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

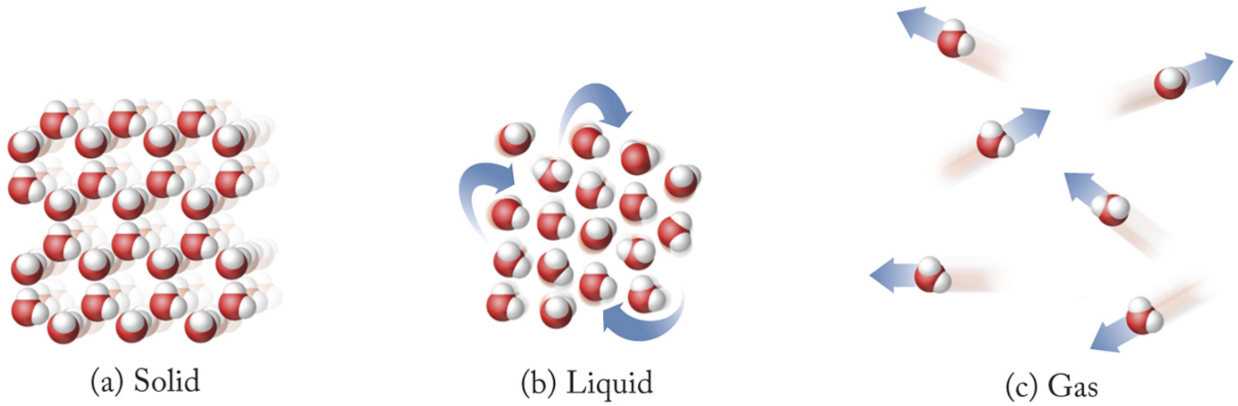
1. Why is something so small (18g/mol) a liquid?
   - Small molecules are almost always gases:
     - N_2 (28 g/mol), CO (28 g/mol), C_2H_6 (30 g/mol), O_2 (32 g/mol), H_2S (34 g/mol), CO_2 (44 g/mol), C_4H_{10} (58 g/mol), etc.
   - But tiny water (18 g/mol) is liquid at normal temp and pressure!
2. 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
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

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

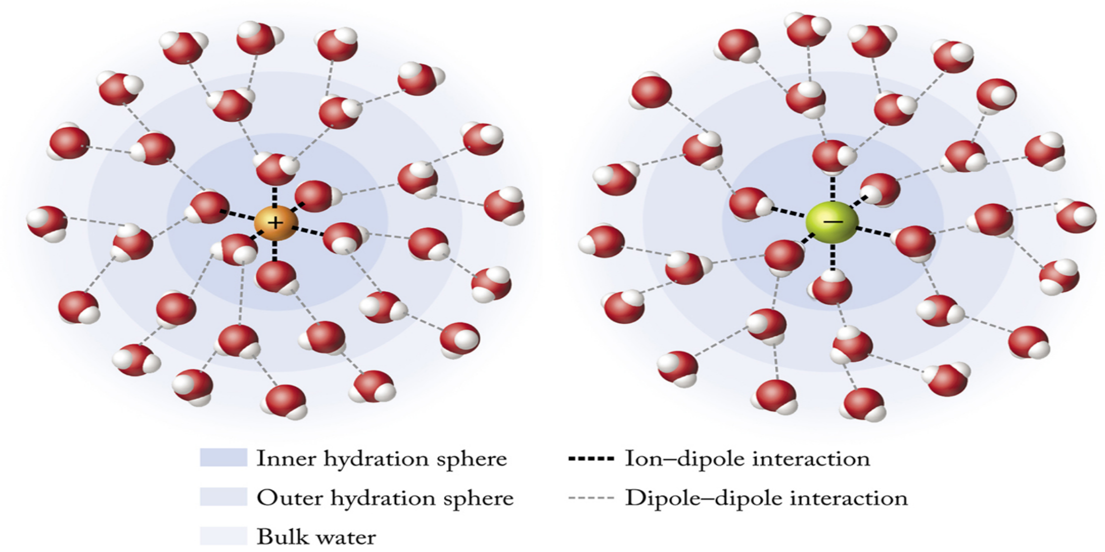
Strategy: Charges First, then Ion Size to Break Ties.

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

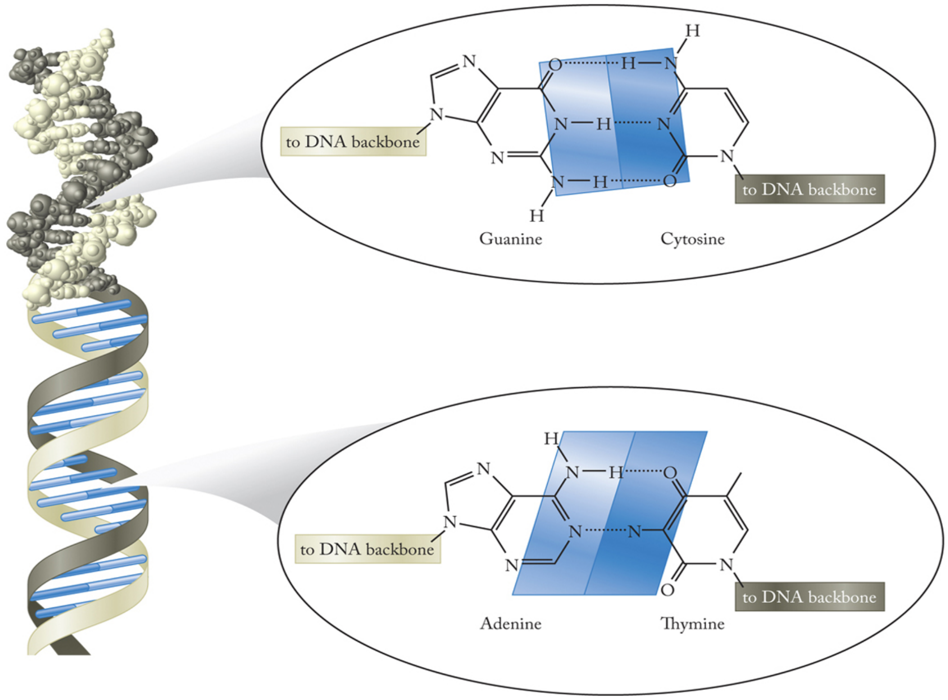
e. H-bonding (→ "hydrophilic") a dominating factor in biological organization

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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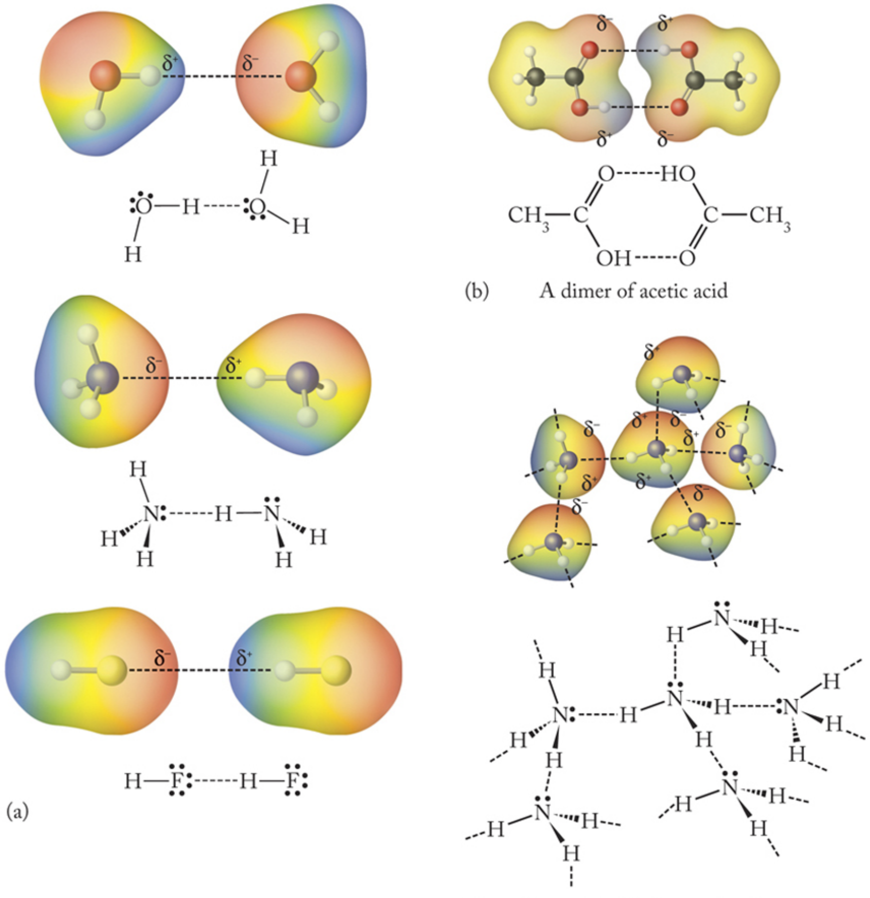
More H-Bonding Examples



(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

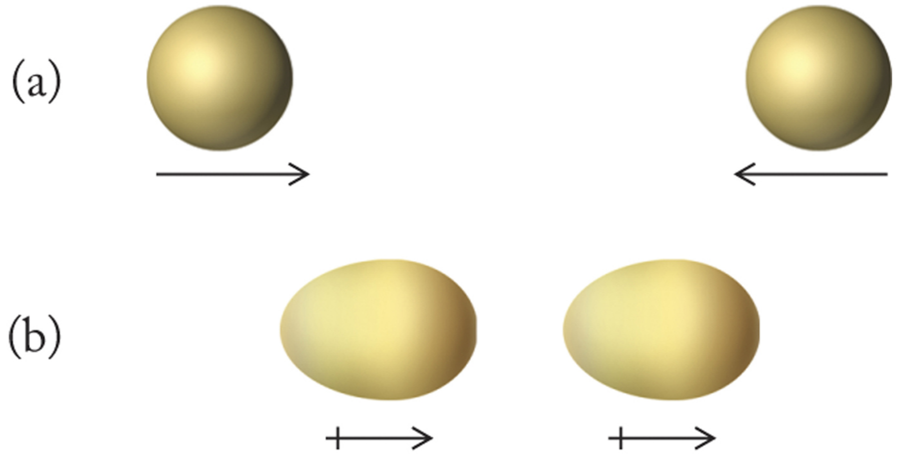
Q1: Rank the boiling points for the following, 1 being highest:

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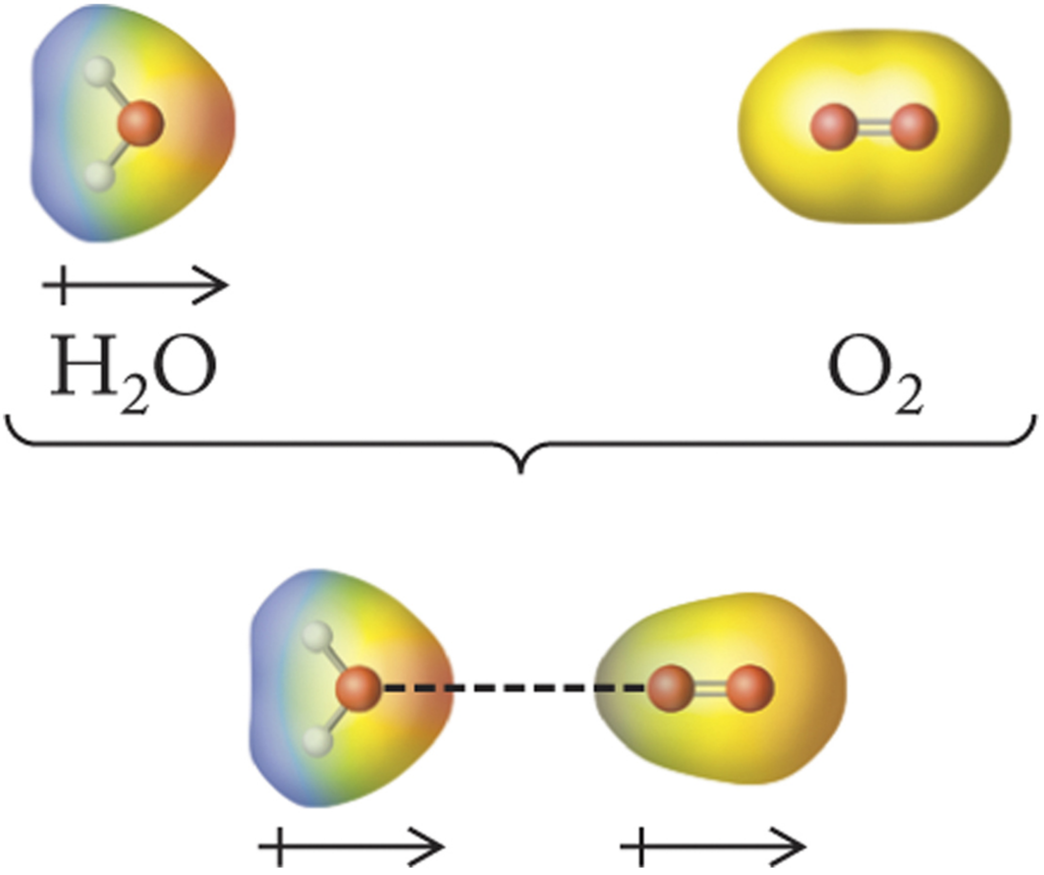
London Dispersion: Polar water induces temporary dipole in initially nonpolar oxygen



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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)

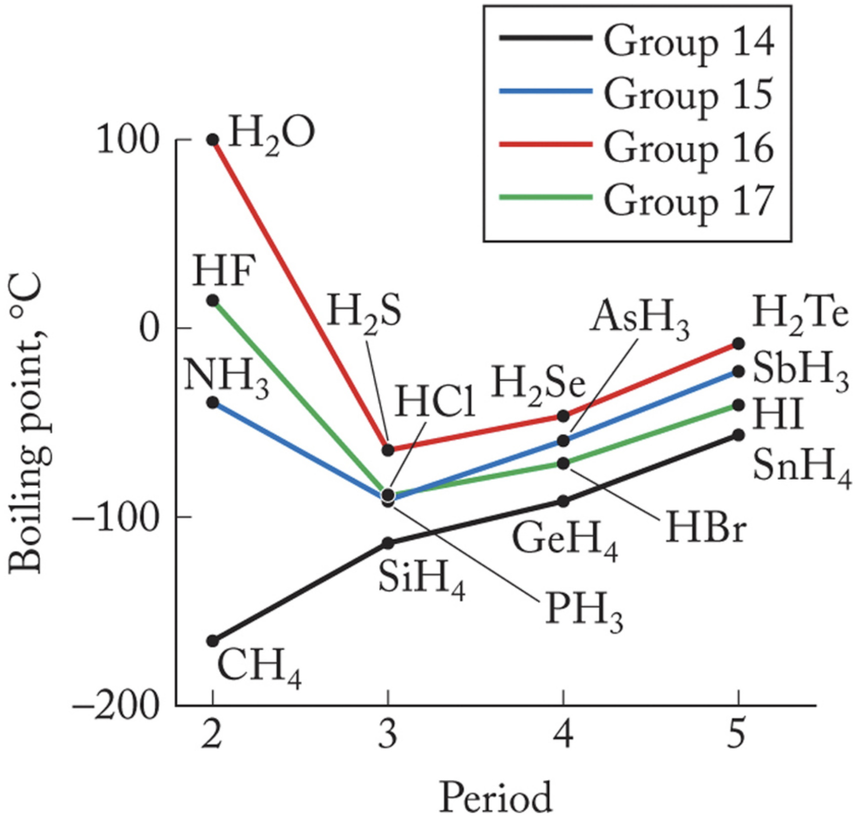
⇨ molecular substances have much lower mp, bp, etc.

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

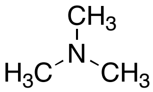
g. HCl

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

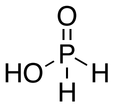
4) Which has H-bonding?

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

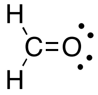
Recognizing Molecular Polarity (9.3)

- 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)

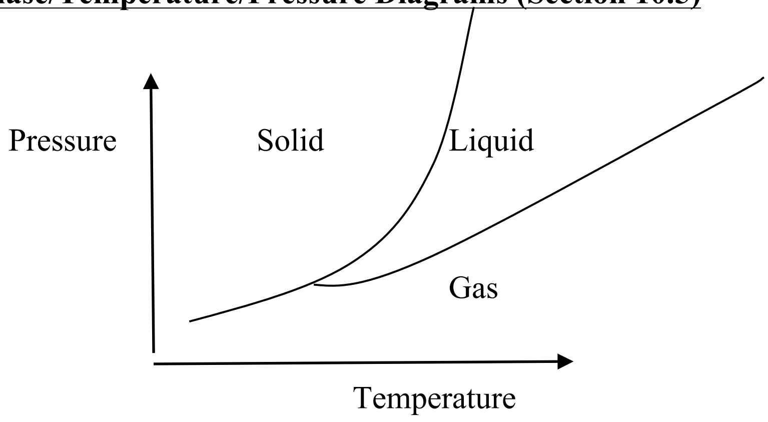
$CH_3CH_2CH_2CH_2CH_2OH$ $CH_3CH_2CH_2OH$ $CH_3CH_2CH_2CH_3$ $CH_3CH_2OCH_3$

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.

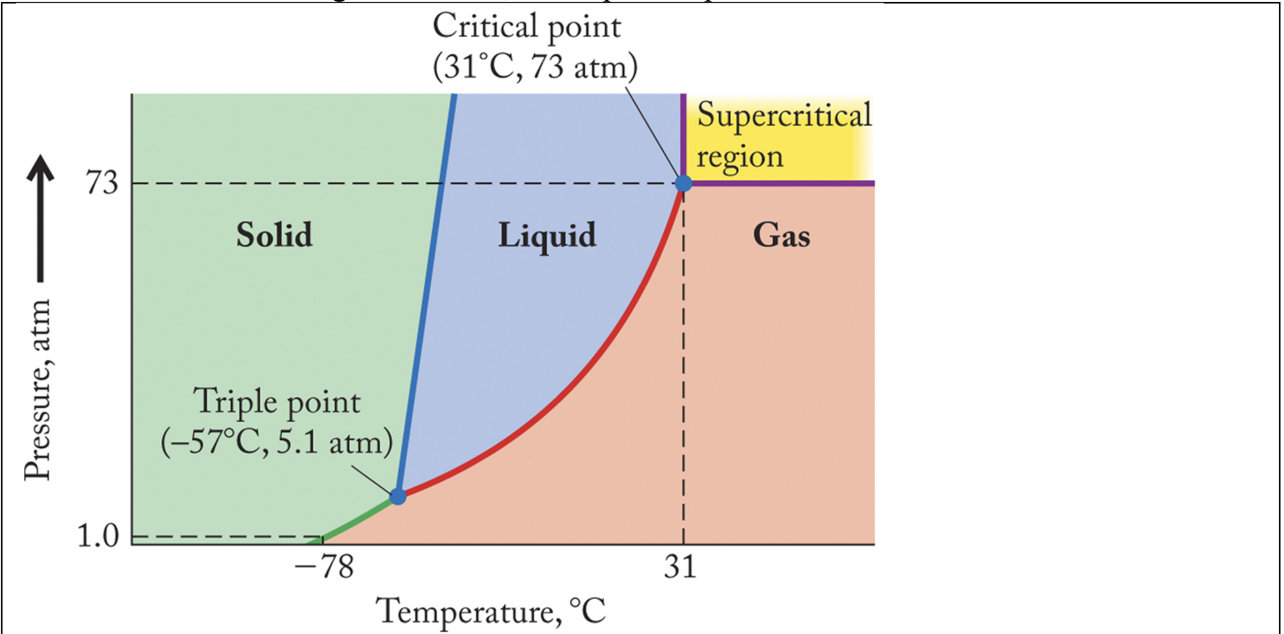
Critical point: (not test, but may need for online homework). Liquid/gas distinction vanishes.

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

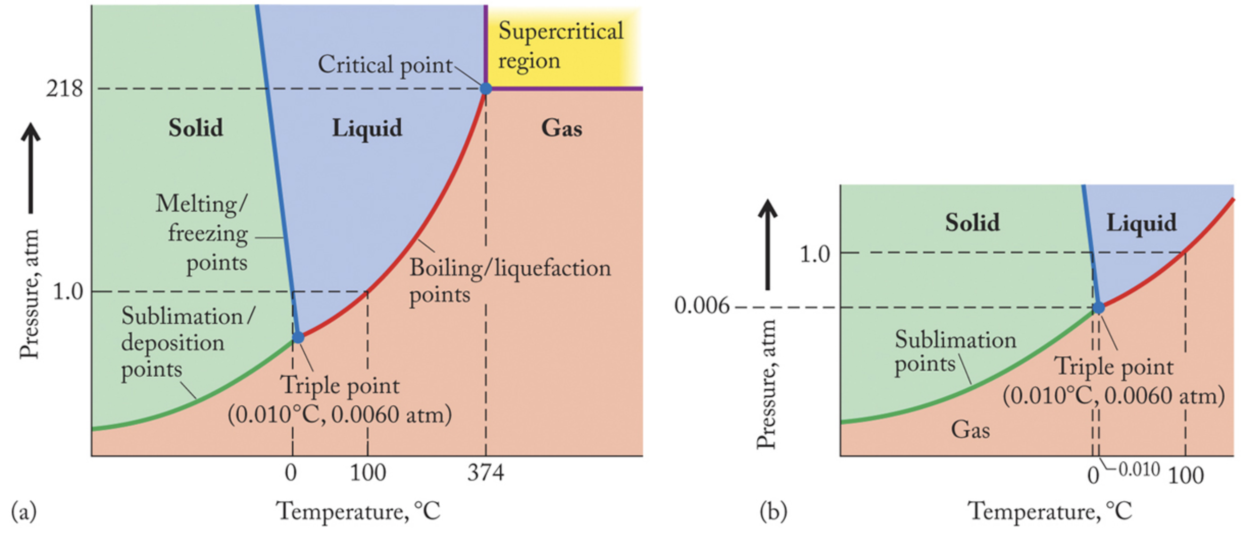
- -notice the angle for the line between solid and liquid: angles to the right (positive slope)
- Due to solid being more dense, has impact on pressure effect.



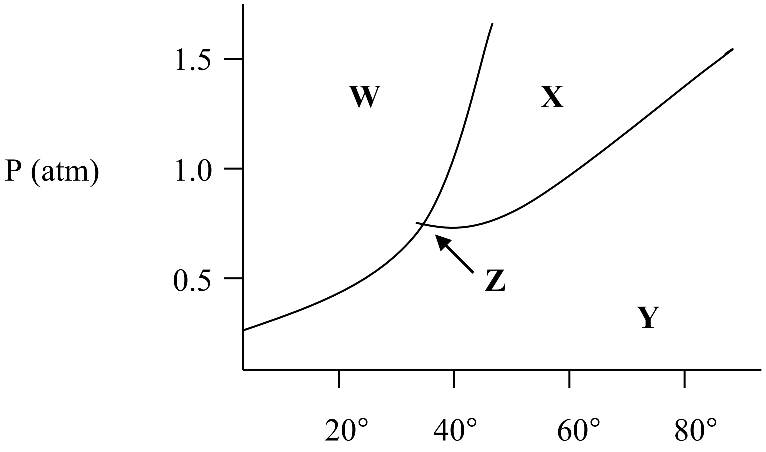
Chemistry: The Science in Context 3/e Figure 10.24

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?

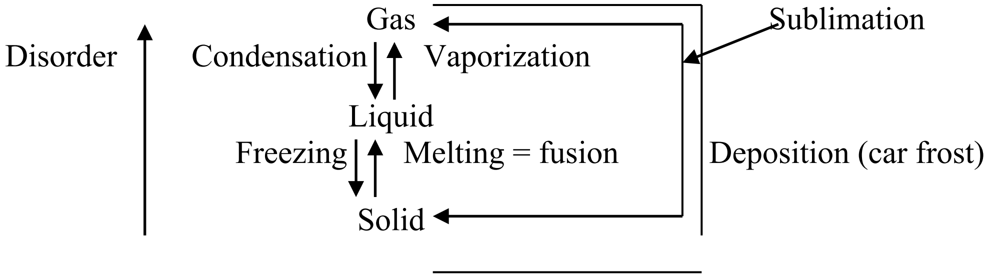
3. When solid at 0.5 atm is warmed, does it: a) melt or b) sublime

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 120° we just evaporate some lake water

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

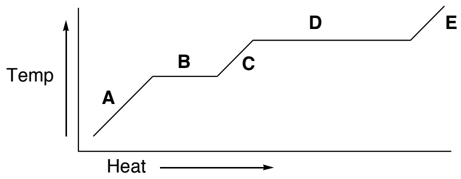
2. Quantitative Energy Calculations
   - Values are given either on a per-mole or a per-gram basis
   - When moles are used, you'll need to use mass-mole interconversions
   - Normally $\Delta H_{vap} > \Delta H_{fus}$

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 1°
   - 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.

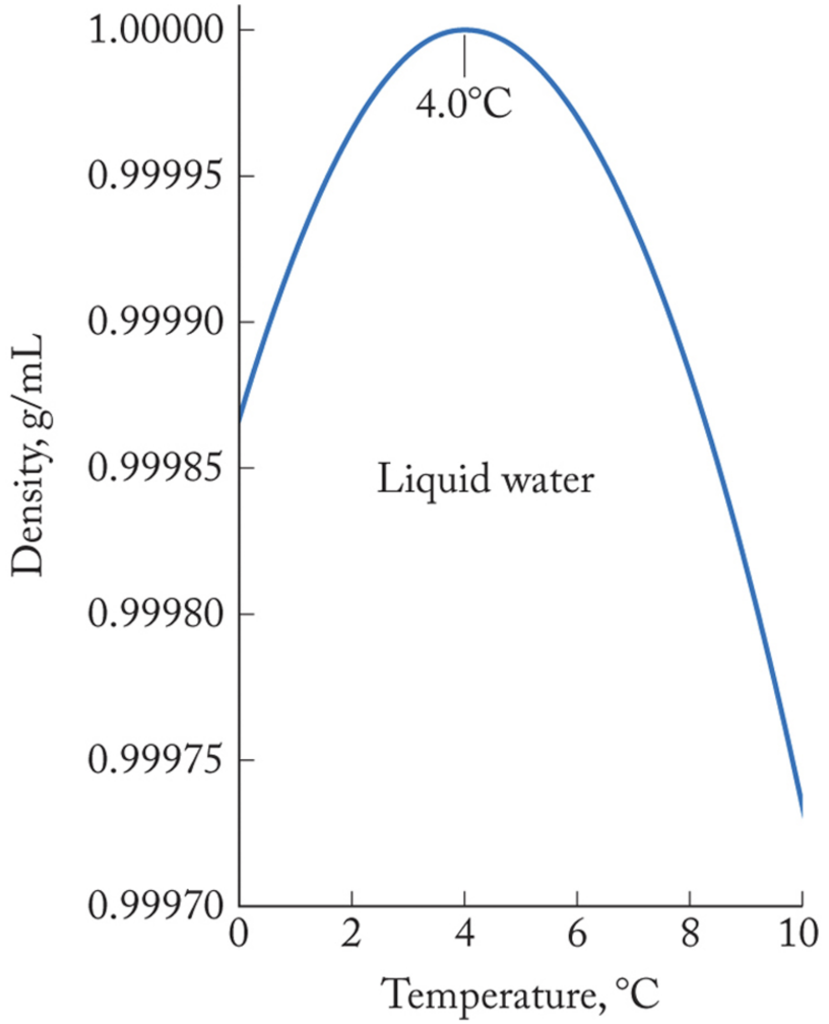
4. Water as Earth and Body Air Conditioner: **Amazingly High Heat Capacity**.
   a. Water has an extraordinarily high heat capacity for a molecular substance or for a liquid
      - A lot of energy is involved to change it's temperature by much
      - This helps to prevent wide temperature variations 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
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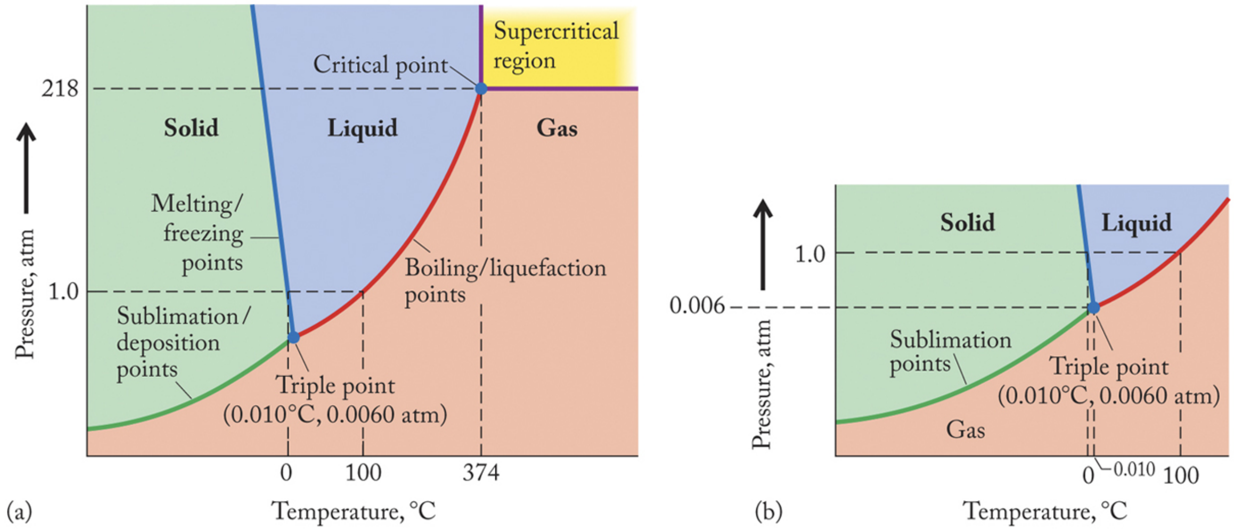
Remember: The weird and wonderful "negative slope" phase diagram for water reflects the unique solid-versus liquid density situation. Critical to water life.



Chemistry: The Science in Context **3/e Figure 10.22**

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

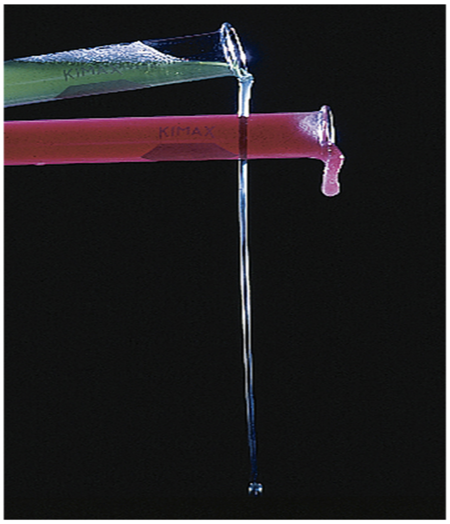
Liquid State (Sections 10.4,5,6, 11.2)

- 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)

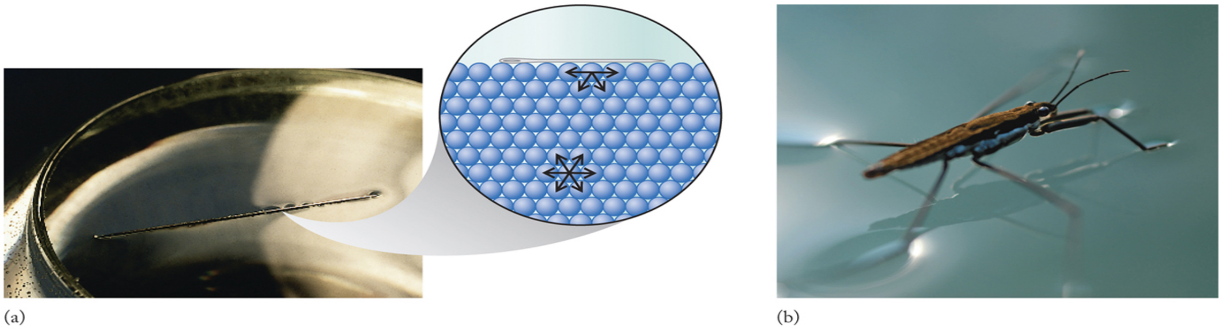
   - Motor Oil issues
   - Water is unusually viscous for a liquid of it's size.



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

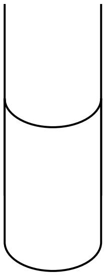
2. Surface Tension (10.6)
   - Water "beads up" on smooth surface, or overfilled glass
   - IMF pull the molecules together, cause them to ball up, pack together as if it had a skin
     - This is why water bugs can "walk" on water
     - To "cut through" the surface would require breaking hydrogen-bonds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

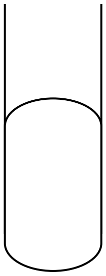


***Chemistry: The Science in Context* 3/e Figure 10.25**
(left): Jeff Daly/Visuals Unlimited; (right): Martin Shields/Photo Researchers Inc.

