Chemistry, The Central Science, 10th edition
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Chapter 11
Intermolecular Forces, Liquids, and Solids

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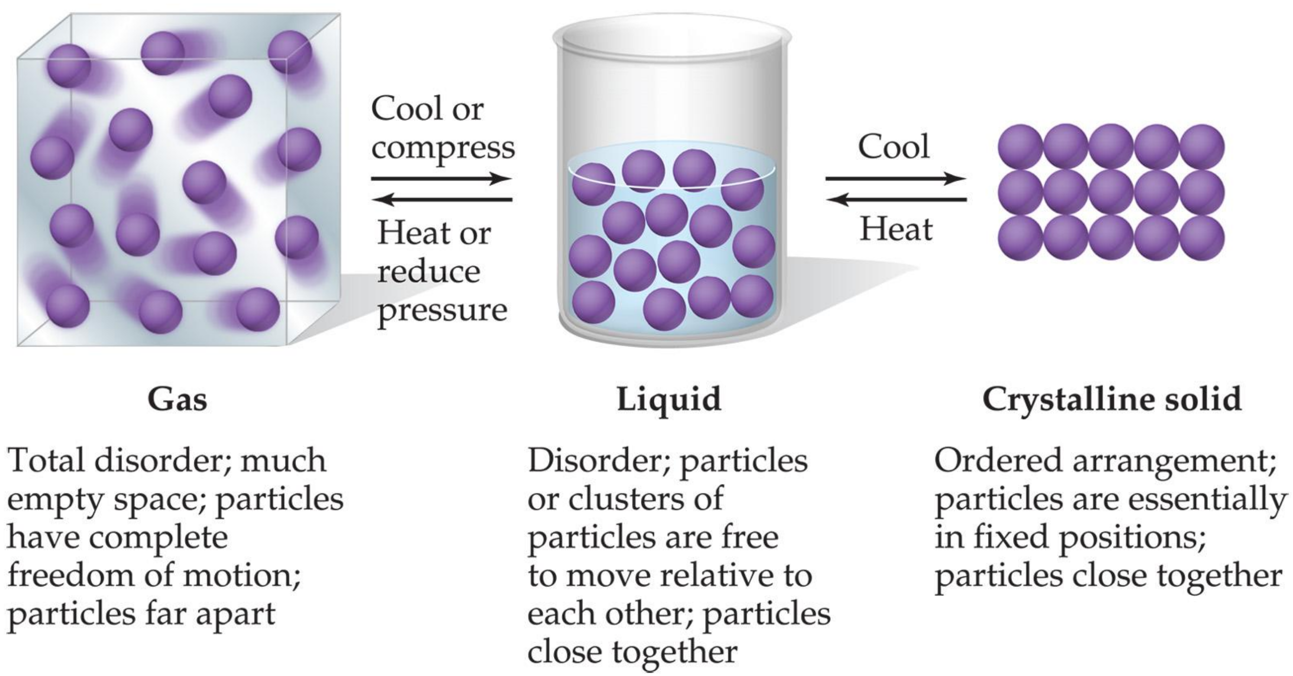
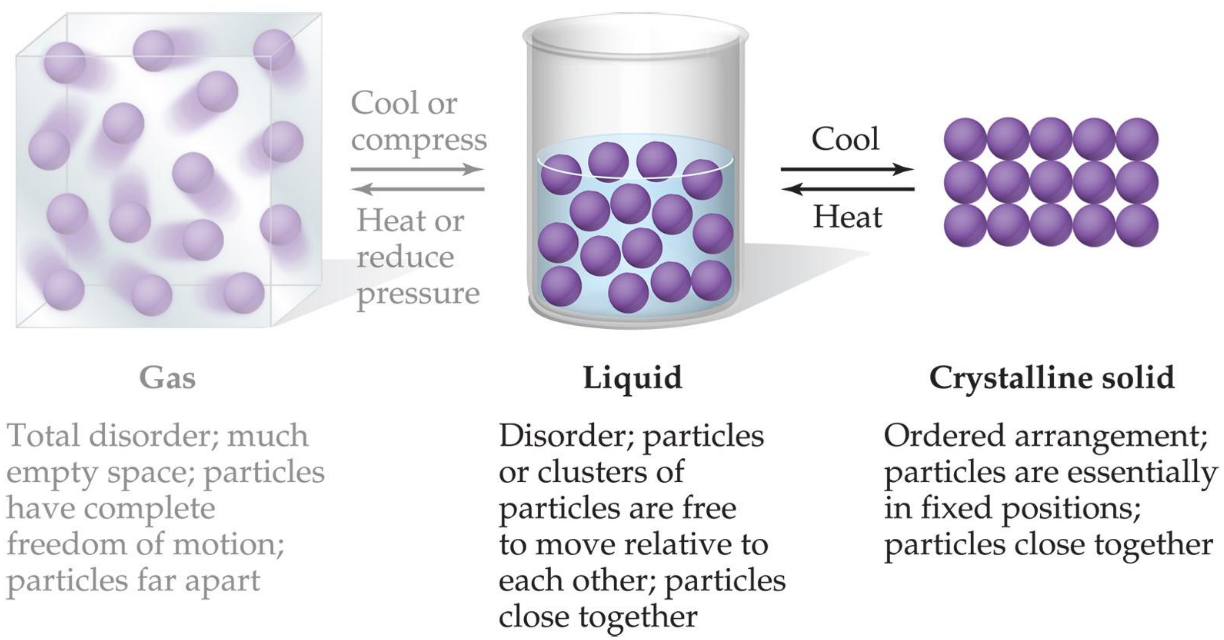
States of Matter

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

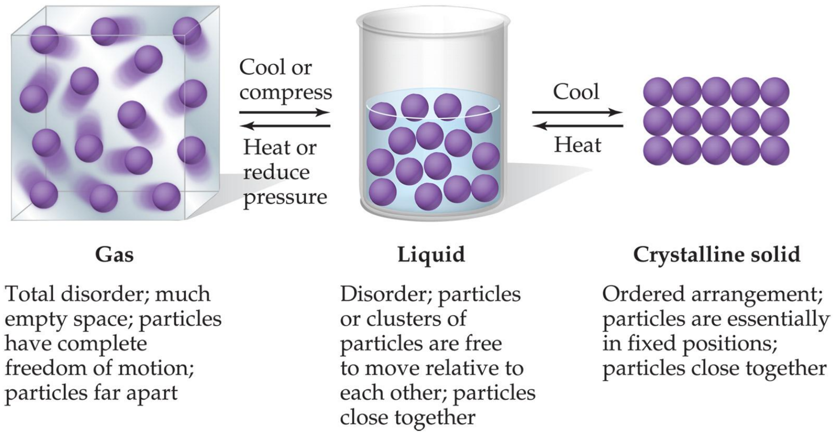


States of Matter

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



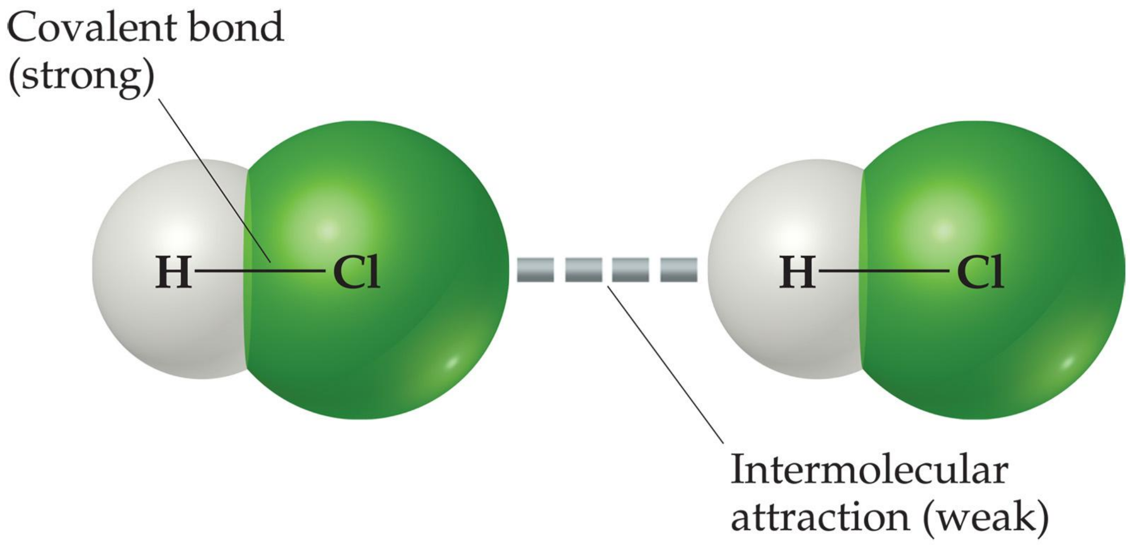
The States of Matter



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

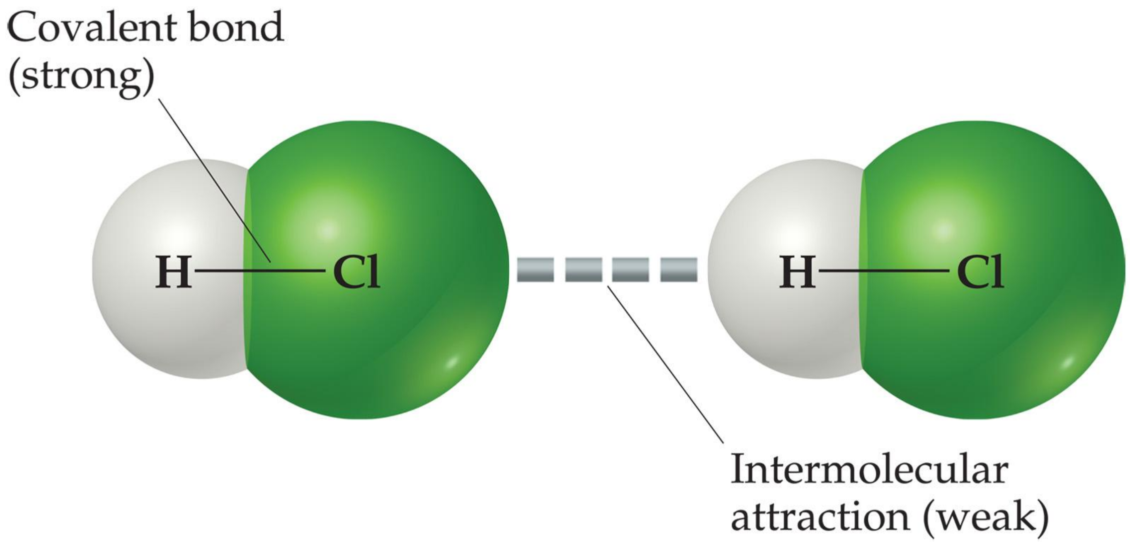
- The state a substance is in at a particular temperature and pressure depends on two antagonistic entities:
  - ➢ The kinetic energy of the particles
  - ➢ The strength of the attractions between the particles

Intermolecular Forces



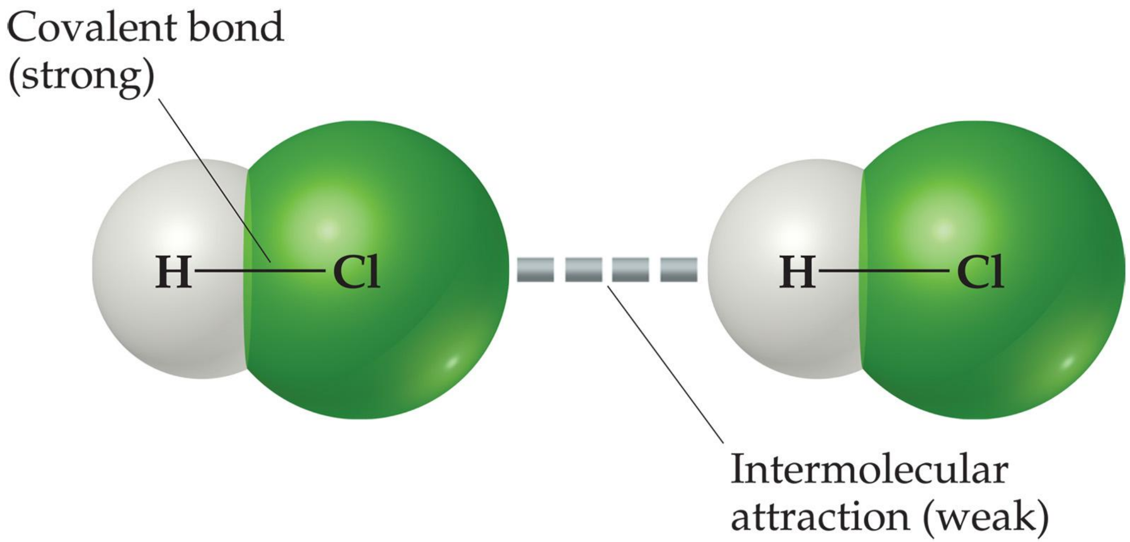
The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compounds together.

