Ch. 10 Forces between Ions and Molecules. Summary/Overview.

Types of Full Bonds/Binding Forces

1. Ionic (strong)
2. Covalent (strong)
3. Metallic (strong)
    - 1-3 are Full Bonds (strong!):

Ion-Dipole: between Charged Ions and Polar Molecules

Intermolecular Forces between Molecules

1. H-Bonding (O-H, N-H, or F-H bonds). Way strongest.
2. Dipole-Dipole (polar, but without O-H, N-H, or F-H bonds)
3. London (only thing that nonpolar molecules have, but applies to all)

Network vs Molecular Substances

1. Network (usually identifiable by presence of a metal!)
    a. Ionic
    b. Metallic
    c. Covalent Network Solid (diamond) (special case, few others)
2. Molecular (usually idenifiable by absence of a metal)
- Network binding forces are stronger

Recognizing Polarity (Necessary for recognizing/evaluating intermolecular forces)

1. AB_m	Nonpolar	If no lone pairs on central, and all outside atoms same, nonpolar.
2. AB_mL_N	Polar.	If lone pairs on central atom.
3. AB_mL_n	Weakly polar	No lone pairs on central atom, but attached atoms not same.
4. Hydrocarbons	Nonpolar	
5. Halocarbons	Very weakly polar	

Ranking substances in terms of relative binding forces:

1. Identify network substances versus molecular substances (Key: are there any metals in formula?)
2. For ion-ion or ion-dipole intereactions, consider the charge.
3. For molecular substances:
    a. H-bonding? (yes or no. If no, proceed to question b. If yes, go to question 3)
    b. Polar? (yes or no)
4. For molecular substances, what is the molecular weight? Greater molecular weight gives greater binding force.

Predictable Properties that Depend on Binding Forces

1	melting point	mp	higher binding force → higher mp
2	boiling point	bp	higher binding force → higher bp
3	evaporation rate ("volatility")		higher binding force → lower evaporation rate
4	vapor pressure		higher binding force → lower vapor pressure
5	heat of fusion (melting)	ΔH_f	higher binding force → higher ΔH_f
6	heat of vaporization (boiling)	ΔH_v	higher binding force → higher ΔH_v
7	viscosity		higher binding force → higher viscosity
8	surface tension		higher binding force → higher surface tension
9	solubility		higher solute/solvent binding force → higher solubility

Intro and Questions: Water, Unique Properties

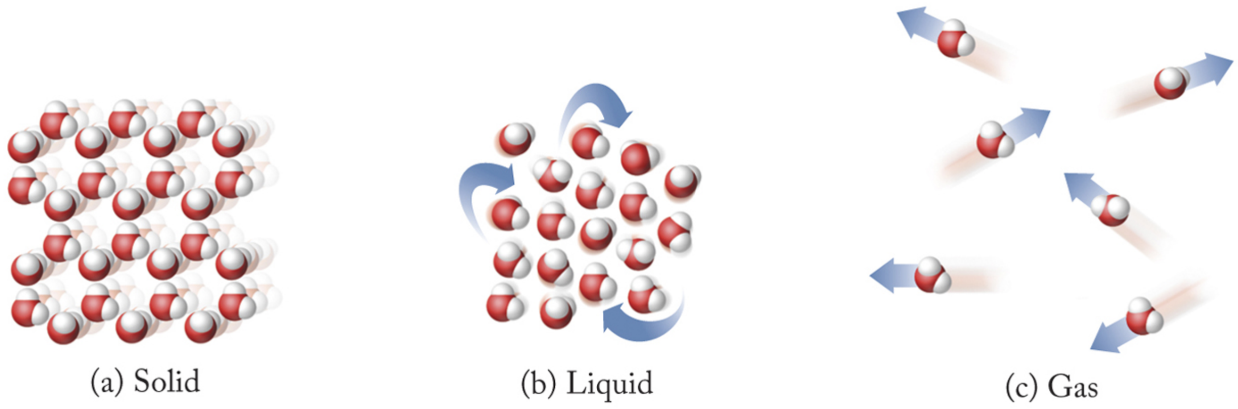
1. Why is something so small (18g/mol) a liquid?
   - Small molecules are almost always gases:
     - N_2 (28 g/mol), CO (28 g/mol), C_2H_6 (30 g/mol), O_2 (32 g/mol), H_2S (34 g/mol), CO_2 (44 g/mol), C_4H_{10} (58 g/mol), etc.
   - But tiny water (18 g/mol) is liquid at normal temp and pressure!
2. Why can water dissolve so many things?
   - Minerals and ions
   - Moleculars (blood…)
   - Gases (oxygen. Blood, lakes…..)
3. Why can ships sail on water?
4. Why does ice float?
5. Why does salt melt ice on Grandma's sidewalk?
6. Why will a can of Pepsi explode in the freezer?
7. Why do water and oil not mix?

- Underlying factors will help us to understand properties for other chemicals, too!

<u>**Review: Liquids, Solids, and Gases**</u> and Attractive/Binding Forces

1. 3 Phases:
   a. Crystalline Solid-
      - <u>**complete order**</u>
      - held closely together by strong forces
      - no "molecular flow"
   b. Liquid-
      - limited disorder
      - -held together, but not fixed; free "molecular flow"
   c. Gas-
      - <u>**complete disorder**</u>
      - Not held together at all, far apart

Gases can be compressed; Solids/liquids are "condensed" states, can't be compressed



(a) Solid (b) Liquid (c) Gas

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2. The state of a given substance depends on balance between **attractive binding forces** (hold together) versus **kinetic energy** (pull particles apart)
   - When energy increases, organization is overcome, particles pull apart
   - **Temperature**: When binding force is the same, but temperature changes:
     - Raising temp increases kinetic order –> increased disorder
     - Raising temp: solid –> liquid –> gas
   - **Binding Force:** At a given temperature, but different substances have different binding forces:

     - Raising binding force → reduces movement → reduces disorder
     - Raising binding force → increasing likelihood of being solid, decreasing likelihood of being gas
     - As attraction grows: gas → liquid → solid

Key: recognizing nature, strength of binding is key to predicting resultant properties

3. **Predictable Properties that Depend on Binding Forces**

1	**melting point**	mp	higher binding force → higher mp
2	**boiling point**	bp	higher binding force → higher bp
3	**evaporation rate**		higher binding force → lower evaporation rate
4	vapor pressure		higher binding force → lower vapor pressure
5	heat of fusion (melting)	ΔH_f	higher binding force → higher ΔH_f
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7	viscosity		higher binding force → higher viscosity
8	surface tension		higher binding force → higher surface tension
9	**solubility**		higher solute/solvent binding force → higher solubility

Concept Questions: **If binding force is stronger**, will something:

Properties

1. Evaporate faster or slower?

2. Boil (or melt) at a higher or lower temperature?

3. Take more energy or less energy to melt? (Or to boil?)

4. Be thicker or thinner (assuming liquid state?)

5. Mix/dissolve more or less easily? (Assuming the binding attraction is stronger between the solvent and the solute?)

10.1-3 Binding Forces

Common to All:

Examples Strength

Types of Bonds/Binding Forces

Summary/Preview/Review

1. Ionic or ion-ion (strong). NaCl
   - Between two charged ions.

2. Covalent (strong) Cl-Cl
   - Between two non-metals

3. Metallic (strong)

The above all involve "full" bonds and are very strong.

Those below are **less than "full" bonds** and are much weaker.

4. Ion-Dipole
   - Between a charged ion and a neutral but polar molecule Na^+ OH_2

5. Intermolecular Forces:
   - Between two molecules. Noncovalent, and variably weak HO-H OH_2

   a. Hydrogen-bonding (OH, NH, or FH)

   b. Dipole-dipole

   c. London dispersion Forces (molecular weight factor)

Ionic Bonds. (Strong). Interactions between ions in Salts (10.1)

a. Ion-ion attraction between opposite charges
b. Full ions with full charges (as opposed to polar molecules like water with partial d+ or d- partial charges)

c. The bigger the charges, the stronger the bonds.
  - **+3 > +2 > +1 cation**
  - **-3 > -2 > -1 anion**

d. Smaller ions make stronger ionic bonds, charge being equal

- **Ion charge take priority over ion size**

e. Formula (don't need to memorize, but illustrates charge/size factors:

$$\text{Ionic bond strength} = \frac{\text{cation charge x anion charge}}{\text{distance}}$$

f. "Lattice energy" = strength of attraction for ionics.

P1: Rank the ionic bond strength for the following ionic formulas, 1 being strongest:

Al_2O_3 MgO $MgCl_2$ NaCl

Strategy: Identify ion charges.

P2: Rank the lattice energy (ionic bond strength) for the following formulas, 1 being strongest:

LiF NaF NaCl NaBr NaI

Strategy: When Charges are Equal, Use Ion Size to Break Ties.

P3: Rank the ionic bond strength for the following ionic formulas, 1 being strongest:

Na_2O NaBr LiCl Fe_3N_2 CaO

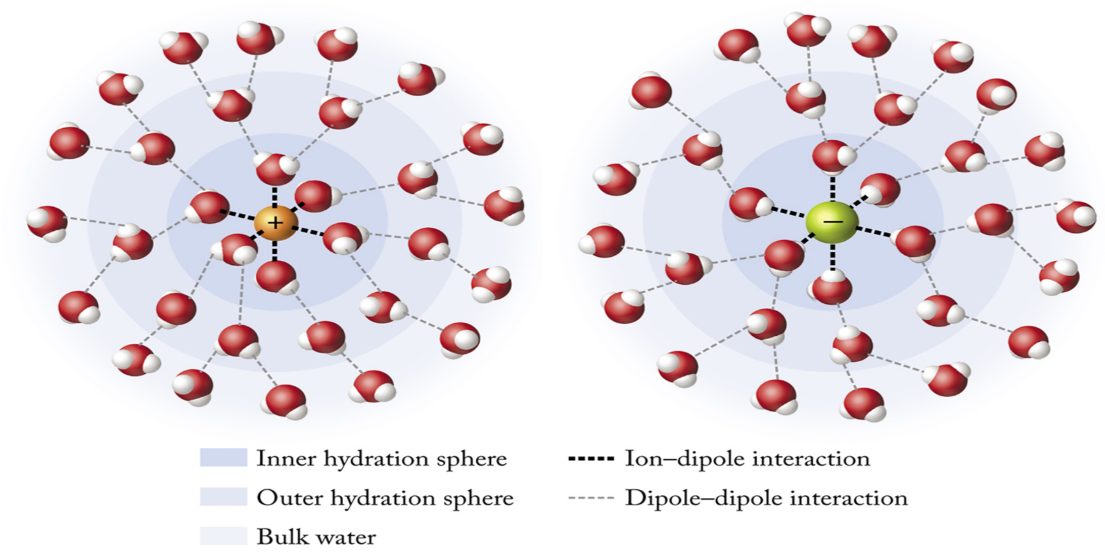
Strategy: Charges First, then Ion Size to Break Ties.

Interactions Involving Polar Molecules (10.2)

Ion-Dipole Involves the attraction between a charged ion and a polar molecule.

Ion Dipole

- between an ion (full charge) and partial charge of polar solvent (water especially)
- why ionic compounds so often dissolve in water
- ex: NaCl in water
- Strength: weaker than an ionic bond, since the charge on the molecule is less
- Water is unusually polar (for a liquid) => better at dissolving ions and salts than other liquids
- **Sphere of Hydration (solvation):**
  - Cluster of water molecules surrounding an ion as it dissolves in aqueous solution.
  - Cations: attract water oxygens Anions: Attract water hydrogens
  - More waters surround those "oriented" waters



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P1: Rank the attractive power for water to the following, 1 being strongest:

Ca^{2+}	Na^{+}	H-Cl	H-H

Key: Amount of charge.

		Intermolecular Forces: Interaction between molecules	
1	Hydrogen-Bonding	**O-H, N-H**, or F-H bonds present	Strongest IMF
2	Dipole-Dipole	Molecule is **polar**, but without O-H, N-H, or F-H bonds	
3	London Dispersion	**Increasing molecular weight** → increased London force. All molecules, whether H-bonders or polar or nonpolar all have London force. But London force is the only intermolecular force that can act between **nonpolar** molecules.	Weakest IMO

http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_10&folder=intermolecular_forces

Intermolecular Forces (IMF): Non-covalent forces between molecules

1. Forces between different molecules
- Key to remember: Bonds within a molecule (covalent, strong) differ from forces between molecules (weak)
- In liquid water:
    a. Covalent bonds (strong) bind oxygen to the two hydrogens in the H_2O molecule.
    b. IMF hold water molecules together in liquid form

2. IMF do not involve full bonds.
    a. Variably weaker interactions,
    b. <10% of a full bond,
    c. easier to overcome (ex bp, etc.)
    d. "Intermolecular forces" attract different molecules
    e. "Intramolecular forces" involve the same attractive factors, but attract and organize otherwise remote parts of the same molecule (key in biology: hydrophobic, hydrophilic, hydrogen-bonding, etc.)

3. If there were no IMF attracting molecules to other molecules, all molecular substances would be gases
    - Some attractive forces are needed in order to have molecular liquids or molecular solids

4. **Like all attractive forces, IMF are based on charge-charge attractions**

5. Key Review: Don't forget the difference between non-covalent IMF and true covalent bond:
    a. H-O in water itself: covalent
    b. One water to another water: noncovalent, IMF

-molecular substances with weak IMF => easy to disorganize (solid → liquid → gas)
one molecule can be removed from others without breaking full bond

2. Dipole-Dipole

- Between polar molecules
- Involve attraction between opposite δ+ and δ- partial charges
- Greater the charges, the stronger the attraction

Ex: HBr, $H_2C{=}O$

- Polarity can vary widely, so the importance of dipole-dipole attractions can vary widely from one polarized molecule to another
- In general, increasing polarity → stronger dipole-dipole force

	Dipole	BP (K)
CH_3OCH_3	1.3	248
CH_3CHO	2.7	294
CH_3CN	3.9	355

1. Hydrogen Bonding

- **Requires the presence of an O-H, N-H bond (or F-H)**

a. Attraction: Between the δ+ charge on Hydrogen (must be OH, NH, or FH) and the δ- charge on Oxygen or Nitrogen (or fluorine).

