Chapter 11
Intermolecular Forces, Liquids, and Solids

States of Matter

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

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

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.

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

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

van der Waals Forces

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

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

London Dispersion Forces

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.

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.

- 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

- 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

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

Summarizing Intermolecular Forces

I
ntermolecular 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.

Surface Tension

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

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

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

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

- 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.

- 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.

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

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

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

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—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.

Crystalline Solids

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

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

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

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

Types of Bonding in Crystalline Solids
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.