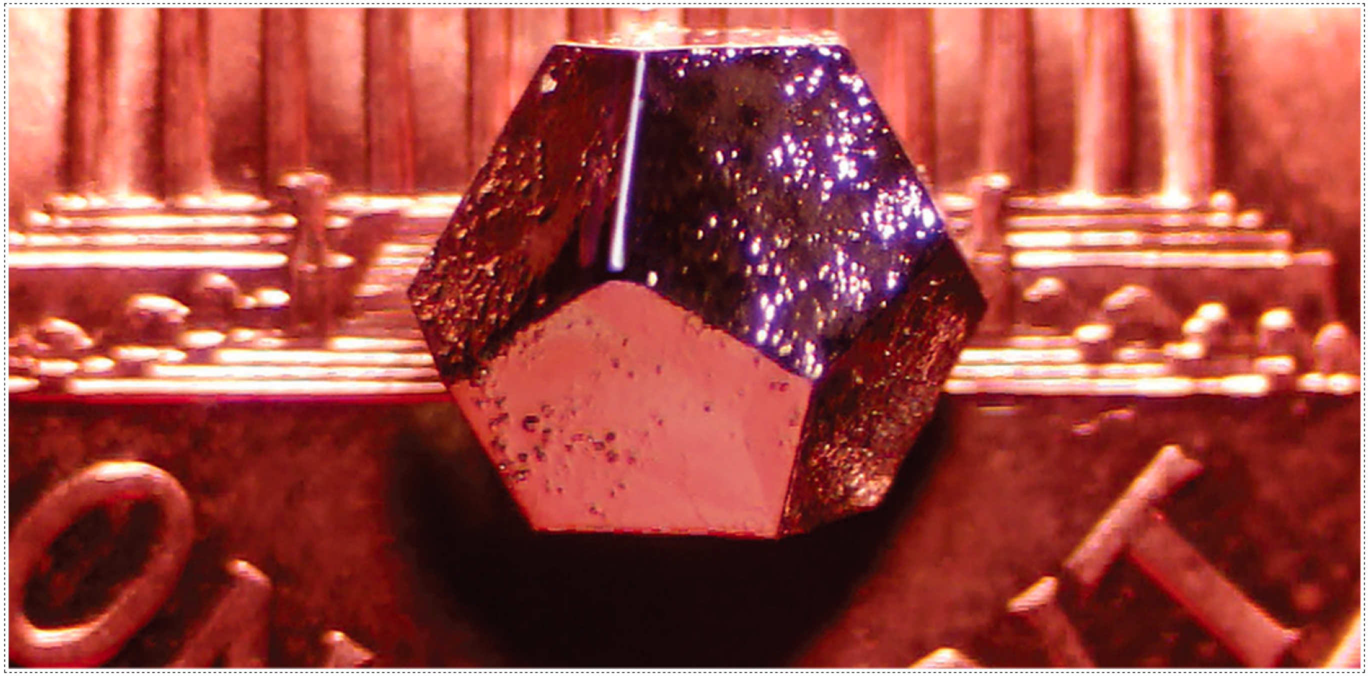
Chapter Twelve

Liquids and Solids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Attractive Forces Review

Strength

Covalent Bonds

- Intramolecular, not intermolecular
- Strongest but NOT broken during melting, boiling
  - -> exception is molecular solids like diamond – they have the highest melting & boiling points

Ionic Bonds

- "Interparticle" attractive force
- Full charge = very strong
- Very high melting & boiling points
- Many ionic solids dissolve in water

Hydrogen "bonds" (H directly bonded to O,N,F)

- Strongest Intermolecular Attractive Force
- Partial charges, so weaker than ionic
- High melting & boiling points
- If have enough make molecules water soluble

Strength

Dipole–Dipole Attraction

- Permanent dipoles
  - Need highly electronegative element bonded to an atom other than H
- Weaker than H bonds
- Increase melting & boiling points & solubility
  - but not as much as H bonds

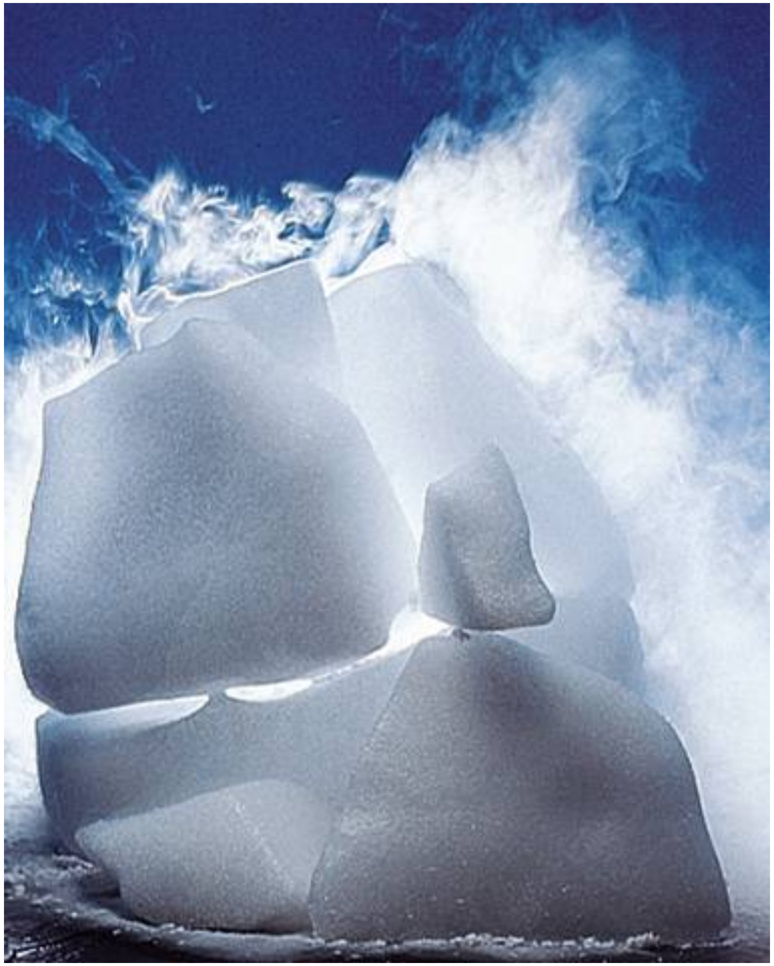
Dispersion Forces

- Weakest Intermolecular Attractive Force
- All molecules have dispersion forces
- Only attractive force available to nonpolar molecules
- Lowest melting & boiling points
  - depend on size & surface area
- Do not help make molecules water soluble
- Nonpolar molecules dissolve in nonpolar solvents
  - “like dissolves like”

