Chapter 16: Phenomena

Phenomena: The tables below show melting points and boiling points of substances. What patterns do you notice from the data?

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting Point</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>2886 K</td>
<td>4123 K</td>
</tr>
<tr>
<td>Cu</td>
<td>1356 K</td>
<td>2840 K</td>
</tr>
<tr>
<td>Fe</td>
<td>1234 K</td>
<td>2485 K</td>
</tr>
<tr>
<td>Cu2Zn</td>
<td>1203 K</td>
<td>1983 K</td>
</tr>
<tr>
<td>NaCl</td>
<td>1081 K</td>
<td>1738 K</td>
</tr>
<tr>
<td>MgCl2</td>
<td>987 K</td>
<td>1691 K</td>
</tr>
<tr>
<td>Al</td>
<td>933 K</td>
<td>2740 K</td>
</tr>
<tr>
<td>MgBr2</td>
<td>984 K</td>
<td>1523 K</td>
</tr>
<tr>
<td>H2O</td>
<td>273 K</td>
<td>373 K</td>
</tr>
<tr>
<td>NO2</td>
<td>262 K</td>
<td>294 K</td>
</tr>
<tr>
<td>CCl4</td>
<td>250 K</td>
<td>349 K</td>
</tr>
<tr>
<td>C8H18</td>
<td>216 K</td>
<td>399 K</td>
</tr>
<tr>
<td>NH3</td>
<td>196 K</td>
<td>240 K</td>
</tr>
<tr>
<td>HF</td>
<td>189 K</td>
<td>293 K</td>
</tr>
<tr>
<td>Cl2</td>
<td>171 K</td>
<td>238 K</td>
</tr>
<tr>
<td>C5H12</td>
<td>143 K</td>
<td>309 K</td>
</tr>
<tr>
<td>FCl</td>
<td>119 K</td>
<td>172 K</td>
</tr>
<tr>
<td>Kr</td>
<td>116 K</td>
<td>120 K</td>
</tr>
<tr>
<td>CH4</td>
<td>91 K</td>
<td>111 K</td>
</tr>
<tr>
<td>Ar</td>
<td>84 K</td>
<td>87 K</td>
</tr>
<tr>
<td>NF3</td>
<td>66 K</td>
<td>144 K</td>
</tr>
<tr>
<td>He</td>
<td>1 K</td>
<td>4 K</td>
</tr>
</tbody>
</table>

Big Idea: Systems that form macromolecules (ionic, metallic, and covalent network) have the strongest interactions between formula units. Systems that cannot form macro molecules still contain intermolecular forces. The strength of the interactions defines the physical properties of the system. Systems with the strongest interactions are solids and weakest are gases.

Intermolecular Forces

Strongest type of interactions occur when large macromolecules can form.

- Ionic
- Covalent Network
- Metallic

Examples: Ionic: NaCl or CaCl2 | Covalent Network: C or SiO2 | Metallic: Cu or Zn

Dipole-Dipole Forces:
The attraction between dipole moments in neighboring molecules.

All polar molecules have dipole-dipole interactions.

Note: The larger the dipole, the greater the dipole-dipole forces.

Student Question

Which molecule is capable of having dipole-dipole intermolecular forces?

- a) trans-dichloroethene
- b) cis-dichloroethene
- c) Both molecules can have dipole-dipole forces
- d) Neither molecules can have dipole-dipole forces
Intermolecular Forces

- **London Dispersion Force**: The force of attraction that arises from the interaction between instantaneous electric dipoles on neighboring molecules.
  - All molecules have London dispersion interactions.

  The rapid fluctuations in the electron distribution in two neighboring molecules result in two instantaneous electric dipole moments that attract each other. The fluctuations flicker into different positions, but each molecule induces an arrangement in the other that results in mutual attraction.

  Note: London forces are also referred to as Van der Waals forces.

- The strength of the London interaction depends on the polarizability ($\alpha$) of the molecules.
  - Polarizability ($\alpha$): The ease with which the electron cloud of a molecule can be distorted.

  **Boiling**: Rapid vaporization taking place throughout a liquid.
  - This implies that the temperature is sufficient so that the atoms can overcome the intermolecular forces in the liquid phase to become a gas.
  - Therefore, the stronger the intermolecular forces the higher the boiling point.

  The boiling points of most of the molecular hydrides of the $p$-block elements show a smooth increase with molar mass in each group. However, three compounds (ammonia, water, and hydrogen fluoride) are strikingly out of line.

  This type of intermolecular force is called **Hydrogen bonding** and only occurs when a $H$ is bonded to an $N$, $O$, or $F$ atom.
Hydrogen bonding dominates all of the other types of intermolecular interactions. Hydrogen bonding is \( \sim 10\% \) as strong as a typical covalent bond.

Hydrogen bonding is strong enough to survive even in the vapor of some substances.

Example: HF contains zigzag chains of HF molecules and the vapor contains short fragments of the chains and (HF)\(_6\) rings.

Student Question

How many of the following substances can form hydrogen bonds?

