CHEM 116

Phase Changes and Phase Diagrams

Lecture 5
Prof. Sevian

Don’t forget your i>clicker

Today’s agenda

Working on chapter 11

- Heating curve vs. phase diagrams vs. vapor pressure curve
- Particle level model of phase changes
- Reminder of polar vs. nonpolar molecules which you learned in first semester chemistry
- Phase diagrams
- Comparison of intermolecular forces of attraction

A clicker question about material we covered in class last lecture

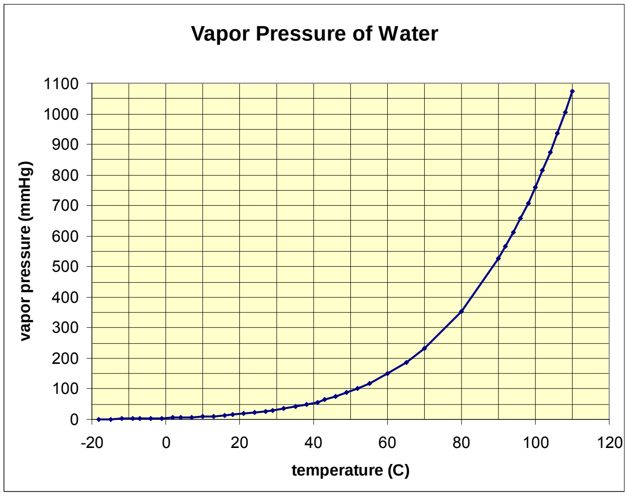
Which statement about the vapor pressure of water is correct?

(A) If atmospheric pressure is 600 mmHg, water will boil at about 93ºC.

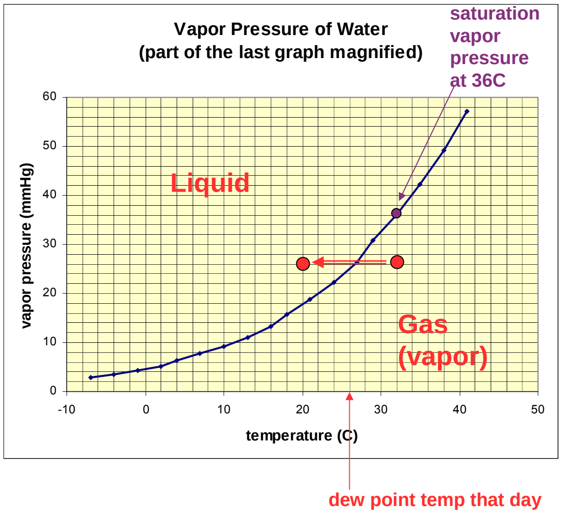
(B) Water cannot boil above 100ºC.

(C) At 100ºC, the vapor pressure of water is about 50 mmHg.

(D) This bears no relevance to my life.



Dew point



- The vapor pressure curve is what weather people more accurately call the saturation vapor pressure – the maximum partial pressure of water that the air can hold at a particular temperature.
- Relative humidity is the actual partial pressure of water in the air on a given day divided by the saturation vapor pressure.
- If the temperature drops (e.g., when night falls), the relative humidity increases because the saturation vapor pressure (denominator in the relative humidity) decreases. When the temperature drops to the point that the saturation vapor pressure of water equals the partial pressure of water in the air, dew forms.

For more plain speak explaining this, see http://www.usatoday.com/weather/whumdef.htm

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)

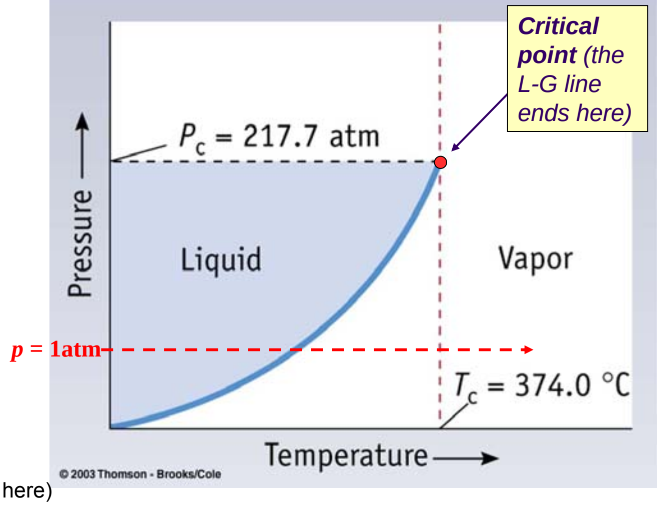
Liquid to gas: As you add heat energy to a liquid below its boiling point, the temperature changes. As the temperature increases, the vapor pressure increases (and vice versa).

