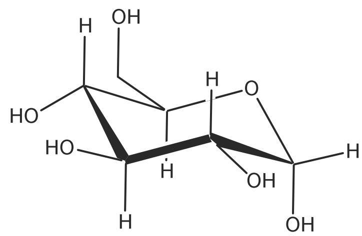
  $CH_4$ $CH_3NH_2$ $CH_2O$ HF $NH_4Cl$

# Hydrogen Bonding and Solubility

- In deciding whether or not certain substances dissolve in each other, chemists have a saying they use:
  "Like dissolves like."
- As a general rule, if a compound can make hydrogen bonds, it is likely to be somewhat soluble in water.
- The more sites a molecule can use to make hydrogen bonds, the more soluble it is likely to be.

## Example

Explain why the sugar glucose dissolves in water.




Glucose

## Dipole-Dipole Forces

- Generally weaker than hydrogen bonds, dipole-dipole forces are the attractions between the positive region of one molecule with the negative regions of another.
- For molecules to engage in this form of attraction, the molecules must have a dipole moment.
- Examples of molecules with dipole-dipole forces are $CH_3Cl$, $H_2S$, and ICl.

## London Dispersion Forces

- London Dispersion Forces are the weakest of the intermolecular forces.
- Even nonpolar molecules can have a *temporary, induced* dipole moment as the electrons move over the molecule.
- The positive side of this temporary dipole will be attracted to the negative pole of another molecule.
- This attraction disappears when the temporary dipole reverses itself.
- These forces become stronger and more important for molecules with larger masses, as well as molecules with a large surface area

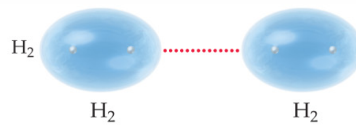
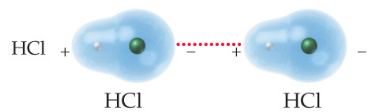
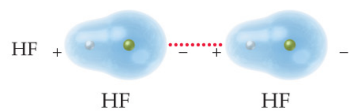
## Comparing Intermolecular Forces

- The *general* order of the strength of intermolecular forces, from strongest to weakest, is

  Hydrogen Bonding>Dipole-Dipole>Dispersion Force

- In comparing intermolecular forces, we generally <u>consider only the strongest force present</u>, as many molecules will display more than one of these forces.

**TABLE 12.5** Types of Intermolecular Forces

| Type of Force | Relative Strength | Present in | Example |
|---|---|---|---|
| dispersion force (or London force) | weak, but increases with increasing molar mass | all atoms and molecules |  |
| dipole–dipole force | moderate | only polar molecules |  |
| hydrogen bond | strong | molecules containing H bonded directly to F, O, or N |  |



# Examples

Which intermolecular force is most significant in for each of the following molecules?

$NH_3$ $CH_3CH_3$ $Br_2$ $CHF_3$

*Important: Always draw the Lewis Structure before answering questions of this type!*

# Optional Material

The remaining material is covered in the textbook but is not included in the students' notes (the material on energy is covered separately in the Energy Topics lecture). It should generally not be covered in Chemistry 120.

# Liquids

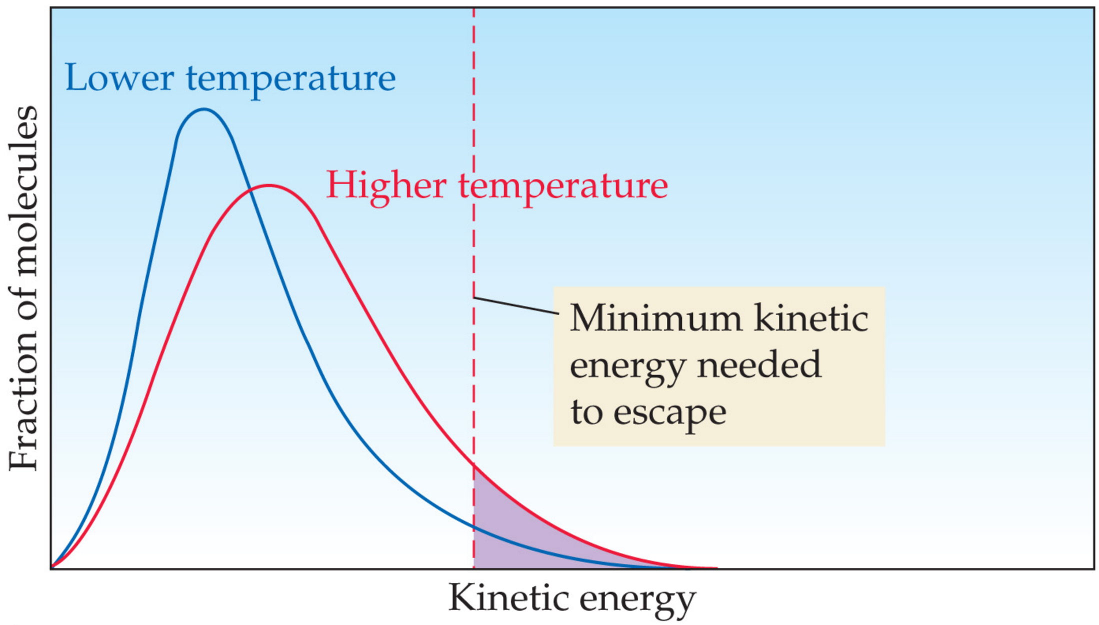
- Liquids take the shape of their container but do not completely fill its volume.
- The particles of a liquid move over one another fairly rapidly, unlike those of a solid which are trapped in place.
- Liquids have several interesting properties we will investigate, largely based on the intermolecular forces which attract the individual molecules together

