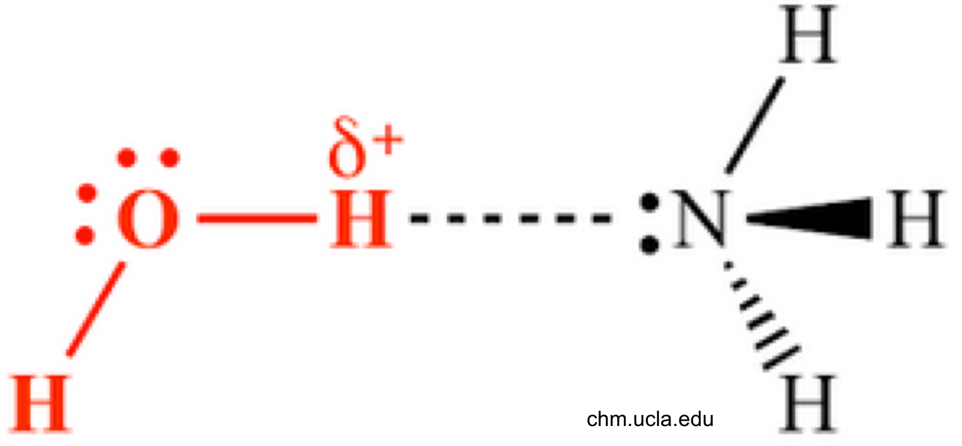
Chapter Twelve

Intermolecular Forces

&

Liquids and Solids



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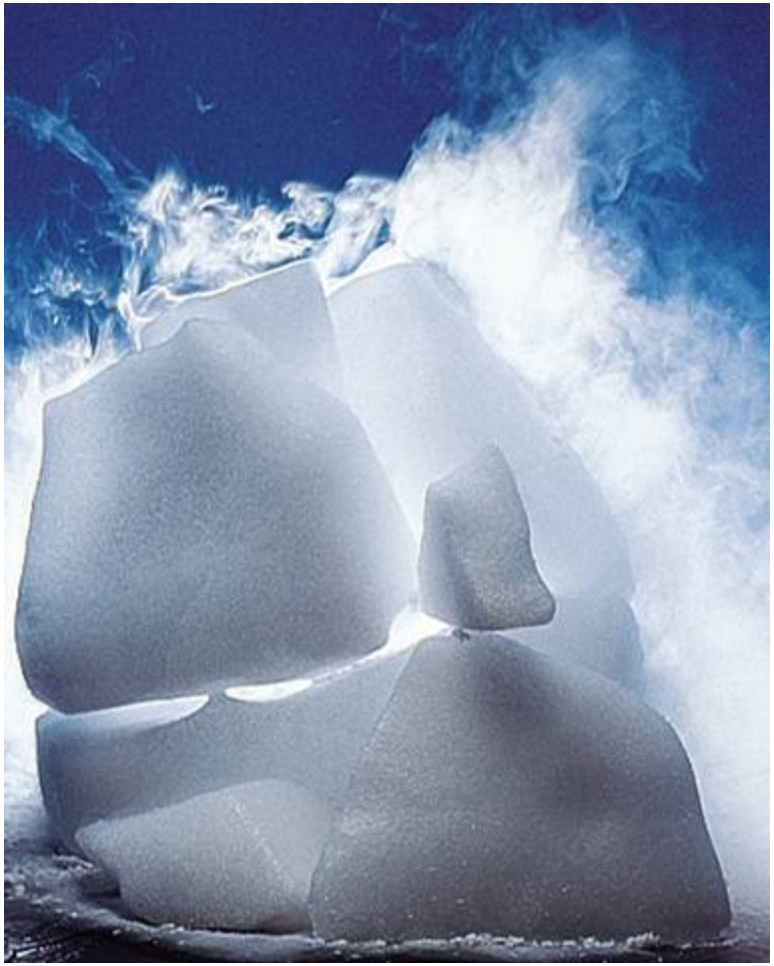
States of Matter

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

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

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



Fluid = liquid + gas

Phase Changes

Change state of matter

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

Vaporization: liquid → gas

Condensation: gas → liquid

Sublimation: solid → gas

Deposition: gas → solid

Fusion (melting): solid → liquid

Freezing: liquid → solid

Intermolecular Attractive Forces

Types of forces

Intermolecular forces: attractive forces between molecules

Intramolecular forces: hold atoms together in a molecule

- covalent bonds

Strength: Intermolecular vs. intramolecular

- Intermolecular: 40 kJ to vaporize 1 mole of water (liquid → gas)
  - attractive forces are disrupted; covalent bonds NOT broken
- Intramolecular: 460 kJ to break O-H bonds in 1 mole of water
- **Intermolecular forces weaker than intramolecular forces!**

Ways to measure strength of intermolecular forces

- Boiling point: disrupt forces holding liquid together
- Melting point: disrupt forces holding solid together
- Enthalpy of these reactions: ΔH_{vap}, ΔH_{fus}, ΔH_{sub}

Dispersion Forces

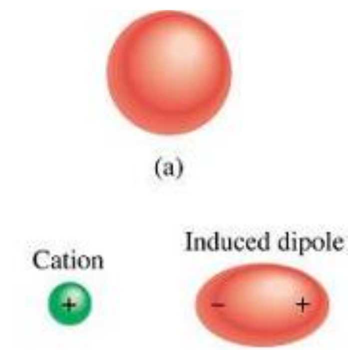
Attractive forces that result from <u>temporary</u> dipoles induced in atoms or molecules

Strength determined by polarizability

- Measure of how easy it is to distort electron density

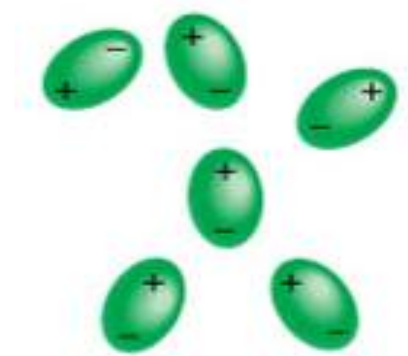
Ion induced dipole

- Dipole induced by attraction to nearby ion



Dipole induced dipole

- Induced dipoles form and fade away.
- Net attraction holds molecules together



- **Temporary**
- **Weak**
- **Only attractive forces available to nonpolar molecules**

