Isoelectric, Lewis Dot

Wednesday, January 03, 2007
9:03 AM

Reading for this week Ch. 10 (10.1 - 10.7), 10.8 - 10.9
Prof. Ken Spears
Wed 1400 - 1600 TA hours Nano building.
Every Thurs, quiz
Every Wed night, review sessions

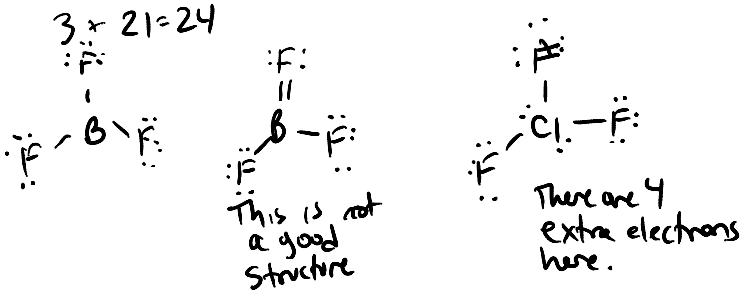
1st quiz on Jan 11

Chemistry (Kenistry)
Why Lewis Dot Formulas for localized bonding?
Valence electrons of common atoms are shared to create an octet around atoms (except H). Both atoms contribute
Formulas usually have central atom listed 1st
Sum all valence electrons including charges
Put a tentative single bond between all bonded atoms

Isoelectronic (CO, CN-, N_2) Count them & add up valence e^-

Rearrange as needed to satisfy octet rule: lone pairs, mult. bonds
(1st, 2nd row use octet C, N, O, F always)
Elmt >= 3rd row can exceed octet rule.

BF_3 $BeCl_3$ ClF_3
B = 3
F = 7·3
3 + 21 = 24



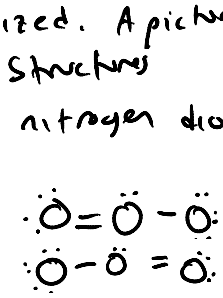
Lewis Dot structures w/ unpaired electrons
Molecular fragments have unpaired e^-'s.
CH_3, CH_2
[illegible] molecules [illegible]

Very few stable molecules w/ unpaired e^-'s.
NO, NO_2 (dimers)

11 e^- 

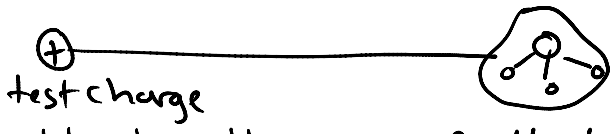
This is actually best

What improvements can be made to electron dot structures?
You have multiple structures.
Assume e^- can create an average bond. The electrons are actually delocalized. A pictorial method of showing is resonance hybrids.
Resonance Structures
Ozone, nitrogen dioxide, sulfate ion, etc.

18 e^- 

Electron dot formulas often put e^- on an atom that are improbable.
Atoms have different nuclear charges & therefore diff ability to attract e^- in a bond. Electronegativity.
Invent a scheme of placing e^- that makes fewer mistakes.
Counting scheme called formal charge.

Polar covalent bonds & electrostatic potential maps.



plot where the energy of attraction is.

From a long distance away, it looks neutral
The closer you get, the easier it is to see imbalances

Qualitative uses of Electronegativity
Organize the bonding trends from Ionic to Covalent

Electronegativity inc → Size/physical stuff Charge/attract inc

dec ↓ inc ↓ $\xrightarrow{\text{dec}}$ dec ↓ $\xrightarrow{\text{inc}}$

Formal charge = # electrons − # lone pair − $\frac{1}{2}$ # bond pair

$FC(O) = 6 - 4 - \frac{1}{2}(4) = 0$

$FC(N) = 5 - 0 - \frac{1}{2}(8) = +1$

$[NO_2]^+$

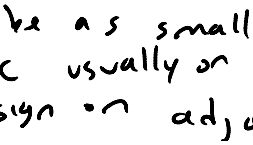
Lewis Dot, VSPER

Thursday, January 04, 2007
9:02 AM

Sum of FC is overall charge
FC should be as small as possible
Negative FC usually on most electronegative elmts
FC of same sign on adjacent atoms is unlikely.

what is the most likely structure, FNO or NFO?

WRONG

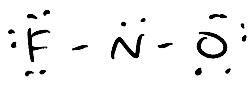


Formal charge F: $7 - \underset{\text{lone pairs}}{6} - \underset{\text{bond pairs}}{1} = 0$
N: $5 - 2 - \frac{1}{2}\cdot 4 = +1$
O: $6 - 6 - \frac{1}{2} = -1$

WRONG

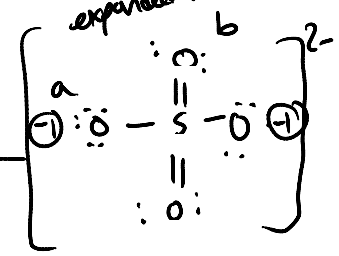
FC
N: $5 - 6 - \frac{1}{2}\cdot 2 = -2$
F: $7 - 2 - \frac{1}{2}\cdot 6 = +2$
O: $6 - 4 - \frac{1}{2}\cdot 4 = 0$

This is a better bond b/c it doesn't have charge inside. All O

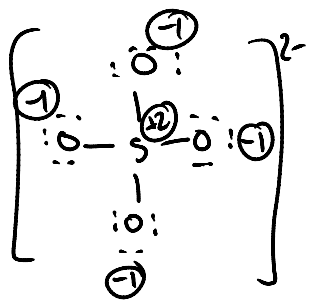


FC
F: $7 - 6 - \frac{1}{2}\cdot 2 = 0$
N: $5 - 2 - \frac{1}{2}\cdot 6 = 0$
O: $6 - 4 - \frac{1}{2}\cdot 4 = 0$

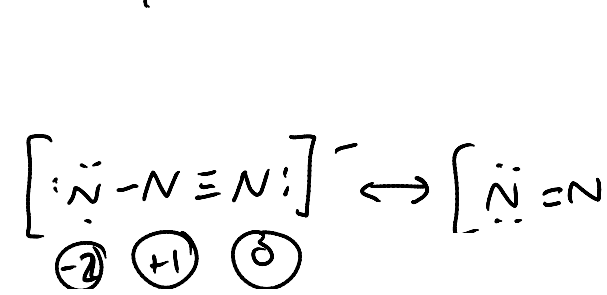
expanded valence shell



	O(a)	O(b)	O(c)	O(d)	S
#valence	6	6			
#LP	-6	-4			
$\frac{1}{2}\cdot$ #bnd	$-\frac{1}{2}\cdot 2$	$-\frac{1}{2}\cdot 4$			
Sum=FC	-1	0			



Normal



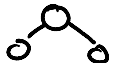
Used in airbags, exothermic rxn

Can we use Lewis Dot Structures for 3D shape information?

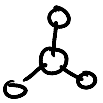
Molecules are not 2D

Double bond isomers have no explanation

Linear

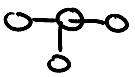


Bent

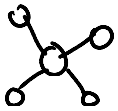


Trigonal planar

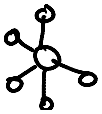
Trigonal Pyramidal



T-shaped



Square planar



VSEPR Valence Shell Electron Pair Repulsion Model

1. Draw structure (Lewis)
2. Sum # bonds + # lone pairs around each atom (in vid.)
3. Pick appropriate e^- pair geometry around central atom + choose molecular shape
4.

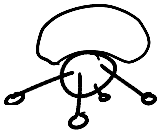
Steric # lets us predict shape of molecule

H_2O → repels itself. δ^- + δ^+ forces

3 atoms bonded to central atom

SN 3 makes Trigonal planar
SN 4 makes Tetrahedral / trigonal pyramidal
SN 5 makes T-shaped

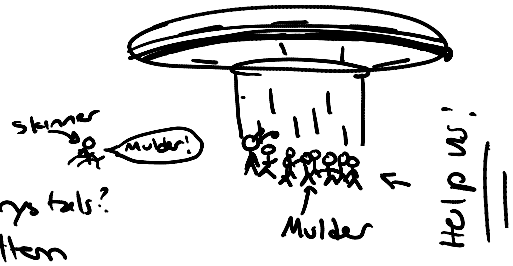
See-saw is when



Properties of Crystals, Lab Procedure

Friday, January 05, 2007
8:59 AM

Bring a can to lab



What are some properties of crystals?
- Atoms arranged in a reg. pattern
- You can grow them
- Often translucent
- Can be different colors

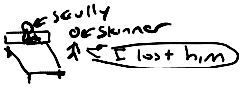
What do you do first?
- Sand can

Then - Dissolve in KOH

Procedure for synthesis of $KAl(SO_4)_2 \cdot 12H_2O$
- Sand can
- Dissolve in KOH (long step)
- Discuss safety issues & do check-in
- Filter out solid
- Add H_2SO_4
- Put in ice bath (b/c you're trying to make crystals)
- Vacuum filter crystals to get rid of excess aq. soln

When you add KOH, can will dissolve & gas will evolve ($H_2(g)$)

$$Al_{(s)} + K^+_{(aq)} + OH^-_{(aq)} \rightarrow H_{2(g)} + K^+_{(aq)} + Al(OH)_4^- + H_2O$$

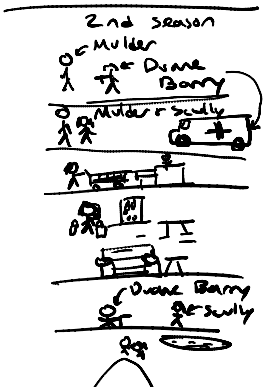


In lab manual

When we add H_2SO_4, a precipitate forms, then dissolves

$$Al(OH)^-_{4(aq)} \rightarrow Al(OH)_{3(s)} \rightarrow Al^{3+}_{(aq)}$$

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$$



We use H_2SO_4 & not some other acid b/c we want potassium aluminum sulfate. So we need H_2SO_4 & KOH

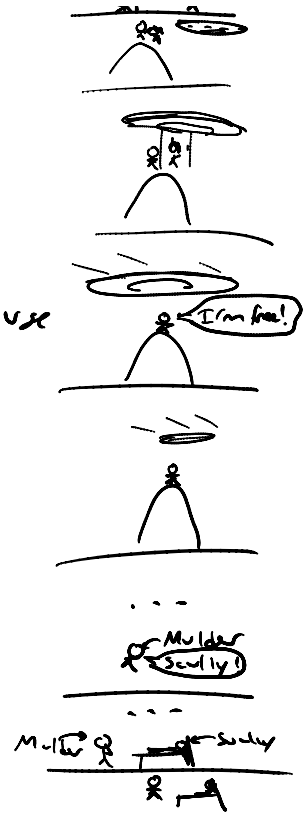
We need an ice bath for the product to form.
Things are less soluble at colder temps.

$KAl(SO_4)_2 \cdot 12H_2O$
Mass of Alum? 466.26g = M overall
1 g aluminum is what we use

$\frac{1}{26.98} = .037$ moles

Theoretical yield = 17.5g
$\left(\frac{\text{Actual yield}}{\text{Theoretical}}\right) 100 = \%$ yield

Growing a single crystal
- Make a saturated soln using the crystals
- Filter into a small vial
- Observe next week



You can see the structure of a crystal by shining x-rays or then

Alum crystals go in white containers, leave aluminum can in lab, filter paper, weighing paper → yellow bags, H_2SO_4 & KOH can go in the sink if it's neutralized.

All lab reports due Thurs, Jan 18 at 6pm

Online Safety Quiz

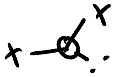
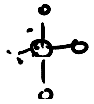
e- Pair Geometry

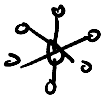
Monday, January 08, 2007
8:58 AM

VSEPR

1. Draw Lewis Structure
2. Sum # bonds + # lone pairs around each atom
3.

The effect of repulsion between nonbonding electrons + bond electrons
Electron pair geometry

No lone pairs	one lone pair	2 L.P.	3 L.P.
			
Trigonal planar	Bent	T-shaped	Linear (see-saw)
AX_3E_0	AX_2E_1	AX_3E_2	AX_2E_3
example	example	example	
BCl_3	$GeCl_2$	F_3Cl	
		ClF_3 ?	
e⁻ pair geometry			
trigonal planar	trigonal planar	Trigonal bipyramidal	"

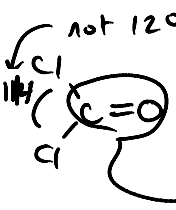
No lone pairs	1 lone pair	2 L.P.
		
AX_6E_0	AX_5E_1	AX_4E_2
SF_6	BrF_5	XeF_4
Mol. Octahedral	Square pyramidal	Square planar
epair Octahedral	Octahedral	Octahedral

Effect of Non-bonding e⁻

Bond ∠ decreases as # L.P. ↑ b/c e⁻ in a bond are attracted to nucleus

LP1/LP2 > LP/Bond > Bond/Bond

e⁻ in double bond



b/c forces big space here

L.P. always placed in equatorial position

5 e^- pairs can make linear molecular geometry.

5 e^- pairs can give T shape.

6 e^- pairs where square pyramidal is distorted by L.P. <90°.

DEMO

Eberhard's special purple plume

NI_3 explosions by touch sensitive detonation.

Ammonia + NI_3 in crystals $NH_3 \cdot NI_3$

source of exothermic energy evolution?

$$8\,NH_3 \cdot NI_3 \rightarrow 5N_2 + 6\,NH_4I + 9I_2$$

exothermic ↑ purple plume

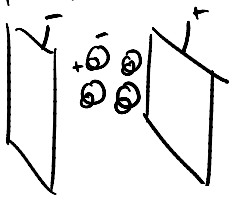
Dipole moment

Polar covalent bonds can have displaced charges due to electronegativity differences. Electrostatic potential plots w/ a + test charge

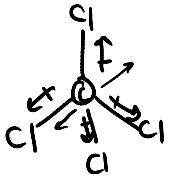
$\delta^+ H - Cl\ \delta^-$ Partial charge δ, distance between partial charge $= d$.

$M = \delta \cdot d$

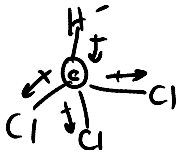
Field or



it would take a lot to orient them



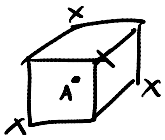
CCl_4, nonpolar no net dipole moment



$CHCl_3$, polar b/c net dipole moment

Tetrahedral molecules can fit inside a cube. 109.5° of AX_4 tetrahedron.

tetrahedron.

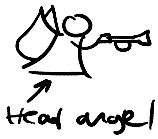


Diff of electronegativity makes bigger dipole moment

Orbitals

Tuesday, January 09, 2007
9:00 AM

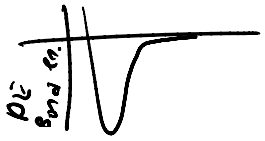
Average bond lengths
Memorize some #s, & decide if you go from single to triple bonds they get short
You can use these to come up w/ radii. Covalent radii, predict new bond lengths.

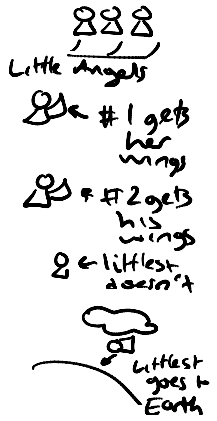


Bond energies are energies needed to break into atoms.

$O=O \rightarrow O+O \quad = +494\ kJ/mol$

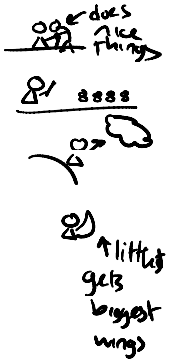
$Br-Cl \rightarrow Br+Cl \quad = +218\ kJ/mol$





reactants → separate atoms → products → formation

$\Delta H = \Sigma BE(\text{reactants}) - \Sigma BE(\text{products})$
Break everything up & put it back together



How atomic orbitals define molecular shapes
Consider Be atoms in gas phase surrounded by H atoms
Unpaired e^- of H very reactive.

Be [↑↓] [↑↓] H [↑]
1s 2s

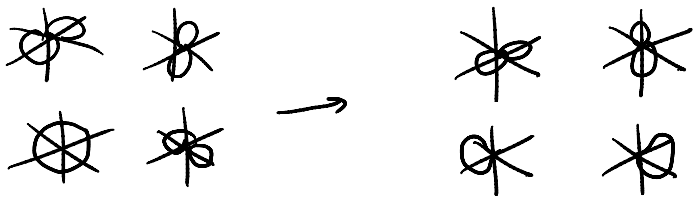
H atoms trolling for atoms w/ unpaired e^-?
H atoms trolling for atoms that can't resist temptation?
<u>Reaction</u> H-Be-H

Why doesn't carbon only make 2 bonds? Lewis Dot structure rules imply 4 e^-.

C [↑↓] [↑↓] [↑][↑][ ]
1s 2s 2p

C [↑↓] [↑] [↑][↑][↑] excited state

Sp orbitals form each having a huge lobe, pointing off directions



Be + 2 Cl atoms

sp^2 hybrids form when you move an $s\uparrow$. Taking a nice pair & moving an e^- up. Can you make a new orbital lower in energy?

Separation ∠s of 109.5°

VSPER concept of trigonal pyramidal geometry. Hybrid orbital

O atoms bond w/ 2 H's. sp^3 hybrids, 2 empty e^-, 2 lone pairs. Tetrahedron, 2 lone pairs

Laughing Gas Eberhard's rxn.

N_2O - nitrous oxide, laughing gas

CS_2 - Carbon disulfide. Bonding similar to CO_2

Exothermic, obviously. Huge explosion.

$$2N_2O + CS_2 \rightarrow 3N_2 + CO_2 + SO_2 + \tfrac{1}{8}S_8$$

Break old bonds (collision velocity, etc) & make new bonds.

