Intermolecular Forces:
Phases of Matter & Colligative Properties

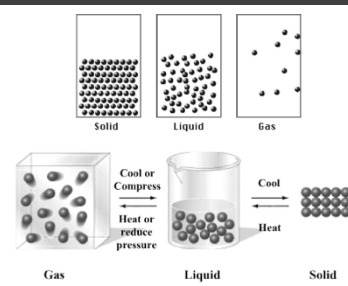
Dr. Ron Rusay

- *Changes of State*
  - Phase transitions
  - Phase Diagrams
- *Liquid State*
  - Pure substances and colligative properties of solutions
- *Solid State*
  - Classification of Solids by Type of Attraction between Units
  - Crystalline solids; crystal lattices and unit cells
  - Structures of some crystalline solids
  - Determining the Crystal Structure by X-ray Diffraction

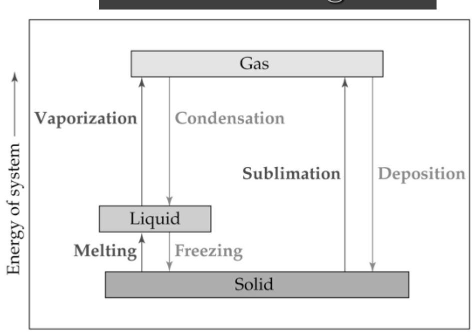
Phase Transitions

• ***Melting**:* change of a solid to a liquid.	$H_2O(s) \rightarrow H_2O(l)$
• ***Freezing**:* change a liquid to a solid.	$H_2O(l) \rightarrow H_2O(s)$
• ***Vaporization**:* change of a solid or liquid to a gas. Change of solid to vapor often called ***Sublimation***.	$H_2O(l) \rightarrow H_2O(g)$ $H_2O(s) \rightarrow H_2O(g)$
• ***Condensation**:* change of a gas to a liquid or solid. Change of a gas to a solid often called ***Deposition***.	$H_2O(g) \rightarrow H_2O(l)$ $H_2O(g) \rightarrow H_2O(s)$

Phases of Matter / Intermolecular Forces



Phase Changes



QUESTION

In which of the following processes will energy be evolved as heat?

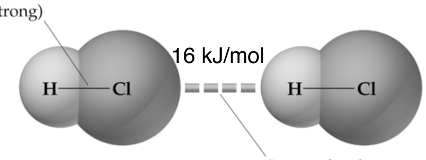
A) Sublimation
B) Crystallization
C) Vaporization
D) Melting
E) None of these

Bonds vs. Intermolecular Forces

(150 - 1000 kJ/mol) (Ionic bond 700-4,000 kJ/mol)

Covalent bond (strong)

16 kJ/mol



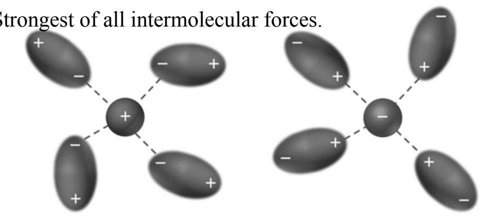
431 kJ/mol

Intermolecular attraction (weak)

Intermolecular Forces

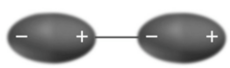
Ion-Dipole Forces (40-600 kJ/mol)

- Interaction between an ion and a dipole (e.g. NaOH and water = 44 kJ/mol)
- Strongest of all intermolecular forces.

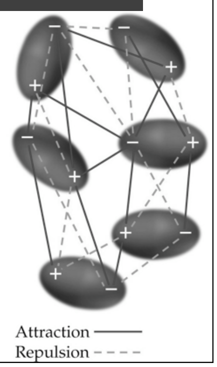


Intermolecular Forces

Dipole-Dipole Forces
(permanent dipoles)



5-25 kJ/mol



Intermolecular Forces

Dipole-Dipole Forces

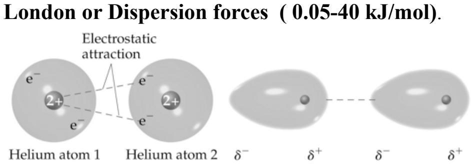
Molecular Weights, Dipole Moments, and Boiling Points of Several Simple Organic Substances

