

*Chemistry, The Central Science*, 10th edition  
Theodore L. Brown; H. Eugene LeMay, Jr.;  
and Bruce E. Bursten

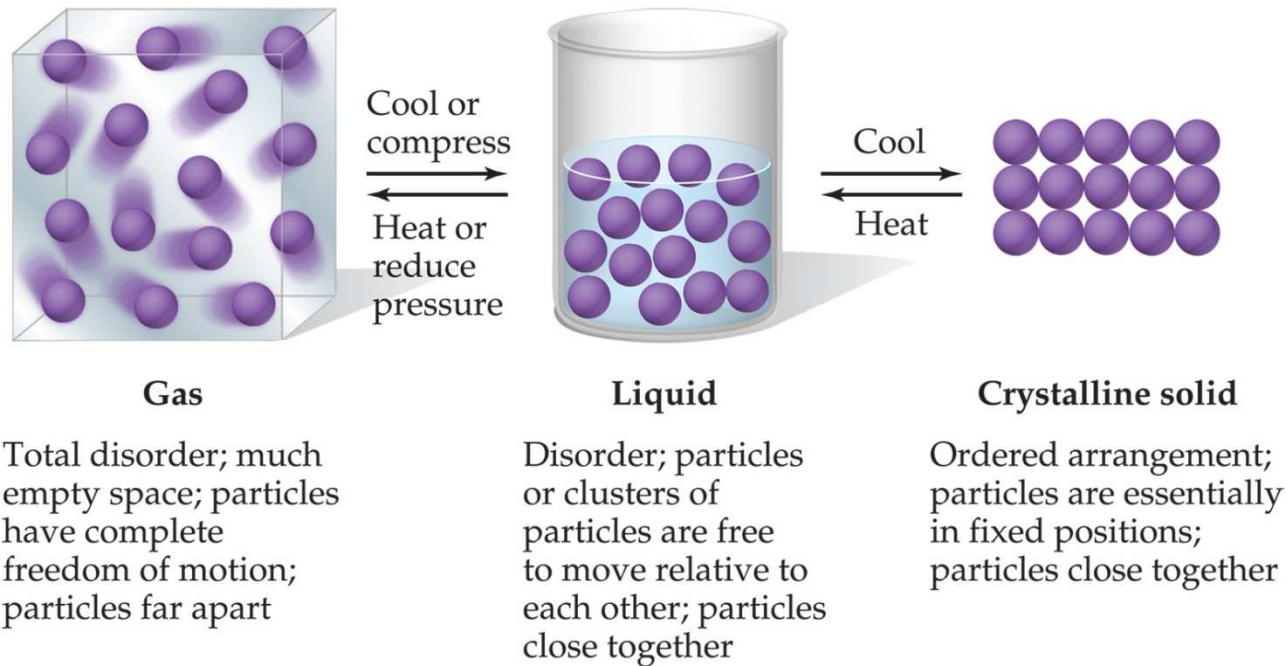
# Chapter 11

# Intermolecular Forces, Liquids, and Solids



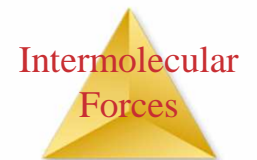
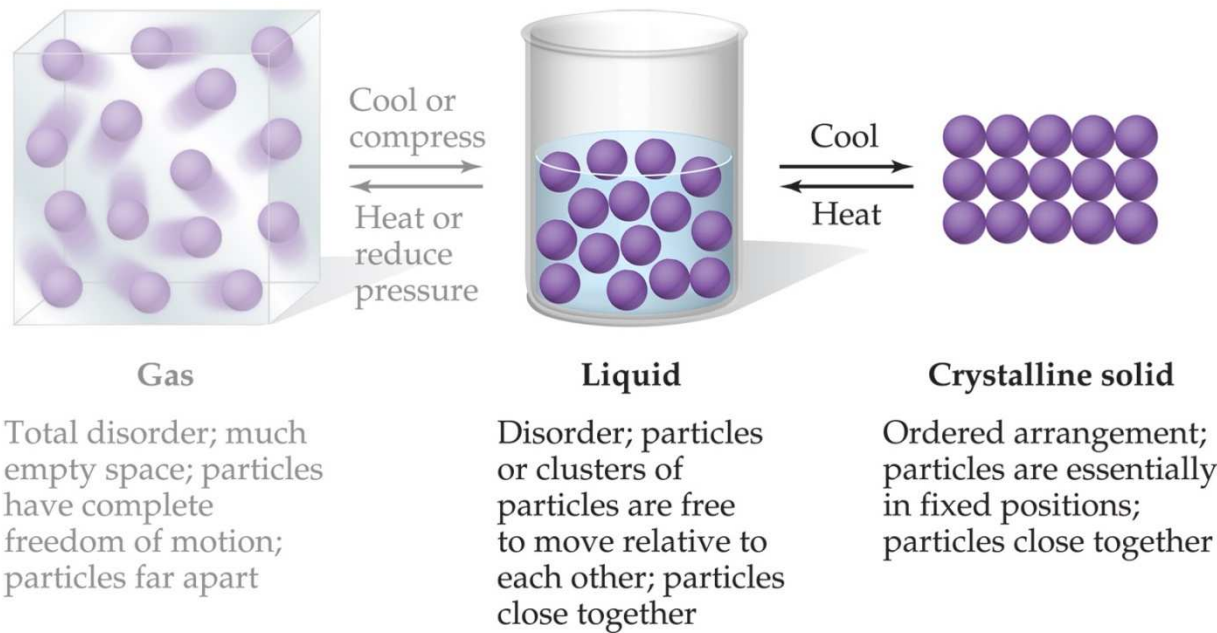
# States of Matter

The fundamental difference between states of matter is the distance between particles.

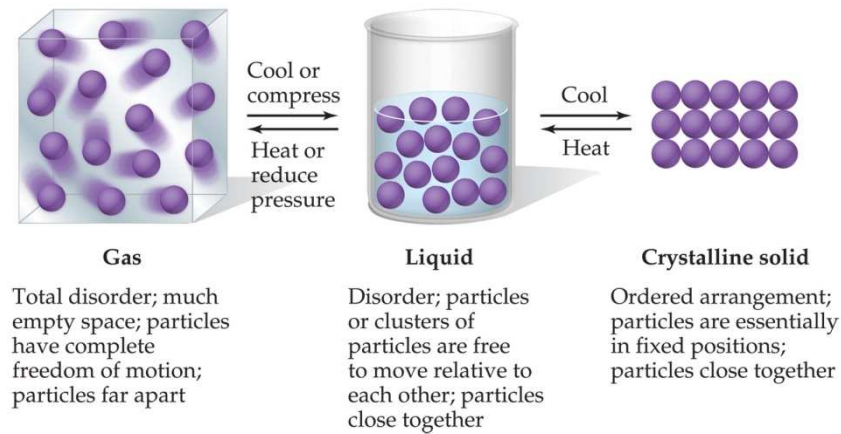


# States of Matter

Because in the solid and liquid states particles are closer together, we refer to them as condensed phases.



# The States of Matter



- The state a substance is in at a particular temperature and pressure depends on two antagonistic entities:

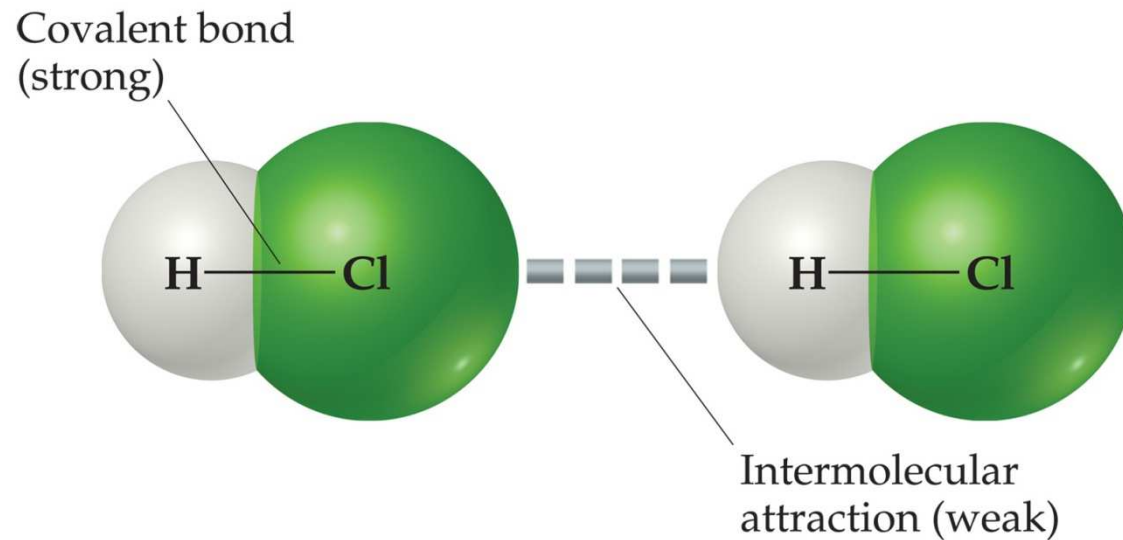
- The kinetic energy of the particles
- The strength of the attractions between the particles



Gas	Assumes both the volume and shape of its container Is compressible Flows readily Diffusion within a gas occurs rapidly
Liquid	Assumes the shape of the portion of the container it occupies Does not expand to fill container Is virtually incompressible Flows readily Diffusion within a liquid occurs slowly
Solid	Retains its own shape and volume Is virtually incompressible Does not flow Diffusion within a solid occurs extremely slowly



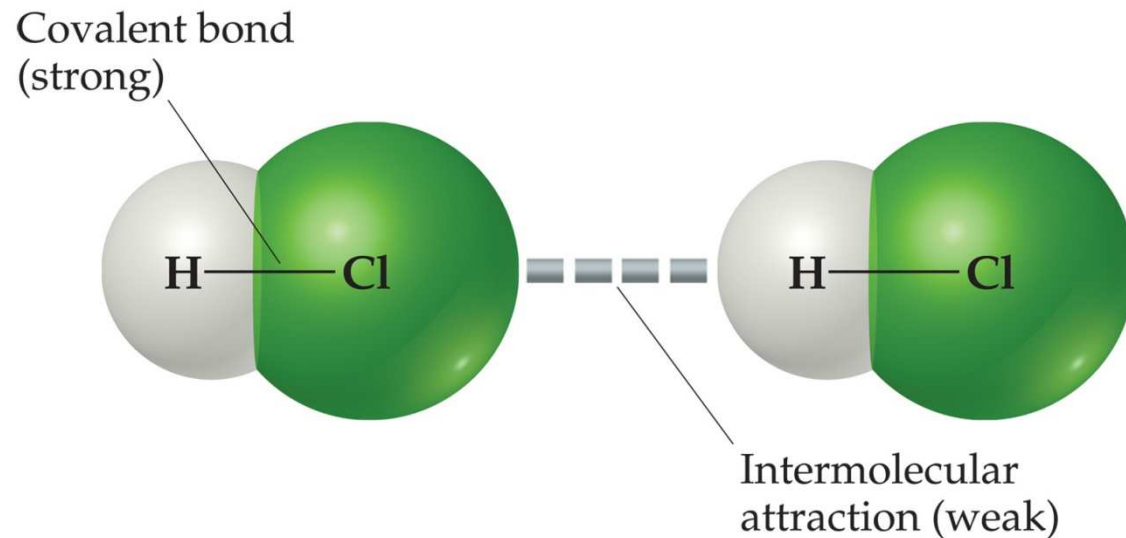
# Intermolecular Forces



The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compounds together.



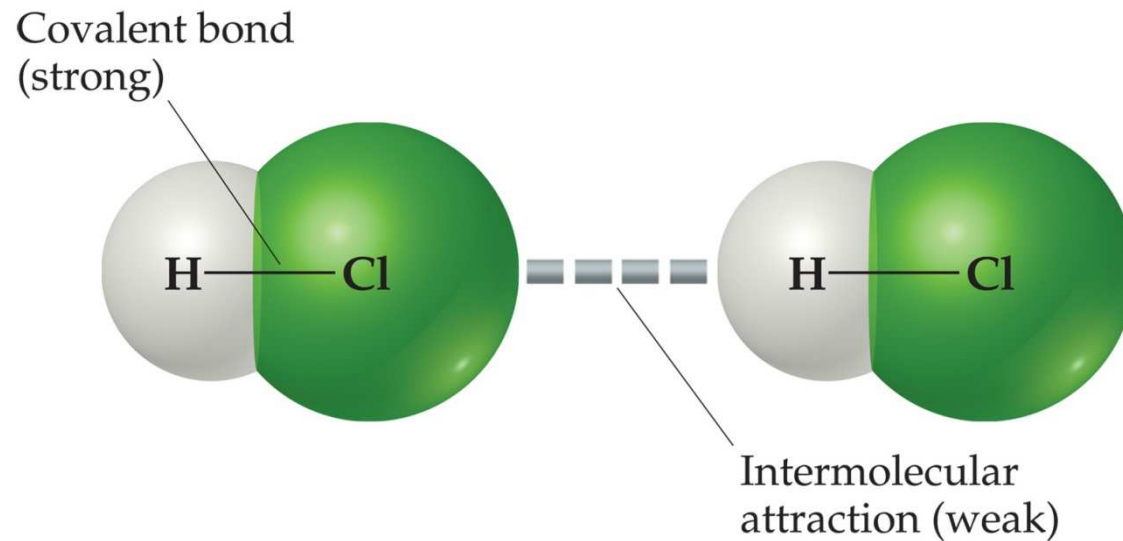
# Intermolecular Forces



They are, however, strong enough to control physical properties such as boiling and melting points, vapor pressures, and viscosities.



# Intermolecular Forces



These intermolecular forces as a group are referred to as **van der Waals forces**.





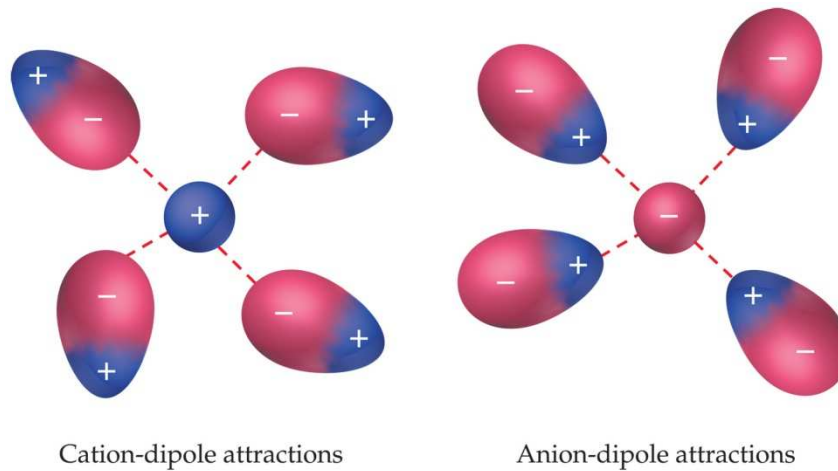
# van der Waals Forces

- Dipole-dipole interactions
- Hydrogen bonding
- London dispersion forces

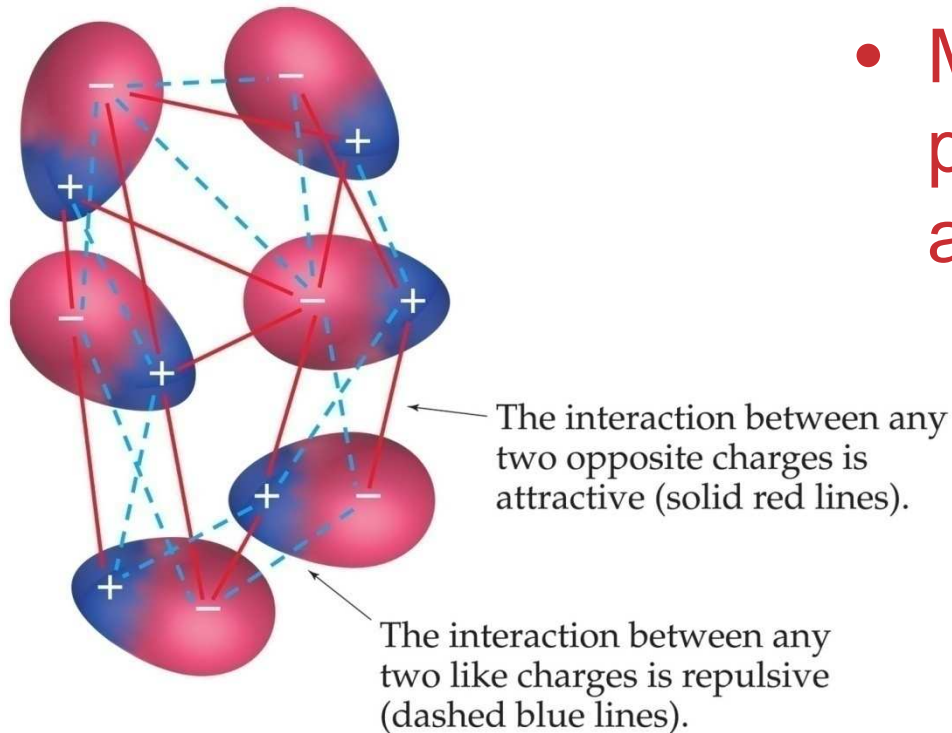


# Ion-Dipole Interactions

- A fourth type of force, ion-dipole interactions are an important force in solutions of ions.
- The strength of these forces are what make it possible for ionic substances to dissolve in polar solvents.



# Dipole-Dipole Interactions



- Molecules that have permanent dipoles are attracted to each other.
  - The positive end of one is attracted to the negative end of the other and vice-versa.
  - These forces are only important when the molecules are close to each other.