b. Ultra-strong dipole-diple interaction
  - Hydrogen-bonding really is an extreme form of dipole-dipole interaction. But hydrogen-bonding is so much stronger and so important that it is given it's own name

c. δ+ Charge on O-H or N-H hydrogens is quite strong, and very attractive to lone pairs on oxygen or nitrogen; the δ- charge on OH or NH oxygens or nitrogens is also strong, and attractive to the δ+ hydrogens.
  - H's on atoms other than Oxygen or Nitrogen don't work; aren't positive enough
  - The δ+ H is then attracted to to

d. Why water is so wonderful

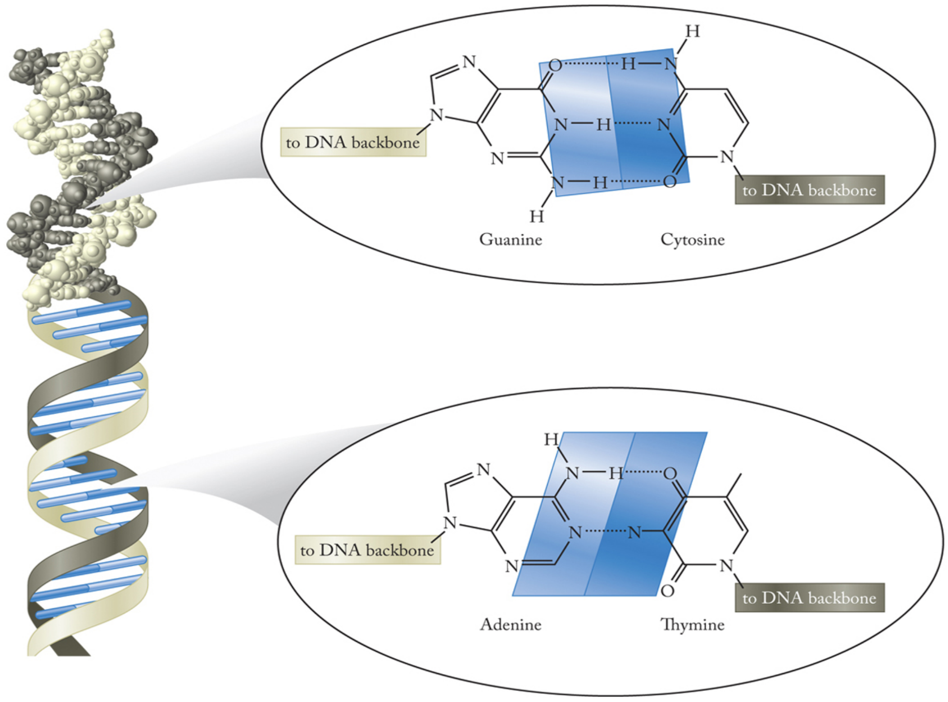
e. H-bonding (→ "hydrophilic") a dominating factor in biological organization

f. While probably 10 times stronger than most dipole-dipole interactions, hydrogen bonding is still <10% of the strength of a full covalent bond

Ex: H_2O

Ex: NH_3

DNA Hydrogen Bonding



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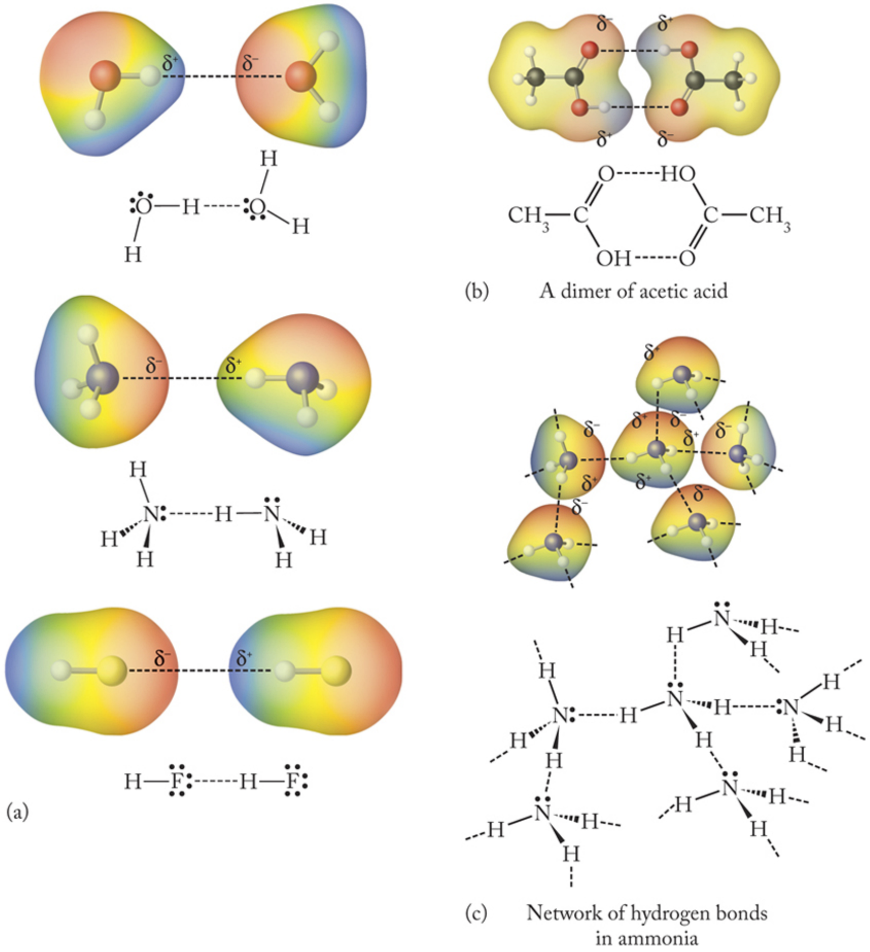
More H-Bonding Examples



(b) A dimer of acetic acid

(c) Network of hydrogen bonds in ammonia

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Ex: Crossed H-Bonding: When one molecule (water?) provide the O-H hydrogen, but a different molecule provides the Oxygen or Nitrogen
-this is why so many oxygenated or nitrogenated molecules are soluble in water.

KEY: Must have an OH or NH (or FH) hydrogen in order for the H to be positive enough. H's that are bonded to other atoms (carbon, for example, or anything other than O, N, or F) can NOT participate in H-bonding because they aren't positive enough.

Q1. Which of the following shows a "hydrogen bond"?

—C······H-F—
—O······H-C—
—N······H-O—
H—H

—N······H-O—
—O······H-N—
—N······H-C—
—C······H-O—

—N······H-N—
—O······H-S—
—S······H-O—
—O······H-N—

Q2. Which of the following will have hydrogen bonding?

$CH_3CH_2CH_2OH$ $CH_3CH_2OCH_3$ $CH_3CH_2NH_2$ CH_3CH_2SH

Q3. Which is higher boiling, and why? (Both have the same formula, C_3H_8O)

$CH_3CH_2OCH_3$ $CH_3CH_2CH_2OH$

3. London Dispersion Force (alias London Force, Dispersion Force, or VanderWaal's Interactions) (Section 10.3)

- Why would a non-polar molecule have any attraction to another non-polar molecule? But if they didn't have at least some, why wouldn't all non-polars be gases?
    - Cl_2 (gas) Br_2 (liquid) I_2 (solid)
- Nonpolar molecules lack permanent dipole, but electon flow → Temporary dipoles
- These temporary, non-permanent dipoles can still cause charge-charge attractions, analogous to regular dipole-dipole attractions.
    - "Polarizability": ease of electron distortion
    - Larger molecules with more electrons can more easily and to greater degree distort their electrons → larger temporary dipoles → large London force

Key: Larger mw = larger molecules => more London force

	Molecular Weight	BP (K)	IMF
F_2		85	
Cl_2		239	
Br_2		332	
I_2		458	

- While London force is the only IMF in nonpolar molecules, it is also important in polar molecules
    - o Electron distortion can **reinforce** existing dipoles and amplify charge attractions
- Key: London force is a great tie-breaker for things with comparable H-bonding or dipole-dipole attraction
    - o It can even override polarity or hydrogen bonding.

	BP	IMF
CH_3OH	348 K	
C_2H_5OH	361 K	

	Dipole	BP	IMF
HCl (mw=30)	1.03 D	190 K	
HBr (mw=80)	0.79 D	206 K	

- For test:
    - o Assume water hydrogen bonding beats anything else
    - o Assume hydrogen bonder overrides London force
    - o Normally I will avoid apples-to-oranges cases unless it's involving water

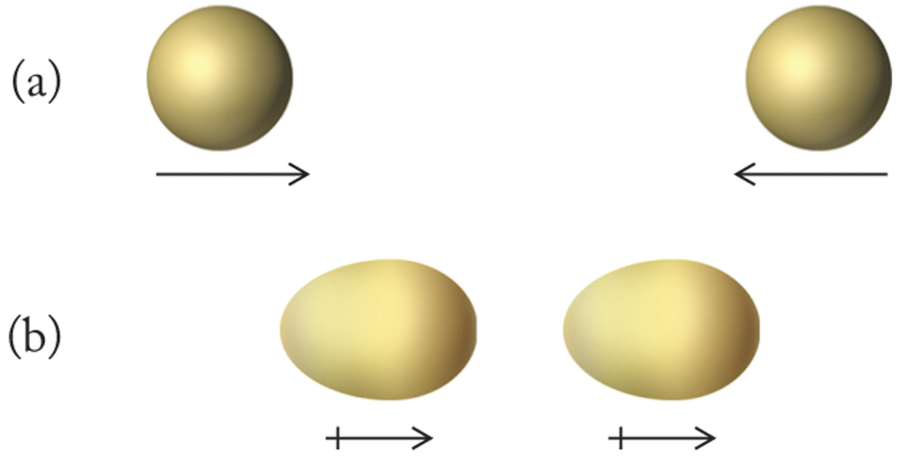
Q1: Rank the boiling points for the following, 1 being highest:

C_4H_{10} C_6H_{14} $C_{10}H_{22}$

Q1: Rank the melting points for the following, 1 being highest:

NaOH $CH_3CH_2OCH_3$ $CH_3CH_2CH_2OH$ $CH_3\ CH_2CH_2CH_2OH$

London Dispersion Force: Initially spherical electron distributions distort into temporary dipoles that attract



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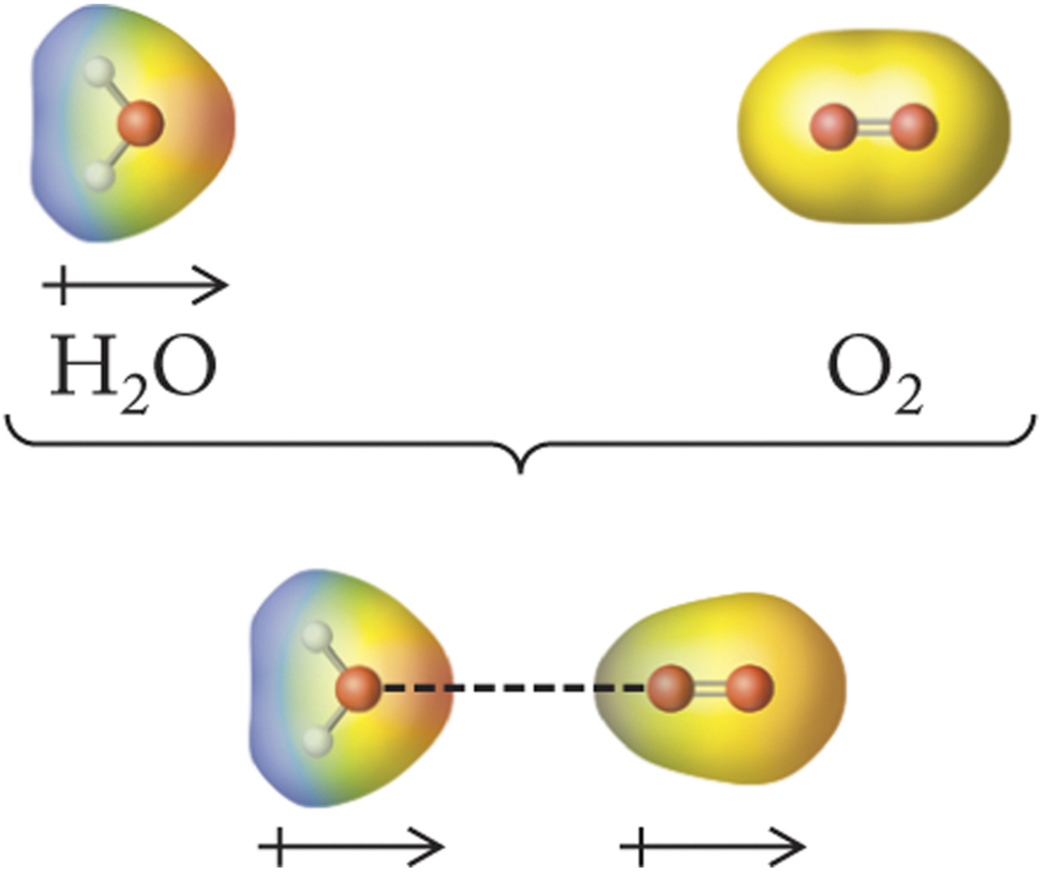
London Dispersion: Polar water induces temporary dipole in initially nonpolar oxygen



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Review:

http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_10&folder=intermolecular_forces

Molecular vs Network Substances: 2 Broad Subsets

1. Molecular
    - Recognition: **Nonmetals only** in formula
    - Different molecules attracted to each other only by IMF, which are relatively weak compared to full bonds
    - Because attractive IMF aren't that strong → molecular substances are relative easy to disorganize
    - One molecule can be moved away from others without breaking full bonds, so the energy price is modest
        - o bp, mp, ΔH_v, ΔH_f, etc. won't be too high
        - o molecular substance can often be gases or liquids
2. Network (these will be solids, Ch 12)
    - 3 Types, all organized and held together using full bonds
        1) Ionic:
            - Recognition: **Metals as well as nonmetal(s)** in formula
        2) Metallic
            - Recognition: **Metal only** in formula
        3) Covalent "Network" Solids (rare) C (diamond), SiO_2 (quartz)
            - Recognition: Exceptionally rare, memorize diamond

a. complete 3-D lattice: can't move one atom without breaking a strong full bond

b. Thus **network substances normally have much stronger binding forces than molecular substances** (there is varation, of course, but as a class network >> molecular)
- o bp, mp, ΔH_v, ΔH_f, etc. will be very high
- o Always solids (almost, mercury the one exception at room temp)

c. Terminology: "network" is often applied (book) only to covalent network, but the broader classification including metals and ionic network substances is useful

KEY Binding: Network Substance (metals involved) >>> Molecular Substance (nonmetals)

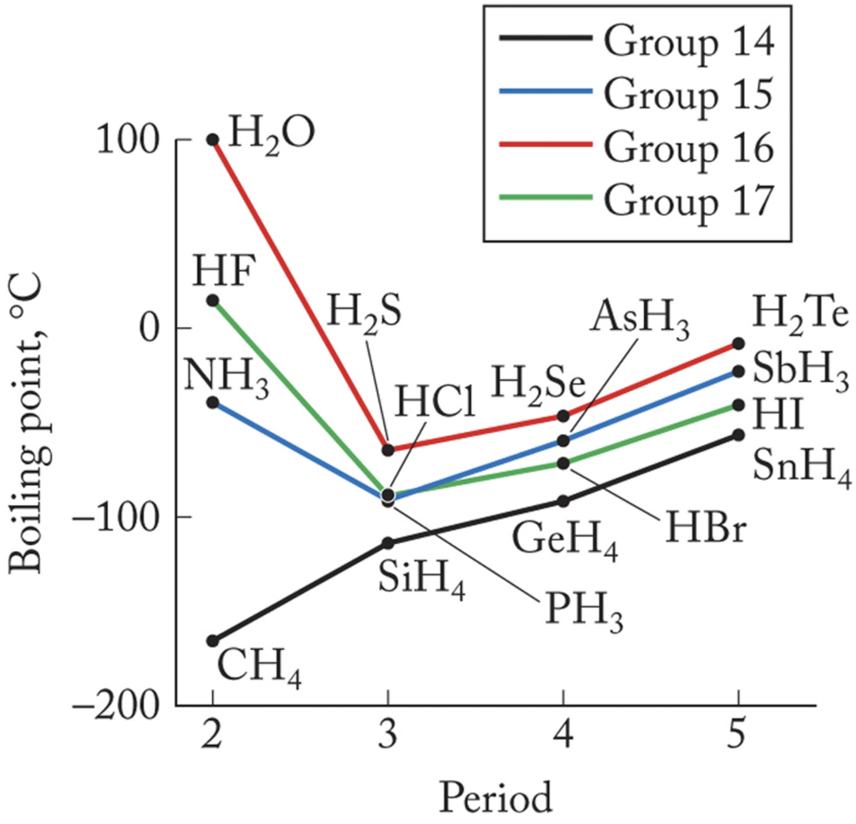
⇨ molecular substances have much lower mp, bp, etc.