- CH\(_3\)CH\(_2\)OH
- CH\(_3\)OCH\(_3\)
- H\(_2\)C=NH–CH\(_3\)
- CH\(_3\)F

a) None of the molecules form H-bonds
b) 1 of the molecules forms H-bonds
c) 2 of the molecules form H-bonds
d) 3 of the molecules form H-bonds
e) All of the molecules form H-bonds

Student Question

Predict which liquid will have the strongest intermolecular forces of attraction (neglect the small differences in molar masses).

a) CH\(_3\)COCH\(_2\)CH\(_2\)CH\(_3\)
b) CH\(_3\)CH\(_2\)CH\(_2\)CH\(_3\)OH
c) CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)OH
d) HOH–C=CH–CH=OH

Note: In a liquid, the kinetic energy of the molecules can partly overcome the intermolecular forces, allowing the molecules to move past one another.

Boiling Point: The temperature at which a liquid boils.

The higher the intermolecular forces the higher the boiling point.

Freezing Point: The temperature at which a liquid freezes.

The higher the intermolecular forces the lower the freezing point.

Viscosity: The resistance of a fluid (a gas or a liquid) to flow.

The higher the intermolecular forces the higher the viscosity.

Viscosity usually decreases as the temperature rises.

Molecules have more energy at higher temperatures and can overcome the intermolecular forces more readily.

In some cases, a change in molecular structure takes place in the course of heating, and viscosity increases.
Chapter 16 – Liquids and Solids

Liquid Interactions

- **Surface Tension**: The tendency of molecules at the surface of a liquid to be pulled inward, resulting in a smooth surface.
  - The higher the intermolecular forces the higher the surface tension.

Student Question

Which of the following should have the highest surface tension at a given temperature?

a) CF₄  
b) CCl₄  
c) CBr₄  
d) Cl₄ (carbon tetraiodide)

Liquid Interactions

- **Vapor Pressure**: The pressure exerted by the vapor of a liquid (or solid) when the vapor and the liquid (or solid) are in dynamic equilibrium.
  - The higher the intermolecular forces the higher the vapor pressure.

Note: When the vapor pressure equals the external pressure a substance boils.

Note: When the vapor pressure of liquid equals the vapor pressure of the solid the system is at the melting temperature.

Solid Structures

<table>
<thead>
<tr>
<th>Class</th>
<th>Examples</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>S₈, P₄, ice, glucose, naphthalene</td>
<td>Relatively low melting/bubbling points, and insulating</td>
</tr>
<tr>
<td>Network</td>
<td>B, C, block P, BN, SiO₂</td>
<td>Hard, rigid, brittle, very high melting/bubbling points, and insoluble in water</td>
</tr>
<tr>
<td>Metallic</td>
<td>s- and d- block elements</td>
<td>Malleable, ductile, lustrous, electrically and thermally conducting</td>
</tr>
<tr>
<td>Ionic</td>
<td>NaCl, KNO₃, CuSO₄·H₂O</td>
<td>Hard, rigid, brittle, high melting/boiling points, and those soluble in water give conducting solutions</td>
</tr>
<tr>
<td>Atomic</td>
<td>Co, I₂, K, As</td>
<td>Made of only 1 type of element; physical characteristics vary dramatically; can be used in conjunction with other class ex: H₂ atomic molecular solid</td>
</tr>
</tbody>
</table>
Solid Structures

- **Crystalline Solid**: A solid in which the atoms, ions, or molecules lie in an orderly array.
  - Examples: NaCl, diamond, and graphite

- **Amorphous Solid**: A solid in which the atoms, ions, or molecules lie in a random jumble with no long-range order.
  - Examples: glass and butter
  - Note: An amorphous solid has a structure like that of a frozen instant in the life of a liquid, with only short-range order.

- **Molecular Solids**: Assemblies of discrete molecules held in place by intermolecular forces.
  - **Amorphous Molecular Solids** (Weak Intermolecular Forces)
    - Very soft
    - Examples: Paraffin wax, which is a mixture of long-chain hydrocarbons that lie together in a disorderly way because the forces between them are so weak.
  - **Crystalline Molecular Solids** (Strong Intermolecular Forces)
    - Hard
    - Brittle
    - Examples: Sucrose molecules C$_{12}$H$_{22}$O$_{11}$ are held together by hydrogen bonding between their numerous –OH groups

- **Network Solids**: Consist of atoms covalently bonded to their neighbors throughout the extent of the solid.
  - Hard
  - Rigid
  - High Melting Points
  - High Boiling Points
  - Ceramics (tend to be network solids)
  - Examples: Diamond and graphite

- **Allotropes**: Alternative forms of an element that differ in the way in which the atoms are linked.

- **Metallic Solids**: Also called metals, consist of cations held together by a sea of electrons.
  - Note: Because the interaction between the nuclei and the electrons is the same in any direction, the arrangement of the cations can be modeled as hard spheres stacked together.