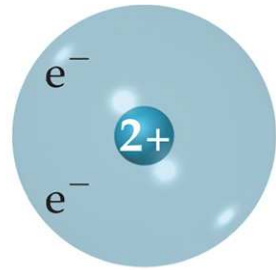
# Dipole-Dipole Interactions

Substance	Molecular Weight (amu)	Dipole Moment $\mu$ (D)	Boiling Point (K)
Propane, CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	44	0.1	231
Dimethyl ether, CH <sub>3</sub> OCH <sub>3</sub>	46	1.3	248
Methyl chloride, CH <sub>3</sub> Cl	50	1.9	249
Acetaldehyde, CH <sub>3</sub> CHO	44	2.7	294
Acetonitrile, CH <sub>3</sub> CN	41	3.9	355

The more polar the molecule, the higher is its boiling point.



# London Dispersion Forces

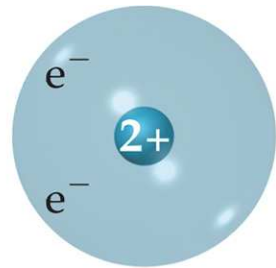


Helium atom 2

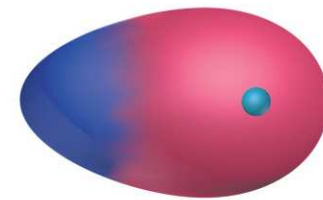
While the electrons in the 1s orbital of helium would repel each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom.



# London Dispersion Forces



Helium atom 2

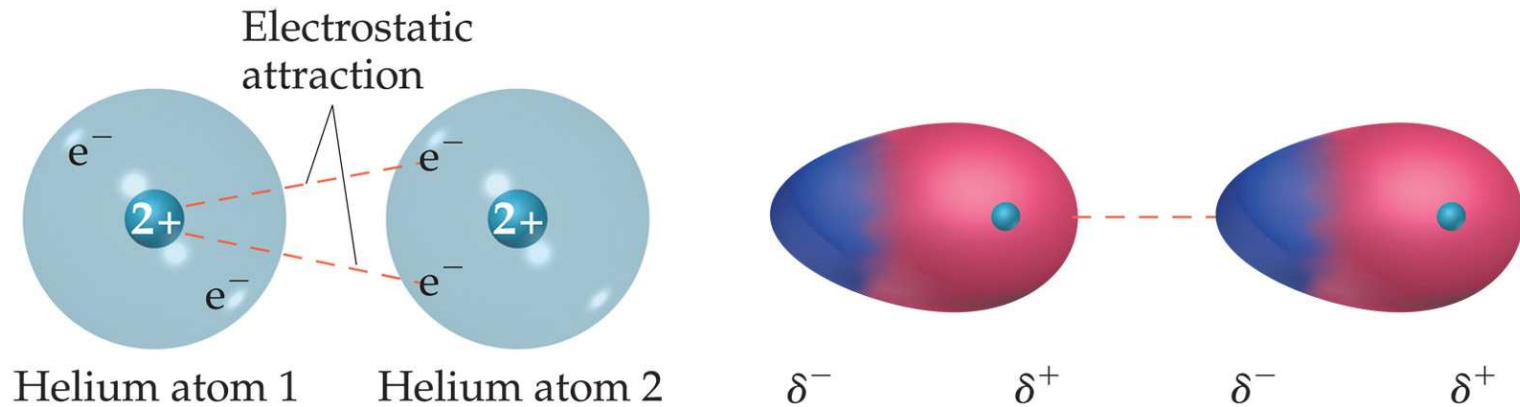


$\delta^-$

$\delta^+$

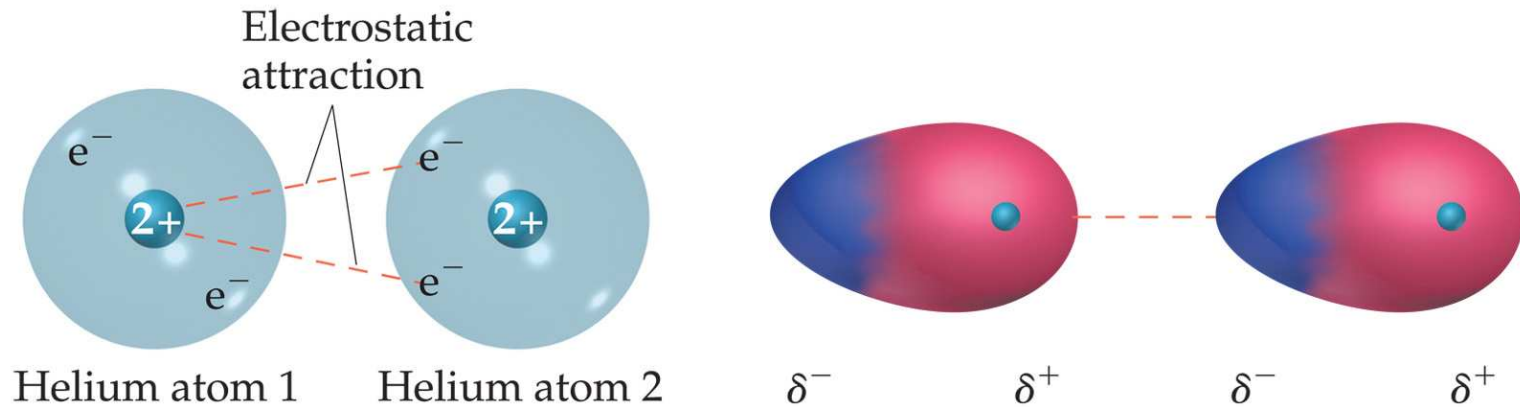
At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.

# London Dispersion Forces



Another helium nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

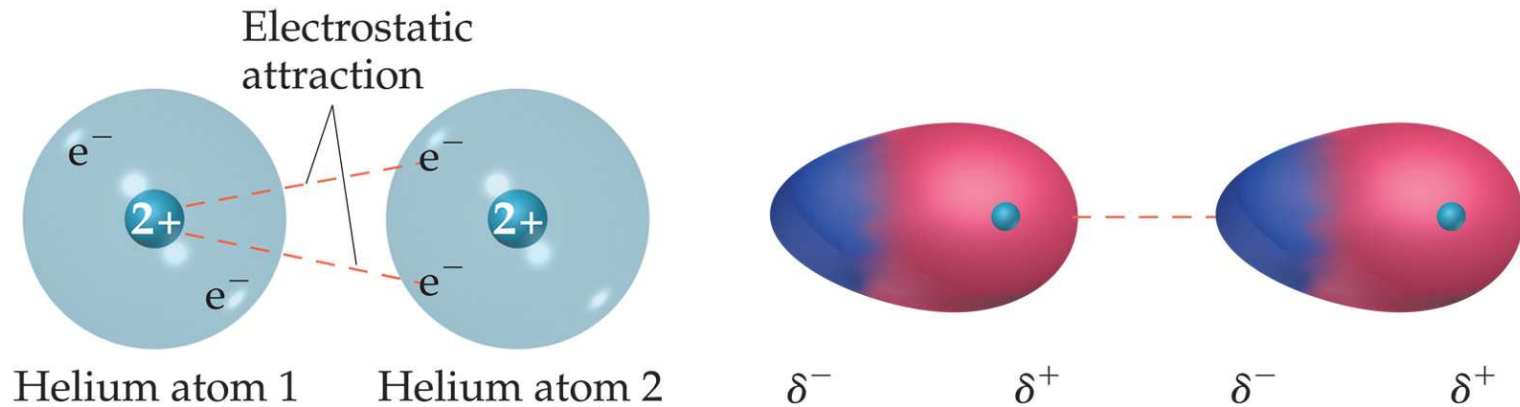
# London Dispersion Forces



London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole.



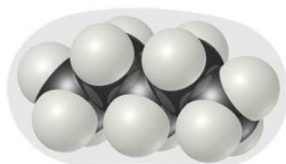
# London Dispersion Forces



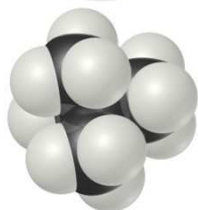
- These forces are present in *all* molecules, whether they are polar or nonpolar.
- The tendency of an electron cloud to distort in this way is called **polarizability** (to give physical **polarity** to).



# Factors Affecting London Forces



*n*-Pentane  
(bp = 309.4 K)



Neopentane  
(bp = 282.7 K)

- The shape of the molecule affects the strength of dispersion forces: long, skinny molecules (like *n*-pentane tend to have stronger dispersion forces than short, fat ones (like neopentane).
- This is due to the increased surface area in *n*-pentane that allows the molecules to make contact over the entire surface area.



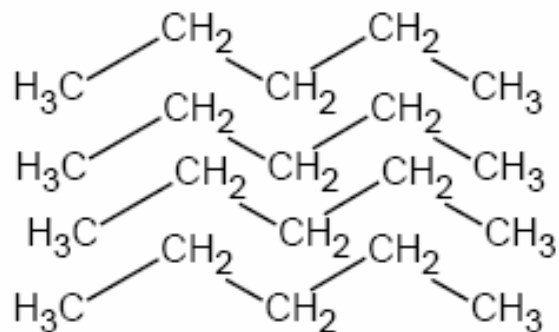
# Factors Affecting London Forces

Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F <sub>2</sub>	38.0	85.1	He	4.0	4.6
Cl <sub>2</sub>	71.0	238.6	Ne	20.2	27.3
Br <sub>2</sub>	159.8	332.0	Ar	39.9	87.5
I <sub>2</sub>	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

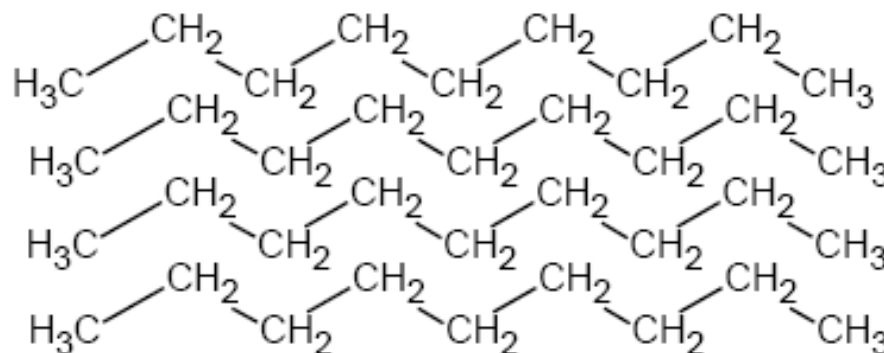
- The strength of dispersion forces tends to increase with increased molecular weight.
- Larger atoms have larger electron clouds, which are easier to polarize.



# Comparing London attractions



four 5-carbon molecules



four 9-carbon molecules

n-pentane, C<sub>5</sub>H<sub>12</sub>

m.p. -130°C

b.p. 36°C

n-nonane, C<sub>9</sub>H<sub>20</sub>

m.p. -54°C

b.p. 151°C



## Explaining macroscopic behavior by reasoning about intermolecular forces

<u>name</u>	<u>formula</u>	<u>melting point</u>
lauric acid	$C_{11}H_{23}COOH$	44° C
myristic acid	$C_{13}H_{27}COOH$	58° C
palmitic acid	$C_{15}H_{31}COOH$	63° C
stearic acid	$C_{17}H_{35}COOH$	70° C



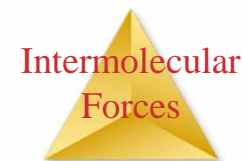
- As the number of carbons increases in a series of fatty acids...
- the melting point increases.
- This is because...
- as the number of carbons increases, the chains get longer. When the chains are longer, the molecules are bigger.
- The larger the molecule, the greater the dispersion forces.
- When the attractive forces holding particles together is greater, you have to get to a higher temperature to break those forces, so the melting point is higher.



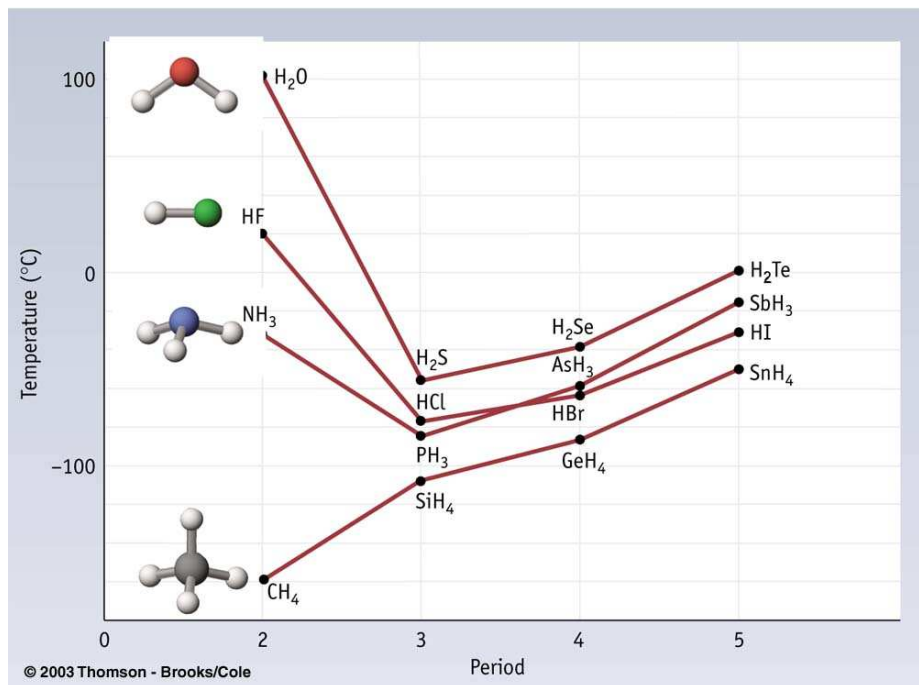
# Which Have a Greater Effect:

Dipole-Dipole Interactions or Dispersion Forces?

- If two molecules are of comparable size and shape, dipole-dipole interactions will likely be the dominating force.
- If one molecule is much larger than another, dispersion forces will likely determine its physical properties.

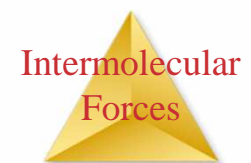


# How Do We Explain This?



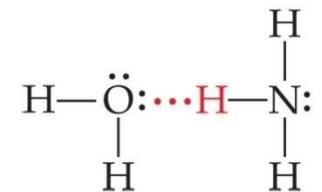
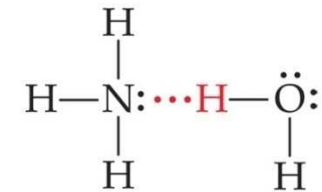
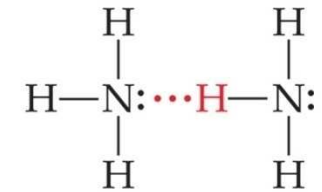
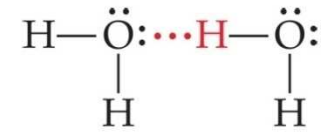


- Water has a high boiling point, high specific heat and high heat of vaporization indicating that intermolecular forces between the water molecules are quite strong.
- HF and NH<sub>3</sub> also behave the same way



# Hydrogen Bonding

- The dipole-dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions **hydrogen bonds**.



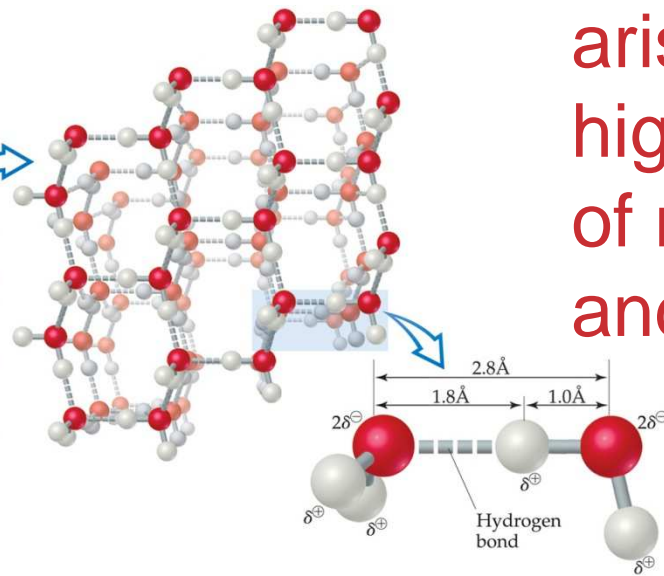
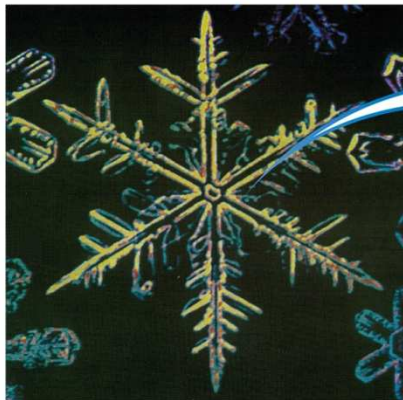
Intermolecular  
Forces



- Hydrogen bonding is a special type of molecular attraction between the hydrogen atom in a polar bond and nonbonding electron pair on a nearby small electronegative ion or atom (usually F, O or N).



# Hydrogen Bonding



Hydrogen bonding arises in part from the high electronegativity of nitrogen, oxygen, and fluorine.

Also, when hydrogen is bonded to one of those very electronegative elements, the hydrogen nucleus is exposed.

