

INTERMOLECULAR FORCES, STATES AND PROPERTIES OF MATTER

INTERMOLECULAR FORCES

- Forces of attraction between particles (including the noble gases and also different parts of some large molecules) are important in determining many macroscopic properties of a substance, including how the observable physical state changes with temperature (EU 2.B)
- Chemical changes involve the making and breaking of chemical bonds. Physical changes involve overcoming weaker intermolecular forces.

Van der Waals Forces:

London Dispersion Forces

- Temporary, instantaneous dipoles can form at any time due to an uneven distribution of electrons around the nucleus.
- Induced dipoles may form in neighboring atoms due to the instantaneous dipoles.
- Dispersion forces (London forces) are attractive forces between instantaneous dipoles and induced dipoles in neighboring molecules. They arise due to Coulombic interactions between the temporary dipoles of neighboring atoms and molecules.
- Dispersion forces increase with the contact area between molecules and increasing polarizability of the molecules.
- Polarizability - how easily electron charge density is distorted by an external electric field -shows how well a dipole can be induced in an atom or molecule.
- The polarizability of a molecule increases with the number of electrons in the molecule and is enhanced by the presence of pi bonding.
- The greater the polarizability of molecules, the stronger the IMF's between them.
- Elongated molecules have stronger IMF's than compact molecules.

Dipole-Dipole Forces

- Result from the attraction among the positive ends and negative ends of polar molecules.
- The larger the dipole moment of a molecule, the stronger the IMF's and the greater the effect on physical properties.
- Intermolecular dipole-dipole forces are weaker than ionic forces or covalent bonds.
- Interactions between polar molecules are usually greater than between nonpolar molecules of comparable size because these interactions act in addition to London dispersion forces.
- Dipole induced dipole interactions are present between a polar and a non-polar molecule. The strength of these forces increases with the magnitude of the dipole of the polar molecule and with the polarizability of the nonpolar molecule.

Hydrogen Bonding

- A relatively strong type of intermolecular interaction that occurs when H is covalently bonded to N, O, or F.
- The H atom in one molecule is attracted to the non-metal atom of a neighboring molecule.
- Greatly affect boiling points, melting points etc. Even small may have strong intermolecular attractions with hydrogen bonding.

Example: For each of the following substances, comment on whether hydrogen bonding is an important intermolecular force: N₂, HI, HF, CH₃CHO, CH₃OH.

STATES OF MATTER

State	Volume	Shape	Compressible?	Particles	Intermolecular forces
gas	indefinite	indefinite	easy to compress	widely spaced, high energy	practically zero
liquid	definite	indefinite	slightly compressible	close together	stronger than gases
solid	definite	definite	difficult to compress	in contact	strong intermolecular forces

Phase Changes:

- Melting (fusion) solid → liquid
- Freezing liquid → solid
- Vaporization liquid → gas
- Condensation gas → liquid
- Sublimation solid → gas
- Deposition gas → solid

HEATING AND COOLING CURVES

- Provide insight into the energetics of solid/ liquid phase changes.

SOLIDS

- Can be **crystalline**, where the particles are arranged in regular 3-D structures or **amorphous**, where the particles do not have a regular arrangement (tars and glass).
- The motion of individual particles is limited and the particles do not undergo any overall translation with respect to each other.
- The properties of solids reflect the nature and strength of the interactions between the particles, The predominant bonding type can generally be inferred from observing the macroscopic properties of the material.

IONIC SOLIDS

- Ionic solids have interionic attractions that extend throughout the solid.

- The cations and anions are arranged in a systematic, periodic 3-D array that maximizes the attractive forces between cations and anions while minimizing the repulsive forces,
- Coulomb's law describes the forces of attraction between the cations and anions in an ionic crystal.
- Lattice energy (which measures the strength of interionic attractions) increases as the charges on the ions increase and as the ionic radii decrease.
- In general, the greater the lattice energy, the higher the melting point of the ionic solid.
- Example: Arrange the following ionic solids in order of increasing melting point: MgO, NaBr, NaCl.

Properties of Ionic Solids

- are related to their structure
- generally have low vapor pressure due to the strong Coulombic interactions of ions.
- Tend to be brittle due to the repulsion of like charges caused when one layer slides over another.
- Do not conduct electricity when solid but do when molten.
- Do conduct electricity when dissolved in water. Dissolving a solid in water and testing for conductivity is one way to identify an ionic compound.
- Tend not to dissolve in nonpolar solvents.