Ranking substances in terms of relative binding forces:

1. Identify network substances versus molecular substances (Key: are there any metals in formula?)
2. If molecular, is there H-bonding?
3. If molecular, is it polar? (not worth asking if you've already ID'd as an H-bonder….)
4. If molecular, what is the molecular weight?

Tiebreakers for molecular substances:

- If mw = comparable, then H-bonding or polarity required to break tie
- If two things are similar in terms of H-bonding or polarity, then mw (London force) should break the tie.
- H-bonding is more important than London dispersion force



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Notice:

1. For Most groups bp increases, due to increasing size/London dispersion force
2. H-bonding makes H2O, HF, and NH3 way different
3. H-bonding is much more important than London dispersion
4. Carbon family doesn't have the H-bonding factor
5. If not for H-bonding raising it's boiling point, water wouldn't be liquid! (Goodbye life!)

Questions

1) Classify as network or molecular, and identify any forces (other than London dispersion) for the following:
   a. CH_3OH
   b. CH_3OCH_3
   c. CH_4
   d. K^+ in H_2O

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Questions

1) Classify as network or molecular, and identify any forces (other than London dispersion) for the following:

a. I_2

b. H-N=O

c. Fe_2O_3

d. CO

e. Zn

f. NH_3

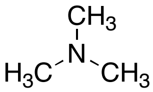
g. HCl

2) Which has highest mp? Lowest bp? (Why)

NaCl $HOCH_2CH_3$ CH_3OCH_3

3) Which has highest bp? Why?

a. OBr_2 OF_2

b. $CH_3CH_2CH_2NH_2$ 

c. CH_3OH CH_3CH_2OH

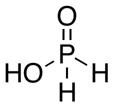
4) Which has H-bonding?

CH_4 $SnCl_4$ NH_3 HCl

5) Which has London dispersion as ONLY IM force?

H_2S Br_2 CH_2O H_2O

6) Which will have highest heat of fusion?

SO_2	Cl_2		$CH_3CH_2CH_2CH_3$
64	70	65	72

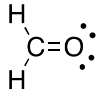
Recognizing Molecular Polarity (9.3)

- an individual **bond** between two atoms is polar when one atom is more electronegative
- An overall **molecular** is polar when one end/side is more negative than the other
  - In other words, when electrons aren't distributed equally
- The unequal distribution of lone pairs often dominated polarity
- When bond dipoles cancel each other out, polarity vanishes or gets minimized

Practical

1	Hydrocarbons	Nonpolar
2	Halocarbons	Very weakly polar (or nonpolar)
3	Diatomic formula, both atoms same	Nonpolar
4	Diatomic formula, two atoms different	Polar
5	AB_mL_X or $AB_mC_nL_x$ (**Lone Pairs on Central Atom**)	**Polar**
6	AB_m (multi-atom, no lone pairs on center, all outside atoms same)	Nonpolar
7	AB_mC_n (outside atoms aren't all the same, but still no lone pairs on central atom)	Weakly polar

Q1: Classify each of the following as polar (molecular), completely nonpolar (molecular), weakly polar (molecular), ionic, or metallic.

1. CO_2
2. CH_3OH
3. O_2
4. NH_3
5. CH_2Cl_2
6. PCl_3
7. CO
8. 
9. $SiCl_4$
10. Fe
11. NaCl

Q2: Identify any for which hydrogen-bonding would apply.

Q3: Which would have dipole-dipole interactions?

Q4: Which would be network solids with high melting points?

Q5: Which would have London force only?

Q1: For the following four structures, rank them from 1-4 according to each of the properties

	$LiCl$ 42 g/mol	$CH_3CH_2CH_2CH_2OH$ 74 g/mol	$CH_3CH_2CH_2OH$ 60 g/mol	$CH_3OCH_2CH_3$ 60 g/mol
Binding Strength (and why?)				
Melting point				
Boiling point				
Evaporation rate				
vapor pressure				
Energy to melt				
Energy to Boil				
Viscosity				
Surface tension				

Notes:

- If you can figure out the relative binding forces at work for different substances, you can rank those substances relative to any of these physical properties
- An understanding of whether a stronger binding force causes an increase or decrease is also required
  - Higher binding raises: mp, bp, energy to melt or boil, viscosity, surface tension
  - High binding reduces: evaporation rate and vapor pressure

General Strategy:
1. Identify network versus molecular substances
2. For molecular: H-bonding? Polar? or London Only?
3. London force (molecular weight) is routinely a tie-breaker.

Q2: Rank the evaporation rate (1 being highest)

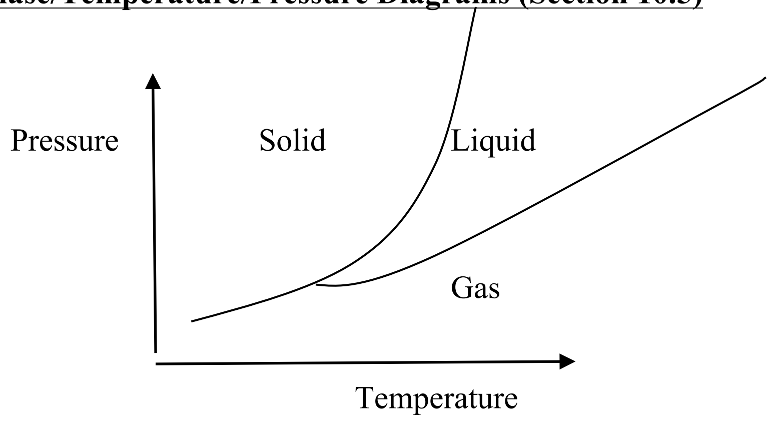
$CH_3CH_2CH_2CH_2CH_2OH$ $CH_3CH_2CH_2OH$ $CH_3CH_2CH_2CH_3$ $CH_3CH_2OCH_3$

Q3: Rank the melting points for the following, 1 being highest:

$CH_3CH_2CH_2NH_2$ $LiCl$ $N(CH_3)_3$ $CH_3CH_2CH_2CH_2CH_2NH_2$

Polarity and Solubility (Section 10.4) I'll cover some of these topics next chapter.

Phase/Temperature/Pressure Diagrams (Section 10.5)



- On lines: phase change situation, two phases present at once
- Triple point: unique temp/pressure situation when all 3 phases are present at once

Phases

- Max temp, minimum pressure ➔ gas (bottom right)
- Min. temp, max pressure ➔ solid (upper left)
- Liquid in between

Use temperature and pressure logic to remind yourself of phase extremes (solid versus gas)

Temperature dependence: increased temperature => increases disorder
Solid => liquid => gas, or solid => gas,

Pressure dependence: increased pressure => increases order (makes harder to escape)
Gas => liquid => solid, or gas => solid

Density: For almost all things, solid > liquid > gas

- Since pressure squeezes things into a small volume, that explains why increasing pressure usually can convert gas to liquid, and then liquid to gas.
- Since solids are usually more dense than liquids, solids almost always sink

Water: Amazing and wonderful Pressure/Density Anomoly

- For water, solid water (ice) is MORE dense than liquid
- Thus ice floats. (Life says thanks!)
- Density reversal means pressure melts ice, rather than vice versa

"Normal" Pressure: 1 atm = 760 mm Hg.
The "normal" melting point or boiling point is the phase-change temperature at 1 atm pressure.

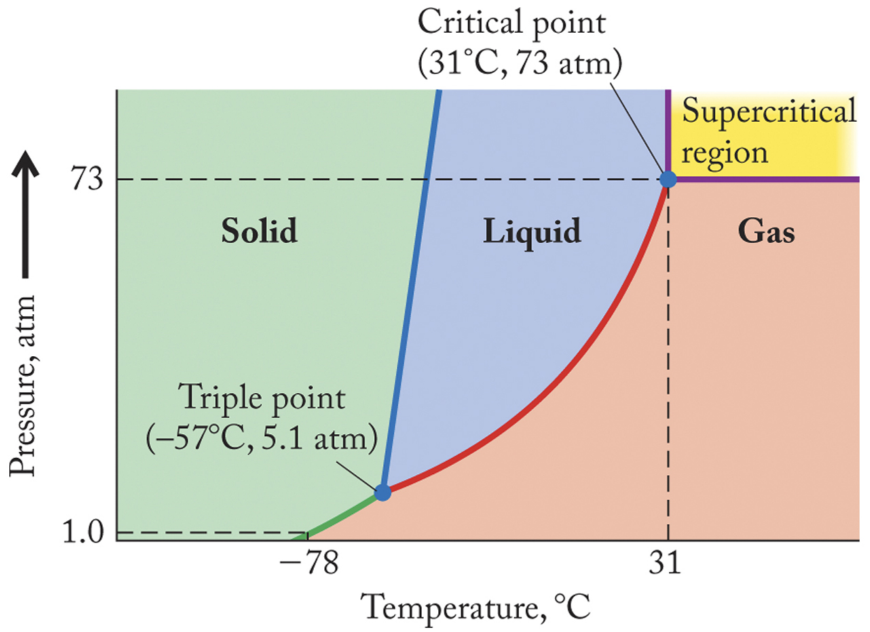
Critical point: (not test, but may need for online homework). Liquid/gas distinction vanishes.

Triple Point: All three phases at meet

Review: http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_10&folder=phase_diagrams

A Normal Phase/Temperature/Pressure Diagrams

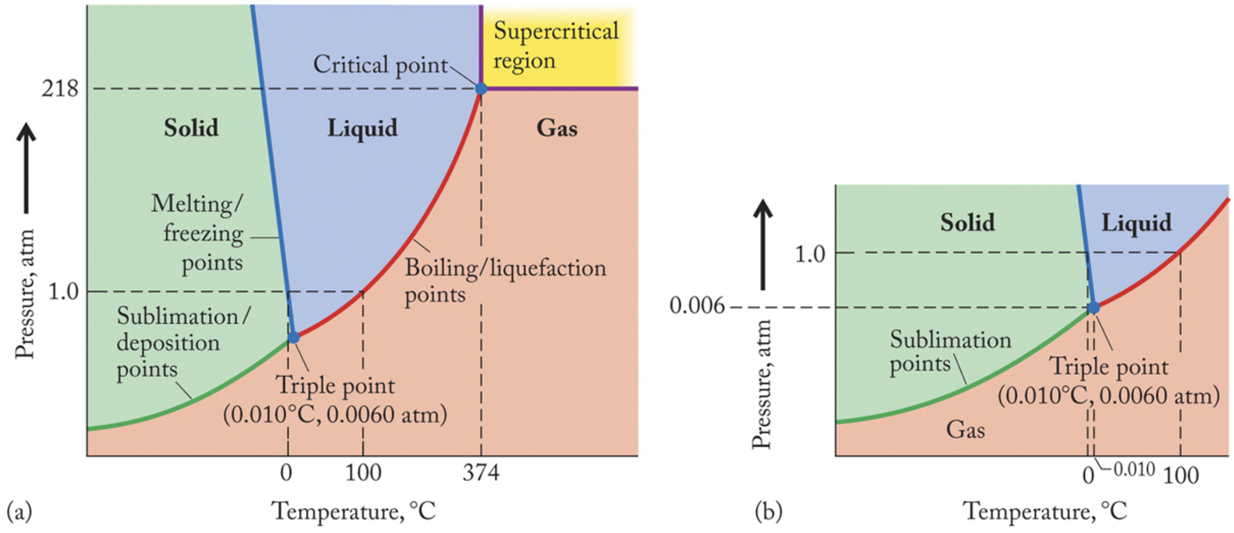
- -notice the angle for the line between solid and liquid: angles to the right (positive slope)
- Due to solid being more dense, has impact on pressure effect.



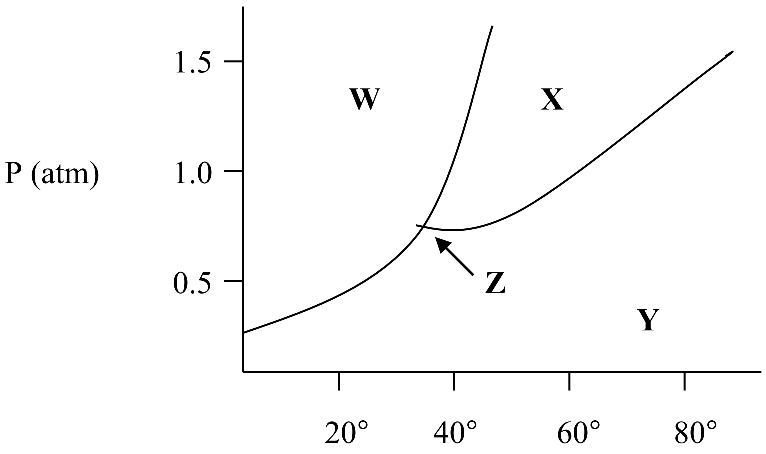
Chemistry: The Science in Context 3/e Figure 10.24

Weird and Wonderful Water

- Notice how the solid-liquid interface line **angles left** (negative slope), not right.
- This causes the unusual **pressure** reversal, such that increasing pressure converts ice to liquid water
- This unusual "angles left" feature reflects the greater density of liquid water compared to solid water, which enables ice to float and saves aquatic life.



Chemistry: The Science in Context 3/e Figure 10.22



1. Which letter represents:

a. Gas Phase b. Liquid c. Solid d. Triple Point

2. What is the normal bp?

a) 20° b) 40° c) 65° d) 80°

1. What is the normal mp?

a) 20° b) 40° c) 80°

2. When a liquid originally at 50° has pressure reduced, at what pressure will it vaporize?

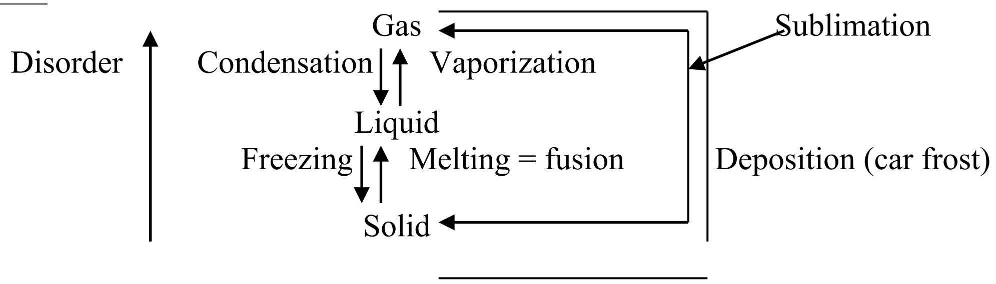
3. When solid at 0.5 atm is warmed, does it: a) melt or b) sublime

4. When solid at 1.5 atm is warmed, does it: a) melt or b) sublime

Review: http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_10&folder=phase_diagrams

Phase Changes (Section 5.3, 5.4 Review)

A. **Terms**:



B. **Energy**

1. Energy is required for change to more disordered state; energy is released during change to a more ordered state

Endothermic: melting, vaporization, sublimation
Exothermic: freezing, condensation, deposition

Water as air-conditioner

- Winter heater: when water freezes, it releases heat. Without freezing water, winter temps would be 30° colder!
- Summer chiller: Evaporation absorbs heat, so instead of hitting 120º we just evaporate some lake water

Refrigeration(Evaporation is cooling!) → fridge: liquid evaporates (chills fridge/freezer) → electrical compressor resqueezes it to liquid

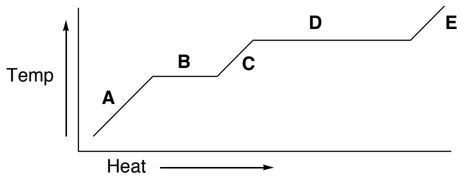
2. Quantitative Energy Calculations
   - Values are given either on a per-mole or a per-gram basis
   - When moles are used, you'll need to use mass-mole interconversions
   - Normally $\Delta H_{vap} > \Delta H_{fus}$

ΔH_{fus}: energy to melt **1 mole** of solid (or 1 g)	ΔH_{vap}: energy to vaporize **1 mole** of liquid (or 1 g)
$^{-}\Delta H_{fus}$: energy released during freezing	$^{-}\Delta H_{vap}$: energy released during condensation

Greater binding force → larger ΔH_{fus}, ΔH_{vap}

3. Specific Heat Capacity: Amount of heat to raise the temperature of a solid, liquid or gas by 1º
   - Applies when you are **not** at a phase change
   - For a given substance, the specific heat will be different for the solid form versus the liquid form versus the gas form

4. Heating "Curves" and Phases



"Horizontals" = phase change. "Diagonals" involve the heating up of a solid, liquid, or gas

Zone	What's Happening	Phases Present
A		
B		
C		
D		
E		

Notes:

- Temperature fixed during phase change. All the energy goes into the phase change rather than temperature increase
- When NOT changing phase, then all the energy goes into temperature (and movement) increase.

