Chapter 10

Liquids, Solids, and Phase Changes

Polar Bonds and Polar Molecules

- Draw Lewis Structures for CCl₄ and CH₃Cl.
- What's the same?
  - What's different?

![Lewis Structures of CCl₄ and CH₃Cl]

Polar Covalent Bonds and Dipole Moments

- Bonds are polar if electrons are shared unequally (differences in electronegativity) (e.g., CH₃Cl)
- Individual bonds can be polar but can cancel each other out to yield a nonpolar molecule (e.g., CO₂)
- Molecules with a lone pair of electrons or atoms with different electronegativities are polar (have a dipole moment)

![Diagram of Chloromethane (CH₃Cl)]

Polar or Nonpolar Molecules?

- Draw Lewis Structures and Dipole Moments along each bond:
  - HCl
  - CCl₄
  - BF₃
  - CH₃Cl
  - NH₃
  - H₂O
- Worked Ex. 10.2, Problems 10.1 - 3

![Diagram of various molecules and their dipole moments]

Dipole Moments

- Polar: HCl, CCl₄, NH₃, H₂O
- Nonpolar: BF₃, CH₃Cl, H₂

![Diagram showing polar and nonpolar molecules]

Intermolecular Forces (IMF)

- Bonds: attractive forces within molecules
- Intermolecular Forces (IMF): attractive forces between molecules
- Intermolecular forces are **weaker** than bonds (intramolecular forces), but have profound effects on the properties of liquids

431 kJ/mol

![Diagram of intermolecular forces and bond strengths]
Intermolecular Forces

- What is the difference between bonds and intermolecular forces?
- IMF affect boiling points, melting points, and solubilities
- As a group, intermolecular forces are called van der Waals forces:
  - London Dispersion
  - Dipole-dipole
  - Hydrogen bonds
  - Ion-dipole

Dispersion Forces

- **London dispersion forces**: attractive forces that result from temporary shift of electrons in atoms or molecules; present in all molecules
- Explains why certain nonpolar substances (benzene, bromine, etc.) are liquids at room temperature.

Dispersion Forces

- Only force in non-polar molecules and in unbonded atoms (e.g., CO₂, Ne)
- Larger atoms or molecules have stronger London forces (and higher boiling points)
  - Larger electron clouds are easier to deform ("squishier", more polarizable) and tend to have more electrons
- Found in mixtures or pure substances

Boiling Points

- Boiling point increases with the size of molecules because of increases in London forces with larger electron clouds

Dipole-Dipole Forces

- Pure substance or mixture made up of polar molecules
- Opposite dipoles (charges) attract; like dipoles repel
- Strength of these forces depends on the polarity of the molecules

Dipole-Dipole Forces

- Like dissolves like (refers to polarity); polar liquids are more soluble in polar liquids
  - It takes 2000 mL of H₂O to dissolve 1 mL of CCl₄
  - It takes 50 mL of H₂O to dissolve 1 mL of CH₂Cl₂
- Which member of each pair has the stronger intermolecular forces?
  - CCl₄ or CHCl₃
  - CO₂ or SO₂
Boiling Points – which is higher?

Hydrogen Bonds (aka bridges)

- **Hydrogen bridge**: special type of dipole-dipole force; attractive force between a hydrogen atom bonded to a very small, electronegative atom (F, O, N) and lone e-pair
- **Ice melting**

Hydrogen Bridges

- Hydrogen bridges are seen in HF, H₂O, NH₃, but not CH₄ or H₂S
- Requirements for hydrogen bridging:
  - H attached to a small, highly electronegative element in one molecule
  - Small, highly electronegative element with one or more unshared electron pairs in the other molecule
- Observed for the elements: F, O, N (rarely S and Cl – too large, not electronegative enough)

Hydrogen Bridging Trends

Hydrogen Bridging

- Which of the following pure substances will experience hydrogen bridging?
  - H₂O
  - H₂Se
  - HBr
  - HF
  - NH₃
  - NF₃
  - DNA
Ion-Dipole Forces

- Ions have full charges that are attracted to the partial charge on polar molecules (dipoles)
- Explains solubility of ionic salts in polar solvents (e.g., NaCl in water)

![Image of NaCl in H2O](NaCl_in_H2O.png)

Figure 10.3

Ion-Ion Forces

- Strength of bonds in ionic compounds (already covered in Lattice Energy section!)