# Properties of Liquids

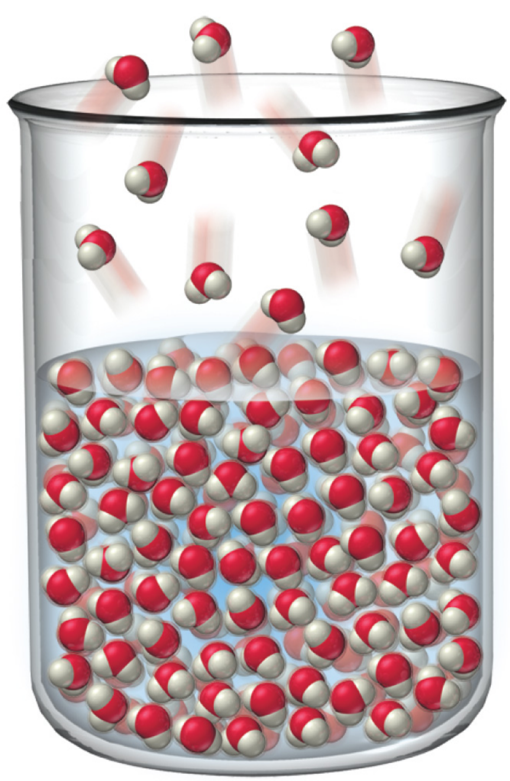
- Liquids possess several interesting properties which can usually be attributed to the strength of the intermolecular forces present.
- The properties we will consider include
  - Vapor Pressure
  - Boiling Point
  - Surface Tension
  - Viscosity

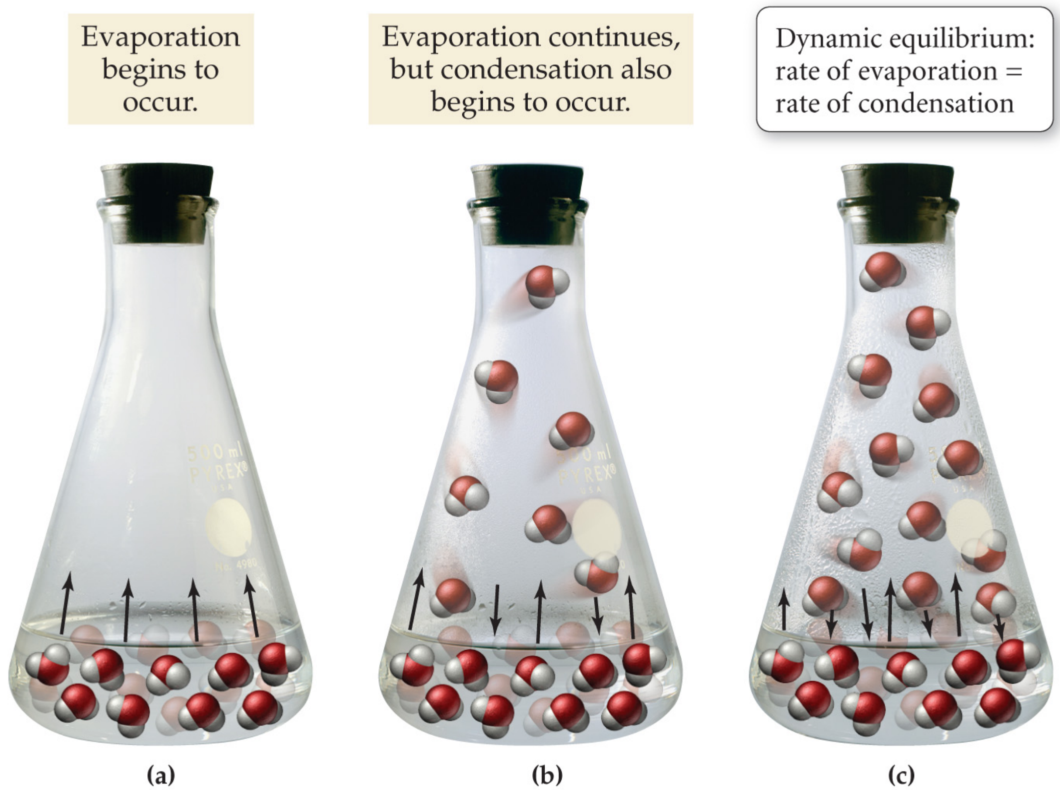
# Vapor Pressure

- A liquid in a sealed container is constantly evaporating, and the vapor above it is being reabsorbed by the liquid. This is called a <u>dynamic equilibrium</u>.
- Liquids which have very strong intermolecular forces tend to have relatively low vapor pressures, as the attractive forces pull the molecules close together.
- Liquids which exert higher vapor pressures tend to have less intermolecular attraction.


Lower temperature
Higher temperature
Minimum kinetic energy needed to escape
Fraction of molecules
Kinetic energy









# Boiling Point

- In order to boil a liquid, the intermolecular forces holding the gas particles together must be overcome.
- If there are strong intermolecular forces then more energy must be expended to separate the molecules into the gas state.
- Liquids with weak intermolecular forces tend to boil at relatively low temperatures, assuming the molecular weight of the compound is not too high.