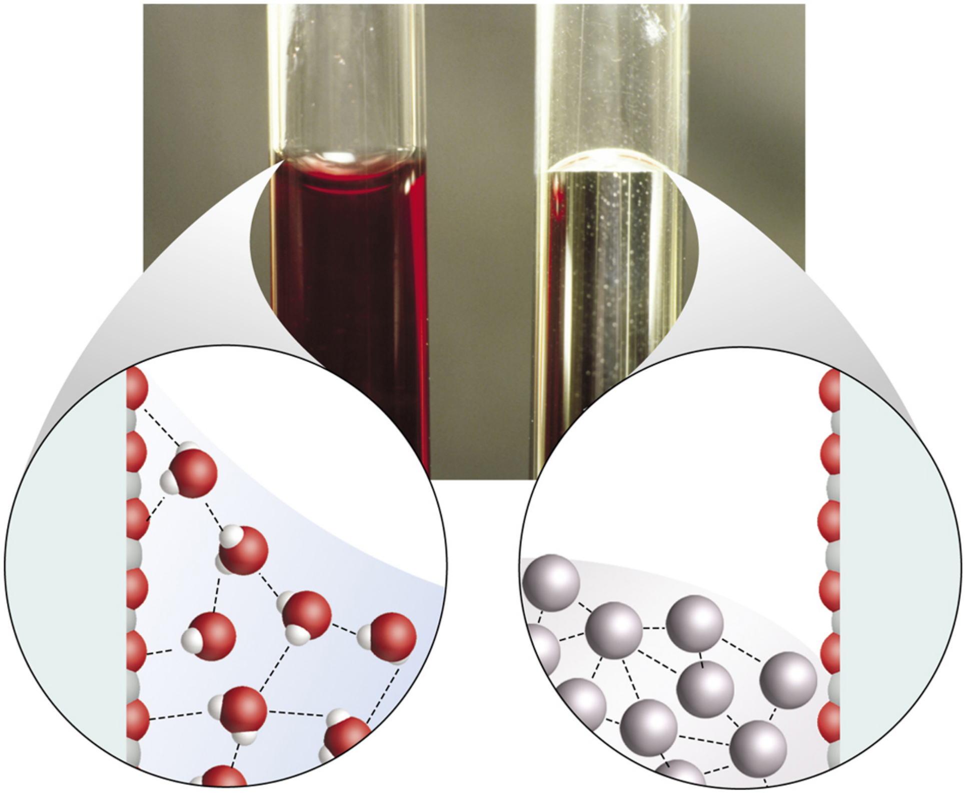
3. Meniscus Chemistry (10.6): Cohesive vs Adhesive Force/Attraction
   - "Cohesive forces" – bind like molecules together (intermolecular force)
   - "Adhesive forces" – bind liquid to surface (non-covalent attractions between a liquid to a solid.)
   - For water, if a surface has strong H-bonding or 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



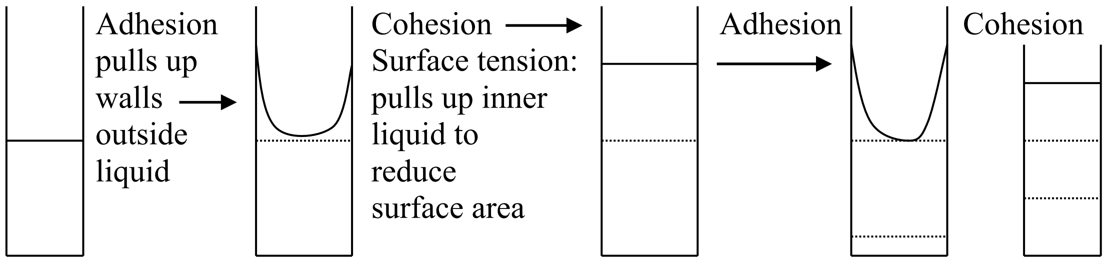
Hg in glass:
Cohesion > adhesion



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

4. <u>Capillary Action (10.6)</u>: 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:
  - o Diameter of the tube
  - o Strength of the cohesive forces
  - o 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?

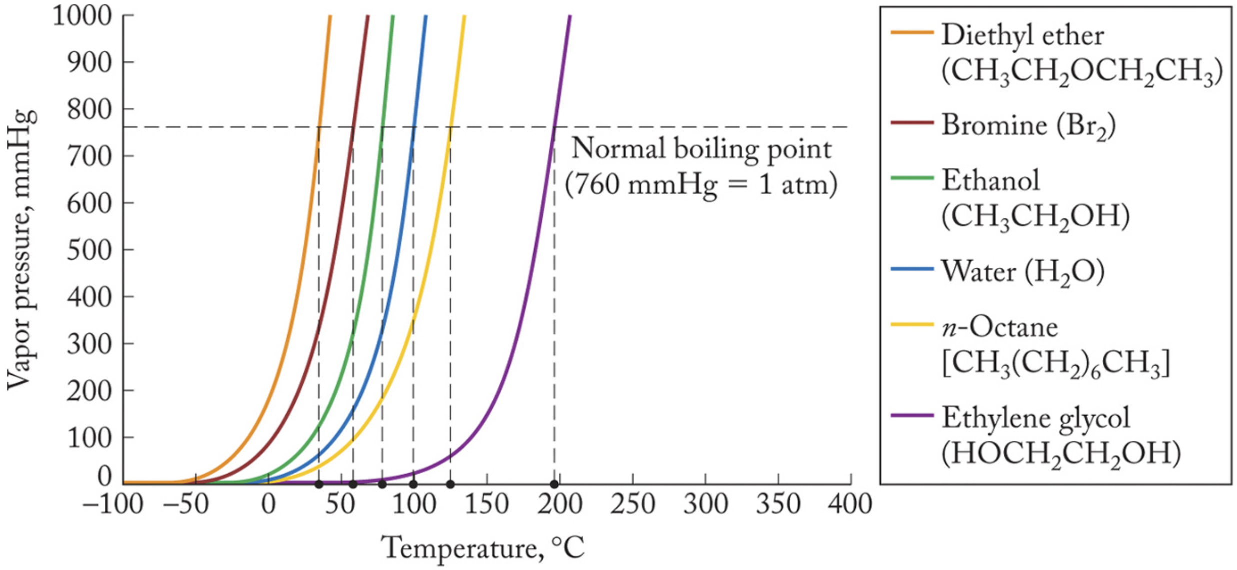
Br_2	F_2	SiH_4	CO_2
160	38	32	44

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

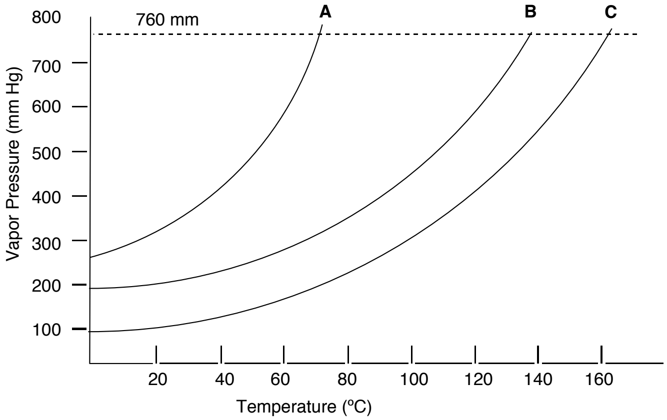
CH_3NO_2	LiF	Cl_2	CH_3OH
61	26	70	32

<u>Vapor Pressure Curves</u>: Show the relationship between temperature and vapor pressure for different substances

E.



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



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)

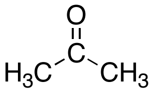
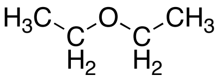
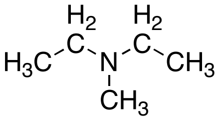
Q: Why does alcohol, salt, and sugar dissolve in water, but oil doesn't?

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 Solute-solute interactions Solvent-solvent interactions		Intermolecular Forces 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
  - $\Delta H >> O$ ➔ 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 12° 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
- **Normally solvent moves from the "dilute" to the "concentrated side"**
  - 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)

Cells have modest salt concentration, and undergo osmosis through cell walls

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

Other Osmosis Trivia

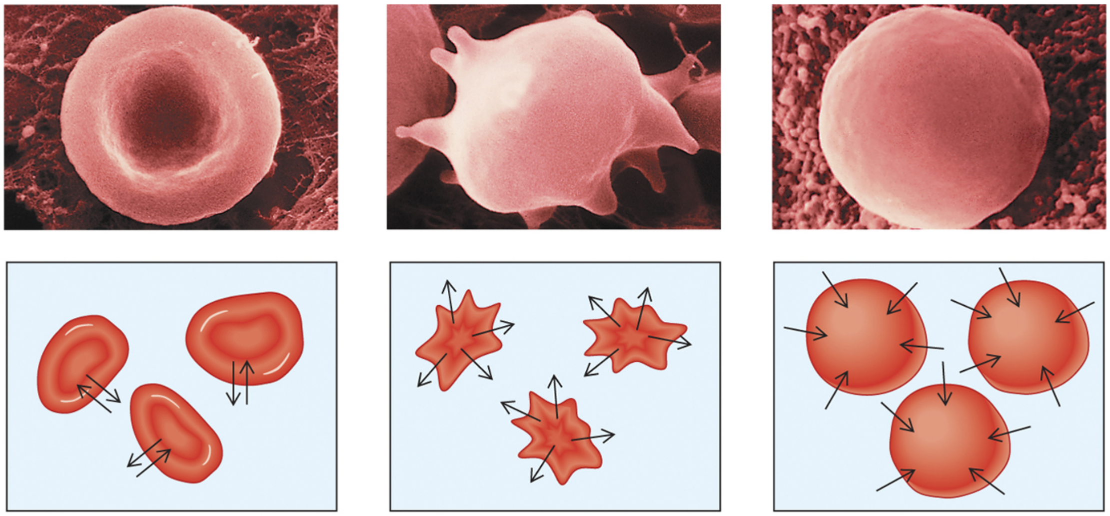
- Pickles: Cucumber shrinks in high salt
- Salt/sugar meats/fruits: bacteria get dehydrated and die → preserves "dried" meat
- H_2O transport in plants: absorb water from soil
- Diabetes: bad metabolism → high concentrations of solutes → need water, high thirst
- Edema: salty food → water retention →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

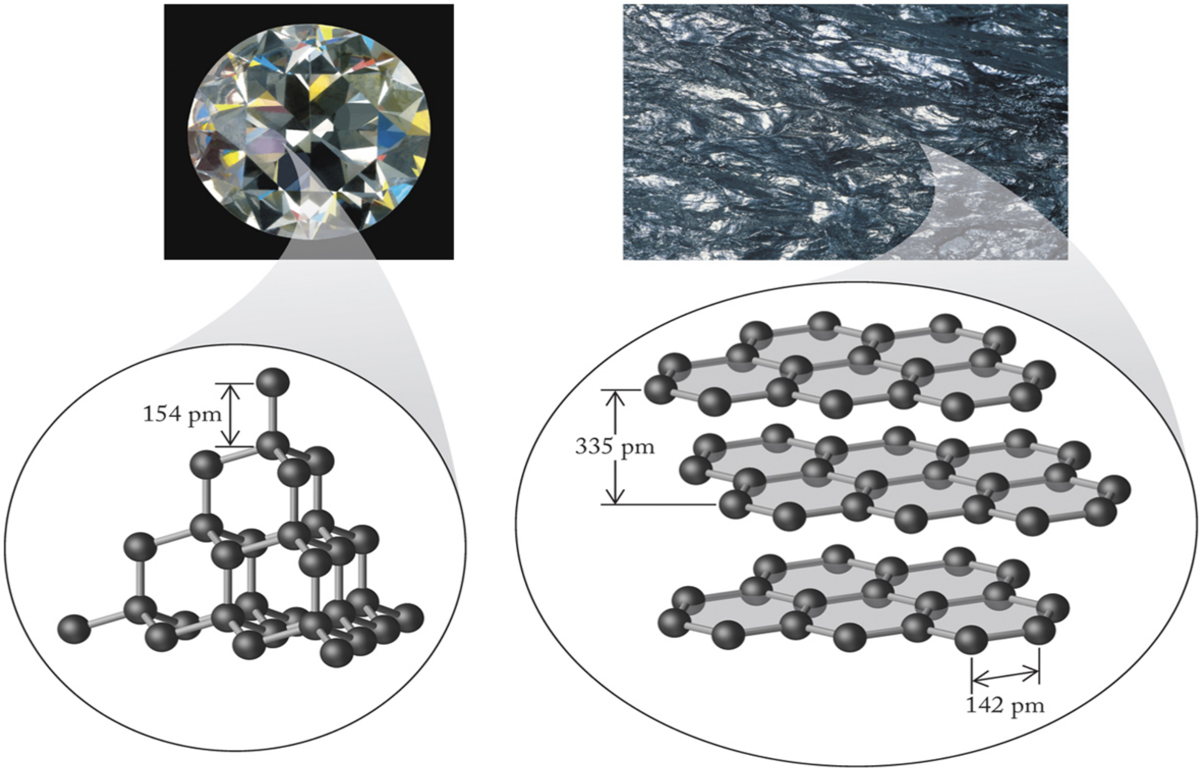
Metals (Section 12.1, 12.3, 12.4)

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

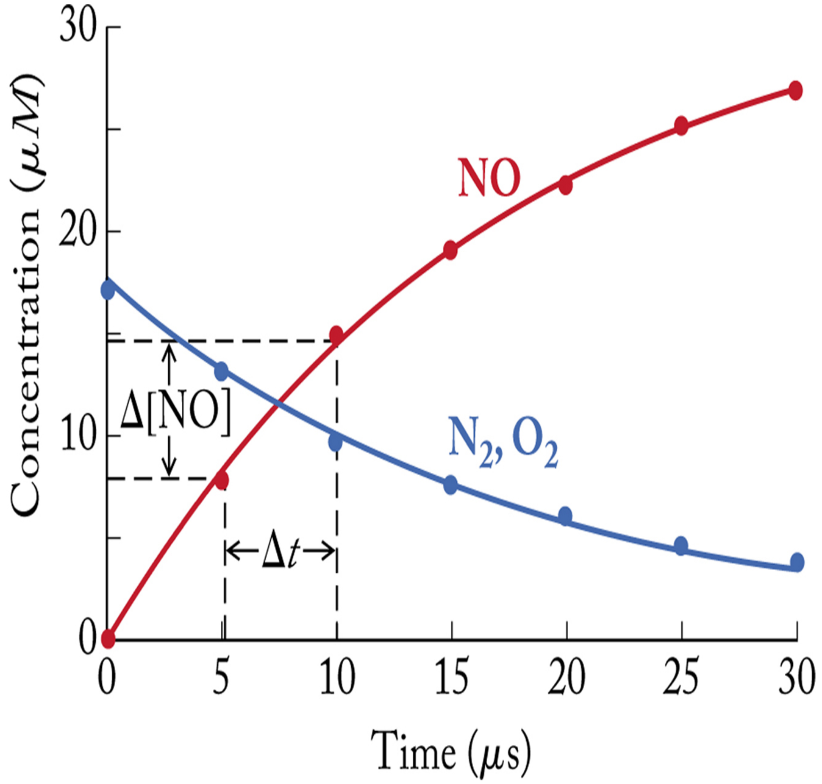
Δ = "change in" $\frac{\Delta x}{\Delta t}$

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

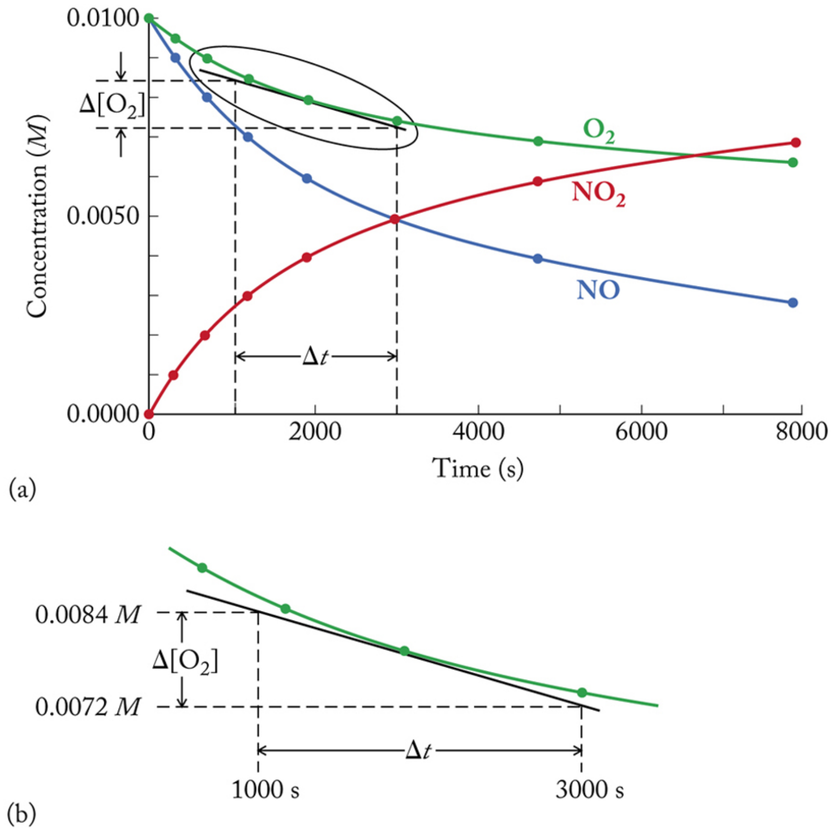
1. Rates can be written based on products or reactants, which are linked by stoichiometry.
   - [B] increases as [A] decreases

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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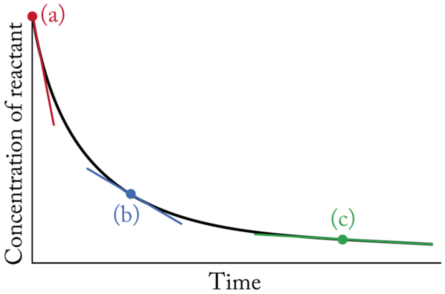
Reaction: $2NO + O_2 \rightarrow 2NO_2$

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 x 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

Ratio of the two actual rates → $\frac{r_2}{r_1} = \left[\frac{[A]_2}{[A]_1}\right]^x$ ← 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 $k = 113\ \text{years}^{-1}$, how long will it take for 10% of A to react?

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

3. **FIND $[A]_t$** If $k = 0.061\ \text{days}^{-1}$, 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

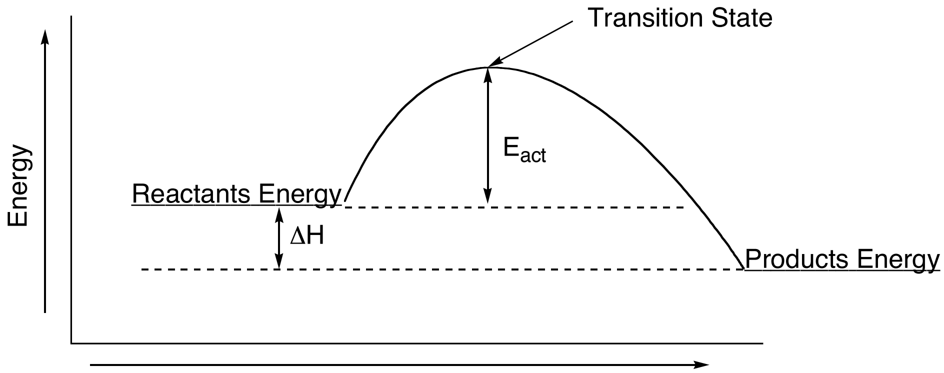
1. Unimolecular: A single molecule either rearranges or decomposes
   - Examples:
     a. $A \rightarrow B$
     b. $A \rightarrow B + C$
   - Energy is required

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



Reaction Progress for a Simple, One-Step Mechanism

- **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 **May be Helpful for Lab**

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

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)

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

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

Applications of Two-Point Solution:

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

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:

Step 1 $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$ fast, but reversible

Step 2 $C + D \xrightarrow{k_2} E + F$ slow

$A + B + D \longrightarrow E + F$

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)

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

Ch. 16 Chemical Equilibrium

16.1 Characteristics of a System at Chemical Equilibrium

1. Not completely on product or reactant side – have some of each
   - "product favored" equilibrium– more product
   - "reactant favored" – mostly reactant

2. "Dynamic Equilibrium"
   - forward rate = reverse rate
   - reactions happen, but cancel each other out, so that no overall change
     - "steady state" = "equilibrium"
   - It may seem like nothing is changing or happening, but is molecular action ("dynamic")

3. Previous Examples
   1. Vapor Pressure (closed container) Liquid $\rightleftharpoons$ vapor
   2. Saturated solution solid $\rightleftharpoons$ dissolved
   3. Weak acid/weak electrolyte HF $\rightleftharpoons H^+ + F^{\ominus}$

3. In achieving an equilibrium it doesn't matter whether you start from left side or right side
   - Either way, you end up with the same balance between reactants and products once equilibrium has been established
   - Figure 14.1 Moore, Fig T-117, 118 Brown

<u>The Equilibrium "Constant"</u>

A. Intro

$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$ $\boxed{\text{At equilibrium, rate}_{\text{forward}} = \text{rate}_{\text{reverse}}}$

Rate forward:

Rate reverse:

Equality:

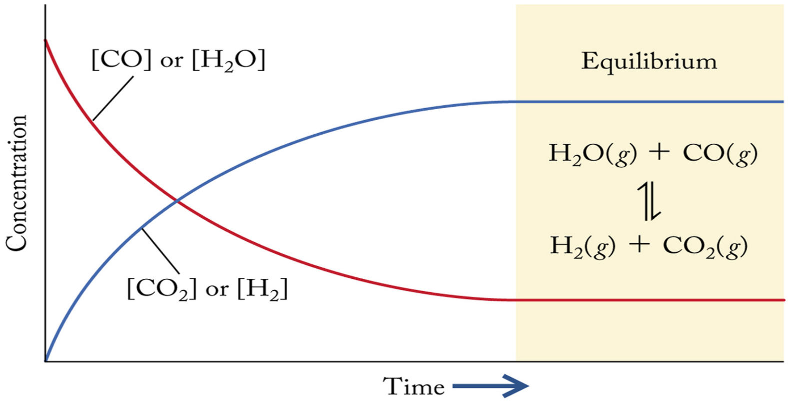
K_c

Rearrange:

<u>Notes</u>

1. K_c is a constant
2. Each reaction has its own unique "K" constant
   - called the "EQUILIBRIUM CONSTANT"
3. Ratio of **<u>product</u>** **<u>over reactant</u>**
   - **<u>concentrations are used</u>** in "M" (Molarity) = mole/liter
4. For gases, a K_p constant based on gas pressures can also be used. (**16.3**)
   - I'll do molarity ones for test problems and home-made problems. But the setup logic is the same for gas problems, in book or online homework or whatever.

Amounts of materials before and after equilibrium is Achieved:



Chemistry: The Science in Context 3/e Figure 16.1
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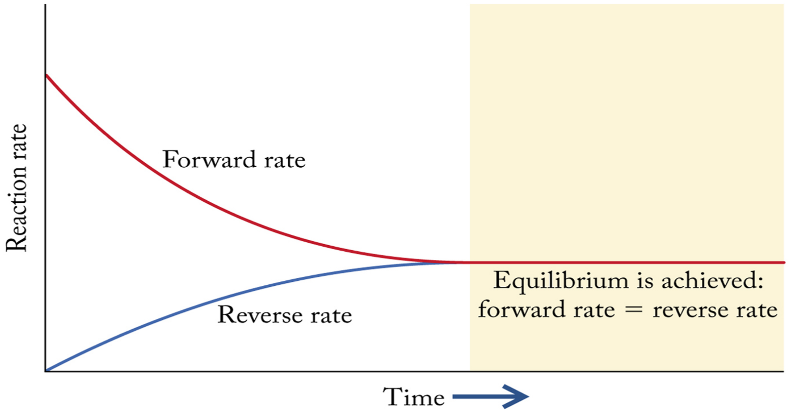
1. At equilibrium, amounts stay constant.
2. Prior to equilibrium amounts were changing.

Forward and Reverse Rates Prior to and After Equilibrium is Achieved:



Chemistry: The Science in Context 3/e Figure 16.2
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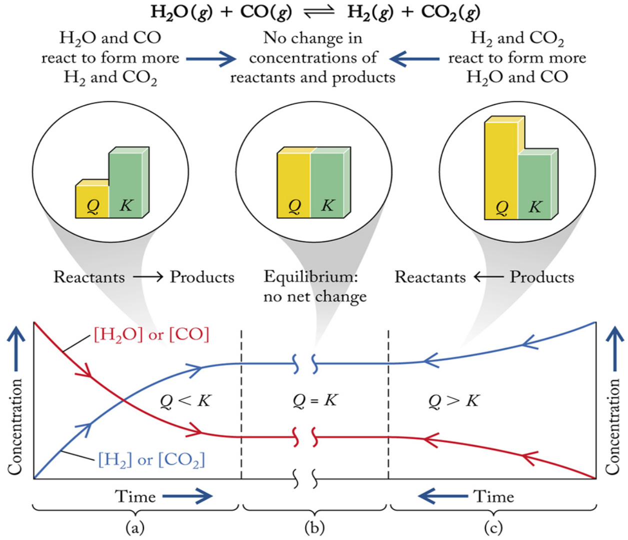
1. At equilibrium, rates are equal
2. Prior to equilibrium, rates were not equal.

Actual Product/Reactant Ratios "Q" versus Equilbrium Product/Reactant Ratios "K"



Chemistry: The Science in Context 3/e Figure 16.5
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1. "K" is the product/reactant ratio, if at equilibrium.
2. "Q" is the actual product/reactant ratio, whether at equilibrium or not
3. If "Q" = "K", you're at equilibrium
4. If "Q"≠ "K", you're NOT at equilibrium.
5. If "Q" < "K", need to make more product.
6. If "Q" > "K", need to make more reactants.

B. Qualitative things the value of K tells us:

1. At equilibrium, is the product favored or the reactant?
    - K >> 1 → product favored
    - K << 1 → reactant favored

Concept Problem: $A \rightleftharpoons B$ Find [B]/[A] ratios if:

a. $K_c=10^3$

b. $K_c = 10^{-3}$

2. If the **actual** initial ratio **Q** does not equal the equilibrium ratio K, in which direction will reaction go to achieve equilibrium? (In other words, if you start out not at equilibrium, how will the system respond to get to equilibrium?) (**Section 16.5**)
    - If actual ratio "Q" < K, the product/reactant ratio will need to increase in order to reach the target "K"
        - Practical:
    - If actual ratio "Q" > K, the product/reactant ratio will need to decrease in order to reach the target "K"
        - Practical:

Concept Problem: $A \rightleftharpoons B$ $K_c=0.20$

How will [A] and [B] change/respond to reach equilibrium (which will go up and which will got down?) if initial conditions are:

a. [A] = 0.20 M and [B] = 0.00 M

b. [A] = 0.10 M and [B] = 0.50 M

3. What will specific concentrations be at equilibrium?
    - If you know K and other information, you can solve for all the equilibrium concentrations

Concept Problem: $A \rightleftharpoons B$ $K_c=0.20$

a. If the system is at equilibrium and [A] = 0.10 M, what must be [B]?

b. If the system is at equilibrium and [B] = 0.10 M, what must be [A]?

c. If the system is **not** at equilibrium, and the initial scenario has [B] = 0.60 M, what will be the concentrations after equilibrium is achieved?

Writing K expressions: General (16.2)

$$aA + bB \rightleftharpoons cC + dD \qquad K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

1. Products over reactants
2. To the "coefficient" power
3. Straight from the balanced equation
   - don't need mechanism, etc.
   - Not like a rate law where equation doesn't really tell you anything

Write K_c Expressions

a. $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

b. $A(g) + 2\ B\ (g) \rightleftharpoons 3\ C(g) + D(g)$

Heterogeneous Equilibria (16.6): Do not include solids or liquids (solvents) in K expressions

- The concentrations of solids and liquids (solvents) are constant, so just wrap into K
- only gases and "aqueous things" (solutes) appear in K expressions
  - these are things whose concentrations are **not** constant
  - A(g), B(aq) Yes
  - C(l), D(s) No
- When water is involved as either a reactant or a product, it does **not** appear in the K expression (when the reaction takes place in aqueous solvent)

Ex. $CuOH(s) \rightleftharpoons Cu^+(aq) + OH^-(aq)$

$$K_1 = \frac{[Cu^+][OH^-]}{\underbrace{[CuOH]}_{\text{Constant}}} \quad \text{so} \quad \mathbf{K_2 = [Cu^+][OH^-]}$$

Write K Expressions

a. $NaF(aq) + H_2O(l) \rightleftharpoons HF(aq) + NaOH(aq)$

b. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

c. $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

Manipulating Equilibrium Constant Expressions. K's for Related Reactions. (16.4)

- When a reaction is written in the reverse direction, the K value is inversed
  - $K_{reverse} = 1/K_{forward}$
- When the coefficients for a reaction are doubled or halved, the K value ends up being squared or "square rooted"

1. Suppose $A + B \rightleftharpoons C$ $K_c=10^4$

   What is K for $C \rightleftharpoons A + B$
   (Draw both the expression and
   the actual K value)

2. Suppose $A + B \rightleftharpoons C$ $K_c=10^4$

   What is K for $2A + 2B \rightleftharpoons 2C$
   (Draw both the expression and
   the actual K value)

16.3 Calculating K values

- Key: You need all equilibrium concentrations. Then you can plug into K expression and solve.

Two ways to know all the equilibrium concentrations.

1. You are simply given all of the equilibrium concentrations. (easy)
2. You are given all of the **initial** concentrations, and **at least one final concentration**, but then must use the "ICE" (**I**nitial-**C**hange-**E**quilibrium) method to figure out what they would all be at equilibrium (harder)

A. Given all of the Equilibrium concentrations, solve for K (easy)

Solution steps:

a. Based on the balanced reaction, write out the correct K expression
b. Enter the known concentrations values and solve for K

1. For $A \rightleftharpoons B + C$, find K_c if [A] = 0.26 M, [B] = 0.26 M, [C] = 0.93 M.

2. For $A + 2B \rightleftharpoons 2C + D$, find K_c if [A] = 0.15, [B] = 0.18, [C]= 2.0×10^{-4}, [D] = 3.0×10^{-6}

B. Given all of the **initial** concentrations, and **at least one final concentration**, solve for K (harder) (**16.8**).

Solution steps:

- a. Based on the balanced reaction, write out the correct K expression
- b. Use the "ICE" (**I**nitial-**C**hange-**E**quilibrium) method to figure out the equilibrium concentrations
- c. Enter the equilibrium concentration values and solve for K

Using the "ICE" Method to Calculate K, Given Initial Concentrations and One Final Concentration

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the knowns
   a. Initial
   b. Change
   c. Equilibrium
3. Find the Change for the chemical whose final concentration is known
4. Use stoichiometric relationship to determine the change in concentrations for the others
5. From the initial concentrations and the deduced changes, determine all equilibrium concentrations
6. With all equilibrium concentrations now known, plug into the K_c expression and solve for K
7. Check: Does Answer Make Any Sense?
   - Note: equilibrium concentrations must be in Molarity, moles/liter. If information is given in grams or moles plus solvent volume, you will need to convert into molarity.

Use the ICE method to find the equilibrium concentrations and the K values for the following:

3.	2A +	2B ⇌	C +	2D	K_c=
I	0.20	0.30	0	0.10	
C					
E	0.10				K_c=

4.	A +	2B ⇌	C +	D	K_c=
I	0.20	0.20	0	0	
C					
E	0.15				K_c=

Chemical Meaning of K

1. $K_c >> 1$ Product Favored
2. $K_c << 1$ Reactant Favored
3. $K_c \approx 1$ Significant quantities of both products and reactants---calculations required

- There are many cases where K_c « 1, but small amount of product are still very important.

Some more Uses for K Values

A. Predicting the direction of a reaction, given information about actual situation. (**16.5 Equilibrium Constants K and Reaction Quotients Q)**

K=equilibrium Q=actual ratios (same format)

- If Q=K, you're at equilibrium. The situation won't change
- If Q<K, you're not at equilibrium. You are short on product, so reactions will go to products to achieve equilibrium. Shift from left to right.
- If Q>K, you're not at equilibrium. You have excess product, so products will go to reactants to achieve equilibrium. Shift from right to left.

1. $A + B \rightleftharpoons C$ $K_c = 72$

Suppose [A], [B], and [C] all begin at 0.33 M:

a. What is Q?

b. Which direction will the reaction go to achieve equilibrium?

c. What will happen to the concentrations of: (will they go up or down?)

[A] [B] [C]

B. Calculating Equilibrium Concentrations, Given K and Some Other Information (16.8, 2)

1. If all but one equilibrium concentration is given: (easy, plug and chug…)

Solution steps:

a. Based on the balanced reaction, write out the correct K expression
b. Enter the known K and the known concentrations values and solve for the unknown concentration

Example. $HF\ (aq) \rightleftharpoons H^{+}(aq) + F^{-}(aq)$ $K_c=6.8 \times 10^{-4}$

a. Find $[H^{+}]$ if $[HF] = 0.10$ and $[F^{-}] = 0.10$.

b. Find $[F^{-}]$ if $[HF] = 0.20$ and $[H^{+}] = 10^{-3}$.

2. If K number and initial concentrations are given, but no equilibrium concentrations are given, use ICE to calculate the equilibrium concentrations.

Using the "ICE" Method to Calculate Equilibrium Concentrations, Given Only Initial Concentrations and K_c

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the known initial concentrations
    a. Initial
    b. Change
    c. Equilibrium
3. Use "x" to define the change of one substance.
4. Use stoichiometric relationships to determine the changes in the concentrations for the others, in terms of "x".
5. Calculate the equilibrium concentrations of all chemicals in terms of initial concentrations and "x", and enter them in the table.
    - Ex: 0.30 – x, or 0.30 – 2x, or 0.00 + x, or 0.00 + 2x …..
    - **If K is small** so that "x" is likely to be small, **use the simplifying assumption** that $[A]_{initial}$ – "x" = $[A]_{initial}$
        - This is often justified, and can greatly simplify the math.
        - Ex: 0.20 – x = 0.20 if x is smaller than 0.01
6. Solve for "x" (This is the hard part!)
7. **Once "x" is known, use it to solve for the actual equilibrium concentrations**
8. Check: Does Answer Make Any Sense?
9. Check: If you made the "simplifying assumption", was it justified? (Was "x" < 5% of $[A]_{initial}$?)

Note: Some hard math!! Quadratics are tedious!

- If possible, being able to avoid needing to solve quadratics saves a lot of time (and mistakes)

***Great simplifying assumption (avoids a lot of quadratics):**

1. changes "x" are often small
    - For something with nonzero original concentration, the change "x" in concentration is often so small that it doesn't significantly change the original concentration
    - [original concentration] – "x" (change in concentration) = [original concentration]

2. Useful strategy:
    a. Make the simplifying assumption
    b. Check at end whether "x" > 5% of the original concentration
        - If not, the simplifying assumption is pretty good
        - If yes, the simplifying assumption is not valid and leads to some nontrivial error. In which case you need to go back and solve completely (often involving quadratic or perhaps even worse).

Concept Example: Why is the Simplifying Assumption Often Justifiable? 0.20-x = ???

If "x" ="	Then 0.20-x =	After roudoff to 2 sig. fig.	Is simplifying assumption valid?
2×10^{-7}	0.20 – 0.0000002 =		
2×10^{-6}	0.20 – 0.000002 =		
2×10^{-5}	0.20 – 0.00002 =		
2×10^{-4}	0.20 – 0.0002 =		
2×10^{-3}	0.20 – 0.002 =		
2×10^{-2}	**0.20 – 0.02 =**		

-Check at end. If x>5% of number, the assumption causes trouble.

