**Chem 20BH: Highlights from the Syllabus**

**READ THE UPDATED SYLLABUS BEFORE AND AFTER EACH CLASS**


Syllabus will be *updated* after each lecture. **Upcoming assignments are finalized** when date is green and underlined.  

**Lecture 1, Monday 7 January**

Textbook: *Principles of Modern Chemistry*, 8th ed, Oxtoby, Gillis, & Campion

Discussions: Tuesday/Thursday 11 AM, 2200 Young Hall

You will learn *both* scientific intuition and how to think through and to work quantitative problems

You will also learn some chemistry

Goals: gain intuition to extend basic knowledge, solve quantitative & qualitative problems, think like a scientist/engineer, be able to read the literature and attend seminars, find scientific interests (& hopefully, get into research labs)

I expect a lot of you, so that we can cover key issues in science and engineering

Come prepared by having read material and be ready to discuss it

Turn in homework in *your* section folder each lecture

You will make up a problem (10 × ) for a set of lectures and answer it

(The top few of the quarter receive nominal extra points + immortality!)

No late homework submission without prior approval of one of our TAs

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**Chem 20BH: Highlights from the Syllabus, cont.**

**Grading:**

Midterms 30% (2 × 15% each)  
Project 15% (10% poster + 5% paper)  
Final 20% *(format depends on the number of students)*  
Homework 30% *(10% creative problems + 10% graded problems + 10% literature assignments, top 5 of 6)*  
Participation 5%

**Exams:**

No notes or calculators or phones or devices

You will receive a periodic table and list of formulas and constants

Recording lectures is not allowed without my explicit permission, and under no circumstances can be posted online or otherwise transmitted

**Tentative office hours (depending on your availability):**

Tuesday 2\textsuperscript{nd}–3\textsuperscript{rd} PM & Thursday 1\textsuperscript{st}–2\textsuperscript{nd} PM, 3041 Young Hall  
*(we may move if crowded)*

Often on iChat, WeChat as psweiss

TA office hours will be on the web site

**READ THE UPDATED SYLLABUS BEFORE AND AFTER EACH CLASS**
Chem 20BH: Foreign Language Immersion Opportunity
Energy

Treat chemistry (and science and engineering) as a foreign language
We are going to jump right in

Energy is to chemistry like money is to economics & everyday life,
so choose your favorite energy unit (like a currency)
eV, kJ/mole, kcal/mole, cm⁻¹
Know the conversions to the others
Also, know conversions to J and to K (absolute temperature)

This course is going to be tailored to your interests
We will explore the science together

Wisdom from Three Leading Interdisciplinary Scientists and “Difference Makers”

Millie Dresselhaus, MIT

Sometimes you just have to trust yourself and
go it alone.

Led to:
Developing understanding of carbon nanomaterials, before many of
them existed

No advisor? Work independently
No colleagues and peers? Find what is interesting and keep going!

ACS Nano 3, 2434 (2009)
George Whitesides, Harvard

When you’re starting a project, is it more important to have the project succeed or to have the project be important?

Imagine a 2×2 matrix and you have columns which are “succeed” and “fail,” and the rows are “important” and “not important.”

Obviously, if you have an important project and it succeeds, + + +.
If you have an unimportant project that fails, - - -.
But, what about the off-diagonal terms?
If you have an unimportant project and it succeeds, it’s still -, because nobody cares.
If you have an important project and it fails, you almost always get credit for identifying an important project and taking a step.

Leroy Hood, Institute for Systems Biology

Assume everything that can be done, has been done.
What would you do next?

Led to:
the development of the automated DNA sequencer, DNA synthesizer, protein sequencer, protein synthesizer;
founding Amgen, ABI, Darwin, Rosetta, etc.
the human genome project;
research in genetics of breast cancer, prostate cancer, multiple sclerosis, Huntington’s Disease, etc.
the development of the field of systems biology

Invest 40% in new technology and be the first to apply it.

ACS Nano 1, 73 (2007)

ACS Nano 1, 242 (2007)
Recap of Lecture #1: Intro & Energies

Simplified class website and link to syllabus & recaps (case matters):
bit.ly/20bh19

Energy and units of energy - kcal/mole, kJ/mole, J, eV, cm⁻¹

Bond strengths, photon energy

Spectroscopies
- Core levels X-ray & deep UV (elemental identification)
- UV-visible – electronic excitation (valence electrons)
- Infrared – vibrations (molecular fingerprints)
- Microwave – rotations

Atomic sizes, bond lengths

Energy level diagrams
- Y-axis is energy
- Quantum states are horizontal lines
- Arrow up – absorbed photon at E = arrow length
- Arrow down – emitted photon at E = arrow length

Fluorescence spectroscopy/imaging
- Absorption followed by emission at different E

Key Chemical Knowledge

How big is an atom?

How strong is a chemical bond?

*NB*- energy is a critical parameter in chemistry and especially this quarter
Choose your favorite energy unit (kcal/mole, kJ/mole, J, eV, cm⁻¹) and learn all the conversions

How energetic is a visible photon?
How does the rest of the electromagnetic spectrum compare?

Dimensional analysis is very useful
What is your native energy unit?
What is the conversion factor for your unit to the following units (other than your own):
eV, cm$^{-1}$, kJ/mole, K (temperature), J, kcal/mole, Hz (frequency of light)

Draw separate energy level diagrams for: a metal, an undoped semiconductor, an $n$-type semiconductor, a $p$-type semiconductor, an insulator, and a semi-metal.
Label the axes, conduction and valence bands, and the Fermi level in each case.

Draw energy level diagrams for: a direct band gap semiconductor and an indirect bandgap semiconductor.
Label the axes and the direct and indirect band gaps in each case. Give typical values of the band gaps.

Draw a Boltzmann distribution at three different temperatures.
Draw a Fermi distribution at three different temperatures.
Label the axes.
Indicate which is the lowest and which is the highest temperature in each case.

Draw separate energy level diagrams for: photoabsorption, photoemission, fluorescence as used in dye labels of biomolecules, Raman spectroscopy, two-photon absorption.
Label axes.

Draw separate energy level diagrams for X-ray photoelectron spectroscopy and X-ray fluorescence.
Label axes.
Single-Molecule Measurements in Chemistry and Biology

Key measurements of heterogeneity and diversity have become possible due to our recent advances across disciplines in sensitivity and resolution.
Finding single molecules is straightforward
Understanding can be hard
Accumulating statistics can be hard

We will discuss
Molecular devices
Single-molecule control
Imaging parts of molecules
Ideas on parallel single-molecule measurements

These topics will introduce key techniques and experiments that we will use many times again.

Single biomolecules have been measured and manipulated for many years.

DNA Content

Fluorescence in-situ Hybridization
Label sites on individual chromosomes.
Specific probes can be made for rapid screens.
Fluorescent Label Example: Chromosomes

Spectral karyotyping
“Chromosome painting”

http://carolguze.com/text/442-4-chromosome_analysis.shtml

DNA Content - Flow Cytometry

Screen single particles or single molecules.
Probe, separate, collect.
Drops produced and sampled at 120 kHz.

Could we boost sensitivity and do this for smaller molecules?

Ger van den Engh
DNA Content - Flow Cytometry, cont.

Ger van den Engh

Single-Molecule Capture and Manipulation

Use optical tweezers to capture and stretch a DNA molecule (λ dimer).

1997 Nobel Physics Prize
Later, Secretary of Energy

Steve Chu & Group

Science 69, 819 (1994)
Single-Molecule Capture and Manipulation

Use optical tweezers to load a single ($\lambda$) DNA molecule into a capillary.

Richard Zare & Group

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Optical Measurements of Chemical Environments

Single-molecule fluorescence maps microcavities in polyacrilimide gels.

*Science* 274, 966 (1996)
W. E. Moerner & Group
Then UCSD, now Stanford
2014 Nobel Chemistry Prize
Recap of Lecture #2: Energies & Measurements

Spectroscopies
- Core levels X-ray & deep UV (elemental identification)
- UV-visible – electronic excitation (valence electrons)
- Infrared – vibrations (molecular fingerprints)
- Microwave – rotations

Atomic sizes, bond lengths

Energy level diagrams
- Y-axis is energy
- Quantum states are horizontal lines
- Arrow up – absorbed photon at $E = \text{arrow length}$
- Arrow down – emitted photon at $E = \text{arrow length}$

Fluorescence spectroscopy/imaging
- Absorption followed by emission at different $E$

Dimensional analysis is very useful

Use fluorescent labels and dyes
- Flow cytometry, fluorescence in-situ hybridization (FISH)
- single-molecule measurements

Recap of Lecture #2, cont.: Energy, Temperature, & Fluorescence

Photon Absorption and Emission, Fluorescence

Fluorescence requires specific excitation energy and has specific emission energy

Use dyes that are fluorescent to “label” species to detect e.g., specific DNA sequences in genome
Boltzmann Distributions

$\varepsilon = \frac{1}{2} \frac{m \mu^2}{N}$

$\varepsilon$ is the average kinetic energy, $\mu$ is the speed (root mean square velocity)
$N$ is Avogadro’s number $6.023 \times 10^{23}$

Ideal Gas Law*

$PV = nRT$

$R$ is the gas constant, $T$ is absolute temperature in K

Units of $R$ are important

$R = 0.08206 \text{ L-atm/mol-K} = 8.314 \text{ J/mol-K} = 1.987 \text{ cal/mol-K}$

$R$ connects temperature with energy
(Stay tuned for the Boltzmann Constant, the same as $R$, but not using moles)

*You should know this one.
Recap of Lecture #3: Ideal Gas Law

Ideal gas law (do know this name)

\[ PV = nRT \]

- \( R \) is the gas constant, \( T \) is absolute temperature in K
- Units of \( R \) are important
- \( R = 0.08206 \text{ L-atm/mol-K} = 8.314 \text{ J/mol-K} = 1.987 \text{ cal/mol-K} \)

\( R \) connects temperature with energy

Stay tuned for the Boltzmann Constant (\( k \)), the same as \( R \), but not using moles

Compare temperature to required energy for reaction, shorthand is “\( kT \)”

Touchstones:

- \( \text{N}_2 \) at room temperature ~0.5 km/sec
- Mole of ideal gas (at STP) 22.4 L
- Liquids and solids are denser than gases by ~1000×
- Water density 1 g/ml, 1 kg/L
- Ionization energies of many solids (~all metals w/out alkali elements) ~ 5 ± 1 eV
Recap of Lecture #4: Ideal & Non-Ideal Gases

First examples: what answer make sense?
Solve problem, then ask if your answer makes sense

Real atoms and molecules interact
Know energy ranges of intramolecular and intermolecular interactions
   (more on this today)

Molecular, interatomic, and intermolecular potentials
Repulsive wall is steep on close approach
Depth of potential well is (~) bond strength
Position of potential well is bond length

Paul’s office hours Thursday moved to 4 PM
(Working on different office hours for next week…)

Speaking of Hydrogen Bombs…

Edward Teller
achievement.org

Sholto Ainslie Design, Wordpress
Data from NASA Goddard
### Solids, Liquids, Gases

<table>
<thead>
<tr>
<th>Solid</th>
<th>Liquid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tightly packed</td>
<td>Close together</td>
<td>Separated</td>
</tr>
<tr>
<td>Condensed phase</td>
<td>Condensed phase</td>
<td></td>
</tr>
<tr>
<td>Arranged in pattern/</td>
<td>Not organized</td>
<td>Not organized</td>
</tr>
<tr>
<td>crystalline</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vibrate but do not</td>
<td>Move past each other</td>
<td>Move freely</td>
</tr>
<tr>
<td>(ex)change place</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Images [https://www.chem.purdue.edu/gchelp/liquids/character.html](https://www.chem.purdue.edu/gchelp/liquids/character.html)

### Transformations: Energy and Order

Forming or breaking bonds? Breaking bonds costs energy ($\Delta H$).
Which state is more ordered ($\Delta S$)?