Wonderful Water: Special Properties (Section 10.6)

1. Liquid Phase, and **Amazingly High Boiling Point**:
    - Given small size/mass/London force, it's amazing that it's a liquid
    - **Liquid** water essential to life

	Molar Mass	Bp (ºC)		Molar Mass	Bp (ºC)
N_2	28	-196	HF	20	-164
O_2	32	-183	H_2S	34	-60
CO_2	44	-78	NH_3	17	-33
CH_4	18	-161	H_2O	18	+100

2. "Universal Solvent": **Amazingly Good and Diverse Dissolving Power**
    - Far more substances dissolve in water than in any other liquid
    - Ionics, moleculars, biological, oxygen
    - Can basically dissolve anything with nitrogens or oxygens in it (through hydrogen bonding)
    - Can dissolve many ionics (through ion-dipole bonding)
    - Can dissolve oxygen (blood, lakes. Less when warmer, lake impact….)
    - Solvent of the blood and of biological cells, delivers everything a body needs

3. Density (Unique Phase Diagram): **Amazingly Unusual and Beneficially Low Density of Solid Water (Ice)**
    a. Solids usually more dense than liquids (because solids normally more organized and packed tighter) → solids sink to the bottom of liquids
    b. Solid water (ice) is unique in being **less dense** than liquid water.
        - Thus ice floats on water
        - Water below is insulated from winter cold, stays liquid
        - Water life is possible.
        - If solid ice fell to the bottom, whole lakes would freeze in cold winters and all biology would die
    c. 4ºC liquid water is denser than warmer or colder liquid water, or solid ice. It sinks to the bottom→ O_2 delivery and nutrient exchange. Spring bloom, etc.

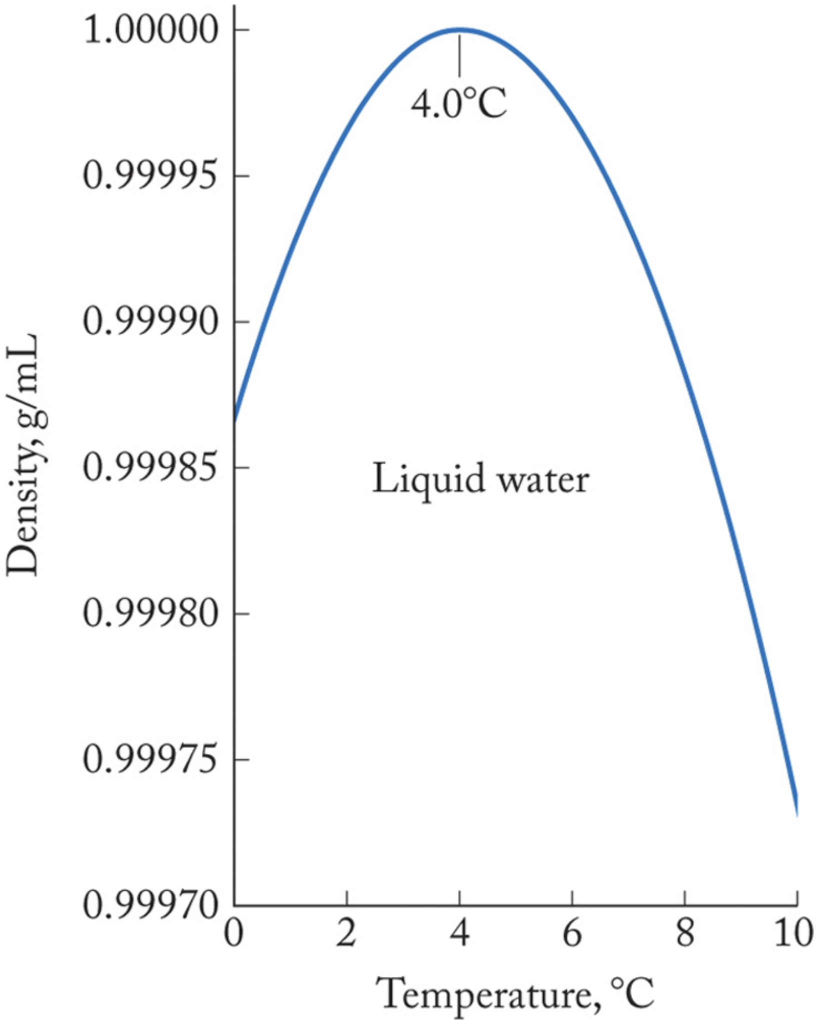
4. Water as Earth and Body Air Conditioner: **Amazingly High Heat Capacity**.
    a. Water has an extraordinarily high heat capacity for a molecular substance or for a liquid
        - A lot of energy is involved to change it's temperature by much
        - This helps to prevent wide temperature variations that are hostile to life.
    b. Winter heater: when water freezes, it releases heat. Without freezing water, winter temps would be 30º colder!
    c. Summer chiller: Evaporation absorbs heat, so instead of hitting 120º we just evaporate some lake water
    d. Sweat/evaporation keeps us from overheating

5. **Amazingly High Surface Tension**
    - Good for bugs, good for ships

The extraordinary Hydrogen-bonding interactions involved with water underlie all of its special properties.

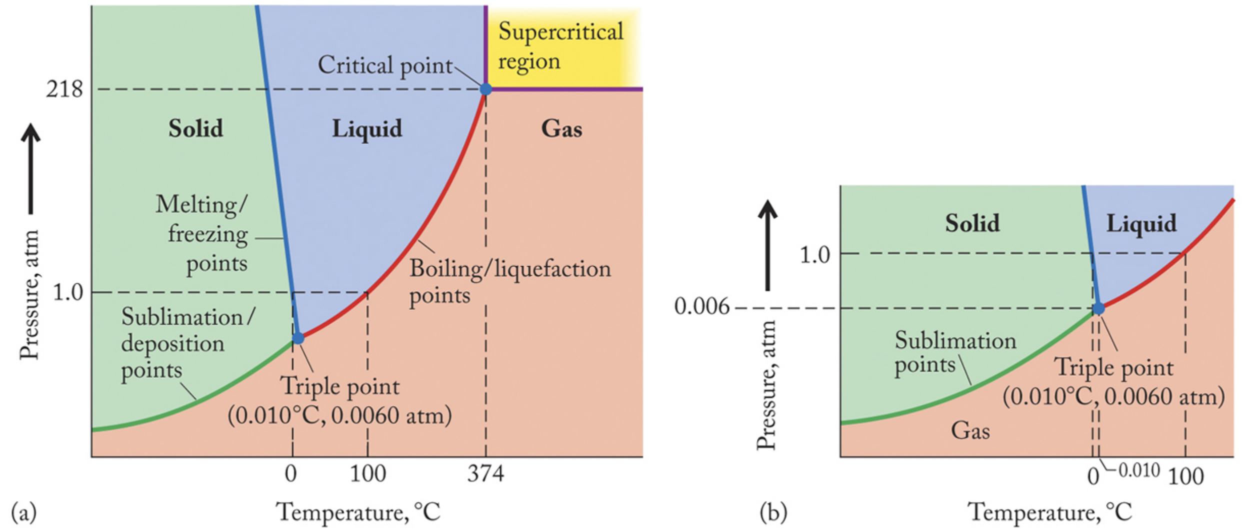
More Weird Water Density Crucial for Aquatic Life (p489)

- Density of solid ice is only 0.92 g/mL, so it floats
- 4ºC water is more dense than colder water (or warmer water), so it sinks and warmer/colder water floats or rises.
- During fall, as water cools it gets denser and sinks, pushing warmer water up
- Critical stirring factor: stirs up nutrients, ready for plant life near the sunny surface next spring.
- Critical air-conditioning factor: Stirring factor exposes all of the water to the surface to release heat which slows onset of cold winter
- Once all the water is 4ºC, subsequent cooling results in ice, which freezes on top and insulates aquatic life underneath
- Spring thaw and spring bloom: When lake melts, nutrients that were stirred up last fall are ready for plant growth.
- As water warms, the nutrients get depleted near the sunny surface and growth slows.



***Chemistry: The Science in Context* 3/e Figure 10.29**

Remember: The weird and wonderful "negative slope" phase diagram for water reflects the unique solid-versus liquid density situation. Critical to water life.



Chemistry: The Science in Context 3/e Figure 10.22

Ch 11 (and some from 10) Liquids and Solutions (mixtures) and their Properties

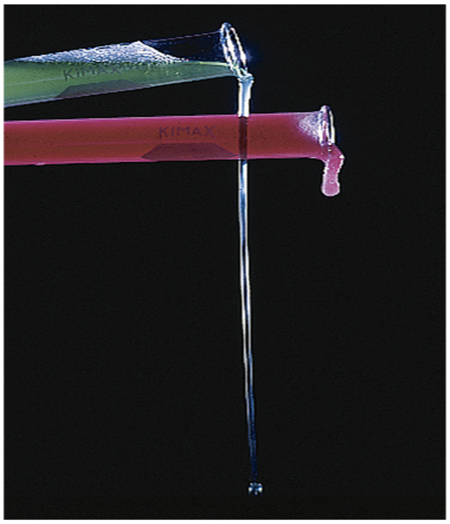
Liquid State (Sections 10.4,5,6, 11.2)

- At room temp, liquids are almost exclusively molecular substances
  - Mercury is the one exception, a non-molecular liquid
- Molecular flow is possible
  - Binding is too weak to lock molecules into a solid
  - Binding is too strong to let the molecules all fly apart into gas phase

1. Viscosity (10.6): Resistence to flow = "thickness" of liquid
   - Examples of viscous liquids: ketchup, syrup, ice-cream topping, motor oil, etc…
   - Liquids get "thick" and "viscous" when the molecules don't want to flow, and instead want to stick together (i.e. controlled by binding force, versus kinetic energy)

Greater IMF → more viscous
Greater temp → less viscous (greater kinetic energy → better flow)

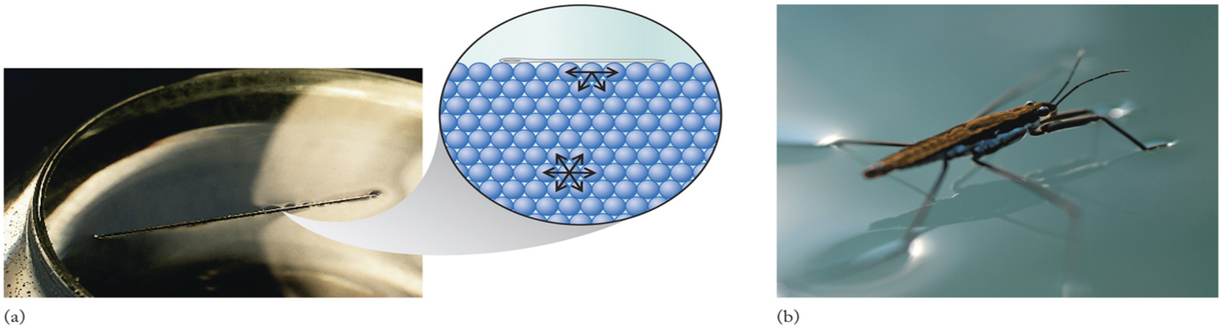
   - Motor Oil issues
   - Water is unusually viscous for a liquid of it's size.



Chemistry: The Science in Context 3/e Figure 10.28
Larry Stepanowicz/Visuals Unlimited

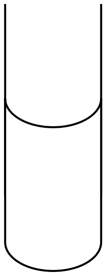
2. Surface Tension (10.6)
   - Water "beads up" on smooth surface, or overfilled glass
   - IMF pull the molecules together, cause them to ball up, pack together as if it had a skin
     - This is why water bugs can "walk" on water
     - To "cut through" the surface would require breaking hydrogen-bonds
   - Mercury has much greater surface tension
   - Rubbing alcohol or turpentine have much less surface tension

Greater IMF → more surface tension
Greater temp → less surface tension (greater kinetic energy → better flow)

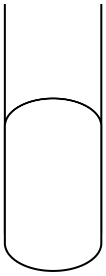


Chemistry: The Science in Context 3/e Figure 10.25
(left): Jeff Daly/Visuals Unlimited; (right): Martin Shields/Photo Researchers Inc.