Electrons moving so much faster than nuclei. Nitrogen molecules bang into us at like 1000 mph. E^- move around trying to find place where they get the lowest energy.

e^- end up in locations that match hybrid orbitals.

Reactive collision between molecules to sample new locations
exothermic rxn encourage more bonds

orbitals are probability density plots that show outer boundary, computed from wave functions.

wavefunctions used to compute probability density - hybrid orbitals result.

5 e^- pairs in sp^3d hybrids

□□□□□ 3d

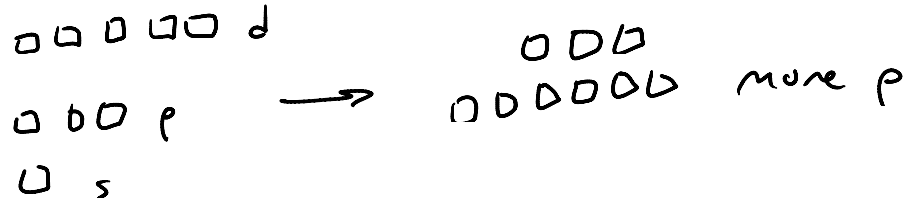
□□□ 3p

□
3s

Hybrid bonds, Orbitals

Wednesday, January 10, 2007
9:04 AM

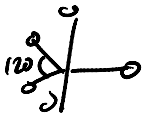
sp^3d^2 hybbonds

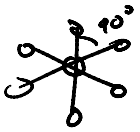


sp Linear

sp^2  Trigonal planar almost a sphere

sp^3 

sp^3d  Trigonal bipyramidal 

sp^3d^2  Octahedral 

<u>Quiz</u>

Lewis Dot Structures — All Ch. 10 possible
Formal charge
VSEPR models
Bond dipoles + electronegativity trend
Resonance
<u>Secondary</u>
Bond length trends
Bond energies & enthalpies of rxn
Eberhard's lab demonstrations

<u>Eberhard's demo</u>

Oxidation w/ bad 17-in oxidants

Nitro-glycerine capsules (explode or save lives w/ heart attacks
$C_3H_5N_3O_9$ — expands arteries)
Nitro cellulose is like cotton
$[C_6H_7O_2(ONO_2)_3]_n$ Guncotton

Black powder: potassium nitrate 75, charcoal 14, sulfur 11
$2KNO_3 + S + 2C \rightarrow K_2O + SO_2 + CO + N_2$
Low velocity explosion

The spark in the hydrogen balloon didn't make the balloon blow up. Explosion occurred from outside in. Hydrogen needs oxygen to explode.

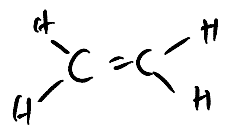
Hybrid orbitals for single, double, triple bonds.
- Overlap of hybrid orbital w/ bonded atoms gives an e^- pair w/ e^- density on bond axis. Called a σ bond (sigma)

- Single bonds are always σ bonds

- Single bonds are cylindrical & can rotate

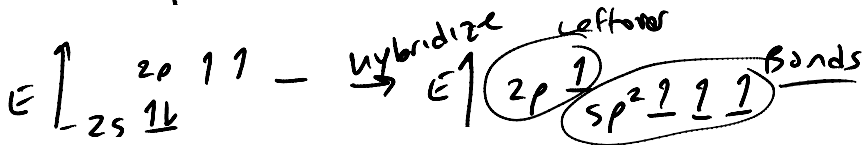
- Double bonds have σ bond & π bond.

Ethylene
C_2H_4



VSPER doesn't explain double bond. Double bond = 1 repulsive group, so trigonal planar. Hybrid that gives trigonal planar might minimize repulsion

Need 3 orbitals
sp^2



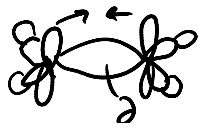
But we have a leftover p orbital

Lower energy region of space to hang out w/out bumping into other e^- pairs

into other e⁻ pairs.

Hanging out is hard to do...

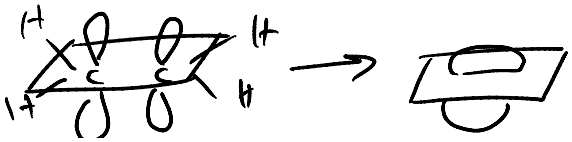
π Bond formation in progress. p orbitals haven't overlapped yet.



This is a new way to use VSEPR. Select hybrid orbitals

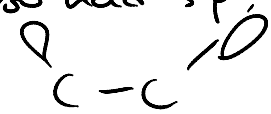
CNOH repeat their bonding patterns

Overlap of 2 p orbitals is a valence bond concept that does explain π bonds.



Carbon is sp^2 for σ bond, not sp^3

If you had sp^3, it'd be sticking out at 109.5°

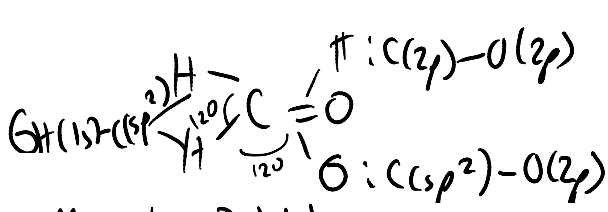


Double & triple bonds easier to understand w/ p orbital overlap & σ framework

C_2H_2

H − C ≡ C − H Linear

Hybridize to make linear sp



$2s\,2p\,2p \rightarrow sp\,2p\,2p$

Molecular Orbitals

π bond model is a local (2 atom) model

Magnetic properties need explaining

Spectroscopic methods show π can delocalize over more

Spectroscopic methods show e^- can delocalize over many atoms w/ alternating double bonds (organic molecules w/ C chains)

Quantum mechanics can be done by allowing e^- to move over whole molecule

Molecular Orbitals, Energy

Tuesday, January 16, 2007
8:55 AM

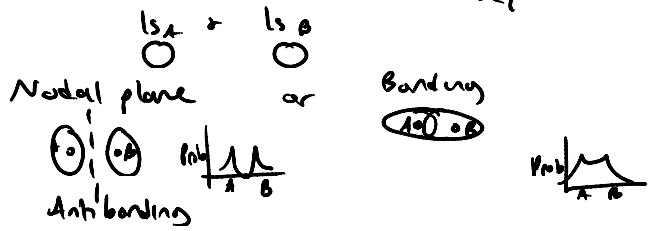
Molecular Orbitals

Core 1s e^- too stable to share

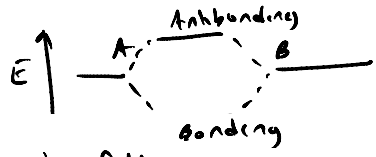
MOs are made from math combos of wavefunctions of similar energy & diff atoms. # MOs = # Atomic orbitals combined.

MO energy order depends on atomic orbital energies

1s orbitals of 2 widely separated H atoms



Create lower energy bonding MO & higher energy antibonding MO



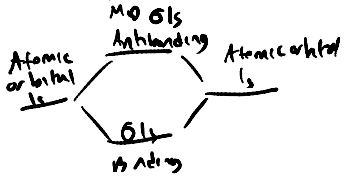
How to fill

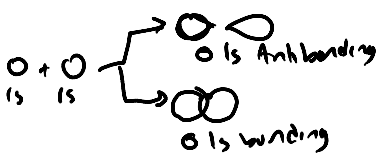
Distribute valence e^- for whole molecule lowest energies 1st.

Each MO holds 2 e^-, each w/ 1 e^- each w/ diff spin properties

Hund: 1st put 1 e^- in each orbital of equal energy (same spin property) before adding 2nd to make a pair.

MOs for 1, 3 e^- H_2 H_2^+ H_2^- He_2^+

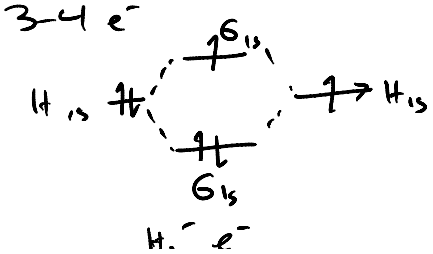




$(\sigma_{1s})^2 (\sigma_{1s}^*)^1$ H_2^- or He_2^+

H_2 $(\sigma_{1s})^2$ H_2^+ $(\sigma_{1s})^1$

3-4 e^-



H_2^- e^-

Stable species have more e^- in bonding order than antibonding

$$\text{Bond order} = \frac{\#\ e^- \text{ in bonding MOs} - \#\ e^- \text{ antibonding MOs}}{2}$$

$$\frac{3-1}{2} = 1$$

$$\frac{2-1}{2} = \tfrac{1}{2} \text{ bond}$$

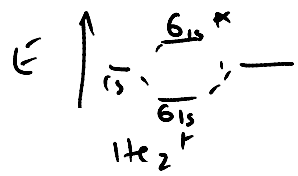
MOs can explain weaker & stronger bonds more effectively

$BO_{H_2^+} = (1-0)/2 = \frac{1}{2}$ bond

$BO_{H_2} = (2-0)/2 = 1$

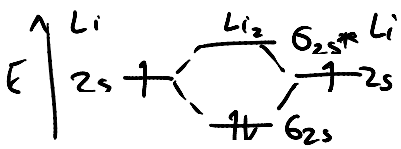
$BO_{He_2^+} = (2-1)/2 = \frac{1}{2}$

$BO_{He_2} = (2-2)/2 = 0$



Is too small to overlap, cannot make MOs

Isoelectronic means same # of e^-

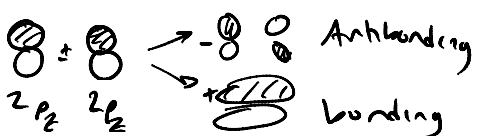


B_2 has 6 valence e^-, 2 in 2s & 1 in p

σ_{2p} is when p overlap

x & y axis p orbitals overlap to make π bonds

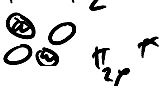
π bonds are MOs, & have same energy.



Ma. Sp EMPS in yellow! What is he talking about?

I AGREE
NO IDEA

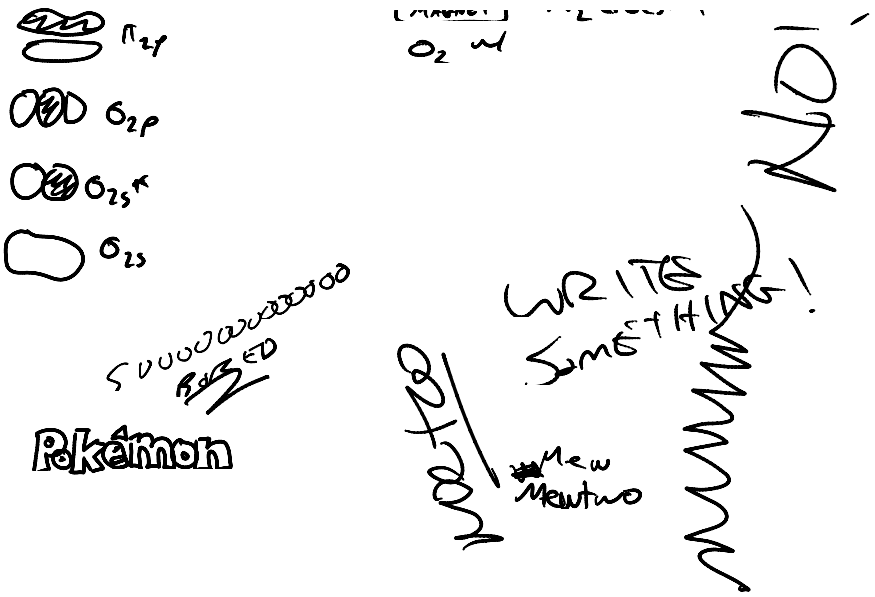
For F_2



Eberhard's Demo

O_2 gets stuck

N_2 doesn't


π_{2p}
σ_{2p}
σ_{2s}^*
σ_{2s}
O_2
NO
WRITE SOMETHING!
Pokémon
Mew
Mewtwo

Quiz Review, Bonding

Wednesday, January 17, 2007
8:56 AM

Quiz
Bond enthalpies, using heats of formation for rxns
Hybrid orbitals & VSPER
Pi & Sigma bonds
Molecular orbitals of diatomic molecules (making MOs, bond order, magnetism)
Delocalized Lewis structures & resonance, simplified MO description.
end of Delocalization in benzene
Eberhard's lab demonstrations

2 possible diagrams.
12+ e^-, no matter molecule, σ lower (see chart online
11− e^- , π

Paramagnetic is ↑ ↑
Diamagnetic is ↑↓

Smaller charge, smaller nuclei, more orbitals collide. Bigger don't collide as easily.

Bonding in diatomics
- Identify bonds in MO models
- Fundamental quantity is e^- density
- Bond order = # of bonds = $(n_B - n_A)/2$

NO, O_2^+ [11e^-] $\{(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2(\pi_{2p})^2(\sigma_{2p})^2(\pi_{2p}^*)^1\}$
2.5 bonds

O_2[12e^-] $\{(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)^1(\pi_{2p}^*)^1\}$
2 bonds

Paramagnetism from unpaired spins
Diamagnetism from paired spins
Ferromagnetism from alignment of many atoms to make magnet

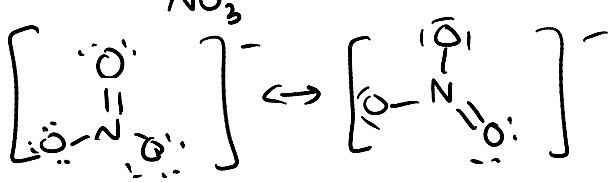
Electronegativity distorts shapes of molecular orbitals

Same rules for bonding work for heteronuclear diatomics & make molecules

Delocalisation occurs when resonance structures can be drawn
If an MO is spread out over 2+ atoms, not like C_2H_4 (isolated double bond).

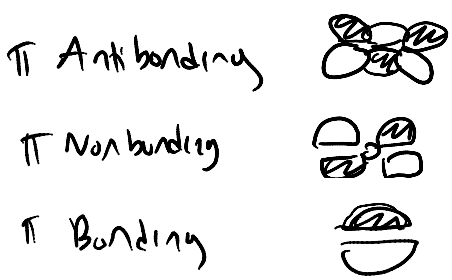
Benzene is a good example, & alternating double bonds in a chain.

NO_3^-



bonds shift but # of each type don't change.

~~Ozone~~
Delocalization could be non-bonding & pi type



1 pi bond shared in 2 bonds is essentially $\frac{1}{2}$ bond order contribution so total is 1.5 bond order between each pair of O's.

Now nonbonding e^- could have unpaired spins

NO_3^-
4 p orbitals
delocalized bonding/antibonding

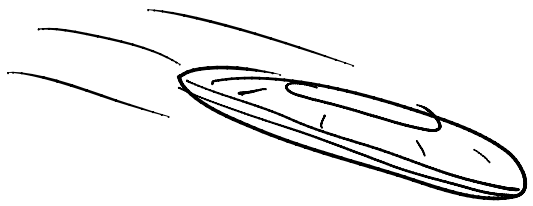
Degenerate non-bonding orbitals

HW 38, 39, 40

Simple Lewis Dot Structures, look at resonance structures.
Delocalized bonds

Can electron charge density plots help? Yes, problem is to discuss unusual bonding in terms of concepts that work for majority of cases.

If you take e^- density as e^-/unit volume, has 1-1 relationship w/ ground state wave function.
~~wavefn~~ e^- density is the bond.



For HF, H has all the motion. F barely moves.
In CO_2, move in many ways

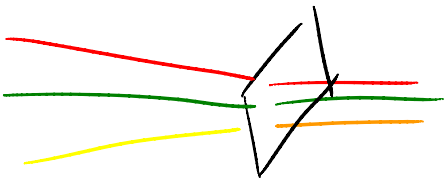
Formaldehyde looks like it's when it moves

Another looks like Medieval torture

Solid State Structures, Refraction

Friday, January 19, 2007
8:59 AM

Solid state structures

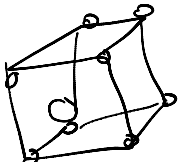


refraction grating
red refracts more

X-ray diffraction can be used to calculate solid state structures

You can take one of the crystals we made, put it under the X-ray (short wavelength) defractometer & from refraction pattern calculate the structure.

Body Centred Cubic

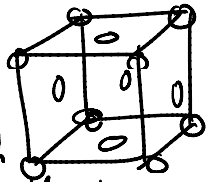


Unit cell has 2 atoms

$\frac{1}{8}$ corner atoms in corners

$\frac{1}{8}$(8 corner atoms) + 1 (central) = 2

Face Centred Cubic



$6(\frac{1}{2}) + 1$ (1 central atom) = 4 atoms in face centered

Polymorphism & allotropy

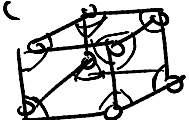
Many - shape
↑
a material that can change its shape

existence of more than 1 crystal structure of a given atom/compound (Carbon [graphite & diamond])

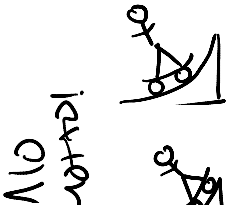
Iron is polymorphous & allotropic

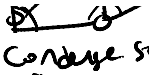
Any regular solid will pack into a repeating structure. Some of the structures are more efficient than others.