Problems

1. If 0.10 mol of N_2O_4 is added to 1L flask, what will be the concentrations at equilibrium?

Quadratic Required. K too large to justify simplification	$N_2O_4 \rightleftharpoons 2NO_2$	K = 0.211
Initial		
Change		
Equilibrium		

Equilibrium:

$[N_2O_4]$

$[NO_2]$

2. Find final concentrations:

	$HA \rightleftharpoons H^+ + A^-$	$K_c = 1.6 \times 10^{-7}$
Initial Concentrations	0.20 0 0	
Change		
Equilibrium		
Equilibrium with Simplifying Assumption		

Equilibrium:

$[HA]$

$[H^+]$

$[A^-]$

3. Find final concentrations given:

	A	$\rightleftharpoons$	B	$+$	C	$K_c = 2.4 \times 10^{-6}$
Initial	0.30					
Change						
Equilibrium						
Equilibrium with Simplifying Assumption						

Equilibrium:

4. Find final concentrations given:

	A	$\rightleftharpoons$	B	$+$	C	$K_c = 0.018$
Initial	0.30					
Change						
Equilibrium						

Equilibrium:

5. Find final concentrations given: **A "Square Root" Simplification**

	A	$+$	B	$\rightleftharpoons$	C	$+$	D	$K_c = 0.060$
Initial	0.30		0.30					
Change								
Equilibrium								

6. Find final concentrations given: Solution with and Without Simplifying Assumption

$$A \rightleftharpoons 2B + C \qquad K_c = 2.0 \times 10^{-8}$$

	A		2B		C
Initial	0.20				
Change					
Equilibrium					
Equilibrium with Simplifying Assumption					

With Simplifying Assumption Without Simplifying Assumption

Solution With and Without Simplifying Assumption: $A \rightleftharpoons 2B + C$ $K_c = 2.0 \times 10^{-8}$

$A \rightleftharpoons 2B + C$

With I 0.20 0 0 C -x 2x x E .20-x 2x x E^* 0.20 x x So K = $2.0 \times 10^{-8} = \frac{(2x)^2 x}{0.20} = \frac{4x^3}{.20}$ $0.4 \times 10^{-8} = 4x^3$ **Easy** $x^3 = 1.0 \times 10^{-9}$ **$x = 1.0 \times 10^{-3}$**	Without (using .20 – x for [A] at eq) $K = 2.0 \times 10^{-8} = \frac{(2x)^2 x}{0.20 - x}$ So $2.0 \times 10^{-8} (0.20 - x) = 4x^3$ So $4.0 \times 10^{-9} - 2.0 \times 10^{-8} x = 4x^3$ So $4x^3 + 2.0 \times 10^{-8}x - 4.0 \times 10^{-9} = 0$ **Not Easy!!!**

16.7 How Systems Respond When an Equilibrium is Disturbed. LeChatelier's Principle.

1. At Equilibrium, there is a steady state of concentrations.
2. How does a system respond when an equilibrium is disturbed?

Le Chatelier's Principle: when a system is disturbed from equilibrium, it responds so as to reduce or counteract the effect of the change.

1. A revised equilibrium gets reestablished
    a. Usually the same K value must still apply
        - unless the temperature is changed
    b. But different actual concentrations result
        - whether you added or subtracted a reactant, a product, some solvent, or the volume
2. The reaction can move in the forward direction (more reactants go to product side) or the reverse direction (more products go back to starting materials) as needed to offset a change

Qual: If something extra is added, react from that side toward the other to remove some of it
If something is removed, react from the other side to replace it

LeChateliers's Principle: Summary

A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner as to reduce or counteract the effect of the change.

Factor that Changes	Direction of the Change	Direction to Restore Equilibrium
1. Concentration	↑ Reactant	Forward
	↑ Product	Reverse
2. Temperature	↑ T, when $\Delta H > 0$	Forward – K increases
	↑ T, when $\Delta H < 0$	Reverse – K decreases
3. Volume	↑ V, when $\Delta n_{gas} > 0$	Forward
	↑ V, when $\Delta n_{gas} = 0$	No effect
A change in volume impacts gas pressure. An increase in volume reduces pressure.	↑ V, when $\Delta n_{gas} < 0$	Reverse

If you reverse any of the Changes above, the **Direction to reach Equilibrium** reverses

3 Factors That can Be Changed	Goals
1) Concentrations	1) restore Q = K
2) Temperature	2) offset change
3) Volume (which impacts gas pressure)	

LeChatelier’s Principle: Response to Disrupted Equilibria

$$2\ A\ (g) \rightleftharpoons B\ (g)\ +\ \text{Heat} \qquad \Delta H < 0\ \text{(exothermic)}$$

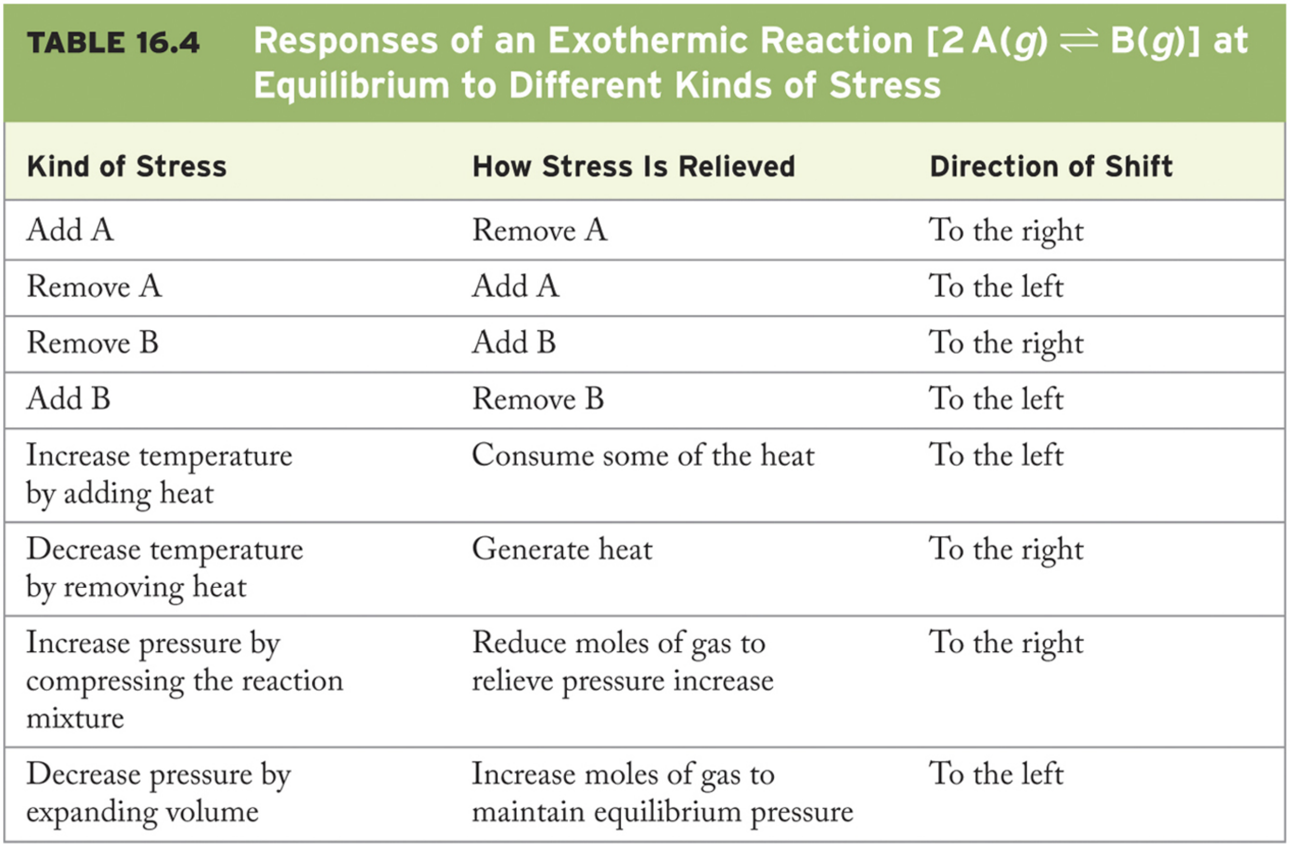


TABLE 16.4 **Responses of an Exothermic Reaction [$2\,A(g) \rightleftharpoons B(g)$] at Equilibrium to Different Kinds of Stress**

Kind of Stress	How Stress Is Relieved	Direction of Shift
Add A	Remove A	To the right
Remove A	Add A	To the left
Remove B	Add B	To the right
Add B	Remove B	To the left
Increase temperature by adding heat	Consume some of the heat	To the left
Decrease temperature by removing heat	Generate heat	To the right
Increase pressure by compressing the reaction mixture	Reduce moles of gas to relieve pressure increase	To the right
Decrease pressure by expanding volume	Increase moles of gas to maintain equilibrium pressure	To the left

***Chemistry: The Science in Context* 3/e Table 16.4**

A. Concentration Change: Addition or Removal of Either a Reactant or a Product

1. If you add (or remove) a chem, at that moment $Q \neq K$
2. The system (and concentrations) will shift forward or backward to adjust Q so $Q = K$
    - **<u>NOTE: K value does not change</u>**
    - many chemical ways to remove a chem (precipitations, acid-base, etc.)

<u>Example</u>

$$A + B \rightleftharpoons C + D$$

<u>Disruption</u>	<u>Immediate Impact on Q</u>	<u>Direction to Restore Eq</u>	Response (following disruption) :			
			[A]	[B]	[C]	[D]
Add A	$Q < K$	Forward	↓	↓	↑	↑
Add B						
Add C						
Add D						
Remove A						
Remove B						
Remove C						
Remove D						

B. Volume Change: Only Relevant When Gases are Involved

1. When the volume changes, it causes a change in concentrations
    - at the instant of change $Q \neq K$
    - note: the actual K value is unchanged

2. Qualitative sense:
    a. **When the volume expands, you want to generate <u>more gas molecules</u> to fill it**
    b. **When the volume shrinks, you want to <u>get rid of gas molecules</u> so it isn't too full**

3. Volume changes will only matter if one side of the equation has more gas on it than the other
    - if moles of gas are equal on both sides, volume changes have no impact

<u>Disruption</u>	**<u>Response</u>**
Volume Increase	**Shift toward side with more gas**
Volume Decrease	**Shift toward side with less gas**

4. Volume and Pressure: A different qualitative way to understand why a system will respond
    - When the volume expands, pressure decreases
    a. When the volume expands and the pressure drops, you want to generate <u>more gas molecules</u> to fill the container and <u>restore pressure</u>
    b. When the volume shrinks, you want to <u>get rid of gas molecules</u> to unclutter the container and to restore the original pressure

Volume Example

$$2H_2\,(g) + O_2\,(g) \rightleftharpoons 2H_2O\,(g)$$

Volume Change	Direction to Restore Eq	Response of moles of: $2H_2\,(g) + O_2\,(g) \rightleftharpoons 2H_2O$
Increase		
Decrease		

C. Temperature Change

1. View heat as either a reactant or a product
    - $\Delta H > 0$ Endothermic Heat is required, on Reactant Side
    - $\Delta H < 0$ Exothermic Heat is produced, on Product Side
2. When the temperature rises, the system responds so as to remove extra heat
3. When the temperature drops, the system responds so as to replace missing heat
4. When the system shifts to the right or to the left in response to a temperature change, this means that chemical concentrations change, too
5. A Temperature Changes Causes a Changes in the K Value
    - Because the Product/Reactant Ratio Changes
    - $\Delta H > 0$ Rise in temp → shift to right → K rises
    - $\Delta H > 0$ Drop in temp → shift to left → K drops
    - $\Delta H < 0$ Rise in temp → shift to left → K drops
    - $\Delta H < 0$ Drop in temp → shift to right → K rises

1. Write in “heat” as reactant or product, and predict the responses when temperature changes:

$$A \rightleftharpoons B \qquad \Delta H < O$$

Temperature Change	Direction to Restore Eq	Response of moles of: $A \rightleftharpoons B$	Response of K Value
Increase			
Decrease			

2. Write in “heat” as reactant or product, and predict the responses when temperature changes:

$$A \rightleftharpoons B \qquad \Delta H > O$$

Temperature Change	Direction to Restore Eq	Response of moles of: $A \rightleftharpoons B$	Response of K Value
Increase			
Decrease			

3. Write in “heat” as reactant or product, and predict the responses to the changes:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H > O$$

Disruption	Direction to Restore Eq	Response of moles of: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Response of K Value
1. Temperature Increase			
2. Volume Increase			
3. Added N_2			
4. Removal of NH_3			
5. Reduced temperature			
6. Added NH_3			
7. Removal of N_2			
8. Volume reduction			

D. Addition Catalyst: Equilibrium is reached faster, but the actual K value or equilibrium product/reactant ratios are unchanged.

Some Math Tips: CHEMICAL EQUILIBRIA Chem 210-Jasperse Ch. 16

1. $(a + b)^2 = a^2 + 2ab + b^2$

example: $(0.24- x)^2 = 0.0576 – 0.48x + x^2 = x^2 – 0.48x + 0.0576$

example: $(3.2e\text{-}5 - x)^2 = 1.02e\text{-}9 – 6.4e\text{-}5\ x + x^2 = x^2 – 6.4e\text{-}5\ x + 1.02e\text{-}9$

2. Quadratic Equation: $ax^2 + bx + c = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

example: $x^2 – 1.48x + 0.0576 = 0$ $x = 1.44$ or 0.04

example: $x^2 – .60\ x + 0.025 = 0$ $x = 0.43$ or 0.17

Note 1: Quadratics are a bother to solve. Avoid them if possible. Often the “simplifying assumption” (see #4) can enable you to avoid quadratic solutions.

Note 2: Quadratics can often give 2 answers, but one will frequently be nonsense.

3. “SIMPLIFYING ASSUMPTION”: If m>>x, then m – x = m (approximately)

examples: $0.14 – 3.6e\text{-}5 = 0.14$ $1.23e\text{-}3 – 1.0e\text{-}6 = 1.23e\text{-}3$

Use: for many equations in which K is small, “x” will also be relatively small. In these circumstances, the degree to which the starting materials react (“x”) will be relatively insignificant from their concentrations perspective, and we can assume the equilibrium concentration of the reactants will not differ significantly from their initial concentration.

- THE SIMPLIFYING ASSUMPTION WILL OFTEN MAKE THE USE OF THE QUADRATIC EQUATION UNNEEDED
- Guide: If “x” is >5% of “m”, then the simplifying assumption is not appropriate.

4. The “Square Root” Simplification: If both numerator and denominator have “squares”, it is convenient to take the square root of both sides to simplify

examples: $0.10 = x^2/(0.050- x)^2$ Take square root of both sides: $0.316 = x/(0.050- x)$
Rearrange: $0.0158 – 0.316x = x$
Solve for “x”: $x = 0.012$

5. $m = x^n$

To solve for x, when “m” and “n” are known:

a. enter “m”
b. hit $x^{1/y}$ or button (depending on your calculator)
c. enter “n”

example:

$25 = x^3$ $x = 2.92$
$1.48e\text{-}6 = x^3$ $x = 0.0114$
$2.14e\text{-}13 = x^4$ $x = 6.80e\text{-}4$

Using the "ICE" Method to Calculate K, Given Initial Concentrations and One Final Concentration

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the knowns
    a. Initial
    b. Change
    c. Equilibrium
3. Find the Change for the chemical whose final concentration is known
4. Use stoichiometric relationship to determine the change in concentrations for the others
5. From the initial concentrations and the deduced changes, determine all equilibrium concentrations
6. With all equilibrium concentrations now known, plug into the K_c expression and solve for K
7. Check: Does Answer Make Any Sense?

- Note: equilibrium concentrations must be in Molarity, moles/liter. If information is given in grams or moles plus solvent volume, you will need to convert into molarity.

Using the "ICE" Method to Calculate Equilibrium Concentrations, Given Only Initial Concentrations and K_c

1. Write balanced equation, and expression for K_c
2. Make an "ICE" table, and enter the known initial concentrations
    a. Initial
    b. Change
    c. Equilibrium
3. Use "x" to define the change of one substance.
4. Use stoichiometric relationships to determine the changes in the concentrations for the others, in terms of "x".
5. Calculate the equilibrium concentrations of all chemicals in terms of initial concentrations and "x", and enter them in the table.
    - Ex: 0.30 – x, or 0.30 – 2x, or 0.00 + x, or 0.00 + 2x …..
    - **If K is small** so that "x" is likely to be small, **use the simplifying assumption** that $[A]_{initial}$ – "x" = $[A]_{initial}$
        - This is often justified, and can greatly simplify the math.
        - Ex: 0.20 – x = 0.20 if x is smaller than 0.01
6. Solve for "x" (This is the hard part!)
7. **Once "x" is known, use it to solve for the actual equilibrium concentrations**
8. Check: Does Answer Make Any Sense?
9. Check: If you made the "simplifying assumption", was it justified? (Was "x" < 5% of $[A]_{initial}$?)

LeChateliers's Principle: Summary

A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner as to reduce or counteract the effect of the change.

Factor that Changes	Direction of the Change	Direction to Restore Equilibrium
1. Concentration	↑ Reactant	Forward
	↑ Product	Reverse
2. Temperature	↑ T, when $\Delta H > 0$	Forward – K increases
	↑ T, when $\Delta H < 0$	Reverse – K decreases
3. Volume	↑ V, when $\Delta n_{gas} > 0$	Forward
	↑ V, when $\Delta n_{gas} = 0$	No effect
A change in volume impacts gas pressure. An increase in volume reduces pressure.	↑ V, when $\Delta n_{gas} < 0$	Reverse

If you reverse any of the Changes above, the **Direction to reach Equilibrium** reverses

Ch. 17 Acids and Bases

Acid/base character (pH) of a solution has enormous impact

a. lake biosystem (acid rain)
b. farming/gardening (soil pH, alkalinity, etc)
c. rusting/corrosion
d. biology

- cells, proteins, blood, enzymes, hormones need very tight pH control
- Most bio reaction mechanisms involve H^+ transfer → $[H^+]$ has huge impact on rates

17.1 Bronsted-Lowry Concept of Acids/Bases

	Bronsted-Lowry Definition	Lewis Definition
Acid	**$H^{\oplus}$ donor**	Lone-pair acceptor
Base	**$H^{\oplus}$ acceptor**	Lone-pair donor

Acid and water: $HCl + H_2O \rightarrow H_3O^{\oplus} + Cl^{\ominus}$

Base and water: $NH_3 + H_2O \rightleftharpoons HO^{\ominus} + NH_4^{\oplus}$

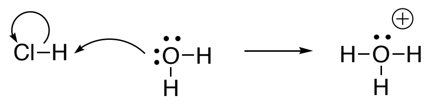
Notes:

1. An **acid** **loses** an $H^{\oplus}$ and gets more negative
    - A neutral acid becomes an **anion** after loss of $H^{\oplus}$ $HCl \rightarrow Cl^{\ominus}$
    - A cationic acid becomes neutral after loss of $H^{\oplus}$ $H_3O^{\oplus} \rightarrow H_2O$
2. A **base** **gains** an $H^{\oplus}$ and gets more positive
    - A neutral base becomes a **cation** after gain of $H^{\oplus}$ $H^{\oplus} + NH_3 \rightarrow NH_4^{\oplus}$
    - An anionic base becomes neutral after gain of $H^{\oplus}$ $H^{\oplus} + {}^{\ominus}OH \rightarrow H_2O$

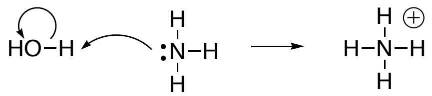
The change in either charge or number of H's can help identify whether a chemical is functioning as an acid or a base.

3. Every base needs a lone pair which gets used to bond to the new hydrogen
    - The two electrons involved in the new bond to hydrogen always come from an electron pair on the base

Water as Base: Uses an Oxygen Lone Pair



Water as Acid: Some Other Base Uses a Lone Pair to Steal An H from Water.



4. Water can function as either a base (accepting an $H^{\oplus}$ when an acid is placed in water) or as an acid (donating an $H^{\oplus}$ when a base is placed in water)

5. In every acid-base reaction, you must have both an acid (a chemical functioning as the $H^{\oplus}$ donor) and also a base (a lone-pair donating chemical functioning as the $H^{\oplus}$ acceptor)
   - An acid can't give unless there is some basic lone-pair to take.….

Terminology: $H^{\oplus}$ = "proton"

Conjugate Acid-Base Pairs

Structures that differ by one H and one charge unit are referred to as conjugate acid-base pairs

Conjugate Acid	Conjugate Base
HF	$F^{\ominus}$
HCl	$Cl^{\ominus}$
H_2SO_4	$HSO_4^{\ominus}$
$HSO_4^{\ominus}$	SO_4^{2-}

Conjugate Acid	Conjugate Base
$H_3O^{\oplus}$	H_2O
H_2O	$HO^{\ominus}$
$NH_4^{\oplus}$	NH_3

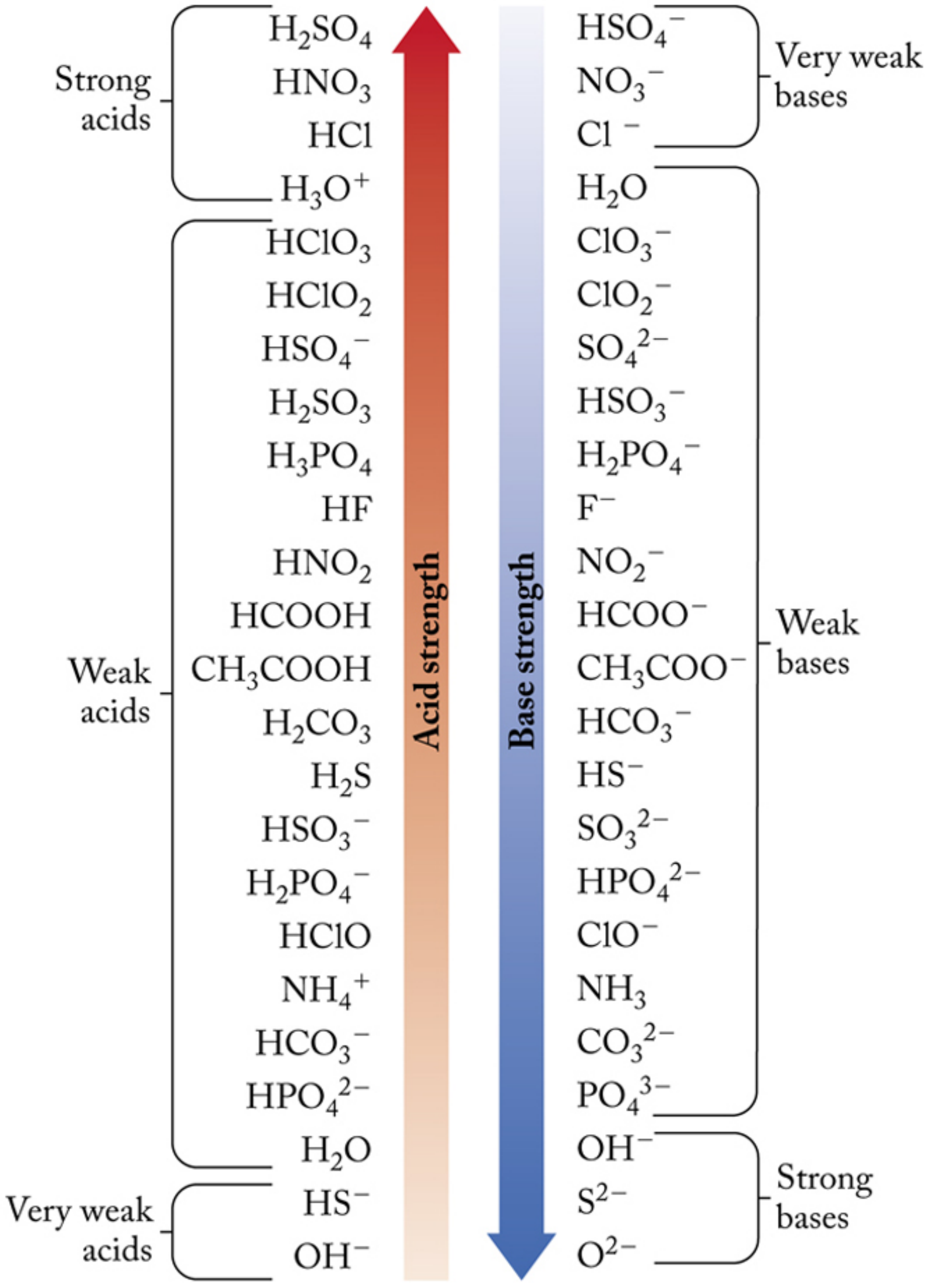
1. Draw the conjugate bases	2. Draw the conjugate acids
a. HCN	a. SO_4^{2-}
b. HBr	b. NH_3
c. CH_4	c. $Cl^{\ominus}$

Relative Strengths of Acids and Bases

	Acid		Base	
Strong acids, 100% Ionized in H_2O	HCl		$Cl^{\ominus}$	Nonbases
	H_2SO_4		$HSO_4^{\ominus}$	
	$H^{\oplus}$ (aq) = H_3O^+		H_2O	
	HSO_4^-		SO_4^{2-}	
	HF		$F^{\ominus}$	
	H_2CO_3		$HCO_3^{\ominus}$	
	$NH_4^{\oplus}$		NH_3	
	$HCO_3^{\ominus}$		CO_3^{2-}	
	H_2O		$OH^{\ominus}$	
Nonacids	$OH^{\ominus}$		O^{2-}	Strong bases, 100% Protonated in H_2O
	H_2		$H^{\ominus}$	

- Stronger acids have weaker conjugate bases and weaker acids have stronger conjugate bases
- Stronger bases have weaker conjugate acids and weaker bases have stronger conjugate acids

Relative Strength of Acids and Bases



***Chemistry: The Science in Context* 3/e Figure 17.4**
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Conjugate Pairs in Acid-Base Reactions and Acid-Base Equilibria

1. Note: Some acid-base reactions go entirely to the product side, or stay entirely on left side
2. But many acid-base reactions involve equilibria, in which a proton is shuffling back and forth from side to side
3. In the example shown, a proton ($H^{\oplus}$) jumps back and forth between F and O.
   a. Going from left to right, F is the giver (HF = acid) and O the acceptor (H_2O = base)
   b. Returning from right back to left, O is the giver ($H_3O^{\oplus}$ = acid) and F the acceptor ($F^{\ominus}$ = base)

$$HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus}$$

Notes

1. Each side of every acid-base reaction has one thing that functions as an acid and the other as a base. (This is true on the right side as well as on the left side).
2. Every acid-base reaction has 2 conjugate pairs
   a. For the acid on the left, it's conjugate base appears on the right side
   b. For the base on the left, it's conjugate acid appears on the right side.

Problems: For each of the species in the following equilibria, mark whether it functions as an acid or a base?

- For each of the species in the following equilibrium, draw an arrow to it's conjugate.

a. $NH_3 + HClO \rightleftharpoons NH_4^{\oplus} + ClO^{\ominus}$

b. $HCN + H_2PO_3^{\ominus} \rightleftharpoons H_3PO_3 + CN^{\ominus}$

c. $CH_3NH_2 + CH_3OH_2^{\oplus} \rightleftharpoons CH_3NH_3^{\oplus} + CH_3OH$

d. $H_2O + HSO_4^{\ominus} \rightleftharpoons H_3O^{\oplus} + SO_4^{-2}$

Notes/Notice:

1. Notice the change in H-count and the change in charge for each of these
2. The acid on the left always loses a hydrogen and becomes one step unit more negative
3. The base on the left always gains a hydrogen and becomes more positive
4. **Cations usually function as acids**
   - They are positive, and want to get rid of $H^{\oplus}$ to alleviate positive charge
5. **An anion usually function as a base**
   - It usually wants to get more positive, and the negative charge always means it has a lone-pair available
   - Some exceptions, such as example "d"

Acid/Base Strength

1. **Strong acids** are better $H^{\oplus}$ donors than **weaker acids**
   Strong bases are better $H^{\oplus}$ acceptors than weaker bases

2. Acid/base strength depends on love for $H^{\oplus}$

- Consider the conjugate pair of $Z^{\ominus}$ and HZ
  a. High $H^{\oplus}$ Love: Suppose $Z^{\ominus}$ really loves $H^{\oplus}$
    1. Then $Z^{\ominus}$ is a strong base
       - It aggressively grabs $H^{\oplus}$ from somebody else
    2. Then HZ is a very weak acid or a total non-acid
       - Z tightly holds onto the $H^{\oplus}$
       - It doesn't let anybody else steal $H^{\oplus}$ unless it's a base who loves $H^{\oplus}$ even more
  b. Low $H^{\oplus}$ Love: Suppose $Z^{\ominus}$ doesn't have much love for $H^{\oplus}$
    1. Then $Z^{\ominus}$ is a weak base or a totally non-base
       - It's very weak about grabbing $H^{\oplus}$ from somebody else
    2. Then HZ is acidic
       - Z is very weak about holding onto the $H^{\oplus}$
       - Some base who loves $H^{\oplus}$ more can easily steal the $H^{\oplus}$ away and leave $Z^{\ominus}$ behind

3. Love for $H^{\oplus}$ and the Competition between Competing Bases

$$\underset{\text{acid}}{HX} + \underset{\text{base}}{Z^{\ominus}} \rightleftharpoons \underset{\text{base}}{X^{\ominus}} + \underset{\text{acid}}{HZ}$$

NOTICE: There is one hydrogen, but two things ($Z^{\ominus}$ and $X^{\ominus}$) competing for it.

a. Whichever base loves $H^{\oplus}$ **more** will be the **stronger base**, and the equilibrium will drive to the opposite direction → to the conjugate acid of the strong base
b. Whichever base loves $H^{\oplus}$ **less** will lose the competition and remain in its basic form

1. Strong love for $H^{\oplus}$ = strong base
2. Equilibrium goes from strong base to weak base, favors the side where the weaker base lies.
3. In the same way, the equilibrium always goes from the stronger acid to the weaker acid, and always favors the side with the weaker acid
4. The weaker acid and weaker base are always on the same side, and the stronger acid and stronger base are always together on the other side

4. Acid-Base Strength and the Direction of Acid-Base Equilibria

*Acid/base reactions **always** go from stronger acid/base to weaker acid + base

K favors weaker

HCl +	$NaOH$ →	H_2O +	$Na^{\oplus}Cl^{\ominus}$	K large (K >>1)
Stronger acid	stronger base	weaker acid	weaker base	

H_2S +	$F^{\ominus}$ ←	HF +	$HS^{\ominus}$	K small (K <1)
weaker acid	weaker base	stronger acid	stronger base	

a. Stronger acid + base always on same side
b. If you know any of relative strengths, can predict sense, K
c. If given K info, can identify weaker/stronger

Problems

1. HF is stronger than HNO_2. Predict the "direction" of the reaction, and say whether K will be greater or less than 1. (ID each as acid or base)

$HF + Na^{\oplus}NO_2^{\ominus}$ $Na^{\oplus}F^{\ominus} + HNO_2$ K 1

2. Predict the "direction" of the reaction, and say whether K will be greater or less than 1.

$HF + Cl^{\ominus}$ $HCl + F^{\ominus}$ K 1

3. Classify each as the weaker or stronger acid or base.

$HA + B^{\ominus}$ $A^{\ominus} + HB$ $K = 10^3$

4. Classify each as the weaker or stronger acid or base.

$HCN + SO_4^{2-}$ $HSO_4^{\ominus} + CN^{\ominus}$ $K = 10^{-5}$

5. **Direct Relationship between strengths of conjugate acid/base**

Acid Strength	**Strength of Conjugate Base**
Strong	Nonbasic
Weak	Weak
Nonacid	Strong base

Note: there is a huge range of strengths within the "weak" category

	Acid	Base	
Strong acids, 100% Ionized in H_2O	HCl	$Cl^{\ominus}$	Nonbases
	H_2SO_4	$HSO_4^{\ominus}$	
	$H^{\oplus}(aq) = H_3O^+$	H_2O	
	HSO_4^-	SO_4^{2-}	
	HF	$F^{\ominus}$	
	H_2CO_3	$HCO_3^{\ominus}$	
	$NH_4^{\oplus}$	NH_3	
	$HCO_3^{\ominus}$	CO_3^{2-}	
	H_2O	$OH^{\ominus}$	
Nonacids	$OH^{\ominus}$	O^{2-}	Strong bases, 100% Protonated in H_2O
	H_2	$H^{\ominus}$	

The weaker the acid, the stronger it's conjugate base
The stronger the acid, the weaker it's conjugate base

6. **Strong Acids versus Weak Acids versus Nonacids. How do they Differ in Water?**

a. **Strong acids** ionize completely in water

$$HCl + H_2O \rightarrow H_3O^{\oplus} + Cl^{\ominus}$$

- There is **NO** acid left, no acid where the H and the Cl are bonded.
- Goes completely to the product side.

b. **Weak acids** ionize incompletely in water
- An equilibrium exists
- Normally only a small amount of product ion is present at equilibrium, and most of the weak acid is in it's undissociated form

$$HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus} \qquad K = 10^{-5}$$

- There is plenty of HF left. But meaningful amounts of $H_3O^{\oplus}$ + $F^{\ominus}$ ions present.
- Some "weak" acids are stronger or weaker than others.

c. **Nonacids:** Don't ionize at all in water.
- No equilibrium exists
- Stays completely on the left side

$$CH_4 + H_2O \leftarrow H_3O^{\oplus} + CH_3^{\ominus}$$

17.1 Recognizing Acids

1) **Memorize** Six **strong acids**

HCl HBr HI HNO_3 H_2SO_4 $HClO_4$

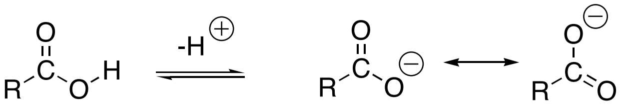
- **Assume all other acids are weak acids**
- The conjugate anions of these strong acids are nonbasic

2) Weak acids

a. Usually formula written with H in front
HF HCN H_2S H_2CO_3 → acids
CH_4
NH_3 SiH_4 → nonacids

*** Note: NOT ALL H's are acidic!!**

b. Carboxylic acids (RCOOH, where R is generic for almost anything)



- The "R" group can be anything, but is usually hydrocarbon
- The anion is stabilized by resonance
- Carboxylic acids are often written as: CH_3COOH, C_2H_5COOH, etc.

c. Ammonium Ions are weak acids (see more under bases, amines)

- Conjugate acids of neutral amine bases
- Formal positive charge on nitrogen
- Unlike most acids, these are cationic species

$NH_4^{\oplus}$, $CH_3NH_3^{\oplus}$, $(CH_3)_2NH_2^{\oplus}$, $C_6H_5NH_3^{\oplus}$, etc.

