

CHEMISTRY

Chapter 10

Liquids and Solids



CHAPTER 10: LIQUIDS AND SOLIDS

10.1 Intermolecular Forces

10.2 Properties of Liquids

10.3 Phase Transitions

10.4 Phase Diagrams

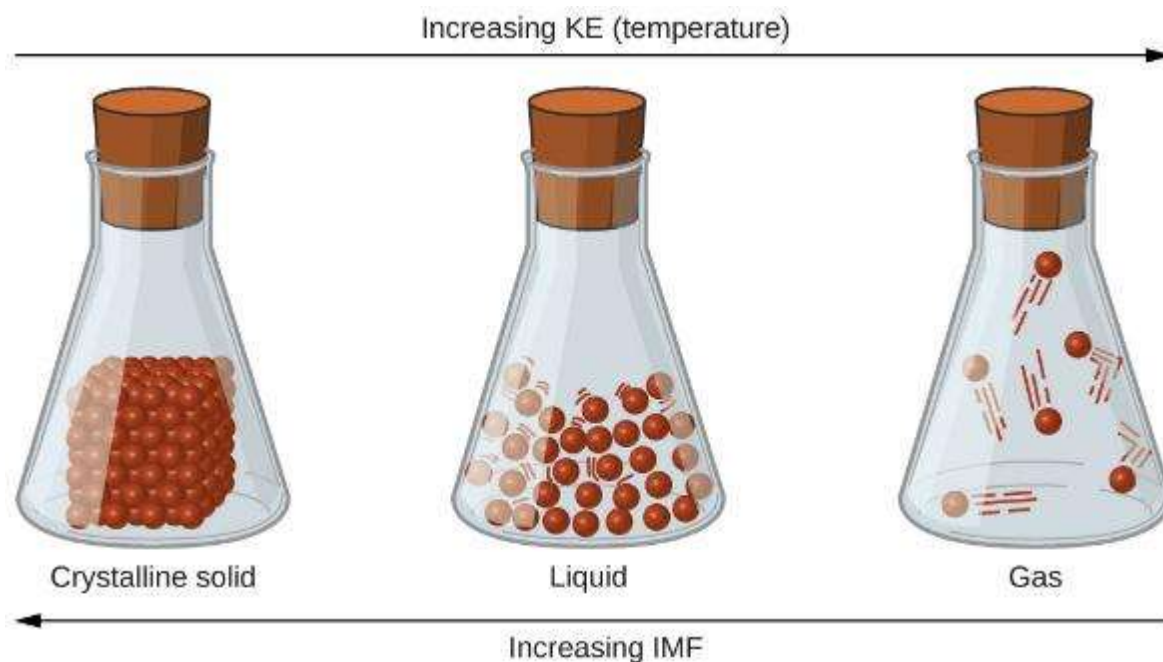
10.5 The Solid State of Matter

10.6 Lattice Structures in Crystalline Solids

10.1 INTERMOLECULAR FORCES

Molecular Structure and Physical Properties

- When discussing an ideal gas, two assumptions were made:
 - Particles are point masses and do not have volume.
 - There are no intermolecular interactions between particles.
- In liquids and solids, the atoms and molecules are very close together and intermolecular forces are very important.



10.1 INTERMOLECULAR FORCES

Atoms/Molecules in Solids and Liquids

- In a solid, particles:
 - are tightly packed and often arranged in a regular pattern.
 - vibrate about fixed positions and do not generally move in relation to one another.
- In a liquid, particles:
 - are close together but have no regular arrangement.
 - can move past each other but remain in constant contact with other particles.
- In a gas, particles:
 - are separated by large distances and have no regular arrangement.
 - move independently except when they collide.

10.1 INTERMOLECULAR FORCES

Solids, Liquids, and Gases

- The different behaviors of solids, liquids, and gases reflect the strength of the attractive forces between the particles in each phase.
- The phase of substance depends upon the extent of the intermolecular forces and the kinetic energies of its atoms or molecules.



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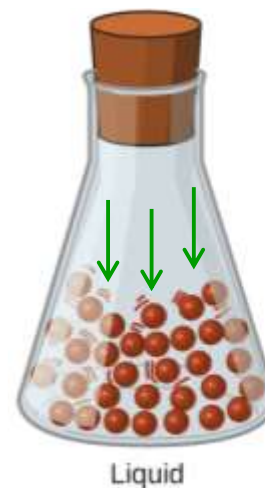
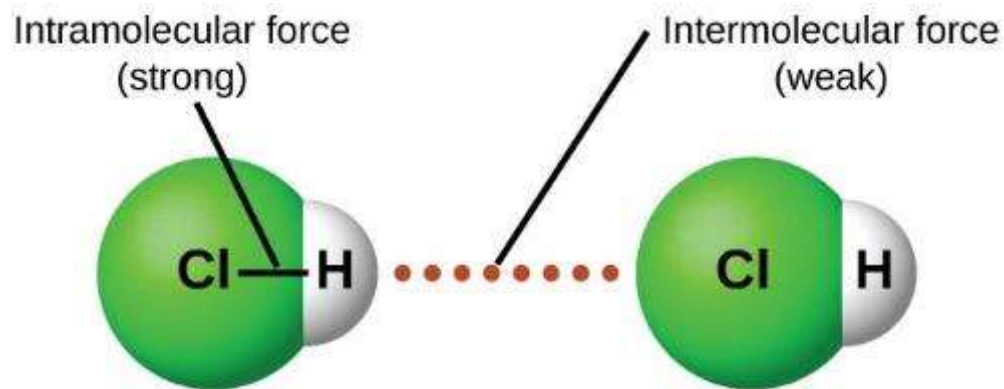


(b)

10.1 INTERMOLECULAR FORCES

Forces Between Molecules

- Under certain conditions, the forces between gas molecules will cause them to form liquids or solids.
 - Intermolecular forces occur between separate molecules.
 - Intramolecular forces such as bonds occur within a molecule.
- Intermolecular forces between molecules give a substance its physical properties.

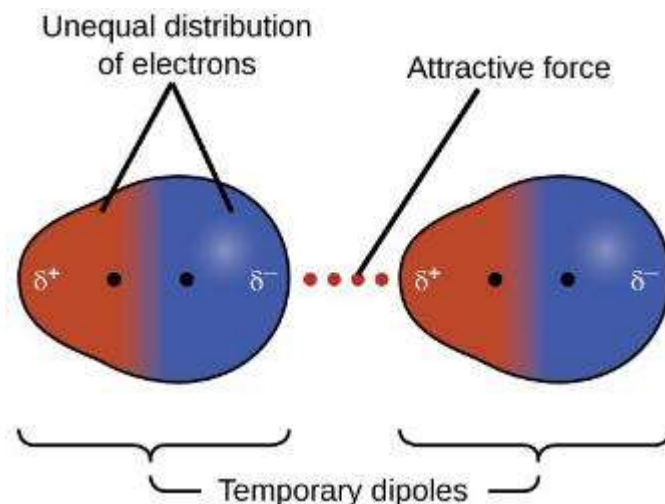


- For instance, a substance with strong intermolecular forces would likely to stay in the liquid phase rather than vaporize.

10.1 INTERMOLECULAR FORCES

Dispersion Forces

- Intermolecular interactions between neutral molecules are known, in general, as van der Waals forces.
- One type of attractive van der Waals force present in all condensed phases is the London dispersion force.
 - Electrons are in constant motion and a molecule can develop an instantaneous dipole.
 - This dipole can affect neighboring atoms and induce dipole formation.



10.1 INTERMOLECULAR FORCES

Dispersion Forces

- Dispersion forces are more significant when molecules are larger and heavier.
- How is this reflected in the data below?

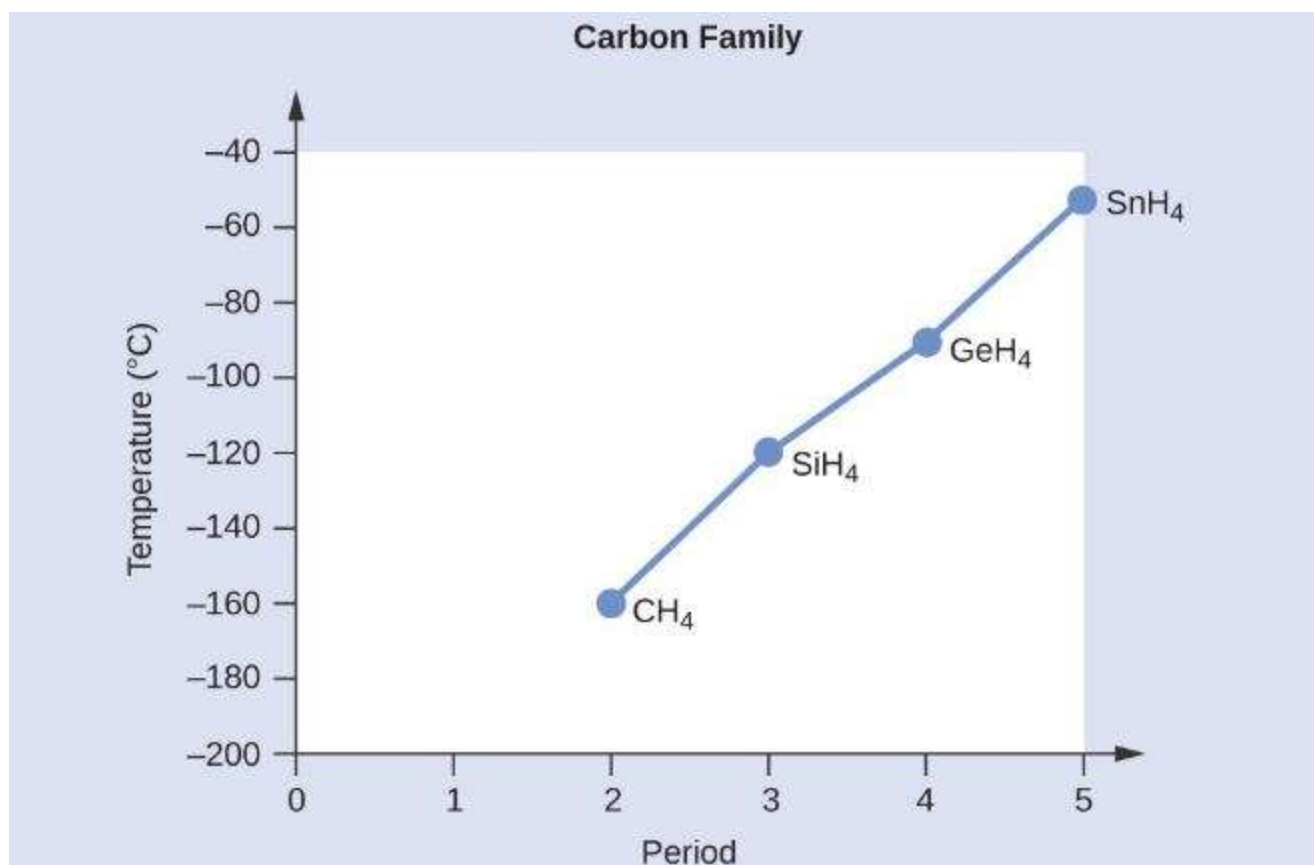
Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F ₂	38 g/mol	72 pm	53 K	85 K
chlorine, Cl ₂	71 g/mol	99 pm	172 K	238 K
bromine, Br ₂	160 g/mol	114 pm	266 K	332 K
iodine, I ₂	254 g/mol	133 pm	387 K	457 K
astatine, At ₂	420 g/mol	150 pm	575 K	610 K

10.1 INTERMOLECULAR FORCES

Example 10.1

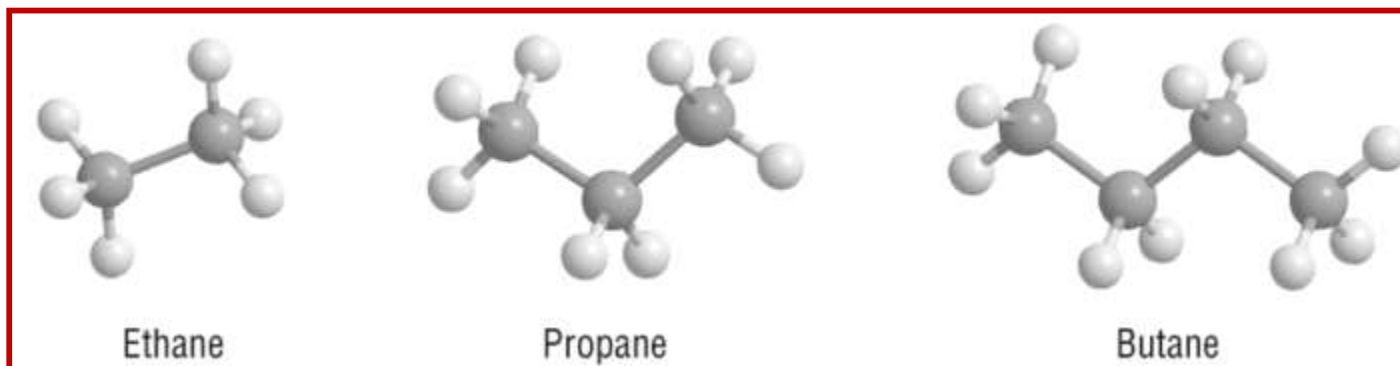
The boiling points for group 14 elements bonded to hydrogen (CH_4 , SiH_4 , GeH_4 , and SnH_4) are shown in the graph. Explain the trend.



10.1 INTERMOLECULAR FORCES

Example 10.1 – Check Your Learning

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6 , C_3H_8 , and C_4H_{10} .



