"A" students work
(without solutions manual)
~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

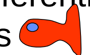
Office Hours Th&F 2-3:30 pm

Module #17A:
Acid Base Visualization

Review Charge Density

FITCH Rules

General

G1: Suzuki is Success
G2. Slow me down
G3. Scientific Knowledge is Referential
G4. Watch out for Red Herrings 
G5. Chemists are Lazy

Chemistry

C1. It's all about charge
C2. Everybody wants to
C3. Size Matters
~~C4. Still Waters Run De~~
C5. Alpha Dogs eat firs

What is an alpha dog?
High charge, low volume

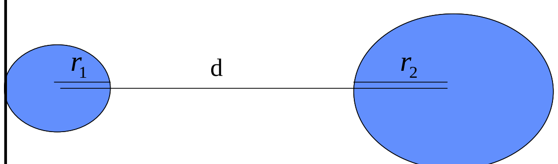
$$k = 8.99x10^9 \frac{J\ m}{C^2}$$

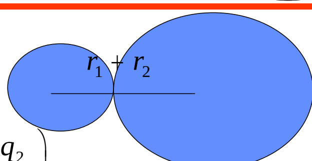
It's all about charge

$$Energy_{electrostatic} = k\left(\frac{q_1 q_2}{d}\right)$$

Charge on object 1 or 2, in coulombs

Distance between the objects



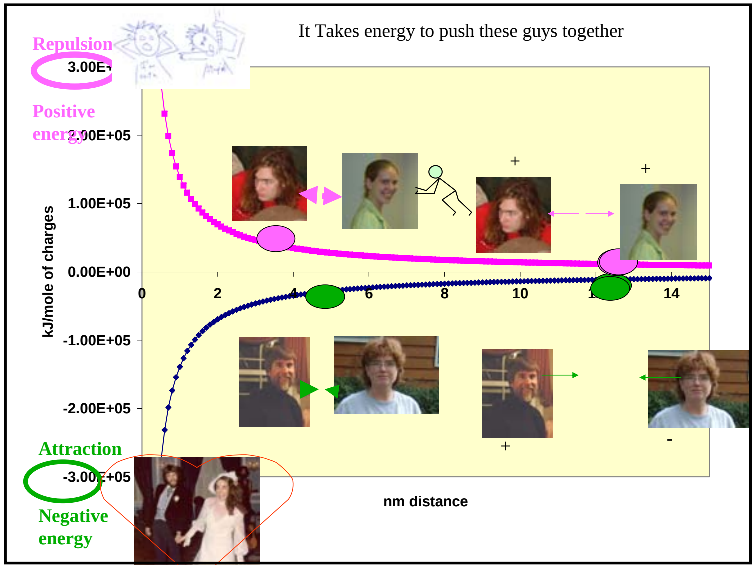


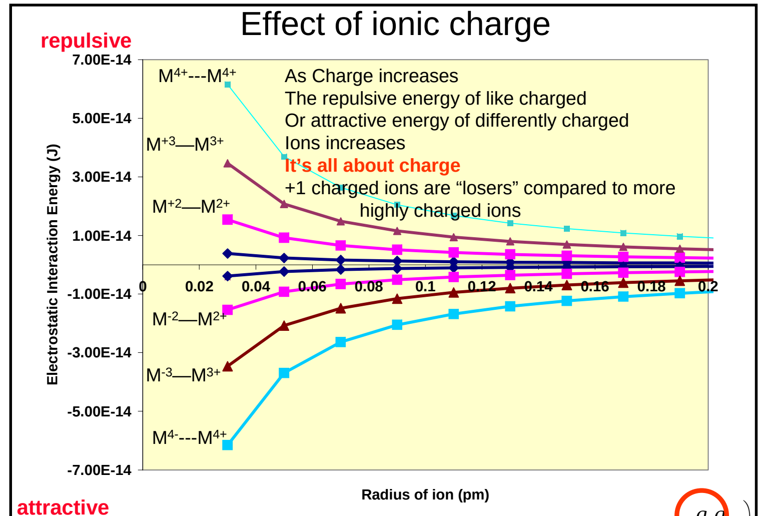
$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

Coulomb's Law

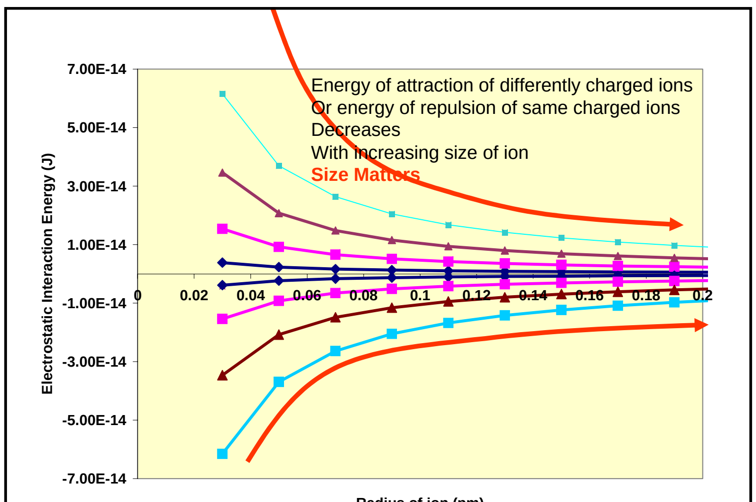
Review: Module 5

Fitch Rule G3: Science is Referential





$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$



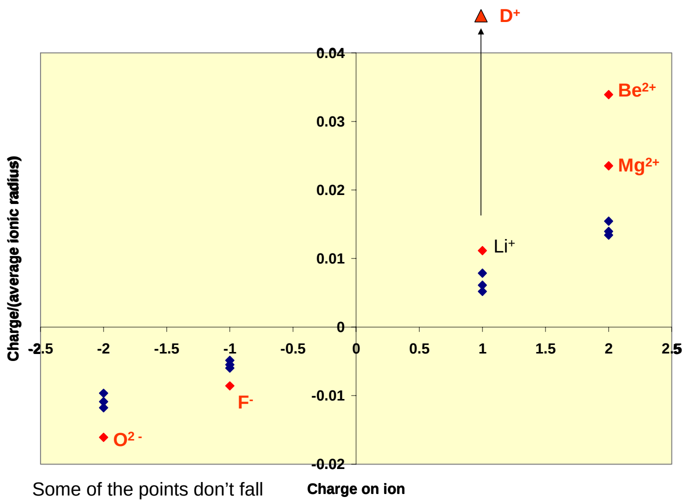
$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

Are there differences in predicted electrostatic effect?

