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>Cu$_2$Zn</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>MgCl$_2$</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>MgBr$_2$</td>
<td>984 K</td>
<td>1523 K</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>273 K</td>
<td>373 K</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>262 K</td>
<td>294 K</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>250 K</td>
<td>349 K</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting Point</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>8$H$</em>{18}$</td>
<td>216 K</td>
<td>399 K</td>
</tr>
<tr>
<td>NH$_3$</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>Cl$_2$</td>
<td>171 K</td>
<td>238 K</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{12}$</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>CH$_4$</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>NF$_3$</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.
Strongest type of interactions occur when large macromolecules can form.

**Examples:**
- Ionic: NaCl or CaCl₂
- Covalent Network: C or SiO₂
- Metallic: Cu or Zn
Intermolecular forces are responsible for the existence of different phases.

**Phase:** A specific state of matter.

**Examples:** Solid, liquid, or gas
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.
Which molecule is capable of having dipole-dipole intermolecular forces?

- **trans-Dichloroethene**
- **cis-Dichloroethene**

**Options:**

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

**Note:** Larger molecules with many electrons are more polarizable than small molecules, therefore, the London interactions play larger role for big molecules than small ones.
**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 effectiveness of London forces also depends on the shapes of molecules.

Molecules of pentane are relatively long and rod shaped. Therefore, the instantaneous partial charges on adjacent rod-shaped molecules can be in contact at several points, leading to strong interactions.

<table>
<thead>
<tr>
<th></th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pentane</strong> C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;12**&lt;/sub&gt;</td>
<td>36°C</td>
</tr>
<tr>
<td><strong>2,2-dimethylypropane</strong> C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;12**&lt;/sub&gt;</td>
<td>10°C</td>
</tr>
</tbody>
</table>
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.
How many of the following substances can form hydrogen bonds?

CH₃CH₂OH, CH₃OCH₃, H₃C–NH–CH₃, CH₃F

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) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$

b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

d) $\text{HOH}_2\text{C}=\text{CH}=\text{CH}=\text{CH}_2\text{OH}$
Although in a liquid the molecules remain in contact with their neighbors, they can move away from one another and have enough energy to push through to a new neighbor. Consequently, the entire substance is fluid.

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

- **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 higher the freezing point.

**Note**: The normal boiling and freezing points are the boiling and freezing point at 1 atm.
Liquid Interactions

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

  **Note:** The higher the viscosity, the slower the 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.
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.
Liquid Interactions

How do we get the $P_{vap}$ at another temperature?

$$\ln(P_{vap_1}) = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1}\right) + C$$

$$\ln(P_{vap_2}) = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2}\right) + C$$

Subtract the two equations from each other

$$\ln(P_{vap_1}) - \ln(P_{vap_2}) = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1}\right) + C - \left(-\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2}\right) + C\right)$$

$$\ln\left(\frac{P_{vap_1}}{P_{vap_2}}\right) = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{P_{vap_2}}{P_{vap_1}}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
Using the following data determine $\Delta H_{vap}$ for the unknown liquid.

<table>
<thead>
<tr>
<th>Vapor Pressure (atm)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>200.</td>
</tr>
<tr>
<td>12.2</td>
<td>300.</td>
</tr>
<tr>
<td>42.9</td>
<td>400.</td>
</tr>
<tr>
<td>90.9</td>
<td>500.</td>
</tr>
</tbody>
</table>

a) $5.53 \times 10^{-6} \frac{kJ}{mol}$
b) $0.00247 \frac{kJ}{mol}$
c) $12.5 \frac{kJ}{mol}$
d) $249 \frac{kJ}{mol}$
e) None of the Above
### 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, naphthalen</td>
<td>Relatively low melting/boiling points, and insulating</td>
</tr>
<tr>
<td>Network</td>
<td>B, C, black P, BN, SiO₂</td>
<td>Hard, rigid, brittle, very high melting/boiling 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.
Solid Structures

- **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.
Solid Structures

Crystalline Ice

Amorphous Ice
Solid Structures

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.
Solid Structures

- (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.
Solid Structures

**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.
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.

**Note:** Unit cells do not have to be square.
Solid Structures

(a) Primitive cubic
(b) Body-centered cubic
(c) Face-centered cubic (ccp)
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)**

- Atom in third layer lies over atom in first layer.
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)

An atom in every fourth layer lies over an atom in the first layer.