Substance	Molecular Weight (amu)	Dipole Moment μ (D)	Boiling Point (K)
Propane, $CH_3CH_2CH_3$	44	0.1	231
Dimethyl ether, CH_3OCH_3	46	1.3	248
Methyl chloride, CH_3Cl	50	1.9	249
Acetaldehyde, CH_3CHO	44	2.7	294
Acetonitrile, CH_3CN	41	3.9	355

Intermolecular Forces

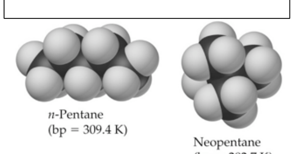
London or Dispersion Forces

- An instantaneous dipole can induce another dipole in an adjacent molecule (or atom).
- The forces between instantaneous dipoles are called **London or Dispersion forces (0.05-40 kJ/mol)**.



Intermolecular Forces

London Dispersion Forces



Which has the higher attractive force?

Intermolecular Forces

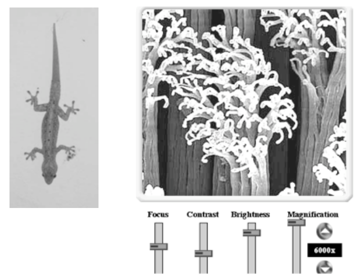
London Dispersion Forces

Boiling Points of the Halogens and the Noble Gases

Halogen	Molecular Weight (amu)	Boiling Point (K)	Noble Gas	Molecular Weight (amu)	Boiling Point (K)
F_2	38.0	85.1	He	4.0	4.6
Cl_2	71.0	238.6	Ne	20.2	27.3
Br_2	159.8	332.0	Ar	39.9	87.5
I_2	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

Gecko: toe, setae, spatulae

6000x Magnification

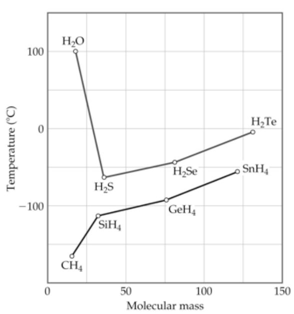


Full et. al., *Nature* (2000)
5,000 setae / mm^2
600x frictional force; 10^{-7} Newtons per seta

Geim, *Nature Materials* (2003)
Glue-free Adhesive
100 x 10^{6} hairs/cm^2

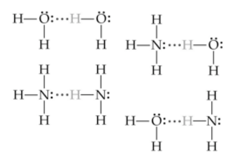
http://micro.magnet.fsu.edu/primer/java/electronmicroscopy/magnify1/index.html

Boiling Points &
Hydrogen Bonding



Hydrogen Bonding

- Hydrogen bonds, a unique dipole-dipole (10-40 kJ/mol).



QUESTION

Which pure substances will not form hydrogen bonds?

