

CHEM 116

End of Course Review

December 12, 2006
Prof. Sevia



Agenda

- Tie together electrochemistry and thermodynamics with a couple of examples
- End of course review
- Important note: gas laws will NOT be on the final exam, though you do need to have facility with some ideas that are described by gas laws (for example, as you increase the temperature, particles move faster)

The **final exam** is scheduled for Monday, December 18, 11:30AM-2:30PM in Lipke Auditorium (our regular lecture hall).

End of course review



- This is a review of everything that has been covered in both semesters of freshman chemistry
- Not all of this will be tested on the final exam, only the material from this semester (minus gas laws) will be tested on the final exam
- To understand the material from this semester, you need a firm grasp on the material from first semester, so I think it's helpful to see all of the chemistry together to see where the pieces fit together

Information about the Final Exam & Suggestions for studying



- The final exam will be 120 minutes long and will have 70 multiple choice questions.
- The exam is the official ACS final exam for second semester general chemistry. The exam covers all the topics in our Chem 116 course except gas laws.
- While there are no math questions about gas laws, in a similar way to all the topics from first semester, you are expected to draw from a conceptual understanding of gas laws.
- The hardest part about taking a comprehensive final exam is knowing how to approach solving a particular problem.
- The problems on the final exam are grouped (e.g., all the questions about intermolecular forces are together).
- Practice recognizing which kind of problem something is – flash cards.
- Know when to use which equations, and know which equations are given on the exam and which ones you have to memorize.

Course Review



Overarching principle: Chemists view nature at three levels.

1. Macroscopic observable
 - Matter that comprises everything
 - Properties of materials
2. Particle level models
 - Structure of matter
 - Energy that governs interactions of particles
3. Symbolic representation
 - Ways of representing behavior of matter

Each level provides information

Overarching principles of chemistry (P.W. Atkins)

1. Matter is made of particles, particles are made of atoms
2. Elements display periodicity
3. Chemical bonds form when electrons pair
4. Molecular shape determines properties of matter
5. There are attractive forces between particles
6. Energy is conserved
7. Entropy tends to increase
8. There are barriers to reaction
9. There are only four types of reactions

Chemistry is about the interaction between matter (structure)
and energy (change)

Atkins, P.W. "Skeletal Chemistry." *Education in Chemistry* (January 2005).
http://www.rsc.org/Education/EIC/issues/2005_Jan/skeletal.asp

1. Matter is made of particles which are made of atoms

- Atoms are comprised of protons, neutrons and electrons.
- All the different kinds of atoms are cataloged in the Periodic table.
- The number of electrons can vary:
 - Neutral atom: same quantity as protons
 - Negative ion: more electrons than protons
 - Positive ion: fewer electrons than protons
- Quantities of matter can be measured either by numbers of particles (in the case of atoms or molecules) or units (in the case of ionic compounds) in a sample of the material, or by the mass of the sample. It is possible to convert between these two measurements of quantity of matter using molar mass.

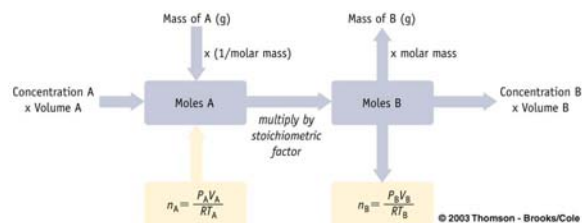
For example,

$$18.5 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 0.686 \text{ mol Al}$$

1. Matter is atomic (continued)

- Atoms are conserved in all processes (except nuclear decay).
 - All stoichiometry calculations are based on this principle: In a chemical change, the number of atoms of each kind that enters the reaction must equal the number of atoms of each kind that exit the reaction.
 - This means you must balance chemical reactions first before doing stoichiometry calculations.
 - The maximum amount of product in a reaction is determined by the least reactant that is available (the most reactant that can be used in a process is equal to the least reactant available).