Ion	Symbol	Charge	Radius (pm)	Charge/radius	
hydrogen	D+	1	4	0.25	H+ should behave differently
lithium	Li+	1	89.66666667	0.011152416	
sodium	Na+	1	127.4285714	0.007847534	
potasium	K+	1	164	0.006097561	
cesium	Cs+	1	192.8333333	0.005185825	
beryllium	Be2+	2	59	0.033898305	Be^{2+} and Mg^{2+} should behave differently
magnesium	Mg2+	2	85	0.023529412	
calcium	Ca2+	2	129.5	0.015444015	
strontium	Sr2+	2	143.3333333	0.013953488	
barium	Ba2+	2	149	0.013422819	
oxide	O2-	-2	124.2	-0.01610306	O^{2-} and, maybe, S^{2-} should behave differently
sulfide	S2-	-2	170	-0.011764706	
selenide	Se2-	-2	184	-0.010869565	
telluride	Te2-	-2	207	-0.009661836	
fluoride	F-	-1	116.625	-0.008574491	F^- should behave differently
chloride	Cl-	-1	167	-0.005988024	
bromide	Br-	-1	182	-0.005494505	
iodine	I-	-1	206	-0.004854369	

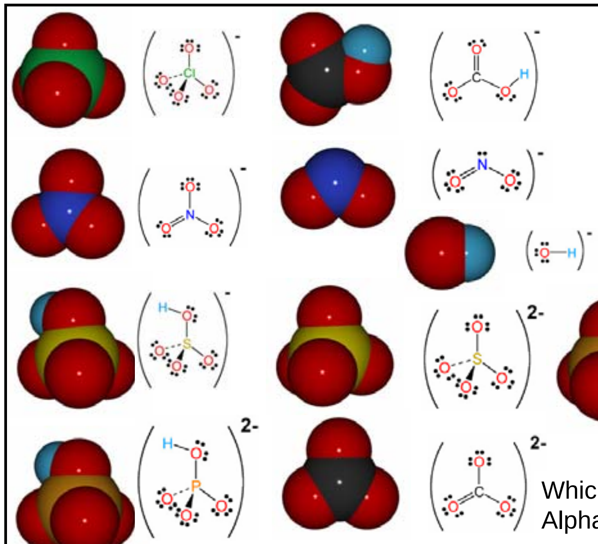
$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

Review: Module 5

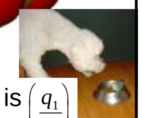


Some of the points don't fall
Within a "cluster"

Review: Module 5

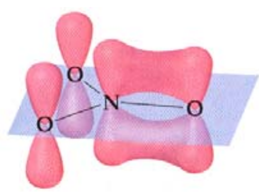


Some
Common
anions



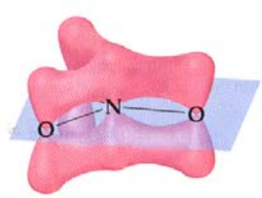
Which is Alpha? $\left(\frac{q_1}{r_1}\right)$

http://www.chemistry.wustl.edu/~courses/genchem/Tutorials/Ions/ions.html



(a) N—O π bond in one of the resonance structures of NO_3^-.

Low charge
Density
NOT an
Alpha dog



(b) Delocalization of the π bonds in the NO_3^- ion.

Charge is
Distributed
Throughout
The volume

Review: Module 5

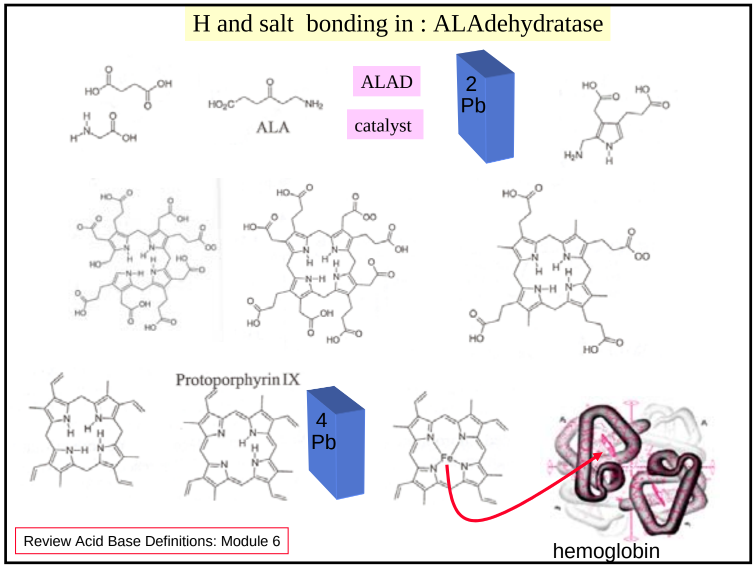
"A" students work
(without solutions manual)
~ 10 problems/night.

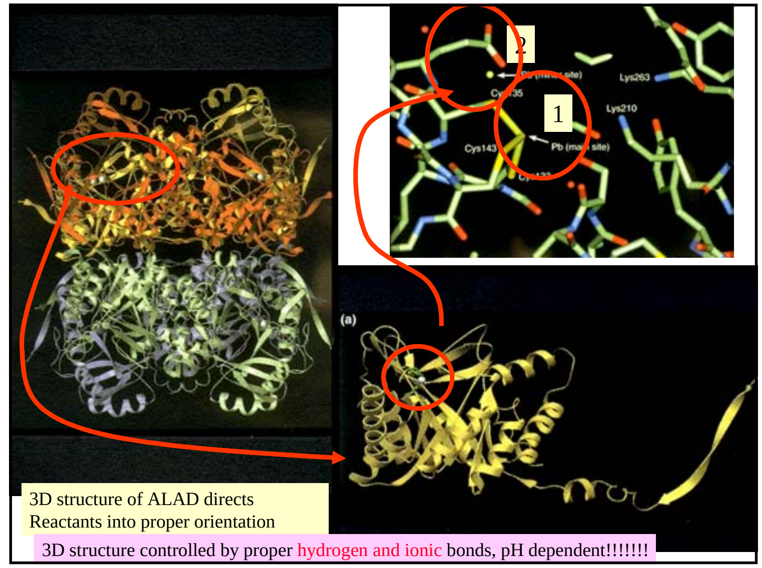
Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

