Test 3

Defects

0 - Point

self interstitial   Vacancy

interstial   substitiliond)

Schotty   - removal local ion pair/vacancy

Frakel - small cation move to interstial site leaves vacancy behind

F-Center

vacancy fraction

vacancy formation $= \frac{n_v}{N} = A \exp \frac{-\Delta H_v}{k_B T} = V_F$

1 - Line
- edge dislocation (born)   tensile + compressive stess from work hardening
- movement like catopillor

2 - Interfacial
- grain boundries
- surfaces

3 - Bulk
- amorphas regions - voids - precipitats

Glass

Atom model Hooke's law
- deformation law
- Crystal has slip lane, glass does not
- compressive stress

XRD will be  vs 

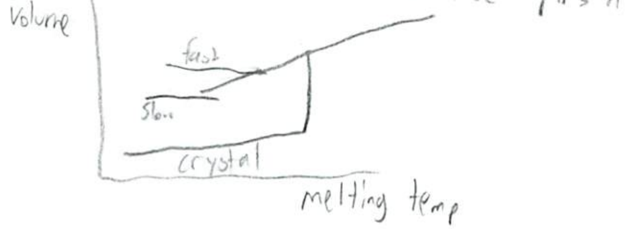
factors
- complexity
- viscosity
- cooling rate

network formors
- covalantly bonded
- high Tg
- O_2

Modifers
- lowers Tg
- forms O_2 briges
- ionically bonded

intermediats formers or modifers
- depends what current state is

Chemically strenghten - compressive forc bulk holds surface in place
or thermal w/ air jet coolled - pins it



kinetics

- time dependent process
- $aA + bB = cC + dD$

$C = \frac{mol}{vol} = \frac{mass}{vol} = \frac{mol}{cm^3} = \frac{n}{V}$ ← $PV = nRT$ $\frac{n}{V} = \frac{P}{RT}$

$A \rightarrow B + 3C$

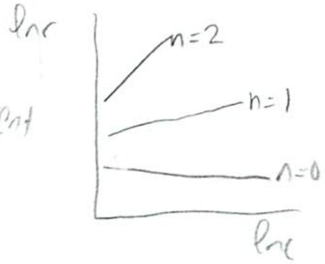
$r = \frac{-dC}{dt} = kC^n$

$k = A \exp\left(\frac{-E_a}{k_B T}\right)$ maxwell boltzman Arrhenius

↳ sum exponents in reaction equation

Orders of Reactions

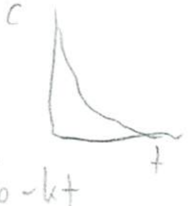
$n=0$
$n=1$
$n=2$
) completly different

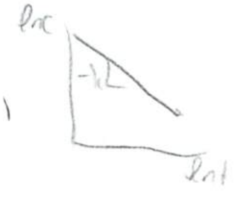


0th
$$-\frac{dc}{dt} = kC^0 = k$$
$$dc = -\int k\,dt$$

$C = C_0 - kt$

1st
$$-\frac{dc}{dt} = kc$$
$$\frac{dc}{dt} = -kt$$
$$\ln C = \ln C_0 - kt$$





2nd

slope = n
intercept log(k)
log r / log c

$$-\frac{dc}{dt} = kc^2$$
$$\frac{1}{c} = \frac{1}{C_0} + kt$$
$$t_{1/2} = \ln(2)/k$$

$k_B = \frac{[BH^+][OH^-]}{[B]} = k[H_2O]$ $k_a \cdot k_B = k_w$

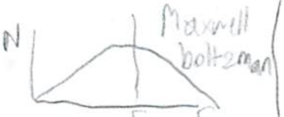
$p[\,] = -\log[\,]$

k changes if have catalyst
- lowers hump

k is orhenius

$k = k_0 \exp\left(\frac{-Q}{RT}\right)$

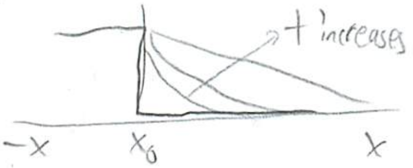
$\ln k = \ln k_0 - \frac{Q}{R} \cdot \frac{1}{T}$



molecules at that E level

273.15 k = 0°C

Diffusion



Ficks 1st lar

- how much mass

$$J_i = -D_i \frac{dc_i}{dx}$$

$\frac{mol}{m^3}$

$\frac{mole}{m^2/sec}$ $\frac{m^2}{sec}$ diffusivity $\frac{mol}{m^4}$

Flux = movement of material through surface

$D = D_0 \exp\left(\frac{-Q}{RT}\right)$ ← energy activation E_a ← $R = k_B N_a$

2nd Law

how concentration evolves over time

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

← partial deriv 1 dimension

$$C(x,T) = A + B\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$A + B\,\mathrm{erf}(\infty)$

$C_0 \to 0 = A + B$

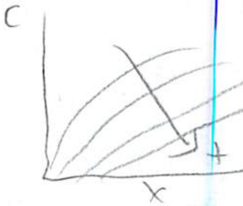
$A = -B$

$C_s = A + B\,\mathrm{erf}(0) = A$

$A = C_s = -B$

$\frac{C}{C_s} = 1 - \mathrm{erf}(\ )$

$$\frac{C(x,t) - C_s}{C_0 - C_s} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$



Steady state = independent of time

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right)$$

$$\frac{D_1 - D_0}{\frac{1}{T} - \frac{1}{T_0}} = \frac{E_a}{R}$$

Solutions

$\text{molar} = \frac{\text{moles solute}}{\text{L solution}}$

solvant = majority
Solute = minority

1. $aA \to B + C \qquad k = \frac{[B][C]}{[A]^a}$

2. $MgF_2 \to Mg^{2+} + 2F^-$ ions

$k_{sp} = [Mg^{2+}][F^-]^2 = k[MgF_2]$

1mole ↓ 0

0 ↓ $1c_{Mg^{2+}}$

0 ↓ $2C_{F^-}$

$\frac{1}{2}$ M

$MgCl_2$

common ion effect - if $[B^{a-}]$ added via anoter compound $[A^{B+}]$ ↓

ksp must remain same

Acid + Bases

	acid	base
Arrhenius	p^+ donor	OH^- donor
Bron-Loer	p^+ donor	p^+ acceptor
Lewis	e^- pair acceptor	e− pair donor

$HA + B \to BH^+ + A$

$$k_a = \frac{[H_3O^+][A^-]}{[HA]} = k[H_2$$

① 3.001 Review

12/14

- ~~a~~ a few hrs before
  - afternoon / evening
- could go through concept sheets
- or past tests - since future similar
- lets do past tests

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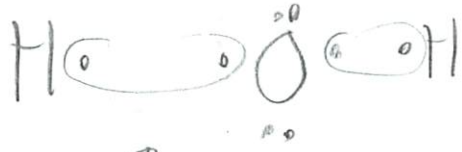
08 Test

Draw a Lewis Dot structure H_2O_2

← look at table 6



So

30 cep

H O O H

H ← fill in H/s

↑ draw Os like that

tablet better in easy Class

② Name of geometry

~~tetra~~ tetrahedral

-where is that from?

-Vespr theory / bonding

-all of the shapes chart, put on cheat sheet

d) % ionic character

no clue on this

think going to skip office hrs - just review myself

$X_o = 3.44$) electronegitivity from the table

$X_h = 2.20$

$3.44 - 2.20 = 1.24$

$1 - \exp\left\{-\frac{1}{4}(\Delta x)^2\right\} \times 100 = 32\%$

e) polar or non polar

H = nonpolar

O = polar - ? net dipole moment

? still unsure on that

no non polar - molecule ~~Symetri~~cal has bonds evenly distributed, Symetrical

Polar bonds ~~coll~~ makes asymetrical molecular - polar

③ Review Polar molecules

- have a net diapole moment
- δ
- in polar molecules
- some seperation of charge in the chemical bonds
- permenant diabole
- water is one

* atoms high electronglitity that bond w/ less
↑ attracts electrons

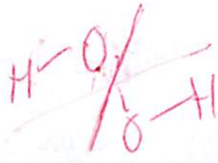
electronegitive atoms

- the more electronegitive atom pulls electrons away from oter atom one end ⊖ and ⊕ charge

Hydrogen bond - so strongly polar attracted to each oter
↑ 10% as strong as covalent bond

e) Is it chiral

- Yes if flip it ↰ will be different
- no is symetric 



← some how I guess
- that I can get answered
- but only 1 person

④

9) Max wave lenght of beam to break

- oh that is te oter formula I copied

$$\sqrt{142 \cdot 432} + 96.3(3.44-2.20)^2 \ \frac{kg}{mol}$$

$$396 \ \frac{kJ}{mol} / N_{AV}$$

$$= 6.57 \cdot 10^{-19} \ J/bond$$

pratice te conversion

So · 1000 to get rid of kJ

~~I would · NAV to get for each~~

No / is right I have

lets say 1 mole = 10000 atoms

10000 atoms to get for each one

↑ think what missed on last test

~~2.83e29 too big wrong way~~

396000 J/mole

· NAV

/NAV

= 2.38 e29

6.57 e-19

- yeah right what did I do wrong before?

- did not follow my own rules right

⑤ But there is more

I just found E_{OH} ← of the bond

now need to shoot some nutrons at it w/ that energy

Calc the E I need to do that with

$$E_{neutron} = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = E_{bond}$$

$$E_{bond} \rightarrow \lambda = \frac{h}{\sqrt{2mE}}$$

$$\frac{6,6 \times 10^{-34}}{\sqrt{2 \cdot 1,67 \cdot 10^{-27} \cdot 6.57 \cdot 10^{-19}}} = 1,41 \times 10^{-11} m$$

← planck's

^ ~~mass of both added from table~~ ^ E

Atomic mass constant

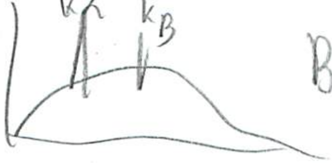
?

More on x-ray difraction

e⁻s crash into a target

and when it hits the e⁻s are released

other e⁻s cascade down



Bremstralung

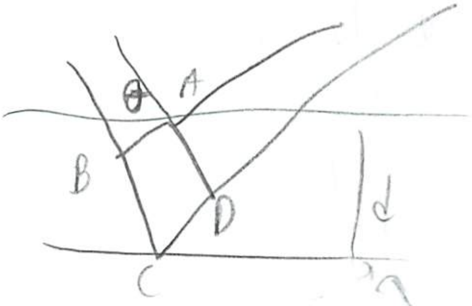
$$\lambda_{SWL} = \frac{hc}{eV}$$

⑥ Mosley $\bar{\nu} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i}\right) - (Z-\sigma)^2$

↑screening factor

XRD → how to determine crystal structure

atoms like mirrors



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

↑ interplanar spacing

$$\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2+k^2+l^2} = \text{Const}$$

$$a = \frac{\lambda}{\sqrt{2}\sqrt{\text{const}}}$$

← can find the different crystal types

2 x ray techniques

- difractrametry - fixed λ variable θ
- Laue variable λ, fixed θ

⑧ On to Qu 2

Structure of CsCl is shown

a) ~~BCC~~ Just simple cubic

- but BCC is body center cubic

- ~~why does it not count~~ - yeah the ~~instructor~~ notes said BCC - ~~and have~~ inside different color

Sadowar office hrs: 2 diff types

b) Name bravais lattice

simple cubic

- perhaps because something inside

C, ask this

basis - smallest repeatable unit

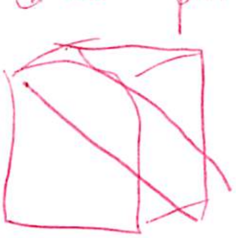
$Cl^- + Cs^+$

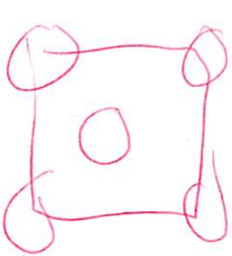
know which is + - from table

3. Sketch (011) plane of Tunstegen to show arangement of iatoms

look up W is BCC

draw plane





← draw slice

b) lable

Fidk how they got this

⑧ Packing density of the (011) plane

$\#$ atoms $4 \cdot \frac{1}{4} + 1 = 2$

area of cell $a \times \sqrt{2}a = \sqrt{2}a^2$

^ the whole cell

BCC $\frac{2}{a^3} = \frac{N_{AV}}{V_{molar}}$

$a = \left(\frac{2 V_{molar}}{N_{AV}}\right)^{1/3} = \left(\frac{2.85}{6.02 \times 10^{23}}\right)^{1/3}$

write on cheat sheet

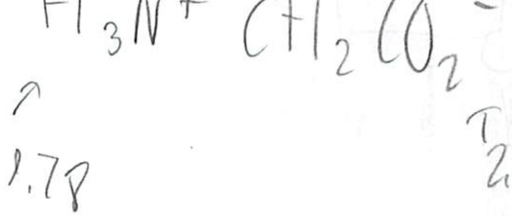
density $\rightarrow \frac{2}{\sqrt{2}a}$ $\frac{\sqrt{2}}{(3.16 \cdot 10^{-8})^2} = 1.42 \times 10^{15}$ atoms/cm²

4) Skeletal structures of 2 amino acids

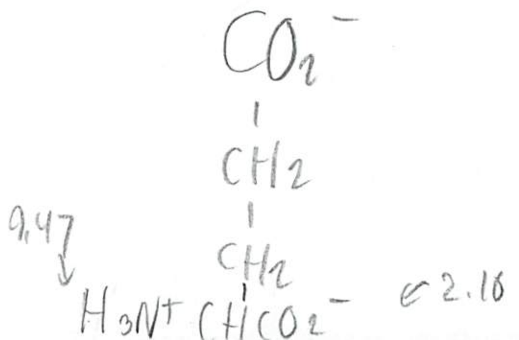
glycie and glutamic acid are given below

along w/ pka

^ never really got the pka thing either



$H_3N^+CH_2CO_2^-$



$H_3N^+CH(CH_2CH_2CO_2^-)CO_2^-$

⑨ Find pH at which the ratio of concentration of neutral zwitterion to deprotonated anion is 10^{-4}

$HA \rightleftharpoons H^+ + A^-$ acids, etc

$\therefore k_{a_2} = \frac{[H^+][A^-]}{[HA]}$

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

what is the p again? $-\log_{10}$

$\therefore pH = pk_{a_2} + \log_{10} \frac{[HA]}{[A^-]}$

$9.78 + \log_{10}(10^4)$

$9.78 + 4$

13.78

← review

⑩ Sadoway office hrs - on that av

Why do bio in chem
- its the basis of proteins
- biologists don't see it as chem

But first diffusion
- when Ficks 1st law

2 States

transient - early
- doping
- drying
- semi infinite
- not based on temp

↙ Ficks 2nd Law

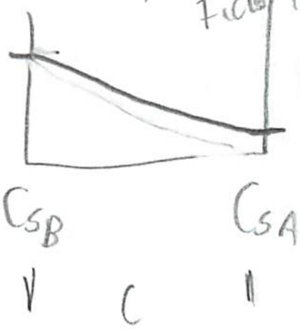
$$\frac{C-C}{C-C} = \text{erf} \ldots$$

↑ fill at

↑ if erf < .6
that just 1 < .6

Steady state - late
- membrane

↙ not time dependent
Ficks 1st law



$$J = -D\frac{dc}{dt}$$

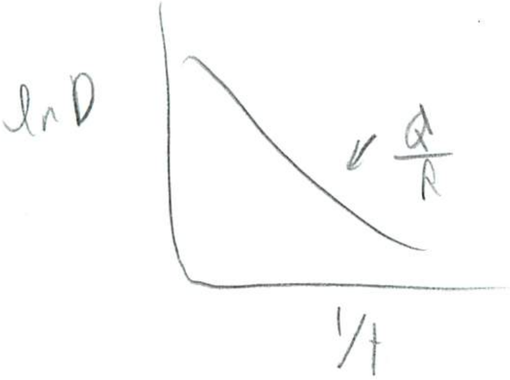
$$= -D\frac{\Delta c}{c}$$

↑ $\frac{\text{moles}}{\text{cm}^2 \cdot \text{sec}}$

area it over a surface of bollon J·A

integrate over total surface area →

⑪



← Diffusion is dependent on temp

- 1st + 2nd law simply isothermic geomatry

← isothermic rate of reaction

Milk is a suspension

fat
aqueous stage) different indexes of refraction
light scatters

NaCl
- transparent
- ionic bonding, high bond gap
- but ground up - cracked up
  - interior interfaces scatter light

- FCC
- 2 ions

⑫ Bonds Strenghts

CoVlant (network)

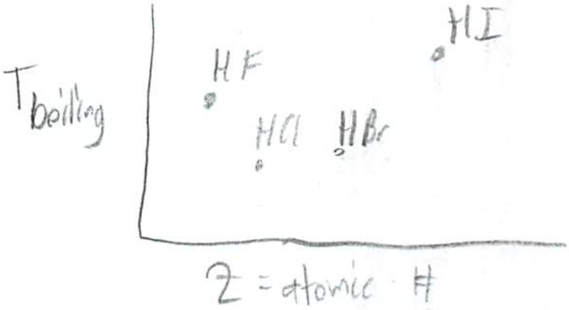
- diamond
- silicate
- ionic

Ionic

H-Bonding

diapole - diapole / polar covalent

Van der Walls / London dispersion / induced diapole



$Mg_3(PO_4)_2 \rightarrow 3\ Mg^{2}$

$2\ PO_4^{3}$ ← remember this stuff

that should be given

what you weigh

$k_{sp} = [Mg^{2+}]^3 [PO_4{}^{3-}]^2$

bracket = concentration

$C_{Mg^{2+}}^{3}$ ←power of 3, cube × $C_{PO_4{}^{3-}}^{2}$

1 mole $Mg_3(PO_4)_2 \rightarrow$ 3 moles Mg^{2+} + 2 moles $PO_4{}^{3-}$

⑬

[ ] [ ] ← other goes down

↑ when one goes ↑

understand the concepts
not the minor rules and hard algebra

— assumed that it disolved completely
- if it disolves partially, too hard

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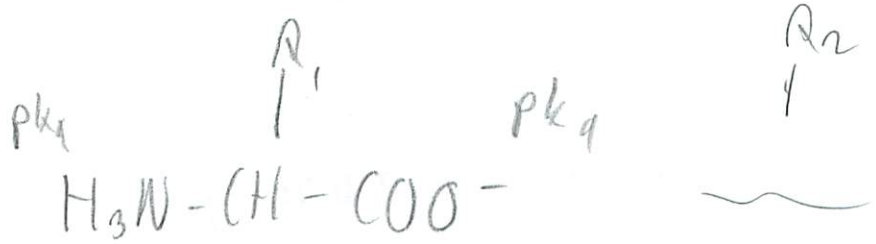
amino acids
- amino end
- R group



$H_3N - \overset{R_1}{CH} - COO^-$

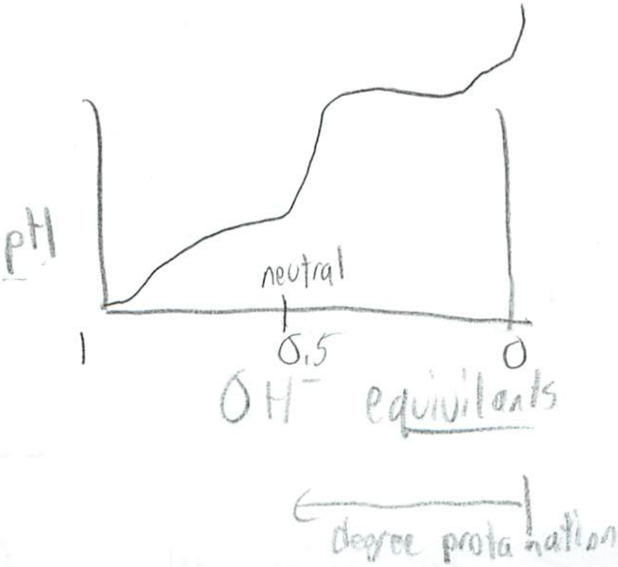
↑chiral - different

these few days good at separating + concentrating
- really learned how to focus again
- clear desk
- write on paper
- can I do it w/o pressure of final

* peptide bond
- inside pka lost on both sides

- but outside pka kinda of dependent

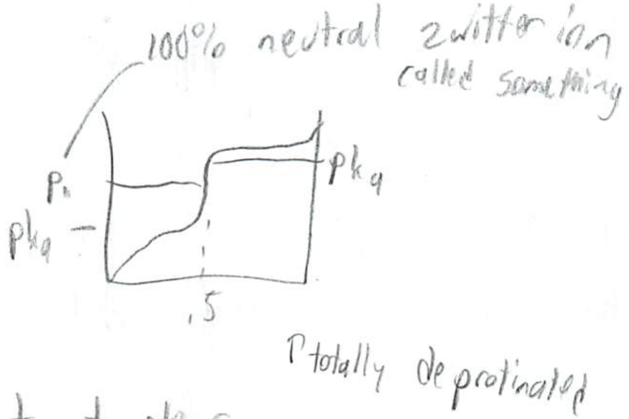
titration curve



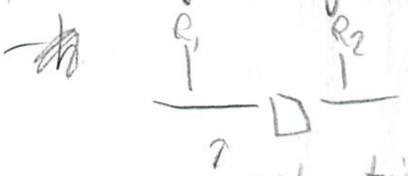
-neutral zwitterion / pH
~~neutral~~

$HA = H^+ + A^-$

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



told which to put together



need this order since chiral remaining functional left standing

Zwitter ion acquires protons at low pH

donates protons in proton deficent

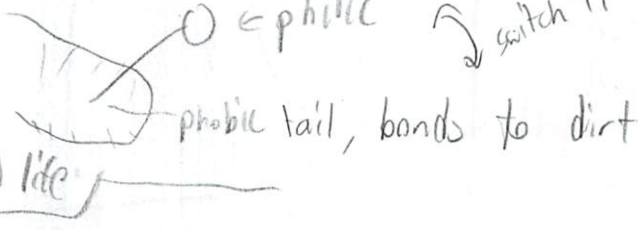
P_i = avg (Pka, Pka)

Still don't get - review which directions

look at R graps
which most compatable w/ detergent

detergent - ~

non polar
- like fat



- delta in polarity turns around → animated ↓ life

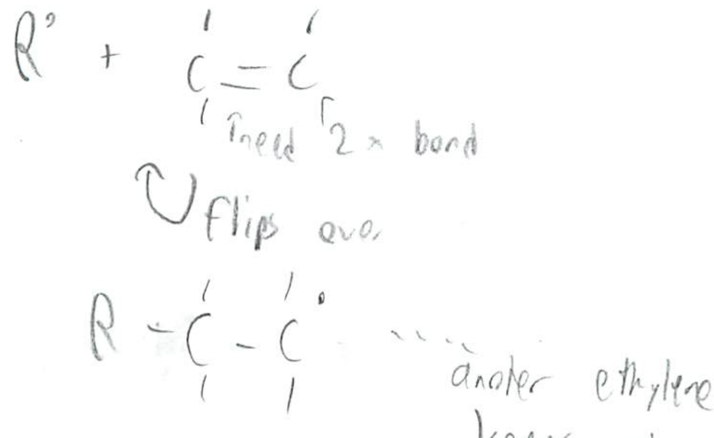
buffering

$\frac{49}{51}$ $\frac{50}{50}$ $\frac{51}{49}$ ~~all~~ very similar — flat

$\frac{98}{2}$ $\frac{99}{1}$ not similar at all / steep

(15)

addition polymerization



dietene – 3 units long

---

thormo plastic
- no cross links

thermo set
- cross links
- rubber

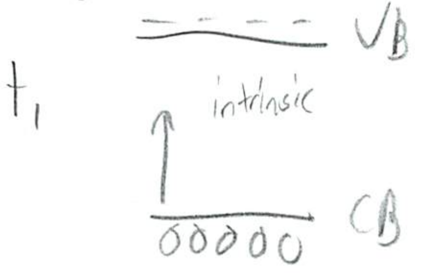
---

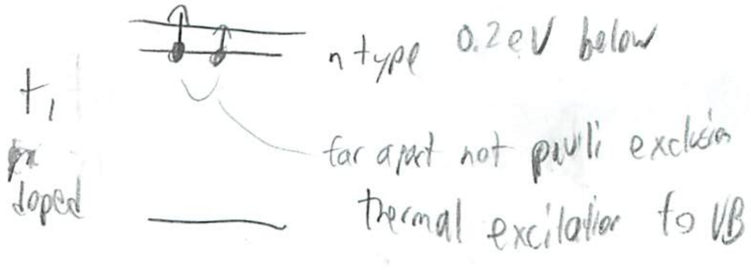
was simple cubic ← my qu since 2 types
if 1 type than it would make sense
was all

but its 2 types (in basis) so simple cubic

---

band gap

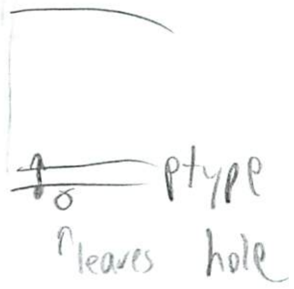




⑯

Skipped
opps

⑰



Lewis acid - e^- pair acceptor / e^- pair doner
-looking for lone pairs

$CaSO_2$ -acid rain
$:\ddot{\underset{..}{O}}^{2-}:$

$SO_2 \rightarrow SO_3$

lewis acid/ base ≠ Ahrenius

Office hrs over

back to test review

Review concentration

- rate of reaction proportional to concentration reactant
- was ~~an~~ always confused on test
- then ~~[illegible] for~~ → learned how for some time
  - now confused

$pH^{+} = -\log_{10}[H^{+}]$

$pOH^{-} = -\log_{10}[OH^{-}]$

$pH + pOH = 14$

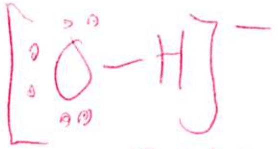
H^{+} ← + means that it lost ~~an~~ its only electron
only a proton + neutron

) Day 1 material

⑱ OH^- c̄ extra electron

look up pic

called hydroxide



↑ where is extra ~~ion~~ electron ?

base (dissiociation of)

- involved in all acid base reactions in water
  - aqueous = disolved in water

So OH^- is a proton acceptor ✓] all bases
electron donator ✓
↑ Lewis base

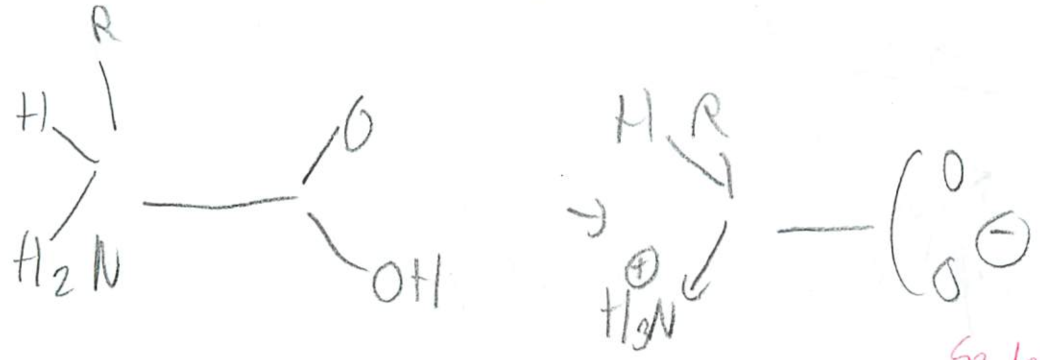
Ok got that set

0	7	14
acid	water	base

↑ low pH = high concentration H^+
very acidic
- donates H^+/protons
- accepts electrons