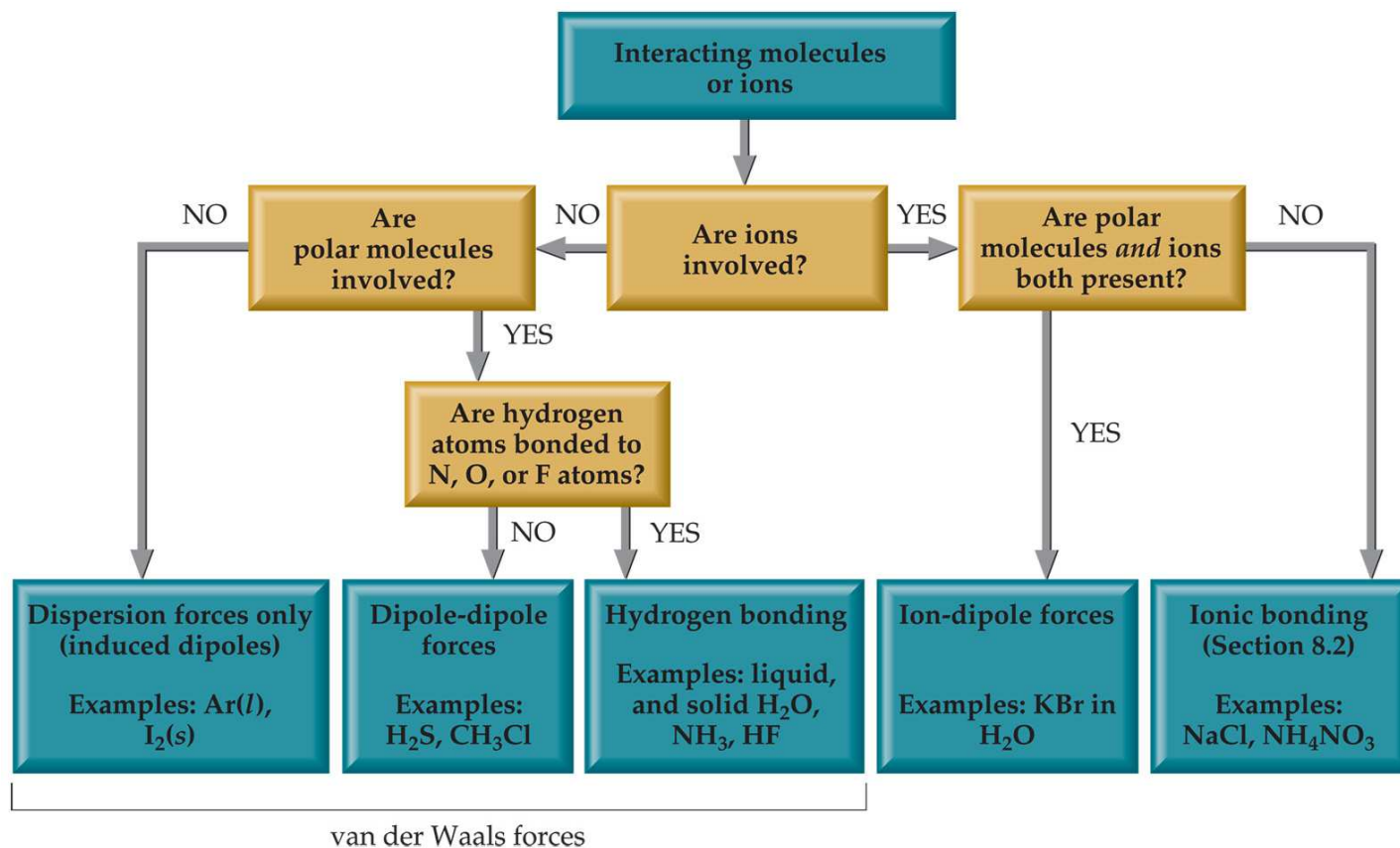
In which of the following substances is hydrogen bonding likely to play an important role in determining physical properties: methane ( $\text{CH}_4$ ), hydrazine ( $\text{H}_2\text{NNH}_2$ ), methyl fluoride ( $\text{CH}_3\text{F}$ ), or hydrogen sulfide ( $\text{H}_2\text{S}$ )?

In which of the following substances is significant hydrogen bonding possible: methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) phosphine ( $\text{PH}_3$ ) hydrogen peroxide ( $\text{HOOH}$ ), or acetone ( $\text{CH}_3\text{COCH}_3$ )?

Page 444

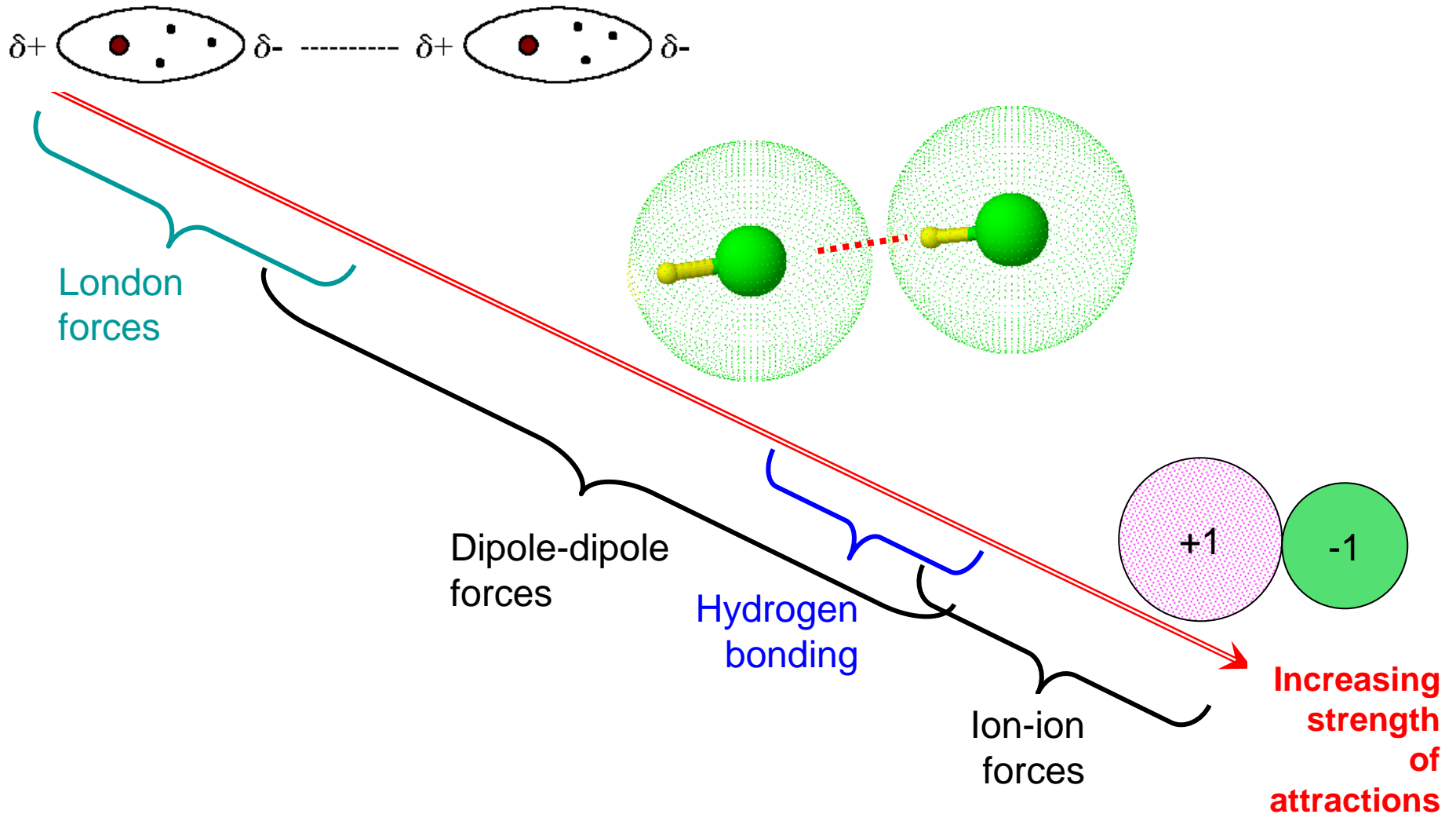


# Summarizing Intermolecular Forces



# Summarizing

From weakest to strongest



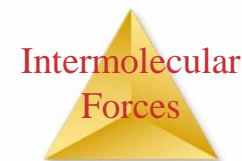
# Complications

- Any molecules that experience one type of attraction, also experience all the weaker types of attractions
- HCl molecules experience:
  - Hydrogen bonding (which is the strongest form of dipole-dipole interactions), and
  - London dispersion forces





- List the substances  $\text{BaCl}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{HF}$ , and  $\text{Ne}$  in order of increasing boiling points.
- The attractive forces are stronger for ionic substances than for molecular ones
- The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are  $\text{H}_2$  (2),  $\text{CO}$  (28),  $\text{HF}$  (20), and  $\text{Ne}$  (20).
- The boiling point of  $\text{H}_2$  should be the lowest because it is nonpolar and has the lowest molecular weight.
- The molecular weights of  $\text{CO}$ ,  $\text{HF}$ , and  $\text{Ne}$  are roughly the same. Because  $\text{HF}$  can hydrogen bond, however, it should have the highest boiling point of the three.
- Next is  $\text{CO}$ , which is slightly polar and has the highest molecular weight. Finally,  $\text{Ne}$ , which is nonpolar, should have the lowest boiling point of these three.
- The predicted order of boiling points is therefore:



(A) Identify the intermolecular forces present in the following substances, and

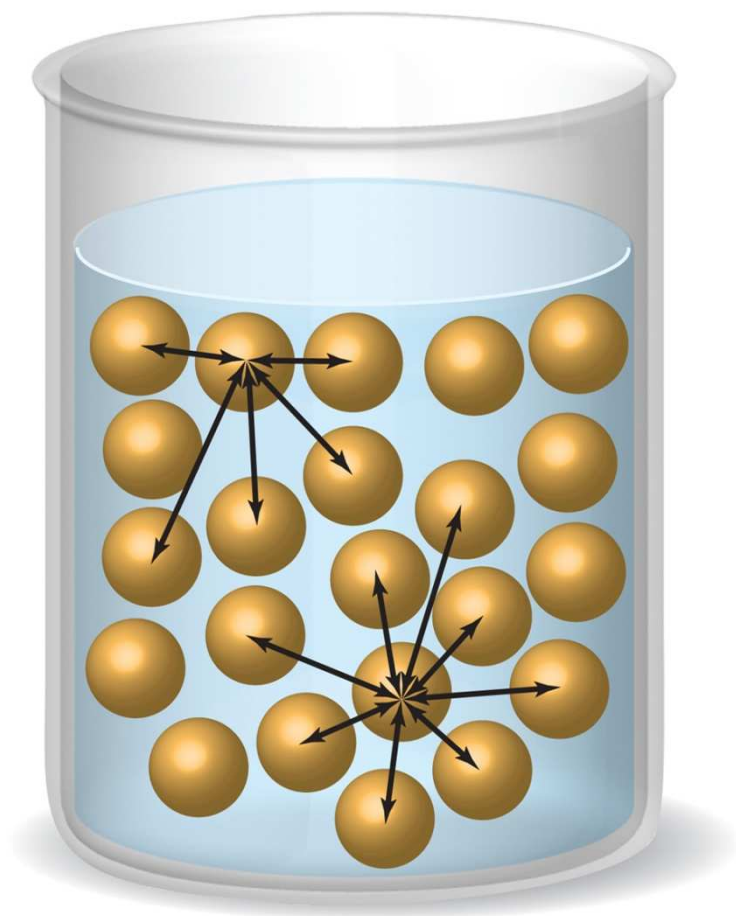
(B) select the substance with the highest boiling point:

$\text{CH}_3\text{CH}_3$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_3\text{CH}_2\text{OH}$

**Answers:** (a)  $\text{CH}_3\text{CH}_3$  has only dispersion forces, whereas the other two substances have both dispersion forces and hydrogen bonds; (b)  $\text{CH}_3\text{CH}_2\text{OH}$



# Intermolecular Forces Affect Many Physical Properties



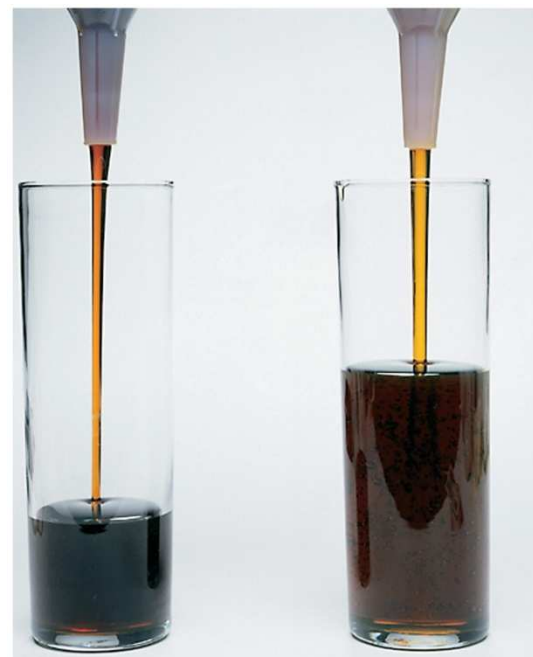
The strength of the attractions between particles can greatly affect the properties of a substance or solution.





# Viscosity

- Resistance of a liquid to flow is called **viscosity**.
- It is related to the ease with which molecules can move past each other.
- Viscosity increases with stronger intermolecular forces caused by increase in the molecular weight, and decreases with higher temperature.



Substance	Formula	Viscosity (kg/m-s)
Hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$3.26 \times 10^{-4}$
Heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$4.09 \times 10^{-4}$
Octane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$5.42 \times 10^{-4}$
Nonane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$7.11 \times 10^{-4}$
Decane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$1.42 \times 10^{-3}$

Intermolecular  
Forces



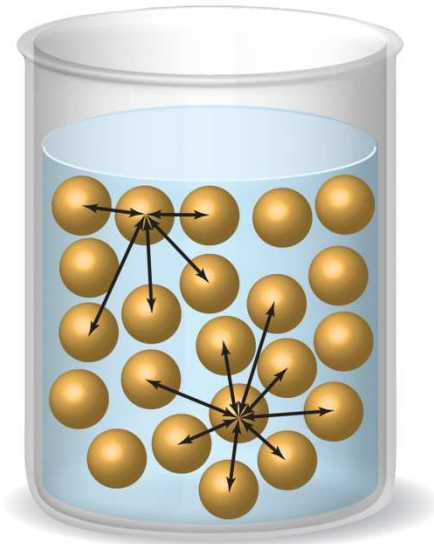
# Explaining macroscopic behavior: viscosity

- Viscosity is the resistance to flow in liquids
- Viscosity is dependent on more than just molecule size – it also depends on the kinds of attractive forces between molecules
- Viscosities of various liquids at 20°C (in centipoise)

<u>Liquid</u>	<u>Viscosity (cp)</u>	<u>Type of IM attraction</u>
water	1.002	H-bonding & London
tetrachloromethane (CCl <sub>4</sub> )	0.969	London
olive oil	84	London
oleic acid	25	London
glycerine	1490	H-bonding & London



# Surface Tension



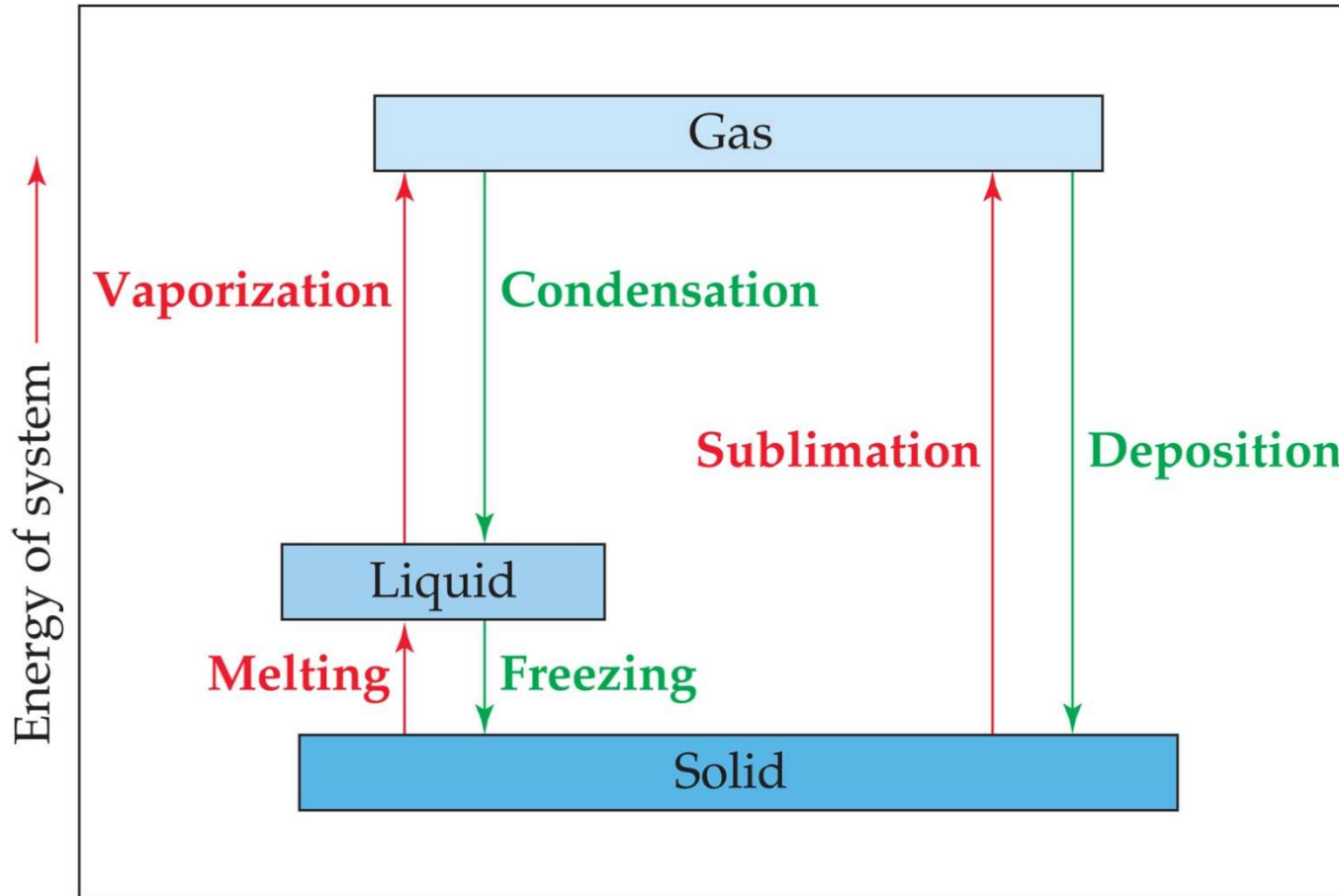
Surface tension results from the net inward force experienced by the molecules on the surface of a liquid.



