

Chapter 11: Intermolecular Forces, Liquids, and Solids

- intermolecular forces – forces that exist between molecules

11.1 A Molecular Comparison of Liquids and Solids

- gases
 - average kinetic energy of the molecules is larger than average energy of attractions between molecules
 - lack of strong attractive forces allows gases to expand
- liquids
 - denser than gases
 - have a definite volume
 - attractive forces not strong enough to keep molecules from moving allowing liquids to hold shape of container
- solids
 - intermolecular forces hold molecules together and keep them from moving
 - not very compressible
 - crystalline – solids with highly ordered structures

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

- state of substance depends on balance between the kinetic energies of the particles and interparticle energies of attraction
 - kinetic energies depends on temperature and tend to keep particles apart and moving
 - interparticle attractions draw particles together
- condensed phases – liquids and solids because particles are close together compared to gases
- increase temperature forces molecules to be closer together → increase in strength of intermolecular forces

11.2 Intermolecular Forces

- intermolecular forces weaker than ionic or covalent bonds
- many properties of liquids reflect strengths of intermolecular forces
- three types of intermolecular forces: dipole-dipole forces, London dispersion forces, and hydrogen-bonding forces
 - also called van der Waals forces
 - less than 15% as strong as covalent or ionic bonds
 - electrostatic in nature, involves attractions between positive and negative species

11.2.1 Ion-Dipole Forces

- Ion-Dipole Force – exists between an ion and partial charge at one end of a polar molecule
- Polar molecules are dipoles
- magnitude of attraction increases as either the charge of ion or magnitude of dipole moment increases

11.2.2 Dipole-Dipole Forces

- dipole-dipole force – exists between neutral polar molecules
- effective only when polar molecules are very close together
- weaker than ion-dipole forces
- for molecules of approximately equal mass and size, the strengths of intermolecular attractions increase with increasing polarity
- increase dipole moment → increase boiling point

11.2.3 London Dispersion Forces

- interparticle forces that exist between nonpolar atoms or molecules
- motion of electrons can create an instantaneous dipole moment
- molecules have to be very close together
- polarizability – ease in which the charge distribution in a molecule can be distorted
 - greater polarizability → more easily electron cloud can be distorted to give momentary dipole
- larger molecules have greater polarizability
- London dispersion forces increase with increasing molecular size
- Dispersion forces increase in strength with increasing molecular weight
- Molecular shape affects intermolecular attractions
 - greater surface contact → greater boiling point and London dispersion forces
- dispersion forces operate between all molecules
- comparing relative strengths of intermolecular attractions:
 - 1) comparable molecular weights and shapes = equal dispersion forces
 - differences in magnitudes of attractive forces due to differences in strengths of dipole-dipole attractions
 - most polar molecule has strongest attractions
 - 2) differing molecular weights = dispersion forces tend to be the decisive ones
 - differences in magnitudes of attractive forces associated with differences in molecular weights
 - most massive molecular has strongest attractions

11.2.4 Hydrogen Bonding

- hydrogen bonding – special type of intermolecular attraction that exists between the hydrogen atom in a polar bond and an unshared electron pair on a nearby electronegative ion or atom
- hydrogen bond with F, N, and O is polar
- density of ice is lower than that of liquid water
- when water freezes the molecules assume the ordered open arrangement → makes ice less dense than water
- a given mass of ice has a greater volume than the same mass of water
- structure of ice allows the maximum number of hydrogen bonding interactions to exist

11.2.5 Comparing Intermolecular Forces

- dispersion forces found in all substances
- strengths of forces increase with increases molecular weight and also depend on shape
- dipole-dipole forces add to effect of dispersion forces and found in polar molecules
- hydrogen bonds tend to be strongest intermolecular force

11.3 Some Properties of Liquids

- two properties of liquids: viscosity and surface tension

11.3.1 Viscosity

- viscosity – resistance of a liquid to flow
- the greater the viscosity the more slowly the liquid flows
- measured by timing how long it takes a certain amount of liquid to flow through a thin tube under gravitational forces
- can also be measured by how long it takes steel spheres to fall through the liquid

- viscosity related to ease with which individual molecules of liquid can move with respect to one another
- depends on attractive forces between molecules, and whether structural features exist to cause molecules to be entangled
- viscosity decreases with increasing temperature

11.3.2 Surface Tension

- surface tension – energy required to increase the surface area of a liquid by a unit amount
- surface tension of water at 20°C is $7.29 \times 10^{-2} \text{ J/m}^2$
- $7.29 \times 10^{-2} \text{ J/m}^2$ must be supplied to increase surface area of a given amount of water by 1 m^2
- cohesive forces – intermolecular forces that bind similar molecules
- adhesive forces – intermolecular forces that bind a substance to a surface
- capillary action – rise of liquids up very narrow tubes

11.4 Phase Changes

11.4.1 Energy Changes Accompanying Phase Changes

- phase changes require energy
- phase changes to less ordered state requires energy
- melting process of solid called fusion
- heat of fusion – enthalpy change of melting a solid
 - $\Delta H_{\text{fus}} \text{ water} = 6.01 \text{ kJ/mol}$
- heat of vaporization – heat needed for vaporization of liquid
 - $\Delta H_{\text{vap}} \text{ water} = 40.67 \text{ kJ/mol}$
- melting, vaporization, and sublimation are endothermic
- freezing, condensation, and deposition are exothermic