States of Matter: Determined by IMAF

Gases: Minimal IMAF

- Low density
- No fixed volume or shape
- Readily compressed
- Atoms/molecules move easily



Liquids: IMAF allow flow

- Relatively high density
- Fixed volume
- Assumes shape of container
- Does not compress
- Molecules flow past each other

Solids: Strongest IMAF

- High density
- Fixed shape and volume
- Does not compress
- Vibrational motion only

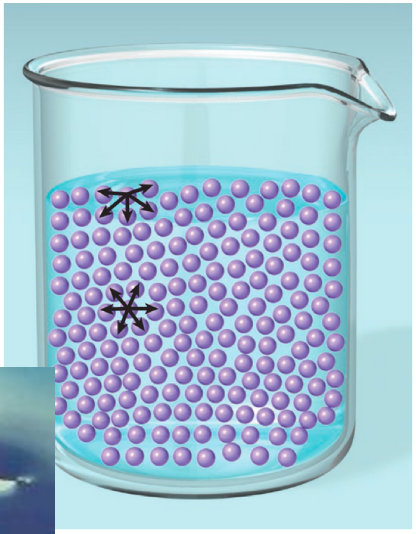
Fluid = liquid + gas

Liquids

Properties of Liquids

Surface Tension

- Energy/unit area needed to form a surface
- Top of liquid has tighter bonds than in liquid
- Higher IMAF = Greater surface tension



Cohesion

- Attraction between like molecules

Adhesion

- Attraction between unlike materials
  - "adhesive" bonds things together

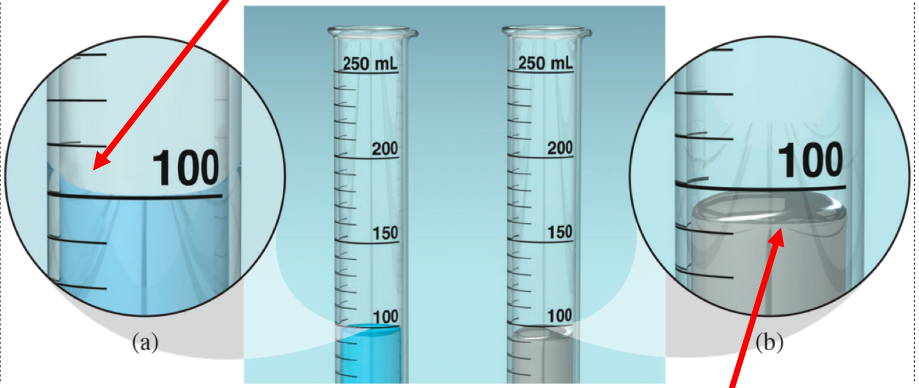
H_2O: A>C
Concave meniscus

Capillary Action

Adhesive forces: liquid sticks to glass

Cohesive forces: molecules stick together

- Allows plants to pull water up through roots



Hg: C>A
Convex meniscus

Properties of Liquids

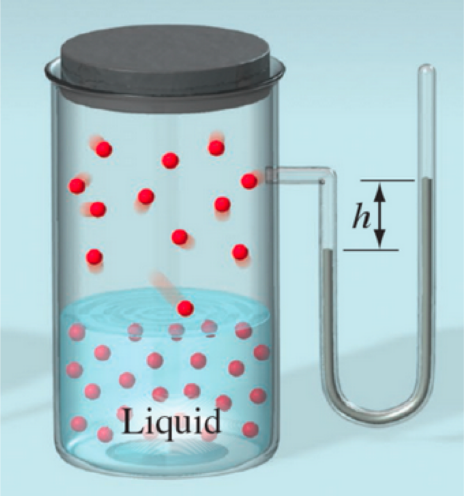
Viscosity: Measure of resistance to flow

- Higher IMAF = higher viscosity
- Higher temperature = lower viscosity (faster flow)
- Higher viscosity = slower flow

TABLE 12.1 Viscosities of Some Familiar Liquids at 20°C	
Liquid	**Viscosity ($N \cdot s/m^2$)**
Acetone (C_3H_6O)	3.16×10^{-4}
Water (H_2O)	1.01×10^{-3}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Mercury (Hg)	1.55×10^{-3}
Blood	4×10^{-3}
Glycerol ($C_3H_8O_3$)	1.49

Properties of Liquids

Vapor pressure: pressure of material in the gas phase above a body of liquid (and some solids).



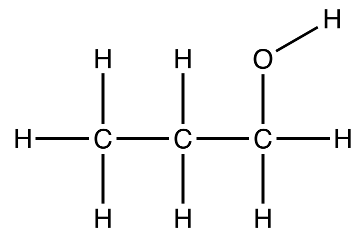
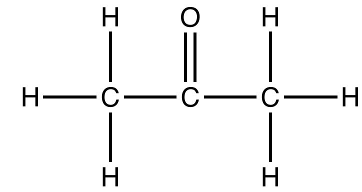
- Equilibrium process – particles constantly moving between gas and liquid phases. Relative amounts remain constant.
- Increases with temp. – more particles moving faster
- Higher IMAF = **lower** vapor pressure

Boiling point: temp. where vapor pressure= atm. pressure

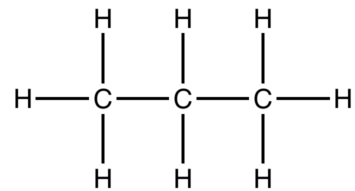
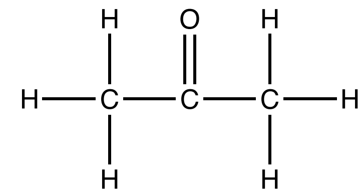
- Lower boiling point = higher vapor pressure!
- Higher IMAF = **higher** boiling (and melting) point!
- Depends on atmospheric pressure, so is different at different elevations
  - Why cooking times can vary based on location

Which of the following would have a higher boiling point?