Recognizing Bases

1. Soluble metal hydroxides ⇒ strong bases
   - All **Group 1 metal hydroxides, many Group 2**…
   - Group 1 metal hydroxides produce 1 mole of hydroxide per mole of formula
   - Soluble Group 2 metal hydroxides produce 2 moles of hydroxide per formula

Group 1	Group 2
LiOH, NaOH, KOH …	$Ca(OH)_2$, $Ba(OH)_2$ …

$NaOH\ (aq) \rightarrow Na^{\oplus}\ (aq) + {}^{\ominus}OH(aq)$ (Complete)
1mole 1 mole

$Ca(OH)_2\ (aq) \rightarrow Na^{\oplus}\ (aq) + 2\ {}^{\ominus}OH(aq)$ (Complete)
1mole 2 mole

- most Transition-metal hydroxides have limited solubility and aren't effectively strong

$CuOH(S) \rightleftharpoons Cu^{+}(aq) + OH^{-}(aq)$
1mole less than 1mole (Incomplete)

2. Amines: Neutral N Compounds ⇒ weak bases

Parent: $H_3N{:} + H_2O \rightleftharpoons {}^{\ominus}OH + NH_4^{\oplus}$
weak base weak acid

- Other amines have N: in common, but replace one or more of the hydrogens with other thing, usually carbon groups

Amines Bases (examples)	Conjugate acids = "Ammonium" Ions
NH_3	$NH_4^{\oplus}$
CH_3NH_2	$CH_3NH_3^{\oplus}$
$(CH_3)_2NH$	$(CH_3)_2NH_2^{\oplus}$
$C_6H_5NH_2$	$C_6H_5NH_3^{\oplus}$

- N lone pairs accept $H^{\oplus}$
- Amines are the only "neutral bases". All other bases have anionic charge.
- The conjugate acids are called "ammonium ions" (see earlier)
  - "Amines" = neutral, weakly basic
  - "Ammoniums" = cationic, weakly acidic
- The ammonium ions have formal $\oplus$ charge on N

3. **Any conjugate base of a weak acid is weak base**

4. **Any conjugate base of a non-acid is a strong base**

5. **Any conjugate base of a strong acid is a non base**

Note: Most Anions are Basic. Whenever you see an anion, consider whether it will be basic!

6. **Evaluating the Basicity of Anions**
   a. Draw the conjugate acid of the anion
   b. Evaluate the acidity of the conjugate "acid" as strongly acidic, weakly acidic, or nonacidic
   c. Based on the acidity of the acid, decide what the strength of the anion base would be.

Conjugate Acid Strength	**Strength of Conjugate Base**
Strong acid	Nonbasic
Weak acid	Weak Base
Non-acid	Strong base

Base Strength	Anion	Conjugate Acid	Acid Strength
	$F^{\ominus}$	HF	
	$^{\ominus}CN$	HCN	
	$H_2PO_4^{\ominus}$	H_3PO_4	
	$Cl^{\ominus}$	HCl	
	$H^{\ominus}$	H_2	
	$^{\ominus}CH_3$	CH_4	

Note: Most anions are basic

- Memorize the six anions derived from strong acids that are not basic
- Assume any other anion is basic

Six strong Acids	HCl	HBr	HI	HNO_3	H_2SO_4	$HClO_4$
Six Non-Basic Anions	$Cl^{\ominus}$	$Br^{\ominus}$	$I^{\ominus}$	$NO_3^{\ominus}$	$HSO_4^{\ominus}$	$ClO_4^{\ominus}$

Recognizing and Classifying Acid/Base Character of Ionic Formulas

1. Distinguish molecular from ionic formulas
2. **For ionics, check each ion separately**
   a. Is the cation acidic?
      1. No if it's a group 1 or group 2 metal cation
      2. Yes if it's a transition metal cation
      3. Yes if it's an ammonium cation
   b. Is the anion basic?
      1. No if it's one of the six non-basic anions derived from strong acids
      2. Yes if it's any other anion

1. Classify as Strong Acid, Weak Acid, Strong Base, Weak Base, or Non-acid/base

   a. HBr

   b. HF

   c. $CH_3CH_2NH_2$

   d. CH_3CH_2COOH

   e. H_2SO_4

   f. H_3PO_4

   g. HClO

   h. $ClO^{\ominus}$

   i. $Cl^{\ominus}$

   j. $NO_3^{\ominus}$

   k. O^{2-}

   l. CH_4

   m. NaOH

   n. NaF

   o. KCl

   p. NH_4NO_3

   q. $FeBr_3$

Autoionization of water (17.2). pH and pOH

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^{\oplus}(aq)^{+}\ OH^{\ominus}(aq) \qquad \mathbf{K_w = 1.00 \times 10^{-14}} =$$

1. Water is both weakly acidic and basic
2. Amount of ions is teensy but very important
3. $K_w = 1.00 \times 10^{-14}$ always true
4. If either $[H_3O^{\oplus}]$ or $[HO^{\ominus}]$ known, can calculate other

$$\boxed{[H_3O^{\oplus}][OH^{\ominus}] = \mathbf{1.00 \times 10^{-14}} \qquad \textbf{Memorize!}}$$

Neutral: $[H_3O^{\oplus}] = 1 \times 10^{-7} = [OH^{\ominus}]$ pH = 7 Acidic: $[H_3O^{\oplus}] > 1 \times 10^{-7} > [OH^{\ominus}]$ pH <7 Basic: $[H_3O^{\oplus}] < 1 \times 10^{-7} < [OH^{\ominus}]$ pH > 7	Note: $H^{\oplus}$ vs. $H_3O^{\oplus}$ • $H^{\oplus}$ (proton) in water exists as $H_3O^{\oplus}$ (hydronium). • But $H^{\oplus}$ is easier to write! • They are really the same thing.

The pH Scale (17.2)

$pH = -\log[H_3O^{\oplus}]$	$[H_3O^+] = 10^{-pH}$	Much nicer numbers
On calculator: enter $[H^+]$, hit "log", and correct the sign from negative to positive	**On calculator**: enter pH, switch the sign from positive to negative, and hit 10^x button (depending on calculator)	

1. Higher numberer pH → less $H^{\oplus}$, less acidic, more basic
   Lower numbered pH → more $H^{\oplus}$, more acidic, more less$^+$

   pH 3.0 4.6 10.2
   ←
   more acidic
   →
   less acidic

2. pH = 7 neutral pH < 7 acidic pH > 7 basic

3. pH change of 1 = tenfold change in $[H^{\oplus}]$
   Change of 2 = 100-fold change
   pH change of 8 → 4 isn't double the acid or half the acid, it's 10 thousand times more!

4. Number of significant figures in $[H^+]$ = number of digits after decimal in pH

   $[H^+] = 3.6 \times 10^{-6}$ → pH = 5.44
   2 sig fig → 2 after decimal

5. Small pH changes → death
   - 7.35 < blood < 7.45
   - bio rates are often strongly H^+ catalyzed, with 2nd or 3rd order rate dependence on $[H^+]$

6. $pOH = -\log[OH^-]$ just like $pH = -\log[H^+]$	**$[OH^-] = 10^{-pOH}$** just like $[H^+] = 10^{-pH}$

7. Since $10^{-14} = [H^+][OH^-]$ → take negative log of both sides → $\boxed{\mathbf{14.00 = pH + pOH}}$

Skills: interconvert among

$\mathbf{[H^+] \Leftrightarrow [OH^-]}$

$\Updownarrow \qquad \Updownarrow$

$\mathbf{pH \Leftrightarrow pOH}$

To know any one allows you to find any of the others!

Problems

1. Find pH for following

a. $[H_3O^+] = 1.0 \times 10^{-4}$

b. $[H^+] = 1.0 \times 10^{-11}$

c. $[H^+] = 3.2 \times 10^{-4}$

d. $[OH^-] = 1.0 \times 10^{-8}$

e. $[OH^-] = 5.8 \times 10^{-4}$

f. pOH = 8.30

2. Find pOH:

a. $[H^+] = 3.9 \times 10^{-5}$

b. $[OH^-] = 3.9 \times 10^{-5}$

c. pH = 3.95

3. Find both	$[H^+]$	$[OH^-]$
a. pH = 3.72		
b. pH = 9.81		
c. $[H^+] = 3.5 \times 10^{-8}$		
d. $[OH^-] = 4.1 \times 10^{-3}$		

<u>Equilibrium Expressions and Ionization Constants for Acids, Bases</u>. (17.3)

A. Acids

$HA\ (aq) + H_20\ (l) \rightleftharpoons H_30^{\oplus}\ (aq) + A^{\ominus}\ (aq)$ $\qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$

Shorthand: $HA \rightleftharpoons H^{\oplus} + A^{\ominus}$ $\qquad \mathbf{K_a} = \frac{[H_3O^+][A^-]}{[HA]}$

1. Strong acids: ionize completely (K_a = infinity)
2. Weak acids: $K_a < 1$
3. Larger $K_a \Rightarrow$ stronger acid Smaller $K_a \Rightarrow$ weaker acid
4. For weak acids, ionizations may be minimal but is still significant
    - for math calculations, the "simplifying assumption" is usually useful
5. Since $A^{\ominus}$ and HA are conjugates:
    - larger $K_a \Rightarrow$ less basic $A^{\ominus}$ (stronger acid → weaker base)
    - smaller $K_a \Rightarrow$ more basic $A^{\ominus}$ (weaker acid → stronger base)

B. Bases

Generic	$Base(aq) + H_20(l) \rightleftharpoons OH^{\ominus}\ (aq) + Base\text{-}H^{\oplus}\ (aq)$ Conjugate acid	$\mathbf{K_b} = \frac{[OH^-][BH^+]}{[B]}$
Anionic Base	$A^{\ominus} + H_20 \rightleftharpoons OH^{\ominus} + HA$ Conjugate acid	$\mathbf{K_b} = \frac{[OH^-][HA]}{[A^-]}$
Neutral Amine Base	$NH_3 + H_20 \rightleftharpoons OH^{\ominus} + NH_4^{\oplus}$ Amine Ammonium	$\mathbf{K_b} = \frac{[OH^-][NH_4^+]}{[NH_3]}$

16.7 Calculations involving K_a, K_b, pH, pOH

A. **<u>Strong Acids</u>**: $[HA] = [H^{\oplus}] \Rightarrow$ pH

- Complete ionization $HCl \rightarrow H^{\oplus} + Cl^{\ominus}$
- To know the concentration of the strong acid is to know the concentration of $H^{\oplus}$

B. **<u>Strong Bases</u>**: complete formation of $OH^{\ominus}$

- $[NaOH] = [OH^{\ominus}] \Rightarrow$ pOH, pH
    - for a group one metal hydroxide (NaOH, etc.), you get exactly as many moles of hydroxide as you put in of NaOH, and $[NaOH] = [OH^{\ominus}]$
    - $NaOH \rightarrow Na^{\oplus} + OH^{\ominus}$
- For a group two metal hydroxide, you get two moles of hydroxide for every one mole of formula that you put in.
    - $1\ Ba(OH)_2 \rightarrow 1\ Ba^{2+} + 2\ OH^{\ominus}$
    - $[OH^{\ominus}] = 2\ ([Ba(OH)_2])$
- Since $[OH^{\ominus}]$ is knowable, you can then plug in, and find pOH, pH, and/or $[H^{\oplus}]$

Some pH Calculations Involving Strong Acids or Bases

1. What is the pH of 1.36×10^{-3} M H_2SO_4?

2. An HCl solution has pH = 2.16. what is [HCl]?

3. What is pH for 0.013 M KOH solution?

4. What is pH for a solution that is 0.013 M in $Ca(OH)_2$?

5. What is the pH if 22 g of $Ba(OH)_2$ (90 g/mol) is dissolved in 760 mL of water?

C. Weak Acids Calculation: Equilibrium, K_a, and pH ICE-able (Section 17.3)

Two Key Equations	$K_a=\frac{[H^+]^2}{[HA]_{init}}$	$[H^+]=\sqrt{K_a\cdot[HA]}$;

1. **Major Application 1**: Given a known K_a, Solve for pH When a Known Amount of Weak Acid is Placed in a Known Amount of Water

Logic: Use K_a → solve for $[H^{\oplus}]$ → solve for pH

Steps

1. Whether it's given in molarity or not, convert the sample/solvent ratio into Molarity
2. Set up an ICE table
3. Solve for equilibrium $[H^{\oplus}]$
   - Use simplifying assumption if K_a is reasonably small
   - Use another simplifying assumption that the original population of $H^{\oplus}$ is also reasonably small relative to the final, equilibrium amount of $H^{\oplus}$
4. Use $[H^{\oplus}]$ to solve for pH

5. Or: If K_a is small enough so that the simplifying assumption is reasonable, you can directly plug into the equation shown above

	HA	$\rightleftharpoons$	$H^{\oplus}$	$+$	$A^{\ominus}$
Initial	$[HA]_{init}$		1.0×10^{-7}		0
Change					
Equilibrium					
Equilibrium After Simplifying Assumptions					

$K_a =$

When is simplifying assumption safe? Use the >100K rule:	If $\frac{[HA]_{init}}{K_a} > 100$ → simplifying assumption is safe

When the simplifying assumptions are used:	$\mathbf{K_a} = \frac{[H^+]^2}{[HA]_{init}}$	$[\mathbf{H}^{\oplus}] = \sqrt{K_a \times [HA]_{init}}$
When the first simplifying assumption is not used (but the second one is)	$K_a = \frac{[H^+]^2}{[HA]_{init} - [H^+]}$	$[H^{\oplus}]$ requires a quadratic solution

2. **<u>Major Application 2</u>**: Given a measured pH, Solve for K_a When a Known Amount of Weak Acid is Placed in a Known Amount of Water

Logic: Use pH → solve for $[H^{\oplus}]$ → solve for K

$$K_a = \frac{[H^+]^2}{[HA]_{init}}$$

<u>Weak Acid pH/K_a Problems</u>

1. pH → K_a What is K_a for an acid if an 0.15 M solution is prepared and found to have pH = 4.86?

Logic:

2. $K_a \rightarrow pH$ What is pH for a 0.15 M solution of an acid with $Ka = 2.2\times10^{-6}$?
Logic:

3. If an 0.23 M solution of an acid gives pH = 3.82, what is K_a for acid?

4. If a 0.11 M solution has a $Ka = 1.3\times10^{-8}$ acid, what is pH?

D. Weak Base Calculations involving K_b and pH (Section 17.3)

	$A^{\ominus}$	$+ H_2O$	$\rightleftharpoons$	HA	+	$HO^{\ominus}$
Initial	$[A^{\ominus}]_{init}$			0		1.0×10^{-7}
Change						
Equilibrium						
Equilibrium After Simplifying Assumptions						

$K_b =$

When is simplifying assumption safe? Use the >100K rule:	If $\frac{[\text{base}]_{init}}{K_b} > 100$ → simplifying assumption is safe

When the simplifying assumptions are used:	$\mathbf{K_b}= \frac{[HO^-]^2}{[A^-]_{init}}$	$\mathbf{[HO^{\ominus}]}=\sqrt{K_b \times [A^-]_{init}}$
When the first simplifying assumption is not used but the second one is	$K_b= \frac{[HO^-]^2}{[A^-]_{init} - [HO^-]}$	$[HO^{\ominus}]$ requires a quadratic solution

Applications

1. pH → K_b Strategy: pH → pOH → $[HO^{\ominus}]$ → K_b
2. K_b → pH Strategy: K_b → $[HO^{\ominus}]$ → pOH → pH

Problems: pH and K_b

1. pH → K_b What is K_b if a 0.123 M solution of a weak base gives pH=10.62?

2. K_b → pH If K_b for a weak base is 1.6×10^{-5}, what is the pH of a 0.222 M solution of the base?

E. Relationship Between K_a and K_b for Conjugate acids/bases (Section 16.7, p 794)

- Review: stronger the acid, weaker the conjugate base (and vice versa)

$$\boxed{K_a \times K_b = 1.0 \times 10^{-14}}$$ Review Table 16.2

1. Given one, can solve for other.
2. Tables routinely provide only one; expect you to solve for other
3. Can rank relative strengths of acids(or bases) given info about conjugates
4. Toughest problem: given K_a for conjugate acid, calculate pH for a solution of weak base
   - Logic: $K_a \rightarrow K_b \rightarrow [HO^{\ominus}] \rightarrow pOH \rightarrow pH$

Derivation of $K_aK_b = 10^{-14}$ (not responsible for derivation, just for interest)

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad K_b = \frac{[OH^-][HA]}{[A^-]}$$

$$\text{So } K_aK_b = \left(\frac{[H_3O^+][A^-]}{[HA]}\right)\frac{[OH^-][HA]}{[A^-]} = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus $\mathbf{K_aK_b = K_w = 10^{-14}}$

Acid Strength	**K_a**	**K_b**	**Strength of Conjugate Base**
Strong	$K_a > 1$	$K_b < 1 \times 10^{-14}$	Nonbasic
Weak	$1 \times 10^{-14} < K_a < 1$	$1 \times 10^{-14} < K_b < 1$	Weak
Nonacid	$K_a < 1 \times 10^{-14}$	$K_b > 1$	Strong base

Problems Involving Relationship between K_a and K_b for Conjugated Acid/Base

Substance	HF	HN_3	HCN
K_a	6.8×10^{-4}	1.9×10^{-3}	4.9×10^{-10}
Relative Acidity			
Conjugate Base			
Relative Basicity			
K_b			

1. Rank the acidity for the three weak acids, 1 being strongest.

2. Rank the basicity, 1 being the stongest, for: NaCN NaF NaN_3

Substance	HF	HN_3	HCN
K_a	6.8×10^{-4}	1.9×10^{-3}	4.9×10^{-10}
Conjugate Base			
K_b			

3. What is K_b for N_3^-?

4. What is pH for a solution that is 0.12 M in NaF^-?

Logic:

5. What is pH for a solution that is 0.20 M in NaCN?

Logic:

Polyprotic Acids: More than One H^+ Available (Section 17.4)

H_2SO_4, H_3PO_4, H_2CO_3,…

1. Each H^+ gets successively **less** acidic (by > 1000)

Relative Acidity	Acid		Conjugate Base	Relative Basicity
	H_3PO_4	$K_{a1} = 10^{-3}$	$H_2PO_4^-$	
	$H_2PO_4^-$	$K_{a2} = 10^{-8}$	HPO_4^{2-}	
	HPO_4^{-2}	$K_{a3} = 10^{-13}$	PO_4^{3-}	

2. As acids in water, only consider the first ionization.
3. When <u>base</u> is added, however, all H^+'s come off (stoichiometry permitting)

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$

But $H_3PO_4 + 3\ OH^- \rightarrow 3\ H_20 + PO_4^{3-}$

4. H_2SO_4: 1st strong, 2nd weak

$$H_2SO_4 \xrightarrow{\text{water}} H^+ + HSO_4^- \xrightleftharpoons{\text{water}} 2H^+ + SO_4^{2-}$$

none $\boxed{\text{Complete}}$ lot $\boxed{\text{weak}}$ little

5. Some anions are complex: both acidic and basic!!

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$HCO_3^- \xrightleftharpoons{H_20} OH^- + H_2CO_3$

Polyprotic Acid/Base Problems

1. Which is the stronger acid?

H_3PO_4 $H_2PO_4^-$

H_2SO_4 HSO_4^-

2. Which is the stronger base?

HCO_3^- CO_3^{2-}

HSO_4^- SO_4^{2-}

Polyprotic Acids: Each H becomes less acidic

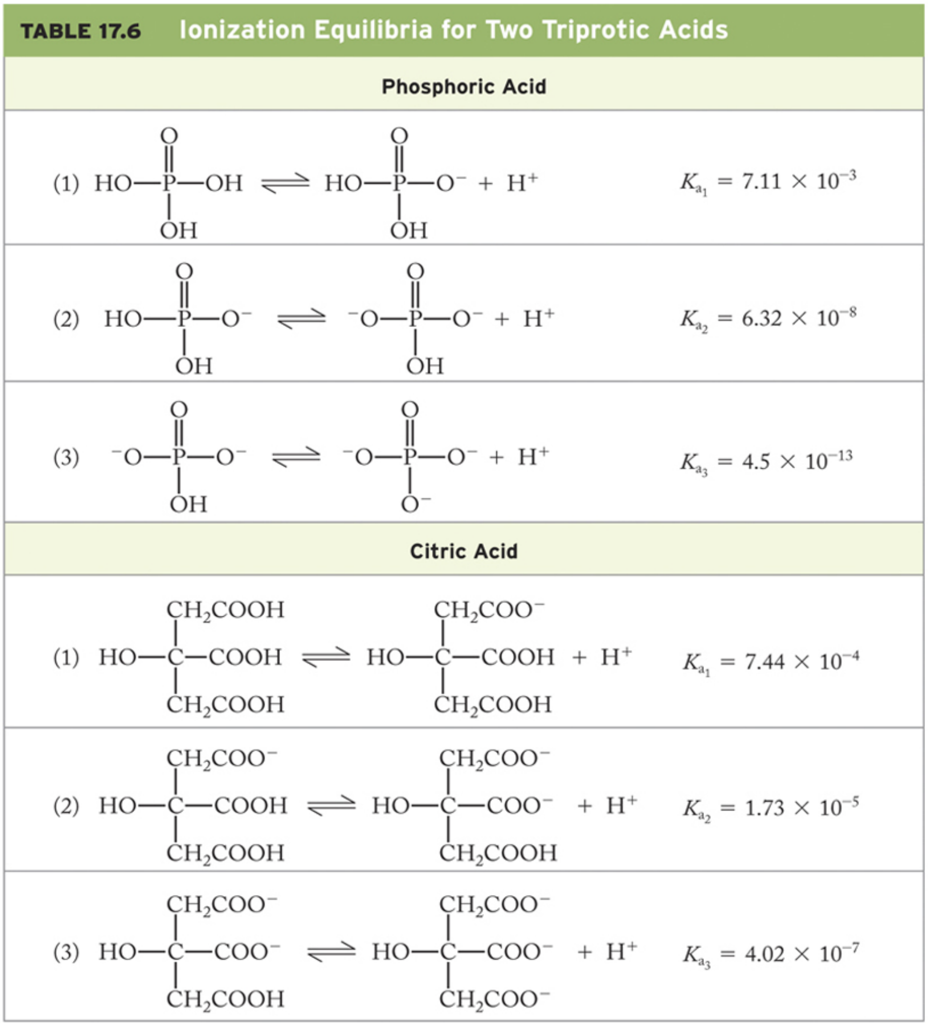


TABLE 17.6 Ionization Equilibria for Two Triprotic Acids

	Phosphoric Acid	
(1)	$\mathrm{HO{-}\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{P}}{-}OH \rightleftharpoons HO{-}\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{P}}{-}O^- + H^+}$	$K_{a_1} = 7.11 \times 10^{-3}$
(2)	$\mathrm{HO{-}\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{P}}{-}O^- \rightleftharpoons {}^-O{-}\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{P}}{-}O^- + H^+}$	$K_{a_2} = 6.32 \times 10^{-8}$
(3)	$\mathrm{{}^-O{-}\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{P}}{-}O^- \rightleftharpoons {}^-O{-}\underset{\underset{O^-}{\vert}}{\overset{\overset{O}{\Vert}}{P}}{-}O^- + H^+}$	$K_{a_3} = 4.5 \times 10^{-13}$
	Citric Acid	
(1)	$\mathrm{HO{-}\underset{\underset{CH_2COOH}{\vert}}{\overset{\overset{CH_2COOH}{\vert}}{C}}{-}COOH \rightleftharpoons HO{-}\underset{\underset{CH_2COOH}{\vert}}{\overset{\overset{CH_2COO^-}{\vert}}{C}}{-}COOH + H^+}$	$K_{a_1} = 7.44 \times 10^{-4}$
(2)	$\mathrm{HO{-}\underset{\underset{CH_2COOH}{\vert}}{\overset{\overset{CH_2COO^-}{\vert}}{C}}{-}COOH \rightleftharpoons HO{-}\underset{\underset{CH_2COOH}{\vert}}{\overset{\overset{CH_2COO^-}{\vert}}{C}}{-}COO^- + H^+}$	$K_{a_2} = 1.73 \times 10^{-5}$
(3)	$\mathrm{HO{-}\underset{\underset{CH_2COOH}{\vert}}{\overset{\overset{CH_2COO^-}{\vert}}{C}}{-}COO^- \rightleftharpoons HO{-}\underset{\underset{CH_2COO^-}{\vert}}{\overset{\overset{CH_2COO^-}{\vert}}{C}}{-}COO^- + H^+}$	$K_{a_3} = 4.02 \times 10^{-7}$

***Chemistry: The Science in Context* 3/e Table 17.6**

Acid-Base Properties of Common Salts

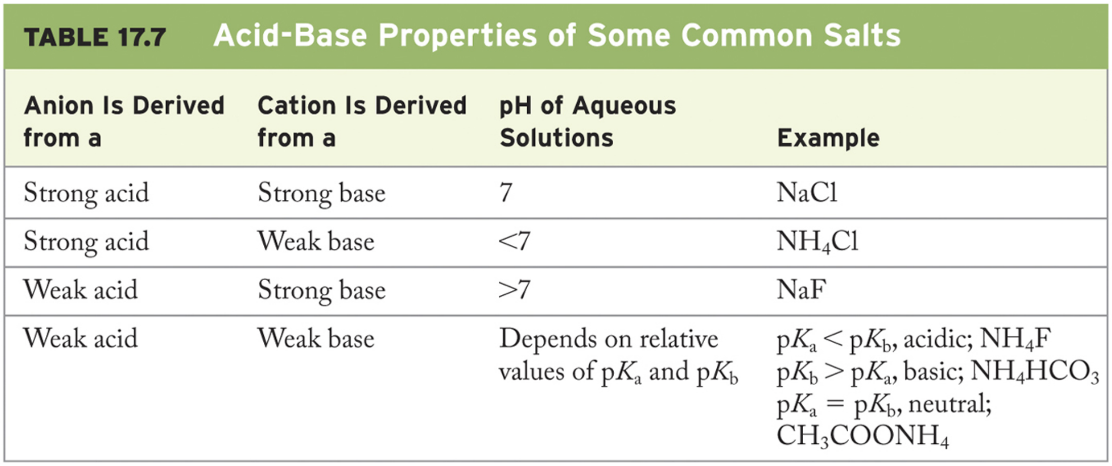


TABLE 17.7 Acid-Base Properties of Some Common Salts

Anion Is Derived from a	Cation Is Derived from a	pH of Aqueous Solutions	Example
Strong acid	Strong base	7	NaCl
Strong acid	Weak base	<7	NH_4Cl
Weak acid	Strong base	>7	NaF
Weak acid	Weak base	Depends on relative values of pK_a and pK_b	pK_a < pK_b, acidic; NH_4F pK_b > pK_a, basic; NH_4HCO_3 pK_a = pK_b, neutral; CH_3COONH_4

***Chemistry: The Science in Context* 3/e Table 17.7**

Acid-Base Properties of Salts (Ionic Compounds) (Section 17.6)

NH_4Cl	$MgBr_2$	NaCN
pH<7	pH=7	pH>7
acidic	neutral	basic

Recall: "salts" formed by acid/base reactions
"salt"=ionic

Example:	SA/SB	$HCl + NaOH \rightarrow H_20 + NaCl$	neutral
	WA/SB	$HF + NaOH \rightarrow H_2O + NaF$	basic
	SA/WB	$HCl + NH_3 \rightarrow NH_4^+Cl^-$	acidic
	WA/WB	$HF + NH_3 \rightarrow NH_4^+F^-$	can't tell

Observations:

1. Salts can be acidic, basic, or neutral.
2. Depends on strengths of acids/bases from which they form.
3. The "ions" in the salts are conjugates; may be acidic or basic!!

A. General Logic to Predict: Identify Ions individually. Check Cation, then Anion.

1. Cations: acidic or neutral
   a. Group I or II metal cations are neutral
      Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}, …
      No impact on pH
   b. Ammoniums are acidic
      NH_4^+, $CH_3NH_3^+$ etc.
   c. Al^{3+}, T-metal cations are acidic in water. (Not for test)

$$Al^{3+} \rightarrow [Al(H_2O)_6]^{3+} \rightleftharpoons H^+ + [Al(OH)(H_20)_5]^{2+}$$

Weak acid

For test purpose, assume metal cations are neutral, ammonium cations acidic

2. Anions: basic or neutral
   a. Neutral: conjugates of strong acids
      Cl^-, Br^-, I^-, NO_3^-, ClO_4^-
   b. basic: conjugates of weak acids (or non acids)
      F^-, ClO^-, …
3. "Amphoteric" anions derived from polyprotic acids: can be acidic or basic
   -not test responsible
   HCO_3^-, $H_2PO_4^-$, HSO_3^-

B. Predicting acidic/neutral/basic (qualitatively)

Cation	anion	salt solution	example
Neutral	neutral	neutral	NaCl, KNO_3
Acidic	neutral	acidic	NH_4Cl, $Fe(NO_3)_3$
Neutral	basic	basic	NaF, K(ClO)
Acidic	basic	can't predict (without K's)	NH_4F, $Fe(N_3)_3$

Predicting Acid/Base Character for Ionic Formulas

1. Predict as acidic, basic, neutral, or can't tell.

a. Na_2SO_3

e. $NaNO_3$

b. $MgCl_2$

f. KN_3

c. NH_4CN

g. Li_2CO_3

d. $Ba(NO_3)_2$

h. CH_3NH_3Br

2. Rank the following in terms of increasing pH, 1 being the lowest. (ID as strong/weak acid, strong/weak base, or neutral first!)

$NaCl$ NH_4Cl ZnF_2 HNO_3 KOH

Molecular Structure and Acid/Base Strength (17.5)

- Why is something strong or weak? Acidic or Basic? Can we predict from structure,without K's?

A. Key Factors on Acid Strength

1. **Stability of conjugate A$^{\ominus}$ and Electronegativity*******
   - Think Anion!
   - Think electronegativity and -electron love

   $CH_4 \rightarrow H^+ + {}^{\ominus}CH_3$ Horrible. Carbon not electronegative, can't handle $\ominus$

   $HF \rightarrow H^+ + F^{\ominus}$ Way stronger. Fluorine electronegative, can handle $\ominus$

2. H-A bond strength: stronger → less acidic
   - Why H-F (strong bond) is weak acid, but H-Cl, H-Br, H-I are strong acids
   - Row 2 bonds (H-F, O-H, N-H, C-H) usually stronger than row 3,4 analogs

3. Resonance
   - For two oxyanions, one with resonance is more stable than one without

B. Practical Pattern

1. Horizontal Periodic Pattern: Acidity increase left → right

	CH_4	NH_3	H_2O	HF
K_a	10^{-50}	10^{-32}	10^{-14}	10^{-4}

Note: e^- love, electronegativity/bond-polarity, anion stability all agree

Rank: Acidity of: SiH_4 SH_2 HCl PH_3

2. Vertical Periodic Pattern: Acidity Increases Top → Bottom
   -due to decreasing H-A bond strength (even though contrary to e^- love)

   $HF < HCl$

   Weak strong

   $H_2O < H_2S < H_2Se$

   $K_a=10^{-14}$ 10^{-9} 10^{-6}

Note: Basicity of conjugates linked!!

Horizontal: ${}^{\ominus}NH_2 > F^{\ominus}$ Vertical: $F^{\ominus} > Cl^{\ominus}$

C. "Oxoacids" : "**Extra" Oxygens's increase acidity** (17.5)

$HClO_4 > HClO_3 > HClO_2 > HClO$	$H_2SO_4 > H_2SO_3$
Strong weak	strong weak

Why? Extra electron-loving oxygen

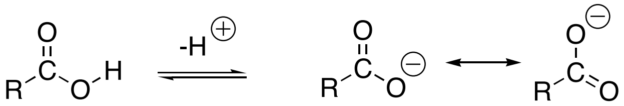
1. Stabilizes resulting anion
2. Polarizes O-H
3. Weakens O-H

- **Any Neutral Oxoacid with ≥ 2 extra O's is a strong Acid**
  - Compare how many oxygens there are versus hydrogens

Strong: H_2SO_4, $HClO_3$ weak: H_2CO_3, H_3PO_4, H_2SO_3

Carboxylic Acids: Famous class of oxoacids: RCOOH or RCO_2H (R is usually an H or a carbon chain.)

- Resonance stabilization of conjugate anion makes the anion more stable



Predicting Acid/Base Properties and Trends Why?

1. Which are acidic vs. basic vs. neutral in water?

   $HClO_3$ CH_3COOH CH_3NH_2 $Ca(OH)_2$

2. Rank Acidity (1 strongest)

   HF H_2O H_2SO_4 CH_4

3. Rank Acidity (1 strongest)

   $HClO_4$ $HClO_3$ H_2SO_4 H_2SO_3

4. Rank Acidity (1 strongest)

   H_2O H_2S H_2Se

5. Rank Acidity (1 strongest)

   HBr H_2Se H_3As H_4Ge

6. Which would be stronger?

   $HBrO_3$ vs $HBrO$

7. Rank Basicity (1 strongest)

   $^{\ominus}CH_3$ $^{\ominus}NH_2$ $^{\ominus}OH$ $F^{\ominus}$

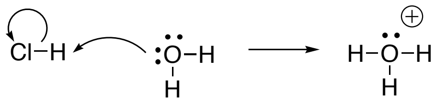
8. Rank Basicity (1 strongest)

   HPO_4^{2-} $H_2PO_4^{\ominus}$ $HSO_4^{\ominus}$

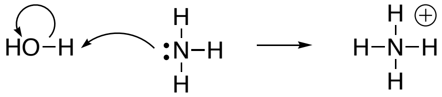
Lewis Acids and Bases: focus on electron pairs, not H^+ movement. (18.1)

Lewis acid: e- pair acceptor **Lewis base: e- pair donor**	Covers "acid-base" chemistry that doesn't involve H^+

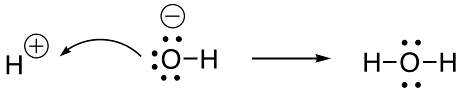
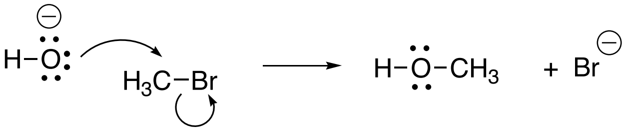
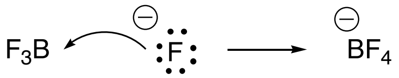
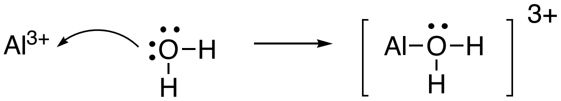
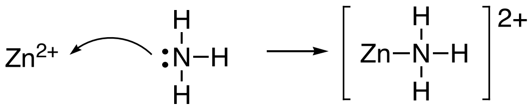
Water as Lewis Base: Uses an Oxygen Lone Pair



Water as Lewis Acid: Accepts Lone Pair



Other Examples

a. 	b. 
c. 	d.  How metal hydrates form
e. 	