Zwitter ion - total net charge = 0
- amino acids

⑲ Amino acids are good examples



gained one here

now ⊕

So lost an H here

now ⊖

Zwitterions online

- electrally neutral overall
- nonadjacent regions ⊕ ⊖, "diapole ions"
- 2 parts of the molecule
  - function as acid / base pair
    - $-COOH$
    - $-NH_2$

as pH nears neutrality

$COOH \rightarrow COO^-$ ← loses OH → ~~gets more ⊕~~ ???

loses H → gets ⊖

$NH_2 \rightarrow NH_3^+$ ← gains H^+ gets ⊕

So ~~now~~ now large, favorable, stabalizing electrostatic interaction develops

⑳ Shifts the =librium constant for the proton transfer reaction towards the formation of charged species

by factor 10x - 50x

Same charged regions have very favorable electrostatic interactions w/ surrounding water so water solvates like cations/anions

- very solvable

Answers.com: ⊕⊖ charge localized at different poles

Bradwell at neutral pH

COOH → COO- } net neutral
amine accepts H^+ } but localized charge

High pH / low [H+]

the H^+ stripped off NH_3^+

* So when there is a low [H+] concentration a zwitter ion donates some [H+] to help balance it

low pH / high [H+]

H^+ added to COO-

So it pulls the extra H^+ in

now writing this all out makes more sense

㉑ Bradwell's notes better than online
- starting to reach that teritory

Back to concentration

Steps
1. Write out reaction equations
2. Set up chart w/
   initial change final
3. Solve for x, ka, km using formulas

$$k_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$ ← well acids + bases

---

When was the normal concentration stuff
- Lect 25 solubility?
- solvent = majority
- solute = minority

measure of solubility → molarity Ⓜ

$$\frac{\text{moles solute}}{\text{Litres solvant}}$$

$C_{solute} < .001$ M insolucably

[ ] ← concentration - moles / L solution

㉒ Solubility product

$k_{sp} = [Ag^+][Cl^-]$

? in AgCl alone $[Ag^+] = [Cl^-]$

concentrations =

$k_{sp} = [Ag^+]^2$ ... i don't get

WP: Solubility Equalibrium / prodct

- Solid and disolved states at saturation
- =librim const for salt disolved to its ions in solution

⇔ can move back and forth

non-ionic $k = \frac{Aq}{Solid}$

? equalibrium constant

[ ] = molar concentration

ionic $$\frac{[Ca^{2+}(aq)][SO_4^{2-}(aq)]}{CaSO_4\ (solid)}$$

pure solid = 1

k_{sp} = soluability product

if only 1 atom than $\sqrt{k_{sp}}$

㉓ Unequal parts

$Ca\,OH_{2\,solid} \leftrightarrows Ca^{2+} + 2OH^-$

↑ how do you know it
splits like that
magic ??
- or what
- I think this given

$k_{sp} = [Ca^{2+}_{aq}]\,[OH^-_{aq}] = [Ca^{2+}]\,2[Ca^{2+}]^2$

$k_{sp} = x(2x)^2 = 4x^3$

$x = \sqrt[3]{\frac{k_{sp}}{4}}$ ← kinda remember this

diff site

actually learning all this

$NaCl \rightarrow Na^+ + Cl^-$ ← 100% dissiocated
very soluable

insoluable salts have a solid precipiate

$Pb^{+2}_{aq} + SO_{4\,aq}^{-2} \rightarrow PbSO_{4\,solid}$

↑ get ions when disolve in water

$k_{sp} = [Pb^{+2}][SO_4^{-2}]$

so this will be in equalibrium with
some solid

㉔

	Start	Δ	End
Pb^{+2}	0	+x	−x
SO_4^{-2}	0	+x	−x
$PbSO_4$	N/a	−x	N/a

→ this should be on every bceblem

I don't really get
- why N/a
- how do x not balance
- how can start w/ everything 0

assumed amt lead sulfate infinite

now plug it in

$$K_{sp} = [Pb^{2+}][SO_4^{-2}] = x \cdot x = x^2$$ ✱ ← find w/ Change table

$$x = \sqrt{K_{sp}} = \sqrt{1.8 \cdot 10^{-8} M^2} = 1.34 \times 10^{-4}$$

↑given

Concentrations =

---

anotor problem

$Cd_3(AsO_4)_2$

$K_{sp} = 2.2 \times 10^{-32}$

Concentrations of 2 components Cd^{+2} AsO_4^{-3}

㉕ Oh what to do

- split it up
- I always get confused w/ coefficents

$$\underbrace{Cd_3\,(AsO_4)_2}\ \rightarrow\ Cd^{2+}\quad AsO_4^{-3}$$

crosses for some reason
why ??????
becomes ions
the subscript is # ~~of~~ of atoms
in the molecules
and + − superscript is # of electrons
lost /gained as ion

~~then~~

$$3\,Cd^{+2} + 2\,AsO_4^{-3}$$

but will have coincidence ?
3 oh when seperated

Now make the table

	Start	Δ	
$Cd_3(AsO_4)_2$	N/a	~~N/a~~	N/a
Cd^{+2}	0	+3x	3
AsO_4^{-3}	0	+2x	2

← oh since none goes to solid

✓ ✓ got this ← why is it adding

(26) Now put it all togeter

$$(3x)^{3} \cdot (2x)^{2} =$$

$$27x^3 \quad 9x^3 \cdot 8x^3 \quad 4x^2$$

$$D\,[Cd^{+2}]^{\boxed{3}}\ \square\,[AsO_4^{-3}]^{\boxed{2}}$$

I think

$$(3x)^3 \cdot (2x)^2 = 108x^5$$

now solve for x

$$x = \left(\frac{ksp}{108}\right)^{1/5} = 1.8 \cdot 10^{-7}\,M$$

what is that even concentration of something

1 more step

$$[Cd^{+2}] = 3x = 3(1.8 \cdot 10^{-7}) = 5.5 \times 10^{-7}\ M$$

$$[AsO_4^{-3}] = 2x = 2(1.8 \times 10^{-7}) = 3.7 \cdot 10^{-7}\,M$$

should do 1 more to get rules down

㉗ try again $Cd_3(AsO_4)_2 \rightarrow Cd^{2+} \quad AsO_4^{-3}$

~~Cd3(As~~ first $3Cd^{2+} + 2(AsO_4^{-3})$

$[Cd^{2+}]^3 \, [AsO_4^{-3}]^2$

table r r

+3 +2

$(3x)^3 \cdot (2x)^2$

$27x^3 \cdot 4x^2$

$108x^3 = ksp$

solve for x

plug in $\leftrightarrow$ do they always = ?

$(3x)^3$

$(2x)^2$

Soluble or insoluble

- ~~A~~ rules
- not on web
- but basically the farther apart on table the more likely it is soluble

salaway said assume soluble

㉘ Now what about general solvability

- like in acids or bases

Like disolves like

$k_{sp} = k_{H_2O} \leftarrow [H_3O^+][OH^-] = 10^{-14}$

$$k_a = \text{constant} = \frac{[H_3O^+][Ac^-]}{[\underset{\uparrow \text{the acid}}{HAc}\ aq]} = 10^{-5}$$

Strong acid → 100 dissication

weak acid → only partial dissication

very weak acid → no dissociation

So back to problem - do I get it now?

$$\frac{[H^+][A^-]}{[HA]} \leftarrow \text{the disociation}$$

$$pH - \log_{10} \frac{[A^-]}{[HA]} \leftarrow \text{what is this}$$

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

(29) ← what is this ? the acid

$HA = H^+ + A^-$ ← is ~~A what the acid actually~~ is

Conjugate base - gains a proton

There is a list of ~~which~~ what is which

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

← constant in dissociation

measure of strenth of acid

↑ Concentration not changing

$BH^+ = H^+ + B$

$pka = -\log_{10} ka$

large = weak

the ion

$$k_a = \frac{[H^+][B]}{[BH^+]}$$

So how does this work on a question

$pH \text{ —? } \frac{\text{start}}{\text{end}}$

↑ why minus

Since $pH = pka - \log \frac{[AH]}{[A^-]}$

↑ henderson haselbach equation

b) Draw the skeletal structures of Glu when solvated under conditions

look at pka

pH = 1.5
acid
- lots of $[H^+]$

CO_2H - so asorbs from on OH region
|
CH ↑ get OH here
|
CH ← neutrall
|
$H_3NCHCOOH$

still ⊕ here
↓
⊕

14
base
- lots of $[OH^-]$

CO_2^- ← loses OH
|
CH loses [H] for some reason
|
CH
|
$H_2N-CHCO_2^-$

still ⊖ here
↓

iso electric
neutra

CO_2^-
|
CH
|
CH
|
N_3N^+ $CHCO_2H$

(30)

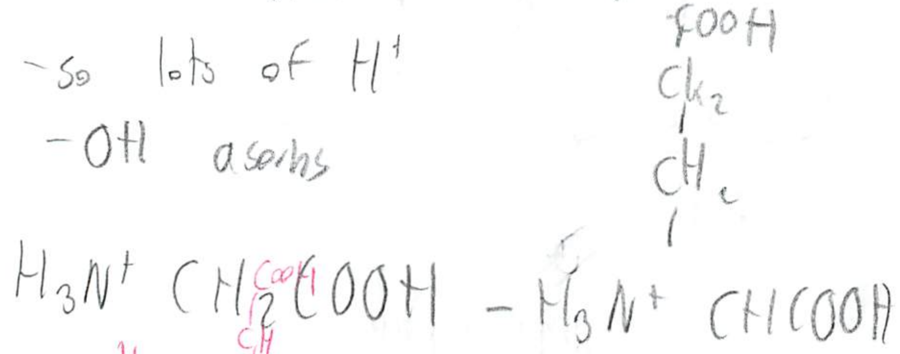
c) Calc the value of pH at neutral zwitter ion

- iso electric pt
- average the ~~X~~ 2 COO⁻ values ← review session ☺

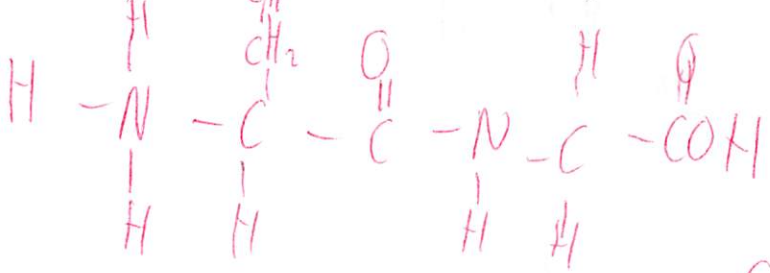
✓

d) draw Sketeal structure at lots of acid pH = 1

- so lots of H^+
- OH asorbs



$H_3N^+ CH_2COOH - H_3N^+ CHCOOH$



← where get that

Gly expands?

well never dren its structure?

e) tertiory structure in aw

- how affected

increase in pH - H_3N^+ do protanatos

chain breaks in 2 + 3

increased detergent - Y will break apart + pulled by hydrophillic tail

open loop

pocket hydrophobic

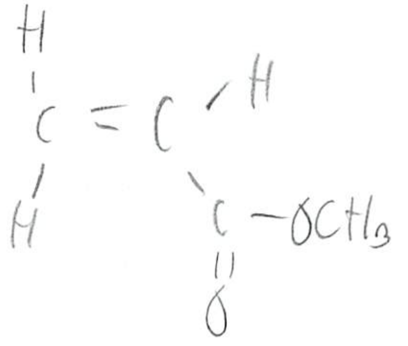
㉛ Problem 5

Methyl methacrylate

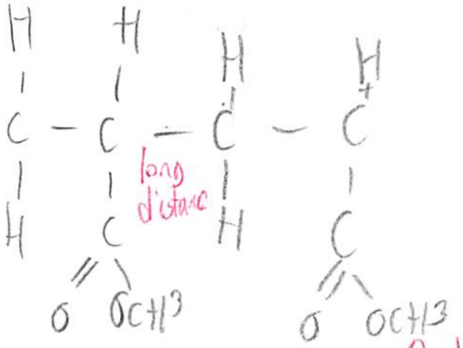
this is polymers

↑ were they on most recent test?

a) draw 5 repeat units



so C=C double bonds break



← 2 units ✓

↑ does switch up + down

b) Calc weight n =3091

- add up weights of each atom from table · 3.091

molecular weights

ans in $\frac{g}{mol}$

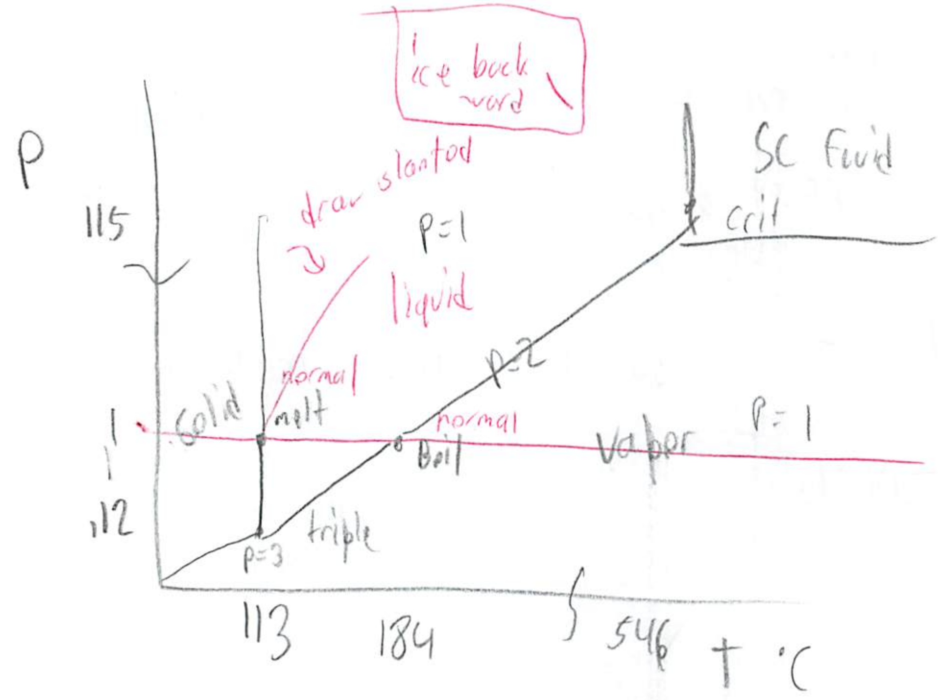
c) Thermo set or plastic

- review session
- are there cross linkages no plastic ✓

(32) Moving quick now
-relearning not reviewing

Ok phase diagram

Iodine

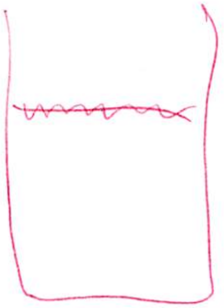


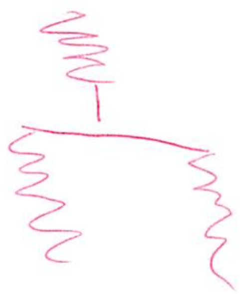
look up rest on table

Melt 113.7 °C
Boil 184.4 °C) 1atm

not bad

7) Lipid trimyristin added to beaker of water neutral pH to enable interaction between lipid molecules draw the arrangement ∿∿ = carbon chain





← wtf is this

Lipids review

→

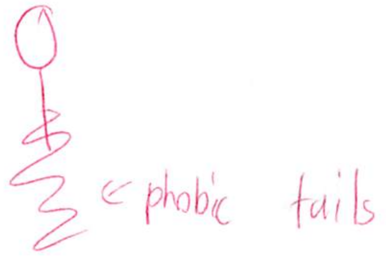
㉝ Protiens denatured (2ndary bonds broken)

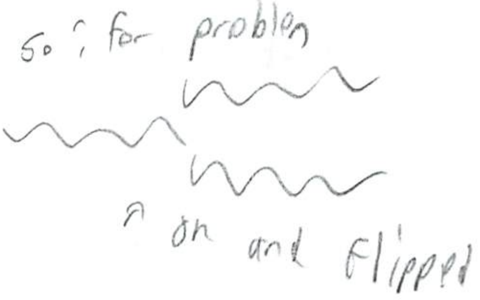
1. Temp
2. PH
3. Oxidizing/reducing agents (-S-S-) bonds
4. detergents

Lipids

- solvable in solvants of low polarity
  - fats, oils, cholestorol, hamones
  - hydrophilic head, -phobic tail

lipid bilayer = cell wall





b) to the beaker add = volume CCl_4

$CCl_4 - H_2O$ agitate

immisible

lower density values float

higher " " sink

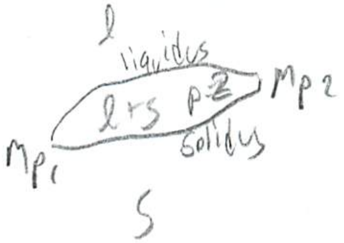
duh now that I see that

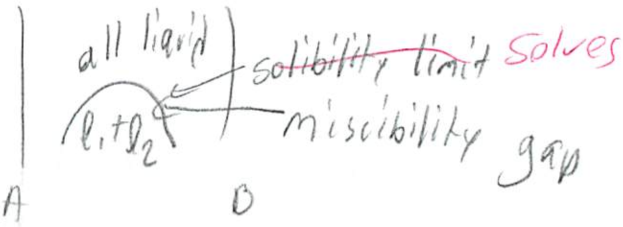
㉞

8. Anoter phase diagram

i lable each region + lable = librium
- oh this is the advanced stuff w/ curves

advanced review





Review tieline

1. ~~Solubility limit~~ solves $\alpha + \beta$ and s ← note both solids

2. Solidus between s+l and s
↑ α in this case

3. liquidus between l and l+s

4. ~~Some point miscibility gap:~~ $\alpha + \beta$
this different temp - composition pair

2hrs studying
40 hrs for physics

$\alpha + \beta$ - nowneed to apply tie line

review tie lines

㉟

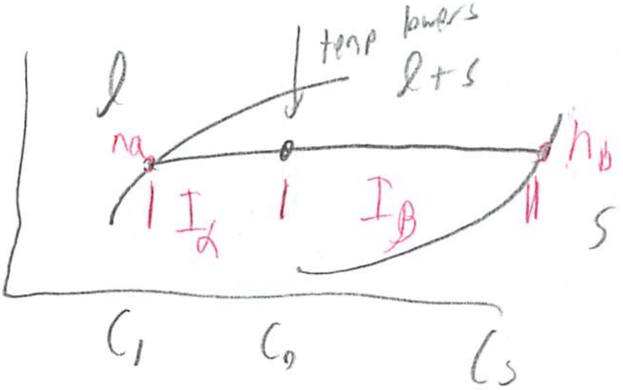
▨ = phases that exist

1. All of material in 1 of the phases

$$W_{sA} + W_{lA} = 1$$

$$W_s C_s + W_L C_L = C_0$$

$$W_L = \frac{C_s - C_0}{C_s - C_L}$$



↑
10% liquid

∴ so what do you actually do?

$$n_\alpha I_\alpha = I_\beta n_\beta$$

↑ ↑
amt of each phase

(36)

~~post~~ Did I ever answer the qu ?

$\alpha = 8\%$

$B = 81$ wt% Ni ~~Al~~

81 % of weight

?, how ~~in all world~~

← go to the line endpoints for α and B

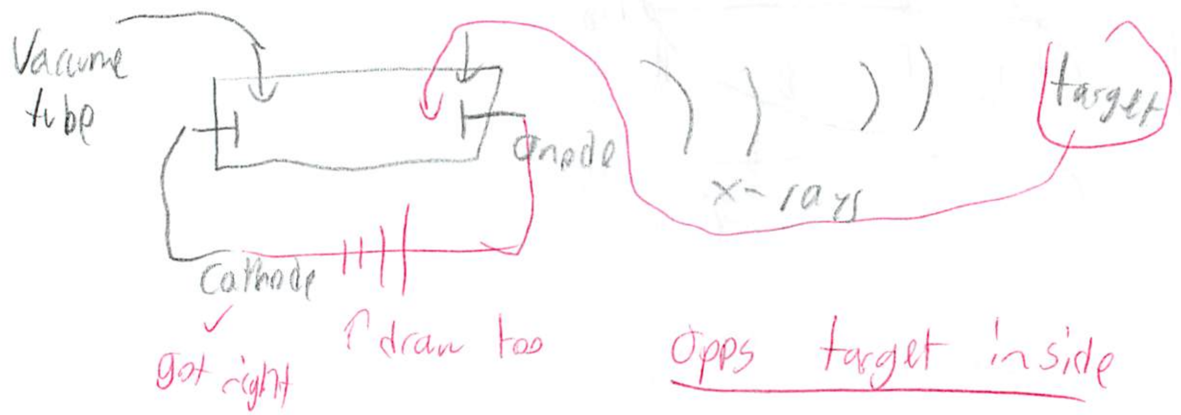
5. is just L   14% weight ← just read

6 l + s   75% solid α 45% weight l   ✓ better

Problem 9

Cartoon of x-ray tube

- invented at MIT) modifications pt b



Opps target inside

b) 1. Vaccume tube – less gas particles to hit ✓

2. Water cooled – less heat, could run longer

Duane - Hunt Law = .666 Å

↑never heard of

for SWL - valve plate voltage

→ Cheat sheet !

$$\lambda_{SWL} = \frac{hc}{eV}$$

c & planks, light

$$\cancel{.666}\ 6.6 \cdot 10^{-11} = \frac{hc}{\cancel{eV}} \leftarrow \text{want}$$

18.6 kV

10. Give rotational symetries of pattern
express n-fold

- oh boy thought this was all a joke / for fun

- why some pics missing

- Review lecture 18

$$\frac{{}^{\circ}\text{ to go back to what have}}{360} = \text{fold}$$

3 fold = ~~360~~ 120°

11. Magnesium phosphate disolves

- solubility product back - lets see !

(38) $Mg_3(PO_4)_2 \Rightarrow 3Mg^{2+} + 2PO_4^{3-}$

?i same I found on web?

$k_{sp} = 1.11 \times 10^{-25}$ at 25°C

$3(Mg^{2+}) + 2(PO_4^{3-})$

n +3 n+2

Ksp = ~~B~~ $[Mg^{2+}]^3 \cdot [PO_4^{3-}]^2$

$(3x)^3 \cdot (2x)^2$

$27x^3 \cdot 4x^2$

$ksp = 108x^5$

solve for x

plug in

$(3x)^3 =$

But this problem is different

$Mg_3(PO_4)_2$ in $5.55 \cdot 10^{-3}$ M Na_3PO_4 solution

express in moles $\frac{Mg_3(PO_4)_2}{l \text{ solution}} = M$

never knew how to do these type of problems

38

✓ $K_{sp} = [Mg^{2+}]^3[PO_4^{3-}]^2$

→ solubility (C_s) $= \frac{1}{3}[Mg^{2+}]$ with Na_3PO_4

?? how find

? were does Na come from

→ oh in here

~~PO4~~

??

↓ ? somehow fully dissociates

$[PO_4^{3-}] = 5.55 \cdot 10^{-3}$ ← given

$$[Mg^{2+}] = \left(\frac{K_{sp}}{[PO_4^{3-}]^2}\right)^{1/3}$$

= something · 3 for C_s

- whish they ~~describ~~ had the table ??

Mg

Po

Na

- still don't get

Should really figure out

(41) 2 problems left

12. Diffusion coefficent

D_o	T
9.2×10^{-11}	1100
$1.4 \cdot 10^{-9}$	1300

- Show that to ↑ value D_o by 10 x [illegible] than 1300°
  would raise of MP Si ← 1414 °C
- So this is solid state 1st law

$D = D_o \exp \frac{-Q}{Rt}$

find T' at which $D = 10 \cdot D_{1300}$

need to get te value of Q

$$\frac{D_{1300}}{D_{1100}} = \frac{\exp \frac{-Q}{R \cdot 1573}}{\exp \frac{-Q}{R 1373}} = 15.22$$

← why those #

$$\exp \frac{-Q}{1573R} = 15.22 \exp \frac{-Q}{1373R}$$

$$\frac{-Q}{1573R} = \ln 15.22 - \frac{Q}{1373R}$$

$$Q = R \ln 15.22 \left(\frac{1}{1373} - \frac{1}{1573}\right)^{-1} = 244 \cdot 10^3 \text{ J/mol}$$

Now solve for T!

$$T = \frac{-244000}{8314\left(\ln 10 - \frac{244000}{1873 \times 8.314}\right.} = 1794\,K$$

$= 1521°C > mps!$

don't get at all

too much math → skipping

watch will be on exam

b) Make a crude estimate showing that feasible to remove O_2 from S_i ribbon of thickness .1 μm

expose to vaccume 10 min 1100°C

~~$x^2 \approx Dt$~~ $x^2 \approx Dt$

$9.2\times10^{-11} \times 10 \times 60$

$5.52 \times 10^{-8}\,cm^2$

$x = 2.35 \cdot 10^{-4}\,cm$

$2.35\,\mu m >> .1\,\mu m$

no clue again

㊸ Last problem

- the bonding again

HI , HF why one higer bonding diff

a) All matter made of atoms

b) Sadoway kinda did this one

H - bonding

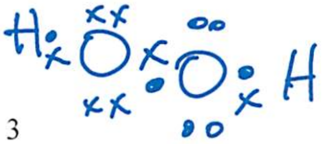
- relative intermolecular bond strenght
  = higher boiling pt
- this is 2ndary bonding
- missed what he said

- go back
  - get qu answered
  - Cheat sheet
  - olivia's stuff

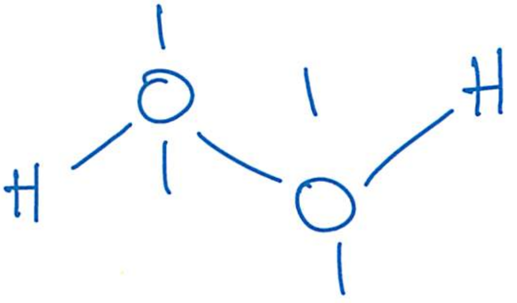
Problem #1 (22 points)
Answer the following questions about

hydrogen peroxide (H_2O_2).

(a) Draw the Lewis structure of H_2O_2.

3 

(b) Draw a 3-dimensional representation of the molecular geometry of the molecule.

3 

(c) Name the geometry of the electron distribution about the oxygen atoms.

1 tetrahedral

(d) Determine the per cent ionic character of the O–H bond.

3 $\chi_O = 3.44$ $\chi_H = 2.20$ $\therefore \Delta\chi = 1.24 \Rightarrow$ % ionic character is $\left[1 - \exp\left\{-\frac{1}{4}(\Delta\chi)^2\right\}\right] \times 100 = \boxed{32\%}$

(e) Is the molecule polar or nonpolar? Explain.

3 nonpolar – symmetric disposal of polar bonds

(f) Is it chiral or achiral? Explain.

3 achiral – symmetric disposal of atoms around center of symmetry

(g) Calculate the maximum wavelength of a beam of neutrons capable of breaking the O–H bond in H_2O_2.