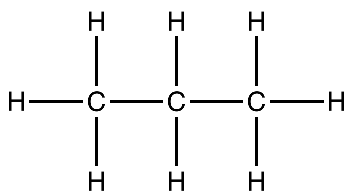
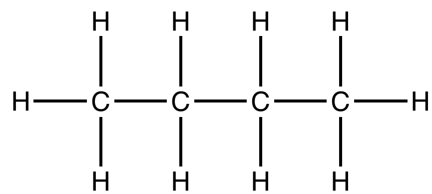
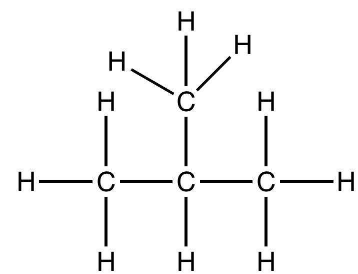
LiF vs CH_3OH

 vs. 

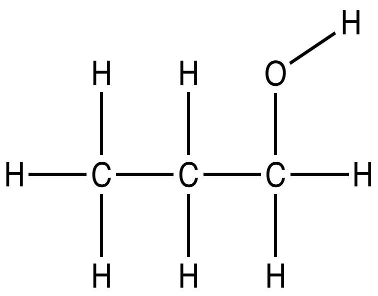
CH_2Cl_2 vs CCl_4

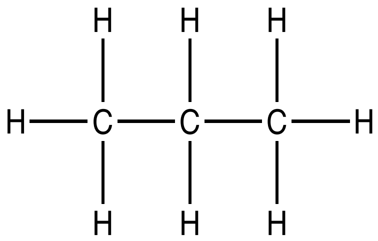
 vs. 

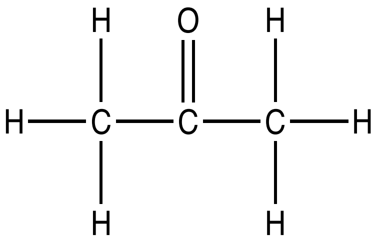
CCl_4 vs CH_4

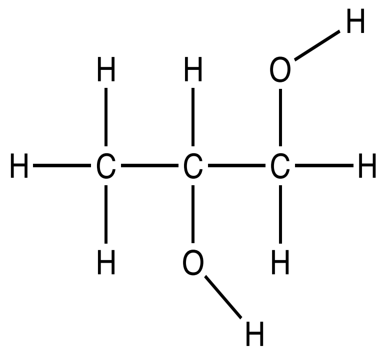
 vs.  vs. 

List the following in order of increasing surface tension.

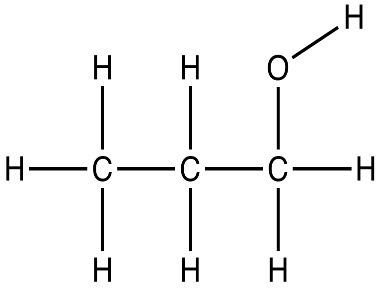


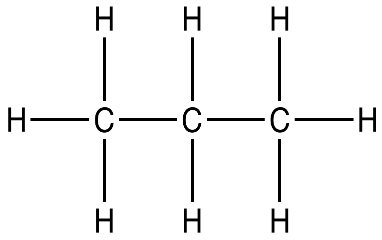


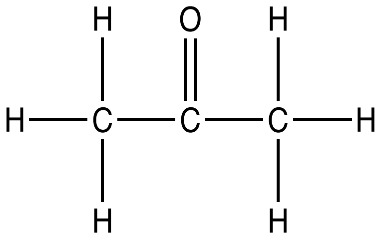


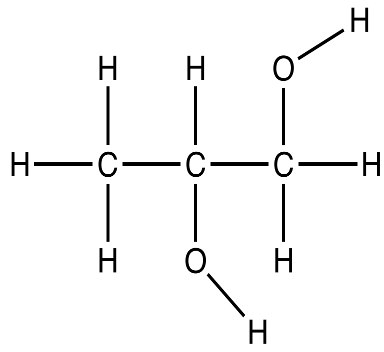


Rank the following in order of increasing water solubility.



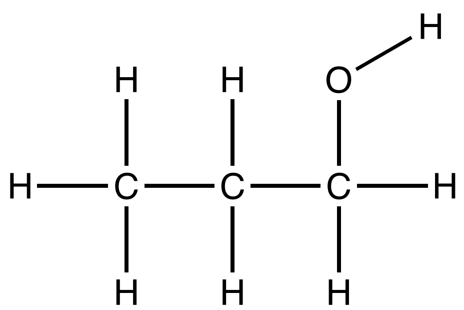


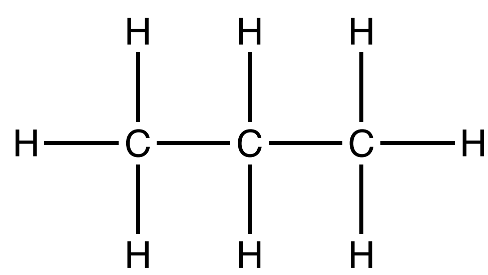


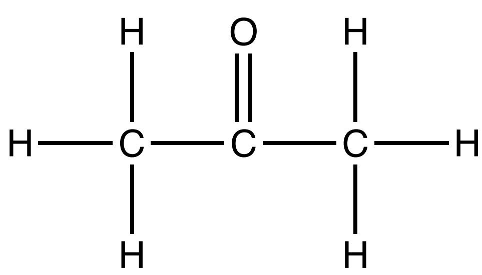


Which of the following would have the highest vapor pressure?

Which would have the lowest vapor pressure?

