

Chapter 16: Phenomena

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

Substance	Melting Point	Boiling Point
CaO	2,886 K	4,123 K
Cu	1,356 K	2,840 K
Fe	1,234 K	2,485 K
Cu ₂ Zn	1,203 K	1,983 K
NaCl	1,081 K	1,738 K
MgCl ₂	987 K	1,691 K
Al	933 K	2,740 K
MgBr ₂	984 K	1,523 K
H ₂ O	273 K	373 K
NO ₂	262 K	294 K
CCl ₄	250 K	349 K

Substance	Melting Point	Boiling Point
C ₈ H ₁₈	216 K	399 K
NH ₃	196 K	240 K
HF	189 K	293 K
Cl ₂	171 K	238 K
C ₅ H ₁₂	143 K	309 K
FCI	119 K	172 K
Kr	116 K	120 K
CH ₄	91 K	111 K
Ar	84 K	87 K
NF ₃	66 K	144 K
He	1 K	4 K

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.

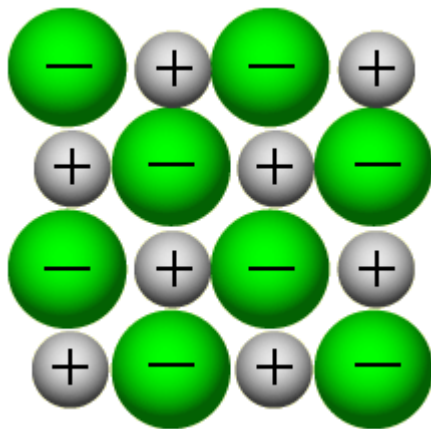
Chapter 16 – Liquids and Solids

- Intermolecular Forces
- Liquid Interactions
- Solid Structures
- Heating Curves/Phase Diagrams

Intermolecular Forces

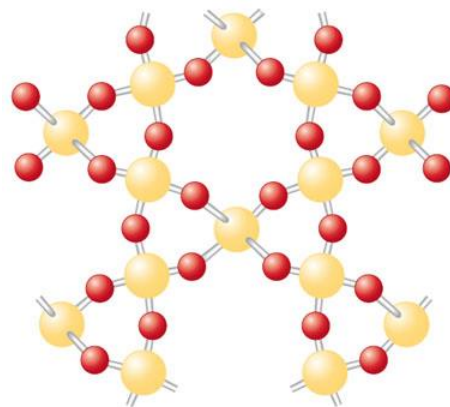
- Strongest type of interactions occur when large macromolecules can form.

Ionic

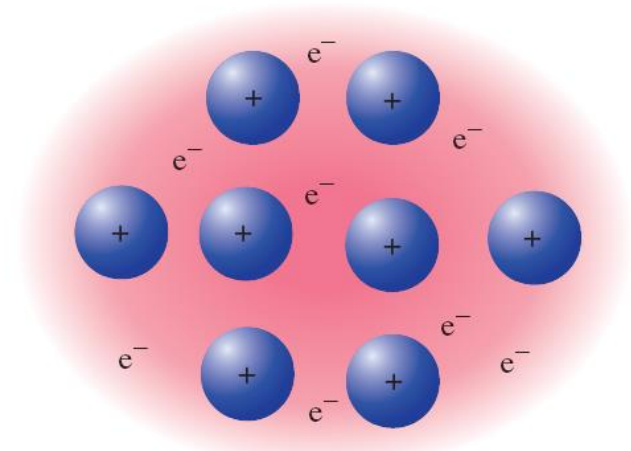


Metal and
Nonmetals

*Covalent
Network*



Metallic



Metals

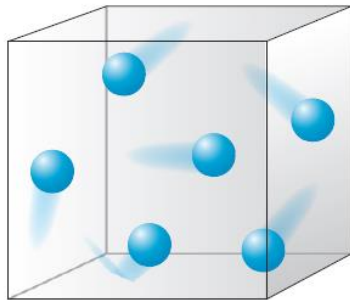
Examples: Ionic: NaCl or CaCl₂ | Covalent Network: C or SiO₂ | Metallic: Cu or Zn

Intermolecular Forces

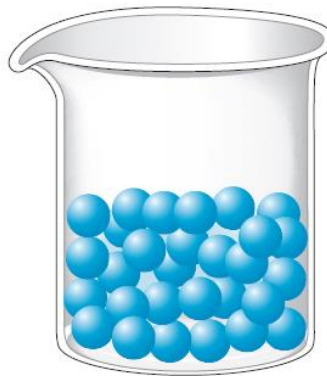
Intermolecular forces are responsible for the existence of different phases.

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

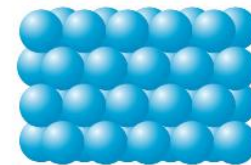
Examples: Solid, liquid, or gas



Gas



Liquid



Solid

Intermolecular Forces

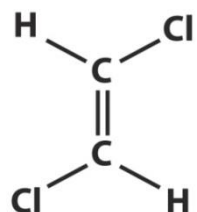
- **Dipole-Dipole Forces:** The attraction between dipole moments in neighboring molecules.
- All **polar** molecules have dipole-dipole interactions.

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

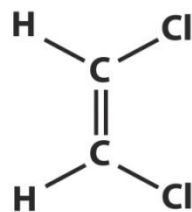
Intermolecular Forces

Student Question

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



6 *trans*-Dichloroethene



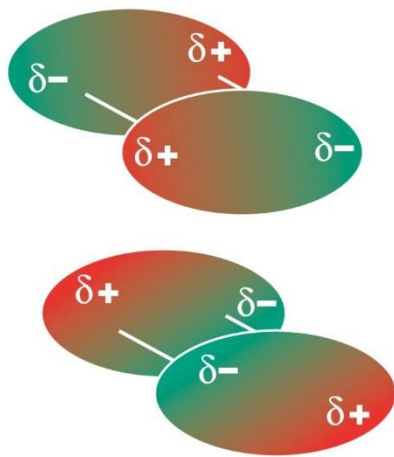
5 *cis*-Dichloroethene

- 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.

Intermolecular Forces

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

1 H 1.00794							2 He 4.0026
3 Li 6.941	4 Be 9.01218	5 B 10.811	6 C 12.011	7 N 14.0067	8 O 16.00	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.305	13 Al 27.98	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K	20 Ca	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra						

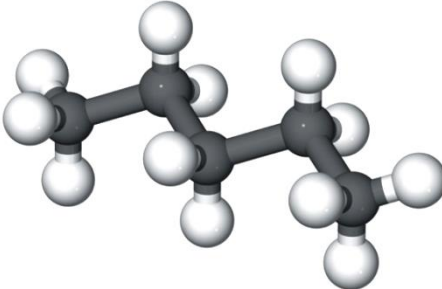
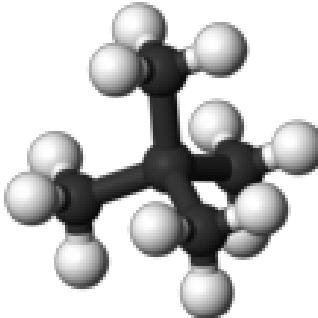
Note: Larger molecules with many electrons are more polarizable than small molecules, therefore, the London interactions play larger role for big molecules than small ones.