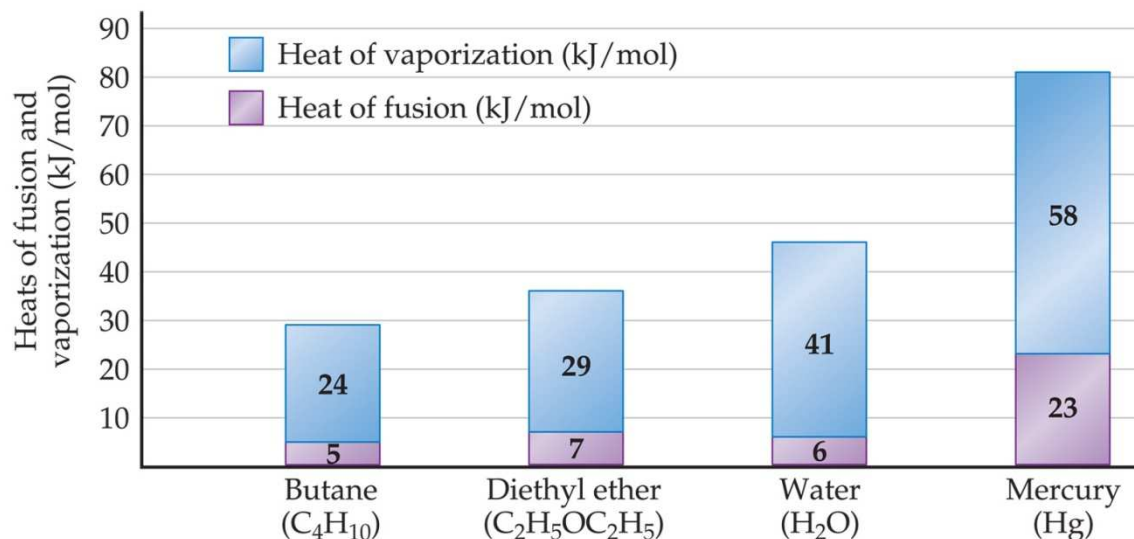
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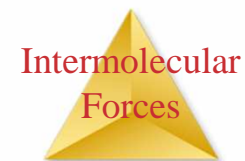
# Phase Changes



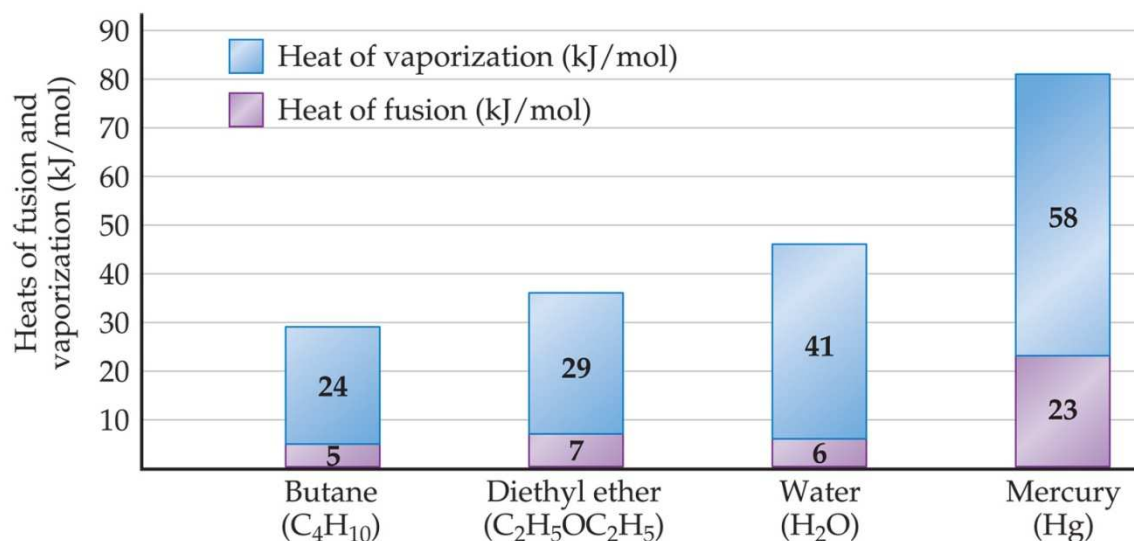
# Energy Changes Associated with Changes of State



- **Heat of Fusion:** Energy required to change a solid at its melting point to a liquid.



# Energy Changes Associated with Changes of State



- **Heat of Vaporization:** Energy required to change a liquid at its boiling point to a gas.



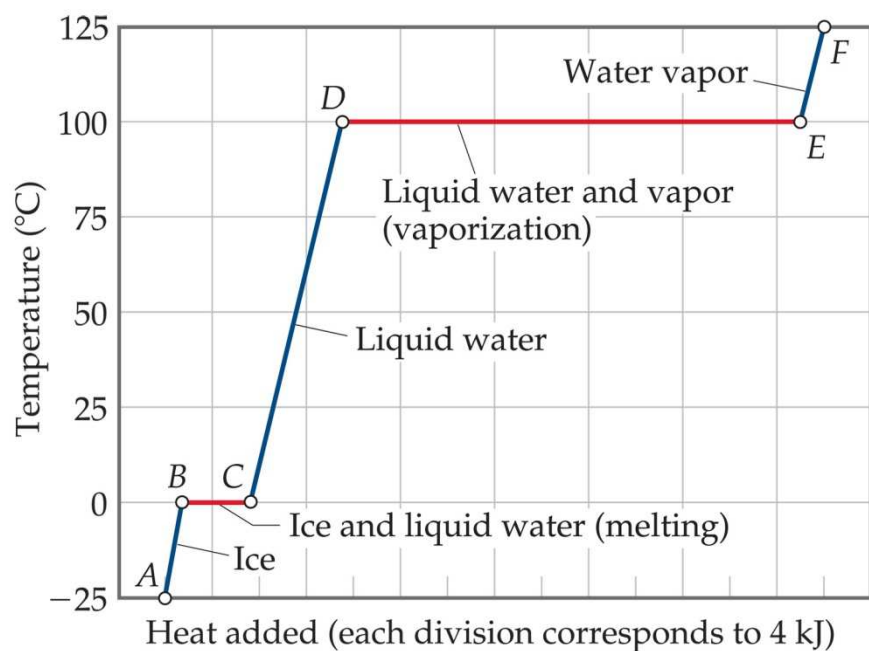
- Heat of Sublimation: Is the enthalpy change required to transform a solid directly into gaseous state.



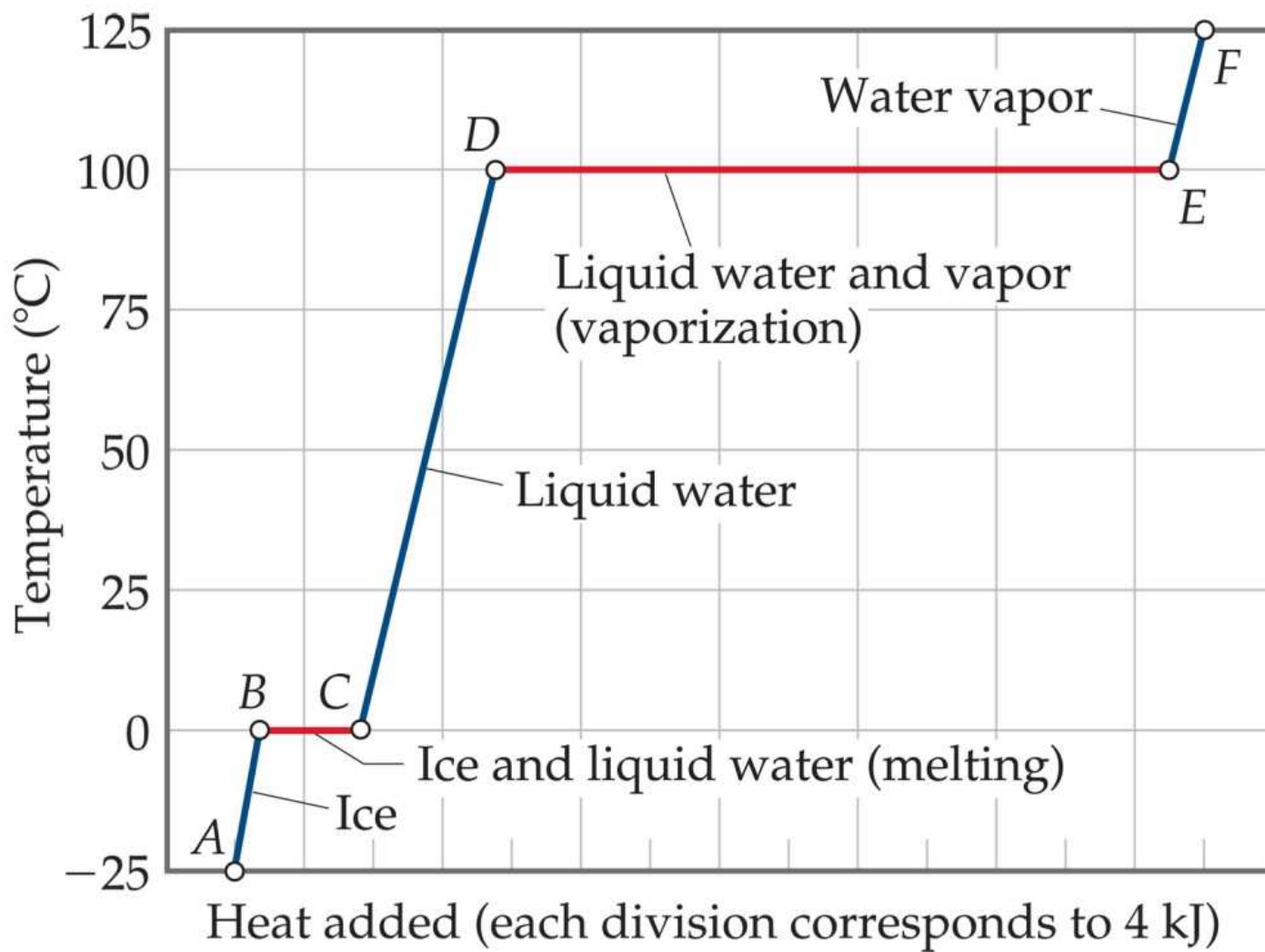
- A refrigerator contains an enclosed gas that can be liquefied under pressure. The liquid absorbs heat as it subsequently evaporates and the refrigerator cools in the process. The vapor is then recycled through a compressor.
- The heat absorbed by the liquid during vaporization is released during condensation. This heat is dissipated through cooling coils at the back of the unit.



# Energy Changes Associated with Changes of State



- The heat added to the system at the melting and boiling points goes into pulling the molecules farther apart from each other.
- The temperature of the substance does not rise during the phase change.



- Calculate the enthalpy change upon converting 1.00 mol of ice at  $-25^{\circ}\text{C}$  to water vapor (steam) at  $125^{\circ}\text{C}$  under a constant pressure of 1 atm. The specific heats of ice, water, and steam are  $2.09\text{ J/g}\cdot\text{K}$ ,  $4.18\text{ J/g}\cdot\text{K}$  and  $1.84\text{ J/g}\cdot\text{K}$ , respectively.

For  $\text{H}_2\text{O}$ ,  $\Delta H_{\text{fus}} = 6.01\text{ kJ/mol}$  and  $\Delta H_{\text{vap}} = 40.67\text{ kJ/mol}$ .

$$\Delta H = mc\Delta T$$

*At the phase change  $\Delta H = m \times$  enthalpy of fusion or vaporization*





- What is the enthalpy change during the process in which 100.0 g of water at 50.0°C is cooled to ice at –30.0°C? The specific heats of ice, water, and steam are 2.09 J/g-K, 4.18 J/g-K and 1.84 J/g-K, respectively.

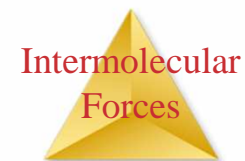
For H<sub>2</sub>O,  $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$  and  $\Delta H_{\text{vap}} = 40.67 \text{ kJ/mol}$ .



Please print another copy of the lab schedule.

### SCHEDULE OF EXPERIMENTS

Week of	#	Experiment Title
Jan 28		No labs this week
Feb 4	1	Limiting Reagent
Feb 11	2	Boyle's Law
Feb 18		No labs this week – Presidents Day 2/18
Feb 25	3	Hexamminenickel(II) Chloride Synthesis
March 3	4	Hexamminenickel(II) Chloride Analysis
March 10	5	Qualitative Analysis of Anions
March 17		No Lab Spring Break
March 24	6	Iodine Clock Reaction Kinetics
March 31	7	Equilibrium Constant Determination
April 7	8	pH Measurement and Titration
April 14	9	Buffer Solutions
April 21		No labs this week – Patriots Day
April 28	10	Electrochemistry Experiment      Last Lab
May 5		No labs this week - Classes end 5/14



# Critical Temperature and Pressure

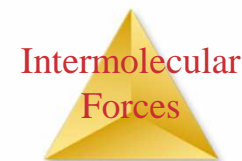
- The highest temperature at which a distinct liquid phase can form is called the critical temperature.
- The critical pressure is the pressure required to bring about liquefaction at this critical temperature
- Above the critical temperature the motion energies of the molecules are greater than the attractive forces that lead to the liquid state.
- At critical temperature the properties of the gas and liquid phases become the same resulting in only one phase: the supercritical fluid.



<u>Substance</u>	<u>Critical temp K</u>	<u>Critical pressure atm</u>
Water	647	217
Ammonia	405	111
H <sub>2</sub> S	374	89
Propane	370	42
Phosphine	324	64
CO <sub>2</sub>	304	73
O <sub>2</sub>	154	50
Argon	150	48
N <sub>2</sub>	126	33

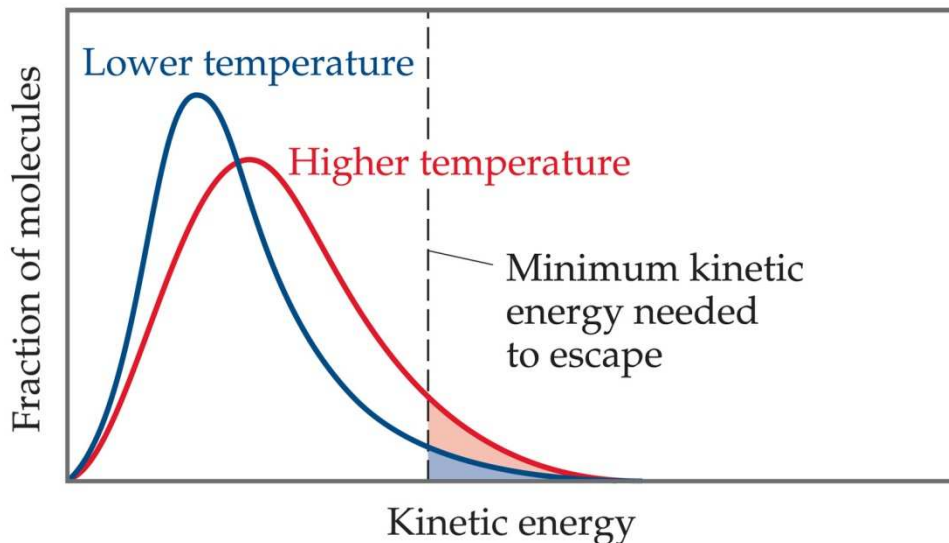
It is useless to try to liquefy the gas if it is above its critical temperature, it needs to be cooled to this temperature before it can be liquefied.

The nonpolar low molecular weight substances have lower critical temperatures.