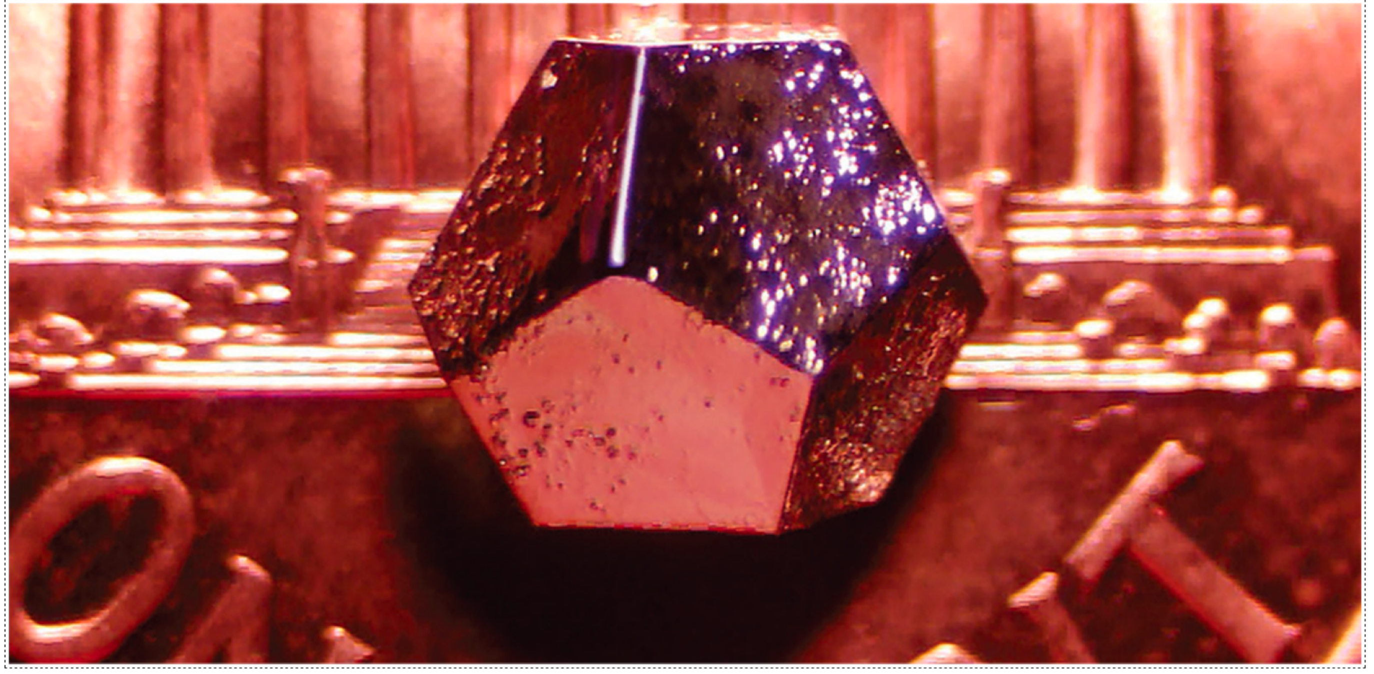






Remember that the trend for vapor pressure is the OPPOSITE of what we have seen for other phenomena (like melting & boiling point & water solubility)

Solids



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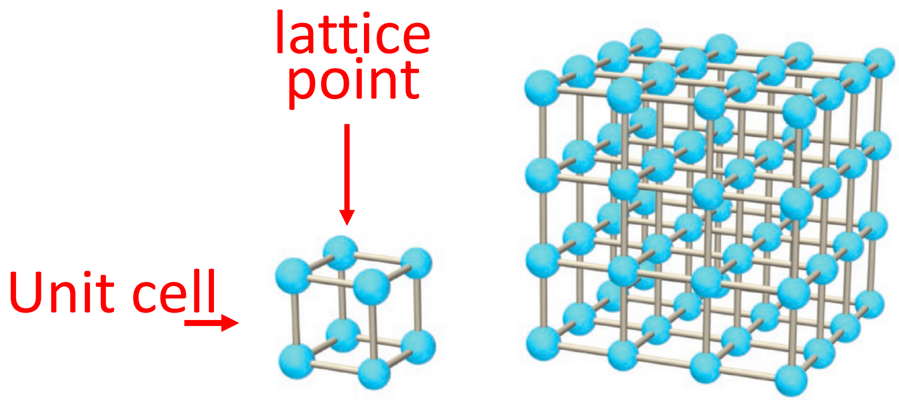
Solids: Crystal Structure

Crystal

- Particles arranged in a well defined order
- Atoms, molecules, or ions occupy predictable positions
- Arrangement based on ratio of particles

Unit cell

- Basic repeating structural unit of a crystalline solid



Lattice points can be:

Atoms
Molecules
Ions

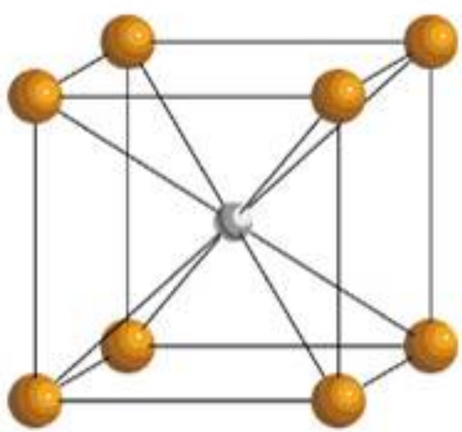
Amorphous solid

- Does not have a well-defined arrangement of particles

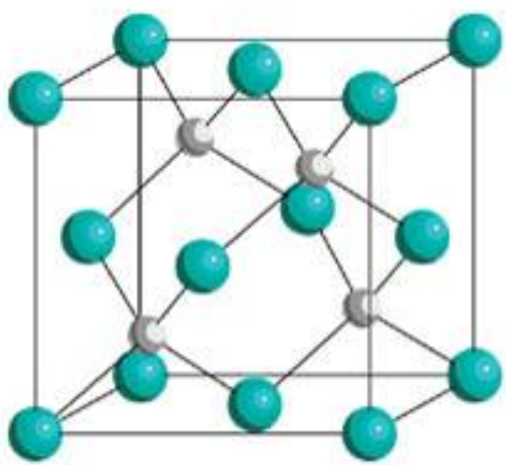
Ionic Crystals

- Lattice points usually occupied by anions (larger)
- Cations usually occupy space between anions
- Held together by electrostatic attraction
- Characteristics:
  - Hard, brittle, high melting point
  - Poor conductors of heat and electricity