Stoichiometry

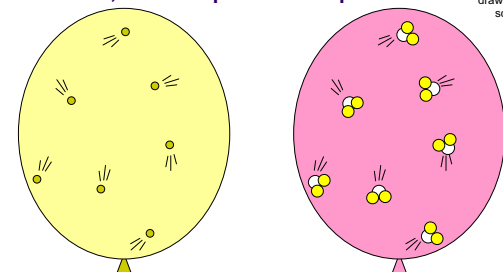


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1. Matter is made of particles (continued)

- Kinetic molecular theory (KMT) of gases is a model which has the assumptions:
 - No attractive forces between particles \Rightarrow collisions are elastic
 - Volume of particles is negligible compared to the space they occupy
 - Temperature is proportional to average kinetic energy
- Kinetic theory leads to the ideal gas law, $pV = nRT$
- Ideal gases behave as particles which are independent of identity
- Real gases condense (to form liquids and solids) because assumptions 1 and 2 break down readily
- The most useful measure of quantity of matter is often "concentration" in some form:
 - Density is mass (grams) of material per space (liters) occupied
 - Molarity is number of particles (moles) of material of interest in a mixture per space that the mixture occupies (liters of solution)

Gas feature #1: No matter what mass a gas particle has, it takes up the same space



Note: not drawn to scale

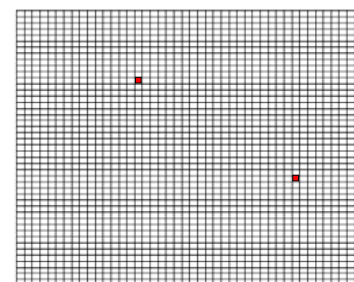
What can you conclude?

If their volume is the same, then the number of particles must be the same.

Gas feature #2: The gas particles are very far apart from each other

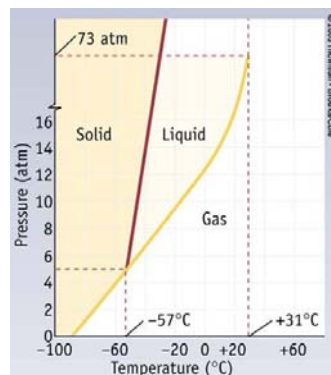


A more accurate depiction: 1 in 1000 at room temperature



CO₂: a typical phase diagram

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



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Characteristics of gases vs. other two phases



Macroscopic observations

Gases

- Very compressible
- Spread out to occupy all the space given in a container
- Low density

Liquids and/or solids

- Not (very) compressible
- Occupy specific volumes, regardless of the container
- High density

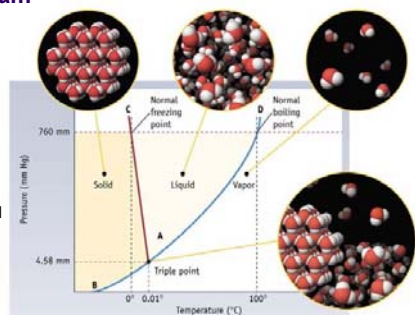
Particle level explanation

- Particles are far apart
- Particles are in rapid motion (kinetic energy)
- Particles are much closer together
- Particles have less kinetic energy than in gases

1. Gases are compressible because the particles are widely separated.
2. Gases immediately fill all available space because the particles are in ceaseless chaotic and rapid motion.

H₂O: an unusual phase diagram

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



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Variables that describe a gas



- Number of particles
 - Quantity: n (moles)
 - Can be converted from/to mass (grams)
- Volume (space) that the gas occupies
 - Three dimensional space: V (liters)
 - Could be given in other units: mL, m³, cm³
- Temperature
 - A measure of the motion of particles: T (degrees Kelvin)
 - Could be given in other units: °C
- Pressure
 - Force per unit area: p (atm)
 - Also used in other units: kPa, Pa, mmHg, torr

Practical uses of KMT model



1. Different gases have different average speeds, so they "effuse" differently (remember our balloons)
 - Useful for identifying gases
2. In a mixture of gases, all gases spread out to occupy the entire volume
 - Useful for measuring how much gas is produced during a reaction