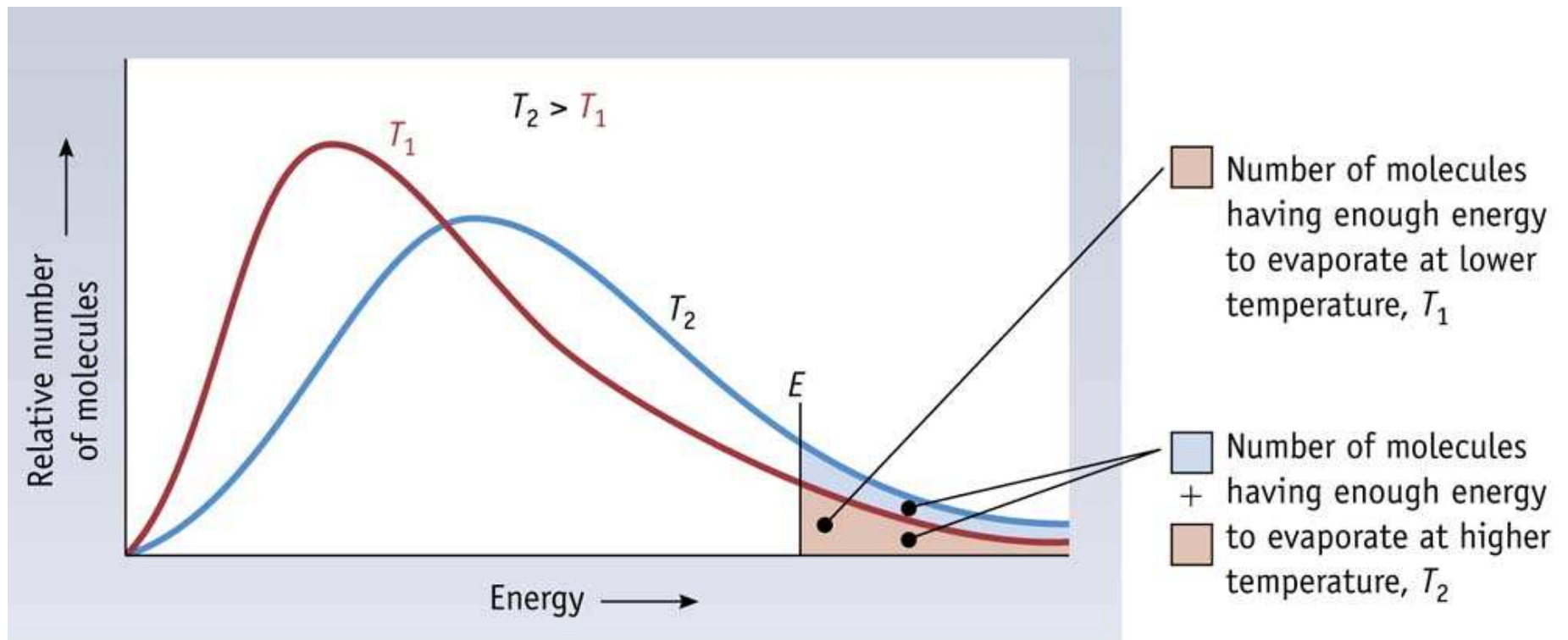


# Vapor Pressure

- At any temperature, some molecules in a liquid have enough energy to escape.
- As the temperature rises, the fraction of molecules that have enough energy to escape increases.



# Comparing a liquid at Particle level two temperatures



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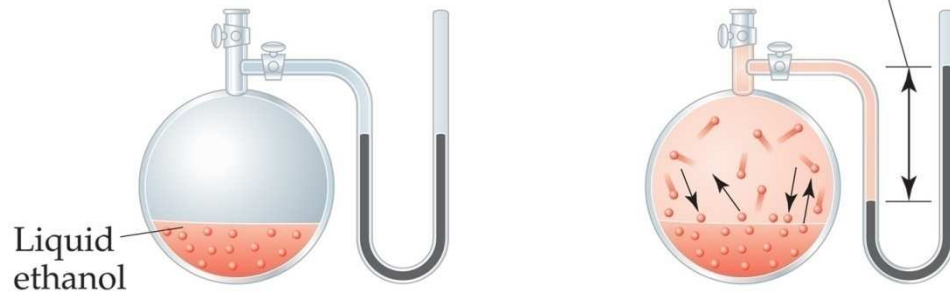
*The effect of temperature on the distribution of kinetic energies in a liquid*

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Intermolecular  
Forces

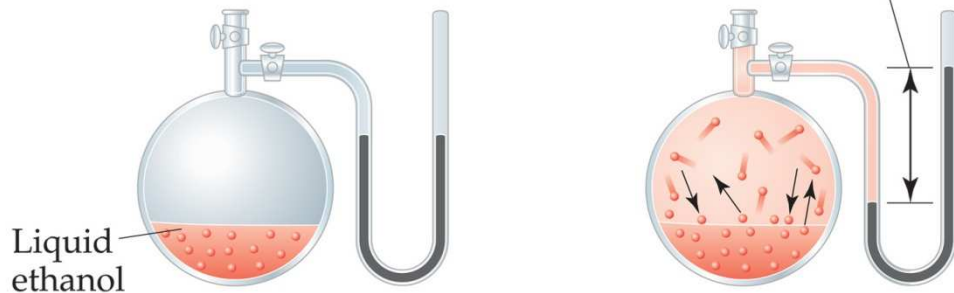


# Vapor Pressure



As more molecules escape the liquid, the pressure they exert increases.

# Vapor Pressure

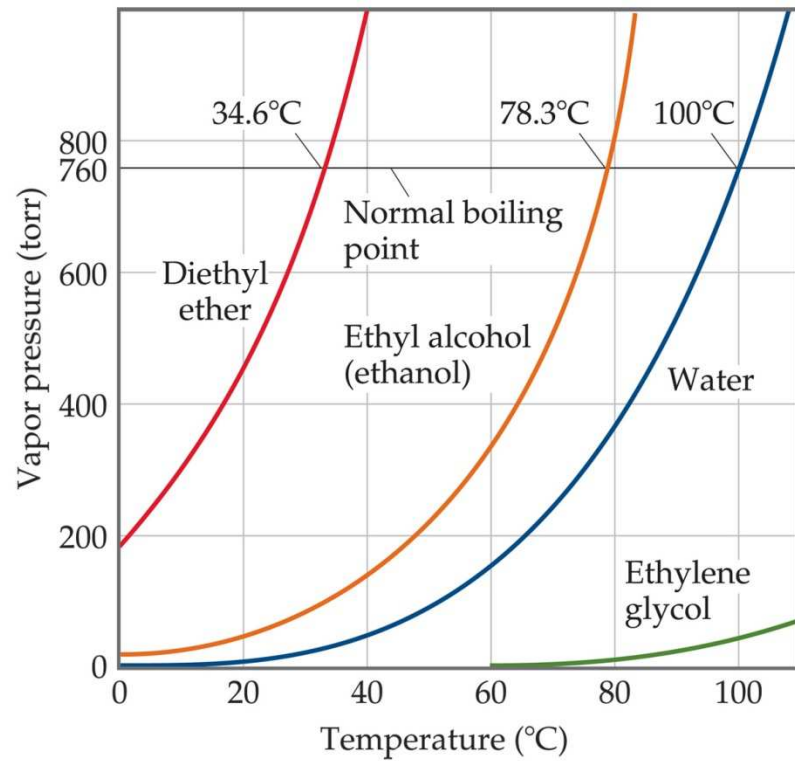


The liquid and vapor reach a state of dynamic equilibrium: liquid molecules evaporate and vapor molecules condense *at the same rate*.

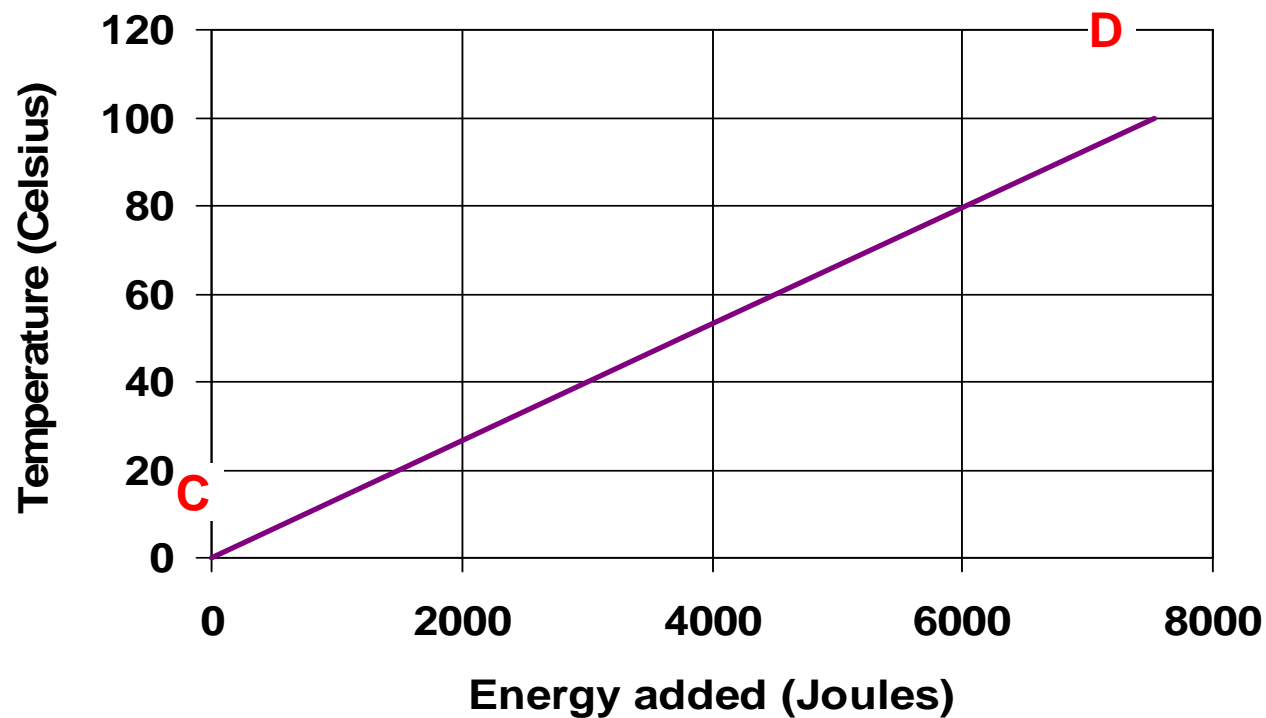


# Vapor Pressure

- The boiling point of a liquid is the temperature at which its vapor pressure equals atmospheric pressure.
- The normal boiling point of a liquid is the temperature at which its vapor pressure is 760 torr.



# Focus on Liquid to Gas: For a 1.00-mol sample of liquid water



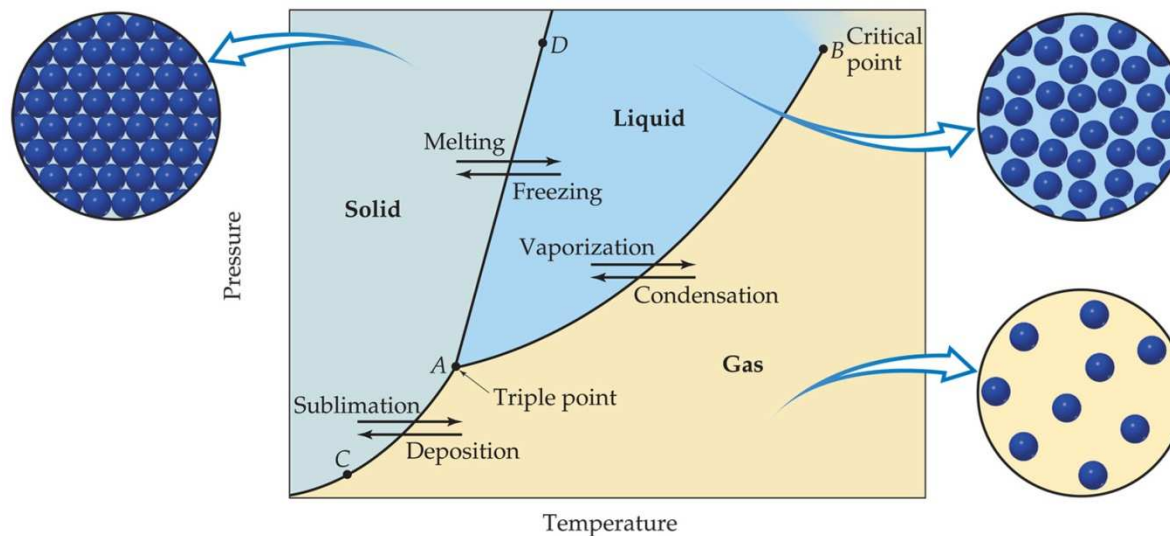
# What happens if you add more heat energy to liquid water at 100°C?

- It boils
- What is boiling?
  - There is a statistical range of kinetic energies (velocities) of particles in the liquid
  - Some particles will always have enough energy to break away from attractive forces that keep them in liquid → evaporation (vapor pressure)
  - As temperature rises, eventually it is high enough that so many particles can break away that their gas pressure (vapor pressure) equals the pressure of the surroundings → boiling
- Boiling continues with no change in temperature until all liquid particles have converted to gas phase
- Normal boiling point is temperature at which vapor pressure reaches atmospheric pressure when  $p_{atm} = 1\text{atm}$



# Phase Diagrams

Phase diagrams display the state of a substance at various pressures and temperatures and the places where equilibria exist between phases.



# Heating curve vs. phase diagram vs. vapor pressure curve

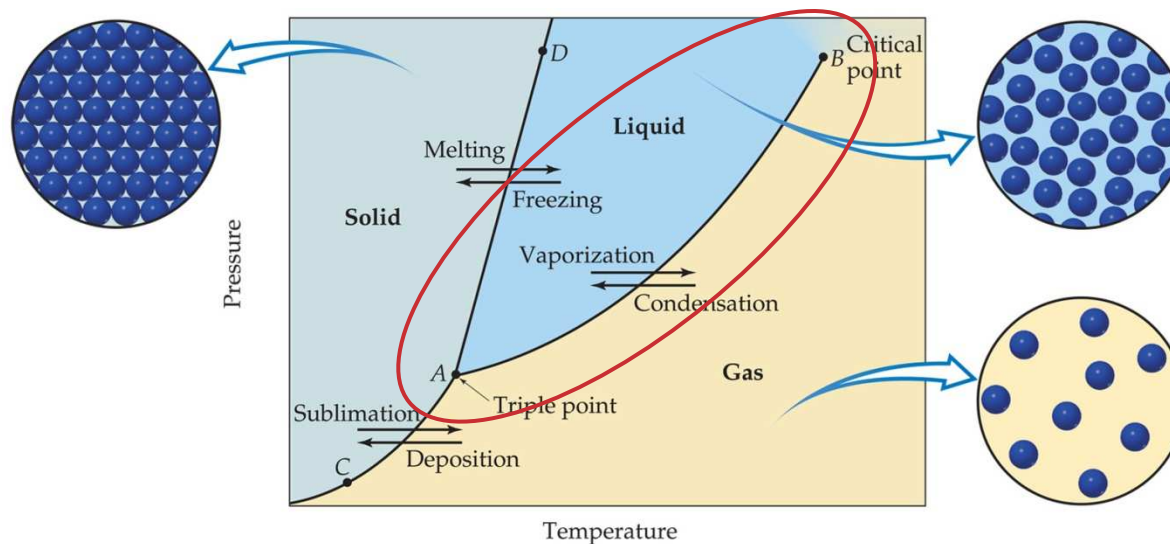
- Heating curve
  - Temperature vs. heat energy added
  - Characteristic up-across-up-across shape
  - Cooling curve is how temperature changes as you remove energy
- Phase diagram
  - Pressure vs. temperature
  - All 3 phases shown with boundaries between them
- Vapor pressure curve
  - The liquid-gas portion of the full phase diagram
  - Vapor pressure line is the boundary between L and G
  - All liquids (and solids too) have vapor pressure

*Liquid to gas: As you add energy, the temperature changes. As the temperature changes, the vapor pressure changes.*



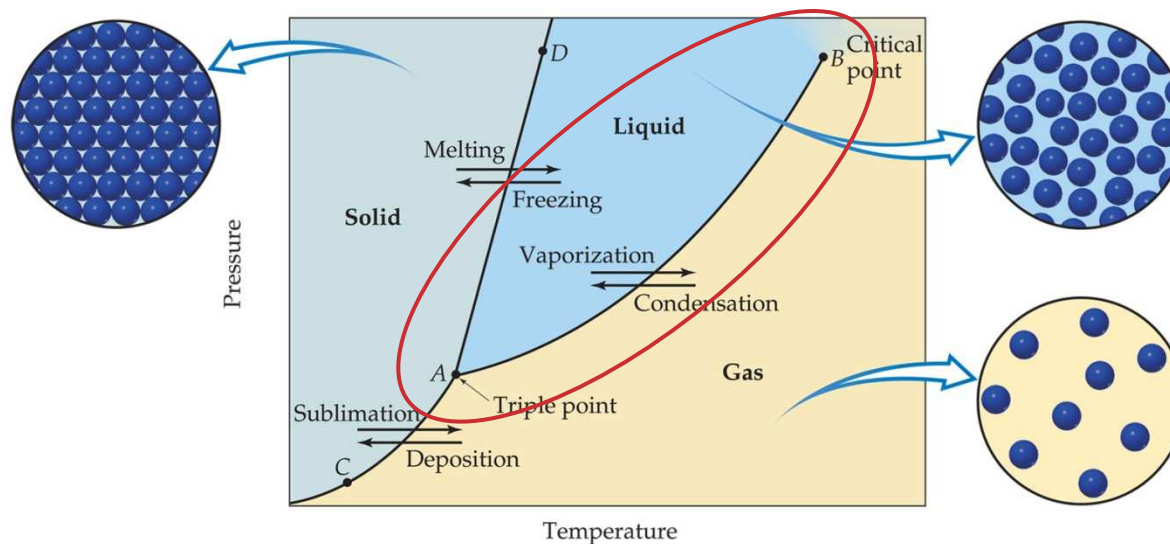
# Phase Diagrams

- The *AB* line is the liquid-vapor interface.
- It starts at the triple point (*A*), the point at which all three states are in equilibrium.