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



***Critical point** (the L-G line ends here)*

p = 1atm

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

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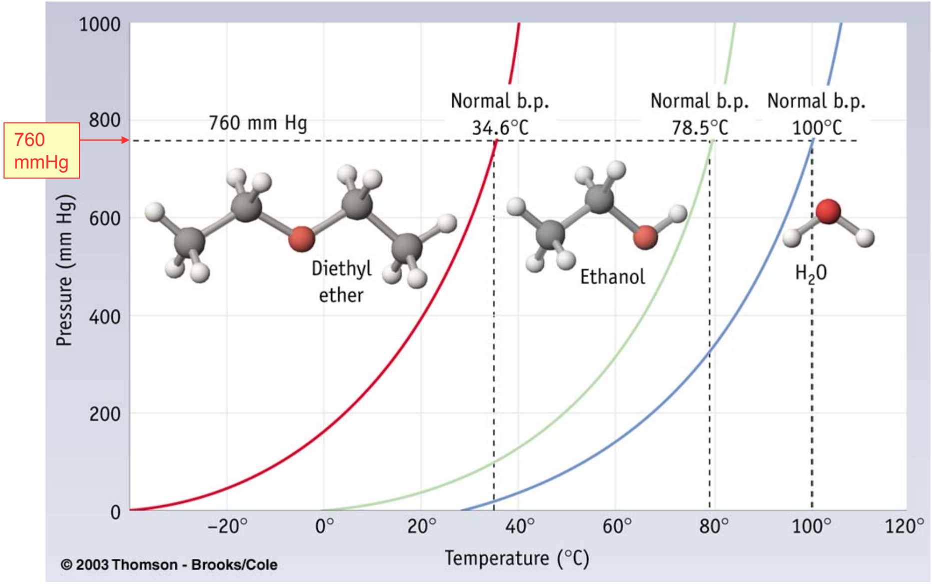
Compare vapor pressure curves for various materials



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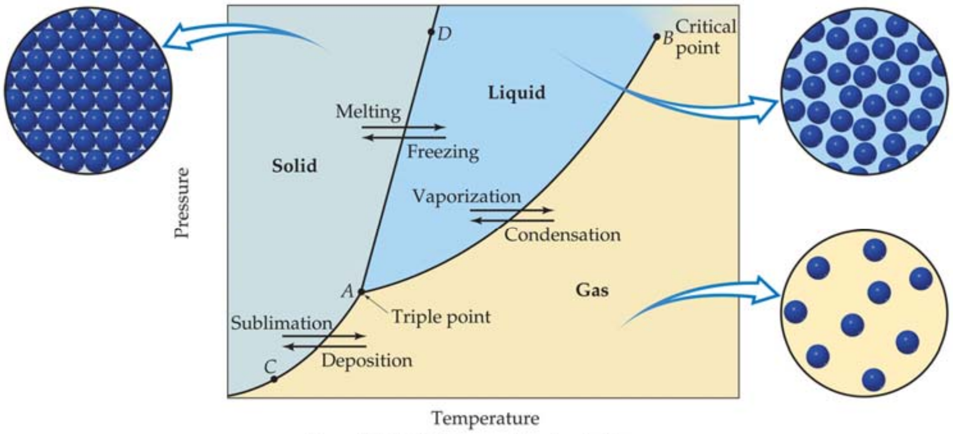
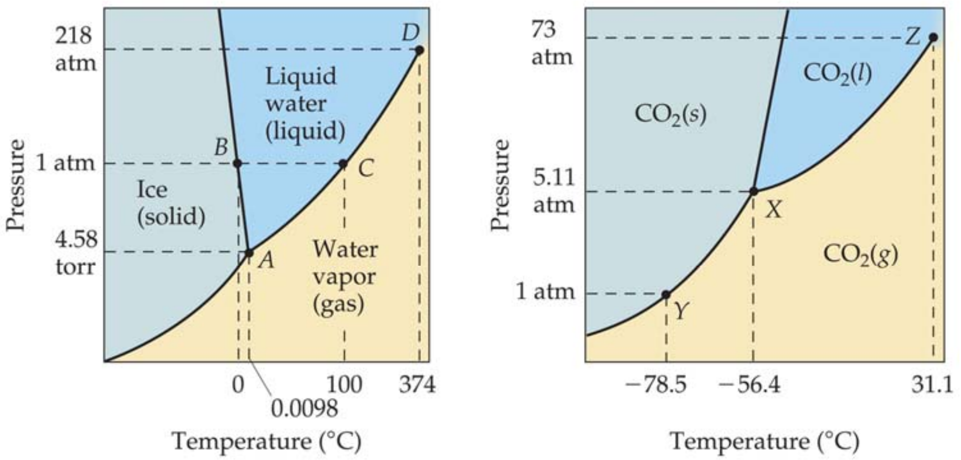
General phase diagram showing all 3 phases