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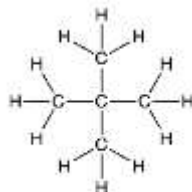
10.1 INTERMOLECULAR FORCES

Dispersion Forces and Surface Area

- Isomers are molecules that have the same molecular formula but different arrangements of atoms.
- C_5H_{12} is the molecular formula for the isomers:

neopentane

BP: 9.5 °C

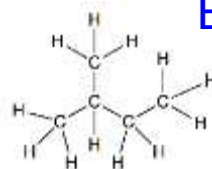


Wolfram|Alpha



isopentane

BP: 27 °C

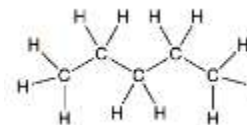


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n-pentane

BP: 36 °C



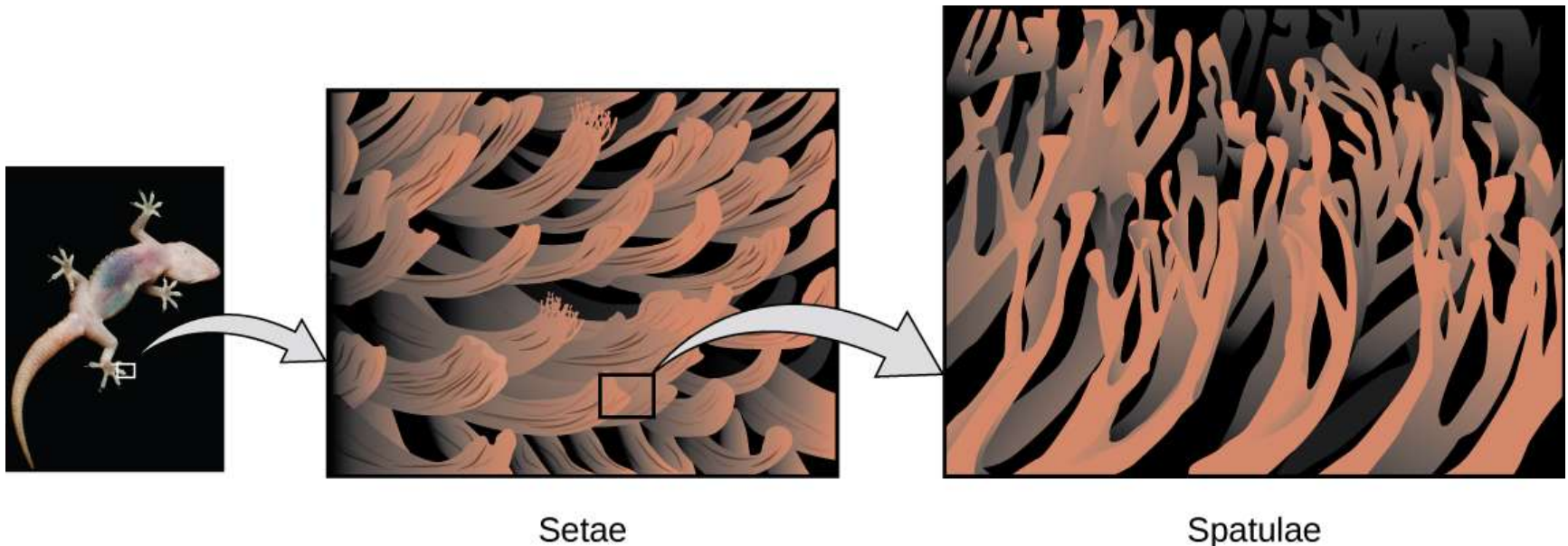
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10.1 INTERMOLECULAR FORCES

Dispersion Forces and Surface Area: Geckos

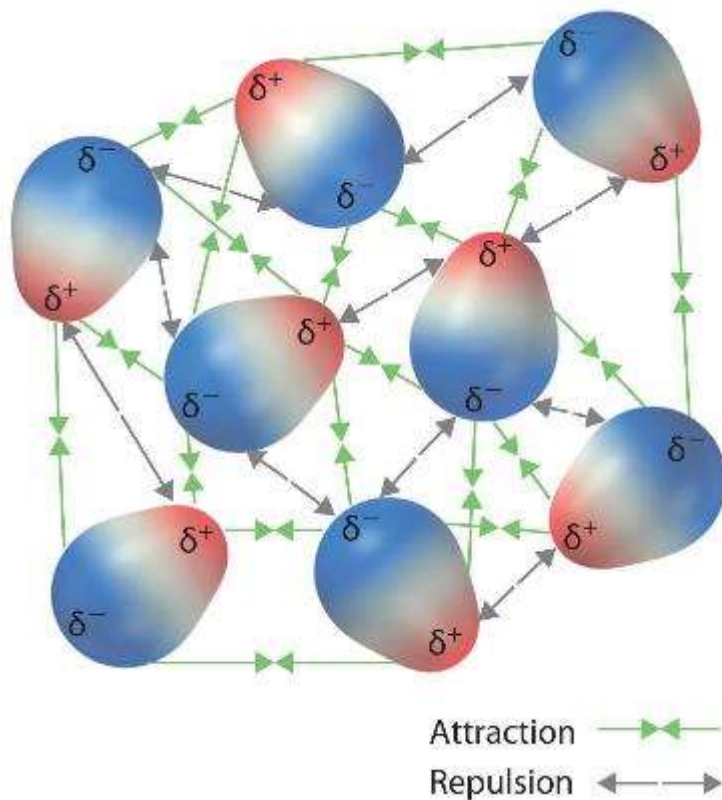
- Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with branching into hundreds of tiny, flat, triangular tips called *spatulae*.
- The huge numbers of spatulae on its setae provide a gecko, shown in with a large total surface area for sticking to a surface.



10.1 INTERMOLECULAR FORCES

Dipole-Dipole Attractions

- Recall that a polar molecule has a dipole: a partial positive charge on one side and a partial negative charge on the other side of the molecule.
- The electrostatic force between dipoles is called a dipole-dipole interaction.



10.1 INTERMOLECULAR FORCES

Dipole-Dipole Attractions

- Consider the molecules HCl and F₂.
- Both HCl and F₂:
 - consist of the same number of atoms.
 - have approximately the same molecular mass.
 - have the same average KE at a temperature such as 150 °C.
- HCl boils at 188 K and F₂ boils at 85 K. Explain.

HCl



F₂

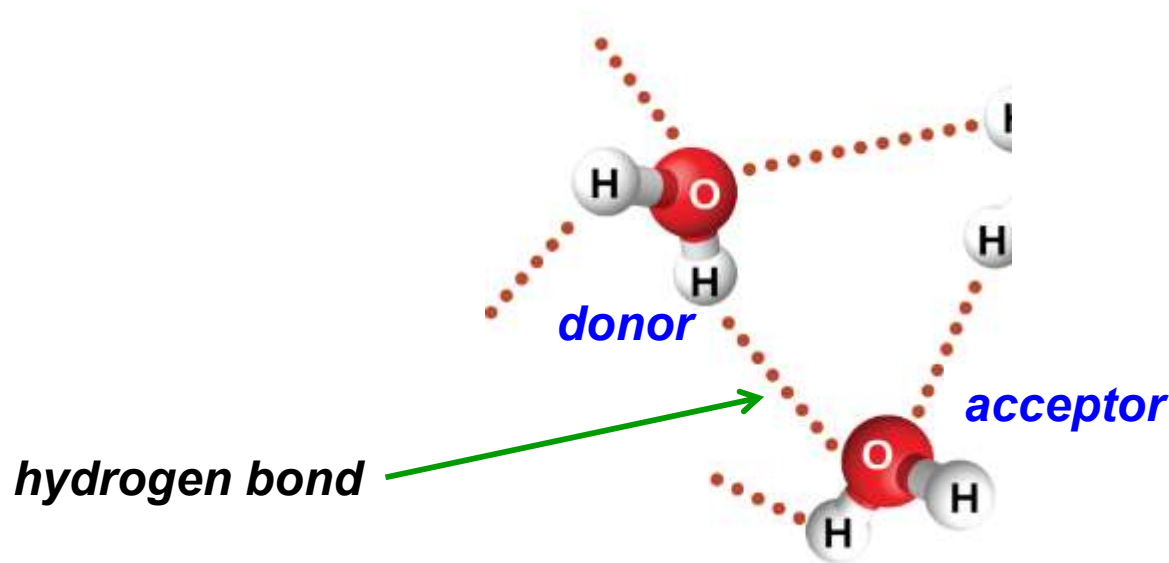


- Predict which will have the higher boiling point: N₂ or CO.

10.1 INTERMOLECULAR FORCES

Dipole-Dipole Attractions: Hydrogen Bonding

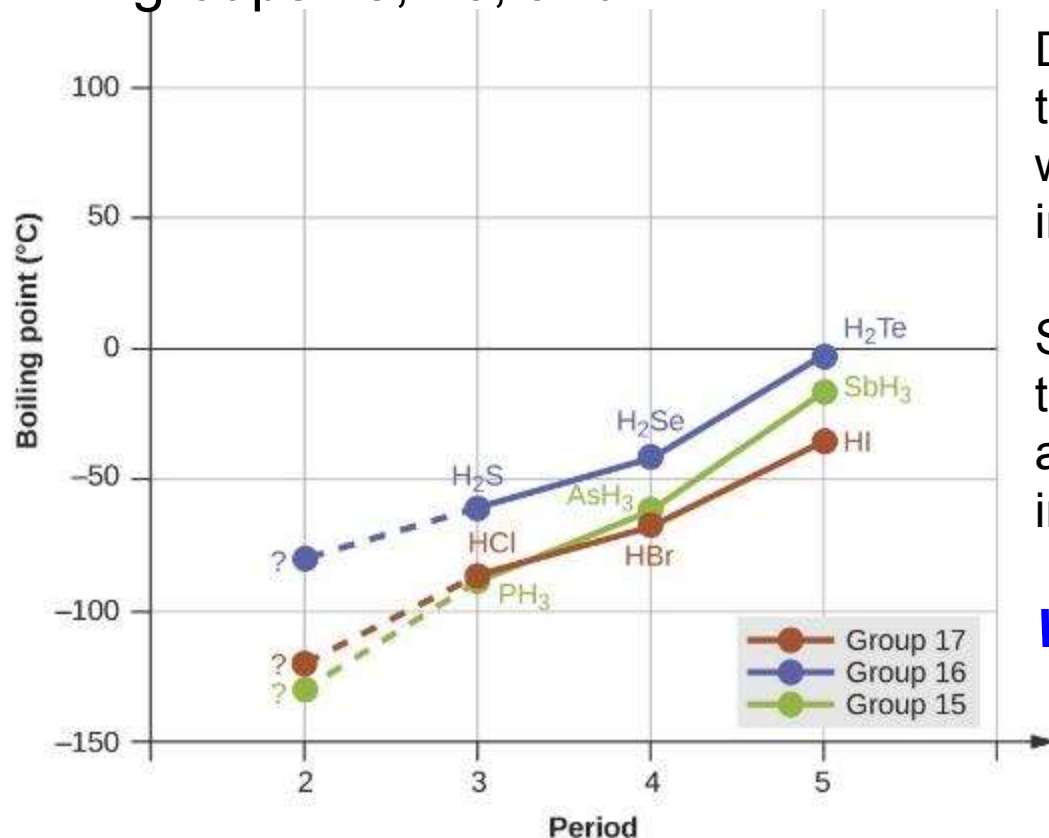
- Hydrogen bonding is a special type of dipole-dipole attraction.
- A particularly strong dipole-dipole attraction (not an actual bond) occurs when a molecule contains a hydrogen atom bonded to F, O, or N (the three most electronegative elements).
- The hydrogen atom of H-F, H-O, or H-N forms a hydrogen bond if an electron pair is available on a nearby molecule.



10.1 INTERMOLECULAR FORCES

Dipole-Dipole Attractions: Hydrogen Bonding

- Hydrogen bonds have a pronounced effect on the properties of condensed phases.
- Consider the trends in boiling points for the binary hydrides of groups 15, 16, and 17.



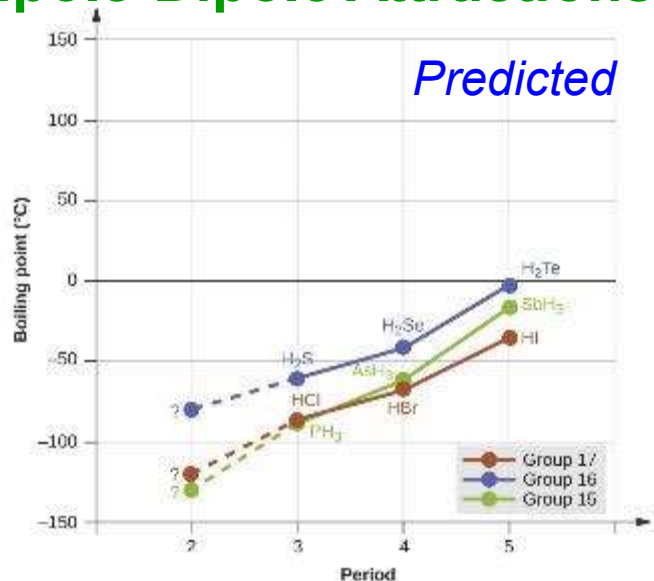
Down each group, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially.

Stronger dispersion forces dominate the increasingly weaker dipole-dipole attractions, and the boiling points increase steadily.

What about NH_3 , H_2O , and HF ?

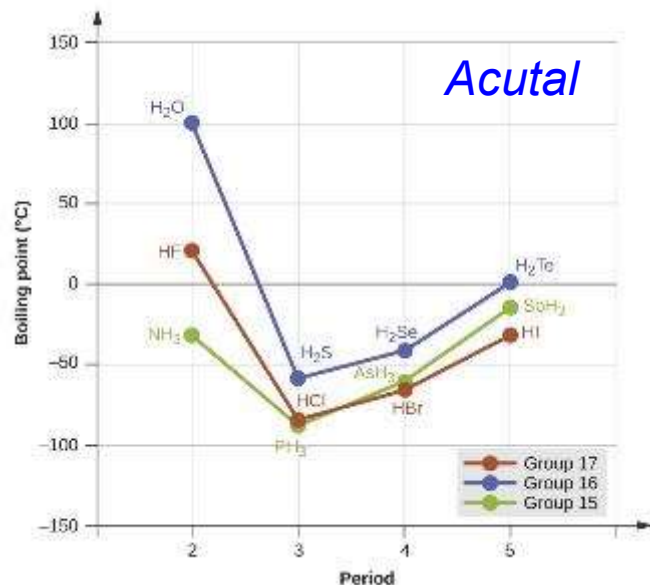
10.1 INTERMOLECULAR FORCES

Dipole-Dipole Attractions: Hydrogen Bonding



What about NH_3 , H_2O , and HF ?