Calculating Packing efficiency of simple cubic



$\frac{1}{8}(8) = 1$





Condense so they touch

Volume, if diameter = 1

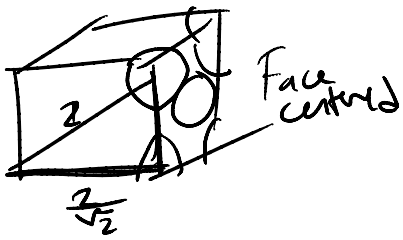
$\frac{4}{3}\pi\left(\frac{1}{2}\right)^3$

$\frac{1}{6}\pi$

Volume of unit cell = 1

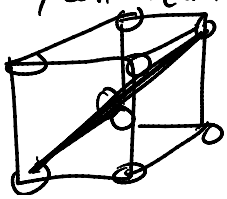
Packing efficiency $= \left(\frac{\frac{1}{6}\pi}{1}\right)100 =$ %

Unit cell is smallest repeating unit.
If atoms weren't touching, distance would not be 1.

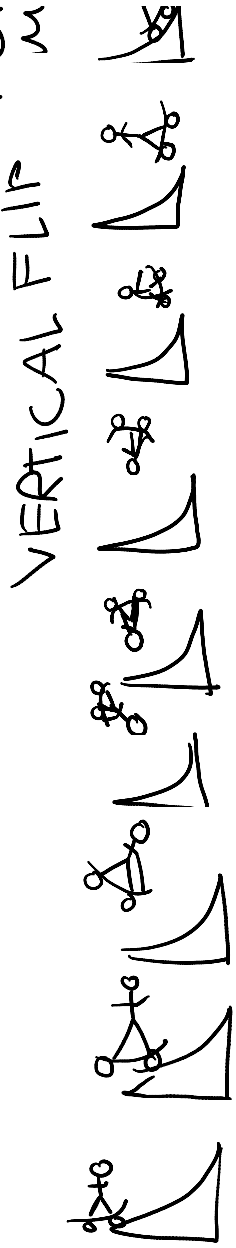


$\left(\frac{2}{\sqrt{2}}\right)^3$ = volume of cell

Body centered cubic



Calculate that



<u>Prelab</u> - do warm-up exercises in lab manual
Title + objective
No procedure (bring lab manual)
In end, write brief conclusion

Interaction Forces

Monday, January 22, 2007
8:58 AM

What are the interaction forces between molecules

Liquids: $10^{-9} - 10^{-12}$ s show changes
internal vibrations fast on this time scale

Solids: Molecules don't translate or rotate, vibrations between molecules
Also fast internal vibrations

Gases: Distances very long range. Need higher P to see non ideal gas behavior

Evidence for forces? Heat of phase transitions
Vaporization is an example

1. Dipole-dipole forces, permanent dipole moments

2. Dispersion / London (transient dipoles)

3. Hydrogen Bonding

<u>Dipole-dipole</u>

- transient alignments, avg. net attraction. Things move.
- Larger = better interactions
- ~~(...)~~ very unlikely to have as much order as pics in book
- Fluctuating order makes avg energy less than expected
- Contributions about ~ 20 kJ/mol. Part of H-bond forces.

<u>Dispersion/London forces</u>

Fast fluctuating. Can make instantaneous dipole (lasts 10^{-15} sec)
A neighbor molecule can respond w/ its own instantaneous dipole that is <u>induced</u> by 1st dipole. While thing is short lived
But on avg there are forces created

Polarize neighboring molecules
Molecular properties enhance this
- Polarizability. distortability of electrons/volume. Larger atoms have more e^- & are more polarizable. Book uses "mass" which ~~bad~~ poor substitute for # e^-.
  Larger polarizability will have greater induced dipole
- Distance dependence: $F \propto 1/(\text{distance})^6$ so closer is better

Implies that close alignment is good
Long molecules in close contact have more London dispersion forces
Range of energies is 0.1–20 kJ/mol

More electrons = higher boiling point (more polarizability)

Hydrogen bonds are dipoles that interact especially strongly, Occur when H atom attached to O, N, F atoms. F-H>O-H>N-H
Interaction is between highly positive H w/ a lone pair. Network of H_2O is b/c there are lone pairs & 2 O-H, 4 H bonds.
Mixture of molecules also H bond. 10–40 kJ/mol

<u>Surface Tension</u> – result of intermolecular forces
Exterior molecules have more symmetric forces, surface molecules have more force pulling them to the bulk. This adds a new energy term for surface molecules, J/m². Energy needed to increase area by 1 m²

Meniscus: Balance between liquid cohesive by surface tension & surface adhesive forces. Hg is diff

<u>Vapor pressure</u> T variation & pressure for equilib closed containers

Eberhard's demo – water + oil went into planes.

Diff slopes for ln P vs $\frac{1}{T} \times 10^3$ graphs.

Diff slope means

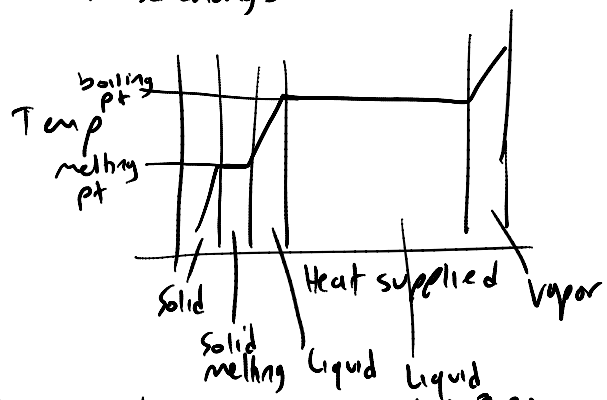
$$\ln \frac{P_2}{P_1} = \left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Prior graphs show slope of water larger than non-polar toluene. (see book)

P vs T curves

Tuesday, January 23, 2007
8:53 AM

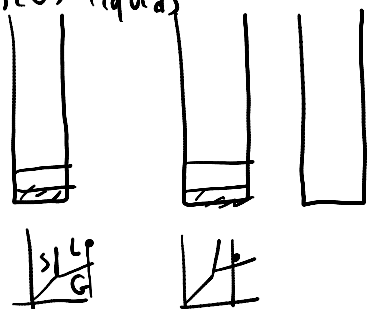
Apply fixed Joules/sec & measure T changes.
phase changes



Slope $\propto \frac{1}{\text{heat capacity}}$

Liquids have biggest heat capacity, then solid, & a little smaller is vapor.

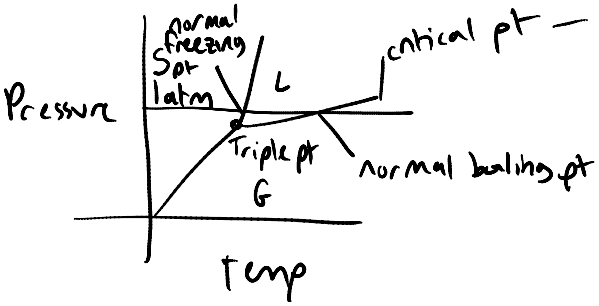
Meniscus liquids



I Paid good money for that

Meniscus!

Supercritical fluid is at same density as a liquid.



Vapor drives back atmosphere (boiling) Open vessel

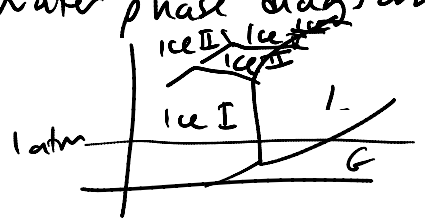
Triple point is lowest temp for a liquid, & point where all 3 are in equilib.

X - FILES

Takes a high P to have a liquid or a triple point and it Sublimes at 1 atm
Supercritical fluid has no meniscus
At the critical point, you go from region w/ meniscus to no

At the critical point, you go from region w/ meniscus to no meniscus. The liquid is reorganizing to make a thing w/out meniscus. Chaos, light scattering over domains.

Water phase diagram



Triple pt. 4.5 Torr

I want to Believe

incomplete.
unacceptable,
despicable,
disgusting
sorry excuse for
a diagram.
There's no ice IV!

Ice has neg. slope. ΔV is neg.

No, yours!

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

Most have + slopes.

$$\ln \frac{P_1}{P_2} = \left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

<u>Sublimation</u>

Triple point of H_2O is 4.58 Torr, .0098°C

$$\Delta H_{subl} = \Delta H_{vap} + \Delta H_{fus}$$

Diff shape for solid-gas line than solid-liquid line.

I WANT TO GET AWAY

WHO BELIEVES?

<u>Types of Solids</u>

Ionic NaCl, $CaCl_2$
Lattice energy from coulomb interactions

Metallic (Au, Cu, etc)

Molecular (H_2O, London dispersion, etc)

Network Solids (quartz, sand, diamond)

MULDER!

Amorphous Solids (glass, polymers)

<u>Crystal lattice</u>

repeating position of atoms (pattern)

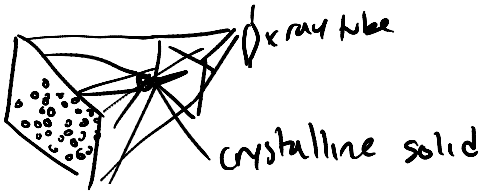
Unit cell is what we use to make a lattice

X-rays have short enough wavelengths to allow spacing between atoms to act like a plane

Unit cells

Wednesday, January 24, 2007
9:03 AM

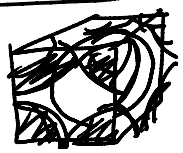
X-ray diffraction of crystals



Quiz Topics

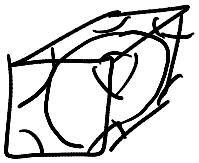
- Intermolecular forces (types, properties, effects)
- Heats of Phase Transitions & Heat Capacities (applications)
- Vapor Pressure of Liquids & B.P.'s
- Phase diagrams
- Crystal Unit cells (SC BCC, FCC)
  Lattice energies, NaCl CsCl, hexagonal close packing not on quiz
- Use KGS Table to organize unit cell info
  Clausius-Clapyron Eqn on exam (don't need to memorize)

Unit cells



Simple cubic
Net count 1 atoms/unit cell

4 touching in same plane. 6 nearest neighbors



Body centered
Net count 2

4 above body & 4 below. 8 nearest neighbors.

Face-centered
Net count 4

Simple cubic – Edge length = e = 2 × atom radius = 2R
Volume of SC unit cel = $e^3 = 8R^3$
1 atom/unit cell
1 atom has $V = \frac{4}{3}\pi R^3$
Ratio $\frac{\text{Atom V}}{\text{Unit cell V}} = \frac{\pi}{6} = .5236$
Only 52.4% of lattice volume is atoms

Simple cubic has most empty space.

Body centered – $(2)^{\frac{1}{2}} e$ is diagonal of a face $(\sqrt{2})$

Sum of squares is $2e^2 + e^2$ & $\sqrt{}$ is body diagonal. body diagonal $= (3)^{\frac{1}{2}} e$

Body diagonal $= 4R$
$= 3^{\frac{1}{2}} e$

Volume unit cell $= e^3 = 64 R^3/(3)^{\frac{3}{2}}$

Volume of 2 atoms in unit cell $= 2(\frac{4}{3}\pi R^3)$

Ratio of volume atoms / volume unit cell $= .680$ or 68% of lattice occupied by atoms

Face centered – $2^{\frac{1}{2}} e$ is diagonal of a face

$4R = 2^{\frac{1}{2}} e$

Volume 4 atoms in unit cell $= 4(\frac{4}{3}\pi R^3)$

Volume unit cell $= e^3$

Ratio volume Atom / unit cell volume $= .740$, 74% of lattice filled w/ atoms.

Highest fraction of space that can be filled by packing same size spheres.

Close Packed Structures

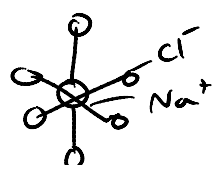
Cubic close packed case means face centered cubic

Coordination #s are 12

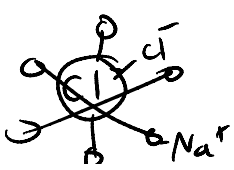
Hexagonal close packed case has no cubic unit cell

both have smallest free volume of 26%

NaCl Lattice



octahedral



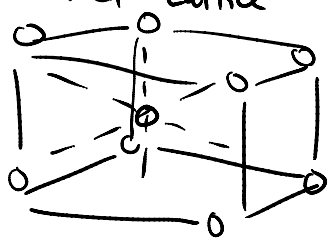
octahedral

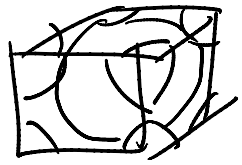
Everything is surrounded by 6 atoms.
Ends up being cubic

4 formula units in unit cell

$(2R_{Na}) + (2R_{Cl}) = 4R$ edge

CsCl Lattice





~~Face~~ Body centered cubic

NaCl requires 4 formula units to describe in the unit cell

CsCl has 1 formula unit, Cs in center. Cs, Cl touch on body diagonal, which has $2R_{Cs} + 2R_{Cl}$ edge $= \frac{\text{Body diagonal}}{\sqrt{3}}$

Nickel has FCC unit cell, density = 6.84 g/cm³. Calculate radius.

We have density.

Unit cell volume = (edge)³. We need to relate edge to R

4R is distance in units of atom Radii. e = edge length.

Always work w/ touching atoms.

$$e = \frac{4R}{\sqrt{2}}$$

Unit cell density = microscopic density. Need # atoms in unit cell, mass of atoms.

Unit cell volume = e^3 density = 6.84 = (mass)/e^3

Mass = 4 (58.69 g/Na) = 3.898 E-22 g

Find e, solve for R.

Bar of X. Density = 10.5 g/cm³. FCC unit cell as 4.09 E-10 m

Atomic weight?

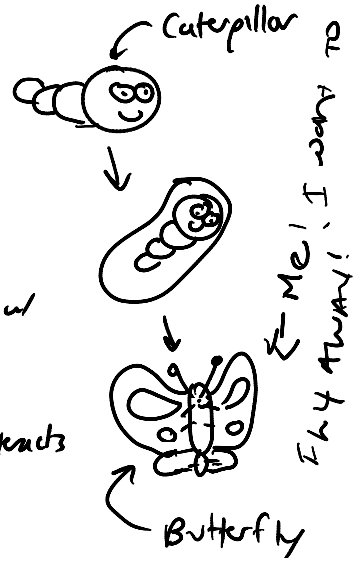
Titanium is BCC Density = 4.5 g/cm³. Edge length & R?

Lab: Diffraction

Friday, January 26, 2007
9:01 AM

Experiment 11 (lab manuals allowed)
Optical Diffraction

OCD are Team 1!



We're using visible light in the lab

Bragg diffraction occurs when x-rays interact w/ crystals.

Fraunhofer diffraction occurs when light interacts w/ the slides

Crystals are constructed of atoms or molecules arranged in a reg. pattern.
http://www.matter.org.uk/diffraction/introduction/default.htm

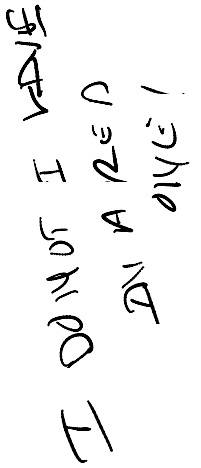
Red light = 670 nm
Green light = higher energy, shorter wavelength

RIDE, captain
Ride upon your
mystery ship!

WE ALL LIVE IN
A YELLOW
SUBMARINE

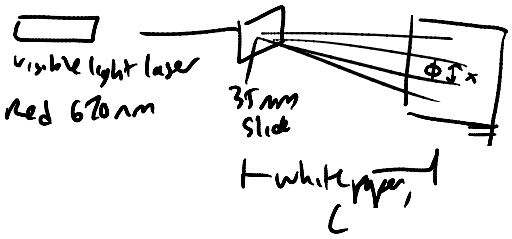
Bring a ruler, bring lab manual

Diffraction caused when you have a repeating, periodic array & the repeat distance is similar to wavelength of waves.
This is on the E-10 angstrom scale
Use X-rays
We use visible light



<u>Result</u>
- Constructive & destructive interference

Fraunhofer Diffraction Exp.



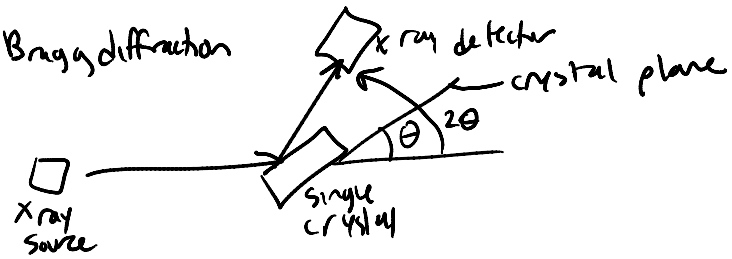
$\tan\Phi \approx \sin\Phi \approx \Phi$ b/c infinite distance

$\tan\Phi = \frac{x}{L}$

d is distance between dots

Constructive interference $d\sin\Phi = n\lambda$ 670nm

Bragg diffraction



RIDE Captain
Ride upon your
mystery ship!

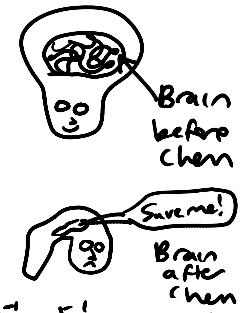
USS
ENTERPRISE
CAPTAIN
JEAN-LUC
PICARD

NX-01
ARCHER
NCC-1701
KIRK
NCC-1701-A
KIRK
NCC-1701-B
HARRISON
NCC-1701-C
GARRETT
NCC-1701-D
PICARD
NCC-1701-E
PICARD

Entropy

Monday, January 29, 2007
9:06 AM

Spontaneous change of natural phenomenon
hot → cold



Decrease entropy, put stuff together.
Phase transitions (solids melt to liquids, etc)
Dissolving (making soln)
Freezing points

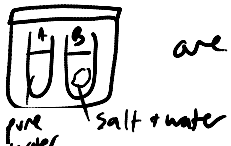
<u>Entropy</u>, S, state function, >= 0 w/ units $J K^{-1} mol^{-1}$, measure of molecular randomness.
Entropy of gases >> liquids > solids
Entropy of a gas increases with increased volume, increased temp (for everything solid, liquid, gas) 0 at 0K, perfect crystal.
Entropy of ideal mixing gases or liquids always is positive.

$$\Delta S = -R\zeta$$

$$S_A + S_B + \Delta S_{mix} = S_{tot}$$

Second Law of Thermodynamics: Entropy of universe either stays the same (equilib) or increases w/ any spontaneous changes.
We have no heat flow in forming an ideal soln, so the increase of entropy is for the universe. It's a spontaneous process.

