

Chem 20BH: Highlights from the Syllabus

READ THE UPDATED SYLLABUS BEFORE AND AFTER EACH CLASS

<https://nano.ucla.edu/chemistry-20bh/> or <http://bit.ly/20Bhw20>

Syllabus will be *updated* after each lecture. Upcoming assignments are finalized when date is green and underlined. **Lecture 1, Monday 6 January**

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

Discussions: Tuesday/Thursday 11 AM, 3069 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 TA

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 2³⁰-3³⁰ PM & Thursday 1²⁰-2³⁰ 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

Paul S. Weiss

California NanoSystems Institute
Departments of Chemistry & Biochemistry and Materials Science & Engineering
UCLA | www.nano.ucla.edu

SB, SM MIT Chemistry 1980

PhD UC Berkeley Chemistry (YT Lee) 1986 

Postdoc Bell Labs 1986-88

Postdoc IBM Almaden (Eigler) 1988-89  

Penn State Chemistry, then Chemistry & Physics 1989-2009

Rewrote freshman chemistry courses, honors course – 3 

U Washington Molecular Biotechnology (Lee Hood) 1996-97 

Kyoto U Electronic Engineering (K Matsushige) 1998

Tohoku U WPI 2007-17

UCLA Chemistry & Biochemistry, Materials Science & Engineering, CNSI 2009-

Cal Tech Kavli Institute 2014-15

Harvard/MIT Wyss Institute 2015-

Nanyang Technological University 2015-18 

INRS Montreal 2016-17

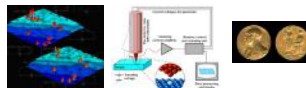
NTU/SKKU 2018-

ACS Nano, Founding Editor-in-Chief 2007- @acs 

Our Research

Paul S. Weiss
www.nano.ucla.edu

Ultimate limits of miniaturization – the smallest switches and motors in the world



Sensors for understanding the brain, by measuring dynamic chemistry *in vivo*
Similar approach to microbiome



Making perfect connections to electronic and other materials



Determining structures of individual biomolecules & how they determine function
Changing how (all) images are recorded and analyzed



High-throughput gene editing to cure genetic diseases & for cancer immunotherapy

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

Selected Upcoming Talks

Wednesday 15 January 3 PM, CNSI Auditorium
Zhong Lin Wang, Georgia Tech – Energy Harvesting

A Conversation with
Prof. Zhong Lin Wang, Energy Harvester



Thursday 16 January, 12 noon, Moss Auditorium (A2-342 MDCC)
Gay Crooks, UCLA – From Stem Cells to T Cells *in Vitro*
(Registration may be required)



Wednesday 22 January 4 PM, CNSI Auditorium
Emily Carter, UCLA Provost – Chemistry Theory & Climate/Energy Issues



Monday 24 February 4 PM, probably 2033 Young Hall
Bogdan Dragnea, Indiana U – Bioinspired Materials



Friday 17 April 5 PM, CNSI Auditorium
Ben Feringa, U Groningen – Molecular Motors



There are MANY, MANY more!
Check bulletin boards, ask your research group members, get on mailing lists.

Proposed Exam and Poster Evenings Fixed Final Exam

Midterm 1
Wednesday 29 January (6-8 PM vs in class)

Poster Presentations
Saturday 22 February (2-6 PM)

Midterm 2
Wednesday 26 February (6-8 PM vs in class)

Final Exam
Tuesday 18 March, 8-11 AM

Recap of Lecture #1: Intro & Energies

Simplified class web site and link to syllabus & recaps (case matters):
bit.ly/20bh20

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 $E = \text{arrow length}$

Arrow down – emitted photon at $E = \text{arrow length}$

Fluorescence spectroscopy/imaging

Absorption followed by emission at different E

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

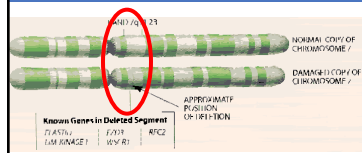
Imaging parts of molecules

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

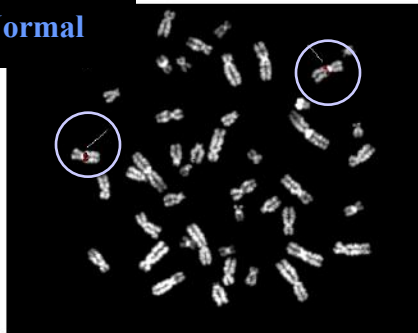


Fluorescence *in-situ* Hybridization

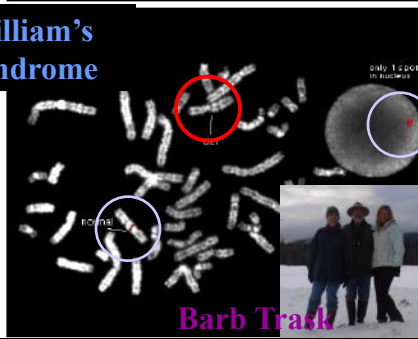
Label sites on individual chromosomes.

Specific probes can be made for rapid screens.

Normal

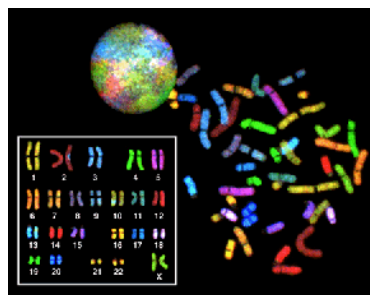


William's Syndrome

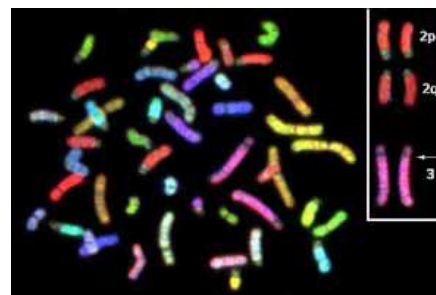


Fluorescent Label Example: Chromosomes

Spectral karyotyping
"Chromosome painting"



Human



Orangutan

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

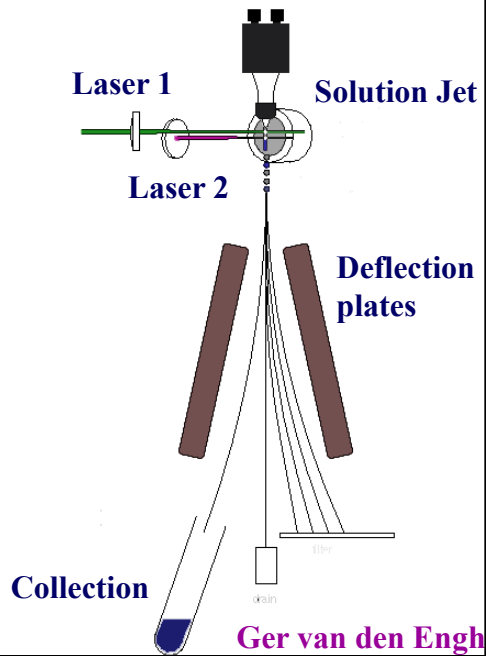
DNA Content - Flow Cytometry

Screen single particles or single molecules.

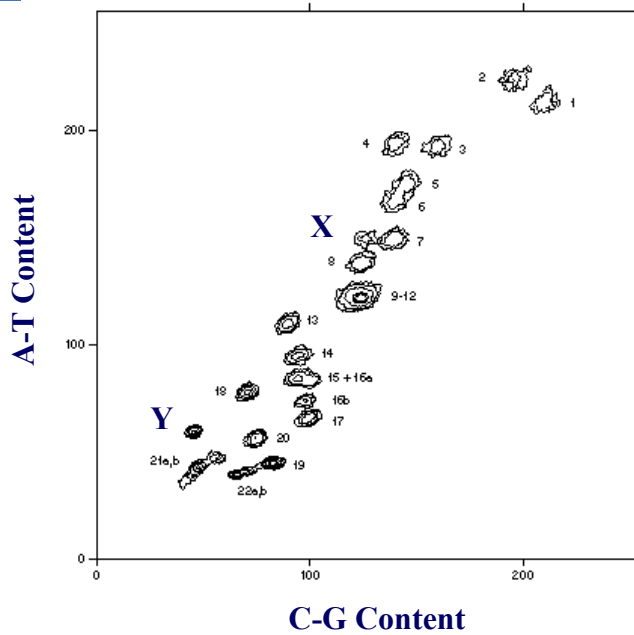
Probe, separate, collect.

Drops produced and sampled at 120 kHz.

Could we boost sensitivity and do this for smaller molecules?



DNA Content - Flow Cytometry, cont.



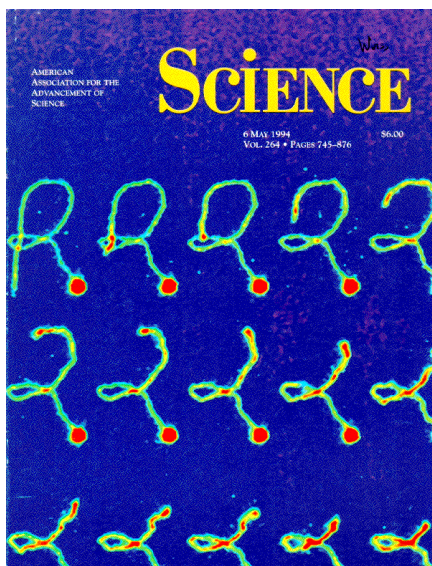
Ger van den Eng

Single-Molecule Capture and Manipulation

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



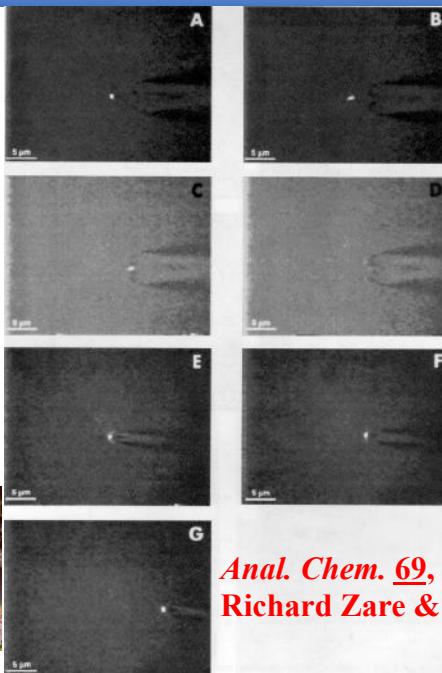
1997 Nobel Physics Prize
Later, Secretary of Energy



Science **69**, 819 (1994)
Steve Chu & Group

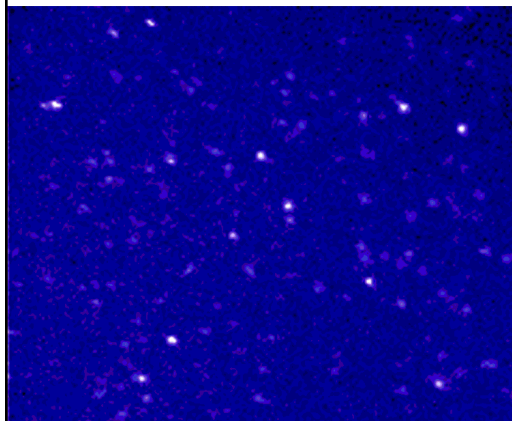
Single-Molecule Capture and Manipulation

Use optical tweezers to load a single (λ) DNA molecule into a capillary.



Anal. Chem. **69**, 1801 (1997)
Richard Zare & Group

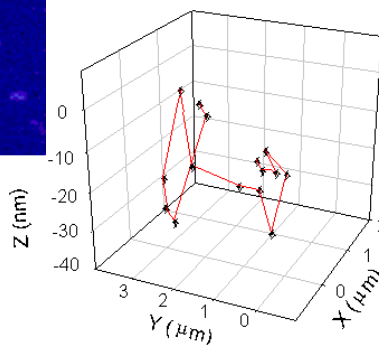
Optical Measurements of Chemical Environments



Single-molecule fluorescence maps microcavities in polyacrilimide gels.



Science 274, 966 (1996)
W. E. Moerner & Group
Then UCSD, now Stanford
2014 Nobel Chemistry Prize



Understanding Scanning Tunneling Microscope Images

How do we understand and predict STM images?

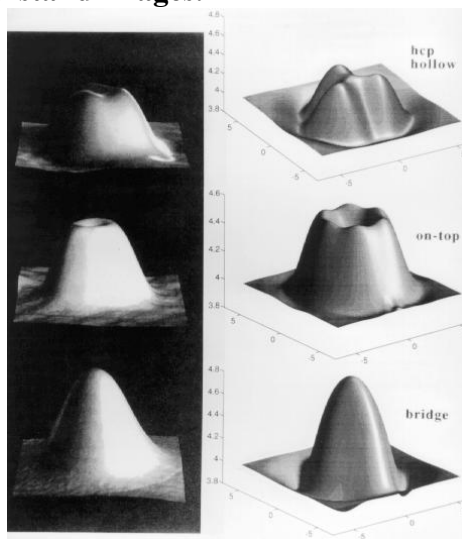
Ultrastable low temperature studies prove the critical data used to understand images.

