CHEM 116

Phase Changes and Phase Diagrams

Lecture 5

Prof. Sevian

Today is the first day that clicker questions count toward your grade. Remember to bring your i>clicker to class with you. There will be a clicker question at the beginning of lecture and another at the end. These clicker questions count as participation points. If you miss the beginning or end of lecture, you will not get all the points.

Today's agenda

Start chapter 11

- Compare the three most common phases of matter
- How to effect phase changes and what can be measured
- Particle level model of phase changes
- Reminder of polar vs. nonpolar molecules which you learned in first semester chemistry
- Phase diagrams

Announcements

FSG's

- One of the FSG times has been established as 11:00-11:50am on Mondays. As of right now, we don't have a classroom assigned for it, so we're temporarily holding it in S-1-89 (chemistry conference room). When the Registrar assigns a classroom, I'll announce the location in class and also post it on the website.
- Shainaz will return at the end of class today to poll the class again to establish a second FSG time. Several students expressed a desire for options on Tuesdays and Thursdays, so she has added some options to the list of times to vote on.

Pre-test

- Pre-test is happening this week. Details about it are in last Thursday's lecture slides. You must take the pre-test this week to get credit for it.
- If you can't take the pre-test at lab, please make arrangements with me to take the pre-test sometime this week.

i>Clickers

- Beginning today (9/16), i>clicker questions will begin to count toward your grade. Bring your clicker to class with you every day.
- If you do not own an i>clicker and do not need one for another class this semester, I will loan you one. Come by my office (W-4-181) to get it. If you do not return it to me at the end of the semester, you will receive an INC for the course. If you lose it, you can buy another one on amazon.com for around $30.

A clicker question that asks about material we covered in class last time

Which answer represents a list in order of increasing deviation from ideal gas behavior?

(A) N_2 at 25ºC and 1 atm,
N_2 at 100ºC and 1 atm,
N_2 at 25ºC and 4 atm

(B) CH_4 at 273 K and 1 atm,
CH_4 at 273 K and 0.4 atm,
CH_4 at 373 K and 1 atm

(C) SO_2 at 20ºC and 1 atm,
SO_2 at 0ºC and 1 atm,
SO_2 at 0ºC and 3 atm

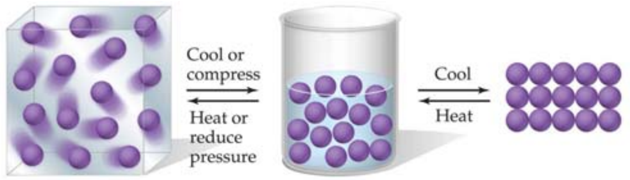
(D) H_2O at 200ºC and 1 atm,
CO_2 at 200ºC and 1 atm,
Ar at 200ºC and 1 atm

Common phases of matter

- Particle level
  - How are these three phases different?
  - How does a material change from one phase to another? What happens at the particle level?
- Macroscopic behavior
  - How do these particle behaviors manifest in different macroscopic behavior?

Three phases of matter: what do the particles do?

- Motion
- Proximity
- Density
- Interactions
- Timescale



Gas

Total disorder; much empty space; particles have complete freedom of motion; particles far apart

Liquid

Disorder; particles or clusters of particles are free to move relative to each other; particles close together

Crystalline solid

Ordered arrangement; particles are essentially in fixed positions; particles close together

Show simulations of methane (CH_4) gas.

Water behaves slightly differently due to H_2O to H_2O interactions being different than CH_4 to CH_4 interactions