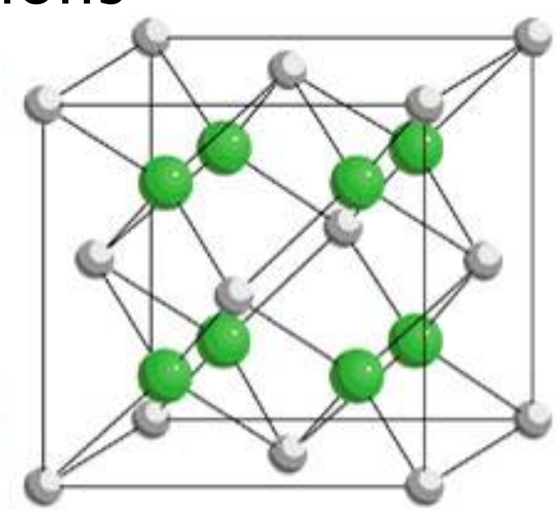
    → charges locked into fixed positions



Simple Cubic
CsCl



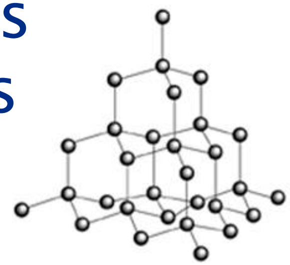
Face Centered Cubic
ZnS

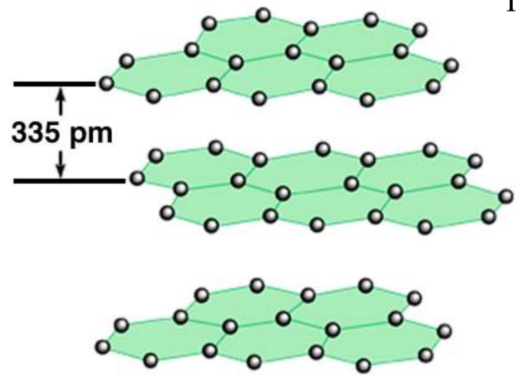


Body Centered Cubic
CaF_2

Covalent Crystals

- Lattice points occupied by atoms
- Held together by covalent bonds
- Hard, very high melting point
- Usually poor conductors of heat and electricity
  - graphite conducts electricity due to pi (π) bonding


diamond



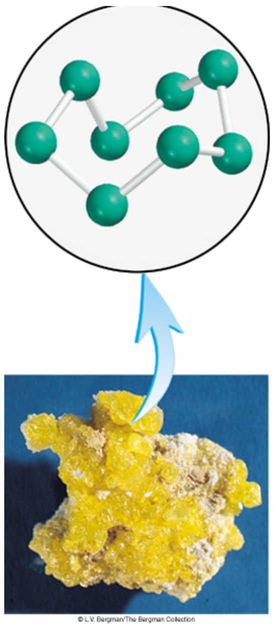
graphite

Molecular Crystals

Note for HW: SiO_2 is a covalent crystal

- Lattice points occupied by molecules
- Held together by intermolecular forces
  - Nonpolar: Dispersion forces
  - Polar: Dipole-dipole or H-bonding
- Soft, low melting point
  - Often don't want to be a solid!
- Poor conductors of heat and electricity
  - Neutral molecules; no free moving e^-