Benzene at three different adsorption sites on Pt{111} at 4 K

Weiss & Eigler



Heine Rohrer
1986 Nobel Physics Prize



Philippe Sautet

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

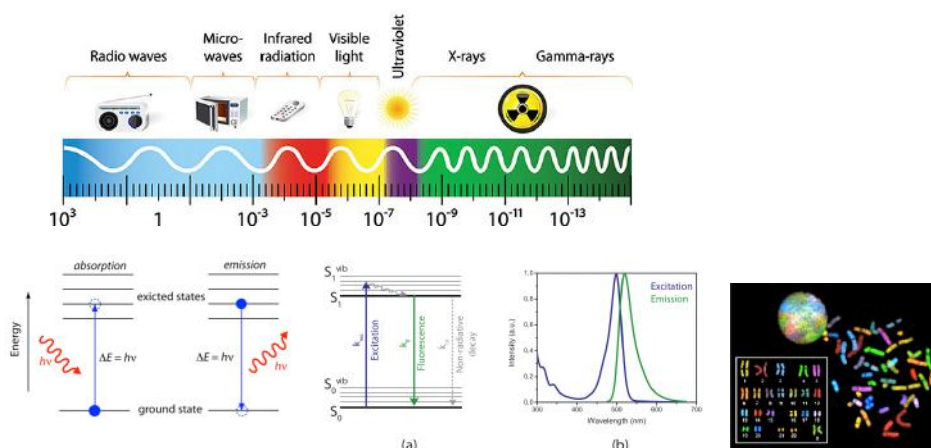
Use fluorescent labels and dyes

Flow cytometry, fluorescence *in-situ* hybridization (FISH)

Single-molecule measurements

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

Photon Absorption and Emission, Fluorescence

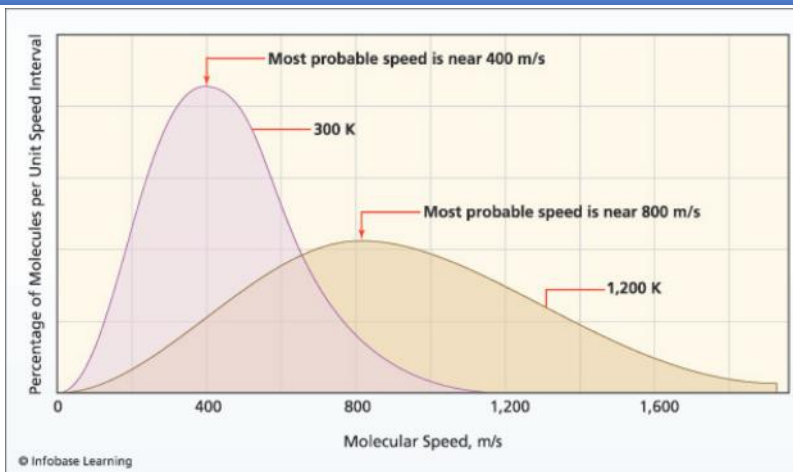


Fluorescence requires specific excitation energy *and* has specific emission energy

Use dyes that are fluorescent to "label" species to detect

e.g., specific DNA sequences in genome

Boltzmann Distributions



Sholto Ainslie Design, Wordpress

$$\varepsilon = \frac{1}{2} m\mu^2 = \frac{3RT}{N}$$

ε is the average kinetic energy, μ is the speed (root mean square velocity)
 N is Avogadro's number 6.023×10^{23}

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:

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 $\sim 1000\times$

Water density 1 g/ml, 1 kg/L

Ionization energies of many solids (\sim all metals w/out alkali elements) $\sim 5 \pm 1$ eV

Recap of Lecture #4: Ideal & Non-Ideal Gases

Real atoms and molecules interact

Know energy ranges of intramolecular and intermolecular interactions

Boiling point gives a crude measure of intermolecular (or interatomic) interaction strength

Molecular, interatomic, and intermolecular potentials

Repulsive wall is steep on close approach

Depth of potential well is (\sim) bond strength

Position of potential well is bond length

State Functions

For equilibrium

Only dependent on state, not on how the material got there

G, H, S

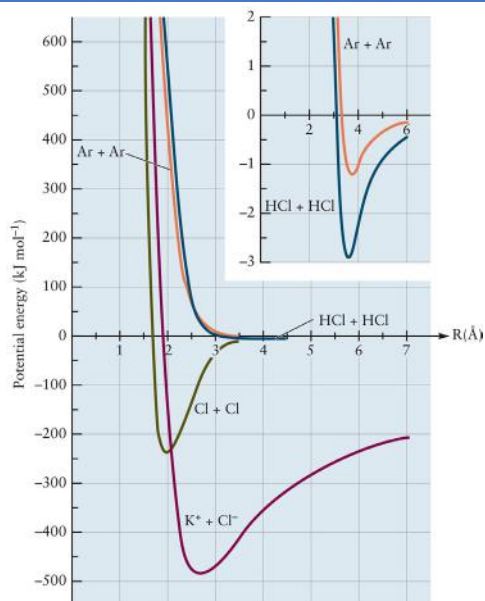
Mass Spectrometry – chemical identification

Make or evaporate ions

Measure parent mass as well as the masses of fragments (daughter masses)

Can fragment multiple times to determine connectivities (*e.g.*, functionalization of proteins)

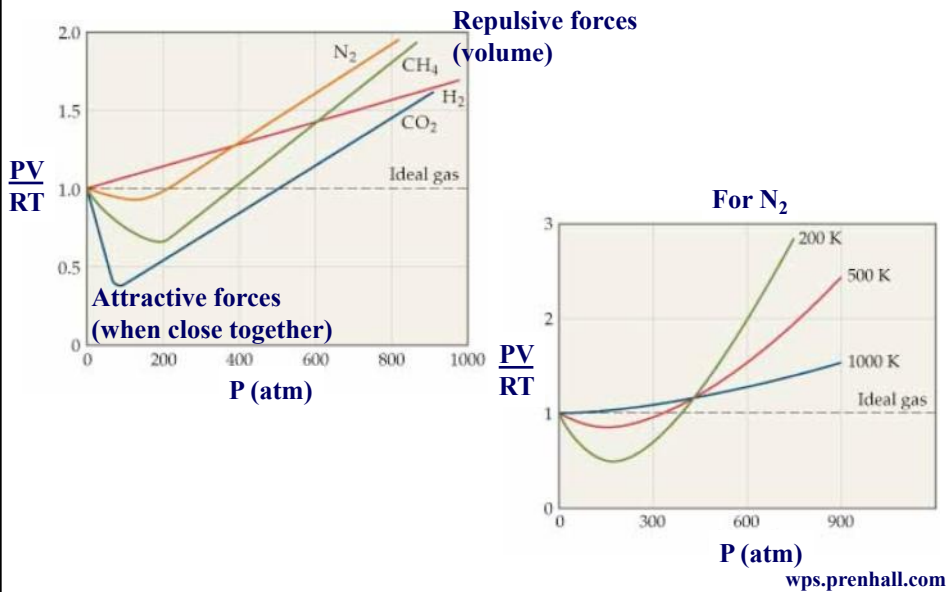
Intramolecular and Intermolecular Potentials



PoMC, Oxtoby, Gillis, & Campion

Real Gases

Deviations from ideal gas

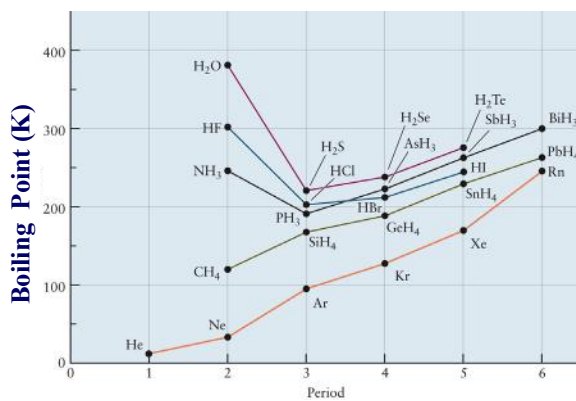


Solids, Liquids, Gases

How will you define them?

What is the phase transition between each (e.g., liquid to gas)?

Does that transition require heat (i.e., are intermolecular interactions overcome)?



PoMC, Oxtoby, Gillis, & Campion

Thermodynamics: State Functions

Recap – State functions

For equilibrium

Only dependent on state, *not* on how the material got there

We consider constant temperature and pressure

Free energy – G

Enthalpy – H

Entropy – S

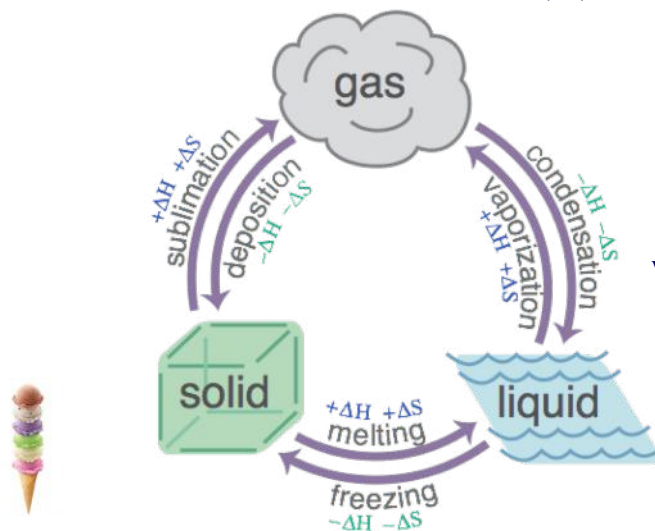
There are equivalents for other situations – chemists and chemical engineers will learn these later, but they will work the same way.

Other quantities (e.g., kinetics) do depend on path

Transformations: Energy and Order

Forming or breaking bonds? Breaking bonds costs energy (ΔH).

Which state is more ordered (ΔS)?

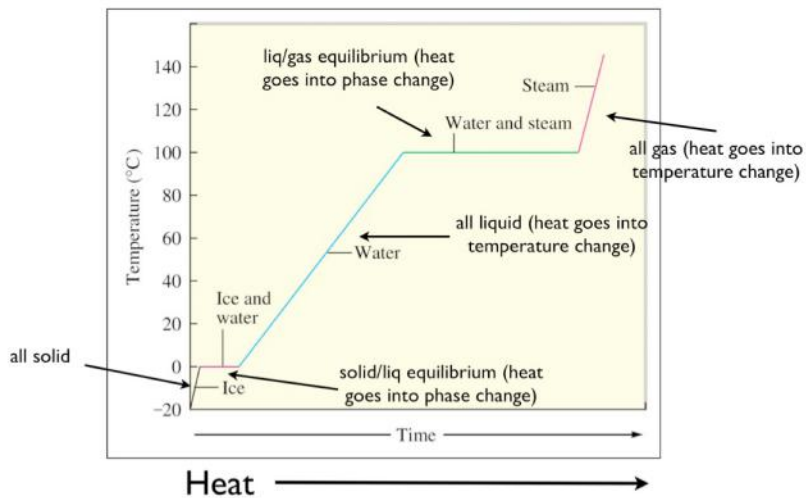


We will come back to this topic quantitatively (Ch. 12)

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

Heat Water, Starting from Ice

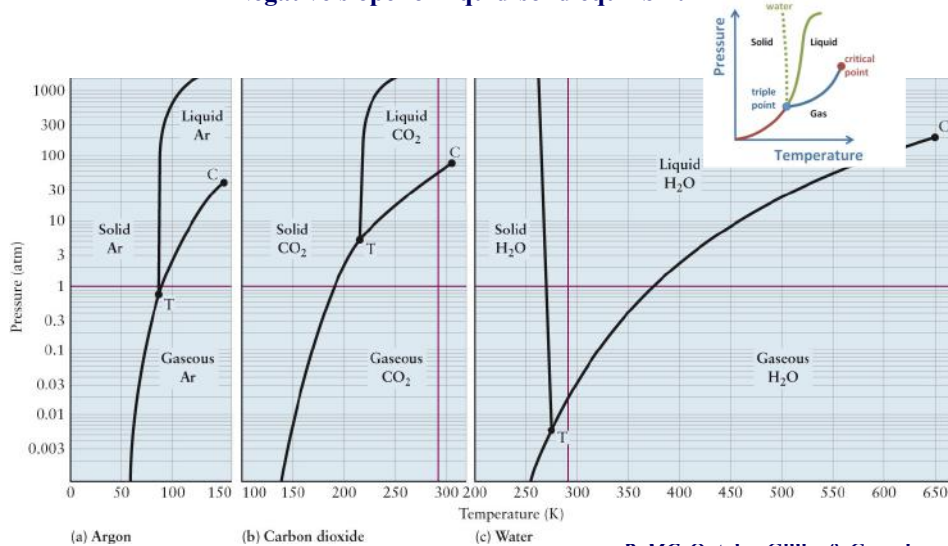
Add heat to go from ice to water to steam



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

Water Is Unusual (Luckily)

Negative slope for liquid-solid equilibrium



PoMC, Oxtoby, Gillis, & Campion
www.boundless.com

Recap: Intermolecular & Intramolecular Forces I

All based on Coulomb's Law (interacting charges)

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Intramolecular	Ionic	Cation–anion	400–4000	NaCl
	Covalent	Nuclei–shared e^- pair	150–1100	H–H
	Metallic	Cations–delocalized electrons	75–1000	Fe