Strength of Dispersion Forces

High polarizability

- Form stronger intermolecular forces
- Greater attraction between molecules (stick together)

High molecular mass

- Larger area to spread out electrons; less repulsion
- Many electrons

Large surface area

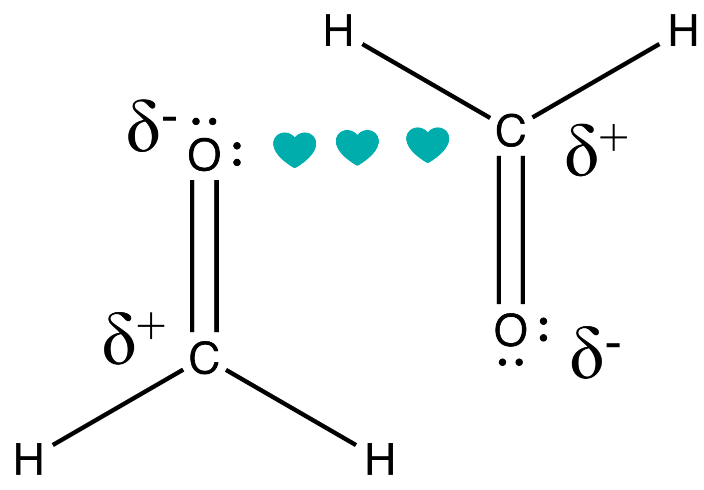
- Long & thin more polarizable; greater charge separation
- More atoms easily “seen” by other molecules

Molecule	Length	BPt
$CH_3CH_2CH_2CH_2CH_2CH_3$	Long	69 °C
$(CH_3)_2CHCH(CH_3)_2$	Branched	50 °C
CCl_4	Heavy	171°C
CH_4	Light	-182 °C

Dipole-Dipole Forces

Exist between molecules with permanent dipoles.

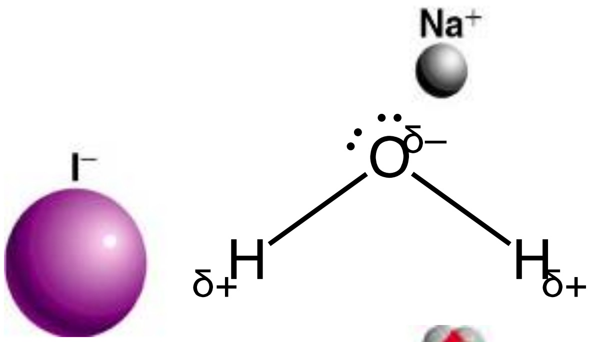
- Need polar bond
- Dipoles align themselves with the positive end of one dipole directed toward negative ends of neighboring dipoles.
  - **Opposites attract!**
- Increase with molecular polarity



Ion-Dipole Forces

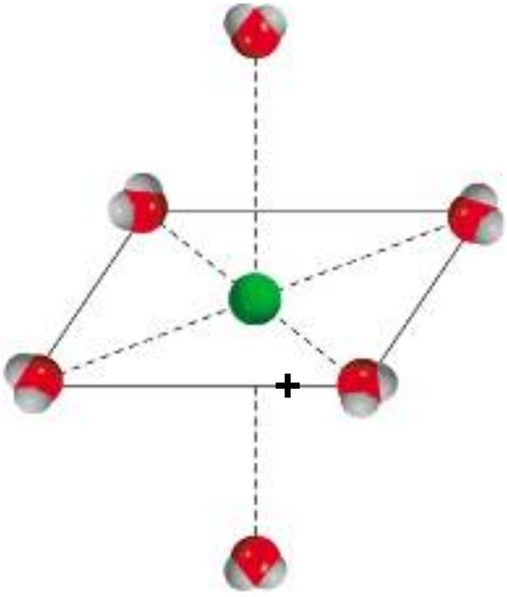
Attractive forces between an ion & a polar molecule

- Electrostatic charges only
- Permanent charges
  (not induced)

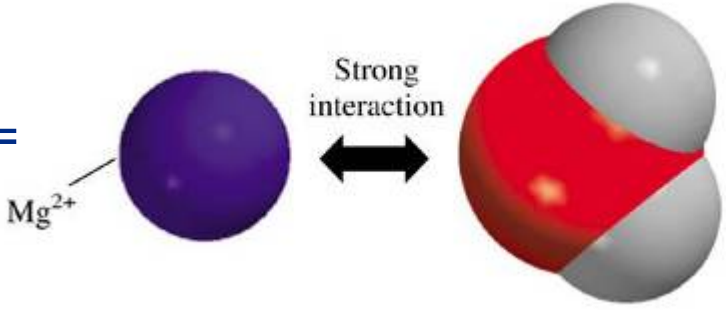


ex: Hydration

- Cations/anions interact with water
- Dissolve ionic salts
- Polar H_2O molecules surround ion