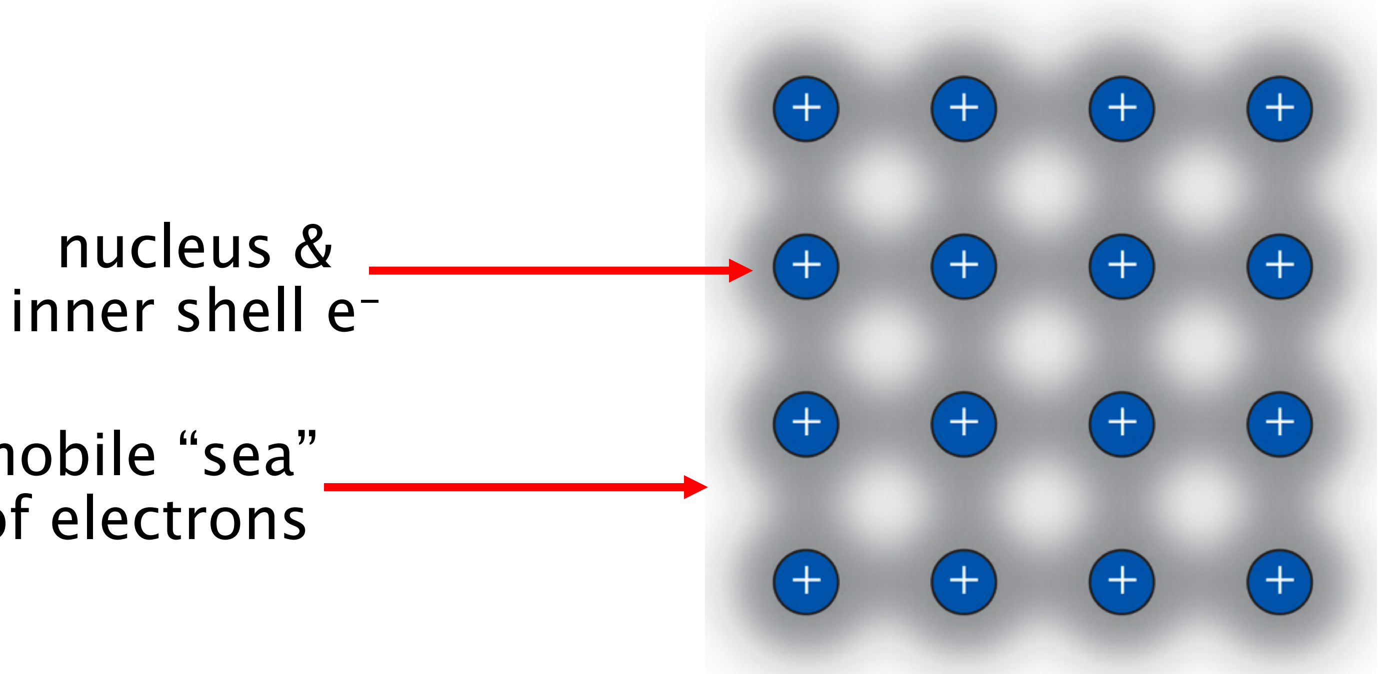
$S_8 \rightarrow$



Metallic Crystals

Lattice points occupied by metal atoms

- Held together by metallic bonds
- Soft to hard, low to high melting point
- Good conductors of heat and electricity
  - movement of electrons between metal atoms
  - “electron sea”



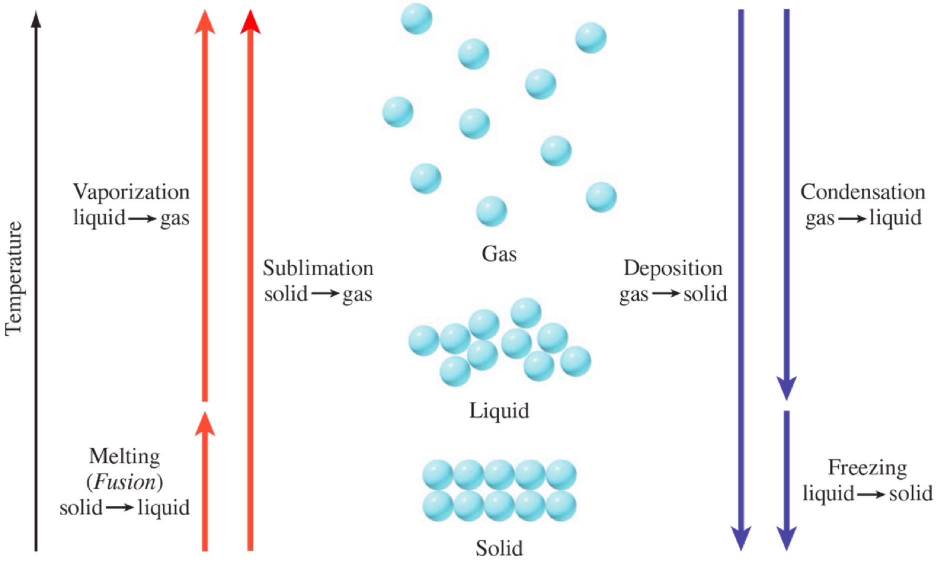
Phase Changes

Phase Changes

Change state of matter

- Forces holding molecules/ions together are disrupted
- Covalent bonds **NOT** broken during phase changes

Fusion (melting): solid → liquid
Freezing: liquid → solid
Vaporization: liquid → gas
Condensation: gas → liquid
Sublimation: solid → gas
Deposition: gas → solid

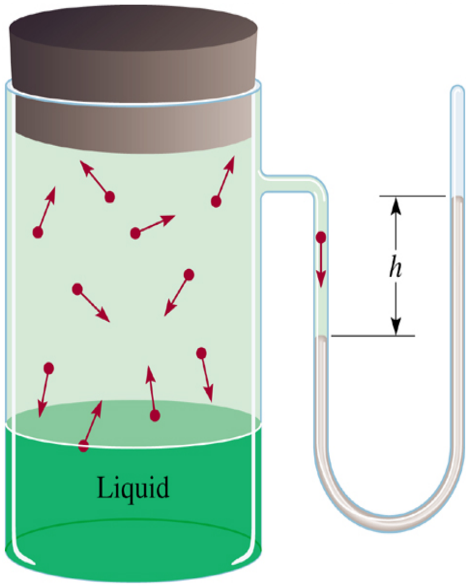


Phase Changes

Liquid–Vapor Equilibrium – molecules constantly moving $\rightleftharpoons$ between liquid & vapor phase

Vaporization: Conversion of liquid to vapor

- Fast molecules leave liquid surface
- Remaining molecules are lower in energy
- Endothermic: molecules need energy to escape liquid surface
- Measure vapor pressure using gas laws



Condensation: Conversion of vapor to liquid

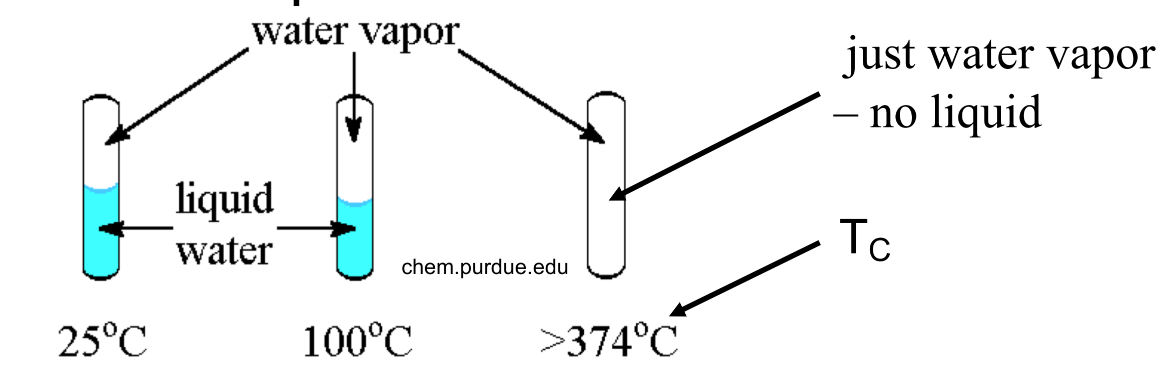
- Slower molecules drop out of gas
- Exothermic: liquid less energetic than gas