Notes: 1. A "base" must have a lone pair
(F^-, OH_2, NH_3, ...)
2. All anions have lone pairs → Lewis Base potential
3. An "acid" must be able to accept a lone pair
-all cations can!!
-some neutrals: BF_3, SO_2, …

Lewis Acid/Base Problems

1. Which would not be a Lewis acid?

$AlCl_3$ Ti^{4+} $NO_3^{\ominus}$ $ZnSO_4$

2. Identify the Lewis acid and Lewis Base

a. $Fe^{3+} + 6\ H_2O \rightarrow [Fe(H_2O)_6]^{3+}$

b. $H^+ + CH_3NH_2 \rightarrow CH_3NH_3$

c. $Br\text{-}CH_3 + I^{\ominus} \rightarrow Br^{\ominus} + I\text{-}CH_3$

d. $Ni^{2+} + 4\ N_3^{\ominus} \rightarrow [Ni(N_3)_4]^{2-}$

CH. 16 Acid-Base Chemistry Math Review

Key Equations, Numerical Relationships

1. $[H^+][HO^-] = 1.00 \times 10^{-14}$

2. $pH = -\log[H^+]$

   $[H^+] = 10^{-pH}$ (on calculator, enter –pH, then punch the **10^x** button)

   $pOH = -\log[OH^-]$

   $[OH^-] = 10^{-pOH}$ (on calculator, enter –pOH, then punch the **10x** button)

3. $pH + pOH = 14$ $pH = 14 - pOH$

Weak acid problems

$K_a = [H^+][A^-]/[HA]$ but when HA is placed in water, $[H^+] = [A^-]$ so:

When the simplifying assumptions are used:	**4.** $K_a = \dfrac{[H^+]^2}{[HA]_{init}}$	**5.** $[H^{\oplus}] = \sqrt{K_a \times [HA]_{init}}$
When the first simplifying assumption is not used (but the second one is)	6. $K_a = \dfrac{[H^+]^2}{[HA]_{init} - [H^+]}$	$[H^{\oplus}]$ requires a quadratic solution

7. Quadratic Equation: for $ax^2 + bx = c = 0$ $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Weak base problems

$K_b = [Base\text{-}H^+][OH^-]/[Base]$ but when Base is place in water, $[Base\text{-}H^+] = [OH^-]$ so:

When the simplifying assumptions are used:	**8.** $K_b = \dfrac{[HO^-]^2}{[Base]_{init}}$	**9.** $[HO^{\ominus}] = \sqrt{K_b \times [Base]_{init}}$
When the first simplifying assumption is not used but the second one is	10. $K_b = \dfrac{[HO^-]^2}{[Base]_{init} - [HO^-]}$	$[HO^{\ominus}]$ requires a quadratic solution

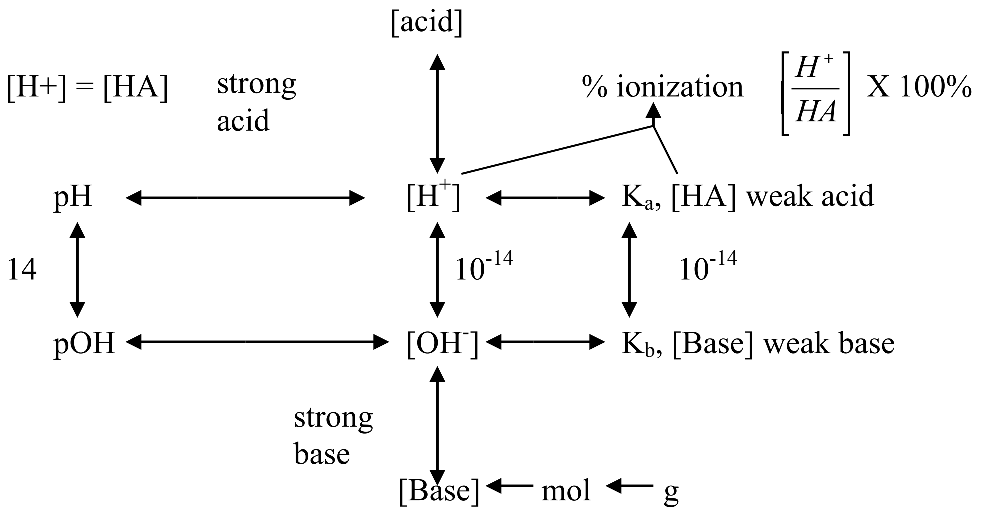
11. $K_aK_b = 10^{-14}$ for a conjugate acid/base pair.

Note: This relationship is routinely used when a K value for your acid or base is not provided, but the K value for it's conjugate is. So get it indirectly.

Some Calculation Logic Scenarios

1. Strong acid → pH [Strong acid] → $[H^{\oplus}]$ → pH
2. Strong base → pH [Strong base] → $[HO^{\ominus}]$ → pOH → pH
3. Weak acid + K_a → pH [Weak acid] + K_a → $[H^{\oplus}]$ → pH
4. pH of weak acid → K_a pH → solve for $[H^{\oplus}]$ → K_a
5. Weak base + K_b → pH [Weak base] + K_b → $[HO^{\ominus}]$ → pOH → pH
6. pH of weak base → K_b pH → solve for $[HO^{\ominus}]$ → pOH → pH
7. Weak base + K_a of conjugate acid → pH K_a → K_b → $[HO^{\ominus}]$ → pOH → pH

Simple Acid-Base Concept Map



Ch. 17b Additional Aqueous Equilibria

- Chapter 17a situations basically only involved one solute: strong or weak acid; strong or weak base; or ionic salt
- Real solutions often have >1 solute
  - ⇒more complex equilibria, pH calculations
  - ⇒extra solute impacts degree to which first chemical dissociates

3 general multi-solute situations:

1. buffers: weak acid and weak base mixture, to which strong acid or base may be added
2. titration: mixing acid and base, at least one of which is normally strong
3. partially soluble solids: impact of pH or other salts on solubility

17.7,8 Buffer solutions: resist change in pH when either acid or base added

- Crucial in nature: blood pH, lake pH, etc. must be tightly controlled.
- Blood: pH ≈7.40 ± 0.05
  - pH < 7.35 → acidosis pH > 7.45 → alkalosis
- The body needs a system for keeping the blood at the target pH, and protecting it from the extreme pH disruption that could result from addition of acid or base
- Many cellular processes likewise depend on precise control of pH
- Buffers provide protection against the addition of H^+ or HO^-

1. Unbuffered: Find pH

a. 1.0 L pure water

b. 1.0 L water + 0.1 mol HCl

c. 1.0 L water + 0.1 mol NaOH

Point: In an unbuffered, unprotected solution, a small addition of strong acid or base can cause a massive and dangerous shift in pH.

A. Reaction of strong acid with weak base. Background Facts:

•While it reacts only slightly with water, a weak acid reacts **almost completely** with strong base
•While it reacts only slightly with water, a weak base reacts **almost completely** with strong acid

WB + water:	$NH_3 + H_2O \rightleftharpoons NH_4^{\oplus} + HO^{\ominus}$	$K = 1.8 \times 10^{-5}$
WB + SA:	$NH_3 + HCl \rightleftharpoons NH_4^{\oplus} + Cl^{\ominus}$	$K = 1.8 \times 10^{+9}$
WA + water:	$HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus}$	$K = 6.8 \times 10^{-4}$
WA + SB:	$HF + NaOH \rightleftharpoons H_2O + NaF$	$K = 6.8 \times 10^{+10}$

1. Key: Strong acid $H^{\oplus}$ can be consumed by weak base.
- Strong acid is replaced by weak acid HCl (SA) in, $NH_4^{\oplus}$ (WA) out

2. Strong base $HO^{\ominus}$ can be consumed by weak acid
- The strong base is replaced by weak base NaOH (SB) in, NaF (WB) out

B. Buffer Action: A buffer system contains both a weak acid (to neutralize any added $OH^{\ominus}$) and a weak base (to neutralize any added $H^{\oplus}$)

- normally the weak acid and weak base are conjugates
- normally they are present in approximately equal quantities, but not always

1. **Since a strong acid reacts with a weak base to produce a weak acid, addition of strong acid results in a weak increase in acidity rather than a strong increase**
2. **Since a strong base reacts with a weak acid to produce a weak base, addition of strong base results in a weak increase in basicity rather than a strong increase**

C. The pH of buffer solutions: Ka, pKa, H^+, pH

1. Formula

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus} \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

rearrange: $$\boxed{\mathbf{pH = pK_a + \log\frac{[base]}{[acid]}}}$$ "**Henderson-Hasselbalch Equation**"

$pK_a = -\log K_a$
$K_a = 10^{-pK_a}$

Practical note: the base/acid ratio can be entered in moles/moles or in molarity/molarity, whichever is easier and more accessible
• since the volume is common to both base and acid

2. Some Practical Simple Stuff

a. A buffer pH depends on:
   1. **pK_a which depends on K_a (weak acid strength)**
   2. **Base/acid ratio**

b. If you have a target pH that you want for a solution, choose an acid with the appropriate K_a and pK_a

c. If the base/acid ratio = 1, then pH = pK_a

- **This is a helpful reference: basically the pH ≈ pK_a, adjusted to the basic or acidic side of pK_a depending on whether you have more of the base or of the acid**
   - **a. More base than acid: → pH number is higher (more basic) than pK_a**
   - b. **Less base than acid: → pH number is lower (more acidic) than pK_a**

d. **Adding base** increases the weak base/weak acid ratio, and **makes the pH more basic**
e. **Adding acid** decreases the weak base/weak acid ratio, and **makes the pH more acidic**

C. Buffer Capacity: determined by the quantity of weak acid/base
-dictates how much strong acid/base is consumed before buffer exhausted
-if more strong acid(base) is added than there is weak base(acid), the capacity is exceeded.

Consider 1.0 L water. Determine the pH's for the following solutions.

1. A solution with 0.5 moles of HF? (K_a for HF = 6.8×10^{-4})

Scenario

2. A solution with 0.5 moles of NaF?

Scenario

3. A solution with 0.5 moles of HF and 0.5 moles of NaF? (K_a for HF = 6.8×10^{-4})

Scenario

4. A solution with 0.5 moles of HF and 0.5 moles of NaF, to which 0.1 moles of HCl is added?

Scenario

5. A solution with 0.5 moles of HF and 0.5 moles of NaF, to which 0.1 moles of NaOH is added?

Scenario

Tips:
1. Diagnose the scenario
2. **For a buffer, use Henderson-Hasselbalch equation**
3. **When strong acid or base is added to a buffer, write out the reaction that would occur with the strong acid or base on the left side, and then work out the ICE change.**

D. Creating/Recognizing a Buffer

-must have or end up with **weak acid/weak base** pair

1. Mix some weak acid with it's conjugate weak base (most common)

HF, NaF H_3PO_4, NaH_2PO_4 $NaHSO_4$,Na_2SO_4 CH_3COOH, CH_3COONa NH_4Cl, NH_3

2. Start with only one of conjugate pair, but create some of the other by adding less than an equivalent amount of strong acid or strong base to create the other (harder to recognize)

Begin	Add(1/2 as much)	Result
Weak Acid	Strong Base	weak acid + conj base
Weak Base	Strong Acid	weak acid + conj base

Ex 1:	HF +	NaOH	$\rightleftharpoons$	H_2O +	NaF
I	0.4 moles	0.20 moles			0
C					
E					

Ex 2:	NH_3 +	HCl	$\rightleftharpoons$	$NH_4^+Cl^-$
I	0.6 mol	0.3 mol		0
C				
E				

Note: doesn't work if you add too much strong acid/base:

Ex 3 (failure):	NH_3 +	HCl	$\rightleftharpoons$	$NH_4^+Cl^-$
I	0.6 mol	0.6 mol		0
C				
E				

Buffer Recognition Practice

1. Which combos would make a buffer solution?

a. HF, KF

b. NH_4Cl, NH_3

c. HCl (0.2 M), NaN_3 (0.4 M)

d. HCl (0.2 mol), NaN_3 (0.1 M)

e. HN_3, NaCl

f. KF, NaF

g. KF, NaOH

h. HF, HCl

i. NH_3, KF

j. HF (0.2 mol), NaOH (0.1 mol)

Key: a) two acids don't work b) two bases don't work
c) an acid and a base is required d) tricky: strong and weak mixtures react, sometimes resulting in a buffer combination (both weak acid and weak base, examples c and j), but sometimes not, depending on ratios (example d)

2. Which could be added to 0.4 mol Na^+CN^- to give a buffer?

a. HCN

b. 0.2 mol HCl

c. 0.2 mol NaOH

d. 0.5 mol HCl

3. Which could be added to 0.4 mol H_3PO_4 to give a buffer?

a. NaH_2PO_4

b. 0.2 mol NaOH

c. 0.4 mol NaOH

d. 0.2 mol HCl

e. KCl

E. Simple Buffer Calcs

a. find pH Logic: $K_a \rightarrow pK_a \rightarrow pH$
b. find K_a Logic: $pH \rightarrow pK_a \rightarrow K_a$
c. solve for quantity of acid or base needed for target pH
Logic: pH and pK_a → base/acid ratio → needed quantity to achieve that ratio

$$\boxed{pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}}$$ "Henderson-Hasselbalch Equation"

- remember: mole/mole ration works as well as molarity/molarity ratio for base/acid

1. **Finding pH**. Find pH for buffer 0.12 M HNO_2, 0.16M $NaNO_2$ $K_a(HNO_2) = 4.5 \times 10^{-4}$

2. **Finding pK_a**. [HA] = 0.11 M [NaA] = 0.13 M. What is K_a for HA if pH = 5.18?

3. **Finding quantity of acid or base**. How many grams of NaF (42 g/mol) should be added to 612 mL solution of 0.4 M HF ($K_a = 6.8 \times 10^{-4}$) to produce a buffer solution in which pH = 3.10?

Logic:

F. pH Changes after Strong Acid or Strong Base is added to a Buffer Solution

(note: the following is written in terms of adding strong acid. Use analogous strategy for addition of strong base)

1. Write out the reaction of the added strong acid with the buffer's weak base
2. Make out an ICE-type table to show how the quantities of weak base and weak acid change as a result of the reaction
   a. Remember that a strong acid basically reacts completely with the weak base
   b. It's often best to do the ICE in terms of moles rather than molarity
   c. The "E" at the end is really the "End" of the acid-base reaction. It may not represent equilibrium
3. **Assess the situation at the end of the ICE analysis. 3 Scenarios**
   a. Are both weak acid and weak base present?
      - buffer situation → Use HH equation

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}}$$

   b. Is only weak acid left? (the strong acid exhausted the weak base?)
      - weak acid situation → use Ch. 17a procedure.
      - Be sure your weak acid is in terms of molarity, and factors in the combined volumes

$$[\mathrm{H}^{\oplus}] = \sqrt{K_a \times [\text{weak acid}]}$$

   c. **Is strong acid as well as weak acid left?** (The strong acid exhausted the buffer's weak base, and you still have some strong acid left over?)
      - Strong acid situation
      - Be sure your strong acid is in terms of molarity, and factors in the combined volumes

$$[\mathrm{H}^{\oplus}] = [\text{strong acid}]$$

Note: Scenario "a" is when the buffer capacity is not exhausted, and you still have a buffer situation at the end. **Scenario's "b" and "c" both represent cases where the buffer capacity is exhausted**, and you do **not** have a buffer scenario at the end of the reaction.

Problems

Given a 1.0 L solution that is initially 0.2 M in both HF and KF, assess the situation and find the pH after the following acids or bases are added.

a. 0.1 mol HCl added Assess:

Reaction:

I

C

E

Problems

Given a 1.0 L solution that is initially 0.2 M in both HF and KF, assess the situation and find the pH after the following acids or bases are added.

b. 0.1 mol NaOH added Assess:

Reaction:

I

C

E

c. 1.0 L of 0.20-M HCl added Assess:

Reaction:

I

C

E

E

d. 1.5 L of 0.20-M mol NaOH added Assess:

Reaction: Web answer key has error on this one, fix

I

C

E

E

17.10 Acid-Base Titration

1. An acid and a base are mixed, at least one being strong
2. “**equivalence point**” or “**end point**:” equal moles of acid/base
3. Indicator often used to turn color, or pH meter used to give “titration curve”
4. pH meter often used. (Lab will use both pH meters and color indicators)
5. **Unlike buffer, pH changes sharply near endpoints**

A. Endpoint Situations: Qualitative, Non-Math Version

Acid In	Base In	Conjugate Acid Out	Conjugate Base Out	Endpoint Outcome	Endpoint pH	Example
Strong Acid	Strong Base	Non-acid	Non-base	Neutral	pH = 7.0	1
Strong Acid	Weak Base	Weak acid	Non-base	Weakly acidic	pH < 7.0	2
Weak Acid	Strong Base	Non-acid	Weak base	Weakly basic	pH > 7.0	3

Example		Endpoint pH
1	HCl + NaOH →	
2	HCl + NaCN →	
3	HF + NaCN →	

1. Would the pH at endpoint be acidic, basic, or neutral when titrated with NaOH?

a. HCN

b. HNO_3

c. HF

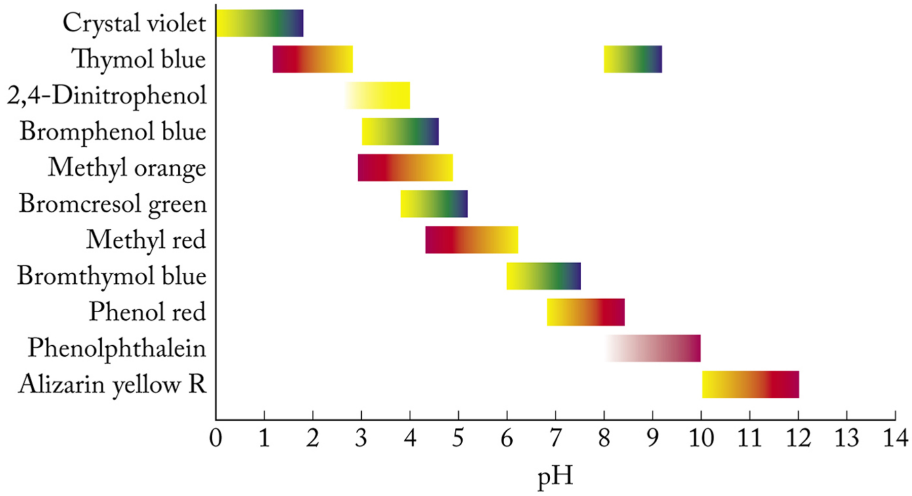
2. Would pH at endpoint be acidic, basic, or neutral when titrated with HCl?

a. NaOH

b. NaF

Some Indicators, and Where they Change pH

- **Phenolphthalein is by far the most famous and common**
- Most have a limited range over which they turn color. You're either on the acid side (one color) or base side (different color). But you can't tell exactly which pH you're at.
- "Universal Indicator" has a mixture, so that your color changes from pH 4 to 5 to 6 etc.
- Note for Organic Lab future: ☺ Indicators and pH paper only work in aqueous solvents



Chemistry: The Science in Context 3/e Figure 17.15
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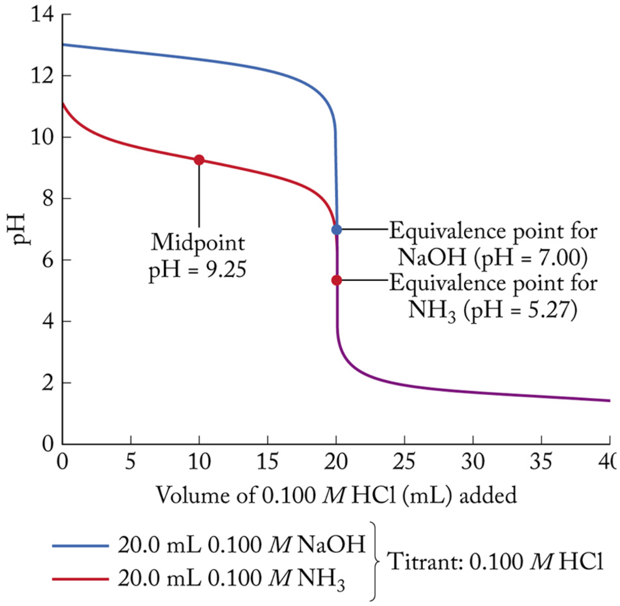
Sample Titration Curves



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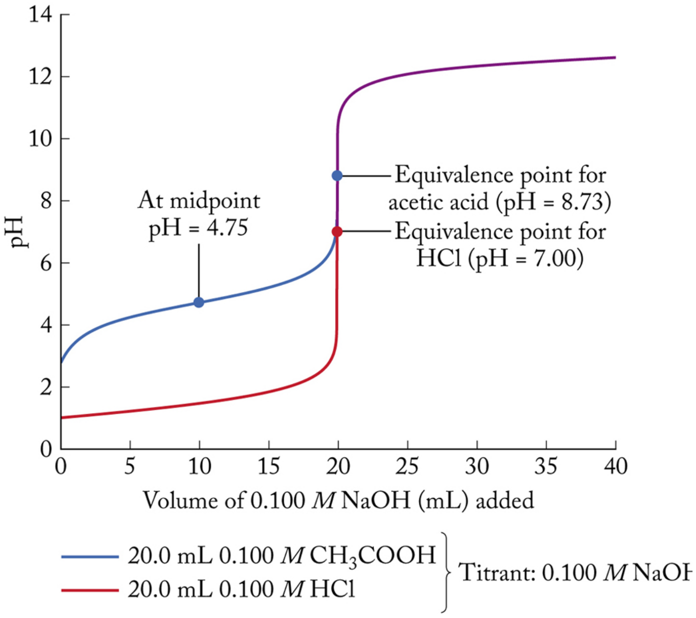

Chemistry: The Science in Context 3/e Figure 17.18
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Notes:

1. Sharp pH change near endpoints
2. Mark the character of original chemical (SA, WA, SB, WB), and what was added (SB or SA)
3. Midpoint starting from WA or WB: Buffer! $pH = pK_a$
4. Buffer capacity exhausted at endpoint
5. pH at Equivalence point: 7 for SA/SB titrations, but not when starting from WA or WB

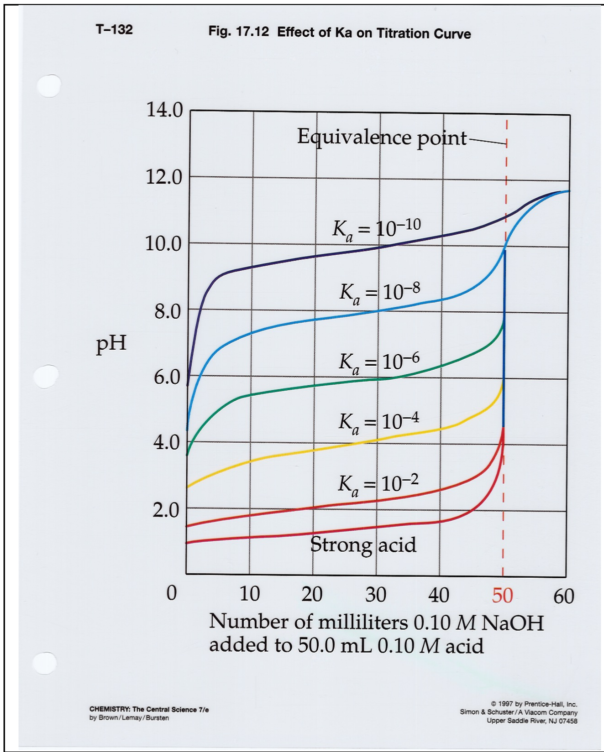
B. Calculation of pH at the **<u>Endpoint=Equivalence Point</u>** for a Titration

- Review: at endpoint equal moles of acid and base have been added. At least one of them was a strong acid or base, and possibly both.
- <u>Three Possible Scenarios</u>

Acid In	Base In	Endpoint Outcome	Endpoint pH	pH Strategy
Strong Acid	Strong Base	Neutral	pH = 7.0	None needed, pH = 7
Strong Acid	Weak Base	Weak acid	pH < 7.0	$K_a \rightarrow [H^+] \rightarrow pH$
Weak Acid	Strong Base	Weak base	pH > 7.0	$K_a \rightarrow K_b \rightarrow [OH^-] \rightarrow pOH \rightarrow pH$

<u>Problem</u>: What is the pH after 40 mL of 0.10-M NaOH is added to 20 mL of 0.20-M HClO? (The K_a for HClO = 3.0×10^{-8})

<u>C. Titration Curves: a plot of how pH changes as strong acid is added to a solution of base, or as a strong base is added to a solution of acid</u>


T–132 Fig. 17.12 Effect of Ka on Titration Curve

CHEMISTRY: The Central Science 7/e by Brown/Lemay/Bursten

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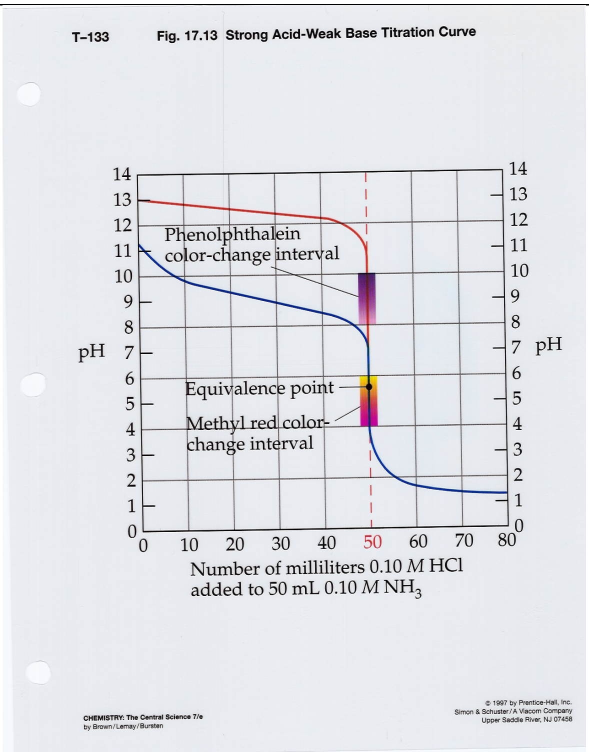
T–133 Fig. 17.13 Strong Acid-Weak Base Titration Curve

CHEMISTRY: The Central Science 7/e by Brown/Lemay/Bursten

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2 Key Diagnostic features:

1. Initial pH
   - Acidic or basic? Strong or weak?
   - This reflects what you started with, before you titrate it with the strong acid or base.

Initial pH	pH < 2	2 < pH < 7	7 < pH < 12	12 < pH
Initial acid/base				

2. The endpoint/equivalence point pH
   - Acidic, neutral, or basic?
   - **If the equivalence point is pH=7, then both the acid and the base involved were STRONG**
   - If the equivalence point is NOT pH=7, then either the acid or the base involved in the titration was WEAK

Odds n ends

1. Endpoint pH is where pH changes most steeply, rapidly
2. When a weak acid is titrated by a strong base, the titration involves an extended "buffer zone" prior to the end-point, during which the pH change is rather gradual
   a. Prior to the endpoint, some of the weak acid is converted to weak base, so a conjugate weak acid/weak base buffer situation exists.
   b. The analogous situation happens when a weak base is titrated by a strong acid
3. When a weak acid "HA" is titrated by a strong base, at the half-way point (half-way to the end-point), half of the original weak acid HA is converted to its weak conjugate base A^-
   - At this point, the pH = pK_a (see HH-equation when [base]/[acid] = 1)
   - The analogous situation happens when a weak base is titrated by a strong acid

Problems

1. An initial pH = 1.3 and an equivalence point of 7 corresponds to a titration curve in which a __

__________________________ is added to a __________________________.

2. An initial pH = 9.3 and an equivalence point of 4.7 corresponds to a titration curve in which a

__________________________ is added to a __________________________.

D. Titration Calculations Involving Endpoint/Equivalence Point

Key: At equivalence point, moles acid = moles base

- know one ⇒ know other

Applications

1. Find volume required
2. Determine unknown concentrations
3. Determine unknown grams

Problems

1. What volume of 0.12 M NaOH is needed to titrate 36 mL of 0.14 M HCl to its endpoint?

2. When 42 mL of aqueous HCl is titrated by 0.10 M NaOH, it takes 25 mL of the NaOH solution to reach the endpoint. What is the [HCl] of the original solution?

3. How many grams of KOH (56 g/mol) would it take to neutralize 86 mL of 1.2 M HNO_3?

E. General pH Strategy: Finding the pH after Acid or Base is added to a solution

- Whether it be to a buffer solution, a strong acid solution, a weak acid solution, a strong base solution or a weak base solution prior to the new addition
- The strategy is similar to when we added acid or base to a buffer

1. Write out the acid-base reaction
   - It helps to recognize which species are acidic or basic or neutral, and weak or strong
2. Calculate the initial moles
   - Number of moles = molarity x volume (in Liters)
3. Use ICE to determine post-reaction ("E") moles
4. **Assess the post-reaction situation, based on what's left at the end**
5. Solve the pH problem from there

	Post-Reaction Situation		
1	Strong acid only	$[H^+] = [SA]$	
2	Strong acid plus weak acid	$[H^+] = [SA]$	Ignore WA, which makes insignificant contribution
3	Strong base only	$[HO^-] = [SB]$	
4	Strong base plus weak base	$[HO^-] = [SB]$	Ignore WB, which makes insignificant contribution
5	Weak acid only	$[H^+] = \sqrt{K_a x[WA]}$	Qual: pH < 7
6	Weak base only	$[HO^-] = \sqrt{K_b x[WB]}$	Qual: pH > 7 May need to find K_b from K_a
7	Weak acid plus weak base	$pH = pK_a + \log \frac{[base]}{[acid]}$	Buffer solution
8	No acid or base; only neutral salts	pH = 7.0	

- For many of these, it will be necessary to calculate molarities
- To do this, make sure that you factor in the total, combined volume

Key: Recognizing the Final Situation!!

Strong base added to weak acid. (Strong acid/weak base combinations would be analogous.)
What is the situation and what is the pH after:

A. **Equal Base**: 20 mL of 0.10 M NaOH is added to 20 mL of 0.10 M HClO? (Ka = 3.0×10^{-8})

B. **Excess Base**: 20 mL of 0.10 M NaOH is added to 10 mL of 0.10 M HClO?

C. **Excess Acid**: 20 mL of 0.10 M NaOH is added to 30 mL of 0.10 M HClO? (Ka = $3.0 * 10^{-8}$)

F. What Happens when a Strong Acid is Added to a Weak Acid? Addition of strong acid to a weak acid solution. (Analog would be strong base to weak base)

1. **Weak Acid Prior to Addition of Strong Acid:** A solution has 1 L of 0.40 M acetic acid (K_a = 1.80 x 10^{-5}). Find the pH and [CH_3COO^-]

Ex: $HA \rightleftharpoons H^+ + A^-$

I

C

E

2. **Weak Acid then Addition of Strong Acid:** Suppose 0.10 moles of HCl is added to the above solution (assume no change in volume). Find the pH and [CH_3COO^-]

Ex: $HA + \qquad \rightleftharpoons H^+ + A^-$

I

C

E

Notice:

1. **The strong acid dominates the pH**
2. **When a weak acid is in water by itself, then [H^+] = [A^-]**
3. **But when strong acid was added (as an additional source of [H^+],) [H^+] >> [A^-]**
4. **The equilibrium constant still applies. With [H^+] up, [A^-] goes down, ala LeChatelier's principle**

17.9 Solubility Equilibria for Ionic Compounds: K_{sp}

- The solubility of ionic compounds is a big deal, from kidney stones to drinking water to stalagtites and stalagmites

A. K_{sp} "Solubility Product Constant"

- **In a "saturated solution," insoluble solid is in equilibrium with aqueous ions**
- Easy to write K expressions, since aqueous ions appear but solid starting chemical doesn't

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ K=

I

C

E (doesn't matter,
not in K!!)

B. Various K_{sp} setups, depending on Formulas and Number of Cations/Anions Produced. Assuming no other source of ions other than from the solid itself.