Intermolecular Forces



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

Intermolecular Forces



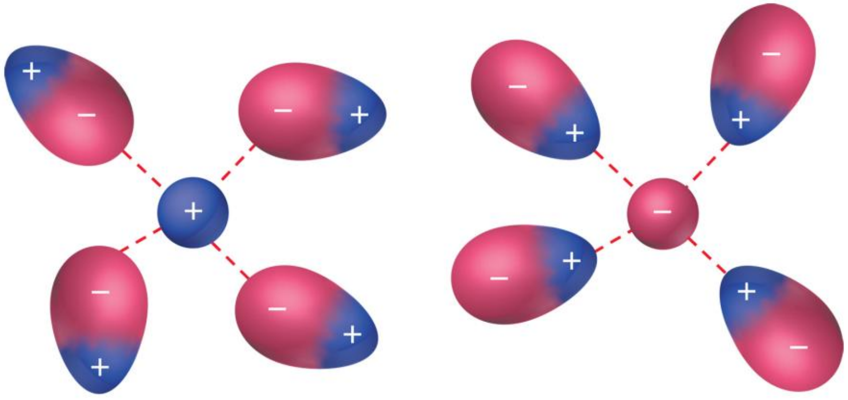
These intermolecular forces as a group are referred to as van der Waals forces.

van der Waals Forces

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

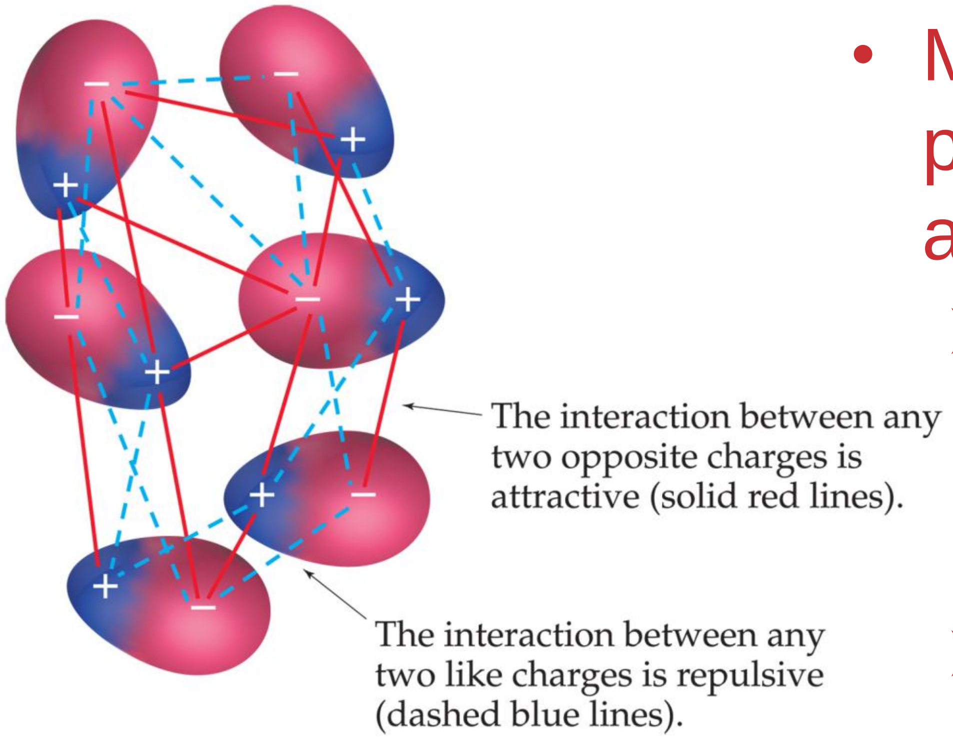
Ion-Dipole Interactions

- 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.



Cation-dipole attractions   Anion-dipole attractions

Dipole-Dipole Interactions



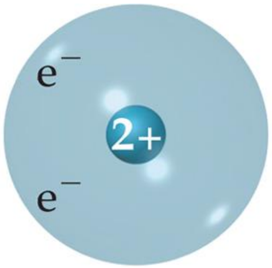
- Molecules that have permanent dipoles are attracted to each other.
  - The positive end of one is attracted to the negative end of the other and vice-versa.
  - These forces are only important when the molecules are close to each other.

Dipole-Dipole Interactions

Substance	Molecular Weight (amu)	Dipole Moment μ (D)	Boiling Point (K)
Propane, $CH_3CH_2CH_3$	44	0.1	231
Dimethyl ether, CH_3OCH_3	46	1.3	248
Methyl chloride, CH_3Cl	50	1.9	249
Acetaldehyde, CH_3CHO	44	2.7	294
Acetonitrile, CH_3CN	41	3.9	355

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

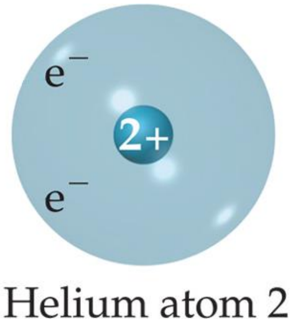
London Dispersion Forces

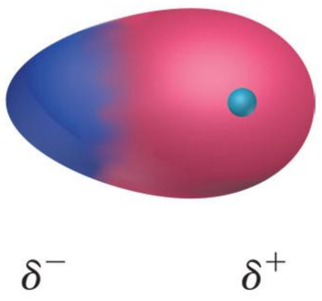


Helium atom 2

While the electrons in the 1*s* 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.

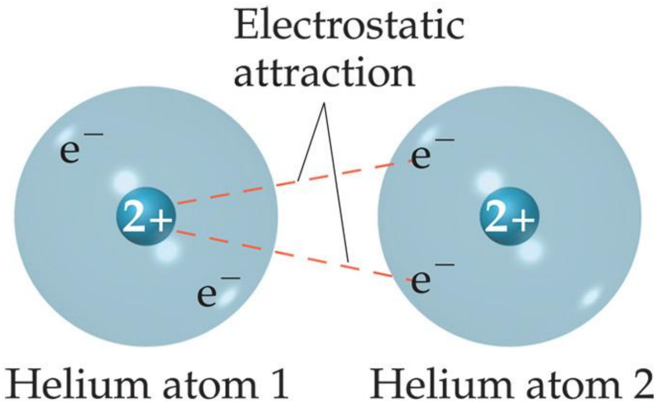
London Dispersion Forces

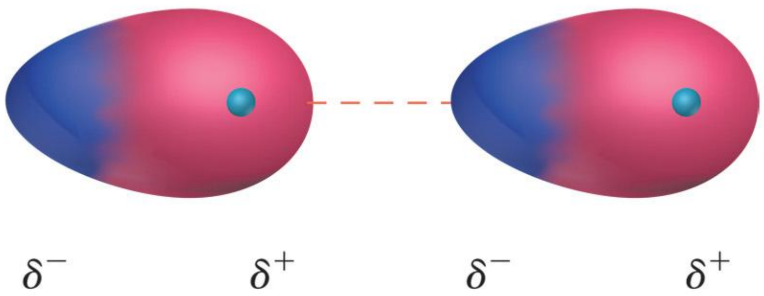




At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.

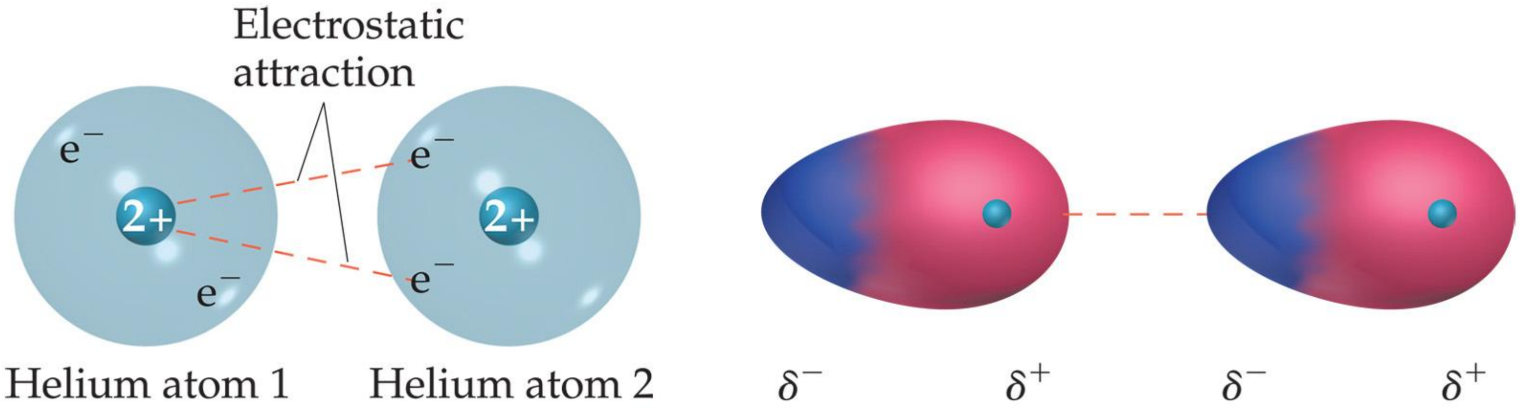
London Dispersion Forces





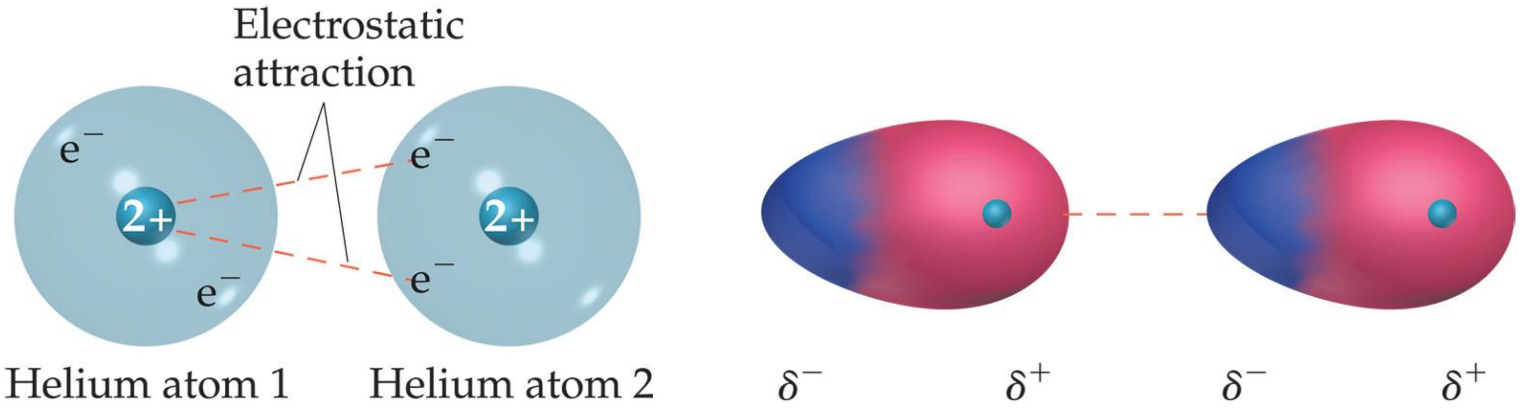
Another helium nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

London Dispersion Forces



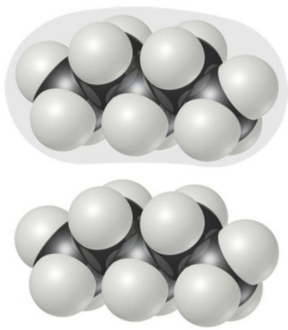
London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole.