Enthalpy Conversions

- $\Delta H_{vap} = -\Delta H_{cond}$

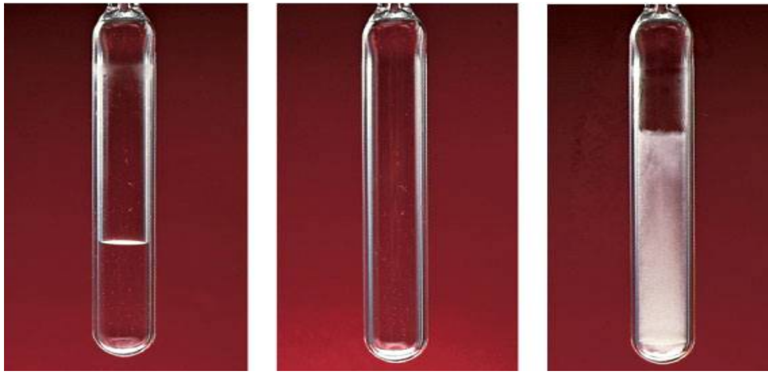
Supercritical Fluid

Critical temp (T_c) – above this temp gas cannot be liquified
Critical pressure (P_c) – Above this pressure, increasing temp will not cause a fluid to vaporize.



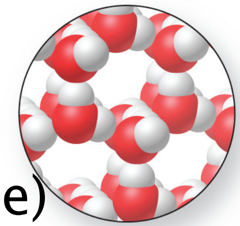
As temperature is raised in a sealed container:

- Start with liquid water & water vapor
- Critical Temp (T_c) is reached, all vapor
- Temp continues to increase – pressure increases to P_c
- Sealed so no way to lower pressure
- Water wants to condense but cannot above T_c
- Liquid & vapor meld into one fluid



Melting and Freezing Solid ⇆ Liquid

Melting

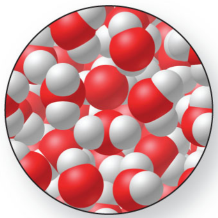

Ice

- Endothermic: requires input of energy (heat)
- Particles move faster & (usually) further apart (less dense)
- Attractive forces decrease; crystalline structure collapses

Freezing

Water is an exception – ice is less dense. Why?

- Exothermic: particles in solid have lower energy
- Particles slow down & (usually) move closer together
- Attractive forces increase; Solid settles into a crystal


Liquid water

Determined by melting / freezing point:

- Temperature at which a substance melts (or freezes)
- Depends on pressure
- Normal melting point: MP at 1 atm

H bonding!

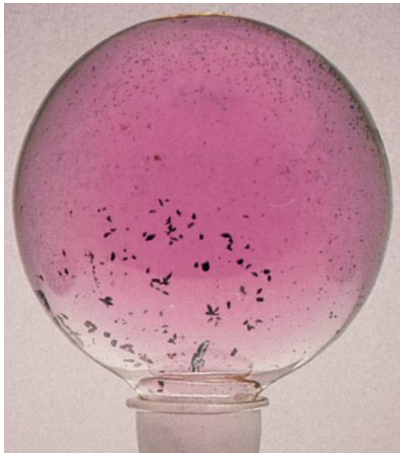
Molar Heat of Fusion/Melting ($\Delta H°_{fus}$)

- Heat absorbed/released when 1 mole solid melts/freezes at constant T & P

Supercooling: Pure liquid cooled slowly may exist below its freezing pt.

Sublimation and Deposition: Solid ⇆ Vapor

Sublimation
- Solid converted directly to gas
- Endothermic: Need heat to increase molecular movement
- Disrupts intermolecular forces



Iodine

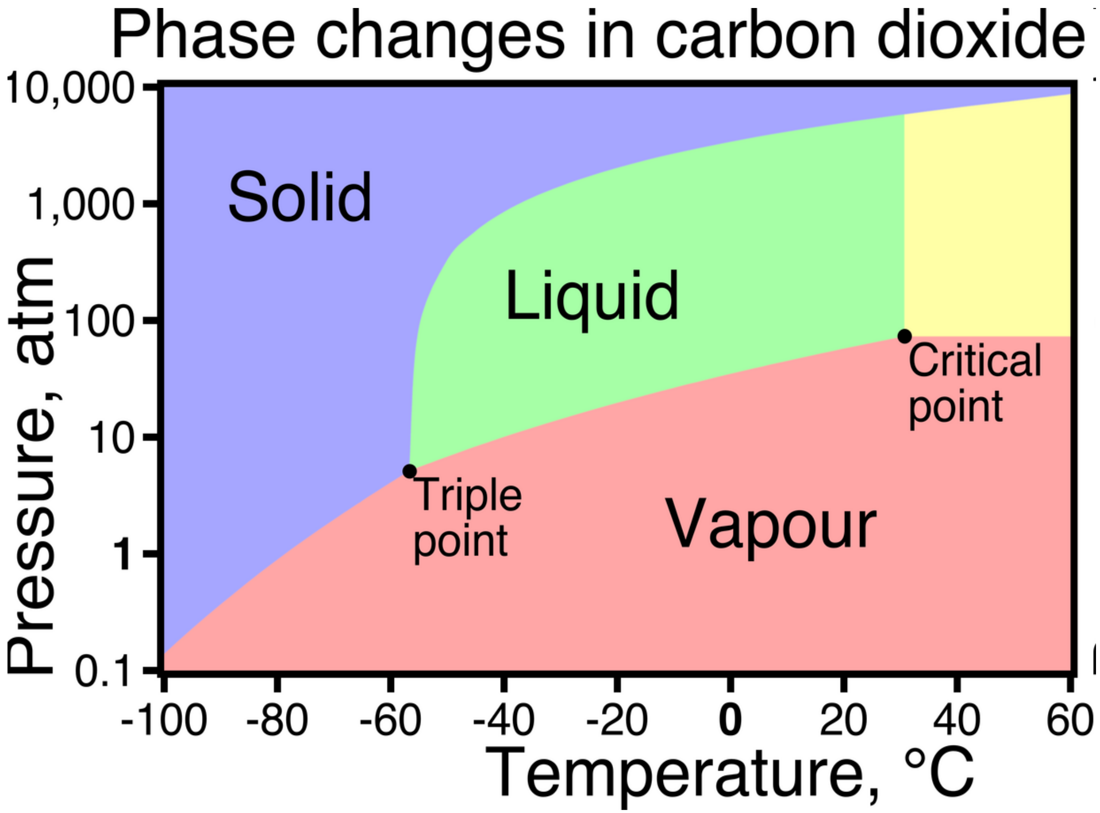
Heat of Sublimation (ΔH°_{sub})
- Combines heat for solid to liquid transition plus liquid to gas transition.
- $\Delta H^\circ_{sub} = \Delta H^\circ_{fus} + \Delta H^\circ_{vap}$