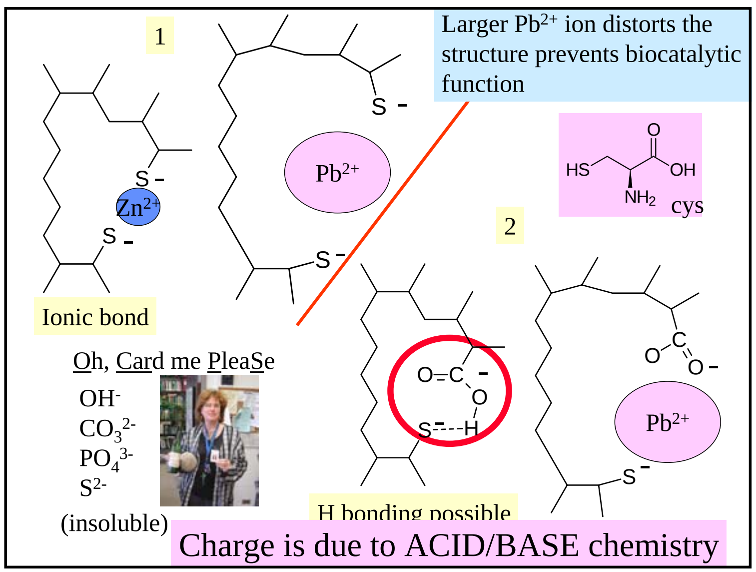
Office Hours Th&F 2-3:30 pm

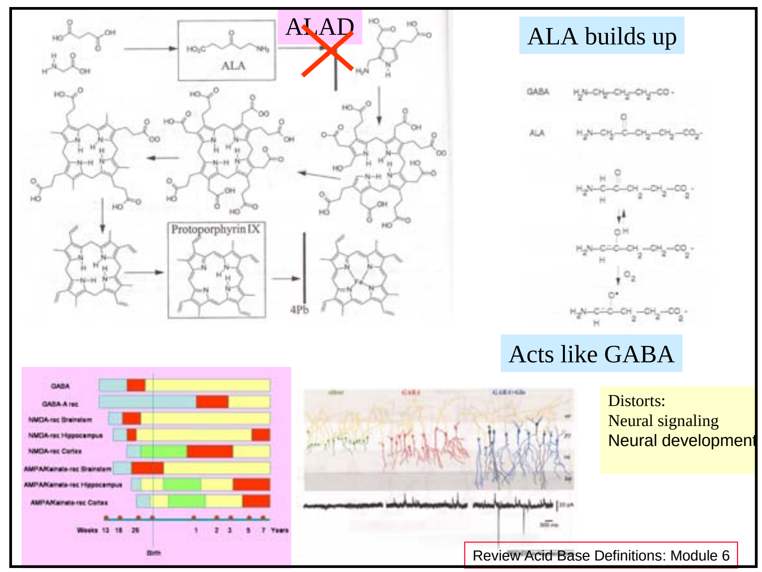
Module #17A:
Acid Base Visualization

Review Biological
Dependence on
Acid/base reactions


H and salt bonding in : ALAdehydratase
ALAD
catalyst
ALA
2 Pb
Protoporphyrin IX
4 Pb
hemoglobin
Review Acid Base Definitions: Module 6

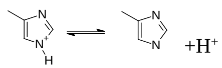

2
1
Lys263
Lys210
Cys143
(a)
3D structure of ALAD directs
Reactants into proper orientation
3D structure controlled by proper hydrogen and ionic bonds, pH dependent!!!!!!!

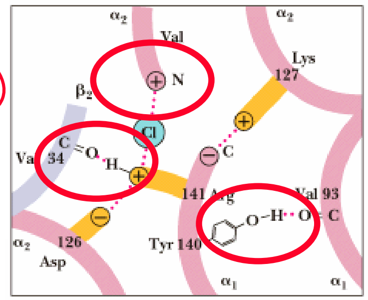

1
Larger Pb2+ ion distorts the structure prevents biocatalytic function
S -
Pb2+
Zn2+
S -
HS
OH
NH2
cys
2
Ionic bond
Oh, Card me PleaSe
OH-
CO3 2-
PO4 3-
S2-
(insoluble)
O=C -
O
S---H
H bonding possible
Pb2+
Charge is due to ACID/BASE chemistry


ALAD
ALA
ALA builds up
Protoporphyrin IX
4Pb
GABA
ALA
Acts like GABA
Distorts:
Neural signaling
Neural development
Review Acid Base Definitions: Module 6

Acid base reactions
With N and COOH, C-OH
Control charge sites on
Proteins, allowing folding

$R3NH^+ \rightleftarrows R3N + H^+$





Hemeglobin

"A" students work (without solutions manual) ~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

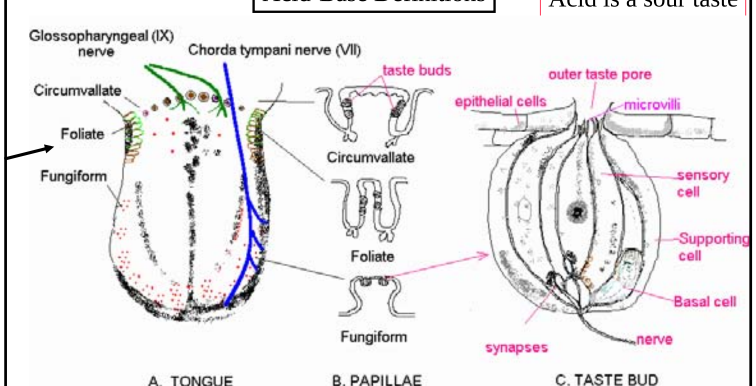
Office Hours Th&F 2-3:30 pm

Module #17A:
Acid Base Visualization

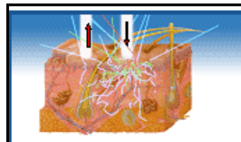
Review Acid/base definitions

Acid-Base Definitions

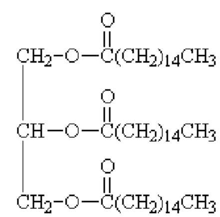
Acid is a sour taste



Foliate papillae are situated on the edge of the tongue slightly anterior of the circumvallate line. They are predominantly **sensitive to sour tastes**. Innervated by the glossopharyngeal (IXth cranial) nerve. On average 5.4 foliate papillae per side of the tongue, 117 taste buds per foliate papillae, total = 1280 foliate taste buds per tongue.