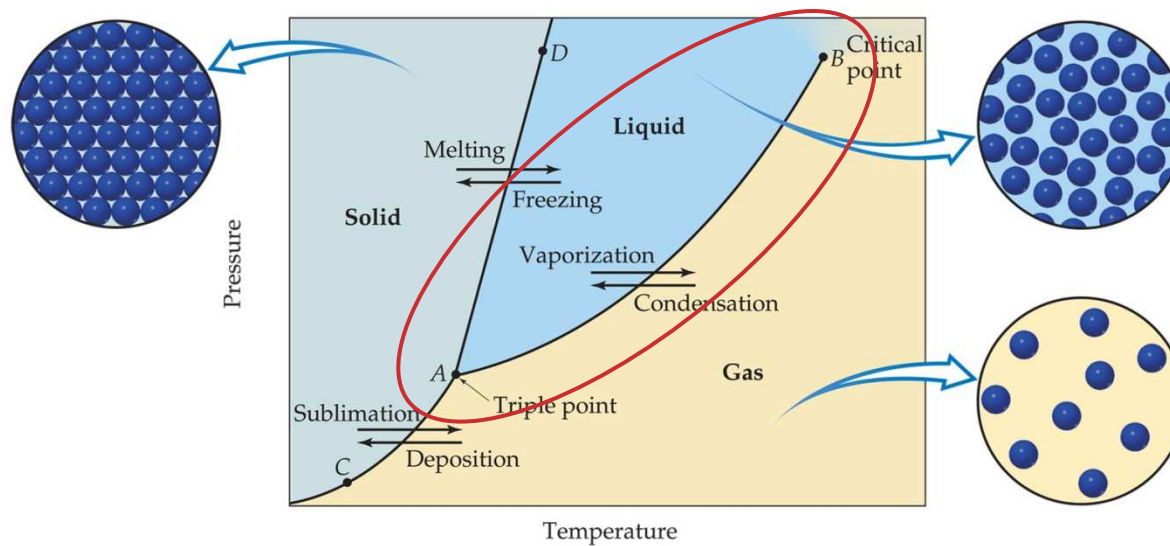
# Phase Diagrams

It ends at the critical point (*B*); which is at the critical temperature and critical pressure, above this critical temperature and critical pressure the liquid and vapor are indistinguishable from each other.



# Phase Diagrams

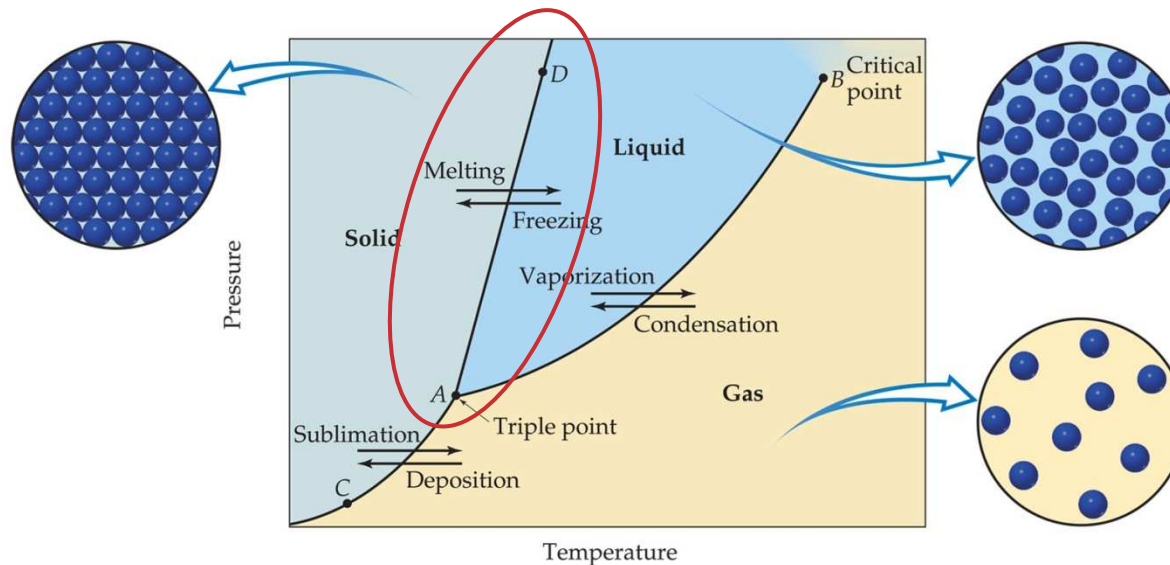
Each point along this line is the boiling point of the substance at that pressure.





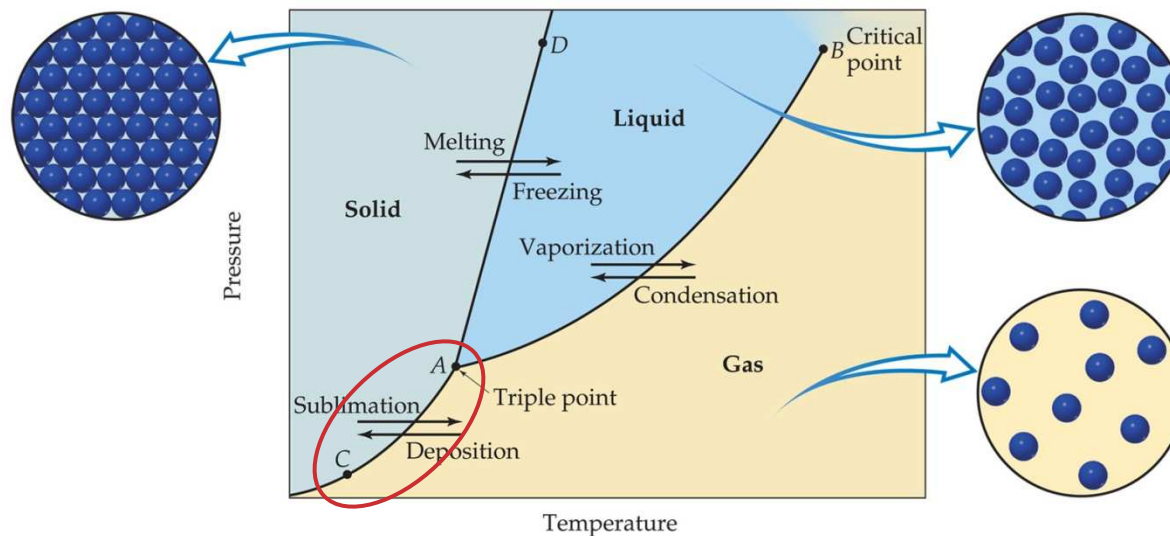
# Phase Diagrams

- The *AD* line is the interface between liquid and solid.
- The melting point at each pressure can be found along this line.

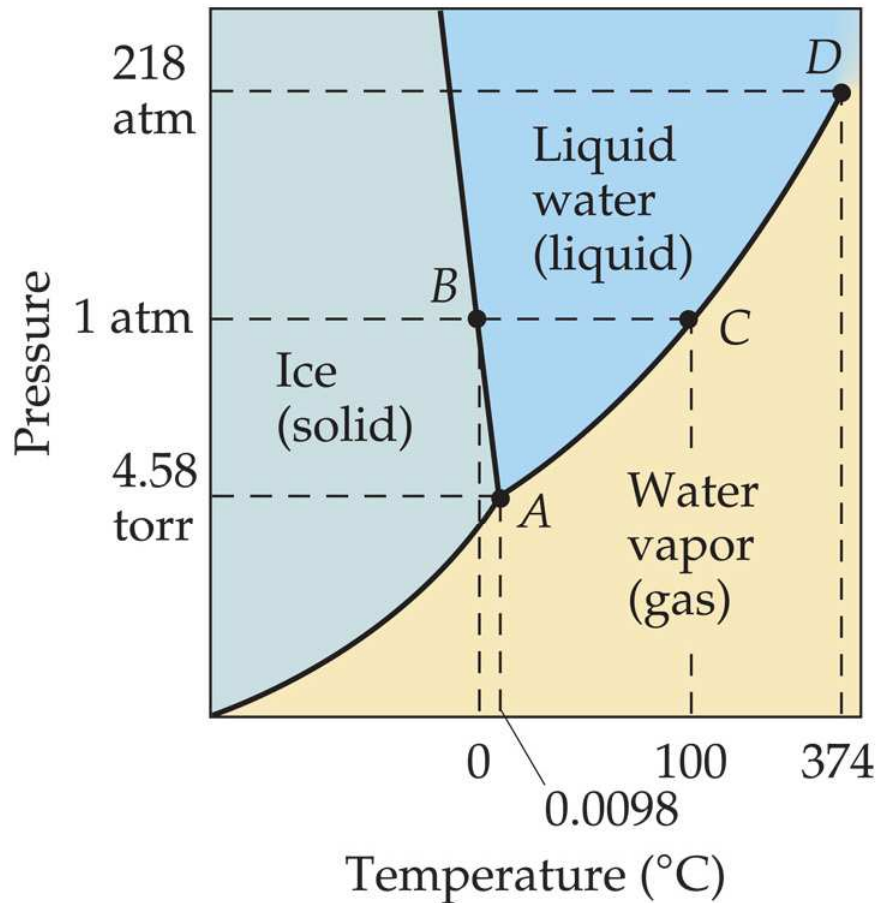


# Phase Diagrams

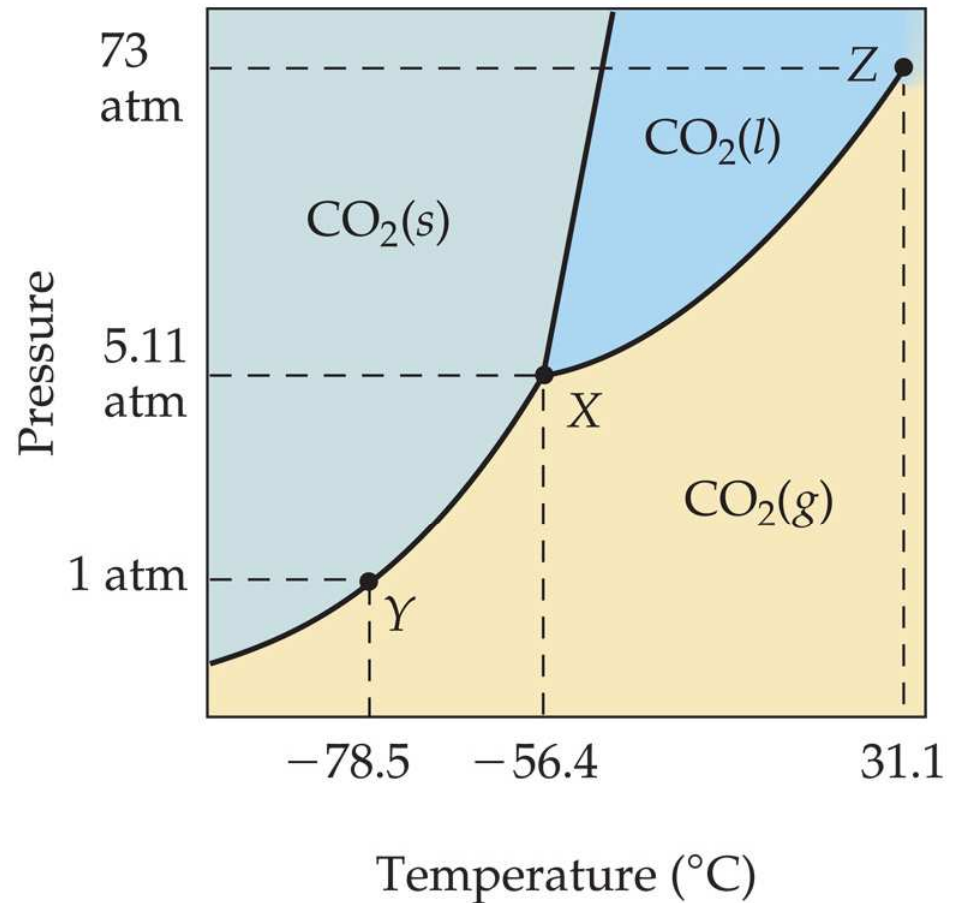
- Below *A* the substance cannot exist in the liquid state.
- Along the *AC* line the solid and gas phases are in equilibrium; the sublimation point at each pressure is along this line.



# Compare phase diagrams of H<sub>2</sub>O and CO<sub>2</sub>

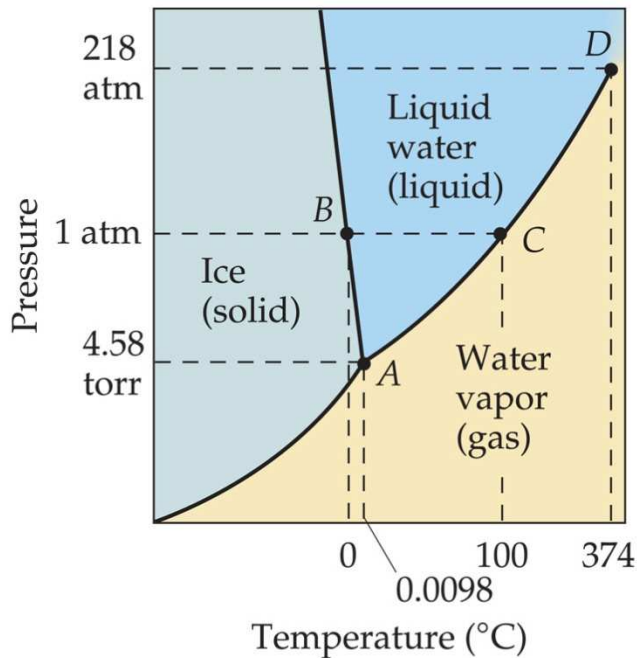


(a)



(b)

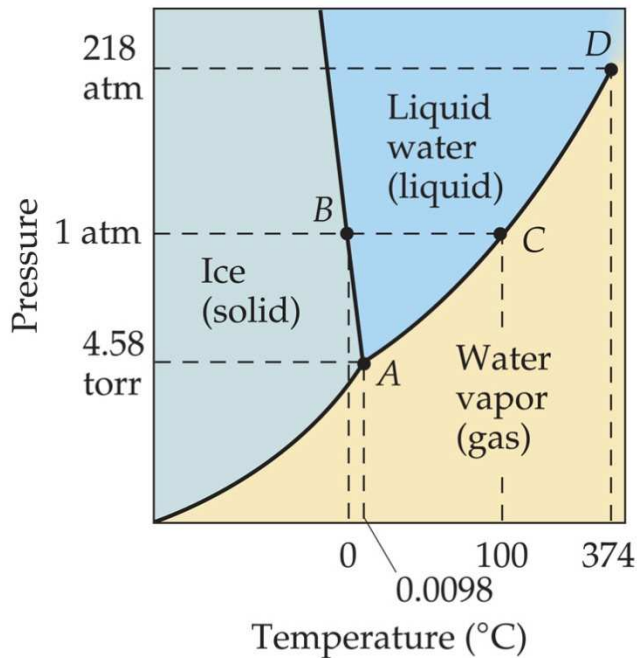
# Phase Diagram of Water



- Note the high critical temperature and critical pressure:
  - These are due to the strong van der Waals forces between water molecules.



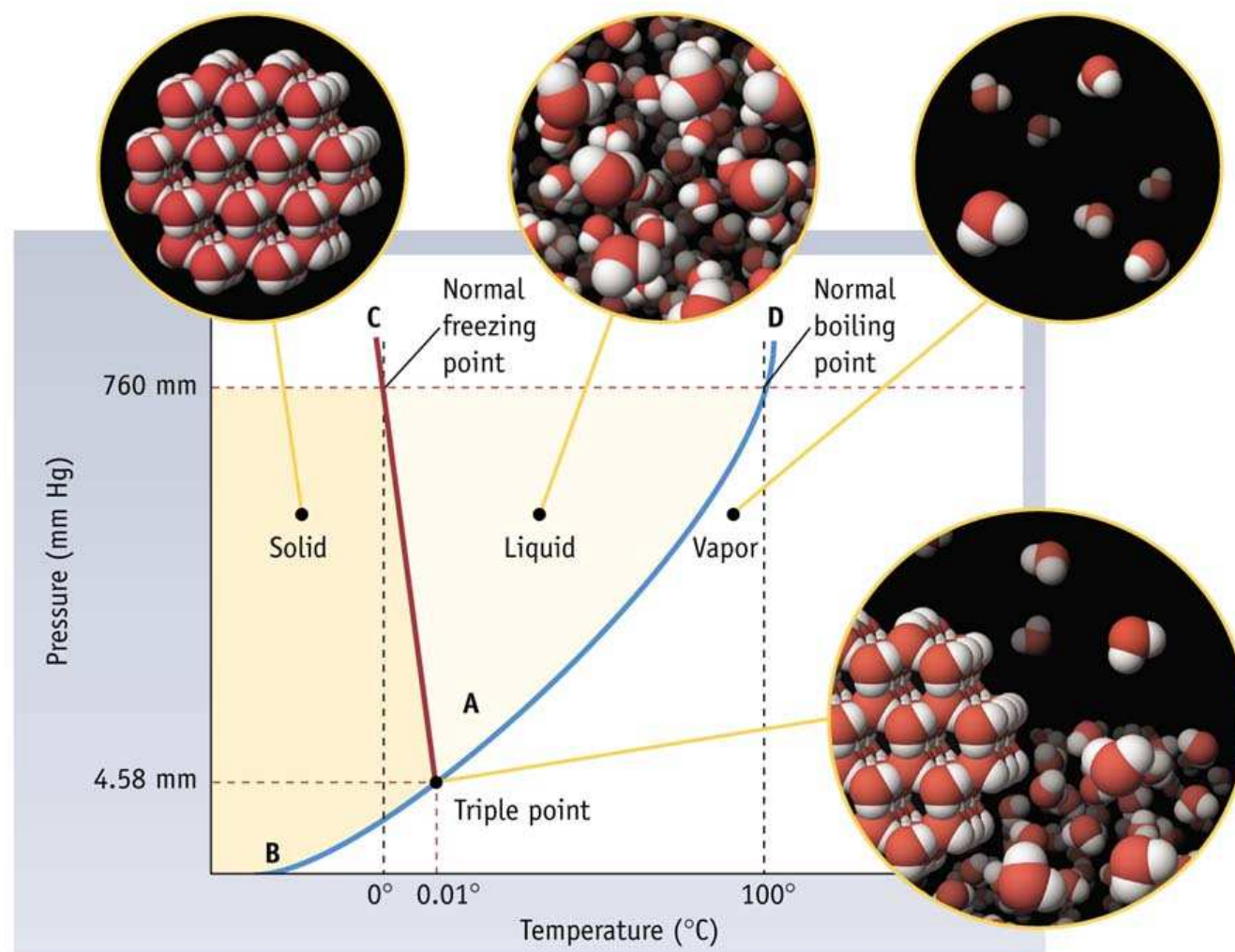
# Phase Diagram of Water



- The slope of the solid–liquid line is negative.
  - This means that as the pressure is increased at a temperature just below the melting point, water goes from a solid to a liquid.