	Predicted boiling point	Actual boiling point
NH_3	-120 °C	-33 °C
H_2O	-80 °C	+100 °C
HF	-110 °C	+20 °C

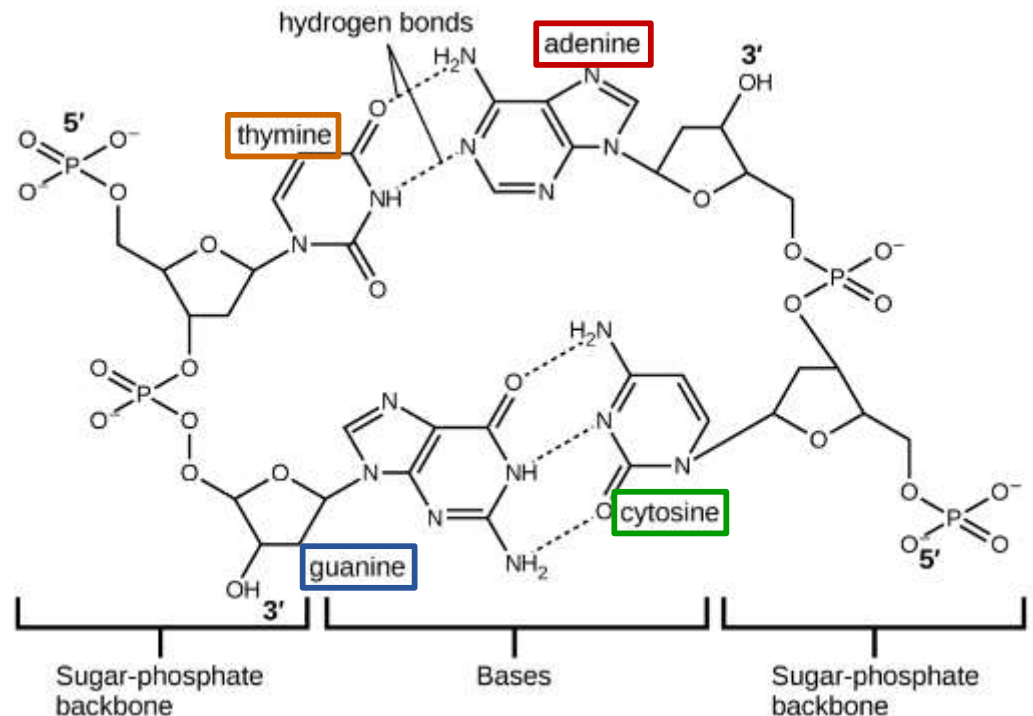
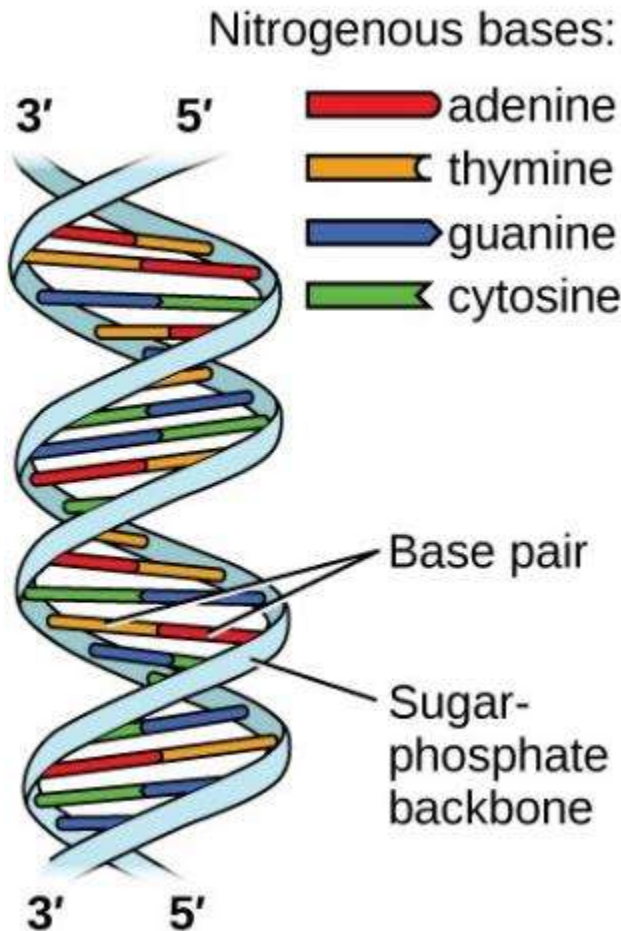


Explain the discrepancy between the predicted and actual boiling points.

10.1 INTERMOLECULAR FORCES

Hydrogen Bonding and DNA

- Hydrogen bonding is responsible for the structure and function of DNA



10.2 PROPERTIES OF LIQUIDS

Viscosity

- Viscosity is the resistance to flow.
 - stronger IMFs – harder for molecules to move past one another
 - higher temperature – greater kinetic energy overcomes IMFs
- The IMFs between identical molecules are cohesive forces.
- At the surface of a liquid sample, cohesive forces give rise to surface tension.
 - Surface tension allows the molecules at the surface of a liquid to act like a membrane stretched over a liquid's surface.

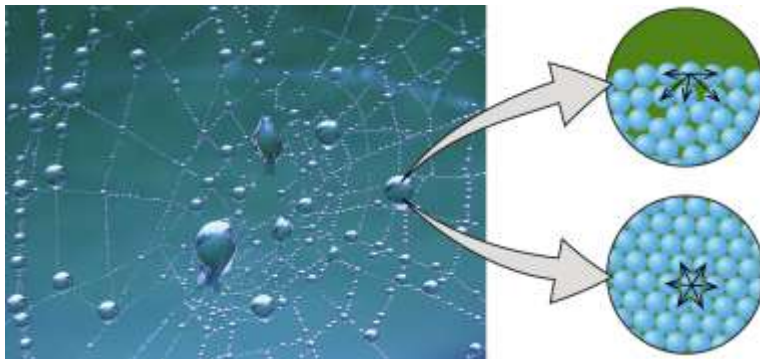


Honey and motor oil are liquids with high viscosities.

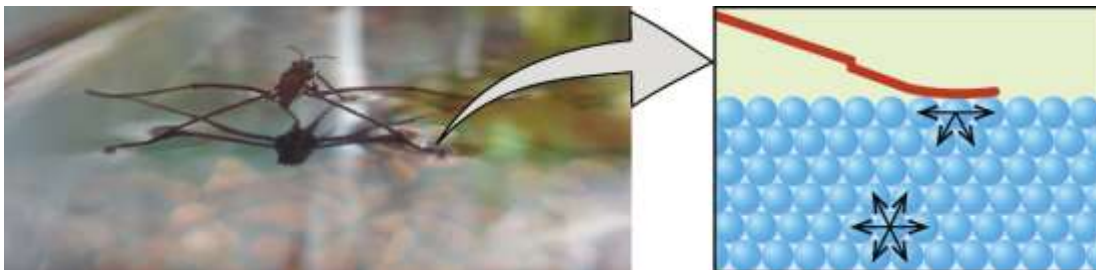
10.2 PROPERTIES OF LIQUIDS

Surface Tension

- Surface tension is defined as the energy required to increase the surface area of a liquid.
- Water exhibits very high surface tension due to very strong interactions between its molecules.
- Some insects, even though they are relative heavy, move across water supported by surface tension.



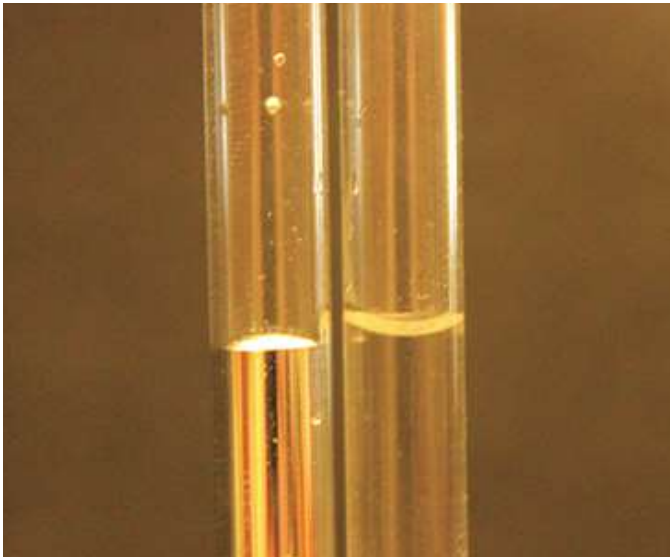
The remarkably high surface tension of water arises from strong intermolecular forces between molecules.



10.2 PROPERTIES OF LIQUIDS

Adhesive Forces

- The interactions between two different types of molecules are known as adhesive forces.
- If adhesive forces $<$ cohesive forces, a substance does not spread out on a surface and droplets form (water, mercury).
- If adhesive forces $>$ cohesive forces, water spreads out on the surface (glass, paper).



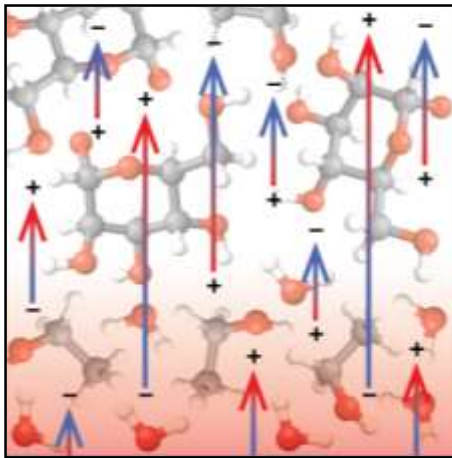
Mercury: the adhesive forces within a sample of mercury are greater than the cohesive forces between mercury and glass.

Water: the adhesive forces within a sample of mercury are greater than the cohesive forces between mercury and glass.

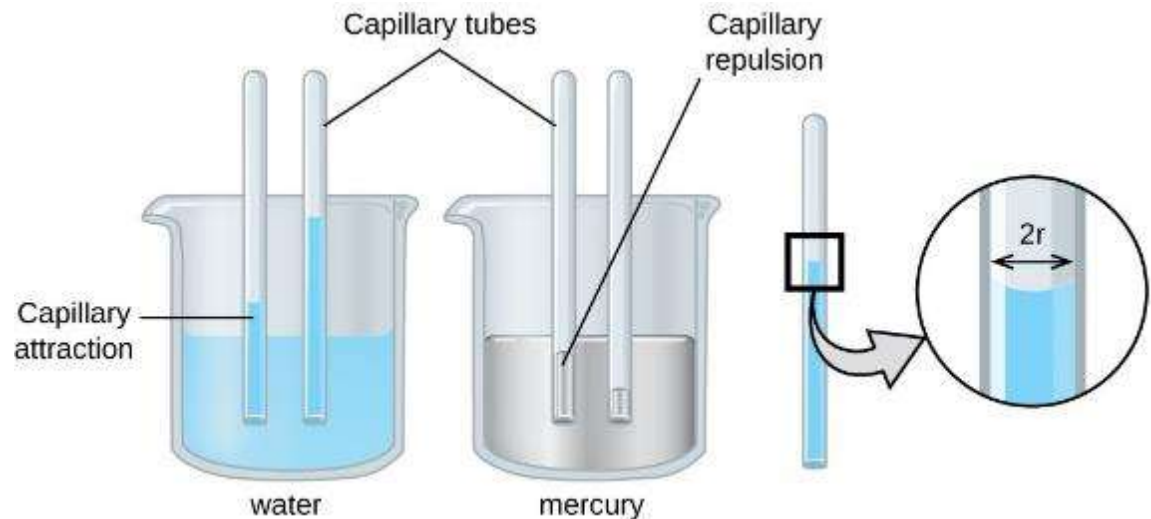
10.2 PROPERTIES OF LIQUIDS

Capillary Action

- When adhesive forces are relatively strong, and liquid molecules can move along a surface, capillary action may occur.
- The adhesive forces between materials, along with the cohesive forces within a liquid, may be strong enough to cause upward movement against gravity.



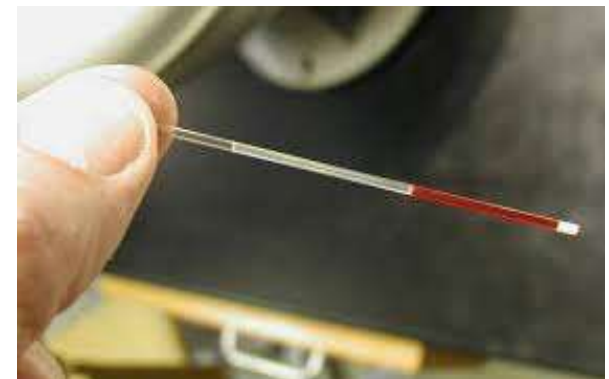
A paper towel soaks up liquid because the fibers are attracted to water molecules.



The behavior of a liquid in a capillary depends upon adhesive vs. cohesive interactions.

CAPILLARY ACTION IN MEDICINE

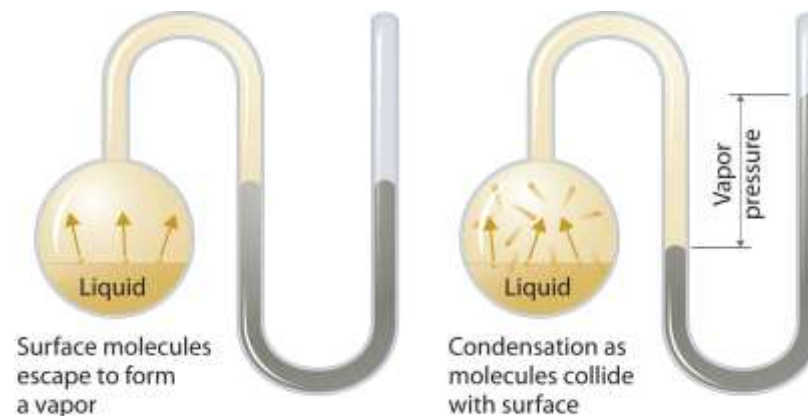
- Many medical tests require drawing a tiny amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete.
- This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity
- When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop.
- When the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube.
- A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces.