Many properties of materials depend on concentration

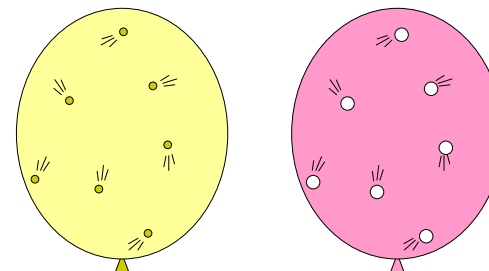


- Ideal gas law contains density (a version of concentration)
 - $D = \text{moles per volume} = n / V$
 - $D = RT / p$
- Colligative properties in mixtures depend on concentration of the species of interest
 - Molality (m) = number of particles of solute per mass of solvent
 - Mole fraction of the solvent (χ_{solvent}) = moles of solvent per total moles
- Molar mass (grams of material per mole) is an intensive property of pure materials and therefore provides a way of identifying pure materials; it also provides a vehicle for converting between expressions of concentration

Density



Why did the SF_6 balloon weigh more than the N_2 balloon?



Solubility, saturation and supersaturation

As you add more solute to a solution →

Below saturation

- Solvent is not yet holding the maximum amount of solute it can at that temperature
- More solute could still dissolve – if you add more, it will mix in

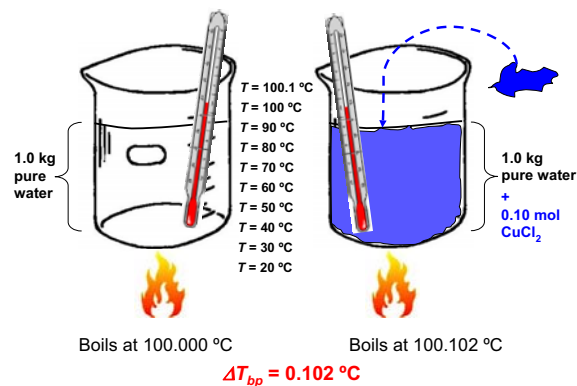
At saturation point

- Solvent is holding the maximum amount of solute it can at that temperature
- If you add any more solute, it will not dissolve (will fall to the bottom – precipitate)
- *Solubility* = often measured in grams of solute per 100 mL of solvent

Beyond saturation

- Solvent is holding more solute than it is able to at that temperature – situation is unstable
- If you add anything to the solution, the excess (beyond saturation point) will crystallize out

Compare boiling points: pure solvent vs. a solution



2. Elements display periodicity

- The Periodic table is a model of how chemists understand the electronic structure of atoms.
- The periodic nature of the elements in the Periodic table gives rise to trends in physical properties of the elements.

3. Chemical bonds form when electrons pair

Two kinds of bonding lead to two kinds of compounds

Ionic Compounds

- Contain ions
- Held together by electrostatic attraction between + and – ions: these attractions called **ionic bonds**
- Ionic formula: simply the ratio of ions present in order for the compound to be neutral, cannot separate a unique unit

Molecular Compounds

- Do not contain ions
- Atoms within molecules held together by **covalent bonds** in which electrons from both atoms are attracted to the nuclei of both atoms in a bond
- In a molecular solid, one molecule held to the next by weaker forces of attraction
- Molecular formula: can separate unique molecules

Reality: bonding is not that simple - there's a gray area in between

Types of pure materials (macroscopic observable level)

- Molecular
 - Non-polar molecules
 - Octane, C_8H_{18}
 - Fats (e.g., olive oil)
 - Polar molecules
 - Water, H_2O
 - Ammonia, NH_3
 - Acetic acid (vinegar is an aqueous solution of it), CH_3COOH
- Ionic
 - Sodium chloride (table salt), NaCl
 - Sodium bicarbonate (baking soda), NaHCO_3
 - Copper (II) sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- Metallic
 - Copper metal, Cu
 - Aluminum foil, Al
- Others that defy categorization
 - Network
 - Quartz, SiO_2
 - Sand, SiO_2
 - Diamond, C
 - Polymeric
 - Any plastic, such as high density polyethylene (HDPE)
 - Amorphous
 - Glasses

The names of these categories are based on the type of bonding

Particle level: materials composed of molecules



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

Particle level: materials composed of ions



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

Particle level: materials composed of metal atoms



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

4. Molecular shape determines properties of matter

- Molecular shape is determined by the underlying geometry of the bonding orbitals.
- Molecules can be either symmetric or not symmetric.
- If a molecule is not symmetric, and if it has at least one polar bond, then the molecule is polar.
- (Polar molecules interact with each other differently than nonpolar molecules do.)