DATA:

	Average Bond Energies (kJ/mol)
O–O	142
H–H	432

6 $$E_{OH} = \sqrt{E_{O-O} \cdot E_{H-H}} + 96.3(\chi_O - \chi_H)^2 = (142 \cdot 432)^{1/2} + 96.3(1.24)^2$$

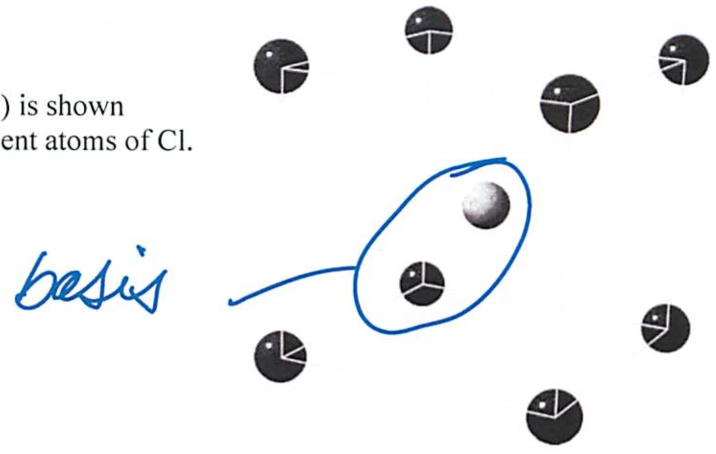
$$= 248 + 148 = 396 \text{ kJ/mol} / N_{Av} = 6.57 \times 10^{-19} \text{ J/bond}$$

$$E_{neutron} = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = E_{bond} \Rightarrow \lambda = \frac{h}{(2mE)^{1/2}}$$

$$\therefore \lambda_{neutron} = \frac{6.6 \times 10^{-34}}{(2 \times 1.67 \times 10^{-27} \times 6.57 \times 10^{-19})^{1/2}} = \underline{\underline{1.41 \times 10^{-11} \text{ m}}}$$

Problem #2 (4 points)

The crystal structure of cesium chloride (CsCl) is shown in the adjacent figure. The dark spheres represent atoms of Cl.



(a) Name the crystal system.

1 cubic

(b) Name the Bravais lattice.

1 Simple Cubic

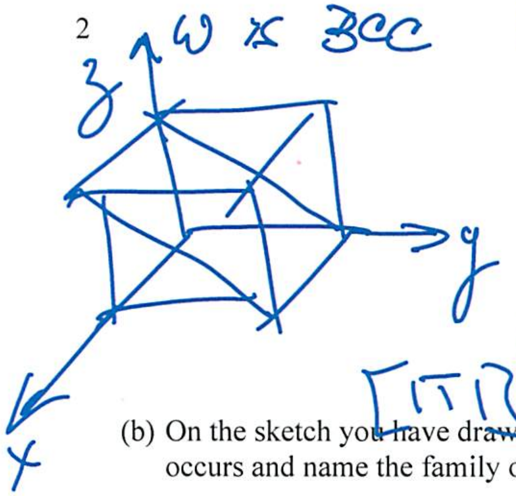
(c) Name the basis of the crystal structure and indicate the basis by markup of the figure.

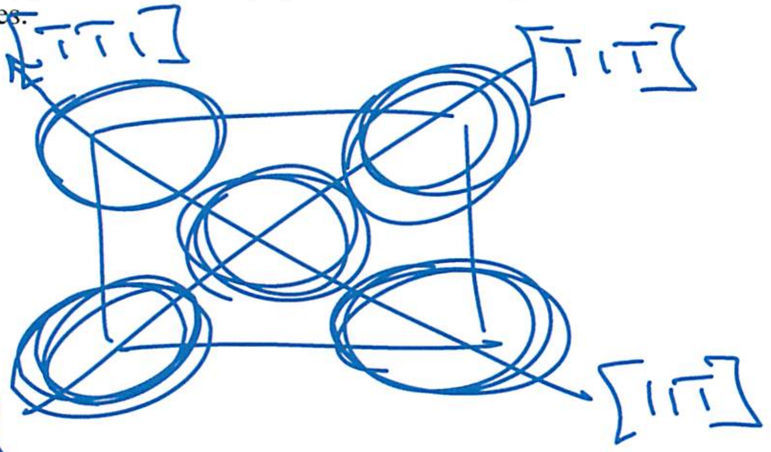
2 $Cl^- \,\&\, Cs^+$

Problem #3 (8 points)

(a) Sketch a fragment of the (011) plane in tungsten (W) to show the arrangement of atoms, which are to be represented as hard spheres.

2 W is BCC





(b) On the sketch you have drawn in answer to part (a), draw and label all directions along which slip occurs and name the family of directions to which they belong.

3

(c) Calculate the atomic packing density in the (011) plane of W. Express your answer in units of atoms cm^{-2}.

3 $$\text{no. atoms / cell} = \left(4 \times \tfrac{1}{4}\right) + 1 = 2$$

$$\text{area of cell} = a \times \sqrt{2}a = \sqrt{2}a^2$$

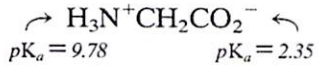
$$\text{for BCC} \quad \frac{2}{a^3} = \frac{N_{AV}}{V_{molar}} \Rightarrow a = \left(\frac{2V_{molar}}{N_{AV}}\right)^{1/3} = \left(\frac{2 \times 9.50}{6.02 \times 10^{23}}\right)^{1/3}$$

$$= 3.16 \times 10^{-8}\ cm$$

$$\therefore \text{density} = \frac{2}{\sqrt{2}a^2} = \frac{\sqrt{2}}{(3.16 \times 10^{-8})^2} = 1.42 \times 10^{15}\ \text{atoms}/cm^2$$

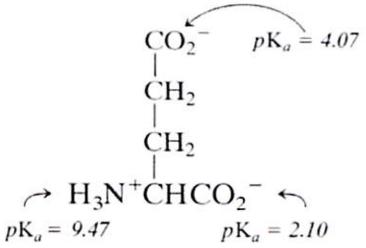
Problem #4 (22 points)

The skeletal structures of the two amino acids, glycine and glutamic acid, are given below along with the values of the relevant acid dissociation constants (pK_a).



$H_3N^+CH_2CO_2^-$

glycine (Gly)



$$\begin{array}{c} CO_2^- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ H_3N^+CHCO_2^- \end{array}$$

glutamic acid (Glu)

(a) For an aqueous solution of glycine (Gly) alone, calculate the value of pH at which the ratio of the concentration of neutral glycine zwitterion to the concentration of deprotonated anion is 10^{-4}.

4

$HA = H^+ + A^-$

$\therefore K_{a_2} = \frac{[H^+][A^-]}{[HA]}$

$\therefore pK_{a_2} = pH - \log_{10}\frac{[A^-]}{[HA]}$

$\therefore pH = pK_{a_2} + \log_{10}\frac{[HA]}{[A^-]}$

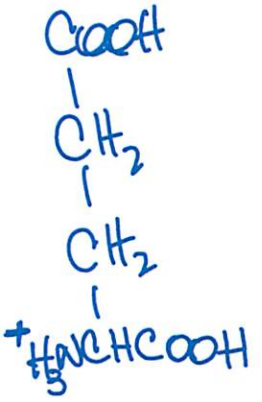
$= 9.78 + \log_{10}(10^4)$

$= 9.78 + 4$

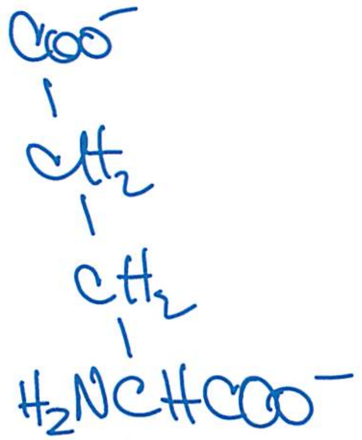
$= 13.78$

(b) Draw the skeletal structure of glutamic acid (Glu) when it is solvated in an aqueous solution under each of the following conditions.

6 (i) $pH = 1.5$ (ii) $pH = 14$ (iii) $pH = pI$, the isoelectric point



$$\begin{array}{c} COOH \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ {}^+H_3NCHCOOH \end{array}$$



$$\begin{array}{c} COO^- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ H_2NCHCOO^- \end{array}$$

$$\begin{array}{c} COO^- \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ {}^+H_3NCHCOOH \end{array}$$

Problem #4 (continued)

(c) Calculate the value of *p*H at which glutamic acid (Glu) exists as the neutral zwitterion.

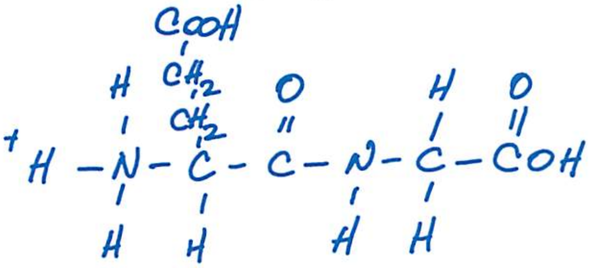
to balance the charge on the ^+H_3N group, the charge must lie ~~st~~ lie

3 at a value between pKa values of the two COO^- groups

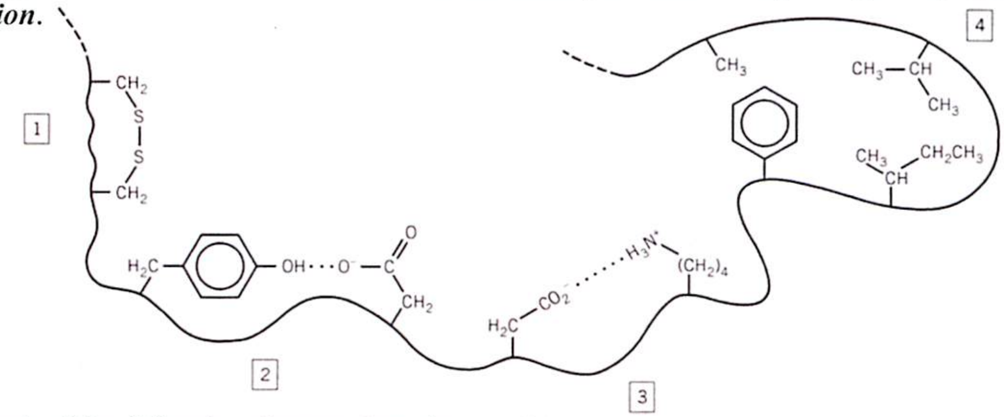
$$\therefore pI = \frac{4.07+2.10}{2} = 3.09$$

(d) Draw the skeletal structure of the dipeptide, Glu-Gly, when it is solvated in an aqueous solution of extreme acidity, i.e., *p*H < 1.

3



(e) The figure below shows various features of the tertiary structure along a length of protein ***in aqueous solution***.



For each of the following changes from the conditions that sustain the structure shown above,
(1) identify the numbered site or sites at which the tertiary structure is affected and
(2) explain the potential impact on the conformation of the protein.

❶ increase in *p*H $\boxed{3}$ inc. in pH will cause H_3N^+ to deprotonate & become neutral => electrostatic attraction will be neutralized & bond will be broken ∴ chain will not be constrained $\boxed{2}$ inc. in pH will cause OH to deprotonate ...

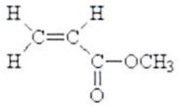
3

❷ increase in concentration of detergent $\boxed{4}$ inc. in detergency will pull on the hydrophobic pocket & open up the loop

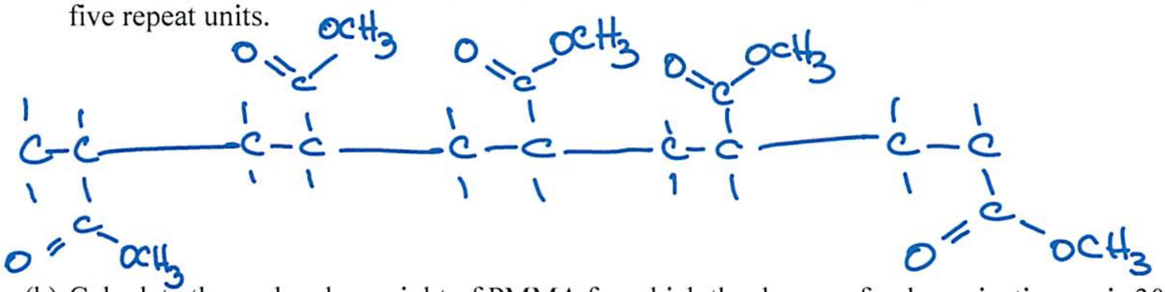
3

Problem #5 (9 points)

(a) Methyl methacrylate (or methyl 2-methylpropenoate in proper IUPAC nomenclature) is the starting material for the synthesis of poly(methyl methacrylate) (PMMA). The molecule is shown at right. Draw a segment of atactic PMMA showing five repeat units.



3



(b) Calculate the molecular weight of PMMA for which the degree of polymerization, n, is 3091.

3 MW of MMA ($C_4H_6O_2$) // $\therefore$ MW(polymer) = $n \times$ MW(mer)

$12 \times 4 = 48$

$1 \times 6 = 6$

$16 \times 2 = 32$

86

$= 3091 \times 86$

$= 2.66 \times 10^5$ g/mol

(c) Classify PMMA as either a thermoset or a thermoplastic, and with reference to its molecular structure assess its recyclability.

3 Thermoplastic — only van der Waals bonds hold chains together ⇒ Thermal reprocessing is feasible

Problem #6 (9 points)

Sketch the unary phase diagram (pressure *vs* temperature) of iodine (I). Indicate the normal melting point (P = 1 atm), normal boiling point, triple point, and critical point. Label all phase fields. Indicate on the diagram ***one example of each:*** (i) one-phase stability; (ii) two-phase coexistence; (iii) three-phase coexistence. For clarity, do not draw to scale.

triple point: P = 0.12 atm, T = 113.5ºC

critical point: P = 115 atm, T = 546ºC

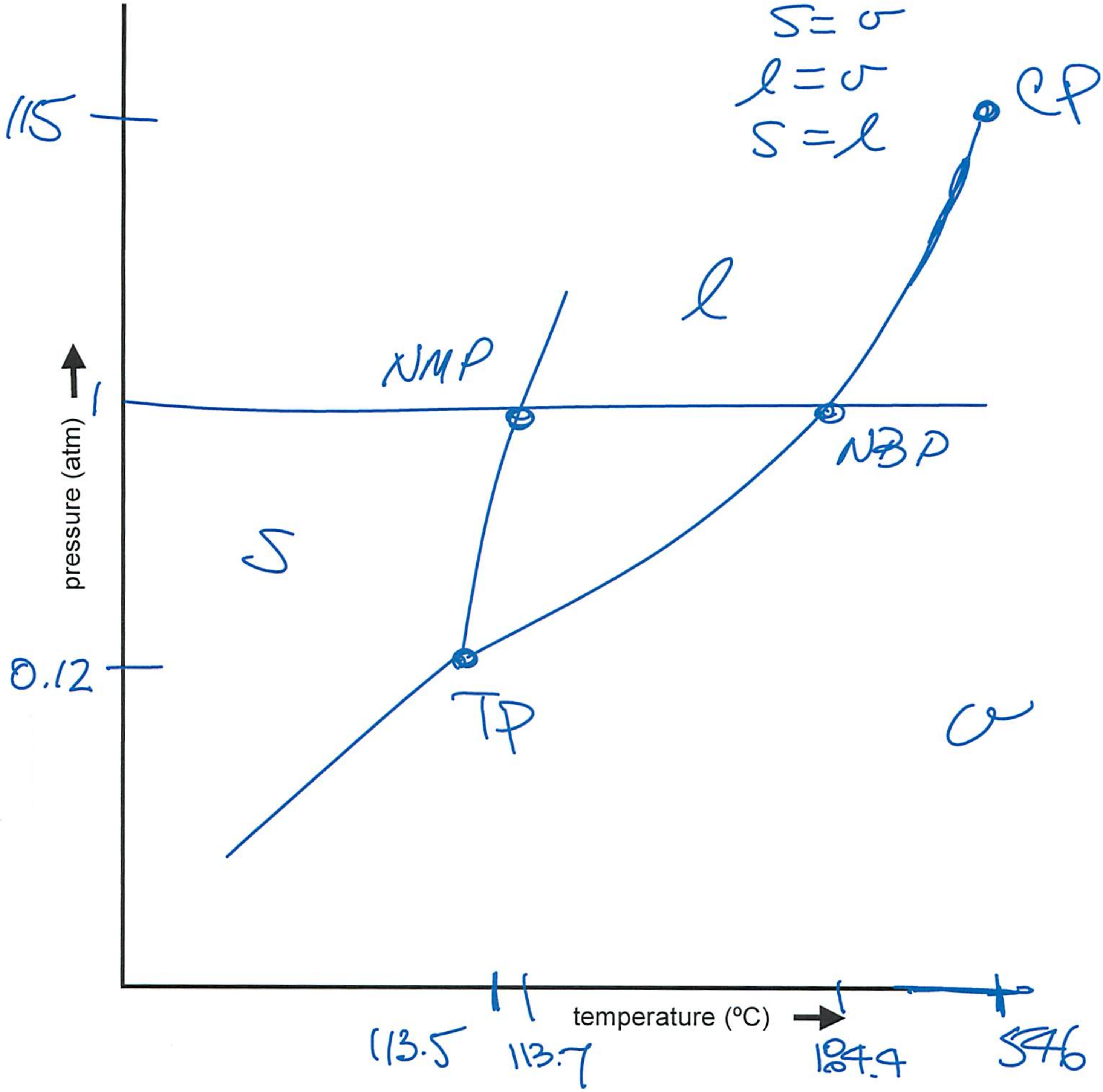
s, l, v

TP

s = v

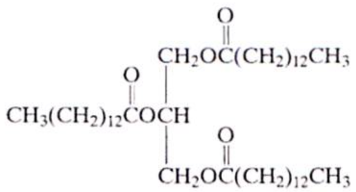
l = v

s = l



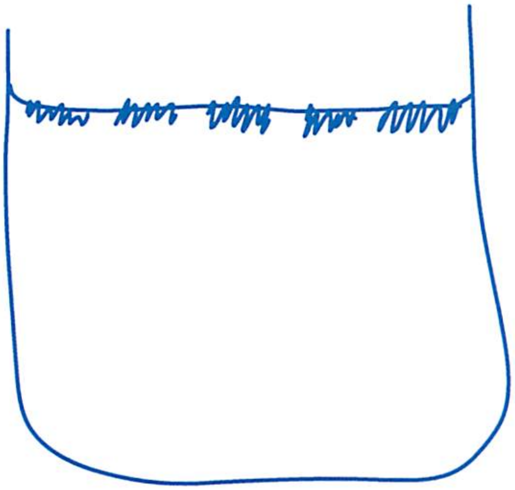
Problem #7 (5 points)

(a) The lipid, trimyristin, (chemical formula given at right) is added to a beaker of water (at neutral *p*H) in sufficient quantity to enable interaction between lipid molecules. Draw a schematic representation depicting one possible molecular arrangement that results. You may stylize the trimyristin molecule, e.g.,  for a carbon chain.


$$\begin{array}{l} \quad\quad\quad\quad\quad\quad\quad CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_{12}CH_3 \\ CH_3(CH_2)_{12}\overset{O}{\overset{\|}{C}}OCH \\ \quad\quad\quad\quad\quad\quad\quad CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_{12}CH_3 \end{array}$$

Trimyristin

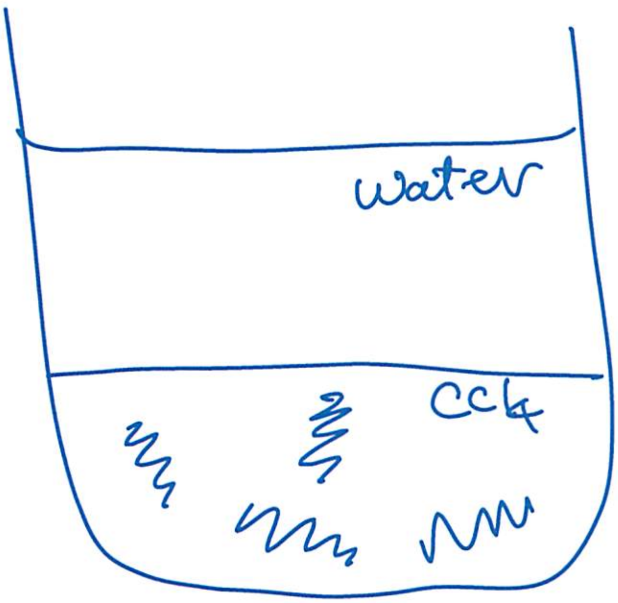
2



represent

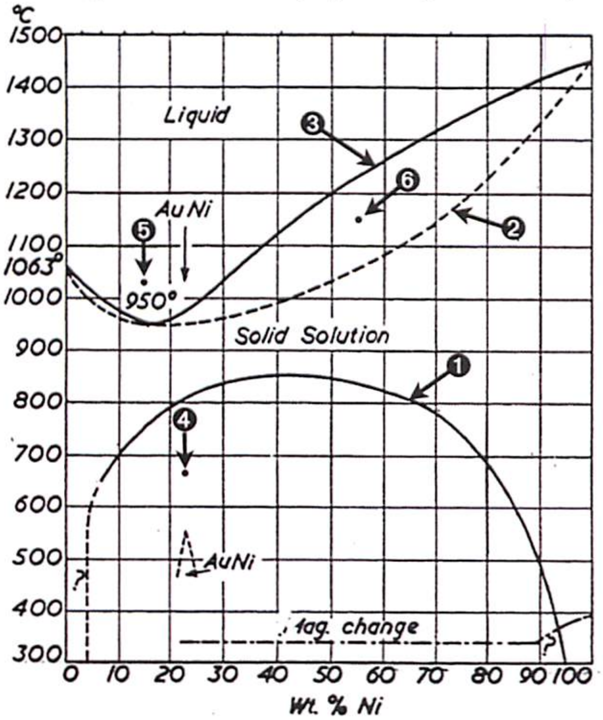
(b) To the beaker described in part (a) an equal volume of carbon tetrachloride (CCl_4) is added. The $CCl_4 - H_2O$ mixture containing the trimyristin is then subjected to vigorous agitation for several minutes and then allowed to equilibrate. Draw a schematic representation depicting one possible molecular arrangement that results. The values of density at room temperature are 1.00 g cm^{-3} for H_2O and 1.58 g cm^{-3} for CCl_4. Assume that CCl_4 and water are mutually immiscible.

3



Problem #8 (18 points)

The phase diagram of the binary system, gold-nickel (Au - Ni), is given below.



A

(a) (i) Name each of the lines labeled on the diagram above, and, for each, (ii) write the equilibrium it represents.

❶ Solvus $S = \alpha + \beta$ 3

❷ Solidus $S = \alpha + L$ 3

❸ liquidus $l = \alpha + L$ 3

(b) At each of the temperature-composition pairs labeled on the diagram above, (i) identify all phases present at equilibrium and (ii) give the composition of each phase present, expressed in wt % Ni.

❹ $\alpha + \beta$ $\alpha \equiv 8$ wt % Ni $\beta \equiv 81$ wt % Ni 3

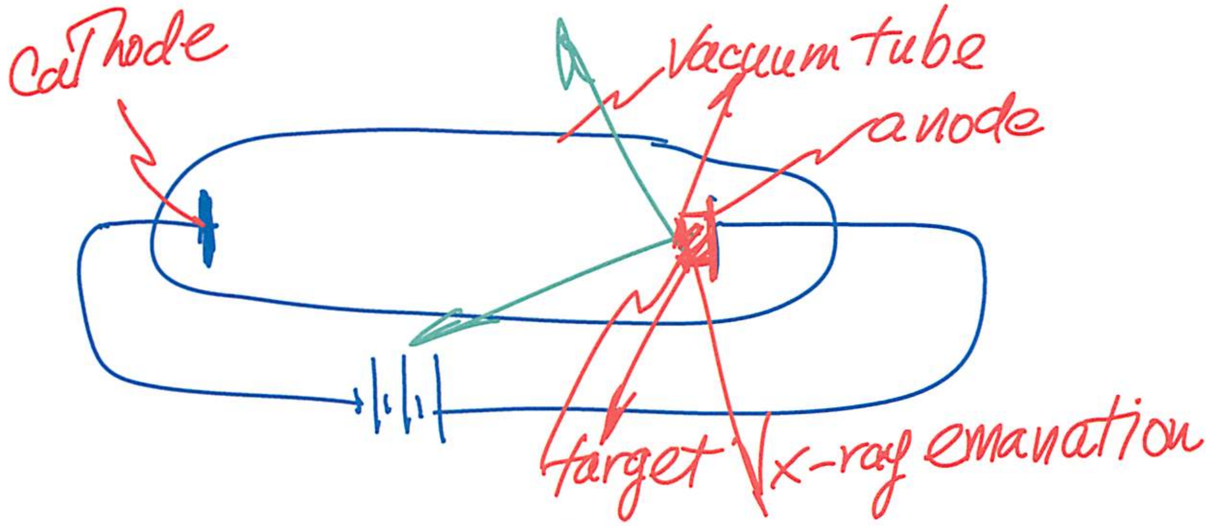
❺ L 14 wt % Ni 3

❻ $\alpha + L$ $\alpha \equiv 70$ wt % Ni $L \equiv 44$ wt % Ni 3

Problem #9 (11 points)

(a) Draw a cartoon depicting the device that generates x-rays. Label the following features: vacuum tube, cathode, anode, target. Indicate on your drawing the emanation of x-rays.

5



(b) Röntgen's gas discharge tube was highly inefficient and unsafe. Among the modifications made by William D. Coolidge (MIT class of 1896), were the following: ❶ vacuum tube instead of tube containing gas; and ❷ water cooled anode. Describe how each modification represents an improvement over Röntgen's device. In your answer specify the problem addressed by the modification and explain how the modification overcomes the problem.

2 ❶ electrons collided w/ gas molecules/atoms ⇒ loss of efficiency ⇒ vacuum tube eliminates the problem —

2 ❷ energy of ballistic electrons heated the target & anode so the tube needed to be operated intermittently ⇒ with water cooling, tube could run continuously.

(c) The Duane-Hunt Law calculation gives a value of 0.666 Å (6.66×10^{-11} m) for the shortest wavelength produced by an x-ray tube. What must be the value of the plate voltage under these circumstances?

2

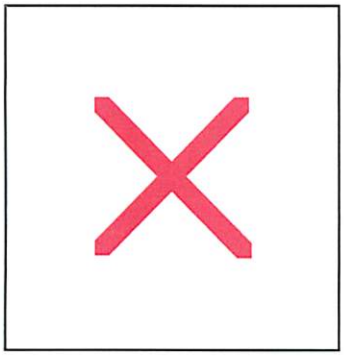
$$\lambda = \frac{12400}{V} \therefore V = \frac{12400}{\lambda} = \frac{12400}{0.666}$$

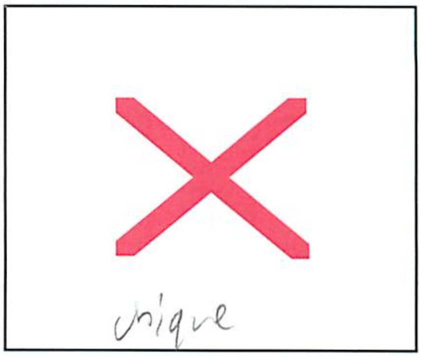
$$= 1.86 \times 10^{4}\, V$$

$$= 18.6\, kV$$

Problem #10 (5 points)

Give the rotational symmetry of each of the following patterns. Express your answer as *n*-fold.