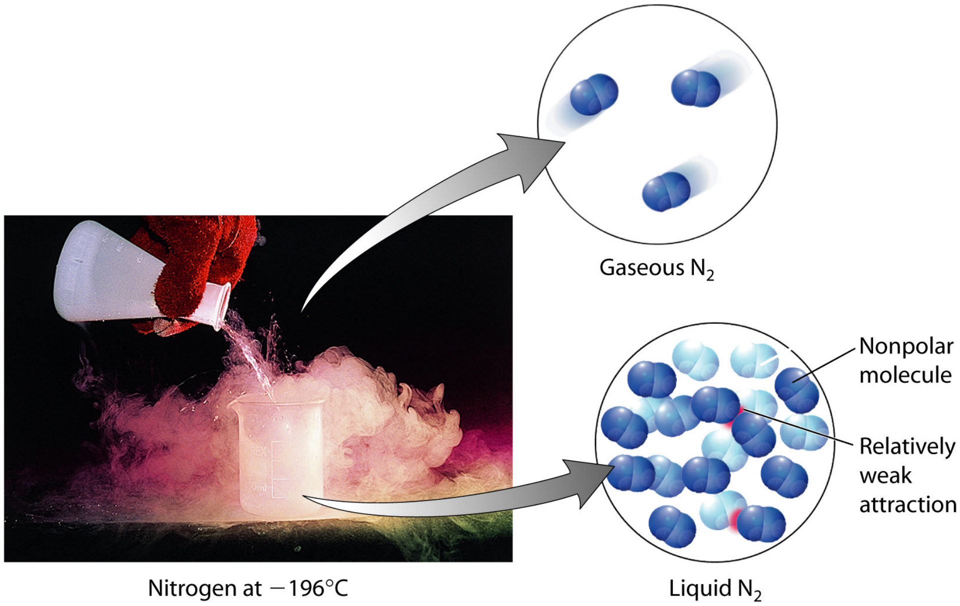
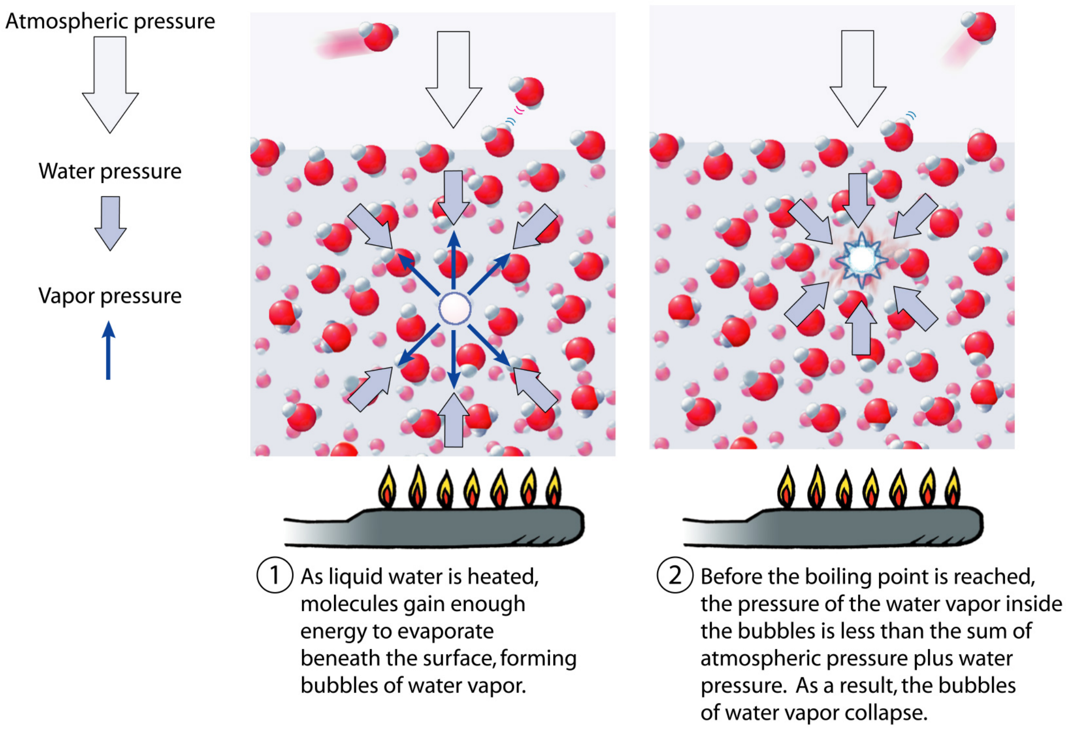
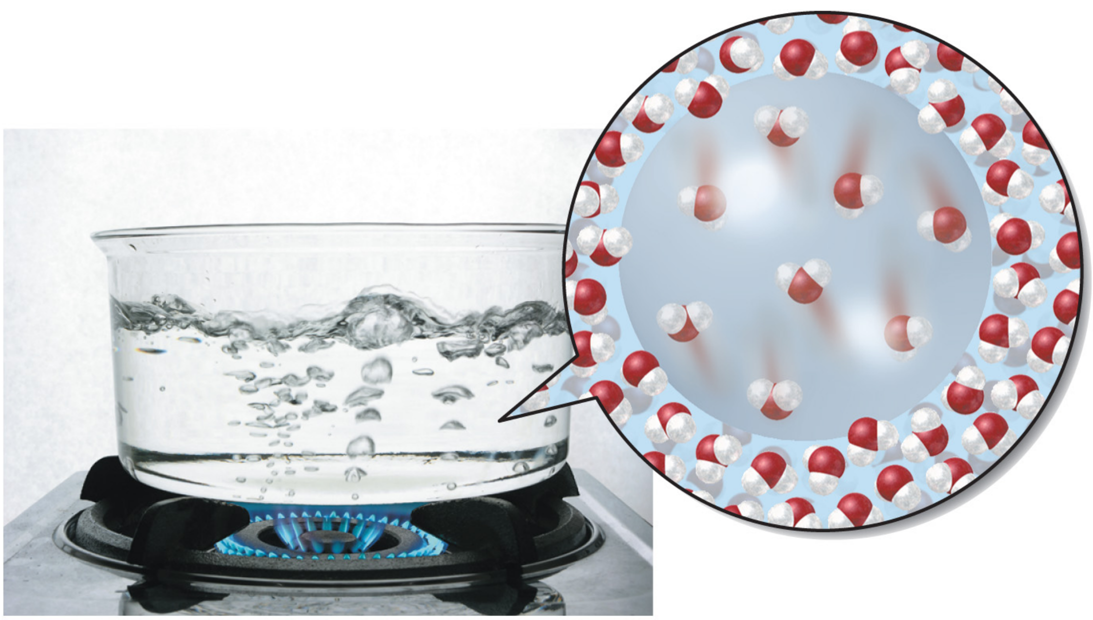


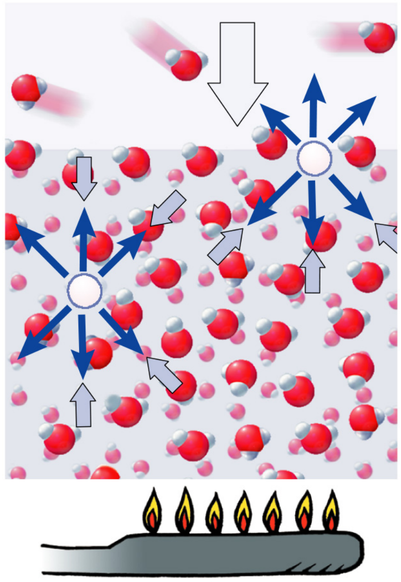

**Table 6.3**

Boiling Points of Some Polar and Nonpolar Substances

| Substance | Boiling Point (°C) |
|---|---|
| *Polar* | |
| Hydrogen fluoride, HF | 20 |
| Water, $H_2O$ | 100 |
| Ammonia, $NH_3$ | −33 |
| *Nonpolar* | |
| Hydrogen, $H_2$ | −253 |
| Oxygen, $O_2$ | −183 |
| Nitrogen, $N_2$ | −196 |
| Boron trifluoride, $BF_3$ | −100 |
| Carbon dioxide, $CO_2$ | −79 |


Atmospheric pressure
Water pressure
Vapor pressure
1 As liquid water is heated, molecules gain enough energy to evaporate beneath the surface, forming bubbles of water vapor.
2 Before the boiling point is reached, the pressure of the water vapor inside the bubbles is less than the sum of atmospheric pressure plus water pressure. As a result, the bubbles of water vapor collapse.



