

Chapter 10 - Liquids and Solids

10.1 Intermolecular Forces

A. Dipole-Dipole Forces

1. Attraction between molecules with dipole moments
 - a. Maximizes (+) ----- (-) interactions
 - b. Minimizes (+) ----- (+) and (-) ----- (-) interactions
2. About 1% of strength of ionic bonds
 - a. Unimportant in gas phase due to distance between molecules

B. Hydrogen Bonding

1. Special dipole-dipole attraction
 - a. Hydrogen covalently bonded to highly electronegative elements (N, O, F) has a higher than normal $\delta+$ charge
2. Bond strength is higher than other dipole-dipole attractions
3. Important in the bonding of molecules such as water and DNA

C. London Dispersion Forces

1. Instantaneous dipoles
 - a. Random movement of electrons can create a momentary nonsymmetrical distribution of charge even in nonpolar molecules
 - b. Instantaneous dipoles can induce a short-lived dipole in a neighboring molecule
2. London dispersion forces exist between all molecules, but are the weakest forces of attraction
3. "Polarizability" increases with the number of electrons in a molecule
 - a. CCl_4 experiences greater London forces than CH_4

10.2 The Liquid State

A. Surface Tension

1. The resistance of a liquid to an increase in its surface area
2. High intermolecular forces greater high surface tension

B. Capillary Action

1. Cohesive forces between liquid molecules
2. Adhesive forces between polar liquid molecules and polar bonds in the material making up the container
 - a. Water's adhesive forces are greater than its cohesive forces, thus the increase in surface area (concave meniscus)
 - b. Oxygen in glass is attracted to hydrogen in water

C. Viscosity

1. Measure of a liquid's resistance to flow
 - a. Viscosity increases with intermolecular forces
 - b. Viscosity increase with molecular size

D. Structural Model for Liquids

1. Strong intermolecular forces (like solids)
2. Considerable molecular motion (like gases)

10.3 An Introduction to Structures and Types of Solids

A. Types of solids

1. Crystalline solids

- Highly regular arrangement of components
- Components organized in a three-dimensional lattice
 - (1) Smallest repeating unit of the lattice is a unit cell

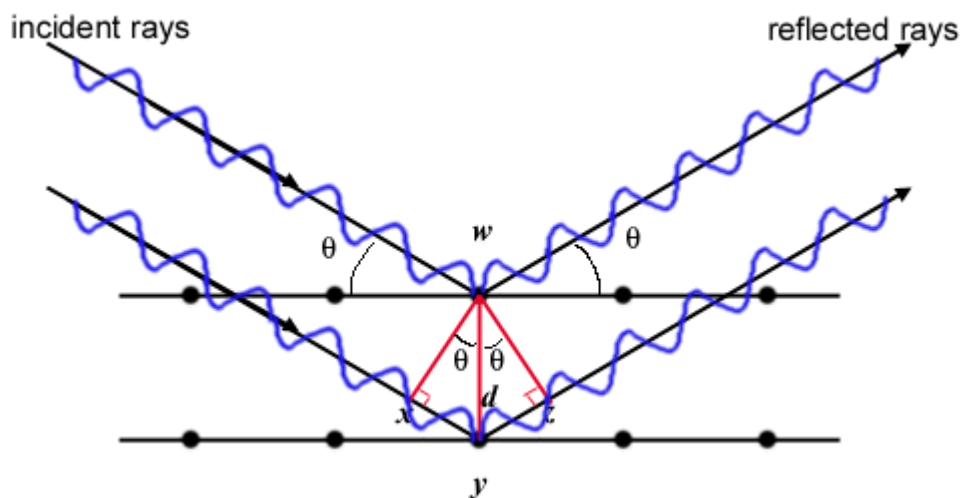
2. Amorphous solids

- Components "frozen in place" and lacking orderly arrangement
 - (1) glass
 - (2) plastic

B. X-ray Analysis of Solids

1. Structure of crystalline solids can be determined by xray diffraction

- waves in parallel beams that are "in phase" produce constructive interference
- waves in parallel beams that are "out of phase" produce destructive interference



θ = angle of incidence and reflection

d = distance between atoms

n = integer

λ = wavelength

2. Bragg's Law

a. $xy + yz = n\lambda$ and $xy + yz = 2d \sin \theta$

$$\therefore n\lambda = 2d \sin \theta$$

3. Diffractometer

- computerized device to rotate crystal samples in an x-ray field, gather incidence and reflection data, and construct models of crystal structure

C. Types of Crystalline Solids

1. Ionic solids
 - a. Ions occupy lattice points
 - b. Sodium chloride is an example
2. Molecular solids
 - a. Discrete covalent molecules occupy lattice points
 - b. Ice and sucrose are examples
3. Atomic Solids (pure elements)
 - a. Metallic solids
 - b. Network solids
 - c. Group 8A solids

10.4 Structure and Bonding in Metals

A. Closest Packing

1. Arrangement of metallic atoms in the tightest pattern possible
 - a. Each atom has twelve nearest neighbors
 - (1) six in same layer
 - (2) three above
 - (3) three below
2. Hexagonal closest packed structure (a, b, a, b, a ...)
 - a. Each layer is identical to the layer two below it
3. Cubic closest packed structure (a, b, c, a, b, c, ...)
 - a. Each layer is identical to the layer three below it
4. Not all metals crystallize in closest packing