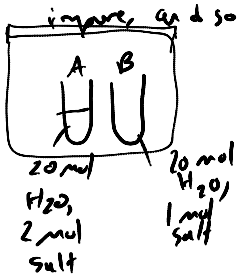
Starting test tubes



are not in equilib

Spontaneous process is B has biggest entropy. Solvent moves through vapor to region w/ higher entropy.
A is empty after vacation.

Equilib point of view is Tube A & B should have same vapor pressure. But pure solvent always have greater vapor pressure than impure, and so stuff will move to soln w/ less vapor pressure.



Less salt has biggest vapor pressure.
Raoult's Law } If salt mole fraction is not too diff then new equilib is possible by equating vapor pressure above each tube.

$$P_{soln} = X_{solvent} P^o_{solvent}$$

$$X_{solvent} + X_{junk} = 1$$

One tube gained 6.86 mol, other loses. A gains. B loses.

Entropy of gas has value that is proportional to partial pressure. At equilib soln entropies in A & B are equal. Gas entropy also equal.

Entropy also of

Gases have biggest entropy. S depends on P or V.

BP elevation, FP depression w/ entropy idea.
How can you create a vapor pressure of 1 atm above a soln? A to original T of BP a soln has less vp due to Raoult's law. Increase T to find a place where vp = 1 atm.
$\Delta T = k_b m_j$ mole fraction of solute

FP Depression: New equilib is between pure solid & junque soln. Solid is pure b/c for most things crystal lattice excludes junque. Original FP is an equilib w/ pure solid & pure solvent. We need to lower entropy of junque by lowering T.
$\Delta T = -k_f m_j$ $T_{final} - T_{initial} = \Delta T$

Quack, Quack, Quack

BP Elevation, Osmotic Pressure

Tuesday, January 30, 2007
8:58 AM

BP elevation Creat vapor pressure of 1 atm above a soln - At original T of BP a soln has < vp due to Raoult's law. Increase T & find a place where vp = 1 atm.

$\Delta T = k_b m_j$

FP depression New equilib is between pure solid & Junque soln. Solid is pureble for most things crystal excludes Junque. original FP is an equilib w/ pure solid & solvent.

$\Delta T = -k_f m_j$

Junque = solute

We don't care what Junque properties are, just moles of Junque

Ionic salts can form multiple ions

At greater dilution there are less interactions between oppositely charged ions so they can act like completely separate entities.

If a diver surfaces too quickly, N_2 dissolves in diver's blood will release quickly resulting in painful & dangerous condition called the bends. This is same as taking off cap on pop bottle

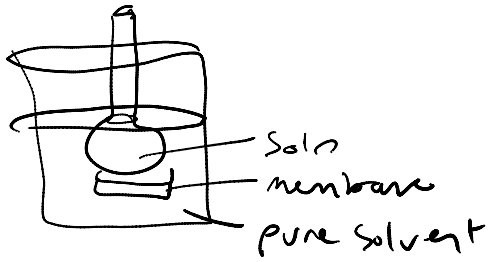
Things have higher b.p. when they break up into ions b/c concentration goes per ion.

2.5 molar $CaCl_2 \rightarrow 3(2.5) = 7.5 CaCl_2$

Osmotic > FP > BP for precision of determining unknown molecular weight

Osmotic Pressure effect

Membrane allows solvent to move, but not solute (Junque)



Pressure changes the entropy of the solid. Pressure on salt side, salt has most entropy, and only takes very small diff in concentration to cause an effect.

Entropy is measurement of how well molecules can occupy diff places + be totally random

Pressure must be lower than entropy of soln,

Volume is very dependent on pressure. V↓ → entropy reduces due to fewer locations for solvent (less random) or fewer microstates in statistical mdl. Higher P → ↓ entropy.

Excess pressure, Π

$\Pi = cRT$, c = solute molality

c becomes ic if i is # ions.

Osmotic Pressure

Hypotonic < .92% m/V rupture

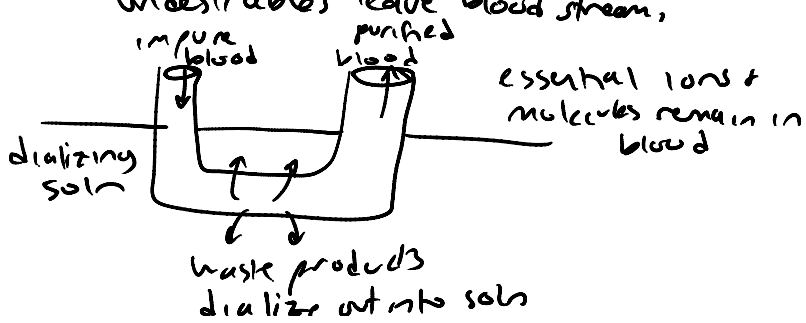
Isotonic saline .92% m/V

Even If solns are not very diff concentrations one can cause enough internal pressure because damage or to dehydrate cells.

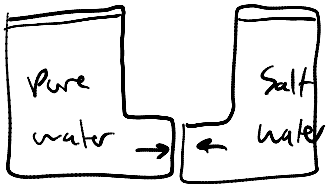
Hypertonic > .92% m/V crenation

Dialysis designed to let many things pass

undesirables leave blood stream,



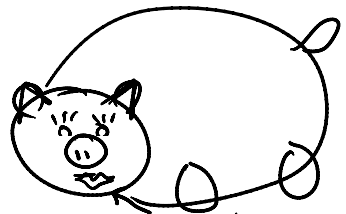
Reverse osmosis – Desalination


Pure
water
Salt
water

Colloids, Distillation

Wednesday, January 31, 2007
9:01 AM

Lewis Dot structures
Formal charge
VSPER Models
Bond dipoles & electronegativity
Resonance (identify cases)
Bond length trends



lipstick on a pig

Bond energies, enthalpies of rxn, heats of formation.
Hybrid orbitals / VSPER relationship
Pi Sigma bonds
MO of Diatomic Molecules (Making MOs, use to describe molecules, bond order, magnetism)
Delocalized Lewis structures & resonance, simplified MO description of MO
Intermolecular Forces (types, properties, effects)
Heats of phase transitions & heat capacities
Vapor pressure of Liquids & BP
Phase Diagrams
Crystal unit cells
NaCl, CsCl unit cells
~~Entropy Supplement~~
Vapor pressure of solns, Raoult's Law
Colligative Properties, FP depression, BP elevation, osmotic Pressure
Henry's Law, Forces in Liquids, Molality
Vapor-composition, BP-composition diagrams. Fractional distillation, azeotropes & non-ideal solns, nBP

$n\lambda = 2d\sin\theta$

$\Pi = iMRT$ $\Delta T_f = -iK_f m_j$ $\Delta T_b = iK_b m_j$

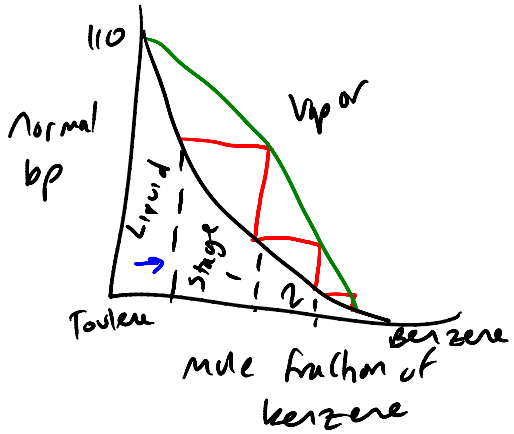
$P_s = X_s P_s^\circ$ non volatile Surque (solute)

$P_i = X_i P_i^\circ$

Raoult's Law gives vp. Benzene: .5 × 95.1 = 47.6 mm Hg
.5 × 28.4 = 14.2 mm Hg

So we know partial pressures Total vp Add together.

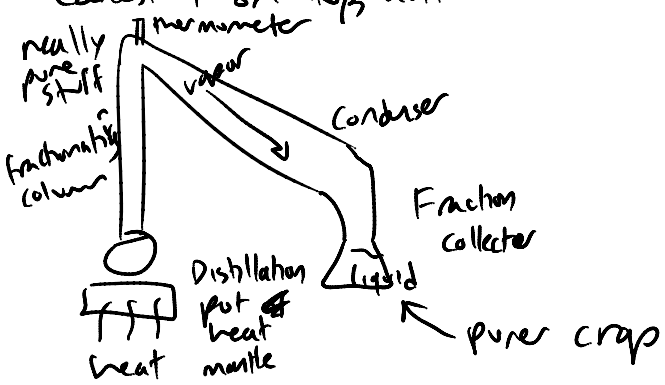
Fractional distillation: Compute BP of liquid vs vapor composition as another curve.



Start at blue arrow. Red lines link vapor comp that is now richer in benzene.

Condense liquid in stage 1, collect vapor in stage 2 that is even richer in benzene, keep repeating & final material is pure benzene.

Coolest T on top, hottest at bottom

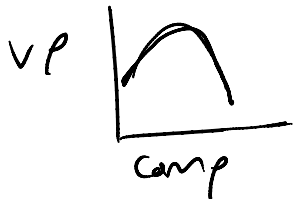


Lower BP has highest vapor pressure & so vapor is richer in lower BP

Intermolecular forces can be weaker than individual species or stronger. This CAN, but not always, generate azeotrope. Azeotrope is soln at particular composition where vapor & liquid have same composition (depends on external pressure). At that special comp., liquid is boiling at pressure T, which is exactly what a single pure liquid would do. Higher total VP than expected by Raoult's law. BP of azeotropes is lower b/c of higher VP.

Mixtures once heated

Mixtures pur = liquid



BUREAU
MULDER!

I ♡ u, Kenisha!

I HATE MUST REPORT!

96% ethanol azeotrope

FBI

<u>Colloids</u>

Nanoparticles of gold in soln. Size controls the color. So light scattering depends on size.

Shorter wavelengths = more intense scattering

Daddy, why is the sky blue?

Well... to match your pretty eyes

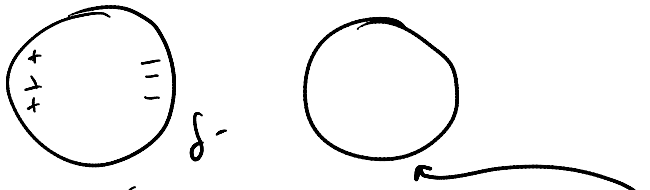
Nope, not even close. See, all colors have wavelengths that are diffused by nitrogen & oxygen. Since blue is the shortest wavelength, it's diffused up to 10 times more.

Our eyes are more sensitive to blue than purple.

Interaction Forces

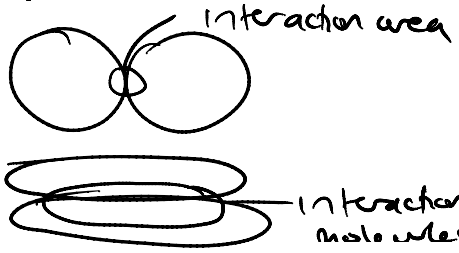
Thursday, February 01, 2007
9:01 AM

London Dispersion Forces



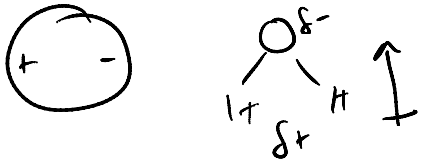
Instantaneous Induced Dipole

London dispersion forces based on polarizability of molecule.
Polarizability related to # electrons per mol.
Also, shapes of molecules affect it.



Dipole-Dipole

Permanent dipole. Always has δ+ & δ-. Water is dipole dipole.



2 molecules w/ always dipoles interact.
These are permanent, so stronger than LDF

Thyophene f.p. -38.3 b.p. 84.4°C used as solvent in place of benzene. Combustion of 2.348g sample produces 4.813g CO_2, 1.005g H_2O & 1.788g SO_2. When a .867g sample of thiophene is dissolved in 44.56g benzene (C_6H_6) the f.p. is lowered by 1.183°C. Molecular formula of thiophene?

$$\Delta T_F = -k_{FP}\, m_J \rightarrow \frac{\text{mol J}}{\text{kg solvent}}$$

$$m = \frac{\Delta T}{-k_{FP}} = \frac{-1.183}{-5.12} = .2 \text{ mol solute (J unit)/kg solvent (benzene)}$$

(benzene)

$$\frac{.2\,mol}{kg\ benzene} = \frac{x\ mol}{44.56\,g\ benzene}$$

$.0103\,mol = x$ mol thiophene

$$\frac{.867\,g\ thiophene}{.0103\ mol\ thiophene} = 84.2\ g/mol$$

thiophene + O_2 → CO_2 + H_2O + SO_2

CO_2: 4.913 g

H_2O: 1.005 g

SO_2: 1.788 g

thiophene: 2.348 g

$$4.913\,g\ CO_2 \left(\frac{1\ mol\ CO_2}{44\,g\ CO_2}\right) = .111\ mol\ CO_2$$

$$1.005\,g\ H_2O \left(\frac{1\ mol\ H_2O}{18\,g\ H_2O}\right) = .0558\ mol\ H_2O$$

$$1.788\,g\ SO_2 \left(\frac{1\ mol\ SO_2}{60\,g\ SO_2}\right) = .0298\ mol\ SO_2$$

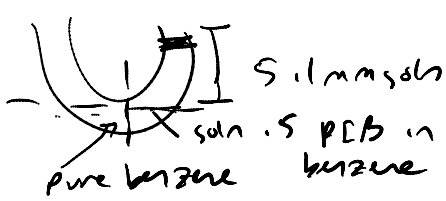
$$2.348\,g \left(\frac{1\ mol}{84.2\,g}\right) = .0279\ mol\ thio$$

Thio: SH_4C_4

SC_4H_4

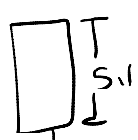
C_4H_4S

At 25°C, 0.5 g sample polyisobutylene in 100 mL benzene soln has osmotic pressure that supports 5.1 mm column of (d = .88 g/mL). Molar mass of polyisobutylene? For Hg, d = 13.6 g/mL



$\Pi = MRT$

$\Pi = \frac{n}{V}RT$



$V = hA$

$V = 5.1A$

$d = .88\,g/cm^3$

$m = Vd$

$m = (.51\,cm)(.88\,g/cm^3)\,A\,cm^2$

$m = X$

we'll pretend this is weight of mercury

$13.6\,g/cm^3 = X/V$

$$A \cdot X_{g\,Hg}\left(\frac{cm^3}{13.6\,g}\right)\left(\frac{1}{A\,cm^2}\right) = h(Hg)\,cm \rightarrow mmHg$$

convert to torr, = pressure

$\pi = MRT$

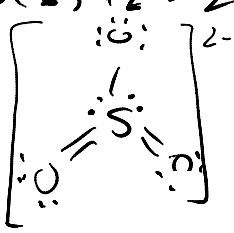
$$mmHg\left(\frac{1\ torr}{1\ mmHg}\right) = MRT$$

$$M(R)(.5\,g)$$

$$= \frac{n}{V}$$

SO_3

$6 + 3(6) + 2 = 26$



$26 - 6 = 20$

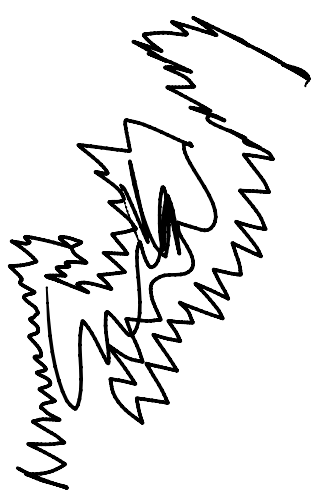
$20 - 12 = 8$

$8 - 4 = 4$

$4 - 4 = 0$

3 resonance structures

$$FC = \#\,valence - L.P - \frac{\#\,bond\ e^-}{2}$$



Lab Prep

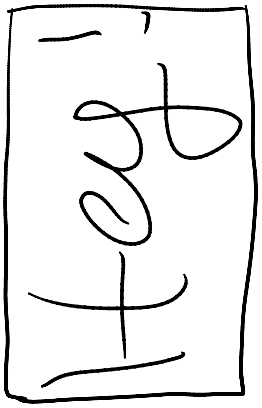
Friday, February 02, 2007
9:08 AM

Prelab
Title
objective
Procedural outline
Chemical eqns
odd exercises p-64

Write eqns w/ states

Rxns
I. A1-A3
II. A1, B1
III. B1-B2, C1-C3
IV. A-D
V. A+B

We won't do red phosphorous rxn, the sodium, or some other thing
We still fill out observations (from here)



Combination rxns.
B. Nonmetal + Nonmetal,
Small quantity of red phosphorous in test tube & heat gently w/ Bunsen Burner

Rxn

$$4P_{(s)} + 5O_{2\,(g)} \xrightarrow{\Delta} P_4O_{10\,(s)}$$

Observations
white

White solid forms, white smoke comes out
Don't just heat bottom of tube (b/c you don't want it just concentrate in one place
Flame inside tube, orange solid Bubbling w/ liquid & flame.

Oxidized/Reduced?