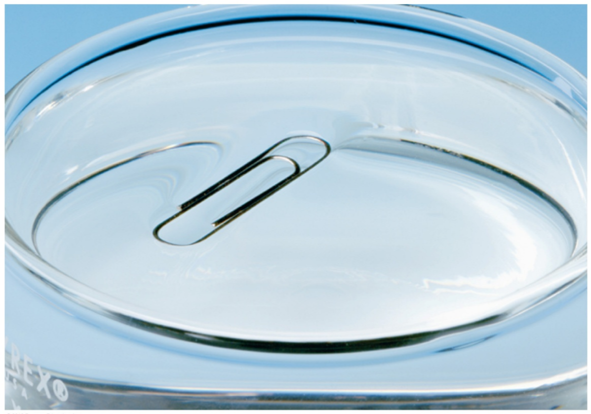


③ At the boiling point, the pressure of the water vapor inside the bubbles equals or exceeds the sum of atmospheric pressure plus water pressure. As a result, the bubbles of water vapor are buoyed to the surface and escape.

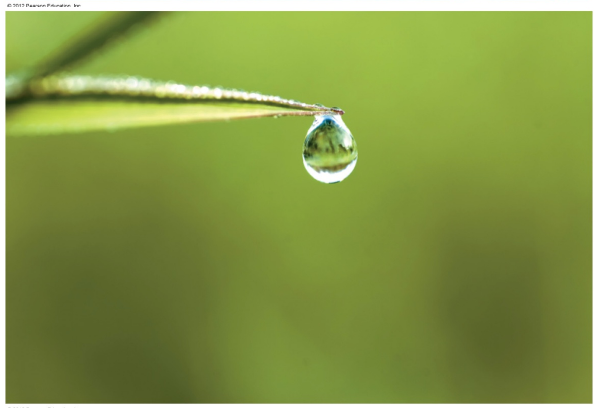
④ We see this evaporation as boiling.

# Surface Tension

- The surface tension of a liquid is its tendency to minimize the area it exposes to the atmosphere.
- For example, water tends to form beads rather than spread out; by beading it is pulling as many molecules as possible into the center of the water drop.
- Force must be applied to penetrate the surface of liquids with high surface tensions
  - Consider insects "walking on water"
- In general, the greater the intermolecular forces, the greater the surface tension of the liquid.







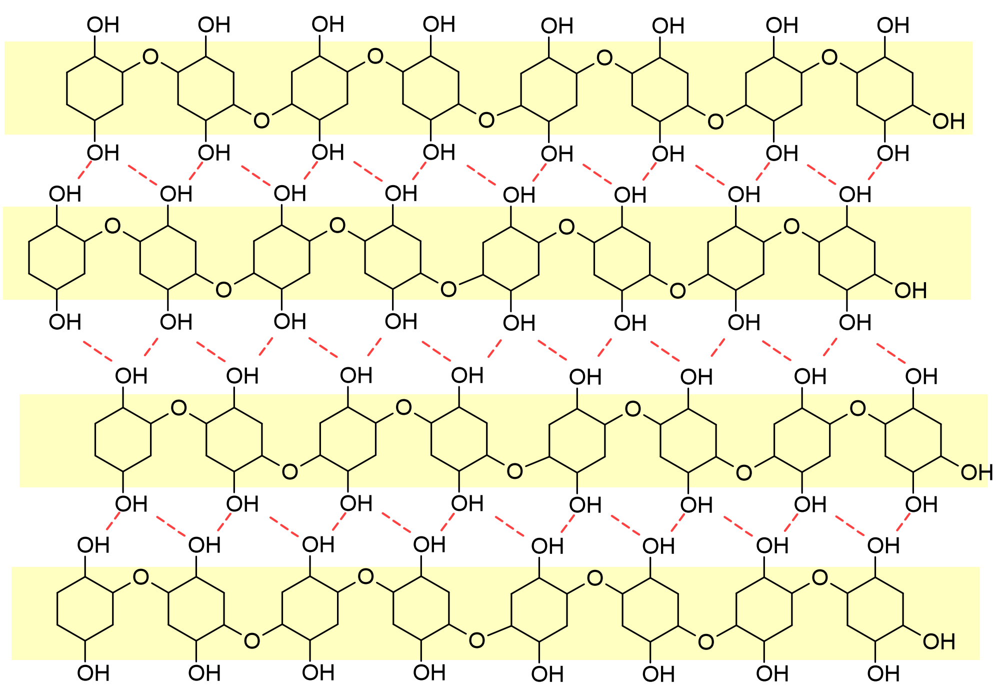


# Viscosity

- The viscosity of a liquid is its tendency to resist flow.
- Honey is an example of a viscous mixture.
- Liquids with greater intermolecular forces tend to be more viscous
- Maple syrup is so viscous because of the extensive hydrogen bonding which occurs between molecules in the liquid
- Many oils contain long chains of carbon and hydrogen atoms with a large surface area, allowing them to form extensive networks of London dispersion forces



Simplified Molecular Structure of a Syrup



# Solids

- Solids neither take the shape nor completely fill their container.
- The particles which make up a solid are generally much closer together than those in a gas or a liquid.
- The particles' motion is restricted, and, at the submicroscopic level, they mainly vibrate in place rather than move over each other like those in a liquid.

# Organization of Solids

- If solids are examined at the smallest levels we will find that some have very well-ordered arrangements of their particles, whereas others lack any organization.
- We can generalize this by categorizing them as follows:
  - Crystalline solids have a well-ordered structure, which is often reflected in the structure of the crystals they may form. They have a definite melting point.
  - Amorphous solids generally lack a clear pattern or organization in their particles. They may gradually melt over a broad temperature range.

## Amorphous Solids

- An amorphous solid is often formed when a substance cools rapidly, trapping the particles in whatever positions they are currently occupying.
- They are generally less stable than crystalline solids, as their particles have not been able to adjust their particles to the most stable positions.
- Examples of amorphous solids include glass, rubber, and many plastics.