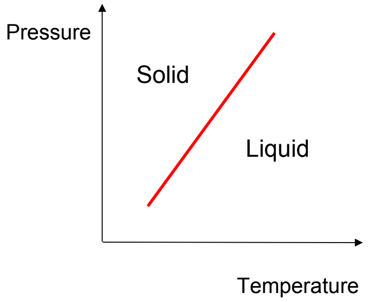


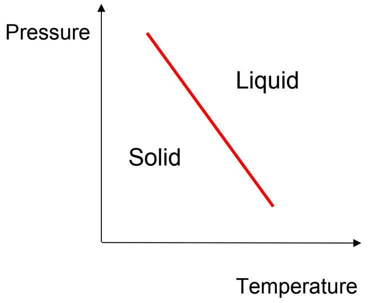
Compare phase diagrams of H_2O and CO_2



(a) (b)

Solid-liquid transition at various pressures





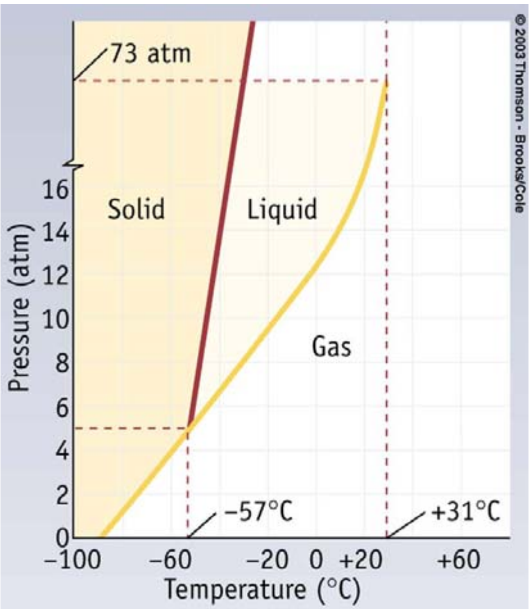
- Typical behavior
- At same T, as you increase p, substance changes from liquid to solid
- Solid more dense than liquid

- 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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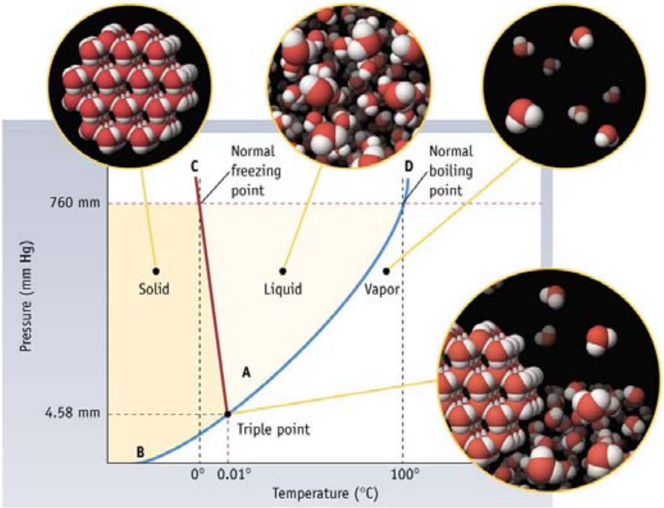
H_2O: an unusual phase diagram