METALLIC SOLIDS

- Positive "cores" consisting of the nucleus and inner electrons surrounded by a sea of mobile valence electrons.
- Are good conductors of heat and electricity because the electrons are delocalized and relatively free to move.
- Are malleable and ductile because deforming the solid does not change the environment immediately surrounding each metal core.
- Have a wide range of melting points.
- Are shiny and readily alloyed.

Metal Alloys

- Mixtures of metals.
- Alloys usually retain a sea of mobile electrons and therefore still conduct.
- The chemistry of the surface is sometimes altered. Ex: The formation of an inert oxide layer in stainless steel.

Interstitial Alloys

- Form between atoms of different radius.
- The smaller atoms fill in the interstitial spaces between the larger atoms.
- The interstitial atoms make the alloy more rigid, decreasing malleability and ductility.
- Example: Steel. Carbon occupies the interstitial spaces between iron atoms.

Substitutional Alloys

- Form between atoms of similar radius
- One atom substitutes for the other in the lattice.
- Density is usually between those of the component metals.
- Alloy remains malleable and ductile.
- Example: Brass. Some copper atoms are substituted with another element such as zinc.

COVALENT NETWORK SOLIDS

- Consist of atoms that are covalently bonded together into a two dimensional or 3 dimensional network.
- Only formed from non-metals, generally in the carbon group because of their ability to form 4 bonds.
- Can be elemental (example diamond or graphite) or molecular (example silicon dioxide and silicon carbide).
- Have high melting points because all of the atoms are covalently bonded.
- 3-D covalent networks tend to be rigid and hard because the covalent bond angles are fixed.
- Are thermal insulators.
- Some conduct electricity.

Carbon Allotropes:

- **Allotrope** - 2 or more forms of an element that differ in their molecular structure.
1. **Diamond.** Each carbon is bonded to 4 other carbons in a tetrahedral structure (sp^3 hybridization). Diamonds do not conduct electricity since the particles are not free to move around. The electrons are localized.
 2. **Graphite.** Each carbon is bonded to 3 others in the same plane. 3 of the valence electrons are localized in sp^2 hybrid orbitals but the 4th valence electron is in a 2p orbital perpendicular to the plane and is between the layers of carbon atoms (delocalized). The carbon-carbon bond between the layers is longer and weaker than the carbon-carbon bonding within the layers, allowing the layers to slide over each other easily (graphite is a good lubricant). Graphite is also a good electrical conductor because the delocalized electrons can move around. Has a high melting point because the covalent bonds between the carbon atoms in each layer are relatively strong. Is soft because adjacent layers can slide past each other easily; the layers are attracted to each other by London Dispersion forces.
 3. **Fullerenes.** (Buckyballs) Roughly spherical molecules of carbon atoms (C_{60} , C_{70} , C_{74} , C_{82})
 4. **Nanotubes.** Hollow cylinders of carbon atoms.

Silicon

- is a covalent network solid and semi-conductor
- Forms a 3-D structure similar to diamond but the energy gap between the filled and empty molecular orbitals is less than in diamonds so some electrons can become excited making silicon a semi-conductor.
- Silicon's conductivity increases as temperature increases (more electrons can become excited).
- Silicon's conductivity at normal temperatures can be enhanced by *doping* the silicon with other elements.
- **n-type semi-conductors** (negative charge carrying) are formed when a small fraction of the silicon atoms is replaced by atoms having one more valence electron than silicon, such as arsenic.
- **p-type semi-conductors** (positive charge carrying) are formed when a small fraction of the silicon atoms is replaced by atoms having one less valence electron than silicon, such as boron.
- junctions between n-doped and p-doped materials are used to control electron flow and are the basis of modern electronics.

MOLECULAR SOLIDS

- Consist of nonmetals, diatomic elements, or compounds formed from two or more nonmetals.
- Are composed of distinct, individual molecules that are weakly attracted to each other.

- Are not expected to conduct electricity because their electrons are tightly held within the covalent bonds of the molecule.
- Generally have low melting points because of the relatively weak intermolecular forces.
- Are sometimes composed of very large molecules or polymers with important commercial and biological applications.

Summary of Crystalline Solids:

Crystal Type	Particles	Attractive Forces	Properties	Examples
Ionic	Cations and anions	Electrostatic interactions	Hard, high MP, brittle, nonconductors as solids (conduct when molten)	NaCl, CaCl ₂ , MgO
Molecular	Atoms or molecules	Dispersion forces, dipole-dipole, H-bonding	Soft, low MP, non-conductors in solid and liquid phases.	H ₂ O(s), HCl(s), H ₂ S, CCl ₄
Covalent (network)	Atoms	Covalent bonds between atoms (one giant covalent molecule)	Very hard, very high MP, most are non-conductors	C (diamond), C (graphite), SiC, SiO ₂
Metallic	Positive ions	Attraction between positive ions and electron clouds that extends throughout the crystal.	Ranges from very hard (Ex: W) to very soft (Ex: Au). MP ranges from very high (Ex: W MP . 3000 C) to very low (Ex: Hg MP = -39 C). Conductors in solid and liquid phases.	Cu, Ag, Fe, Hg (all metals).