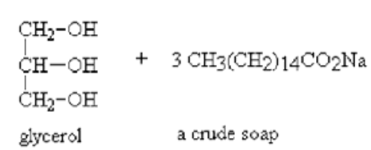
Optical Deep-Tissue Measurement



a fat

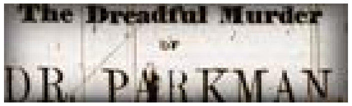
+ Hard soap NaOH (lye) Soft soap Or KOH (pot ash) $Ca(OH)_2$ (lime)

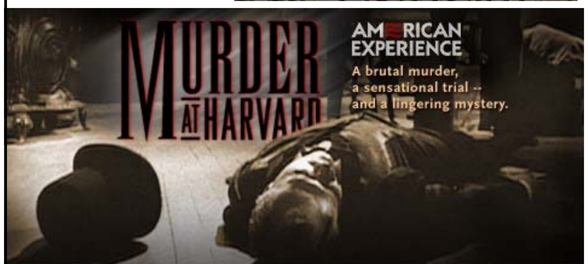
saponification
Latin for soap



Bases dissolve fatty acids and oils from your skin, making soaps (**feel slippery**)

In 1849 a **Harvard chemistry professor**, John Webster argued with a colleague, Dr. Parkman, about money he owed the colleague for some dinosaur bones. He killed his fellow Professor and attempted to hide the crime by dissolving the body in a vat Of “lime” ($Ca(OH)_2$) and then burning the remaining bones.





Review Acid Base Definitions: Module 6

Chemical Definition of Acid/Base

Svante Arrhenius

An acid is a species that produces proton ions in solution

Solution

Acid: HX

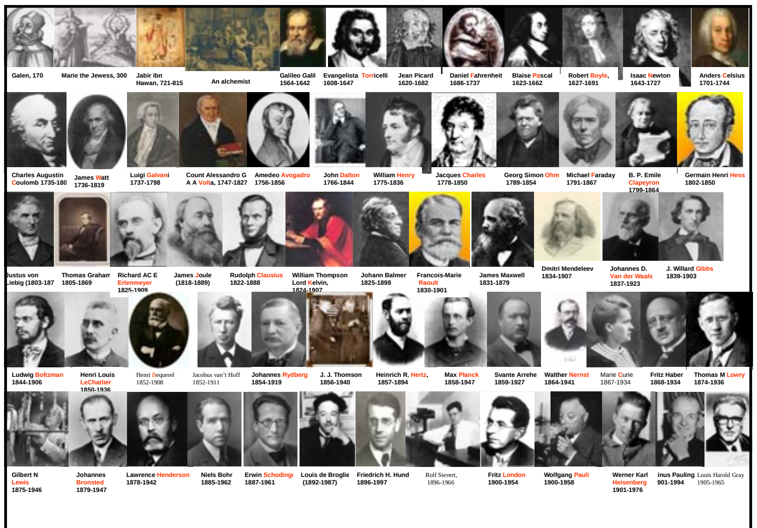
Strong acid | Weak acid

X^- or A^- is an anion who is partnered with the cation, H^+

$$HX_{aq} \rightarrow H^+_{aq} + X^-_{aq}$$

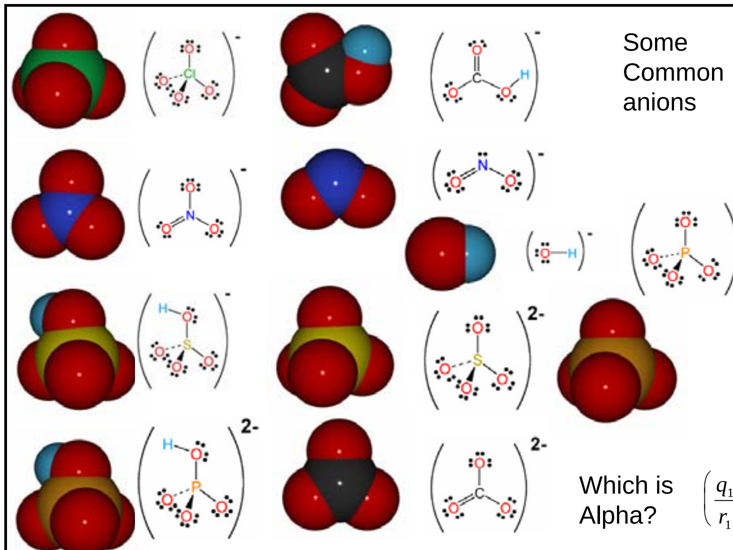
$$HA_{aq} \rightarrow H^+_{aq} + A^-_{aq}$$

In a **STRONG** acid the anion can not provide enough electrostatic attraction to hold onto the H^+ (proton)
In a **WEAK** acid the anion is very charge dense and holds onto the H^+



Fitch Rule G3: Science is Referential

Some Common anions



Which is Alpha? $\left(\frac{q_1}{r_1}\right)$

http://www.chemistry.wustl.edu/~courses/genchem/Tutorials/Ions/ions.html

We saw that q/r > ~0.08 seemed to be "big"
Which of these anions are not "alpha dogs"

No Clean Socks

	name	formula	charge	radius	charge/radius
No Clean Socks	perchlorate	ClO4-	1	236	0.004237288
	nitrate	NO3-	1	189	0.005291005
	bromide	Br-	1	182	0.005494505
	chloride	Cl-	1	167	0.005988024
		HSO4-	1	?	?
		H2PO4-	1	?	?
	hydrogen sulfide	HS-	1	?	?
		HPO42-	2	?	?
	hydrogen carbonate	HCO3-	1	163	0.006134969
	acetate	CH3COO-	1	159	0.006289308
	formate	HCOO-	1	158	0.006329114
	nitrite	NO2-	1	155	0.006451613
Oh Card Me PleaSe	hydroxide	OH-	1	140	0.007142857
	fluoride	F-	1	116.625	0.008574491
	sulfate	SO42-	2	230	0.008695652
	carbonate	CO32-	2	185	0.010810811
	sulfide	S2-	2	170	0.011764706
	phosphate	PO43-	3	238	0.012605042

Who gives up and who holds onto a proton?

Low Charge Density
Intermediate Charge Density
High Charge Density

No Clean Socks | Oh Card me PleeeeaSe!!