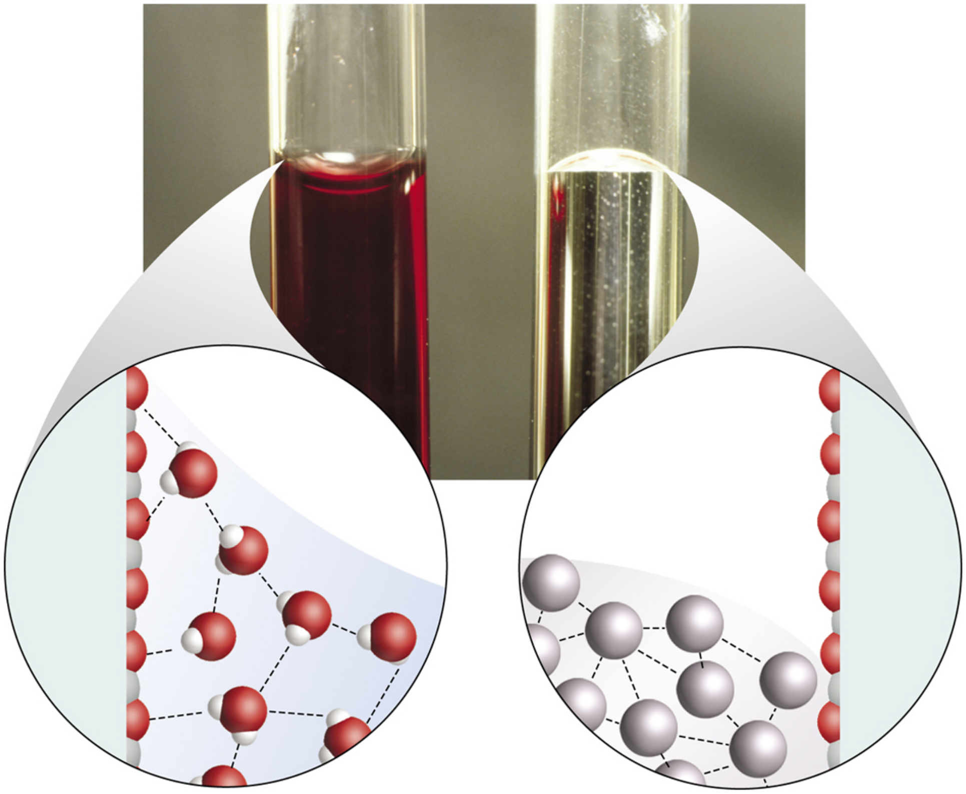
3. Meniscus Chemistry (10.6): Cohesive vs Adhesive Force/Attraction
   - “Cohesive forces” – bind like molecules together (intermolecular force)
   - “Adhesive forces” – bind liquid to surface (non-covalent attractions between a liquid to a solid.)
   - For water, if a surface has strong H-bonding or even ionic character, adhesive attraction (to surface) will exceed cohesive attraction (to itself). If not, cohesive attraction (to itself) will exceed adhesive attraction (to the surface)
     - The balance between adhesive vs cohesive force determines the shape of the meniscus
     - In glass tubes (glass is very strongly polar), water has a downwards meniscus
     - In plastic tubes (plastic is nonpolar), water has an upward meniscus



H_2O in glass (very H-bonding):
Adhesion > cohesion

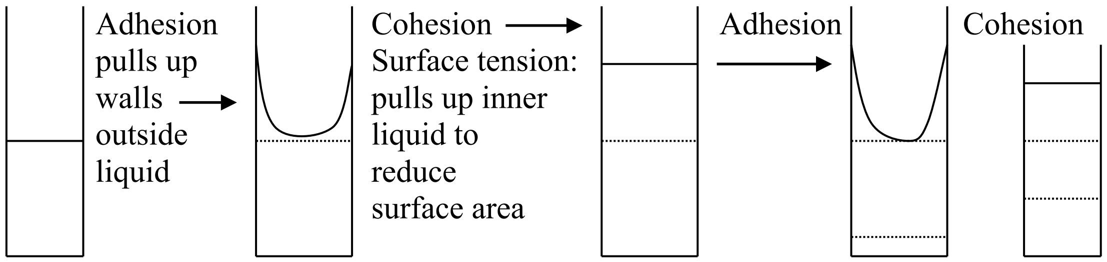


Hg in glass:
Cohesion > adhesion



***Chemistry: The Science in Context* 3/e Figure 10.26**
Sinclair Stammers/Science Photo Library/Photo Researchers, Inc.

4. Capillary Action (10.6): Liquids climb up narrow tubes!
Review: http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_10&folder=capillary_action
- Contrary to gravity
- Key to plant biology! It's the way water climbs up from the roots through the stalks/trunks and gets distributed to the leaves
- Combined adhesion/cohesion "steps" liquid up narrow tube (simplified picture)
  1) Adhesion pulls up "outside"
  2) Cohesion pulls up "inside"
- Three variable:
  - Diameter of the tube
  - Strength of the cohesive forces
  - Strength of the adhesive forces



Q1: Rank the viscosity (1 being highest)

$CH_3CH_2CH_2OH$ $CH_3CH_2CH_2CH_3$ $CH_3CH_2OCH_3$ $CH_3CH_2CH_2CH_2CH_2OH$

Q2: Rank the surface tension, 1 being highest:

$CH_3CH_2CH_2NH_2$ $CH_3CH_2CH_2CH_2CH_2NH_2$ $N(CH_3)_3$ $CH_3CH_2CH_2CH_3$

Volatility, Evaporation, and Vapor Pressure, (Section 11.2)

- Why does nail polish, gas, turpentine evaporate faster than water?
- Why does "Latex" paint dries faster than oil-based gloss?
- Does Pepsi get "flat" when bottle almost empty or uncapped?

A. Intro

1) **Vaporization**: When molecules break away from the liquid phase and escape into the gas phase
2) Temp reflects **average** kinetic energy, but some molecules are above average
3) Even below bp temp., some above-average molecules often have enough KE to vaporize
   ➔ **Molecules Routinely Escaping** (see 2, 4, 5 on following)

http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_11&folder=molecular_motion

4) Higher temp → Higher fraction of molecules with enough energy to escape → higher vaporation rate
5) At a given temp, the greater the binding force → less likely that molecules will have enough energy to escape → lower vaporization rate

Greater IMF → lower vaporization rate
Greater temp → higher vaporization rate

B. Vaporization in **Open Containers**

1. Breakaway ➔ Evaporation
2. "**Volatility**"—rate of evaporation
3. Weaker the IMF => more volatile
4. Higher the temp => more volatile

Greater IMF → lower rate of evaporation = lower volatility
Greater temp → higher rate of evaporation = lower volatility

C. Vaporization in a **Closed Container**

1. Molecules still vaporize out of the liquid into the gas, but can't escape the container
   - The population of gas molecules increases
2. With more gas molecules flying around, a lot of them fly into the liquid and rejoin the liquid phase
   - (liquifaction or "condensation")
3. Eventually: rate of vaporization = condensation
   - Achieve "**dynamic equilibrium**"
   - Constant population of gas: new ones forming as fast as old ones re-liquifying
4. When gas molecules fly around and hit a surface (whether the liquid surface or the surface of the closed container), they create **pressure**
5. The **Vapor Pressure** of a substance at a given temperature is the pressure exerted by its vapor when liquid/vapor are in dynamic equilibrium.
6. The vapor pressure depends on how much vapor is present, so basically whatever is good for vaporization increases vapor pressure

Greater IMF → lower rate of vaporization → lower vapor pressure
Greater temp → higher rate of vaporization → higher vapor pressure

Practice Problems

1. Increasing the amount of liquid in a **closed** container will cause vapor pressure to:
   a) increase b) decrease
   c) remain the same d) depends on the liquid

2. **Increasing temperature** will cause vapor pressure to:
   a) increase b) decrease
   c) remain the same d) depends on the liquid

3. Which will have **highest vapor pressure**? **Lowest**?
   a) CH_3OCH_3 b) CH_3CH_2OH c) $CH_3CH_2CH_2CH_2OH$

D. Vaporization and **Boiling Point** in the open

1. Boiling occurs when the vapor pressure of the escaping gas pressing up equals the total combined external pressure down
   - Most of the external pressure comes from air (nitrogen and oxygen) in an open container
   - In a sense, the external pressure is pushing molecules down. To boil, molecules from the liquid need to be jumping into the gas phase and pushing up as hard or harder than the external pressure is pushing down.
2. **BP and External Pressure:** The boiling point is highly dependent on external pressure
   - Higher pressure → higher boiling point (temp needs to go up for vaporization escape pressure to match external pressure)
   - Lower pressure → lower boiling point (temp doesn't need to be that high to produce enough vaporization to match external pressure)
3. "**Normal boiling point**" = boiling temperature under normal atmospheric pressure, when external pressure = 1 atm = 760 mm Hg = 760 torr
   - mostly when we refer to "boiling point", we mean the "normal boiling point"

Greater IMF → lower rate of vaporization → higher normal boiling point (need more temp to make up for the otherwiselow vaporization rate)
Greater external pressure → higher boiling point (need more temp for escape pressure to match the external pressure)
Lower external pressure → lower boiling point (need less heat to generate the escape pressure needed to match the external pressure)

Q4: Benzene boils at 80°. Is its vapor pressure at room temperature higher or lower than that of water? Will it's vapor pressure be higher at room temperature or at 40º?

Q5: Hexane has higher vapor pressure than water. Which has higher bp?

Miscellany:

- Takes longer to boil an egg in Denver (higher elevation → reduced pressure → reduced boiling point → boiling water isn't as hot)
- Water would boil on the moon (low external pressure), or Mercury and Venus (hot)
- Pressure cooker cooks fast: high pressure → higher bp for water → hotter → cook fast

More Practice Problems

5. Which will have highest bp?

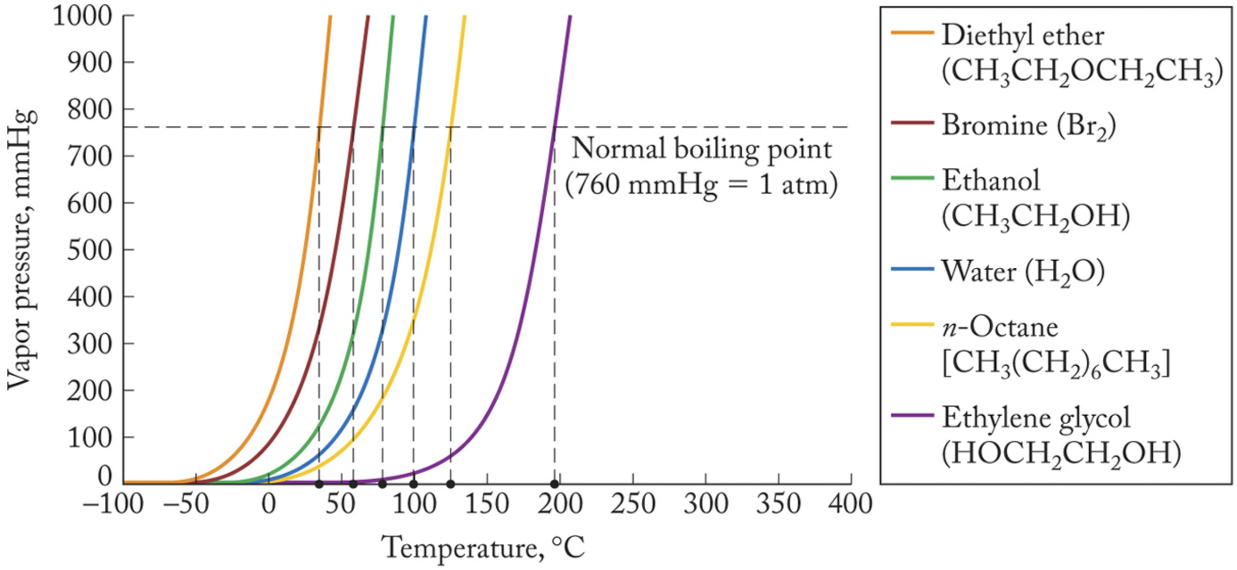
Br_2	F_2	SiH_4	CO_2
160	38	32	44

6. Which will have highest bp? Which would you guess would be lowest? Try to rank all four.

CH_3NO_2	LiF	Cl_2	CH_3OH
61	26	70	32

Vapor Pressure Curves: Show the relationship between temperature and vapor pressure for different substances

E.



***Chemistry: The Science in Context* 3/e Figure 11.7**
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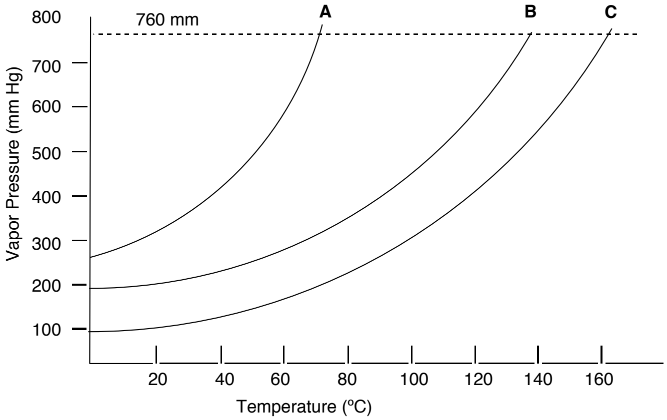


For each of the following, fill in the information:

	A	B	C
1. "Normal boiling point"			
2. BP at 400 mmHg			
3. Vapor Pressures at 40ºC			
4. Rank the three substances in terms of IMF			

Properties of "Solutions"

- A "Solution" is a **homogeneous** (uniform) **mixture**, usually liquid (also gas)

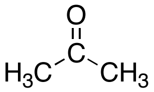
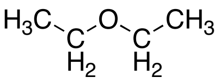
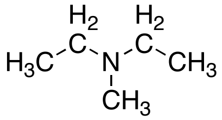
Q: Why does alcohol, salt, and sugar dissolve in water, but oil doesn't?

Facts

1. All gases mix fully
2. Water has awesome dissolving powers. Great for blood, and biology
3. Only some liquids and solids "dissolve" in a given "solvent". (Review 4.1)
    - "**solvent**": major liquid
    - "**solute**": minor component dissolved
    - solids: "soluble" or "insoluble"
    - liquids: "miscible" or "immiscible"

Polarity, Solubility and Noncovalent Forces (10.4)

1. **Water** is strongly polar.

Water Will Dissolve:	Strong Solvent-Solute Interaction	Examples
a) many ionics		NaCl, KBr, $LiNO_3$
b) H-bonders		C_3H_7OH, $C_2H_5NH_2$
c) molecules with N or O		  

Q1: For each of the three groups, fill in what kind of solvent-solute interaction is involved

- Each of these three groups are "**hydrophilic**"

- Hydrophilic things have **strong solvent-solute** interactions in water
    - hydrogen-bonding or ion-dipole
    - the solute-water interactions may be similar, better, or not much worse than the original solute-solute and water-water interactions

Q2: How can "case c" molecules that have N or O hydrogen bond to water when they don't hydrogen-bond themselves?

Q3: Sketch interaction of water with NaCl and CH_3OH

Water Won't Dissolve:	Solvent-Solute Interaction	Examples
a) nonpolar molecules	Dipole-induced dipole	Br_2, N_2, SiH_4
b) hydrocarbons, halocarbons	Dipole-induced/weak dipole	C_6H_{14}, C_2H_5Cl
c) weakly polar molecules without N or O	Dipole-weak dipole	PCl_3, $SiHCl_3$

- These groups are "hydrophobic"
- all end up with **weak solvent-solute** interactions in water
    - none can hydrogen-bond with water
    - at best they end up with dipole (water)-weak dipole (solute), or dipole (water)-induced dipole (solute) interactions which are quite weak
    - the solute-water interactions are much inferior to water-water interactions. Therefore the energy penalty of breaking waters apart in order to allow solute into the water is prohibitively high.

For water to dissolve something, it must exchange H-bonding with other water molecules for different interaction with the solute. That's fine if the new interactions (H-bonding or ion-dipole) are comparably strong. But not if the new solute can't even H-bond with water.

☆ **2. Adding C's to a molecule reduces polarity, reduces water solubility**

- adding more carbons is like adding more non-polar grease to a molecule

	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$	$C_6H_{11}OH$	$C_7H_{13}OH$
Water Solubility:	Infinite	Infinite	9.1g/100mL	2.7g/100mL	0.6g/100mL	0.1g/100mL

☆ **3. Hydrocarbons/Halocarbons are "Nonpolar"/"Weakly Polar"**

- Oils, grease, fat, gasoline
- Don't dissolve in water
    - Hydrocarbon-water interactions are too weak
- Dissolve weakly polar, nonpolar things
    - Interactions between solute-solvent may be weak, but not any weaker than the original solute-solute or solvent-solvent interactions

4. "Like dissolves like" (general principle)

	Soluble?
Hydrophilic-hydrophilic	Yes
Hydrophobic-hydrophobic	Yes
Hydrophilic-hydrophobic	No

- More alike, more soluble

Why?