We will come back to this topic quantitatively (Ch. 12)

http://ch302.cm.utexas.edu/physEQ/physical/physical-all.php
Heat Water, Starting from Ice

Add heat to go from ice to water to steam

Recap: Intermolecular & Intramolecular Forces I

All based on Coulomb’s Law (interacting charges)

<table>
<thead>
<tr>
<th>Force</th>
<th>Model</th>
<th>Basis of Attraction</th>
<th>Energy (kJ/mol)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding</td>
<td>Ionic</td>
<td>Cation–anion</td>
<td>400–4000</td>
<td>NaCl</td>
</tr>
<tr>
<td></td>
<td>Covalent</td>
<td>Nuclei–shared e⁻ pair</td>
<td>150–1100</td>
<td>H–H</td>
</tr>
<tr>
<td>Intramolecular</td>
<td>Metallic</td>
<td>Cations–delocalized electrons</td>
<td>75–1000</td>
<td>Fe</td>
</tr>
</tbody>
</table>

http://ch302.cm.utexas.edu/physEQ/physical/physical-all.php

www.umkc.edu
Recap: Intermolecular & Intramolecular Forces II

All based on Coulomb’s Law (interacting charges)

<table>
<thead>
<tr>
<th>Force</th>
<th>Model</th>
<th>Energy (kJ/mol)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-dipole</td>
<td><img src="image" alt="Ion-dipole" /></td>
<td>40–600</td>
<td>$\text{Na}^+\cdots\text{O}H$</td>
</tr>
<tr>
<td>H bond</td>
<td><img src="image" alt="H bond" /></td>
<td>10–40</td>
<td>$\text{O}H\cdots\text{O}H$</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td><img src="image" alt="Dipole-dipole" /></td>
<td>5–25</td>
<td>I–Cl⋯I–Cl</td>
</tr>
<tr>
<td>Ion–induced dipole</td>
<td><img src="image" alt="Ion–induced dipole" /></td>
<td>3–15</td>
<td>Fe$^{2+}\cdots\text{O}_2$</td>
</tr>
<tr>
<td>Dipole–induced dipole</td>
<td><img src="image" alt="Dipole–induced dipole" /></td>
<td>2–10</td>
<td>H–Cl⋯Cl–Cl</td>
</tr>
<tr>
<td>Dispersion (London)</td>
<td><img src="image" alt="Dispersion (London)" /></td>
<td>0.05–40</td>
<td>F⋯F⋯F⋯F</td>
</tr>
</tbody>
</table>

www.umkc.edu
Recap of Lecture #5: Phase Transitions

**Phases**

*Solid* – Condensed (close together), organized
  - Has vibrational but not translational nor rotational motion

*Liquid* – Condensed, not organized
  - Has translational, vibrational, and rotational motion

*Gas* – Separated (*much more randomness ➔ higher entropy than condensed phases*)
  - Has translational, vibrational, and rotational motion

*Plasma* – high energy, ionized gas
  - Ionization potentials are several eV (UV)

**Transitions**

Breaking bonds takes energy, SO making bonds gives off energy (heat)

Ionization energies are comparable to bond energies

Chemical Identification

**Elemental identification**

Core level spectroscopies
  - (*e.g.*, X-ray photoemission and X-ray fluorescence)

**Chemical identification**

Vibrational spectroscopy (infrared absorption, Raman, other)

Mass spectrometry (*more today*)

**Bond lengths**

X-ray diffraction

Rotational spectroscopy (microwave)
  - *only* for small molecules in the gas phase

**Energies**

Know photon energies:
  - X-ray, UV, visible, infrared, microwave

Know bond energies.

Know conversions between various units:
  - kJ/mole, kcal/mole, eV, cm\(^{-1}\) (for light), K, Hz (for light), J (,.cal)
Solvated Protons

Acids

Sour taste:
Lemon Juice - Citric acid
Vinegar - Acetic Acid

Dissolve active metals, usually liberating H₂

Corrosive - dissolve compounds that are otherwise hard to dissolve.

Examples:
Precious metals such as gold (Au) dissolve in HNO₃ + HCl (aqua regia)
Hard water deposits dissolve in vinegar

(Turn litmus paper RED)
Bases

Bitter taste

Dissolve oil and grease

Drano and lye soap contain NaOH

Slippery to the touch - dissolve hair and skin

React with many metal ions to form precipitates.

Example:

Hard water (=Ca^{2+}, Mg^{2+}) + soap

White precipitate (ppt)

(bathtub rings and scale – try a weak acid like distilled vinegar)

(Turns litmus paper BLUE)

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Arrhenius Acids and Bases

ACID

Any compound that releases H^+ when dissolved in H_2O

Example:

\[
\text{HCl}(g) \xrightarrow{\text{H}_2\text{O}} \text{H}^+(aq) + \text{Cl}^-(aq)
\]

BASE

Any compound that releases OH^- when dissolved in H_2O

Example:

\[
\text{KOH}(s) \xrightarrow{\text{H}_2\text{O}} \text{K}^+(aq) + \text{OH}^-(aq)
\]
**Bronsted & Lowry Acids and Bases**

**ACID**
Any compound capable of donating a $H^+$ ion

*Example:*

\[
\text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)
\]

**BASE**
Any compound capable of accepting a $H^+$ ion

*Example:*

\[
\text{NH}_3(g) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq)
\]

**Conjugate Acid-Base Pairs**
Differ only by the presence or absence of a proton ($H^+$)

Conjugate Acid = Conjugate Base + $H^+$

*Examples:*

- $\text{H}_3\text{O}^+ / \text{H}_2\text{O}$
- $\text{H}_2\text{O} / \text{OH}^-$
- $\text{HCl} / \text{Cl}^-$
- $\text{NH}_4^+ / \text{NH}_3(g)$

*Note:*

The *stronger* the acid, the weaker its conjugate base.
The *weaker* the acid, the stronger its conjugate base.
We will make this quantitative
Acids and Bases

_Acid/Base Definitions_

**Arrhenius:**
- **Acid** - Proton donor
- **Base** - Hydroxide donor

**Bronsted-Lowry:**
- **Acid** - Proton donor
- **Base** - Proton acceptor

**Lewis:**
- **Acid** - Electron pair acceptor
- **Base** - Electron pair donor

_Solvation shells_
Solvent orients around central ion (hydronium as shown)

---

**Equilibria**

Strong acids and bases dissociate completely. 
**Know the strong acids & bases.**

\[ K_a \cdot K_b = [H^+][OH^-] = K_w = 10^{-14} \]

\[ pH = -\log_{10}X \]

\[ pK_a + pK_b = 14 = pH + pOH \]
Recap of Lecture #6: Interactions

Interactions and Interaction Strengths

Ionic bonding
- Charges and separation
Covalent bonding
Metallic bonding
- Delocalized electrons
- Comparable cohesive energies (bond strengths)

Weaker Interactions
- Ion-dipole
- Hydrogen bonding
- Dipole-dipole
- Ion – induced dipole
- Dipole – induced dipole
- Dispersion (fluctuating dipole – induced dipole)

Office hours: Today 245-300 PM, Thursday 1-2 PM
Lecture 4 PM today: Prof. Joanna Aizenberg, Harvard
CNSI Auditorium

Recap of Lecture #6, cont.: Acids & Bases

Acid/Base Definitions

Arrhenius:
- Acid - Proton donor
- Base - Hydroxide donor

Bronsted-Lowry:
- Acid - Proton donor
- Base - Proton acceptor

Lewis:
- Acid - Electron pair acceptor
- Base - Electron pair donor

Conjugate Acid = Conjugate Base + H⁺
The stronger the acid, the weaker its conjugate base.
The weaker the acid, the stronger its conjugate base.

Kₐ Kₐ = [H⁺][OH⁻] = K_w = 10⁻¹⁴
pK_a + pK_b = 14 = pH + pOH

Solvation shells
Solvent orients around central ion
Periodic Trends Reminder

**Periodic Trends**
Know which direction across the periodic table determines property.
Based on filling electron shells

**Ionization Energy**
Low if resulting ion has filled shell rare gas configuration.
(or to a lesser extent – has filled or half-filled subshells)
Same rules for higher oxidation states (e.g., Mg^{2+})

**Electron Affinities**
(Negative values for species with stable anions)
Related to **electronegativity** – many ways to define this.
Determine dipoles within molecules.

**Atomic & Ionic Sizes**
Size decreases with more positive oxidation state for isoelectronic atoms/ions.

Office hours: Today 1-2 PM

Balancing Reactions

Same number of atoms of each element on each side of reaction*
Same total charge on each side

In electrochemistry – we will also cover half-cell reactions.
In reduction, electrons will be a reactant (on left)
In oxidation, electrons will be a product (on right)
Total reaction will eliminate electrons from both sides.

**Losing electrons at Anode is Oxidation &**
**Gaining electrons is Reduction at the Cathode**

**LAnOx & GRedCat**

*Except in nuclear reactions
Solutions, Vapor Pressures, Azeotropes

For an ideal solution, the more volatile component should have a higher partial pressure.