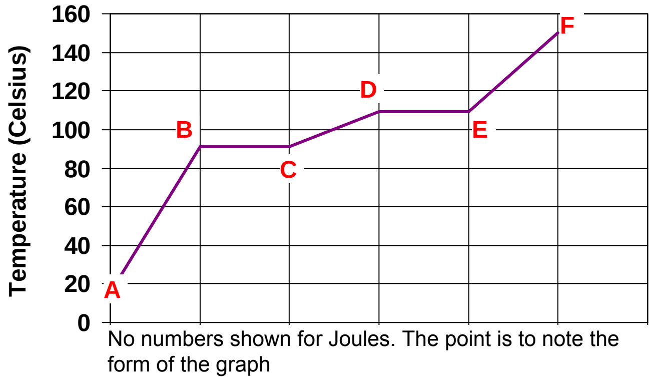
Particle level

Change from one phase to another

- What kinds of energy are involved?
  - Kinetic energy = motion
  - Potential energy = separation
- How do particles get from one phase to another? Surfaces!
- Some vocabulary
  - Solid to liquid: melting
  - Liquid to solid: fusion (freezing)
  - Liquid to gas: vaporization (boiling)
  - Gas to liquid: condensation
  - Solid to gas: sublimation
  - Gas to solid: deposition

Macroscopic

Heating Curve of 1.00-gram Sample of Methane (CH_4) at Standard Pressure



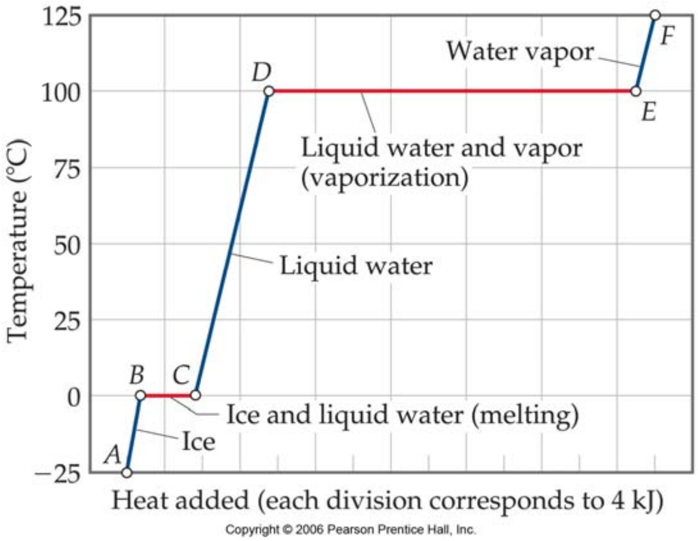
No numbers shown for Joules. The point is to note the form of the graph

A = solid below melting*
B = solid has reached melting temperature, and is beginning to melt*
C = liquid at melting temperature, has just completed melting
D = liquid has reached boiling temperature, and is beginning to boil*
E = gas at boiling temperature, has just completed boiling*
F = gas above boiling temperature

Horizontal parts vs. sloped parts

See http://www.chemistry.wustl.edu/~gelb/gchem/materials/phases/

Heating curve of water
(1.00 mol at standard pressure)



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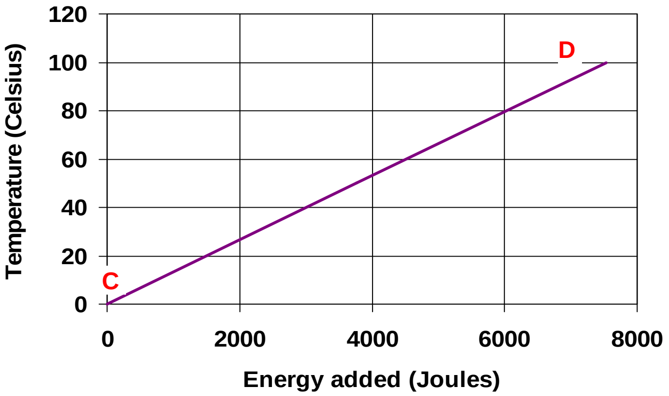
Macroscopic