Molecular structure informs properties of acids



1. Binary acids (HX where X is a nonmetal)
2. Oxoacids (formula HOXO_n where X is a nonmetal)
3. Carboxylic acids (RCOOH where R is a carbon group)

The question is – how easily can the H⁺ be let go?
It always depends on how much electron density gets drawn away from the H in the acid molecule

5. There are attractive forces between particles

- Forces of attraction and repulsion are explained by the Coulomb model, where the force is proportional to two things:
 1. The magnitudes of the charges that interact.
 2. The distance separating the charges.

Coulomb's Law:

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

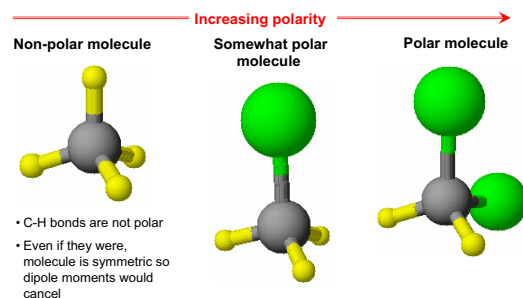
Annotations:

- proportionality constant (points to k)
- Force of attraction (points to F)
- Charge on positive ion (points to Q_+)
- Charge on negative ion (points to Q_-)
- distance between ions (points to r^2)

- Changes in matter are due to the energetics dictated by the forces in matter. Energy is conserved in all changes.
 - Two atoms that are bonded have lower potential energy than two atoms separated, so when atoms bond they give off energy.
- Energy changes are path independent.

What is a dipole?

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



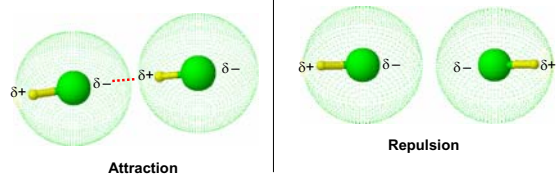
Interactions between particles



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

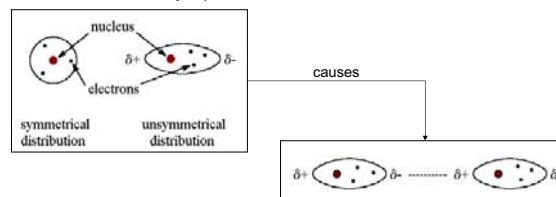
Polar molecule – polar molecule attractions

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



Non-polar molecule – Non-polar molecule attractions

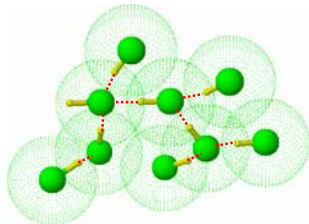
- A non-polar molecule can have a momentary, fleeting dipole
- When it does, it can induce a dipole in a neighboring molecule
- Two momentary dipoles attract each other



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

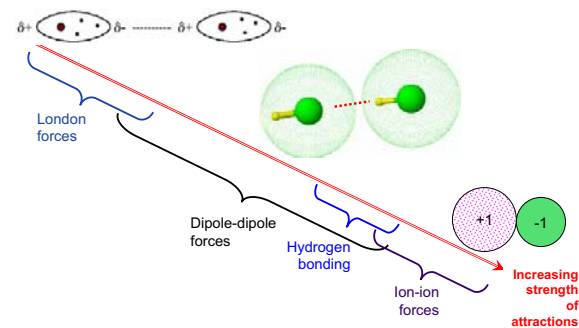
How dipole-dipole attractions help keep a liquid together