PHASE CHANGES IN SOLIDS:

- **Melting Point (or freezing point)** - solid and liquid states exist in equilibrium (vary slightly with pressure).

Enthalpy of Fusion:

- The heat required to melt a given amount of solid.
- Endothermic.
- Freezing takes the same amount of energy but is exothermic.

- **Cooling curve** - plots temp v's time as a liquid cools.
- **Heating curve** - plots temp v's time as a solid melts.

LIQUIDS

- Particles are very close to each other and they are constantly moving and colliding.
- Particles are able to undergo translation.

PROPERTIES OF LIQUIDS

Surface Tension

- Molecules in a liquid attract each other therefore those in the center pull together leaving a minimal surface area (free-falling liquids tend to form spheres).
- **Surface tension** - the amount of work required to extend a liquid surface.
- Decreases with higher temperatures.
- **Adhesive forces** - intermolecular forces between unlike molecules (water molecules and the container).
- **Cohesive forces** - intermolecular forces between like molecules (the interaction between neighboring water molecules).
- If the adhesive forces are stronger than the cohesive forces, the liquid will wet the surface.
- **Meniscus** - concave if the liquid wets the surface of its container (ex: water in glass). Convex if the liquid pulls away from the container (Ex: mercury in glass).
- **Capillary action** - meniscus formation is greatly exaggerated in thin tubes, causing it to be drawn up the tube (Ex: water in a sponge).

Viscosity

- A liquid's resistance to flow.
- Decreases with higher temperatures.
- Is partly related to the strength of the IMF's - stronger IMF's give greater viscosity.

PHASE CHANGES IN LIQUIDS:

Vaporization:

- Some surface molecules have enough kinetic energy to escape the liquid - they vaporize (go into a gaseous state). The average kinetic energy of the remaining liquid is the lower and the temperature decreases.

Enthalpy of Vaporization:

- the quantity of heat that must be absorbed to vaporize a certain amount of liquid at a constant temperature.
- an endothermic process (ΔH is positive).
- Enthalpy of condensation is the same amount of heat but has the opposite sign (it is exothermic).

Example: 1. How many kilojoules of energy are required to vaporize 175 g of methanol at 25° C ($\Delta H_{\text{vap}} = 38.0$ kJ/mol methanol)? 2. To vaporize a 1.50 g sample of benzene (C_6H_6) requires 652 J of heat. What is the ΔH_{vap} of benzene?

Vapor Pressure:

- the partial pressure exerted by the vapor above a liquid in a closed container once it has reached dynamic equilibrium.
- **Dynamic equilibrium** - two opposing processes take place at the same rate.
- vapor pressures of liquids increase with temperature.
- **volatile** substances have weak intermolecular forces and high vapor pressures.
- **nonvolatile** substances have strong intermolecular forces and low vapor pressures.

Boiling Point:

- the temperature where vapor pressure equals atmospheric pressure.
- Normal boiling point - boiling point for a liquid at 1 atm.

Critical Point:

- **Critical temperature (T_c)** - the highest temperature at which liquid and vapor can coexist in equilibrium.
- **Critical pressure (P_c)** - The vapor pressure at critical temp.
- **Critical point** - corresponds to T_c and P_c .
- **Supercritical fluids** - fluids above the critical point. Supercritical fluids are used as solvents in the food industry for processes such as decaffeinating coffee.

PREDICTING PHYSICAL PROPERTIES OF SUBSTANCES:

Relative Strength of IMF's

ion-ion interactions > H-bonding > dipole-dipole > dispersion forces

- Stronger IMF's give higher boiling points and melting points.

For Ionic Substances:

- Higher charges and smaller ionic radii give higher melting points.

For Polar Substances:

- Dispersion forces are stronger with increasing molar mass and elongation of the molecules. They occur in all molecular substances. (For non-polar substances, molar mass and molecular shape are essential to consider).
- Dipole-dipole and induced dipole forces are found in polar substances. IMF's are generally stronger in polar substances. The more polar, the stronger the IMF.
- For molecules with the same IMF's, the larger the molecular mass, the higher the BP/MP.
- Example: Arrange the following substance in order of increasing boiling points: carbon tetrabromide, butane, fluorine, acetaldehyde (CH_3CHO).