London Dispersion Forces

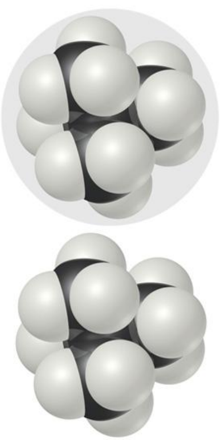


- These forces are present in *all* molecules, whether they are polar or nonpolar.
- The tendency of an electron cloud to distort in this way is called polarizability.

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.

Factors Affecting London Forces

Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F_2	38.0	85.1	He	4.0	4.6
Cl_2	71.0	238.6	Ne	20.2	27.3
Br_2	159.8	332.0	Ar	39.9	87.5
I_2	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

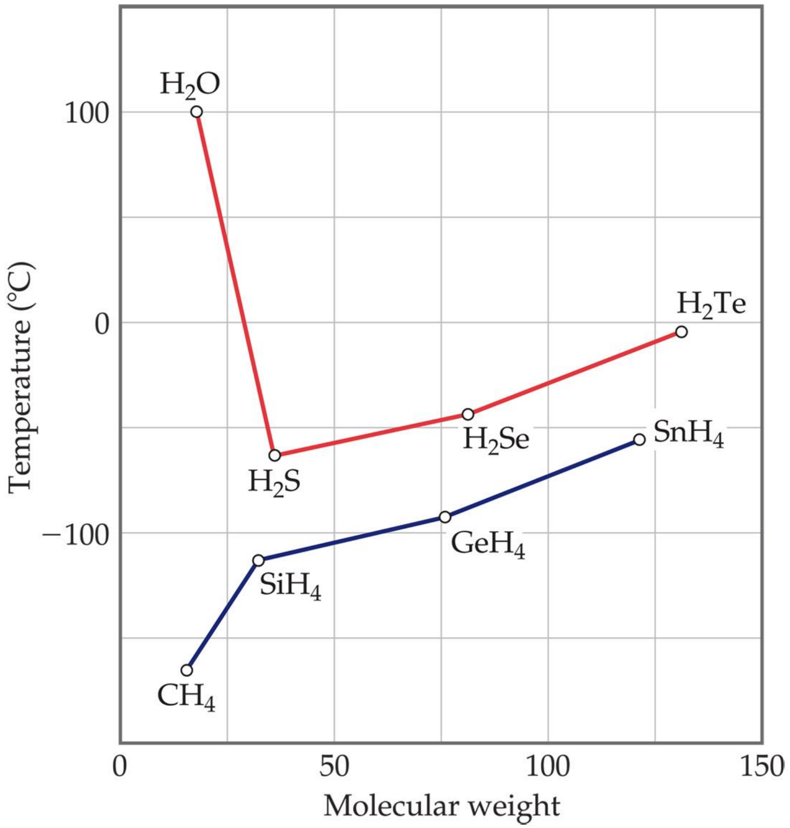
- The strength of dispersion forces tends to increase with increased molecular weight.
- Larger atoms have larger electron clouds, which are easier to polarize.

Which Have a Greater Effect:

Dipole-Dipole Interactions or Dispersion Forces?

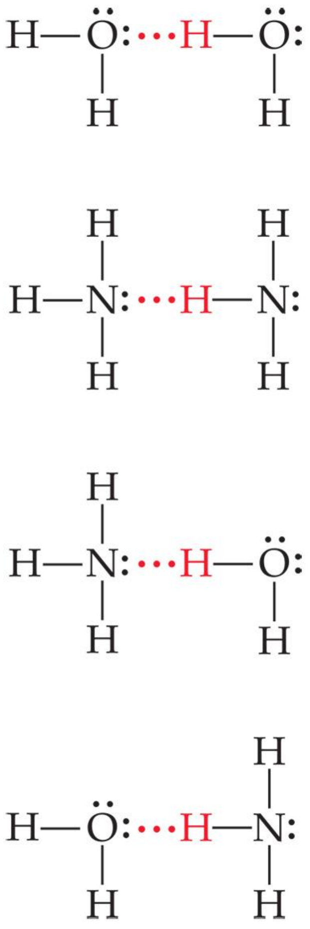
- If two molecules are of comparable size and shape, dipole-dipole interactions will likely be the dominating force.
- If one molecule is much larger than another, dispersion forces will likely determine its physical properties.

How Do We Explain This?



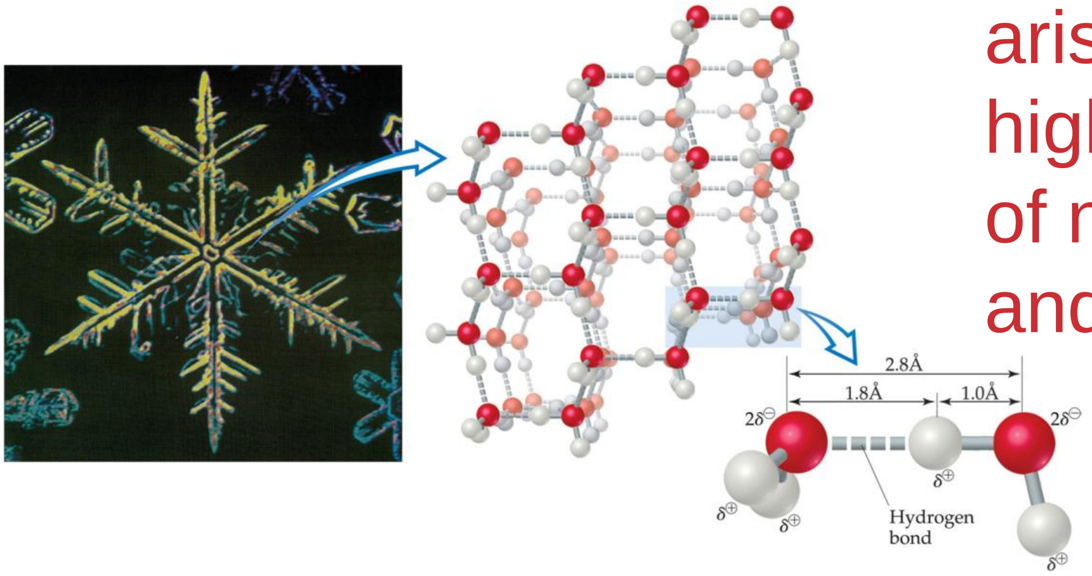
- The nonpolar series (SnH_4 to CH_4) follow the expected trend.
- The polar series follows the trend from H_2Te through H_2S, but water is quite an anomaly.

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.