Focus on Liquid to Gas:
For a 1.00-mol sample of liquid water



Particle level

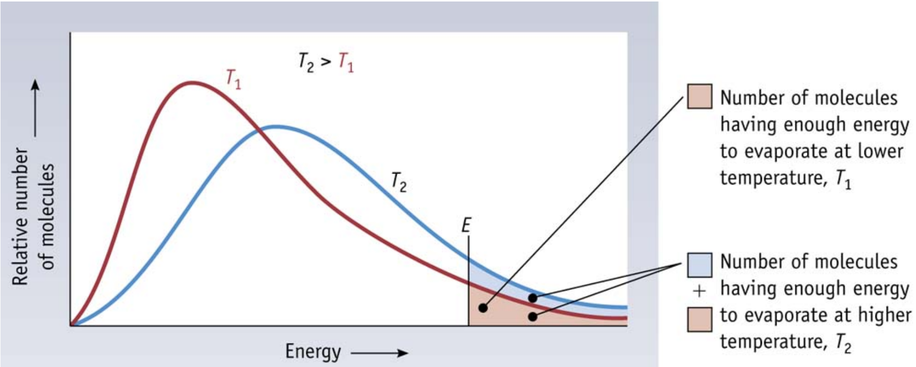
What happens if you add more heat energy to liquid water at 100ºC and 1 atm?

Molecular dynamics simulation of water evaporating

- It boils
- What is boiling?
  - There is a statistical range of kinetic energies (velocities) of particles in the liquid
  - Some particles will always have enough energy to break away from attractive forces that keep them in liquid → evaporation (vapor pressure)
  - As temperature rises, eventually it is high enough that so many particles can break away that their gas pressure (vapor pressure) equals the pressure of the surroundings → boiling
- Boiling continues with no change in temperature until all liquid particles have converted to gas phase
- Normal boiling point is temperature at which vapor pressure reaches atmospheric pressure when p_{atm} = 1atm

Particle level

Comparing a liquid at two temperatures



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The effect of temperature on the distribution of kinetic energies in a liquid

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What we've learned about liquids and solids so far

- The same as in gases, there is a distribution of speeds of particles
- Both liquids and solids have *vapor pressure* at <u>every</u> temperature (even low temperatures)
- Vapor pressure is the pressure exerted by the gas particles that evaporate (L→G) or sublime (S→G) from a liquid or solid, respectively
- Evaporation and sublimation happen at the surface of the liquid or solid, where particles can escape from the surface
- When the vapor pressure reaches the pressure of whatever gas is surrounding the substance, we say that the substance is boiling (if it's changing from L→G) or subliming (S→G)

Heating curve vs. phase diagram vs. vapor pressure curve

1. Heating curve
    - Temperature vs. heat energy added
    - Characteristic up-across-up-across shape
    - Cooling curve is how temperature changes as you remove energy
2. Phase diagram
    - Pressure vs. temperature
    - All 3 phases shown with boundaries between them
3. Vapor pressure curve
    - Usually refers to the liquid-gas portion of the full phase diagram
        - (but could also be used to refer to the solid-gas line)
    - Vapor pressure line is the boundary between L and G
    - All liquids (and solids too) have vapor pressure
        - (most materials that are solids at standard pressure will go through a phase change to liquids, not gases, as the temperature is raised, but those that sublime to gases have S→G vapor pressure curves at standard pressure)

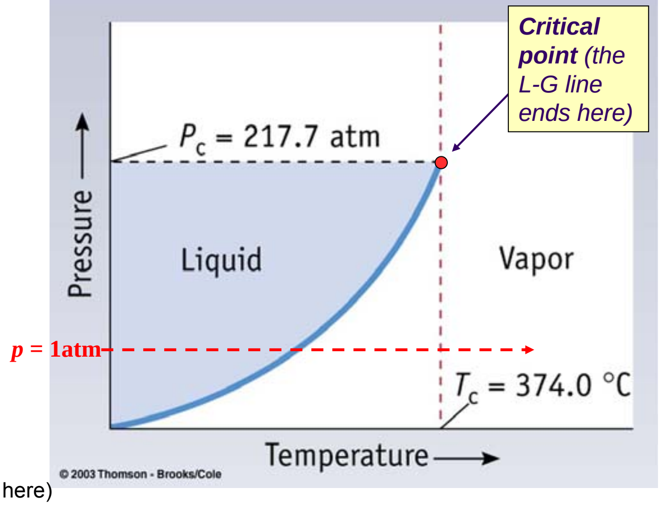
Liquid to gas: As you add heat energy to a liquid below its boiling point, the temperature changes. As the temperature increases, the vapor pressure increases (and vice versa).