10.3 PHASE TRANSITIONS

Vaporization and Condensation

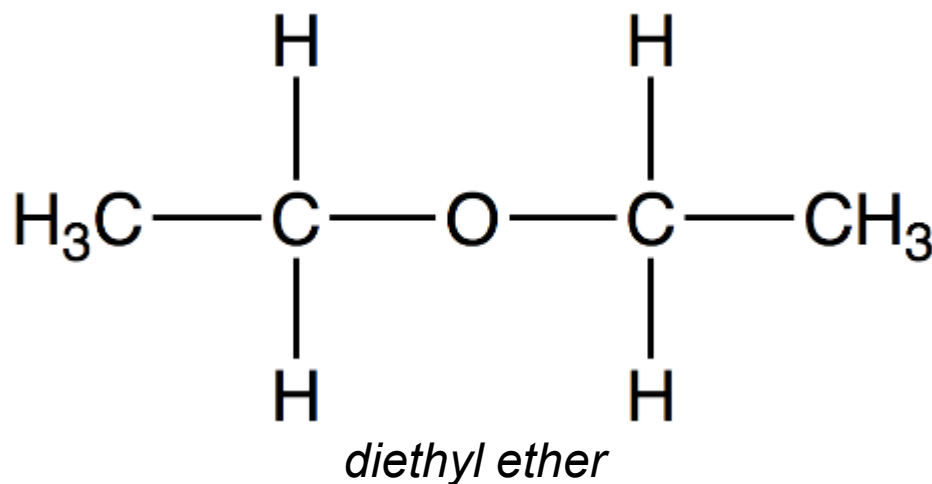
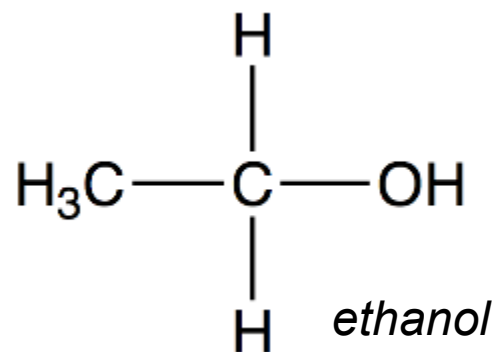
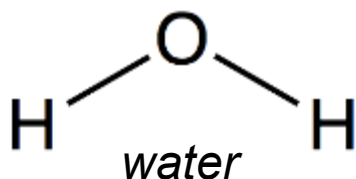
- When a liquid vaporizes in a closed container, an equilibrium forms between the liquid and vapor phases.
- This is a dynamic equilibrium where $R_{\text{vaporization}} = R_{\text{condensation}}$.
- The vapor pressure in the closed container depends upon the intermolecular interactions in the liquid.
 - Strong intermolecular interactions prevent vaporization.
 - Weak intermolecular interactions allow molecules to escape the liquid phase and enter the vapor phase.



10.3 PHASE TRANSITIONS

Vaporization and Condensation

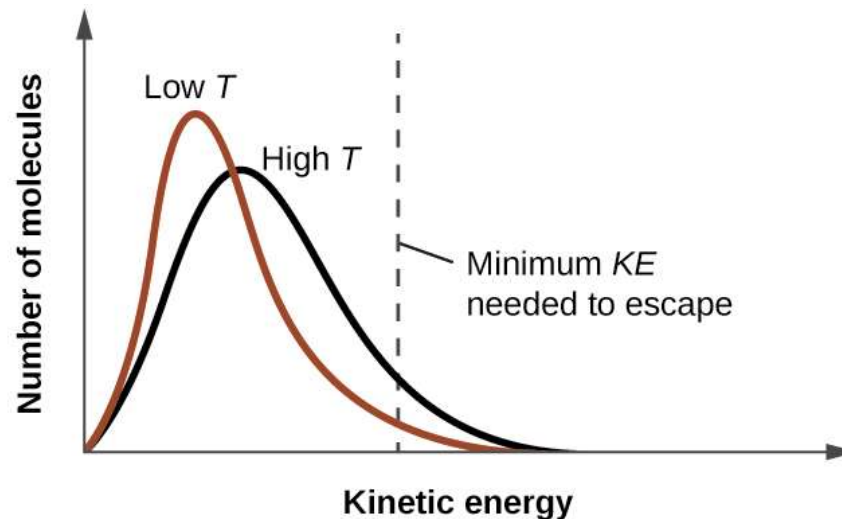
- Which of the following substances would have the highest vapor pressure? Explain.
- Which would have the lowest vapor pressure? Explain.



10.3 PHASE TRANSITIONS

Vaporization and Condensation

- As temperature increases, the kinetic energy of the molecules in a liquid increases.
- More molecules with the kinetic energy to overcome intermolecular forces mean that the vapor pressure of the liquid increases.
- At higher temperature, a greater fraction of molecules have enough energy to escape from the liquid.



10.3 PHASE TRANSITIONS

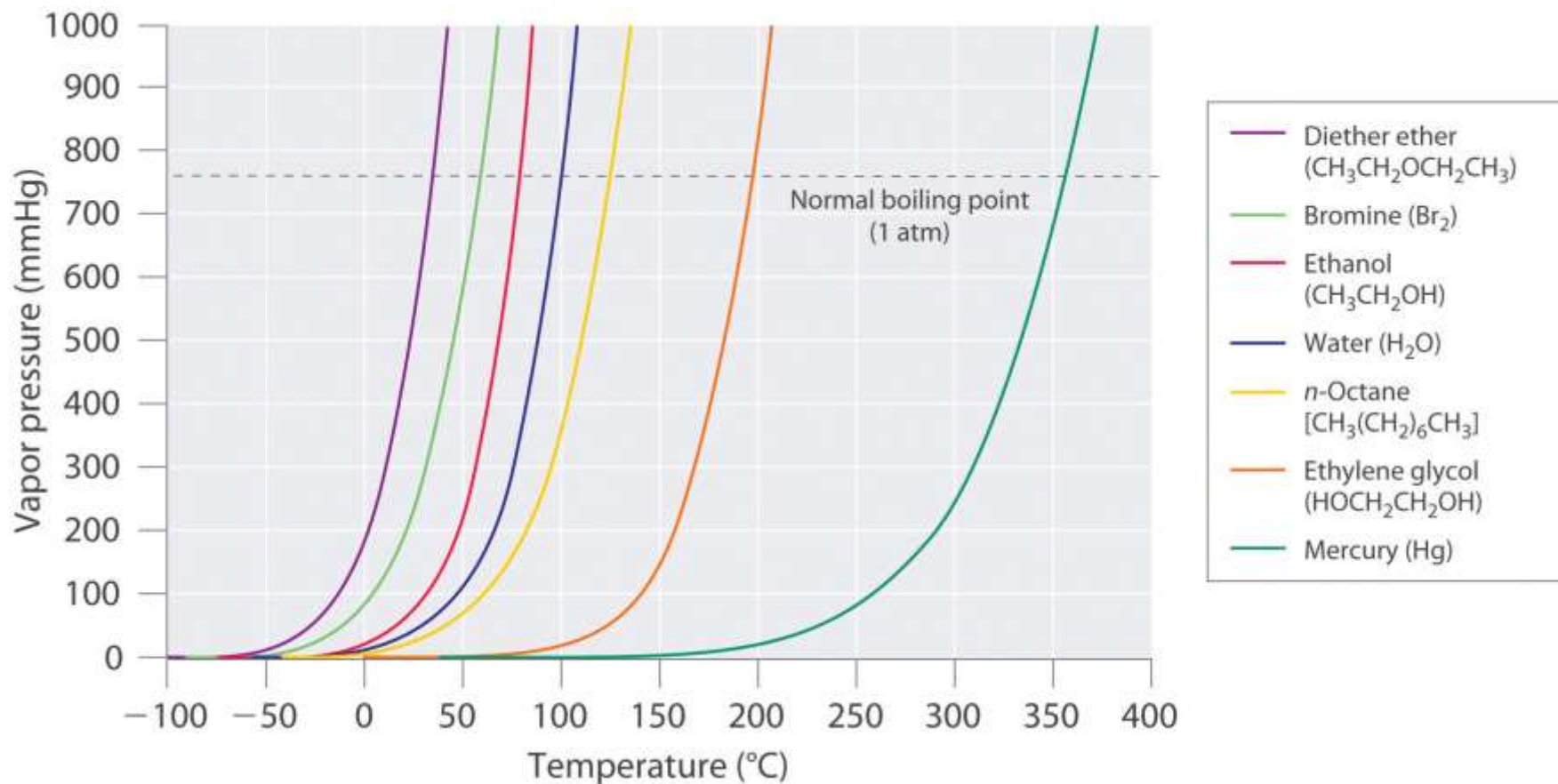
Boiling Points

- When the vapor pressure of a liquid increases enough to equal the atmospheric pressure, the liquid reaches its boiling point.
- The normal boiling point of a liquid is defined as the boiling point when the surrounding pressure is 1 atm.
 - What happens to the boiling point of water in a place like Denver, CO where the atmospheric pressure is about 0.817 atm.
 - What happens to the boiling point of water in a place like Siberia where the atmospheric pressure is sometimes as high as 1.07 atm.



10.3 PHASE TRANSITIONS

Boiling Points and Pressure



10.3 PHASE TRANSITIONS

Vapor Pressure and Temperature

- The quantitative relationship between vapor pressure and temperature is given by the Clausius-Clapeyron equation:

$$P = Ae^{-\Delta H_{\text{vap}}/RT}$$

P = pressure

A = constant for the substance

ΔH_{vap} = enthalpy of vaporization

R = gas constant

T = temperature in Kelvin

Linear version of the equation:

$$\ln P = -\frac{\Delta H_{\text{vap}}}{RT} + \ln A$$

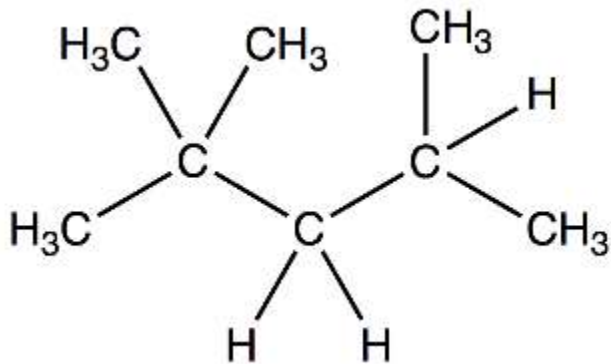
Two-point version of the equation:

$$\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

10.3 PHASE TRANSITIONS

Example 10.7 – Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapor pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapor pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

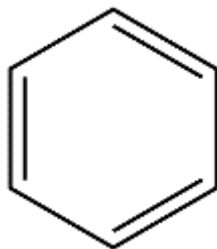


$$\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

10.3 PHASE TRANSITIONS

Example 10.8 – Estimating Temperature or Vapor Pressure

For benzene (C_6H_6), the normal boiling point is $80.1\text{ }^\circ\text{C}$ and the enthalpy of vaporization is 30.8 kJ/mol . What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa ?



10.3 PHASE TRANSITIONS

Melting and Freezing

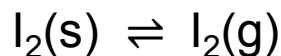
- The process of transitioning from the solid state to the liquid state is melting; the opposite is freezing.
 - When a solid is heated, the average KE of its atoms, molecules, or ions increases.
 - If the average energy of the particles is large enough to overcome the energy holding particles together, a phase change begins to occur.
- The temperature remains constant throughout the phase change and only starts to rise again once all particles are in the liquid state.
- The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fusion} .



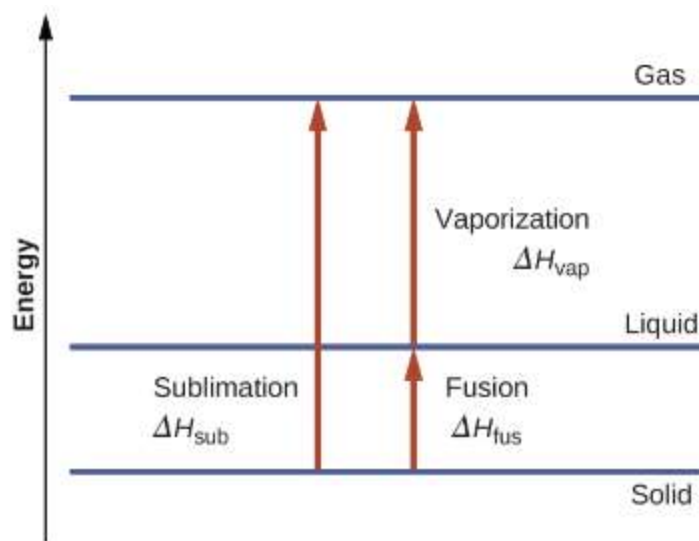
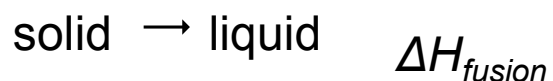
10.3 PHASE TRANSITIONS

Sublimation and Deposition

- Some substances transition directly from the solid state to the gaseous state via sublimation.