Boiling point based on mole ratio in vapor

Boiling point based on mole ratio in solution

Spontaneity and Work

Useful work can be extracted from a spontaneous process

Example:
Water in a tower ➔ Water on the ground
   can be used to drive a turbine

Work must be done to drive a non-spontaneous process

Example:
Water on the ground ➔ Water in a tower
   Work is done to pump (or carry) the water up
Free Energy & Spontaneity

\[ \Delta H < 0 \]
Exothermic reactions are *usually* spontaneous

\[ \Delta S > 0 \]
Favors being spontaneous if
\[ \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \]

Function that combines \( \Delta H \) and \( \Delta S \) and can predict spontaneity:
*Free Energy:*
\[ \Delta G = \Delta H - T \Delta S \]
\( T \) is absolute temperature (in K)

\( \Delta G \) is the Gibbs free energy
\( \Delta G \) is state function
\( \Delta G \) refers to a reaction at constant temperature and pressure
(there are equivalents for other reaction arrangements)

- \( \Delta G < 0 \) Spontaneous
- \( \Delta G > 0 \) Not spontaneous
- \( \Delta G = 0 \) System at equilibrium

Entropy

A thermodynamic parameter that is a *measure of the disorder or randomness in a system*

The more disordered a system, the greater its entropy.

*Entropy is a state function* – its value depends only upon the state of the system (not how it got there).
We are usually concerned with the change in entropy (\( \Delta S \)) during a process such as a chemical reaction.

\[ \Delta S = S_{\text{final}} - S_{\text{initial}} \]
Laws of Thermodynamics

1st Law:
The total energy in the universe is constant
\[ \Delta E_{\text{universe}} = 0 \]
\[ \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} \]
\[ \Delta E_{\text{system}} = -\Delta E_{\text{surroundings}} \]

2nd Law:
The total entropy in the universe is increasing
\[ \Delta S_{\text{universe}} > 0 \]
\[ \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \]

3rd Law:
The entropy of every pure substance at 0 K (absolute zero temperature) is zero
\[ S = 0 \text{ at } 0 \text{ K} \]

Entropy

Gases much more entropy than solids or liquids
Reactions that form gases usually have \( \Delta S > 0 \)

Entropy is a state function – its value depends only on the systems initial and final states

Standard state: \( S = 0 \) at \( T=0 \text{ K} \) \( (\text{Third Law}) \)
Effect of Temperature on Spontaneity

\[ \Delta G = \Delta H - T \Delta S \]

\( \Delta H \) and \( \Delta S \) do not change substantially with temperature, but \( \Delta G \) does.

<table>
<thead>
<tr>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>( \Delta G )</th>
<th>Spontaneous?</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
<td>-</td>
<td>At all temperatures</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>At low temp</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>+</td>
<td>Not at high temp</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>-</td>
<td>At high temp</td>
</tr>
<tr>
<td></td>
<td>+</td>
<td>+</td>
<td>Not at low temp</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>+</td>
<td>Never</td>
</tr>
</tbody>
</table>

Compare potential energy and free energy.
Exam #1 Topics

Exam #1 covers through last week’s lectures and reading:
Define temperature, pressure, state function
Bond lengths and strengths
Energy scales
  - Interactions and potentials – intramolecular, intermolecular, solids, liquids
  - Photons
Spectroscopies
  - Fluorescence and fluorescent labeling
  - Nuclear
Energy distribution (e.g., Boltzmann distribution in gas)
Elemental and chemical identification
Ideal gas law and deviations
Partial pressures
Phase transitions and equilibria
  - Typical, water, CO₂
  - Solid, liquid, gas, supercritical fluid
  - Energy changes with making and breaking bonds, heat
Thermodynamics – free energy, enthalpy, entropy
Oxidation states

Chemical Identification

*Elemental identification*
Core level spectroscopies
  - (e.g., X-ray photoemission and X-ray fluorescence)
*Chemical identification*
Vibrational spectroscopy (infrared absorption, Raman, other)
Mass spectrometry
*Bond lengths*
X-ray diffraction
  - Rotational spectroscopy (microwave)
    - only for small molecules in the gas phase
*Energies*
Know photon energies:
  - X-ray, UV, visible, infrared, microwave
Know bond energies.
Know conversions between various units:
  - kJ/mole, kcal/mole, eV, cm⁻¹ (for light), K, Hz (for light), J (cal)
Question 1 (15 points):

a) What is the approximate bond energy for Ar₂ in cm⁻¹ and in your favorite energy units (which must be one of the following: eV, kcal/mol, kJ/mol, or J)? (10 points)

b) What is the approximate bond length of Ar₂? (5 points)

EC) Which has a larger bond strength, Ar₂ or Ar₂⁺? Why (concisely)?
Chemistry 20BH, Winter 2019
30 January 2019
x questions + 1 small extra credit problem, x pages.
Answer on these sheets only. Additional space on last page.
If you need extra sheets, please ask your TA.

Note: Only these papers can be used; no other notes are allowed.

Please answer each question concisely. Show your calculations.
You may (and in some cases, must) draw explanatory diagrams.
Label all axes and features on graphs and diagrams. Total) /100

You may not use a calculator, computer, watch, smart device, or electronics of any sort.
Irrelevant and/or incorrect material will result in loss of points.

Table of constants and conversions
Speed of light: c = 3 × 10^8 m/s
Faraday constant = 96500 coul/mole
Electron charge magnitude: e = 1.6 × 10^{-19} C
Plank's constant: ħ = 1.1 × 10^{-34} J-s
Gas constant: R = 0.08206 L-atm/mol-K = 8.314 J/mol-K = 1.987 cal/mol-K
Boltzmann constant: k_B = 1.4 × 10^{-23} J/K
Electron rest mass: m = 9.1 × 10^{-31} kg
Proton rest mass: M = 1.7 × 10^{-27} kg
1 mole = 6.02 × 10^{23}

<table>
<thead>
<tr>
<th>Energy Conversion Table</th>
</tr>
</thead>
<tbody>
<tr>
<td>eV</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>8.06573</td>
</tr>
<tr>
<td>0.00861705</td>
</tr>
<tr>
<td>4.1355 × 10^{-14}</td>
</tr>
</tbody>
</table>

ΔG° = -nFE° = -2.303 RT log_{10}K_{eq}
pH = pK_a - log_{10} ([HA]/[A^-])

You will find a periodic table for your reference on the next page.
Recap of Lecture #11: Mass Spectrometry

1) Ion Sources:
   - Start with gaseous ions
     - Ionize neutral gas with electrons, wire, chemically, or photons
     - Evaporate solution leaving behind ions (electrospray)
     - Good for proteins and biomolecular complexes
   - Ion impact on solids (atomic sandblasting)
   - Embed material in photon absorber that blows up on illumination
     (matrix-assisted laser desorption ionization (MALDI))

1.5) Accelerate all ions to same energy with electric field
[Vacuum required]

2) Mass filters:
   - Bending magnet
   - Time-of-flight
   - Orbital trap
   - Quadrupole

3) Detector:
   - Accelerate ions and count charges
   - Keep in mind:
     - Fingerprint of molecular identity
     - Fragmentation patterns
     - Isotopic ratios
     - Isotopic substitution

2.5) Optional collision chamber
followed by another mass filter
[Asking: Which ions are stable?]

Relationship between ΔG and E

ΔG = -nFE

Standard States: ΔG° = -nFE°

n = number of electrons transferred in a balanced redox reaction

F = Faraday = 96,500 coulomb/mole e-
1 coulomb = 1 Amp-sec
1 J = 1 Amp-sec-V = 1 coulomb-V
1 F = 96,500 J/V-mole e-
### ΔG and E, cont.

\[ ΔG° = -2.303 \, RT \, \log K_{eq} \]
\[ ΔG° = -nF \, E° \]

\[ E° = \frac{2.303 \, RT \, \log K_{eq}}{nF} \]

R = 8.314 J/K-mole
F = 96,500 J/V-mole e⁻

At 25 °C = 298 K:

\[ E° = \frac{(2.303)(8.314 \, J/K-mole)(298 \, K) \, \log K_{eq}}{n(96,500 \, J/V-mole \, e^{-})} \]

\[ E° = \frac{0.059}{n} \, \log K_{eq} \]

### Effect of Concentration

#### Half Reactions

\[ aA + bB + ne^{-} \rightleftharpoons cC + dD \]

\[ E_{1/2} = E_{1/2}^{o} - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

#### Cell Reactions

\[ aA + bB \rightleftharpoons cC + dD \]

\[ E_{cell} = E_{cell}^{o} - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \]
**Thermodynamics & Electrochemistry**

*Le Chatelier’s Principle*: Disturb a system from equilibrium and it will move to restore that equilibrium.

- One way to drive a reaction is to remove product.

Next, quantify with concentration dependence of $\Delta G$ and $E$.

*You do not need to know the name for this class, but it will be useful/needed later.*

---

**Effect of Concentration on $\Delta G$**

*Half Reactions*

\[ aA + bB + ne^- \rightarrow cC + dD \]

\[ E_{1/2}^\circ = E_{1/2}^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

*Cell Reactions*

\[ aA + bB \rightarrow cC + dD \]

\[ E_{\text{cell}}^\circ = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

Looks like equilibrium constant, but does not have to be at equilibrium.

$Q$ in your book (and all freshman chemistry books).
ΔG and Work

For a spontaneous process,
ΔG = W_{max} = The maximum work that can be obtained from a process at constant T and p

For a non-spontaneous process,
ΔG = W_{min} = The minimum work that must be done to make a process go at constant T and p
A spontaneous reaction is one that is capable of proceeding in the forward direction to a substantial extent under a given set of conditions.

*NB*- spontaneity has nothing to do with the rate at which a reaction will occur

A spontaneous reaction may be fast or slow

Exothermicity usually determines spontaneity

Use your intuition

If you cannot intuit reaction as written, look at reverse

---

Electrochemistry relates electrical energy and chemical energy

**Oxidation-reduction reactions**

Quantitate reactions

Assign oxidation states

**Spontaneous reactions**

Can extract electrical energy from these

Examples: voltaic cells, batteries

Positive cell potentials

**Non-spontaneous reactions**

Must put in electrical energy to make them go.

Examples: electrolysis, electrolysis cells.