- 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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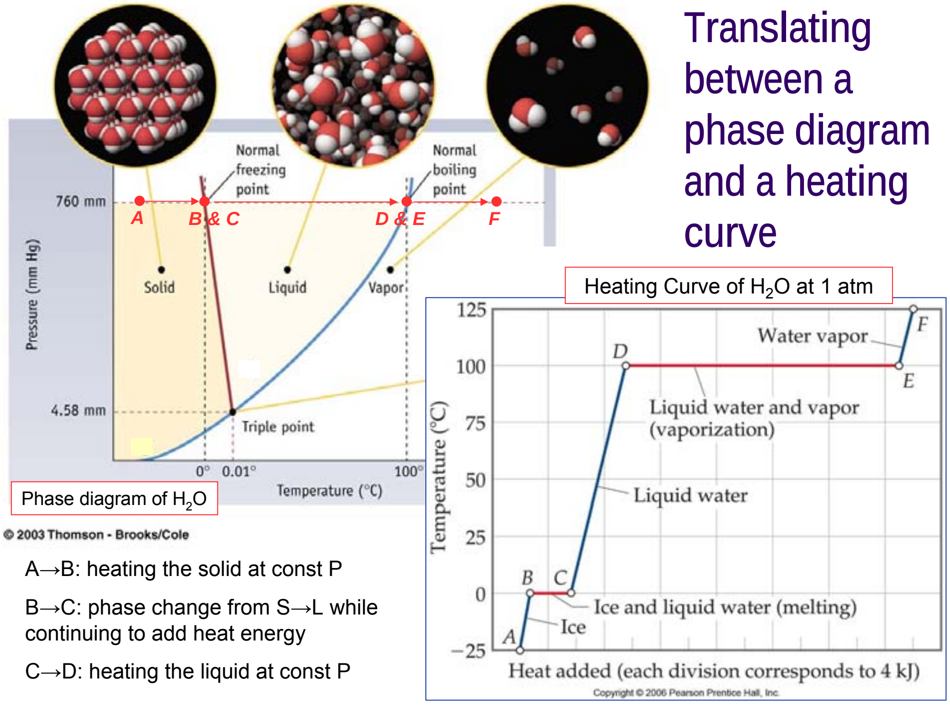
Translating between a phase diagram and a heating curve



Phase diagram of H_2O

Heating Curve of H_2O at 1 atm

A→B: heating the solid at const P

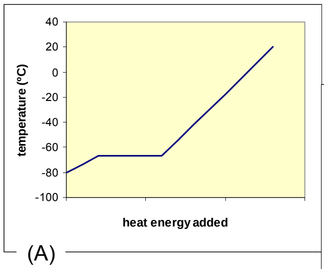
B→C: phase change from S→L while continuing to add heat energy

C→D: heating the liquid at const P

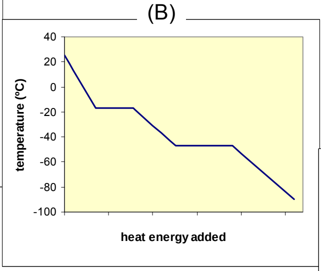
A clicker question that asks about material we covered in class today

i>clicker

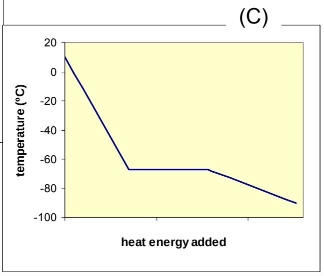
Which of the following graphs represents a cooling curve for CO_2 at P = 3 atm?



(A)



(B)



(C)

Key points so far

- 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.

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?

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

Particle level: materials composed of Molecules

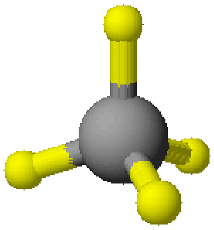
- Solid state
    - Molecules arranged in lattice
    - Individual molecules are neutral
    - Molecules restricted to vibration in lattice space
    - To change to liquid, must overcome molecule-molecule attraction that bind molecules to each other in solid state
- Liquid state
    - Molecules occupy similar amount of space as in solid
    - Molecules have enough kinetic energy to surmount energetic barrier and move past each other
- Gas state
    - Molecules are in rapid random motion and travel in straight lines until they collide with something (each other, walls)
    - The space that an individual molecule occupies is negligible compared with the space available for the molecule to move in

Reminder: What is a dipole?

Molecules can be dipoles or non-polar (actually, it's more about the degree of polarity)

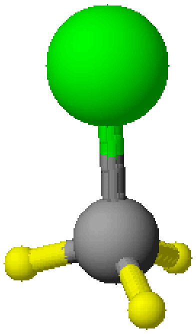
Increasing polarity →

Non-polar molecule

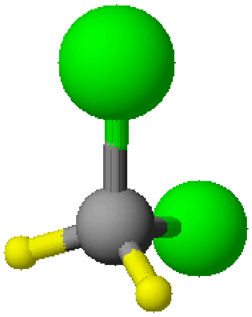


- C-H bonds are not polar
- Even if they were, molecule is symmetric so dipole moments would cancel