- **Solvent-solute interactions come at the expense of some solvent-solvent and solute-solute interactions**
    - To dissolve something in water, you need to separate water molecules from each other (at the expense of water-water hydrogen bonding) and also separate the solute molecules from each other (at the expense of solute-solute interactions)
- If the solute-solvent interactions are superior → good, soluble ($H_2C=O$ in H_2O)
- If solute-solvent interactions are comparable → good, soluble (CH_3OH in H_2O or CH_4 in CH_2Cl_2)
- If the solute-solvent interactions are way worse → bad, insoluble (CH_4 in H_2O)

1) For each of the following substances, mark whether they would be more soluble in H_2O or C_6H_{14}.

Substance	H_2O	C_6H_{14}
a. NH_3		
b. Br_2		
c. $C_{12}H_{26}$		
d. $CHCl_3$		
e. CH_3OCH_3		

2) For each pair, circle the one that would be more soluble in water?

a. CH_3NH_2 or CH_3Cl

b. $MgCl_2$ or C_6H_5Cl

c. $CH_3CH_2CH_2OH$ or CH_3CH_2OH

3) Which is more soluble in CCl_4?

a) C_6H_{10} or C_3H_7OH

b) $CH_3CH_2CH_2OH$ or CH_3OH

Energy Changes during Dissolving (11.1)

Enthalpy, Entropy, and Dissolving Solutes. The Solution Process.

A. 2 Factors Influence spontaneity of any process

1. Energy/**enthalpy**: Exothermic (good) or Endothermic (bad) or energy neutral

2. "**Entropy**": the **order/disorder** or a system
   - increasing disorder is natural
     - desk, office, brain, etc.
   - entropy/disorder increases → favorable, spontaneous event
   - entropy/disorder decreases → unfavorable, spontaneous event
   - work/energy is required to fight the natural tendency towards disorder

3. If both enthalpy and entropy are in agreement, it's easy to decide whether a process will be favorable or not. If they disagree, you need to know which factor dominates.

B. Dissolving always increases entropy

- When a solute, which is originally organized together, dissolves and disperses throughout a solvent, the result is less order and more entropy

Solubility is primarily entropy-driven

Entropy always favors solubility

Q: But, why will some things not dissolve in water?

A: Only if enthalpy is so bad (endothermic) that it overrules the entropy factor

4 Scenarios for dissolvings:

Enthalpy	ΔH	Entropy	Will Dissolving Occur?	Why?
1. Good	$\Delta H < 0$	Good	Yes	Entropy + Enthalphy
2. Indifferent	$\Delta H \sim 0$	Good	Yes	Entropy Driven
3. Slightly bad	$\Delta H > 0$, but only a little	Good	Yes	Entropy Driven
4. Very Bad	$\Delta H >> 0$	Good	No	Enthalpy Driven

Point: Solubility fails only if strongly endothermic

- If exothermic, energy neutral, or only weakly endothermic, solubility succeeds
  - Endothermic dissolving is how ice fast packs work

C. Solubility Enthalpy (10.4, 11.1)

Solute + solvent → Dissolved Solution

Intermolecular Forces		Intermolecular Forces
Solute-solute interactions Solvent-solvent interactions		Solute-solvent interactions

Old interactions are traded for new solute-solvent interactions

- If the new are comparable or better than the old → $\Delta H \leq 0$ (exothermic or neutral)
- If the new are weaker → $\Delta H > 0$ (endothermic)

Only if the new solute-solvent interactions are substantially weaker than original interactions will ΔH be sufficiently endothermic to veto solubility

D. Why Like Dissolves Like

- in **like/like**, new solute/solvent IMF are similar to original
  - hydrophilic + hydrophilic: strong in, strong out (dissolving in water)
  - hydrophobic + hydrophobic: weak in, weak out (dissolving in nonpolar solvent)
  - $\Delta H \approx O$ → soluble (**entropy gets it's way**)

- in **like/unlike case**, new solute/solvent IMF are much weaker than the original
  - hydrophilic (water) + hydrophobic (nonpolar): strong H-bonding in, weak dipole-induced dipole out
  - $\Delta H \gg O$ → insoluble (**lousy enthalphy vetos entropy**)

Solubility, Equilibrium, and Temperature (4.7)

2 Terms

1. "**unsaturated**" solution: the solvent could dissolve more solute.
2. "**saturated** solution": the solvent has dissolved as much solute as it can hold
   - Caveat: as much as it can hold if it's *at equilibrium* (supersaturation exception later)
   - A saturated solution will normally have some undissolved solid sitting at the bottom.

- Temperature: "saturation" is temperature dependent. **At a higher temperature, a solvent will be able to dissolve more solute**.
- Basis for recrystallization (you'll do in lab)
  - Dissolve all solid in just enough **hot** solvent
  - Then cool the homogeneous solution.
  - As it cools, solubility drops, the solvent become saturated, and pure solid forms
  - Yields are NEVER 100% because some of the solute remains soluble even when cold

Impact of Solutes on 3 Properties of Solutions. "Colligative" Properties (11.4)

- Phase change properties of a pure liquid differ when the liquid has solutes dissolved
- The **molar** quantity of **dissolved PARTICLES** is what matters
  - ***Ionic electrolytes may give variable moles of particles***
- "Molality" = moles solute **particles**/kg of solvent

1. **Vapor Pressure** is Reduced
   - If solution is only 95% solvent → vapor pressure will be only 95% of normal

2. **Boiling Point** is **Elevated**
   - Salt raises the boiling point of water
   - Increased molality of solute → reduced vapor pressure (solvent escape rate) → temperature needs to rise to reach the boiling point
     - (since vapor pressure must equal external pressure at boiling point…)

3. **Freezing Point/Melting Point** is **Depressed**
   - Why Grandma put salt on icy sidewalk ($CaCl_2$ usually): frozen ice melts
   - Why does it work?
     - As solvent is diluted, fewer are able to crystallize, so need to get colder to force it
   - Freezing range is not only lowered, but is also greatly broadened
     - Ice freezes as pure water, so the remaining water gets more and more concentrated in salt, resulting in further depression, etc..
   - Note: pressure also reduces melting point
     - At many temperatures, ice skates melt the ice and the thin film of water makes the skates go faster

Key: Impact on melting point, boiling point, and vapor pressure depends on **moles** of **particles**
- **One mole of an ionic substance produces more than one mole of particles**

Q1: For the following, how many moles of solute particles are produced when 1 mole of "formula" is dissolved? If one mole of each is placed into a liter of water, rank them in terms of how much they would depress the boiling point.

	C_3H_8O	$NaCl$	Na_2SO_4	$Mg_3(PO_4)_2$
Moles:				
Rank:				

Q2: Which would depress more, adding 1 mole of CH_3OH or 0.5 moles of $Al(NO_3)_3$?

Q3: If adding 1 mole of CH_3OH caused a 12º depression, how much depression would occur upon adding 0.5 moles of $Al(NO_3)_3$?

Q4: Which would cause more depression, adding 13 g of LiF (26 g/mol) or 90g of $C_6H_{12}O_6$ (180 g/mol)?

15.7 Osmosis: Selective Movement of Solvent Through a Semipermeable Membrane

- Membrane is selective: only some things (usually solvent) can pass through
    - Like a sieve or a filter
    - Usually based on size (water is small)
    - Cell walls
- Movement is motivated (usually) by a desire to equalize concentrations
- **<u>Normally solvent moves from the "dilute" to the "concentrated side"</u>**
    - This makes the dilute side more concentrated, and the concentrated side more dilute, until ideally they eventually equalize their concentrations

Volume of "concentrated" side grows (as more solvent comes over)
Volume of "dilute" side shrinks (as solvent leaves)

<u>Cells have modest salt concentration, and undergo osmosis through cell walls</u>

1. Placed in concentrated salt solution ("hypertonic"), cell passes water out, shrinks, dehydrates
2. Placed in pure water ("hypotonic"), cell passes water in, swells, and bursts
    - "lyse" a cell for biology purposes
    - impact on "hydrating" a dehydrated person: just water will burst the cells

<u>Other Osmosis Trivia</u>

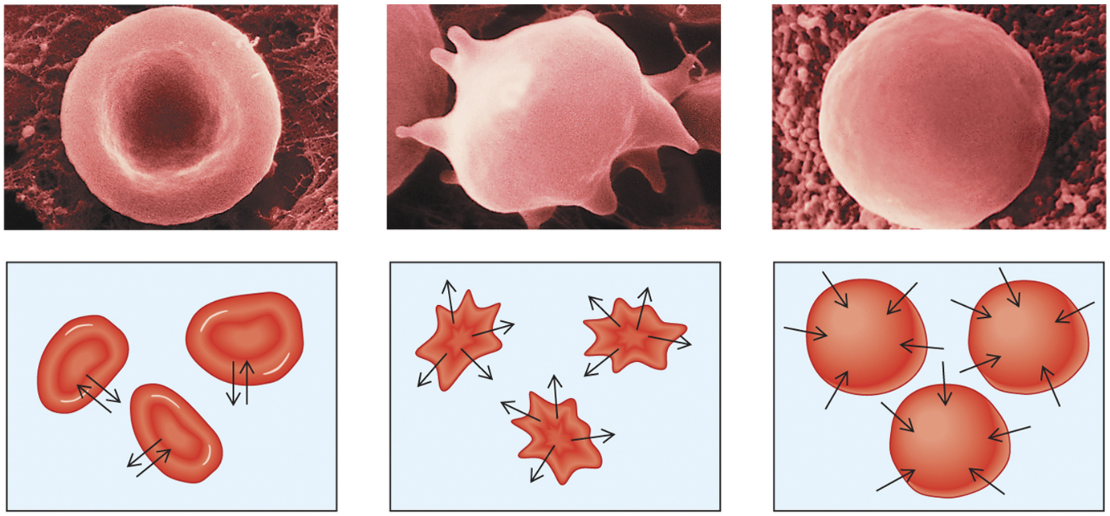
- Pickles: Cucumber shrinks in high salt
- Salt/sugar meats/fruits: bacteria get dehydrated and die → preserves "dried" meat
- H_2O transport in plants: absorb water from soil
- Diabetes: bad metabolism → high concentrations of solutes → need water, high thirst
- Edema: salty food → water retention → puffiness________________________

“Hyptonic” (case c): “Lysing” (popping open) a cell: putting a cell in solute-free water

- don’t do this when hydrating a dehydrated person!

“Hypertonic” (case b): shrinks when placed in a high-salt solution

“Isotonic” (case a): when water flow is equal both directions, no shrinkage or inflate/explosion



(a) Isotonic: total solute concentration in the solution matches that inside the cell

(b) Hypertonic: total solute concentration in the solution is greater than that inside the cell

(c) Hypotonic: total solute concentration in the solution is less than that inside the cell

Chemistry: The Science in Context **3/e Figure 11.22**
David M. Phillips/Visuals Unlimited

Ch 12. The Chemistry of Solids

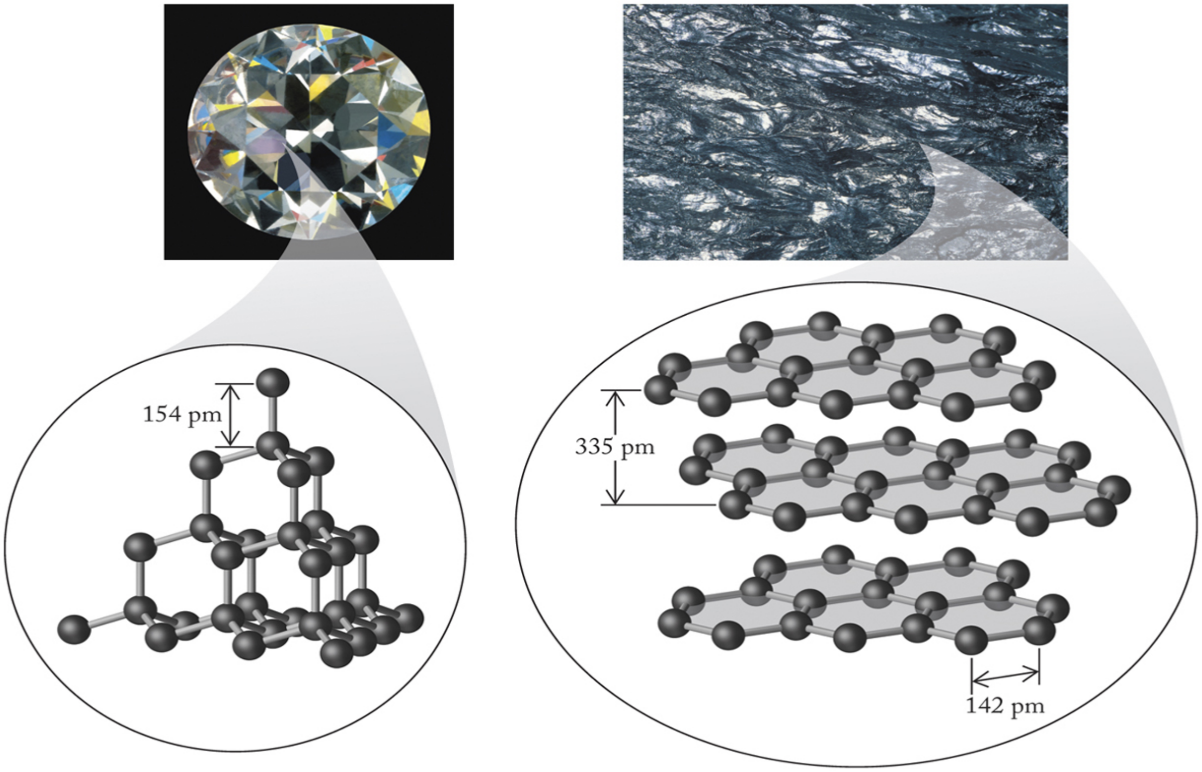
Metals (Section 12.1, 12.3, 12.4)

1. View as metal cations immersed in sea of electrons
    - The charge attraction is between the positive cations and the negative electrons
2. Network substance → solid (except mercury)
3. Unlike covalent bonds, where two electrons are precisely localized between two nuclei, metallic electrons are free-flowing
4. Resulting properties:
    a. mobile e's → **electrical** (and thermal) **conductivity**
    b. variable hardness, mp
    c. malleable, ductile: not brittle
        - can pound, bend, shape, draw into wires…..
        - an atom can be moved without really breaking a full bond, unlike an ionic crystal where it's really hard to move anything without breaking the bonding
    d. Very high bp: you can move an atom/ion within the sea of electrons, but to remove it altogether is very difficult
5. Shiny appearance
6. Alloys: Blends of metal with something else, enhanced properties

Overview: Types of Solids (Ch 12) Structures, Bonding, and Properties of Various Solids

Type	Examples	Structural Units	Forces Holding Units Together	Typical Properties
Ionic 12.6 10.1	NaCl, K_2SO_4, $CaCl_2$, $(NH_4)_3PO_4$	Positive and Negative ions (some polyatomic); no discrete molecules	Ionic bonding: attractions among charges on positive and negative ions	**Hard; brittle, high melting point**; **poor electrical conductivity as solid, good as liquid; often water-soluble**
Metallic 12.1 12.3 12.4	Iron, silver, copper, other metals and alloys	Metal atoms (or positive metal ions surrounded by an electron sea)	Metallic bonding; electrostatic attraction among metal ions and electrons	**Malleability**; ductility; **good electrical conductivity** in solid and liquid; good heat conductivity; wide range of hardness and melting point; **low water solubility**
Molecular	H_2, O_2, I_2, H_2O, CO_2, CH_4, CH_3OH, CH_3COOH	Molecules with covalent bonds	London forces, dipole-dipole forces, hydrogen bonds	**Low to moderate melting points and boiling points; soft; poor electrical conductivity in solid and liquid;** variable water solubility
Covalent Network Solids 12.5	Graphite, diamond, quartz, feldspars, mica	Atoms held in an infinite two-, or three-dimensional network	Covalent bonds; directional	Variable but **often very hard**; variable but **often very high mp**; **poor water solubility; low electrical conductivity**

1. Diamond and graphite



(a) Diamond (b) Graphite

***Chemistry: The Science in Context* 3/e Figure 12.27**
(left): Jon Stokes/Photo Researchers Inc.; (right): Ken Lucas/Visuals Unlimited

2. Classify the following as ionic, molecular, metallic, or network covalent solids.
   a. High mp, great hardness, low electrical conductivity

   b. Low mp, soft, low electrical conductivity

   c. High water solubility, low electrical conductivity alone, good conductivity in water

   d. High electrical conductivity

3. Which property is **not** characteristic of a metallic solid?
   a. Excellent thermal conductivity
   b. Excellent electrical conductivity
   c. Variable hardness
   d. Extreme brittleness
   e. Variable melting point

Chapter 15 Chemical Kinetics

- Some reaction are faster than others!