Add 5 mL H_2O to the residue, shake to dissolve, test w/ pH paper.

$$P_{(s)}^{0} + O_{2(g)}^{0} \rightarrow P_4^{+5}O_{10}^{-2}$$

So P oxidized, Oxygen reduced. From 0 → -2. And O → +5

Rxn

$$P_4O_{10(s)} + H_2O_{(l)} \rightarrow$$

Observations

Turns chocolate color, then reddish thing. Some suspended solid. P is probably in there (unreacted Phosphorous) but P_4O_{10} is dissolving.

Displacement of a Halide ion from a Salt

Add 10 drops $Br_{(aq)}$ + 5 mL $KI_{(aq)}$ & shake. Add 3 mL hexane & shake again

Rxns

$$Br_{2(aq)} + 2\,KI_{(aq)} \rightarrow I_{2(aq)} + 2\,KBr_{(aq)}$$

Observations

Clear soln, add Br. Br makes brown color soln. Both aqueous
Add hexane to make soln nonpolar (hexane nonpolar) & Br is nonpolar, polar KI
Hexane layer ontop b/c less dense than water.
Purple color on top layer, and that means something has reacted Br is brown. Bottom layer is yellow
Iodine I_2 & KBr
Bromine reduced to Bromide.
Iodine oxidized to Iodide.

Add 10 drops $I_{2(aq)}$ + 5 mL $KBr_{(aq)}$ + shake. Add [illegible] shake again.

3 mL hexane & shake again.

$I_2 + KBr \rightarrow$?

No rxn

If bromine strong enough to oxidize iodide then iodide cannot ~~oxidize~~ oxidize bromine.

Observations

Hexane layer would be Clearish purple.

Exercises

1. $CuCO_{3(s)} + \Delta \rightarrow CuO_{(s)} + CO_{2(g)}$ Dissociation

3. $Cl_{2(g)} + 2KI_{(aq)} \rightarrow I_{2(s)} + 2KCl_{(aq)}$ Displacement

5. $Pb(NO_3)_{2(aq)} + K_2SO_{4(aq)} \rightarrow 2KNO_{3(aq)} + PbSO_{4(s)}$ Double displacement

7. $K_2O_{(aq)} + H_2O_{(l)} \rightarrow 2KOH_{(aq)}$ or NR ?

Superconductors, Colloids

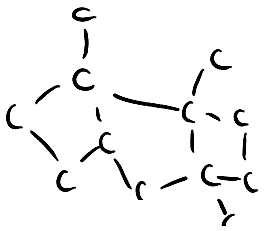
Monday, February 05, 2007
8:57 AM

<u>Superconductors</u> 991-994
<u>Colloids/Nanocrystals</u> 557-559, 992
Self-Assembled Materials } Handouts
Nanomaterials
Silicon 452-456 Ch 11: 45-47, 49-51
Silicates/Silicone 901-906
LEDs 908-959
Liquid Crystals/Polymers 1117-1121 Ch 21 45, 48 Ch 26 91

Diff between intrinsic & extrinsic semiconductor is intrinsic is not doped, extrinsic is.

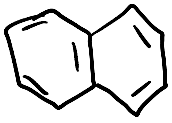
Metals have ~~a small~~ no gap between valence & conduction bands
Semiconductors have a small band gap
Insulators have a large band gap.

<u>Network Solids</u>
Crystal is a structure where it is one big molecule. For instance, diamond. A network of carbon



One huge network of carbon.
Carbon is tetrahedral.

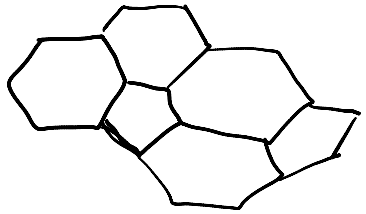
<u>Allotrope</u> – 3 classes of allotropes of carbon. Diamond, graphite, & things called fullerings
Crystalline forms of a material
Graphite has a sheet-like structure.



Weak interactions between the sheets.

So graphite has diff types of bonds. Lower melting pt, easily broken. Alternating double bonds means it can

absorb light, and so it's darker.



Soccer ball pattern for fullerings

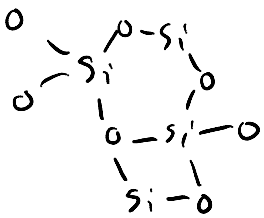
Very small amts are very highly colored. Alternating double bonds gives a very deep purple. All carbons are sp^2 hybridized instead of sp^3 hybridized

SiO_2 vs CO_2

sand, glass, quartz

$O=C=O$

(structure is diff for these (not molecular solids))



Like diamond

One molecule stays in molecular form, other forms a network solid.

You have to break double bonds & form single bonds to make CO_2 a network solid, & they don't want to do that.

SiO_2 double bonds aren't natural. They're weaker than SiO_2 single bonds.

SiO_2 high melting pt

Glass, quartz, <u>doped structures</u>

B_2O_3 labware

K_2O lenses

<u>Si</u> Similar structure to diamond

Semiconductor

We determine if something is a semiconductor by its properties

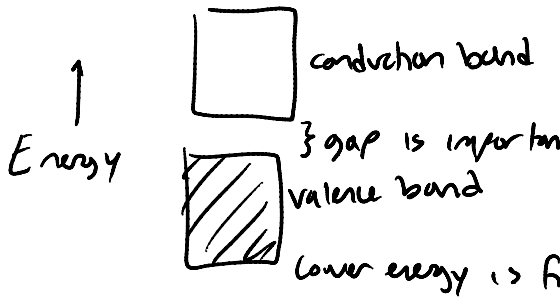
Same for metals & insulators.

Metals (structures that have atoms that share e^-)

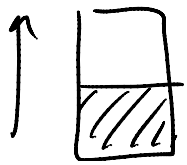
As you add elmts to the structure, you get more molecular

orbitals. Ones in bonding & antibonding overlap. These form a band. The bands formed are <u>valence band</u> or <u>conduction band</u>

bonding antibonding



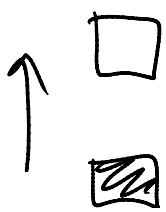
No gap = metal. Small gap = semiconductor. Large gap = insulator



Metal — good conductor b/c e^- can freely move throughout structure.

Semiconductor

At certain cases at room temp, you get a small gap & e^- jump. Silicon is a semiconductor. Small gap.

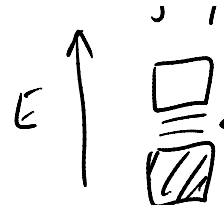


Insulator — Not enough energy to jump. And diamond is a good example.

For a material to conduct, we should be able to move e^- freely throughout the bands.

If you heat the system, the semiconductor conductivity will increase. Metals become worse conductors w/ temp. It decreases w/ a metal b/c it vibrates atoms, more collisions w/ e^- & nuclei, & impedence in free e^-.

Doping is the adding of elements. Take a material & add a small amt of another elmt. Like adding P to Si. Extra valence electrons & more will jump. Create levels:



← levels. Decrease gap. Take insulator & make it a semiconductor. N-dope.

Ga instead of P, has less e^-. Still becomes a better conductor. P-dope. Changes whether you have full shells. Take away full valence shell on bonding square, allow more to jump.

Types of Conductors, Insulators

Tuesday, February 06, 2007
9:01 AM

$$SiO_2 + Mg \rightarrow Si + MgO$$

Eberhard's demo + how you make silicon.

$$Si + 2Mg \rightarrow Mg_2Si$$

$$Mg_2Si + 4HCl \rightarrow SiH_4 + 2MgCl_2$$

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

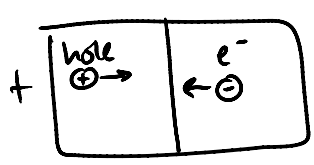
Semiconductors are better conductors when heated.
Metals are better conductors at low temps.

Light - insulators have large band gap & don't absorb visible light. semiconductors absorb some, & metals are dark b/c they have no band gap.

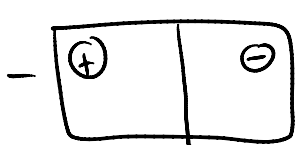
P is doped w/ an element to the left

N is doped w/ an element to the right

PN junction, PN diode (2 types of semiconductors brought close to one another makes current naturally flow)



moves toward p-n junction



Doesn't move

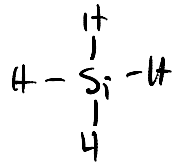
Monomers coupled w/ each other make polymers

<u>Superconductors</u> - Mainly ceramic materials. Certain materials were discovered in the 80s that could be superconductors at high temps.

$YBa_2Cu_3O_7$ is a superconductor
↓
will conduct w/ 0 resistance.

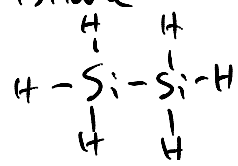
Polymers/Liquid crystals

Monosilane

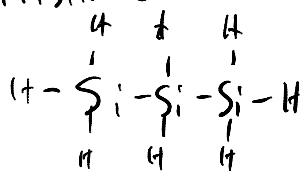


Ligomer is something smaller than a polymer but bigger than a monomer.

Disilane



Trisilane



If you keep adding, you get a polymer.

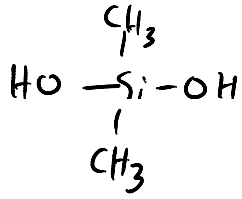
Organosilanes

$$2CH_3Cl + Si \rightarrow (CH_3)_2SiCl_2$$

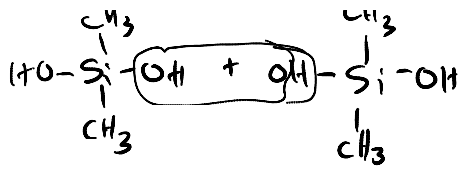
↑ organic groups attached to Si

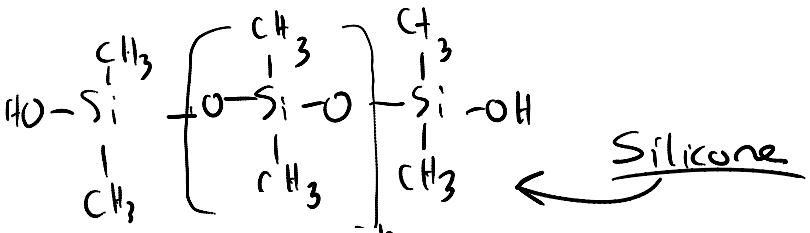
These types of structures react with water

$$(CH_3)_2SiCl_2 + H_2O \rightarrow$$



That creates a situation where this can happen:





n ← # of these guys. And N can be anything from 1 – 1E6 or something.

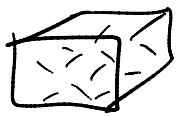
Silicone acts as oils that doesn't degrade under high temps. So it's awesome for cars.

Liquid crystals are not polymers. They're diff. Made from macromolecules

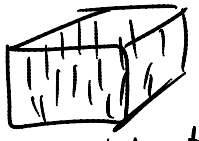
Molecules w/in liquid are not completely disordered. Align w/ themselves. Build things.
Rod-shaped molecules do this.

Ordering in Liquid-Crystal phases

1) Normal liquid
Random

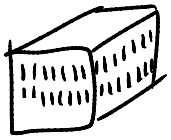


2) Nematic liquid crystals



oriented but not in planes.

3) Smectic A liquid crystals



oriented in planes

4) Smectic C liquid crystals

tilted & in planes & oriented

LCD display is a liquid crystal display.

Liquid crystals can also be thermometers. Change color when you touch them w/ diff temp. Fingerprint analysis, laptop touch pad

laptop touch pad
They exhibit LC behavior at diff temps.

Kevlar is made up of repeating chains (Amides NHCO group
Molecules align a bit and that lets it stop projectiles
Chains can interact + it leads to strength

Polymers

Wednesday, February 07, 2007
9:03 AM

Hydrogen bonding between Kevlar

Addition polymers

Polypropylene 23 billion lbs/yr — bottles, film, packaging, clothing, kitchenware

Polystyrene

Polyvinyl chloride

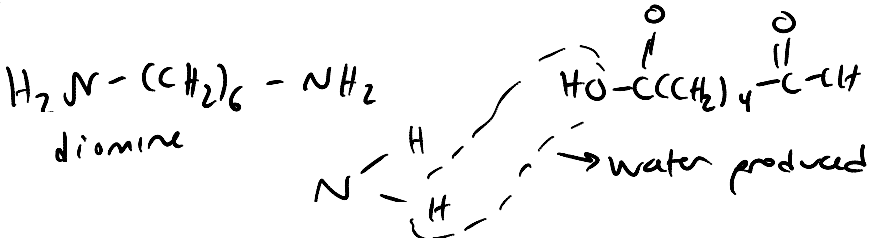
> All come from double bonds, go to single bonds.

Condensation polymers — 2 types of molecules come together

Polyurethane

Polyethylene terephthalate (polyester)

Nylon

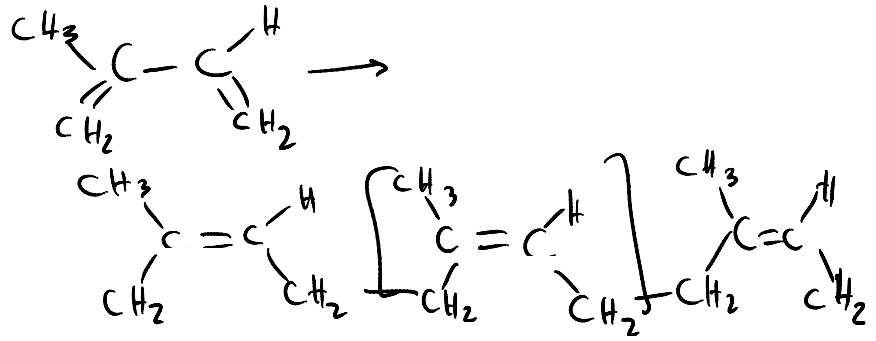


Rubber is another important polymer.

There are naturally occuring polymers.

DNA, rubber, latex, proteins, cotton, skin

Rubber:



At the ends, sometimes polymers grab whatever they can find. The ends don't matter to the whole polymer's properties. This is why grabbing whatever & not completing the octet.

Polyisoprene is the above. You have to add vulcanization (add sulfur) to it to make it cross-link. This changes properties of the polymer. This is how they make tires.

If you covalently attach the polymers w/ the sulfur, it becomes stronger.

DNA is made up of sugar & phosphate. Bases hang off the sugars, and are chemicals that are there for recognition purposes

DNA strands recognize each other through H bonding.
H bond interaction through bases.

Electrons used b/c of their charge & short wavelength

Electron microscope works like a CRT TV

Gold Particles, Light Interactions

Friday, February 09, 2007
8:59 AM

Nano = 10^{-9}

edge of dime is 1mm thick. Slicing edge 1000 times is a micron. Take <u>that</u> & slice it 1000 times, nanometer.

Introduction, works cited due in prelab.

Gold colloids are solid gold but are in tiny pieces suspended in soln.

In the medieval ages, people were making nanoparticles. They didn't know this, but diff metals, concentrations, etc they made colored glass.

On a macroscopic scale, things don't change color b/c they change size. But at a nano scale, they do b/c it changes size & shape & how light interacts.

Quantum Mechanics
Schrodinger Equation
Particle in a Box

Gold soln fed to alphalpha plants & plants reduce Ag^{3+} ions to solid gold, $Ag_{(s)}$.

Use type of spectroscopy to realize what the plants were doing.

Gold particles interact w/ light waves the way a boat interacts w/ water.

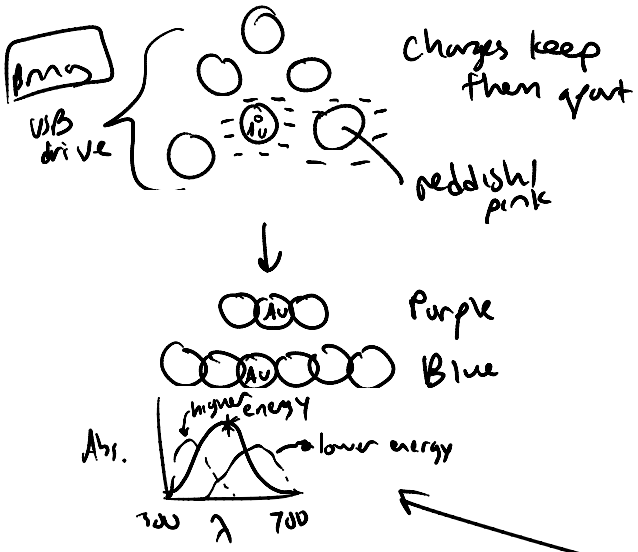
When you change the size & shape, you perceive a diff color & you can track those changes in the visible region of the spectrum. ≈ 320 nm → 670 nm
high energy blue — low energy red

If you see red, everything but red is being absorbed & there will be an absorbance peak in the green area.

Whatever light is absorbed you'll see the complimentary color w/ your eyes.

At purple range (absorbed) you'll see clear.
At red range (absorbed) you'll see green.

Hydrogen tetrachlorate trihydrate + sodium citrate



NanoHUB

Put gold metal in
In solvent → H_2O, refractive index of H_2O = 1.3 ish
Size of particles (change size until you match λ_{max}*

Scattered light

Look for scattered light

Formal reports 7 pages maximum including graphs & pics double spaced.

Graphs should be integrated into text, should not be larger than ½ page.

Past tense passive voice.

Experimental section should be brief. Any modifications made to lab summary sited.

Due week of Feb 19th on Blackboard & TA.

Prelab

Title, Objective, Procedure.

Introd references submitted to TA

References

Book, ACS journal article, Lab manual, Other.