Higher charge =
Stronger force

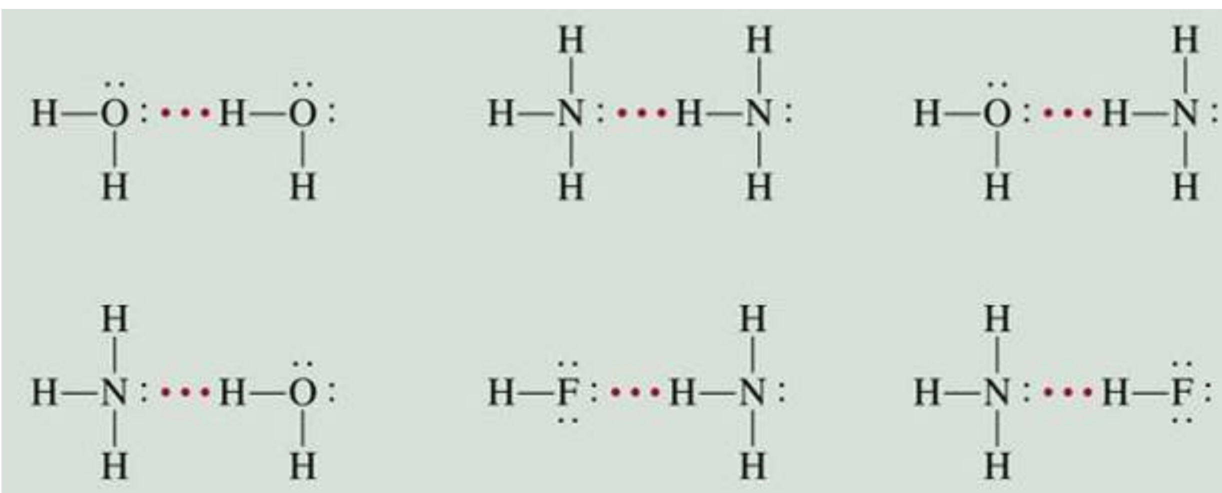


Hydrogen Bonds

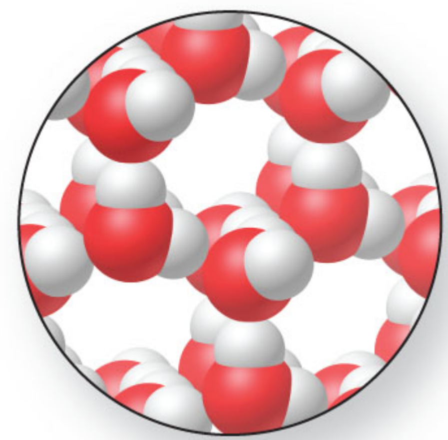
Bond between **H** atom (δ+) bonded to a highly electronegative atom (δ-) and attracted another highly electronegative atom (δ-)

Highly electronegative atom = O,N,F

Strength > dipole-dipole
(basically just a super strong dipole-dipole force)



Represented by dotted line

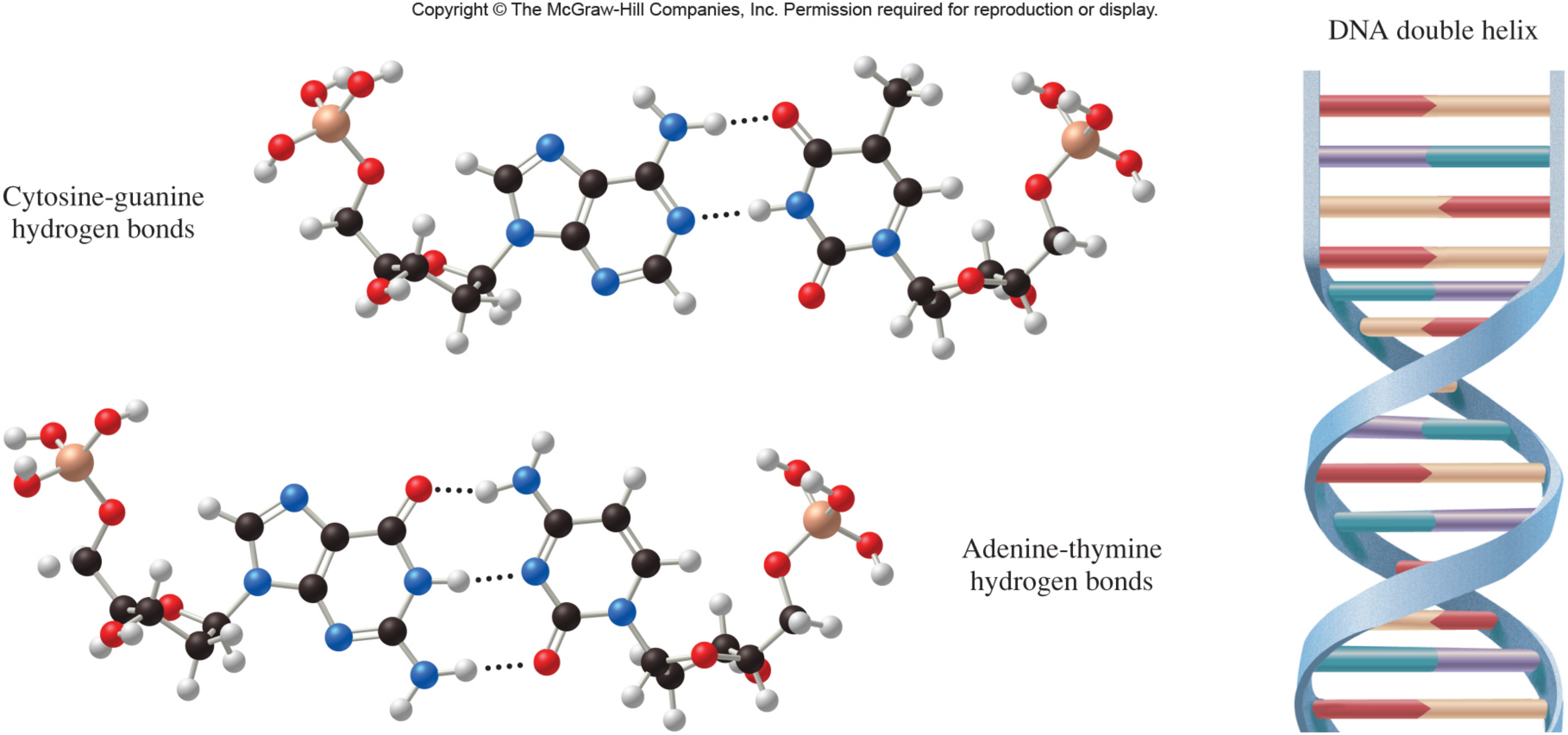


Ice

Why ice is less dense than water

Hydrogen Bonds are Essential to Life

- Hold together double helix in DNA



- Help to give proteins their shape

Comparison & Impact of Attractive Forces:

Boiling & Melting Points; Solubility

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

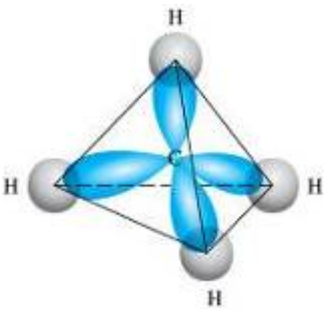
- Weakest Intermolecular Attractive Force
- All molecules have dispersion forces
- Only attractive force available to nonpolar molecules
- Lowest melting & boiling points
  - depend on size & surface area
- Do not help make molecules water soluble
- Nonpolar molecules dissolve in nonpolar solvents
 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

What type(s) of intermolecular forces exist between each of the following molecules?