NO_3^- Cl^- HSO_4^- | OH- | CO_3^{2-} PO_4^{3-} S^{2-}

H+

Low Charge Density Anions Give up protons | H_2O | **High Charge Density Anions hold onto protons**

STRONG acids | **WEAK acids**

Weak to Intermediate

$$HX_{aq} \rightarrow H^+_{aq} + X^-_{aq}$$

Completely falls apart

$$HX_{aq} \rightleftarrows H^+_{aq} + X^-_{aq}$$

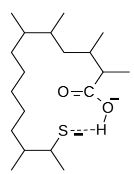
X- tries to hold onto some protons; are "alpha dogs"
Double arrow

$$H_2O_\ell \rightleftarrows H^+_{aq} + OH^-_{aq}$$

Review Acid Base Definitions: Module 6

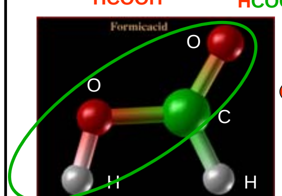
Water is an Arrhenius acid

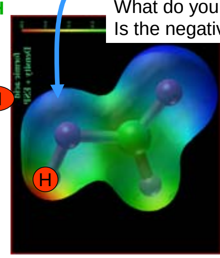
Another very common type of Weak Acid - ....COOH



Condensed Structural Formula gives a clue as to the Important Functional Group

HCOOH **HCOOH**





Blue represents negative charge causes potential field

What do you see?
Is the negative charge fully localized?

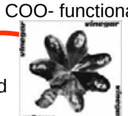
Dissociate temporarily

Proton actually resides Somewhere between Two highly negatively Charged oxygen

Review Acid Base Definitions: Module 6

Some Weak Acids with COO- functional group **(Carboxylate)**

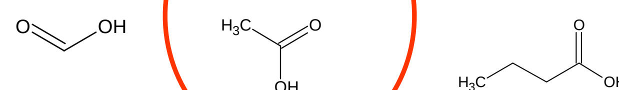
Formic Acid (Ants)

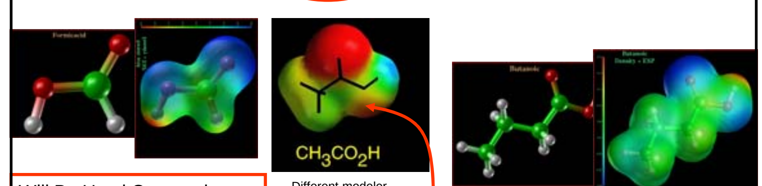


Acetic Acid
Vinegar
HOAc (OAc = acetate)

Butanoic Acid

Gives Smell of Rancid butter





Will Be Used Over and Over In Example Problems

Different modeler
Gave opposite color scheme (Red = large neg charge)

http://academic.reed.edu/chemistry/alan/ED/JCE/figlist.html

Chemical Definition of Acid/Base

Svante Arrhenius

An acid is a species that produces proton ions in solution

A base is a species that produces hydroxide ions in solution

- Solution
  - Acid: HX
    - Strong acid
    - Weak acid
  - Base:
    - Strong base

$$MOH \rightarrow OH^-_{aq} + M^+_{aq}$$

Where M⁺ is some cation

Review Acid Base Definitions: Module 6

Strong Bases (SB)

hydroxides which have low charge density cations as partners

$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

1. q is low (+1)
   Group 1 (Li^+, Na^+, K^+)

$$LiOH \xrightarrow{completely} Li^+_{aq} + OH^-_{aq}$$

2. r is large
   Group 2 cations

Be^{2+}
Mg^{2+}
Ca^{2+}
Sr^{2+}
Ba^{2+}
Ra^{2+}

But only larger ones

Not Ra^{2+} because dispersion forces come into play

$$Ca(OH)_2 \xrightarrow{completely} Ca^{2+}_{aq} + 2OH^-_{aq}$$

Who gives up and who holds onto a hydroxide?

Low Charge Density
Intermediate Charge Density
High Charge Density

	No	Clean	Socks	Oh	Card me		PleeeeaSe!!
	NO_3^-	Cl^-	HSO_4^-	OH^-	CO_3^{2-}	PO_4^{3-}	S^{2-}
H+	STRONG acids				WEAK acids		
Group 1 cations (1+)				Strong Bases			
Group 2 cations (2+)							

Weak bases are produced by an alternative manner

Our next step is to look
To an alternative definition

Review Acid Base Definitions: Module 6

"A" students work (without solutions manual)
~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

Office Hours Th&F 2-3:30 pm

Module #17A: Acid BaseVisualization

Review More Acid Base Definitions

Bronsted and Lowry definitions

B^- and X^- are bases (anions) which can accept protons

$$B^-_{aq} + H^+_{aq} \rightleftarrows HB_{aq}$$

$$X^-_{aq} + H^+_{aq} \rightleftarrows HX_{aq}$$

HX and HB are species which can donate protons

$$HX_{aq} \rightleftarrows X^-_{aq} + H^+_{aq}$$

$$HB_{aq} \rightleftarrows B^-_{aq} + H^+_{aq}$$

$$B^-_{aq} + H^+_{aq} \rightleftarrows HB_{aq}$$

$$HX_{aq} \rightleftarrows X^-_{aq} + H^+_{aq}$$

A proton donor Bronsted acid

$$B^-_{aq} + HX_{aq} \rightleftarrows HB_{aq} + X^-_{aq}$$

A proton acceptor (Bronsted base)

Fitch Rule G3: Science is Referential

$$B^-_{aq} + H^+_{aq} \rightleftarrows HB_{aq}$$

Mass balance for B

1. Occurs as both a “base” and “acid” form
2. The 2 forms are “linked” by the reaction
3. The 2 forms are “conjugated”
4. The anion B^- is the “conjugate” base of HB

$$HX_{aq} \rightleftarrows X^-_{aq} + H^+_{aq}$$

Mass balance for X

1. Occurs as both a “base” and “acid” form
2. The 2 forms are “linked” by the reaction
3. The 2 forms are “conjugated”
4. The HX is the conjugate acid of X^-

1. Write the linking rx
2. Identify the mass balance component

Example:

What is conjugate base of:

$$HClO_{4,aq} \rightarrow H^+_{aq} + ClO^-_{4,aq}$$

$$H_2O_l \rightarrow H^+_{aq} + OH^-_{,aq}$$

$$PH_4^+ \rightarrow H^+_{aq} + PH_3$$

Linking reactions

Mass balance component

$HClO_4$

H_2O

PH_4^+

What is conjugate acid of:

$$CN^-_{,aq} + H^+_{aq} \rightarrow HCN_{aq}$$

$$SO^{2-}_{4,aq} + H^+_{aq} \rightarrow HSO^-_{4,aq}$$

Linking reactions

CN^-

SO_4^{2-}

conjugate base	charge	radius	charge/radius	conjugate acid
ClO4-	1	236	0.004237288	HClO4
NO3-	1	189	0.005291005	HNO3
Br-	1	182	0.005494505	HBr
Cl-	1	167	0.005988024	HClO4
HSO4-	1	?	?	H2SO4
H2PO4-	1	?	?	H3PO4
HS-	1	?	?	H2S
HPO42-	2	?	?	H2PO4-
HCO3-	1	163	0.006134969	H2CO3
CH3COO-	1	159	0.006289308	H(CH3COO)
HCOO-	1	158	0.006329114	H(HCOO)
NO2-	1	155	0.006451613	HNO2
OH-	1	140	0.007142857	HOH
F-	1	116.625	0.008574491	HF
SO42-	2	230	0.008695652	HSO4-
CO32-	2	185	0.010810811	HCO3-
S2-	2	170	0.011764706	HS-
PO43-	3	238	0.012605042	HPO42-

Notice, that some anions occur in multiple rx

In every Bronsted-Lowry Acid-base reaction the position of the equilibrium favors transfer of the proton to the **stronger** base.