❶ 4-fold ❷ 3-fold ❸ 1-fold

Problem #11 (5 points)

Magnesium phosphate dissolves in water according to

$Mg_3(PO_4)_2 = 3\ Mg^{2+}(aq) + 2\ PO_4^{3-}(aq)$ $K_{sp} = 1.11 \times 10^{-25}$ at 25°C

have 3
want 1 = $\frac{1}{3}$

Calculate the solubility of magnesium phosphate ($Mg_3(PO_4)_2$) in a 5.55×10^{-3} *M* sodium phosphate (Na_3PO_4) solution. Express your answer in moles $Mg_3(PO_4)_2$ per liter of solution (*M*).

$$K_{sp} = [Mg^{2+}]^3[PO_4^{3-}]^2 \Rightarrow \text{solubility} = c_s = \frac{1}{3}[Mg^{2+}]$$

with Na_3PO_4, $[PO_4^{3-}] = 5.55\times10^{-3}$

$$\therefore [Mg^{2+}] = \left(\frac{K_{sp}}{[PO_4^{3-}]^2}\right)^{1/3} = \left(\frac{1.11\times10^{-25}}{(5.55\times10^{-3})^2}\right)^{1/3} = 1.53\times10^{-7}\,M$$

$$\Rightarrow c_s = 5.11\times10^{-8}\,M$$

Calc concentration Mg and $\cdot\frac{1}{3}$

Problem #12 (10 points)

(a) The diffusion coefficient of oxygen in silicon, D_O, has been measured to have the following values:

D_O (cm^2 s^{-1})	T (°C)
9.2×10^{-11}	1100
1.4×10^{-9}	1300

Show that in order to increase the value of D_O by a factor of 10× greater than it is at 1300°C would require raising the temperature above the melting point of silicon.

7 $D = D_0 \exp -\frac{Q}{RT} \Longrightarrow$ find T' at which $D = 10 \times D_{1300}$

need to get the value of Q // $\frac{D_{1300}}{D_{1100}} = \frac{\exp -\frac{Q}{R1573}}{\exp -\frac{Q}{R1373}} = \frac{1.4\times10^{-9}}{9.2\times10^{-11}} = 15.22$

$\Rightarrow \exp\frac{-Q}{1573R} = 15.22 \exp -\frac{Q}{1373R}$

$\therefore \frac{-Q}{1573R} = \ln 15.22 - \frac{Q}{1373R}$

$\therefore Q = R \ln 15.22 \left(\frac{1}{1373} - \frac{1}{1573}\right)^{-1}$

$= 244 \times 10^3$ J/mol

now solve for $T' \Longrightarrow$

$\exp -\frac{Q}{RT} = 10 \exp \frac{-Q}{R1573}$

$\therefore \frac{-Q}{RT} = \ln 10 - \frac{Q}{R1573}$

$\therefore T = \frac{-Q}{R\left(\ln 10 - \frac{Q}{1573R}\right)}$

$\therefore T = \frac{-244000}{8.314\left(\ln 10 - \frac{244000}{1573\times8.314}\right)} = 1794K$
$= 1521°C >$ mp Si

(b) Make a crude estimate showing that it is feasible to remove oxygen from a silicon ribbon of thickness 0.1 µm by exposing the ribbon to vacuum for 10 minutes at a temperature of 1100°C.

$x^2 \approx Dt = 9.2\times10^{-11} \times 10\times60 = 5.52\times10^{-8}$ cm^2

3 $\therefore x = 2.35\times10$ cm $= 2.35\,\mu$m $\gg 0.1\,\mu$m

Problem #13 (10 points)

In this question you are going to be asked to draw a cartoon that illustrates bonding differences between HI and HF and explains why one compound has a higher boiling point than the other.

(a) Before you begin drawing, state the most important scientific idea that should be included in your cartoon to communicate these bonding differences.

3

(b) Draw a cartoon illustrating bonding differences between HI and HF and explain why one compound has a higher boiling point than the other.

6 (i) Incorporate the idea you cited in answer to part (a).

(ii) Label all operative bonding.

1 (c) Circle the compound with the higher boiling point: HI HF

Grading Scheme
MIT / 3.091 / Fall 2008
Chemical Bonding
10 points possible

		Points Earned	Points Possible
1	**Text response: the most important scientific concept that must be included in the drawing to explain the science** 3 points = relative inter-molecular bond strength determines which bond is stronger and a stronger bond equates to a higher boiling point 1 point = secondary bonding		**3**
2	**Is the compound with the correct boiling point identified?** 1 point = earned ONLY if text response is valid		**1**
3	**Graphical representation** 6 points = Relative strength of secondary bonding correctly depicted 4 points = Secondary bonding depicted w/out relative bond strength but multiple molecules ARE shown 2 points = Secondary bonding capability depicted w/out multiple molecules shown		**6**
	Total points		**10**

Cheat sheet ideas

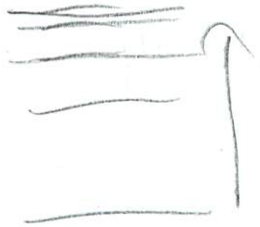
shapes -vespr -tetrahedral

% ionic character $1-\exp\left(-\frac{1}{4}(\Delta x)^2\right)\cdot 100$

Energy Heteronuclear bonds

$$\sqrt{E_{AA}\cdot E_{BB}} + 96.3\,(x_a - x_b)^2 \ \frac{kJ}{mol}$$

1) $E_{\text{~~neutron~~ electron}} = -k\,\frac{Z^2}{n^2}$ ← the different energy levels



$$r(n) = \frac{a_0 n^2}{Z}$$

$$v(n) = \frac{hZ}{2\pi m a_0 n}$$

$$E_{neutron} = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

↑ planks constant

↑ atomic mass constant

$$\lambda_{SWL} = \frac{hc}{eV}$$

$$\bar{v} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)\cdot(Z-\sigma)^2$$

↑ screening factor

~~Mosley~~

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

$$\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2+k^2+l^2} = const$$

$$a = \frac{\lambda}{\sqrt{2}\sqrt{const}}$$

Vacency formation $f_v = \frac{n_v}{N} = A\exp\left(-\frac{\Delta H_v}{k_B T}\right)$

plane notation, etc

Cell packing densities

HA -stuff orgo ✓ review orgo

erf function

acid base definitions

$k_a = k[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$

amphiprotic → acid or base

~~when was base concentration stuff~~

~~- Lec 25? Solubility~~

~~- Solvent - majority~~

~~- solute - minority~~

~~Measures of solvability → molarity Ⓜ~~

$\frac{\text{moles solute}}{\text{liters solvent}}$

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

$pH = pka - \log\frac{[AH]}{[A^-]}$

$k_a = \frac{[H^+][B]}{[BH^+]}$

$$W_L = \frac{C_s - C_0}{C_s - C_L}$$

$$W_s = \frac{C_0 - C_L}{C_s - C_L}$$

$h_a I_a = I_B n_b$

fricks 1st, 2nd law

solid, transient from class today

the $\frac{VB}{CB} \longrightarrow \lambda$ x levels Silicon

Solvant - majority
solute - minority

$pH = pka - log \frac{[A+1]}{[A^-]}$ $pKa = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+][B]}{[BH^+]}$

Produced by Kenny Mandel

Q=Activation Energy, $R = K_B N_{Av}$

$Q_{substitutional} = Q_{migration} + Q_{vacancy\ formation}$

$Q_{interstitial} = Q_{migration}$

Fick's Second Law: $\frac{dc}{dt} = D\frac{d^2c}{dx^2} \rightarrow \frac{c_1 - c_s}{c_0 - c_s} = erf\frac{x}{2\sqrt{Dt}}$

Note: They will tell u how to calculate an erf, it is usually is equal to the argument.

Solutions, Acids, and Bases:

$AB \rightarrow A^+ + B^-$, $K_{sp} = [A^-][B^+]$

(Acids/Bases)

Arrhenius- donates H^+/OH^-

Bronsted-Lowry- donates proton/accepts proton

Lewis- Electron pair acceptor/donor

$pH = -\log[H^+]$, $pOH = -\log[OH^-]$

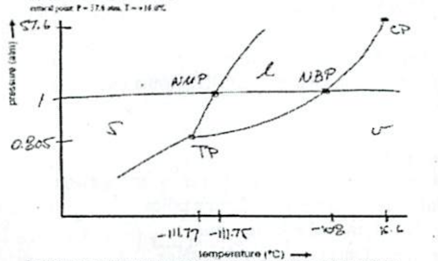
$K_a = \frac{[H^+][A^-]}{[HA]}$, $K_a > 1$ = strong acid

$K_a < 1$ = weak acid   amphiprotic - acid or base

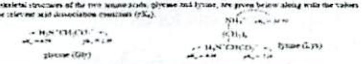
Old Test Answers:

Sketch the unary phase diagram (pressure vs temperature) of xenon (Xe). Indicate the normal melting point (P = 1 atm), normal boiling point, triple point, and critical point. Label all phase fields. For clarity, do not draw to scale.

triple point: P = 0.805 atm, T = -111.77°C
critical point: P = 57.6 atm, T = +16.6°C



The skeletal structures of the two amino acids, glycine and lysine, are given below along with the values of the relevant acid dissociation constants (pK_a).



(a) For an aqueous solution of glycine alone, calculate the value of pH at which the ratio of the concentration of neutral glycine zwitterion to the concentration of protonated cation is 10^2.

$HA + H^+ \rightleftharpoons HAH^+$

$K_1 = \frac{[H^+][HA]}{[HAH^+]}$

$\therefore pK_1 = pH + \log_{10}\frac{[HAH^+]}{[HA]}$

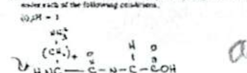
$\therefore pH = pK_1 + \log_{10}\frac{[HA]}{[HAH^+]}$

$\rightarrow pH = 2.35 + \log_{10} 10^2$
$= 2.35 + 2$
$= 4.35$

pH

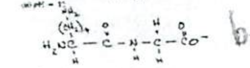
(b) Draw the skeletal structure of the dipeptide, Lys-Gly, when it is solvated in an aqueous solution under each of the following conditions.

(i) pH = 1



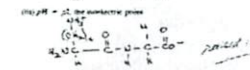
acid

(ii) pH = 13



base

(iii) pH = pI, the isoelectric point



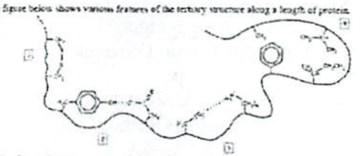
paired states

(c) Calculate the value of pI of the dipeptide, Lys-Gly, assuming that there is negligible shift in the values of acid dissociation constants from the values of the constituent amino acids.

To balance The charge on The COO^- group, pH must lie at a value btw pK_a values of The Two NH_3^+ groups

$\therefore pI = \frac{0.77+9.18}{2} = 9.97$

(d) The figure below shows various features of the tertiary structure along a length of protein.



At sites 2 and 4 in the protein shown above, (i) name the sidechain interaction, (ii) identify one chemical agent that can denature the molecule at that site; and (iii) explain what happens at the atomic level to disrupt the structure.

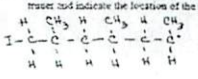
- at site 2 H-bonding p^+ is chem. agent denature by drop in pH which will protonate COO^- → break bond
- at site 4 hydrophobic interactions
detergent
denature by addition of amphipathic molecules whose hydrophobic tails bind to nonpolar sidegroups & whose hydrophilic heads bind to water.

(a) The absorption edge of aluminum nitride (AlN) has been measured to be 196 nm or 1.96×10^{-7} m at room temperature. Would AlN be classified electrically as a conductor, a semiconductor, or an insulator? Justify your choice.

$E_g = \frac{hc}{\lambda_{edge}} = \frac{6.6\times10^{-34} \times 3\times10^8}{1.96\times10^{-7}} = 1.01\times10^{-18} J$

$= 6.31 eV \Rightarrow$ insulator

(a) Propylene (or propene in proper IUPAC nomenclature), $H_2C{=}CH{-}CH_3$, can be reacted by addition polymerization to form polypropylene (PP). The process is initiated with the radical, $I^\bullet$. Draw a segment of isotactic PP showing three repeat units. Place the radical initiator at the left end of the trimer and indicate the location of the unpaired electron.



$I-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}\cdot$

(b) What is the degree of polymerization, n, of PP with a molecular weight of 3.091×10^5 g mol^{-1}?

MW of PP (C_3H_6)
$12\times3 = 36$
$1\times6 = 6$
42

$n = \frac{MW\ polymer}{MW\ mer} = \frac{3.091\times10^5}{42} = 7.36\times10^3$

(b) Do you expect the electrical conductivity of gallium nitride (GaN) to be greater or less than that of AlN at room temperature? Justify your choice.

Conductivity ∝ carriers ∝ $e^{-(E_g/k_BT)}$

expect $E_g(GaN) < E_g(AlN)$ b/c Ga is in 4th period vs Al in 3rd period ∴ Ga larger ∴ weaker bonding → Ga is more conductive.

Problem #4 (9 points)

(a) A single-crystal wafer of germanium (Ge) is doped with gallium (Ga) to the level of 3.091×10^{21} Ga atoms m^{-3} at a depth of 33 μm from the surface of the Ge. The effective surface concentration of Ga is 5.55×10^{21} atoms m^{-3}. How long must the Ge be processed to meet specification? Assume that initially the concentration of Ga in the Ge crystal is zero. The diffusion coefficient of Ga in Ge, D_{Ga}, has a value of 7.77×10^{-19} m^2 s^{-1} at the processing temperature.

Error Function Values: use the approximation erf(z) = z for 0 < z < 0.6
erf(1.0) = 0.84   erf(1.5) = 0.97   erf(z) = 1.00 for z > 1.9

$\frac{c-c_s}{c_0-c_s} = erf\frac{x}{2\sqrt{Dt}}$

$\frac{3.091-5.55}{0-5.55} = 0.443 < 0.6$

$\therefore erf\frac{x}{2\sqrt{Dt}} = \frac{x}{2\sqrt{Dt}}$

$(0.443)^2 \times 4Dt = x^2$

$\therefore t = \frac{x^2}{4D(0.443)^2}$

$\therefore t = \frac{(33\times10^{-6})^2}{4\times7.77\times10^{-19}(0.443)^2}$

$= 1.79\times10^3 s$

(b) Name the majority charge carrier in the Ga-doped Ge.

h^+ hole

(c) Name another suitable dopant that would introduce the same type of charge carrier into Ge as does Ga.

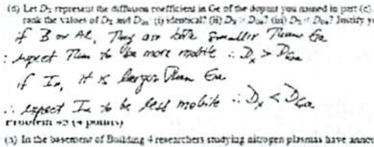
group 3: B, Al, In

(d) Let D_X represent the diffusion coefficient in Ge of the dopant you named in part (c). How do you rank the values of D_X and D_{Ga}: (i) identical? (ii) $D_X > D_{Ga}$? (iii) $D_X < D_{Ga}$? Justify your choice.

if B or Al, They are both smaller Than Ga
∴ expect Them to be more mobile ∴ $D_x > D_{Ga}$
if In, it is larger Than Ga
∴ expect In to be less mobile ∴ $D_x < D_{Ga}$

Problem #5 (4 points)

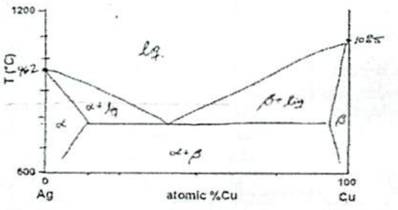
(a) In the basement of Building 4 researchers studying nitrogen plasmas have announced the existence of the gas-phase species N_2^-. Use energy-level diagrams from LCAO-MO theory (linear combination of atomic orbitals - molecular orbitals) to show that N_2^- is stable and paramagnetic. The filling sequence of molecular 2p orbitals in N_2^- is $\pi_{2p}, \sigma_{2p}, \pi^*_{2p}, \sigma^*_{2p}$.



- stability shown by no electrons in bonding orbitals > no. electrons in antibonding orbitals
- paramagnetism shown by the (unpaired) e^- in uppermost orbital

Silver (Ag) and copper (Cu) are completely miscible as liquids but exhibit limited solid solubility. The Ag-rich solid solution with the highest Cu concentration contains 14% Cu at 779°C. The Cu-rich solid solution with the highest Ag concentration contains 5% Ag at 779°C. The lowest point on the Ag-Cu binary phase diagram at which a single-phase liquid solution is in equilibrium is 40% Cu and 779°. All concentrations are stated in units of atomic per cent.

(a) Draw a schematic representation of the Ag-Cu phase diagram (T vs c) over the temperature interval 600 - 1200°C. Label all phase fields. For simplicity, do not draw to scale.



(b) Identify the different types of coexistence curve and, for each, write the equilibrium it represents.

liquidus. $l = l+\alpha$ or $l = l+\beta$
Solidus. $\alpha = \alpha+l$ or $\beta = \beta+l$
Solvus: $\alpha = \alpha+\beta$ or $\beta = \alpha+\beta$

(c) Name the lowest point on the Ag-Cu binary phase diagram at which a single-phase liquid solution is stable, and write the equilibrium involving the liquid under these conditions.

eutectic

$l = \alpha + \beta$ or

In 1951 Linus Pauling and Robert Corey discovered that in proteins the secondary structure (analogous to conformation in polymers) takes three forms: one of them disordered and two of them ordered.

(a) Name the two ordered secondary structures and explain what drives their formation.

3 α-helix
β-sheet   maximize H-bonding

(b) Name the disordered secondary structure.

1 random coil

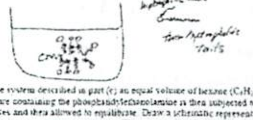
(c) Identify the chemical feature in the protein that dictates the choice of local secondary structure.

1 amino acid sequence

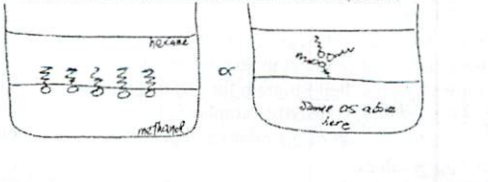
(d) Methanol (CH_3OH) is a liquid at room temperature and has gained some notoriety in recent years as a candidate liquid fuel to replace gasoline. The phospholipid phosphatidylethanolamine, (chemical formula given at right) is added to methanol in sufficient quantity to enable interaction between phospholipid molecules. Draw a schematic representation depicting one possible molecular arrangement that results.

[illegible]

2



(e) To the system described in part (c) an equal volume of hexane (C_6H_{14}) is added. The $C_6H_{14} - CH_3OH$ mixture containing the phosphatidylethanolamine is then subjected to vigorous agitation for several minutes and then allowed to equilibrate. Draw a schematic representation depicting one possible molecular arrangement that results. The values of density at room temperature are 0.79 g cm^{-3} for CH_3OH and 0.66 g cm^{-3} for C_6H_{14}. Assume that hexane and methanol are mutually immiscible.



Tungsten and lead are thought to be immiscible. Recently, a group at Indigo Institute announced that it had prepared a homogeneous, single-phase W-Pb alloy consisting of 30 mole per cent W. They base their conclusion on PES (photoelectron spectroscopy) data. Their findings are being challenged by a group at Crimson College (no reference to Harvard intended) who claim to have prepared the same material. Relying on x-ray diffraction (XRD) data the Crimson researchers claim that Indigo's material is not homogeneous and single phase, but rather a two-phase mixture of pure W and pure Pb. Who is correct, Indigo or Crimson? Support your answer with the data provided.

Here are Crimson's XRD data taken with Ag K_α radiation (λ = 0.573 Å).
$\theta_1 = 5.747°$; $\theta_2 = 6.640°$; $\theta_3 = 7.356°$; $\theta_4 = 9.408°$; $\theta_5 = 10.41°$; $\theta_6 = 12.81°$.

Lattice constant, a: 3.16 Å for W   4.95 Å for Pb

W is BCC ⇒ (110), (200), (211)...
Pb is FCC ⇒ (111), (200), (220)...
} Calculate θ values & compare

$\lambda = 2d\sin\theta$ $d = \frac{a}{(h^2+k^2+l^2)^{1/2}} \Rightarrow \theta_{hkl} = \sin^{-1}\left(\frac{\lambda(h^2+k^2+l^2)^{1/2}}{2a}\right)$

for W

$\theta_{110} = \sin^{-1}\frac{0.573(1^2+1^2+0^2)^{1/2}}{2\times3.16} = 7.37° = \theta_3$ ✓

$\theta_{200} = \sin^{-1}\frac{0.573(2^2+0^2+0^2)^{1/2}}{2\times3.16} = 10.45° = \theta_5$ ✓

$\theta_{211} = \sin^{-1}\frac{0.573(2^2+1^2+1^2)^{1/2}}{2\times3.16} = 12.83° = \theta_6$ ✓

for Pb

$\theta_{111} = \sin^{-1}\frac{0.573(1^2+1^2+1^2)^{1/2}}{2\times4.95} = 5.75° = \theta_1$ ✓

$\theta_{200} = \sin^{-1}\frac{0.573(2^2+0^2+0^2)^{1/2}}{2\times4.95} = 6.65° = \theta_2$ ✓

$\theta_{220} = \sin^{-1}\frac{0.573(2^2+2^2+0^2)^{1/2}}{2\times4.95} = 9.42 = \theta_4$ ✓

Consistent with both elements present in Their pure states, i.e., unalloyed

⇒ Crimson is Correct

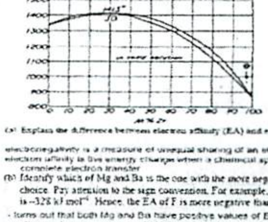
The binary phase diagram of the scandium - zirconium (Sc-Zr) is shown below.

(a) At ① and ②, name all phases present and give the composition of each.

- $l + \beta$ $l_{iq} \cong 10\% Zr$ $\beta \cong 22\% Zr$
- β 97% Zr

(b) Using zone refining, does the phase diagram indicate that it should be possible to raise the content of a Zr-Sc alloy, from 20 atom % scandium to > 80 atom % Sc? If so, describe how to do it. If not, explain why this is the case.

yes
① heat 20% Sc to Solidus & collect liquid which is ≈ 40% Sc
② cool 40% Sc to its Solidus & collect liquid which is ≈ 60% Sc
③ Cool 60% Sc to its Solidus & Collect liquid which is ≈ 85% Sc



moles solute / L solvant = M

(a) Explain the difference between electron affinity (EA) and electronegativity (χ).

electronegativity is a measure of unequal sharing of an electron within a covalent bond
electron affinity is the energy change when a chemical species acquires an electron by complete electron transfer

(b) Identify which of Mg and Ba is the one with the more negative EA. Explain the reason for your choice. Pay attention to the sign convention. For example, the EA of Li is −59.6 kJ mol^{-1}; the EA of F is −328 kJ mol^{-1}. Hence, the EA of F is more negative than that of Li.

- turns out that both Mg and Ba have positive values of EA.
- both are strong metals (good electron donors) so forcing either of them to accept an electron takes effort, thus the energy change is positive
- thus, since Mg is n=3 and Ba is n=6, the energy levels are much farther apart in Mg than in Ba; so the acquisition of the extra electron is accompanied by a greater energy penalty in Mg than in Ba
- so, in full respect of the wording of the question, the EA of Ba is less positive or MORE NEGATIVE than the EA of Mg

For each pair of substances listed below (i) identify the one with the lower melting point and (ii) explain in terms of the relevant bonding the basis for your choice.

(i) lithium fluoride (LiF), hydrogen fluoride (HF)

HF. LiF is ionic whereas HF is polar covalent with H bonding. Ionic trumps.

(ii) tetrafluoromethane (CF_4), tetrachloromethane (CCl_4)

CF_4. Both are nonpolar covalent molecules. Van der Waals secondary bonding operative but CCl_4 is larger and more polarizable.

(iii) nitrogen (N_2), nitric oxide (NO)

N_2. N_2 is nonpolar so secondary bonding is van der Waals. NO is polar so secondary bonding is dipole-dipole which is stronger than vdW.

(iv) potassium fluoride (KF), calcium oxide (CaO)

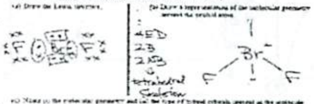
KF. Both are ionic but coulombic forces are greater between doubly charged Ca^{2+} and O^{2-} than between K^+ and F^-.

(v) hexane (C_6H_{14}), hexanol ($C_6H_{13}OH$)

C_6H_{14}. C_6H_{14} is nonpolar with weak van der Waals secondary bonding, while $C_6H_{13}OH$ is polar and has H-bonding capability.

Answer the following questions about the difluorobromate ion (BrF_2^-).

(a) Draw the Lewis structure.   (b) Draw a representation of the molecular geometry around the central atom.



(c) Name (i) the molecular geometry and (ii) the type of hybrid orbitals present in the molecule.

2 bent sp^3

(d) Is the molecule polar or nonpolar? Explain.

2 polar. asymmetry with δ^- on F legs and δ^+ on Br

(e) Determine the minimum de Broglie wavelength of an electron capable of breaking the Br-F bond.

Bond energies (kJ/mol)   F-F 160   Br-Br 195

$E_{Br-F} = \sqrt{E_{Br_2} \times E_{F_2}} + 96.3(\chi_{Br}-\chi_F)^2$

$= \sqrt{195\times160} + 96.3(2.96-3.98)^2$

$= 177 + 100 = 277$ KJ/mol

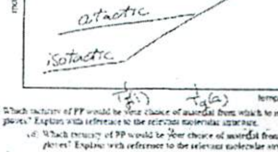
$E_{kinetic} = \frac{1}{2}mv^2 = \frac{p^2}{2m}$ where $p = \frac{h}{\lambda} \Rightarrow E_e = \frac{h^2}{2m\lambda^2}$

$\therefore \lambda_e = \frac{h}{\sqrt{2mE}} = \frac{6.6\times10^{-34}}{\left(2\times9.11\times10^{-31}\times\frac{277\times10^3}{6.02\times10^{23}}\right)^{1/2}}$

$= 7.21\times10^{-10} m = 7.21 Å$

$erf = \frac{2}{\pi}\int_0^x e^{-t^2} dt$

(c) On the graph below, draw a schematic representation of the temperature dependence of the molar volume of isotactic PP and of atactic PP, assuming both to be of comparable molecular weight. Label the glass transition temperature, T_g, of each substance.



(d) Which tacticity of PP would be your choice of material from which to manufacture stretchable gloves? Explain with reference to the relevant molecular structure.

2

choose the form that is less likely to crystallize, which means atactic

the isotactic has a higher propensity for crystallization because it is more regular and therefore can pack better which explains its lower value of T_g

intrinsic = pure

supervalent n —e^-— CB

subvalent p —e^-, h^+— VB subvalent

$E_{neutron} = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$

r atomic mass constant

Produced by Kenny Mandel

Polymers: n = polymerization index

$MW_{polymer} = n(MW_{mer})$

Primary bonds:covalent, secondary:VanderWaals

Partial xtalinity: xtal regions w/i polymer

Architecture:

1) Composition: homopolymer-same unit

Copolymer: block-AABBAAABBB

Alternating- ABABABAB

Graft: AAAAA-BBB (sidechains)

2) Tacticity: where side groups are.

Syndiotactic-alternating

Isotactic-same side

Atactic- Random

3) Linear vs. Branched vs. X-linked

Linear, isotactic, homopolymer is most crystalline.