![Image of NaCl and CaF2](NaCl_CaF2.png)

Strengths of Intermolecular Forces

- Intermolecular forces generally increase in strength as:
  - London < Dipole-Dipole < H-bridging < Ion-Dipole < Ion-ion forces (ionic bonding)
- Summary:
  - Nonpolar molecules: London Dispersion
  - Polar molecules: Dipole-dipole
  - Polar with H-N, H-O, or H-F: Hydrogen bridging
  - Ionic compound: Ion-ion forces

Intermolecular Forces

- For each substance below, indicate the strongest type of intermolecular force observed.
  - H2O, CH4, HCN, CO2
  - CO, NH3, CH3OH, CO2
  - CH3Cl, H2S, CH3NH2, F2

- Worked Ex. 10.3, Problem 10.5

Trends in Intermolecular Forces

- Which member of each pair has stronger intermolecular forces (and higher boiling point)?
  - CH3OH or CH3SH
  - CH4 or CH3CH2CH3
  - CO or F2
  - CH3Cl or HF
  - CO2 or NH3
  - NH3 or N2
- Problem 10.6

Surface Tension

- Surface tension: attraction of molecules to each other on a liquid’s surface
- Molecules must break IMF in order to move to the surface and increase the surface area (large IMF, high surface tension)

![Image of surface tension](Surface_Tension.png)
**Properties of Liquids**

- Properties (e.g., IMF) in between those of gases and solids
- **Viscosity**: resistance to flow
- Depends on intermolecular forces and sizes
- Ethanol vs Glycerol

**Phase Changes**

- **fusion (melting)**: s → l
- **freezing**: l → s
- **vaporization**: l → g
- **condensation**: g → l
- **sublimation**: s → g
- **deposition**: g → s

In gases, the particles feel little attraction for one another and are free to move about randomly.

In liquids, the particles are held close together by attractive forces but are free to move over one another.

In solids, the particles are rigidly held in an ordered arrangement.

**Phase Changes - note structures**

Nitrogen molecules are weakly attracted to one another at low temperature by intermolecular forces, causing nitrogen to become liquid.

At higher temperatures, intermolecular forces are no longer able to keep molecules close together, so nitrogen becomes a gas.

**10.11 Phase Diagram: Water**

- **Phase diagram**: plot of temperature vs. pressure; solid lines are phase equilibria

**10.5 Vapor Pressure**

- Liquid evaporates, gaseous molecules exert a pressure (vapor pressure) that can be measured as shown below.

**Phase Diagram**

- Features of a phase diagram:
  - **Triple point**: temperature and pressure at which all three phases (s, l, and g) are in equilibrium
  - **Vaporization curve**: equilibrium between liquid and gas
  - **Melting curve**: equilibrium between solid and liquid
  - **Normal melting point**: melting point at 1 atm
  - **Normal boiling point**: boiling point at 1 atm

http://www.chm.davidson.edu/ChemistryApplets/PhaseChanges/PhaseDiagram.html
Critical Temperature and Pressure

- **Critical point**: liquid and gas phases are indistinguishable
- **Critical temperature, \( T_c \)**: highest temperature at which a substance can exist as a liquid (cannot be liquified) no matter how much pressure is applied
- **Critical pressure, \( T_p \)**: minimum pressure that must be applied to bring about liquefaction at the critical temperature

Phase Diagram: Carbon Dioxide

Worked Ex. 10.11, Problems 10.17, 10.18

10.6 Kinds of Solids

- Amorphous: random arrangement (rubber)
- Ionic: ordered arrangement of ions (salt)

Kinds of Solids

- Molecular (left): covalent molecules in an ordered arrangement (sucrose, ice); intermolecular forces hold molecules together
- Covalent network (right): atoms connected by covalent bonds in 3D array (quartz)

Cubic Crystal Systems

- Cubic is the most common
- Three forms of cubic crystals - simple, body-centered, face-centered