## Crystalline Solids

- The particles in a crystalline solid organize themselves into patterns which generally stabilize the compound.
- Crystalline structures may be formed from ions (NaCl), from molecules ($H_2O$ in ice, $CO_2$ in dry ice), from metal atoms (copper, sodium, etc.), and non-metal atoms (carbon in diamond, graphite, and buckyballs).

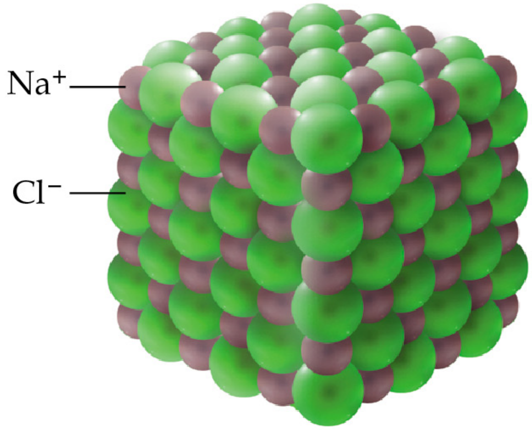
# Organization of Crystalline Solids

- Many interesting types of crystal structures can be found in solids.
  - Many consist of ions or atoms at the points of a cube, with other atoms or ions in the center, on a face, or at the edges of the cube.
  - Some position their atoms or ions in hexagonal pattern, with other atoms or ions sitting in the "holes" between the layers of these patterns.
  - Even more elaborate patters exist.
- Careful examination of these structures is beyond the scope of this course.

# Types of Crystalline Solids

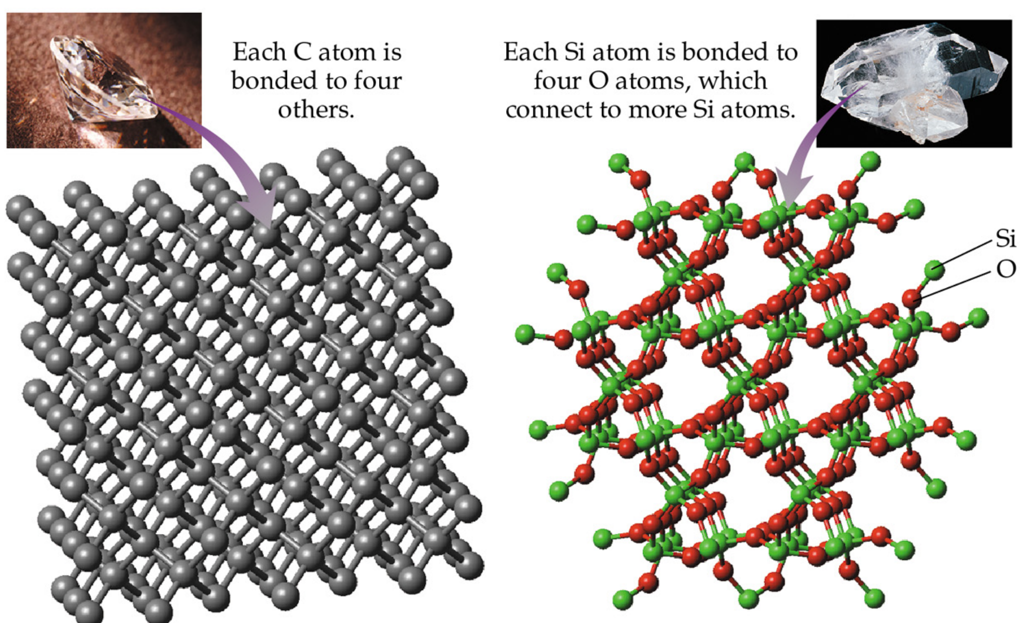
- We generally classify crystalline solids into three distinct types:
  - <u>Molecular solids</u>, composed of molecules held together by intermolecular forces
  - <u>Ionic solids</u>, composed of ions held together by ionic bonds.
  - <u>Atomic solids</u>, composed of individual atoms held together by bonds or forces, depending on the particular element
  - We can categorize atomic solids even further
    - <u>Covalent solids</u>, (sometimes called "network covalent") which feature atoms covalently bonded to one another over an extensive network
    - <u>Metallic solids</u>, in which the nuclei of metal atoms are suspended in a regular pattern in a "sea of electrons"
    - <u>Non-bonding</u>, in which individual atoms are held together by dispersion forces