1. $AgCl(s) \rightleftharpoons$ K =

2. $Zn(OH)_2(s) \rightleftharpoons$ K =

3. $ScCl_3(s) \rightleftharpoons$ K =

4. $Al_2(SO_4)_3(s) \rightleftharpoons$ K =

Points:

1. Manipulating equations with x^3 or x^4 is common!
2. **While the solid itself doesn't appear in the K expression, the value of "x" does tell how many moles/L of the original solid can dissolve.**
    - If you know how many moles/Liter of product solute is present, you know how many moles/Liter of parent solid actually dissolves

C. Technical note: often K_{sp} problems end up with x^3 or x^4 type terms. What does this mean and how do I solve them?

- Ex 1: $x^3 = 100$ meaning: x times x times x = 100. Or, $x = 100^{1/3}$ ($x = 4.64$)
    - Calculator: find your calculator's $\sqrt[x]{y}$ key, enter 100 for "y" and 3 for "x"
    - In other words, solve as $x = \sqrt[3]{100}$
    - On my Texas Instruments Calculator (yours may differ):
        - enter 100 first
        - click the $\sqrt[x]{y}$ key second
        - enter 3 third

- Ex 2: $0.26^3 = x$ meaning: 0.26 times 0.26 times 0.26 = x. ($x = 0.0176$)
    - Calculator: find your calculator's y^x key, enter 0.26 for "y" and 3 for "x"
    - On my Texas Instruments Calculator (yours may differ, x^y for Casio?):
        - enter 0.26 first
        - click the y^x key second
        - enter 3 third

Calculator Practice

x equals

1. $x^3=125$
    - enter 125
    - click the $\sqrt[x]{y}$ key
    - enter 3
2. $x^3=200$
3. $x^4=12.7$

x equals

4. $12^3=x$
    - enter 12
    - click the y^x key
    - enter 3
5. $8^4=x$
6. $3.2^3=x$

D. Definitions

1. **"Solubility": g/L of solid that dissolves**
2. **"Molar solubility": mol/L of solid that dissolves**

- For problems, always be aware of whether you're dealing with g/L or mol/L

E. Interconverting Solubility and K_{sp}: Calculations

1. Working from K_{sp} to solubility:

K_{sp} $\rightleftharpoons$ moles/L of ions $\rightleftharpoons$ moles/L of solid $\rightleftharpoons$ (g/L) of solid

2. Working from solubility to K_{sp}:

Solubility of compound (g/L) $\rightleftharpoons$ Molar solubility of compound (mol/L) $\rightleftharpoons$ Molar concentration of ions $\rightleftharpoons$ K_{sp}

Working from K_{sp} to solubility:

K_{sp} $\rightleftharpoons$ moles/L of ions $\rightleftharpoons$ moles/L of solid $\rightleftharpoons$ (g/L) of solid

1. $PbCl_2$ (278 g/mol) $K_{sp}=1.6 \times 10^{-5}$ $PbCl_2\ (s) \rightleftharpoons$ K =

a. Calculate $[Pb^{2+}]$ and $[Cl^-]$ for a saturated solution of $PbCl_2$.

b. Calculate molar solubility (mol/L) for $PbCl_2$

c. Calculate mass solubility (g/L) for $PbCl_2$

d. What mass of $PbCl_2$ (278 g/mol) would dissolve in 140 mL?

Working from solubility to K_{sp}:

Solubility of compound (g/L) $\rightleftharpoons$ Molar solubility of compound (mol/L) $\rightleftharpoons$ Molar concentration of ions $\rightleftharpoons$ K_{sp}

1. Find K_{sp} for CaF_2 whose molar solubility is 2.1×10^{-4} mol/L.

Molar solubility plus stoichiometry tells us what ion concentrations are, from which K can be found.

2. $BaCO_3$ (197g/mol) has a solubility of 0.014 g/L. Find K_{sp} for $BaCO_3$.

17.9,17.7 Factors that affect Solubility of Ionic Compounds (LeChatelier's Principle)

A. pH Factor: If anion is basic, (weakly or strongly), => solubility increases at low pH (high $[H^+]$)

1. Via selective removal of anion (product side)
2. Many basic anions: OH^-, F^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} etc.
3. Few non-basic anions (the strong acid big-6!): Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-

Question: In Which of the following will adding Acid Impact Solubility?

Example 1: $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

Add acid:

By selective removal of $[OH^-]$,
Q < K, so ala LeChatelier,
solid $Cu(OH)_2$ keeps dissolving,
and $[Cu^{2+}]$ keeps rising

Notice: In pure water, when $Cu(OH)_2$ dissolves $[HO^-] = 2\,[Cu^{2+}]$
But when acid is added (low pH), $[HO^-] \neq 2\,[Cu^{2+}]$

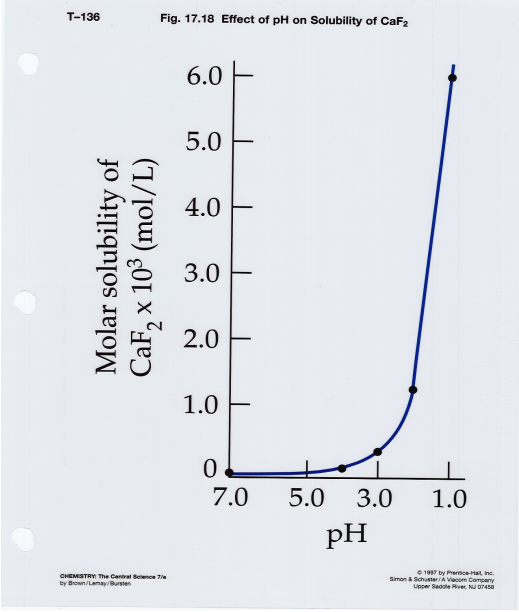
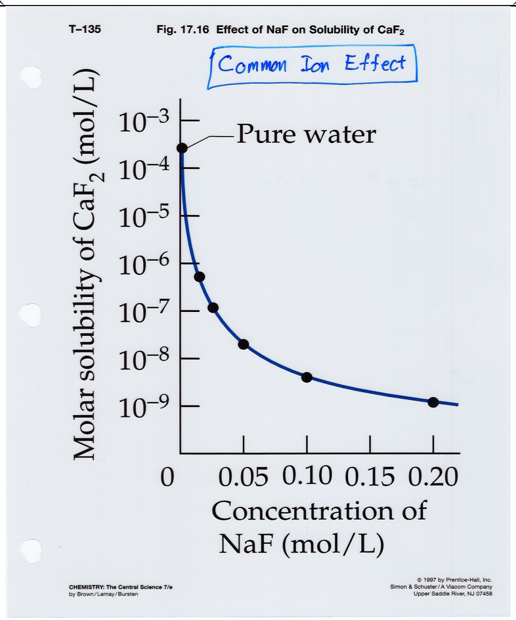
Example 2: $PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$ $K=[Pb^{2+}][F^-]^2$

Add acid:

Example 3: $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$ $K=[Pb^{2+}][Br^-]^2$

Add acid:

Notice:

pH Effect on CaF_2 (fluoride is a basic anion)	**Common Ion Effect on CaF_2** (fluoride from NaF is the "common ion")
	

Example: $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^{-}(aq)$

- Adding H^+ (reducing pH) raises solubility from 10^{-3} to >6, (factor of over a thousand
- Adding F^- reduces solubility from 10^{-3} to 10^{-9} (factor of a million)
- In terms of LeChatelier's Principle, H^+ is a product ion remover (shift equilibrium to the right), while NaF is a product ion source (shifts equilibrium to the left).

B. Common Ion Effect (17.7): A "common ion" DECREASES solubility. (LeChatelier)

Example: $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

	Additive	Equilibrium Shift Response	Impact on:		Ratio of $[Ba^{2+}]$ to $[SO_4^{2-}]$	Impact on Solubility of $BaSO_4$
1	Add $Ba^{2+}(aq)$ (for example, $Ba(NO_3)_2$)		$[SO_4^{2-}]$		$[Ba^{2+}]$ $[SO_4^{2-}]$	
2	Add SO_4^{2-} (aq) (for example, Na_2SO_4)		$[Ba^{2+}]$		$[Ba^{2+}]$ $[SO_4^{2-}]$	

Notes:

1. If Ba^{2+} or SO_4^{2-} is added as a common ion from a different source, that pushes the equilibrium to left, so solubility decreases
2. Case 1, where $Ba(NO_3)_2$ was added:
   a. The barium ion concentration $[Ba^{2+}]$ is dominated by the fully soluble $[Ba(NO_3)_2]$ source
   b. Simplifying assumption allows the contribution "x" from $BaSO_4$ to be ignored
   c. As a result, solving for $[SO_4^{2-}]$ and thus the molar solubility of $BaSO_4$ under these conditions becomes easy.

Equilibrium Calculations when a "Common Ion" is Present: Way Easier!

When a known concentration of a common ion is present, you can easily:

1. **Calculate molar concentrations of ions**
2. **Calculate molar solubility of the solid**

Example **WITHOUT common ion**:

1. What is the molar solubility of $BaSO_4$ when added to regular water?

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$$

Example **WITH common ion**:

2. What is the molar solubility of $BaSO_4$ in the presence of 0.10-M $Ba(NO_3)_2$?

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$$

I

C

E (doesn't matter)

Example **WITH common ion**:

3. What is the molar solubility of $BaSO_4$ in the presence of 0.50-M Na_2SO_4?

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$$

I

C

E (doesn't matter)

How would the solubility of the salts be affected?

Q's: 1. Is there a common ion? 2. Is there a basic anion that might be impacted by pH?

	Added $Ca(NO_3)_2$	Added NaF	Added HNO_3	More soluble at Low or High pH?
1. CaF_2				
2. $CaCO_3$				
3. $Ca(OH)_2$				
4. ZnF_2				
5. $PbCl_2$				
6. AgI				
7. $ZnSO_4$				

Example **WITHOUT common ion**:

8. What is molar solubility of AgBr ($K_{sp}=3.3x10^{-13}$) in a solution with 0.20 M NaBr (which of course dissolves fully)?

I

C

E (doesn't matter)

Example **WITH common ion**:

9. What would AgBr solubility be without NaBr present? ($K_{sp}=3.3x10^{-13}$)

I

C

E (doesn't matter)

Calculating Solubility for Metal Hydroxides, given pH.

- Any ionic formula with a basic anion is more soluble under acidic conditions. (LeChatelier)
- With metal hydroxide, knowing pH enables easy quantitative solubility calculations
- Essentially when you know pH, you can know $[HO^-]$,which simplies the math

10. Determine molar solubility for $Mg(OH)_2$ (K_{sp}=1.5 x 10^{-11}) at the following pH's:

Equation:

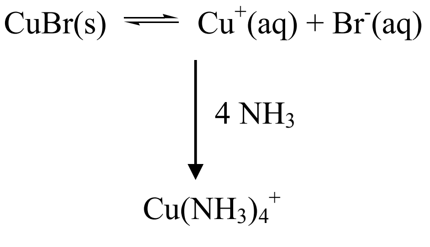
a. pH=12.00

b. pH=6.00

pH can define the concentration of hydroxide

C. Complex Ion Formation (not for test, but lab relevant)

- many Lewis bases can increase the solubility of a solid by irreversible removal of a product cation
- NH_3, ^-CN common



$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$ K = 5.3 x 10^{-9}

$\downarrow$ 4 NH_3

$Cu(NH_3)_4^+$

- Selective, irreversible removal of the copper ion via ammonia complexation drives the equilibrium in the right direction.
    - Thus, the solubility of the original solid increases.

General pH Strategy: Finding the pH after Acid or Base is added to a solution

- Whether it be to a buffer solution, a strong acid solution, a weak acid solution, a strong base solution or a weak base solution prior to the new addition
- The strategy is similar to when we added acid or base to a buffer

1. Write out the acid-base reaction
    - It helps to recognize which species are acidic or basic or neutral, and weak or strong
2. Calculate the initial moles
    - Number of moles = molarity x volume (in Liters)
3. Use ICE to determine post-reaction ("E") moles
4. Assess the post-reaction situation, based on what's left at the end
5. Solve the pH problem from there

	Post-Reaction Situation		
1	Strong acid only	$[H^+] = [SA]$	
2	Strong acid plus weak acid	$[H^+] = [SA]$	Ignore WA, which makes insignificant contribution
3	Strong base only	$[HO^-] = [SB]$	
4	Strong base plus weak base	$[HO^-] = [SB]$	Ignore WB, which makes insignificant contribution
5	Weak acid only	$[H^+] = \sqrt{K_a x [WA]}$	Qual: pH < 7
6	Weak base only	$[HO^-] = \sqrt{K_b x [WB]}$	Qual: pH > 7 May need to find K_b from K_a
7	Weak acid plus weak base	$pH = pK_a + \log \frac{[base]}{[acid]}$	Buffer solution
8	No acid or base; only neutral salts	pH = 7.0	

- For many of these, it will be necessary to calculate molarities
- To do this, make sure that you factor in the total, combined volume

Key: Recognizing the Final Situation!!

APPENDIX
Table of Solubility Product Constants (K_{sp} at 25^o C)

Bromides	$PbBr_2$	6.3 x 10^{-6}		Iodides	PbI_2	8.7 x 10^{-9}
	AgBr	3.3 x 10^{-13}			AgI	1.5 x 10^{-16}
Carbonates	$BaCO_3$	8.1 x 10^{-9}		Oxalates	BaC_2O_4	1.1 x 10^{-7}
	$CaCO_3$	3.8 x 10^{-9}			CaC_2O_4	2.3 x 10^{-9}
	$CoCO_3$	8.0 x 10^{-13}			MgC_2O_4	8.6 x 10^{-5}
	$CuCO_3$	2.5 x 10^{-10}		Phosphates	$AlP0_4$	1.3 x 10^{-20}
	$FeCO_3$	3.5 x 10^{-11}			$Ba_3(P0_4)_2$	1.3 x 10^{-29}
	$PbCO_3$	1.5 x 10^{-13}			$Ca_3(P0_4)_2$	1.0 x 10^{-25}
	$MgCO_3$	4.0 x 10^{-5}			$CrP0_4$	2.4 x 10^{-23}
	$MnCO_3$	1.8 x 10^{-11}			$Pb_3(P0_4)_2$	3.0 x 10^{-44}
	$NiCO_3$	6.6 x 10^{-9}			Ag_3P0_4	1.3 x 10^{-20}
	Ag_2CO_3	8.1 x 10^{-12}			$Zn_3(P0_4)_2$	9.1 x 10^{-33}
	$ZnCO_3$	1.5 x 10^{-11}		Sulfates	$BaS0_4$	1.1 x 10^{-10}
Chlorides	$PbCl_2$	1.7 x 10^{-5}			$CaS0_4$	2.4 x 10^{-5}
	AgCl	1.8 x 10^{-10}			$PbS0_4$	1.8 x 10^{-8}
Chromates	$BaCrO_4$	2.0 x 10^{-10}			Ag_2S0_4	1.7 x 10^{-5}
	$CaCrO_4$	7.1 x 10^{-4}		Sulfides	CaS	8 x 10^{-6}
	$PbCrO_4$	1.8 x 10^{-14}			CoS	5.9 x 10^{-21}
	Ag_2CrO_4	9.0 x 10^{-12}			CuS	7.9 x 10^{-37}
Cyanides	$Ni(CN)_2$	3.0 x 10^{-23}			FeS	4.9 x 10^{-18}
	AgCN	1.2 x 10^{-16}			Fe_2S_3	1.4 x 10^{-88}
	$Zn(CN)_2$	8.0 x 10^{-12}			PbS	3.2 x 10^{-28}
Fluorides	BaF_2	1.7 x 10^{-6}			MnS	5.1 x 10^{-15}
	CaF_2	3.9 x 10^{-11}			NiS	3.0 x 10^{-21}
	PbF_2	3.7 x 10^{-8}			Ag_2S	1.0 x 10^{-49}
	MgF_2	6.4 x 10^{-9}			ZnS	2.0 x 10^{-25}
Hydroxides	AgOH	2.0 x 10^{-8}		Sulfites	$BaS0_3$	8.0 x 10^{-7}
	$Al(OH)_3$	1.9 x 10^{-33}			$CaS0_3$	1.3 x 10^{-8}
	$Ca(OH)_2$	7.9 x 10^{-6}			Ag_2S0_3	1.5 x 10^{-14}
	$Cr(OH)_3$	6.7 x 10^{-31}				
	$Co(OH)_2$	2.5 x 10^{-16}				
	$Cu(OH)_2$	1.6 x 10^{-19}				
	$Fe(OH)_2$	7.9 x 10^{-15}				
	$Fe(OH)_3$	6.3 x 10^{-38}				
	$Pb(OH)_2$	2.8 x 10^{-16}				
	$Mg(OH)_2$	1.5 x 10^{-11}				
	$Mn(OH)_2$	4.6 x 10^{-14}				
	$Ni(OH)_2$	2.8 x 10^{-16}				
	$Zn(OH)_2$	4.5 x 10^{-17}				

Ch. 14 Thermodynamics and Direction of Reactions

Product Favored Processes that Proceed Spontaneously (14.1)

- Chemical events can be strongly product favored, reactant favored, or in some cases in equilibrium

Examples

Product-Favored Chemistry Examples	Other Examples of Spontaneous Events
1. H_2O (s) → H_2O (l) at 50°	1. Ball falling
2. 2Na + Cl_2 → 2NaCl + heat	2. Desk getting messy
3. Gasoline + O_2 (+ spark) → CO_2 + H_2O + heat	3. Forgetting first semester chemistry…
4. NaCl (s) in water → NaCl (aq)	

Reactant Favored Chemistry Examples	Other Examples of Non-Spontaneity
1. H_2O (s) ← H_2O (l) at -50°	4. Automobile self-assembly
2. $2H_2O$ ← $2H_2$ + O_2	5. Learning organic chemistry

1. Product-favored events may be slow at room temperature, but a catalyst or spark can initiate them so that once started, they can **continue spontaneously**, without requiring continuous energy input
   - Once started, they are self-sustaining
   - The reason they may not start on their own is because of activation barriers
2. Reactant-favored chemical events require **continuous energy input** from the outside
3. Most (but not all) product-favored processes are **exothermic**
4. Most (but not all) reactant-favored processes are **endothermic**
5. The spontaneity of chemical events may depend on temperature

Probability and Reactions

Facts

1. Exothermic processes usually product favored
2. Some highly favorable processes are not exothermic:
   - Expansion of gas into vacuum
   - Heat/energy transfer from something hot to cold
   - The mixing of colored liquids
   - NaCl dissolving in water'
   - My desk gets messy, your chemistry knowledge gets disordered

Fact: Common to **All** Favorable Chemical Events: An Increase in the **Disorder** of **Energy or Matter**

1. Dispersal of energy
   a. Exothermic processes: disperse energy to the surrounding
      - Chemicals → surroundings (small # particles → large # particles)
      - Eating candy bar: concentrated energy → energy dispersed through body → energy dispersed outside of body
   b. More probable for energy to be dispersed than concentrated in small number of particles

2. Dispersal of matter
   a. Concentrated matter tends to disperse (gases filling a room or filling a vacuum; sodium chloride dissolving in water; colored liquids mixing….)
   b. More probable for matter to be dispersed than concentrated in a small space
      - More probable for matter to be dispersed than highly organized

3. Dispersal of matter usually involves dispersal of energy, so in either case 1 or case 2, dispersal of energy results
   - Chemists often recognize the dispersal/disorganization of atoms as being inherently favorable, but the underlying reason is really the corresponding but less obvious dispersal of chemical energy

1. **If both energy and atoms are more dispersed ⇒ product favored**
2. **If neither energy and atoms are more dispersed ⇒ reactant favored**
3. **If one of energy or atoms is more dispersed but the other is less dispersed ⇒ ????**

Energy dispersal: **enthalphy** issue	Atoms dispersal: **entropy** issue

"Entropy" = S = Amount of Disorder

1. Each chemical has a finite entropy "S°" under standard conditions
2. **Standard conditions: 25°C, 1atm, per mole**
   - Factors in size, motion
     - more motion, more disorder
     - translational, rotational, vibrational motion
3. Higher S → higher entropy (which will normally mean more atom movement)
4. Even elements have $S \neq O$ (unlike $\Delta H_f°$)

Qualitative Guidelines for Entropy (Memorize)

- use these to rank things in terms of entropy
- Use these to compare which side of a reaction (left/reactant side or right/product side) has more entropy
- This will enable you to decide whether entropy is increasing or decreasing
- You can do this without having charts or entropy numbers given to you; you just look at the chemicals and anticipate which will have more entropy
-

1. **Phase**: Gases >>> Liquids > Solids
   a. Huge difference for gases
   b. Related to movement disorder

   For any equation, if one side has more gas, always has more entropy

   c. Phase charges ⇒ predictable ΔS

2. **Molecular Size:** larger molecule > smaller molecule (Assuming phase is equal)
   $C_5H_{12} > C_4H_6 > C_3H_8 > C_2H_6$

3. **Number of Molecules**: more molecules > fewer molecules (Assuming phase is equal)
   $2NO + O_2 >> 2NO_2$ (3 molecules versus 2 molecules)
   - For any combination reaction, ΔS negative (entropy decreases)
     Ex: $Ti + O_2 \rightarrow TiO_2$ ($\Delta S < 0$)

   - For any fragmentation reaction, ΔS positive (entropy increases)
     Ex: $CaCO_3 \rightarrow CaO + CO_2$ ($\Delta S > 0$)

4. **Dissolving:** Entropy increases when a solid is dissolved in a solvent
   - Matter get more disorganized
   - Resulting ions/molecules have more motion (translational, rotational)
   - Entropy increases specially for ionics, which dissociate
     - Ionic dissolving is really a special class of fragmentation reaction

$$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

5. **Temperature:** Higher temperature = higher entropy for a given substance
   - At higher temperature, the motion is greater and the atoms are less organized

Skill: Predict Entropy Changes ΔS = S products – S reactants
   a. if products have more entropy, ΔS positive
   b. if products have less entropy, ΔS negative

Class Problems

1. From each pair, which has more entropy? Why?

a. H_2O(l) vs. H_2O(g)

b. H_2O(l) at 80° vs. H_2O(l) at 20°C

c. $Ca_3(PO_4)_2$ (s) vs. FeO(s)

d. $CaBr_2$ (s) vs. $CaBr_2$ (aq)

e. C_3H_8O (l) vs. C_3H_6 (l) + H_2O (l)

2. Will ΔS be Positive or Negative? ΔS Why?

a. 2Mg (s) + O_2 (g) → 2MgO (s)

b. $NaNO_3$ (s) → $NaNO_3$ (aq)

c. $2C_2H_6$ (l) + $7O_2$ (g) → $4CO_2$ (g) + $6H_2$ (g)

d. $C_4H_8Br_2$ (l) → C_4H_8 (l) + Br_2 (l)

e. $AgNO_3$ (aq) + NaCl (aq) → AgCl (s) + $NaNO_3$ (aq)

f. C_7H_{14} (s) → C_7H_{14} (l)

g. CO_2 (g) → CO_2 (s)

h. $CaCO_3$ (s) → CaO (s) + CO_2 (g)

Calculating ΔS (14.3,4)

$$\boxed{\Delta S° = S° \text{ (products)} - S° \text{ (reactants)}}$$

Units: $\frac{J}{\text{mole} \times K}$ (note: J, not kJ)

- Same as for ΔH° but:
  1) units (J not kJ)
  2) elements $\Delta H°_f = O$ $S° \neq O$

- **Remember to factor in the number of moles**

1. Find ΔS° for:

	$CaCO_3(s)$	→	$CaO(s)$	+	$CO_2(g)$
S° =	93		38		213

Note: ΔS° assumes molar amounts of everything.

2. Calculate overall ΔS when 2.3 moles of $CaCO_3$ decomposes.

	$CaCO_3(s)$	→	$CaO(s)$	+	$CO_2(g)$
S° =	93		38		213

Note: ΔS° versus actual ΔS.
When non-molar amounts are used,
multiply ΔS° accordingly.

3. Find ΔS° for:

	C_2H_6 (l)	+	$3O_2$ (g)	→	$2CO_2$ (g)	+	$3H_2O$ (l)
S° =	161		205		214		70

Note: Factor coefficients when calculation ΔS°.

Note: this "combustion" reaction is actually very favorable.

- But it is NOT ΔS favorable.
- It is favorable due to enthalpy, not entropy.

Second Law of Thermodynamics: The Total Entropy of Universe is Increasing

- First Law: Energy is neither created nor destroyed
- Third Law: Entropy at Abolute Zero is Zero

Notes

1. Unlike energy, entropy is not conserved
   a. The universe is constantly getting more messy!
   b. Increasing disorder a fundamental law of nature

2. Total Entropy Changes for the Universe: Whether a Reaction is Product or Reactant Favored

Product-favored Processes: $\Delta S_{univ} > O$
Reactant-favored Processes: $\Delta S_{univ} < O$
Equilibrium Situation: $\Delta S_{univ} = O$

3. $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$
   1. The "system" would the reacting chemicals, or the solution in your beaker
      - Measuring changes on the "system" is relatively easy
      - For example, it's easy to tell whether a reaction is exothermic or endothermic by seeing whether a solution gets hotter or colder
   2. But the surroundings count too!!
      - Measuring what happens to the entire surrounding universe is less convenient…

4. A Convenient Way to Find $\Delta S_{surroundings}$: Use the ΔH_{system} (which is easy to measure)
   - Easily measurable enthalpy changes for the "system" essentially measure entropy changes for the surroundings

$$\boxed{\Delta S_{surroundings} = \frac{-\Delta H_{system}}{T}}$$

5. A Convenient Way to Find ΔSuniverse Using Only System Measurements

Given: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$ and $\Delta S_{surroundings} = \frac{-\Delta H_{system}}{T}$

Then: $$\boxed{\Delta S_{universe} = \Delta S_{system} - \frac{\Delta H_{system}}{T}}$$

   1. ΔS_{system} and ΔH_{system} can be found relatively easily, but can tell us what happens to the universe
   2. By knowing changes in both the **enthalpy** (ΔH_{system}) and **entropy** (ΔS_{system}) for the **system** alone, you can figures out whether $\Delta S_{universe}$ is favorable or unfavorable
   3. **The more exothermic the reaction, the more positive and favorable is the $\Delta S_{surroundings}$**
      - The energy released heats up the surroundings and makes the surroundings become more disordered

6. A process can have an unfavorable negative ΔS for the system, but the overall process can still be favorable if the surroundings have a favorable positive ΔS as a result of an exothermic reaction

7. Product favored processes associated with:
   a. dispersal of matter (ΔS_{system} positive)
   b. dispersal of energy $\Rightarrow \Delta S$ surroundings positive!!
      1. **Exothermic usually favorable because results in positive $\Delta S_{surroundings}$**
      2. energy release causes heat, faster motion, etc.

8. Nothing is ever spontaneously "ordered "
   1. Only at the expense of something else
   2. Outside work/energy/effort (all of which disorder surroundings) is needed

9. Qualitative Predictions for ΔSuniv, Favorability

- consider ΔS, ΔH for systems
- If there is **agreement** between enthalpy and entropy factors, then it's easy to predict the overall favorability

4 Scenarios:

	Enthalpy ΔH_{system}	ΔH Sign	Entropy ΔS_{system}	ΔS Sign	Enthalpy Entropy	$\Delta S_{universe}$	ΔS_{univ} Sign
1	Good	$\Delta H < 0$	Good	$\Delta S > 0$	Good-Good	Good	$\Delta S_{univ} > 0$
2	Bad	$\Delta H > 0$	Bad	$\Delta S < 0$	Bad-Bad	Bad	$\Delta S_{univ} < 0$
3	Good	$\Delta H < 0$	Bad	$\Delta S < 0$	Good-Bad	Depends	???
4	Bad	$\Delta H > 0$	Good	$\Delta S > 0$	Bad-Good	Depends	???

a. When enthalpy and entropy both agree (cases 1 and 2), it's easy.

b. When enthalpy and entropy **disagree**, the overall favorability depends on the relative magnitudes for the enthalpy and entropy factors, and on the temperature

c. The relative importance of system enthalpy versus entropy decreases at higher temperatures

d. When there is a disagreement, there is normally some cutoff temperature at which the enthalpy and entropy factors cancel each other out and the resulting $\Delta S_{universe} = 0$. This results in a perfect equilibrium situation

e. If product favored, may be entropy driven, enthalpy driven, or driven by both.

Problems: Classify Each of the Following Processes as Product-Favored, Reactant-Favored or impossible to tell without further temperature information (see later). Also note whether $\Delta S_{universe}$ would be positive or negative.

Product or Reactant Favored?	$\Delta S_{universe}$ Sign

1. A → B $\Delta S° = +52$ J/K $\Delta H° = -32$ KJ/mol

2. A → B $\Delta S° = -116$ J/K $\Delta H° = +12$ KJ/mol

3. A → B $\Delta S° = +76$ J/K $\Delta H° = +4$ KJ/mol

The following Reactions are all **Product-Favored.** Which are enthalpy driven, entropy driven, or favored by both?

4. C → D $\Delta S° = -28$ J/K $\Delta H° = -112$ KJ/mol

5. E → F $\Delta S° = +563$ J/K $\Delta H° = +7.3$ KJ/mol

6. G → H $\Delta S° = +89$ J/K $\Delta H° = -42$ KJ/mol

Free Energy and Free-Energy Changes. Gibbs "Free Energy" = G and (14.5)

G^o = free energy per exactly one mole under standard conditions
ΔG = change in free energy (for a reaction)
ΔG^o = change in free energy for a reaction on a per mole basis
ΔG_f^o = standard free energy of formation for a substance from elements in their standard states

A. $\boxed{\Delta G = \Delta H - T\Delta S}$ Definition: $\Delta G = -T\Delta S_{universe}$

B. Derivation (not test responsible)

1. Given: $\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{system}$
2. Recall: $\Delta S_{surroundings} = \dfrac{-\Delta H_{system}}{T}$
3. After substituting: $\Delta S_{universe} = \dfrac{-\Delta H}{T} + \Delta S$
4. Multiply by –T: $-T\,\Delta S_{universe} = \Delta H - T\Delta S$
5. By definition: $\Delta G = -T\Delta S_{universe}$
6. After substituting: $\Delta G = \Delta H - T\Delta S$

Notes

1. ΔG reflects $\Delta S_{universe}$. Since ΔG reflects $\Delta S_{universe}$ it tells whether any process is product favored or not.

2. Value 1: by measuring ΔH, ΔS for system, can find ΔG ($\Delta S_{universe}$) for universe
   - needn't measure surroundings!! Local system information can tell you everything.

3. Value 2: Each chemical has a standard "free energy" G, so can easily calculate $\Delta G_{reaction}$ (see later)

4. Sign Meaning:

$\Delta G < O$	product-favored
$\Delta G > O$	reactant-favored
$**\Delta G = O$	equilibrium

   - Sign sense is Opposite to that for $\Delta S_{universe}$
   - Given $\Delta G \Rightarrow$ predict whether a reaction is product- or reactant-favored (or equilibrium)
   - Given whether a reaction is product-favored $\Rightarrow$ predict ΔG

5. Sign Review

	Negative	Positive
ΔG	Good	Bad
ΔH	Good	Bad
ΔS	Bad	Good

C. Calculations Involving $\Delta G = \Delta H - T\Delta S$

- given any 3, solve for 4th
- Sometimes you'll need to determine one of these from

Units

ΔG kJ/mol	T Kelvin (not °C)
ΔH kJ/mol	ΔS normally given in J/mol·K (not kJ), so need to be converted from J → kJ

1. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H° = -394$ kJ/mol
$\Delta S° = 42.9$ J/mol·K

   a. What is $\Delta G°$ (in kJ/mol) at 25°C?

   b. what is ΔG (in kJ) when 0.32 mol of C reacts? (Note: No ° by the ΔG, so you need to adjust for the actual supply of moles.)

2. $C + 2H_2 \rightarrow CH_4$ $\Delta G° = -50.8$ kJ/mol $\Delta H° = -74.5$ kJ/mol
What is $\Delta S°$ (by definition, at 25°C)

D. Calculating $\Delta G°_{rxn}$ based on $\Delta G_f°$

- $\Delta G_f°$ = standard free energy of formation from elements in standard state
- For elements in standard state: $\Delta G_f° = 0$, $\Delta H_f° = 0$, $S° \neq 0$

$$\boxed{\Delta G°_{rxn} = \Delta G_f° \text{ (products)} - \Delta G_f° \text{ (reactants)}}$$

- Same format as ΔH, ΔS

3. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
$\Delta G_f° = -51$ -394 -237

Calculate $\Delta G°_{rxn}$ in kJ/mol:

Qualitative: Predict the signs for:

$\Delta S°$

$\Delta G°$

$\Delta H°$ Note: **ΔH dominates over $-T\Delta S$**

E. Temperature and ΔG

$\Delta G = \Delta H - T\Delta S$ High temp ⇒ entropy more important
Low temp ⇒ entropy less important

ΔH	ΔS	-TΔS	ΔG	Temp	Product-Favored	
-	+	-	-	Any	Yes	Enthalpy/entropy agree
-	-	+	-	Low	Yes	enthalpy wins
			0	Crossover	Equilibrium	Enthalpy/entropy cancel
			+	High	No	entropy
+	-	+	+	Any	No	Enthalpy/entropy agree
+	+	-	+	Low	No	enthalpy
			0	Crossover	Equilibrium	Enthalpy/entropy cancel
			-	High	Yes	entropy

1. If enthalpy, entropy agree, sense of ΔG is same regardless of temp.
2. If enthalpy, entropy disagree, the sense of ΔG changes between low temp (enthalpy control) and high temp (entropy control)
    a. Enthalpy dominates at low temp, entropy takes over at higher temps (TΔS)
    b. There will be a crossover temperature at which enthalpy and entropy cancel, and the system is at equilibrium

F. Equilibrium and the Crossover Temperature

1. At equilibrium, $\Delta G = 0$
2. $\Delta G = \Delta H - T\Delta S$
3. Therefore, at equilibrium $\boxed{\Delta H = T\Delta S}$
4. Therefore the equilibrium temperature: $\boxed{T_{equil} = -\Delta H / \Delta S}$
5. Remember that T must be in Kelvin, not ºC, and that both ΔH and ΔS must be converted to common units (kJ or J)

G. Phase change: The melting or boiling temperature always involves equilibrium between two phases, and thus always occurs at a crossover temperature with $\Delta G = 0$

- So the temperature at which something will melt or boil can be determined from the ΔH and ΔS for the phase change
    - given ΔH, ΔS calculate mp or bp!!

1. a) What is the melting temp for A? b) Under what temp conditions is process favorable?

$A(s) \rightarrow A(l)$ $\Delta H° = +13.2$ KJ/mol $\Delta S° = +34.3$ J/mol·K

Provide sense of ΔG, ΔH, ΔS (Given Reaction Knowledge!)

	Favorable?	ΔG	ΔH	ΔS
1. $H_2O\ (l) \rightarrow H_2O\ (g)$ at 50°C				
2. $H_2O\ (l) \rightarrow H_2O\ (g)$ at 200°C				
3. $C_6H_{12}\ (l) + 9O_2\ (g) \rightarrow 6CO_2\ (g) + 6H_2O\ (l)$				

4. Qualitatively, under what temperature conditions will the following be Product-Favored?

a.	ΔH neg	ΔS neg
b.	ΔH neg	ΔS pos
c.	ΔH pos	ΔS neg
d.	ΔH pos	ΔS pos

5. $A \rightarrow B$ $\Delta H = -14.9$ kJ/mol $\Delta S = -48$ J/mol•K

At what temperatures is the process product-favored?