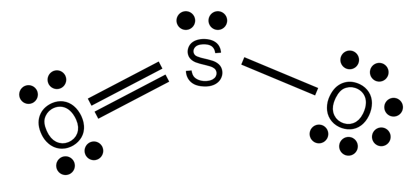
HBr

H – Br

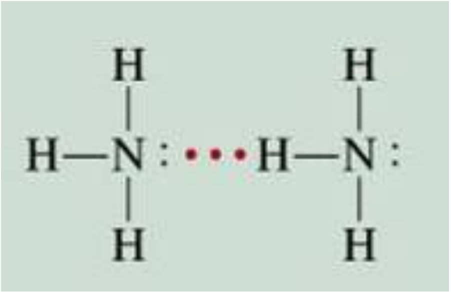
CH_4



SO_2



NH_3

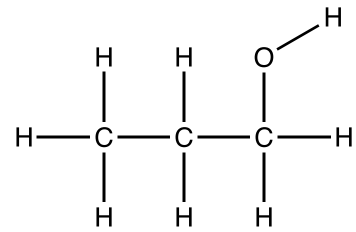
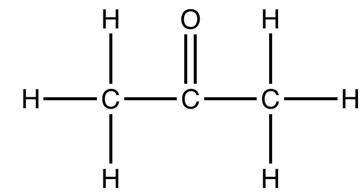


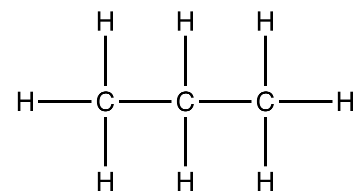
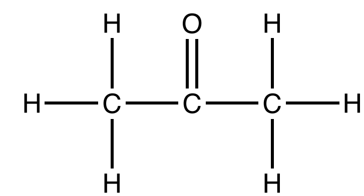
Which of the following would have a higher boiling point?

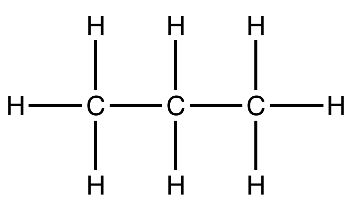
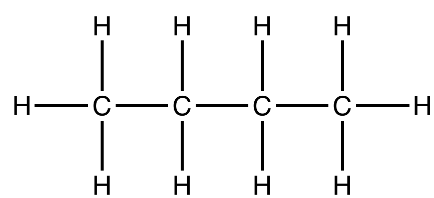
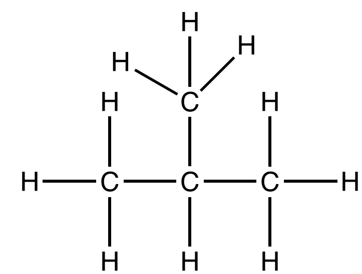
LiF vs CH_3OH

CH_2Cl_2 vs CCl_4

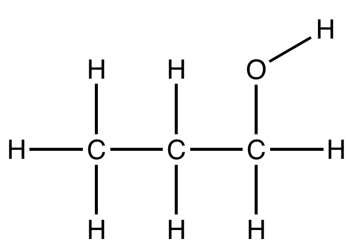
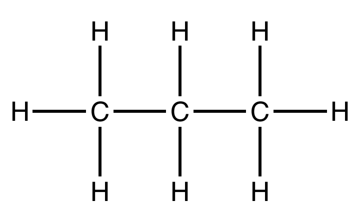
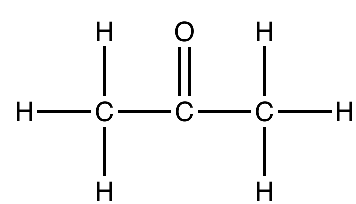
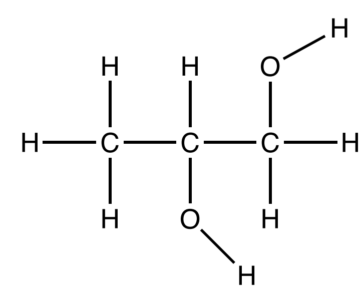
CCl_4 vs CH_4

 vs. 

 vs. 

 vs.  vs. 

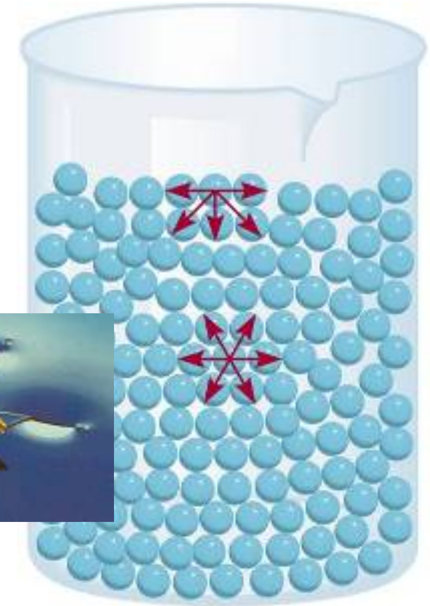
Rank the following in order of increasing water solubility.