## Portion of a NaCl Lattice



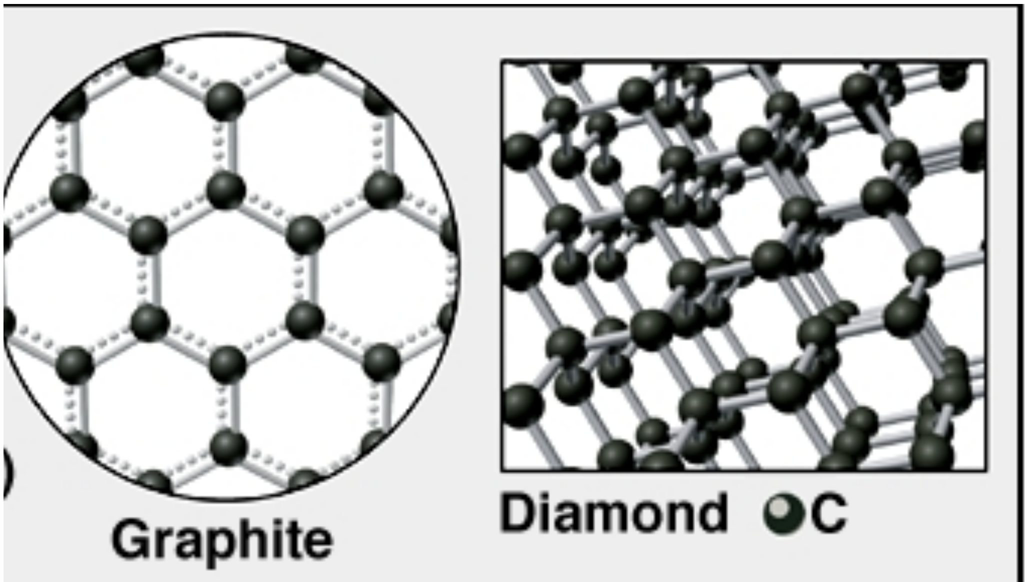



## Two Network Solids

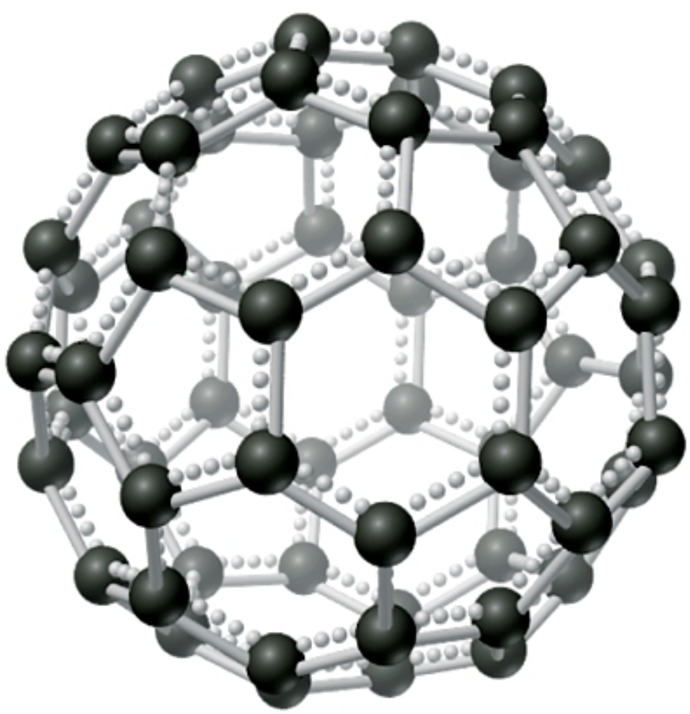



Diamond, C

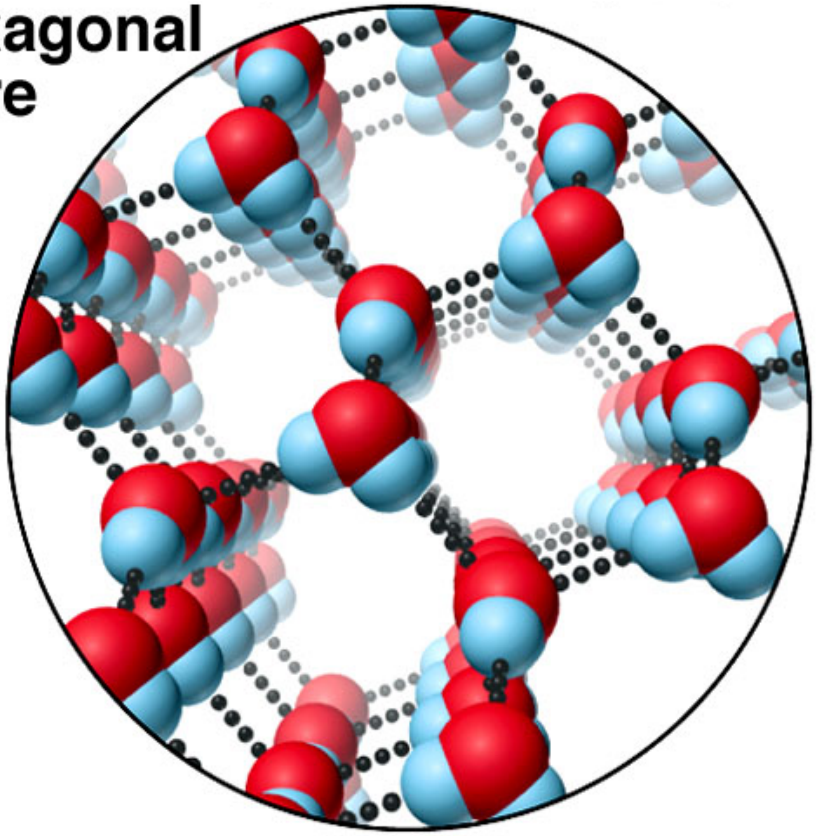
Quartz, $SiO_2$

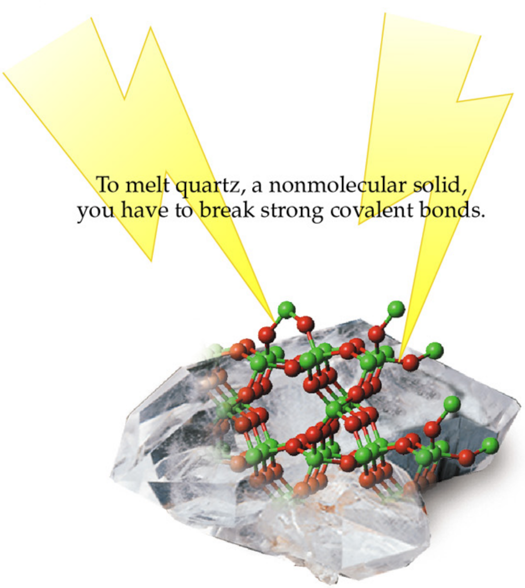



## Buckyball

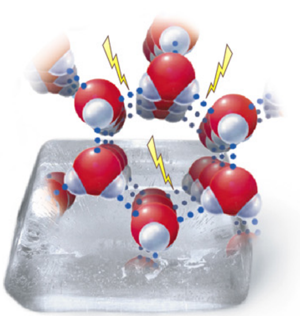


# The Hexagonal Structure of Ice

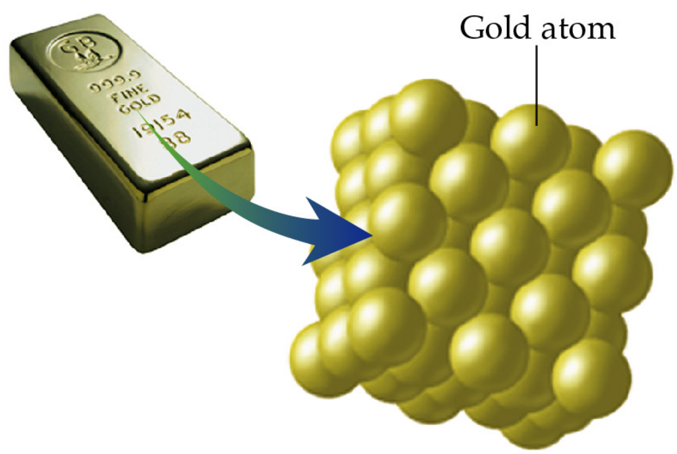




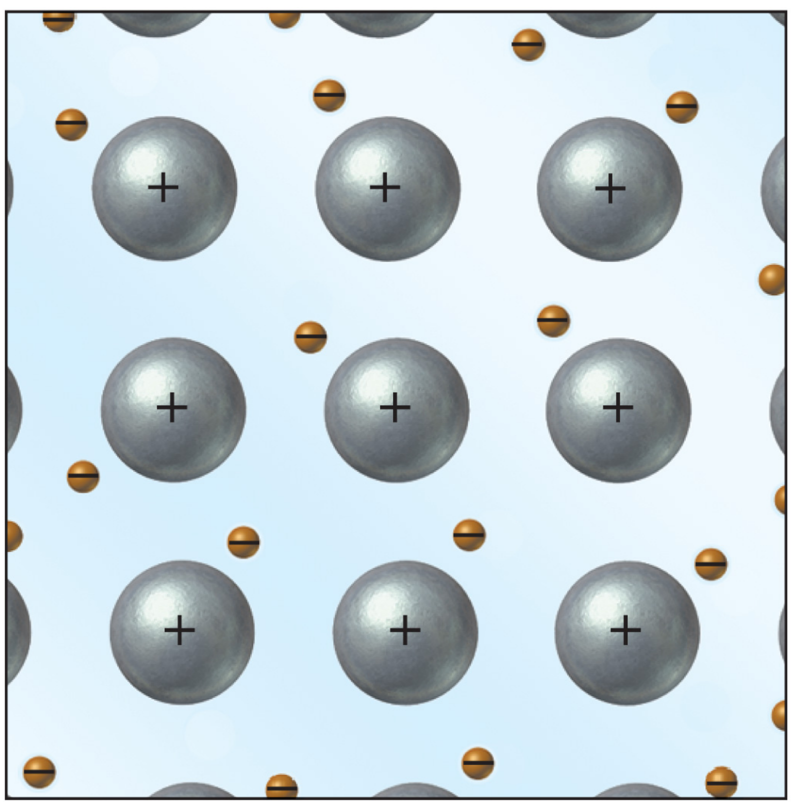