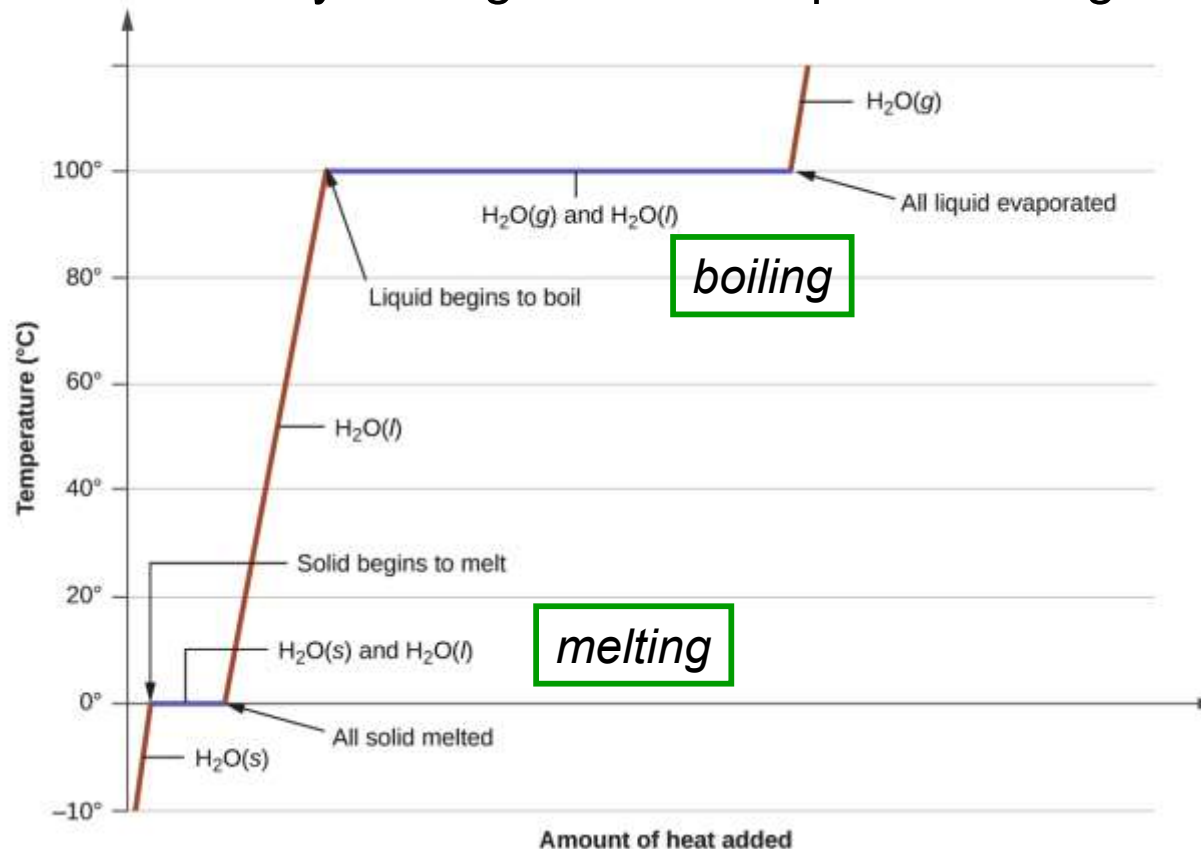
sublimation of iodine



10.3 PHASE TRANSITIONS

Heating and Cooling Curves

- A heating curve depicts the changes in temperature that result as a substance absorbs increasing amounts of heat.
- While undergoing a phase change, the temperature remains constant; the temperature can only rise again after the phase change is complete.



10.3 PHASE TRANSITIONS

Example 10.10 – Total Heat for a Phase Change

How much heat is required to convert 135 g of ice at $-15\text{ }^{\circ}\text{C}$ into water vapor at $120\text{ }^{\circ}\text{C}$?

The transition involves the following steps:

1. Heat ice from $-15\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$

$$q_1 = mc\Delta T \text{ for ice}$$

2. Melt ice

$$q_2 = n \cdot \Delta H_{\text{fusion}}$$

3. Heat water from $0\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$

$$q_3 = mc\Delta T \text{ for water}$$

4. Boil water

$$q_4 = n \cdot \Delta H_{\text{vaporization}}$$

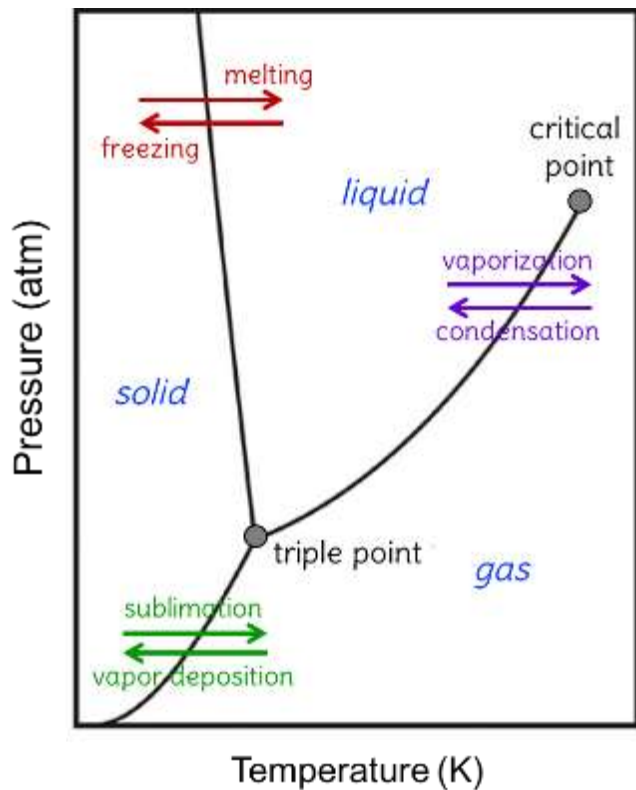
5. Heat steam from $100\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$

$$q_5 = mc\Delta T \text{ for steam}$$

10.4 PHASE DIAGRAMS

Phase Diagrams

- In the previous section, heat/cooling curves were used to show the relationship between vapor pressure and temperature.
- Making such measurements over a wide range in pressures yields data that may be used to construct a phase diagram.



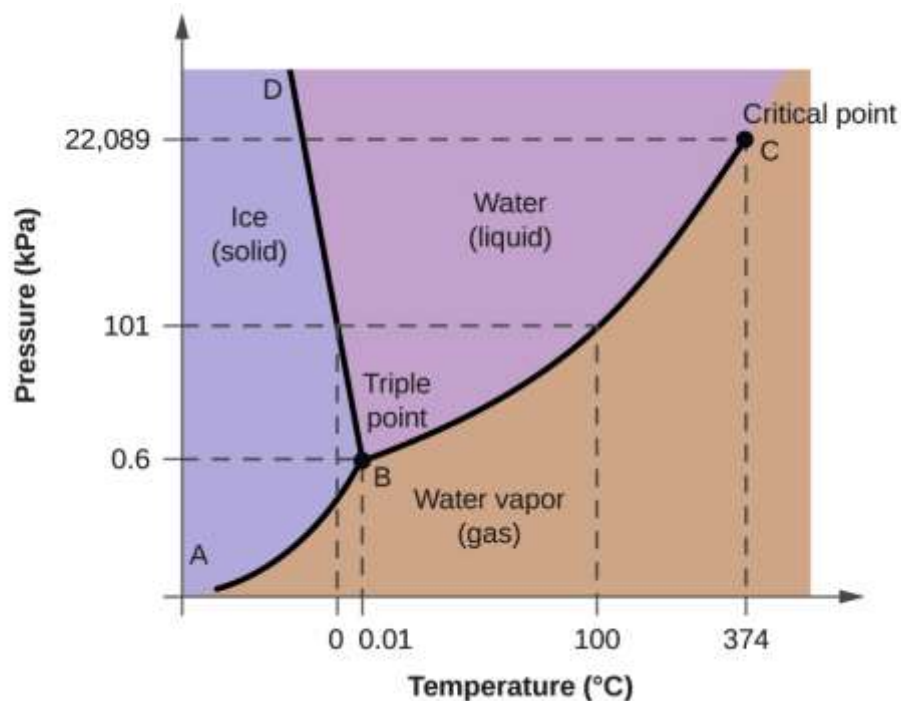
- The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram.
- At the pressure and temperature of the triple point, all depicted phases exist in equilibrium.
- Above the critical point, gas cannot be condensed into a liquid.

10.4 PHASE DIAGRAMS

Example – Using the Phase Diagram for Water

What is the phase of water at:

- a. a pressure of 50 kPa and -10°C ?
- b. a pressure of 50 kPa and 50°C ?
- c. a pressure of 25 kPa and 200°C ?



What are the conditions:

- 4. at the triple point?

What does this mean?

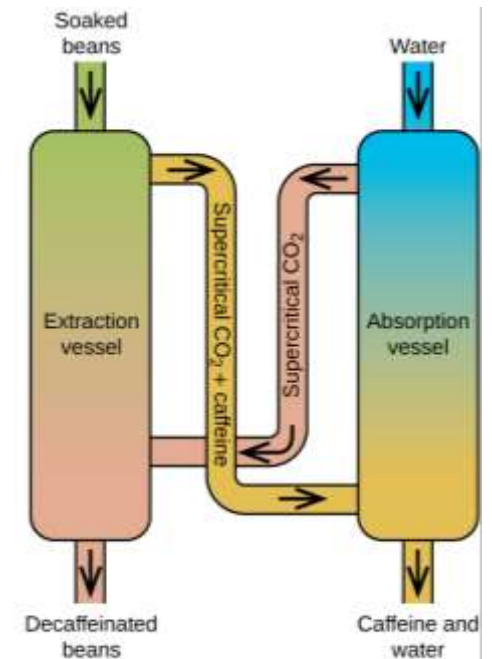
- 5. at the critical point?

What does this mean?

DECAFFEINATION: SUPERCRITICAL FLUID

At a temperature and pressure higher than its critical point, a substance is a supercritical fluid (SCF) and exhibits properties intermediate between the gaseous and liquid state.

- Coffee can be decaffeinated by using supercritical CO₂.
- Solvents to remove caffeine (a polar molecule) also remove molecules responsible for the flavor and aroma of coffee.
- Supercritical CO₂ can be used to effectively remove caffeine.
- The fluid penetrates deep into beans (like a gas) and dissolves certain substances (like a liquid).
- The caffeine extracted from coffee is commodity itself and is used in other food and drug products.

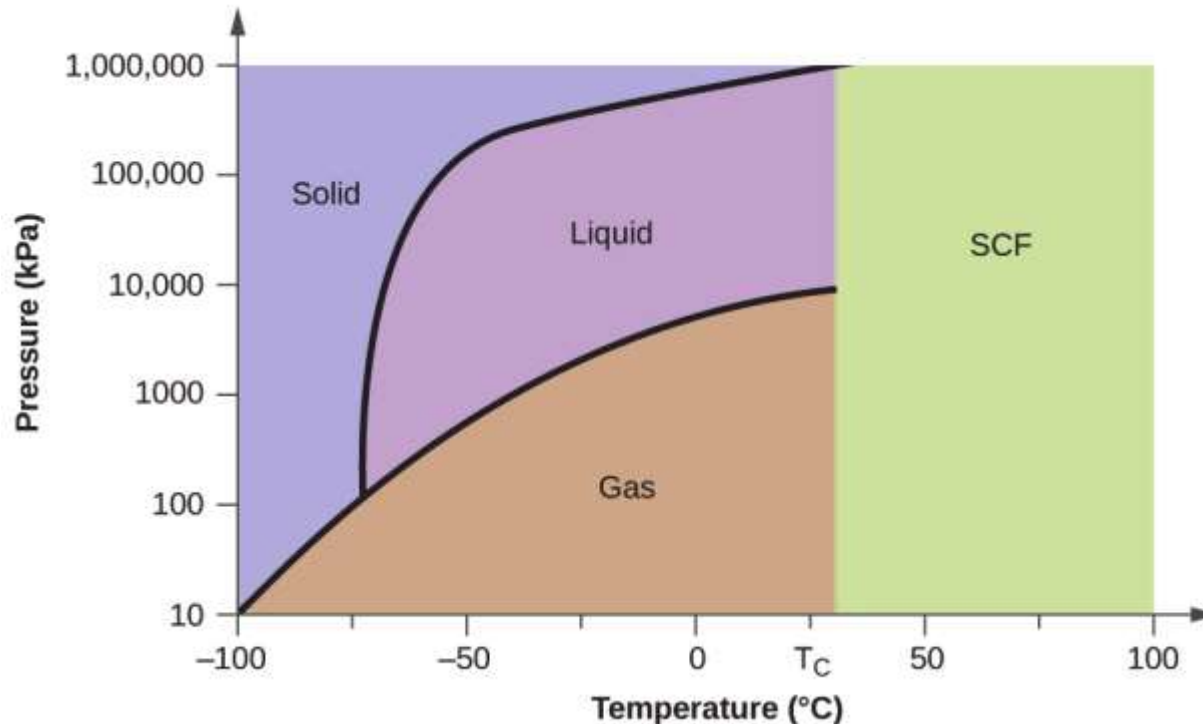


10.4 PHASE DIAGRAMS

Example 10.12 – Using the Phase Diagram for Carbon Dioxide

What is the phase of CO₂ at:

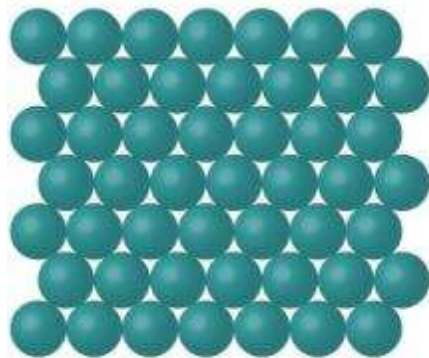
- a. -30 °C and 2000 kPa
- b. -60 °C and 1000 kPa
- c. -60 °C and 100 kPa
- d. 20 °C and 1500 kPa
- e. 0 °C and 100 kPa
- f. 20 °C and 100 kPa



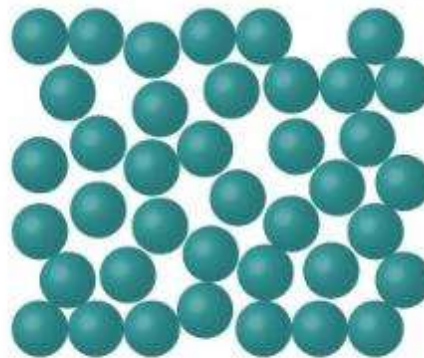
10.5 THE SOLID STATE OF MATTER

Types of Solids

- When most liquids are cooled, they eventually freeze into crystalline solids where particles are arranged in a repeating pattern.
 - ionic solids
 - metallic solids
 - covalent network solids
 - molecular solids
- If a substance freezes before a repeat pattern is established, it is a material called an amorphous solid.