Properties of Liquids

Surface Tension

- Work/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
  - An "adhesive" bonds things together

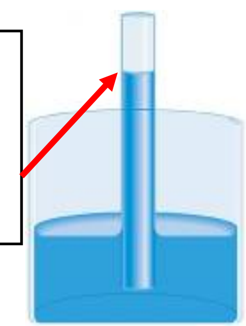
Capillary Action

Adhesive forces: liquid sticks to glass

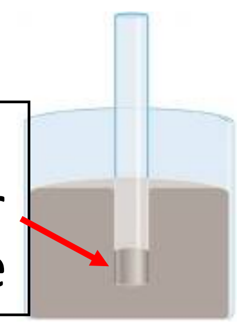
Cohesive forces: molecules stick together

- Allows plants to pull water up through roots

H_2O:A>C
Liquid higher than surface

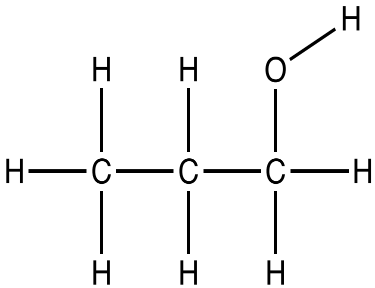


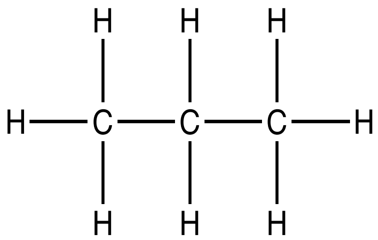
Hg: C>A
Liquid lower than surface

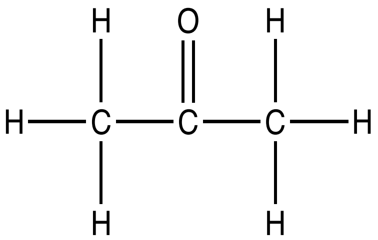


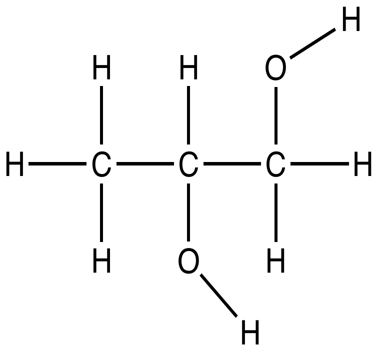
Viscosity: Measure of resistance to flow

List the following in order of increasing surface tension.







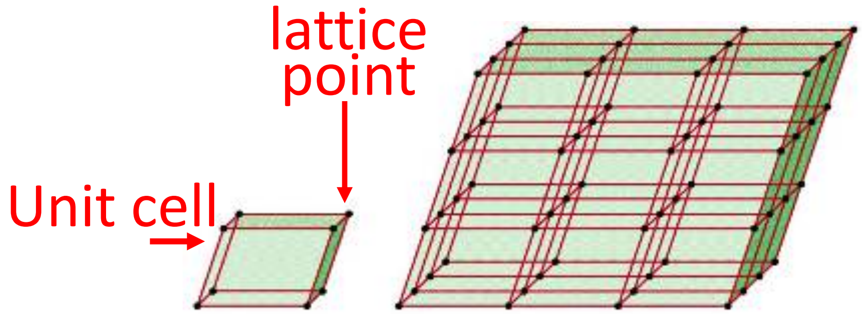


Remember that the trend for vapor pressure is the OPPOSITE of what we have seen for other phenomena (like melting & boiling point & water solubility)

Solids: 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:

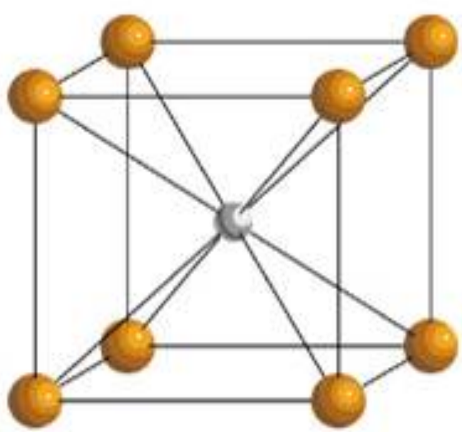
Atoms
Molecules
Ions

Amorphous solid
- Does not possess a well-defined arrangement of particles

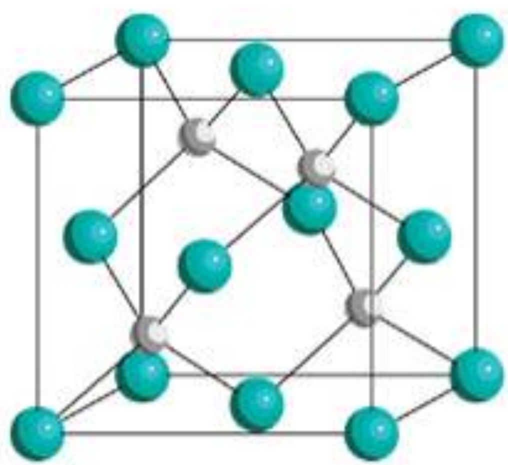
Ionic Crystals

- 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

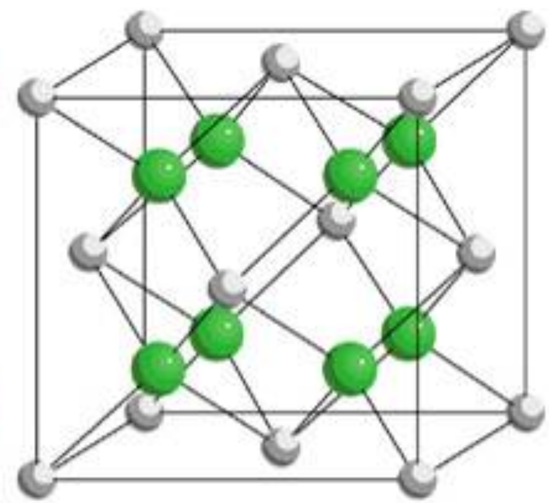
    → electrons locked in place due to connection to anions