At what temperature is the process at equilibrium?

At what temperatures is the process reactant-favored?

Key Ch. 14 Equations:

1. $\Delta S^\circ = S^\circ$ (products) – S° (reactants)
2. $\Delta G^\circ = \Delta G_f^\circ$ (products) – ΔG_f° (reactants)
3. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (T in Kelvin)
4. at equilibrium $\Delta H = T\Delta S$

Chapter 19 Electrochemistry Math Summary

Relating Standard Cell Potential to Standard Half Cell Potentials

$E^o_{cell}=E^o_{oxidation} + E^o_{reduction}$ (standard conditions assume 1.0 M concentrations)

Relating Half Cell Potentials when Written in Opposite Directions

$E^o_{ox} = -E^o_{red}$ for half reactions written in opposite directions

Relating Standard Cell Potentials to ΔG

$\Delta G^o = -nFE^\circ_{cell}$ (to give answer in kJ, use F = 96.485)

F = 96,500 C/mol
n=number of electrons transferred

Relating Actual Cell Potential to Standard Cell Potential when Concentrations aren't 1.0-M

$E_{cell} = E^o_{cell} -[0.0592/n] \log Q$ (Q = ratio of actual concentrations)

Relating Standard Cell Potential to Equilibrium Constant

$\log K = nE^o/0.0592$

Relating Actual Cell Potential to Actual Concentrations in Concentration Cells

$E_{cell} = -[0.0592/n] \log Q$ for concentration cells, where anode and cathode differ only in concentration, but otherwise have same ions

Relating # of Moles of Electrons Transferred as a Function of Time and Current in Electrolysis

1 mol e^- = 96,500 C

moles of electrons = [current (A)•time (sec)]/96,500 for electrolysis, moles, current, and time are related.

rearranged: time (sec)=(moles of electrons)(96500)/current (in A)

Note: 3600 sec/hour

so time (hours)=(moles of electrons)(26.8)/current (in A)

Electrochemistry-Related Units

C = Coulomb = quantity of electrical charge = $6.24 \cdot 10^{18}$ electrons

- 1 mole of electrons = 96,500 C

A = amp = rate of charge flow per time = C/sec
V = volt = electrical power/force/strength = J/C

$$F = \text{Faraday} = \frac{96{,}500\text{C}}{\text{mole } e^-} = \frac{96.5 \text{ kJ}}{\text{mole } e^- \bullet \text{V}}$$

Assigning Oxidation Numbers (See Section 4.9)

Use these rules in order.
The sum of all oxidation numbers of all elements = charge on substance.

		Oxidation Number:	Examples:
1.	Atoms in their elemental state	= 0	Fe, H_2, O_2
2.	Monatomic ions	= charge	F^{1-}, Na^{1+}, Fe^{3+}

IN COMPOUNDS

3.	Group 1A	= +1	NaCl, KNO_3
4.	Group 2A	= +2	MgO
5.	Fluorine	= -1	HF, ClF
6.	Hydrogen	= +1	H_2O
7.	Oxygen	= -2	SO_2, $HClO_4$
8.	Group 7A (Halogen family)	= -1	HCl
9.	Group 6A (Oxygen family)	= -2	PbS_2

The sum of all oxidation numbers of all elements = charge on substance.

Key: For anything else, (or for a group 7A or group 6A in the presence of higher priority atoms), set it's oxidation number = "x", and solve for "x" such that the ox. #'s = actual charge.

Balancing Redox: Simple Cases where all Reactants and Products are Provides

1. Identify oxidation numbers for redox actors
2. **2.** Set coefficients for them so that the **#e's released = #e's accepted**
   - focus completely on the atoms whose oxidation numbers change
3. Then balance any redox spectators
4. Check at the end to make sure:
   - Charges balance
   - Atoms balance

Standard Reduction (Electrode) Potentials at 25° C (Appendix 6, shortened)

Half-cell reaction	**Eo (volts)**		**Half-cell reaction**	**Eo (volts)**
$F_2 + 2e \rightarrow 2F^-$	2.87		$Pb^{2+} + 2e \rightarrow Pb$	-0.126
$Ce^{4+} + e \rightarrow Ce^{3+}$	1.61		$Sn^{2+} + 2e \rightarrow Sn$	-0.136
$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	1.507		$Ni^{2+} + 2e \rightarrow Ni$	-0.257
$Cl_2 + 2e \rightarrow 2Cl-$	1.36		$Co^{2+} + 2e \rightarrow Co$	-0.277
$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$	1.33		$Fe^{2+} + 2e \rightarrow Fe$	-0.447
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	1.229		$Cr^{3+} + 3e \rightarrow Cr$	-0.74
$Br_2 + 2e \rightarrow 2Br^-$	1.066		$Zn^{2+} + 2e \rightarrow Zn$	-0.7618
$Ag^+ + e \rightarrow Ag$	0.7996		$2H_2O + 2e \rightarrow H_2 + 2OH^-$	-0.8277
$Fe^{3+} + e \rightarrow Fe^{2+}$	0.5355		$Al^{3+} + 3e \rightarrow Al$	-1.662
$I_2 + 2e \rightarrow 2I^-$	0.48		$Mg^{2+} + 2e \rightarrow Mg$	-2.37
$Cu^{2+} + 2e \rightarrow Cu$	0.3419		$Na^+ + e \rightarrow Na$	-2.71
$2H^+ + 2e \rightarrow H_2$	0.0000		$K^+ + e \rightarrow K$	-2.95
$Cu^{2+} + e \rightarrow Cu^+$	0.153		$Li^+ + e \rightarrow Li$	-3.05

Ch. 19 Electrochemistry and its Applications

- electron flow = electricity
- electrochemistry = the study of electron transfer
- "reduction" and "oxidation" ("redox") chemistry is central

1. Product-favored redox reactions run batteries
2. Voltmeters quantify electrochemistry
   - measure reactivity of redox reactions
3. Reactant-favored redox reactions can be pushed to product side by external electricity
   - "Electrolysis"
   - Electrolysis is the source of many pure metals and other not found in nature ("Electroplating")

     $Cr^{3+} + 3e^- \rightarrow Cr$ (chrome-plating)
4. One can also force oxidation reactions under the appropriate conditions

   $2\,Cl^- \rightarrow Cl_2 + 2e^-$ (for disinfecting water)
5. "Corrosion", "rusting" are redox processes that are undesirable and that we need to prevent

Assigning Oxidation Numbers (19.1, See Section 4.9 to review)

This is a more complete set of rules than your textbook. It always works.

Use these rules in order.

The sum of all oxidation numbers of all elements = charge on substance.

		Oxidation Number:	Examples:
1.	Atoms in their elemental state	= 0	Fe, H_2, O_2
2.	Monatomic ions	= charge	F^{1-}, Na^{1+}, Fe^{3+}

IN COMPOUNDS

3.	Group 1A	= +1	NaCl, KNO_3
4.	Group 2A	= +2	MgO
5.	Fluorine	= -1	HF, ClF
6.	Hydrogen	= +1	H_2O
7.	Oxygen	= -2	SO_2, $HClO_4$
8.	Group 7A (Halogen family)	= -1	HCl
9.	Group 6A (Oxygen family)	= -2	PbS_2

The sum of all oxidation numbers of all elements = charge on substance.

Key: For anything else, (or for a group 7A or group 6A in the presence of higher priority atoms), set it's oxidation number = "x", and solve for "x" such that the ox. #'s = actual charge.

Find Ox #'s for

1. H_2OC C:
2. PCl_3 P:
3. HSO_4^- S:
4. $KMnO_4$ Mn:
5. $Mg_3(PO_4)_2$ P:
6. $HClO_2$ Cl:

19.1 Redox Reactions (Review: 4.9)

ex: $2Al + 3ZnBr_2 \rightarrow 3Zn + 2AlBr_3$

<u>Recognizing Redox Reactions</u>:

1. Any reaction in which an <u>elemental</u> substance is involved is always a redox reaction
   - The element can be on either reactant or product side, or both
2. Any reaction involving a Change in "oxidation number" is a redox reaction (review 5.4)
   - Oxidation numbers count charges in molecular as well as ionic compounds
   - In a polar covalent bond, a more electronegative atom is given negative charge (credited with bonding electrons), and a less electronegative atom is given positive charge (as if it wasn't seeing the bonding electrons at all)

$$\overset{\delta+}{H} - \overset{\delta-}{Cl} \qquad\qquad \overset{\delta-}{O} = \overset{\delta+}{C} = \overset{\delta-}{O}$$

$$H^{\oplus}\ Cl^{\ominus} \qquad\qquad O^{2-}\ C^{4+}\ O^{2-}$$

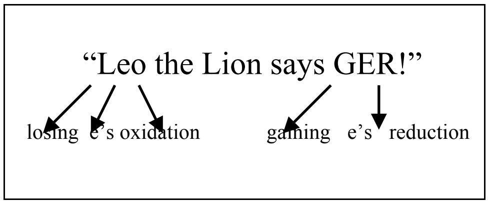
<u>Notes, Terms</u>

1. Oxidation: loss of e's
   - Ox # increases (more positive or less negative)

$Al^0 \rightarrow Al^{3+}$	$CO \rightarrow CO_2$	$2\ Cl^- \rightarrow Cl_2$	$H_2S \rightarrow H_2SO_4$	$H_2O \rightarrow H_2O_2$
$0 \rightarrow 3$	C: $+2 \rightarrow +4$	$-1 \rightarrow 0$	S: $-2 \rightarrow +6$	O: $-2 \rightarrow -1$

2. Reduction: gain of e's
   - Ox # is "reduced" (less positive or more negative)

$Zn^{2+} \rightarrow Zn^0$	$CO_2 \rightarrow C$	$H_2SO_4 \rightarrow NaHSO_3$	$Cl_2 \rightarrow 2\ Cl^-$	$CO_2 \rightarrow CH_4$
$+2 \rightarrow 0$	C: $+4 \rightarrow 0$	S: $+6 \rightarrow +4$	S: $0 \rightarrow -1$	C: $+4 \rightarrow -4$



3. All redox reactions require both an electron giver (the thing that is oxidized) and an electron taker (the thing that is reduced)
   a. Essentially a redox reaction involves a competition for a limited supply of electrons
   b. In the example shown, there aren't enough electrons for both Al and Zn to be in their reduced zero-charge form. One or the other must be in it's electron-deficient oxidized form

$$2Al + 3ZnBr_2 \rightarrow 3Zn + 2AlBr_3$$

   c. That Al^{3+} ends up oxidized and Zn^0 ends up reduced suggests that Zn has a higher electron-love than Al
   d. Competition for limited electrons not unlike acid/base competition for limited H^+'s

$$2Al + 3ZnBr_2 \rightarrow 3Zn + 2AlBr_3$$

4. "Oxidizing Agent" or "Oxidant": causes something else to be oxidized
   - is itself reduced
   - Zn^{2+}, which is itself reduced, is the "oxidizing agent" because it causes Al to be oxidized

5. "Reducing Agent": causes something else to be reduced
   - is itself oxidized
   - by giving it's electrons to the other guy, it causes the other guy to be reduced, but is oxidized in the process
   - Al, which is itself oxidized, is the "reducing agent" because it causes Zn^{2+} to be reduced

6. "Redox" reduction – oxidation

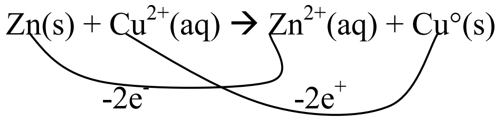
7. Electrons must balance in a redox reaction: the number given up by the reducing agent must equal the number accepted by the oxidizing agent

Identify the oxidizing and reducing agents and count how many electrons transfer

1. $2Na + 2HCl \rightarrow 1H_2 + 2NaCl$

2. $2KMnO_4 + 6NaCl \rightarrow 2MnO_2 + 3Cl_2$ (some H_2O, KOH, NaOH also involved)

Half Reactions, Redox, and Balancingn (19.2)



$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu°(s)$

- both oxidation and reduction must occur
- electrons must balance

Half Reactions

Ox: $Zn \rightarrow Zn^{2+} + 2e^-$
Red: $2e^- + Cu^{2+} \rightarrow Cu°$
Sum: $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

Suppose: Zn^{2+} reacts with Na. Draw the oxidation and reduction half reactions, and balance them for electrons. Combine them to make the sum redox reaction:

Reduction	Oxidation	Net Sum

Balancing Redox

2. Identify oxidation numbers for redox actors
3. Set coefficients for them so that the **#e's released = #e's accepted**
   - focus completely on the atoms whose oxidation numbers change
4. Then balance any redox spectators
5. Check at the end to make sure:
   - Charges balance
   - Atoms balance

Note: Test problems will give you all of the species involved. Some OWL problems will be harder and will not include all of the chemicals

Balance (Test Level)

1. $H^+ + \quad I^{\ominus} + \quad NO_3^{\ominus} \rightarrow I_2 + \quad NO + \quad H_2O$

2. $H_2O + \quad MnO_4^{\ominus} + \quad Br^{\ominus} \rightarrow MnO_2 + \quad BrO_3^{\ominus} + OH^{\ominus}$

3. $Al \quad O_2 \rightarrow Al_2O_3$

4. $NaIO_3 + Mn \rightarrow MnO_2 + NaI$

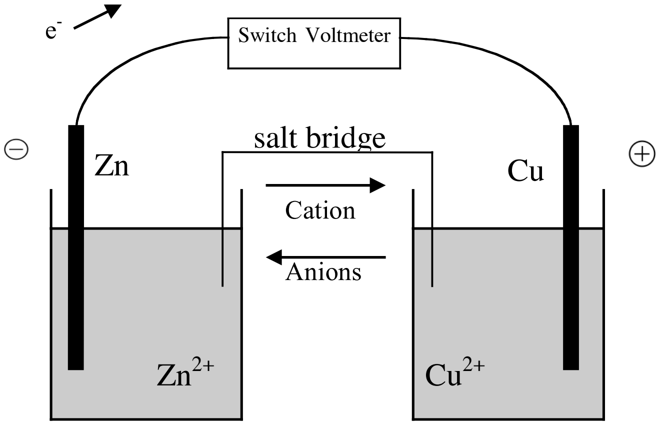
Electrochemical Cells (19.2)

Example: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ 2 electron flow

- when redox partners are in direct contact (in the same beaker, in the same solution) direct electron transfer occurs: no measurable or useful electron flow

Electrochemical ("Voltaic") Cell: redox reactants are separated, so electron flow is forced to go through external circuit ⇒ measurable, useful electricity

Setup



2 Solid metals = "electrodes"

- electrodes can be metal, plates or wires, or graphite or some other materials: (conductive)
- "Anode" = electrode Oxidized (vowels) $Zn \rightarrow Zn^{2+}$
    - electron source
    - dissolving
    - negative sign on a battery
- "Cathode" = electrode reduced (consonant) $Cu^{2+} \rightarrow Cu$
    - e- receiver
    - physically electrode grows (Cu° forming)
    - positive sign on battery

Two "Half Cells" and "Half Reactions"

- "Anode" side = Where the oxidation half reaction occurs ($Zn \rightarrow Zn^{2+}$ beaker)
- "Cathode" side = Where the reduction half reaction occurs ($Cu^{2+} \rightarrow Cu$ beaker)

Salt Bridge Connector or Semipermeable Membrane

- In an electrochemical cell, cations are being produced in the anode half ($Zn \rightarrow Zn^{2+}$), and cations are being removed in the reduction side ($Cu^{2+} \rightarrow Cu$)
- Solutions need to maintain charge balance, so the anode side needs to either gain anions or lose excess cations, and the cathode side needs to either gain cations or lose anions in order to charge-balance.
- This is accomplished via either a "salt bridge" or "semipermeable membrane" ("porous barrier"): something that allows ions to pass

Direction of Ion flow:
- Cations move from anode (being produced) to cathode (to replace cations reduced)
- Anions move from cathode to anode, to balance forming cations

Cell Shorthand Convention

$Zn(s)/Zn^{2+}(aq)//Cu^{2+}(aq)/Cu(s)$
ANODE CATHODE

// = barrier between half cells
/ = distinction between electrodes and ions

Many variations on electrochemical cell engineering (not for test)

- Special cells when H_2 gas is produced
- Many types use conductive graphite electrodes on which surface redox half-reactions occur
- "Dry cells" involving thick paste mixtures rather than any solvent (many batteries)

Electrochemical Cells and Voltage (19.3)

- Voltage depends on redox reactivity, the chemical force for electron transfer

E_{cell} = cell potential in volts (V = J/C C = coulomb of electricity)

$E°_{cell}$=**standard** potential

Standard Conditions

a. 1.0 M concentration
b. 25°C
c. gases (if any) at 1.0 atm

Since a cell consists of 2 half cells:

$$\boxed{E°_{cell} = \underset{\textbf{Anode}}{E°_{oxidation}} + \underset{\textbf{Cathode}}{E°_{reduction}}}$$

Each half reaction has an E°, relative to self-defined **reference half reaction**

$2H^+ + 2e^- \rightarrow H_2$ E°=0

Show Appendix 6.1, APP-26, Standard Redox Potentials

Example: $Zn + 2\,HCl \rightarrow H_2 + ZnCl_2$ $E_{cell}° = +0.76$

Ox half $Zn \rightarrow Zn^{2+} + 2e^-$ $E_{ox} = ??$
Red half $2\,H^+ + 2\,e^- \rightarrow H_2$ $E_{red} = 0$

$E°_{cell} = +.76 = E_{ox} + E_{red} = E_{ox} + 0$ so $\boxed{E°_{ox} = +0.76\text{ V}}$

The same approach can be used to find the potentials for any other half reaction.

Using $E°_{cell}$ and known Half Potentials (19.3)

$$\boxed{E°_{cell} = E°_{ox} + E°_{red}}$$

1. Tables list reduction halves $E°_{red}$ (Appendix 6.1 App-26)

$Fe^{3+} \rightarrow Fe^{2+}$	+0.77V
$Cu^{2+} \rightarrow Cu$	+0.34V
$2\ H^{+} \rightarrow H_2$	0.00
$Pb^{2+} \rightarrow Pb$	-0.13
$Ni^{2+} \rightarrow Ni$	-0.25
$Cr^{3+} \rightarrow Cr^{2+}$	-0.74

2. When a half is reversed, sign reverses. $\boxed{\mathbf{E_{ox}° = -\ E_{red}°}}$

Red: $Zn^{2+} \rightarrow Zn$ $E°_{red} = -\ 0.76V$
Ox: $Zn \rightarrow Zn^{2+}$ $E°_{ox} = +\ 0.76$

$$\boxed{\mathbf{E_{ox}° = -\ E_{red}°}}$$

Q: What is the oxidation potential for $Cu \rightarrow Cu^{2+}$?

3. Key skill: Given known halves, deduce $E°_{cell}$.

Ex: $Ni + Fe^{3+} \rightarrow Fe^{2+} + Ni^{2+}$ Balance and find $E°_{cell}$

4. Stoichiometry coefficients don't matter to E°'s
   - In previous example, the reduction potential for Fe^{3+} was still +0.77 V, even though the balanced reaction had 2 Fe^{3+} ions being reduced.

5. Key skill: Given an overall $E°_{cell}$ and one known or knowable half potential (Cu^{2+} redn = +034V), calculate the half potentials for the other half (without needing or having table access).

$Cu + Sn^{2+} \rightarrow Sn + Cu^{2+}$ $E°_{cell} = -0.48V$

Find $E°_{red}$ for: $Sn^{2+} \rightarrow Sn$

Find $E°_{ox}$ for: $Sn \rightarrow Sn^{2+}$

6. **Hydrogen Reference**: All redox half-reaction potentials are relative to H^+ reduction ($E^\circ_{red}=0$) or H_2 oxidation ($E^\circ_{ox}=0$) (19.5)

$Fe^{3+} \rightarrow Fe^{2+}$	+0.77V
$Cu^{2+} \rightarrow Cu$	+0.34V
$2\ H^+ \rightarrow H_2$	**0.00**
$Pb^{2+} \rightarrow Pb$	-0.13
$Ni^{2+} \rightarrow Ni$	-0.25
$Cr^{3+} \rightarrow Cr^{2+}$	-0.74

7. For a **good, product-favored** reaction, $\boxed{\mathbf{E^\circ_{cell} = positive}}$
   - more positive the better

Q: Which of the following are favorable redox reactions?

a. $Cu + Sn^{2+} \rightarrow Sn + Cu^{2+}$ $E^\circ_{cell} = -0.48V$

b. $Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+}$ $E^\circ_{cell} =$

c. $Cu^{2+} + Ni \rightarrow Ni^{2+} + Cu^{2+}$ $E^\circ_{cell} =$

Logic: 1. Find E°_{cell} from $\mathbf{E_{ox}}^\circ$ and $\mathbf{E_{red}}^\circ$
2. Check if E°_{cell} is positive or negative.

8. For half reactions, the more positive the more favorable

Reductions			Oxidations		
$F_2 \rightarrow 2\ F^-$	+2.87	great	$2\ F^- \rightarrow F_2$	-2.87	terrible
$Cu^{2+} \rightarrow Cu$	+0.34	good	$Cu \rightarrow Cu^{2+}$	-0.34	bad
$Ni^{2+} \rightarrow Ni$	-0.25	bad	$Ni \rightarrow Ni^{2+}$	+0.25	good
$Li^+ \rightarrow Li$	-3.0	terrible	$Li \rightarrow Li^+$	+3.0	great

9. **Chemical Logic**: Redox patterns depend on electron love (predictable periodic trends)
   - Higher love for electrons → more favorable to be reduced (gain electrons)
   - Higher love for electrons → more unfavorable to be oxidized (lose electrons)

   - Fluorine is the most electronegative of the four elements, lithium the least
     - Neutral: F_2 loves to be reduced (gain electrons), so has best reduction potential
     - Anions: F^- holds negative charge best, so has the worst anion oxidation potential
     - Lithium has low electron love, so is easily oxidized
     - Because unattractive towards electrons, lithium cation has poor oxidation potential

Q1: Based on table, rank the electron affinities for Cu, H_2, Ni, and Pb

Q2: Which would be a stronger oxidizing agent (stealer of e's), Cu^{2+} or Ni^{2+} ?

Q3: Which would be a stronger reducing agent (giver of e's), Cu or Ni ?

Redox conjugates: Oxidizing vs. Reducing Agents, Oxidized versus Reduced Forms

Love For Electrons	Strength as Oxidizing Agents		Strength as Reducing Agents	Love For Electrons
		$Fe^{3+} \rightarrow Fe^{2+}$ +0.77V $Cu^{2+} \rightarrow Cu$ +0.34V $2\ H^{+} \rightarrow H_2$ 0.00 $Pb^{2+} \rightarrow Pb$ -0.13 $Ni^{2+} \rightarrow Ni$ -0.25 $Cr^{3+} \rightarrow Cr^{2+}$ -0.74		

On table:

	Left Side	Right Side
1	**Oxidized form** (less electrons)	**Reduced Form** (more electrons)
2	**Oxidizing Agents** (may wish to grab electrons from something else and so oxidize the other thing)	**Reducing Agents** (able to give electrons to something else and so reduce the other thing)
3	Higher up = stronger oxidizing agent	Lower down = stronger reducing agent
4	Higher up = greater love for electrons	Lower down = lesser love for electrons
5	Higher E°_{red} ⇒ a. more easily reduced b. stronger love for e's c. stronger oxidizing agent	

- Often things aren't charted like this. But for two things in their oxidized forms, the one with the higher E°_{red} ⇒
  a. more easily reduced
  b. stronger love for e's
  c. stronger oxidizing agent

If charting reduction potentials:

- upper left = strongest oxidizing agent = max electron love = most easily reduced
- bottom right = strongest reducing agent = minimum electron love = most easily oxidized.

Some Representative Problem Types

a. Rank the oxidizing agents by strength

b. Rank the reducing agents by strength

c. Which will react with Cu^{2+}?

d. Which will react with Cu°?

Love For Electrons	Strength as Oxidizing Agents			Strength as Reducing Agents	Love For Electrons
		$Fe^{3+} \rightarrow Fe^{2+}$	+0.77V		
		$Cu^{2+} \rightarrow Cu$	+0.34V		
		$2\ H^{+} \rightarrow H_2$	0.00		
		$Pb^{2+} \rightarrow Pb$	-0.13		
		$Ni^{2+} \rightarrow Ni$	-0.25		
		$Cr^{3+} \rightarrow Cr^{2+}$	-0.74		

- Strongest Oxidizing agent: top left (max e- love)
- Strongest Reducing agent: bottom right (min e- love)

Odds and Ends

1. An oxidizing agent on table will react (product-favored) with any reducing agent lower
   - Will not react with any reducing agent higher (reactant favored)
   - A reducing agent will only react with an oxidizing agent higher on the chart

   a. What species would react with Pb^{2+}?

   b. What species would react with Pb?

2. For two species to react, one must be in reduced form (reducing agent), and the other in oxidized form (oxidizing agent)

   c. What of the following species could react with Cu^{2+}?

   $2\ H^{+}$ H_2 Pb^{2+} Pb Ni Ni^{2+} Cr^{2+} Cr^{3+}

   d. What of the following species could react with Cr^{2+}?

   $2\ H^{+}$ H_2 Pb^{2+} Pb Ni Ni^{2+}

3. Given redox chart, rank electron love and basically predict which reactions are or aren't favorable

4. Based on periodic table, predict reactivity **without redox table** (based on general periodic patterns in electron love)
   - General Activity as Reducing Agents (increasing e- love)

	G1 >	G2 >	Al >	most T-metals >	H_2 >	coinage metals
	(active metals)					
Ex.	Li	Mg	Al	Zn, Fe, Cr	H_2	Cu, Au

$Fe^{3+} \rightarrow Fe^{2+}$	+0.77V
$Cu^{2+} \rightarrow Cu$	+0.34V
$2\ H^{+} \rightarrow H_2$	0.00
$Pb^{2+} \rightarrow Pb$	-0.13
$Ni^{2+} \rightarrow Ni$	-0.25
$Cr^{3+} \rightarrow Cr^{2+}$	-0.74

5. Given 2 reduction potentials, figure out how a product-favored cell would be constructed and calculate the standard voltage

- A real cell needs an oxidation half reaction, so one of the reductions must be reversed.
- Keep the more favorable reduction potential as the reduction half, but reverse the other into it's oxidation version
- Then sum $E°_{red} + E°_{ox}$ to get $E°_{cell}$

Examples

a. Determine what the voltage would be for a cell consisting of Pb^{2+}/Pb and Ni^{2+}/Ni.

b. Determine what the voltage would be for a cell consisting of Pb^{2+}/Pb and Cu^{2+}/Cu.

6. Use observed reactivities to determine:
   a. relative love for electrons
   b. relative strength as reducing agents
   c. relative strength as oxidizing agents
   d. relative redox table ("activity series")

Example A: $X + Y^{2+} \rightarrow Y + X^{2+}$ Product-favored redox. Questions: Between X and Y:

a. Which element loves electrons more?

b. What thing is the strongest reducing agent?

c. Which thing is the strongest oxidizing agent?

d. Draw a little reduction potential chart, with the strongest oxidizing agent in the upper left corner as usual

A Redox Reaction Always favors "weaker" side

Example B: $Q + P^{2+} \leftarrow P + Q^{2+}$ Non-reaction (Reactant-favored redox).

- In other words, no reaction when Q is mixed with P^{2+}).
- Between P and Q:

a. Which element loves electrons more?

b. What thing is the strongest reducing agent?

c. Which thing is the strongest oxidizing agent?

d. Draw a little reduction potential chart, with the strongest oxidizing agent in the upper left corner as usual

A Redox Reaction Always favors "weaker" side.

- The side with the weaker reducing agent and weaker oxidizing agent.

Miscellaneous Problems

1. $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$ E° = 0.32V

- What is the "reduction potential" for Fe^{2+} ($Fe^{2+} \rightarrow Fe°$) given the above potential, and given that: $Zn^{2+} \rightarrow Zn$ $E°_{red} = -0.76$

2. Find E° for product favored reaction involving the following, and balance the reaction

$Fe^{3+} \rightarrow Fe^{2+}$ 0.77
$Cu^{2+} \rightarrow Cu$ 0.34

a. keep more favorable one as reduction
b. reverse less favorable to make it an oxidation
c. sum $E°_{ox}$ and $E°_{red}$
d. adjust coefficients to balance e's

3. Ditto for $Br_2 \rightarrow 2\,Br^-$ +1.06
$Zn^{2+} \rightarrow Zn$ -0.76

4. Reduction potentials for Ni^{2+} and Sn^{2+} are -0.25V and -0.16V.

   a. Which of Ni^{2+} and Sn^{2+} is a stronger <u>oxidizing</u> agent?

   b. Which of Ni and Sn is a stronger <u>reducing</u> agent?

   c. Would either or both of Ni and Sn react with H^+?

<u>Periodic Table-Based Predictions</u>

5. Predict/Rank $E°_{ox}$ for:

   Li Mg Fe H_2 Ag

6. Rank/predict $E°_{red}$ for

   Li^+ Mg^{2+} Fe^{2+} H^+ Ag^+

7. Rank F_2 Cl_2 I_2 as oxidizing agents.

8. Rank F^- Cl^- I^- as reducing agents.

<u>Activity Series</u>

<u>Reducing Activity</u> <u>Electron Love</u>

$3 A + 2 B^{3+} \rightarrow 2 B + 3 A^{2+}$

$B + C^{2+} \rightarrow C + B^{2+}$

$A + D^{2+} \rightarrow$ No reaction

9. Rank "activity" of A, B, C, D

10. Rank "activity" of A^{2+}, B^{3+}, C^{2+}, D^{2+}

11. Rank electron love

$Ag^+ \rightarrow Ag$	+0.80 V
$Cu^{2+} \rightarrow Cu$	+0.34 V
$Zn^{2+} \rightarrow Zn$	-0.76 V
$Al^{3+} \rightarrow Al$	-1.66 V
$Mg^{2+} \rightarrow Mg$	-2.36 V

12. Which species react with Cu^{2+}?

13. Which species react with Zn°?

14. Which element loves e’s the most?

15. Which element loves e’s the least?

16. $NiCl_2 + H_2 \rightarrow Ni + 2\,HCl$ E° = -0.28 V

a. Product favored or not?

b. Is reduction potential for Ni^{2+} positive?

Relating $E°_{cell}$ to $\Delta G°$ and K. Chemical Energy and Electrical Work (19.4)

	ΔG	$E°_{cell}$	K
Product Favored	neg	pos	large
Reactant Favored	pos	neg	small
**Equilibrium	0	0	1

$\Delta G°$ and $E°_{cell}$ have opposite signs, but are related

- both provide measurements for the favorability or unfavorability of a reaction
- obviously $E°_{cell}$ is more limited, to redox reactions
- K is also related, since it too relates to how favorable or unfavorable a reaction is
- $\Delta G°$ = "free energy" available to do be released and do work
- $E°_{cell}$ also reflects the amount of energy that is released to do work when a favorable redox transfer occurs
    - The "free energy" in an electrical cell is really the free energy to do the work of moving electrons and to the work that flowing electricity can do

Key Formula for relating $\Delta G°$ and $E°_{cell}$

$$\Delta G° = -nFE°_{cell} \qquad \boxed{\Delta G° = -96.5nE°_{cell}}$$

n = number of electrons transferred in the balanced equation (now coefficients matter!!!!)

- crucial that you have a correctly balanced redox reaction, and can count how many electrons transfer
- **F** = Faraday's constant **= 96.5** to get ΔG in kJ/mol

Math derivation (not for test):

Units $F = \frac{96{,}500C}{\text{mole } e^-}$ $V = \frac{J}{C}$ so $C = \frac{J}{V}$ C = coulomb, unit of electricity, amount of charge

Substituting $F = \frac{96{,}500J}{\text{mole } e^- \bullet V}$ $F = \frac{96.5 \text{ kJ}}{\text{mole } e^- \bullet V}$ Thus when "n" is moles of electrons, and $E°_{cell}$ is in volts, the units cancel and only kJ are left.

Electrochemistry-Related Units/Terms: For interest, not for test

C = Coulomb = quantity of electrical charge = $6.24 \bullet 10^{18}$ electrons

- 1 mole of electrons = 96,500 C

A = amp = rate of charge flow per time = Coulombs/second

V = volt = electrical power/force/strength; difference in electrical potential energy = J/C

- Force for moving electrons and charge
- Not all Coulombs of charge have the same energy/power/force/ability to do work
- Just like dropping a brick from one cm has less force than dropping it from two meters high

F = Faraday = charge per chemical amount (the mole) = $\frac{96{,}500C}{\text{mole } e^-} = \frac{96.5 \text{ kJ}}{\text{mole } e^- \bullet V}$

Watt = amount of energy

$$\boxed{\Delta G^\circ = -96.5nE^\circ_{cell}}$$

1. Balance the reaction, and find ΔG° given the reduction potentials shown

$Cu + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+}$

+0.77V +0.34V

2. Balance the reaction, and calculate E°_{cell}.

$Zn + Cr^{3+} \rightarrow Zn^{2+} + Cr$ $\Delta G^\circ = -11.6$ kJ/mol

3. If the reduction potential for Zn^{2+} is -0.76V, what is the reduction potential for Cr^{3+}?

Cell Voltage and K Voltage and K are also linked!!