Crystalline



Amorphous

10.5 THE SOLID STATE OF MATTER

Crystalline vs. Amorphous Solids

- Metals and ionic compounds typically form ordered, crystalline solids.
- Substances composed of large molecules or a mixture of molecules can form either crystalline or amorphous solids depending upon the preparation conditions.

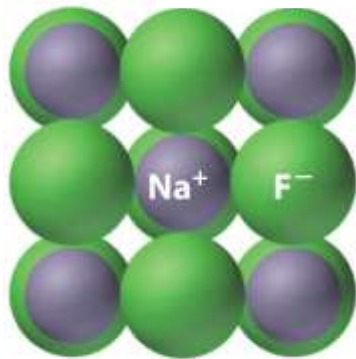


- Obsidian is an amorphous solid. It is a volcanic glass that forms when lava is cooled rapidly (therefore minimal crystal growth is allowed).
- Obsidian has a typical composition of KAlSi_3O_8 and tends to have curved, irregular surfaces when carved.
- Obsidian is hard and brittle and can form extremely sharp edges when fractured. Aztec weapons were sometimes made of obsidian.

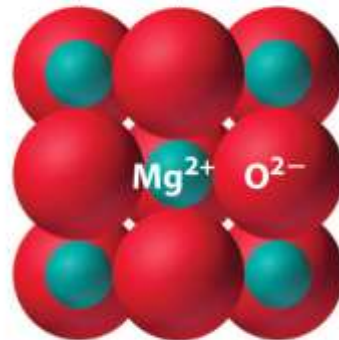
10.5 THE SOLID STATE OF MATTER

Crystalline Solids: Ionic Solids

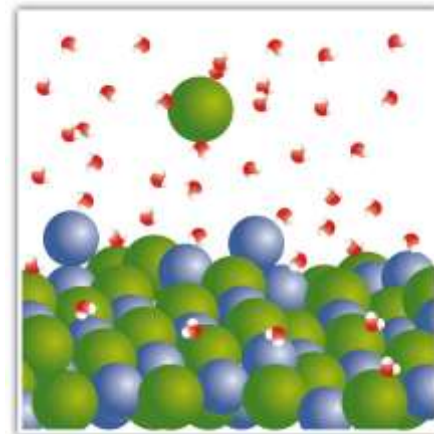
- Solid composed of positive and negative ions that are held together by electrostatic forces are known as ionic solids.
- The lattices are held together by relatively large forces (full positive and full negative charges) and have a high lattice energy.
- Ionic solids:
 - tend to be hard and brittle.
 - do not conduct electricity in the solid state.
 - can conduct electricity when dissolved and ions are free to move.



NaF



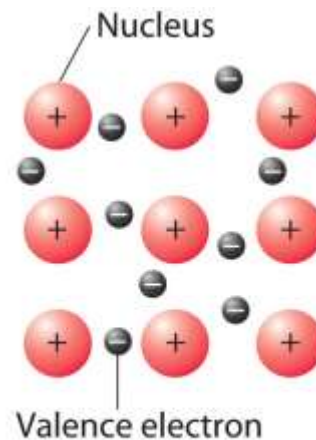
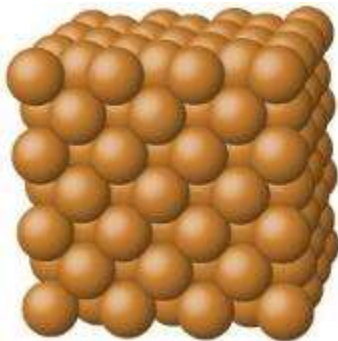
MgO



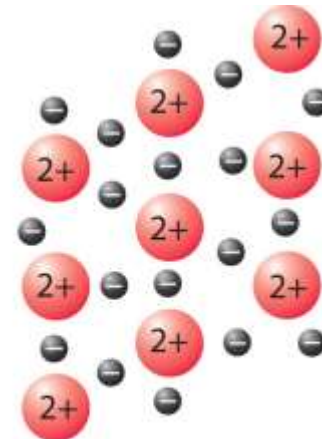
10.5 THE SOLID STATE OF MATTER

Crystalline Solids: Metallic Solids

- Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms.
- Metallic solids are sometimes described as a distribution of atomic nuclei within a sea of electrons.
- Metallic solids:
 - exhibit high thermal and electrical conductivity.
 - have a metallic luster and are malleable.



(a) Group 1 metal

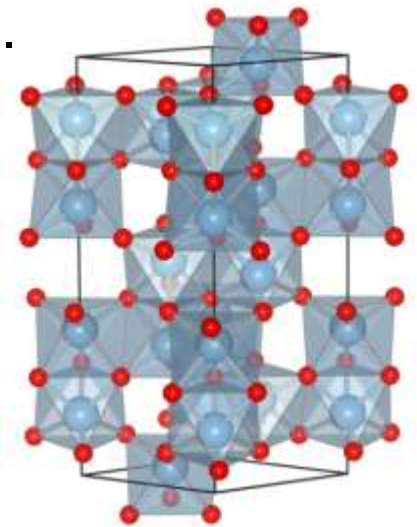
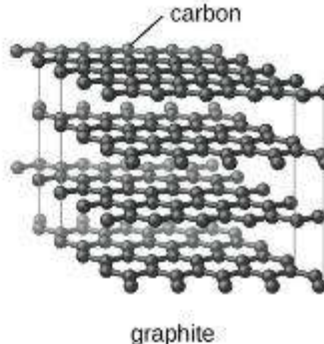
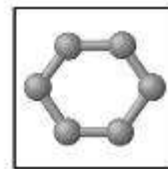
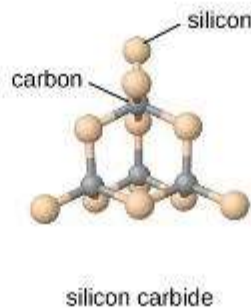
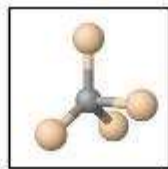
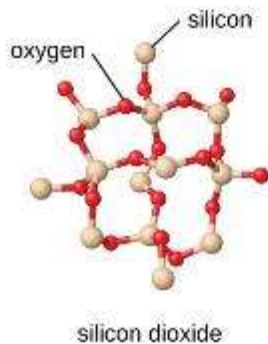
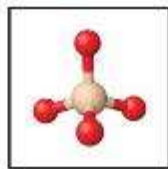
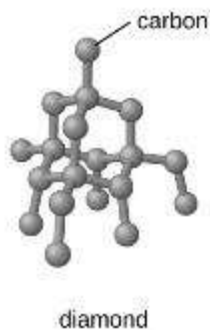
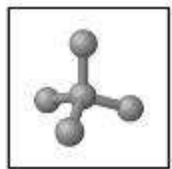


(b) Group 2 metal

10.5 THE SOLID STATE OF MATTER

Covalent Network Solids

- Diamond and graphite are examples of covalent network solids.
- Covalent network solids have strong, covalent bonds and are characterized by:
 - strength
 - hardness
 - high melting points
- There are no individual molecules in these solids – the covalent bond network is continuous.
- Many minerals have networks of covalent bonds.

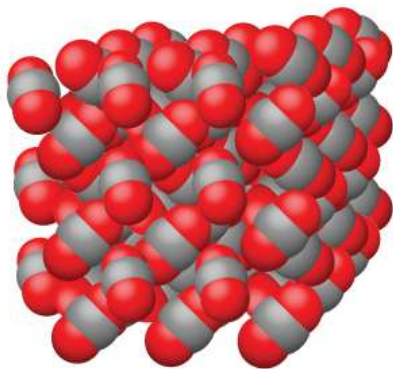


*The structure of ruby:
aluminum and oxygen.*

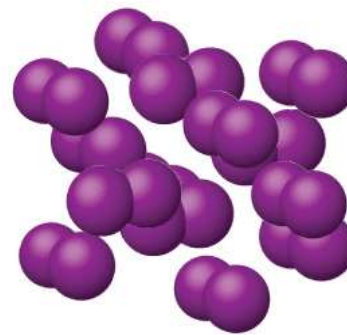
10.5 THE SOLID STATE OF MATTER

Molecular Solids

- Solids composed of neutral molecules are molecular solids.
- The attractive forces in such solids differ widely depending upon the molecules present.
- Molecular solids composed of polar molecules have larger attractive forces and therefore higher melting points.



CO₂ consists of small, nonpolar molecules and forms a molecular solid with a melting point of -78°C .



I₂ consists of larger, nonpolar (but polarizable) molecules and has a melting point of 114°C .

10.5 THE SOLID STATE OF MATTER

Properties of Solids

- A pure crystalline solid has a precise melting temperature because each type of particle is held in place with the same forces/energy.
- The forces all have the same strength and require the same amount of energy to be broken.
- Amorphous materials soften gradually with the weakest intermolecular forces breaking first.

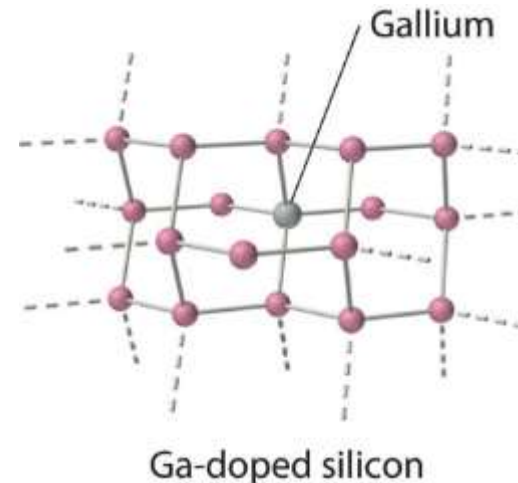
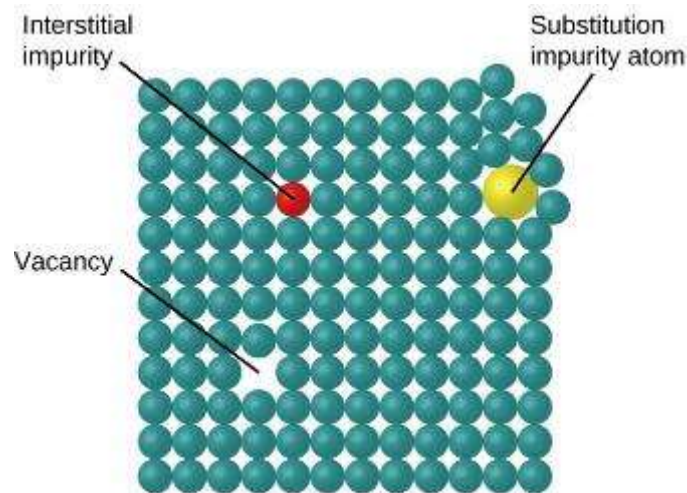
Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al ₂ O ₃
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO ₂ , SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H ₂ O, CO ₂ , I ₂ , C ₁₂ H ₂₂ O ₁₁

10.5 THE SOLID STATE OF MATTER

Crystal Defects

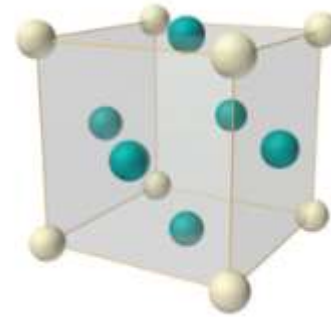
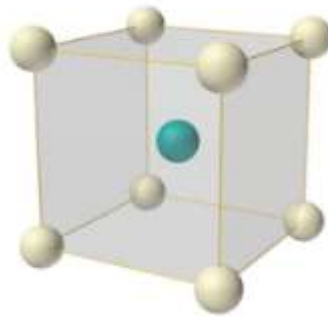
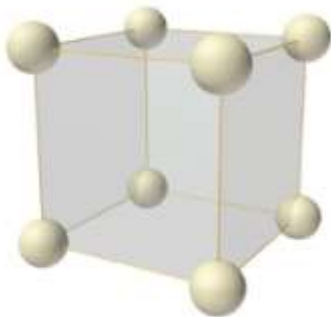
- In a crystalline solid, particles are arranged in a definite repeating pattern.
- Defects that occur when atoms are missing are called vacancies.
- Another type of defect occurs when an atom occupies an interstitial site and takes the place of another atom.
- Trace amounts of impurities can be added to a crystal in a process called doping and may lead to desirable changes in properties.



10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

The Structure of Metals

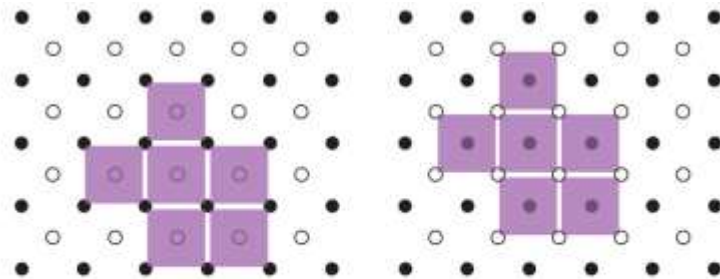
- Over 90% of naturally occurring and made-made solids are crystalline.
- Crystalline structures are favored because because
 - attractive interactions between particles is maximized.
 - intermolecular energy is minimized.
 - particles pack in the most efficient manner.
- Elemental metals are composed of just one type of atom, packed closely together in a repeating pattern.
- There are some common types of geometries in such crystals.