Intermolecular Forces

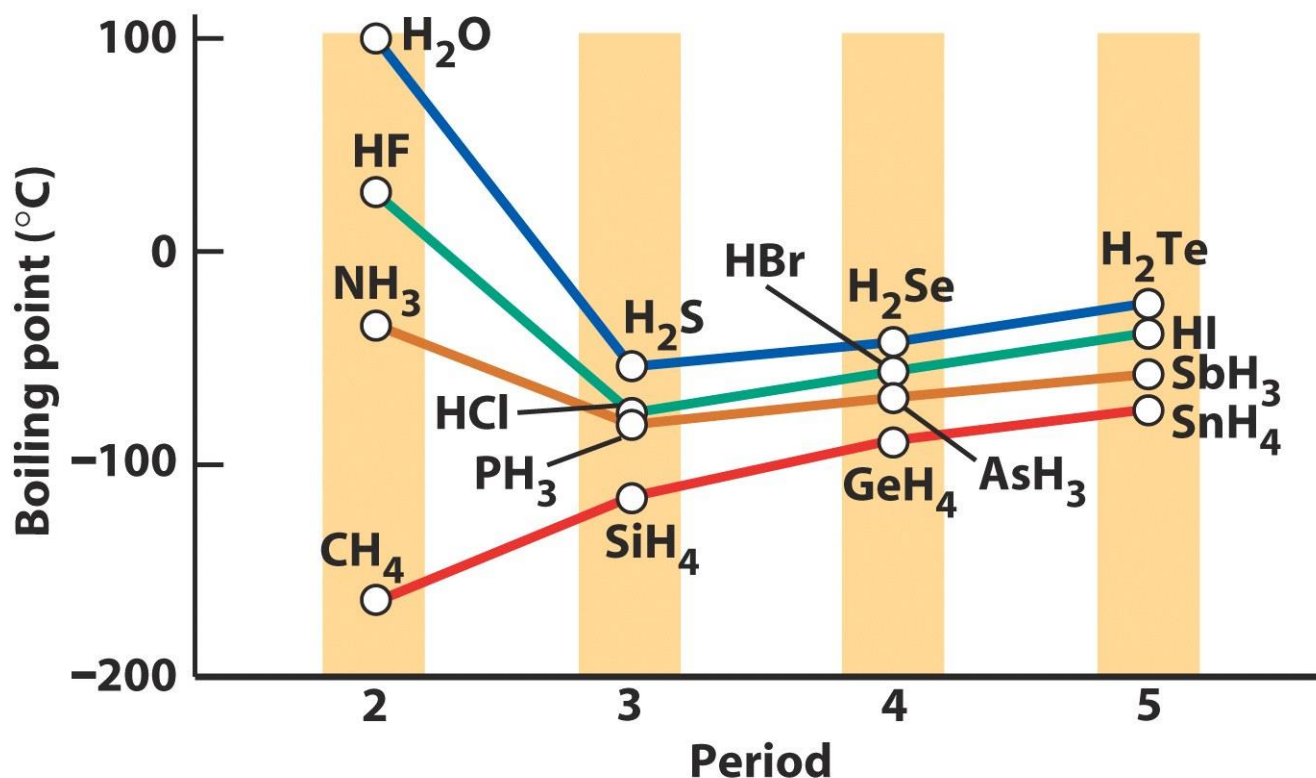
- **Boiling:** Rapid vaporization taking place throughout a liquid.
- This implies that the temperature is sufficient so that the atoms can overcome the intermolecular forces in the liquid phase to become a gas.
- Therefore, the stronger the intermolecular forces the _____ the boiling point.

Intermolecular Forces

- 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.

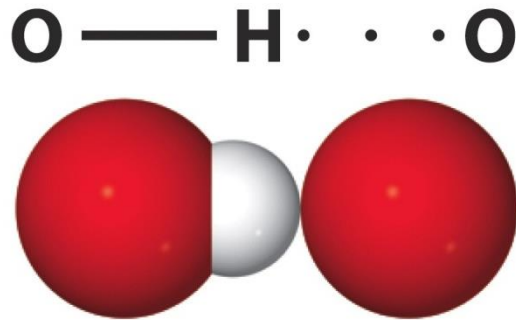
	Boiling Point
Pentane C_5H_{12} 	36°C
2,2-dimethylpropane C_5H_{12} 	10°C

Intermolecular Forces



- 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.

Intermolecular Forces

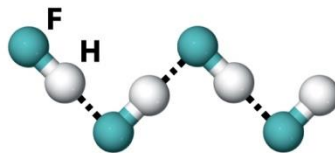


- The electronegative O atom exerts a strong pull on the electrons in the bond and the proton of the H atom is almost completely unshielded. Because it is so small, the hydrogen atom with its partial positive charge can get very close to one of the lone pairs of electrons on the O atom of another water molecule. The lone pair and the partially positive charge attract each other strongly and form a hydrogen bond.
- This type of intermolecular force is called **Hydrogen bonding** and **only occurs** when a **H** is bonded to an **N, O, or F** atom.

Intermolecular Forces

- Hydrogen bonding dominates all of the other types of intermolecular interactions. Hydrogen bonding is ~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 $(\text{HF})_6$ rings



11 Hydrogen Fluoride, $(\text{HF})_n$

Intermolecular Forces

Student Question

How many of the following substances can form hydrogen bonds?



- 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

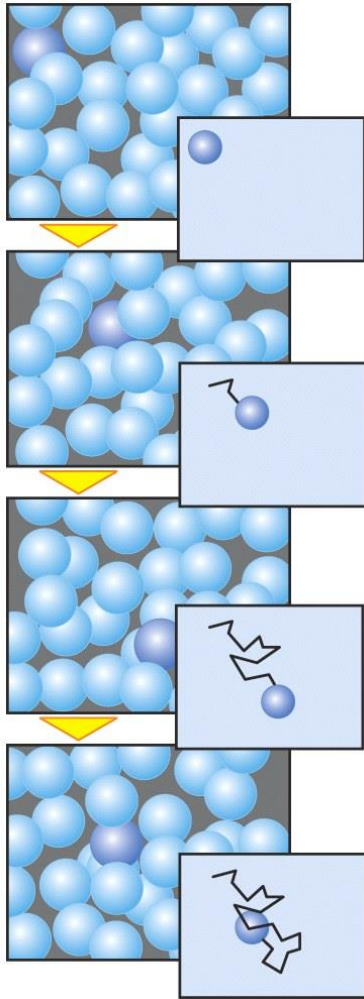
Intermolecular Forces

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) $\text{HOH}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$

Liquid Interactions



- 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 _____ the boiling point.

- **Freezing Point:** The temperature at which a liquid freezes.
- The higher the intermolecular forces the _____ the freezing point.

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

Liquid Interactions

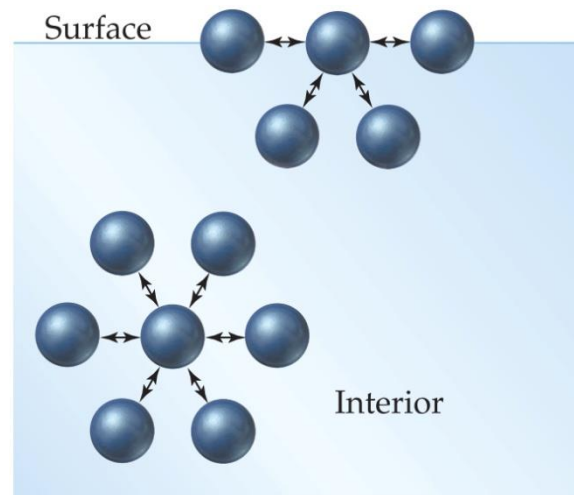
- **Viscosity:** The resistance of a fluid (a gas or a liquid) to flow.

Note: The higher the viscosity, the slower the flow.

- The higher the intermolecular forces the _____ 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 surface tension.

Student Question

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

- a) CF_4
- b) CCl_4
- c) CBr_4
- d) CI_4 (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 _____ 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?

$$\ln(P_{\text{vap}_1}) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1}\right) + C$$

$$\ln(P_{\text{vap}_2}) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2}\right) + C$$

Subtract the two equations from each other

$$\ln(P_{\text{vap}_1}) - \ln(P_{\text{vap}_2}) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1}\right) + C - \left(-\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2}\right) + C\right)$$

$$\ln\left(\frac{P_{\text{vap}_1}}{P_{\text{vap}_2}}\right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{P_{\text{vap}_1}}{P_{\text{vap}_2}}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Liquid Interactions

Student Question

Using the following data determine ΔH_{vap} for the unknown liquid.

Vapor Pressure (atm)	Temperature (K)
1.00	200.
12.2	300.
42.9	400.
90.9	500.

- a) $5.53 \times 10^{-6} \frac{\text{kJ}}{\text{mol}}$ b) $0.00247 \frac{\text{kJ}}{\text{mol}}$
c) $12.5 \frac{\text{kJ}}{\text{mol}}$ d) $249 \frac{\text{kJ}}{\text{mol}}$
e) None of the Above

Solid Structures

Class	Examples	Characteristics
Molecular	S ₈ , P ₄ , ice, glucose, naphthalen	Relatively low melting/boiling points, and insulating
Network	B, C, black P, BN, SiO ₂ , semiconductors	Hard, rigid, brittle, very high melting/boiling points, and insoluble in water
Metallic	s- and d- block elements	Malleable, ductile, lustrous, electrically and thermally conducting
Ionic	NaCl, KNO ₃ , CuSO ₄ ·H ₂ O	Hard, rigid, brittle, high melting/boiling points, and those soluble in water give conducting solutions
Atomic	Co, I ₂ , K, As	Made of only 1 type of element; physical characteristics vary dramatically; can be used in conjunction with other class ex: H ₂ atomic molecular solid

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.