↓

NU Library

→ electronic resources

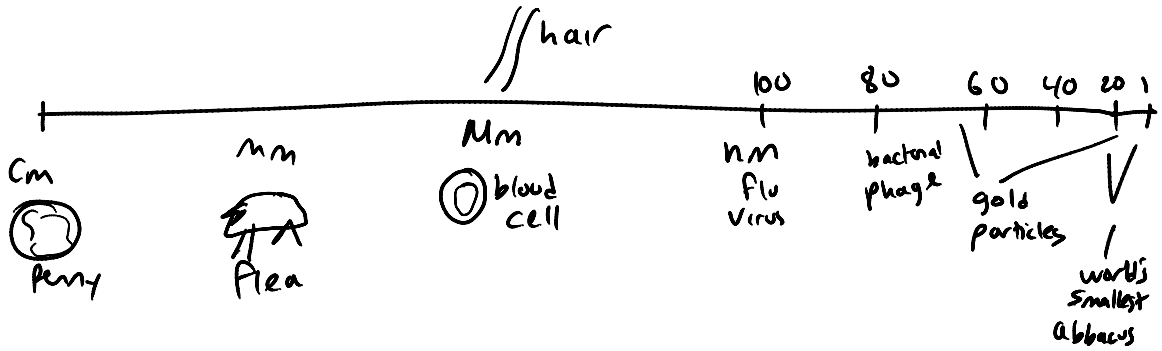
→ ACS American Chemical Society

Use ACS style guide.

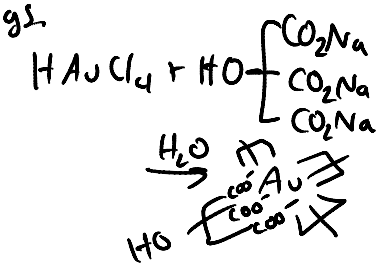
Nanotechnology

Monday, February 12, 2007
9:02 AM

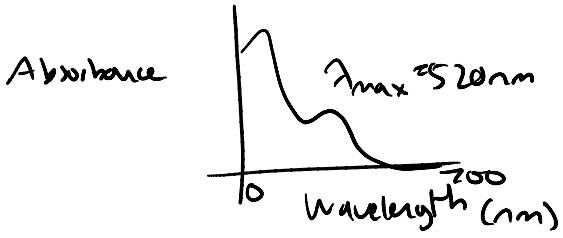
Take gold & shrink it down to 13 nm, changes color.
If you take any material & shrink it down, it forms a new material w/ new properties.



Nanotubes are cousins to fullerings.
Gold nanoparticles form a colloid



The size is much smaller than the wavelength of light



On the interior, surface atoms see below atoms like themselves & atoms on top. Surface diff from bulk.
Many more bulk than surface materials. Majority of atoms in bulk. Shrinking down, ratio of surface-bulk goes up

All diff color silver. Ag is neat b/c if you take a soln of silver particles (yellow in color) you can see silver nanocrystals (colored) & spherical particles break down & become silver Δ's.

By making silver in diff sizes & shape you modulate diff optical properties. Photosynthesis of Silver Prisms.

Composition, size, & shape matter.

100 nm	100 nm	50 nm	90 nm
Nanoprisms	Ag spheres	Ag spheres	Spheres

<u>Tools</u>

Electron microscopes — 1990's developed these

Scanning tunneling Microscopes (IBM in Switzerland Binnings & Rora?)

Atomic Force Microscopes

Scanning Probe Microscopes — Really sharp tip.

Really sharp tip feels atoms on surface (Metal & surface conductor pops electrons from atoms at tip to surface e^-)
You can get this thing for only $10,000.

Limitation → has to be a conducting surface. We can't look at insulators.
Atomic Force Microscope allows us to look at insulators. Bring tip down & measure repulsive interactions. Deflections from tip is monitored as $f(x)$ tip → surface
You can measure the stickiness of a surface too.

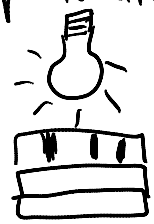
Get a topological map of the surface, & figure out if the atoms are hydrophillic or hydrophobic.
Tips are not as sharp in AFM tips.

If the chemical is reactive, you put chemicals on the tip to manipulate the reactive substance.

Printing tools (electronics)
Computation is a huge industry, making computer chips.

We can make smaller & smaller features.

We can make a mol (6.022 E 23 !) of transistors through photo lithography.



Mask w/ desired pattern
Photo resist, light sensitive / reactive material
Substrate, material to be patterned

If you take the mask away, areas that were irradiated have insoluble layer you can etch.

Transfer info to substrate. Lift polymer

Limit of how far you can go → limit of light wavelength
(smaller & smaller features, cost ↑. Physical limits)

So they tried etching tips but you damage the tips.

<u>Dip Pen Nanolithography.</u>

Deposit materials on a surface. Use surface like a pen & move molecules.

Water collects at point of contact b/c of thermodynamic minimum to move molecules from tip to surface.

Single layer of molecules on a surface to write out stuff w/ them

We use the water droplet as a carrier solvent instead of the inks in your pen.

Richard Feynman's Plenty of Room At The Bottom predicts that nanotechnology will become a reality.

Photolithography is a serial process. We want to print structures in parallel. Take a single pen system & go to printer.

Nanotechnology 2

Tuesday, February 13, 2007
9:05 AM

Top → down chisels bulk materials
Bottom → up breaks down material into almost elemental state & deforms.

You get a soln of particles in a colloid, repulsive charge stabilizes it.

We can determine that the particles do this by looking at them w/ an electron microscope or:

When you add salt to the colloid, particles grow together & eventually fall out of soln, form bulk gold.

Color change from red → blue. Changes wavelength of light, as it grows. Bigger particles scatter wavelength of light.

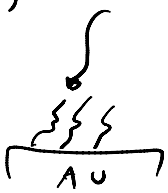
You can come up w/ detection systems based on this principle. DNA detection w/ nanoprobes. You can tack DNA on the surface of a gold particle. You can design things coded w/ anthrax, infectious diseases, etc. When the DNA is recognized, the particles come together & change color.

DNA Litmus Test (Test is almost to the point of cure— you can detect stuff on the spot)

If you heat the new soln, it would turn back to red b/c it breaks apart.

We use e^- or sharp tips to etch and move nanoparticles around.
Dip Pen Nanolithography.
Water condenses at point of contact (from air)
Ink based w/ composition (molecules that react w/ surface)

$CH_3(CH_2)_{17}-SH$



Molecules crystalize on surface. Self-assembled monolayer.

Whole process = surface modification

Octadecanethiol (ODT) - properties of surface change - surface has a lot of organic properties (terminated by an organic compound, slippery nature). Change the tail end & make it a carboxyllic acid. Something that looks more like water won't be hydrophobic like SH, but hydrophillic like OH.

Pip pen lithography lets you modify it on smallest scale

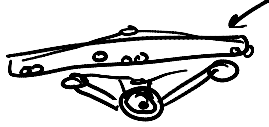
Hydrophillic materials are stickier. White correlates w/ hydrophillic. Blue correlates w/ hydrophobic

4000 yrs ago Quill pen	120 years ago Fountain pen	60 yrs ago Ballpoint pen	20 yrs ago Photolithography
"Quill" 3 yrs ago	"Fountain" 1.5 yrs ago	"Ballpoint" 1 yr ago	engage/disengage tips based on heating 6 mo. ago

You can print on the nanoscopic view (you can pattern anything you want)

One chip could screen for every disease out there can do same thing w/ proteins

You can etch the Enterprise !!!



on nano-scale!

$A + B \xrightarrow{?} C$

$NO_{2(g)} + NO_{2(g)} \rightleftharpoons N_2O_4$

brown colorless

Does the amt of NO_2 & N_2O_4 change as a function of external conditions?

As we heat it, it gets darker meaning more NO_2 forms. If you cool it down, turns clear meaning more N_2O_4.

$2H_2 + O_2 \rightarrow 2H_2O$

$2CaO \rightarrow 2Ca + O_2$

Calcium wants to be Ca^{2+}. Wants to be oxidized. So $CaO \rightarrow Ca + O_2$ will favor Calcium oxide at equilibrium. So!

$$2CaO \rightleftharpoons 2Ca + O_2$$

Hydrogen & Oxygen will react violently to form water.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

Activation energy has to start a reaction. High activation energy means it needs a real kick to get started. Some bonds are harder to break than others.

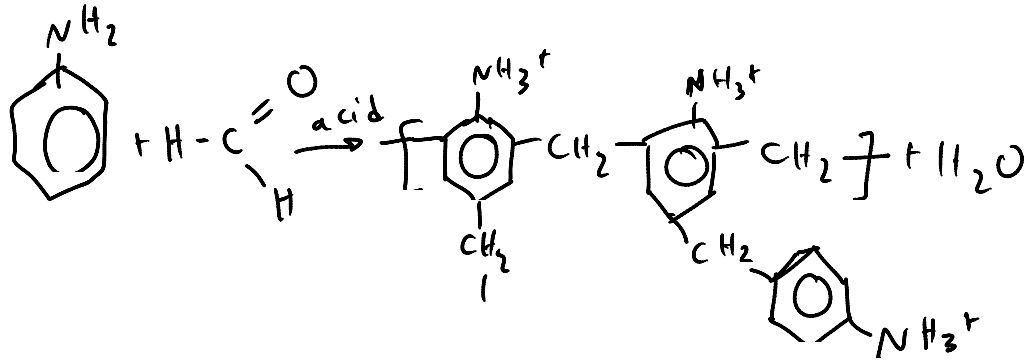
$\langle O = O \rangle$ is hard to break.

But at equilibrium, you're going to see a lot of product.

Learn how to use concept of chemical equilib & how it works. How to get to equilib, will it stay in equilib? Thermodynamics & kinetics.

K value

Wednesday, February 14, 2007
8:59 AM

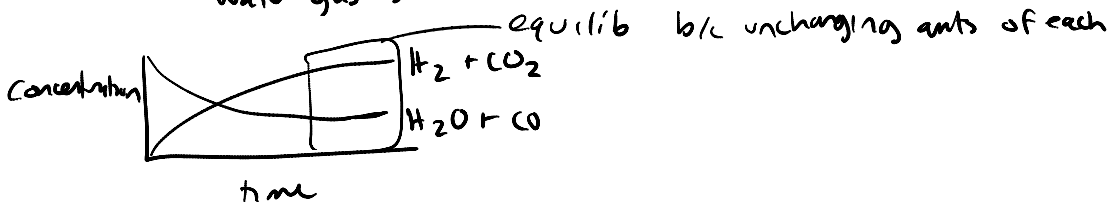


Just b/c a rxn is favored in equilib doesn't mean there's enough activation energy to get it to go.

1st have to figure out if you can get rxns to go fast enough to get product (thermodynamically possible)

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_2{}_{(g)} + CO_{2(g)}$$

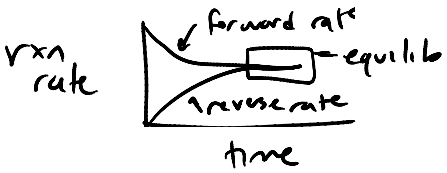
water-gas shift rxn



Syn-gas is CO & H_2. People used to rely a lot on these.

$$CO + H_2 \longrightarrow C_xH_y + H_2O$$

hydrocarbons



rate of rxn dependent on amt of materials

$H_2 + N_2 \rightleftharpoons NH_3$ ← 20 million tons/yr

H_2 & N_2 do not react by themselves.

N_2 has a really strong bond.
We want to be able to predict what conditions it'll break.

Lesson: do not approach alien blood.

Rm temp, no rxn. At equilib, we have rxn that doesn't favor products. Large activation energy.

So we heat it. What happens?

$$jA + kB \rightleftharpoons lC + mD$$

$$K = \boxed{\frac{[C]^l[D]^m}{[A]^j[B]^k}} = \boxed{\frac{\text{products}}{\text{reactants}}}$$

Balanced equation 1st.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

[ ] = concentration at equilib.

associated w/ rxn as written & as balanced.

Multiplying eqn by 2 means K^2
Reversing eqn means $\frac{1}{K}$

Coordination Complex

Friday, February 16, 2007
8:59 AM

Chemical equilibrium is dynamic. Reactants form products, products form reactants

Temperature, Pressure add stressor therefore change R & P. Remove R or P, add R or P

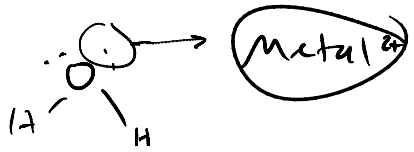
Change Volume, Concentration... pH... stuff like that.

Coordination complex

Consists of a transition metal ion & ligands

Ligands are things that attach other things. Neutral molecules or anions. Water could be a ligand but that does not account for all ligands.

E^- in a coordinate covalent bond, both e^- come from the ligand.



Distance between D orbitals is smaller, making color.

NaCl in soln is clear

$CuSO_4$ in soln is blue.

Transition metals tend to make color complexes

If you change the ligands, you change energy of D orbitals & therefore color.

You can tell, they, if you have Co^+Cl vs $Co + H_2O$.

Complex 1 ⇌ complex 2
pink blue

Add acid, & soln is pink. Adding acid has changed

equilib so you have small amt complex 2 & large amt complex 1.

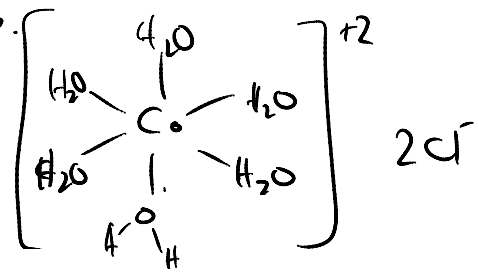
If you saw purple, equal amts of complex 1 & 2.

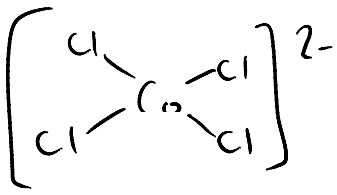
1st part of lab, just observe Cu & Co.
2nd part, disrupt equilib & observe

$[Cu(H_2O)_6]Cl_2$ Hexaaquacobalt (II) Chloride,

octahedral shape.

perfect octahedron





overall charge can be +, −, or 0 depending on oxidation state of metal.

Depending on neutral/neg. charged ligands, charge on complex can change.

Complex Ion	Color
Stuff	
Cobalt	
Copper	
Not Chromium/nickel	

All of part A
1st half of B (equilibria of Co complexes)

2nd week
Equilibria of Cu complexes

Diff d orbitals of a transition metal ion have diff energies when that ion is surrounded by ligands.

When light of a particular λ corresponds to the spacing btw 2 energy levels, an e^- is raised to that energy level & light of that λ is absorbed

Dynamic equilibrium

Products making reactants & vice versa at equal rates.

Forward:

$[Fe(H_2O)_6]^{3+} + SCN^- \rightarrow [Fe(H_2O)_6SN]^{2+} + H_2O$

Reverse:

$[Fe(H_2O)_5SN]^{2+} + H_2O \rightarrow [Fe(H_2O)_6]^{3+} + SCN^-$

Equilib: $\rightleftharpoons$

Part A: Color of Coordination Cmpds (Complex ions)

1. Cobalt (II) Complex ions
2. Copper (II) Complex ions & coordination cmpds
3. Summary of colors

Part B: Shifting Chemical Equilibria

1. Cobalt (II) Equilibria
2. Copper (II) Equilibria.

Concentrated acids & bases used. Goggles & gloves.

Chem Rxn, Equilib State

Monday, February 19, 2007
9:00 AM

Chemical rxns, equilibrium state

1st have to know if rxn is possible.
2nd have to know if it will occur in a reasonable period of time.

We can relate products & reactants

There are strong bonds in some reactants that have to be broken, requires activation energy.

At equilib & 300°C

$[N_2] = .25$ mol/L
$[H_2] = .15$ mol/L
$[NH_3] = .090$ mol/L

$N_{2(g)} + 3H_{2(g)} = 2NH_{3(g)}$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} = 9.6 \ L^2/mol^2$$

units depend on coefficients

9.6, or 10^{45}, or 10^{-32} tells you whether it favors reactants or products

If $K > 1$, products favored
If $K < 1$, reactants favored
If $K = 0$, NR
If $K = 1$, equal amts of reactants & products.

At 127°C,

$[NH_3] = 3.1E-2$
$[N_2] = 8.5E-1$
$[H_2] = 3.1E-3$

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = 3.8E4$$

There's 1 equilib constant for a given rxn at each temp. This tells us it greatly favors products when temp is lower. This is a rxn where if you lower temp, you get more product

In theory, you could run it at a really low temp, but the lower you go, the slower the rxn goes. You want to still get to equilib.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Initially 1 M $[H_2]$
1 M $[N_2]$
0 M $[NH_3]$ hasn't been created yet

Finally .921 M $[N_2]$
.963 M $[H_2]$
.157 M $[NH_3]$
6.02 E-2 = Keq

Immediately, you know it was a higher temp. You actually know it's higher than 300°C, b/c it's lower Keq.

Initially 1 M $[NH_3]$
0 M $[H_2]$
0 M $[N_2]$

We work under conditions where we get to equilib

Finally .399 M $[N_2]$
1.197 M $[H_2]$
.203 M $[NH_3]$
Keq = 6.02 E -2

So we have to be working at same temp. [ ] not the same.

This is equilib position. There are ∞ equilib position systems. 1 equilib constant.

Solids & liquids (pure) not included in equilib constant
If you add more reactants, you still get same Keq at one temp.