# H<sub>2</sub>O: an unusual phase diagram

- Unusual behavior
- At same T, as you increase p, substance changes from solid to liquid
- Liquid more dense than solid
- Exhibits triple point where all three phases coexist



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- If you have this equilibrium and increase the pressure on it, according to Le Chatelier's Principle the equilibrium will move to reduce the pressure again. That means that it will move to the side with the smaller volume. Liquid water is produced



- since water fills a smaller volume when it's liquid, rather than solid, it will go to a lower melting point -- allowing more solid to become liquid.

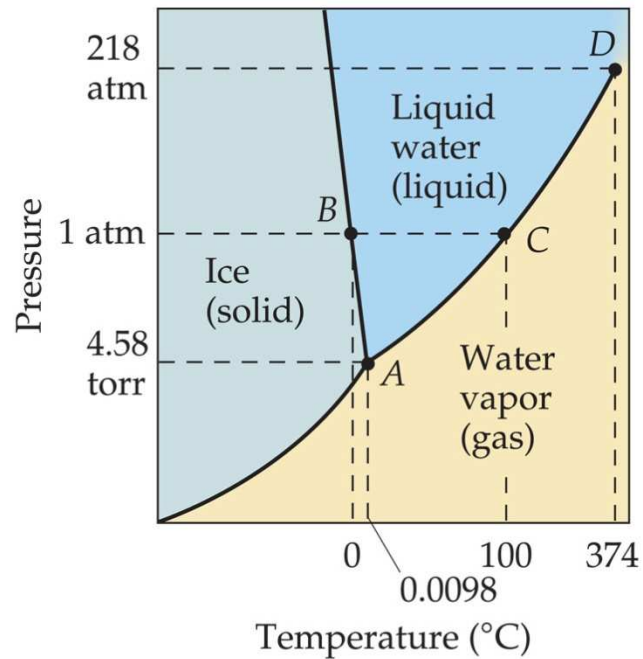






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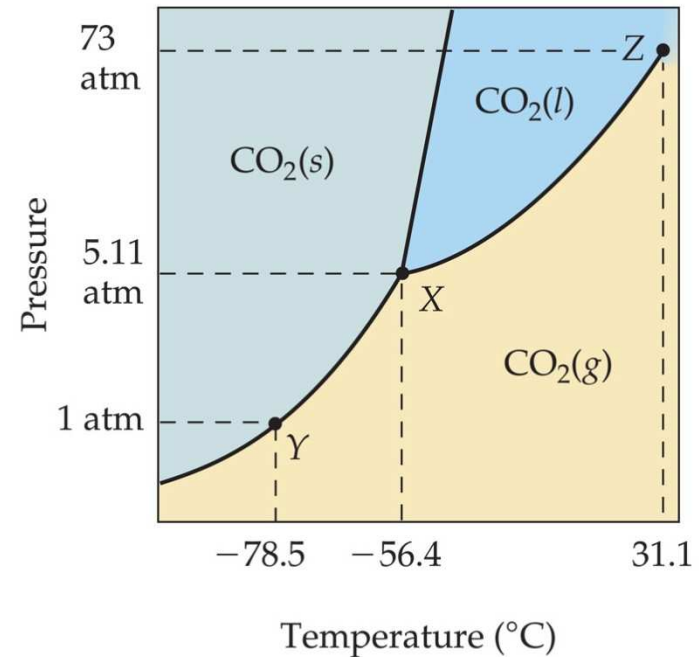
# Phase Diagram of Water



- Water is a substance whose liquid form is more compact than its solid form

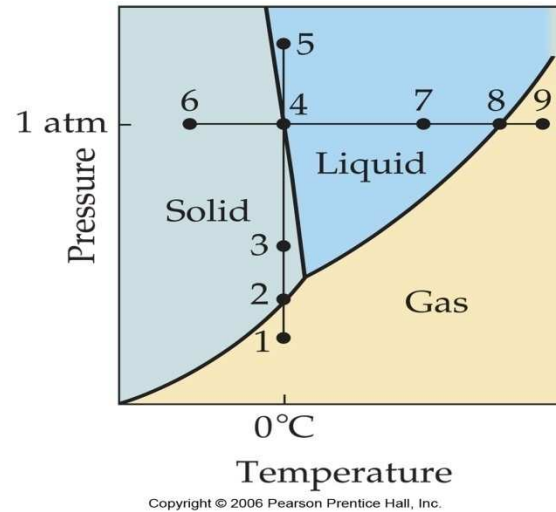
# Phase Diagram of Carbon Dioxide

Carbon dioxide cannot exist in the liquid state at pressures below 5.11 atm;  $\text{CO}_2$  sublimates at normal pressures.



Referring to Figure describe any changes in the phases present when is

- (a) kept at  $0^{\circ}\text{C}$  while the pressure is increased from that at point 1 to that at point 5 (vertical line),
- (b) kept at 1.00 atm while the temperature is increased from that at point 6 to that at point 9 (horizontal line).



# Types of materials

- Molecular

- Non-polar molecules

- Octane,  $C_8H_{18}$
- Fats (e.g., olive oil)

- Polar molecules

- Water,  $H_2O$
- Ammonia,  $NH_3$
- Acetic acid (vinegar is an aqueous solution of it),  $CH_3COOH$

- Ionic

- Sodium chloride (table salt),  $NaCl$
- Sodium bicarbonate (baking soda),  $NaHCO_3$
- Copper (II) sulfate pentahydrate,  $CuSO_4 \cdot 5H_2O$

- Metallic

- Copper metal,  $Cu$
- Aluminum foil,  $Al$

- Others that defy categorization

- Network

- Quartz,  $SiO_2$
- Sand,  $SiO_2$
- Diamond,  $C$

- Polymeric

- Any plastic, such as high density polyethylene (HDPE)

- Amorphous

- Glasses

- Mixtures

- Butter, see

**Notice that the names of these categories are based on the type of bonding**



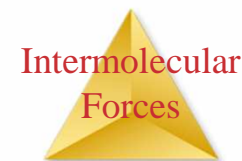
# Properties that molecular materials exhibit

- Most are liquids or gases at room temperature
- Smallest molecules are gases at room temperature
- Only very large molecules are solids at room temperature
- All have relatively low melting points (near or below room temperature)
- Most feel soft
- Chemical composition is usually carbon, hydrogen, oxygen, nitrogen and a few others (“organic”)
- In liquid state, *usually* do not conduct electricity
- Some can dissolve in water and others cannot



# Properties that ionic materials exhibit

- All are solids at room temperature
- Very high melting points
- Do not conduct electricity in solid state
- Conduct electricity in liquid state
- Crystalline
- Brittle, break along flat/planar surfaces
- When they contain transition metals, usually are colored; when they do not contain transition metals, usually are white
- Generally called “salts” because they can be made from mixing together an acid and a base
- Some can dissolve in water and others cannot



# Properties that metallic materials exhibit

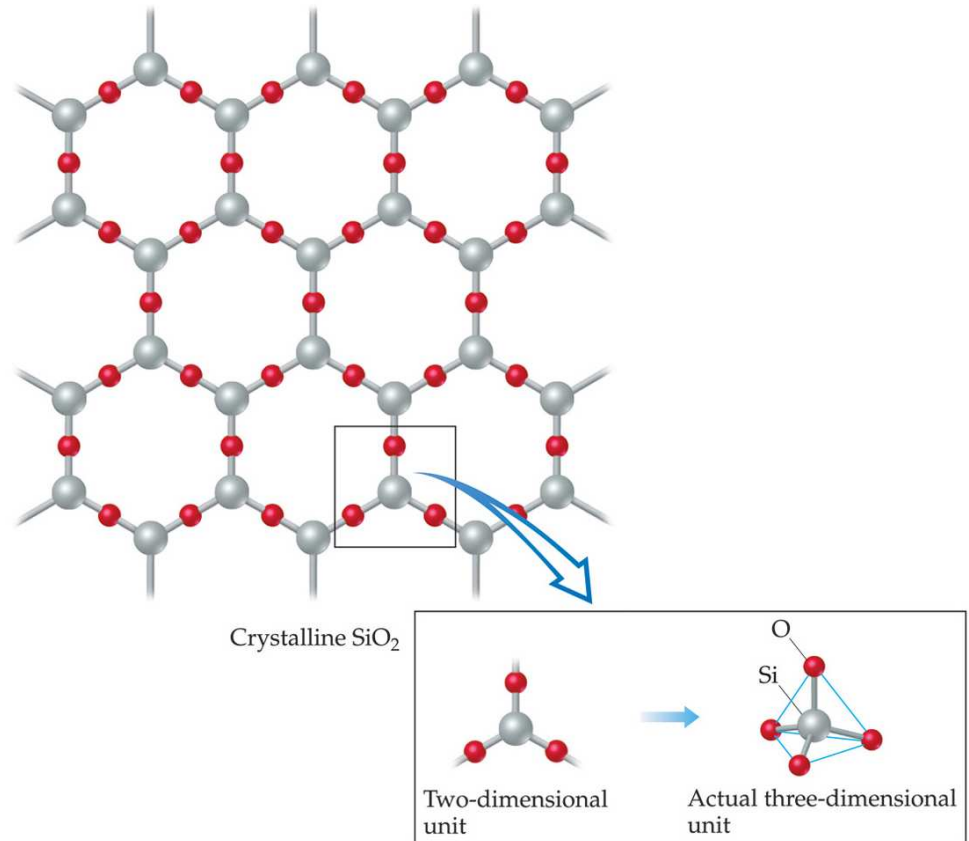
- Lustrous (shiny)
- Malleable (can be pounded into a pancake)
- Ductile (can be bent)
- Conduct electricity
- Sometimes rust (oxidize)
- Never dissolve in water





# Solids

- We can think of solids as falling into two groups:
  - Crystalline—particles are in highly ordered arrangement.



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Forces

# Solids

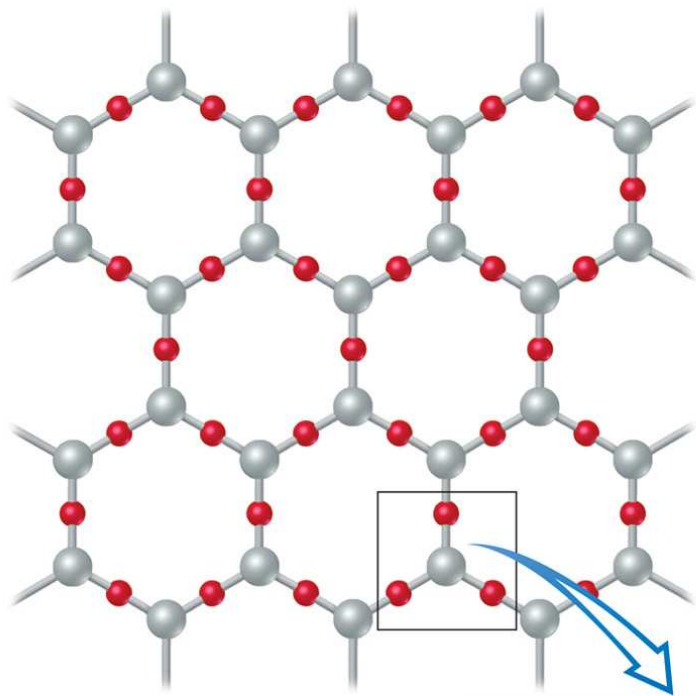
Solids can be:

Amorphous—no particular order in the arrangement of particles

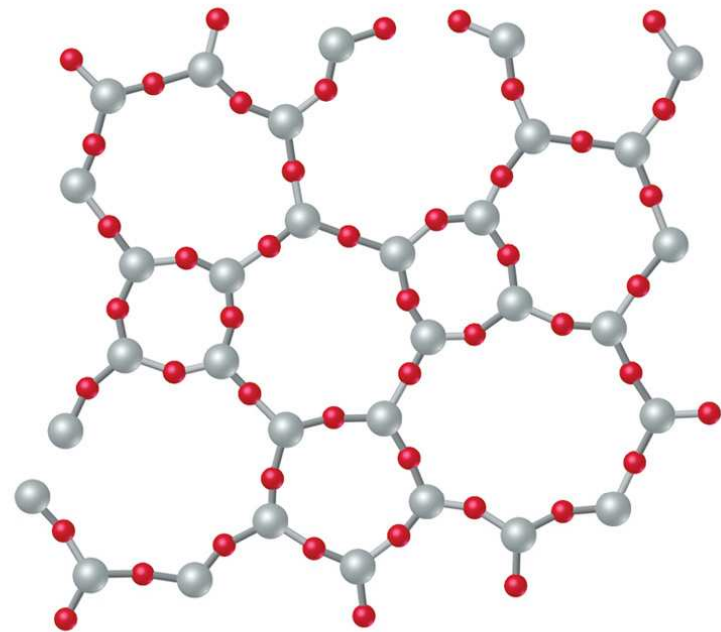
or

Crystalline

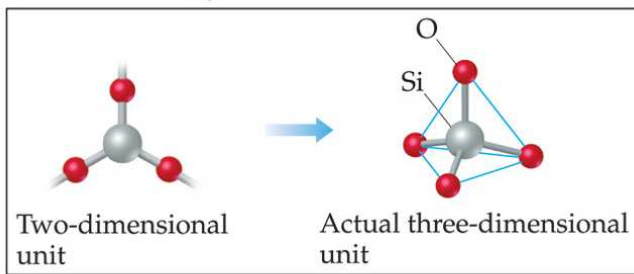




Crystalline SiO<sub>2</sub>



Amorphous SiO<sub>2</sub>



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(a)



(b)



(c)

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# Unit Cells

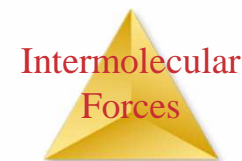
- We can think of a crystalline solid as being built of bricks.
- Each brick is a unit cell.
- Each crystalline solid is represented by a crystal lattice.

The crystal lattice is like a scaffolding for the solid.

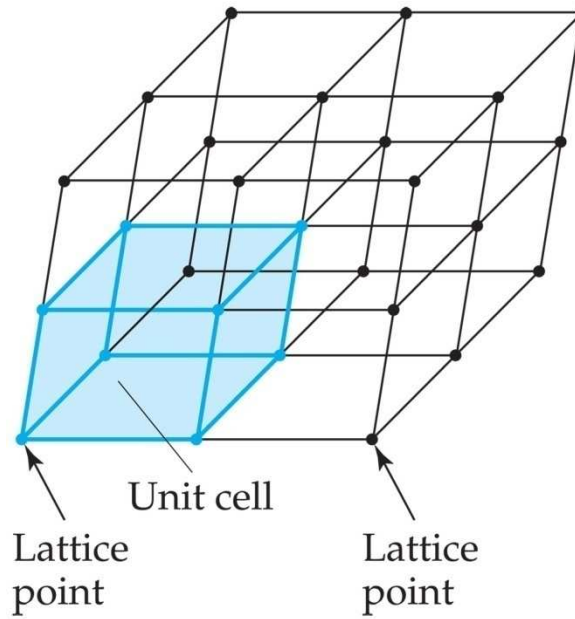


# A Unit Cell

- The unit cell is the fundamental concept in solid state chemistry
- It is the smallest representation of structure which carries all the information necessary to construct unambiguously an infinite lattice.