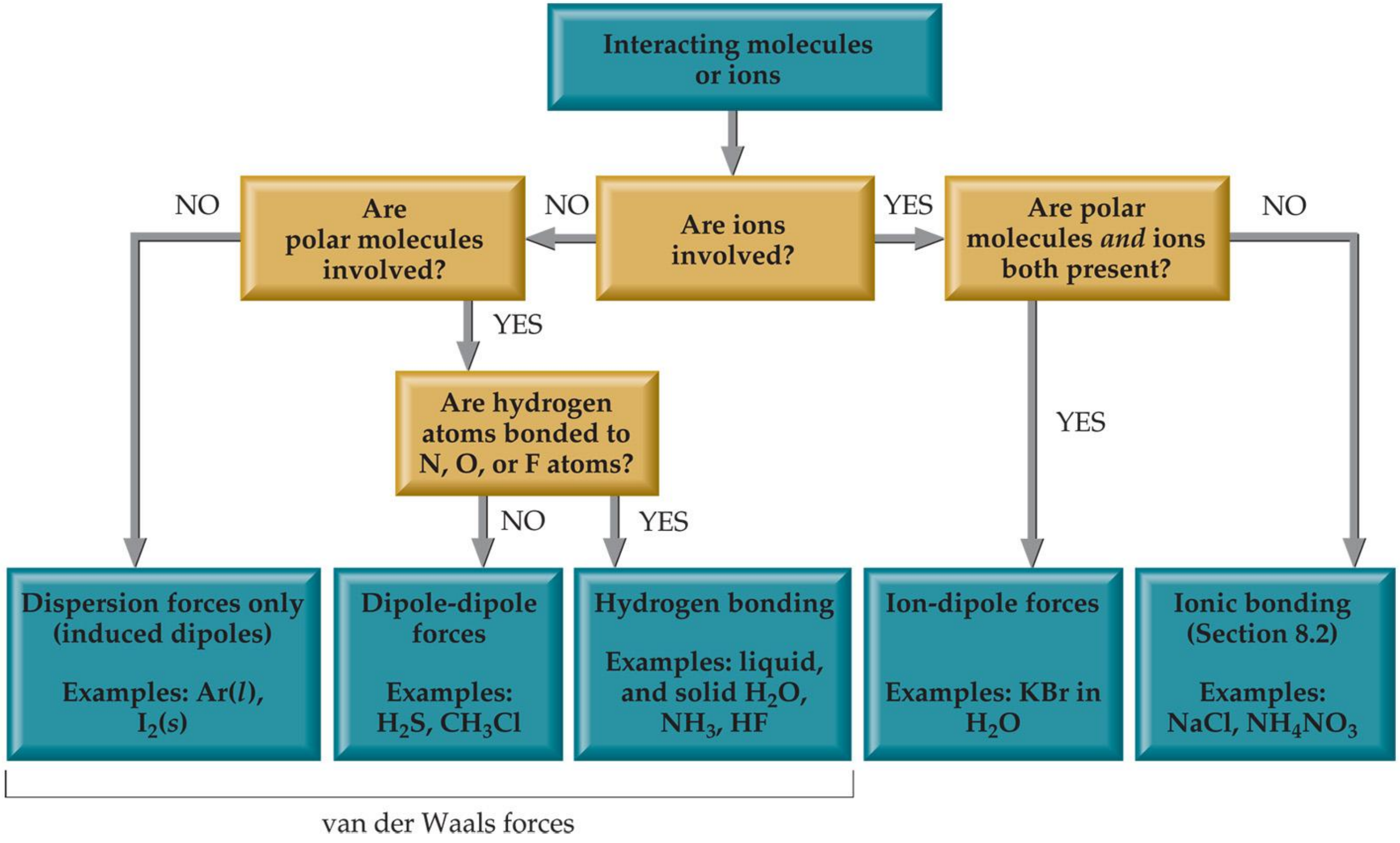
Hydrogen Bonding



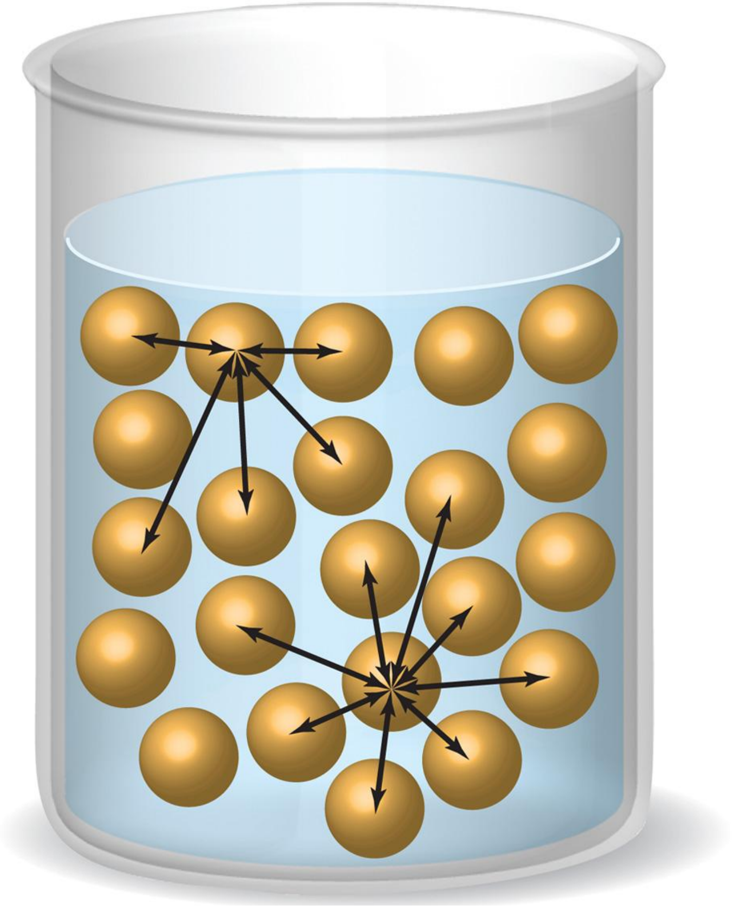
Hydrogen bonding arises in part from the high electronegativity of nitrogen, oxygen, and fluorine.

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

Summarizing Intermolecular Forces



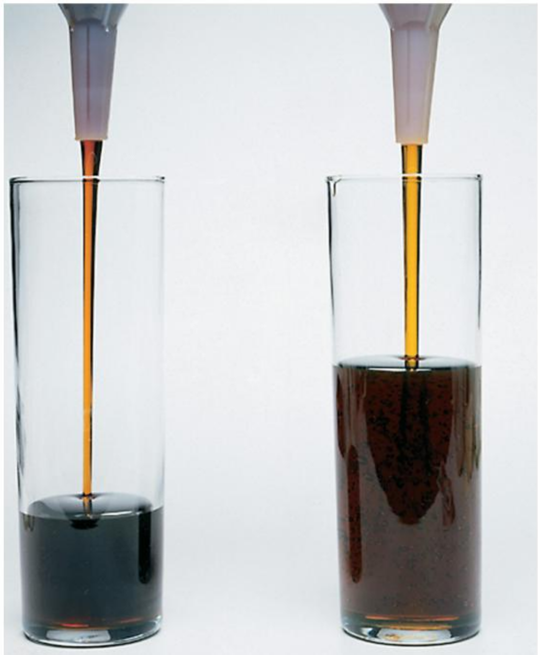
Intermolecular Forces Affect Many Physical Properties



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

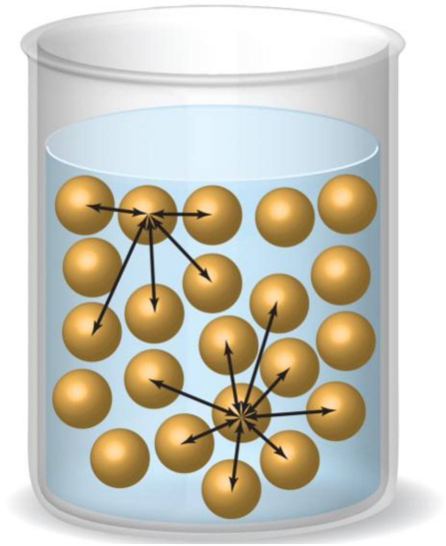
Viscosity

- 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 and decreases with higher temperature.

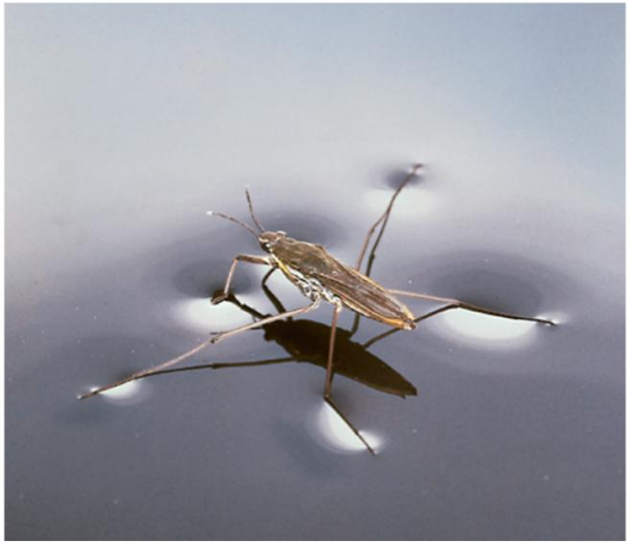


Substance	Formula	Viscosity (kg/m-s)
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	$3.26 * 10^{-4}$
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	$4.09 * 10^{-4}$
Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	$5.42 * 10^{-4}$
Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	$7.11 * 10^{-4}$
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	$1.42 * 10^{-3}$