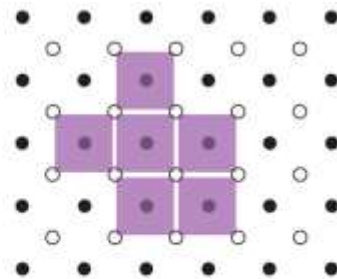
10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Unit Cells in Two Dimensions

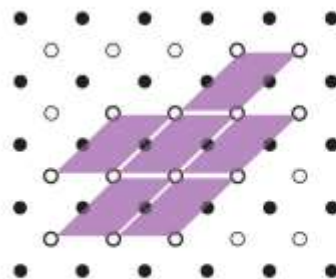
- The structure of a crystalline solid is described by considering its simplest repeating unit, the unit cell.
- Examples of unit cells in two dimensions are:



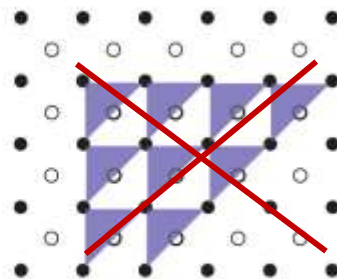
(a)



(b)



(c)



(d) *not a unit cell: space is not completely filled*

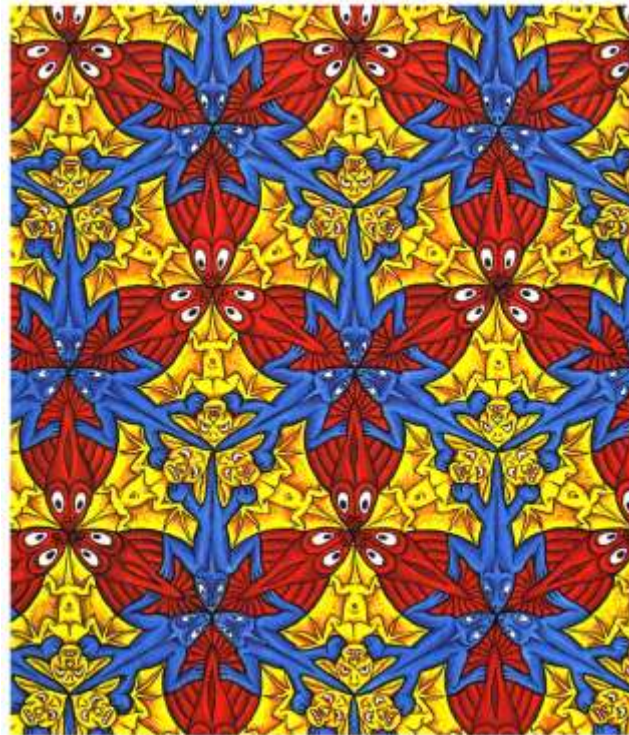


M. C. Escher

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Unit Cells in Two Dimensions

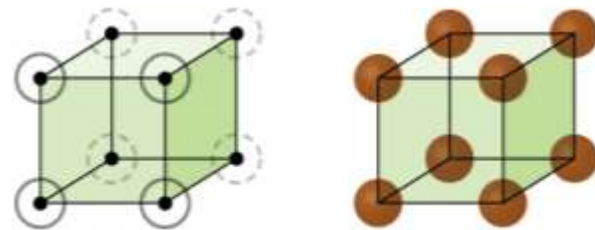
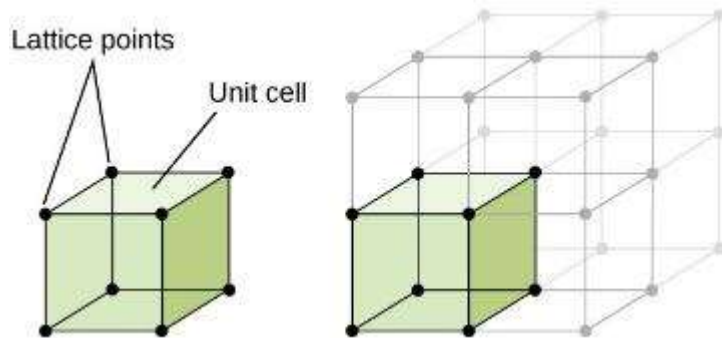
- Study the Escher drawings and draw in a possible unit cell for each.



10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Unit Cells in Three-Dimensions

- In three dimensions, the unit cell consists of lattice points representing particles (atoms or ions).
- The unit cell is repeated in all directions for a crystal.
- In the simplest arrangement, atoms in one layer are located directly above the layer below.
- This is a simple cubic structure or a simple cubic unit cell or primitive cubic unit cell.

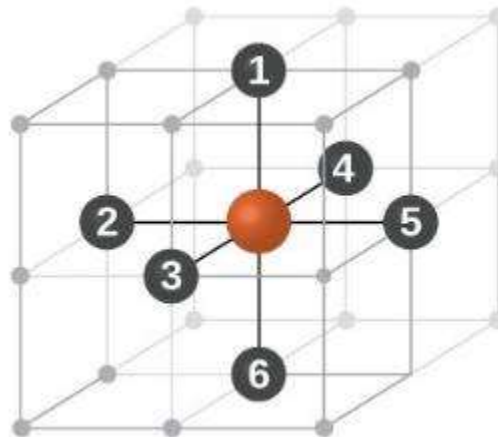
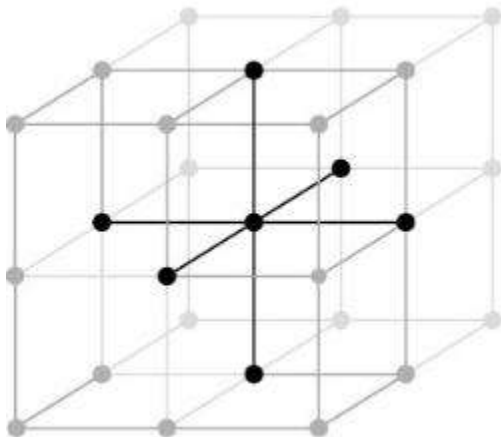


simple cubic unit cell

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Simple Cubic Lattices

- In a simple cubic structure, the spheres are not packed as closely as they could be; it is an inefficient arrangement.
- Only one metal, polonium (Po) crystallizes in this arrangement.
- Each atom in this type of lattice contacts four nearest neighbors in its layer, one atom in the upper layer, and one atom in the lower layer.
- The number of crystalline contacts is the coordination number.



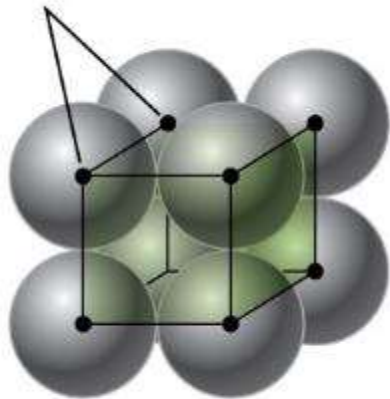
A polonium atom in a simple cubic array has a coordination number of six.

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Simple Cubic Lattices

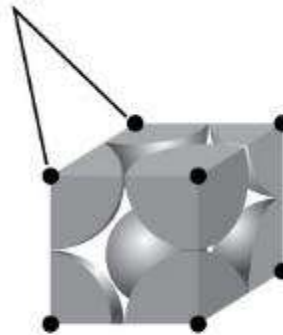
- In a simple cubic lattice, the unit cell that repeats in all directions is a cube defined by the centers of eight atoms.
- Atoms at the corner are in contact, so the edge length is two atomic radii.
- A unit cell only contains the parts of the atom within it.
- In total, a simple cubic unit cell contains a total of one atom.

Lattice points



Simple cubic lattice cell

Lattice points



8 corners

Each corner contains 1/8 of an atom. Eight corners added together gives a total of one atom in total.

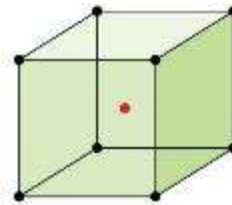
52% of the cell volume is occupied.

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

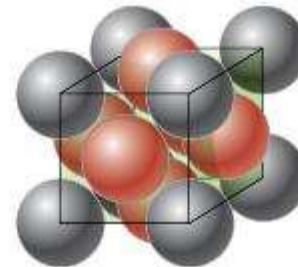
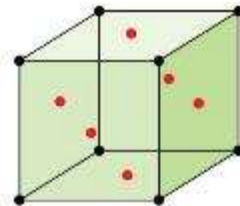
Other Cubic Lattices: Body-Centered and Face-Centered

- There are three types of cubic unit cells:
 - simple
 - body-centered
 - face-centered

- A body-centered cubic structure has atoms at all corners and one atom in the center of the cell.
- A face-centered cubic structure has atoms at all corners and an atom in the center of each face.



Body-centered cubic structure

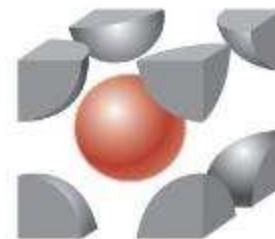
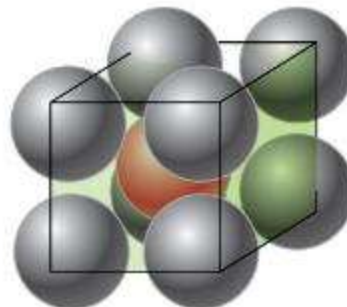
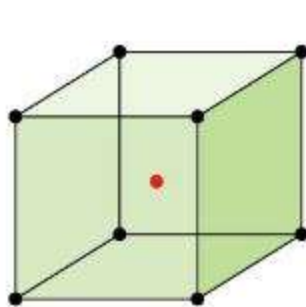


Face-centered cubic structure

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Other Cubic Lattices: Body-Centered Cubic

- A body-centered cubic (BCC) structure has atoms at all corners and one atom in the center of the cell with 68% of the cell filled.
- Atoms at the corners are not in direct contact with one another, but they do contact the atom situated in the center of the cell.
- In total, a BCC unit cell contains a total of two atoms:
 - one from the $\frac{1}{8}$ atom at each corner
 - and one from the atom in the center

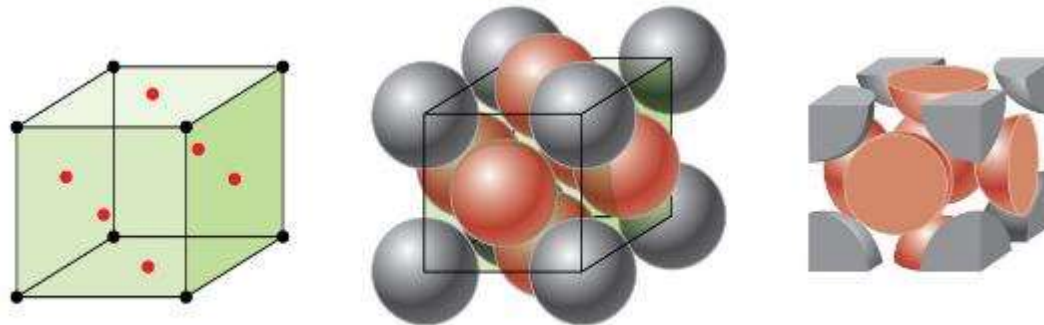


Body-centered cubic structure

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Other Cubic Lattices: Face-Centered Cubic

- A face-centered cubic (FCC) structure has atoms at all corners and one atom in the center of each face, with 74% of the cell filled.
- Atoms at the corners are not in direct contact with one another, but they do contact the atom situated in the center of each face.
- In total, a FCC unit cell contains a total of four atoms:
 - one from the $\frac{1}{8}$ atom at each corner
 - and three from $\frac{1}{2}$ atom on each of the six faces



Face-centered cubic structure

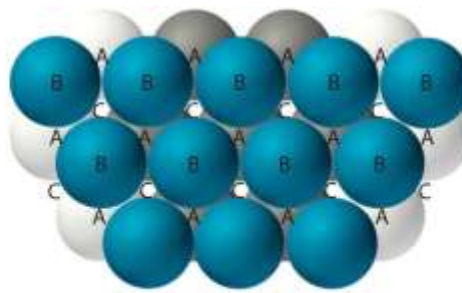
10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Other Cubic Lattices: Closest Packed Arrangements

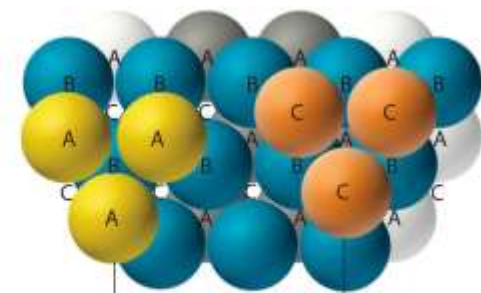
- Atoms in an FCC arrangement are packed as closely together as possible, with 74% of the cell volume occupied.
- This structure is also called cubic closest packed (CCP).
- In a CCP lattice, there are three repeating layers of hexagonally arranged atoms.
- Each atom is in contact with six atoms in the same layer, three in the layer above, and three in the layer below – for a coordination number of 12.



(a) Single layer



(b) Two layers

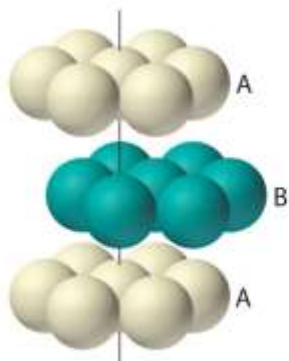


(c) Three layers

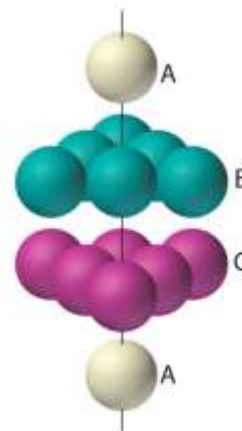
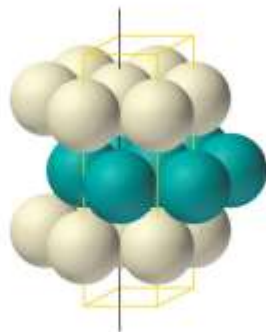
10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Other Cubic Lattices: Closest Packed Arrangements

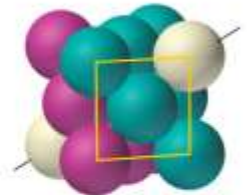
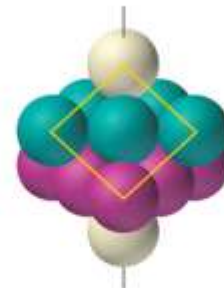
- Consider a single layer (A) of closest-packed spheres:
- The second layer (B) is placed above (A) such that each sphere is in contact with three spheres in the layer above it.
- The third layer can be placed in two different orientations.
 - If the third layer is placed directly above the first layer, a hexagonal closest-packed (HCP) structure is formed (ABABAB).
 - If the third layer is offset from both the (A) and (B) layers, a cubic-closest packed (CCP) structure forms.