Get proton

$$\frac{q_1}{r_1}\uparrow\uparrow\uparrow > \frac{q_1}{r_1}\uparrow$$

$$\frac{q_1}{r_1}\uparrow > \frac{q_1}{r_1}\downarrow$$

Alpha dogs eat first

Predict who gets the proton B- or X- :

$$B^-_{aq} + HX_{aq} \rightleftarrows HB_{aq} + X^-_{aq}$$

$\frac{q_1}{r_1}\downarrow$ | $\frac{q_1}{r_1}\uparrow$

No Clean Socks

Cl-
Br-
I-
NO_3^-
ClO_4^-
HSO_4^-

OH-
CO_3^{2-}
PO_4^{-3}
S^{-2}

Oh
Card (me)
P(lea)
S(e)

H_2O
PO_4^{-3}
Neither one

Water Is intermediate

Water can be one of the conjugate pairs

$$HX_{aq} \rightleftarrows H^+_{aq} + X^-_{aq}$$

$$H_2O_\ell + H^+_{aq} \rightleftarrows H_3O^+_{aq}$$

$$H_2O_\ell + HX_{aq} \rightleftarrows H_3O^+_{aq} + X^-_{aq}$$

The acid HX donates a proton to water
it is a proton donor = acid
The water molecule takes a proton from HX
it is a proton acceptor = base

Water is a Bronsted-Lowry Base

We looked at 2 water reactions

$$H_2O_\ell \rightleftarrows H^+_{aq} + OH^-_{,aq}$$

Acts as Arrhenius Acid
source of protons

$$H_2O_\ell + H^+_{aq} \rightleftarrows H_3O^+_{,aq}$$

Acts as Bronsted-Lowry Base
proton acceptor

$$H_2O_\ell + H_2O_\ell \rightleftarrows H_3O^+_{aq} + OH^-_{,aq}$$

Base 2 Acid 2

Acid 1 Base 1

The ability of water to act as both acid/base
Is called amphoteric

Weak bases are made by a BL reaction with water

$$R + H_2O_\ell \rightleftarrows RH^+_{aq} + OH^-_{aq}$$

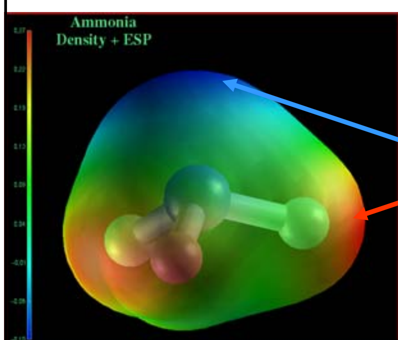
$$NH_{3(aq)} + H_2O_\ell \rightleftarrows NH^+_{4(aq)} + OH^-_{aq}$$

Who is a proton donor (BL acid)? Water

Who is a proton acceptor (BL base)? Ammonia

What functional groups are "R"?

http://core.ecu.edu/phys/flurchickk/AtomicMolecularSystems/molecularStructures/molecularStructures.html



net neutral Molecule ammonia, NH_3

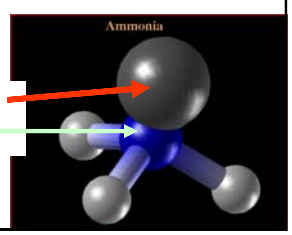
Is the charge evenly distributed?

Is there a region of high charge Density?

In this model blue is negative charge causing a potential field and red is Positive charge opposite potential field

Nitrogen typically contains a set of unbonded electrons

which give Large charge density near the N atom



Review Acid Base Definitions: Module 6

Write reaction to show the unbonded electrons on R (where R is N in ammonia)

$$H_2O + :R \rightarrow OH^-_{aq} + RH^+_{aq}$$

Write the reaction to show that electrons on R are attracted to proton on water

$$HO\cdot\cdot H + :R \rightarrow OH^-_{aq} + RH^+_{aq}$$

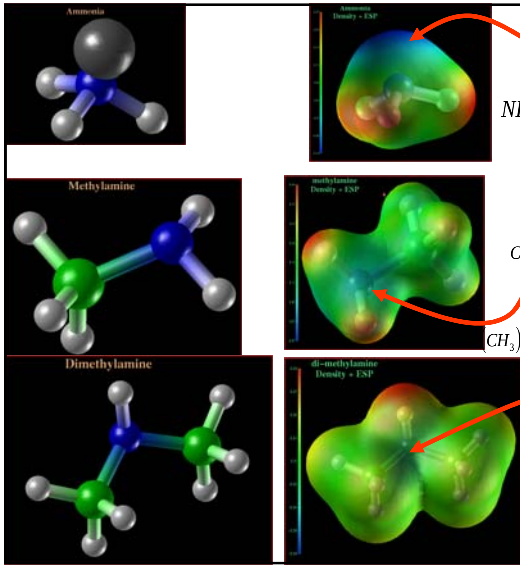
$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