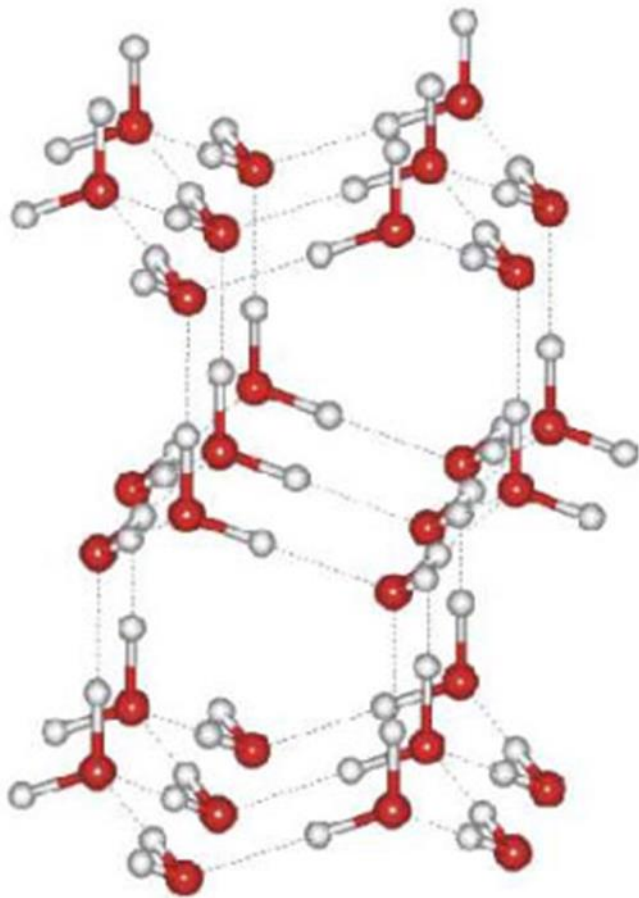
- **Crystalline Molecular Solids** (Strong Intermolecular Forces)

- Hard
- Brittle

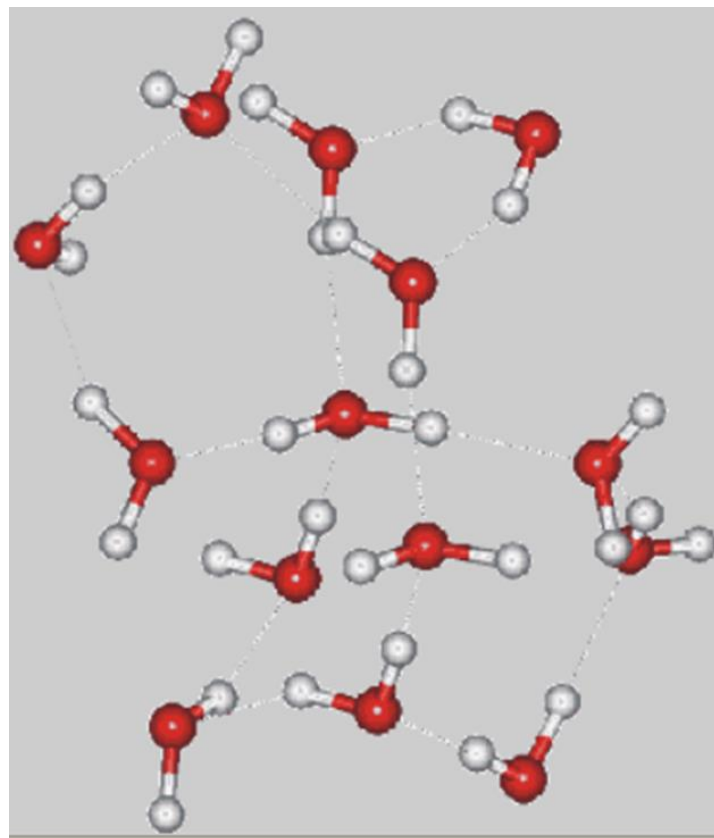
Examples: Sucrose molecules $C_{12}H_{22}O_{11}$ are held together by hydrogen bonding between their numerous -OH groups

Solid Structures

Crystalline Ice



Amorphous Ice

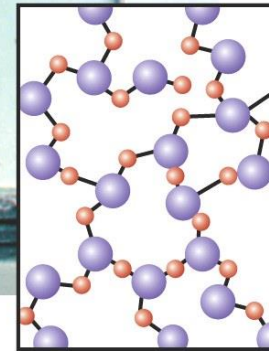
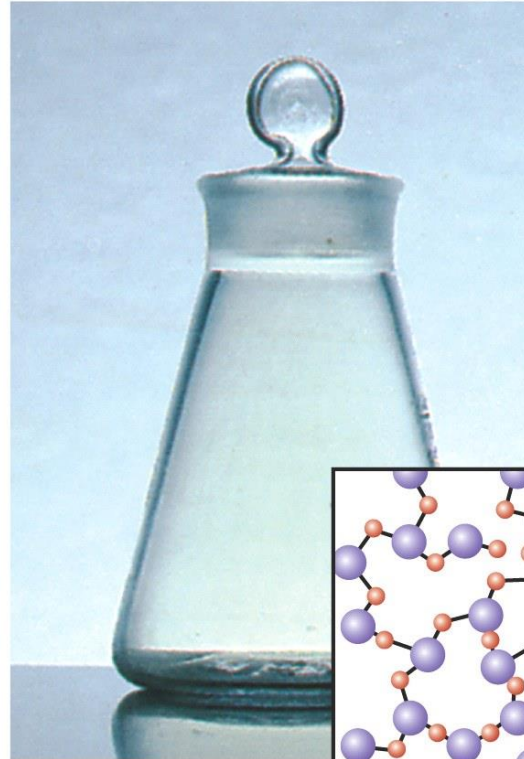
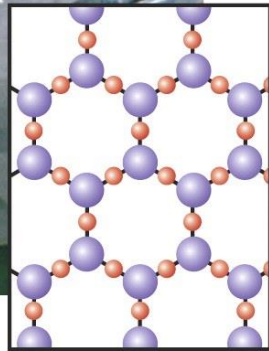
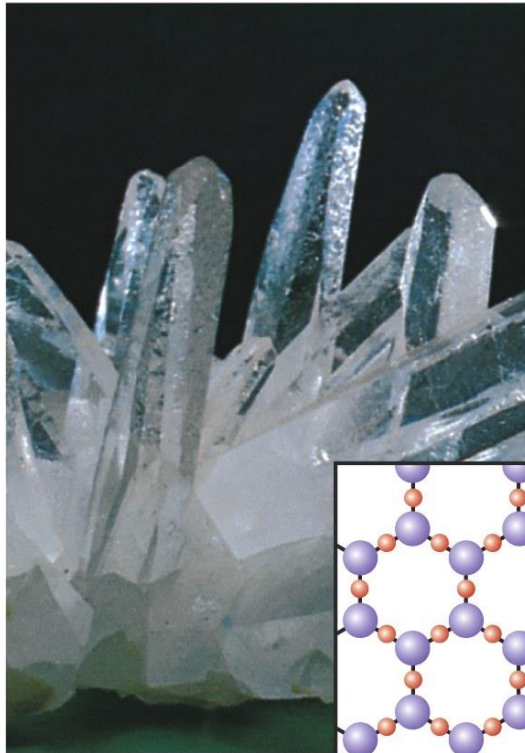


- **Network Solids:** Consist of atoms covalently bonded to their neighbors throughout the extent of the solid.
 - Hard
 - Rigid
 - High Melting Points
 - High Boiling Points
 - Ceramics (tend to be network solids)