Linkages: disulfide bonds→elasticity

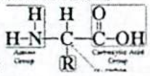
Synthesis:

1) Addition: Free radical makes mers bond

2) Condensation: R-OH + H-P →H_2O+R-P

BioChem: Proteins, Lipids, Nucleic Acids

Amino Acid: mer of protein:



$$H_2N-CH(R)-COOH$$

Have Chirality: L (ccw) vs. D (cw)

In Solution: ^+H_3N-CHR-COO^- →zwitterion

Low pH- HAH^+ High pH- A^-

$$K_a = \frac{[H^+][HA]}{[HAH^+]} \quad pK_a = pH + \log\left(\frac{HAH^+}{HA}\right)$$

$$pI = \frac{pK_{a-1} + pK_{a-2}}{2}$$

Protein Structure:

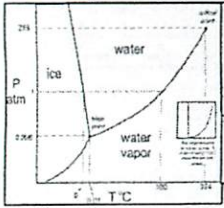
Primary: AA sequence

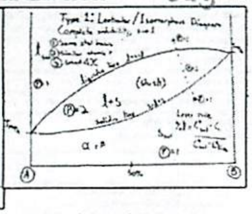
2ndary: packing: alpha helix or beta sheet

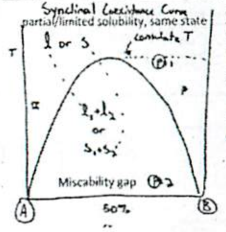
Tertiary: conformation S-S linkages

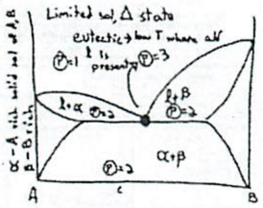
Denaturing: temp., pH, ox/red, detergents $n_a I_a = n_b I_b$

Phase Diagrams: I, II, III in that order









Packing density

$\frac{\text{atoms}}{\text{unit cell}} \cdot V_{atom}$

V_{cell}

$V_{atom} = \frac{4}{3}\pi r^3$

$V_{cell} = a^3$

$$p(momentum)_{photon} = \frac{h}{\lambda}$$

Bound Electrons:

$$\Delta p \cdot \Delta x \geq \frac{h}{2\pi}$$

$$E = E_0\frac{Z^2}{n^2}, E_0 = 13.6eV$$

$$p = mv = \frac{h}{\lambda}$$

Unbound Electrons/Protons/Neutrons:

$Kinetic - Energy = \frac{1}{2}mv^2 = \frac{h^2}{2m\lambda^2}$ ----> PARTICLES ONLY

$$p = mv = \frac{h}{\lambda_{deBrolie}}$$

$$\frac{1}{2}mv^2 = |q| \cdot V$$

1 Electron Model:

$$E_{n-shell} = E_0\frac{Z^2}{n^2}, E_0 = 13.6eV$$

$$r_n = \frac{n^2 a_0}{Z}, a_0 = .529 Angstroms$$

$E_{heteronuclear}$ $\sqrt{E_{AA} \cdot E_{BB}} + 96.3(\chi_a - \chi_b)^2 = \frac{kJ}{mole}$

$$v_n = \frac{Zh}{n \cdot 2\pi m a_0}$$

$$\Delta E = -E_0 Z^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), E_0 = 13.6eV$$

$$\Delta E = -RhcZ^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$E_{electron} = -k\frac{Z^2}{n^2}$

$$\Delta E = \frac{hc}{\lambda_{emmited - photon}}$$

$r(n) = \frac{a_0 n^2}{Z}$

$$Rhc = 2.18 \times 10^{-18} J$$

$v(n) = \frac{hZ}{2\pi m a_0 n}$

Bonding:

$\frac{b}{r^n}$ = repulsive force, n = borne exponent, b = constant

$$E(r_0) = \frac{Q_+Q_-}{4\pi\varepsilon_0 r_0}(1 - \frac{1}{n}), r_0 = r_+ + r_-$$

$$Lattice\ Energy = \frac{-MQ_+Q_- \cdot N_{Av}}{4\pi\varepsilon_0 r_0}(1 - \frac{1}{n})$$

$$E_{x-y} = \sqrt{E_{xx} \cdot E_{yy}} + 96.3(\chi_x - \chi_y)^2$$

$$Ionic\ Character = \left(1 - e^{-.25(\Delta\chi)^2}\right) \times 100\%$$

Visible Light: 400 to 700nm

Test 2:

Lattices and Crystals:

[hkl] → Vector, <hkl> → Vector Family,

i.e. <001> = $[001][010][100][00\bar{1}][0\bar{1}0][\bar{1}00]$

(hkl) → Plane, {hkl} → Plane Family,

i.e. {001} = $(001)(010)(100)(00\bar{1})(0\bar{1}0)(\bar{1}00)$

Note: Vector [hkl] is the normal to plane (hkl).

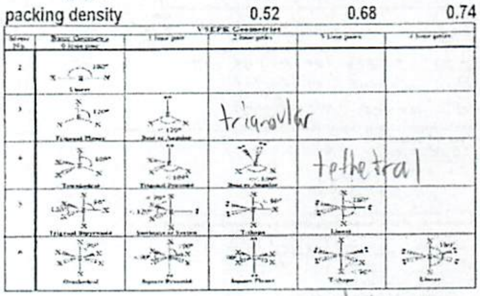
$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ → Distance between planes

Lattice Constant = a = $\left(\frac{x \cdot V_{molar}}{N_{Avagadro}}\right)^{1/3}$, where

x = {1 for SC, 2 for BCC, 4 for FCC}

Closest Packed Direction: SC=[100], BCC = [111], FCC = [011]

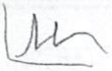
	Simple	Body-Centered	Face-Centered
Unit Cell Volume	a^3	a^3	a^3
Lattice Points Per Cell	1	2	4
Nearest Neighbor Distance	a	$\frac{a\sqrt{3}}{2}$	$\frac{a}{\sqrt{2}}$
Number of Nearest Neighbors	6	8	12
Second Nearest Neighbor Distance	$a\sqrt{2}$	a	a
Number of Second Neighbors	12	6	6
a = f(r)	2r	$4r/\sqrt{3}$	$2\sqrt{2}r$
or 4r =	$\sqrt{4}$ a	$\sqrt{3}$ a	$\sqrt{2}$ a
packing density	0.52	0.68	0.74



octaleardl

X-Rays:

Mosley's Law: $\frac{1}{\lambda} = \bar{\nu} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)(Z - \sigma)^2$, sigma = 1 for K_α, sigma = 7.4 for L_α



Simplified Mosley's Laws:

$$\frac{1}{\lambda_{K_\alpha}} = (8.175 \times 10^6)(Z - 1)^2 \quad \frac{1}{\lambda_{L_\alpha}} = (1.524 \times 10^6)(Z - 7.4)^2$$

ehC

$\lambda_{swl} = \frac{12400}{Voltage} angstroms$, 1 angstrom = 10^{-10} meters

Bragg's Law: $\lambda \cdot n = 2d\sin\theta$, where n is a positive integer and d is d_{hkl}, found in above formula.

"Sadoway's Five Step Program for Determining Crystal Structure:" (Heavily Paraphrased)

1. Start with a set of 2θ values and generate $\sin^2\theta$ values.
2. Normalize these values (divide all values by the smallest $\sin^2\theta$ value)
3. Clear Fractions from normalized column. These are $h^2 + k^2 + l^2$ values.
4. Speculate on what values of hkl make $h^2 + k^2 + l^2$ = normalized column (i.e 3 is 111, 4 is 200, etc.)
5. Compute $\frac{\sin^2\theta}{h^2 + k^2 + l^2}$ for each data point. If all of these values are identical, you are correct in hkl assumptions.

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

SC: $h^2 + k^2 + l^2$ = 1, 2, 3, 4, 5, 6, 8 (NOTE: no 7)

BCC: h + k + l = any even number, $h^2 + k^2 + l^2$ = 2, 4, 6, 8, 10, 12, 14

FCC: h, k, and l are either all even or all odd, $h^2 + k^2 + l^2$ = 3, 4, 8, 11, 12, 16

Band Theory:

$np = n_i^2$

Intrinsic (pure): $n = p$

Extrinsic (impure): $n \neq p$

VSEPR:

Vertical Axis: Electron Domains

Horizontal Axis: Non-Bonding (NB) Domains

Test 3:

Defects:

0D- Point Defects

Substitutional- the wrong atom, but on a lattice point

Interstitial- any atom not on a lattice point

Vacancy- No atom at the lattice site

Schottky (Ionic Only)- missing ion pair

Frankel (Ionic Only)- wrong site for an ion

$f_v = \frac{n_v}{N} = A^{\frac{-H_v}{k_B T}}$

1D- Line Defects

Dislocation- "Line of Vacancies"- This is the mechanism for plastic deformation.

2D- Plane Defect

Grain Boundary- Edge of each individual crystal- "boundaries arrest dislocations"

3D- Precipitate/Inclusion

Insertion of a separate crystal into the lattice

Vacancies, Dislocations, Grain Boundaries→ increased diffusion

Grain Boundaries→Improved Strength of material

Elastic Deformation: Bonds Stretched, no permanent changes

Plastic Deformation: broken bonds, moving atom planes

Glasses:

-short range order, no long range order

-factors favoring glass formation: Viscosity, Complexity of Arrangement, Faster Cooling Rate

Networks:

Formers: Covalent network with oxide bridges (SiO_2, GeO_2, B_2O_3)

-Insulating, Colorless

Modifiers: (Li_2O, CaO, MgO) Ionic Oxides.

-Introduces O^{2-}, scission of oxide bridges

Intermediates: Covalent Oxides with Different Coordination #s

-Disrupts packing – thermal shock resistance

Strengthening Glasses: Thermal or Chemical Treatment:

-Thermal: surface compressed, increases tensile strength

-Chemical: insert larger molecules→tenses material→stronger

Kinetics:

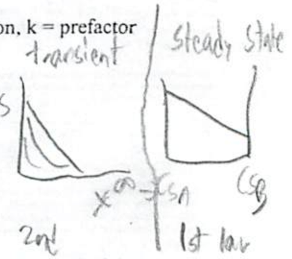
$r = -\frac{dc}{dt} = kc^n$, n = order of reaction, k = prefactor

$$k = A\exp(-E_A / k_B T)$$

If $n = 1$, $\ln(c) = \ln(c_0) - kt$

If $n = 2$, $\frac{1}{c} = \frac{1}{c_0} + kt$

Else: $\ln r = \ln k + n\ln c$



Diffusion:

Fick's First Law: $J = -D\frac{dc}{dx}$, $D = D_0\exp(-Q / RT)$

Fi what are tus

Angstrom 10 $^{-10}$ m 1eV = 1.6×10^{-19} J

	Quantity	Symbol	Value	Units (SI)	Relative uncertainty ppm
1	Speed of light in vacuum	c	299 792 458 $\times 10^8$	m s^{-1}	exact
2	Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$	N A^{-2}	exact
3	Permittivity of vacuum	ε $\epsilon_0 = 1/\mu_0 c^2$	8.854 187 817... $\times 10^{-12}$	F m^{-1}	exact
4	Newtonian constant of gravitation	G	6.672 59(85) $\times 10^{-11}$	m^3 kg^{-1} s^{-2}	128
5	Planck constant	h	6.626 075 5(40) $\times 10^{-34}$	J s	0.60
6	h-bar	$\hbar = h/2\pi$	1.054 572 66(63) $\times 10^{-34}$	J s	0.60
7	Elementary charge (oil drop experiment)	e	1.602 177 33(49) $\times 10^{-19}$	C	0.30
8	Electron mass	m_e	9.109 389 7(54) $\times 10^{-31}$	kg	0.59
9	Proton mass	m_p] almost same	1.672 623 1(10) $\times 10^{-27}$	kg	0.59
10	Neutron mass	m_n	1.674 928 6(10) $\times 10^{-27}$	kg	0.59
11	Avagadro constant	N_A, L	6.022 136 7(36) $\times 10^{23}$	mol^{-1}	0.59
12	Atomic mass constant	m_u	1.660 540 2(10) $\times 10^{-27}$	kg	0.59
13	Molar gas constant	R	8.314 510(70)	J mol^{-1} K^{-1}	8.4
14	Boltzmann constant	$k = R/N_A$	1.380 658(12) $\times 10^{-23}$	J K^{-1}	8.5
15	Molar volume (ideal gas), STP	V_m	0.022 414 10(19)	m^3 mol^{-1}	8.4
16	Faraday constant	$F = N_A e$	96 485.309(29)	C mol^{-1}	0.30
17	Magnetic flux quantum	$\Phi_0 = h/2e$	2.067 834 61(61) $\times 10^{-15}$	Wb	0.30
18	Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 015 4(31) $\times 10^{-24}$	J T^{-1}	0.34
19	Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.050 786 6(17) $\times 10^{-27}$	J T^{-1}	0.34
20	Fine structure constant	$\alpha = \mu_0 c e^2/2h$	7.297 353 08(33) $\times 10^{-3}$		0.045
21	Inverse fine structure constant	$1/\alpha$	137.035 989 5(61)		0.045
22	Rydberg constant	$\mathcal{R}$ $R_\infty = m_e c \alpha^2/2h$	10 973 731.534(13)	m^{-1}	0.0012
23	Rydberg constant in eV	$R_\infty hc/\{e\}$	13.605 698 1(40)	eV	0.30
24	Bohr radius .529 Å	$a_0 = \alpha/4\pi R_\infty$	0.529 177 249(24) $\times 10^{-10}$	m	0.045
25	Quantum of circulation	$h/2m_e$	3.636 948 07(33) $\times 10^{-4}$	m^2 s^{-1}	0.089
26	Electron specific charge	$-e/m_e$	-1.758 819 62(53) $\times 10^{11}$	C kg^{-1}	0.30
27	Electron Compton wavelength	$\lambda_C = h/m_e c$	2.426 310 58(22) $\times 10^{-12}$	m	0.089
28	Electron classical radius	$r_e = \alpha^2 a_0$	2.817 940 92(38) $\times 10^{-15}$	m	0.13
29	Electron magnetic moment	μ_e	928.477 01(31) $\times 10^{-26}$	J T^{-1}	0.34
30	Electron mag. moment anomaly	$a_e = \mu_e/\mu_B - 1$	1.159 652 193(10) $\times 10^{-3}$		0.0086
31	Electron g-factor	$g_e = 2(1 + a_e)$	2.002 319 304 386(20)		0.00001
32	Muon mass	m_μ	1.883 532 7(11) $\times 10^{-28}$	kg	0.61
33	Muon magnetic moment	μ_μ	4.490 451 4(15) $\times 10^{-26}$	J T^{-1}	0.33
34	Muon mag. moment anomaly	$a_\mu = [\mu_\mu/(e\hbar/2m_\mu)] - 1$	1.165 923 0(84) $\times 10^{-3}$		7.2
35	Muon g-factor	$g_\mu = 2(1 + a_\mu)$	2.002 331 846(17)		0.0084
36	Proton magnetic moment	μ_p	1.410 607 61(47) $\times 10^{-26}$	J T^{-1}	0.34
37	Proton gyromagnetic ratio	γ_p	26 752.212 8(81) $\times 10^{4}$	T^{-1} s^{-1}	0.30
38	Neutron magnetic moment	μ_n	0.966 237 07(40) $\times 10^{-26}$	J T^{-1}	0.41
39	Stefan-Boltzmann constant	$\sigma = (\pi^2/60)k^4/\hbar^3 c^2$	5.670 51(19) $\times 10^{-8}$	W m^{-2} K^{-4}	34
40	First radiation constant	$c_1 = 2\pi hc^2$	3.741 774 9(22) $\times 10^{-16}$	W m^2	0.60
41	Second radiation constant	$c_2 = hc/k$	0.014 387 69(12)	m K	8.4
42	Electron volt	eV = (e/C)J = {e}J	1.602 177 33(49) $\times 10^{-19}$	J	0.30
43	Atomic mass unit	u	1.660 540 2(10) $\times 10^{-27}$	kg	0.59
44	Standard atmosphere	atm	101 325	Pa	exact
45	Standard acceleration of gravity	g_n	9.806 65	m s^{-2}	exact

Notation: 1.602 177 33(49) $\times 10^{-19}$ C means (1.602 177 33 ± 0.000 000 49) $\times 10^{-19}$ C

C = A s F = (C/V) = m^{-2} kg^{-1} s^4 A^2 Pa = N m^{-2} = m^{-1} kg s−2 T = kg s^{-2} A^{-1} W = J s^{-1} = m^2 kg s^{-3}

Wb = V s = m^2 kg s^{-2} A^{-1} F m^{-1} = (C/V) m^{-1} = m^{-3} kg^{-1} s^4 A^2 T s = kg s^{-1} A^{-1} J T^{-1} = m^2 A

Ground state electron level H $k = \mathcal{R}hc$ 2.18×10^{-18} J 1.312 MJ/mole

$k = \mathcal{R}hc$ 13.6 eV] $= \frac{1}{4\pi\epsilon_0 m_e}$

Lattice energy k 2.31×10^{-28}

Prefix	Exponent	symbol	Prefix	Exp.	symbol	Prefix	Exp.	symbol	Prefix	Exp.	symbol
deci	-1	d	deca	1	da	centi	-2	c	hecto	2	h
milli	-3	m	kilo	3	k	micro	-6	μ	mega	6	M
nano	-9	n	giga	9	G	pico	-12	p	tera	12	T
femto	-15	f	peta	15	P	atto	-18	a	exa	18	E
zepto	-21	z	zetta	21	Z	yocto	-24	y	yotta	24	Y

Note: "giga" is pronounced with the first g soft, the second g hard, as in "gigantic".

Metric Prefixes

unit		unit	definition
name	symbol	of	
meter	m	length	The length of the path travelled by light in vacuum during a time interval of $^1/299\ 792\ 458$ of a second. [1983]
kilogram	kg	mass	The mass of the international prototype of the kilogram. [1901]
second	s	time	The duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom. [1967]
ampere	A	electric current	That constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 meter apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per meter of length. [1948]
kelvin	K	temperature	The fraction $^1/273.16$ of the thermodynamic temperature of the triple point of water. [1967]
mole	mol	amount of substance	The amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles. [1971]
candela	cd	luminous intensity	The luminous intensity, in a given direction, of a source which emits monochromatic radiation of frequency 540×10^{12} Hz radiant intensity in that direction of $(^1/683)$ W per steradian. [1979]
radian	rad	plane angle	$^1/2\pi$ of a circle
steradian	sr	solid angle	$^1/4\pi$ of a sphere

The radian and steradian are not properly base units, they are usually considered to be derived units, $(\mathrm{m} \cdot \mathrm{m}^{-1})$ and $(\mathrm{m}^2 \cdot \mathrm{m}^{-2})$ respectively. They are of dimension 1 and may be omitted if they are not needed for clarity.

SI base units

from	to S.I.	multiply by	from	to S.I.	multiply by
inch	m	0.0254	foot	m	0.3048
BTU	J	1055	cal	J	4.186
ounce (mass)	kg	0.02835	pound (mass)	kg	0.453 592 37
horsepower	W	746	mph	$\mathrm{m\ s^{-1}}$	0.44704
mmHg	$\mathrm{N\ m^{-2}}$	133.322	psi	$\mathrm{N\ m^{-2}}$	6894.76
fluid ounce	m^3	$2.957\ 353 \times 10^{-5}$	pint	m^3	$4.731\ 765 \times 10^{-4}$
gallon	m^3	$3.785\ 412 \times 10^{-3}$	°F	°C	$t_C = (5/9)(t_F - 32)$

English to S.I. Conversions

References:

"Guide for metric practice", Robert A. Nelson, Physics Today, August 1993, pp. 15-16

"Symbols, Units, and Nomenclature", E. Richard Cohen, Encyclopedia of Physics, pp. 1217-1232

"Symbols. Units, Nomenclature and Fundamental Constants in Physics, 1987 revision", E. Richard Cohen and Pierre Giacomo, Document I.U.P.A.P.-25 (SUNAMCO 87-1), Physica, **164A**, (1987) pp. 1-64

"Guide for the Use of the International System of Units", NIST Special Publication 811.

3.091 Review Notes 12/13

-def look at old tests

Lecture 1 – Sept 9:

- Intro.

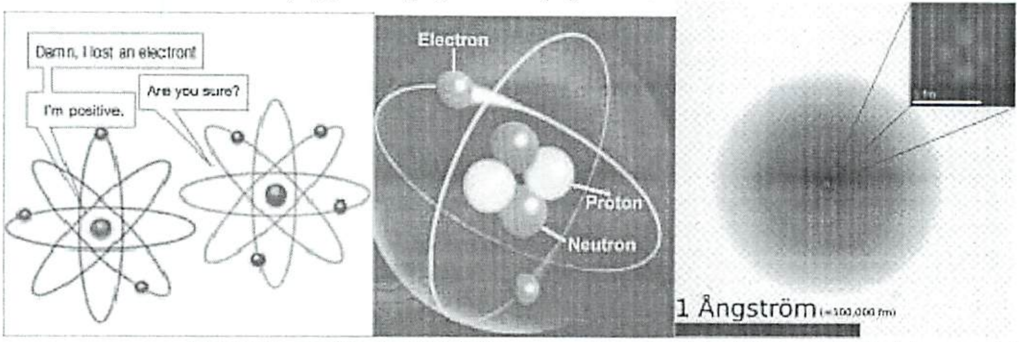
Lecture 2 – Sept 11: PERIODIC TABLE, ATOMIC NOMECLATURE

- History of the Periodic Table
  - Atoms - Dalton (1803) (*nearly got it right) – pg 14-15*
    - *Dalton's Atomic Theory*
  - Mendeleyev (1869) → predicted "missing elements" and their properties
- Structure of the atom
  - Electron (e^-), proton (p^+), neutron (n^o) **see table below**

want to study physics not this

a perhaps skip this session are don't have as prepared

will go through this mon afternoon



  - Electrons are tiny (~1/1830 the mass of a proton), but their orbital's take up a lot of space, the nucleus is tiny.
- Method of labeling elements: ${}^{A}_{Z}X$
  - A= mass # ~= # nucleons(protons + neutrons)
  - Z = proton # (defines chemical properties. An element's "social security identification #")
  - A,Z are integer numbers
  - ex. ${}^{23}_{11}Na$
- Ions
  - positive (+): e^- deficient = cation (**"paws"itive = cat**… meow)
  - negative (-): e^- rich = anion (extra 'n' = negative)
- Molar masses
  - 'Relative' masses of each element determined by mass spectroscopy, average elemental mass amongst its various isotopes
- Faraday's const (**F = 96,485 C/mol**)
  - "Oil drop experiment" (Millikan) → **$e=1.6\times10^{-19}C$**
  - Electrochemistry: $Ag^+ + e^- \rightarrow Ag^o$.
    - Count e^- ($=n_{Ag}$). Weigh Ag. Determine mass per atoms
    - From 'relative mass' values, we now know atomic mass of each element
- Avogadro, **$N_{Av} = 6.02 \times 10^{23}$ moles** :
  - Simply for convenience (easier units that 10^{23} atoms)
  - Defined such that 1 mole of ${}^{12}_{6}C$ weighs 12g
- **Chemical Reaction Equations**
  1. Write out a balanced equation
  2. convert mass to moles
  3. determine limiting reagent
  4. calculate amount of product
  - ex. $TiCl_{4\,(g)} + 2\,Mg_{(l)} = 2MgCl_{2(l)} + Ti_{(s)}$
- **Isotope calculations** (iso=isotope)
  - $X(m_{iso1}) + (1-X)(m_{iso2}) = m_{avg}$, solve for X. If X>0.5, iso1 is more abundant.

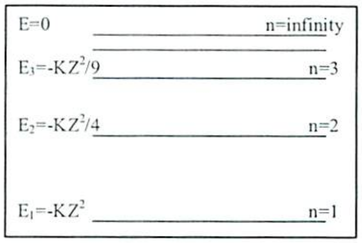
Bradwell

Lecture 3 – Sept 14 – MORE HISTORY

- Structure of atom
  - JJ Thomson (1904): "Plum Pudding"
    - e^-'s distributed uniformly throughout an atom
  - Ernest Rutherford (1911): "Nuclear Model"
    - Conclusion from gold foil expt
    - Majority of mass is found in the nucleus ($r_{nucleus}/r_{atom}=1/10,000$)
    - e^- orbiting around nucleus
  - Niels Bohr (1913): introduces quantization condition
    - Needed to explain blackbody radiation and atomic spectra
    - Postulated
      - e^- follow circular orbits around a nucleus
      - Orbital angular momentum is quantized, hence only certain orbits possible
      - e^- in stable orbits do not radiate
      - e^- change orbits by radiating or by absorbing radiation

Lecture 4 – Sept 16: BORH MODEL

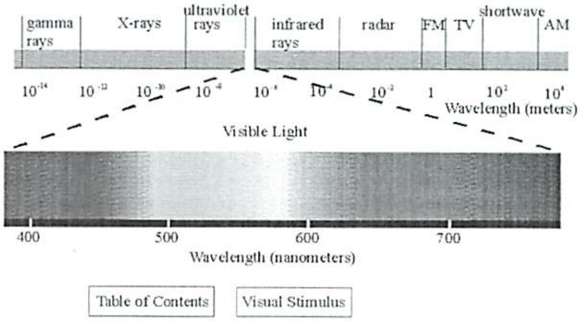
- Bohr Model
  - **Developed for H-atom, applicable to any one electron system (e.g. Li^{3+}, etc)**
  - Quantized energy states (n=1,2,3…)
  - $r(n) = \frac{a_o n^2}{Z}$, $E_{electron} = -K\frac{Z^2}{n^2}$, $v(n) = \frac{hZ}{2\pi m a_o n}$
  - a_o=borh radius = 0.529 Angstroms
  - Z = proton number
  - e = elementary charge
  - m = mass of e^-
  - h=plank's constant
  - n = e^- principal quantum number
  - K = a constant = 1.312MJ/mol = 13.6 eV/atom
  - 1eV = 1.6×10^{-19}J



- Energy Level diagram
  - E=0 at n=infinity
  - E_1 = ground state energy, when n=1 (e.g. E_1 =-13.6 eV for H)
  - Spectrum from cathode ray tube with known gas
- Stimulated emission
  - Photons: $E_{incident} = E_{transition} + E_{scattered}$
  - $E_{transition} = -KZ^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$
- Photons:
  - $E = h\nu = \frac{hc}{\lambda}$
  - h=Planck's constant, ν = photon freq., λ= wavelength, c=speed of light
- Traveling Particle (in other words, particles with definite mass)
  - $E = \frac{1}{2}mv^2$

Lecture 5 – Sept 18: EMISSIONS SPECTRA, QUANTUM NUMBERS

- **Reading: Avril 6.5**
- Visible light: 400-700nm = 3.1-1.8eV



- Bohr model for hydrogen (1 electron system) resulted in quantized energy level
  - Generalized eqn.: $\bar{\nu} = \Re Z^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$,
  - $\bar{\nu} = \frac{1}{\lambda}$ =wave number
  - $\Re$ = Rydberg constant = 1.097 x $10^7\, m^{-1}$
  - Berlin – Frank – Hertz: Hg (mercury vapor) experiment showed quantized energy levels applies to other elements/atoms as well.

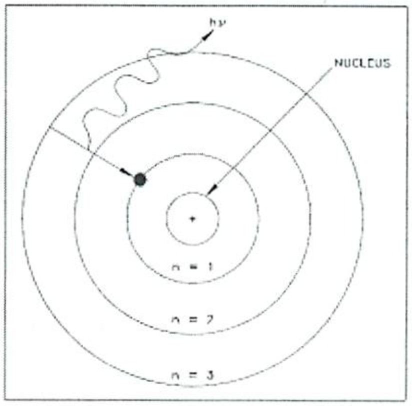


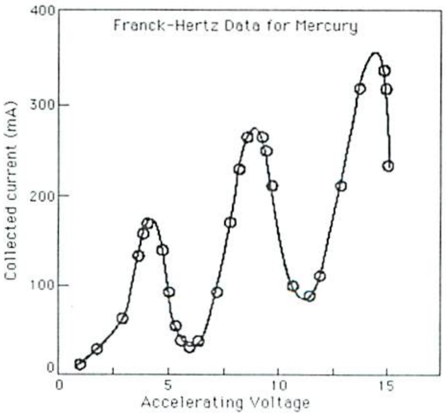
Figure 1 Bohr's Model of the Hydrogen Atom

- Limitations of Borh model:
  - Fine structure (doublet)
  - Zeeman splitting (under an applied magnetic field (B))

- Sommerfeld proposed 'elliptical shape' to the electron orbitals
  - Quantum numbers: n, l, m, s

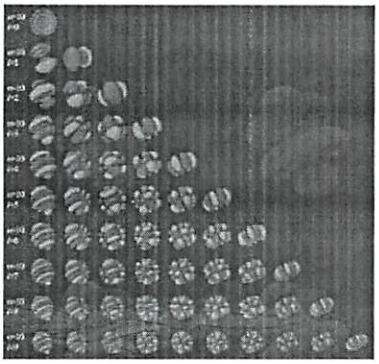
- ex. Ag metal beam split by magnetic field (atoms with spin-up e^- go one way, atoms with spin-down e^- go the other way).