(a) Hexagonal close-packed (hcp)



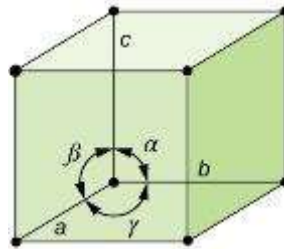
(b) Cubic close-packed (ccp)



10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Other Types of Unit Cells

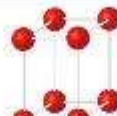
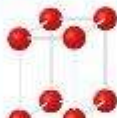
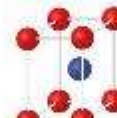
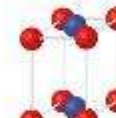
- A unit cell is generally defined by the lengths of its axes (a , b , and c) and the angles (α , β , and γ) between them.



10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Other Types of Unit Cells

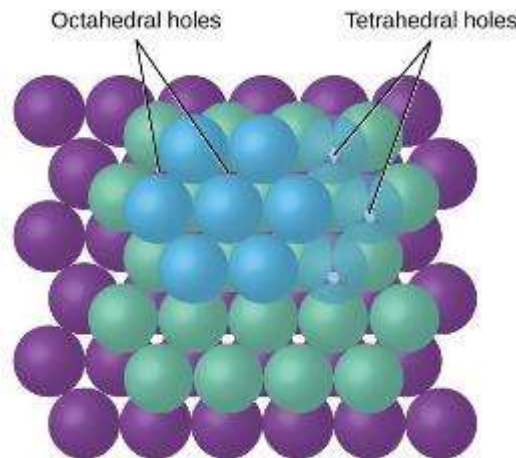
- There are seven lattice systems and a total of fourteen types of unit cells.

System/Axes/Angles	Unit Cells			
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Face-centered	Body-centered	
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Body-centered		
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
	Simple	Body-centered	Base-centered	Face-centered
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$				
	Simple	Base-centered		
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$				
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$				
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$				

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

The Structures of Ionic Crystals

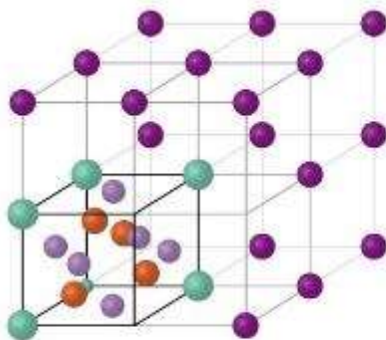
- A unit cell in ionic crystals consists of two or more different kinds of ions that usually have different sizes.
- The smaller cations commonly occupy one of two types of holes (or interstices) remaining between the anions.
 - The smaller of the holes is found between three anions in one plane and one anion in an adjacent plane; this is a tetrahedral hole.
 - The larger type of hole is found at the center of six anions located at the corners of an octahedron; this is an octahedral hole.



10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

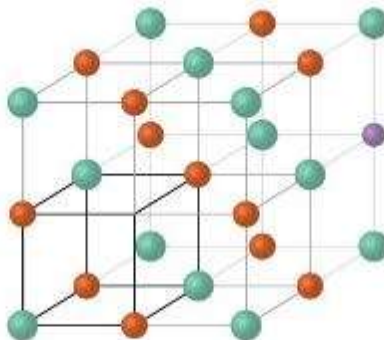
The Structures of Ionic Crystals

- Depending on the relative sizes of the cations and anions, the cations of an ionic compound may occupy tetrahedral or octahedral holes.
- Relatively small cations occupy tetrahedral holes, and larger cations occupy octahedral holes.
- A cation's size and shape and the hole occupied are directly related.



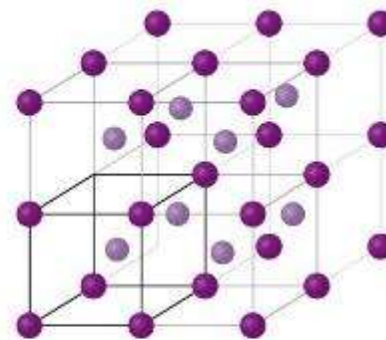
Tetrahedral hole

Cation radius is about 22.5 to 41.4% of the anion radius



Octahedral hole

Cation radius is about 41.4 to 73.2% of the anion radius



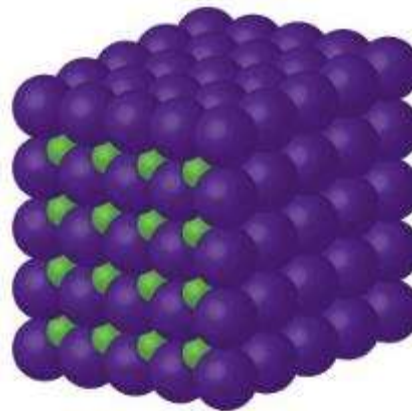
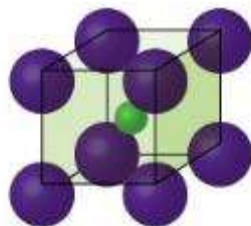
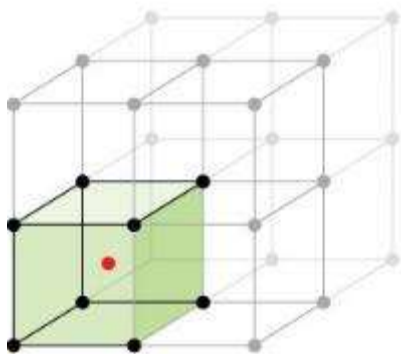
Cubic hole

Cation radius is about 73.2 to 100% of the anion radius

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Unit Cells of Ionic Compounds

- When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure.
- Cesium chloride, CsCl , is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm, respectively.
- One cesium ion and one chloride ion are present per unit cell, giving the 1:1 stoichiometry required by the formula for cesium chloride.

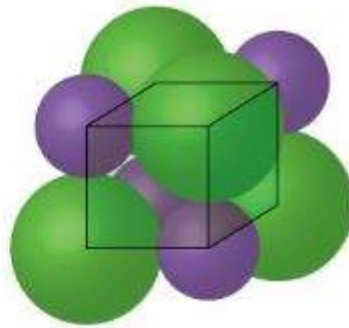
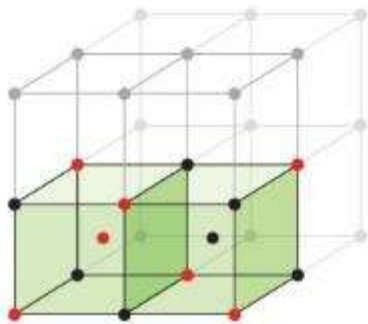


Simple cubic structure

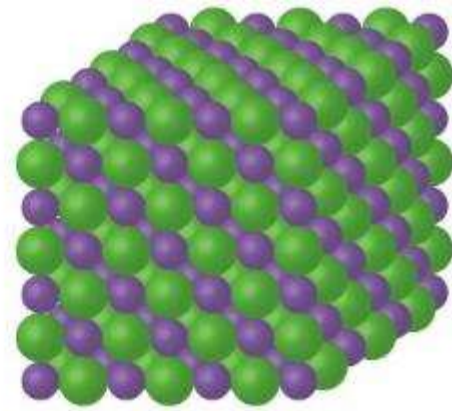
10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Unit Cells of Ionic Compounds

- When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell.
- Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively.



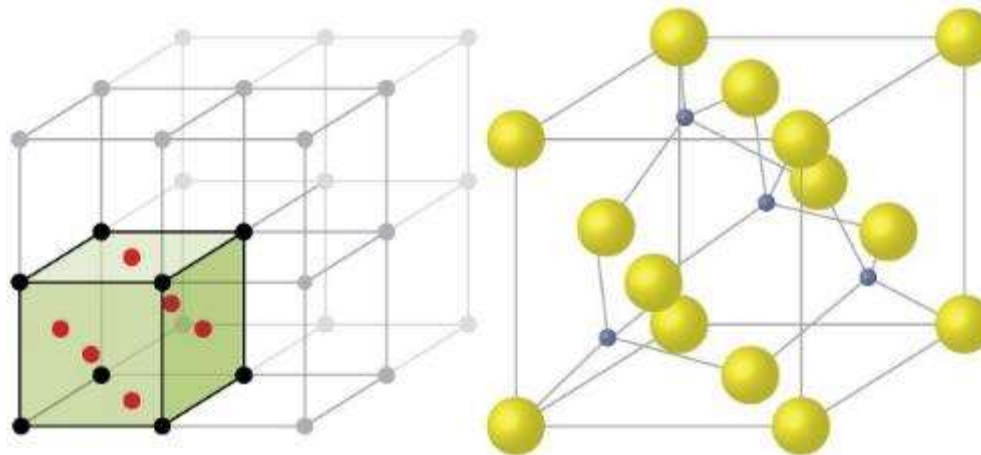
Face-centered simple cubic structure



10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Unit Cells of Ionic Compounds

- The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit .
- Small Zn^{2+} ions are located in alternating tetrahedral holes, that is, in one half of the tetrahedral holes.
- There are four zinc ions and four sulfide ions in the unit cell, giving the empirical formula ZnS .

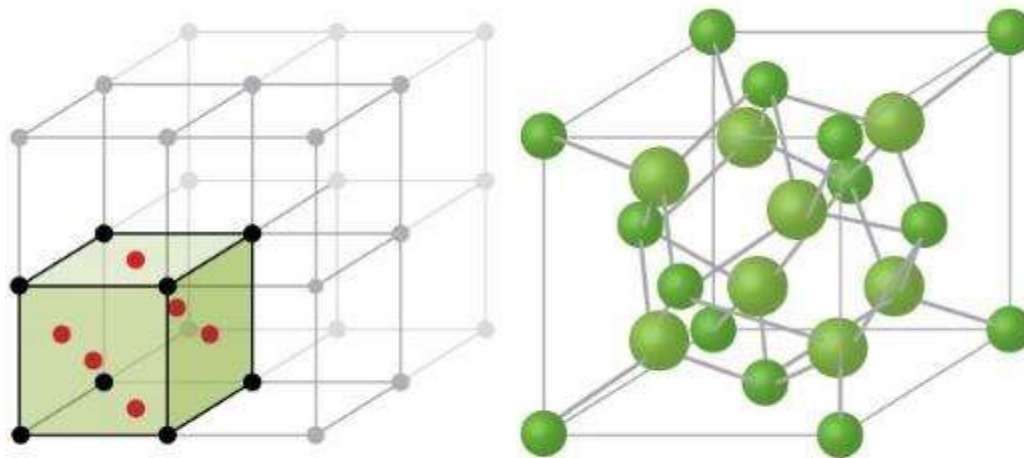


ZnS face-centered unit cell

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Unit Cells of Ionic Compounds

- A calcium fluoride unit cell is also an FCC unit cell, but in this case, the cations are located on the lattice points.
- All of the tetrahedral sites in the FCC array of calcium ions are occupied by fluoride ions.
- There are four calcium ions and eight fluoride ions in a unit cell, giving a chemical formula of CaF_2 .

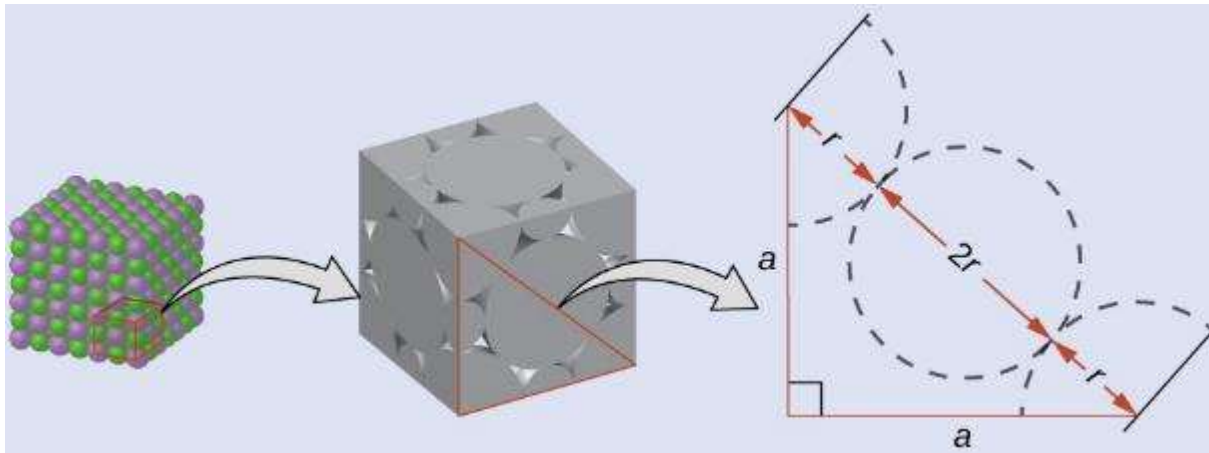


CaF_2 face-centered unit cell

10.6 LATTICE STRUCTURES IN CRYSTALLINE SOLIDS

Example 10.18 – Calculation of Ionic Radii

The edge length of the unit cell of LiCl (NaCl-like structure, FCC) is 0.514 nm or 5.14 Å. Assuming that the lithium ion is small enough so that the chloride ions are in contact, calculate the ionic radius for the chloride ion.



END OF CHAPTER PROBLEMS – CHAPTER 10

Intermolecular Forces: #12, 18, 21

Vapor Pressure: #45, 50, 55, 63

For detailed solutions to these problems, go to the OpenStax Chemistry website and download the [Student Solution Guide](#).

VIDEOS – CHAPTER 10

Overview of Intermolecular Forces

<http://screencast.com/t/qghSO0thk>

Dipole-Dipole Forces

<http://youtu.be/aUcMfSOPPX>

Hydrogen Bonding

<http://youtu.be/B2ZMZFdPm-Q>

Ion Dipole Forces

<http://youtu.be/zLcY8EAdhVQ>

Predicting Physical Properties Based on IMF

<http://screencast.com/t/0On9BZ6J>

**All videos were created by MC Chemistry faculty unless otherwise indicated.*

SIMULATIONS – CHAPTER 10

States of Matter (States of matter, phase transitions)

<https://phet.colorado.edu/en/simulation/states-of-matter>