How do we describe K for gases in terms of pressure?

$$PV = nRT$$
$$P = \left(\frac{n}{V}\right)RT$$
$$P = CRT$$ Partial Pressure
$$C = \frac{n}{V}$$, C = molar concentration.

$$K = \frac{[NH_3]^2}{\ } = \frac{C_{NH_3}^{\ 2}}{\ }$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}^2}{C_{N_2} C_{H_2}^3}$$

$$C = \frac{P}{RT}$$

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} \qquad \frac{\left(\frac{P_{NH_3}}{RT}\right)^2}{\left(\frac{P_{N_2}}{RT}\right)\left(\frac{P_{H_2}}{RT}\right)^3} = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}(RT)^2$$

So $K_{eq} = K_p(RT)^2$

When # moles balanced equation total on products = reactants. $3X + 3Y \rightarrow 3XY$

Coefficients in balanced eqn determine K_{eq} in terms of K_p.

$$H_2 + F_2 \rightleftharpoons 2HF$$

This'll work b/c # moles reactants = # moles products.

$$K_p = K_c(RT)^{\Delta n} \leftarrow \Sigma \text{coefficients products} - \Sigma \text{coefficients reactants}$$

Anytime $\Delta n \neq 0$, $K_p \neq K_c$

Synthesis of NH_3 from N_2 & H_2 at 472°C has an equilib constant K_c of .105. K_p for this rxn?

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$\Delta n = -2$ $\qquad 2-(3+1) = -2$

$K_c = K_p(RT)^{-2}$ $\qquad R = .821$, $T = 472°C$,

$.105(.821 \cdot 472)^2 = K_p$ $\qquad K_c = .105$

$$CaCO_{3(s)} \overset{\Delta}{\rightleftharpoons} CaO_{(s)} + CO_{2(g)}$$

$K = \frac{[CO_2]\cancel{[CaO]}}{\cancel{[CaCO_3]}}$ Solids don't get included b/c The concentration is a constant

$K = [CO_2]$

$3Fe + 4H_2O_{(g)} \rightarrow Fe_3O_4 + 4H_2$ $\qquad$ 1000°C

$$K_c = \frac{[H_2]^4}{[H_2O]^4}$$

At lower temp, $H_2O = l$

$$K_c = [H_2]^4$$

Reaction quotient

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3}$$ Initial Concentrations!

If $Q = K$, system is at equilib
If $Q > K$, products get consumed & go to reactants' side.
If $Q < K$, too many reactants & to get to equilib form more products

Q is a great predictor

Keq, LeChatlier

Tuesday, February 20, 2007
8:56 AM

Predictive power comes from Keq.

As you increase temp, it effects Keq.
Q = initial concentration equilib constant.
Compare Q to K

1. Write balanced eqn, w/ phases
2. Write equilib expression
3. List initial concentrations
4. Calculate Q, determine which way the shift to equilib will be.
5. Define change needed to reach equilib, apply changes to initial concentrations to find equilib concentrations
6. Substitute equilib concentrations. Calculate unknown.
7. check K vs. equilib concentration.

eqn: $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

water-gas shift rxn
1 mol CO
1 mol H_2O in 50L flask.
$K_c = .58$ at 1000°C

expression: $K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$

$.58 =$

concentrations: $C = \frac{mol}{V} = \frac{1 \text{ mol CO}}{50 \text{ L flask}} = \text{mol } H_2O = .02 \text{ M } [CO]$

$[CO_2] = [H_2] = 0$ b/c nothing yet.

Q: We know we aren't at equilib & so we have to go from reactants' side to products' side.

	Initial	Change	Equilibrium
$[CO] = [H_2O]$	$= .02$	$-x$	$.02 - x$
$[CO_2] = [H_2]$	$= 0$	$+x$	x

ICE chart

Equilib/unknown: $K = .58 = \frac{[CO_2]_{eq}[H_2]_{eq}}{[CO]_{eq}[H_2O]_{eq}} = \frac{(x)(x)}{(.02+x)(.02-x)} = \frac{x^2}{(.02-x)^2}$

$$\pm .76 = \frac{x}{.02-x}$$

$x = .0086$
$x = \cancel{-.0086}$ no neg concentration.

Plug into <u>Equilibrium</u>

$$.02 - .0086 = .0114 = [H_2O]_{eq}$$

<u>LeChatelier's Principle</u>

Allows us to predict changes that occur in a disturbed equilib sys.

<u>Häber Process</u>

$N_{2(g)} + H_{2(g)} \rightleftharpoons NH_{3(s)}$ Temp ↑, Keq ↓

Very important to shift to right

Häber noted pressure favors equilib concentration of NH_3

If a change is imposed on a sys @ equilib, position of equilib will shift to reduce change.

$CaCO_{3(g)} \rightleftharpoons CO_{2(g)} + CaO_{(s)}$

↑ Add ↑, get more $CaCO_3$

Add $CaCO_3$, get more product. $Q > K$, shift to left.
$Q < K$, shift to right

Add anything that changes Q (more CO_2), reaction will respond. But $CaCO_3$ & CaO don't enter into Q.

Pressure change

$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Add H_2 or N_2, drive sys toward product.
Add NH_3, drive sys toward reactants.
Add inert gas, no effect
Change overall pressure, but not equilib b/c partial pressures don't change.
Half the volume, change [ ] & p.p.'s ∴ change Q.

Remove NH_3, drive toward product.

Increase volume, move toward side w/ most gas molecules.
Decrease, Drive from right to left. Larger # gas molecules → smaller #.

Exothermic rxn, heat on product side. If you want product, don't heat then up.
Endothermic, heat on reactant side.

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H = 58$ kJ/mol. Endothermic, so heat will favor reactants. Heat it & will drive toward product.

Add N_2O_4, get more product.
Inc. volume, more product.
Half volume, more reactants.

$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ $K = 1.6E-5$ mol/L (M)
initial $[NOCl] = .5M$

$$\frac{[NO]^2[Cl_2]}{[NOCl]^2} = 1.6E-5 \text{ M}$$

$[NOCl]_0 = .5M$
$[NO]_0 = [Cl_2]_0 = 0$

So we don't need to calculate Q. We know rxn →.

$2NOCl \rightarrow 2NO + Cl_2$
$-2x \quad 2x \quad x$

Initial	Change	Equilib
$[NOCl]$ .5M	$-2x$	$.5-2x$
$[NO] = 0$	$2x$	$2x$
$[Cl_2] = 0$	x	x

$$\frac{(2x)^2(x)}{(.50-2x)^2} = 1.6E-5$$ Solve for x

pretty small equilib constant, so reactants aren't favored. Means change is small. get rid of 2x on bottom.

$$\frac{4x^3}{(.5)^2} = 1.6E-5$$

$$x^3 = \frac{(1.6E-5)(.5)^2}{4}$$

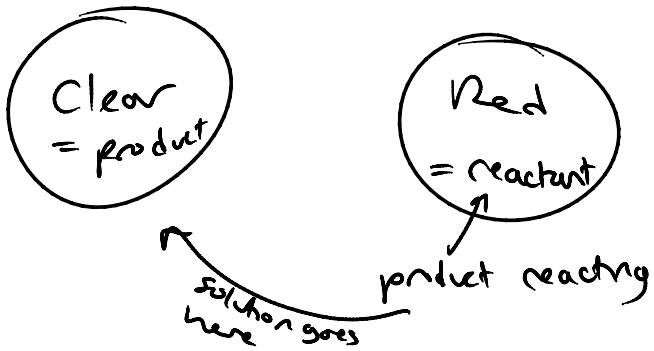
$$x = \#$$

Plug # back in.

Laws of Thermodynamics

Wednesday, February 21, 2007
9:05 AM

If you add something the product that reacts w/ product, you get more product b/c you're using some of it up during the rxn.



Change in pressure <u>does</u> not <u>change</u> the equilib constant.

Laws of Thermodynamics.

1st In any process, spontaneous or nonspontaneous, total energy of a system & its surroundings is constant

2nd In any spontaneous process, total entropy of a system & its surroundings increases

Spontaneous process is a possible process.

3rd Entropy of a perfect crystal at 0K is 0.

ΔS_{sys} change in entropy

$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr}$

ΔS for spontaneous process is (+)

DNA Double helix

Entropy of system goes down when it forms.

However, the entropy of everything else increases.

This is a spontaneous process b/c S_{surr} ↑ while

$S_{sys} \downarrow$.

$$\Delta S_{uni} = \underset{(-)}{\Delta S_{sys}} + \underset{(+)}{\Delta S_{surr}}$$

The entropy change must be positive for the universe for the process to be spontaneous.

You can't get back to an ordered state b/c of probability – there is only 1 ordered state, and very many disordered states. The probability of getting the ordered state is slim. Alex is a testimonial to that. So nature favors disorder.

Phase Changes, Gibbs Free Energy

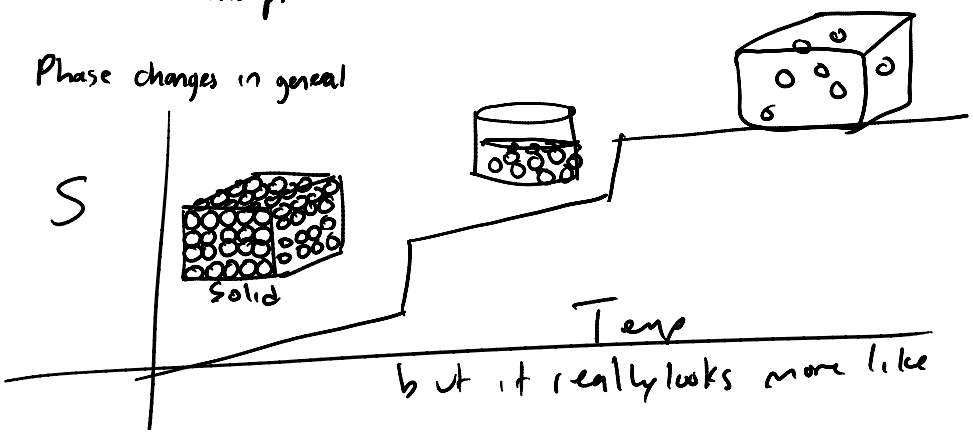
Thursday, February 22, 2007
8:58 AM

$H_2O_{(l)} \rightarrow H_2O_{(g)}$ 1atm, 1mol $H_2O_{(l)}$, 18mL; 1mol $H_2O_{(g)}$, 31L

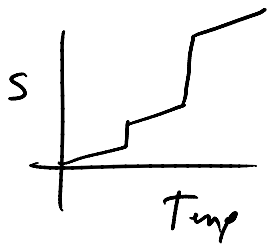
ΔS_{sys} has (+) sign

endothermic process. Takes heat in.

Phase changes in general



but it really looks more like



$$S \underset{\Delta S<0}{\overset{\Delta S>0}{\rightleftharpoons}} L \underset{\Delta S<0}{\overset{\Delta S>0}{\rightleftharpoons}} G$$

As ΔS_{sys} has (+) sign b/c sys gets more disordered, ΔS_{surr} has (-) sign b/c one must drive rxn to go from $L \rightarrow G$ or $G \rightarrow L$ under diff situations. Can't be spontaneously going back, so ΔS_{surr} has to be (-).

Temperature plays a key role.

Heat flows out of surroundings & into sys to decrease entropy. This is b/c it's an endothermic process.

ΔS_{sys} or ΔS_{surr} controls ΔS_{uni}

ΔS_{surr} controlled by heat flow

Higher the temp of the surroundings, less significant impact of heat flow is

ΔH_{sys} is (+) , ΔS_{surr} is (-).

ΔS_{surr} exothermic : $\frac{+q\,(J)}{Temp\,(K)}$

endothermic : $\frac{-q\,(J)}{Temp\,(K)}$

$\Delta S_{surr} = \frac{-\Delta H}{T}$, ΔH for rxn. If ΔS_{sys} is (-), ΔS_{surr} is (+)

Constant T & P

Water melting

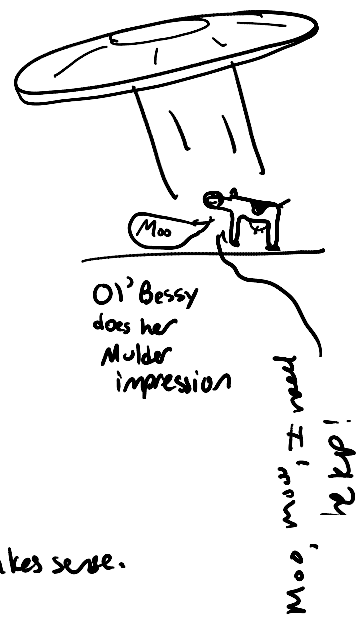
ΔS_{sys} is (+)

ΔS_{surr} is (-) when does ΔS_{sys} win?

At high temp.

$\Delta S_{sys} \equiv$ inherent for physical state

$\Delta S_{surr} = \frac{-\Delta H}{T}$ # gets smaller at higher T.



25°C

$H^+ + OH^- \rightarrow H_2O$ $\Delta H = -58$ kJ/mol

$\frac{(58\,kJ)(1000\,J)}{298\,K}$ (+) ΔS_{surr}

so (-) ΔS_{sys}. More ordered. Makes sense.

Gibb's Free Energy

$$\Delta G = \Delta H - T\Delta S_{sys}$$

$\Delta S_{uni} = \frac{-\Delta G}{T}$ (-)ΔG means spontaneous process

$\Delta G = \Delta H - T\Delta S_{sys}$

$\frac{-\Delta G}{T} = \frac{-\Delta H}{T} + \Delta S_{sys}$

$\frac{-\Delta G}{T} = \Delta S_{surr} + \Delta S_{sys}$

$\Delta S_{uni} = \Delta S_{surr} + \Delta S_{sys}$

$\frac{-\Delta G}{T} = \Delta S_{uni}$ ✓ It works

$nCH_2 = CH_2 \rightarrow (CH_2 - CH_2)_n$ addition polymerization

ΔS_{sys} (-).

$\Delta G = \Delta H - (-T\Delta S) = \Delta H + T\Delta S$

must be (-) b/c it is spontaneous.

When ΔH is (+) & ΔS is (-) then ΔG will be (+) & it

When ΔH is (+) & ΔS is (-), the ΔG will be (+) & it will always be nonspont.

When ΔH is (-) & ΔS is (+), the ΔG will be (-) & it will always be spont

When ΔH is (-) & ΔS is (-), the ΔG will be spont if T is low. Will be nonspont if T is high. Exothermic.

When ΔH is (+) & ΔS is (+), the ΔG will be spont if T is high. Will be nonspont if T is low. Endothermic Ice melting.

Enthalpically driven vs. Entropically driven.
ΔH is (-) ΔH is either (+) or very small.

Endothermic can never be enthalpically driven. Ice melting is entropically driven.

Level of predictability.

I ♡ CHEESE

Gibbs Free Energy, Entropy

Monday, February 26, 2007
8:59 AM

Gibb's Free energy was a restatement of the 2nd law of Thermodynamics

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

You can make predictions w/ this.
(−) is spont, ΔS is (+)
(+) is non spont

Quantitative Predictions
Calculate how much Ag_2O must be heated (to what T) to decompose Ag_2O to O_2 gas & Ag metal.

$Ag_2O \rightarrow 2Ag + \frac{1}{2}O_2$

$\Delta H = 62.1\ kJ$
$\Delta S = 132.7\ J/K$

Endothermic process, so entropically driven. Must be heated to work.

$0 = \Delta H - T\Delta S$
$T\Delta S = \Delta H$
$T = \frac{62.1\ kJ\left(\frac{1000\ J}{1\ kJ}\right)}{132.7\ J/K} = 468\ K$ Anything ↑ 468 K will be spont.

$Fe_2O_{3(s)} + 3H_{2(g)} \rightarrow 2Fe_{(s)} + 3H_2O_{(g)}$

$\Delta H° = 98.8\ kJ$
$\Delta S° = 141.5\ J/K$

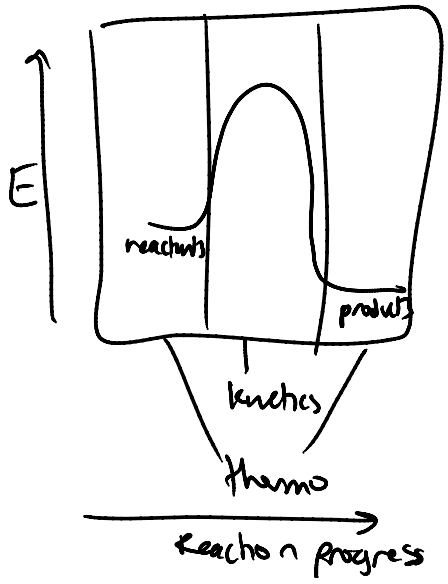
$\Delta G = \Delta H - T\Delta S$
$\Delta G = 98.8E3\ J - (298\ K)(141.5\ J/K)$ given
$\Delta G = +56.6\ kJ$, not even close to spontaneous.
Have to calculate T to make it so.
It will be spont when 298 is way higher.

$0 = 98.8E3\ J - T(141.5\ J/K)$
$T = \frac{98.8E3\ J}{141.5\ J/K}$
$T = 698\ K$ any temp above this makes spont process

$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + Fe$

Fe_2O_3 $\Delta H = -824\ kJ/mol$ $S = +87.4\ J/mol \cdot K$
Al_2O_3 $\Delta H = -1673\ kJ/mol$ $S = +50.92\ J/mol \cdot K$
$\Delta H°_{298} = -849\ kJ/mol$ enthalpically driven
$\Delta S° = -36.48\ J/mol \cdot K$

free energy change at 298K = −838 kJ/mol
If you reverse it, it's pos. so it shouldn't go.
Eberhard's demo



Entropy change

$I_{2(s)} \rightarrow I_{2(g)}$	This is (+).	
$KNO_{3(s)} \rightarrow KNO_{3(aq)}$	This is (+)	
$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$	(−)	ordered solid
$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$	(−)	4 molecules → 2
$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$	Can't tell w/out values	
$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$	(−)	ordered solid

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ Entropically or enthalpically given.
As written, (+) entropy change.

N_2O_4 S° 304.2 J/K·mol This has a greater value b/c it's a more complex molecule.
NO_2 S° 240 J/K·mol ← This is a smaller molecule.