Examples: Diamond and graphite

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

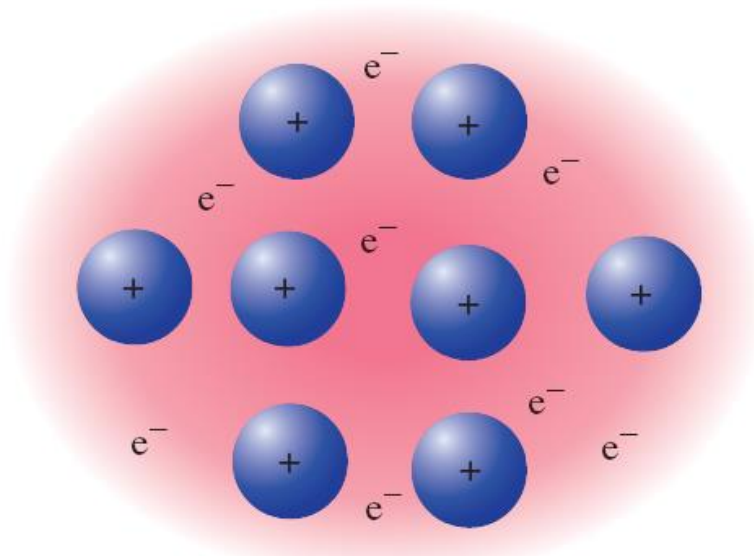
Solid Structures



- (Left) Quartz is a crystalline form of silica, SiO₂ 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.

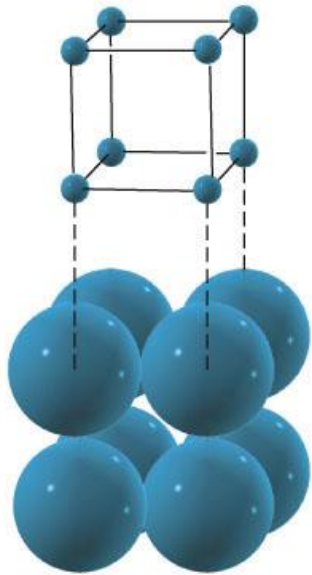
Student Question

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

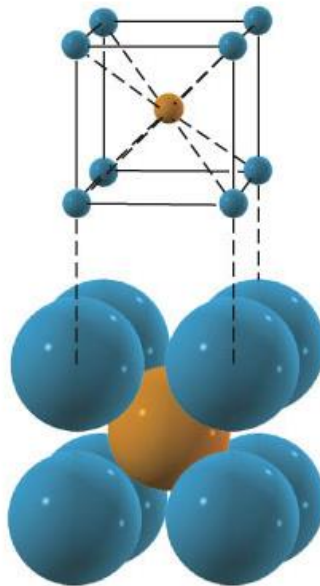
- a) 0.103 nm
- b) 0.169 nm
- c) 0.193 nm
- d) 0.412 nm
- e) None of the Above

Solid Structures

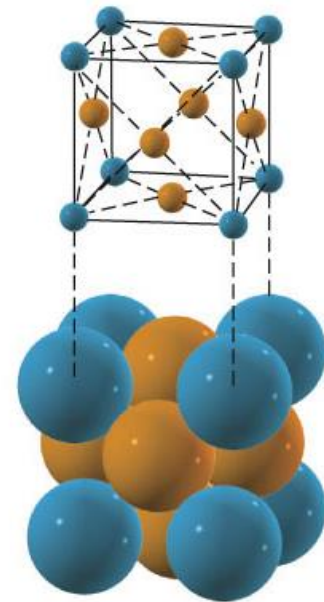
- **Unit Cell:** The smallest unit that, when stacked together repeatedly without any gaps and without rotations, can reproduce the entire crystal.



Primitive Cubic



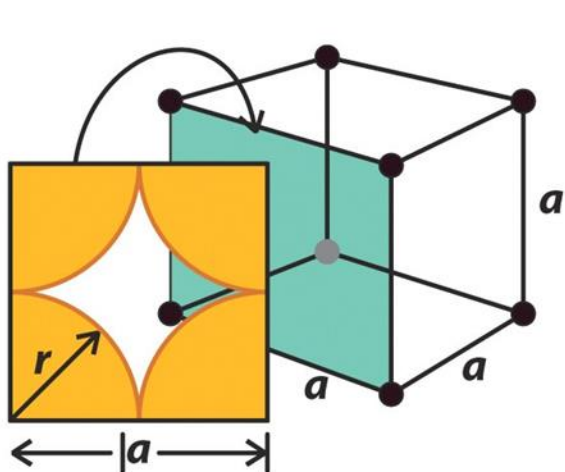
**Body Centered Cubic
(BCC)**



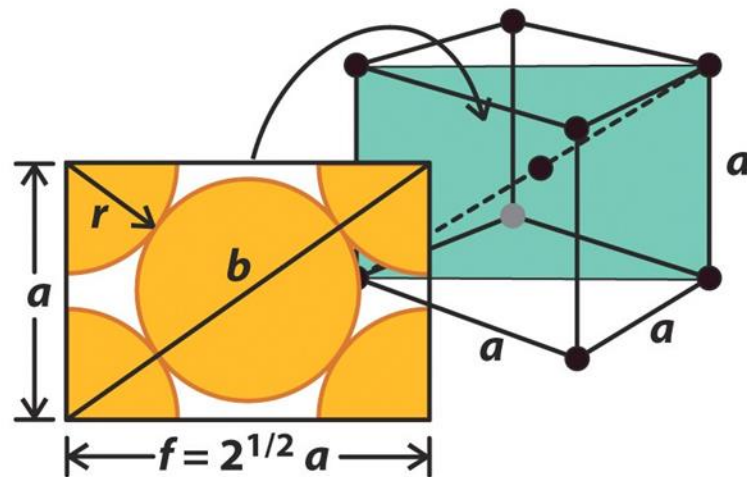
**Face Centered Cubic
(FCC)**

Note: Unit cells do not have to be square.