Macroscopic

Phase diagram for water showing liquid and gas states

- Curve shows where phase change occurs
- All materials display a critical point, above which there is no interface between liquid and vapor
- Supercritical fluids are useful

Vapor pressure curve for water



Comparison of water (shown here) to a different substance:
CO_2 T_c = 30.99°C, P_c = 72.8 atm

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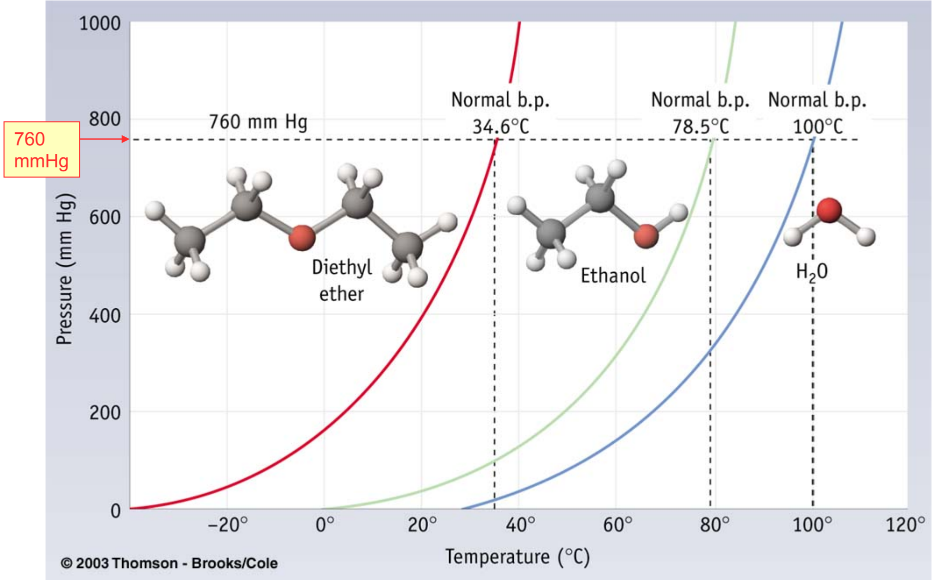
Compare vapor pressure curves for various materials