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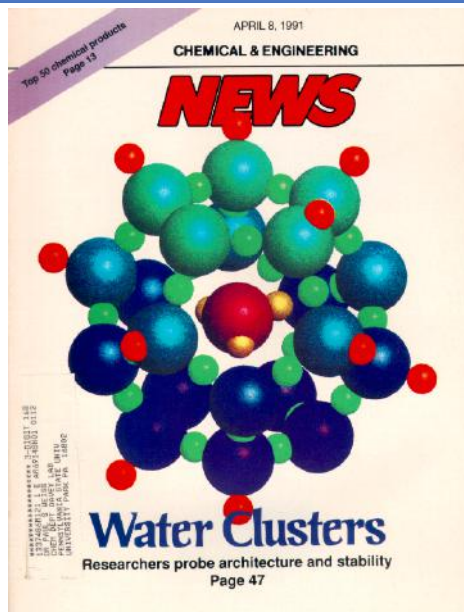
Recap: Intermolecular & Intramolecular Forces II

All based on Coulomb's Law (interacting charges)

Force	Model	Energy (kJ/mol)	Example
Ion-dipole		40–600	$\text{Na}^+ \cdots \text{O} \begin{matrix} \text{H} \\ \diagup \\ \text{H} \end{matrix}$
H bond	$\begin{matrix} \delta^- & \delta^+ & \delta^- \\ -\text{A}-\text{H} \cdots \cdots \text{:B}- \end{matrix}$	10–40	$\begin{matrix} \text{:}\ddot{\text{O}}-\text{H} \cdots \cdots \text{:}\ddot{\text{O}}-\text{H} \\ \qquad \qquad \qquad \\ \text{H} \qquad \qquad \qquad \text{H} \end{matrix}$
Dipole-dipole		5–25	$\text{I}-\text{Cl} \cdots \cdots \text{I}-\text{Cl}$
Ion-induced dipole		3–15	$\text{Fe}^{2+} \cdots \cdots \text{O}_2$
Dipole-induced dipole		2–10	$\text{H}-\text{Cl} \cdots \cdots \text{Cl}-\text{Cl}$
Dispersion (London)		0.05–40	$\text{F}-\text{F} \cdots \cdots \text{F}-\text{F}$

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Solvated Protons



Will Castleman, Penn State

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?
(matrix-assisted laser desorption ionization (MALDI))

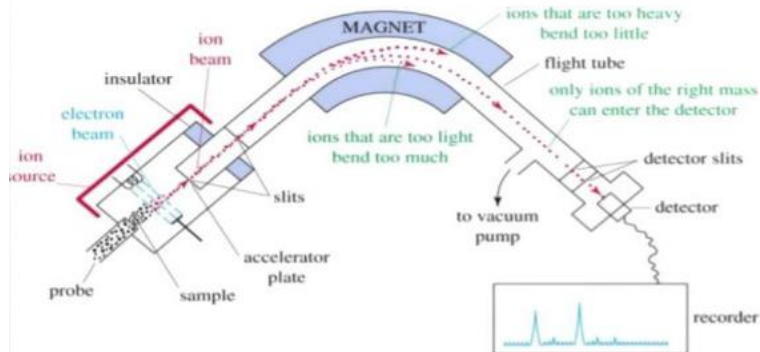
2002 Nobel Chemistry Prize



¹John Fenn
Yale > VCU



²Koichi 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

2.5) Optional collision chamber
followed by another mass filter

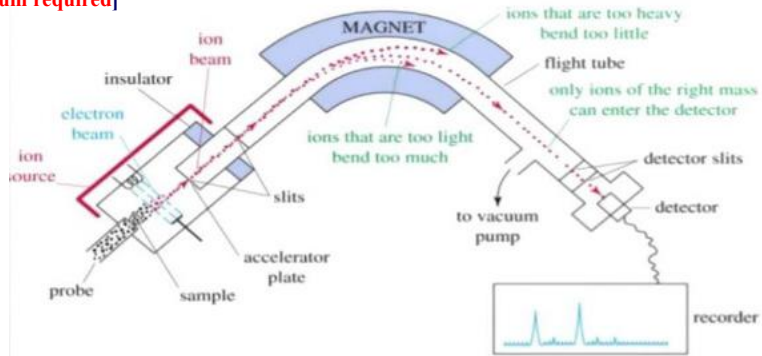
[Asking: Which ions are stable?]

3) Detector:

Accelerate ions and
count charges

1.5) Accelerate all ions to
same energy with electric field

[Vacuum required]



<https://www.slideshare.net/ssuser3375a9>

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)

Acids

Sour taste:

Lemon Juice - Citric acid

Vinegar - Acetic Acid

Dissolve active metals, usually liberating H_2

Corrosive - dissolve compounds that are otherwise hard to dissolve.

Examples:

Precious metals such as gold (Au) dissolve in $HNO_3 + HCl$ (*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)

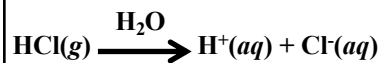
(Turns litmus paper **BLUE**)

Arrhenius Acids and Bases

ACID

Any compound that releases H^+ when dissolved in H_2O

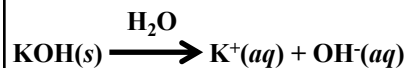
Example:



BASE

Any compound that releases OH^- when dissolved in H_2O

Example:

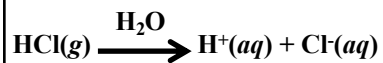


Bronsted & Lowry Acids and Bases

ACID

Any compound capable of donating a H^+ ion

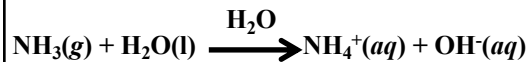
Example:



BASE

Any compound capable of accepting a H^+ ion

Example:



Conjugate Acid-Base Pairs

Differ only by the presence or absence of a proton (H^+)

Conjugate Acid = Conjugate Base + H^+

Examples:

$\text{H}_3\text{O}^+ / \text{H}_2\text{O}$ $\text{H}_2\text{O} / \text{OH}^-$

HCl / Cl^-

$\text{NH}_4^+ / \text{NH}_3(\text{g})$

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)

Acids and Bases

Equilibria

Strong acids and bases dissociate completely.

Know the strong acids & bases.

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

$$\text{pX} = -\log_{10} X$$

$$\text{p}K_a + \text{p}K_b = 14 = \text{pH} + \text{pOH}$$

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

Exam #1 Topics

Exam #1 covers through today's lectures *and* reading:

Recaps and coverage online

Define temperature, pressure, state function

Bond lengths and strengths

Office Hours today 1³⁰ PM

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

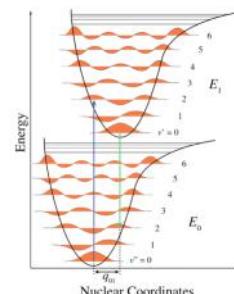
Phase transitions and equilibria

Typical, water, CO₂

Solid, liquid, gas, supercritical fluid

Energy changes with making and breaking bonds, heat

Thermodynamics – free energy, enthalpy, entropy



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

Office Hours today 1³⁰ PM

X-ray diffraction

Rotational spectroscopy (microwave)

– *only* for small molecules in the gas phase

Energies

Know photon energies:

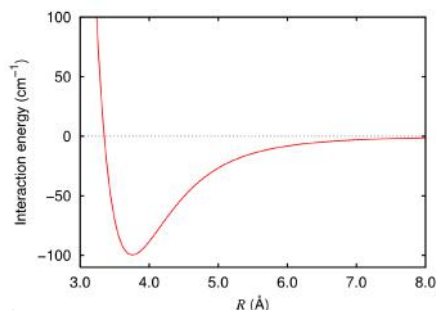
X-ray, UV, visible, infrared, microwave

Know bond energies.

Know conversions between various units:

kJ/mole , kcal/mole , eV , cm^{-1} (for light), K , Hz (for light), J (cal)

Example Question



Question 1 (15 points):

- a) What is the approximate bond energy for Ar_2 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 Ar_2 ? (5 points)

EC) Which has a larger bond strength, Ar_2 or Ar_2^+ ? Why (concisely)?

Data Sheets

Name _____ Student ID # _____

Signature _____ TOTAL = _____

- Chemistry 208H, Winter 2020 1) /20
 29 January 2020
 x questions + 1 small extra credit problem, y pages. 2) /20
 Answer on these sheets only. Additional space on last page.
 If you need extra sheets, please ask your TA. 3) /20
- Note: Only these papers can be used; no other notes are allowed. 4) /20
- Please answer each question concisely. Show your calculations. 5) /20
 You may (and in some cases, must) draw explanatory diagrams.
 Label all axes and features on graphs and diagrams. EC) /5
- 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: $c = 3 \times 10^8 \text{ m/s}$
 Faraday constant = 96500 coul/mole
 Electron charge magnitude: $e = 1.6 \times 10^{-19} \text{ C}$
 Planck's constant: $h = 1.1 \times 10^{-34} \text{ J}\cdot\text{s}$
 Gas constant: $R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} = 8.314 \text{ J}/\text{mol}\cdot\text{K} = 1.987 \text{ cal}/\text{mol}\cdot\text{K}$
 Boltzmann constant: $k_B = 1.4 \times 10^{-23} \text{ J/K}$
 Electron rest mass: $m = 9.1 \times 10^{-31} \text{ kg}$
 Proton rest mass: $M = 1.7 \times 10^{-27} \text{ kg}$
 1 mole = 6.02×10^{23}

	eV	cm ⁻¹	kcal/mol	kJ/mol	K	J	lit
1 eV	1	8065.7	0.239	0.239	11604.5	1.60218 × 10 ⁻¹⁹	2.118916 × 10 ⁻¹¹
1 cm ⁻¹	1.23984 × 10 ⁻⁴	1	0.0230589	0.0119627	1.43879	1.98630 × 10 ⁻²³	2.99792 × 10 ⁻¹⁰
1 kcal/mol	0.034868	29979.2	1	4.184	9632.0	6.94783 × 10 ⁻²¹	8.0658 × 10 ⁻¹¹
1 kJ/mol	0.0238846	19900.0	0.238846	1	238.046	4.57182 × 10 ⁻²¹	5.03418 × 10 ⁻¹¹
1 K	8.61733 × 10 ⁻⁵	0.695035	0.00238846	0.00238846	1	1.380658 × 10 ⁻²³	1.60138 × 10 ⁻¹⁰
1 J	6.24151 × 10 ¹⁸	8341.45 × 10 ¹⁸	0.239 × 10 ¹⁸	0.239 × 10 ¹⁸	2.38046 × 10 ¹⁷	1	1.55052 × 10 ²¹
1 lit	4.13568 × 10 ¹⁵	3.13568 × 10 ¹⁵	0.237 × 10 ¹⁵	0.237 × 10 ¹⁵	4.799 × 10 ¹⁴	6.62543 × 10 ¹⁴	1

$$\Delta G^\circ = -nFE^\circ = -2.303 RT \log_{10} K_{eq}$$

$$\text{pH} = \text{p}K_a - \log_{10} \left(\frac{[\text{HA}]}{[\text{A}^-]} \right)$$

Periodic Table of the Elements

Recap of Lecture #1: Intro & Energies

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 $E = \text{arrow length}$

Arrow down – emitted photon at $E = \text{arrow length}$

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

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.

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

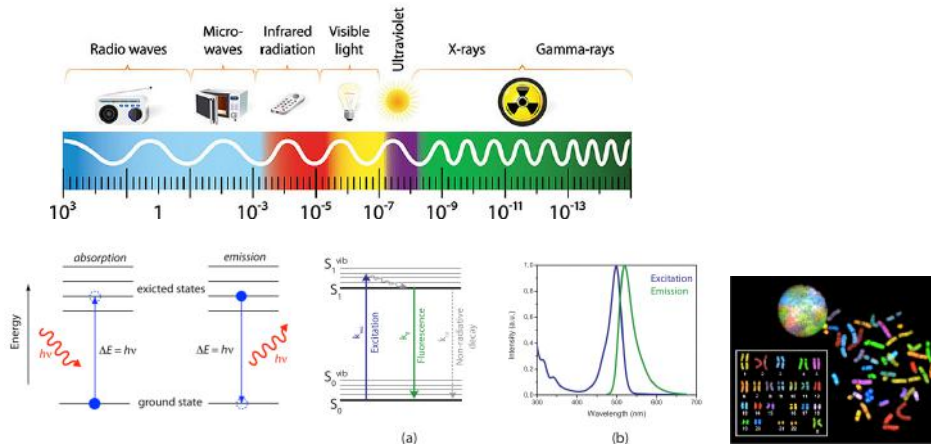
Use fluorescent labels and dyes

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

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 $E = \text{arrow length}$

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Fluorescence spectroscopy/imaging

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Use fluorescent labels and dyes

Flow cytometry, fluorescence *in-situ* hybridization (FISH)

Single-molecule measurements

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

Energy scales

Reaction free energy changes and interaction strengths vs. photon energies

State functions – thermodynamic energies that do not depend on reaction path

(more to come on these)

Measurements & spectroscopies

Energies and wavelengths

e.g., for diffraction, we match photon wavelength to bond length

choose X-rays

Infrared – vibrational transitions →

Useful for chemical identification of functional groups (*e.g.*, -CH₃)

Visible & near UV – electronic transitions (not generally used for chemical ID)

X-ray – core level electronic excitations →

Useful for identifying elements, Li and beyond

Touchstones:

N₂ 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×

Recap of Lecture #4: Ideal & Non-Ideal Gases

Real atoms and molecules interact

Know energy ranges of intramolecular and intermolecular interactions

Boiling point gives a crude measure of intermolecular (or interatomic) interaction strength

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

State Functions

For equilibrium

Only dependent on state, not on how the material got there

G, H, S

Mass Spectrometry – chemical identification

Make or evaporate ions

Measure parent mass as well as the masses of fragments (daughter masses)

Can fragment multiple times to determine connectivities (*e.g.*, functionalization of proteins)

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

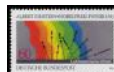
Plasma – high energy, ionized gas

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



Recap: Intermolecular & Intramolecular Forces I

All based on Coulomb's Law (interacting charges)

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

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Recap: Intermolecular & Intramolecular Forces II

All based on Coulomb's Law (interacting charges)

Force	Model	Energy (kJ/mol)	Example
Ion-dipole		40–600	$\text{Na}^+ \cdots \text{O} \begin{array}{l} \text{H} \\ \text{H} \end{array}$
H bond		10–40	$\begin{array}{c} \text{:}\ddot{\text{O}}\text{---H} \\ \\ \text{H} \end{array} \cdots \begin{array}{c} \text{:}\ddot{\text{O}}\text{---H} \\ \\ \text{H} \end{array}$
Dipole-dipole		5–25	$\text{I---Cl} \cdots \text{I---Cl}$
Ion-induced dipole		3–15	$\text{Fe}^{2+} \cdots \text{O}_2$
Dipole-induced dipole		2–10	$\text{H---Cl} \cdots \text{Cl---Cl}$
Dispersion (London)		0.05–40	$\text{F---F} \cdots \text{F---F}$

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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.

