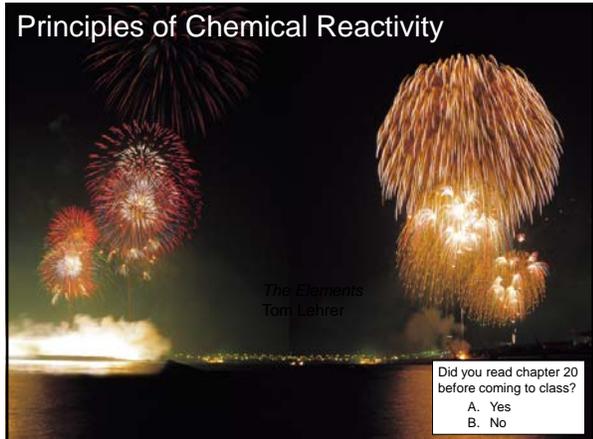


Principles of Chemical Reactivity

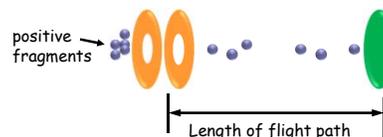


The Elements
Tom Lehrer

Did you read chapter 20 before coming to class?
A. Yes
B. No

Review: In a mass spectrometer, which fragments reach the detector first?

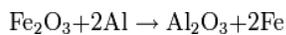
- The most reactive fragments
- The heaviest fragments
- The lightest fragments
- The biggest fragments



We'll start off with some fireworks



- We will combine some rust (Fe_2O_3) with some aluminum powder.
- We will light a ribbon of magnesium, and let it burn into the combination, and see what happens...



Learning objectives

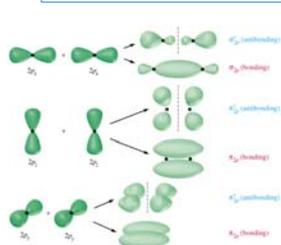
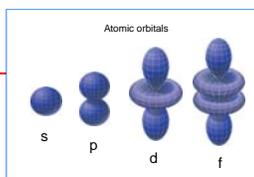
- Why do atoms form chemical bonds?
- Why are some reactions fast, and others slow?
- How do energy and entropy play a role
- What is equilibrium

Molecular Orbitals

- Orbitals are electron probability standing waves
- Shape of orbital depends on placement of the different nuclei.
- New standing wave patterns (new orbitals) form when there are multiple nuclei
- Molecular orbitals follow same rules as atomic orbitals:
 - 2 electrons per orbital (opposite spins)
 - Fill lowest energy orbitals first

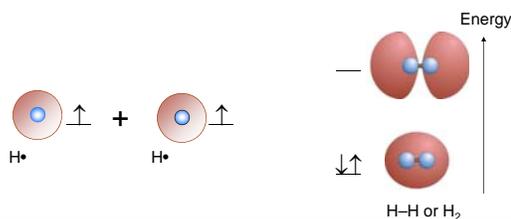


Molecular orbitals



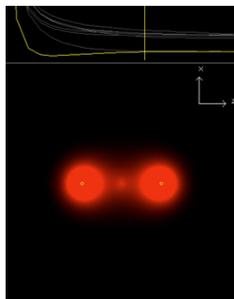
Molecular Orbitals and Bonding

- When atoms get close, molecular orbitals can form
 - If the electrons are lower in energy in the resulting molecular orbital than they were in the atomic orbitals, bonds form
 - Bonding and antibonding orbitals are possible



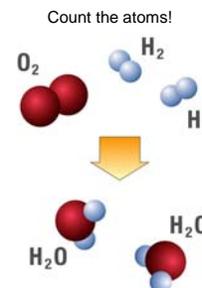
Molecular Orbitals on the Web

- See www.falstad.com/qmimo
- Two positive nuclei mean new electron probability standing wave patterns work (different from atomic orbitals)
- Bonding molecular orbitals have high electron density between nuclei



Conservation of Matter: Balancing Chemical Reactions

- Matter is not created or destroyed in chemical reactions
- This is reflected in the way we write them
- Write a balanced equation for the conversion of hydrogen and oxygen into water.



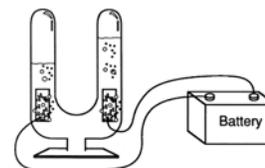
Which way of writing the reaction of hydrogen with oxygen to make water best complies with conservation of matter and describes what happens?

- $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$
- $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$
- $2\text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$



Electrolysis

- You can run the reaction backward:
 - $2\text{H}_2\text{O} + \text{energy} \rightarrow 2\text{H}_2 + \text{O}_2$
 - Pumping energy back into the system
- For each water molecule that reacts, how many molecules of H_2 are produced?
- Same question, for O_2 ?



Reactions Take Time

- Going in the direction $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$, reaction is fast
 - Or is it? What if you don't have a match?
- Electrolysis clearly takes time
- Clock reaction (oscillating clock demo)
 - Really a complex set of racing reactions
 - When one set leads, yellow
 - When the other leads, purple

Iron and Oxygen combine at different speeds depending on conditions

- Write a balanced reaction for combining Iron (Fe) and Oxygen (O_2) into rust (Fe_2O_3)
 - $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$
 - $3\text{Fe}(s) + 2\text{O}_2(g) \rightarrow \text{Fe}_3\text{O}_4(s)$



Reactions Go at Different Speeds

- Cellulose + O₂ → CO₂ + H₂O
 - Dead tree in forest
 - Wood in fire
 - Sawdust in explosion
- Why?