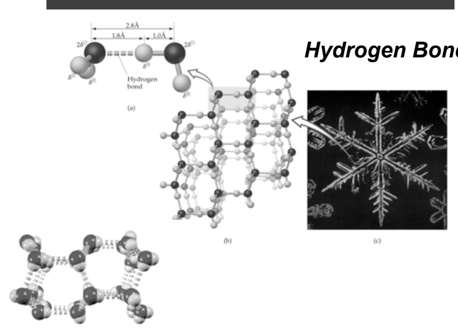
I) CH_3CH_2OH II) CH_3OCH_3

III) $H_3C{-}NH{-}CH_3$ IV) CH_3F

A) I and II B) I and III C) II and III D) II and IV

Intermolecular Forces

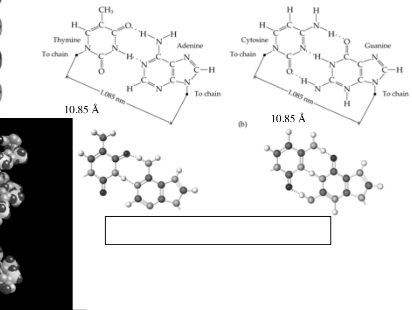
Hydrogen Bonding



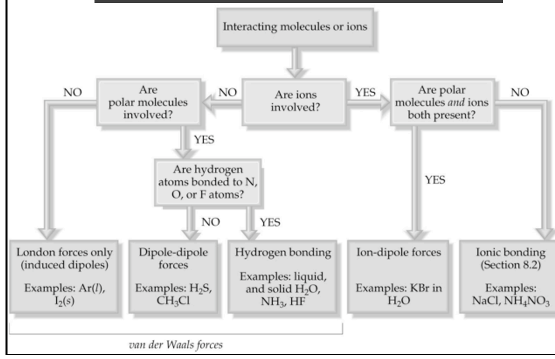
DNA: Size, Shape & Self Assembly

http://www.umass.edu/microbio/chime/beta/pe_alpha/atlas/atlas.htm

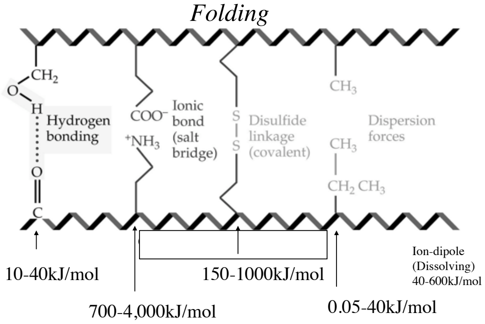
Views & Algorithms



Intermolecular Forces



Protein Shape: Forces, Bonds, Self Assembly, Folding



QUESTION

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

A) $CH_3COCH_2CH_2CH_3$ (molar mass = 86 g/mol)

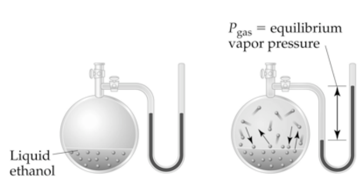
B) $CH_3CH_2CH_2CH_2CH_2OH$ (molar mass = 88 g/mol)

C) $CH_3CH_2CH_2CH_2CH_2CH_3$ (molar mass = 86 g/mol)

D) $HOH_2C{-}CH{=}CH{-}CH_2OH$ (molar mass = 88 g/mol)

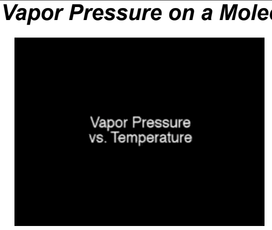
Vapor Pressure

Vapor Pressure on the Molecular Level



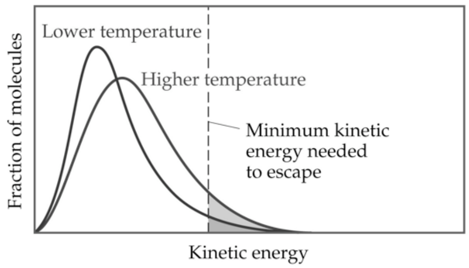
Vapor Pressure

Explaining Vapor Pressure on a Molecular Level



Vapor Pressure

Volatility, Vapor Pressure, and Temperature



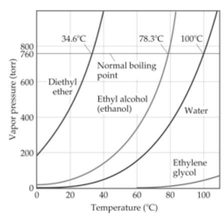
QUESTION

Which one of the following decreases as the strength of the attractive intermolecular forces increases?

A) The heat of vaporization.
B) The normal boiling temperature.
C) The extent of deviations from the ideal gas law.
D) The sublimation temperature of a solid.
E) The vapor pressure of a liquid.

Temperature Dependence of Vapor Pressures

- The vapor pressure above the liquid varies exponentially with changes in the temperature.
- The Clausius-Clapeyron equation shows how the vapor pressure and temperature are related.

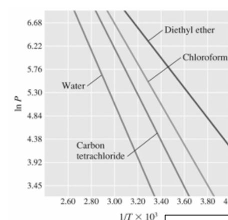


$$\ln P = -\frac{\Delta H_{vap}}{RT} \times \frac{1}{T} + C$$

Clausius – Clapeyron Equation

- A straight line plot results when ln P vs. 1/T is plotted and has a slope of ΔH_{vap}/R.
- Clausius – Clapeyron equation is true for any two pairs of points.

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



QUESTION

You are given the following boiling point data:

A. water, H_2O	100°C
B. methanol, CH_3OH	64.96°C
C. ethanol, CH_3CH_2OH	78.5°C
D. diethyl ether, CH_3OH_2–O–CH_2CH_3	34.5°C
E. ethylene glycol, HO–CH_2–CH_2–OH	198°C

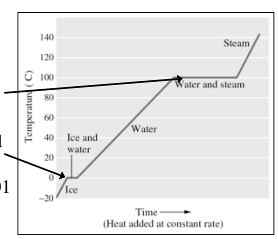
Which one of the above liquids would you expect to have the highest vapor pressure at room temperature?