Recap of Lecture #6 & 6.5: Interactions

Interactions and Interaction Strengths

Stronger Interactions

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 2³⁰ and Friday afternoon 1³⁰ – *NOT* Thursday and Tuesday

Recap of Lecture #6 & 6.5, 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.

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

$$\text{p}K_a + \text{p}K_b = 14 = \text{pH} + \text{pOH}$$

Solvation shells

Solvent orients around central ion

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 ΔH and ΔS and can predict spontaneity:

Free Energy:

$$\Delta G = \Delta H - T\Delta S$$

T is absolute temperature (in K)

ΔG is the Gibbs free energy

ΔG is state function

ΔG 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

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

$S=0$ at 0 K

Effect of Temperature on Spontaneity

$$\Delta G = \Delta H - T\Delta S$$

ΔH and ΔS do not change substantially with temperature, but ΔG does

ΔH	ΔS	ΔG	<i>Spontaneous?</i>
-	+	-	At all temperatures
-	-	- +	At low temp Not at high temp
+	+	- +	At high temp Not at low temp
+	-	+	Never

Compare potential energy and free energy

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.

Recap of Lecture #12: Electrochemistry

Oxidation State Rules

(+ exceptions, *e.g.*, peroxides, superoxides)

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

$$E_{1/2}^{\circ}(\text{oxid}) = -E_{1/2}^{\circ}(\text{reduc})$$

Standard half-cell is a hydrogen electrode:



$$E_{1/2}^{\circ}(\text{oxid}) = E_{1/2}^{\circ}(\text{reduc}) = 0 \text{ V}$$

$$\Delta G = -nFE$$

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

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^-

UCLA Physical Sciences
UCLA Chemistry & Biochemistry

PHYSICAL CHEMISTRY SEMINAR



Prof. Shelley A. Claridge
Department of Chemistry and
Weldon School of Biomedical Engineering
Purdue University

Monday, Feb. 3, 2020
4:00 PM
2033 Young Hall

"Standing, Lying, and Sitting: Phospholipid
Striped Phases for nm-Resolution
Patterning of Interfaces"

Early polling:

Exam average = 8*

Range = ~7*~10*

Standard Potential for an Electrochemical Cell

The *standard potential* for an electrochemical cell is the potential (voltage) generated when reactants and products of a redox reaction are in their standard states.

Standard States:

T = 25 °C

Gases, p = 1 atm

[Solutions] = 1 M

Half-Cell Potential

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:

$$E_{\text{cell}}^{\circ} = E_{\frac{1}{2}}^{\circ}(\text{oxid}) + E_{\frac{1}{2}}^{\circ}(\text{reduc})$$

2. For any half-reaction:

$$E_{\frac{1}{2}}^{\circ}(\text{oxid}) = -E_{\frac{1}{2}}^{\circ}(\text{reduc})$$

3. Standard half-cell is a hydrogen electrode:



$$E_{\frac{1}{2}}^{\circ}(\text{oxid}) = E_{\frac{1}{2}}^{\circ}(\text{reduc}) = 0 \text{ V}$$

Relationship between ΔG and E

$$\Delta G = -nFE$$

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

n = number of electrons transferred in a balanced redox reaction

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

$$1 \text{ coulomb} = 1 \text{ Amp-sec}$$

$$1 \text{ J} = 1 \text{ Amp-sec-V} = 1 \text{ coulomb-V}$$

$$1 F = 96,500 \text{ J/V-mole } e^-$$

The cell potential does not change with more reaction (moles), the free energy does - n

ΔG and E, cont.

$$\Delta G^\circ = -2.303 RT \log K_{eq}$$

$$\Delta G^\circ = -nFE^\circ$$

$$E^\circ = \frac{2.303RT \log K_{eq}}{nF}$$

$$R = 8.314 \text{ J/K-mole}$$

$$F = 96,500 \text{ J/V-mole } e^-$$

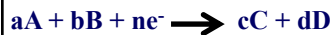
At 25 °C = 298 K:

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

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

Effect of Concentration

Half Reactions



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

Cell Reactions



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

Recap of Lecture #13: Thermodynamics & Electrochemistry

$\Delta G = -nFE$ 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^-

$$\Delta G^\circ = -2.303 RT \log_{10} K_{\text{eq}}$$

$$E^\circ = \frac{0.059}{n} \log_{10} K_{\text{eq}}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants})$$

For elements, $\Delta G_f^\circ = 0$

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

$$\Delta G > 0, K_{\text{eq}} < 1, E_{\text{cell}} < 0$$

INORGANIC CHEMISTRY SEMINAR



Professor Katherine Mirica
Dartmouth College, Department of Chemistry
Molecular Engineering of Materials for
Chemical Sensing and Microelectronics

Wednesday, February 16, 2011 8:30 a.m.
3000 Hall 301
www.semester.dartmouth.edu/ics
DCLA Chemistry Department

Exam average = 92.5

Range = ~76-103

Wow!

Effect of Concentration on ΔG

Half Reactions



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

Cell Reactions



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

Looks like equilibrium constant,
but does *not* have
to be at equilibrium
Q in your book (and *all*
freshman chemistry books)

Recap of Lecture #14: 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 ΔG 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, HNO₃, HClO₄, H₂SO₄

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:

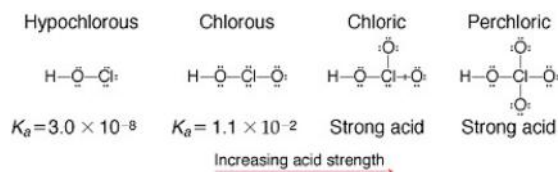
Rank by K_b – the highest K_b is the strongest base

The lowest K_a for the conjugate acid is the strongest base

Oxyacids

The (labile) proton is attached to oxygen

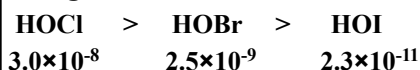
The higher the oxidation state of the central atom, the stronger the acid



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{p}K_a = -\log_{10} K_a$$

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



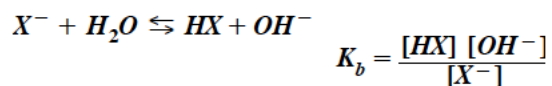
$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

$$\text{p}K_b = -\log_{10} K_b$$

Chemistry: The Central Science

Equilibria in Acid/Base Dissociation

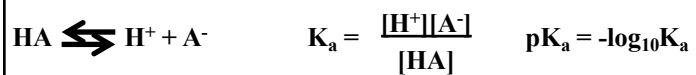
ACIDS AND BASES



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

Buffers

Both acid and conjugate base are present



$$pH = pK_a - \log_{10} \frac{[HA]}{[A^-]}$$

So, pH should be within ~1 unit of pK_a

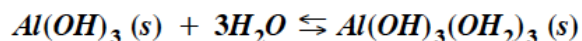
The more of the acid and base present, the greater the capacity of the buffer

Amphoterism

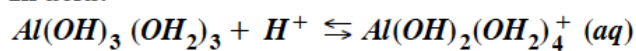
Amphoterism is the ability of a molecule to act both as an acid and as a base.

This results in metal hydroxides which are soluble in both acids and bases.

Hydration: $Al^{3+}(aq) \equiv Al(H_2O)_6^{3+}$

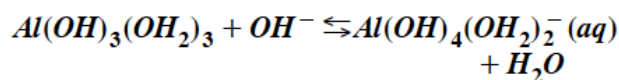


In acid:



Solubility increases

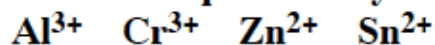
In base:



Solubility increases

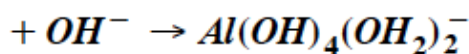
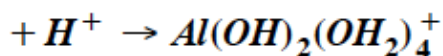
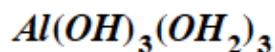
Amphoteric Metal Hydroxides

There are amphoteric hydroxides of:



many transition metal ions

These involve formation of complex ions, such as:



Recap of Lecture #17: Peroxides, Superoxides, Acid/Base Equilibria

Peroxide: O_2^{2-} Superoxide: O_2^-

Disproportionation reactions

Acids and bases

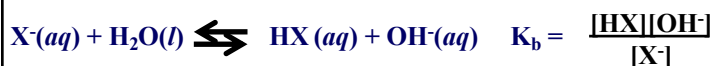
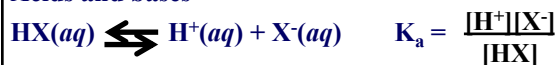


Table of initial and equilibrium conditions

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

$$pH + pOH = pK_a + pK_b = 14 \quad K_w = 10^{-14} = [H^+][OH^-] = K_a K_b$$

Recap of: Solubility, Simultaneous Equilibria

Acid-Base Equilibria

Amphoterism

e.g., $Al(OH)_3(H_2O)_3$ is more soluble (as an ion) in acid or base than in neutral solution - $Al(OH)_3(H_2O)_3$ vs $[Al(OH)_2(H_2O)_4]^+$ or $[Al(OH)_4(H_2O)_2]^-$

Buffers

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

$$pH = pK_a - \log_{10} \frac{[HA]}{[A^-]}$$

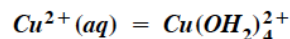
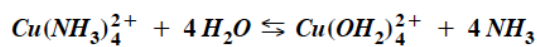
Solubility product



In solving equilibria, keep track of stoichiometry

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

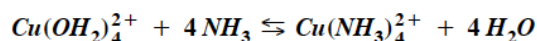
Metal Complex Stability



$$K = \frac{[\text{Cu}(\text{OH}_2)_4^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}][\text{H}_2\text{O}]^4}$$

↖ = constant

Dissociation constant $K_D = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]} = 2 \times 10^{-13}$



Formation constant $K_F = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 5 \times 10^{12}$

$$K_D = \frac{1}{K_F}$$

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 (Δ) to the spin pairing energy (P)

Spectrochemical series – relative ligand effect on Δ

Paramagnetic – having one or more unpaired spins

Colors

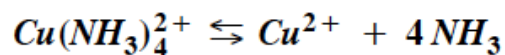
Complementary colors – if a color is absorbed, the absorbing material will appear as the complementary color

Red-green, orange-blue, yellow-violet

Other means of color: emission, interference

Metal Ion Buffer

Can supply metal ions from “reservoir” of complex:



$$[\text{Cu}^{2+}] = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{K_F [\text{NH}_3]^4}$$

$$[\text{Cu}(\text{NH}_3)_4^{2+}] = 1 \text{ M}$$

$$[\text{NH}_3] = 1 \text{ M}$$

then: $[\text{Cu}^{2+}] = 3 \times 10^{-13} \text{ M}$

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? $K_F = 1.1 \times 10^{13}$



Chelation

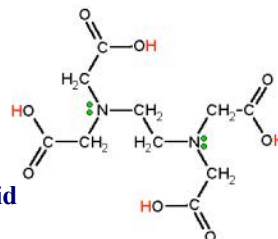
More than one Lewis base site in a molecule

Entropically favored over comparable monodentate ligands



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

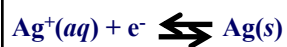
EDTA = ethylenediaminetetraacetic acid



Thermodynamics and equilibria

Measure thermodynamics (and equilibria) electrochemically
e.g., by comparing complex ions to aqueous ions.