Somewhat polar molecule



Polar molecule

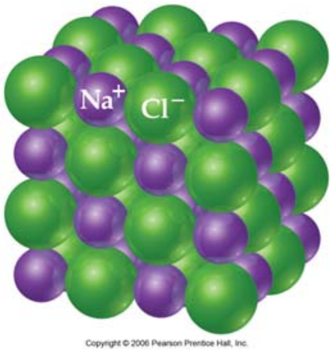


Particle level: materials composed of Ions

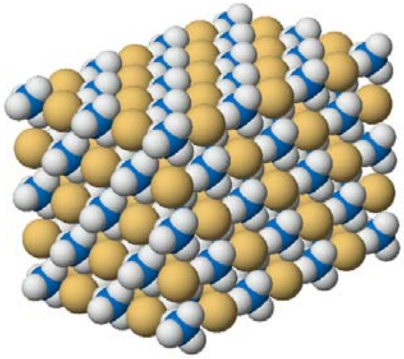
- Solid state
  - Ions arranged in lattice, with individual ions occupying lattice points
  - Ions have alternating arrangement (+ then – then +, etc.) in such a way that every + ion is surrounded by – ions, and vice versa
  - Individual ions are charged
  - Ions restricted to vibration in lattice space
  - To change to liquid, must overcome positive ion – negative ion attractions that bind ions to each other in solid state
- Liquid state
  - Ions occupy similar amount of space as in solid
  - Molecules have enough kinetic energy to surmount very large energetic barrier and move past each other
- Gas state
  - Not realistic

Some examples of ionic solids (particle level illustrations)

Sodium chloride (NaCl)



Ammonium chloride (NH_4Cl)



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Particle level: materials composed of metal atoms

- Solid state
  - Metal ions (missing valence electrons) arranged in lattice, with individual metal ions occupying lattice points
  - Every lattice point is occupied by a + charged metal ion
  - Valence electrons from all the metal atoms surround the metal ions (a “sea” of electrons)
  - Metal ions restricted to vibration in lattice space
  - Electrons free to roam and can be influenced by static charge or by voltage potential across the metal
  - To change to liquid, must overcome metal ion – negative electron sea attractions that bind metal ions to bulk solid

Interactions between particles

- What kinds of particles are we considering?
  - Molecules
    - Non-polar molecules
    - Polar molecules
  - Ions
- The variations that matter
  - Molecules
    - Sizes of molecules
    - Degree of polarity
  - Ions
    - Sizes of ions
    - Magnitude of charge

Precision in language matters in chemistry

The basic idea

- Strength of attractive force governs difficulty of breaking the force (amount of energy required)
- Two factors matter in determining the strength of the attractive force:
  - Separation (distance) between the point charges or dipoles
  - Magnitudes of the point charges or dipoles
- However, there are significant differences between how these factors manifest in dipoles (neutral molecules) and monopoles (charged ions, point charges)

Every possible interaction

1. Non-polar molecule with non-polar molecule
2. Non-polar molecule with polar molecule
3. Polar molecule with polar molecule
4. Polar molecule with ion
5. Ion with ion
6. Ion with non-polar molecule (rare, we won’t worry about this)

Another way of organizing all the different kinds of interactions

A with A

Attraction can be between identical particles or different particles

- Non-polar with non-polar
- Polar with polar (dipole-dipole)

A with B

Attraction must be between two particles that are different from each other

- Non-polar with polar
- Polar with ion
- Ion with ion

Ion-ion attractions

Coulomb's Law:

$$F = \frac{k\,Q_{+}\,Q_{-}}{r^{2}}$$

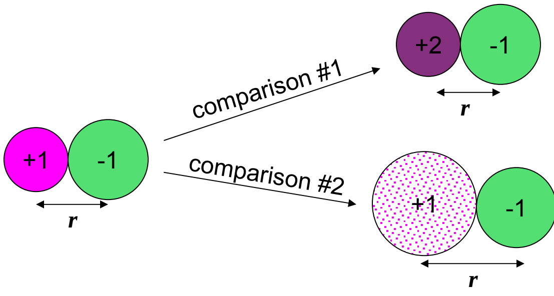
proportionality constant

Charge on positive ion

Charge on negative ion

Force of attraction

distance between ions



Is the force of attraction stronger or weaker? Should this ionic compound require greater or smaller "lattice energy" than the (+1)(-1) original?