Example: liquid HCl



Summarizing inter-particle attractions

From weakest to strongest



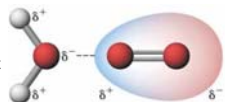
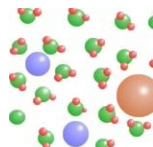
Mixed intermolecular forces

- Ion – dipole

- The ion causes the dipoles to orient in ways that increase attractions
- This explains solvation of an ionic compound in water or other polar solvents (e.g., Na^+ and Cl^- ions in water)

- Dipole – non-polar molecule

- The dipole causes the non-polar molecules to form more temporary dipoles
- This causes the non-polar molecules to orient in ways that increase attractions
- This explains why it is possible to dissolve tiny amounts of non-polar chemicals in a polar solvent (e.g., oxygen gas in water)

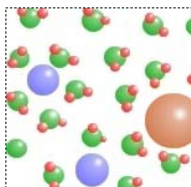


What's significant about how particles are arranged inside a solution?



In the bulk

- Solute particles surrounded by solvent particles
- Solute-solvent attraction is stronger than a solvent-solvent attraction



At the surface

- Phase changes occur at surfaces
- Only solvent particles change phase (solute particles remain dissolved)
- As solvent particles leave the liquid phase, the solution becomes more concentrated in solute

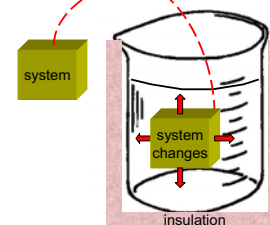
6. Energy is conserved

- Energy changes that occur can be understood when the universe is divided into the *system* and the *surroundings*
- The total energy of the universe (system + surroundings) is conserved
- Endothermic and exothermic refer to heat energy flow into and out of the system – that energy flows from or to the surroundings
- Energy (called “enthalpy” in a closed system with constant pressure) is a state function, i.e., it is path independent

Liquid Water's Capacity to Absorb Heat Energy

Can be used as the standard for comparison:
Calorimetry!

Measuring heat transferred from a system



Problem Solving Strategy

$$q_w = m_w C_w \Delta T_w$$

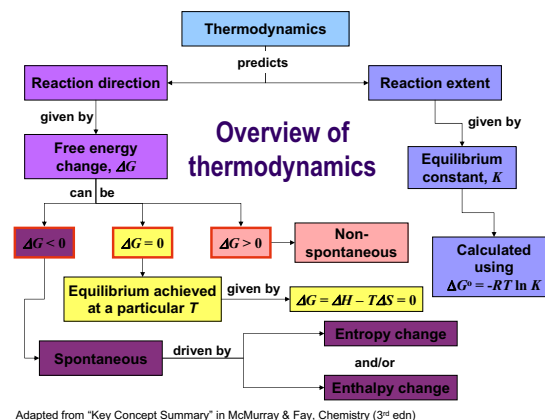
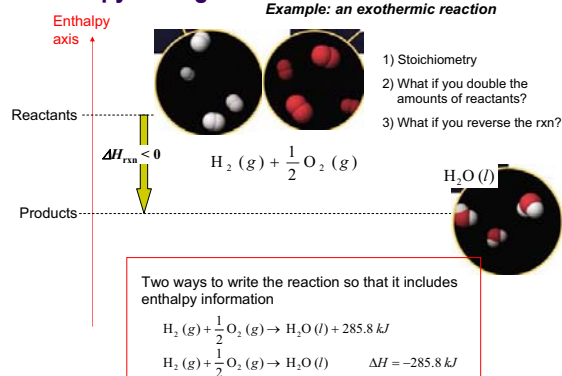
where $\Delta T_w = \text{temp change of } \text{H}_2\text{O}$
 q_{sys} is opposite of q_w