Measuring Stability Metal Ion Complexes



$$E_{1/2}^\circ = +0.80 \text{ V}$$



CN^- is *not* a chelate because it is monodentate

Transition Metal Ions, Review

Transition metal ions are Lewis acids \Rightarrow
they accept electron pairs

Ligands are Lewis bases \Rightarrow
molecules or ions which donate electron pairs

Ligands bonded to metal ions \Rightarrow
metal complexes or coordination compounds

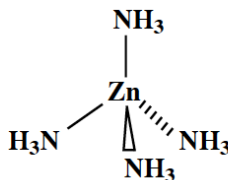
Coordination number: number of electron donor atoms attached to the metal

Chelates are ligands possessing two or more donor atoms

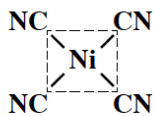
Tetrahedral and Square Planar Coordination Compounds

Coordination # = 4

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

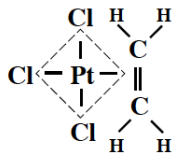


Square Planar, *e.g.*, $[\text{Ni}(\text{CN})_4]^{2-}$



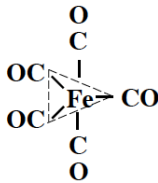
More Coordination Compounds

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



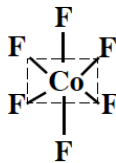
Coordination # = 5

Trigonal Bipyramidal, *e.g.*, $[\text{Fe}(\text{CO})_5]$

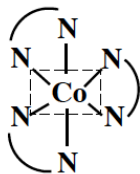


Octahedral Coordination Compounds

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



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



Chelate Reminder

More than one Lewis base site in a molecule

Entropically favored over comparable monodentate ligands



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



$$\Delta G^\circ = -37.2 \text{ kJ/mol}, \Delta H^\circ = -57.3 \text{ kJ/mol}$$

$$\Delta S^\circ = -67.3 \text{ J/mol-K}$$



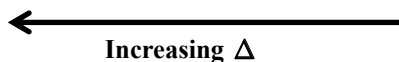
$$\Delta G^\circ = -60.7 \text{ kJ/mol}, \Delta H^\circ = -56.5 \text{ kJ/mol}$$

$$\Delta S^\circ = +14.1 \text{ J/mol-K}$$

Coordination Compounds

Δ – the crystal field splitting

Spectrochemical Series:



Δ depends upon:

1. Metal
2. Oxidation state
3. Ligands

P – Spin pairing energy.

P does not depend upon the ligands.

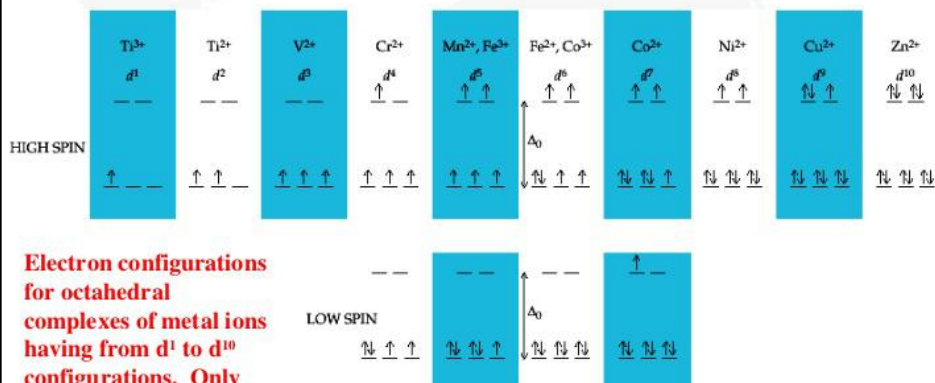
$P < \Delta \Rightarrow$ Low spin complexes.

$P > \Delta \Rightarrow$ High spin complexes.

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

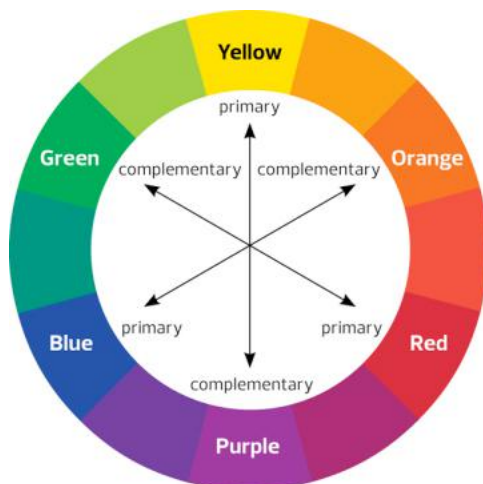
Electron Configuration for Octahedral complexes of metal ion having d^1 to d^{10} configuration $[M(H_2O)_6]^{+n}$.

Only the d^4 through d^7 cases have both high-spin and low spin configuration.



<https://www.slideshare.net/surya287/crystal-field-theory>

Color Wheel: Complementary Colors



Color: A Photographer's Guide to Directing the Eye, Creating Visual Depth, and Conveying Emotion

Color Absorption of Co^{3+} Complexes

The Colors of Some Complexes of the Co^{3+} Ion

Complex Ion	Wavelength of light absorbed	Color of Light Absorbed	Color of Complex
$[\text{CoF}_6]^{3+}$	700 (nm)	Red	Green
$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3+}$	600, 420	Yellow, violet	Dark green
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	600, 400	Yellow, violet	Blue-green
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475, 340	Blue, violet	Yellow-orange
$[\text{Co}(\text{en})_3]^{3+}$	470, 340	Blue, ultraviolet	Yellow-orange
$[\text{Co}(\text{CN})_6]^{3+}$	310	Ultraviolet	Pale Yellow

The complex with fluoride ion, $[\text{CoF}_6]^{3+}$, 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>

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.

Semiconductor and insulators become *more* conductive with increasing T
Increasing thermal population of carriers

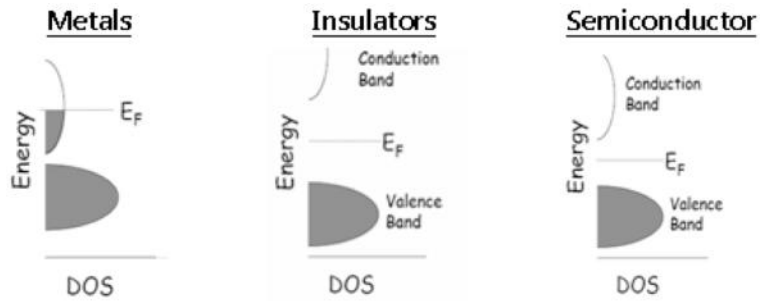
Metals become *less* conductive with increasing T
Increasing scattering of electrons by moving lattice

Metals: heat carried by electrons

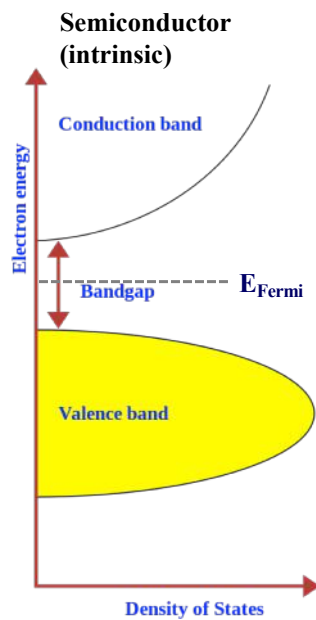
Semiconductors & insulators: heat carried by vibrations

Back to energy level diagrams!

Energy and Excitations in Solids



Semiconductor Electronic Structure



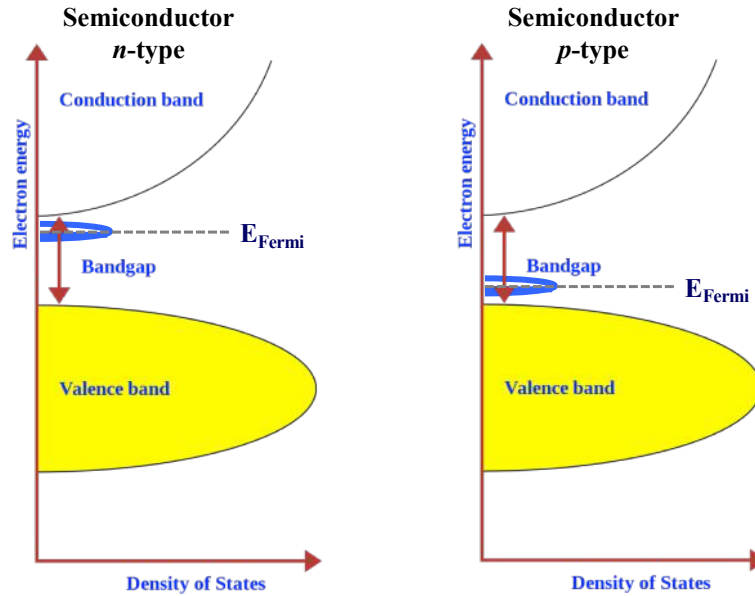
Raising temperature increases conductivity (*i.e.*, decreases resistivity), because carriers are thermally excited

With impurities, semiconductors have shifted Fermi energies, from/to which carriers can be thermally excited

wikipedia.com

Doping in Semiconductors

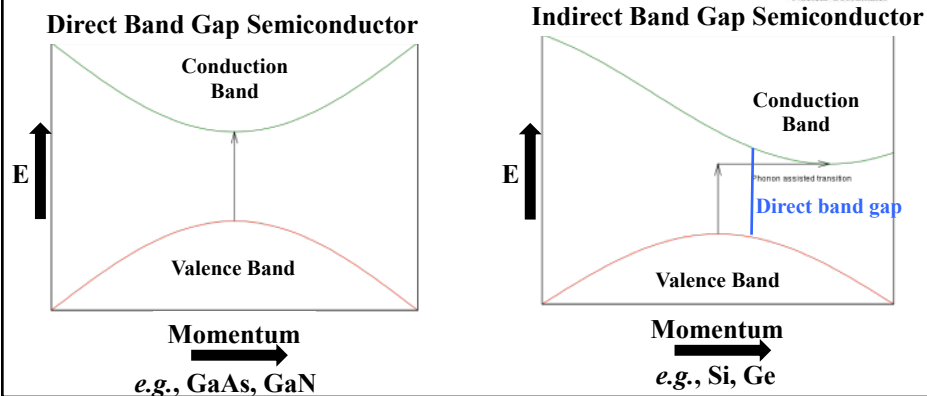
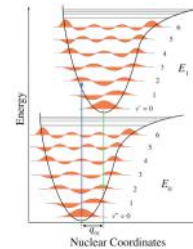
Thermally excite carriers from/to dopant level in the band gap



Direct vs Indirect Band Gap Semiconductors

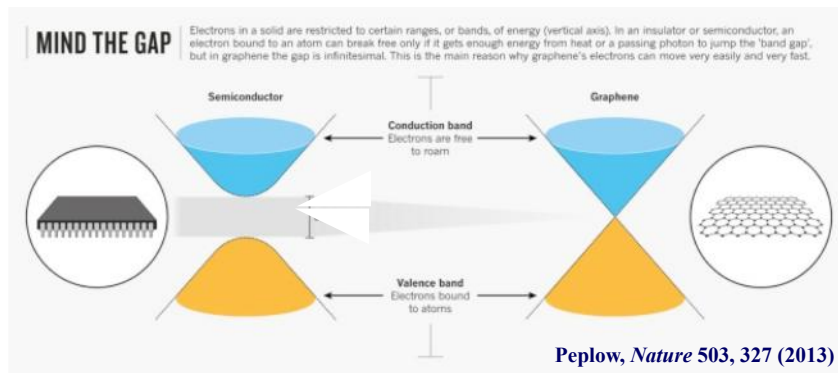
Energy and momentum are conserved in photoexcitation
Photons carry little momentum

Direct band gap semiconductors absorb and emit light more efficiently than indirect band gap semiconductors



Semimetals

Semimetals have no band gap, but no states at the Fermi energy
e.g., graphite, graphene



Millie
Dresselhaus
MIT



Kostya
Novoselov
Manchester

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 T , 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

Dopants in semiconductors

Elemental identity determines energy of dopant level

which then determines *p*- or *n*-type

Energy of dopant level *and* concentration determine conductivity of material

more dopant atoms \rightarrow higher conductivity

Do *not* form a “band” – serve as a source or sink for thermally excited electrons

Conductivity increases with increasing T , because of thermal excitation of carriers

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

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

Amphoterism

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

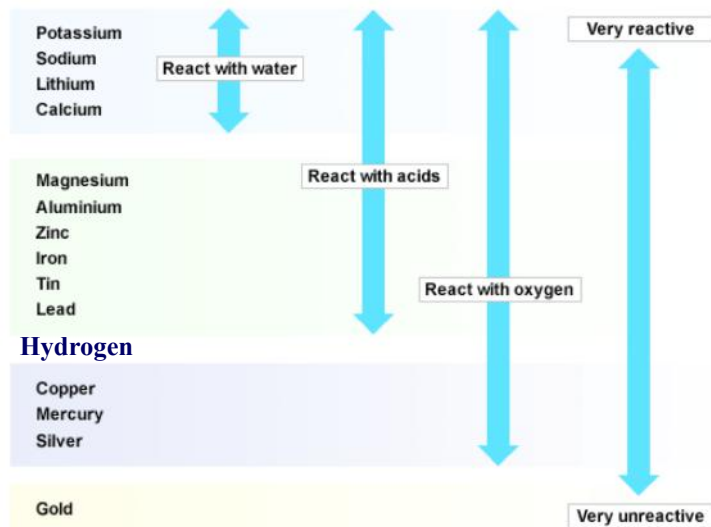
Quantitate reactions

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

Activity Series



bbc.co.uk

Half-Cell Potential

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:

$$E_{\text{cell}}^{\circ} = E_{\frac{1}{2}}^{\circ}(\text{oxid}) + E_{\frac{1}{2}}^{\circ}(\text{reduc})$$