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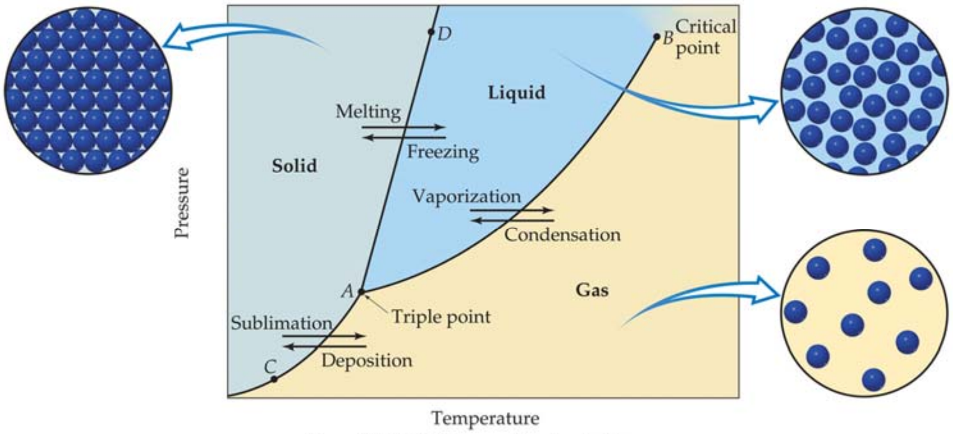
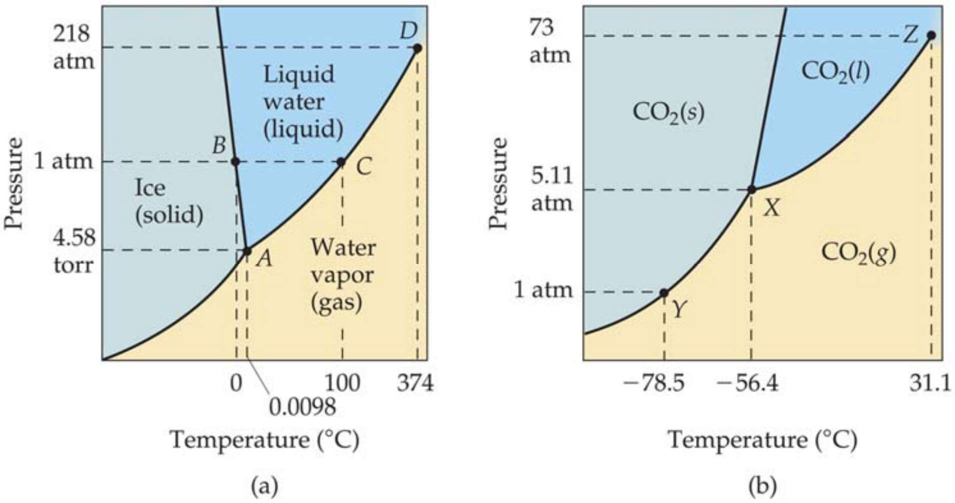
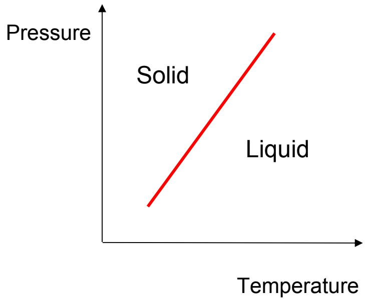
General phase diagram showing all 3 phases

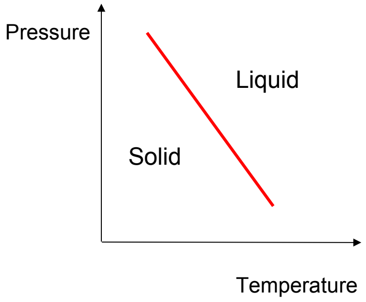


Compare phase diagrams of H_2O and CO_2



Solid-liquid transition at various pressures





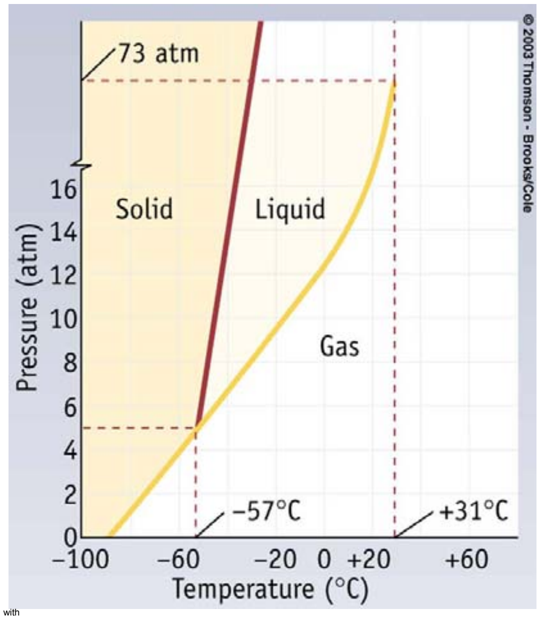
- Typical behavior
- At same T, as you increase p, substance changes from liquid to solid
- Solid more dense than liquid

- Unusual behavior
- At same T, as you increase p, substance changes from solid to liquid
- Liquid more dense than solid

Consequence: solid melts when pressure exerted on it

CO_2: a typical phase diagram

- Typical behavior
- At same T, as you increase p, substance changes from liquid to solid
- Solid more dense than liquid
- Exhibits triple point where all three phases coexist