- The more favorable and positive E^o_{cell}, the larger and more favorable is K
- Again, "n" = number of electrons transferred, so you need balanced reaction
- Caution: K values often work out to be enormous (calculator problems)

$$\boxed{\log K = nE^\circ_{cell} / (0.0592)}$$

4. Calculate K, given reduction potentials.

$Ag^+ + Fe^{2+} \rightarrow Ag^\circ + Fe^{3+}$

+0.80V +0.77V

The Effect of Concentration on Cell Potential: Voltages when Concentrations are not 1.0 M (19.6)

1. E° assumes 1.0 M concentrations for any soluble species (and 1.0 atm pressure for any gas)
   - rarely actually true!
2. For any real reaction, concentrations change as the reaction procedes
   - As the concentrations change, the voltage drops
   - Actual voltage continues to drop until the battery is dead = 0V = equilibrium
   - At equilibrium, $E_{actual} = 0$ V

Nernst Equation: $$\mathbf{E_{actual} = E° - \frac{.0592}{\mathit{n}} \log Q}$$

n = number of e's transferred (need balanced equation, coefficients)
Q = ratio of <u>actual</u> concentrations (K format, but using actual concentrations)

- Recall: solids, liquids don't appear in K or Q, only aqueous solutes or gases

<u>Problems</u>

1. Calculate actual voltage for $Mg/Mg^{2+}(0.10M)//Cu^{2+}(0.001M)/Cu$ given the following reduction potentials:

$Mg^{2+} = -2.37V$
$Cu^{2+} = +0.34V$

<u>Logic Steps</u>

2. Calculate actual voltage for $Cu/Cu^{2+}(1.0M)//Ag^{+}(0.032M)/Ag$

$E_{red}°$	
Ag^{+}	+0.80V
Cu^{2+}	+0.34V

3. $2\ Ag^{+}(aq) + Zn(s) \rightarrow 2\ Ag(s) + Zn^{2+}(aq)$
$E_{red}°$ +0.80 -0.76
If a cell with $[Ag^{+}] = 0.20$ M has $E_{actual} = 1.63V$, what is $[Zn^{2+}]$

Using Nernst Equation to Calculate the Cell Potential and Equilibrium Equation (not for test)

$$\boxed{\text{Nernst Equation:} \qquad \mathbf{E_{actual} = E° - \frac{.0592}{\mathit{n}} \log Q}}$$

At equilibrium:

a. $E_{actual} = 0$ V

b. Q=K

So, at equilibrium $0 = E° - \frac{.0592}{n} \log K$

At equilibrium: $\boxed{E° = \frac{.0592}{n} \log K}$ Finding E° given K

Rearranged: $\boxed{\log K = nE°_{cell} / (0.0592)}$ Finding K given $E°_{cell}$

“**Concentration cells**”, **pH meters, and neurons**:

- anode and cathode use the same chemicals, but with ions at different concentrations
- at equilibrium, the concentrations would be equal, so the voltage drive is to equalize

Example: $H_2 + 2\,H^+ \rightleftharpoons H_2 + 2\,H^+$ E° = 0

So $E_{actual} = (-0.592/n)\log Q$

This kind of voltage is key to pH meters, neurons (19.8)

- pH meter: dip meter with known $[H^+]$ into a solution, measured voltage reflects solution $[H^+]$
- neurons: The H^+ concentration differs inside and outside cell membranes. This creates a voltage which is the key for nerve sensation

Common Batteries (19.7-9)

A. Primary: Nonrechargeable

- run till concentration achieves equilibrium = dead = toss

1. Alkaline batteries

$$H_2O + Zn(s) + MnO_2(s) \rightarrow ZnO(aq) + 2\ MnO(OH)(s) \qquad E° = 1.54V$$

anode cathode
oxidized reduced

- flashlights, radio, toys, Jasperse insulin pump, Jasperse blood testers, tooth brush, etc.

2. Lithium batteries $Li(s) + CoO_2(s) \rightleftharpoons LiCoO_2(s) + \text{energy}$ $\boxed{E° = 3.4V}$

- Lithium is actually in a polymer with carbon graphite)

Pros:

- Big voltage → good for fueling energy eaters, like laptops, cameras, cell phones
- Light weight

Cons

- More expensive

B Secondary Batteries (“nicad” and “car”) = **Rechargeable**

1. Lead-acid (car battery) (19.8)

$$Pb°(s) + \overset{+4}{PbO_2}(s) + 2\ H_2SO_4 \rightleftharpoons 2\ PbSO_4(s) + 2\ H_20 \quad + \text{energy} \qquad E° = 2.0V$$

Anode cathode ↑
CAREFUL!
Leakage caused corrosion!

- Each cell is 2.0V: six alternating cathode/anodes in series sums to 12V
- Energy during a recharge drives it in the reverse direction, to the left

2. NiCad E°=1.3

- electric shavers, dustbusters, video camcorders, rechargeable power toothbrush, any rechargeable cordless appliances

$$\overset{0}{Cd}(s) + 2\ \overset{+3}{Ni}O(OH)(s) + 2\ H_20 \rightleftharpoons \overset{+2}{Cd}(OH)_2 + 2\ \overset{+2}{Ni}(OH)_2(s) \ + \text{energy} \qquad E°=1.3$$

Anode cathode

- reaction can reverse upon treatment with electrical energy

3. Fuel Cell: continuous feed of reactants from outside to electrodes (19.9, interest, not test)

$$2\ H_2 + O_2 \rightarrow 2\ H_2O \qquad E° = 0.9V$$

Anode cathode

- $H_2 + O_2$ light, so good fuels, high energy efficiency
- Spaceships: 500 pounds of fuel enough energy for 11 days
- Dream: come up with way to use solar/wind energy to produce H_2 from water
- Fuel cells for cars: Need to “stack” lots to multiply the power

Electrolysis: Using outside electricity to drive unfavorable redox reactions (19.18)

- key process in recharging rechargeable batteries
- key route to elements not found in nature: metals, H_2, Cl_2,…

A. Electrolysis of Molten Salts ("molten" = melted, pure liquid salts in absence of solvent, super hot!!)

Ex. Energy + $2\ Na^+Cl^- \rightarrow 2\ Na + Cl_2$ $E° = -4.07V$

Cathode
e- acceptor

Anode
e- source

- products must be kept separate so can't react

B. Electrolysis of salts in Water: Can only process ions that are more reactive than water

- At each electrode, the most reactive candidate reacts
    - In water, water competes at both the cathode (reduction) and anode (oxidation)
- Reduction/Cathode

Water reduction: $2\ H_2O + 2\ e- \rightarrow H_2 + 2\ OH^-$ $E° = -0.83$ (when hydroxide is 1M)
$2H_2O + 2e \rightarrow H_2 + 2OH^-\ (10^{-7}\ M)$ $E = -0.41$ (when hydroxide is 10^{-7} M)

- Easily reduced cations (Zn^{2+}, Ni^{2+}, Cr^{3+}, Sn^{2+}, etc.) can be reduced to elemental form in water.
- Cations of Active metals can't (K^+, Mg^{2+}, Na^+,…). If they are to be reduced to elemental form, they must be reduced as molten salts.

Oxidation/Anode
Water Oxidation: $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4e-$ $E° = -1.23$ ($[H^+] = 1.0$ M)
$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4e-$ $E = -0.82$ ($[H^+] = 1 \times 10^{-7}$ M)

C. Electroplating: metal cation → elemental metal (reduction at cathode)

- metal forms on surface of cathode
- many metals are "plated" on outside of things in their way
- "Silverware" for a long time involved plating a coating of silver over something else
- Art objects, etc.
- Materials that are otherwise subject to rust, corrosions are often electroplated with a coating that is resistant to air, rain, and acid.

Electrolysis Calculations

- **1 mol electrons = 96,500 C (Coulombs)**

current, time, and moles of electrons are related

A (amp) = C/sec

A Derivation and 3 Permutations of an equation:

$$\boxed{\textbf{Moles electrons} = \frac{current(A)\cdot \sec}{96{,}500}} \qquad \textbf{Sec} = \frac{(moles)96{,}500}{A} \qquad \textbf{A} = \frac{(moles)96{,}500}{\sec}$$

Finding moles, given current and time

Finding time, given moles and current

Finding current, given moles and time

Qualitative Relationship (and vice versa):

Amps + time → **moles of electrons** → **moles of substance redoxed** → **grams of substance**

Keys:

1. Grams of substance and moles of substance are interconverted by molecular weight
2. Be sure to factors how many moles of electron are involved per moles of chemical formula

1. How many grams of Al (27g/mol) is produced in 1.0 hour by electrolysis of $AlCl_3$ at 10.0A current?

2. At 3.2A, how long will it take to make 10g of Zn (65.4 g/mol) from $ZnBr_2$?

3. What current in amps is required to make 10 grams of Cl_2 (71 g/mol) from $AlCl_3$ in one hour?

Corrosion

- Corrosion involves a product-favored oxidation of a metal exposed to environment (O_2, H^+, H_2O,…)
- The metal being oxidized always functions as the oxidation half
- Molecular oxygen is reduced to water in the presence of acid as the reduction half

  $O_2 + 4H^+ \rightarrow 2\ H_2O$ $E°_{red} = +1.23V$ very good under standard conditions!!

- Most metals can oxidize/corrode, especially under acidic conditions!!
- Why most metals are not found in their elemental form in nature, but rather as ions
- Exception: gold!!
- Metals usually end as metal oxides or sometimes metal hydroxides

  Ag tarnish
  Cu "greening"
  Fe rusting
  Rust: $2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe(OH)_2 \rightarrow \rightarrow \rightarrow Fe_2O_3$ red-brown rust

Practical notes:

1. Corrosion often speeded by H^+ and/or ionic salts that acidity water
2. Gold has always been valued because unlike other oxidizable metals, it retains it's elemental form and it's lustrous golden elemental surface appearance.
3. Most metals get coated with a film of hard metal oxide, which ends up protecting the interior or the metal.
   - The interior stays elemental metal, but is protected by sheath of hard metal oxide from exposure to air.
   - Sometimes it takes chemical activation to clear the oxide film and enable the elemental metal inside to be exposed for chemical reactions.
4. Why does iron have such a special rusting problem?
   - Iron is bad because iron oxide (rust) forms flakes that break off.
   - As a result, the interior iron is **not** protected and is continuously exposed for further corrosion.

Prevention

1. Coat iron surface with something that resists corrosion and protects.
   - Development of improved and more resistant sealants has been a major priority of auto-industry
2. "Galvanized iron"-Iron materials are electroplated with Zn, which is more easily oxidized than iron but oxidizes to give a hard, protective $Zn(OH)_2$ coating.

Chapter 20 Nuclear Chemistry Math Summary

Particles Involved in Nuclear Reactions, either as Nucleons, Emitted particles or Particles that React with a Nucleus and Induce a Decay

(Memorize these for Test)

-the first three, alpha, beta, and positrons are the crucial ones for balancing radioactive nuclear decay reactions

$\frac{4}{2}\text{He}$	α-particle (alpha)	$\frac{0}{0}\gamma$	gamma
$\frac{0}{-1}\text{e}$	ß-particle (beta), electron	$\frac{1}{0}\text{n}$	neutron
$\frac{0}{+1}\text{e}$	positron	$\frac{1}{1}\text{H}$	proton

Radioactive Decay Math

$t = (t_{1/2}/0.693)\ \ln (A_o/A_t)$ When solving for time, given half life and quantities of material

$\ln (A_o/A_t) = 0.693\ (t/t_{1/2})$ When solving for the amount of material left after a given time, given the half life

Handling "ln y = x" on calculator, when you know "x" but want to solve for "y": enter "x", then hit your "e^x" button.

Mass Defect/Binding Energy Math

Proton mass: 1.00783

Neutron mass: 1.00867

$E = \Delta mc^2$ Δm = (sum mass of protons plus neutrons) – actual mass

- The binding energy will depend on the Δm difference between the summed weight of the protons and neutrons minus the actual mass of the nucleus.
- Δm in terms of kilograms (you'll normally need to convert from grams to kg)
- The energy answer from the formula comes out in terms of Joules, not kJ; you'll routinely need to convert from J to kJ to fit the answers

Ch. 21 Nuclear Chemistry

1. Some rules for chemical reactions that do not apply to nuclear reactions:
   a. Balanced reactions: the same atoms that go into a reaction come out
   b. Conservation of mass (no mass is gained or lost)
   c. Conservation of energy

2. In nuclear reactions:
   a. Nuclei do change! (C→N, U→Ba, etc.)
   b. Mass does change (slightly) ⇒ large energy changes
   c. Energy is not conserved: energy is produced
   - Mass is actually converted to energy via Einstein's $e=mc^2$
   - The real conservation is of energy/mass, but in nuclear reactions mass can be converted into energy

Applications of Nuclear Energy

1. Energy source
   - ~20% of US electricity, ~17% world-wide
   - cheap! Efficient
   - no greenhouse gases: environmentally 'clean', no acid rain, etc.
   - Currently, all the nuclear waste from one reactor can be stored in one barrel of "glass"
2. Medicinal
   a) diagnostic tracers, "imaging"
      PET: position emission tomography
      -thyroid, heart, tumors, bone studies, brain imaging, blood flow tracking
   b) therapy: anti-cancer radiation therapy
3. Radioactive tracers, labelling
   - Incorporating radioactive nuclei into reactive molecules enables scientists to figure out which atoms go where in chemical and biochemical reactions
   - This enables researchers to unravel many biological pathways
4. Age dating
   - ^{14}C for archeological dates: recent several thousand years while people have been around (Carbon dating)
   - K/Ar dating for geological dates (dates for rocks, on the order of millions or billions rather than thousands of years)
5. Food irradiation: kill/retard Bacteria, molds, yeast (ala pasteurization)
6. Bombs!!
   - Fission: original WWII uranium bombs, in which big uranium nuclei break into smaller nuclei
   - Fusion (Hydrogen bomb): more powerful subsequent cold-war developed bombs that are much, much more destructive. Involve small hydrogen nuclei fusing into larger nuclei
7. Sun energy. All of the energy from the sun is produced by hydrogen and helium fusion.
   - All of the energy that we live on originally began with the sun
   - Plants harvest solar energy via photosynthesis
   - People and animals harvest energy by eating plants or by eating animals that ate plants
   - The solar energy harvested by plants also ends up being converted to fossil fuels and firewood

Radioactivity: Spontaneous Disintegration of Nucleus (21.1,2)

- although spontaneous, this may still be very slow. Rates vary widely, which is good.

A. Nuclear Review: Symbols for "Nuclide"

↙ Mass # A= protons + neutrons sum

$^{A}_{Z}\mathrm{E}$

↖ Atomic number Z= number of protons (redundant, given element symbol)

1. Number of protons = Z (atomic number)
2. Number of neutrons = A (mass number) – Z (number of protons)
3. Number of electrons = Number of protons for a neutral atom
   - For an anion, negative charge means more electrons than protons
   - For a cation, the positive charge means fewer electrons than protons

"isotopes": nuclei that have the same number of protons but differing number of neutrons

- ^{12}C, ^{13}C, ^{14}C all have six protons
- Stability often depends on the neutron/proton ratio, so frequently different isotopes will have different stability

"radioisotopes": particular isotopes that spontaneously disintegrate and release radiation

Shorthands: $^{12}_{6}\mathrm{C} = {}^{12}\mathrm{C}$ = C12 = 12C

B. Common "Particles" involved in Radioactivity and Nuclei (memorize these for test)

$\frac{4}{2}\mathrm{He}$	α-particle (alpha)	$\frac{0}{0}\gamma$	gamma ray (no mass, just energy)
$\frac{0}{-1}\mathrm{e}$	ß-particle (beta), electron	$\frac{1}{0}\mathrm{n}$	neutron
$\frac{0}{+1}\mathrm{e}$	positron	$\frac{1}{1}\mathrm{H}$	proton

1. Memorize names, symbols, constitution
2. Crucial in balancing nuclear reactions
3. The radiation emitted by radioactive elements is normally alpha, beta, or gamma. Positron emission and neutron emission is more rare.
   - Protons and neutrons are often involved when nuclei are being intentionally bombarded
4. Different radiation has different penetrating power. (20.8) Biological impact depends on:
5. The number or rays/particles that strike
6. The energy and penetration depth of the rays
7. Whether the radiation originates inside or outside the body

γ **Max damage, due to high energy, deep penetration**	ß Penetrate only a few mm	α Little penetration, only irritates outer skin. But bad if generated internally.

Nuclear Reactions: Equations and Balancing

Keys:
1. balance mass sum (top)
2. balance charge sum (bottom)

Five Types of Radioactive Reactions (Spontaneous)

	Isotope Change	Effect on n/p ratio		
1. Alpha emission	$\frac{A}{Z} \rightarrow \frac{4}{2}\text{He} + \frac{A-4 \text{ change}}{Z-2 \text{ change}}$	$\frac{n-2}{p-2}$ Little impact		
2. Beta emission	$\frac{A}{Z} \rightarrow \frac{0}{-1}e + \frac{A \text{ no change}}{Z+1 \text{ increase}}$	$\frac{n-1}{p+1}$	Lower	Neutron becomes a proton
3. Positron emission	$\frac{A}{Z} \rightarrow \frac{0}{+1}e + \frac{A \text{ no change}}{Z-1 \text{ decrease}}$	$\frac{n+1}{p-1}$	Higher	Proton becomes a neutron
4. Electron capture	$\frac{0}{-1}e + \frac{A}{Z} \rightarrow \frac{A}{Z-1}\ \frac{\text{no change}}{\text{decrease}}$	$\frac{n+1}{p-1}$	Higher	Proton becomes a neutron
5. Gamma emission	$\frac{A}{Z} \rightarrow \frac{0}{0}\gamma + \frac{A}{Z}\ \frac{\text{no change}}{\text{no change}}$	No change		

- Radioactive Series: many decays give unstable daughter nuclei, which then undergo subsequent serial decays
- A very common sequence when the n/p ratio is two high is emission of one 〈 and two ® particuls (in any sequence)
- This results in the effective removal of 4 neutrons

$$\frac{4}{2}\text{He} + \frac{0}{-1}e + \frac{0}{-1}e = 4\ \frac{1}{0}n$$

Fill in the Holes, Name the process

1. ^{234}Pu ⟶ $^{4}_{2}He$ +

2. ^{14}C ⟶ ^{14}N+

3. ^{230}U ⟶ ^{226}Th+

4. ${}^{99}_{43}Tc^{*} \longrightarrow {}^{99}_{43}Tc +$

5. ${}^{0}_{-1}e + {}^{81}_{37}Rb \longrightarrow$

6. ${}^{210}\mathrm{Pb} \longrightarrow {}^{0}_{+1}e +$

<u>Artificial Transmutations</u>: The human-induced conversion of one nucleus into another by Bombardment with ${}^{1}_{0}n$ or other nuclei. (21.5)

1. Key: reactions must still balance in the same way.
2. Often products are accompanied by production of side particles, often multiple neutrons
3. Few radioactive nuclei are still found in nature. Most fast-decay nuclei used for research or medicine are made by bombardment.

7. ${}^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr +$ = neutron bombardment

8. ${}^{35}_{17}Cl + {}^{1}_{1}H \longrightarrow {}^{32}_{16}S +$ proton bombardment

9. ${}^{239}_{92}U + {}^{4}_{2}He \longrightarrow {}^{1}_{0}n +$ Alpha Bombardment

The Stability of Atomic Nuclei (21.4)

A. Physics background

a. 3 fundamental forces
  1. gravity
  2. electrostatic attraction: opposite charges attract
  3. "strong nuclear force"

b. **proton-proton repulsion destabilizes** all nuclei except hydrogen **BAD**

- This repulsion increases sharply with increasing number of protons
- In other words, as nuclei increase in atomic number, this destabilizing repulsion increases exponentially
- This is a destabilizing electrostatic force
- If proton-proton repulsion is destabilizing, why do nuclei exist at all for atoms other than hydrogen?

c. "**strong nuclear force**" between protons or neutrons **GOOD**

- This attracts nuclides, holds nucleus together
- Unknown how the strong nuclear force works. It's existence and strength is really known by deduction!
- The neutron/proton ratio increases with larger nuclei.
  - This enables the strong nuclear force to increase at a pace that can balance the proliferating proton-proton repulsion
- Beyond atomic-number of 83, it becomes impossible for the nuclear force to keep up with the destabilizing proton-proton repulsion, so nuclei cease to be stable.
  Fig. 20.2, 21.2 Brown

B. Decay Patterns: The Band of Stability Target Ratio: A range of n/p ratios that appropriately balance the electrostatic repulsion and the nuclear attraction and give stable nuclei

1. Rule of 83: Atoms/nuclei with atomic number of Z > 83 are radioactive
  -nuclear force can't keep up!
  -most elements Z < 83 have at least one stable isotope ($_{43}$Tc, $_{61}$Pm)
  -**Z > 83 emit α** to reduce Z

Normal solution: For unstable nuclei with Z > 83, **alpha emissions** normally occurs, to reduce the atomic number and move it toward stability

2. For atoms with Z < 83, but above the band of stability: **atoms whose n/p ratio is too high**

- Conversion of a neutron into a proton would help

Normal solution: For nuclei whose n/p ratio is too high, **beta emissions** normally occurs, to reduce the n/p ratio by converting a neutron into a proton

β–emission (n → p) $\quad {}^{0}_{1}n \rightarrow {}^{0}_{-1}e + {}^{1}_{1}p \quad \frac{A}{Z} \rightarrow \frac{0}{-1}\text{e} + \frac{A \text{ no change}}{Z+1 \text{ increase}}$

3. For atoms with $Z < 83$, but below the band of stability: **atoms whose n/p ratio is too low**
    - Conversion of a proton into a neutron would help

Normal solution: For nuclei whose n/p ratio is too low, either **positron emission or electron capture** normally occurs, to increase the n/p ratio by converting a proton into a neutron

- Electron capture tends to be more likely for higher-Z elements

Positron emission	$\frac{A}{Z} \rightarrow \frac{0}{+1}e + \frac{A\ \text{no change}}{Z-1\ \text{decrease}}$	$\frac{n+1}{p-1}$	Higher	Proton becomes a neutron
Electron capture	$\frac{0}{-1}e + \frac{A}{Z} \rightarrow \frac{A}{Z-1}\ \frac{\text{no change}}{\text{decrease}}$	$\frac{n+1}{p-1}$	Higher	Proton becomes a neutron

Practical: How do I recognize whether a nucleus is likely to be stable or not? And if it isn't, how do I predict what it will do?

1. **Check Z. Is Z > 83**? If so, then **expect alpha emission**. If not, proceed to step two.
2. **Compare the n/p ratio to the ratio found in the periodic table for the same atom.**
3. If the **n/p ratio is similar**, it's probably a **stable** nucleus.
4. If the **n/p ratio is significantly higher** than in the periodic table, **expect beta emission**.
5. If the **n/p ratio is significantly lower** than in the periodic table, then **expect either positron emission or electron capture**.

- Note: There are some not-well-understood kind of stability pattern
- Pairing seems to be preferred, although it's not understood why
    - Even numbers of protons and even numbers of neutrons seem to be preferred, all else being equal

Problems: Predict how the following would decay by α, ß, or positron emission, or by electron capture. Then draw the nuclide produced.

1. ^{40}Cl

2. ^{134}Ba

3. $^{237}_{93}$Np

Binding Energy (21.3)

- the mass of an actual nucleus is always less than the sum of its component neutrons and protons
- The **missing mass (Δm) is called the "mass deficit".**

Δm=(mass sum of protons + neutrons) – actual nuclear mass

$^{1}_{1}$proton	1.00783	$^{1}_{0}$neutron	1.00867

- **The mass deficit (Δm) equals the "nuclear binding energy" = "strong nuclear force"**

$$E=\Delta mc^2$$

Δm in kg (convert from grams to kg)
E in J (convert to kJ)

- Get answers in either kJ/mol (of nucleus) or kJ/"mole nucleon"
  - The number of "nucleons" is the sum of protons and neutrons

4. What is the binding energy in kJ/mol for $^{16}_{8}$O?

Given: $^{16}_{8}$O 15.978 $^{1}_{1}$proton 1.00783 $^{1}_{0}$neutron 1.00867

5. For the above, what is the binding energy in kJ/mol **nucleons**?

Miscellaneous

1. Fe-56 is the most stable of all nuclei, has the greatest binding energy per nucleon
2. In nuclear reactions, the great amounts of energy are provided by nuclear "binding energy" that is released

Fig. 20.3

3. Fission reactions (Section 20.6): large nuclei fragment into smaller nuclei
4. Fusion reactions (20.7): small nuclei combine to give bigger nuclei
5. Both fission and fusion occurs to draw nearer the maximum stability of Fe-56

Rates of Radioactive Decay (21.10)

A. Nuclear half-life: radioisotope decay with 1st order rate laws, have characteristics half-lives ($t_{1/2}$)

Isotope	Half-Life	Notes
$^{238}_{92}U$	$5 * 10^9$ years (5 billion years)	Slow enough so that plenty is still left from when earth was made
^{40}K	$1 * 10^9$ years (1 billion years)	• Daughter nucleus is ^{40}Ar. • Used to date old rocks. The ratio of ^{40}Ar to ^{40}K reflects how much time has passed.
^{14}C	5730 years	Medium half life, used to measure the ages of artifacts used during human history
^{131}I	8 days	Short, used in medical imaging
^{24}Na	15 hours	Short, used in medical imaging
^{99}Tc	6 hours	Short, used in medical imaging

Notes:

1. For radioactive nuclei to be around, they must either have:
    a. Long half-lives so that there hasn't been enough time for the original stuff to decay away. (^{238}U and ^{40}K)
    b. Have some source by which they have been made more recently.
    - ^{14}C is continuously made in the atmosphere as result of cosmic rays acting on ^{14}N
    - Radioactive nuclei used in medical imaging techniques (^{131}I, ^{24}Na, ^{99}Tc) must be made fresh by laboratory techniques.
2. Radioactive nuclei used in medical imaging techniques or in chemotherapy must have relatively short life times.
    - You want them radiating so the doctors can detect whether the solution is going where it should.
    - But once the analysis is completed, you'd like the body to be free from them as soon as possible. (Rather than irradiating your DNA for weeks for no reason.)

B. Radioactive Decay Math

- Radioactive nuclei decay via first-order rate laws
- Formulas for First Order Reactions: $kt = \ln([A_o]/[A_t])$ $kt_{1/2} = 0.693$

$\ln(A_o/A_t) = 0.693 \cdot t / t_{1/2}$	When solving for the amount of material left after a given time, given the half life
$t = (t_{1/2}/0.693) \ln(A_o/A_t)$	When solving for time, given half life and quantities of material
$t_{1/2} \cdot \ln(A_o/A_t) = 0.693 \cdot t$	Rearranged version when solving for $t_{1/2}$

- A_o = original amount of material
- A_t = amount after time t
    - Amounts can be in mass, or in emission rate, or activity, or 100% → percent.
- $t_{1/2}$ = half life, the time for half of the material to decay
- Boxed formulas are the ones you'll be given on the test
- Handling "ln y = x" on calculator, when you know "x" but want to solve for "y": enter "x", then hit your "e^x" button.

1. ^{99}Tc is used for brain imaging scan. The half-life for ^{99}Tc = 6.0 hours. What percentage of a dose of ^{99}Tc is left after 24 hours?

2. ^{131}I has a half-life = 8.0 days. How long will it take to decay for a sample to decay so that only 10% of the original ^{131}I survives?

3. ^{90}Sr $t_{1/2}$ = 28.8 g If 42 g of ^{90}Sr is buried, how much is left after 120 years?

C. C-14 and Carbon Age Dating: Measurement of Human History Dates.

- carbon-14 is a very small, low abundance isotope of carbon. C-12 is the major isotope, C-13 next. But the C-14 is good for finding human history dates.
- ^{14}C $t_{1/2} = 5730$ years
- Since most of human history has been within the last few thousand years, the half-life for carbon-14 ends up being pretty appropriate.

The logic of Carbon dating:

1. A steady state percentage of CO_2 in the air is radioactive $^{14}CO_2$.
   a. The $^{14}CO_2$ in the air is produced from ^{14}N as the result of cosmic rays
   b. Plants take in $^{14}CO_2$ directly from the air via photosynthesis.
   c. Animals and humans take in ^{14}C indirectly, either by eating plants that have ^{14}C or by eating animals that ate the plants with the ^{14}C.
2. All living things (plant or animal) have a known steady state percentage of ^{14}C relative to total carbon
   - This results in a known ^{14}C radioactivity rate, relative to total carbon
   - A_o is known
3. Once a living thing dies, it stops incorporating ^{14}C.
   - Plants stop photosynthesizing, people and animals stop eating
4. After death, the radioactive ^{14}C decays at $t_{1/2}$ rate, and the ^{14}C radioactivity rate declines, relative to total carbon
5. By looking at the ^{14}C activity, you can determine approximately how long it's been since something that was formerly alive has died
   - Wood, cloth, anything ex-biological…
   - After a couple of half lives, the amount of ^{14}C radiation gets too low to allow much accuracy

Problem. ^{14}C has a half-life = 5730 years. "Live" carbon has activity of 15.3. A shirt is claimed to be Jesus's, but is found to have carbon activity of 14.0. How old is the shirt, and can the claim be true?

Rock dating similar:

$^{40}K \rightarrow {}^{40}Ar$ $t_{1/2} = 1 \cdot 10^9$ years $^{238}U \rightarrow {}^{206}Pb$ $t_{1/2} = 4.5 \cdot 10^9$ years

- When lead is formed by sources other than ^{238}U decay, isotopes other than just ^{206}Pb are formed, so you can tell that the ^{206}Pb came from the ^{238}U.
- By measuring the ratio of ^{40}K to ($^{40}K + {}^{40}Ar$), or ^{238}U to ($^{238}U + {}^{206}Pb$), you can determine what fraction of the original ^{40}K or ^{238}U is left, figure out how many half-lives have passed, and figure out how long ago a rock formed.

Nuclear Fission

${}^{1}_{0}n + {}^{235}_{92}U \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3{}^{1}_{0}n$ + Energy!! $\Delta E = -2 \bullet 10^{10}$ kJ/mol!! (Lots!!)

Fig. 20.6

Keys

1. Fission: When a larger nucleus breaks to give smaller nuclei
2. Humongous energy release!!
3. Fact: neutron bombardment doesn't always result in the same fission. Sometimes the ${}^{235}U$ fragments in other ways to produce other daughter nuclei. Fig. 20.7
4. Neutron: both a reactant and a product!!
   - more neutrons are produced than are absorbed!
5. Branching and the uranium fission "chain reaction" Fig. 20.7
   - more neutrons produced than absorbed ⇒ more neutrons can strike other uraniums and cause more fission reaction ⇒ more neutrons ⇒ more fissions (and energy), etc..
   - Proliferating neutrons → proliferating fissions → proliferating energy, proliferating chain reaction (and maybe a uranium fission bomb, WWII Japan…)
6. "Critical Mass": enough ${}^{235}U$ is required to support chain
   - "subcritical"- There isn't a large enough block of ${}^{235}U$ to absorb the neutrons. While a given fission may absorb only one neutron and produce several neutrons, most of those neutrons produced just escape, rather than hitting another ${}^{235}U$, causing another fission reaction, and propagating/proliferating the chain
   - "supercritical": more than enough ${}^{235}U$ so that more than enough of the neutrons produced bump into another ${}^{235}U$, cause another fission, and propage/proliferate the chain.
   - Nuclear fission bomb: 2 subcritical masses are smashed together to achieve supercritical mass. The chain reaction then propagates/proliferates!!
     - A chemical bomb is actually used to propels one mass into the other!

Nuclear Reactors: Major Components

1. **${}^{235}U$ fuel rods** (last for years)
   - subcritical: can't explode
   - these are not pure natural uranium; rather they are enriched in ${}^{235}U$
2. **Cadmium control rods** to control the rate of reaction and provide emergency security
   a. The control rods are adjustable and are suspended in between the fuel rods
   b. The control rods absorb neutrons.
   c. They can block the spray of neutrons from one fuel rod to another and prevent chain reaction.
   d. The rate of chain reaction is controlled by raising the control rods just high enough so that enough neutrons can get through and sustain the chain reaction.
   e. As a fuel rod ages and becomes less active, it needs more neutron hits to sustain the chain reaction, so the fuel rods get raised higher and higher.
   f. Many automatic controls are in place to drop the control rods and stifle chain reaction in case of any emergency
3. **A coolant (water) absorbs energy**, produces steam that drives turbine⇒⇒electricity

Concern: what do with spent fuel rods, still with some radioactive content?

- Current process: "vitrifactions"
  - Fuel rods get "melted" and dissolved in liquid glass;
  - The liquid glass gets poured into a steel can, cools, and glasses over.
  - For one year plant: only one barrel gets produced!!

"Breeder Reactors" $^{238}U + ^{1}_{0}n \Rightarrow ^{239}Pu$

- Active Plutonium is "bred" from relatively inactive ^{238}U by bombardment with high-speed neutrons

Nuclear Fusion

$4\,^{1}_{1}H \rightarrow ^{4}_{2}He + 2\,^{0}_{+1}e$ $\Delta E = -2.5 \cdot 10^{9}$ kJ/mol

$2\,^{2}_{1}H \rightarrow ^{4}_{2}He$

- Solar process, hydrogen and deuterium fusion is how the sun produces it's energy!
- Ideal energy dream: no radioactive byproducts, huge energy, cheap H_2O provides lots of hydrogen (and a good amount of deuterium) for fuel!!
- Problem: huge temperatures are needed (to overcome nuclear repulsion) in order to push Hydrogens together in order for them to fuse
  - Materials that can contain and support such high temperatures are not currently practical
- Hydrogen-bomb (cold war, never used in actual wars): a uranium fission bomb is used to provide the heat needed to support fusion!

Radiation: Effects and Units

1. rad = energy absorbed/body mass (dosage)

   (1 food calorie = ½ million rads)
2. rem = biological damage

   effective dose = rads x impact factor
   (dose) (quality)

Key: "rems: measures risk
 a) not all rays equal
 b) dosage doesn't consider variance in penetration

Typical: < 0.4 rems/year (cosmic, x-rays, radon…)
 > 25 rems to cause trace damage
 > 500 rems → 50% chance of death within 30 years

Rays and damage (depends on whether internal or external)

α: little penetration, only irritates outer skin (bad if generated internally)

ß: penetrates a few mm

- γ While external α and ß radiation does little serious harm because it never penetrates to vital organs, internal α and ß radiation is much more harmful
- if the source of the radiation is inside the lungs or liver or kidney or brain, etc., large doses of these rays can be damaging even without penetrating far

γ: high energy, deep penetration, maximum damage

- γ radiation can generate DNA mutation
- γ radiation generated internally is actually not all that bad, because many of the γ rays largely escape!

Radon: Uranium →→ $^{222}_{86}\text{Rn}$ (gas) → $^{218}_{84}\text{PO} + ^{4}_{2}\text{He}$ → $^{4}_{2}\text{He} + ^{214}_{82}\text{Pb}$

1. Radioactive radon gas is produced from certain natural underground uranium sources
2. The radon gas seeps through basement cracks or into underground mines
3. Because the radon is heavy, it kind of sits in the basement, rather than just floating away
4. Because the radon is a gas, when you breathe the air you breathe some radon in, into your lungs
5. The radon is a major alpha emitter
6. From outside that wouldn't be much of a problem, but when you breathe it into your lungs and it's alpha-emitting in your lungs, the radiation can damage lung tissue ⇒ lung cancer.