- [Left] Quartz is a crystalline form of silica, SiO$_2$, with the atoms in an orderly network, represented here in two dimensions. [Right] When molten silica solidifies in an amorphous arrangement, it becomes glass and atoms form a disorderly network.
Chapter 16 – Liquids and Solids

Solid Structures

Student Question

Calculate the interplanar distance that has a second order reflection of 43.2° for x-rays of wavelength of 0.141 nm.

a) 0.103 nm
b) 0.169 nm
c) 0.193 nm
d) 0.412 nm
e) None of the Above

Solid Structures

Unit Cell: The smallest unit that, when stacked together repeatedly without any gaps and without rotations, can reproduce the entire crystal.

Primitive Cubic
Body Centered Cubic (BCC)
Face Centered Cubic (FCC)

Note: Unit cells do not have to be square.

Solid Structures

Closed-Packed Structure: A crystal structure in which atoms occupy the smallest volume with the least empty space.

Hexagonal Closed-Packed Structure (hcp)

Solid Structures

Closed-Packed Structure: A crystal structure in which atoms occupy the smallest volume with the least empty space.

Hexagonal Closed-Packed Structure (hcp)

Solid Structures

Coordination Number (Metals): The number of nearest neighbors of each atom.

What is the coordination number for the hcp unit cell?
3 nearest neighbors in the plain below
6 nearest neighbors in the plain of the atom
3 nearest neighbors in the plain above

Coordination Number = 12

Solid Structures

Cubic Closed-Packed Structure (ccp)

Note: The coordination number is still 12 for ccp.
Solid Structures

Tetrahedral Holes:
- Made when 4 atoms come together

Octahedral Holes:
- Made when 6 atoms come together

Note: The holes in the close-packed structure of a metal can be filled with smaller atoms to form alloys.

Chapter 16 – Liquids and Solids

Ionic Solids: Are built from the mutual attractions of cations and anions.

Example: Metal and a non-metal, NaCl, MgBr₂, K₂O

Note: For ionic species the unit cell must reflect the stoichiometry of the compound and be electrically neutral.

Note: Cations (Na⁺) are usually smaller than anions (Cl⁻)

Note: This structure has a radius ratio (ρ) between 0.4 and 0.7

Note: Other structures that have the rock salt structure include: KBr, RbI, MgO, CaO, and AgCl

The cesium chloride structure is found for compounds whose cations and anions are similar in size to each other (ρ > 0.7).

Note: Other structures that have the cesium chloride structure include: Salt, Ox, TlCl, and TIlBr

The zinc-blend structure occurs for structures who cations and anions differ in size greatly, ρ < 0.4. In the zinc-blend structure the cations are located in the tetrahedral holes of a cubic closed-packed system.

Note: Other structures that have the cesium chloride structure include: Salt, Ox, TlCl, and TIlBr

Note: This structure has a radius ratio (ρ) between 0.4 and 0.7

Note: Other structures that have the zinc-blend structure include: CdZn, ZnO, CuO, and AgCl

Rock-Salt Structure

This structure is found in compounds whose cations and anions differ in size. The cations are located in the octahedral holes of the cubic closed-packed structure.

Green = Anions
Orange = Cations

Note: Cations (Na⁺) are usually smaller than anions (Cl⁻)

Note: This structure has a radius ratio (ρ) between 0.4 and 0.7

Note: Other structures that have the rock salt structure include: KBr, RbI, MgO, CaO, and AgCl

Zinc-Blend

Zn²⁺
Solid Structures

- **Coordination Number ( Ionic Solids):** The number of opposite charged ions immediately surrounding a specific ion.
  - In the rock-salt structure the coordination number of Na⁺ (orange) is 6 and the coordination number of Cl⁻ (green) is also 6.
  - NaCl is said to have (6,6)-coordination [(cation, anion)-coordination]

  **Note:** Cesium chloride structures have (8,8)-coordination and zinc-blend structures have (4,4)-coordination.

Heating Curves/Phase Diagrams

- **Heat of Fusion (ΔH\text{fus}):** The amount of heat that needs to be supplied to turn a solid into a liquid.
- **Heat of vaporization (ΔH\text{vap}):** The amount of heat that needs to be supplied to turn a liquid into a gas.

Heating Curve of H₂O

- **Supercooled:** Refers to a liquid cooled to below its freezing point.

- **Triple Point:** The point where three phases (solid, liquid, gas) meet in a phase diagram. Under the conditions represented by the triple point, all three adjoining phases are in dynamic equilibrium.

- **Critical Pressure:** The pressure required to produce liquefaction (a liquid) at the critical temperature.
- **Critical Temperature:** The temperature above which the vapor cannot be liquefied no matter what pressure is applied.
- **Critical Point:** The point defined by the critical pressure and critical temperature.
The normal boiling point of the substance with the phase diagram shown below is ______ °C.

- a) 10
- b) 15
- c) 40
- d) 50
- e) None of the Above
Take Away From Chapter 16

- **Heating Curves/Phase Diagrams**
  - Be able to draw/interpret heating curve (91, 96)
  - $\Delta H_{\text{vap}} > \Delta H_{\text{fus}}$ (13)
  - Slope of the line inversely proportional to heat capacity
  - Be able to interpret phase diagram (103)
  - Know where and what triple point, critical point, and each phase should be located
  - Know that the slope of the solid/liquid line should favor the more dense phase