$$R + H_2O \rightarrow RH^+_{aq} + OH^-_{aq}$$

Compounds in which H on NH_3 has been replaced by –C groups react Similarly

- NH_3
- CH_3NH_2
- $C_2H_5NH_2$
- $(C_2H_5)_2NH$
- $C_6H_5NH_2$

} R



NH_3

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

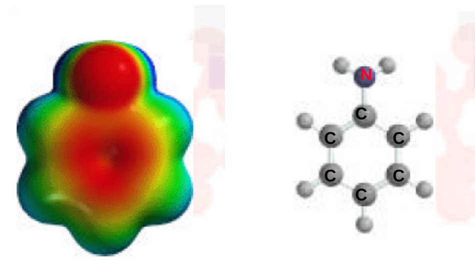
CH_3NH_2

$$CH_3NH_2 + H_2O \rightleftarrows CH_3NH_3^+ + OH^-$$

$$(CH_3)_2NH + H_2O \rightleftarrows (CH_3)_2NH_2^+ + OH^-$$

$(CH_3)_2NH$

http://www.chem.uic.edu/web1/PDF/CH13.PDF

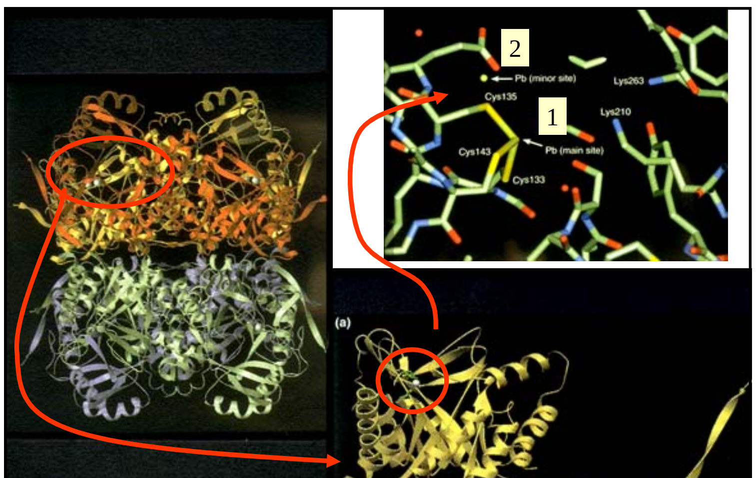


In this image electrons are red

aniline

$(C_6H_5)NH_2$

$$(C_6H_5)NH_2 + H_2O \rightleftarrows (C_6H_5)NH_3^+ + OH^-$$



3D structure of ALAD directs
Reactants into proper orientation

3D structure controlled by proper ionization of COO^- and RNH_3^+

There is one more type of acid/ Base reaction to consider

- Solution
  - Acid: HX
    - Strong acid
    - Weak acid
  - Base:
    - Strong base: $MOH \rightarrow OH^-_{aq} + M^+_{aq}$ — Arrhenius hydroxide donor (base)
    - Weak base: $R + H_2O \rightarrow RH^+_{aq} + OH^-_{aq}$ — Bronsted Lowry proton acceptor (base)

Review Acid Base Definitions: Module 6

"A" students work (without solutions manual) ~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

Office Hours Th&F 2-3:30 pm

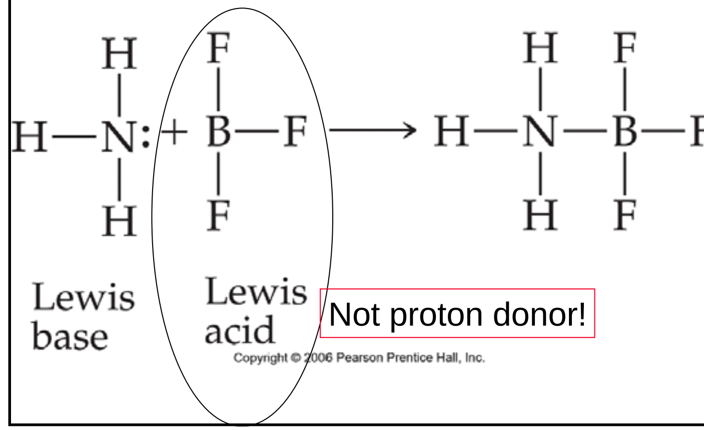
Module #17A:
Acid Base Visualization

One more kind of Acid/Base reaction

Lewis Acids and Bases:

Base is an electron pair donor

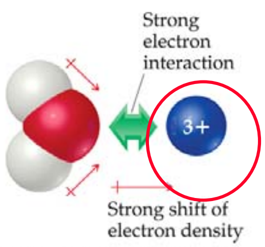
Lewis acid is an electron-pair acceptor;



Highly chared Cations can Act as Lewis acids

$$E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$$

$q\uparrow$ $r\downarrow$ = stronger effect

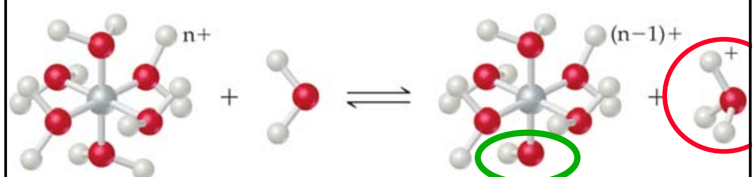


$$Al^{3+} + :\ddot{O}\cdot\cdot H \rightarrow \left[Al^{3+}\cdots:\ddot{O}\cdot\cdot H\right] + H^{+}_{aq}$$

(with H bonded to O)

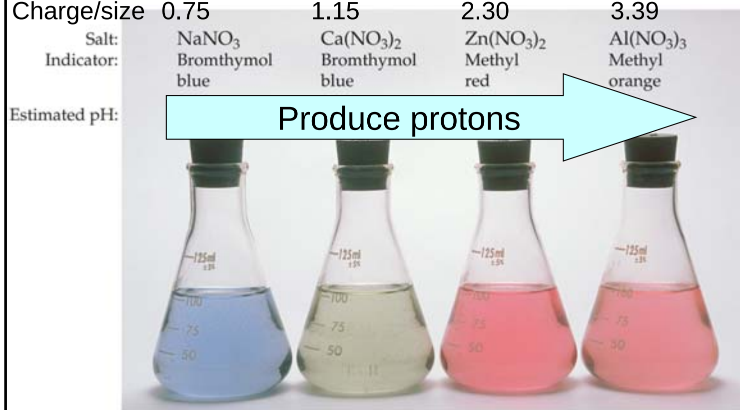
Aluminum ion is an electron pair acceptor = **Lewis acid**

$$Fe(H_2O)^{3+}_{6(aq)} + H_2O_{\ell} \rightleftarrows Fe(OH)(H_2O)^{2+}_{5(aq)} + H_3O^{+}$$



ATOM SIZE (NOT ION)

Size (A)	1.34	1.74	1.31	1.18
Charge	+1	+2	+2	+3
Charge/size	0.75	1.15	2.30	3.39



"A" students work (without solutions manual)
~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

Office Hours Th&F 2-3:30 pm

Module #17A: Acid BaseVisualization

Salts

Ionic salts can act as acids and bases

$$MX_s \rightarrow M^+_{aq} + X^-_{aq}$$

$$X^{n-}_{aq} + H_2O \rightarrow HX^{(n-1)-}_{aq} + OH^-_{aq}$$

Bronsted-Lowry Base

$$Al^{3+} + :\ddot{O}\cdot\cdot H \rightarrow \left[Al^{3+} \cdots :\ddot{O}\cdot\cdot H\right] + H^+_{aq}$$