B. Bonding Models for Metals

1. Electron sea model
 - a. Metal cations
 - b. Mobile sea of valence electrons that conduct heat and electricity
2. Band Model (Molecular Orbital Model)
 - a. Electrons travel within molecular orbitals formed by the valence orbitals of the metallic atoms
 - b. Molecular orbitals occupied by conducting electrons are called conduction bands

C. Metal Alloys

1. Alloys are substances that contain a mixture of elements and have metallic properties
2. Substitutional alloys
 - a. Host metal atoms are replaced in the lattice by other atoms of similar size
 - (1) Brass, sterling silver, pewter
3. Interstitial alloys
 - a. Holes in the closest packed metallic structure are filled by small atoms
 - b. Carbon is often added to iron to produce steels with higher than normal hardness

10.5 Carbon and Silicon: Network Atomic Solids

A. Network Solids

1. Atomic solids with strong directional covalent bonds

B. Diamond

1. Large gap in energy between occupied orbitals and unoccupied orbitals makes diamond a poor conductor of electricity
2. Bonds formed by overlap of hybridized sp^3 orbitals

C. Graphite

1. Very strong σ bonds between carbons in fused rings using sp^2 hybridization
2. π molecular orbitals provide weaker π bonding between layers
 - a. Delocalized electrons make graphite an electrical conductor

D. Silica

1. Quartz (SiO_2) is actually based on interconnected SiO_4 tetrahedra
2. Glass is produced by quickly cooling silica, producing an amorphous solid
 - a. Other compounds added to molten silica prior to cooling produce glass with varying properties (see table 10.5)

E. Ceramics

1. Made from clays containing silicates (silicon-oxygen anions)
2. Heterogeneous
 - a. crystals of silicates suspended in a glassy cement
3. Remarkable range of uses

F. Semiconductors

1. Silicon
 - a. Energy gap between occupied and unoccupied orbitals is smaller than in diamond, allowing some electrons to be conducted
 - b. Conductivity increases with temperature
2. n-type semiconductors
 - a. "Dope" silicon with elements such as arsenic
 - (1) extra valence electron increases conductivity
3. p-type semiconductors
 - a. "Dope" silicon with elements such as boron
 - (1) shortage of valence electrons creates a "hole" that electrons fill as they move (conduct)

10.6 Molecular Solids

A. Examples

1. Water
2. Dry ice
3. P_4
4. S_8

B. Bonding

1. London dispersion forces
2. Dipole-dipole (including hydrogen bonding)
 - a. Only in polar molecules

10.7 Ionic Solids

A. Closest Packing

1. Large particles (usually anions) arrange in closest packing
2. Smaller particles (usually cations) fit into holes between anions
 - a. not all holes need be filled
3. Maximize (+) ---- (-) attraction
4. Minimize (+) ---- (+) and (-) ---- (-) repulsion

B. Types of holes

1. Trigonal holes - three spheres in the same layer
2. Tetrahedral holes - a sphere sits in the dimple of three spheres in the same layer
3. Octahedral holes - two layers of three spheres in adjoining layers

10.8 Vapor Pressure and Changes of State

A. Vaporization (Evaporation)

1. The escape of molecules of a liquid from the surface to form a gas
2. Vaporization is always endothermic
 - a. Heat of vaporization (Enthalpy of vaporization, ΔH_{vap}) is the energy required to vaporize one mole of a liquid at 1 atm

B. Vapor Pressure

1. Pressure of the vapor present at equilibrium (also called equilibrium vapor pressure)
***remember vapor pressure corrections made in gas law problems involving water displacement
2. Variation in Vapor Pressure
 - a. Liquids with high intermolecular attraction have relatively low vapor pressures
 - b. Liquids with low intermolecular attraction have relatively high vapor pressures (the are "volatile")
 - c. Vapor pressure increases with temperature
3. Clausius-Clapeyron equation