What Governs Speed of a Reaction?

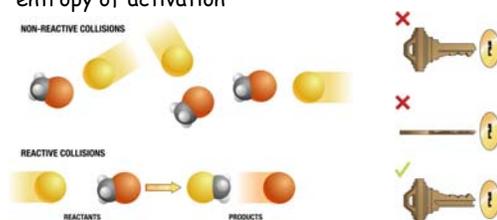
- Definition: rate that reactants are consumed, or products are produced
- Reactants must get close for electron clouds to interact
- Factors:
 - Collision rate
 - Temperature (a reflection of molecular speed)
 - Pressure (for gases) or concentration (for liquids)
 - Physical state
 - Energetic requirements
 - Entropic (organization) requirements

A Thermodynamic View of Bonding

- Bond formation is favorable if it leads to decreased energy for the system, and/or increased entropy for system + surroundings
- 3 ways to accomplish this
 - Lots of atoms share lots of electrons: metals
 - Nonmetals "take" electrons from metals: ionic materials
 - Nonmetals share electrons with each other: covalent materials

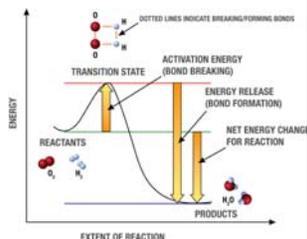
The effect of entropy on reaction rates

- Reactants frequently must have a certain orientation at the transition state, or reaction will not occur
- This corresponds to order in the transition state: entropy of activation



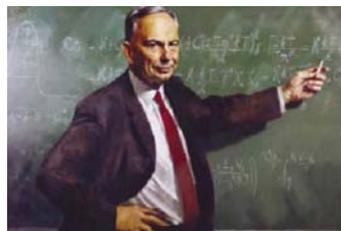
Effect of Energy

- The net energy released (or consumed) does not affect rates
- The energy required to reach the *transition state* ("activation energy") has large effect
- Transition state
 - The critical arrangement of atoms where the reacting system "decides" whether or not to make products
 - Typically involves breaking and/or formation of bonds

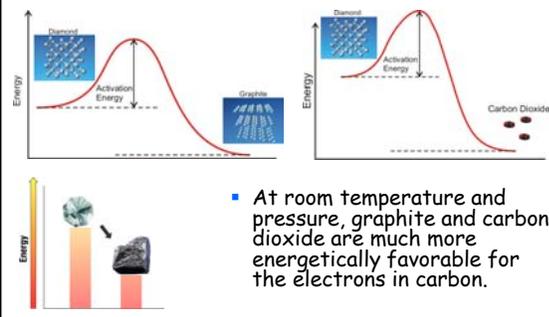


A famous LDS connection

- Professor Henry Eyring, 1901-1981



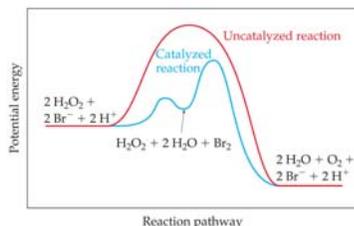
Why doesn't your diamond turn into pencil lead or burst into flames?



- At room temperature and pressure, graphite and carbon dioxide are much more energetically favorable for the electrons in carbon.

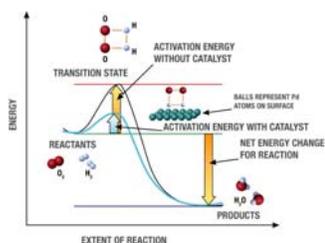
Catalysts Decrease energy or increase entropy of activation without themselves being consumed; speed up rate

- H_2O_2 decomposes spontaneously
- Much faster in presence of Br^- or I^-
- Catalyst makes new, lower energy route possible



Catalyzing the formation of water

- $H_2 + O_2$ w/ Pd/C catalyst
- Pd surface stretches the H-H bond, helping it break and lowering transition state energy

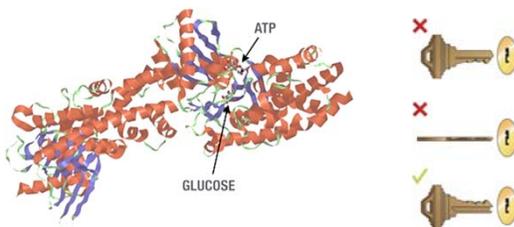


Why do we need to use a match to explode the balloon?

- Products of combustion of the match catalyze reaction of $H_2 + O_2$
- Heat from the match provides the required energy of activation
- We need the match to pop the balloon and expose the H_2 to the O_2
- Matches contain small amounts of palladium (Pd)



Catalysts in biology



Hexokinase - Enzyme that catalyses the transfer of phosphate from ATP to glucose to form glucose-6 phosphate, the first reaction in the metabolism of glucose via the glycolytic pathway.

Equilibrium

- Reactions go in both directions:



- You've already seen this in the $H_2 + O_2$ reaction
- When forward and reverse rates are equal, amount of reactant & product no longer changes
- This dynamic balance is called "chemical equilibrium"
- Equilibrium is the state of lowest energy, and maximum entropy; everything moves toward it