Quartz, melting point 1710°C

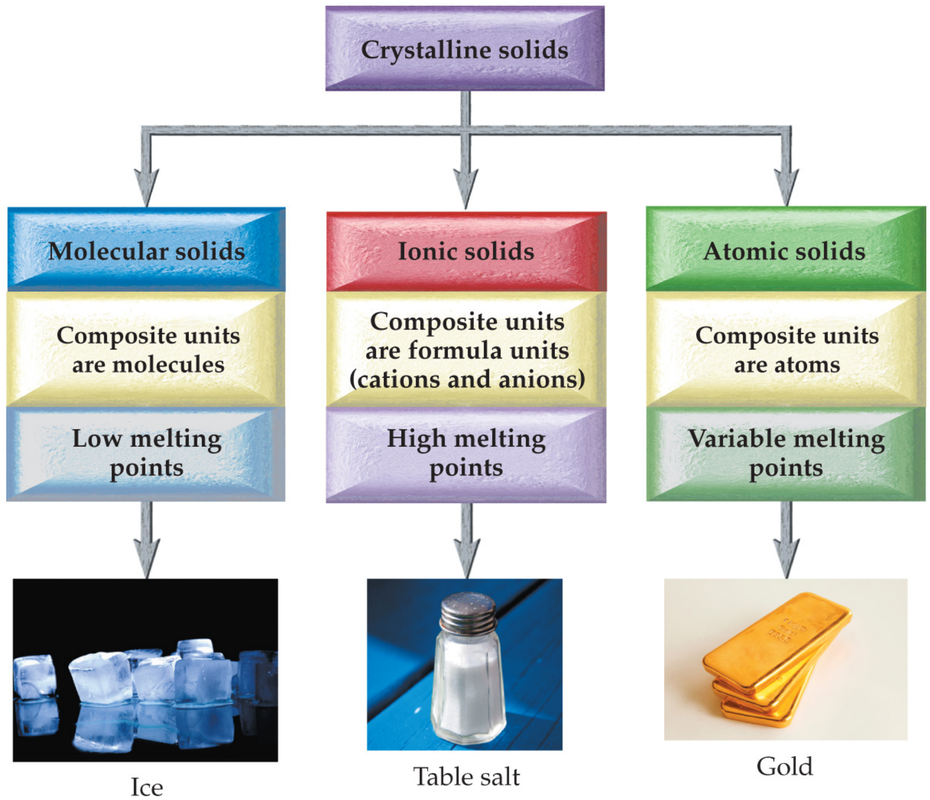



Ice, melting point 0°C


Gold atom
999.9
FINE
GOLD
19154

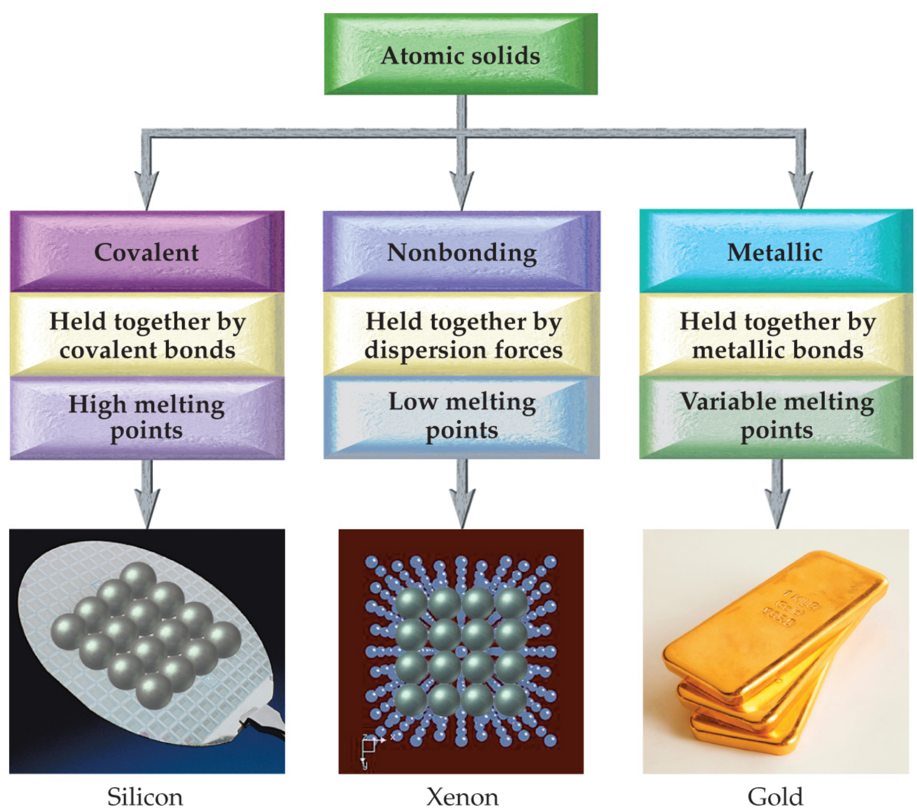






Crystalline solids
Molecular solids
Composite units are molecules
Low melting points
Ice
Ionic solids
Composite units are formula units (cations and anions)
High melting points
Table salt
Atomic solids
Composite units are atoms
Variable melting points
Gold