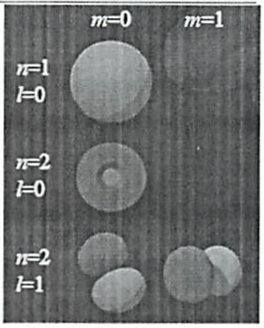
- Franck & Hertz Expt.:
  - Gas discharge tube, Hg vapor
  - Demonstrated existence of a threshold energy required to excite electrons in Hg atoms → electron energy levels are true to all atoms



Lecture 6 – Sept 21: QUANTUM NUMBERS, PARTICLE-WAVE DUALITY

- **Reading: Avril 6.4**
- Quantum numbers defining the 'state' of the electron
    - n = principle quantum number n=1,2,3…, (or K,L,M…)
    - ℓ = angular momentum ("shape"), $\ell = 0..n\text{-}1$ (s,p,d,f,g…)
    - m = magnetic quantum number, $m = -\ell..0..\ell$
    - s = spin +/- ½
- Examples of orbital shapes http://www.orbitals.com/orb/orbtable.htm :





- Aufbau Principle
    1. Paul exclusion principle: in any atom, each e^- has a unique set of quantum no.'s (n,l,m,s)
    2. e^- fill orbitals from lowest E to highest
    3. Degenerate electrons (same energy level) strive to be unpaired

  → Filling electron states:
    - Ex. Carbon, C: $1s^2 2s^2 2p^2$

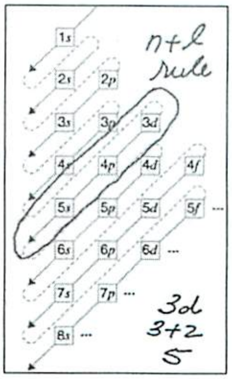
- de Broglie – *an electron can act as a wave*
    - He asked: "if photons can behave as particles, can electrons behave as a wave?"
    - Geometric constraint: $2\pi r = n\lambda$, n=1,2,3… (circular wave path)
    - Wavelength of an electron: $\lambda_e = h/p = h/mv \rightarrow mvr = nh/2\pi$!
        - p=momentum = mv
    - Demonstration of diffraction of electron 'beam' using a crystal lattice
    - ***Particle-wave duality confirmed!***

- Heisenberg – uncertainty principle
    - $(\Delta p_x)(\Delta x) >= h/2\pi$
    - You can't know the exact position and momentum of a particle at the same time
    - Deterministic models (billiard balls) turn into probabilistic models
        - Einstein: "God doesn't play dice with the universe"
        - Bohr: "Einstein, stop telling God what to do!"

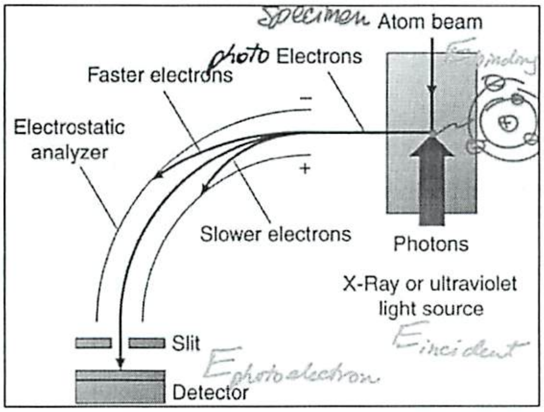
- Schrodinger equation (NOT TESTED ON FINAL)
    - $$i\frac{\partial}{\partial t}\Psi(x,t) = -\frac{1}{2m}\nabla^2\Psi(x,t) + V(x)\Psi(x,t).$$
    - It's a *defining equation* for quantum mechanics
    - Think of it as equivalent to Newton's equation: *F=ma*
    - Complex equation that allows us to calculate measurable quantities, such as position, momentum, energy of microscopic systems.
    - Well beyond the scope of this class…

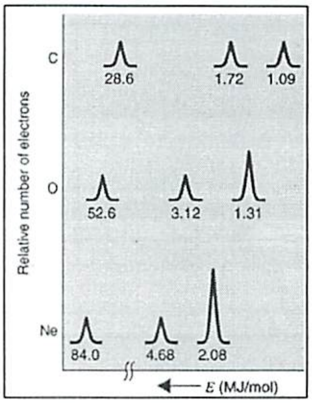
Lecture 7 – Sept 23: AUFBAU PRINCIPLE X-RAY PHOTON SPECTROSCOPY

- **Reading : Avril 8.1-8.2, 12.5, 8.3**
- n+l rule for filling orbitals. Fill in ascending n.
    - 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s…

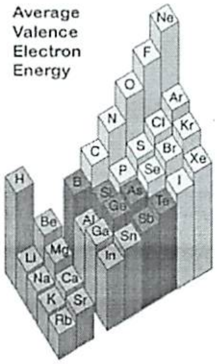


- Measurement of ionization energies ($E_{inc} = E_{binding} + E_{kin}$)
    - Peak height tells # of electrons in shell
    - Energy tells shell (n)



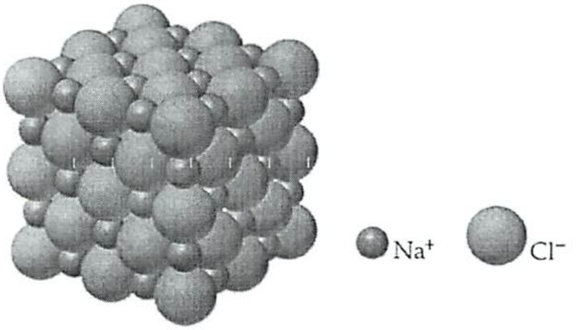


- Average Valence Electron Energy (AVEE)
    - <11eV → e^- weakly held = metals
    - >13ev → e^- tightly bound = non-metals
    - >11ev, <13ev = semi-metals



- Noble gases → filled valence shell → energy well = extremely stable

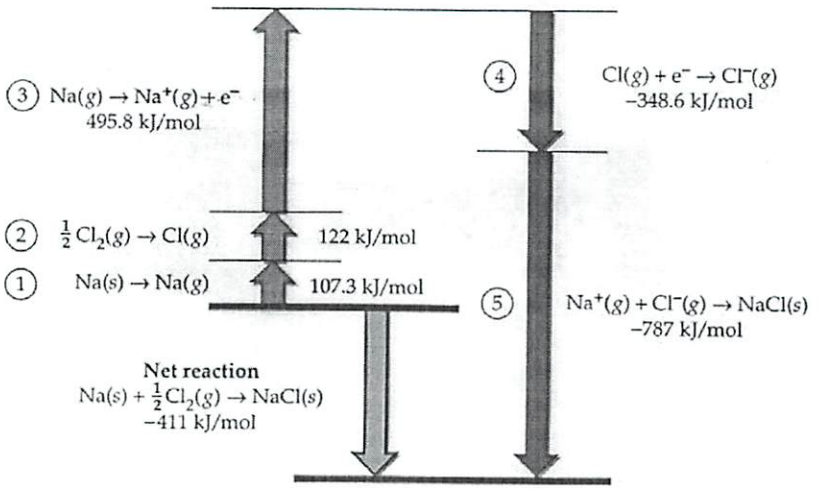
- Electron transfer *to achieve valence shell filling*
    - Ion pair production
    - $Na \rightarrow Na^+ + e-$
    - $Cl + e^- \rightarrow Cl^-$
    - Agglomerate without limit due to coulombic attraction
      → **Crystal**!



Lecture 8 – Sept 25 :

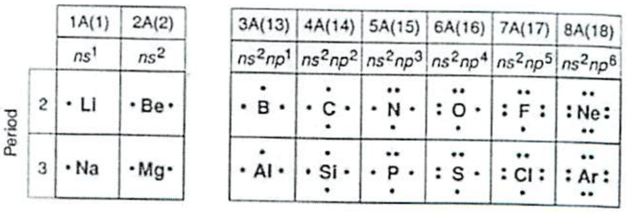
- **Reading : Avril 8.3-8.6, 8.8, 9.2**
- Energetics of pair attraction
  - → energy gained upon converting a gas of ion pairs, to a crystal array
  - $E_{attr} = \frac{q_1 \cdot q_2}{4\pi\varepsilon_o r}$, $E_{rep} = \frac{b}{r^n}$, $E_{net} = E_{attr} + E_{rep}$
    - b,n = constants, n~=6-12
  - Madelung constant, M → energy related term of a crystal, based on atomic geometry
    - Generally, an infinite sum
    - For a material with +1 and -1 charged species
    - Energy per mole of ions:
    - $E_{line} = \frac{-M \cdot z^+ \cdot z^- \cdot N_{AV} \cdot e^2}{4\pi\varepsilon_o r_o}\left(1 - \frac{1}{n}\right)$ (sum of all ion interactions)
    - n = borh exponent, n~=6-12
    - If M > 1 → a solid will form
    - If M < 1 → material will remain as a gas
- Transparent materials:
  - If $E_{hv,incident} < \Delta E_{trans}$, visible light doesn't have enough energy to promote electron excitation → the photon passes straight through material
- Hess's Law: *energy change in a chemical rxn is path independent*
  - Energy is a *State Function*
  - i.e. $Na_{(s)} + 1/2Cl_{2(g)} \rightarrow NaCl_{(xstal)}$
  - a) convert reactants to their independent gaseous forms (steps 1,2)
  - b) remove/add electrons (steps 3,4)
  - c) crystallize (step 5)

Figure 6.6 A Born-Haber cycle for NaCl



Lecture 9 – Sept 28 :

- **Reading : Avril 7.3, 8.9**
- Problems with ionic-bonding for diatomic molecules: H_2, N_2, O_2 → can't be ionic
- G.N. Lewis (1916) – shell filling by ***electron sharing***
    - Lewis Dot notation
    - Cooperative use of valence e⁻'s to achieve octet stability = ***covalent bonds***

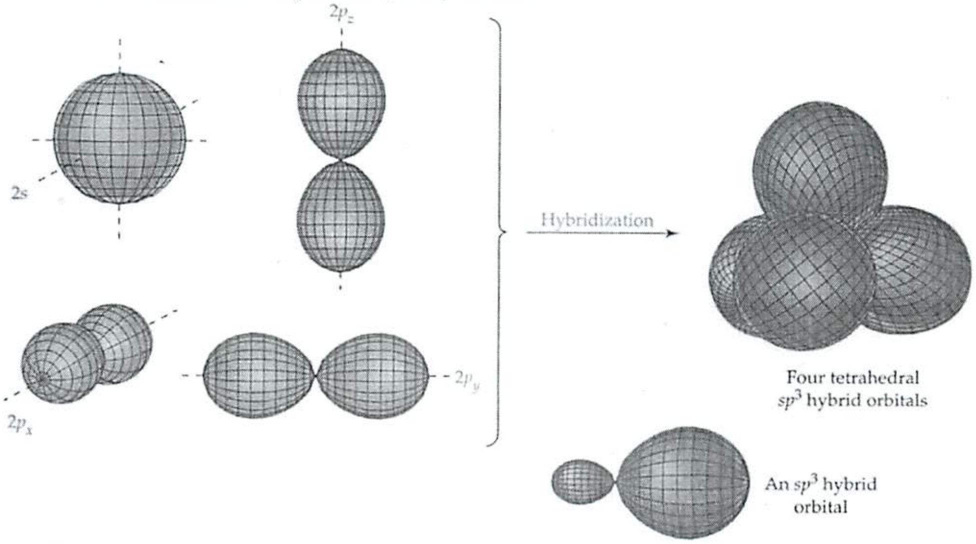


Period	1A(1)	2A(2)
	ns^1	ns^2
2	• Li	• Be •
3	• Na	• Mg •

3A(13)	4A(14)	5A(15)	6A(16)	7A(17)	8A(18)
ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
• B •	• C •	• N •	: O •	: F :	:Ne:
• Al •	• Si •	• P •	: S •	: Cl :	: Ar :

- Ionic Bond = e⁻ transfer
- Covalent Bond = e⁻ sharing (directional)

- Carbon → only has 2 unpaired (bonding) electrons in p-orbital
    - s-orbitals 'merge' with p-orbitals → ***sp^3 hybridized***
    - Results in 4 unpaired e⁻, ready to bond



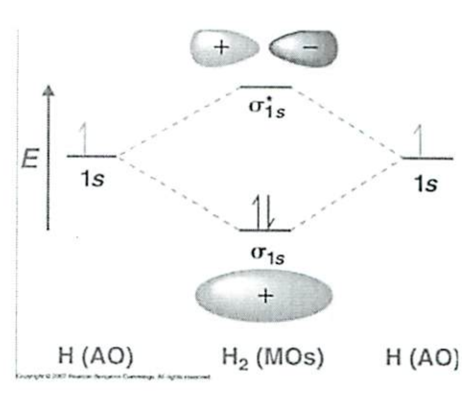
- Energy of heteronuclear bonds :
    - $E_{A-B} = \sqrt{E_{AA} \cdot E_{BB}} + 96.3 \cdot (\chi_A - \chi_B)^2$ *(in kJ/mol)*

- % ionic character = $\left\{1 - \exp\left(-\frac{1}{4}(\Delta\chi)^2\right)\right\} \cdot 100\%$

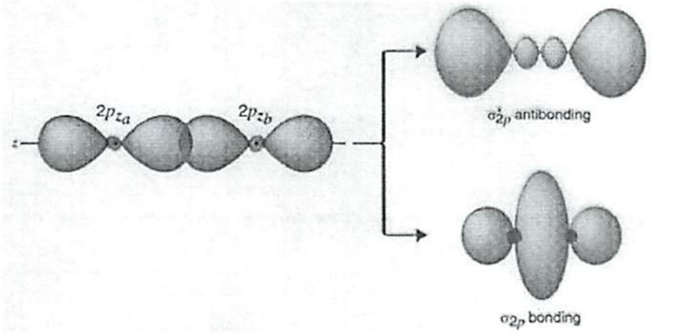
- Polar bonding → can lead to a polar molecule – but only if there's asymmetry

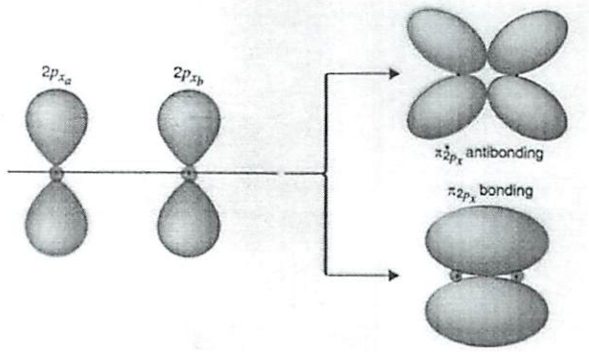
Lecture 10 – Sept 30 : LCAO-MO

- **Reading : Avril 9.2, 9.3, 9.4**
- LCAO-MO (Linear Combination of Atomic Orbitals – Molecular Orbitals)
  - Orbitals split into a bonding (lower) and anti-bonding (higher) orbitals. Electrons fill from lowest energy up.

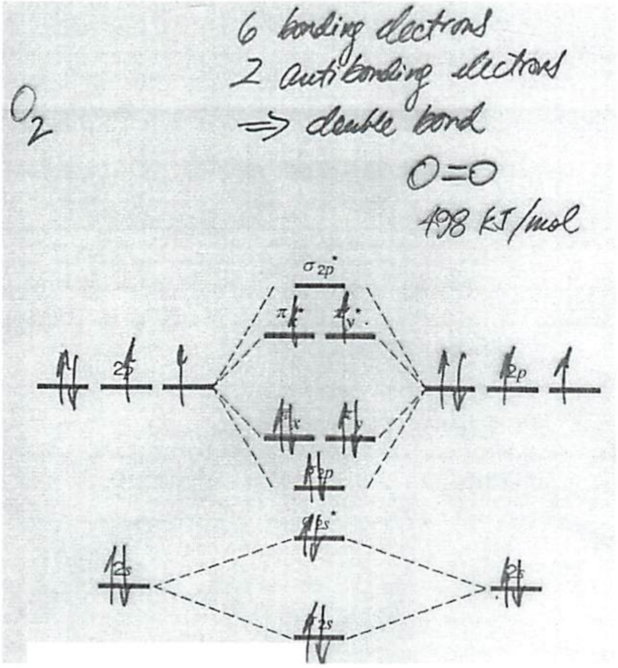


- Types of bonds:
  - σ = no nodal plane separates nuclei
    - eg. s + s, $p_z + p_z$, s + p
  - π = a nodal plane separates nuclei
    - eg. $p_y + p_y$, $p_x + p_x$
  - don't need to worry about *d* or *f* orbitals





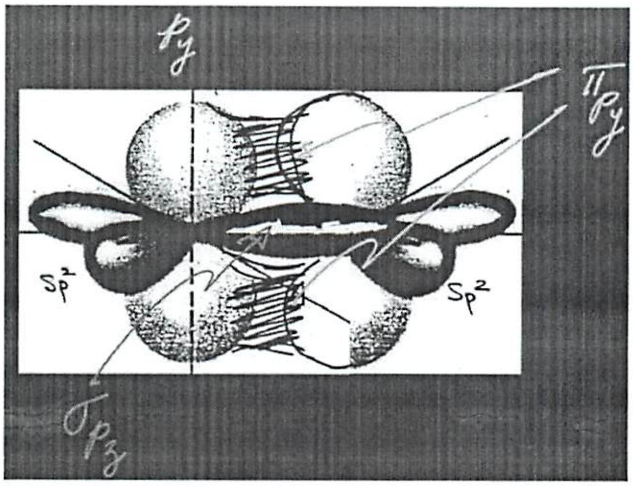
- Paramagnetism: from unpaired electrons in MO
  - eg. liquid oxygen is paramagnetic – can be held by a magnetic field



6 bonding electrons
2 antibonding electrons
⇒ double bond
O=O
498 kJ/mol

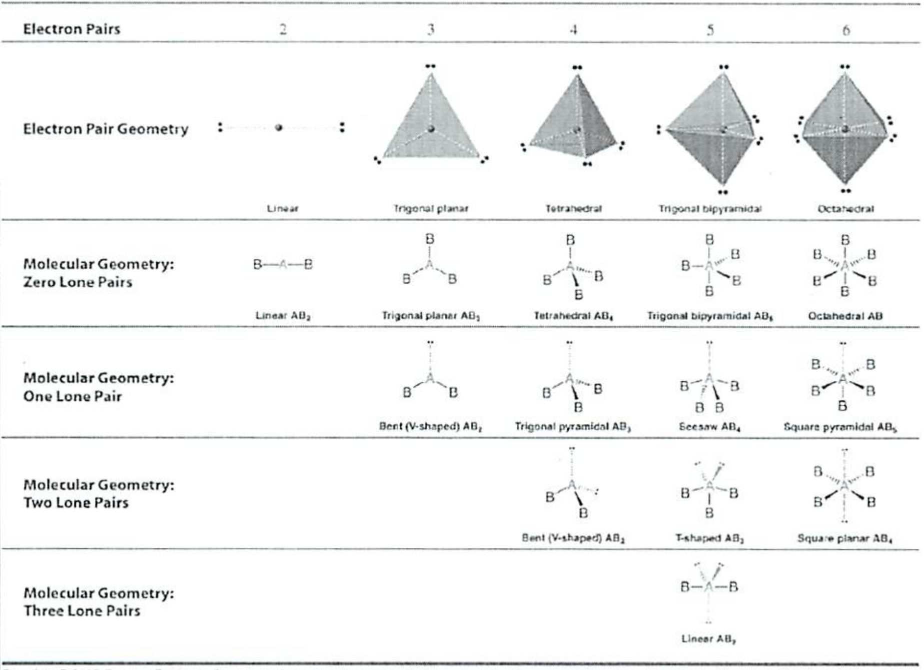
Lecture 11 – Oct 2 : HYBRIDIZED ORBITALS AND BONDING, SHAPES OF MOLECULES

- **Reading : Avril 9.1, Shakelford 2.5**
- Hybridized bonding in molecules
  - i.e. C_2H_4 (C=C double bond has one σ-bond, and one π_x -bond), and C-H bonds are from sp^2 hybridized orbital in C.



- VSEPR (Valence Shell Electron Pair Repulsion)
  - Electron Pair Geometry vs. Molecular Geometry

TABLE 9.3 Overview of molecular geometries



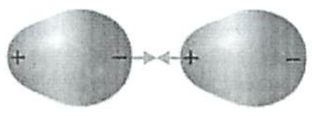
Electron Pairs	2	3	4	5	6
Electron Pair Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Molecular Geometry: Zero Lone Pairs	Linear AB_2	Trigonal planar AB_3	Tetrahedral AB_4	Trigonal bipyramidal AB_5	Octahedral AB
Molecular Geometry: One Lone Pair		Bent (V-shaped) AB_2	Trigonal pyramidal AB_3	Seesaw AB_4	Square pyramidal AB_5
Molecular Geometry: Two Lone Pairs			Bent (V-shaped) AB_2	T-shaped AB_3	Square planar AB_4
Molecular Geometry: Three Lone Pairs				Linear AB_2	

- Elements that can undergo an expanded octet are: Al→Cl, Ga→Kr, In→Xe, Tl→At

Lecture 12 – Oct 5 : SECONDARY BONDING

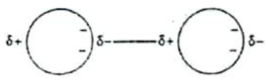
Averill 12.5, 12.6; Shackelford 2-5, 2-4, 15-1, 15-2, 15-5

1. dipole-dipole:
    - applies to polar molecules (i.e. HCl)
    - $E_{d\text{-}d} \sim 5$ kJ/mol (vs. 780kJ/mol for an ionic bond)
    - Much weaker!



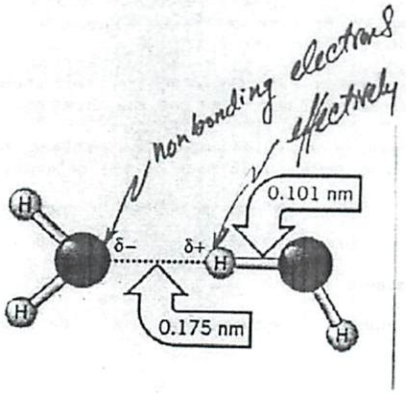
(b) Attraction

2. induced dipole – induced dipole
    - operative in non-polar species
    - explains why non-polar species can exists as a liquid or solid (i.e. N_2 bp = 77k)
    - Van der Waals bond or London Dispersion forces
    - $E_{VdW} \propto \alpha^2 / r^6$
    - Force is larger for larger atoms → higher bp for larger atoms



induced dipole –
induced dipole

3. Hydrogen Bonding
    - Between exposed proton side of H, and e^- on other atom
    - Only applies between H+ F, O, or N. (i.e. HCl does not have a "H-bonding")
    - i.e. (H-F) ··· (H-F)



non bonding electrons

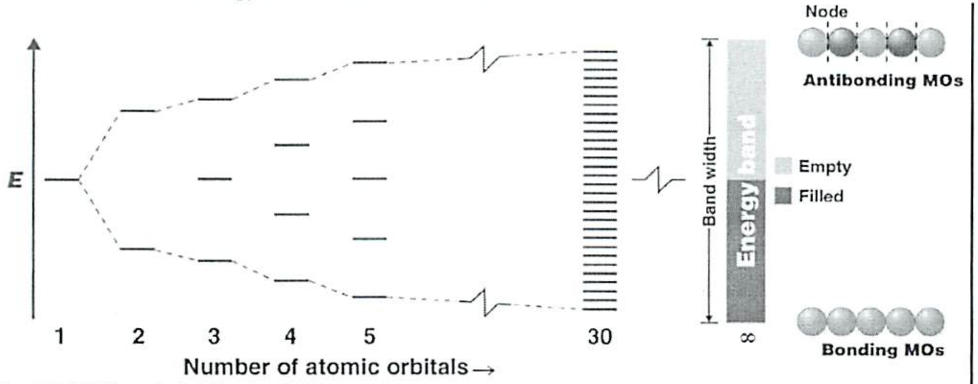
effectively

Lecture 13 – Oct 9: E^- BAND STRUCTURE: METALS, CONDUCTORS, INSULATORS

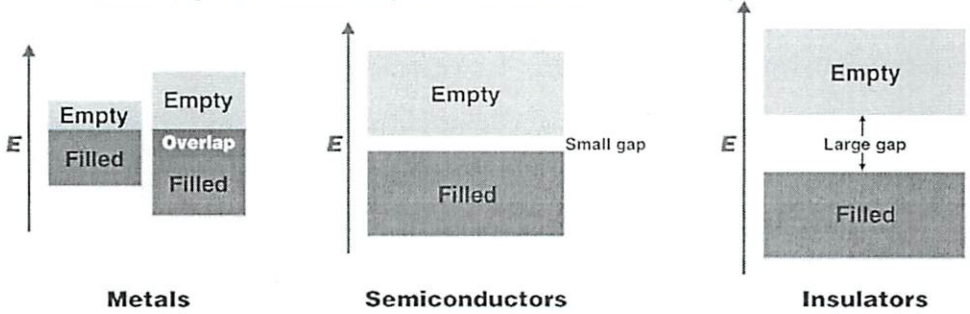
Averill 12.6

- Drude model:
  - "Free e^- gas" model → e^- in valence shell can move → some success
  - Couldn't explain insulators vs. metals → needed quantum mechanics!