Simple Cubic
CsCl



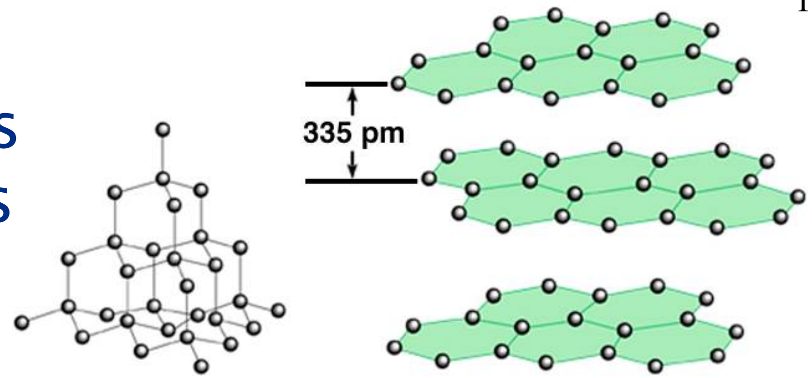
Face Centered Cubic
ZnS



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

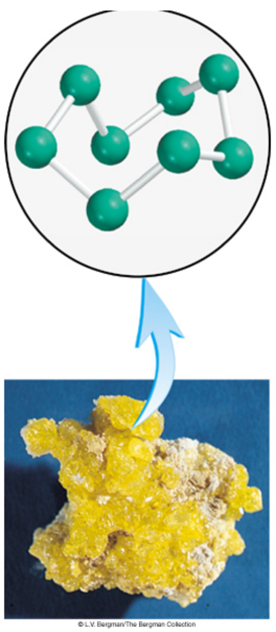


diamond graphite

Molecular Crystals

- 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
  - No electron movement

Note for HW: SiO_2 is a covalent crystal

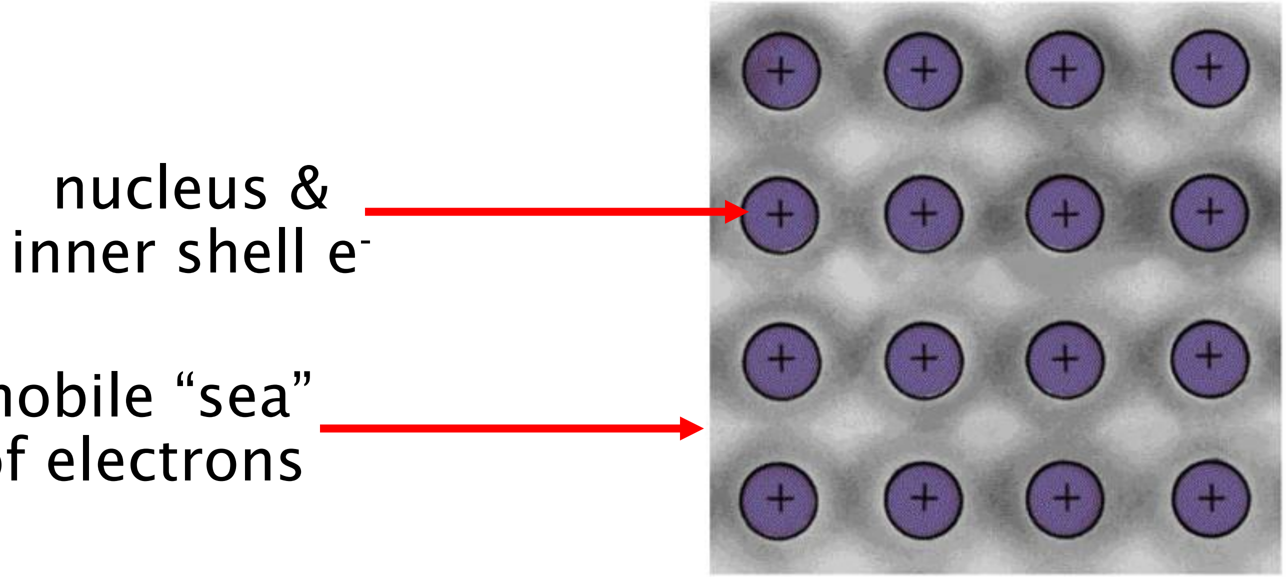


$S_8 \rightarrow$

Metallic Crystals

Lattice points occupied by metal atoms

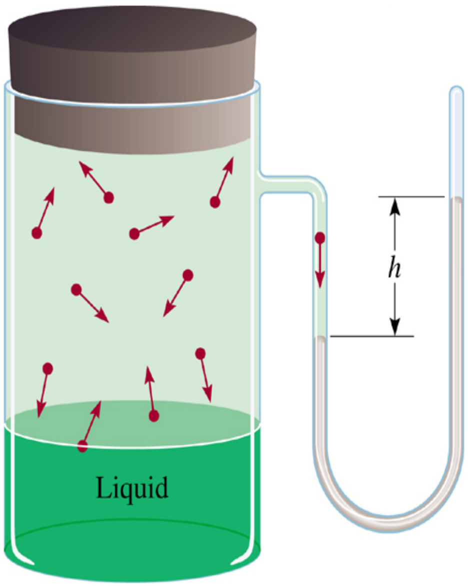
- Held together by metallic bonds
- Soft to hard, low to high melting point
- Good conductors of heat and electricity
  - movement of electrons between metal atoms
  - “electron sea”



Phase Changes

Liquid-Vapor Equilibrium – molecules constantly moving between liquid & vapor phase

$\rightleftharpoons$



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

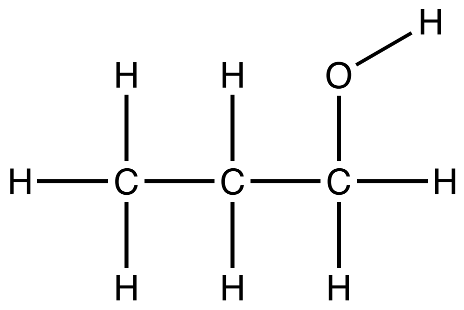
Enthalpy Conversions
- $\Delta H_{vap} = - \Delta H_{cond}$

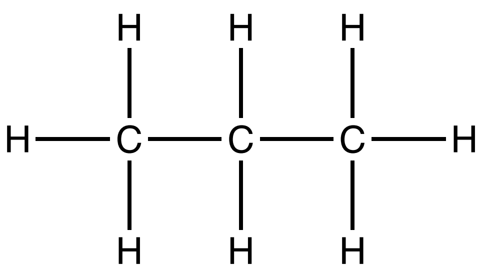
Boiling point: temp. where vapor pressure= atm. pressure

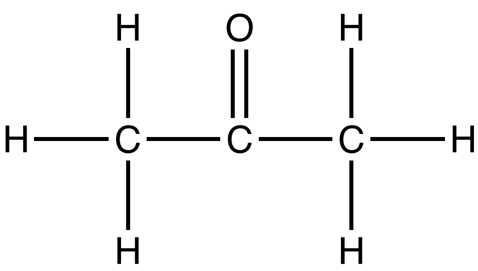
Lower bpt = higher vapor pressure!