Deposition: Opposite of sublimation
- Gas directly to solid
- Exothermic – solid at lower energy than gas

Triple Point: Pressure & temperature at which solid, liquid, & gas (or any 3 phases) exist simultaneously

Phase Diagrams

Phase diagrams summarize the conditions (temp & press.) at which a substance exists as a solid, liquid, or gas.

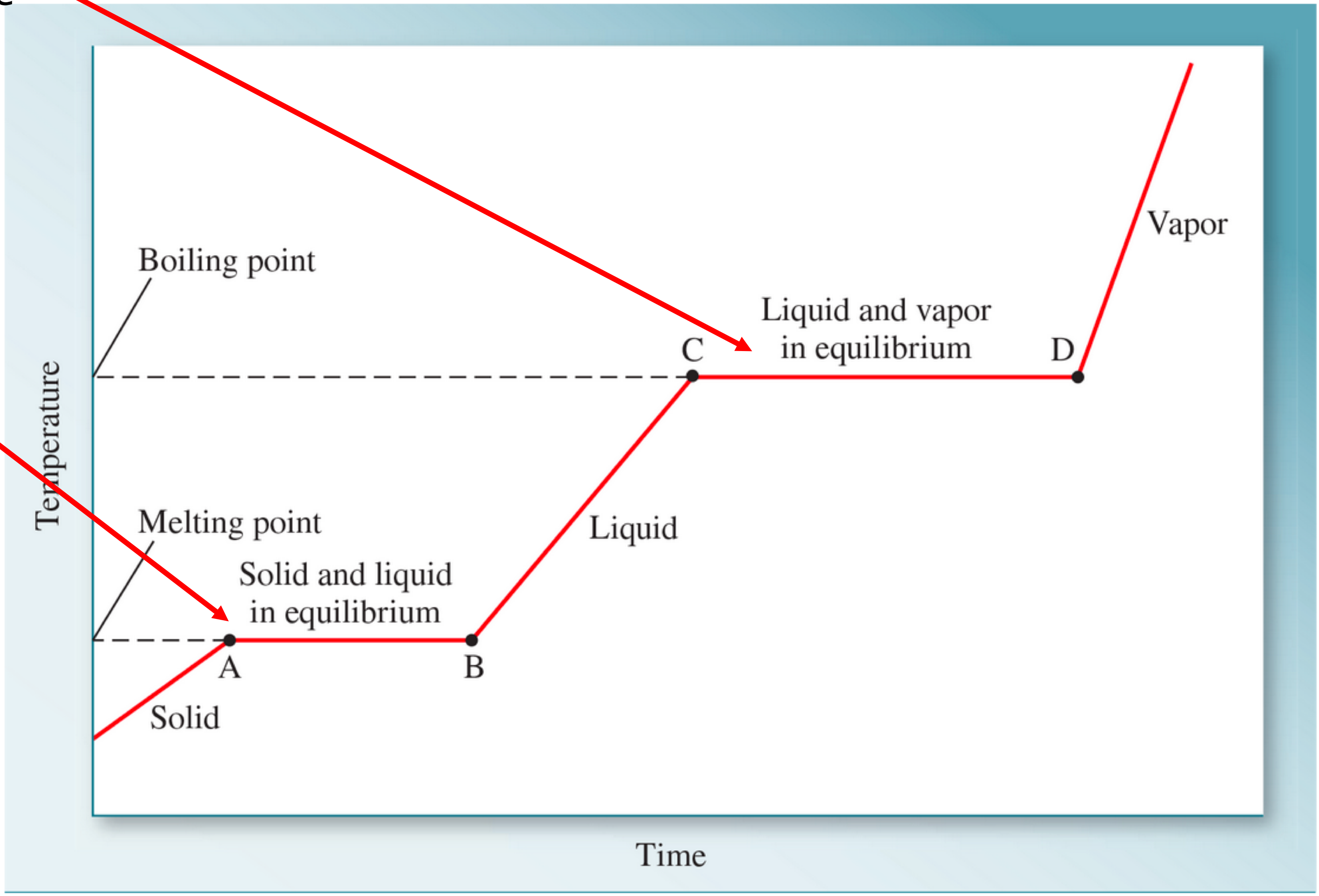


At 1 atm

CO_2 (s) $\longrightarrow$ CO_2 (g)

Heating Curve

Note that at bpt. & mpt., temperature remains constant until all material has changed phase



Enthalpy Problems involving Phase Changes

1.) How much heat (in kJ) is required to convert 25.4 g water into steam at 100°C? (ΔH_{vap}=40.79 kJ/mol for water)

A: 57.5 kJ

2.) A beaker of ethanol requires 15.67 kJ heat to fully evaporate the ethanol. What is the mass of the ethanol? (Heat of vaporization of ethanol is 918 J/g.)

A: 17.1g

3.) How much heat (in kJ) is required to convert 150.0 g ice at – 5.0°C into steam at 130.0°C?

ΔH_{fus} = 6.01 kJ/mol, ΔH_{vap} = 40.79 kJ/mol;
specific heat values: water = 4.184 J/g°C, ice = 2.03J/g°C, steam = 1.99 J/g°C

This is basically just a Hess's Law problem involving calorimetry!

A: 462.9 kJ