Four factors (in addition to the nature of the reacting chemicals themselves…)	
1. Concentrations of the reactants	3. “Catalysts”
2. Temperature	4. Reaction Mechanism

15.1 Intro: Cars, Trucks, air Quality: Smog Formation includes sunlight and mix of NO, NO_2, O_3

15.2 Reaction Rates

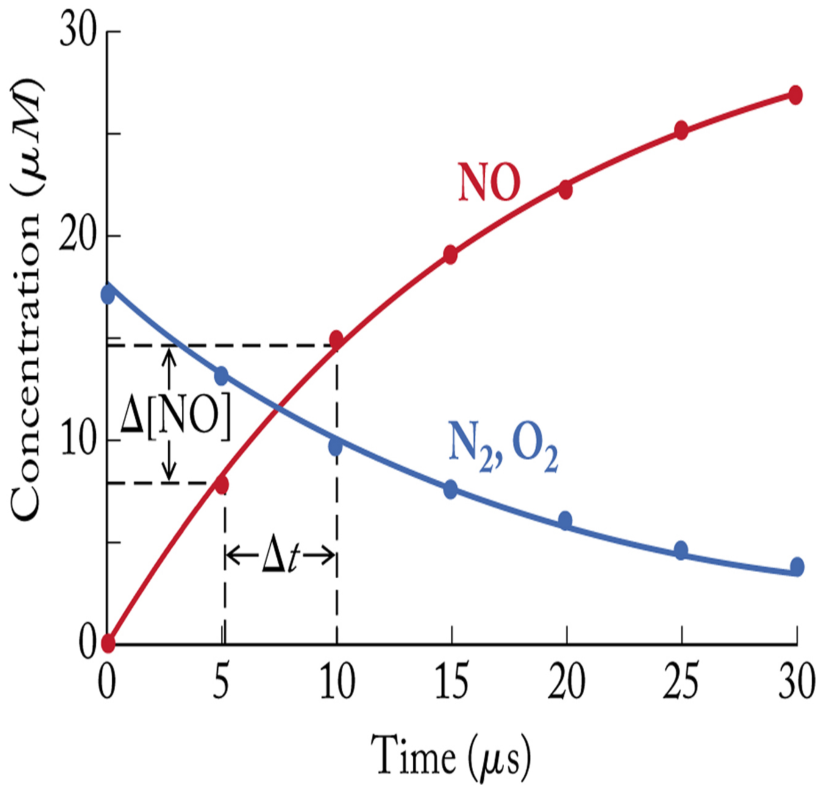
Rate: Change in something (x) per time interval

$$\Delta = \text{“change in”} \qquad \frac{\Delta x}{\Delta t}$$

> Any **average rate** can be determined between measurements at 2 points in time.
> - Unfortunately, chemical rates keep changing, getting slower and slower with time…

Car Example: What is the **average speed** of a car that between 1:00 (t_1) and 1:30 (t_2) travels from point O (x_1) to 30 miles away (x_2) ?

http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_15&folder=reaction_rateReaction Example: $1N_2 + 1O_2 \rightarrow 2NO$



Chemistry: The Science in Context 3/e Figure 15.3
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Notice:

1. The rate of change for red NO between 5 and 10 seconds:
2. Rate of change for Blue N_2:
3. Rate of change for NO is twice that for O2 (just like stoichiometry suggests)
4. Product concentrations decrease, products increase
5. The rate is constantly changing

Chemical Reaction Example: **A → B**

Chemical rates are defined by change in concentration (M, moles/L) per time interval.

$$\text{rate} = \frac{\Delta [B]}{\Delta t} = \frac{-\Delta [A]}{\Delta t} \qquad \text{Units} = \frac{M}{\text{sec}}$$

Notes

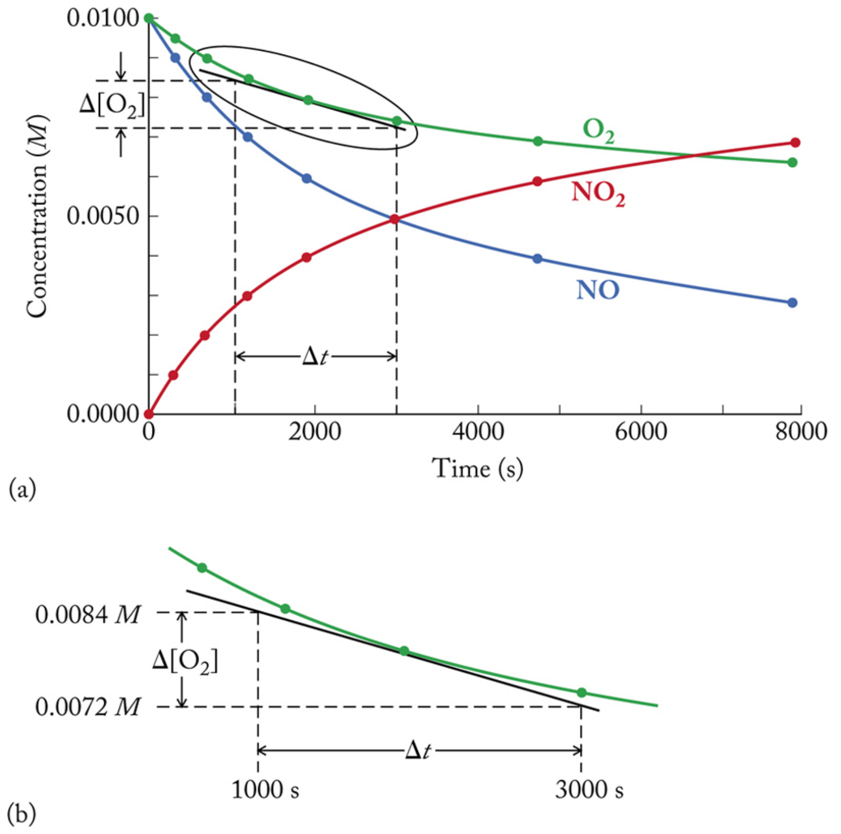
1. Rates can be written based on products or reactants, which are linked by stoichiometry.
   - [B] increases as [A] decreases

2. **Rate of changes decrease with time**
   - declines as starting reactant is depleted
   - especially for reactions involving two or more chemicals that need to collide
   - the lower the concentration, the less probable a collision

3. Rate can be found from:
   - **a. 2 time points (Average rate)**
   - b. Graphical analysis (Instantaneous Rate, not tested)
     - tangent slope, or calculus! $\text{rate}_t = \frac{d[B]}{dt}$
   - **c. Known rate of change for another chemical (factor in coefficients)**

4. Extra emphasis: The Relative Rate of Change for reactants/products has a **stoichiometric relationship**.

Instantaneous Rate Illustration.



Chemistry: The Science in Context 3/e Figure 15.4
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Reaction: $2NO + O_2 \rightarrow 2NO_2$

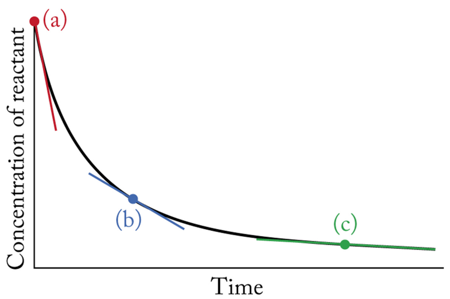
a. The "instantaneous rate" is constantly changing. Can be measured by taking the slope of a tangent line.

b. Notice that given 2:1 stoichiometry, the concentration of NO is dropping faster than O_2.

c. The concentration of NO_2 is increasing as fast as NO is decreasing.

d. No instantaeous tangents for our tests!

e. Typical decline in rate as time and concentration drop



Chemistry: The Science in Context 3/e Figure 15.6
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Calculating the rates of change for one chemical given the rate of change for some other chemical

- Seeing the relationship between stoichiometry, rate of change, and directions of change.

Reaction: **$2A + B \rightarrow 1C + 2D$**

1. For the above reaction, if the concentration of B is dropping by 0.5 M/min, what is the rate of change for the following?

[A]: [C]: [D]:

2. If [A] is dropping by 0.8 M/min, what is the rate of change for:

[B]: [C]: [D]:

3. Write the rate law, relative to each reactant or product, beginning with [B]. (Put +/- signs to reflect whether the concentration is dropping or increasing.):

4. Reaction: **$2A \rightarrow B$** If $\Delta[A]/\Delta t = -0.10$ M/s, what is $\Delta[B]/\Delta t$?

Two-Point "Average Rate" Calculation: Calculating the average rate of change based on measurements at two points in time

5. Reaction: **$A \rightarrow B$**
   a. Calculate the average rate (per second) from 0 → 10 sec if [A] goes from 0.100M → 0.080M?

   b. If [B] = 0 M at 0 sec, what is [B] after 5 sec, based on the average rate?

15.3 **Rate Laws and the Effect of Concentrations on Rates**.

- since reactants must collide to react, rates depend on concentrations

A. General Form for a "Rate Law"

Rate = $k[A]^x [B]^y [C]^z$…… A, B, C reactants (or catalyst)

http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_15&folder=reaction_order

1. Describes dependence of rate on concentration of each reactant
   - Concentrations in molarity M, mole/liter

Rate $\infty[A]^x$ Rate $\infty [B]^y$ Rate $\infty [C]^z$

If:	Effect of Doubling [A]	Effect of Tripling [A]	Effect of Multipying [A] by Ten-fold
$x = 1$			
$x = 2$			
$x = 0$			

2. k is "rate constant":
   - the rate changes with time and concentration, k doesn't
   - k is a fixed constant for a given reaction at a given temperature
   - if the temperature changes, then k changes too….

3. Each reaction has it's own rate law and rate constant (not like ideal gas law)
   - **both must be determined experimentally**

Problem 1: Given rate law, actual concentration, and actual rate, solve for k

Example: What is the rate constant for a reaction given the following info:

- rate law: rate = $k[A]^2$
- $[A] = 0.20$ M
- rate = 3.6×10^{-3} M/s $^{-1}$

Problem 2: Given rate law, actual concentration, and actual k, solve for actual rate

Example: What is the rate constant for a reaction given the following info:

- rate law: rate = $k[A]^2$
- $[A] = 0.60$ M
- $k = 0.090\ M^{-1}s^{-1}$

4. Rate laws can't be predicted from balanced equation.

5. Reactant "Order" Terminology
   a. For a given reactant

rate $\infty [A]^x$ $x = 0$ zero order
$= 1$ first order
$= 2$ second order

   b. Overall reaction order = sum of individual orders (x+y+z…..)

6. Units for k: Whatever it takes to balance units!
rate = M/s = k $M^{x+y+z....}$

First Order	M/s = k M	$k = 1/s = s^{-1}$
Second Order	$M/s = k\ M^2$	$k = M^{-1}s^{-1}$
Third Order	$M/s = k\ M^3$	$k = M^{-2}s^{-1}$

Examples of Rate Laws	Overall Reaction Order	Order of A	Effect on rate of Doubling [A]	Rate Constant Units
r = k[A]				
r = k[A][B]				
$r = k[A]^2$				
$r = k[A]^{½}[B]$				
$r = k[A]^2[B]$				
$r = k[A]^3[B]$				

B. Determination of Rate Laws

Need Either:
1. Known mechanism (see later, section 15.5) OR,
2. Systematic variation of each reactant, with experimental measurement of rate (lab experiment)
   - each reactant, one at a time!
   - Only one reactant should vary at a time

General determination of reactant "order", when numbers aren't simple:
- Set the ratio of 2 rates = the ratio of the 2 concentrations to the "x" power.
- "x" gives you the actual "order" for the reactant

$$\text{Ratio of the two actual rates} \rightarrow \frac{r_2}{r_1} = \left[\frac{[A]_2}{[A]_1}\right]^x \leftarrow \text{Ratio of the two concentrations to the "x" power}$$

Routinely the concentration are varied by nice ratios: 2:1, or 3:1, or 10:1, or 1:2, or something …..

Example Problem: Figure out the order of A if the concentration of [A] is Doubled, with the effect on rate shown:

Rate	Order of [A]	Means
doubles		
x 4		
x 8		
unchanged (1)		
x 1.4		

Problems: Determining Rate Laws from Actual Rate Measurements Using Different Concentrations

1. $A + B \rightarrow C + D$

	[A]	[B]	rate
1)	0.20	0.20	0.0078
2)	0.40	0.20	0.0156
3)	0.20	0.40	0.0078

Order of A:
Order of B:
Rate law:
k (number + units):
What is rate when [A]= 0.80, [B]= 0.80

2. $A + B \rightarrow C + D$

[A]	[B]	rate
0.20	0.20	0.15
0.40	0.20	0.30
0.20	0.40	0.30
0.40	0.40	0.60
0.80	0.40	
0.80	0.80	

Rate law:

Number for k:

3. $A + B + C \rightarrow D + 2E$

[A]	[B]	[C]	rate
0.20	0.20	0.20	0.15
0.40	0.20	0.20	0.60
0.20	0.40	0.20	0.30
0.20	0.20	0.40	0.15

4. $A + B \rightarrow C$

[A]	[B]	Rate
0.1	0.1	1
0.2	0.1	4
0.1	0.2	1

5. $A + B \rightarrow C$

[A]	[B]	Rate
.1	.1	3
.2	.1	6
.1	.2	24

6. The effect of Solvent on Concentrations and Rates. Shown below are three scenarios using the same amount of reactants but differing volumes of solvent. Calculate the relative rates, assuming r= k[A][B]

Moles A	[A]	Moles B	[B]	Liters of Solvent	Relative Rate
0.5		0.5		1	1
0.5		0.5		2	
0.5		0.5		0.5	

7. Which is true for: $A + 2B \rightarrow C + D$ $r = k[A]^1[B]^1$?
   a) doubling [A] will not affect rate
   b) doubling both [A] and [B] will make rate 4 times faster
   c) doubling both [A] and [B] will multiply rate by 8
   d) doubling [B] will double rate

Some Specific Calculations Available for First Order Reactions (15.3, p 716-720)

rate = k[A] = -Δ[A]/Δt use calculus, integrate: $\boxed{\ln [A]_t = -kt + \ln[A]_o}$

- Equation in the form of a linear plot: y = mx + b form.
  - If actual concentration $[A]_t$ is measured and plotted (y axis) as a function of time (x axis), the slope of the line equals –k.
  - Note: only in the case of a 1st order reaction will this plot as a straight line.