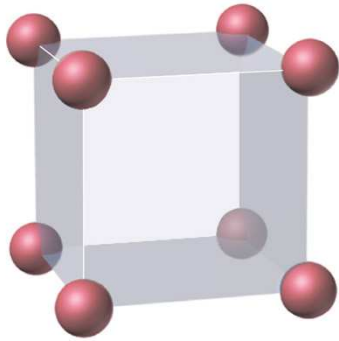
# Crystalline Solids



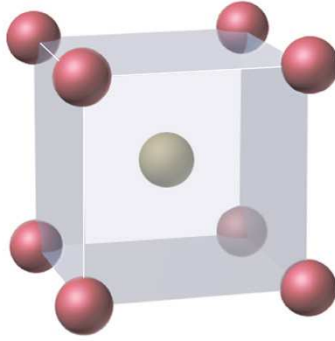
- There are three kinds of unit cells
- Primitive cubic
- Body - centered cubic
- Face - centered cubic



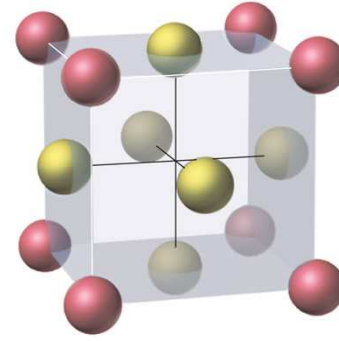




Primitive cubic



Body-centered cubic

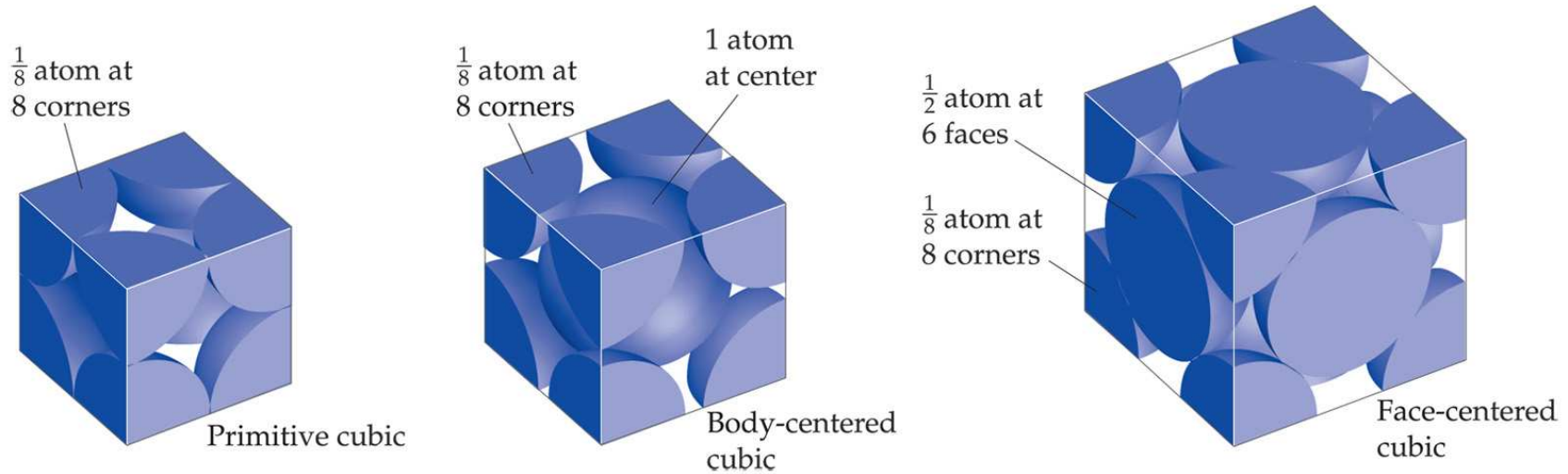


Face-centered cubic

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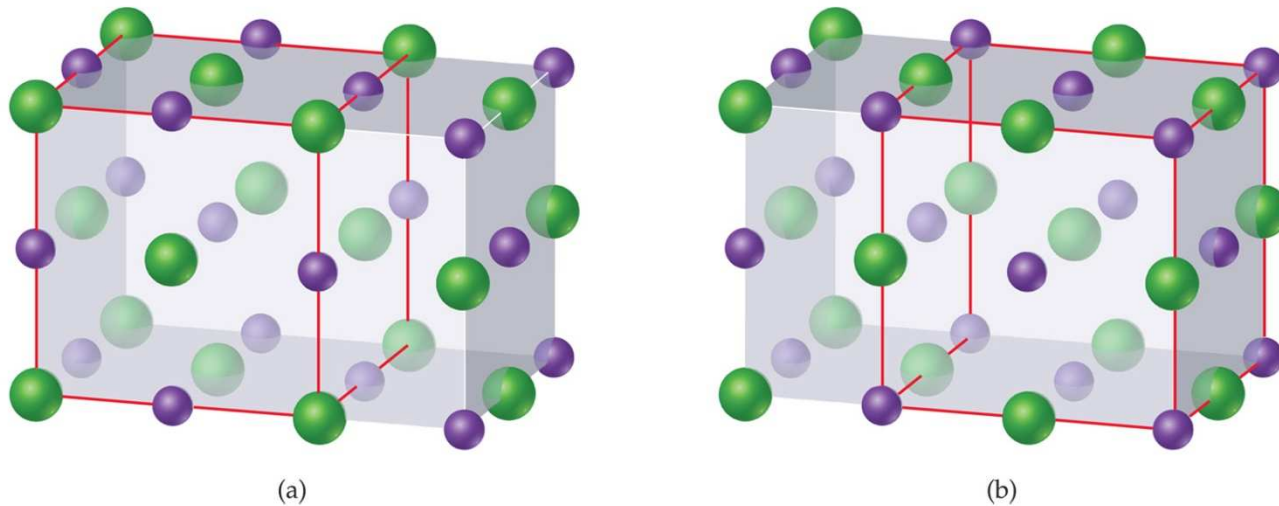
- Primitive cubic : When lattice points are at the corners only
- Body centered cubic: When the lattice point also occurs at the center of the unit cell
- Face centered cubic: When the cell has lattice points at the center of each face as well as at each corner.

# Crystalline Solids



There are several types of basic arrangements in crystals, such as the ones shown above.

# Crystal Structure of Sodium Chloride

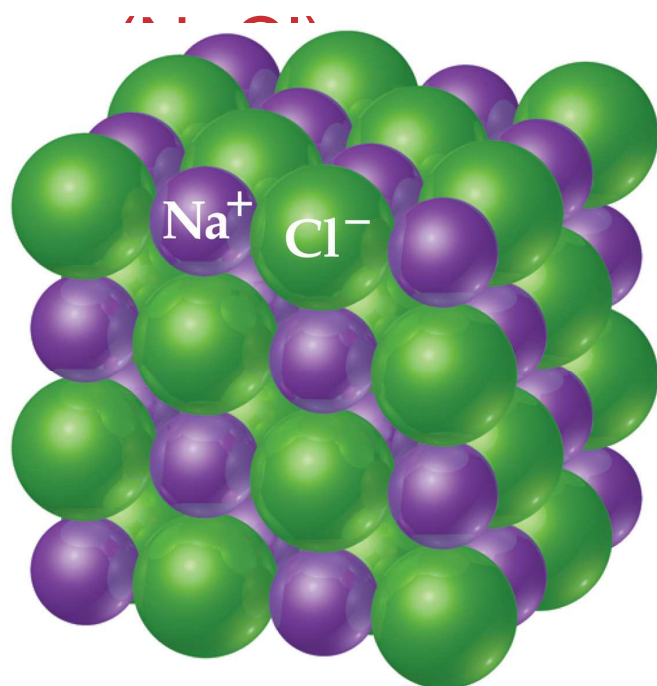


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- NaCl is a face centered cubic as we can center either the  $\text{Na}^+$  ion or the  $\text{Cl}^-$  ion on the lattice point of a face centered cubic unit cell

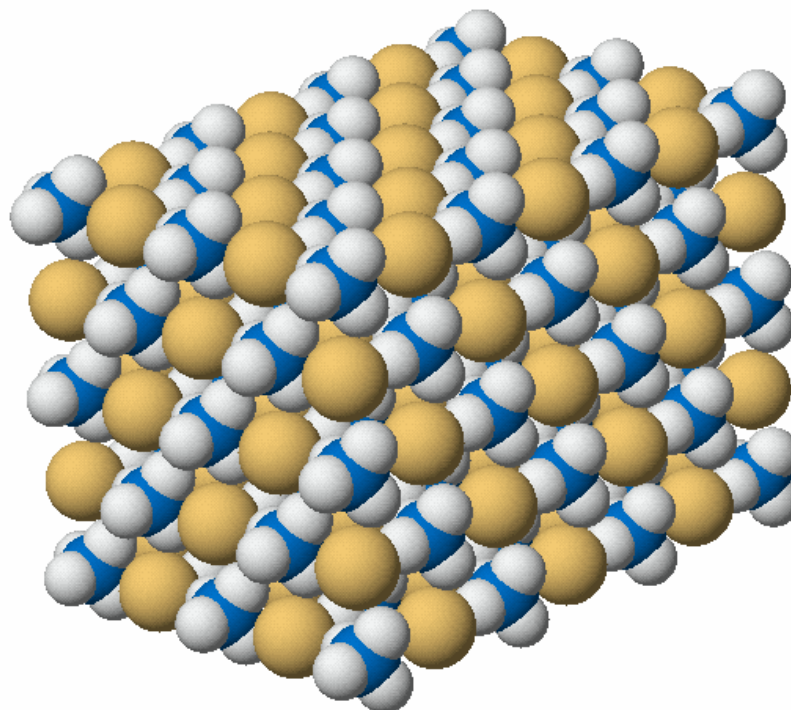
# Some examples of ionic solids (particle level illustrations)

## Sodium chloride



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## Ammonium chloride



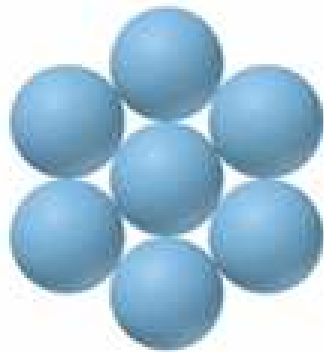
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# Attractions in Ionic Crystals

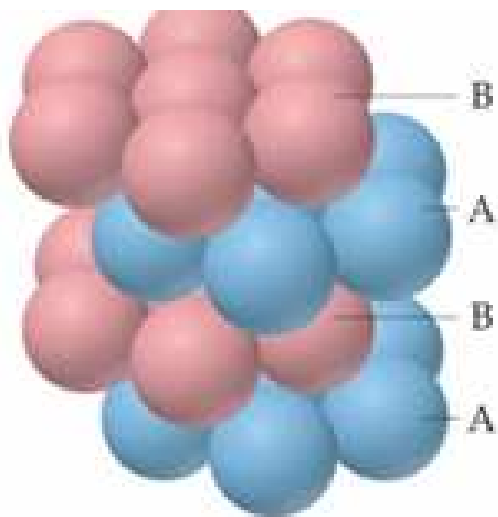
In ionic crystals, ions pack themselves so as to maximize the attractions and minimize repulsions between the ions.





Close-packed  
layer of spheres

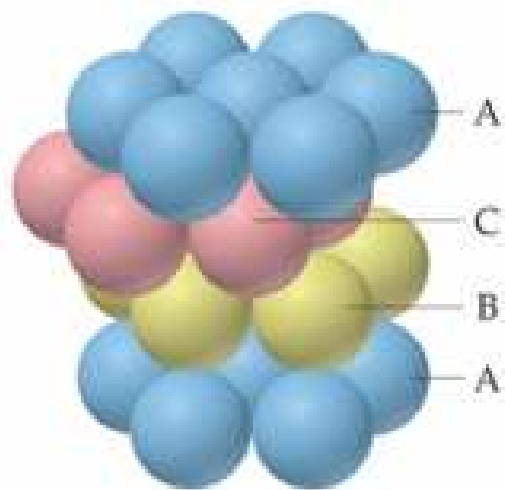
- Equal sized spheres can be arranged like this



(b)

- Hexagonal close packing

# Cubic close packing



(c)

nc



- In each of these structures there are 12 equidistant neighbors.
- Thus the particles are thought to have a coordination number of 12.
- The coordination number is the number of particles immediately surrounding a particle in the crystal.



- In both types of close packing 74% of the total volume of the structure is occupied by the spheres and 26% is empty space.



- In comparison each sphere in the body centered cubic structure has a coordination number of 8 and only 68% of the space is occupied. In the primary cubic structure the coordination number is 6 and only 52% of the space is occupied.



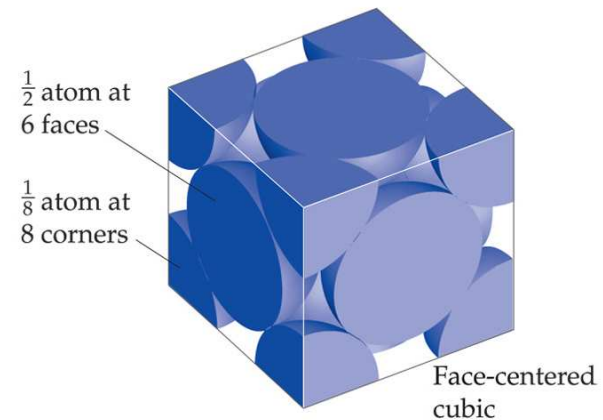
- The higher the coordination number the greater the packing efficiency



# Crystalline Solids

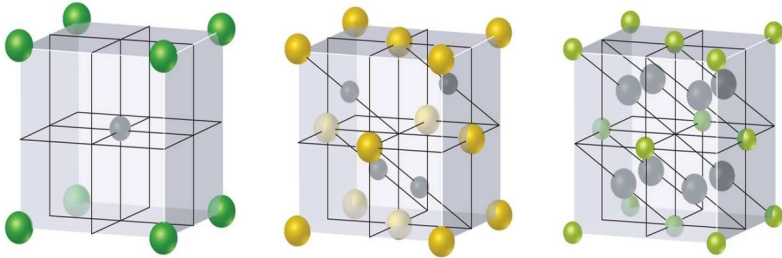
We can determine the empirical formula of an ionic solid by determining how many ions of each element fall within the unit cell.

Position in Unit Cell	Fraction in Unit Cell
Center	1
Face	$\frac{1}{2}$
Edge	$\frac{1}{4}$
Corner	$\frac{1}{8}$



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# Ionic Solids



Position in Unit Cell	Fraction in Unit Cell
Center	1
Face	$\frac{1}{2}$
Edge	$\frac{1}{4}$
Corner	$\frac{1}{8}$

What are the empirical formulas for these compounds?

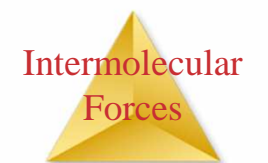
(a) Green: chlorine; Gray: cesium

(b) Yellow: sulfur; Gray: zinc

(c) Green: calcium; Gray: fluorine



- Start here



# Types of Bonding in Crystalline Solids

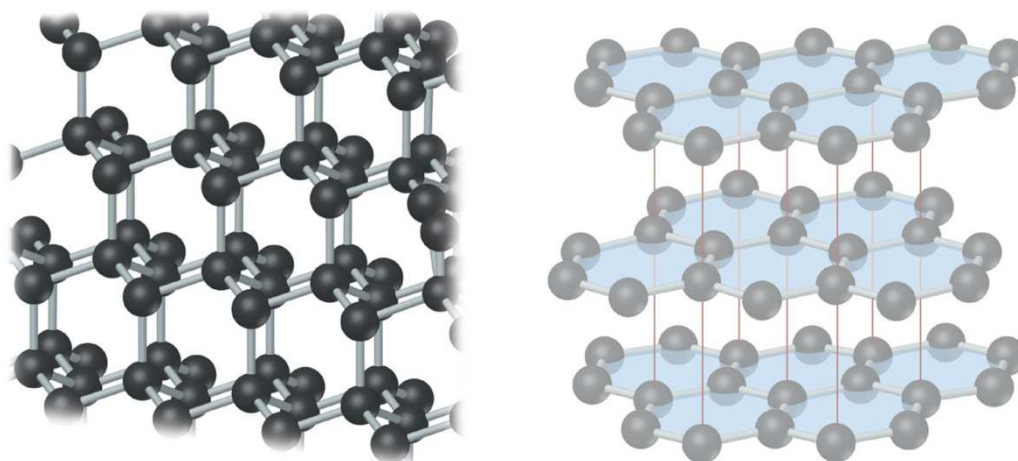
Type of Solid	Form of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms or molecules	London dispersion forces, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, Ar; methane, CH <sub>4</sub> ; sucrose, C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> ; Dry Ice™, CO <sub>2</sub>
Covalent-network	Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, often poor thermal and electrical conduction	Diamond, C; quartz, SiO <sub>2</sub>
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts—for example, NaCl, Ca(NO <sub>3</sub> ) <sub>2</sub>
Metallic	Atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements—for example, Cu, Fe, Al, Pt

Intermolecular  
Forces



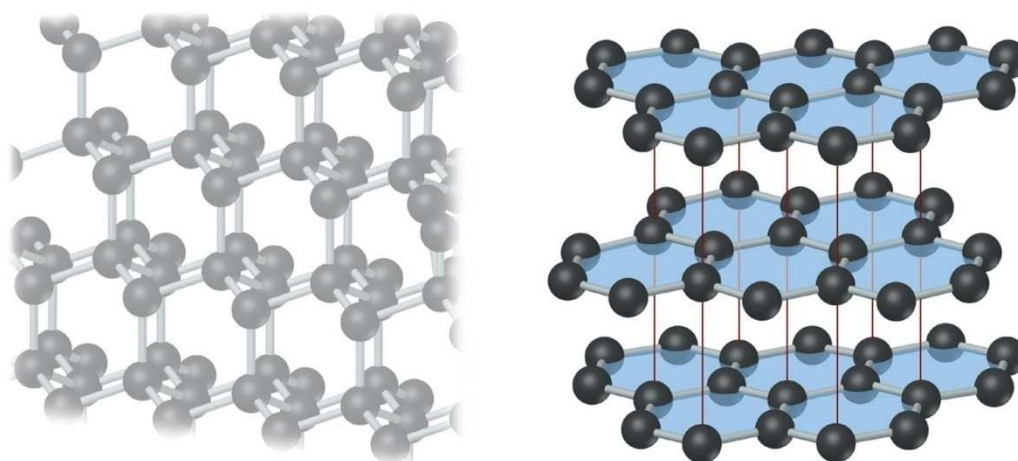


# Covalent-Network and Molecular Solids



- Diamonds are an example of a covalent-network solid in which atoms are covalently bonded to each other.
  - They tend to be hard and have high melting points.

# Covalent-Network and Molecular Solids



- Graphite is an example of a molecular solid in which atoms are held together with van der Waals forces.
  - They tend to be softer and have lower melting points.

# Metallic Solids

- Metals are not covalently bonded, but the attractions between atoms are too strong to be van der Waals forces.
- In metals, valence electrons are delocalized throughout the solid.