Energy of Heat and Phase Change

- ***Heat of vaporization***: heat needed for the vaporization of a liquid.

  $H_2O(l) \rightarrow H_2O(g)$ ΔH = 40.7 kJ/mol
- ***Heat of fusion***: heat needed for the melting of a solid.

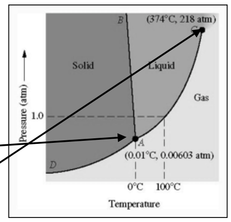
  $H_2O(s) \rightarrow H_2O(l)$ ΔH = 6.01 kJ/mol
- *Temperature does not change during the change from one phase to another.*



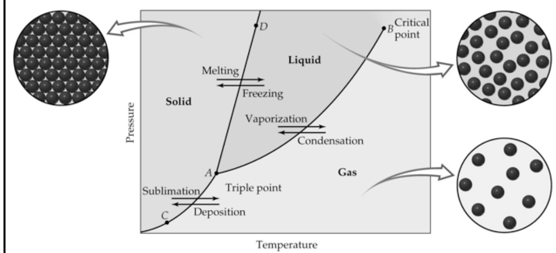
50.0 g of H_2O(s) and 50.0 g of H_2O(l) were mixed together at 0°C. Determine the heat required to heat this mixture to 100.0°C and evaporate half of the water.

Phase Diagrams

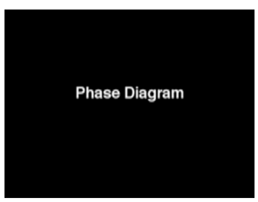
- Graph of pressure-temperature relationship; describes when 1,2,3 or more phases are present and/or in equilibrium with each other.
- Lines indicate equilibrium state between two phases.
- ***Triple point***- Temp. and press. where all three phases co-exist in equilibrium.
- ***Critical temp.***- Temp. where substance must always be gas, no matter what pressure.
- ***Critical pressure***- vapor pressure at critical temp.
- ***Critical point***- system is at its critical pressure and temp.



Phase Diagrams

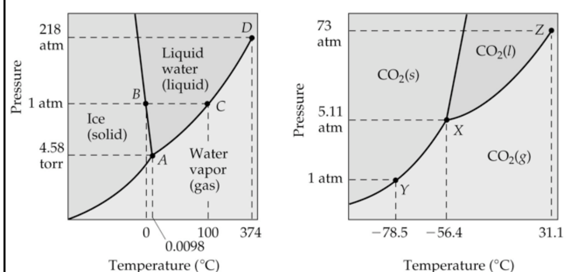


Phase Diagrams

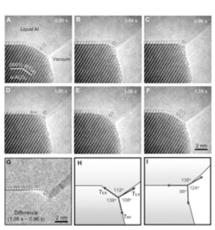


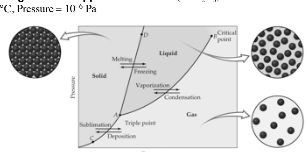
Phase Diagrams

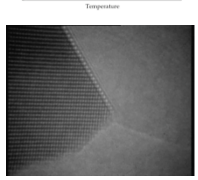
The Phase Diagrams of H_2O and CO_2



Oscillatory Vapor-Liquid-Solid growth of sapphire nanowires (α-Al_2O_3)
660°C, Pressure = 10^{-6} Pa







S. H. Oh et al., Science 330, 489-493 (2010)

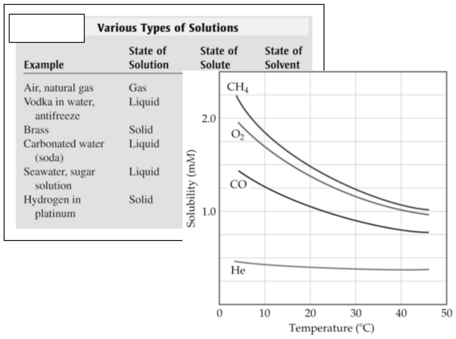
Published by AAAS

Phase Changes

Critical Temperature and Pressure

Critical Temperatures and Pressures of Selected Substances

Substance	Critical Temperature (K)	Critical Pressure (atm)
Ammonia, NH_3	405.6	111.5
Phosphine, PH_3	324.4	64.5
Argon, Ar	150.9	48
Carbon dioxide, CO_2	304.3	73.0
Nitrogen, N_2	126.1	33.5
Oxygen, O_2	154.4	49.7
Propane, $CH_3CH_2CH_3$	370.0	42.0
Water, H_2O	647.6	217.7
Hydrogen sulfide, H_2S	373.5	88.9



Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas		
Vodka in water, antifreeze	Liquid		
Brass	Solid		
Carbonated water (soda)	Liquid		
Seawater, sugar solution	Liquid		
Hydrogen in platinum	Solid		

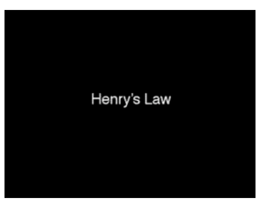
QUESTION

A salt solution sits in an open beaker. Assuming constant temperature and pressure, the vapor pressure of the solution:

A) increases over time.
B) decreases over time.
C) stays the same over time.
D) Need to know which salt is in the solution to answer this.
E) Need to know the temperature and pressure to answer this.

Factors Affecting Solubility

Pressure Effects



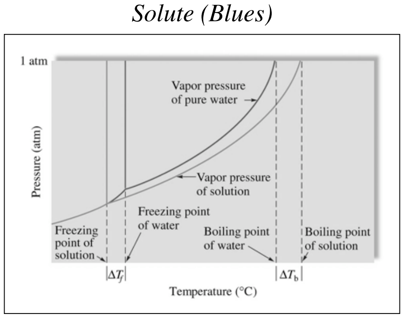
If S_g is the solubility of a gas, k is a constant, and P_g is the partial pressure of a gas, then Henry's Law gives: $S_g = kP_g$

QUESTION

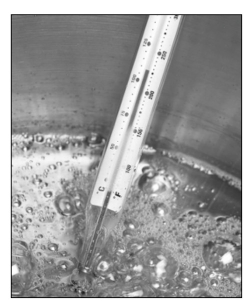
A minimum of 1.3×10^{-4} *M* O_2 must be maintained in freshwater supplies to sustain aquatic life. In the mountains of Montana, the partial pressure of O_2 may drop to 0.15 atm. What is the water concentration of O_2 there? Henry's constant for $O_2 = 1.3 \times 10^{-3}$ mol/L-atm. At the lower elevations at the base of those mountains, would **more or less** O_2 be dissolved in water?

A. $M = 2.0 \times 10^{-4}$; more dissolved
B. $M = 8.7 \times 10^{-4}$; more dissolved
C. $M = 2.0 \times 10^{-4}$; less dissolved
D. $M = 8.7 \times 10^{-4}$; less dissolved

Phase Diagrams for Pure Water (Red) and for an Aqueous Solution Containing a Nonvolatile Solute (Blues)



Sugar Dissolved in Water to Make Candy Causes the Boiling Point to be Elevated



Spreading Salt on a Highway

The Addition of Antifreeze Lowers the Freezing Point of Water in a Car's Radiator

Colligative Properties

- *Colligative properties depend on quantity and type of solute/solvent molecules. (E.g. freezing point depression and melting point elevation.)*

Lowering Vapor Pressure

- Non-volatile solvents reduce the ability of the surface solvent molecules to escape the liquid.
- Therefore, vapor pressure is lowered.
- The amount of vapor pressure lowering depends on the amount of solute.

Colligative Properties

Lowering Vapor Pressure

- ***Raoult's Law: P_A is the vapor pressure with solute, $P_A°$ is the vapor pressure without solvent, and X_A is the mole fraction of A, then***

$$P_A = X_A P^\circ_A$$

- ***Recall Dalton's Law:***

$$P_A = X_A P_{total}$$

QUESTION

If 2.00 g of helium gas and 4.00 g of oxygen gas are mixed together what is the mole fraction of helium in the solution?