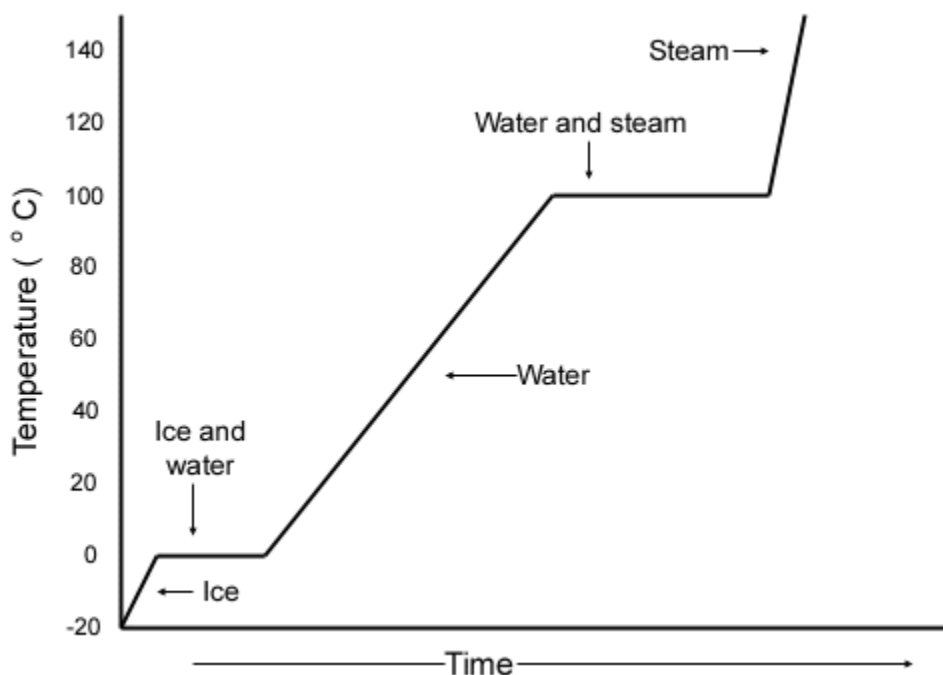
$$\ln\left(\frac{P_{T_1}^{\text{vap}}}{P_{T_2}^{\text{vap}}}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

C. Sublimation

1. A process in which a substance goes directly from the solid to the gaseous state
2. Reasons for sublimation
 - a. Solids have vapor pressure, but it is normally very low
 - b. Solids with little intermolecular attraction may have substantial vapor pressures and be able to sublime at room conditions

D. Changes of State

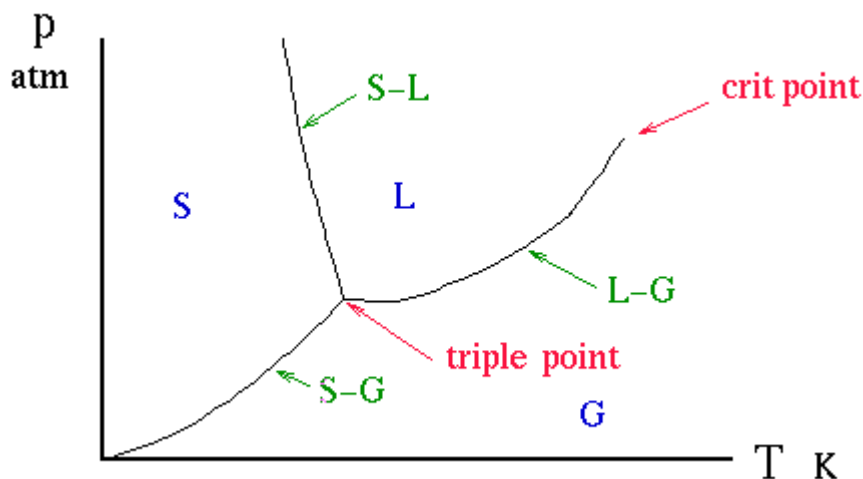
1. Heating curve



- a. Note that temperature remains constant during a phase change
 - b. Chemical bonds are not being broken during phase changes
2. Heat of fusion (Enthalpy of fusion, ΔH_{fus})
 - a. Energy required to convert a mole of solid substance to a mole of liquid substance
 3. Normal melting point
 - a. The temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is 1 atm
 4. Normal boiling point
 - a. The temperature at which the vapor pressure of the liquid is exactly 1 atmosphere
 5. Supercooling
 - a. Rapid cooling of a liquid may allow it to exist as a liquid at temperatures below its normal melting point
 - (1) quick temperature change does not allow time for molecules to become organized as they must be to become solids
 - (2) When crystallization does begin, it occurs rapidly
 6. Superheating
 - a. Rapid heating of a liquid may allow it to exist as a liquid at temperatures above the normal boiling point
 - (1) not enough high energy molecules accumulate in one place to form bubbles
 - (2) when bubbles do form, they tend to be very large
 - (3) superheating can be avoided by adding boiling chips

10.9 Phase Diagrams

A. Diagram for a closed system



1. Triple Point

- a. Solid and liquid have identical vapor pressure
- b. All three phases exist together in equilibrium

***Note that the "great outdoors" does not constitute a closed system. Seeing snow, water, and water vapor on a day at the slopes does not constitute the triple point, since the system is not closed and is not at equilibrium

2. Critical temperature

- a. The temperature above which the substance cannot exist as a liquid, regardless of how great the pressure

3. Critical pressure

- a. The pressure required to produce liquefaction at the critical temperature

4. Critical point

- a. Point defined by the critical temperature and critical pressure
- b. For water: 374°C and 218 atm

Location	Feet above sea level	P_{atm} (torr)	Boiling Point (°C)
Top of Mt. Everest, Tibet	29,028	240	70
Top of Mt. Denali, Alaska	20,320	340	79
Top of Mt. Whitney, California	14,494	430	85
Leadville, Colorado	10,150	510	89
Top of Mt. Washington, N.H.	6,293	590	93
Boulder, Colorado	5,430	610	94
Madison, Wisconsin	900	730	99
New York City, New York	10	760	100
Death Valley, California	-282	770	100.3