Solid Structures

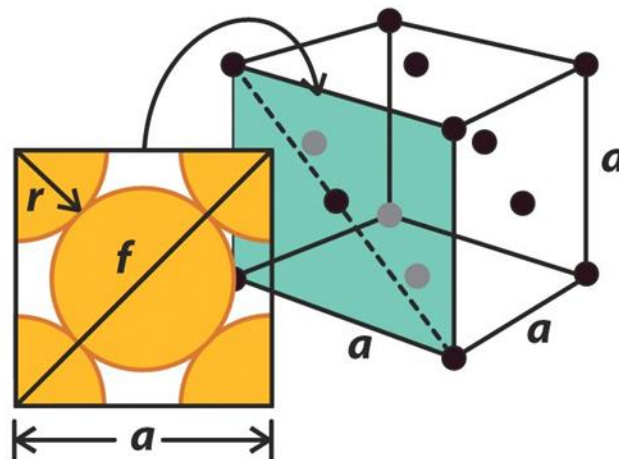


(a) Primitive cubic



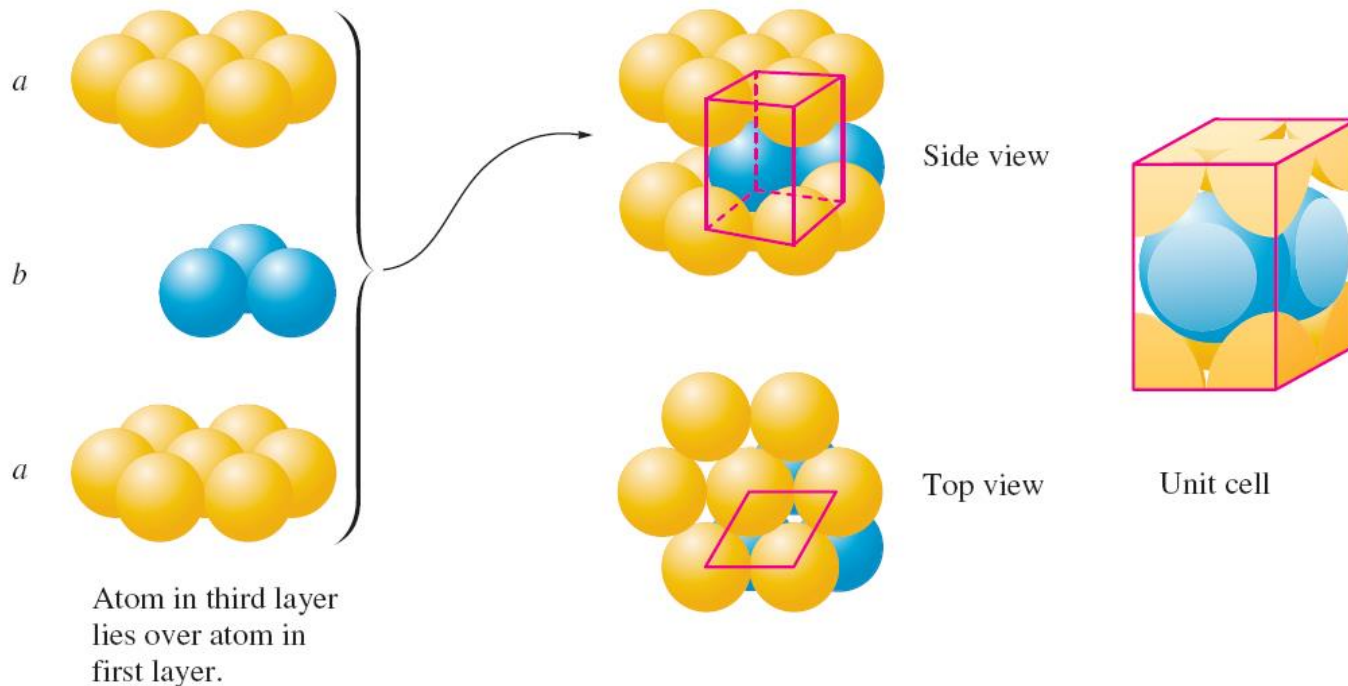
(b) Body-centered cubic

(c) Face-centered cubic (ccp)



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

Hexagonal Closed-Packed Structure (hcp)



- **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



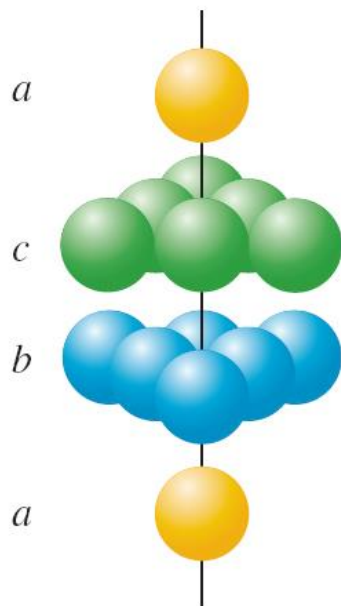
6 nearest neighbors
in the plain of the atom



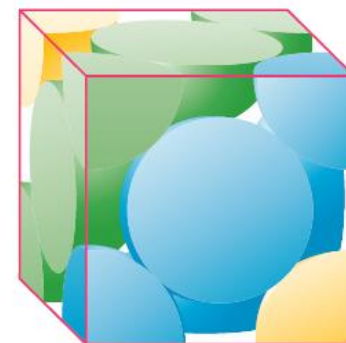
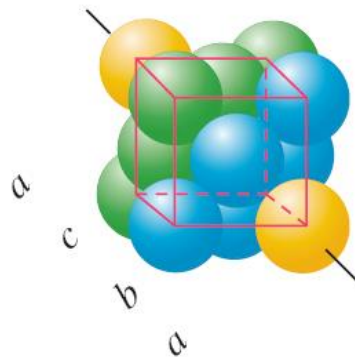
3 nearest neighbors
in the plain above

Coordination Number = 12

○ Cubic Closed-Packed Structure (ccp)

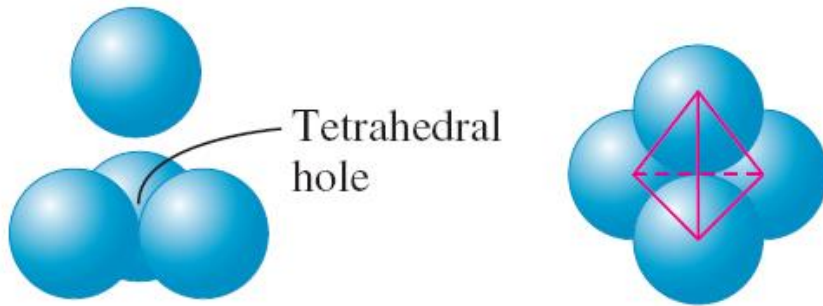


An atom in every fourth layer lies over an atom in the first layer.



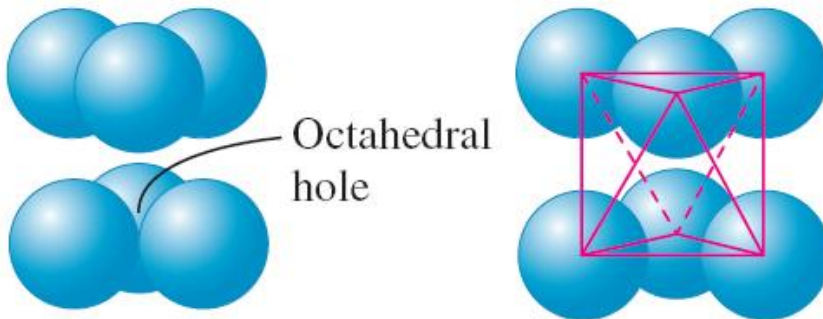
Unit cell

Note: The coordination number is still 12 for ccp.



Tetrahedral Holes:

- Made when 4 atoms come together



Octahedral Holes:

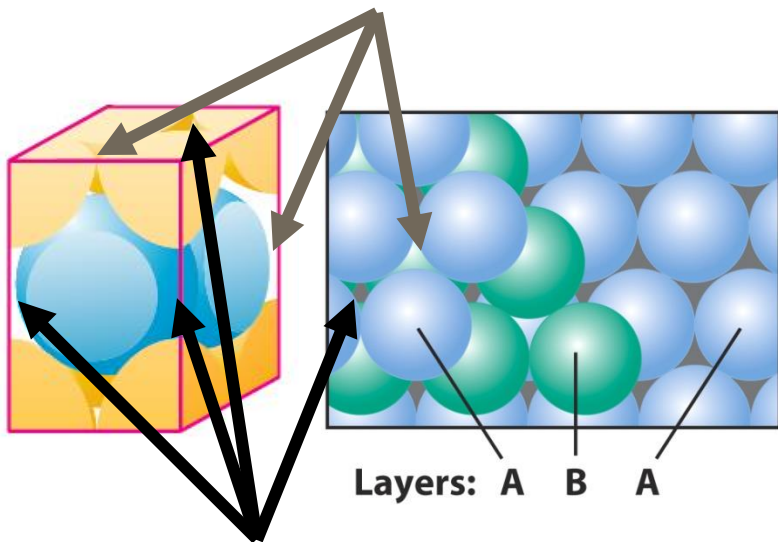
- Made when 6 atoms come together

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

Solid Structures

HCP

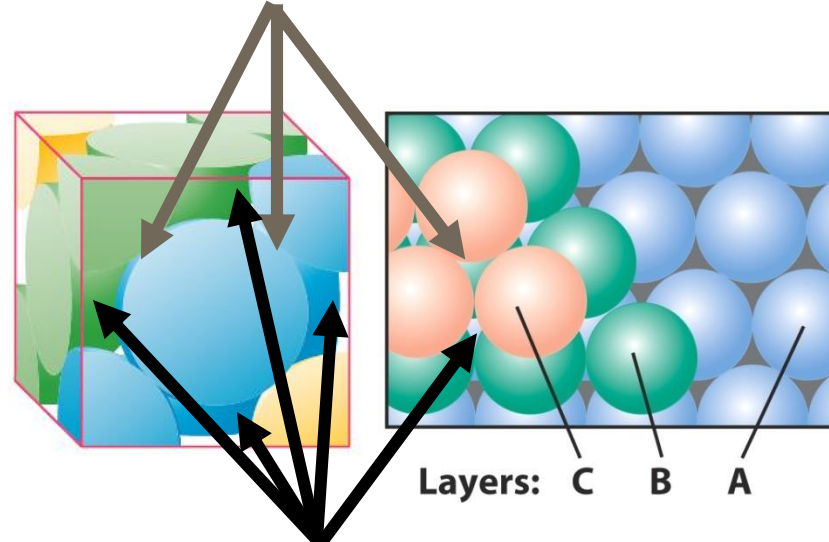
Tetrahedral Holes



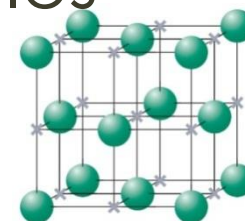
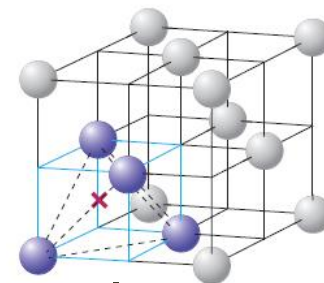
Octahedral Holes