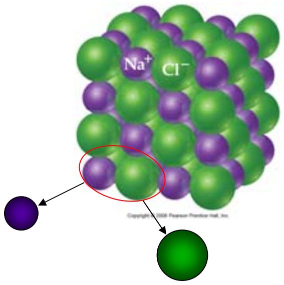
Is the force of attraction stronger or weaker? Should this ionic compound require greater or smaller "lattice energy" than the (+1)(-1) original?

Explaining macroscopic behavior by reasoning based on ion-ion attractions

Lattice energies* of some ionic compounds

(You can think of lattice energy as the amount of energy required to break apart an ionic crystal into its separated constituent ions far apart, *i.e.*, in the gas phase)

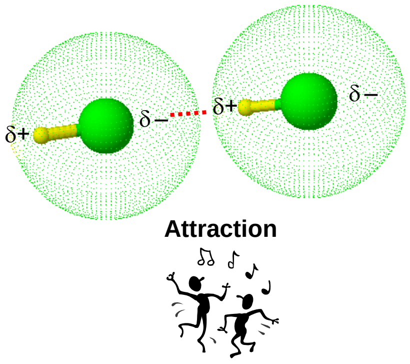
Compound	Lattice energy (kJ/mol)*
LiF	1037
LiCl	852
LiBr	815
LiI	761

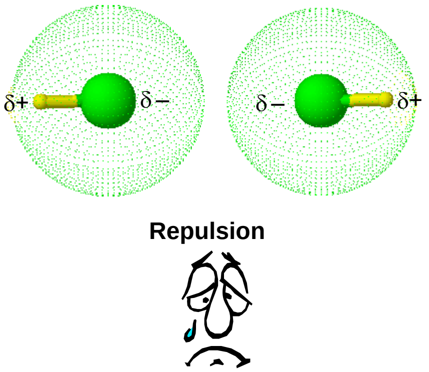


*Actually, lattice energy is defined as the energy to do exactly the opposite, so the values are all negative. But the main point here is to look at the magnitudes of the numbers.

Polar molecule – polar molecule attractions

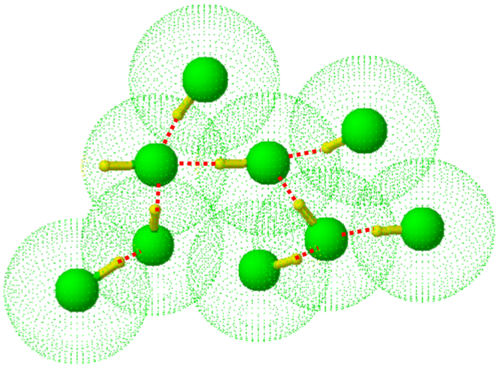
- Often called dipole-dipole interactions
- Remember that dipoles are permanent
- Bar magnets are magnetic dipoles, some molecules are electric dipoles, the behavior is analogous mathematically





How dipole-dipole attractions help keep a liquid together

Example: liquid HCl



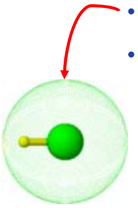
Explaining macroscopic behavior by reasoning based on dipole-dipole attractions

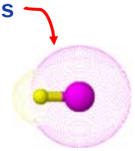
The stronger the permanent dipole, the stronger the attractions

Molecule	dipole moment (debyes)	b.p. (ºC)
HCl	1.08	-84.9
HF	1.92	19.5

Which are stronger?

- **Attractions between HCl and other HCl molecules, or**
- **Attractions between HF and other HF molecules**