Versions of the equation that are useful for 2-point analyses.

$\ln\left(\frac{[A]_o}{[A]_t}\right) = kt$	Variations:	$\frac{[A]_o}{[A]_t} = (kt)^e$	$[A]_o = [A]_t(kt)^e$	$[A]_t = \frac{[A]_o}{(kt)^e}$	$t = \frac{1}{k}\ln\left(\frac{[A]_o}{[A]_t}\right)$

Applications: Solve for
1. $[A]_t$ at any time, given k and t
2. the time "t" for an original $[A]_o$ to decline to $[A]_t$
3. k

Handling “In"

1. Enter $[A]_o/[A]_t$ ratio, then hit LN button
2. “antiln” Find “x”, given: $\ln\frac{100}{x} = 1.83$

    a. Solution: enter 1.83, hit e^x
    b. Set the resulting number = 100/x
        - In the general case, whatever follows “ln”
    c. Solve from there.

Practice using ln:

a. ln 1.8 =

b. ln (100/18) =

c. ln (18/7.2) =

d. ln x =1.43

e. ln (14/x) =1.86

f. ln (100/x) =1.13

Assume 1st Order Rate Laws for the Following:

$$\boxed{\ln\left(\frac{[A]_o}{[A]_t}\right) = kt}$$

Variations: $\frac{[A]_o}{[A]_t} = (kt)^e$

1. **FIND k**. What is rate constant if [A] goes from 1.0 M → 0.32 M in 46 sec?

2. **FIND t**. If k = 113 years^{-1}, how long will it take for 10% of A to react?

Hint: $[A]_o =$
$[A]_t =$

3. **FIND $[A]_t$** If k = 0.061 days^{-1}, what % of a spilled poison remains after 12 days?

Hint: set $[A]_o =$
$[A]_t =$

C. Half-Life $t_{1/2}$: Time for Concentration to Drop by Half (for 1st order reaction)

at $t_{1/2} \Rightarrow [A]_t = {}^{1}/_{2}\,[A]_o$

$$kt_{\frac{1}{2}} = \ln\frac{[A]_t}{[A]_0} = \ln 2 = 0.693$$

$$\boxed{\mathbf{kt_{1/2} = 0.693}}$$

Assume 1st Order Rate Laws for the following Problems

1. Concept Q (no calculator needed): The half life for A is 30 sec. If you start with 128 A, how many will be left after

t (sec)	Amount		t (sec)	Amount
0	128		120	
30			150	
60			180	
90			210	

2. If k is 0.36 days^{-1}, what is $t_{1/2}$ and how long will it take for 75% to decay?

3. ^{14}C decomposes with $t_{1/2}$ = 5730 years. What is k for decomposition?

Higher Order Reactions (p720)

- -time/concentration/half-life relationships more complex
- -not responsible

15.4 Reactions, Energetics, and Temperature Q: Why are rates influenced by concentration, temp?

A. Nanoscale Reactions

- While an overall reaction mechanism may involve many steps (15.5), elementary steps are either unimolecular or bimolecular

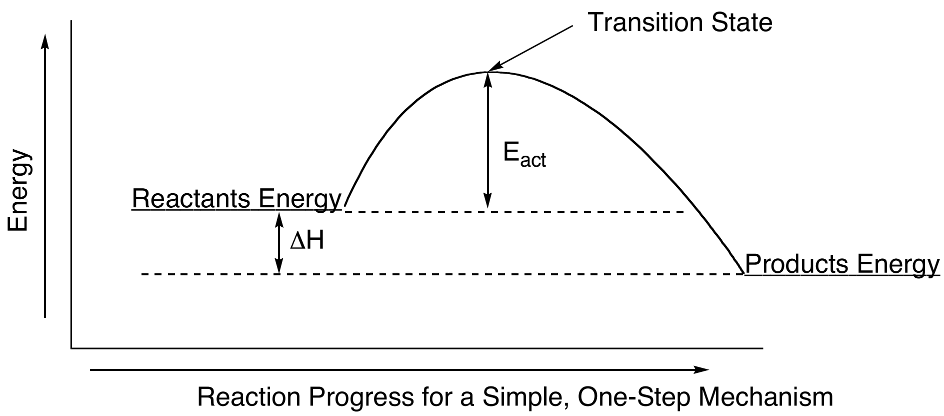
1. Unimolecular: A single molecule either rearranges or decomposes
   - Examples:
     a. A → B
     b. A → B + C
   - Energy is required

2. Bimolecular: **2 molecules collide**
   a. Orientation, angle must be suitable
      - Most collisions do not succeed
   b. Reactants must collide with enough energy
      - Called “**activation energy**, E_a”

http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_15&folder=collision_theory

Higher concentration → mole collisions → faster rate
Higher temperature → higher energy → more of the collisions that do occur succeed

B. Energy Diagrams, Activation Energy, Transition State



- **Transition State**: the energy maximum on the road to products (worst spot energetically)
- **Activation Energy E_a or E_{act}**: the energy gap between reactants and Transition-state
- **ΔH**: The energy gap between reactants and products

1. **the higher the activation barrier, the slower the reaction**
2. the transition-state is higher in energy than either the reactants or the products, but it must be crossed
3. even exothermic reactions have activation barrier
   - because the cost of breaking old bonds precedes the payoff of making new and improved bonds
4. the higher the **temperature**, the higher the odds that the reactants have enough energy to clear the barrier
   - at a higher temperature, a higher fraction of the molecules are able to clear the barrier
   - note: at higher temperature, the rate law for the reaction will stay basically the same, but the k value will be higher (p5)

http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_11&folder=molecular_motion

5. E_{act} is unique for each reaction
6. E_{act} has no correlation with ΔH
7. **Catalysts** change a reaction mechanism in such a way that the transition state is lowered

C. Arrhenius Equation: Not for Test, but **<u>May be Helpful for Lab</u>**

$k = Ae^{-Ea/RT}$

R = constant = 0.00831

A = constant unique to each reaction

Qualitative:
1. Large E_{act} → smaller k (and slower rate)
2. higher temperature → larger k (and faster rate)

<u>Math: take the natural log of both sides, end up with some practical variations:</u>

a. Graphical Format

$$\ln k = \frac{-E_{act}}{0.00831}\left(\frac{1}{T}\right) + \ln A$$

- y = mx + b form
- Graph ln k vs 1/T
  - slope solves for E_{act} and intercept solves for A constant

b. Two-Point Format

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_{act}}{0.00831}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

E_{act} in kJ/mol

T in Kelvin

<u>Applications of Two-Point Solution:</u>

1. Given measured k's at 2 temps, can find E_{act}
2. Given E_{act} and the k at one temp, can find the k at any other temp
3. Given E_{act} and the k at one temp, can find whatever temperature is required to produce a desired rate constant (for example, if I know a reaction is way too slow, and I want to know what it would take to make it ten times faster…)

Reaction Mechanisms, Rate Laws, and the Rate-Determining Step (15.5)

A. Miscellaneous and Examples

http://media.wwnorton.com/college/chemistry/chemtours/interface.asp?chapter=chapter_15&folder=mechanisms

1. Elementary steps are **unimolecular** or **bimolecular** (terminology)

2. Most reactions are multistep (especially catalyzed reactions)

3. "Intermediates": shortlived, forms in one step, destroyed in another
   - observed on both product and reactant sides, cancel out
   - since concentrations normally too low to measure → they do not appear in the final rate law

4. **The final rate law should only include reactants (in the balanced reaction) and perhaps catalyst. NOT INTERMEDIATES.**

5. Rate laws of elementary steps depend directly on reactants! Examples:
   - Note: this is in complete contrast to balanced reactions

$A \rightarrow B$	$r = k[A]$
$A + A \rightarrow B + C$	$r = k[A]^2$
$A + B \rightarrow C + D$	$r = k[A][B]$

6. **Given a mechanism, you can deduce the rate law**
   - **Any reactant that appears in or before the rate determining step is in the rate law**

7. Elementary steps must sum to give the overall balanced equation

B. Deducing Rate Laws from Multistep Mechanisms: Determined/Influenced by the **Slow**est Step = "**The Rate Determining Step**"

1. The slowest step is the bottleneck
2. Any step after the slow step has no impact on the overall rate of conversion
   - **Any reactant after the slow step does not appear in the rate law**
3. **Any reactant in or before the slow step does appear in rate law**
   - **If it appears twice in or before the slow step, it will be 2nd order, etc..**
4. No intermediates should appear in any overall rate law

Some practical skills

Given a mechanism → write the rate law

Given a rate law → distinguish plausible from implausible mechanisms

For the following, classify the molecularity of the elementary steps (mono- or bimolecular), identify intermediates (scratch them out), and then determine the overall rate laws, given identification of which step is rate-determining.

			Molecularity	Intermediates	Overall Rate Law
1.		$A \rightarrow B$			
2.		$CH_3Br + {}^{\ominus}OH \rightarrow CH_3OH + Br^{\ominus}$			
3.		$2A \rightarrow B + C$ slow			
		$B + D \rightarrow E$ fast			
	Sum:				
4.		$A + B \rightleftharpoons C$ fast			
		$C + D \rightarrow E + F$ slow			
	Sum				
5.		$A + A \rightarrow B$ fast			
		$B + C \rightarrow D + E$ slow			
	Sum				
6.		$A \rightarrow B + C$ slow			
		$B + C + D \rightarrow E + F$ fast			
	Sum				

Distinguishing among possible mechanisms, given a rate law:

1. Which mechanism is plausible for the reaction shown, given the rate law:

$A + 2B \rightarrow C$ rate = k[A]

a. $A + B \rightarrow D$ (slow)
$D + B \rightarrow C$ (fast)

b. $B + B \rightarrow E$ (slow)
$A + E \rightarrow C$ (fast)

c. $A \rightarrow F$ (slow)
$F + B \rightarrow G$ (fast)
$G + B \rightarrow C$ (fast)

d. $B + B \rightarrow H$ (fast)
$A + H \rightarrow C$ (slow)

Identifying a Rate Law, given the Mechanism:

2. Given the mechanism shown, what is a reasonable rate law?

$2A + 2B \rightarrow C$

Mechanism: $A + B \rightarrow D$ (slow)
$D + B \rightarrow E$ (fast)
$A + E \rightarrow C$ (fast)

a. $r = k[A][B]$

b. $r = k[A][E]$

c. $r = k[A]^2[B]^2$

d. $r = k[A]^2[B]^2[D][E]$

Derivation of Rate Law when 1st Step Is Not the Slow Step, and which Proceed Via a Reactive Intermediate (not for test)

Example Mechanism:

$$\begin{array}{lll} \text{Step 1} & A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C & \text{fast, but reversible} \\ \text{Step 2} & C + D \xrightarrow{k_2} E + F & \text{slow} \\ \hline & A + B + D \longrightarrow E + F & \end{array}$$

Overall rate law:

- Intermediates (C in this example) don't build up. They reach a steady state (usually a very low concentration), in which the rate of formation equals the rate of destruction

  Rate of formation = Rate of destruction

  $k_1[A][B] = k_{-1}[C] + k_2[C]$
- Since step 2 is slow, it probably makes a small contribution to the rate of destruction and can be dropped.

  Thus, the equality can be simplified to: $k_1[A][B] = k_{-1}[C]$
- Rearrange: $[C] = \frac{k_1}{k_{-1}}[A][B]$
- The overall rate is given by the slow step: $r = k_2[C][D]$
- Substitution in for [C] → $r = k_2(\frac{k_1}{k_{-1}}[A][B])[D]$
- Since $k_2\frac{k_1}{.}$ is itself a constant, the overall rate can be rewritten as: $r = k' [A][B][D]$

15.6 Catalysts

General Considerations

1. Increase Rates
2. Tiny quantities of catalysts suffice (because they are continuously recycled)
3. Not used up, the final quantity of catalyst equals the initial quantity
    - They are recycled ("catalytic converter")

Mechanistic and Energetics Considerations

4. A catalyst speeds up a reaction by providing a **new mechanism** with a lower transition-state
    - "Tunnel" through energy barrier
5. The new mechanism is always more complex
6. While E_{act} is reduced, the overall ΔH is unchanged. (metabolism…)
7. Catalysts dramatically reduce temperature/heat requirements for reactions (metabolism…)
    - Industrial Attraction: cost effective, small amounts, lower temperatures, easier engineering, reduces waste disposal, etc..
8. A catalyst reacts early in a mechanism, but is then regenerated later in a mechanism

	At Beginning	In Between	At End
"Intermediates"	Not present	They form but then react away	Not present
"Catalysts"	Present	They react away, but then reform again	Present

Recognition:

9. A catalyst does not appear in balanced equation
10. A catalyst does appear in rate law

Enzymes (Section 20.2)

11. Enzymes are Big Proteins that Catalyze Biochemical Reactions (Ch 20)
    - >100,000 enzymes
    - can increase rates by millions or billions!
    - Remarkable specificity
    - Most diseases involve enzyme malfunction
    - Medicinal research addresses these problems, why enzymes don't turn on or off correctly

Chapter 15 Kinetics Math Summary

- Handling "ln y = x" on calculator:
  1. When you know "y" but want to solve for "x", enter "y" and hit your "ln" button. (On some calculators, you will instead hit "ln" button first, then enter "y")
  2. When you know "x" but want to solve for "y", enter "x", then hit your e^x button

- Determining the "Order" of a Particular Reactant in a Rate Law

  Use two different concentrations ($[A]_1$ and $[A]_2$), and then measure the rates (r_1 and r_2). Set the rate ratio (r_2/r_1) equal to the concentration ratio ($[A]_2/[A]_1$) to the "x" power. "x" is the "Order" for reactant A. Usually "x" will be a small whole number [0, 1, 2, occasionally 3].

  $$\mathbf{r_2/r_1 = ([A]_2/[A]_1)^x}$$

  - In general, for $y = m^x$, what does the "x" mean? It's the number of times you would have to multiply "m" times "m" to equal "y". Examples: $2 = 2^x$ then x = 1; $4 = 2^x$ then x = 2, since 2 x 2 = 4. For $8 = 2^x$ then x = 3, since 2 x 2 x 2 = 8. And for $16 = 2^x$ then x = 4, since 2 x 2 x 2 x 2= 16.
  - In general for $y = m^x$ then $x = (\ln y)/(\ln m)$.

- Rate Constants, Quantities and Half-Lives for First-Order Reactions

  $$\mathbf{kt_{1/2} = .693}$$

  - Given k, can find $t_{1/2}$
  - Given $t_{1/2}$ can find k.

  $$kt = \ln([A]_o/[A]_t)$$

  - $[A]_o$ is the amount of material at time zero
  - $[A]_t$ is the amount of stuff at time "t"
  - when dealing with problems involving "percents", the original percent is 100%

- The Arrhenius Equation (won't be test-responsible)

  $$k = Ae^{(-E_a/RT)}$$

  - R = constant = 0.00831
  - T in Kelvin
  - E_a is the activation energy in kJ/mol
  - A is a constant for each reaction

- Solving for E_a (activation energy) given known rate constants at two temperatures (won't be test responsible, but used for laboratory)

  $$E_a = [0.00831\ln(k_2/k_1)] / (1/T_1 - 1/T_2) \qquad \text{Answer in kJ/mol}$$