2. For any half-reaction:

$$E_{\frac{1}{2}}^{\circ}(\text{oxid}) = -E_{\frac{1}{2}}^{\circ}(\text{reduc})$$

3. Standard half-cell is a hydrogen electrode:



$$E_{\frac{1}{2}}^{\circ}(\text{oxid}) = E_{\frac{1}{2}}^{\circ}(\text{reduc}) = 0 \text{ V}$$

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))

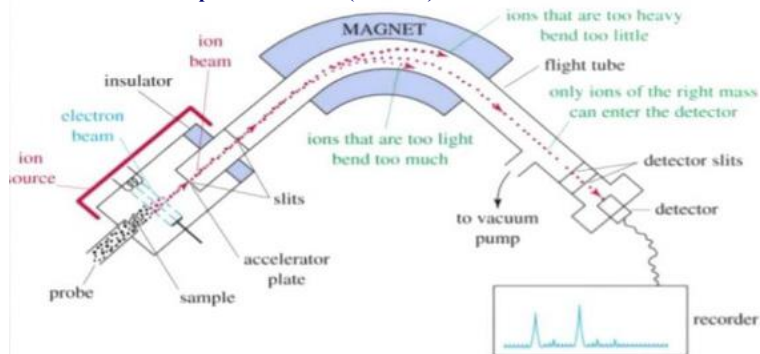
2002 Nobel Chemistry Prize



¹John Fenn
Yale > VCU



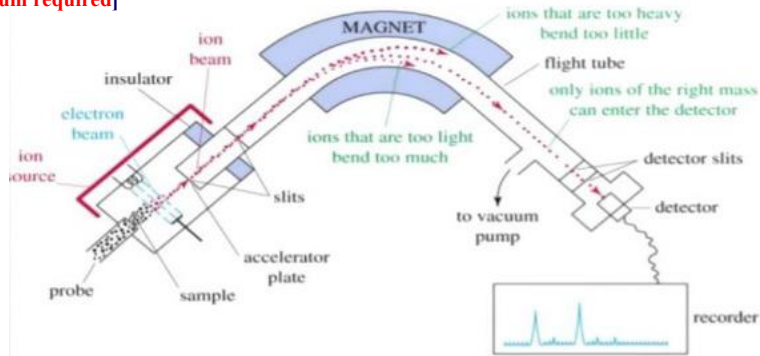
²Koichi Tanaka
Shimadzu



<https://www.slideshare.net/ssuser3375a9>

Mass Spectrometry

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



<https://www.slideshare.net/ssuser3375a9>

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

$$S=0 \text{ at } 0 \text{ K}$$

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 ΔH and ΔS and can predict spontaneity:

Free Energy:

$$\Delta G = \Delta H - T\Delta S$$

T is absolute temperature (in K)

ΔG is the Gibbs free energy

ΔG is state function

ΔG 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

ΔH and ΔS vary little with temperature. ΔG *does* vary with T \rightarrow effect of ΔS

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

$$\Delta G > 0, K_{eq} < 1, E_{cell} < 0$$

Thermodynamics & Electrochemistry

$$\Delta G = -nFE \text{ and for standard states: } \Delta G^\circ = -nFE^\circ$$

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, $\Delta G_f^\circ = 0$

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 ΔG 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

Peroxides and Superoxides

Peroxide: O_2^{2-} Superoxide: O_2^-

$2\text{H}_2\text{O}_2(l, aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$ bottles have vented caps

Autooxidation and disproportionation

In self-contained breathing apparatus:

Peroxide

$2\text{Na}_2\text{O}_2(s) + 2\text{CO}_2(g) \longrightarrow 2\text{Na}_2\text{CO}_3(s) + \text{O}_2(g)$

Superoxide

$4\text{KO}_2(s) + 2\text{H}_2\text{O}(g) \longrightarrow 3\text{O}_2(g) + 4\text{KOH}(s)$

$\text{KOH}(s) + \text{CO}_2(g) \longrightarrow \text{KHCO}_3(s)$

Acid/Base Equilibria

Acids and bases

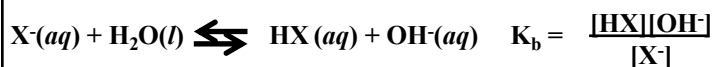
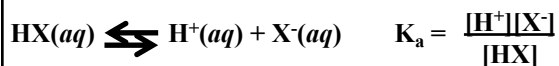


Table of initial and equilibrium conditions

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%)

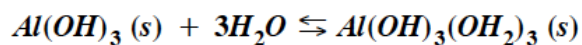
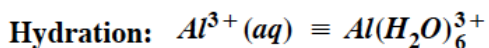
Fractional dissociation and dilution

$$\text{pH} + \text{pOH} = \text{p}K_a + \text{p}K_b = 14 \quad K_w = 10^{-14} = [\text{H}^+][\text{OH}^-] = K_a K_b$$

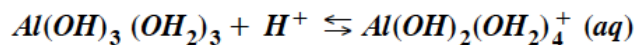
Amphoterism

Amphoterism 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.

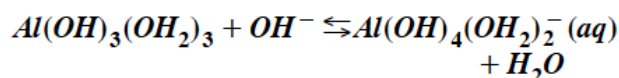


In acid:



Solubility increases

In base:



Solubility increases

Polyprotic Acid Equilibria

Polyprotic acid: >1 acidic proton

For 0.1 M H₂S, what are the concentrations of H₂S, H⁺, HS⁻, and S²⁻?

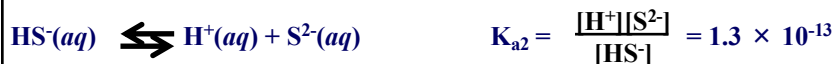


Table 1:	H ₂ S	H ⁺	HS ⁻	
Init	0.1	(10 ⁻⁷) ~ 0	0	
Final	0.1-x	x	x	$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{x^2}{0.1-x} \sim \frac{x^2}{0.1}$

Table 2:	HS ⁻	H ⁺	S ²⁻	
Init	x	x	0	
Final	x-y~x	x+y~x	y	$K_{a2} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{(x+y)y}{x-y} \sim y$

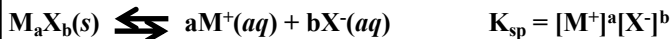
Buffers, Solubility, & Simultaneous Equilibria

Buffers

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

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

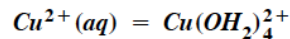
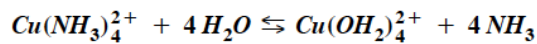
Solubility product



In solving equilibria, keep track of stoichiometry

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

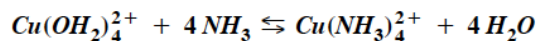
Metal Complex Stability



$$K = \frac{[\text{Cu}(\text{OH}_2)_4^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}][\text{H}_2\text{O}]^4}$$

↙ = constant

Dissociation constant $K_D = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]} = 2 \times 10^{-13}$



Formation constant $K_F = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 5 \times 10^{12}$

$$K_D = \frac{1}{K_F}$$

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 (Δ) to the spin pairing energy (P)

Spectrochemical series – relative ligand effect on Δ

Paramagnetic – having one or more unpaired spins

Colors

Complementary colors – if a color is absorbed, the absorbing material will appear as the complementary color

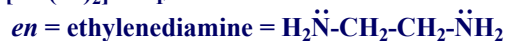
Red-green, orange-blue, yellow-violet

Other means of color: emission, interference

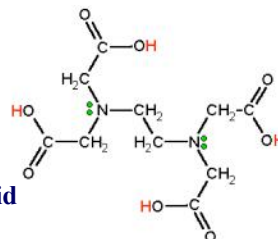
Chelation

More than one Lewis base site in a molecule

Entropically favored over comparable monodentate ligands



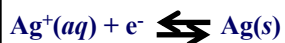
EDTA = ethylenediaminetetraacetic acid



Thermodynamics and equilibria

Measure thermodynamics (and equilibria) electrochemically
e.g., by comparing complex ions to aqueous ions.

Measuring Stability Metal Ion Complexes



$$E_{1/2}^\circ = +0.80 \text{ V}$$



CN^- is *not* a chelate because it is monodentate

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.

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

Semi-metals

No gap, but 0 density of states at the Fermi level

Kinetics

Rate laws

Reaction order

First-order reactions

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 equilibria

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 equilibria

Enzymes are biological catalysts with greater specificity and control than synthetic catalysts

Posters

What did we learn from posters? **Lots!**

1D Materials – carbon nanotube growth

2D Materials – black phosphorus, graphene

Batteries (Zn-air)

Catalysis & green chemistry including catalytic converters

Electronic nose (lung cancer detection)

Indirect detection of neutrinos

Mechanical transmission in electric cars

Metal-organic frameworks (MOFs) for CO₂ capture and catalysis

Molecular dynamics simulations (macromolecules)

Neurodegenerative disease detection (synucleinopathies)

Nuclear reactors (Th/fluorides)

Optigenetics for neuroscience

Protein structure

Paramagnetic tags for nmr

Raman detection in porous materials

Redox flow electrochemical cells

Solar cells (perovskites, black phosphorus)

Supercapacitors

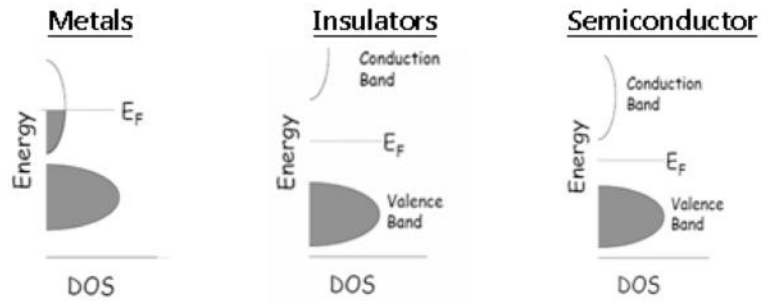
Triboelectric energy harvesters (wearables, blue energy)

Two-photon microscopy

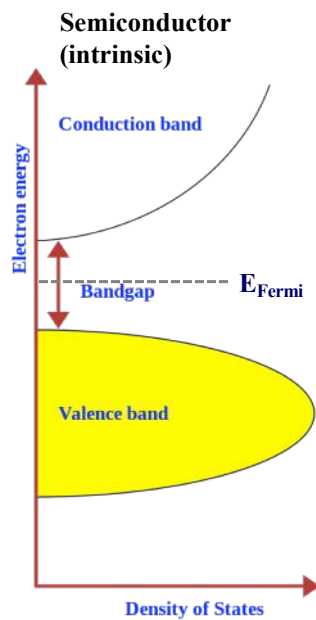
Viruses – capsid assembly, coronavirus

Wound-healing hydrogels

Energy and Excitations in Solids



Semiconductor Electronic Structure



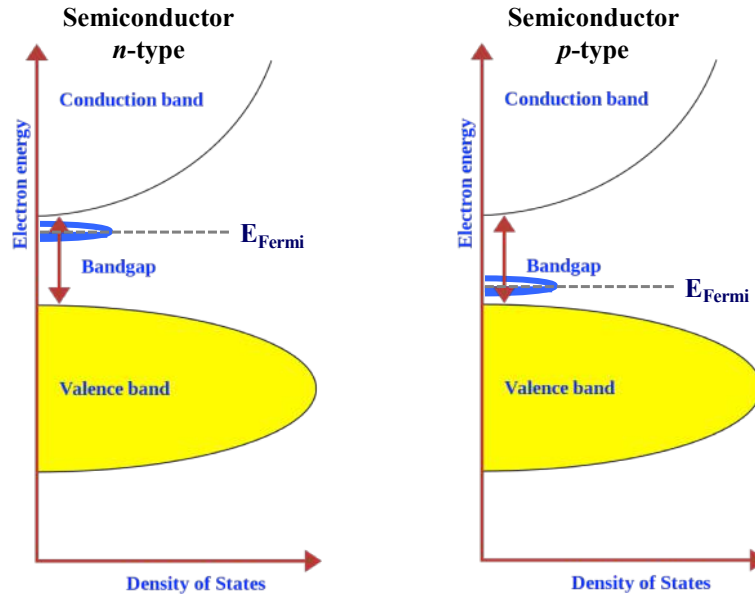
Raising temperature increases conductivity (*i.e.*, decreases resistivity), because carriers are thermally excited