- Quantum mechanics → LCAO-MO applied to many atoms (solids)
  - Energy levels turn into bands



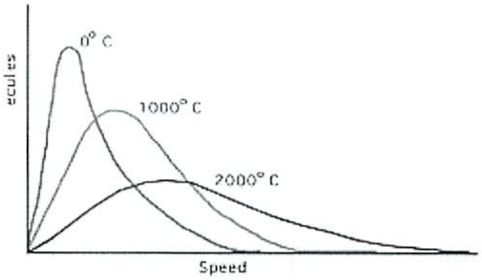
- Electrons can only move (e^- conduction) if they are in an energy level adjacent to unoccupied states
- Metals (Eg=0), Insulators (Eg>3eV), Semiconductors (1ev<Eg<3ev)



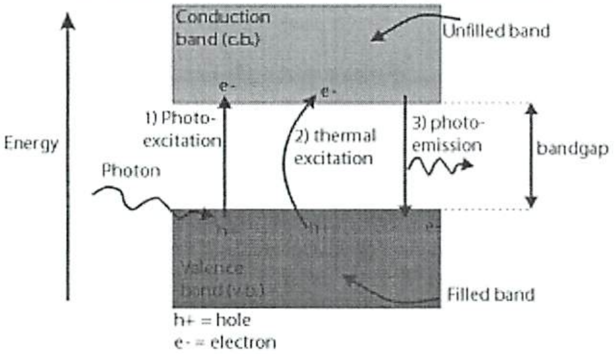
Lecture 14 – Oct 13: SEMICONDUCTORS

Averill 12.6

- Photo-excitation of e^- from valence band to conduction band
    - Recall: absorption edge plot
- Photo-emission: from an e^- in the valence band falling down to an empty state in the conduction band.
- Thermal excitation
    - $E_{e^-} \sim 1/40$ eV at room temperature
    - Maxwell-Boltzmann distribution of e^- energy

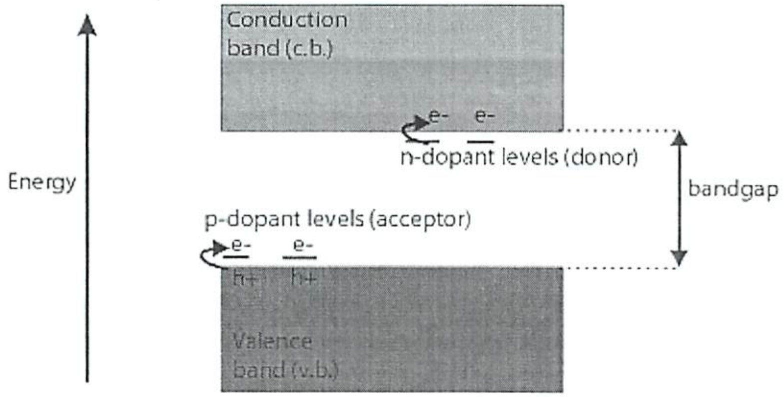


Three different processes for charge carrier creation/destruction in an intrinsic (undoped) semiconductor



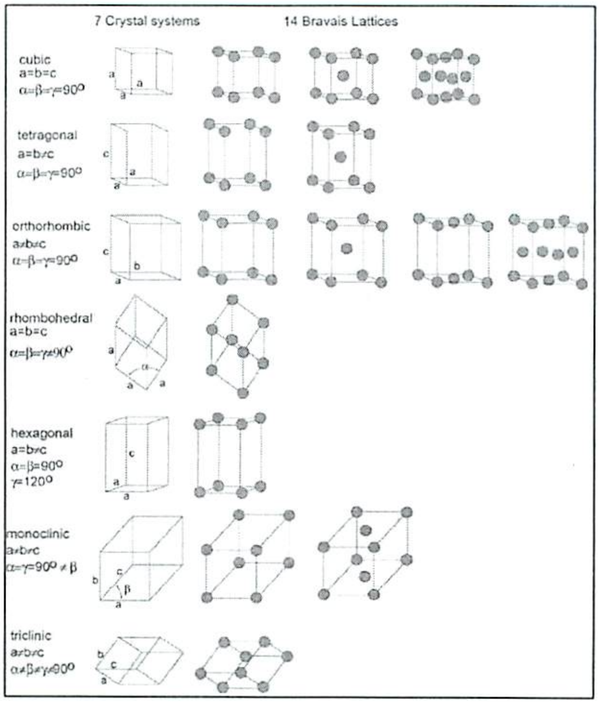
- "Chemoexcitation" = doping of a semiconductor
    - **Intrinsic** = pure Si, Ge, or compound
    - **Extrinsic** = intentional impurity added to inject charge carriers
        - n-type: supervalent (i.e. P) → adds e^- to conduction band
        - p-type: subvalent (i.e. B) → adds h^+ to valence band

Doped semi-conductors



Lecture 15 – Oct 14: CRYSTALLOGRAPHY

Averill 12.1, 12.2; Shackelford 3-1.



- 7 Crystal systems
  - o 7 unique ways to fill space with volume elements
- 14 Bravais lattices
  - o Crystal systems, plus lattice sites
  - o i.e. sc, fcc, bcc, hcp…
  - o Lattice sites are interchangeable – all sites are equivalent
- Basis
  - o Atoms or molecules per lattice site
  - o i.e. 1 atom, or a molecule
  - o i.e. Au atom, or NaCl ion pair, of CH_4 molecule, or C-C pair
- Crystal Structure
  - o Bravais lattice & basis
  - o i.e. fcc, rocksalt, diamond cubic structure
- Closest Packed structure: 12 nearest neighbors → fcc, and hcp = 74% APD
- Atomic Packing Density, APD: $APD = \left(\frac{volume\_matter}{total\_volume}\right) = \frac{\left(\frac{atoms}{unit\_cell}\right)\cdot V_{atom}}{V_{cell}} \cdot 100\%$
  - o $V_{atom} = 4/3\ \pi\ r^3$
  - o $V_{cell} = a^3$ (if cubic)
- Calculating lattice constant (a) or atomic radius (r)
  - o Molar Volume (V_{molar}) = moles/volume = constant
  - o For volume of unit cell, (V_{cell}) (= a^3 for cubic),
    1. (atoms)/(unit volume) = (N_{av}) / (V_{molar}) = (# atoms/cell) / V_{cell}
       → solve for **'a'** via V_{cell}
    2. Get a = f(r) based on unit cell geometry (i.e. a = 4r/sqrt(3) for bcc)
       → solve for **'r'**

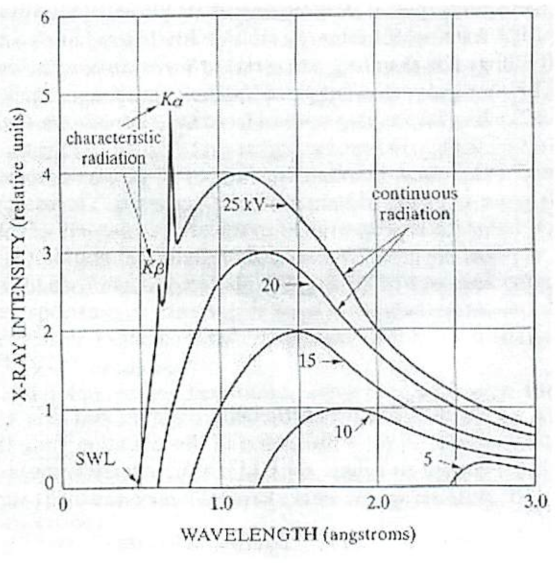
Lecture 16 – Oct 16: MILLER INDICES, X-RAY SPECTRA

Averill 12.1, 12.2; Shackelford 3-2, 3-6

- Miller Indices (ref. handout from class)
  - Point: h,k,l
  - Direction [h k l]
  - Family of directions <h k l>
  - Plane[1]: (h k l)
  - Family of planes[1]: {h k l}
    - [1] *direction [h k l] is normal to plane (h k l)*
    - [1] *h,k,l are reciprocal of axial intercepts*

- Distance between adjacent planes with miller indices (h k l)
  - $d_{hkl} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$
  - a = lattice spacing of unit cell

- X-ray Spectra
  - e^- discharge tube (vacuum tube with a large voltage (~35,000V's) applied between two electrodes (cathode and anode (target))
  - accelerate e^- through a vacuum
  - e^- 'crash' into anode (target), ejecting bound e^- from core shells
  - e^- from higher orbitals 'cascade down', releasing high energy photons → x-rays
  - K_α, K_β, L_α, L_β, etc.
    - i.e. K = final shell number of transition (if n=1→K, 2→L, 3→M, 4→N...)
    - i.e. $\alpha = \Delta n$ of falling electron ($1=\alpha$, $2=\beta$, $3=\gamma$)
  - Underlying **whale-like shape** from continuous e^- deflections → **Bremsstrahlung**
  - Shortest wavelength of Bremsstrahlung curve $\lambda_{SWL} = \dfrac{hc}{eV}$



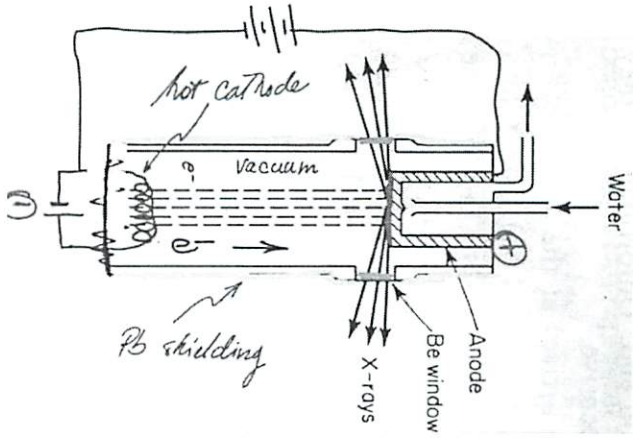
Lecture 17 – Oct 19: MOSELEY FIT OF X-RAY SPECTRA

Averill pp. 305, 535, 536; Cullity pp. 1E-11E, 19E-22E.

- X-ray spectra data fitted to Rydberg-type equation
- $\bar{\upsilon} = \Re\left(\frac{1}{n_f^{2}} - \frac{1}{n_i^{2}}\right)\cdot(Z-\sigma)^2$
  - $\bar{\upsilon} = 1/\upsilon$ = inverse frequency
  - σ = screening factor
    - =1 for K_α, and =7.4 for L_α

- Results of **Moseley's** work:
  - A plot of $\bar{\upsilon}$ vs. Z^2 demonstrated a linear relationship
  - Corrected Mendeleyev: periodic table should be arranged via Z, and not A (atomic mass number)
  - Placed Lanthenides in periodic table

- Improvements to x-ray spectra apparatus by W. D. Coolidge, MIT alum
  - Lead-shielding
  - Beryllium window
  - Water-cooled anode (target)
  - Heated cathode
  - Better vacuum



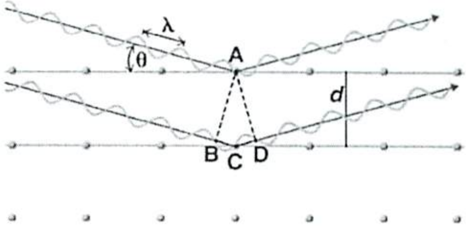
Therefore: We can now accurately identify relative amounts of elemental species within a sample!

Lecture 18 – Oct 21: PROBING ATOMIC ARRANGEMENT BY X-RAYS, BRAGGS LAW

Shackelford 3-7.

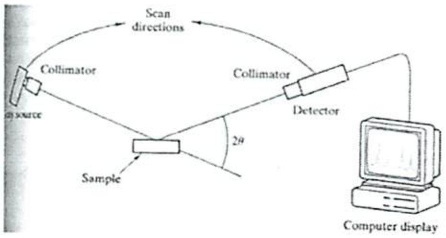
→ *See 'lecture notes' for Lecture 18 on steps to determine crystal structure*

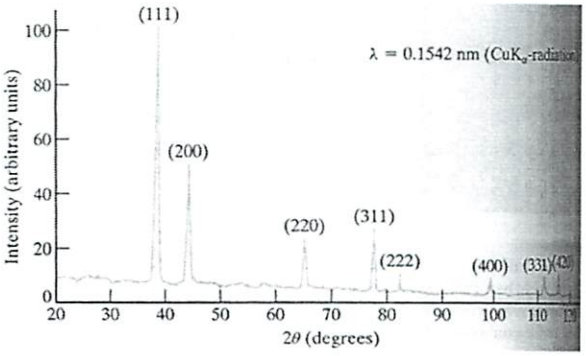
- X-Ray Diffraction (XRD) → ***A means to determine crystal structure!***
  1. Model atoms as mirrors
  2. Apply interference criterion – constructive or destructive
  - Parallel monochromatic x-rays (i.e. K_α line from a specific target) are sent to sample.
  - X-rays reflect off of various planes, constructively or destructively interfering, based on extra distance traveled by ray reflecting off of lower atomic plane.



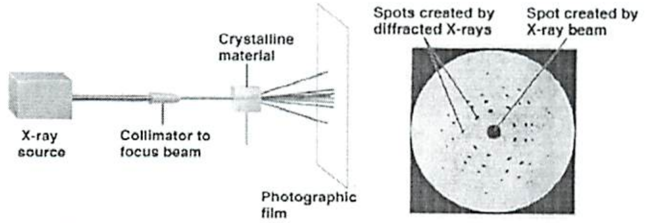
- $n\lambda = 2d\sin\theta$
  - For 3.091, n=1
  - d=interplanar spacing (Lect 16)
- $\dfrac{\lambda^2}{4a^2} = \dfrac{\sin^2\theta}{h^2+k^2+l^2} = const$
- Can determine appropriate values of h,k,l, based on θ (handout)
- Can also determine 'a': $a = \dfrac{\lambda}{\sqrt{2}\sqrt{const}}$
- Determine different crystal types by values of $h^2+k^2+l^2$
  - sc: 1,2,3,4,5,6,8,9 (no 7!)
  - bcc: 2,4,6,8,10,12,14,16 (would appear as 1,2,3,4,5,6,7,8 → there is a 7!)
  - fcc: 3,4,8,11,12… (the first two terms are a ¾ ratio, not ½)

- Two XRD Techniques:
  1. **Diffractometry** (fixed λ, variable θ)





  2. **Laue** (variable λ, fixed θ)
  - Spot pattern → atomic symmetry



(a) X-ray diffraction

(b) X-ray diffraction pattern captured on photographic film

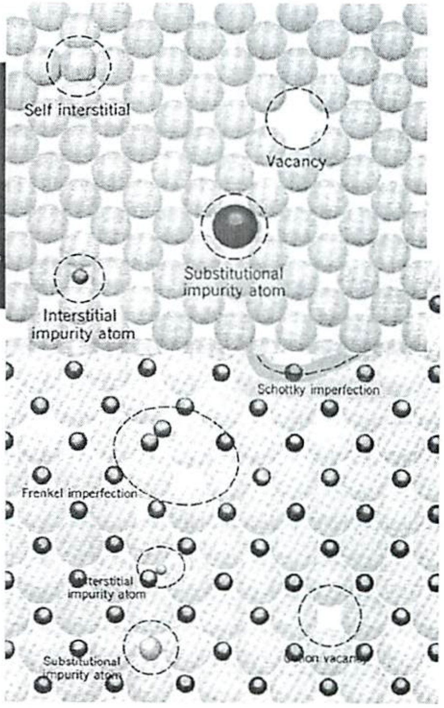
Therefore, we can now determine crystal structure!

Lecture 19,20 - Oct 23,26: DEFECTS

- Reading : Averill 12.4; Shackelford 4-1, 4-2, 4-3, 4-4, 5-1.

Taxonomy of Defects: Classify by Dimensionality

***0-dimensional*: point defects**
***1-dimensional*: line defects**
***2-dimensional*: interfacial defects**
***3-dimensional*: bulk defects**



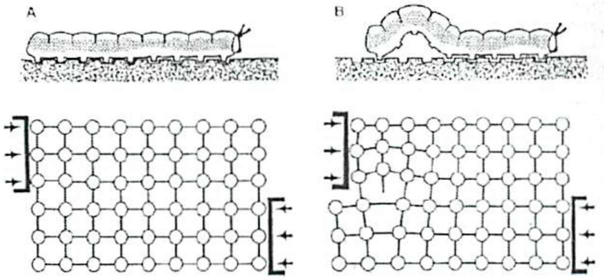
Point Defects (0-D):

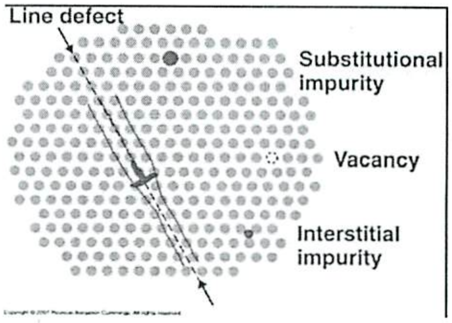
- i)Self interstitial, ii) Interstitial impurity, iii) substitution impurity, iv) vacancy

- Vacancies: i) Schotty, ii) Frenkel, iii) F-center
  - *Should be able to calculate vacancy fraction based on enthalpy of vacancy formation.* $f_v = \frac{n_v}{N} = A \cdot \exp\left(-\frac{\Delta H_v}{k_B T}\right)$
  - Also be able to show 'reaction' equation for forming a vacancy. (i.e. null $\rightarrow V_{Zr}^{''''} + 2V_{o}^{oo}$)

Line Defect (1-D):

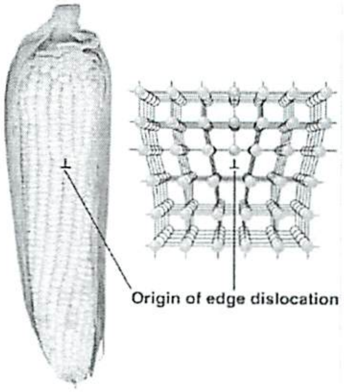
- Edge dislocation – extra half-plane of atoms.
- Crystals deform via. dislocation motion.





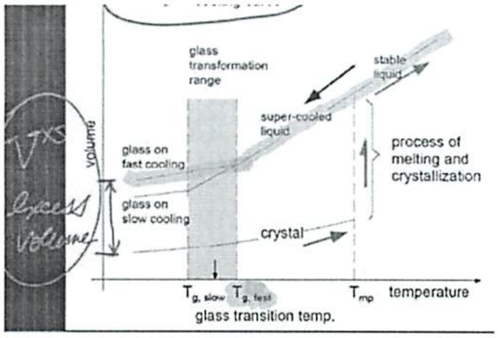
Interfacial Defects (2-D) - Grain Boundaries, surfaces

Bulk Defects (3-D) – Amorphous regions in crystal, voids, inclusions, precipitates

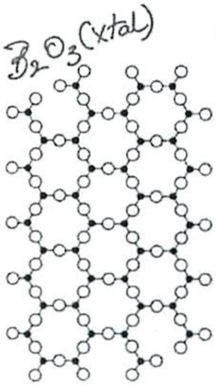


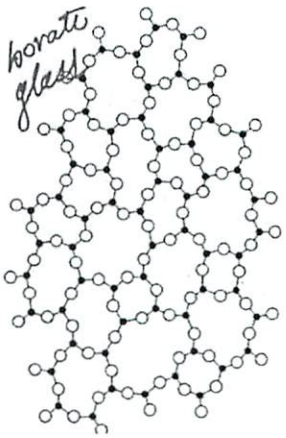
Lecture 21 – Oct 30: GLASSES

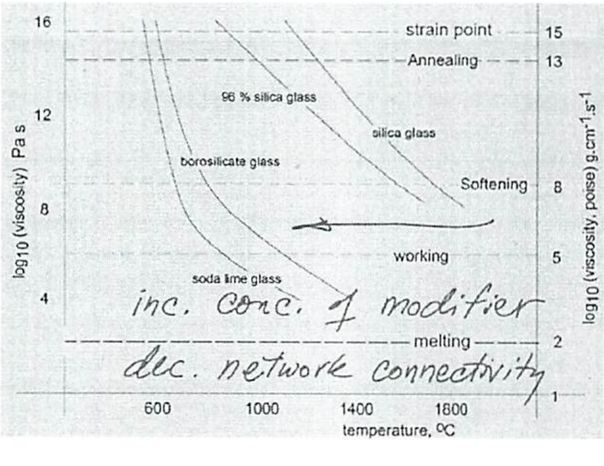
- Atomistic model of Hooke's law (E vs. r → F vs. r graphs)
- Factors promoting glass formation:
    - **(viscosity)** x **(complexity of xtal structure)** x **(cooling rate)**
    - The larger each of these values, the more likely it is to form a glass instead of a crystal
- Silicate glasses
    - Bridging oxygens, –O–
    - Chemical formula: SiO_2
    - Structural formula: SiO_4^{4-}



- Volume vs. Temperature heating/cooling curves for glasses.
    - Know: excess volume, effect of different cooling rates, T_g, T_m.
- Energy comparison: xstal has lower energy than glass
- Properties of oxide glasses:
    1. Chemically inert
    2. Electrically insulating
    3. Mechanically brittle
    4. Optically transparent
    - → but high melting point → tough to process → add modifiers to lower T_g
- Net work formers: have bridging oxygens, i.e. SiO_2, B_2O_3,
- Network modifiers (lower T_g): ionic bonds → O^{2-} breaks bridging –O– bonds
    - i.e. CaO, Na_2O, Li_2O…
    - i.e. CaO → $Ca^{2+} + O^{2-}$
- Intermediates:
    - A glass that has a cation that makes a different number of oxygen bonds than the majority glass former. It breaks up the network, results in poorer packing, and increases the thermal shock resistance (i.e. Al_2O_3 in a SiO_2 glass)



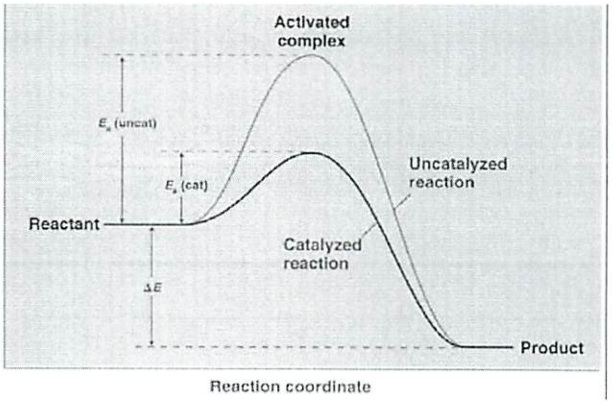




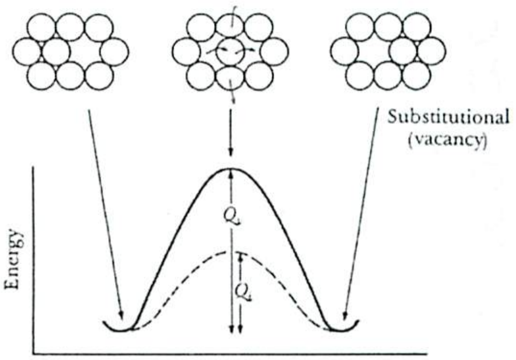
Lecture 22,23 – Nov 2, 4: GLASS STRENGTHENING MECHANISMS

- Two assumptions: i) Glasses break by crack formation and propagation, which starts at the surface. ii) Glasses are strong under compression, but fail because their weak under tension. Solution: create internal stresses that place the surface layer under compression, thereby increasing its strength.
  - Thermal treatment → tempering
    - Air jets cool outside of glass faster → larger volume, compressed by slower-cooled internal region → surface under compression yields higher strength
    - $V_{outer} > V_{bulk}$
  - Chemical Treatment
    - Ion exchange. A larger ion replaces a smaller ion in the glass (i.e. K^+ (from KCl salt bath) replaced Na^+ from the glass). K^+ is larger → puts a compressive strain on surface region → increases strength

- **KINETICS:**
  - Reaction rates, including nuclear decay.
  - Rate of reaction is proportional to concentration of reactant.
  - Reaction: $aA + bB \rightarrow cC + dD$
  - Rate Equation:
    - $r = -\dfrac{dC}{dt} = kC^n$
    - $k = A\exp\left(-\dfrac{E_a}{k_B T}\right)$
    - 'k' is related to Maxwell-Boltzmann distribution of energy → Arrhenius relationship
    - Solution depends on value of n (rate of reaction = sum of exponents in reaction equation)
    - Solutions to rate equation:
      - n=1 → $\ln C = \ln C_o - kt$
      - n=2 → $1/C = 1/C_o + kt$
        - $t_{1/2} = \ln(2) / k$
      - n=other → plot log(r) vs. log (C) → slope = n, intercept = log(k)

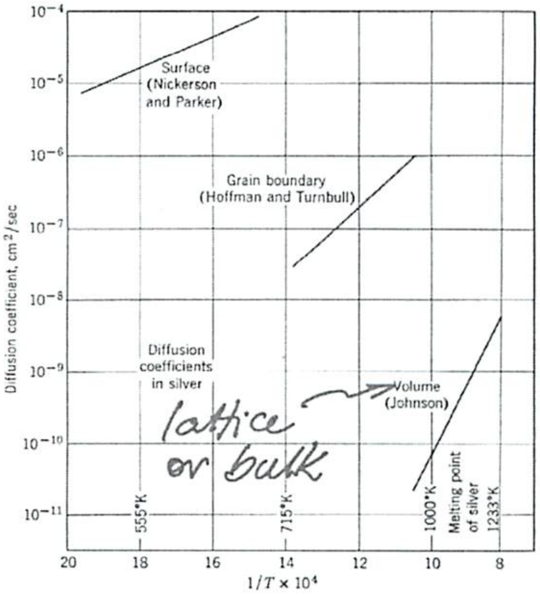


Lecture 24 – Nov 6: DIFFUSION



- Random movement of particles, resulting in a 'spreading out' of particles tending towards equal concentration.
- Rate Process "d/dt"
- **Rate at which atoms vibrate. = 10^{13} Hz**
- **Jump Freq = 10^8 Hz → very fast!!**
- Diffusion occurs only if there is a free space to move into (vacancy for self or substitutional diffusion)
- Diffusion (D) is proportional to the concentration of free sites. D also increases with a looser packed atomic structure.
  - i.e. # vacancies, or other defects, such as grain boundaries
- Surface, brain boundary, and volume diffusion occur at different rates → proportional to # of free sites!

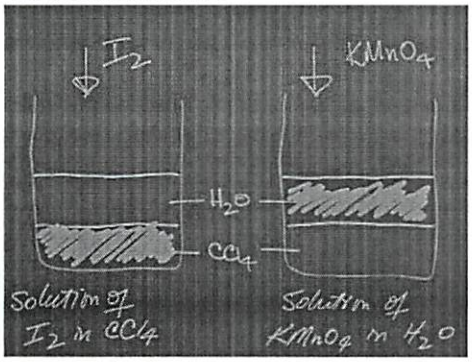
- **Fick's First Law (FFL)**
  - Flux is proportional to the concentration gradient
  - $J = -D\dfrac{dC}{dx}$
  - → Use if in stead-state
  - In steady-state, this results in a linear concentration gradient (i.e. straight line) through a material
  - D=diffusivity, units = cm^2/s,
  - $D = D_o \exp\left(-\dfrac{Q}{RT}\right)$, $R = k_B N_A$
    - Maxwell-Boltzmann distribution again

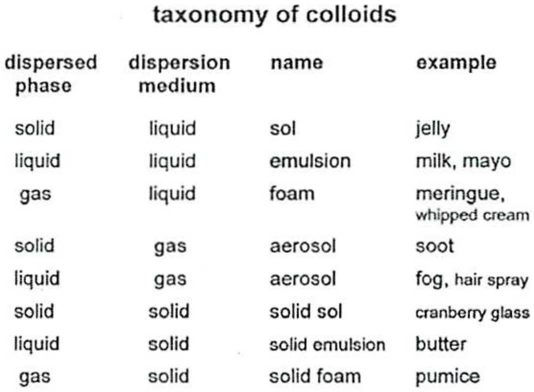


- **Fick's Second Law (FSL)**
  - Introduce time-varying concentration profile.
  - $\dfrac{dC}{dt} = -D\dfrac{d^2C}{dx^2}$, → one solution is:
    $\dfrac{C(x,t) - Cs}{Co - Cs} = erf\left(\dfrac{x}{2\sqrt{Dt}}\right)$
    - Note: solution is for semi-infinite system with constant surface concentration
  - erf = special function. erf (0) = 0, erf(infinity) = 1, erf (x) ~= x for 0<x<0.6
  - Approximate diffusion distance (distance an impurity will dissolve into a sample to an appreciable level over a given time): $x \approx \sqrt{Dt}$

Lecture 25 – Nov 9: SOLUTIONS

- *"Like Dissolves Like"*





taxonomy of colloids

dispersed phase	dispersion medium	name	example
solid	liquid	sol	jelly
liquid	liquid	emulsion	milk, mayo
gas	liquid	foam	meringue, whipped cream
solid	gas	aerosol	soot
liquid	gas	aerosol	fog, hair spray
solid	solid	solid sol	cranberry glass
liquid	solid	solid emulsion	butter
gas	solid	solid foam	pumice

- Measure of solubility:
  - Molar (M) = (moles solute) / (liters of solution – both solute and solvent)

- Soluble if $C_{solute} > 0.1$ M, insoluble if $C_{solute} < 0.001$ M
- Equilibrium Constant, K: $aA + bB \Leftrightarrow cC + dD$
  - $K = [A]^a[B]^b / [C]^c[D]^d$
  - Most other "K's" are based on the form of this 'K', but exclude one term.
- Solubility Product $A_aB_b \rightarrow aA^{b+} + bB^{a-}$ (i.e. $MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$)
  - Coefficients become the exponents in K_{sp} eqn.
  - $K_{sp} = [A^{b+}]^a[B^{a-}]^b = K[A_aB_b]$
- Common Ion Effect:
  - If $[B^{a-}]$ added via another compound, K_{sp} must remain the same, therefore, $[A^{b+}]$ must decrease.