CCP

Tetrahedral Holes

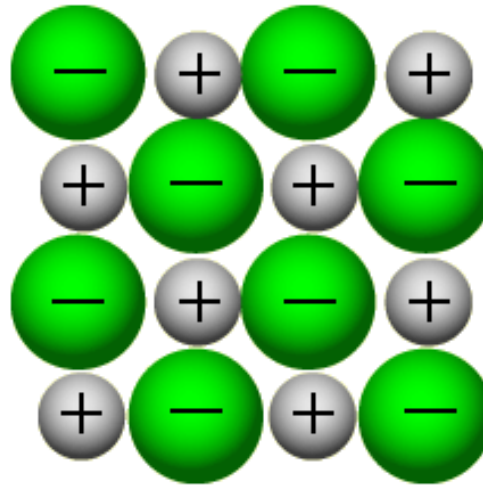


Octahedral Holes



Solid Structures

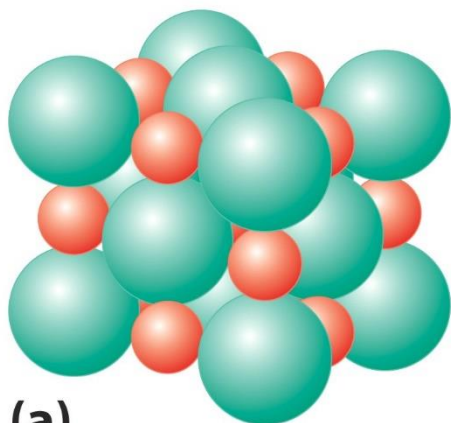
- **Ionic Solids:** Are built from the mutual attractions of cations and anions.



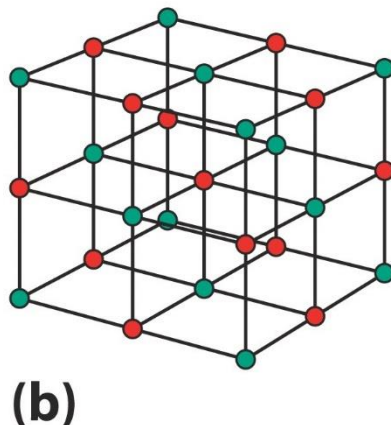
Example: Metal and a non-metal, NaCl, MgBr₂, K₂O

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

Rock-Salt Structure



Green = Anions
Orange = Cations



- 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.

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

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

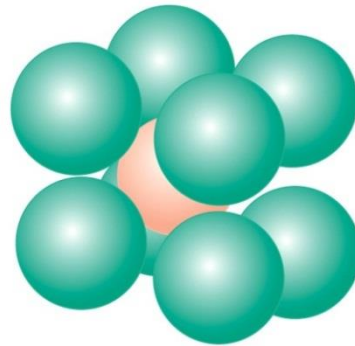
Note: Other structures that have the rock salt structure include:
KBr, RbI, MgO, CaO, and AgCl

Solid Structures

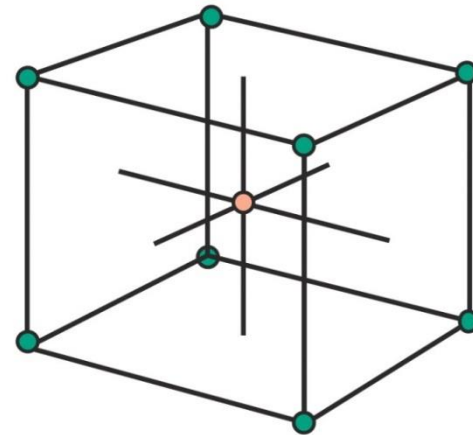
- The cesium chloride structure is found for compounds whose cations and anions are similar in size to each other ($\rho > 0.7$).

Cesium Chloride Structure

Green = Anions
Orange = Cations



(a)

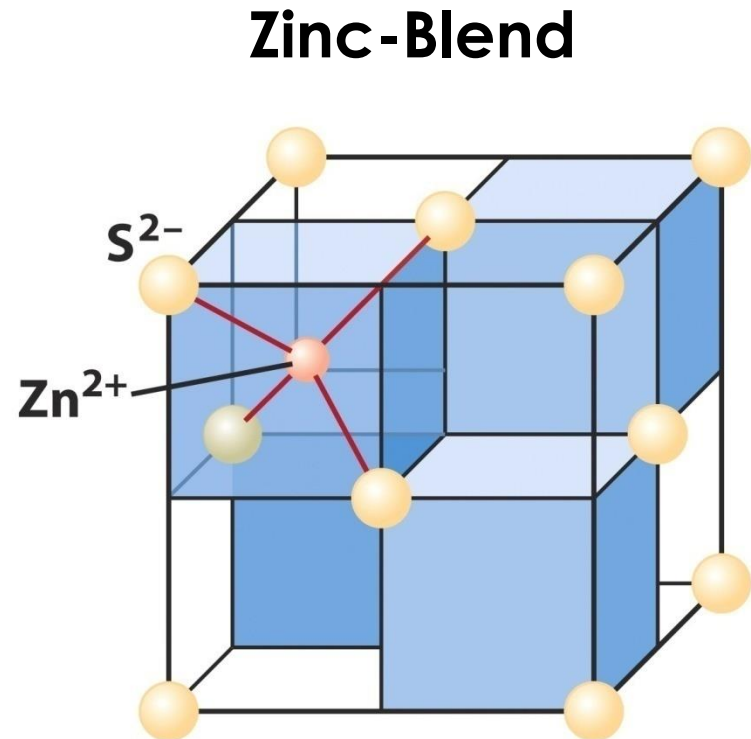


(b)

Note: Other structures that have the cesium chloride structure include:
CsBr, CsI, TlCl, and TlBr

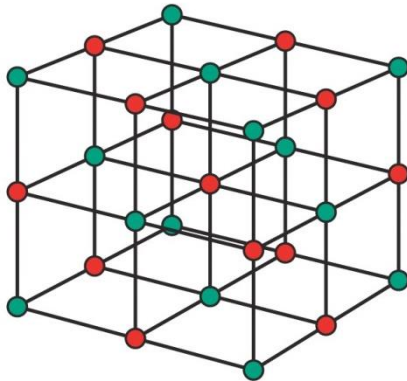
Solid Structures

- 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.



Solid Structures

- **Coordination Number (Ionic Solids):** The number of opposite charged ions immediately surrounding a specific ion.