With impurities, semiconductors have shifted Fermi energies, from/to which carriers can be thermally excited

wikipedia.com

Doping in Semiconductors

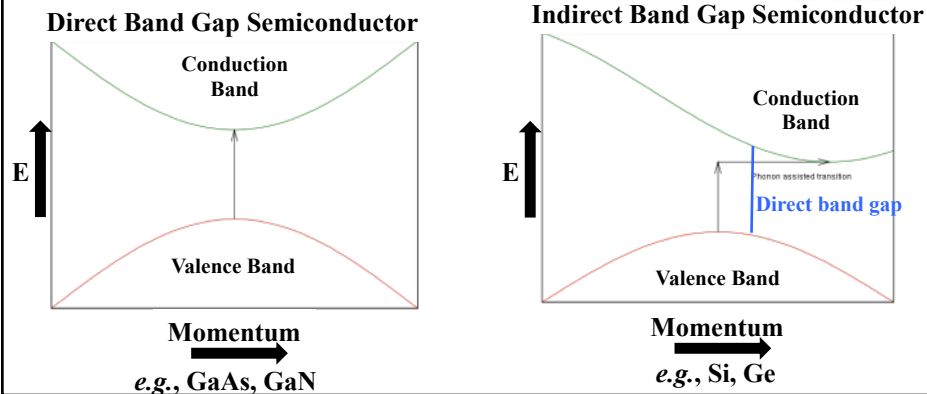
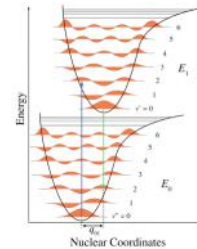
Thermally excite carriers from/to dopant level in the band gap



Direct vs Indirect Band Gap Semiconductors

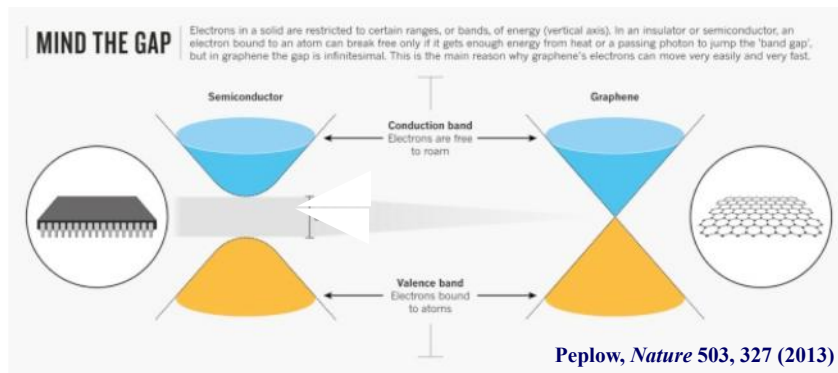
Energy and momentum are conserved in photoexcitation
Photons carry little momentum

Direct band gap semiconductors absorb and emit light more efficiently than indirect band gap semiconductors



Semimetals

Semimetals have no band gap, but no states at the Fermi energy
e.g., graphite, graphene



Millie
Dresselhaus
MIT



Kostya
Novoselov
Manchester

Energy and Excitations in Solids

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Conductivity *decreases* with increasing T , because of electron scattering

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Differentiate with magnetic field (Hall effect)

Energies of (dopant) states in the band gap determine conductivity and whether
 electrons or holes dominate current

Dopants in semiconductors

Elemental identity determines energy of dopant level

which then determines *p*- or *n*-type

Energy of dopant level *and* concentration determine conductivity of material

more dopant atoms \rightarrow higher conductivity

Do *not* form a “band” – serve as a source or sink for thermally excited electrons

Conductivity increases with increasing T , because of thermal excitation of carriers

Recap of Crystal Field Theory & Inorganic Complexes

Transition metal ions are Lewis acids \Rightarrow they accept electron pairs

Ligands are Lewis bases \Rightarrow molecules or ions which donate electron pairs

Ligands bonded to metal ions \Rightarrow metal complexes or coordination compounds

Coordination number: number of electron donor atoms attached to the metal
Determines symmetry, splitting arrangement

Metal, oxidation state, ligands (spectrochemical series) determine splittings

High spin / low spin - compare Δ to P

$P < \Delta \Rightarrow$ Low spin complexes

$P > \Delta \Rightarrow$ High spin complexes

Color wheel & other sources of color

Chelates - entropy effects

Recap of Energy and Excitations in Solids

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Conductivity increases with increasing T, because of thermal excitation of carriers

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

Half-Life: First-Order Reactions Only

$$\frac{dA}{dt} = -k[A] \rightarrow$$

$$A = A_0 e^{-kt}$$

$$\ln[A] = \ln[A]_0 - kt$$

What is t when:

$$[A] = 0.5 [A]_0$$

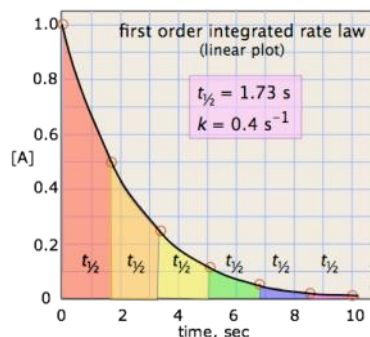
$$\ln(0.5 [A]_0) = \ln[A]_0 - kt_{1/2}$$

$$kt_{1/2} = \ln[A]_0 - \ln[A]_0 - \ln 0.5 = -\ln 0.5$$

$$t_{1/2} = (\ln 2)/k = 0.693/k$$

Note that the half-life is independent of $[A]_0$

This is the same half-life as in radioactivity



chemwiki.ucdavis.edu

Reaction Rates

Express Rate in terms of *RATE LAW*

Rate Constant

Reaction Order

Dependence on Concentration

Dependence on Time

Dependence on Temperature

Activation Energy



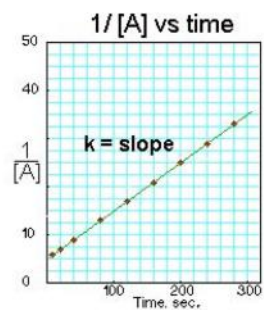
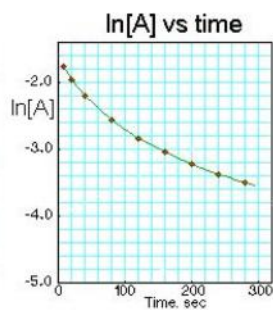
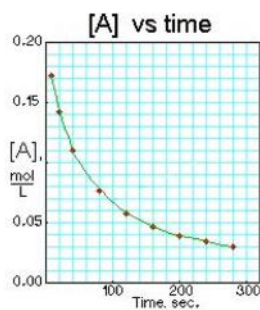
Rudy Marcus at Caltech

Second-Order Reactions



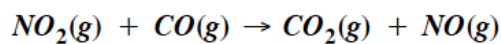
$$\text{Rate} = k[\text{NO}_2]^2$$

$$\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}$$



chem.purdue.edu

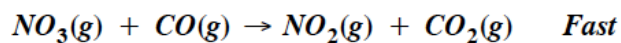
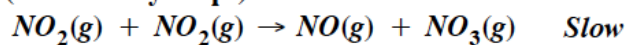
Rate-Limiting Step



$$\text{Rate} = k[\text{NO}_2]^2$$

Mechanism:

(Elementary Steps)



Slow step determines rate
"Bottleneck"

$$\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}$$

Catalysis

Catalytic Converters – catalyze multiple reactions

Oxidation



Reduction



Catalysts

CuO, Cr₂O₃, Pt, Rh

Enzymes

Enzymes are biological *catalysts*

Enzymes are produced by organisms to *accelerate* and to *control* reaction rates

Enzymes are typically large protein molecules or combinations of proteins with other molecules

The region where the substrate/s (reactant/s) bind is called the *active site*

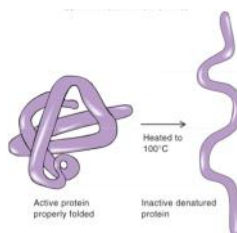
Enzymes differ from man-made catalysts:

More efficient

More specific

Rate can be controlled by changing enzyme activity

Enzymes can be denatured



Recap of Lecture #25: Kinetics

Rate laws – depend on slow elementary steps of reaction

Reaction order – not the same as stoichiometry

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 hydrocarbons, reduces NO_x

Homogeneous catalysis – catalyst in solution of compounds in solution

Heterogeneous catalysis – catalyst is in a different phase (usually solid) than reactants and products (usually gas or solution)

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



Exam 2

74-104

87±10

Enzymes

Metal ions are often bound at the active site and serve as the reaction center of the enzyme

The enzyme *carbonic anhydrase* uses a Zn^{2+} ion at its active site to accelerate the reaction:



In red blood cells, CO_2 is converted to H_2CO_3 which deprotonates to form HCO_3^- . HCO_3^- leaves the cell and serves as a buffer for blood plasma

In the lungs, HCO_3^- is re-protonated to form H_2CO_3 .
Carbonic anhydrase converts H_2CO_3 back to $CO_2(g)$ and H_2O
Exhale!

Control of Enzymes

Some enzymes wait in the “off” state, such as blood-clotting and digestive proteins. They are activated (reacted to make the active form) when needed

The active site depends on the enzyme conformation (shape)

Metal ions are held in place by different sections of the protein sitting in close proximity

If this shape is altered, the active site no longer functions and the enzyme is “turned off”

Molecular shape depends on pH, temperature, and reactions of the enzyme

Another way to inhibit an enzyme is to bind a molecule to its active site, blocking any catalytic activity

Many drugs and poisons work by this mechanism

Drugs

Penicillin (antibiotic) blocks an enzyme that bacteria use to build cell walls

People do not have this enzyme

Bacterial cells only are poisoned

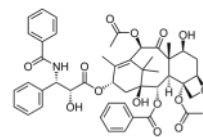
Penicillin is produced by a fungus



Taxol is an anti-cancer drug that blocks enzymes responsible for cell growth, slowing the growth or even shrinking malignant tumors

Caps microtubules and prevents their dynamics

cf. abraxane



Vitamins

Vitamins are non-protein parts of enzymes, called co-enzymes

When combined with the protein part they make enzymes

Enzymes derived from vitamins play critical roles in redox chemistry in the body – the source of heat and energy

Polymerase Chain Reaction

Polymerase is an enzyme that forms a polymer

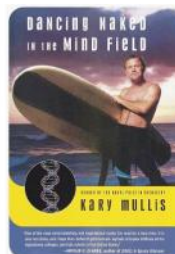
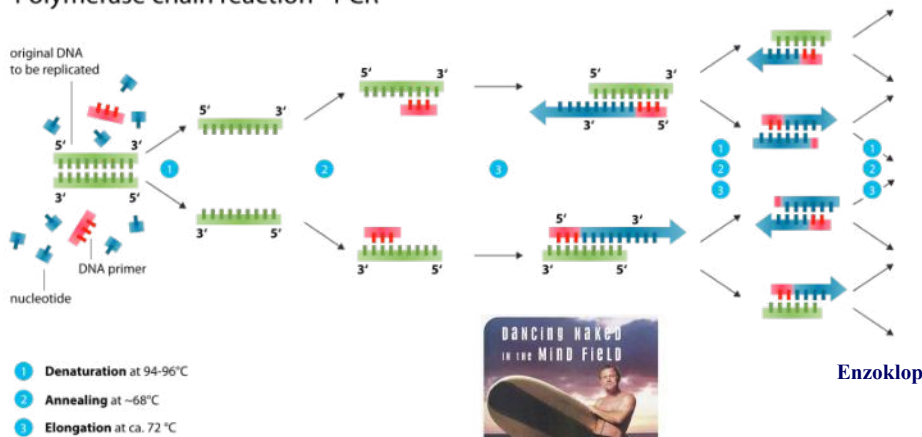
PCR depends on a polymerase that catalyzes the replication of DNA (the polymer) from the nucleotides (the monomers)

- 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.)