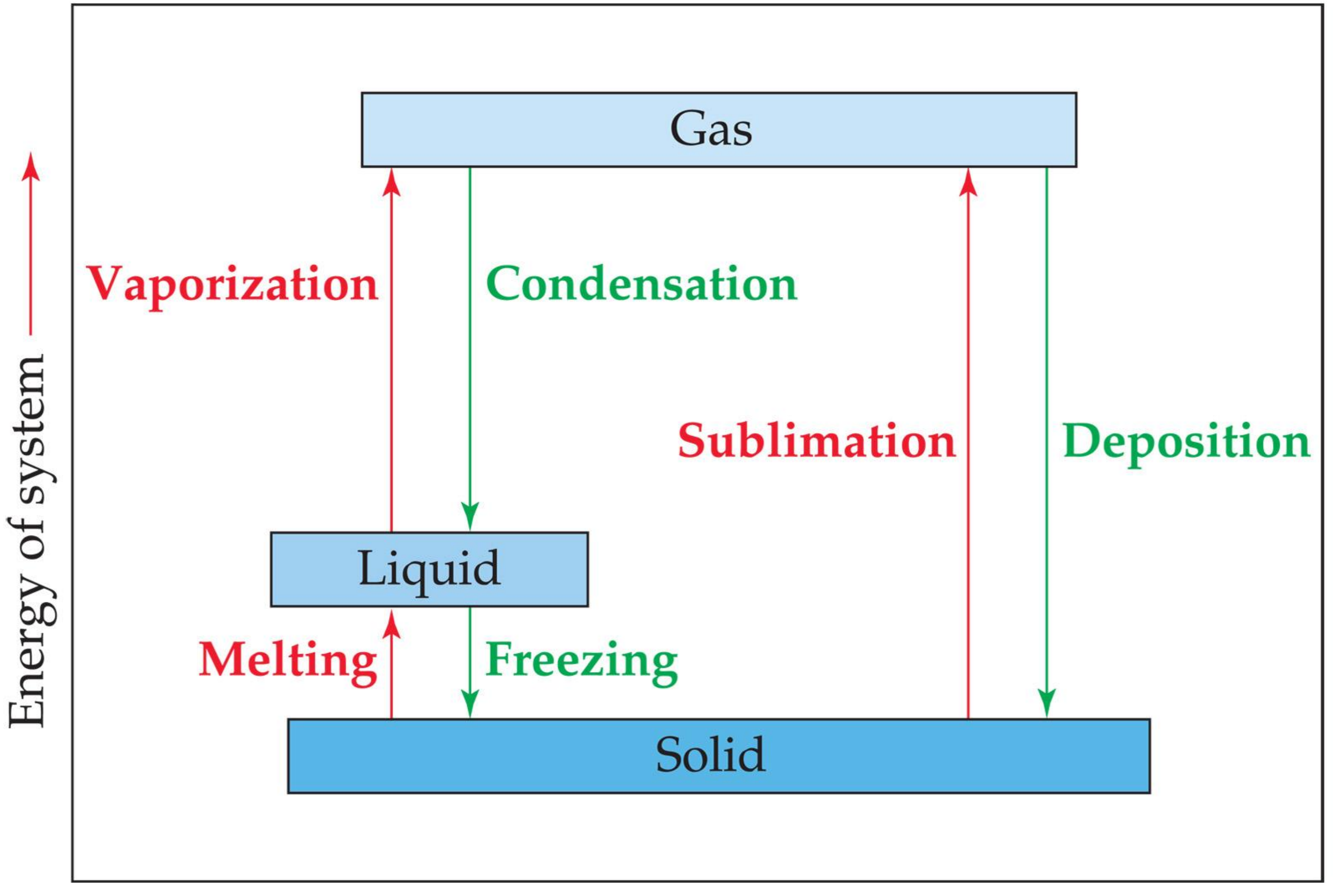
Surface Tension



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

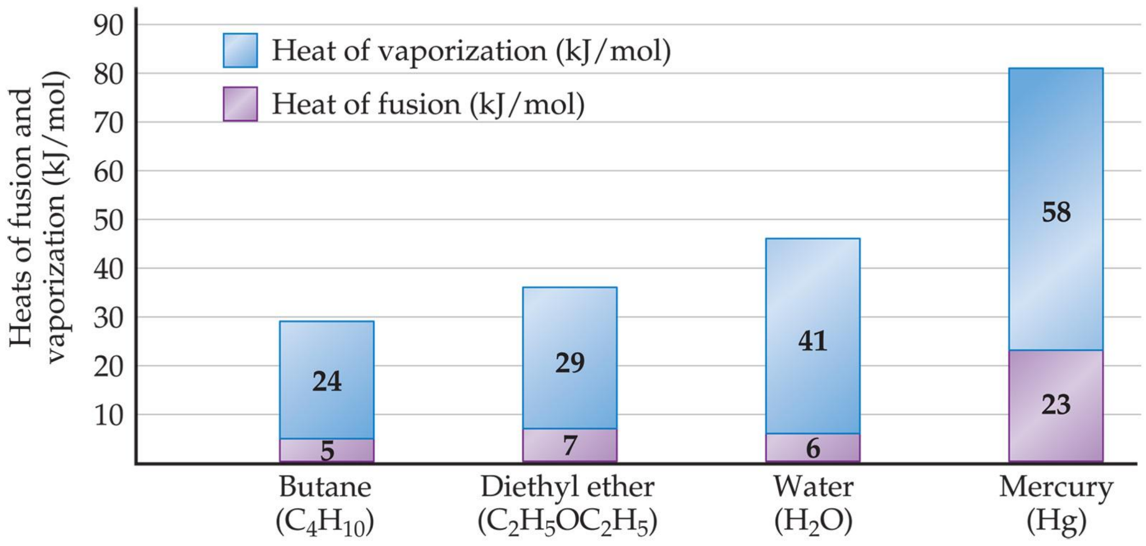


Phase Changes



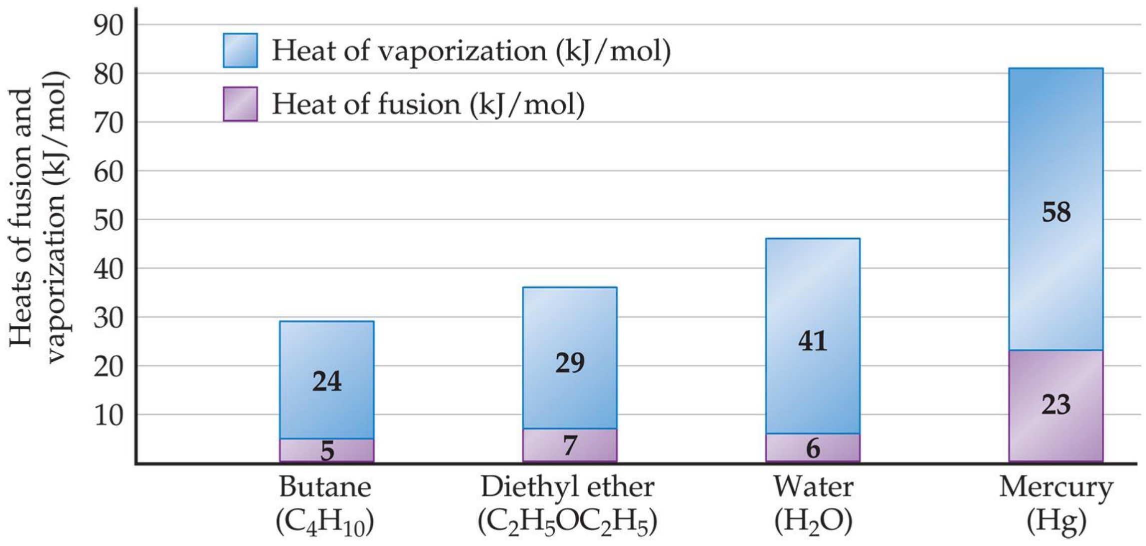
Intermolecular Forces

Energy Changes Associated with Changes of State



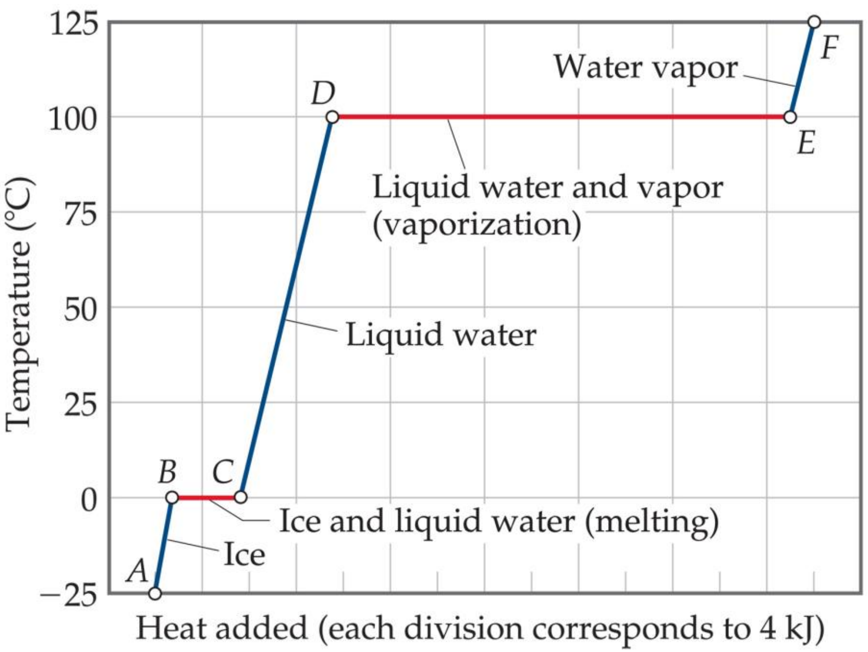
- **Heat of Fusion:** Energy required to change a solid at its melting point to a liquid.

Energy Changes Associated with Changes of State



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

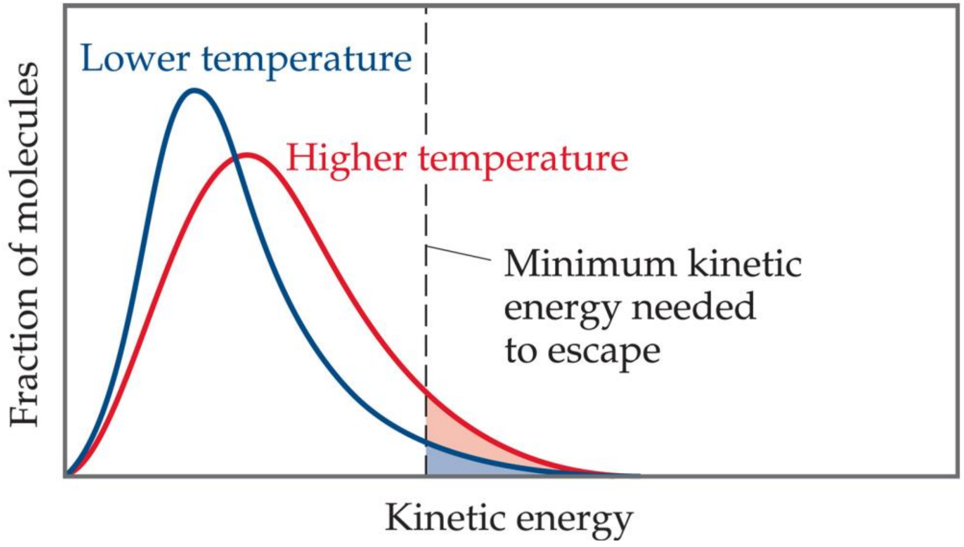
Energy Changes Associated with Changes of State



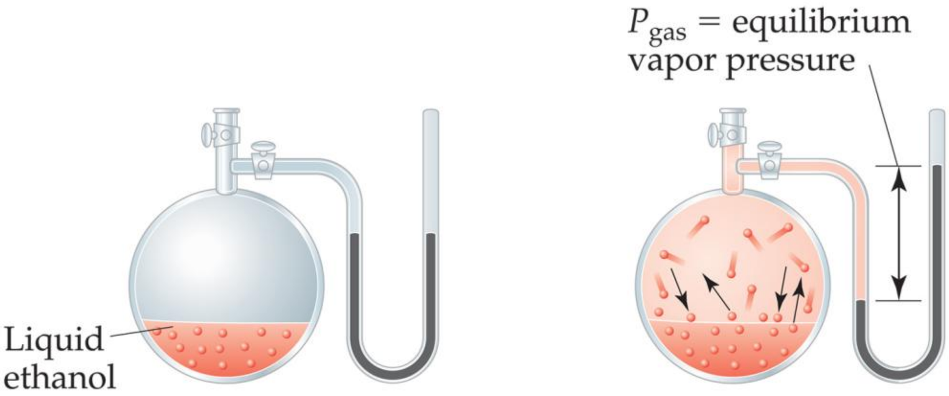
- The heat added to the system at the melting and boiling points goes into pulling the molecules farther apart from each other.
- The temperature of the substance does not rise during the phase change.

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.