(b)

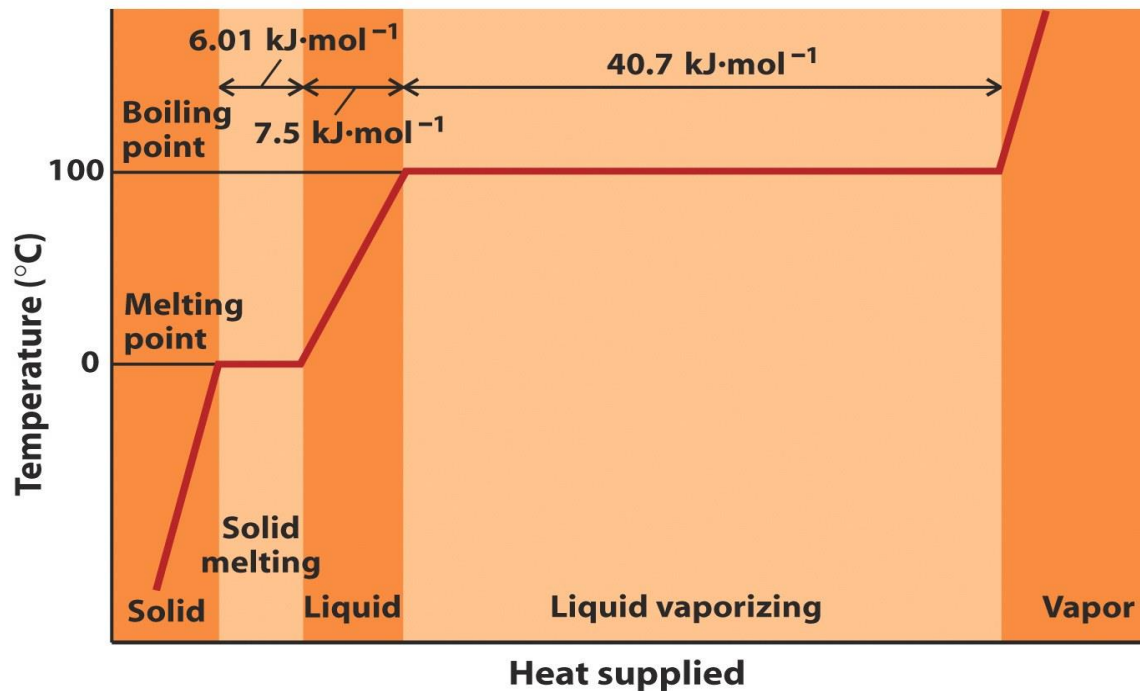
Green = Anions
Orange = Cations

- 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

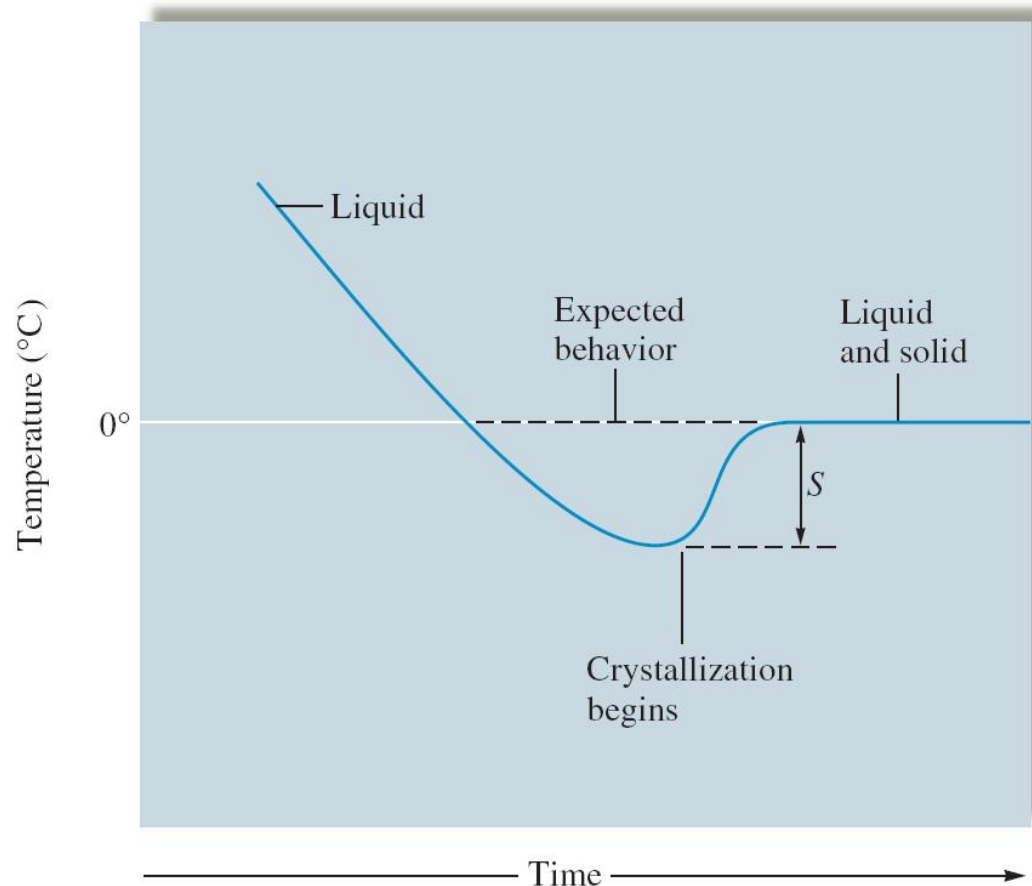
Heating Curves/Phase Diagrams

Heating Curve of H₂O



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

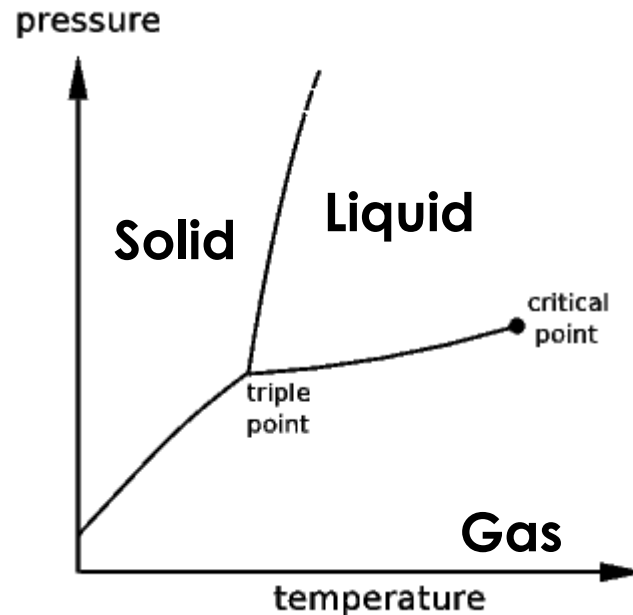
Heating Curves/Phase Diagrams



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

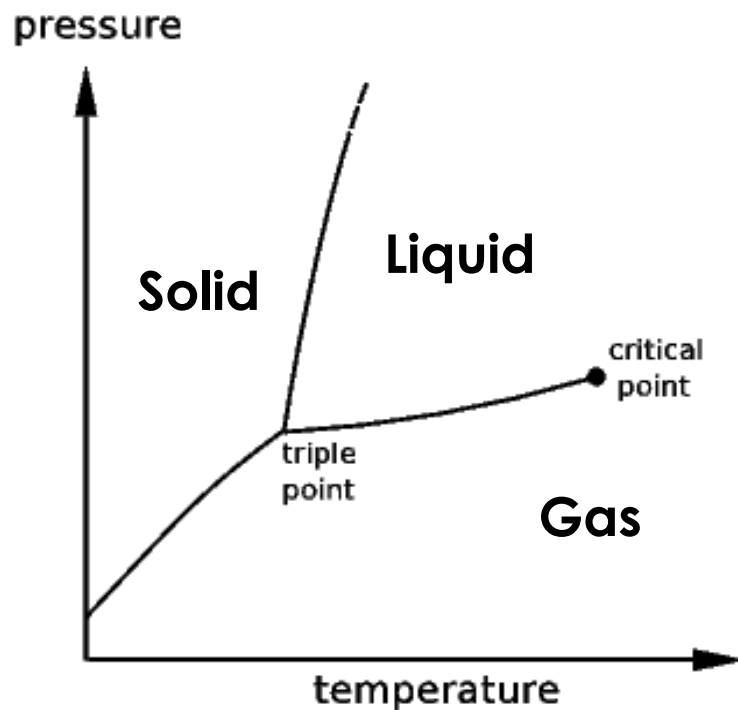
Heating Curves/Phase Diagrams

Phase Diagram



- **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.