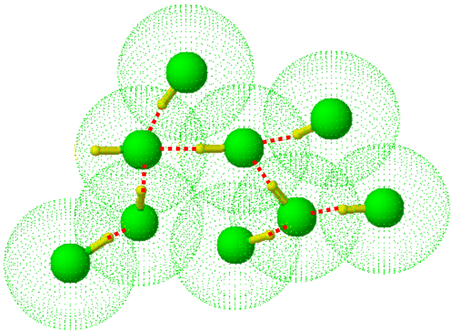




Compare HCl and HF

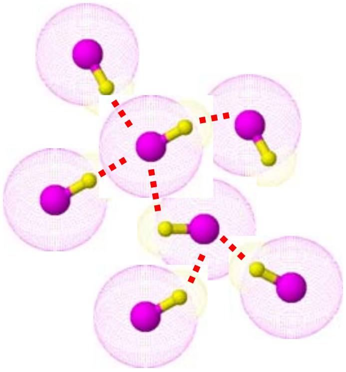
Liquid HCl

...... Strength of attraction proportion to dipole moment which is 1.08



Liquid HF

.... Strength of attraction proportion to dipole moment which is 1.92

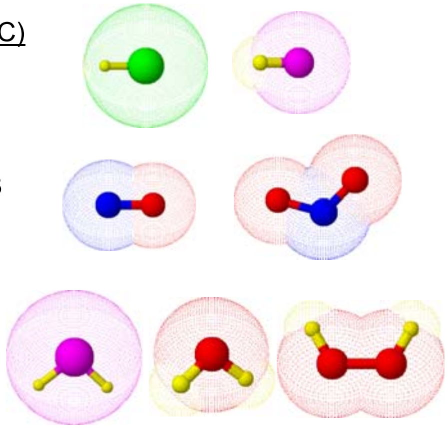


Question to consider: In which liquid does it require more energy to break intermolecular forces and move molecules into the gas state?

Explaining macroscopic behavior by reasoning based on dipole-dipole attractions

The stronger the permanent dipole, the stronger the attractions

Molecule	dipole moment (debyes)	b.p. (ºC)
HCl	1.08	-84.9
HF	1.92	19.5
NO	0.16	-151.8
NO_2	0.29	21.2
H_2S	1.10	-60.7
H_2O	1.87	100
H_2O_2	2.13	150.2



Key points about intermolecular forces

- Intermolecular forces (IM forces) are attractive forces that hold particles together in the liquid and solid phases
- What kinds of IM forces exist depends on what kinds of particles they are
    - Molecular particles
        - Non-polar molecules
        - Polar molecules
            - Polar molecules that have an H bonded to either N, O, F or Cl
    - Ionic particles
- Some IM forces are stronger than others

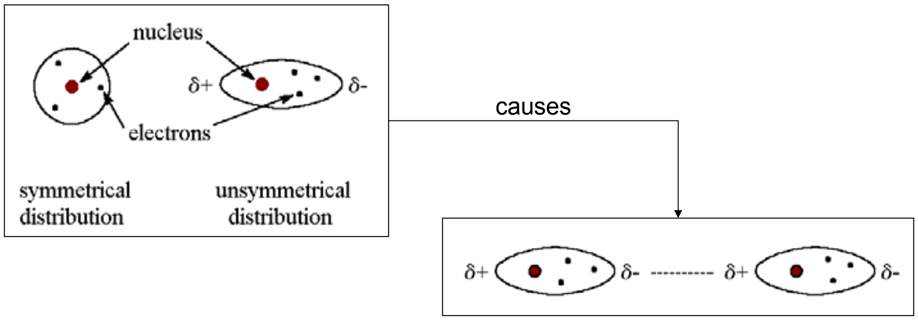
Some dipole-dipole interactions are very strong

They get their own special name: hydrogen bonding

- Hydrogen bonding is a category of dipole-dipole IM forces
- It is just the strongest of the dipole-dipole interactions
- When H is bonded to either N, O, F or Cl in a molecule
- Examples of substances in which there is hydrogen bonding
    - HCl
    - H_2O
    - CH_3COOH
    - NH_3
    - NH_2Cl
- Not hydrogen bonding (why not?)
    - CH_3-O-CH_3

Non-polar molecule – Non-polar molecule attractions (London dispersion forces)

- A non-polar molecule can have a momentary, fleeting dipole
- When it does, it can induce a dipole in a neighboring molecule
- Two momentary dipoles attract each other

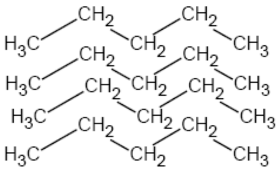


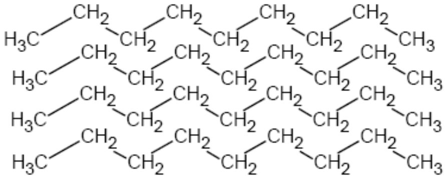
Source: http://www.chem.purdue.edu/gchelp/liquids/disperse.html

More about non-polar – non-polar attractions (dispersion forces)

- Often called London dispersion forces
- Sometimes called induced dipole – induced dipole attractions
  - To *induce* means to cause
- The larger the molecule, the greater the possible separation of partial electric charge, therefore the larger the momentary dipole moment can be
  - Caution: molecular mass is often, but not always, a good indicator of molecular size
- The stronger the temporary dipoles, the stronger the attractions