Negative cell potentials
Recap of Lecture #10+:
Thermodynamics & Electrochemistry

Laws of Thermodynamics
1 Energy is conserved
2 Entropy increases
3 At 0 K, S = 0 for a pure element

\[ \Delta G = \Delta H - T \Delta S \]
So, \( \Delta H < 0 \), making stronger bonds, is favorable
So, \( \Delta S > 0 \), increased disorder, is favorable

\( \Delta H \) and \( \Delta S \) vary little with temperature. \( \Delta G \) does vary with T \( \Rightarrow \) effect of \( \Delta S \)

Spontaneous reactions produce energy (generally make stronger bonds)
\( \Delta G < 0 \), \( K_{eq} > 1 \), \( E_{cell} > 0 \)

Nonspontaneous reactions require energy, \( e.g. \), electrolytic reactions, Al reduction
\( \Delta G > 0 \), \( K_{eq} < 1 \), \( E_{cell} < 0 \)

Assigning Formal Oxidation States

1. Oxygen is almost always -2.

2. Halogens (F, Cl, Br, I) always are -1, \( except \) when Cl, Br, I are bound to oxygen or fluorine, in which case they have positive oxidation numbers.

3. Hydrogen is always +1, \( except \) when bound to group I, II, or III metals, in which case it is -1.

4. Determine the oxidation states of other elements in a compound by difference. Most elements tend to lose or gain enough electrons to achieve a filled shell.
Oxyacids

The (labile) proton is attached to oxygen

The higher the oxidation state of the central atom, the stronger the acid

\[
\begin{align*}
\text{Hypochlorous} & \quad \text{Chlorous} & \quad \text{Chloric} & \quad \text{Perchloric} \\
\text{H--O--Cl} & \quad \text{H--O--Cl} & \quad \text{H--O--Cl} & \quad \text{H--O--Cl} \\
K_a = 3.0 \times 10^{-8} & \quad K_a = 1.1 \times 10^{-2} & \quad \text{Strong acid} & \quad \text{Strong acid}
\end{align*}
\]

\[
\text{HX} \rightleftharpoons H^+ + A^- \quad K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{p}K_a = -\log_{10}K_a
\]

For the same oxidation state, the more electronegative the central atom, the stronger the acid

\[
\begin{align*}
\text{HOCl} & > \text{HOBr} & > \text{HOI} \\
3.0 \times 10^{-8} & > 2.5 \times 10^{-9} & > 2.3 \times 10^{-11}
\end{align*}
\]

\[
\begin{align*}
\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{HB}^+ + \text{B}^- \quad K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} \quad \text{p}K_b = -\log_{10}K_b
\end{align*}
\]

Mass Spectrometry

1) Ion Sources:
Start with gaseous ions
Ionize neutral gas with electrons, wire, chemically, or photons
Evaporate solution leaving behind ions (electrospray)\(^1\)
Good for proteins and biomolecular complexes
Ion impact on solids (atomic sandblasting)
Embed material in photon absorber that blows up on illumination\(^2\)
(matrix-assisted laser desorption ionization (MALDI))

2002 Nobel Chemistry Prize
\(^1\)John Fenn, Yale > VCU
\(^2\)Koichi Tanaka, Shimadzu

https://www.slideshare.net/ssuser3375a9
Mass Spectrometry

2) Mass filters:
   Bending magnet
   Time-of-flight
   Orbital trap (1989 Nobel Prize in Physics)
   Quadrupole

1.5) Accelerate all ions to same energy with electric field
   [Vacuum required]

2.5) Optional collision chamber followed by another mass filter
   [Asking: Which ions are stable?]

3) Detector:
   Accelerate ions and count charges

https://www.slideshare.net/ssuser3375a9

Relationship between $\Delta G$ and $E$

$\Delta G = -nFE$

Standard States: $\Delta G^\circ = -nFE^\circ$

$n = \text{number of electrons transferred in a balanced redox reaction}$

$F = \text{Faraday} = 96,500 \text{ coulomb/mole e}^-$

1 coulomb = 1 Amp-sec

1 J = 1 Amp-sec-V = 1 coulomb-V

1 F = 96,500 J/V-mole e$^-$
ΔG and E, cont.

\[ \Delta G^\circ = -2.303 \text{RT} \log K_{eq} \]
\[ \Delta G^\circ = -nFE^\circ \]
\[ E^\circ = \frac{2.303RT\log K_{eq}}{nF} \]

\[ R = 8.314 \text{ J/K-mole} \]
\[ F = 96,500 \text{ J/V-mole e}^- \]

At 25 °C = 298 K:

\[ E^\circ = \frac{(2.303)(8.314 \text{ J/K-mole})(298 \text{ L}) \log K_{eq}}{n(96,500 \text{ J/V-mole e}^-)} \]

\[ E^\circ = \frac{0.059 \log K_{eq}}{n} \]

Effect of Concentration

Half Reactions

aA + bB + ne^- \rightarrow cC + dD

\[ E_{1/2} = E_{1/2}^\circ - \frac{2.303RT}{nF} \log \frac{[C]^d[D]^d}{[A]^a[B]^b} \]

Cell Reactions

aA + bB \rightarrow cC + dD

\[ E_{cell} = E_{cell}^\circ - \frac{2.303RT}{nF} \log \frac{[C]^d[D]^d}{[A]^a[B]^b} \]
# Recap of Lecture #13: Thermodynamics, Electrochemistry, and Concentrations

**Le Chatelier’s Principle**
Disturb a system from equilibrium and it will move to restore that equilibrium
- One way to drive a reaction is to remove product
Quantify with concentration dependence of $\Delta G$ and $E$.

**Batteries**
- Lead acid battery
- Dry cell, alkaline cell
- Rechargeable Ni-Cd battery
To get higher voltages, stack up cells in series (e.g., car battery $6 \times 2 \text{V} = 12 \text{V}$)

**Electrolysis**
Driving non-spontaneous reactions by applying electrical energy
The least unfavorable potential reaction goes first (there can be overlap)
Overpotentials and concentrated reactants are used
Quantify the amount of reaction – $n$, $F$, and number of moles

---

## Weak Acids and Bases

**Strong acids**
- HCl, HBr, HI, HNO$_3$, HClO$_4$, H$_2$SO$_4$
  These dissociate completely to form $H^+ + X^-$

Other (weak) acids:
- Dissociate partially to $H^+ + X^-$
- Rank by $K_a$ – the highest $K_a$ is the strongest acid.

**Strong bases**
- LiOH, NaOH, KOH, RbOH, CsOH
- Ca(OH)$_2$, Sr(OH)$_2$, Ba(OH)$_2$
  These dissociate completely to form $OH^- + M^+$

Other (weak) bases:
- Rank by $K_b$ – the highest $K_b$ is the strongest base
- The lowest $K_a$ for the conjugate acid is the strongest base
Buffers

### Phosphate

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^- & pK_a &= 2.2 \\
\text{H}_2\text{PO}_4^- & \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} & pK_a &= 7.2 \\
\text{HPO}_4^{2-} & \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-} & pK_a &= 12.7
\end{align*}
\]

### Carbonate

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3
\]

\[
\begin{align*}
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- & pK_a &= 6.4 \\
\text{HCO}_3^- & \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} & pK_a &= 10.2
\end{align*}
\]

---

Recap of Lecture #16: Solubility, Complex Ions, Simultaneous Equilibria

**Solubility product**

\[\text{M}_a\text{X}_b(s) \rightleftharpoons a\text{M}^{(aq)} + b\text{X}^{(aq)} \quad K_{sp} = [\text{M}]^a[\text{X}]^b\]

**In solving equilibria, keep track of stoichiometry**

Solubility – how much of the solid (in moles/L) dissolves in a given solution

Metal complexes, \(K_F, K_D\)
Metal Complex Stability

\[
\begin{align*}
\text{Cu(NH}_3\text{)}^2{+}_4 + 4 \text{H}_2\text{O} & \rightleftharpoons \text{Cu(OH}_2\text{)}^2{+}_4 + 4 \text{NH}_3 \\
\text{Cu}^{2+}(aq) & = \text{Cu(OH}_2\text{)}^2{+}_4 \\
K & = \frac{[\text{Cu(OH}_2\text{)}^2{+}_4][\text{NH}_3]^4}{[\text{Cu(NH}_3\text{)}^2{+}_4][\text{H}_2\text{O}]^4} \Rightarrow \text{constant} \\
\text{Dissociation constant } K_D & = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu(NH}_3\text{)}^2{+}_4]} = 2 \times 10^{-13} \\
\text{Cu(OH}_2\text{)}^2{+}_4 + 4 \text{NH}_3 & \rightleftharpoons \text{Cu(NH}_3\text{)}^2{+}_4 + 4 \text{H}_2\text{O} \\
\text{Formation constant } K_F & = \frac{[\text{Cu(NH}_3\text{)}^2{+}_4]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 5 \times 10^{12} \\
K_D & = \frac{1}{K_F}
\end{align*}
\]

Metal Complexes

Coordination compounds
Lewis acid – Lewis base adducts
Important in enzymes, catalysis, metal/salt dissolution
Orbitals and oxidation state of central metal ion determine coordination.
Electronic excitation – absorption and emission
Lewis base ligands split electronic energies of metal ions – leading to color and spin
Lone pair electrons repel and stay farthest away (as compared to ligands)
Spin
High spin vs. low spin compounds
Compare crystal field splitting (\(\Lambda\)) to the spin pairing energy (\(P\))
Spectrochemical series – relative ligand effect on \(\Lambda\)
Paramagnetic – having one of more unpaired spins
Colors
Complementary colors – if a color is absorbed, the absorbing material will appear as the complementary color
Red-green, orange-blue, yellow-violet
Other means of color: emission, interference
Dissolve Insoluble Salts

CuCO$_3$ is a sparingly soluble salt  
$K_{sp} = [\text{Cu}^{2+}][\text{CO}_3^{2-}] = 2.3 \times 10^{-10}$

What if we add ammonia?  
$K_F = 1.1 \times 10^{13}$

$$\text{CuCO}_3(\text{s}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + [\text{Cu(NH}_3)_4]^{2+}(\text{aq})$$

Chelation

More than one Lewis base site in a molecule
Entropically favored over comparable monodentate ligands

$[\text{Cu(NH}_3)_4]^{2+}$  $K_F = 1.1 \times 10^{13}$

$[\text{Cu(en)}_2]^{2+}$  $K_F = 1.0 \times 10^{30}$

$\text{en} = \text{ethylenediamine} = \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$

$\text{EDTA} = \text{ethylenediaminetetraacetic acid}$

Thermodynamics and equilibria
Measure thermodynamics (and equilibria) electrochemically  
$e.g.$, by comparing complex ions to aqueous ions.
### Chelation – Entropy Effect

More than one Lewis base site in a molecule

**Entropically** favored over comparable monodentate ligands

\[
\begin{align*}
[Ni(NH_3)_6]^{2+} & \quad K_F = 4 \times 10^8 \\
[Ni(en)_3]^{2+} & \quad K_F = 2 \times 10^{18}
\end{align*}
\]