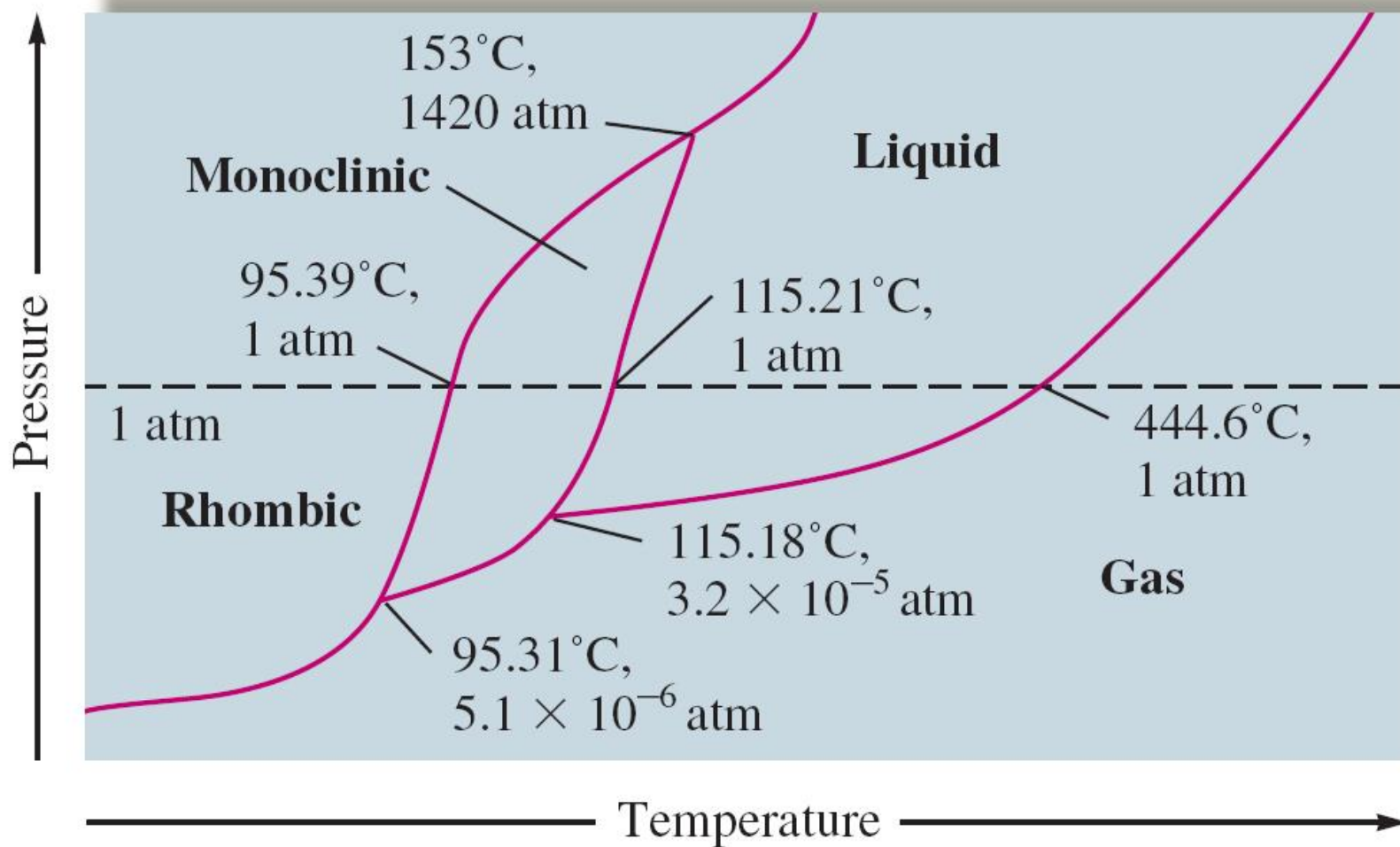
Heating Curves/Phase Diagrams



- **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

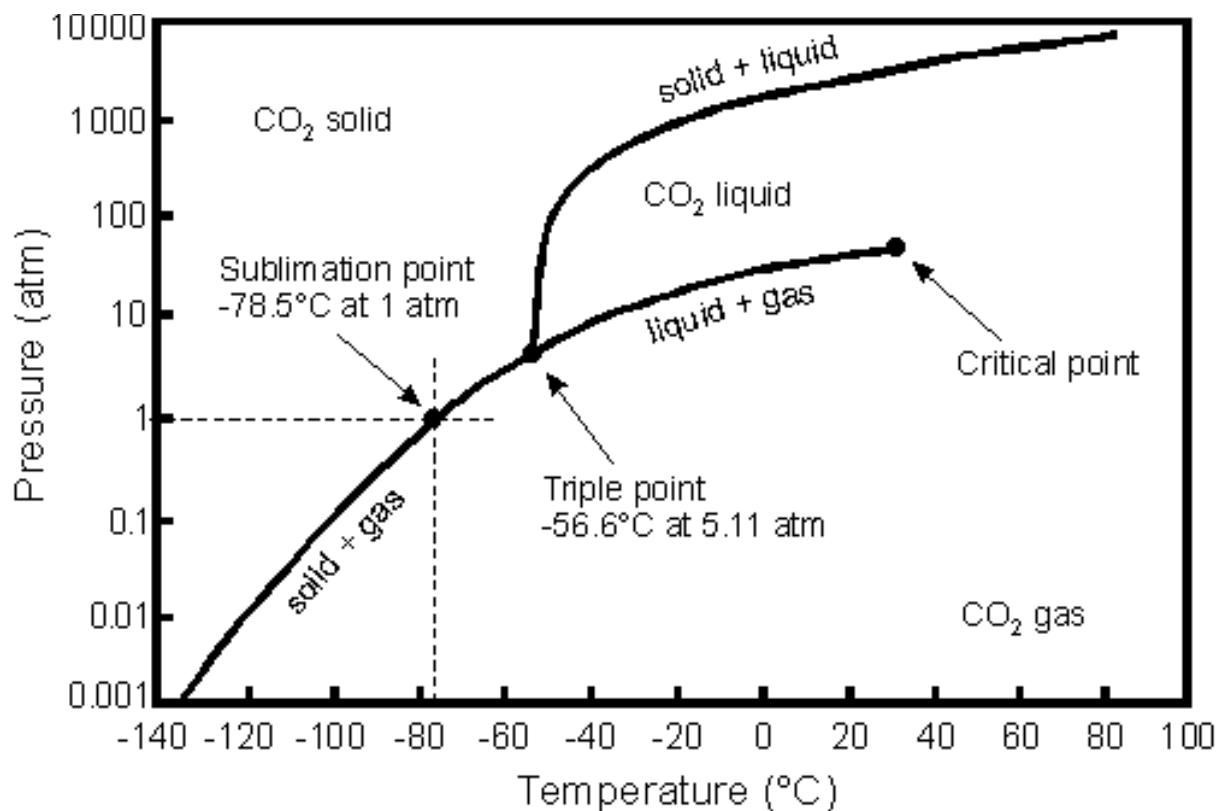
Heating Curves/Phase Diagrams

● Sulfur Phase Diagram



Heating Curves/Phase Diagrams

● CO₂ Phase Diagram

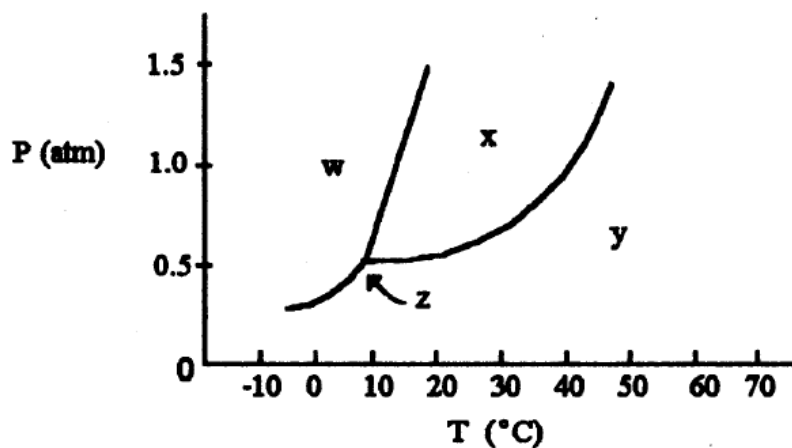


Pressure-Temperature phase diagram for CO₂.

Heating Curves/Phase Diagrams

Student Question

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



- 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 effects 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)
 - $\ln(P_{vap}) = -\frac{\Delta H_{vap}}{R} \left(\frac{1}{T}\right) + C$
 - $\ln\left(\frac{P_{vap}^1}{P_{vap}^2}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

○ 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.

Take Away From Chapter 16

○ 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, $\rho = \frac{r_{smaller}}{r_{larger}}$, 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

Numbers correspond to end of chapter questions.

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.