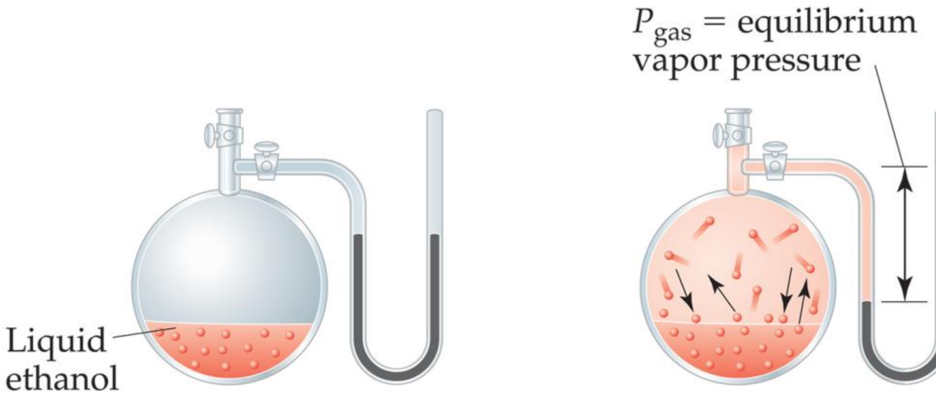


Vapor Pressure



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

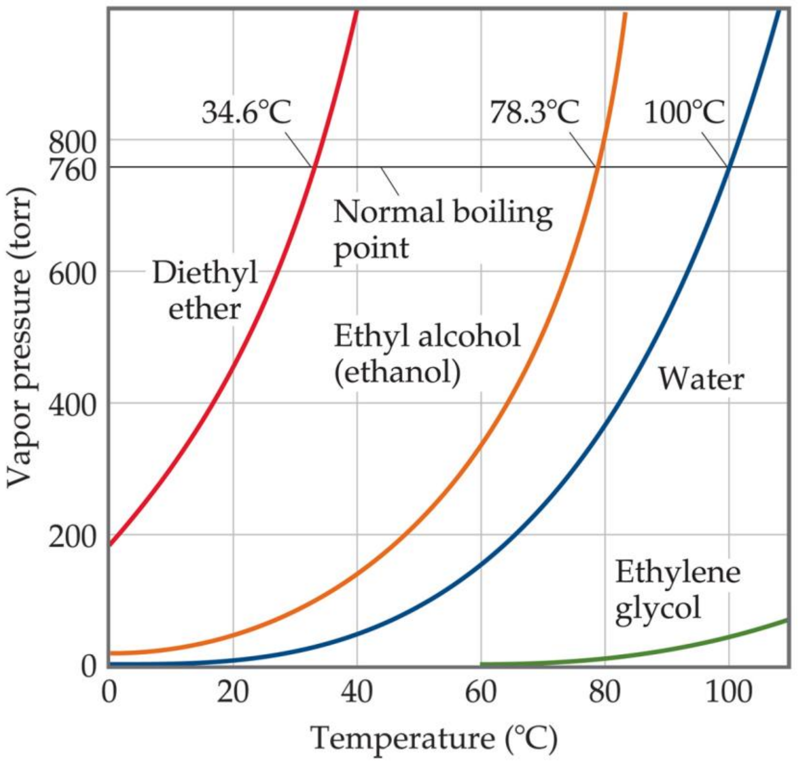
Vapor Pressure



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

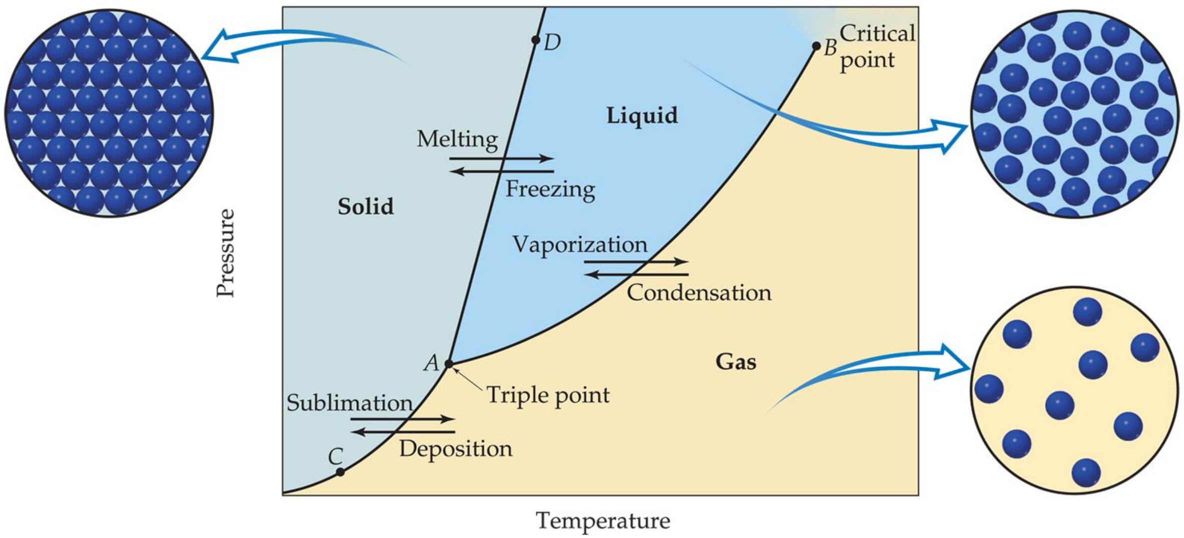
Vapor Pressure

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



Phase Diagrams

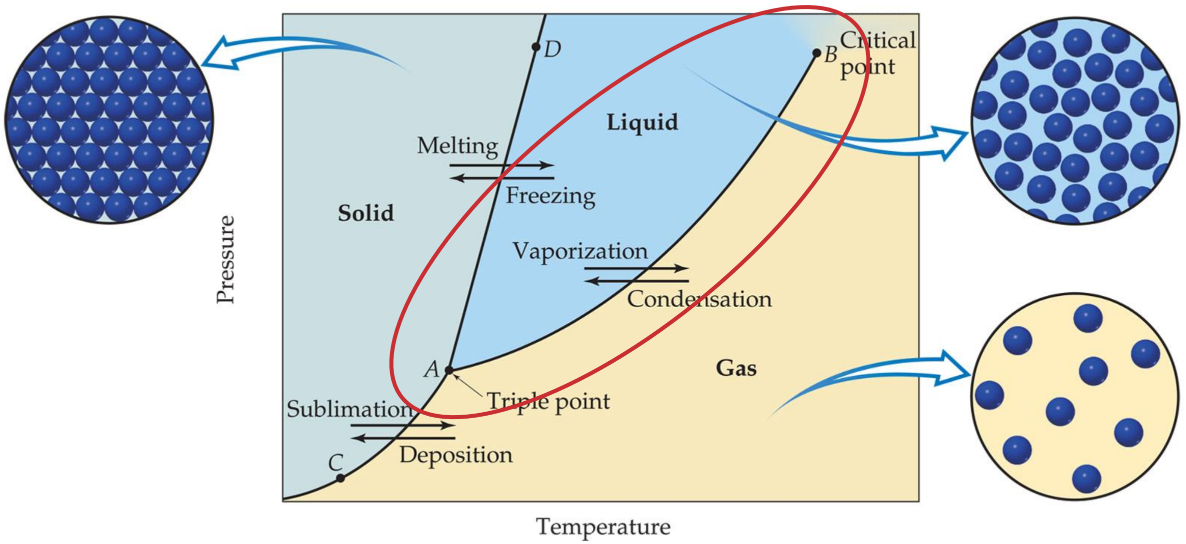
Phase diagrams display the state of a substance at various pressures and temperatures and the places where equilibria exist between phases.



Intermolecular Forces

Phase Diagrams

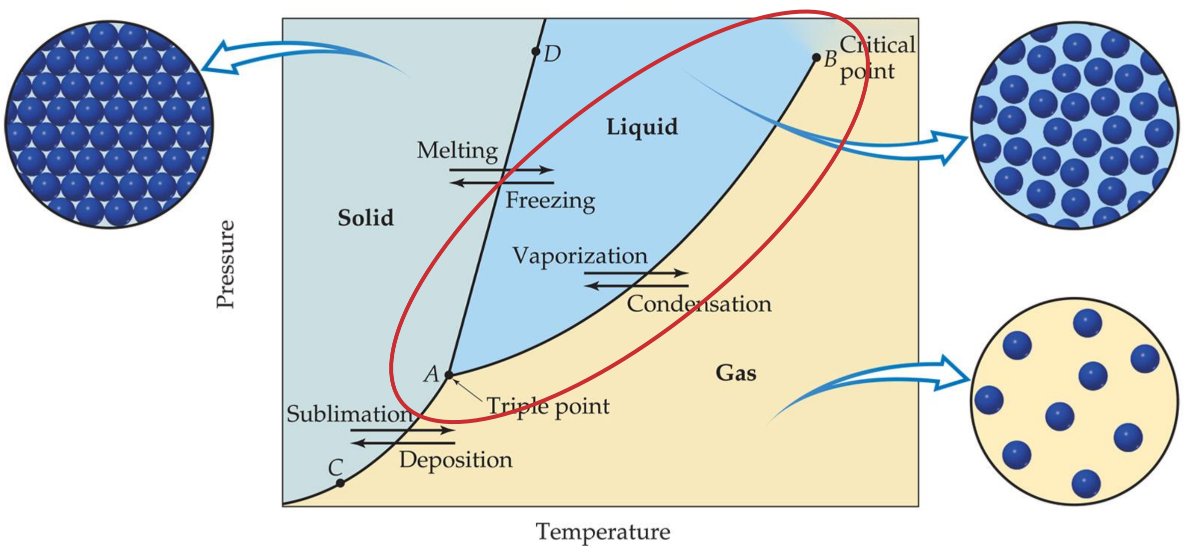
- The *AB* line is the liquid-vapor interface.
- It starts at the triple point (*A*), the point at which all three states are in equilibrium.



Intermolecular Forces

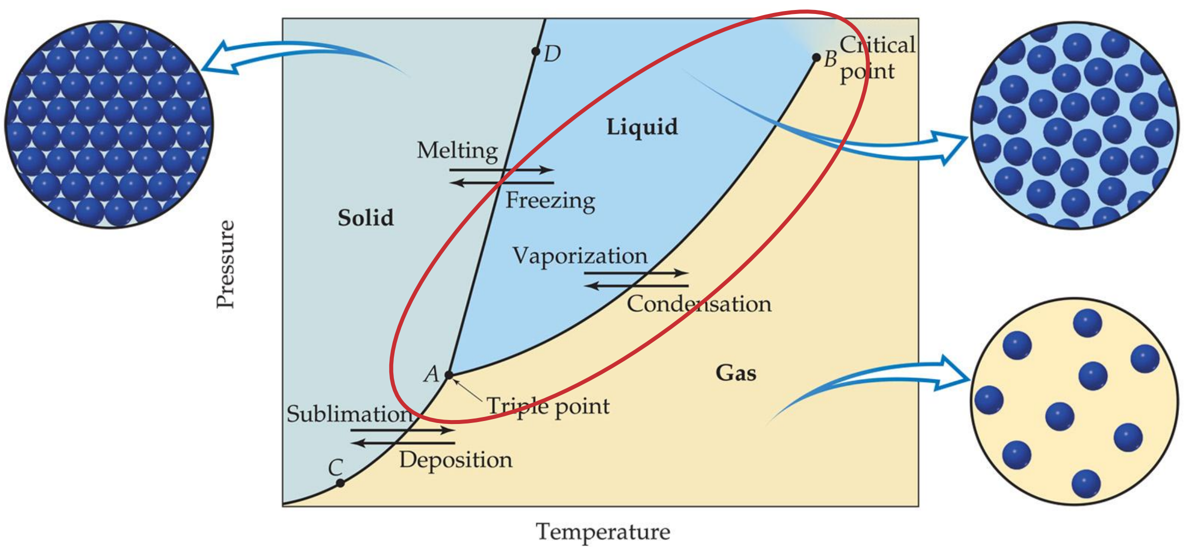
Phase Diagrams

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



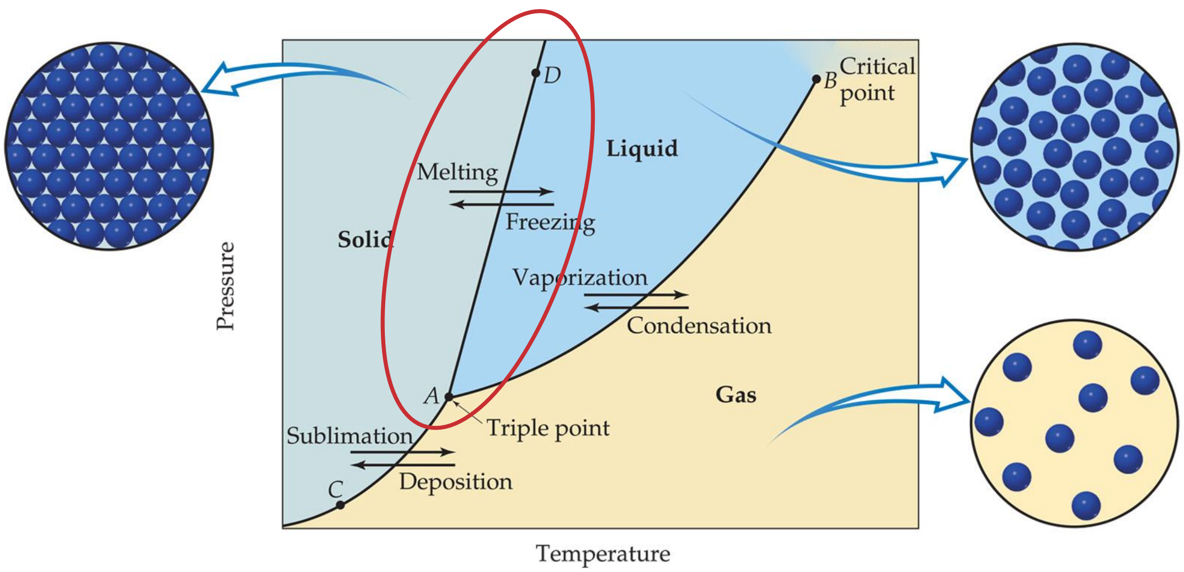
Phase Diagrams

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



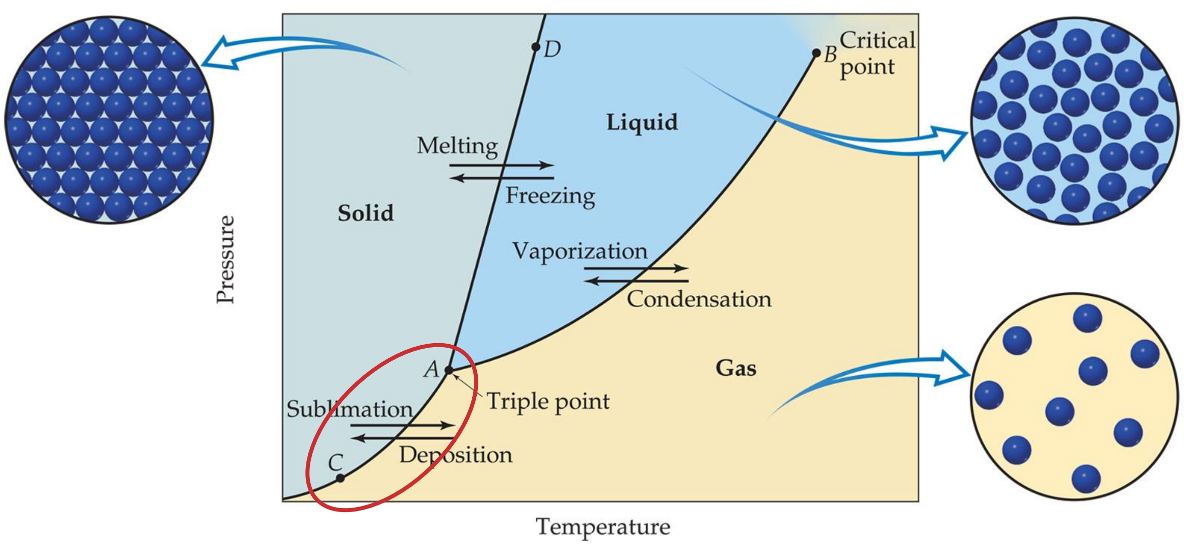
Phase Diagrams

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

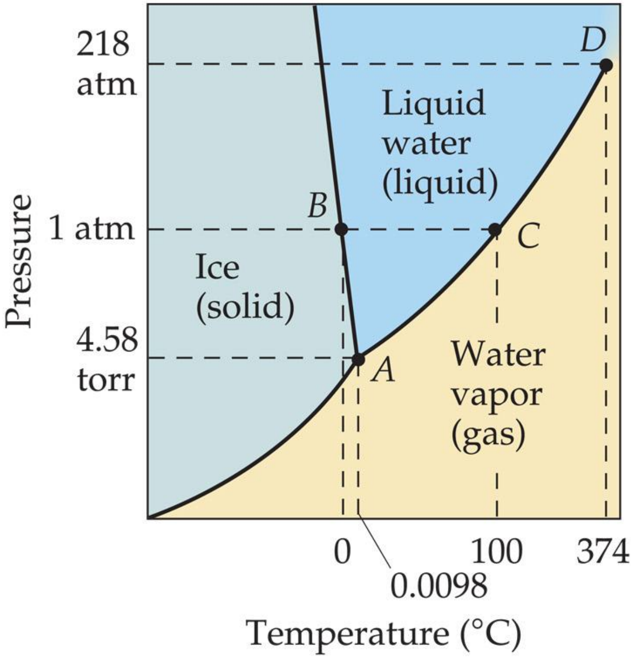


Phase Diagrams

- 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.