\(en = \text{ethylenediamine} = H_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}H_2\)

\[
\begin{align*}
\text{Cd}^{2+} + 4\text{CH}_3\text{NH}_2 & \rightleftharpoons [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+} \\
\Delta G^\circ & = -37.2 \text{ kJ/mol}, \Delta H^\circ = -57.3 \text{ kJ/mol} \\
\Delta S^\circ & = -67.3 \text{ J/mol-K}
\end{align*}
\]

\[
\begin{align*}
\text{Cd}^{2+} + 2en & \rightleftharpoons [\text{Cd}(en)_2]^{2+} \\
\Delta G^\circ & = -60.7 \text{ kJ/mol}, \Delta H^\circ = -56.5 \text{ kJ/mol} \\
\Delta S^\circ & = +14.1 \text{ J/mol-K}
\end{align*}
\]

### Measuring Stability Metal Ion Complexes

\[
\begin{align*}
\text{Ag}^{+}(aq) + e^- & \rightleftharpoons \text{Ag}(s) \quad E^\circ_{\frac{1}{2}} = +0.80 \text{ V}
\end{align*}
\]

\[
\begin{align*}
[\text{Ag(CN)}_2]^{-}(aq) + e^- & \rightleftharpoons \text{Ag}(s) + 2\text{CN}^- \quad E^\circ_{\frac{1}{2}} = -0.31 \text{ V}
\end{align*}
\]

\(\text{CN}^- \text{ is not a chelate because it is monodentate}\)
Transition Metal Ions, Review

Transition metal ions are Lewis acids ➞
they accept electron pairs

Ligands are Lewis bases ➞
molecules or ions which donate electron pairs

Ligands bonded to metal ions ➞
metal complexes or coordination compounds

Coordination number: number of electron donor atoms attached to the metal

Chelates are ligands possessing two or more donor atoms

---

Tetrahedral and Square Planar Coordination Compounds

Coordination # = 4

Tetrahedral, e.g., [Zn(NH$_3$)$_4$]$^{2+}$

Square Planar, e.g., [Ni(CN)$_4$]$^{2-}$
More Coordination Compounds

Square Planar, e.g., \([\text{PtCl}_3(\text{C}_2\text{H}_4)]^-\)

Coordination #: 5
Trigonal Bipyramidal, e.g., \([\text{Fe(CO)}_5]\)

Octahedral Coordination Compounds

Octahedral, e.g., \([\text{CoF}_6]^{3-}\)

Octahedral, e.g., \([\text{Co(en)}_3]^{3+}\)
Chelate Reminder

More than one Lewis base site in a molecule
Entropically favored over comparable monodentate ligands

\[
\begin{align*}
[Ni(NH_3)_6]^{2+} & \quad K_F = 4 \times 10^8 \\
[Ni(en)_3]^{2+} & \quad K_F = 2 \times 10^{18} \\
en & = \text{ethylenediamine} = H_2N-CH_2-CH_2-NH_2
\end{align*}
\]

\[
\begin{align*}
\text{Cd}^{2+} + 4\text{CH}_3\text{NH}_2 & \quad [\text{Cd}((\text{CH}_3\text{NH}_2)_4]^{2+} \\
\Delta G^\circ & = -37.2 \text{ kJ/mol, } \Delta H^\circ = -57.3 \text{ kJ/mol} \\
\Delta S^\circ & = -67.3 \text{ J/mol-K}
\end{align*}
\]

\[
\begin{align*}
\text{Cd}^{2+} + 2en & \quad [\text{Cd}(en)_2]^{2+} \\
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\Delta S^\circ & = +14.1 \text{ J/mol-K}
\end{align*}
\]

Coordination Compounds
Coordination Compounds

\( \Delta \) – the crystal field splitting

Spectrochemical Series:

\[ CN^- > NO^- > en > NH_3 > H_2O > F^- > Cl^- \]

Increasing \( \Delta \)

\( \Delta \) depends upon:
1. Metal
2. Oxidation state
3. Ligands
P – Spin pairing energy.
P does not depend upon the ligands.

P < \( \Delta \) \( \Rightarrow \) Low spin complexes.
P > \( \Delta \) \( \Rightarrow \) High spin complexes.

High Spin Vs. Low Spin (d\(^1\) to d\(^{10}\))

Electron Configuration for Octahedral complexes of metal ion having d\(^1\) to d\(^{10}\) configuration [M(H\(_2\)O)\(_6\)]\(^{n+}\).

Only the d\(^1\) through d\(^5\) cases have both high-spin and low spin configuration.

Electron configurations for octahedral complexes of metal ions having from d\(^1\) to d\(^{10}\) configurations. Only the d\(^1\) through d\(^5\) cases have both high-spin and low-spin configurations.

https://www.slideshare.net/surya287/crystal-field-theory
**Color Wheel: Complementary Colors**

![Color Wheel Diagram]

**Color Absorption of Co²⁺ Complexes**

The Colors of Some Complexes of the Co³⁺ Ion

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Wavelength of light absorbed</th>
<th>Color of Light Absorbed</th>
<th>Color of Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CoF₆]³⁻</td>
<td>700 (nm)</td>
<td>Red</td>
<td>Green</td>
</tr>
<tr>
<td>[Co(C₂O₄)₂]³⁻</td>
<td>600, 420</td>
<td>Yellow, violet</td>
<td>Dark green</td>
</tr>
<tr>
<td>[Co(H₂O)₆]³⁻</td>
<td>600, 400</td>
<td>Yellow, violet</td>
<td>Blue-green</td>
</tr>
<tr>
<td>[Co(NH₃)₆]²⁺</td>
<td>475, 340</td>
<td>Blue, violet</td>
<td>Yellow-orange</td>
</tr>
<tr>
<td>[Co(en)₃]³⁺</td>
<td>470, 340</td>
<td>Blue, ultraviolet</td>
<td>Yellow-orange</td>
</tr>
<tr>
<td>[Co(CN)₆]³⁻</td>
<td>310</td>
<td>Ultraviolet</td>
<td>Pale Yellow</td>
</tr>
</tbody>
</table>

The complex with fluoride ion, [CoF₆]³⁻, is high spin and has one absorption band. The other complexes are low spin and have two absorption bands. In all but one case, one of these absorptions is in the visible region of the spectrum. The wavelengths refer to the center of that absorption band.

[https://www.slideshare.net/surya287/crystal-field-theory](https://www.slideshare.net/surya287/crystal-field-theory)
# Energy and Excitations in Solids

## Metals vs. Semiconductors & Insulators (along with a few other less common flavors)

For metals, there is **no** energy gap between highest occupied and lowest unoccupied orbitals.

For semiconductors & insulators, there is an energy gap between highest occupied and lowest unoccupied orbitals.

This difference has significant consequences in appearance, electrical conduction, thermal conduction, and thus, how they are used.

Back to energy level diagrams!

## Metals
- No band gap - HOMO, LUMO are at the same energy
- Electronic excitation is small $\text{vs. } kT$
- High electrical and thermal conductivity
- Conductivity *decreases* with increasing temperature because of electron scattering

## Semiconductors and Insulators
- Have a band gap between valence (lower) band and conduction (upper) band – electronic excitation is $>kT$
- This determines insulator vs. semiconductor
- Direct band gap can be excited by photons (very little momentum)
- Indirect band gap cannot be photoexcited efficiently
- Electrons and “holes” can carry charge
- Differentiate with magnetic field (Hall effect)
- Energies of (dopant) states in the band gap determine conductivity and whether electrons or holes dominate current
- Conductivity increases with increasing temperature because of thermal excitation of carriers
Exam #2 Topics

Exam #2 covers through last week’s lectures, readings, homework, and posters.
Nearly the same data sheet as for exam #1, same periodic table
No trick questions, no multiple choice. Be rested and ready to think.

Electrochemistry, equilibria, free energy, and how they are related
Acid-base equilibria, polyprotic acids, buffers
Amphotericism
Laws of thermodynamics, state functions, free energy, enthalpy, and entropy
Mass spectrometry
Spectroscopies, energy level diagrams
Metals, semiconductors – n- & p-type, direct vs indirect band gaps
Chemical and elemental fingerprinting methods

Quantifying reactions with electrochemistry
Quantifying free energies and equilibrium constants with electrochemistry
Batteries, corrosion, electrolysis

Complex ions, formation, dissociation, Lewis acid-Lewis base complexes
Chelates

Periodic Trends Reminder

Periodic Trends
Know which direction across the periodic table determines property.
Based on filling electron shells

Ionization Energy 🔄
Low if resulting ion has filled shell rare gas configuration.
(or to a lesser extent – has filled or half-filled subshells)
Same rules for higher oxidation states (e.g., Mg^{2+})

Electron Affinities 🍀
(Negative values for species with stable anions)
Related to electronegativity 🍀 – many ways to define this.
Determine dipoles within molecules.

Atomic & Ionic Sizes 🍀
Size decreases with more positive oxidation state for isoelectronic atoms/ions.

Important (lifetime/career/GRE/MCAT scale)
Electrochemistry

Electrochemistry relates electrical energy and chemical energy

Oxidation-reduction reactions

Spontaneous reactions
Can extract electrical energy from these
Examples: voltaic cells, batteries
Positive cell potentials

Non-spontaneous reactions
Must put in electrical energy to make them go.
Examples: electrolysis, electrolysis cells.
Negative cell potentials

Quantitate reactions

Assigning Formal Oxidation States

1. Oxygen is almost always -2.*

2. Halogens (F, Cl, Br, I) always are -1, except when Cl, Br, I are bound to oxygen or fluorine, in which case they have positive oxidation numbers.

3. Hydrogen is always +1, except when bound to group I, II, or III metals, in which case it is -1.

4. Determine the oxidation states of other elements in a compound by difference. Most elements tend to lose or gain enough electrons to achieve a filled shell.

*Except for molecular oxygen, peroxides, superoxides
The half-cell potential is the potential associated with the half-reaction.