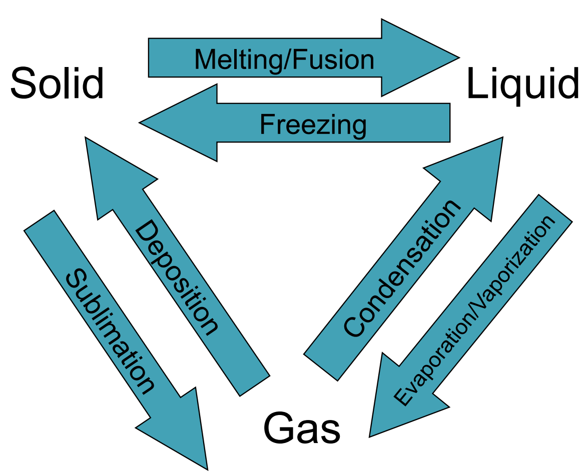
Atomic solids
Covalent
Held together by covalent bonds
High melting points
Silicon
Nonbonding
Held together by dispersion forces
Low melting points
Xenon
Metallic
Held together by metallic bonds
Variable melting points
Gold

# Example

- How would you classify each of the following crystalline solids?
  - Dry ice (solid $CO_2$)
  - Sodium
  - Potassium chloride
  - Sucrose crystals (sucrose is $C_{12}H_{22}O_{11}$)
  - Diamond

# Changes of State (Review)

- Special terms are associated when matter changes from one state to another.



## Energy Changes Associated with Changes of State

- Energy must be added or removed from a substance for a change of state to occur
  - This is true assuming that the ambient pressure does *not* change.
- We know from everyday experience that we must add energy to melt ice and to boil water. Energy must be taken away in the reverse process.

## Energy Changes Associated with Changes of State

- The *heat of fusion* ($\Delta H_{fus}$) is the amount of energy required to convert one mole of a substance from its solid state to its liquid state *at the melting/freezing point*
- The *heat of vaporization* ($\Delta H_{vap}$) is the amount of energy required to convert one mole of a substance from its liquid state to its gas state *at the boiling point*
- Both quantities are always positive
  - Why?
- The units of both quantities are typically reported in kJ/mol (although sometimes you will find them in kJ/gram)

## Energy Changes Associated with Changes of State

- When energy is added to a pure *solid* at its *melting* point, the temperature of the solid should remain constant, with all energy directed towards overcoming the heat of *fusion*
- Similarly, when energy is added to a pure *liquid* at its *boiling* point, the temperature of the liquid should remain constant, with all energy directed towards overcoming the heat of *vaporization*
- The reverse is true when energy is taken away from a liquid or gas

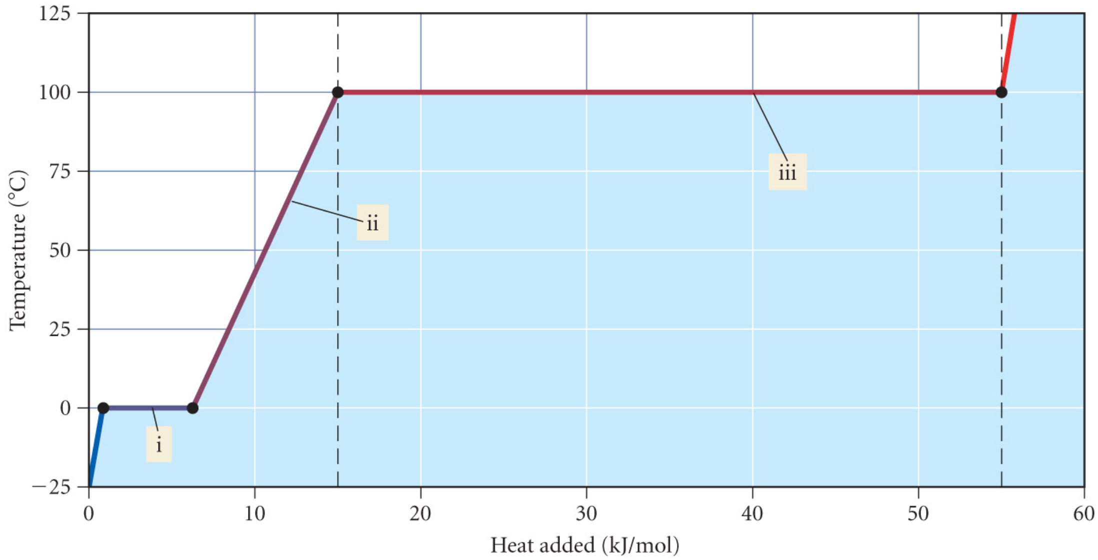
## Energy Changes Associated with Changes of State

Suppose we wanted to carry out the following process:

"Take 5.00 grams of solid $H_2O$ at
-10 °C and convert it to steam at 120 °C."

(assume constant pressure)

Construct a *heating curve* to show the various stages involved in this process. Then, describe the necessary calculations you would need to carry out to calculate the total amount of heat required to accomplish this.






# Examples

*Always assume constant pressure for this type of problem unless told otherwise!*

a. How much energy is required to convert 10.0 g of solid $H_2O$ to liquid $H_2O$ at 0 °C?

b. What is the change in energy when 10.0 g of liquid $H_2O$ is changed to solid $H_2O$ at 0 °C?

c. How much energy is required to convert 10.0 g of liquid $H_2O$ to gaseous $H_2O$ at 100. °C?

# Example

How much energy is required to convert 5.00 grams of solid $H_2O$ at -15.0 °C to liquid $H_2O$ at 45.0 °C?