Which of the following would have the highest vapor pressure?

Which would have the lowest vapor pressure?



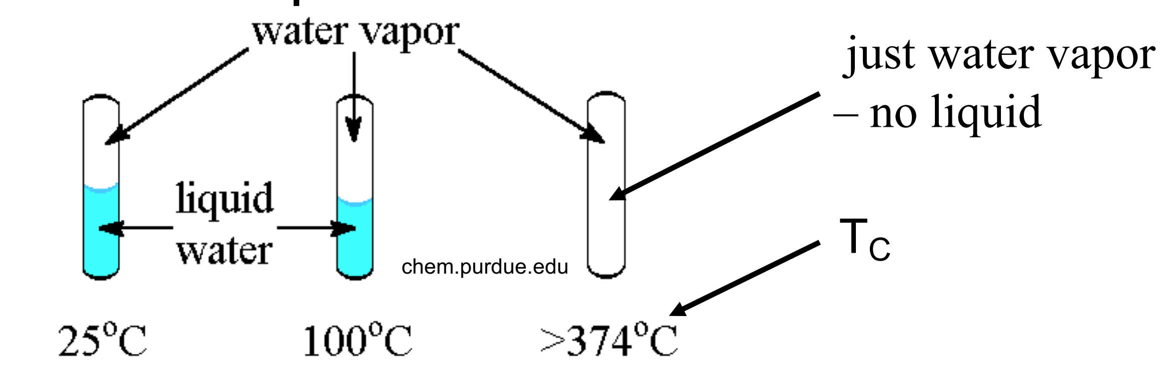




Remember that the trend for vapor pressure is the OPPOSITE of what we have seen for other phenomena (like melting & boiling point & water solubility)

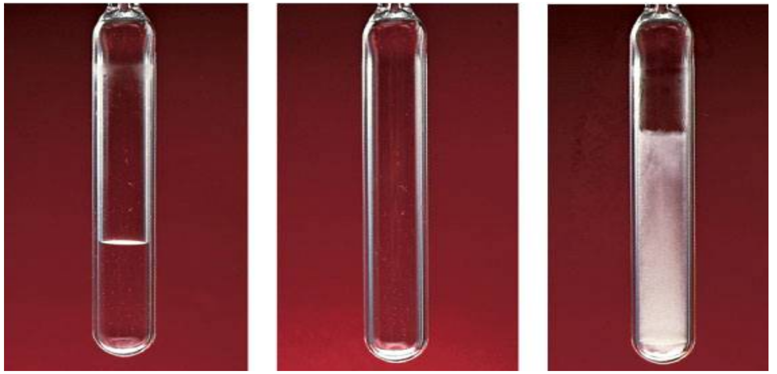
Supercritical Fluid

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:

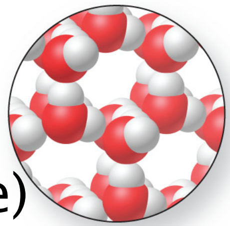
- Start with liquid water & water vapor
- Critical Temp (T_c) is reached, all vapor
- Temp continues to increase – pressure increases to P_c
- Sealed so no way to lower pressure
- Water wants to condense but cannot above T_c
- Liquid & vapor meld into one fluid



Melting and Freezing Solid ⇆ Liquid

Melting

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

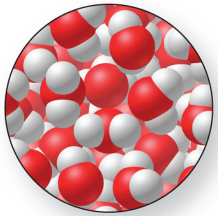


Ice

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

Freezing

- 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

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

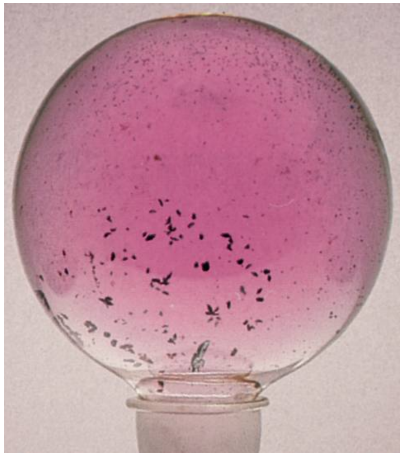
- Heat absorbed/released when 1 mole solid melts/freezes at constant T & P

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.
- $\Delta H^\circ_{sub} = \Delta H^\circ_{fus} + \Delta H^\circ_{vap}$