Rules for half-cell potentials:

1. The sum of two half-cell potentials in a cell equals the overall cell potential:

\[ E_{\text{cell}}^\circ = E_{\text{oxid}}^\circ + E_{\text{reduc}}^\circ \]

2. For any half-reaction:

\[ E_{\text{oxid}}^\circ = -E_{\text{reduc}}^\circ \]

3. Standard half-cell is a hydrogen electrode:

\[ \text{H}_2(\text{g},1 \text{ atm}) \rightleftharpoons 2\text{H}^+(\text{aq},1 \text{ M}) + 2e^- \]

\[ E_{\text{oxid}}^\circ = E_{\text{reduc}}^\circ = 0 \text{ V} \]
Chemical Identification

**Elemental identification**
Core level spectroscopies
  *(e.g., X-ray photoemission and X-ray fluorescence)*

**Chemical identification**
Vibrational spectroscopy (infrared absorption, Raman, other)
Mass spectrometry

**Bond lengths**
X-ray diffraction
  Rotational spectroscopy (microwave)
  – only for small molecules in the gas phase

**Energies**
Know photon energies:
  X-ray, UV, visible, infrared, microwave
Know bond energies.
Know conversions between various units:
  kJ/mole, kcal/mole, eV, cm$^{-1}$ (for light), K, Hz (for light), J (cal)

Mass Spectrometry

1) Ion Sources:
Start with gaseous ions
Ionize neutral gas with electrons, wire, chemically, or photons
Evaporate solution leaving behind ions (electrospray)$^1$
  Good for proteins and biomolecular complexes
Ion impact on solids (atomic sandblasting)
Embed material in photon absorber that blows up on illumination$^2$
  (matrix-assisted laser desorption ionization (MALDI))

2002 Nobel Chemistry Prize
1. John Fenn
2. Koichi Tanaka
Yale > VCU
Shimadzu

https://www.slideshare.net/ssuser3375a9
Mass Spectrometry

2) Mass filters:
   - Bending magnet
   - Time-of-flight
   - Orbital trap (1989 Nobel Prize in Physics)
   - Quadrupole

3) Detector:
   Accelerate ions and count charges

1.5) Accelerate all ions to same energy with electric field
   [Vacuum required]

2.5) Optional collision chamber followed by another mass filter
   [Asking: Which ions are stable?]

Laws of Thermodynamics

1st Law:
The total energy in the universe is constant
\[ \Delta E_{\text{universe}} = 0 \]
\[ \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} \]
\[ \Delta E_{\text{system}} = -\Delta E_{\text{surroundings}} \]

2nd Law:
The total entropy in the universe is increasing
\[ \Delta S_{\text{universe}} > 0 \]
\[ \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \]

3rd Law:
The entropy of every pure substance at 0 K (absolute zero temperature) is zero
\[ S=0 \text{ at } 0 \text{ K} \]
Mass Spectrometry

1) Ion Sources:
   Start with gaseous ions
   Ionize neutral gas with electrons, wire, chemically, or photons
   Evaporate solution leaving behind ions (electrospray)
   Good for proteins and biomolecular complexes
   Ion impact on solids (atomic sandblasting)
   Embed material in photon absorber that blows up on illumination
   (matrix-assisted laser desorption ionization (MALDI))

1.5) Accelerate all ions to same energy with electric field
   [Vacuum required]

2) Mass filters:
   Bending magnet
   Time-of-flight
   Orbital trap
   Quadrupole
   2.5) Optional collision chamber
   followed by another mass filter
   [Asking: Which ions are stable?]

3) Detector:
   Accelerate ions and count charges

   Keep in mind:
   Fingerprint of molecular identity
   Fragmentation patterns
   Isotopic ratios
   Isotopic substitution

Thermodynamics

A spontaneous reaction is one that is capable of proceeding in the forward direction
to a substantial extent under a given set of conditions.

NB - spontaneity has nothing to do with the rate at which a reaction will occur
A spontaneous reaction may be fast or slow

Exothermicity usually determines spontaneity

Use your intuition
If you cannot intuit reaction as written, look at reverse
Free Energy & Spontaneity

- \( \Delta H < 0 \)
- Exothermic reactions are *usually* spontaneous

- \( \Delta S > 0 \)
- Favors being spontaneous if
  - \( \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \)

Function that combines \( \Delta H \) and \( \Delta S \) and can predict spontaneity:

*Free Energy:*

\[
\Delta G = \Delta H - T \Delta S
\]

- \( \Delta G \) is the Gibbs free energy
- \( \Delta G \) is state function
- \( \Delta G \) refers to a reaction at constant temperature and pressure
  - (there are equivalents for other reaction arrangements)

- \( \Delta G < 0 \)  Spontaneous
- \( \Delta G > 0 \)  Not spontaneous
- \( \Delta G = 0 \)  System at equilibrium

Thermodynamics:

*Laws of Thermodynamics*

1. Energy is conserved
2. Entropy increases
3. At 0 K, \( S = 0 \) for a pure element

\[
\Delta G = \Delta H - T \Delta S
\]

- So, \( \Delta H < 0 \), making stronger bonds, is favorable
- So, \( \Delta S > 0 \), increased disorder, is favorable

\( \Delta H \) and \( \Delta S \) vary little with temperature. \( \Delta G \) *does* vary with \( T \) ➔ effect of \( \Delta S \)

- Spontaneous reactions produce energy (generally make stronger bonds)
  - \( \Delta G < 0 \), \( K_{\text{eq}}>1 \), \( E_{\text{cell}}>0 \)

- Nonspontaneous reactions require energy, *e.g.*, electrolytic reactions, Al reduction
  - \( \Delta G > 0 \), \( K_{\text{eq}}<1 \), \( E_{\text{cell}}<0 \)
\[ \Delta G = -nFE \] and for standard states: \[ \Delta G^\circ = -nFE^\circ \]

\( n \) = number of electrons transferred in a balanced redox reaction

\( F \) = Faraday = 96,500 coulomb/mole e\(^-\) = 96,500 J/V-mole e\(^-\)

**Standard States:**
- **Solid** = Pure solid
- **Liquid** = Pure liquid
- **Gas** = 1 atm pressure
- **Solution** = 1 M
- **Temperature** = (Usually) 25 °C

\[ \Delta G^\circ = -2.303 \, RT \log_{10} K_{eq} \]

\[ E^\circ = \frac{0.059}{n} \log_{10} K_{eq} \]

\[ \Delta G^\circ = \Sigma \Delta G_f^\circ (\text{products}) - \Sigma \Delta G_f^\circ (\text{reactants}) \]

For elements, \( \Delta G_f^\circ = 0 \)

---

**Le Chatelier’s Principle**
Disturb a system from equilibrium and it will move to restore that equilibrium

⇒ One way to drive a reaction is to remove product
Quantify with concentration dependence of \( \Delta G \) and \( E \).

**Batteries**
- Lead acid battery
- Dry cell, alkaline cell
- Rechargeable Ni-Cd battery
To get higher voltages, stack up cells in series (e.g., car battery \( 6 \times 2 \, V = 12 \, V \))

**Electrolysis**
Driving non-spontaneous reactions by applying electrical energy
The least unfavorable potential reaction goes first (there can be overlap)
Overpotentials and concentrated reactants are used
Quantify the amount of reaction – \( n \), \( F \), and number of moles
### Peroxides and Superoxides

<table>
<thead>
<tr>
<th>Peroxide: $O_2^-$</th>
<th>Superoxide: $O_2^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H_2O_2(l,aq)$ $\rightarrow$ $2H_2O(l) + O_2(g)$</td>
<td>bottles have vented caps</td>
</tr>
</tbody>
</table>

**Autooxidation and disproportionation**

*In self-contained breathing apparatus:*

**Peroxide**

$2Na_2O_2(s) + 2CO_2(g)$ $\rightarrow$ $2Na_2CO_3(s) + O_2(g)$

**Superoxide**

$4KO_2(s) + 2H_2O(g)$ $\rightarrow$ $3O_2(g) + 4KOH(s)$

$KOH(s) + CO_2(g)$ $\rightarrow$ $KHCO_3(s)$

### Acid/Base Equilibria

**Acids and bases**

$HX(aq) \leftrightarrow H^+(aq) + X^-(aq)$  \hspace{1cm} $K_a = \frac{[H^+][X^-]}{[HX]}$

$X^-(aq) + H_2O(l) \leftrightarrow HX(aq) + OH^-(aq)$  \hspace{1cm} $K_b = \frac{[HX][OH^-]}{[X^-]}$

**Table of initial and equilibrium conditions**

Solve problems by following the amount of reaction

Make and test assumptions about relative significance of initial concentrations and amount of reaction (our limit here will be $<3\%$)

**Fractional dissociation and dilution**

$pH + pOH = pK_a + pK_b = 14$  \hspace{1cm} $K_w = 10^{-14} = [H^+][OH^-] = K_aK_b$
Amphoterism

Amphotericism is the ability of a molecule to act both as an acid and as a base. This results in metal hydroxides which are soluble in both acids and bases.

Hydration:  \( \text{Al}^{3+} (aq) \rightleftharpoons \text{Al}(H_2O)_6^{3+} \)

\[
\text{Al(OH)}_3 (s) + 3H_2O \rightleftharpoons \text{Al(OH)}_3(OH_2)_3 (s)
\]

In acid:

\[
\text{Al(OH)}_3(OH_2)_3 + H^+ \rightleftharpoons \text{Al(OH)}_2(OH_2)_4^{+} (aq)
\]

Solubility increases

In base:

\[
\text{Al(OH)}_3(OH_2)_3 + OH^- \rightleftharpoons \text{Al(OH)}_4(OH_2)_2^{-} (aq) + H_2O
\]

Solubility increases

Polyprotic Acid Equilibria

Polyprotic acid: >1 acidic proton

For 0.1 M \( \text{H}_2\text{S} \), what are the concentrations of \( \text{H}_2\text{S}, \text{H}^+, \text{HS}^-, \) and \( \text{S}^{2-} \)?

\[
\begin{align*}
\text{H}_2\text{S}(aq) & \rightleftharpoons \text{H}^+(aq) + \text{HS}^-(aq) \quad \text{\( K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} \)} \\
\text{HS}^-(aq) & \rightleftharpoons \text{H}^+(aq) + \text{S}^{2-}(aq) \quad \text{\( K_{a2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = 1.3 \times 10^{-13} \)}
\end{align*}
\]

Table 1:

<table>
<thead>
<tr>
<th></th>
<th>( \text{H}_2\text{S} )</th>
<th>( \text{H}^+ )</th>
<th>( \text{HS}^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init</td>
<td>0.1</td>
<td>(10^{-7})</td>
<td>0</td>
</tr>
<tr>
<td>Final</td>
<td>0.1-x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
\text{K}_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{x^2}{0.1-x} \approx \frac{x^2}{0.1}
\]

Table 2:

<table>
<thead>
<tr>
<th></th>
<th>( \text{HS}^- )</th>
<th>( \text{H}^+ )</th>
<th>( \text{S}^{2-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Init</td>
<td>x</td>
<td>x</td>
<td>0</td>
</tr>
<tr>
<td>Final</td>
<td>x-y~x</td>
<td>x+y~x</td>
<td>y</td>
</tr>
</tbody>
</table>

\[
\text{K}_{a2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{(x+y)y}{x^2} \approx y
\]
Buffers, Solubility, & Simultaneous Equilibria

Buffers
pH should be within 1 unit of pKₐ of acid-base equilibrium used

\[ \text{pH} = \text{pK}_a - \log_{10} \frac{[HA]}{[A^-]} \]

Solubility product
\[ M_aX_b(s) \rightleftharpoons aM^{+}(aq) + bX^{-}(aq) \quad K_{sp} = [M^{+}]^a[X^{-}]^b \]

In solving equilibria, keep track of stoichiometry
Solubility – how much of the solid (in moles/L) dissolves in a given solution

Metal Complex Stability

\[ \text{Cu(NH}_3\text{)}_{4}^{2+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Cu(OH}_2\text{)}_{4}^{2+} + 4 \text{NH}_3 \]

\[ \text{Cu}^{2+}(aq) = \text{Cu(OH}_2\text{)}_{4}^{2+} \]

\[ K = \frac{[\text{Cu(OH}_2\text{)}_{4}^{2+}][\text{NH}_3]^4}{[\text{Cu(NH}_3\text{)}_{4}^{2+}][\text{H}_2\text{O}]^4} \]

Dissociation constant
\[ K_D = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu(NH}_3\text{)}_{4}^{2+}]} = 2 \times 10^{-13} \]

\[ \text{Cu(OH}_2\text{)}_{4}^{2+} + 4 \text{NH}_3 \rightleftharpoons \text{Cu(NH}_3\text{)}_{4}^{2+} + 4 \text{H}_2\text{O} \]

Formation constant
\[ K_F = \frac{[\text{Cu(NH}_3\text{)}_{4}^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 5 \times 10^{12} \]

\[ K_D = \frac{1}{K_F} \]
### Metal Complexes

**Coordination compounds**
- Lewis acid – Lewis base adducts
- Important in enzymes, catalysis, metal/salt dissolution
  - Orbitals and oxidation state of central metal ion determine coordination.
  - Electronic excitation – absorption and emission
    - Lewis base ligands split electronic energies of metal ions – leading to color and spin
    - Lone pair electrons repel and stay farthest away (as compared to ligands)
  - Spin
    - High spin vs. low spin compounds
    - Compare crystal field splitting ($\Delta$) to the spin pairing energy (P)
  - Spectrochemical series – relative ligand effect on $\Delta$
  - Paramagnetic – having one of more unpaired spins

**Colors**
- Complementary colors – if a color is absorbed, the absorbing material will appear as the complementary color
- Red-green, orange-blue, yellow-violet
- Other means of color: emission, interference

### Chelation

**More than one Lewis base site in a molecule**
- Entropically favored over comparable monodentate ligands

\[
[Cu(NH_3)_4]^{2+} \quad K_F = 1.1 \times 10^{13}
\]

\[
[Cu(en)_2]^{2+} \quad K_F = 1.0 \times 10^{20}
\]

- $en = \text{ethylenediamine} = H_2\tilde{N}-\text{CH}_2-\text{CH}_2-\tilde{N}H_2$
- EDTA = ethylenediaminetetraacetic acid

**Thermodynamics and equilibria**
- Measure thermodynamics (and equilibria) electrochemically, e.g., by comparing complex ions to aqueous ions.
### Measuring Stability Metal Ion Complexes

\[
\text{Ag}^+(aq) + e^- \rightleftharpoons \text{Ag}(s) \quad E^\circ_{\text{Ag}} = +0.80 \text{ V}
\]

\[
[\text{Ag(CN)}_2]^- (aq) + e^- \rightleftharpoons \text{Ag}(s) + 2\text{CN}^- \quad E^\circ_{\text{Ag}} = -0.31 \text{ V}
\]

CN\(^-\) is **not** a chelate because it is monodentate

### Energy and Excitations in Solids

**Metals vs. Semiconductors & Insulators**

(\text{along with a few other less common flavors})

For metal, there is no energy gap between highest occupied and lowest unoccupied orbitals.

For semiconductors & insulators, there is an energy gap between highest occupied and lowest unoccupied orbitals.

This difference has significant consequences in appearance, electrical conduction, thermal conduction, and thus, how they are used.
# Energy and Excitations in Solids

**Metals**
- No band gap - HOMO, LUMO are at the same energy
- Electronic excitation is small vs. $kT$
  - High electrical and thermal conductivity
- Conductivity decreases with increasing temperature because of electron scattering

**Semiconductors and Insulators**
- Have a band gap between valence (lower) band and conduction (upper) band – electronic excitation is $>kT$
  - This determines insulator vs. semiconductor
- Direct band gap can be excited by photons (very little momentum)
- Indirect band gap cannot be photoexcited efficiently nor is emission efficient
- Electrons and “holes” can carry charge
  - Differentiate with magnetic field (Hall effect)
- Energies of (dopant) states in the band gap determine conductivity and whether electrons or holes dominate current
- Conductivity increases with increasing temperature because of thermal excitation of carriers
Recap of Lecture #21: Kinetics

Rate laws
Reaction order
Order and stoichiometry are not the same
   Clue to mechanism
Reaction dynamics = kinetics + mechanism
   Location of reaction barrier determines effectiveness of translation vs.
   vibration at promoting reaction.

Recall the mechanism and kinetics do NOT affect the thermodynamics (state functions) and equilibra.

Reaction Order
Statistical/graphical analysis of kinetics

First order reactions result in exponential changes in [reactants], [products]

Exam 2 Results:
73.5 ± 14.4
30’s-90’s range

Recap of Lecture #22: Kinetics, cont.

Rate laws
Reaction order
We covered first and second order reactions

Strategy: linearize data by transformation – extract parameters like rate constant
   and activation energy

Catalytic converter
   Complex mixture of supported catalysts
   Oxidizes CO and hydro carbons, reduces NOx

Enzymes
Biological catalysts
Both accelerate and control reactions
Control comes from reactions (post-translational modification), context
Often have metal center(s) function as Lewis Acids for reagents/ligands
Recap of Lecture #24:
More on Kinetics

\[ \text{Slope} = \frac{-E_a}{k_B} \]

\[ \ln A \]

Recap of Lecture #24:
More on Catalysis

Lower activation energy

Stabilized intermediate

Images: Wiki commons
Polymerase Chain Reaction

Polymerase is an enzyme that forms a polymer
PCR depends on a polymerase that catalyzes the replication of DNA (the polymer) from the nucleotides (the monomers)

1) Create two short complementary sequences that “prime” replication of a single length of the DNA molecule
2) Heat DNA to separate paired strands
3) Add primers
4) Cool, then add bases and polymerase
   Chains are copied starting at the primers
5) Repeat steps 2-4
25 cycles make 1,000,000 copies of the sequence between the two primers from a single DNA molecule

People’s DNA are different enough to be used as extremely accurate identification (Microbiomes, too.)
Recap of Lecture #24: Enzymes, Polymerase Chain Reaction

Enzymes
Biological catalysts
Better specificity, turnover numbers, and control than artificial catalysts
Most are proteins, and can also include co-factors (vitamins) and metal ions
(There are also some RNA enzymes.)

Proteins –
Copolymer of 20 amino acids, with ~100 possible post-translational modifications
Function depends on chemical modifications, environment, conformation
Lewis base sites coordinate metals

Polymerase chain reaction – enzyme to copy DNA

Drugs often interfere with enzyme activity (e.g., bind up active site)

Radioactive Decay: First-Order Kinetics

Radioactive Decay Rates:

\[
\frac{dN}{dt} = -kN
\]

where: 
- \( k \) is a constant, and 
- \( N \) is the number of decaying nuclei.

By rearranging and integrating:

\[
\int_0^t \frac{dN'}{N'} = - \int_0^t k dt'
\]

\[
\ln \frac{N(t)}{N_0} = -kt
\]

where \( N_0 \) is the number of decaying nuclei at \( t=0 \).

\[
N(t) = N_0 e^{-kt}
\]

Because the rate is proportional to the number of nuclei, this is called a first-order process.
Radioactive Decay: Half Life

**Half-Life:** the time required for half of a radioactive sample to decay.

\[ N(t_{1/2}) = \frac{N_0}{2} \]

\[ \ln(\frac{1}{2}) = -kt_{1/2} \]

\[ k = \frac{0.693}{t_{1/2}} \; \text{or} \; t_{1/2} = \frac{0.693}{k} \]

**Examples:**

<table>
<thead>
<tr>
<th>Isotope</th>
<th>( t_{1/2} )</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{238}\text{U})</td>
<td>4.5x10^9 yr</td>
<td>(\alpha)</td>
</tr>
<tr>
<td>(^{235}\text{U})</td>
<td>7.1x10^8 yr</td>
<td>(\alpha)</td>
</tr>
<tr>
<td>(^{14}\text{C})</td>
<td>5.7x10^3 yr</td>
<td>(\beta)</td>
</tr>
</tbody>
</table>

Recap of Lecture #25: Nuclear Chemistry

**Radioactive Dating**

First-order (exponential) decay kinetics

Measure elapsed time by following decay of an isotope

Example – \(^{14}\text{C}\) decay measures the time since respiration stopped (end of carbon uptake)

\(^{14}\text{C}\) half-life of 5700 years, \(^{238}\text{U}\) half-life of 4.5x10^9 years

Accessible ages must be on these scales

After \(n\) half-lives, \((\frac{1}{2})^n\) of original amount remains

**Nuclear Stability**

Unstable elements decay so as to move toward the band of stability

Transuranium elements undergo a series of \(\alpha\) decays

Neutron-rich isotopes undergo \(\alpha\) decays

Neutron-deficient isotopes undergo positron emission or electron capture

Even proton and neutron numbers + closed shells favor stability
**Nuclear Chemistry**

*Spontaneous nuclear reactions:*
Radioactive Decay.

1) Emission of $\alpha$-particles: $^4_2\text{He}$

\[ \text{e.g. } ^{238}_{92}\text{U} \rightarrow ^{234}_{90}\text{Th} + ^4_2\text{He} \]

In air, $\alpha$-particles travel several cm.
In Al, $\alpha$-particles travel $10^{-3}$ mm.