Lecture 26 – Nov 13: ACIDS AND BASES

- $pH = -\log_{10}[H^+]$,
- $pOH = -\log_{10}[OH^-]$,
- $pH + pOH = 14$

Definitions:

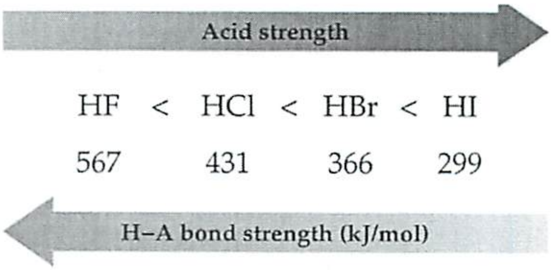
	Arrhenius	Bronsted-Lowry	Lewis
Acid:	p^+ donor	p^+ donor	e^- pair acceptor
Base:	OH^- donor	p^+ acceptor	e^- pair donor

- General Rxn: $HA + B \rightarrow BH^+ + A^-$
    - Conjugate acid-base pairs
    - HA & A^-
    - B & BH^+
    - For an acid, B can equal $[H_2O]$

- K_a and K_b describe the degree of dissociation of an acid/base, respectively.

- In aqueous systems, with $B = [H_2O]$:
    - $K_a = K\,[H_2O] = [H_3O^+][A^-] / [HA]$

- Amphiprotic: can act as an acid or a base (i.e. H_2O)
- Strong acids → complete dissociation ($K_a >> 1$)

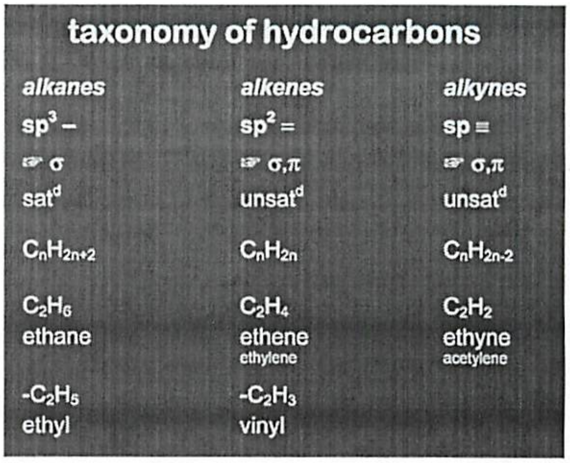


To solve some of these problems,

1. write out reaction equation
2. set up chart: initial, change, and final concentrations, with 'x' as the change the concentration of the base or acid.
3. solve for x and K_a or K_b are related, using formula above.

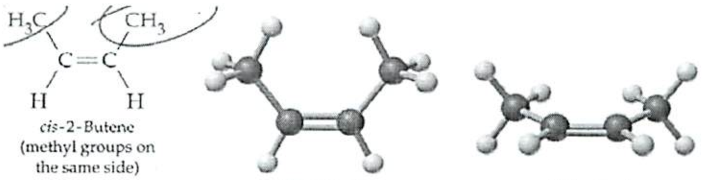
Lecture 27 – Nov 16: ORGANIC CHEMISTRY

- Naming Nomenclature
- Prefix (# of carbons in chain)
  - 1 = meth
  - 2 = eth
  - 3 = prop
  - 4 = but
  - 5 = pent
  - 6 = hex
  - 7 = hept
  - 8 = oct
- Add '-ane' or '-ene', or '-yne' based on bond type.
- Isomer: same chemical formula, but different configuration
  - **Constitutional Isomers:** Same chemical formula, but atoms bonded together in a different order (different side-groups)
    - (i.e butane vs. 2-methyl propane)
  - **Stereoisomers**: Same chemical formula, same side-groups, but different configuration (i.e. left-hand vs. right-hand). cis- vs. trans-
- Aromatic compounds:
  - Double and single bonds 'share' delocalized π-bond
  - e⁻ conductivity.



taxonomy of hydrocarbons

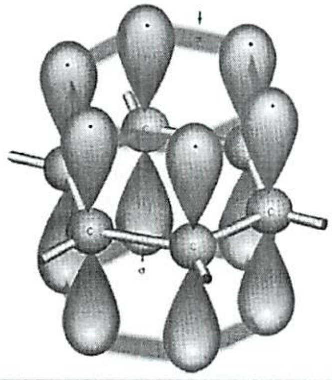
alkanes	alkenes	alkynes
sp^3 –	sp^2 =	sp ≡
☞ σ	☞ σ,π	☞ σ,π
sat^d	unsat^d	unsat^d
C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
C_2H_6 ethane	C_2H_4 ethene ethylene	C_2H_2 ethyne acetylene
-C_2H_5 ethyl	-C_2H_3 vinyl	



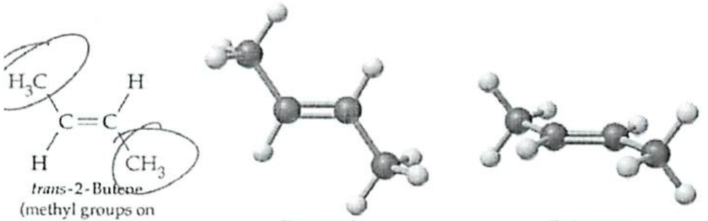
cis-2-Butene (methyl groups on the same side)

(Top view)

(Side view)



delocalized π-bonding in benzene



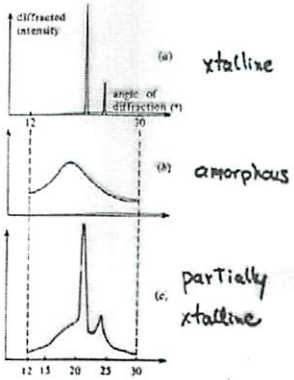
trans-2-Butene (methyl groups on opposite sides)

(Top view)

(Side view)

Lecture 28 – Nov 18: POLYMERS I

- Applied organic chem => polymers
- Polymers are macromolecules – long chains of molecules with repeating chemical structure. Poly = "many" mer = "repeat unit"
  - Can be xtalline, amorphous, or a combination of both → XRD can verify this



Polyethylene

Tailoring Molecular Architecture:

I. Composition:

- Random copolymer (AABBBABBAAA…)
- Regular copolymer (ABABA…)
- Block copolymer (AAAAAABBBBBBB…)
- Graft copolymer (BBBBBBBBB… with AAA…and S side chains)

II. Tacticity

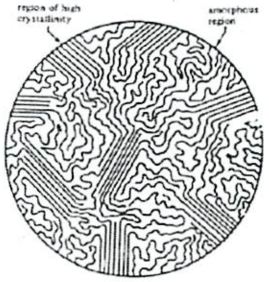
- Polymer can also be classified by side-group orientation
  - atactic, syndiotactic, isotactic

III.

Backbone:

- Linear chain
- Branched chain: harder to xtalize
- Crosslinked: Enabled by sulfur. Rubbery!

partially xtallized polyethylene

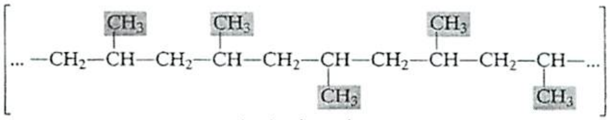


Synthesis:

- Addition polymerization
  - Need free radicals and double bonds to carry synthesis
- Condensation polymerization
  - Formed by rxns between the start and ends of mers
  - Polymer looses mass when synthesized (e.g. the condensation)

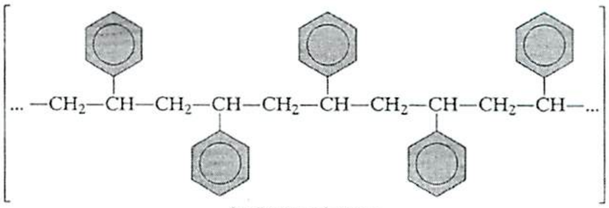
Thermoplastic: only Van der Waals acting between neighboring polymers, liquefies upon melting and are easy to recycle.

Thermoset: caused by the cross linking of polymers with disulfide bonds. There are covalent bonds between polymers, so the material strengthens but as a result is extremely hard to recycle.

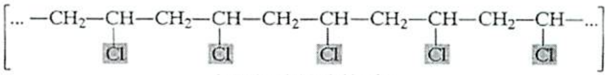


$$\left[\ldots -CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\underset{CH_3}{\underset{|}{C}H}-\ldots\right]$$

Atactic polypropylene



Syndiotactic polystyrene



$$\left[\ldots -CH_2-\underset{Cl}{\underset{|}{C}H}-CH_2-\underset{Cl}{\underset{|}{C}H}-CH_2-\underset{Cl}{\underset{|}{C}H}-CH_2-\underset{Cl}{\underset{|}{C}H}-CH_2-\underset{Cl}{\underset{|}{C}H}-\ldots\right]$$

Isotactic poly(vinyl chloride)

Lecture 29 – Nov 20: POLYMERS II:

Polymer Synthesis:

1. Addition Polymerization
    - Uses an initiator (R radical) to break a double or triple C-C bond (of a mer unit)
    - i.e. $R^* + CH_n{=}CH_n \rightarrow R\text{-}CH_n\text{-}CH_n^*$
    - growth by subsequent mer attachment
2. Condensation Polymerization
    - Uses the reaction between an H and an OH on two separate molecules to form an amide or peptide both, and releasing H_2O
    - i.e. $R_1H + R_2OH \rightarrow R_1\text{-}R_2 + H_2O$
    - mass polymer < Sum (mass of reactants)

Thermoplastics → weak VdW bonds connecting linear chains. Can reheat and reprocess → recyclable!
Thermoset → crosslinked chains → difficult to recycle

Plastics can have zones of random configuration and zones of crystallization, which can make the material stronger and denser.
Factors favoring crystallization:

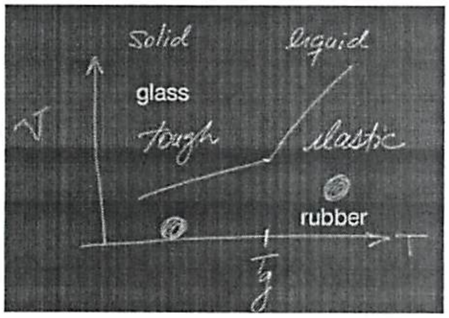
1. composition - homopolymer over copolymer)
2. tacticity – isotactic attractive
3. conformation – linear over branched

Properties of polymers

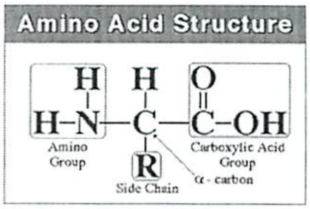
- e^- insulating, transparent to visible light, low density, solid at room temp.

Recall:

- Nylon pull-out video
- glass transition temperature of different polymers



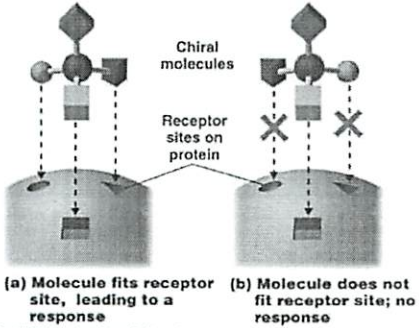
Lecture 30 – Nov 25: BIOCHEMISTRY:



Amino Acids:

- Contain an amine group, carboxylic acid group, and a side chain, R.
- R can be anything. But in our bodies, there are just 20 different R's, giving rise to twenty different amino acids
- R can be 1) nonpolar, 2) polar, 3) hydrophilic + acidic, 4) hydrophilic + basic
  - 3) and 4) can be 'titratable' (i.e. can accept or give off a H^+, depending on the local pH)

Amino acids are usually Chiral (i.e. Left (L) or Right (D) handedness → L- or D-enantiomers)



(a) Molecule fits receptor site, leading to a response **(b) Molecule does not fit receptor site; no response**

Amino acids are **Zwitterions**:

- In water at neutral pH, COOH group gives up an H^+, and the amine group accepts an H^+, causing the molecule to be net neutral, but have local +'ive and –'ive charges
- At high pH (low $[H^+]$), H^+ are stripped off of NH_3^+
- At low pH (high $[H^+]$), H^+ are added to COO^-

For titratable groups on the amino acid (i.e. a group that can gain or lose a H^+):

$HA + H^+ \rightarrow HAH^+$

$K_1 = [H^+][HA]/[A^-]$ (K is basically the equilibrium constant)

$pK_1 = pH + \log_{10}([HAH^+]/[HA])$

Similarly, at high pH

$A^- + H^+ \rightarrow HA^+$

$K_2 = [H^+][A^-]/[HA]$ (K is basically the equilibrium constant)

$pK_1 = pH + \log_{10}([HA^+]/[A^-])$

pI = isoelectric point.

When net charge of all molecule is zero (i.e. $[HA] >> [HAH^+],[A^-]$)

It happens ½ way between pK_1 and pK_2.

$pI = (pK_1 + pK_2)/2$

Lecture 31 – Nov 30: PROTEIN STRUCTURE:

Plot of pH as a function of 'extent of reaction':
"Equivalents of OH^-" is the same as the negative of $[H^+]$. i.e. the number of $[H^+]$ in the system (both free, and bound to the Zwitterion) increases from right to left.

Gel Electrophoresis:
Apply a voltage across a gel tube with varying pH. Amino acids (zwitterions) introduced at one end.
Zwitterions are propelled to migrate in the electric field as long as they have charge. When they reach the pH equivalent to their pI, they no longer have net charge, so they stop.
This allows researchers to measure the pI of an amino acid / zwitterion.

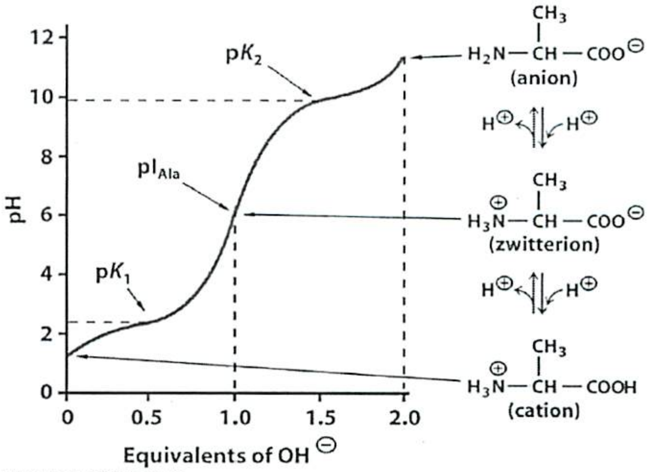


Figure 3-6 Principles of Biochemistry, 4/e © 2006 Pearson Prentice Hall, Inc.

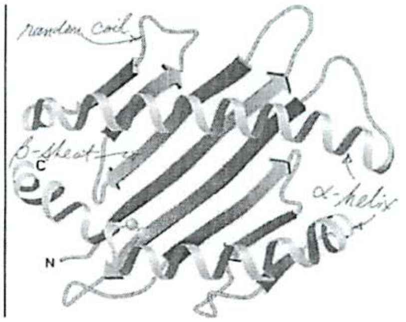
Proteins formed by condensation reaction between amides, forming polyamides.

TABLE P.2 Common Condensation Polymers

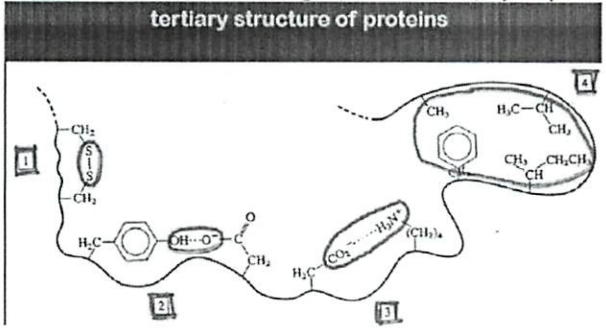
Structure	Trade Name Common N
Polyamides	
amino end · amide bond $(\text{—NH—}(CH_2)_6\text{—NH—}\overset{\overset{O}{\|}}{C}\text{—}(CH_2)_4\text{—}\overset{\overset{O}{\|}}{C}\text{—})_n$ carboxylic acid end	Nylon 6, 6

Protein exhibiting secondary structures:

- regions: α-helix, β-sheets, random coils



Tertiary structure of proteins ("random" coils):
- "random" structure determined by secondary bonding, ie. 1) disulfide bonds, 2) H-bonding, 3) columbic, 4) hydrophobic regions



Lecture 32 – Dec 2: LIPIDS, NUCLEIC ACIDS, DNA

Proteins can be denatured (i.e. breaking secondary bonding) by changes in:

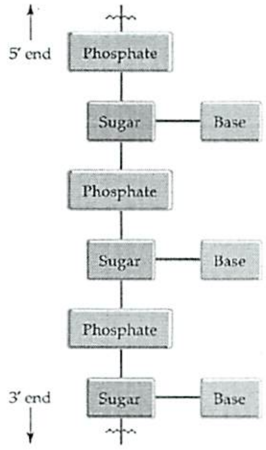
- 1) Temperature, 2) pH, 3) oxidizing/reducing agents to create/destroy -S-S- bonds), 4) detergents

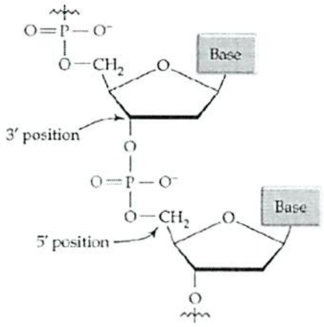
Lipids: defined by their properties – soluble in solvents of low polarity – includes fats, oils, cholesterol, hormones.

- Some have a hydrophilic head and a hydrophilic tail (amphipathic molecules)
- can arrange in a lipid bilayer in a polar solvent → Cell wall!

Nucleic acids

- Building block of nucleotides → DNA
- DNA contain sugar (amine link) and a phosphate backbone, with one of four of five amine groups that make up the 'code' (AGCU for RNA, and AGCT for DNA)
- A pairs with T (2 H bonds), C pairs with G (3 H bonds). Spacing is important.
- These chains makeup a double-helix structure → DNA





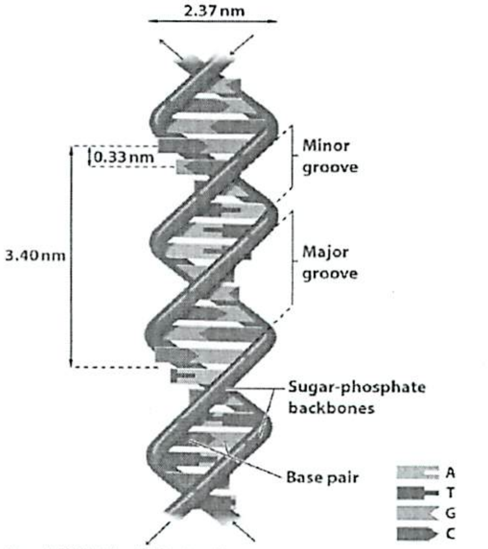


Figure 19-14 Principles of Biochemistry, 4/e
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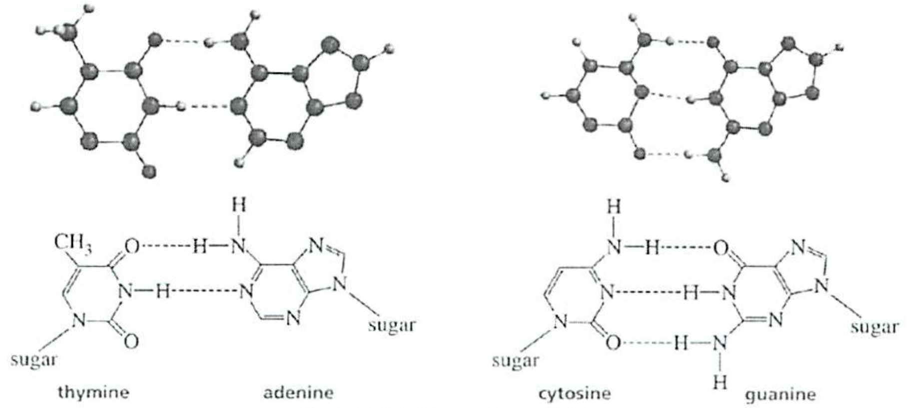

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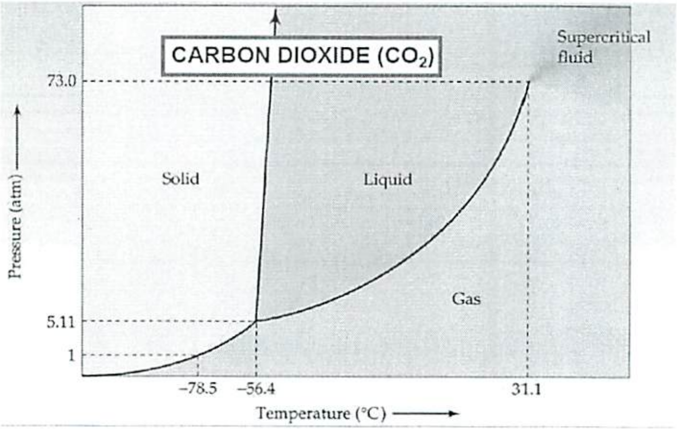
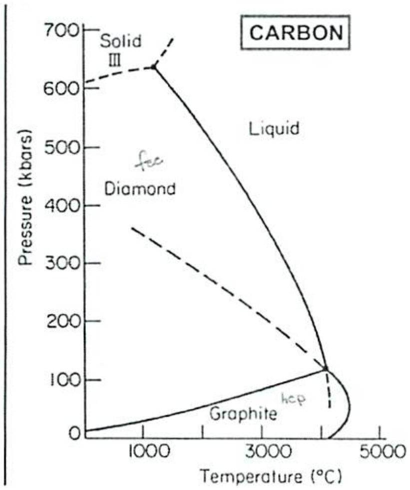
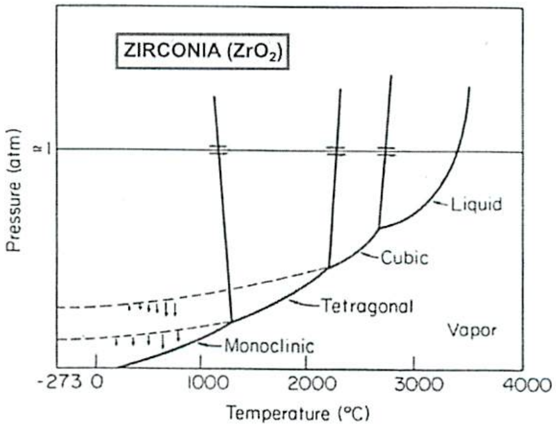
Lecture 33 – Dec 4: PHASE DIAGRAMS, ONE COMPONENT - UNARY

- Triple point is where the three lines meet, a region where three phases coexist in equilibrium
- Slope of solid/liquid interface (2 phase region) characterized the density of the material in either phase
- Super critical fluid is a one phase regime
- "Normal" conditions means 1 atm of pressure

more examples

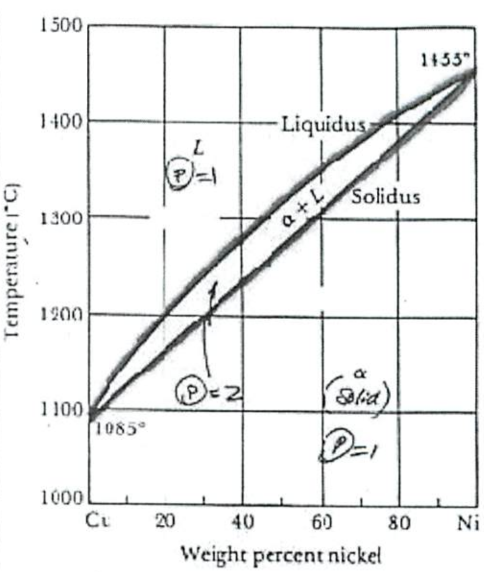




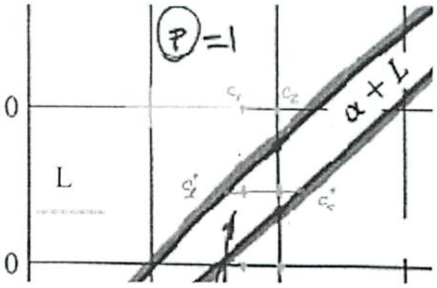


Lecture 34 – Dec 7: PHASE DIAGRAMS – BINARY – LENTICULAR/IMMISCIBILITY

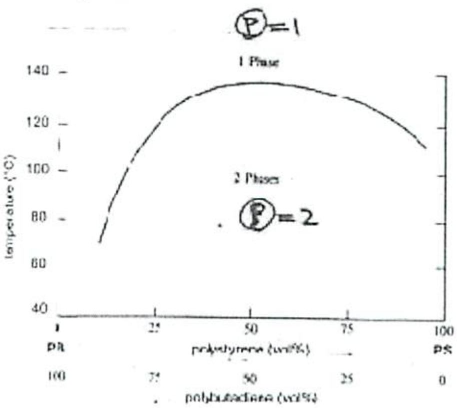
- Sadoway's system classification
  - Type 1
    - Complete solubility as solids and liquids
    - Isomorphism – lens shape
    - Properties include:
      - Identical crystal structures
      - Similar atomic volumes
      - Small electronegativity differences
    - When (c) > 1, impossible to move from one single phase field to another single phase field
    - **Liquidus:** lowest temperature at which all liquid is stable
    - **Solidus:** highest temperature at which all solids are stable



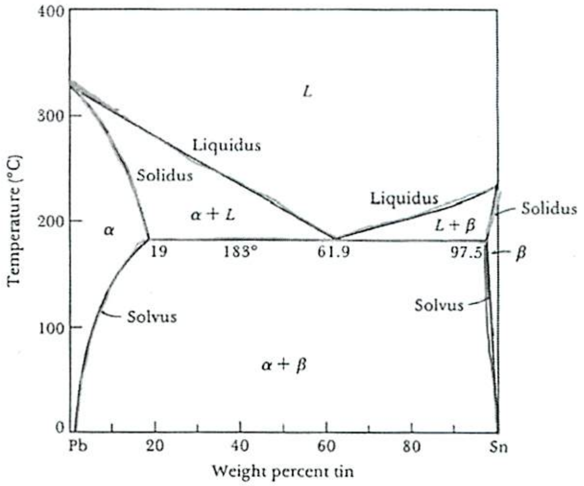
  - LEVER RULE
    - (P) = 2
    - Used to compute percentages of the relevant phases in equilibrium
    - For the example on the right:
      - Held at c_2 (you can do the same for c_1)
      - $\%liquid = \dfrac{c_s^* - c_2}{c_s^* - c_l^*}$
      - $\%solid = \dfrac{c_2 - c_l^*}{c_s^* - c_l^*}$
      - c_l^* is the equilibrium concentration in the liquid phase
      - c_s^* is the equilibrium concentration in the solid phase



  - Type 2
    - partial or limited solubility of both components in each other
    - no change of state – always solid or always liquid
    - generates "Synclinal" coexistence curve



Lecture 35 – Dec 9: PHASE DIAGRAMS – BINARY – LIMITED SOLUBILITY



- Type 3
  - Partial solubility of A and B
  - Change of state
  - "hybrid between lens and syncline"
  - Freezing point depression of both components
  - Eutectic: composition and temperature where three phases coexist in equilibrium.
  - **APPLY LEVER RULE TO TWO PHASE REGIONS!!!**
    - $\alpha+\beta$, $\alpha+L$, $L+\beta$
  - Top example:
    - α is a Pb-rich phase
    - β is a Sn-rich phase
  - You can tell a lot about the history of a material by looking at the microstructure