However, there are more NO_2's than N_2O_4's, &
$2(240) > 304.2$

$\Delta S^\circ_{rxn} = \Delta S_{prod} - \Delta S_{reac}$
$\Delta S^\circ_{rxn} = 480 - 304.2 = +175.8$ J/K·mol

$H_2O_{(l)}$ has a really low S° value b/c of H bonding keeps order.

$H_2O(l)$ [illegible]

$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ Combustion rxn.

Spontaneous?

Need to know ΔG values. $\Delta G_{prod} - \Delta G_{reactants}$.

<u>OR</u> Find ΔH & ΔS. Find ΔG

<u>OR</u> Find related rxns.

$2CH_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{(g)} + 4H_2O_{(g)}$ ΔG° -1088 kJ

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$ -801 kJ

Flip one, mult, add, & get ΔG°

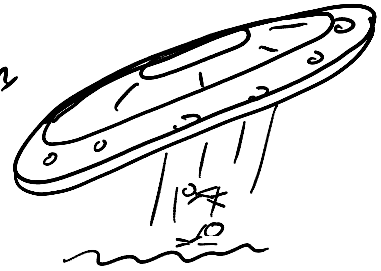
Gibbs Free Energy, Hess's Law

Tuesday, February 27, 2007
9:01 AM

1a/ 33, 37, 39, 43, 47, 53, 63, 69, 74, 79, 84, 88, 89

ΔG tells us the driving force for a rxn, and the spontaneity. Can be calculated w/ Hess' Law, directly calculating $\Delta G_{prod} - \Delta G_{reactants}$, or $\Delta H - T\Delta S$

Hess's Law takes 2 eqns, rearranges them, & adds together to get ΔG°

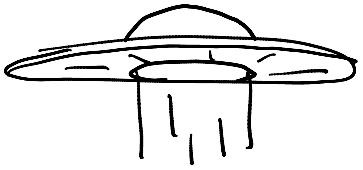


$\Delta G_{rxn} = \Sigma n_p \Delta G_f^\circ{}_{prod} - \Sigma n_r \Delta G^\circ_{reac}$

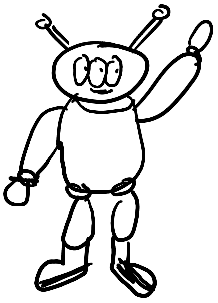
$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(l)}$

$\Delta G^\circ = (4\text{ mol } 86.6\text{ kJ/mol NO}) + 6\text{ mol}(-237.2\text{ kJ/mol } H_2O) - (4\text{ mol})(-16.5\text{ kJ/mol } NH_3) + 5\text{ mol}(0\text{ kJ/mol } O_2)$

elmts in standard states, ΔG° of formation is 0



ΔG_f° is change in free energy that will occur if standard states are added



Convert reactants all the way to products → ΔG°.
In the lab, we can't do this b/c you start w/ diff concentrations, temps, & pressures.

If you change the temp & pressure of rxn, you change the rxn (where it goes)

$\Delta G = \Delta G^\circ + RT\ln Q$

- ΔG: any conditions
- ΔG°: standard set of conditions
- $RT\ln Q$: equilib expression w/ concentration at start of experiment

Q is rxn quotient

We can calculate ΔG° for each rxn we're interested in. $RT\ln Q$ will give us correction term.

$\Delta G^\circ = -33.5$

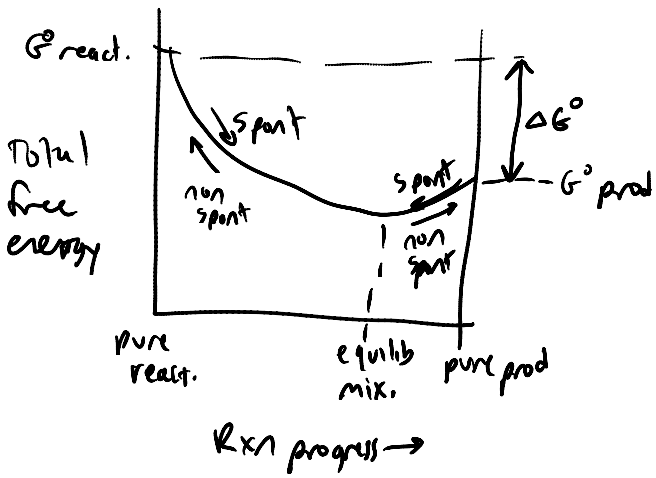
$N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta G^\circ = -33\ kJ$

1 atm N_2, 3 atm H_2, .020 atm NH_3
.01 atm N_2 .03 Amt H_2,

$$Q_p = \frac{(.020)^2}{(1)(3^2)} = 1.5E-5$$

$$\Delta G = (-33E3) + (8.3/k)(298)\ln(1.5E-5)$$
$$\Delta G = -60.5\ kJ$$

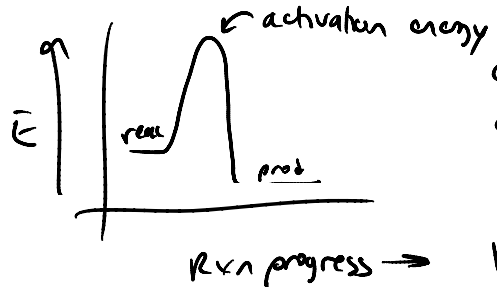
You use a diff R value per Q_p + Q_c



once you get to equilib, $G = 0$

$0 = \Delta G^\circ + RT\ln Q$
$-\Delta G^\circ = RT\ln Q$ at equilib
$\Delta G^\circ = -RT\ln K$
Now we can calculate K.

If it goes to equilib, + its activation energy is reasonable, then the ΔG will tell what direction it will lean.



catalysts lower activation energy w/o changing pos of react. + prod.

Heating breaks up bonds + might help. It will change K. Change relative positions, though.

A catalyst interacts w/ reactants to stretch + weaken bonds.

Demo – H_2O_2 goes to H_2 + O_2. Thermodynamically unstable, Spontaneous → Meaning large activation barrier keeps it from going right away.
Add catalyst + see what happens

Free Energy, Nuclear Rxns

Wednesday, February 28, 2007
9:04 AM

You can calculate ΔG for any conditions as long as you had ΔG°. ΔG° for a rxn is taking all reactants & converting them all to products. We don't really do this.

At equilib, $\Delta G = 0$

$0 = \Delta G^\circ + RT \ln Q$ ← at equilib, $Q = K$

$-RT \ln K = \Delta G^\circ$

Now we can calculate K w/ ΔG° temp & R.

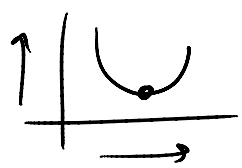
Enormous equilib K or really small K have been tabulated w/ calculation, not rxn. This is why $-RT\ln K = \Delta G^\circ$ is really important

$\Delta G^\circ < 0$, then it is spont. Will go to prod, & so $K > 1$.

$\Delta G^\circ > 0$, then it is nonspont. Will favor reactants, so $K < 1$

If you know RT & K, you can find ΔG°.

At equilib, ΔG is 0. So it's uphill both ways & forward & reverse are nonspont.



$N_2 + 3H_2 \rightleftharpoons 2NH_3$

ΔG° 0 0 −16.5 kJ/mol

$\Delta G^\circ = 2\text{ mol}(-16.5\text{ kJ/mol}) = -33.0\text{ kJ}$

$\Delta G^\circ = -RT\ln K$

At 25° $\ln K = \frac{-(-33E3\text{ J})}{(8.3)(298\text{ K})}$

$K = 6E5$ This is K_p

$K_p = K_c RT^{\Delta n}$ (R is .0821)

b/c $K_c = K_p RT^{-\Delta n}$

ΔG°_f Mercury at 25°C is 31.85 kJ/mol. Vapor pressure of mercury at 25°C?

$K_p = P_{Hg}$ b/c pure liquid not in eqn.

$\ln K_p = \frac{\Delta G^\circ}{RT} = \frac{-31.85E3\ J}{(8.314)(298K)} =$, $K_p = 2.6E^{-6}$

this is pretty high, and that's why it's volatile.

As T↑, K↑ endo. As T↑, K↓ exo.

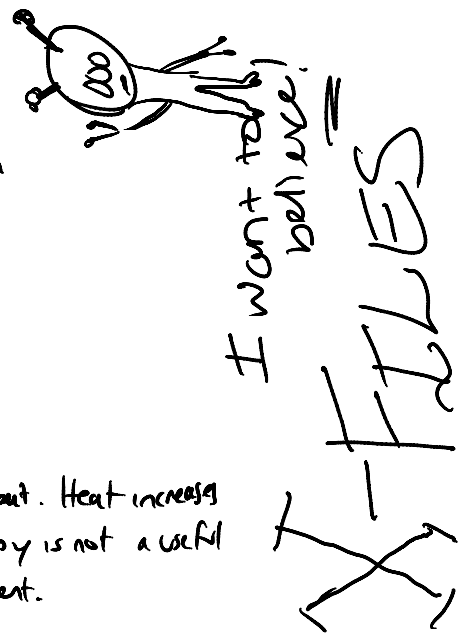
$\Delta G^\circ = -RT\ln K = \Delta H^\circ - T\Delta S^\circ$

$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{T\Delta S^\circ}{RT}$

$\ln K = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$

2 variables here – K & T, so you get a linear graph

I ♡ Keisha!



How does W relate to ΔG?

Max theoretical work is ΔG.

$W_{max} = \Delta G$

We can never get to W_{max}, though.

As you do work, you lose energy to heat. Heat increases entropy of the environment. And entropy is not a useful form of energy – there's no function component.

Thermal energy increases entropy of the surroundings.
1st law – the best one can do w/ this process is break even.

Calculate ΔG° for

$CO + Cl_2 \rightarrow COCl_2$ $K = 5.3E9$, 373 K

$\Delta G = \Delta G^\circ + RT\ln Q$

At equilib $\Delta G = 0$

$\Delta G^\circ = -RT\ln K$

$\Delta G^\circ = (-8.314)(373K)\ln(5.3E9)$

$\Delta G^\circ = -69{,}400\ J$ $\underbrace{-69.4\ kJ}_{\text{Max work}}$

It's spontaneous process. If ΔG° was >0, most work you could get out is 0 b/c it's a nonspont process.

Nuclear rxns, nuclear chemistry

Radioactive materials, radioactive dating, power & other operation of

Radioactive materials, radioactive dating, power & other generation of stuff. Homer Simpson works at a Nuc power plant.

$^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}He$

↑ alpha particle
α

$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}e$

↑ beta particle (electron)
β

$^{99m}_{43}Tc \rightarrow ^{99}_{43}Tc + ^{0}_{0}\gamma$

↑ high energy radiation, gamma ray (effectively an x-ray)

lead blocks radioactive particles.
goes through glass

The Los Alamos sample is no longer radioactive. It's all decayed now. Nuclear radiuss is unstable.

There's radioactive radon in the air in dust particles.

Nuclear Rxns

Monday, March 05, 2007
8:58 AM

Nuclear Rxn

Fundamentally, rxn occurs in nucleus. No molecules reacting. You can have nuc. rxns occurring in molecules, but actual rxn occurs in nucleus. Radioactive sugar leads to labelling.

Radioactive material is constantly decaying, so we're constantly losing radioactive material.

α $^{4}_{2}He$

β $^{0}_{-1}e$

positron $^{0}_{+1}e$

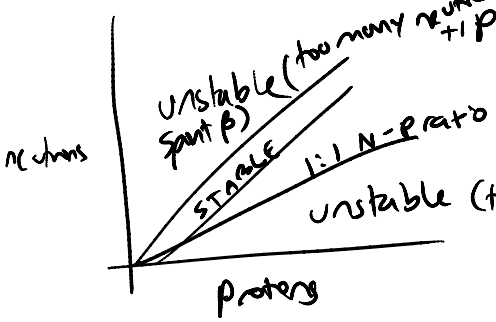
annihilation $^{0}_{-1}e + ^{0}_{+1}e \rightarrow ^{0}_{0}\gamma$

γ $^{0}_{0}\gamma$ gamma

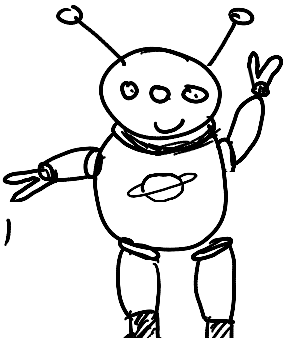
electron capture $^{0}_{-1}e + ^{40}_{19}K \rightarrow ^{40}_{18}Ar$

21 neutrons, 19 protons — 22 neutrons, 18 protons — proton converted to neutron.

$^{1}_{+1}p + ^{0}_{-1}e \rightarrow ^{1}_{0}n$



β particle emission	Decrease in N-P ratio
Positron	Inc.
e^- capture	Inc
α	Inc
γ	Nada
Spont. fission	Nein



Halflife is time required for half of material to go through half of decay

Halflife is time required for half of material to go through half of decay

Uranium has a halflife of 4 billion years.
Some materials have haflives of seconds.

If we know how old something is by halflives, then it's important to know this.

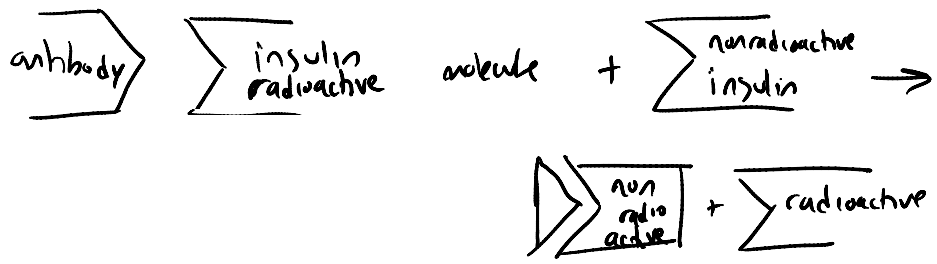
You need to see the types of particles liberated (like you don't want γ b/c too high energy) and the halflives for storage purposes.

$t_{\frac{1}{2}} = \boxed{\frac{.693}{k}}$ ← rate constant associated w/ decay rxn

Nuclear reactors are not great things to have in the backyard for safety concerns and terrorism concerns.

70% of Illinois is powered by nuc. reactors.
Radioactive hydrogen is tritium. Mass 3
Deuterium is H w/ mass 2. Heavy water.

^{131}I used for thyroid
^{60}Co used for cancer treatment
Thallium 201 used as tracer after heart attacks
Tc-99m for bone abnormalities, heart damage in heart attack



displacement reaction.
Calculate amt radioactive material, calculate amt insulin.

Radiation pill is how you protect yourself from radiation → saturate thyroid w/ I before attack so radioactive I doesn't come in.

Radioactive Dating, Fusion

Tuesday, March 06, 2007
9:05 AM

Radioactive Dating $t_{\frac{1}{2}} = \frac{.693}{k}$

Derivation $\ln \frac{N_t}{N_0} = -kt$ Integrated 1st order rate law.
N_0 is amt radioactive material at start of process.
N_t is amt left

$\ln \frac{50}{100} = -kt_{\frac{1}{2}}$

$-.693 = -kt_{\frac{1}{2}}$

C^{14} $t_{\frac{1}{2}}$ - 5730 y

^{14}C exists in atm due to cosmic ray bombardment of earth
react w/ C & N.

$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$

Then $^{14}_{6}C$ reacts w/ O, converts to $^{14}CO_2$
plants consume it (CO_2)

Libby recognized that once animals & plants die, they no longer consume ^{14}C & they liberate it.

$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}e$

If we know amt ^{14}C in living things & something dies, we can back calculate how old object is.
Biggest assumption is that $^{14}C - ^{12}C$ ratio hasn't changed in thousands of years

Tree died, gave 7 disintegrations of ^{14}C per minute per gram carbon.
Present day gives 15.3 disintegrations/min. When did it die?

We use ^{14}C b/c it's accurate but long.
^{14}C $t_{1/2}$ = 5730 y

$\ln \frac{N_t}{N_0} = -kt$

$t_{\frac{1}{2}} = \frac{.693}{k}$

$k = \frac{.693}{t_{\frac{1}{2}}}$

$\ln \frac{7}{15.3} = -\frac{.693\,t}{5730}$

$t = 6.563$ yrs old

Fission splits
Fusion puts together

It's possible to do fusion w/ certain things below 60 b/c of the relative stabilities of elmts.
60 is mass #

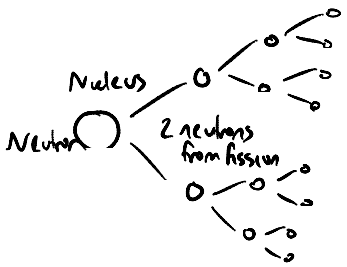
Any time you go toward a more stable nucleus, it is a spont. process.

The prob w/ having 2 nuclei or making them fuse is spont. but the rate is really slow unless we know something about activation barrier. W/ fusion, activation barrier is huge.

Fission is splitting of nuclei. Release a lot of energy when they do that.

ATLANTA

Peace up,
A-Town
Yeah Yeah



As this happens, it rises in energy. Basis for bomb is the chain reaction that cascades out of control & explodes.

To control process, control amt of neutrons.
Nuclear reactors don't have chain rxn or we'd die.
Neutrons are controlled by control rods – they absorb neutrons.

Fusion brings them together.

$^{2}_{1}H + ^{3}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$ Fusion process
deuterium + tritium → helium / α particle + neutron
This generates an enormous amt of energy
Another benefit is just helium and a neutron vs all that radioactive waste.
No chain rxn. Very controllable. No cascading out of control.

Activation energy, however, is enormous & we don't have a catalyst.
Other option is really high temps. 40 million° on sun.
So have to generate that kind of heat w/out melting everything around the reactor.
Hydrogen bomb is uncontrolled fusion. You have those starting materials & you initiate the rxn by slamming them into each other. You use fission to produce enough heat to initiate fusion.