Comparing dispersion forces


four 5-carbon molecules


four 9-carbon molecules

n-pentane, C_5H_{12}
m.p. -130ºC
b.p. 36ºC

n-nonane, C_9H_{20}
m.p. -54ºC
b.p. 151ºC

Explaining macroscopic behavior by reasoning about intermolecular forces

name	formula	melting point
lauric acid	$C_{11}H_{23}COOH$	44° C
myristic acid	$C_{13}H_{27}COOH$	58° C
palmitic acid	$C_{15}H_{31}COOH$	63° C
stearic acid	$C_{17}H_{35}COOH$	70° C

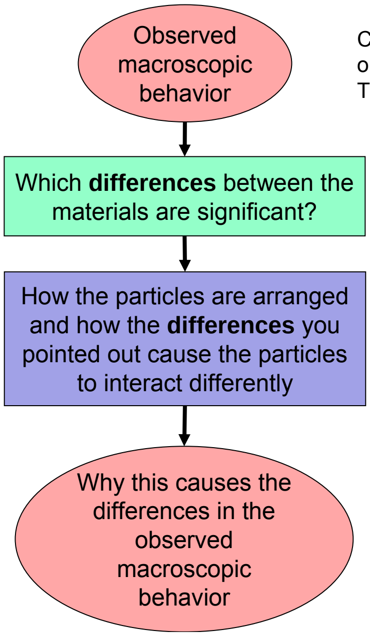
- **What is “melting point”?**
- **If one substance has a higher melting point than another, what is true about the substance with the higher melting point?**
- **What trend exists in the melting points of the fatty acids listed? (As ___, the melting points ____.)**
- **What is the cause of the trend seen in the melting points of the fatty acids listed?**

Reasoning based on IM forces

- As the number of carbons increases in a series of fatty acids…
- the melting point increases.
- This is because…
- as the number of carbons increases, the chains get longer. When the chains are longer, the molecules are bigger.
- The larger the molecule, the greater the dispersion forces.
- When the attractive forces holding particles together is greater, you have to get to a higher temperature to break those forces, so the melting point is higher.

- State the trend
- State the physical property that is changing
- Point out the important point about the particles that is different
- Explain which IM forces are different and how they are
- Explain why that causes the physical property to be different

The structure of scientific explanations (in chemistry)



Comparison of properties exhibited by two materials
or
Trend in properties exhibited by a series of related materials

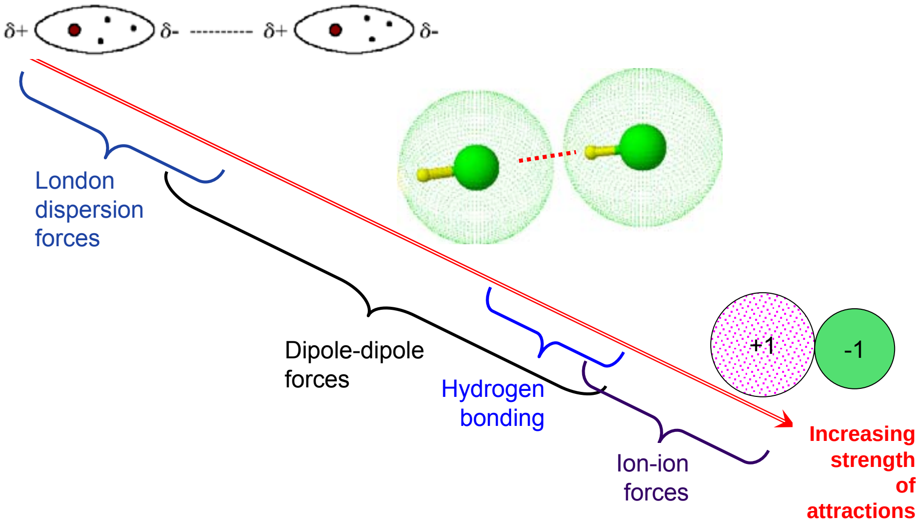
What things are the same about the materials?
What things are different?

What kinds of interactions are there?
Which of these are affected by the differences in the materials?

Questions to help you think about what to say

Summarizing

From weakest to strongest



London dispersion forces

Dipole-dipole forces

Hydrogen bonding

Ion-ion forces

Increasing strength of attractions

Key points about IM forces of attraction

- Intermolecular forces (IM forces) are <u>attractive forces that act between one particle (e.g. molecule) and another</u> in the liquid and solid phases
- What kinds of IM forces exist depends on what kinds of particles they are
  - Molecular particles
    - Non-polar molecules
    - Polar molecules
      - Polar molecules that have an H bonded to either N, O, F or Cl
  - Ionic particles
- Some IM forces are stronger than others
- If a substance has one kind of IM forces, it also has all the weaker ones as well