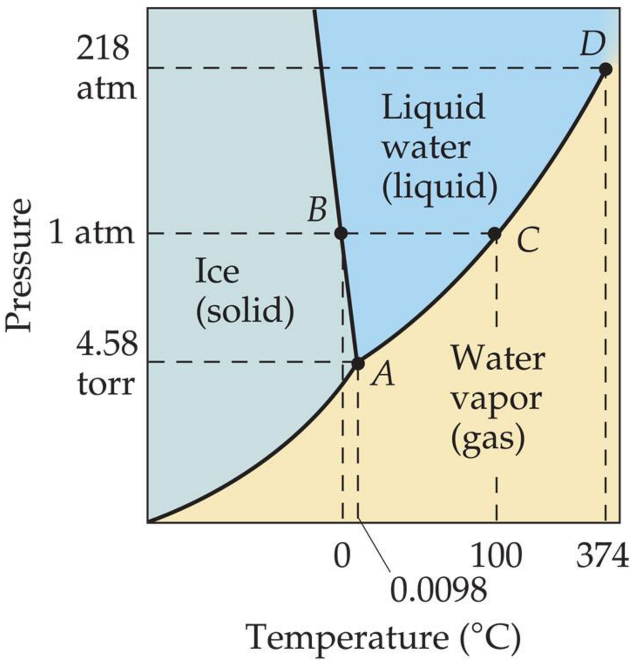


Phase Diagram of Water



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

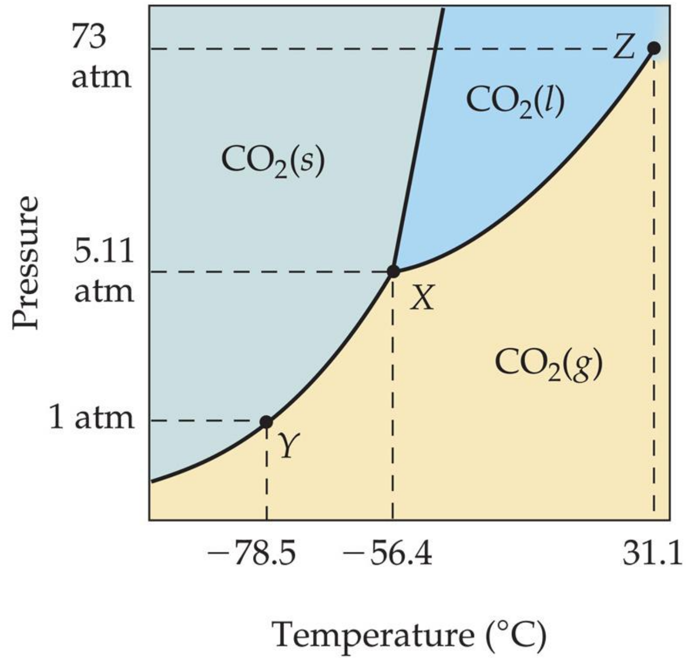
Phase Diagram of Water



- 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.

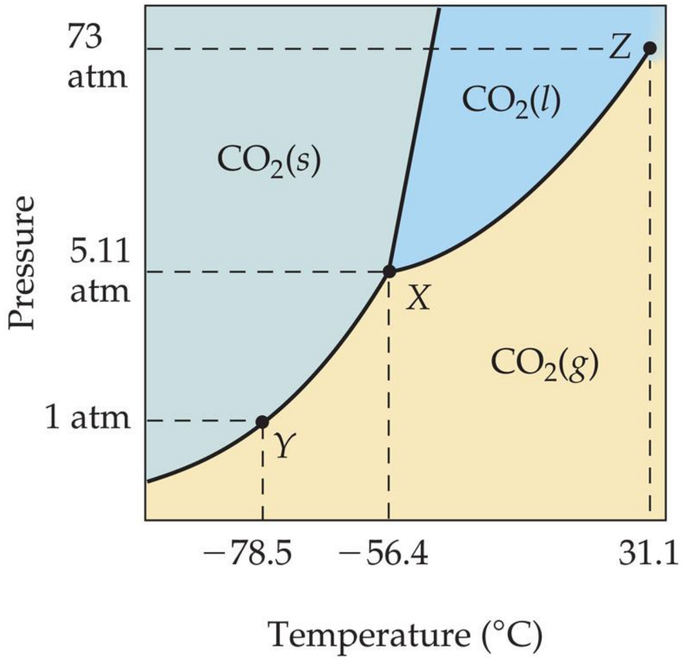
Phase Diagram of Carbon Dioxide

Carbon dioxide cannot exist in the liquid state at pressures below 5.11 atm; CO_2 sublimes at normal pressures.



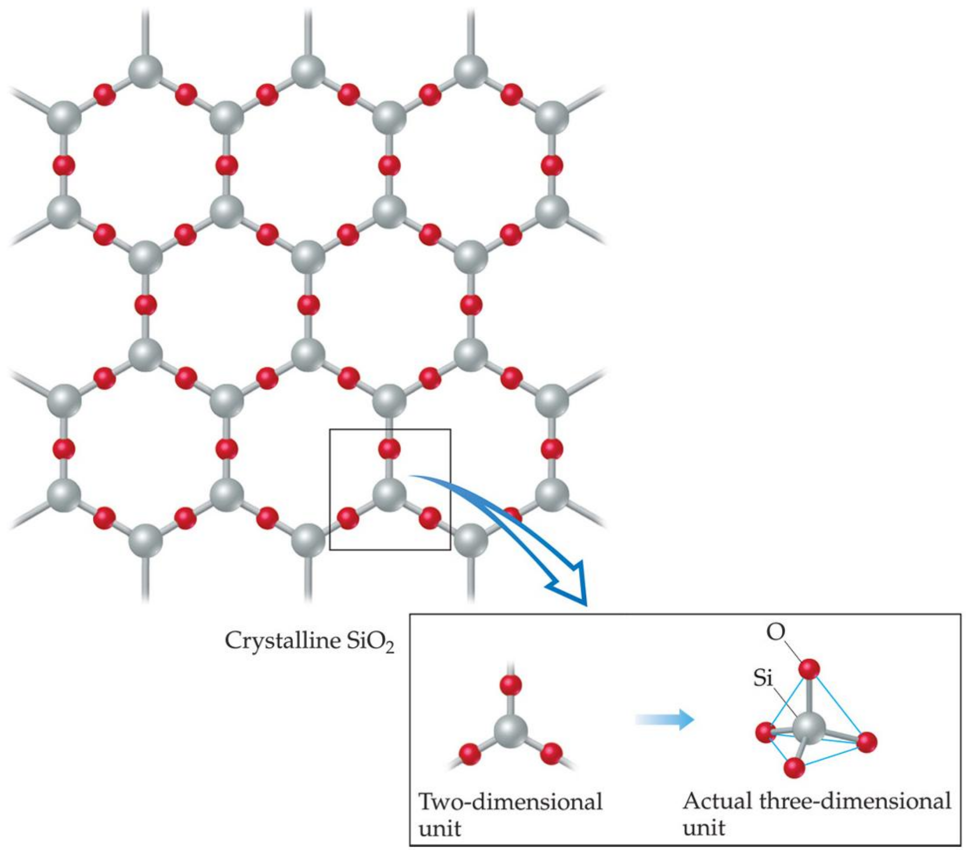
Phase Diagram of Carbon Dioxide

The low critical temperature and critical pressure for CO_2 make supercritical CO_2 a good solvent for extracting nonpolar substances (such as caffeine).

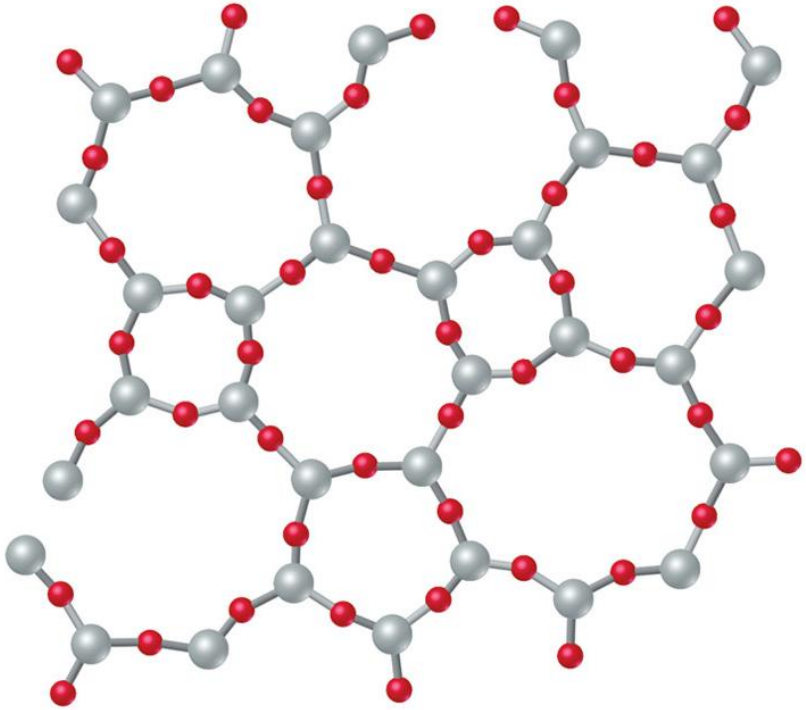


Solids

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



Solids

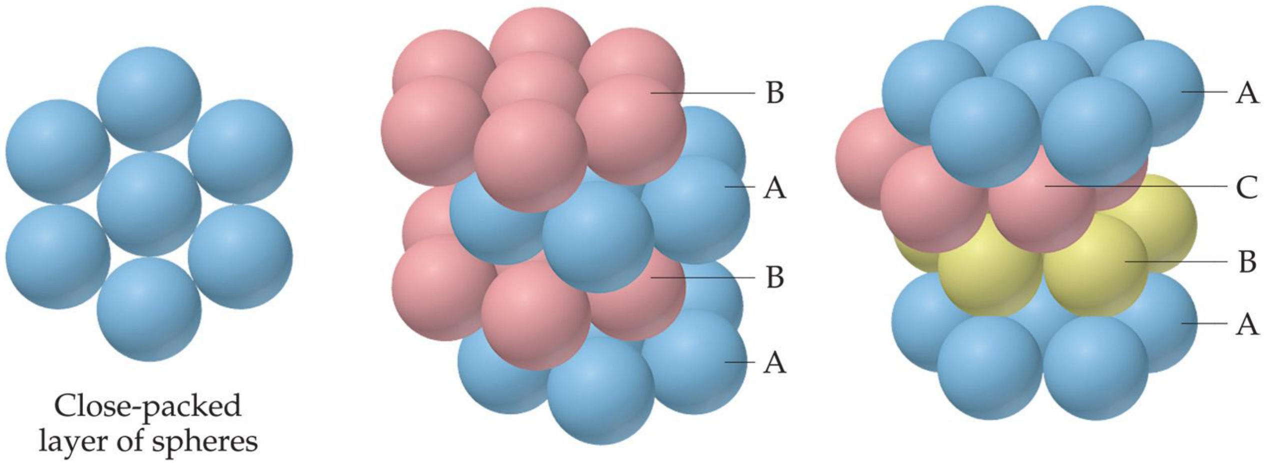


Amorphous SiO_2

- Amorphous—no particular order in the arrangement of particles.