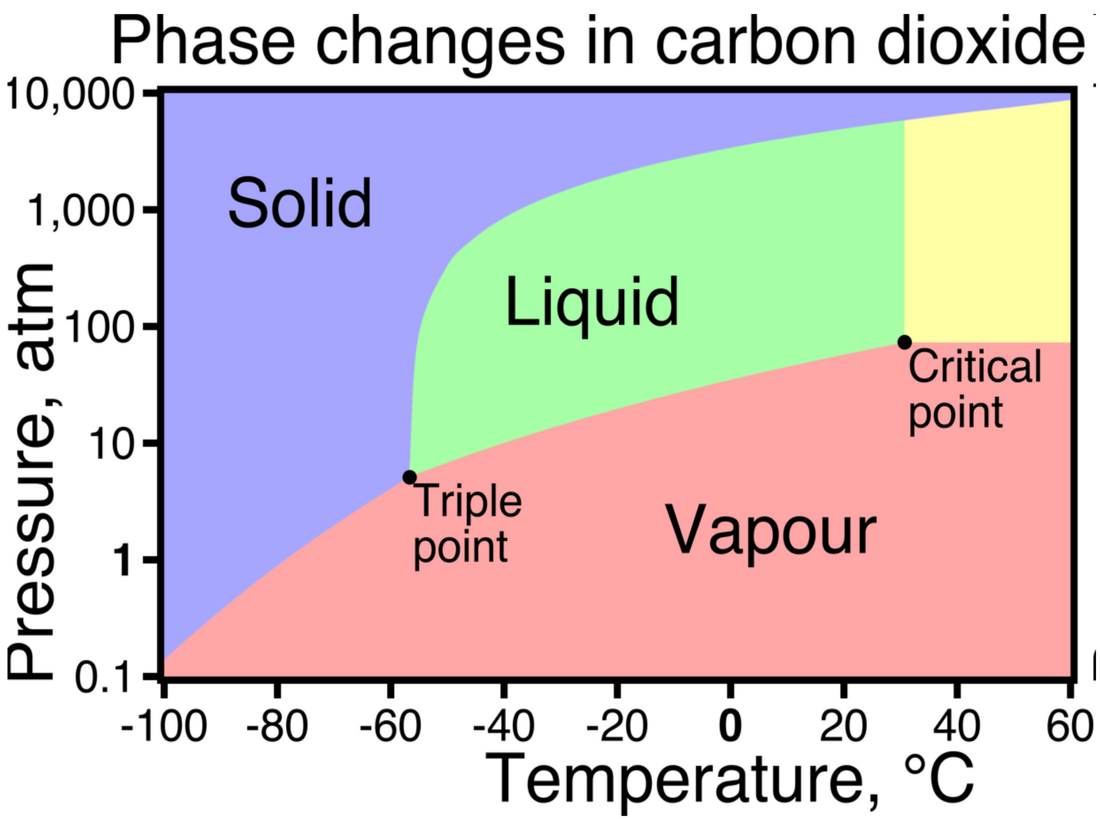
Deposition: Opposite of sublimation

- 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.

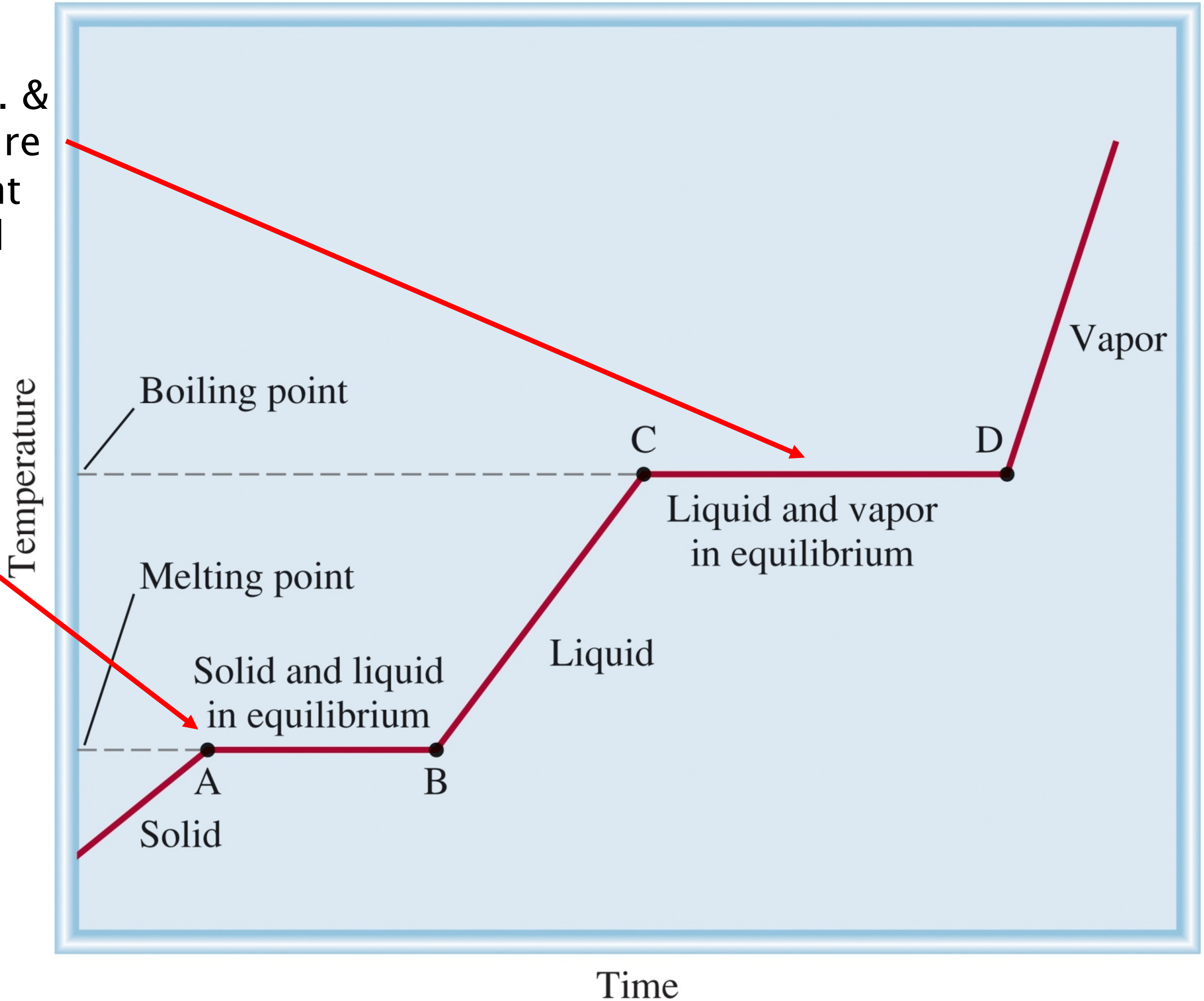


At 1 atm

CO_2 (s) ⟶ 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