---

2) Emission of $\beta$-particles: $^0_{-1}\text{e}$ - electrons.

\[ \text{e.g. } ^{131}_{53}\text{I} \rightarrow ^{131}_{54}\text{Xe} + ^0_{-1}\text{e} \]

$\beta$-particle emission converts a neutron to a proton:

\[ ^1_0\text{n} \rightarrow ^1_1\text{p} + ^0_{-1}\text{e} \]

In air, $\beta$-particles travel 10 m.
In Al, $\beta$-particles travel 0.5 mm.
3) Emission of $\gamma$-rays: $^0_0\gamma$

$\gamma$-ray emission changes neither atomic number nor mass.

In Al, $\gamma$-particles travel 5-10 cm.

---

4) Emission of positrons ($\beta^+$-particles): $^0_1e$

E.g. $^{11}_6C \rightarrow ^{11}_5B + ^0_1e$

Positron emission converts a proton to a neutron:

$^{1}_1p \rightarrow ^1_0n + ^0_1e$

Positrons have a short lifetime because they recombine with electrons and annihilate:

$^0_1e + ^0_{-1}e \rightarrow 2^0_0\gamma$

Detect the $\gamma$. 
Nuclear Chemistry

5) Electron Capture: an electron from the orbitals surrounding the nucleus can be captured:

\[ \text{e.g. } \frac{81}{37}\text{Rb} + 0_{-1} e \rightarrow \frac{81}{36}\text{Kr} \]

Electron capture converts a proton to a neutron:

\[ 1_{-1}p + 0_{-1} e \rightarrow 0_{-1}n \]

Nuclear Stability

Rules:
1) Up to atomic number 20, n=p is stable.
2) Above atomic number 20, n>p is stable.
3) Above atomic number 84, all nuclei are unstable.
4) Nuclei with 2, 8, 20, 28, 50, or 82 protons, or 2, 8, 20, 28, 50, 82, or 126 neutrons are particularly stable. These are the nuclear equivalent of closed shell configurations (and are called magic numbers).
5) Even numbers of protons and neutrons are more stable.

<table>
<thead>
<tr>
<th># Stable Nuclei With This Configuration:</th>
<th># Protons</th>
<th># Neutrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>157</td>
<td>Even</td>
<td>Even</td>
</tr>
<tr>
<td>52</td>
<td>Even</td>
<td>Odd</td>
</tr>
<tr>
<td>50</td>
<td>Odd</td>
<td>Even</td>
</tr>
<tr>
<td>5</td>
<td>Odd</td>
<td>Odd</td>
</tr>
</tbody>
</table>
Nuclear Chemistry: Decay towards Stability

An isotope with a high n/p ratio is proton deficient. To convert neutrons to protons, it can undergo β-decay:

\[ ^1p \rightarrow ^1p + ^0_e \]

e.g. \( ^{97}\text{Zr} \rightarrow ^{97}\text{Nb} + ^0_e \)

An isotope with a low n/p ratio is neutron deficient. To convert protons to neutrons, there are two possibilities:

i) Positron emission:

\[ ^1p \rightarrow ^0n + ^0_e \]

e.g. \( ^{20}\text{Ne} \rightarrow ^{20}\text{Ne} + ^0_e \)

ii) Electron capture:

\[ ^1p + ^0_e \rightarrow ^0n \]

Nuclear Chemistry: Decay towards Stability, cont.

Elements with atomic numbers greater than 84 undergo α-decay in order to reduce both the numbers of neutrons and protons:

\[ ^{235}\text{U} \rightarrow ^{231}\text{Th} + ^4\text{He} \]
Band of Stability for Nuclei

Decay of $^{238}\text{U}$
Recap of Lecture #26: Nuclear Chemistry

Balance Nuclear Reactions

Nuclear Stability
Unstable elements decay so as to move toward the band of stability
Transuranium elements undergo a series of α decays
Neutron-rich isotopes undergo β⁻ decays
Neutron-deficient isotopes undergo positron emission or electron capture

Even proton and neutron numbers + closed shells favor stability
Nuclear Binding Energy

\[ ^1p + ^1n \rightarrow ^2He \]

\(^1p\) mass is 1.00728 amu

\(^1n\) mass is 1.00867 amu

\(^2He\) mass is 4.00150 amu

Mass defect = \(2(1.00728) + 2(1.00867) - 4.00150 = 0.03040\) amu = \(5.047 \times 10^{-29}\) kg

\[ E = mc^2, \text{ really } \Delta E = \Delta mc^2 \]

\[ E = (5.047 \times 10^{-29} \text{ kg})(3 \times 10^8 \text{ m/sec})^2 = 4.543 \times 10^{-12} \text{ J/}^2He \]

Binding \(E/\text{nucleon} = 4.543 \times 10^{-12} \text{ J/}^2He\)

\[ 1.41 \times 10^{-12} \text{ J for } ^{56}\text{Fe} \]

\[ 1.22 \times 10^{-12} \text{ J for } ^{238}\text{U} \]

For mass > \(\sim 50-60\) amu nuclei: nuclear fission is exothermic

For mass < \(\sim 50-60\) amu nuclei: nuclear fusion is exothermic
An average of 2.4 neutrons are produced per $^{235}\text{U}$ fission.

**Chain reactions:**

- **Small:** Most neutrons are lost, subcritical mass
- **Medium:** Constant rate of fission, critical mass
  - Nuclear reactor
    - e.g., 3% $^{235}\text{U}$ in $^{238}\text{U}$ – $\text{UO}_2$ pellets in metal rods
    - Heat liquid to drive turbines – need lots of cooling water
      - (see also breeder reactors)
- **Large:** Increasing rate of fission, supercritical mass
  - Bomb
Nuclear Chain Reactions: Fusion

“Chemistry of the stars”

The sun contains 73% H and 26% He

\[ ^1\text{H} + ^1\text{H} \rightarrow ^2\text{H} + 9\beta \]

\[ ^1\text{H} + ^2\text{H} \rightarrow ^3\text{He} \]

\[ ^2\text{He} + ^3\text{He} \rightarrow ^4\text{He} + 2^1\text{H} \]

\[ ^3\text{He} + ^1\text{H} \rightarrow ^4\text{He} + 9\beta \]

Initiation of these reactions requires temperatures of \(4 \times 10^7\) K

(not currently obtainable on Earth on a stable basis)
**Energy-Level Diagrams +**

- Metals, semiconductors, insulators, semi-metals, doped semiconductors, direct & indirect band gap semiconductors, semi-insulating semiconductors, superconductors
- Boltzmann distribution (vs T), Fermi distribution
- Photoexcitation, emission, fluorescence, photoionization, two-photon excitation, multiphoton excitation, Raman spectroscopy, stimulated emission, Jablonski diagram
- X-ray photoelectron spectroscopy, X-ray fluorescence, Auger spectroscopy
- Reaction coordinate, activation energy, catalysis
- Conversion of energy units, temperature, frequency, photon wavelength, particle wavelength, magnetic field
- Fingerprint spectroscopies and methods

**Thermodynamics and Equilibria**

- Thermodynamics, free energy ($\Delta G$), enthalpy ($\Delta H$), entropy ($\Delta S$), cell potential (E)
- Use intuition, rules of forming stronger bonds ($\Delta H<0$)
- Entropy changes – gas/solution/liquid/solid
- Know sign conventions
- Relate thermodynamics, equilibrium constants, and electrochemistry (vs kinetics)
- Phase transitions
- Acids & bases, buffers
- Solubility
- Complex formation – Lewis acid – Lewis base interactions (including enzymes)
- Periodic trends
- Interaction strengths
- Chemical bonds – covalent, ionic, metallic
- Weaker interactions – hydrogen bonding, ion-dipole, dipole-dipole,
- Electrochemistry – LAnOx & GRedCat
- Oxidation states, half reactions, spontaneous & non-spontaneous reactions
- Batteries, electrolysis
**Kinetics**

Rate laws
Reaction order
Order and stoichiometry are *not* the same
  Clue to mechanism
Reaction dynamics = kinetics + mechanism
  Location of reaction barrier determines effectiveness of translation vs.
  vibration at promoting reaction
Recall the mechanism and kinetics do *NOT* affect the thermodynamics (state
functions) and equilibra

*Reaction Order*
Statistical/graphical analysis of kinetics

*Catalysis*
Lower barrier to accelerate reaction equilibration
Recall the mechanism and kinetics do *NOT* affect the thermodynamics (state
functions) and equilibra
Enzymes are biological catalysts with greater specificity and control than synthetic
catalysts

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**Materials**

*Semiconductors*
  Conduction and valence bands
  Band gap, Fermi level
  Density of states
  *n*- and *p*-type, semi-insulating
  Direct and indirect band gaps
  Reactions of Si to make: insulators, metals, and to add dopants
  Conductivity increases with increasing temperature
    thermal excitation to conduction band or from valence band

*Insulators*
  Conductivity increases with increasing temperature
  Energy level diagram looks like semiconductor but bigger gap (compare to kT)

*Metals*
  No band gap
  Conductivity decreases with increasing temperature

*Semi-Metals*
Nuclear Chemistry

Decays - α, β⁻, β⁺, γ, electron capture
Balance decay reactions
Band of stability – also, use periodic table (what are average/common masses?)

Nuclear Stability
Unstable elements decay so as to move toward the band of stability
Transuranium elements undergo a series of α decays
Neutron-rich isotopes undergo β⁻ decays
Neutron-deficient isotopes undergo positron emission or electron capture
Even proton and neutron numbers + closed shells favor stability

Radioactive Dating
First-order (exponential) decay kinetics
Measure elapsed time by following decay of an isotope
Example – 14C decay measures the time since respiration stopped (end of carbon uptake)
14C half-life of 5700 years, 238U half-life of 4.5x10⁹ years
Accessible ages must be on these scales
After n half-lives, (1/2)^n of original amount remains

Nuclear Energy
Mass defect, AE = Δmc² – binding energy per nucleon peaks at ⁵⁶Fe
Fission and chain reactions, fusion

Chemical Measurements

Infrared spectroscopy – vibrations, chemical fingerprint (isotopes)
Optical and ultraviolet spectroscopy – electronic excitation
X-ray spectroscopies – core levels, elemental identification

Fluorescence
Mass spectrometry
  Fragmentation, isotopes

Electrochemical – thermodynamics
Balance cells and half-cells, count electrons
  Quantitative
  Important in energy harvesting and storage

X-ray diffraction – spacings in and between molecules

Microscopies – real-space measurements

Know energy scales, both for photons and interaction strengths
Photon Energies

Infrared spectroscopy – vibrations, chemical fingerprint
Optical and ultraviolet spectroscopy – electronic excitation
X-ray spectroscopies – core levels, elemental identification
X-ray diffraction – bond lengths in crystals
(Microwave spectroscopy – rotations)