ΔH_{sys} is just q_{sys} per mole of reactant

Known quantity (mass, m_w) of water in beaker

Beaker image: core.ecu.edu/chem/chemlab/equipment/beaker.htm

Enthalpy Change



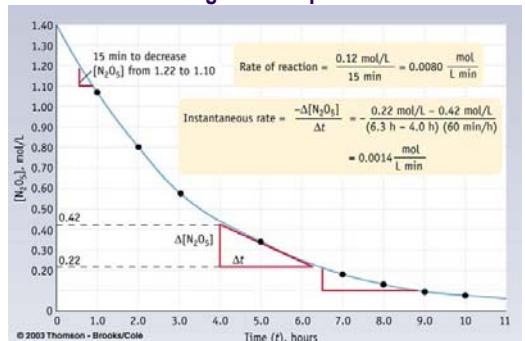
7. Entropy tends to increase

- Energy and matter both tend to disperse
- This is represented by the equation, $\Delta G = \Delta H - T\Delta S$
- The dispersal of energy and matter may be linked to a constructive process, such as assembly of constructed objects or of amino acids into a protein, but always in such a way that the entropy of the universe (system + surroundings) increases
- When a given (system + surroundings) reaches maximum entropy, it exists at a dynamic equilibrium
 - All species in a system exist (even if only in very small quantities) at equilibrium
 - Rate of forward reaction equals rate of reverse reaction

8. There are barriers to reaction

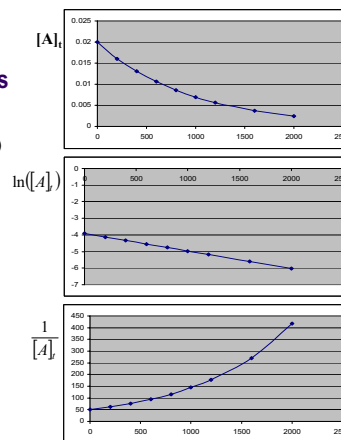
- The world is collapsing into chaos, but the existence of barriers prevents it from occurring quickly
- Activation energy is proportional to the time it takes for a reaction to occur
- The rate (speed) that a reaction occurs at depends on two things:
 - Concentrations of reactants
 - Rate constant, which depends on
 - Temperature (direct relation: as $T \uparrow$, $k \uparrow$)
 - Activation energy (inverse relation: as $E_a \uparrow$, $k \downarrow$)

The rate of a reaction changes over time because reactants get used up



Method 1: Comparing graphs

Time (min)	$[H_2O_2]$ (M)
0	0.0200
200	0.0160
400	0.0131
600	0.0106
800	0.0086
1000	0.0069
1200	0.0056
1600	0.0037
2000	0.0024



Two ways to figure out the dependence of the rate on concentration of chemicals in the reaction

- Graph concentration vs. time and examine mathematical shape of curve

Zero order

$$\text{rate} = k[A]^0$$

$$-\frac{d[A]}{dt} = k \rightarrow \int_{\text{when } t=0}^{\text{at time } t} d[A] = -\int_0^t k dt \rightarrow [A]_t = [A]_0 - k t$$

$$y = a + bx$$

First order

$$\text{rate} = k[A]^1$$

$$-\frac{d[A]}{dt} = k[A] \rightarrow \int_{\text{when } t=0}^{\text{at time } t} \frac{d[A]}{[A]} = -\int_0^t k dt \rightarrow \ln[A]_t = \ln[A]_0 - k t$$

$$y = a + bx$$

Second order

$$\text{rate} = k[A]^2$$

$$-\frac{d[A]}{dt} = k[A]^2 \rightarrow \int_{\text{when } t=0}^{\text{at time } t} \frac{d[A]}{[A]^2} = -\int_0^t k dt \rightarrow \frac{1}{[A]_t} = \frac{1}{[A]_0} + k t$$

$$y = a + bx$$

- Measure initial rate at many different initial concentrations and compare

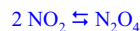
Method 2: Determining rate law by measuring initial rate at various concentrations

Given the following measurements of initial rate of reaction under various conditions of initial concentrations of reactants, determine:

- the rate law
- the value of the rate law constant, k
- the units of k

Experiment	Initial Concentration (M)		Initial rate (M/s)
	[NO]	[O ₂]	
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

What is equilibrium?