A) 0.500
B) 0.333
C) 0.800
D) 0.200
E) 0.666

Concentration

Molality and Molarity

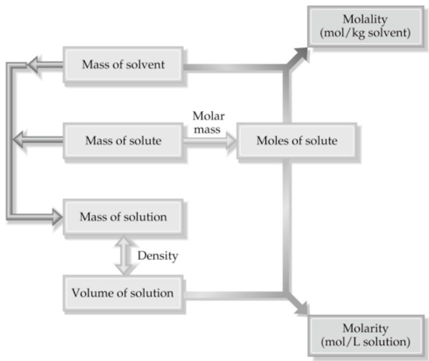
$$\text{Molality}, m = \frac{\text{moles solute}}{\text{kg of solvent}}$$

- Molality relates to colligative properties.
- Converting between molarity (*M*) and molality (*m*) requires density.
- Therefore Molarity and molality are most often **not** equal

QUESTION

What is the molality of a solution of 50.0 g of propanol ($CH_3CH_2CH_2OH$) in 152 mL water, if the density of water is 1.0 g/mL?

A) 5.47 m
B) 0.00547 m
C) 0.833 m
D) 0.183 m
E) None of these



QUESTION

Household bleach is an aqueous solution of sodium hypochlorite. If 5.25 g of NaOCl (molar mass = 74.5 g/mol) were placed in 94.75 g of water, what would you calculate as the molality? The density of the solution is slightly greater than water. Would the molarity of the solution be greater, less or the same as the molality?

A. 0.0705 m; M would be greater
B. 0.705 m; M would be the same
C. 0.744 m; M would be greater
D. 0.744 m; M would be less

Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C · kg/mol)	Freezing Point (°C)	K_f (°C · kg/mol)
Water (H_2O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl_4)	76.5	5.03	−22.99	30.
Chloroform ($CHCl_3$)	61.2	3.63	−63.5	4.70
Benzene (C_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	−111.5	3.83
Ethyl ether ($C_4H_{10}O$)	34.5	2.02	−116.2	1.79
Camphor ($C_{10}H_{16}O$)	208.0	5.95	179.8	40.

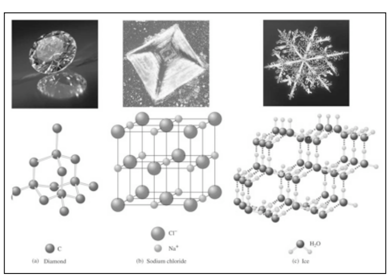
QUESTION

Suppose you want to keep the water in your car cooling system from freezing during a cold Alaska winter night. If you added 5.00 Kg of ethylene glycol ($C_2H_4(OH)_2$ mm = 62.0 g/mol) to 5.50 kg of water, what would be the freezing temperature of the coolant/water mixture in your automobile?

$k_{f.p.}$ H_2O = –1.86°C kg/ mol

A. –0.0367°C
B. –7.90°C
C. –14.7°C
D. –27.3°C

Atomic Solid / Ionic Solid / Molecular Solid

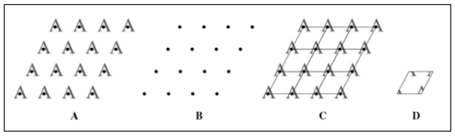


Structure of Solids

- *Types of solids*:
  - Crystalline – a well defined arrangement of atoms; this arrangement is often seen on a macroscopic level.
    - ***Ionic solids*** – ionic bonds hold the solids in a regular three dimensional arrangement.
    - ***Molecular solid*** – solids like ice that are held together by intermolecular forces.
    - ***Covalent network*** – a solid consists of atoms held together in large networks or chains by covalent networks.
    - ***Metallic*** – similar to covalent network except with metals. Provides high conductivity.
  - Amorphous – atoms are randomly arranged. No order exists in the solid.

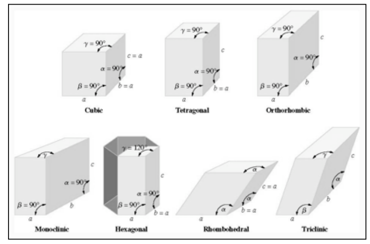
Unit Cells

- Crystals are made up of atoms in regular arrays – the smallest of repeating array of atoms is called the unit cell.
- There are 14 different unit cells that are observed which vary in terms of the angles between atoms some are 90°, but others are not.



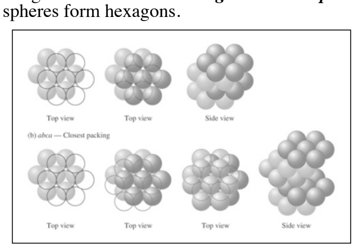
Unit Cells

- Length of sides a, b, and c as well as angles α, β, γ vary to give most of the unit cells.