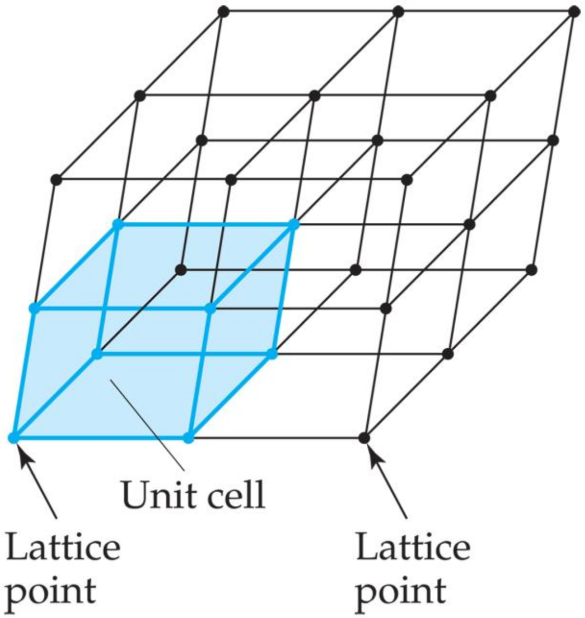
Attractions in Ionic Crystals

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

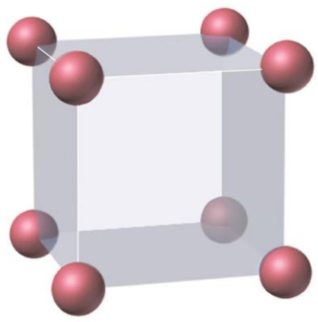


Close-packed layer of spheres

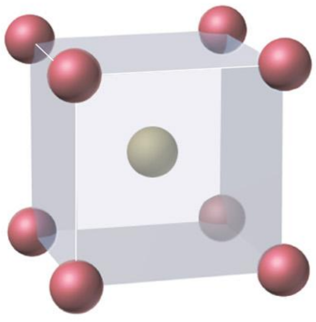
Crystalline Solids



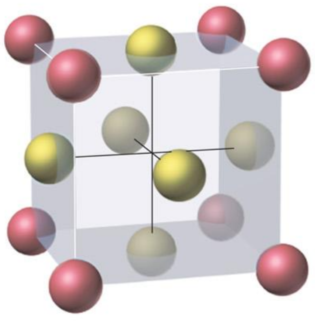
Because of the order in a crystal, we can focus on the repeating pattern of arrangement called the unit cell.



Primitive cubic

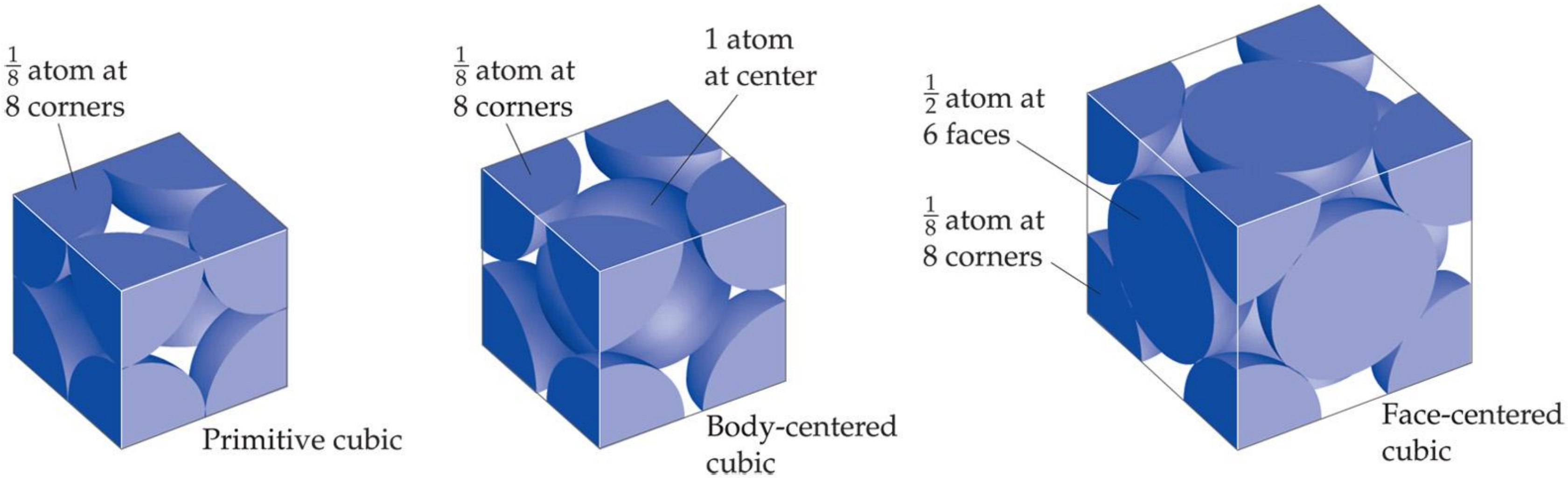


Body-centered cubic



Face-centered cubic

Crystalline Solids

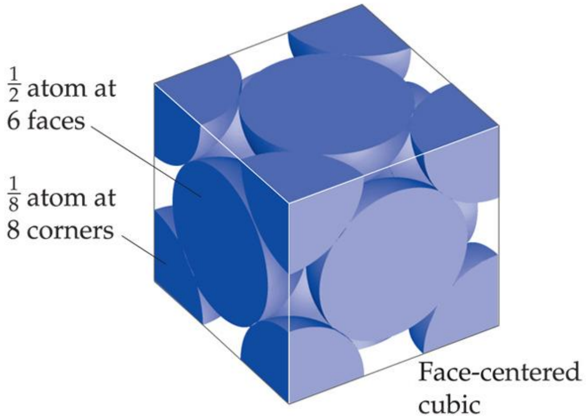


There are several types of basic arrangements in crystals, such as the ones shown above.

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	$\frac{1}{8}$



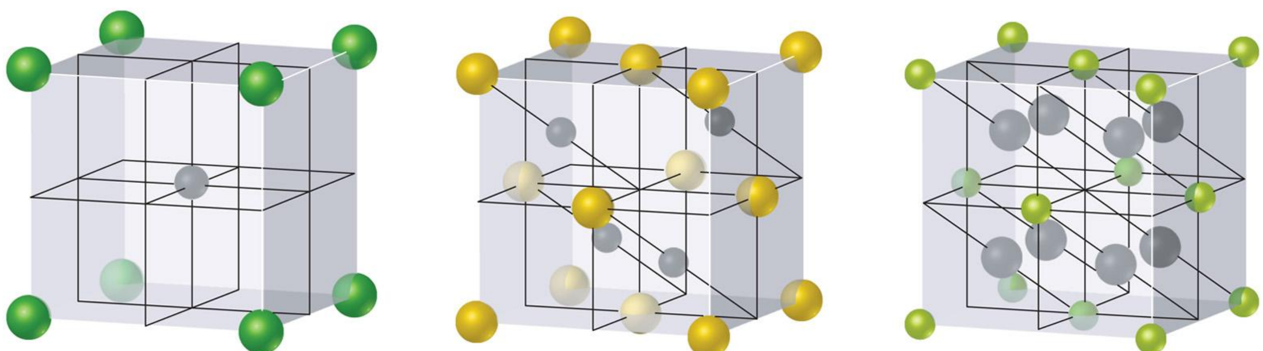
Ionic Solids

What are the empirical formulas for these compounds?

(a) Green: chlorine; Gray: cesium

(b) Yellow: sulfur; Gray: zinc

(c) Green: calcium; Gray: fluorine

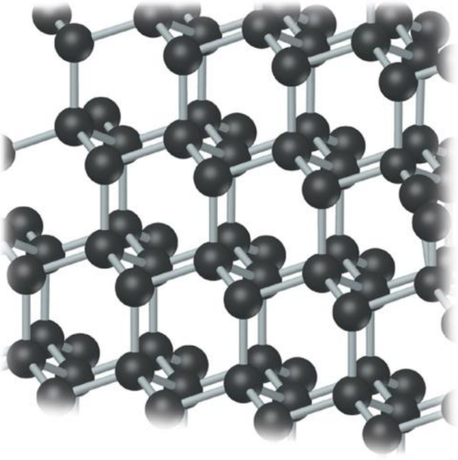


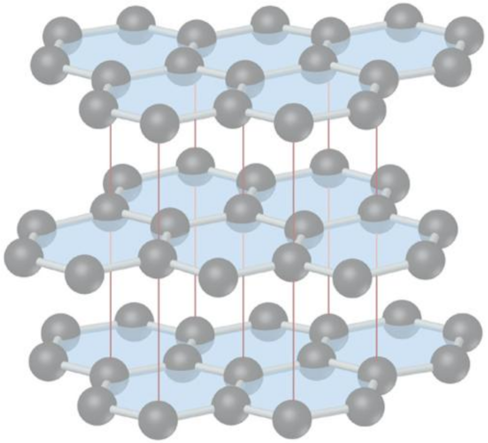
(a) CsCl (b) ZnS (c) CaF_2

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_4 ;sucrose, $C_{12}H_{22}O_{11}$; Dry Ice™, CO_2
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_2
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts—for example, NaCl, $Ca(NO_3)_2$
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

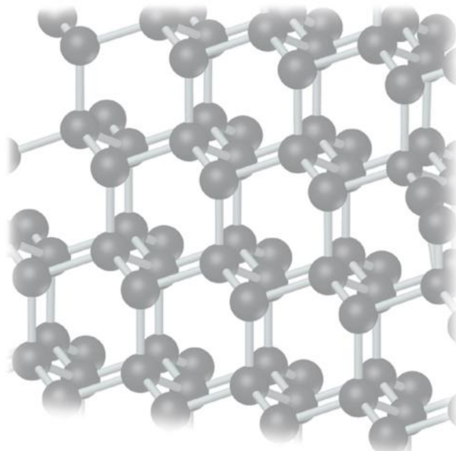
Covalent-Network and Molecular Solids

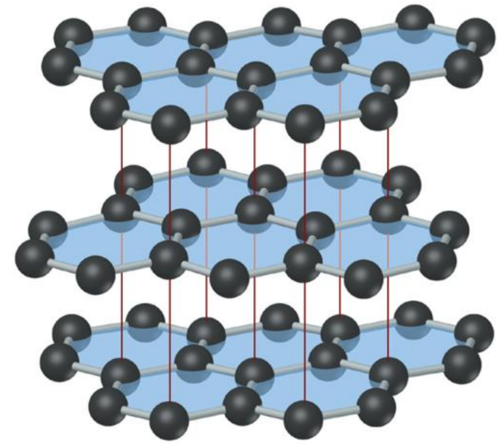




- Diamonds are an example of a covalent-network solid in which atoms are covalently bonded to each other.
  - They tend to be hard and have high melting points.

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.