<http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/no2n2o4equilV8.html>

In this animation of the system at the particle level, what indication is there that the system is at equilibrium?

- Concentration of each chemical remains constant in time
- Both the forward and reverse reactions are occurring
- The rate of the forward reaction is EQUAL to the rate of the reverse reaction

At the macroscopic observable level:

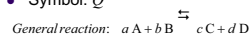
When a system is at equilibrium, it looks like nothing is happening!

Reaction Quotient vs. Equilibrium Constant



Reaction Quotient

- Symbol: Q

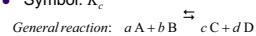


$$\text{Reaction quotient: } Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

- Situation: when the system is not at equilibrium
- The concentrations of the chemicals in the reaction continue to change as the reaction progresses toward equilibrium

Equilibrium Constant

- Symbol: K_c



$$\text{Equilibrium constant: } K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

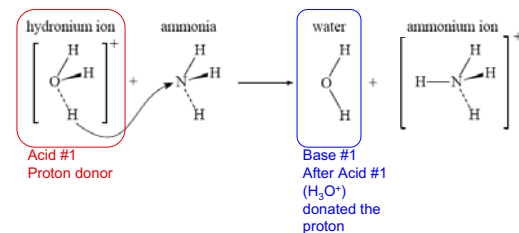
- Situation: when the system is at equilibrium
- Once the system has reached equilibrium, the concentrations of chemicals involved in the reaction do not change

9. There are only four types of reactions

There is really only one type of reaction, but for convenience we think of all chemical changes as one of four processes which each have personalities:

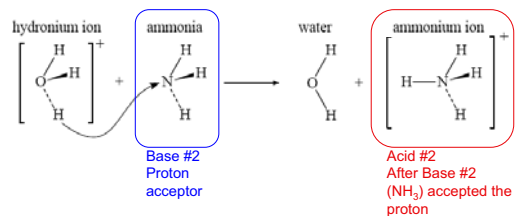
- Transfer of a proton (Bronsted-Lowry acid-base reactions)
 - $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$
 - $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{HB}^+ + \text{OH}^-$
 - $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{HB}^+$
- Transfer of an electron (redox reactions)
 - Can be separated into oxidation ($\text{M} \rightarrow \text{M}^+ + e^-$) and reduction ($\text{N} + e^- \rightarrow \text{N}^-$)
- Sharing of a pair of electrons (Lewis acid-base reactions, also called "exchange" or double-replacement reactions)
 - Precipitation: ($\text{M}^+ + \text{N}^- \rightleftharpoons \text{MN}$)
 - Sometimes gas forming (e.g., $\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2$)
- Sharing of single electrons (radical reactions)

Conjugate acid-base pairs



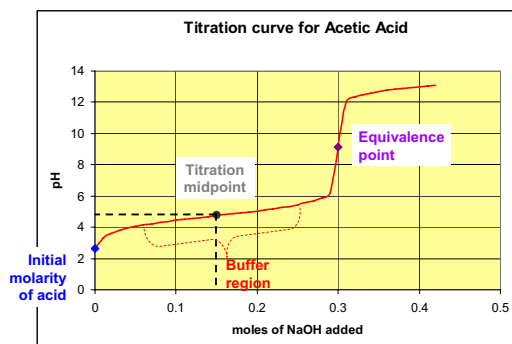
Pair #1: an acid on one side and its conjugate base on the other side

Conjugate acid-base pairs



Pair #2: a base on one side and its conjugate acid on the other side

Main points about titration



Redox rxns in symbolic representation

- Non-redox reactions
 - Sodium sulfide + cadmium nitrate → cadmium sulfide + sodium nitrate
<http://www.jce.divched.org/JCESoft/CCA/samples/cca4CuNO.html>
 - Copper (II) nitrate + ammonia → copper (II) hydroxide + ammonium ions
<http://www.jce.divched.org/JCESoft/CCA/samples/cca4CuNO.html>
- Redox reactions
 - Iron (III) oxide + aluminum metal → aluminum oxide + iron metal
<http://www.jce.divched.org/JCESoft/CCA/samples/cca7thermite.html>
 - Sodium metal + hydrochloric acid → sodium chloride + hydrogen gas
http://www.jce.divched.org/JCESoft/CCA/samples/cca4Na_acid.html
 - Sodium metal + nitric acid → sodium ions + nitrogen dioxide (brown gas)