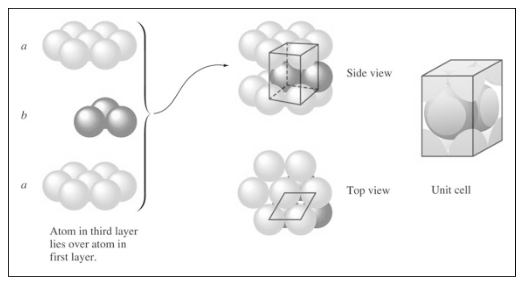


Closest Packing Arrangement of Uniform Sphere

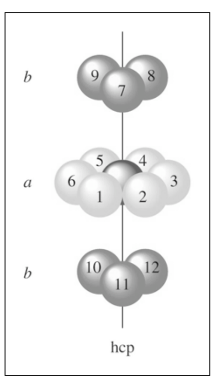
•Arrays of atoms act as if they are spheres. Two or more layers produce a 3-D structure.
•Angles between groups of atoms can be 90° or can be in a more compact arrangement such as the ***hexagonal closest pack*** (see below) where the spheres form hexagons.



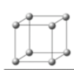
Hexagonal Closest Packed Structure

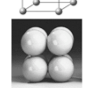


Hexagonal Close Packed: The Red Sphere has 12 Nearest Neighbors



QUESTION



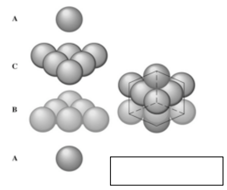


Consider an interior atom in the simple cubic crystal lattice. What is the maximum number of unit cells that share this atom in the three-dimensional crystal lattice?

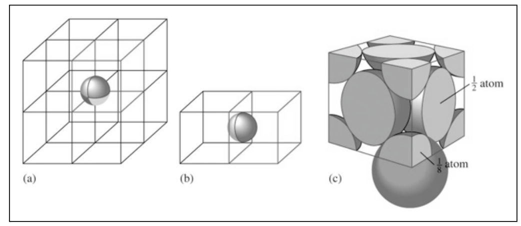
A) 2 **B) 4** **C) 6** **D) 8**

Unit Cells

- Face Centered Cubic structure has *a-b-c-a-b-c* stacking. It takes three layers to establish the repeating pattern and has 4 atoms per unit cell and the coordination number is 12.

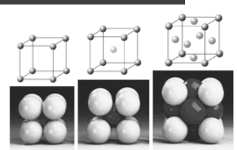


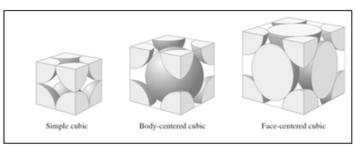
The Net Number of Spheres in a Face-Centered Cubic Unit Cell



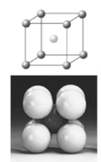
Unit Cells

- ***Simple-cubic***
- ***Body-centered cubic***
- ***Face-centered cubic***





QUESTION

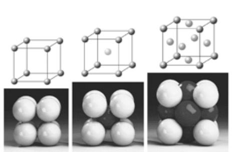


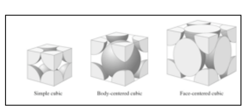
The number of atoms per unit cell in the body-centered cubic lattice is

A) 1 **B) 2** **C) 3** **D) 4**

Unit Cells

- **Simple-cubic** shared atoms are located only at each of the corners. **1 atom per unit cell**.
- **Body-centered cubic** 1 atom in center and the corner atoms give a net of **2 atoms per unit cell**.
- **Face-centered cubic** corner atoms plus half-atoms in each face give **4 atoms per unit cell**.

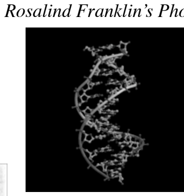


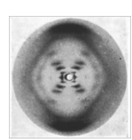


X-ray Crystallography

http://info.bio.cmu.edu/courses/03231/ProtStruc/ProtStruc.htm

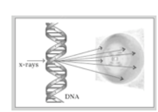
Rosalind Franklin's Photo 51





12 base sequence

(1953-2003)



http://molvis.sdsc.edu/pdb/dna_b_form.pdb