Polymerase Chain Reaction

Polymerase chain reaction - PCR



Recap of Lecture #27: Nuclear Chemistry

Balance nuclear reactions using Z and isotope mass

Nuclear Decay – energy scales in MeV

α is a ${}^4\text{He}$ nucleus – not very penetrating

Neutron-rich isotopes undergo β^- decays ($-e$) – more penetrating

Neutron-deficient isotopes undergo positron emission (${}_{+1}\beta^+$) or electron capture

Electron capture (from 1s orbital) is more likely for higher Z elements

Positrons are the anti-particles of electrons and annihilate with them, producing 2 γ rays that go in opposite directions ($\Delta E = \Delta mc^2$ & conservation of momentum)

γ rays are produced when excited nuclei relax (photon emission), no change in Z or mass

Nuclear Stability

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

Transuranium elements undergo a series of α decays

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

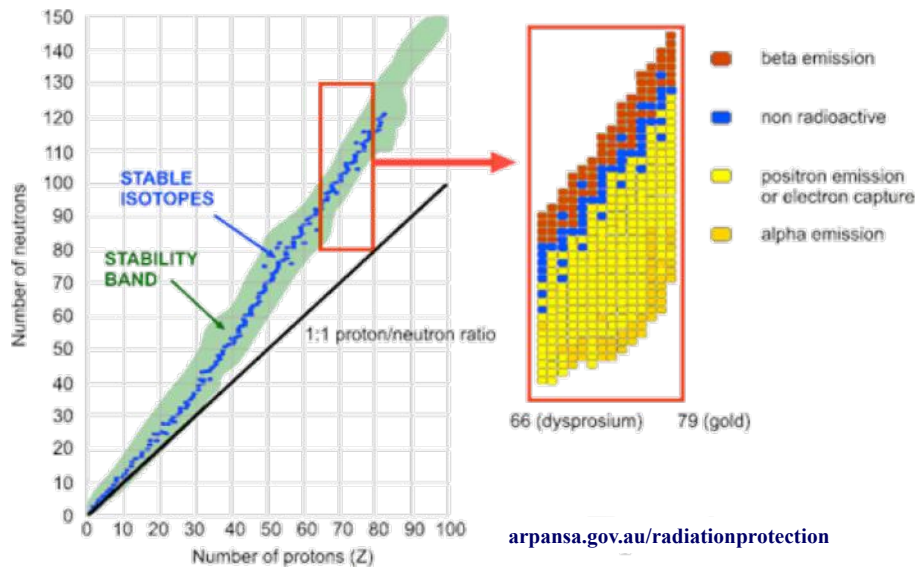
Example – ${}^{14}\text{C}$ decay measures the time since respiration stopped (end of carbon uptake)

${}^{14}\text{C}$ half-life of 5700 years, ${}^{238}\text{U}$ half-life of 4.5×10^9 years

Accessible ages must be on these scales

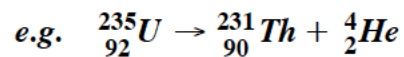
After n half-lives, $(\frac{1}{2})^n$ of original amount remains

Band of Stability for Nuclei

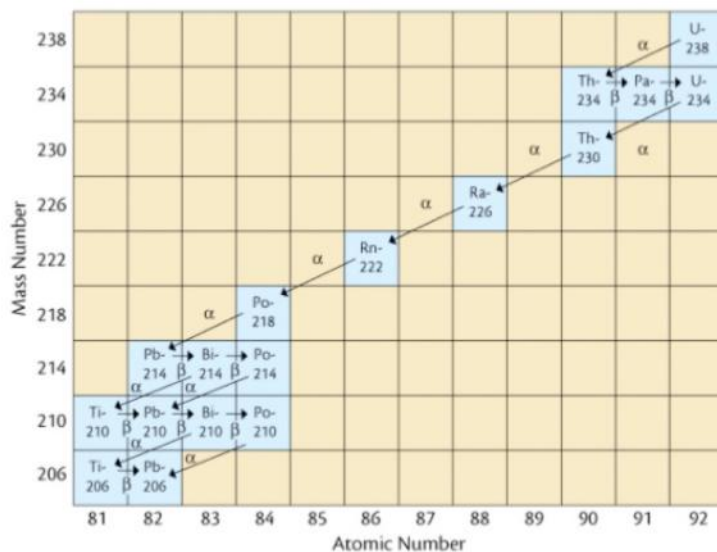


Nuclear Chemistry: Decay towards Stability, cont.

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

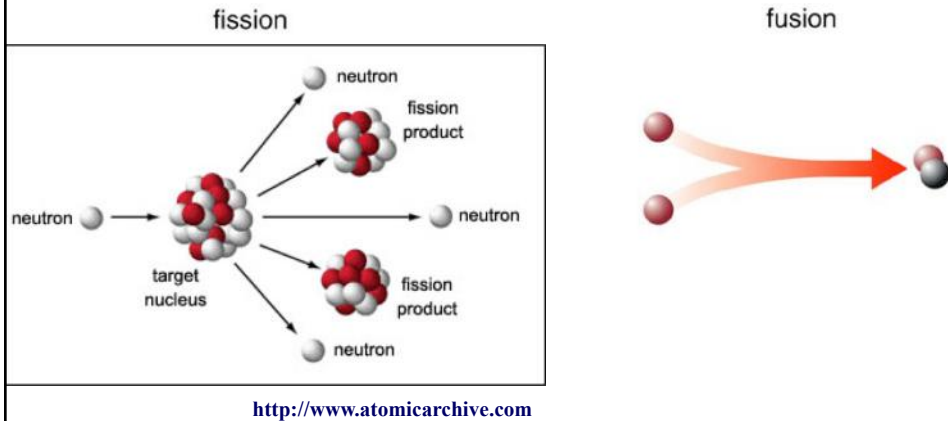


Decay of ${}^{238}\text{U}$



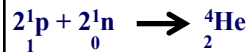
www.david-s.org

Fission vs. Fusion



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Nuclear Binding Energy



$\text{}^1_1\text{p}$ mass is 1.00728 amu

$\text{}^1_0\text{n}$ mass is 1.00867 amu

$\text{}^4_2\text{He}$ mass is 4.00150 amu

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

$E = mc^2$, really $\Delta E = \Delta mc^2$

$E = (5.047 \times 10^{-29} \text{ kg})(3 \times 10^8 \text{ m/sec})^2 = 4.543 \times 10^{-12} \text{ J/}^4_2\text{He}$

Binding E/nucleon = $4.543 \times 10^{-12} \text{ J/}^4_2\text{He} = 1.14 \times 10^{-12} \text{ J}$ for $\text{}^4_2\text{He}$ vs.

$1.41 \times 10^{-12} \text{ J}$ for $\text{}^{56}_{26}\text{Fe}$

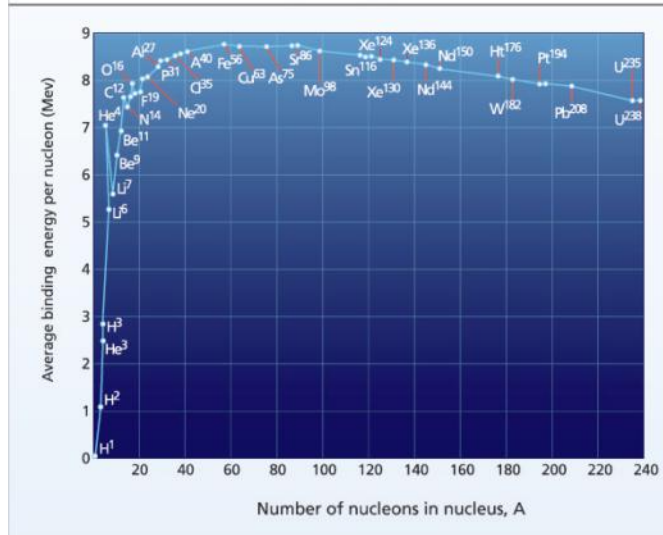
$1.22 \times 10^{-12} \text{ J}$ for $\text{}^{238}_{92}\text{U}$

For mass > ~50-60 amu nuclei: nuclear fission is exothermic

For mass < ~50-60 amu nuclei: nuclear fusion is exothermic

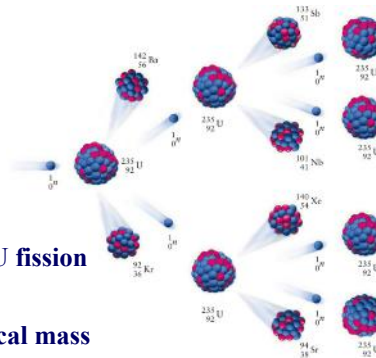
Nuclear Binding Energy

Binding Energy Curve



Sholto Ainslie Design, Wordpress
Data from NASA Goddard

Nuclear Chain Reactions: Fission

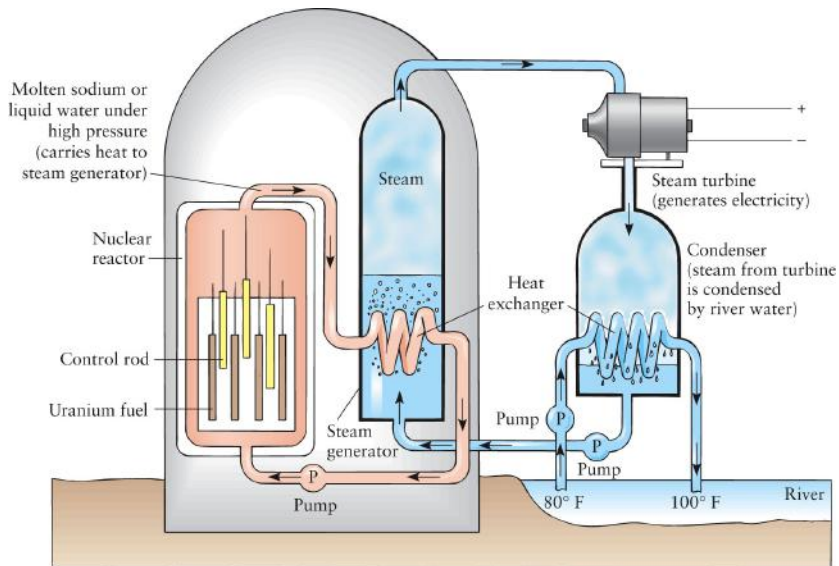


An average of 2.4 neutrons are produced per ${}^{235}\text{U}$ fission

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 ${}^{238}\text{U}$ – 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

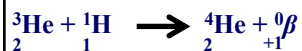
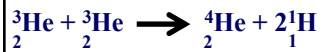
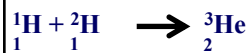
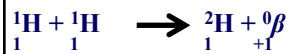
Nuclear Power Reactor



Nuclear Chain Reactions: Fusion

“Chemistry of the stars”

The sun contains 73% H and 26% He



Initiation of these reactions requires temperatures of 4×10^7 K
(not currently obtainable on Earth on a stable basis)

Recap of Lecture #28: Fission and Fusion

Mass Defect

$$\Delta E = \Delta mc^2$$

Energy scales are much higher than chemical energies (*KNOW THEM!*)

Exothermic Nuclear Reactions

Rate stability as mass deficit per nucleon.

Binding energy per nucleon peaks at ^{56}Fe

Lighter elements can undergo **fusion** exothermically

Heavier elements can undergo **fission** exothermically

Nuclear Chain Reactions

More neutrons produced than absorbed

Subcritical mass – not sustained

Critical mass – self-sustaining reaction

Supercritical mass – increasing reaction rate – bomb

Nuclear Reactors

Fission reactors – most common

Heat water to drive steam turbines

Use moderators to determine neutron capture rate and thus reaction rate

Breeder reactors produce more fuel than they consume

Fusion reactors do not exist due to difficulty in sustaining high temperatures required

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 (ΔG), enthalpy (ΔH), entropy (ΔS), 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 equilibria

Reaction Order

Statistical/graphical analysis of kinetics

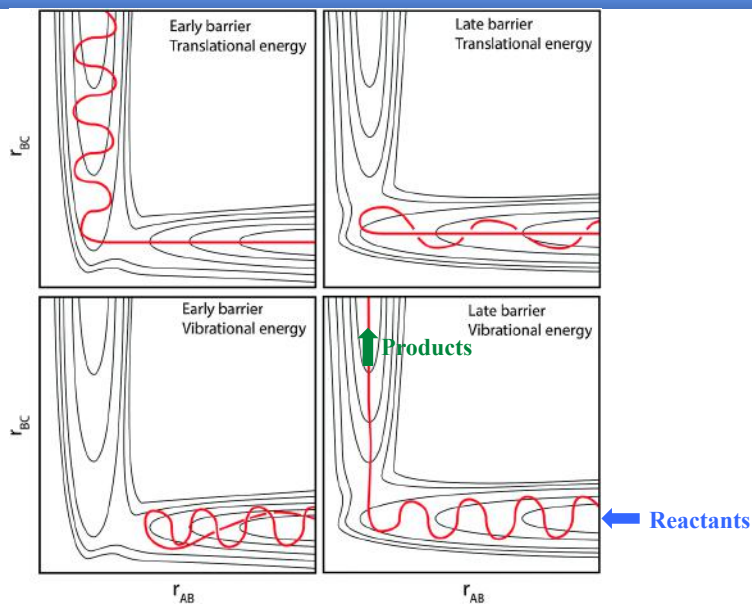
Catalysis

Lower barrier to accelerate reaction equilibration

Recall the mechanism and kinetics do **NOT** affect the thermodynamics (state functions) and equilibria

Enzymes are biological catalysts with greater specificity and control than synthetic catalysts

More on Reaction Coordinates



Chadwick & Beck, *Chem Soc Rev* **45**, 3576 (2016)

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

^{14}C half-life of 5700 years, ^{238}U half-life of 4.5×10^9 years

Accessible ages must be on these scales

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

Nuclear Energy

Mass defect, $\Delta E = \Delta mc^2$ – binding energy per nucleon peaks at ^{56}Fe

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

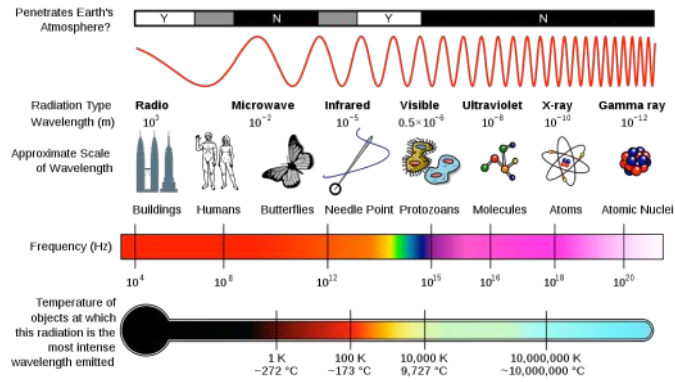
X-ray diffraction – spacings in and between molecules

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)



NASA, via *Earth & Sky*