Redox rxns at the particle level

- Electrons are exchanged between one species and another
- One species is an electron donor, another species is an electron acceptor
- Therefore, one species must lose one or more electrons, the other species must gain one or more electrons
- A redox reaction can be broken into two halves: the electron donation (called oxidation) and the electron acceptance (called reduction)
- If these half-reactions are separated in space, electrons can be forced to flow through a wire
- If $Q < K$ for the starting concentrations, then the reaction is product-favored and the reaction progresses toward products, generating electricity as it does

Skills

Part I: Foundational

- Assigning oxidation numbers
- Balancing redox equations

Part II: Applied

- Diagramming electrochemical cells
- Facility with cell notation

Part III: Making mathematical predictions of properties

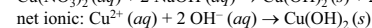
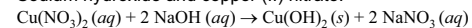
- Calculating cell potential at standard conditions
- Calculating cell potential at non-standard conditions
- Relating the amount of a substance oxidized or reduced to the electrical current and the time during which current is allowed to flow



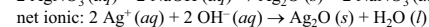
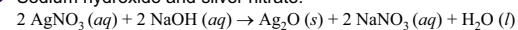
Precipitation reactions

Examples

- Sodium hydroxide and copper (II) nitrate:

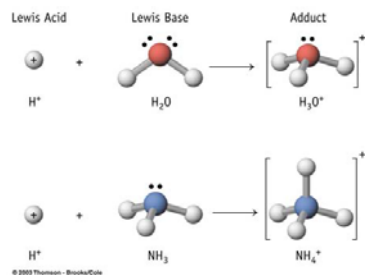


- Sodium hydroxide and silver nitrate:



Lewis acids and bases

- Lewis acid = accepts a pair of electrons
 - Lewis base = donates a pair of electrons
- Definition is more general than Bronsted-Lowry



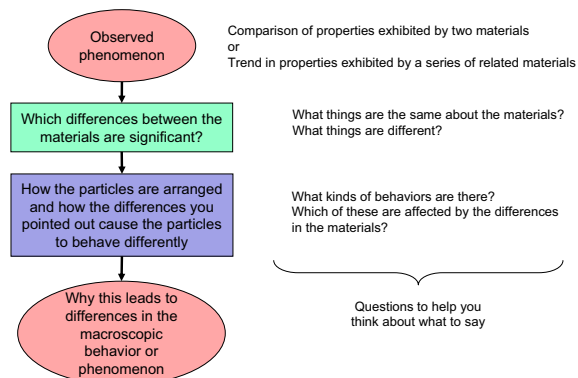
From Chemistry A Chemical Reaction in Action by K. J. Laidler, C. 2003. Reprinted with permission of Thomson, a division of Thomson Learning. All rights reserved. 0-03-02522-5.

What we study in chemistry

- First, learn these principles
- Then explore their ramifications for synthesis and analysis
- Understand how these principal ideas were established (what experimental evidence exists)
- Use tools that rely on these principles to study specific systems (spectroscopy, diffraction, etc.)



The structure of scientific explanations (in chemistry)



Overarching principles of chemistry (P.W. Atkins)

1. Matter is made of particles, particles are made of atoms
2. Elements display periodicity
3. Chemical bonds form when electrons pair
4. Molecular shape determines properties of matter
5. There are attractive forces between particles
6. Energy is conserved
7. Entropy tends to increase
8. There are barriers to reaction
9. There are only four types of reactions

Chemistry is about the interaction between matter (structure)
and energy (change)

Atkins, P.W. "Skeletal Chemistry." *Education in Chemistry* (January 2005).
http://www.rsc.org/Education/EIC/issues/2005_Jan/skeletal.asp