11.4.2 Heating Curves

- heating curve – graph of temperature of system versus the amount of heat added
- used to calculate enthalpy changes
- supercooled water – when water is cooled to a temperature below 0°C

11.4.3 Critical Temperature and Pressure

- critical temperature – highest temperature at which a substance can exist as a liquid
- critical pressure – pressure required to bring about liquefaction at critical temperature
- the greater the intermolecular attractive forces, the more readily gases liquefy → higher critical temperature
 - cannot liquefy a gas by applying pressure if gas is above critical temperature

11.5 Vapor Pressure

- vapor pressure – measures tendency of a liquid to evaporate

11.5.1 Explaining Vapor Pressure on the Molecular Level

- dynamic equilibrium – condition when two opposing processes are occurring simultaneously at equal rates
- vapor pressure of a liquid is the pressure exerted by its vapor when the liquid and vapor states are in dynamic equilibrium

11.5.2 Volatility, Vapor Pressure, and Temperature

- volatile – liquids that evaporate readily
- vapor pressure increases with increasing temperature

11.5.3 Vapor Pressure and Boiling Point

- liquids boil when its vapor pressure equals the external pressure acting on the surface of the liquid
- temperature of boiling increase with increasing external pressure

- normal boiling point – boiling point of a liquid at 1 atm
- higher pressures cause water to boil at higher temperatures

11.6 Phase Diagrams

- phase diagrams – graphical way to summarize conditions under which equilibria exist between the different states of matter
- three important curves:
 - 1) vapor pressure curve of liquid
 - shows equilibrium of liquid and gas phases
 - normal boiling point = point on curve where pressure at 1 atm
 - 2) variation in vapor pressure of solid at it sublimates at different temperatures
 - 3) change in melting point of solid with increasing pressure
 - slopes right as pressure increases
 - higher temperatures needed to melt solids at higher pressures
 - melting point of solid identical to freezing point
 - differ only in temperature direction from which phase change is approached
 - melting point at 1 atm is the normal melting point
- triple point – point at which all three phases are at equilibrium
- gas phase stable at low pressures and high temperatures
- solid phase stable at low temperatures and high pressures
- liquid phase – stable between gas and solids

11.6.1 the Phase diagrams of H₂O and CO₂

- melting point of CO₂ increases with increasing pressure
- melting point of H₂O decreases with increasing pressure
- triple point of H₂O (0.0098°C and 4.58 torr) at lower pressure than CO₂ (-56.4°C and 5.11 atm)
- solid CO₂ does not melt but sublimates
- CO₂ does not have a normal melting point but a normal sublimation point
 - CO₂ absorbs energy at ordinary temperatures

11.7 Structures of Solids

- crystalline solid – solid whose atoms, ion, or molecules are ordered in well-defined arrangements
 - flat surfaces or faces that make definite angles
 - regular shapes
- amorphous solid – solid whose particles have no orderly structure
 - lack well-defined faces and shapes
 - mixtures of molecules that do not stack together well
 - large, complicated molecules
 - intermolecular forces vary in strength
 - does not melt at a specific temperature but soften over a temperature range

11.7.1 Unit Cell

- unit cell – repeating unit of a solid
- crystal lattice – three-dimensional array of points, each representing an identical environment within the crystal
- three types of cubic unit cell: primitive cubic, body-centered cubic, and face-centered cubic
- primitive cubic – lattice points at corners only
- body-centered cubic – lattice points at corners and center
- face-centered cubic – lattice points at center of each face and at each corner

11.7.2 The Crystal structure of Sodium Chloride

- total cation-to-anion ratio of a unit cell must be the same as that for entire crystal

11.7.3 Close Packing of Spheres

- structures of crystalline solids are those that bring particles in closest contact to maximize the attractive forces
- most particles that make up solids are spherical
- two forms of close packing: cubic close packing and hexagonal close packing
- hexagonal close packing – spheres of the third layer that are placed in line with those of the first layer
- coordination number – number of particles immediately surrounding a particle in the crystal structure
 - both forms of close packing have coordination number of 12

11.8 Bonding in Solids

Type of Solid	Forms of Unit Particles	Forces Between Particles	Properties	Examples
Molecular	Atoms of molecules	London dispersion, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, methane, sucrose, dry ice
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, quartz
Ionic	Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts
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

11.8.1 Molecular Solids

- molecular solids – atoms or molecules held together by intermolecular forces
- soft, low melting points
- gases or liquids at room temperature from molecular solids at low temperature
- properties depends on strengths of forces and ability of molecules to pack efficiently in three dimensions
- intermolecular forces that depend on close contact are not as effective

11.8.2 Covalent-Network Solids

- covalent-network solids – atoms held together in large networks or chains by covalent bonds
- hard, high melting points

11.8.3 Ionic Solids

- ionic solids – ions held together by ionic bonds
- strength depends on charges of ions
- structure of ionic solids depends on charges and relative sizes of ions

11.8.4 Metallic Solids

- metallic solids – metal atoms
- usually have hexagonal close-packed, cubic close-packed, or body-centered-cubic structures

- each atom has 8 or 12 adjacent atoms
- bonding due to valence electrons that are delocalized throughout entire solid
- strength of bonding increases as number of electrons available for bonding increases
- mobility of electrons make metallic solids good conductors of heat and electricity

11.2.5 (continued)