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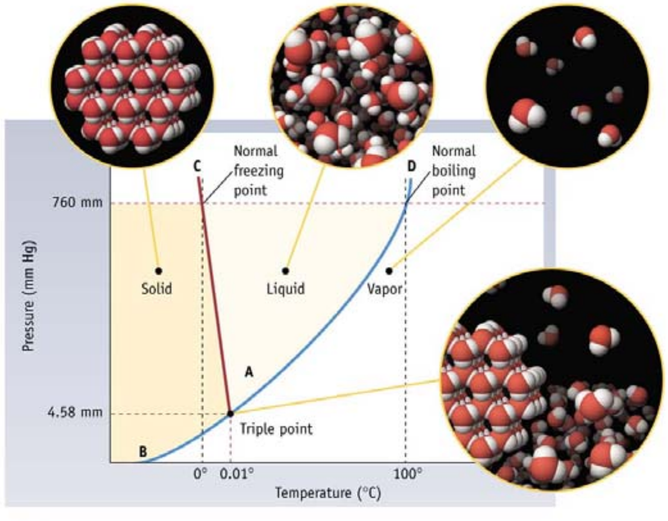
H_2O: an unusual phase diagram

- Unusual behavior
- At same T, as you increase p, substance changes from solid to liquid
- Liquid more dense than solid
- Exhibits triple point where all three phases coexist



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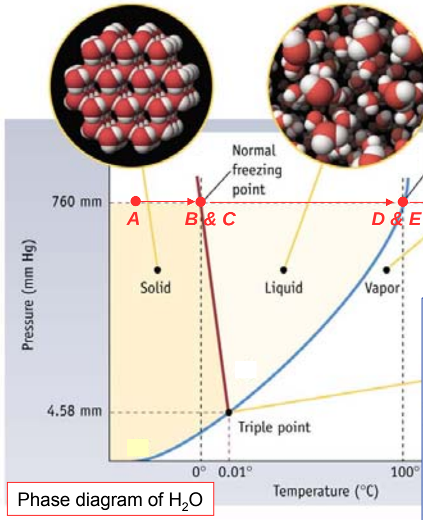
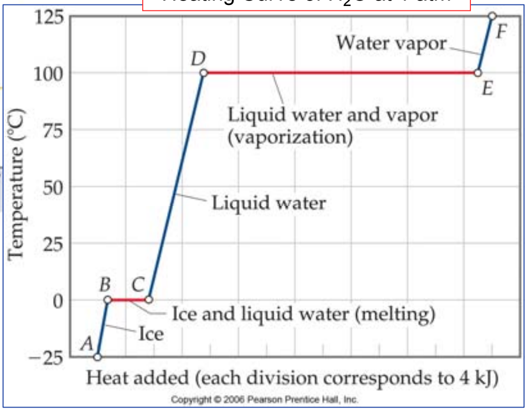
Translating between a phase diagram and a heating curve



Phase diagram of H_2O

Heating Curve of H_2O at 1 atm



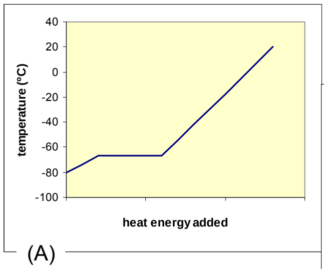
A→B: heating the solid at const P

B→C: phase change from S→L while continuing to add heat energy

C→D: heating the liquid at const P

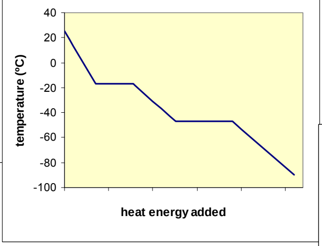
A clicker question that asks about material we covered in class today

Which of the following graphs represents a cooling curve for CO_2 at P = 3 atm?