Unit cell

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.
Solid Structures

HCP
Tetrahedral Holes

Octahedral Holes

Layers: A B A

CCP
Tetrahedral Holes

Octahedral Holes

Layers: C B A
Solid Structures

**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.
Solid Structures

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

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 ($\rho > 0.7$).

**Cesium Chloride Structure**

Green = Anions
Orange = Cations

**Note:** Other structures that have the cesium chloride structure include: CsBr, CsI, TICl, and TIBr
The zinc-blend structure occurs for structures where cations and anions differ in size greatly, $\rho < 0.4$. In the zinc-blend structure, the cations are located in the tetrahedral holes of a cubic closed-packed system.
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
Heat of Fusion ($\Delta H_{\text{fus}}$): The amount of heat that needs to be supplied to turn a solid into a liquid.

Heat of vaporization ($\Delta H_{\text{vap}}$): The amount of heat that needs to be supplied to turn a liquid into a gas.
Supercooled: Refers to a liquid cooled to below its freezing point.
**Triple Point:** The point where three phases boundaries meet in a phase diagram. Under the conditions represented by the triple point, all three adjoining phases are in dynamic equilibrium.
Heating Curves/Phase Diagrams

- **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.
Heating Curves/Phase Diagrams

Sulfur Phase Diagram

- Monoclinic
  - 153°C, 1420 atm

- Rhombic
  - 95.39°C, 1 atm
  - 115.18°C, 3.2 × 10⁻⁵ atm
  - 95.31°C, 5.1 × 10⁻⁶ atm

- Liquid
  - 115.21°C, 1 atm

- Gas
  - 444.6°C, 1 atm
**CO₂ Phase Diagram**

Pressure-Temperature phase diagram for CO₂.
Heating Curves/Phase Diagrams

**Student Question**

The normal boiling point of the substance with the phase diagram shown below is ______ °C.

![Phase Diagram](image)

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

Big Idea: Systems that form macro molecules (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** (11, 12)
  - Be able to identify what intermolecular forces are present. (15, 16)
    - Dipole-Dipole
      - Molecule must be polar.
      - The larger the dipole moment the larger the force.
    - London Dispersion
      - Present in all molecules.
      - The larger the molecule the larger the force.
      - The more contact the molecule can make with other molecules the larger the force.

Numbers correspond to end of chapter questions.
Take Away From Chapter 16

- **Intermolecular Forces (continued)**
  - H-Bonding
    - Present when a H is bonded to a F, N, or O.

- **Liquid Interactions**
  - Know the definition of the following and how the strength of intermolecular forces affects each.
    - (9, 16, 17, 19, 20, 21, 22, 23, 27, 29, 126)
  - Boiling Point
    - Larger the intermolecular forces the higher the boiling point.
  - Freezing Point
    - Larger the intermolecular forces the higher the freezing point.
  - Viscosity
    - Larger the intermolecular forces the larger the viscosity.
  - Surface Tension
    - Larger the intermolecular forces the larger the surface tension.

Numbers correspond to end of chapter questions.
Take Away From Chapter 16

**Liquid Interactions (continued)**
- Vapor Pressure (7,81)
  - Larger the intermolecular forces the smaller the vapor pressure.
- Be able calculate the vapor pressure from experimental data.(86,87,89)
  \[
  \ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T}\right) + C
  \]
  \[
  \ln\left(\frac{P_{\text{vap}}^1}{P_{\text{vap}}^2}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
  \]

**Solid Structure**
- Know the types of solids and be able to classify solids by their types. (33,40)
  - Molecular, covalent network, metallic, ionic, and atomic
- Know that x-ray diffraction can be used to determine the internuclear spacing in crystalline solids.(43)
  \[
  n\lambda = 2d \sin\theta
  \]
- Know that unit cells are the smallest unit that when stacked together makes the overall crystal.

Numbers correspond to end of chapter questions.
Solid Structure (Continued)

- Be able to calculate the number of atoms per unit cell. (78)
- Be able to calculate the density based on unit cell. (45, 48)
- Be able to calculate the atomic radii based on unit cell.
- Know that many metals have closed packed structures.
- Know how to predict, \( \rho = \frac{r_{\text{smaller}}}{r_{\text{larger}}} \), which structure ionic compounds will form.
  - \( \rho > 0.7 \) cesium chloride structure
  - \( 0.7 > \rho > 0.4 \) rock salt structure
  - \( \rho < 0.4 \) zinc-blend
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

Numbers correspond to end of chapter questions.