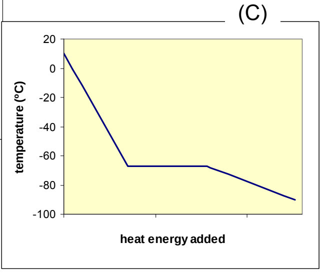


(A)

(B)



(C)



Key points from today

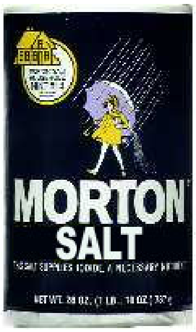
- All solids and liquids have some vapor pressure. Vapor pressure increases as temperature increases (L-G line in phase diagram always has a positive slope). If the temperature is high enough that the vapor pressure equals atmospheric pressure, then the substance boils.
- Phase diagrams show P vs. T for all three phases, with lines indicating where phase transition occurs.
- Heating curves show how the temperature changes as heat energy is added to a sample at constant pressure (cooling curve is the opposite: removing heat energy)
- Vapor pressure line is the L-G part of the phase diagram (also refers to the S-G part since solids also have vapor pressure if below the triple point pressure)
- S-L line can have either a positive (usual) or negative (unusual) slope. Water is unusual.

What's next

- Review types of materials
  - Macroscopic level characterization
  - Particle level theoretical models
  - Symbolic level representation

Types of materials

- Look at examples of common materials on the next page
- Categorize these materials – create your own categories
- Be prepared to justify what makes each material belong to each category
  - In other words, How do you justify placing specific materials in one category and not another?

Octane C_8H_{18} 	Acetic acid (main component of vinegar) CH_3COOH 	Aluminum Al 
Copper sulfate pentahydrate $CuSO_4{\cdot}5H_2O$ 	Sodium bicarbonate (baking soda) $NaHCO_3$ 	Oleic acid triglyceride (main component of olive oil) 
High density polyethylene (HDPE) $-(CH_2-CH_2)_n-$  (container)	Ammonia NH_3 	Sodium chloride (table salt) NaCl 
Water H_2O 	Sand SiO_2 	Copper Cu 

Macroscopic

Types of materials

- Molecular
  - Non-polar molecules
    - Octane, C_8H_{18}
    - Fats (e.g., olive oil)
  - Polar molecules
    - Water, H_2O
    - Ammonia, NH_3
    - Acetic acid (vinegar is an aqueous solution of it), CH_3COOH
- Ionic
  - Sodium chloride (table salt), NaCl
  - Sodium bicarbonate (baking soda), $NaHCO_3$
  - Copper (II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$
- Metallic
  - Copper metal, Cu
  - Aluminum foil, Al
- Some others that don't neatly fit in the first three categories
  - Network
    - Quartz, SiO_2
    - Sand, SiO_2
    - Diamond, C
  - Polymeric
    - Any plastic, such as high density polyethylene (HDPE)
  - Liquid crystals
  - Amorphous
    - Glasses
  - Mixtures
    - Butter, see http://www.foodsci.uoguelph.ca/dairyedu/butter.html)

Notice that the names of most of these categories are based on the type of bonding.

Properties that molecular materials exhibit

- Most are liquids or gases at room temperature
- Smallest molecules are gases at room temperature
- Only very large molecules are solids at room temperature
- All have relatively low melting points (near or below room temperature)
- Most feel soft
- Chemical composition is usually carbon, hydrogen, oxygen, nitrogen and a few others ("organic")
- In liquid state, *usually* do not conduct electricity
- Some can dissolve in water and others cannot

Properties that ionic materials exhibit

- All are solids at room temperature
- Very high melting points
- Do not conduct electricity in solid state
- Conduct electricity in liquid state
- Crystalline
- Brittle, break along flat/planar surfaces
- When they contain transition metals, usually are colored; when they do not contain transition metals, usually are white
- Generally called “salts” because they can be made from mixing together an acid and a base
- Some can dissolve in water and others cannot

Properties that metallic materials exhibit

- Lustrous (shiny)
- Malleable (can be pounded into a pancake)
- Ductile (can be bent)
- Conduct electricity
- Sometimes rust (oxidize)
- Never dissolve in water