(with H bonded below the O on the left)

Lewis Acid

$$M^{3+} + H_2O_\ell \rightarrow M(OH)^{(n-1)+} + H^+_{aq}$$

Generic Lewis Acid

Require High charge Density ions

$$NH^+_{4,aq} + H_2O \rightarrow NH_{3,aq} + H_2O^+_{3q}$$

Arrhenius acid

Predict what happens when the following salts Are added to water

$Na^+ Cl^-$

Na^+ does not "grab" OH from water, no effect
Cl^- does not "grab" H from water, no effect

neutral

$NH_4^+Cl^-$

$$NH^+_{4,aq} + H_2O \rightarrow NH_{3,aq} + H_2O^+_{3q}$$

Arrhenius Acid: forms protons
acidic

$Na^+ CH_3COO^-$

Bronsted Lowry Base: Proton acceptor

$$CH_3COO^-_{aq} + H_2O_\ell \rightarrow CH_3COOH_{aq} + OH^-_q$$

basic

What about NH_4F?

$NH^+_{4,aq} + H_2O_\ell \rightleftarrows NH_{3,aq} + H_2O^+_{3q}$

Arrhenius Acid: forms protons

acidic

$F^-_{aq} + H_2O_\ell \rightleftarrows HF_{aq} + OH^-_{aq}$

Bronsted Lowry Base: Proton acceptor

basic

Who controls the pH?

Here we need to define one of our comparison numbers

FITCH Rules

General

G1: Suzuki is Success

G2. Slow me down

G3. Scientific Knowledge is Referential

G4. Watch out for Red Herrings 

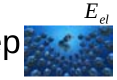
G5. Chemists are Lazy

Chemistry

C1. It's all about charge $E_{el} = k\left(\frac{q_1q_2}{r_1 + r_2}\right)$

C2. Everybody wants to "be like Mike"

C3. Size Matters $E_{el} = k\left(\frac{q_1q_2}{r_1 + r_2}\right)$

C4. Still Waters Run Deep  Piranhas lurk

C5. Alpha Dogs eat first

Definition of K_a

"a" stands for "acid dissociation"

$$H_2O_\ell + HA_{aq} \rightarrow H_3O^+_{,aq} + A^-_{aq}$$

$$K_{eq}[55M] = K_a = \frac{[A^-_{aq}][H_3O^+_{aq}]}{[HA_{aq}]}$$

$$K_{eq} = \frac{[A^-_{aq}][H_3O^+_{aq}]}{[HA_{aq}][H_2O_\ell]}$$

$$K_a = \frac{[A^-_{aq}][H_3O^+_{aq}]}{[HA_{aq}]}$$

Density of water is 1 g/mL

What is the molarity of liquid water?

$$\left(\frac{1gH_2O}{mL}\right)\left(\frac{10^3 mL}{L}\right)\left(\frac{1mole\ H_2O}{18gH_2O}\right) = 55.55M$$

Definition of K_b

"b" stands for "base reaction"

$$R + H_2O \rightarrow RH^+_{aq} + OH^-_{aq}$$

$$K_{eq} = \frac{[RH^+_{aq}][OH^-_{aq}]}{[R][H_2O]}$$

$$K_{eq}[H_2O] = K_b = \frac{[RH^+_{aq}][OH^-_{aq}]}{[R]}$$

$$K_b = \frac{[RH^+_{aq}][OH^-_{aq}]}{[R]}$$

What about NH_4F?

$$NH^+_{4,aq} + H_2O \rightarrow NH_{3,aq} + H_2O^+_{3q} \qquad K_a = 5.6x10^{-10}$$

$$F^-_{aq} + H_2O_\ell \rightleftarrows HF_{aq} + OH^-_{aq} \qquad K_b = 1.4x10^{-11}$$

Who controls the pH?

Since the concentrations of NH_4^+ and F^- are equal the reaction with the largest K_{eq} will be in control

Ammonium controls, solution goes acidic

What about NH_4ClO?

$$NH^+_{4,aq} + H_2O \rightarrow NH_{3,aq} + H_2O^+_{3q} \qquad K_a = 5.6x10^{-10}$$

$$ClO^-_{aq} + H_2O_\ell \rightleftarrows HClO_{aq} + OH^-_{aq} \qquad K_b = 3.6x10^{-7}$$

Who controls the pH?

Reaction with largest K_{eq}

ClO^- controls, solution goes basic

"A" students work (without solutions manual)
~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

Office Hours Th&F 2-3:30 pm

Module #17A: Acid BaseVisualization

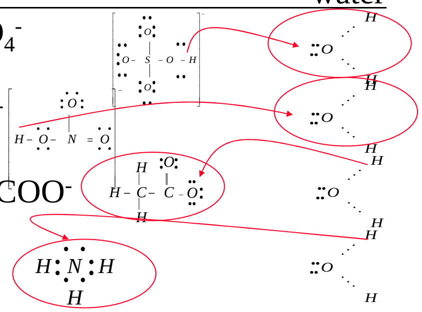
Using Ka and Kb Values for comparison

conjugate base	charge	radius	charge/radius	conjugate acid	Ka
ClO4-	1	236	0.004237288	HClO4	
NO3-	1	189	0.005291005	HNO3	
Br-	1	182	0.005494505	HBr	
Cl-	1	167	0.005988024	HClO4	
HSO4-	1	?	?	H2SO4	
H2PO4-	1	?	?	H3PO4	0.01
HS-	1	?	?	H2S	1.0X10-7
HPO42-	2	?	?	H2PO4-	6.1X10-8
HCO3-	1	163	0.006134969	H2CO3	4.4x10-7
CH3COO-	1	159	0.006289308	H(CH3COO)	1.8x10-5
HCOO-	1	158	0.006329114	H(HCOO)	1.9x10-4
NO2-	1	155	0.006451613	HNO2	6.0x10-4
OH-	1	140	0.007142857	HOH	1.OX10-14
F-	1	116.625	0.008574491	HF	6.9x10-4
SO42-	2	230	0.008695652	HSO4-	0.01
CO32-	2	185	0.010810811	HCO3-	4.7x10-11
S2-	2	170	0.011764706	HS-	1.2x10-13
PO43-	3	238	0.012605042	HPO42-	4.5x10-13

$$H_2O_\ell + HA_{aq} \underset{?}{\overset{?}{\rightleftarrows}} H_3O^+_{,aq} + A^-_{aq}$$

Who will the proton, "A" or water?

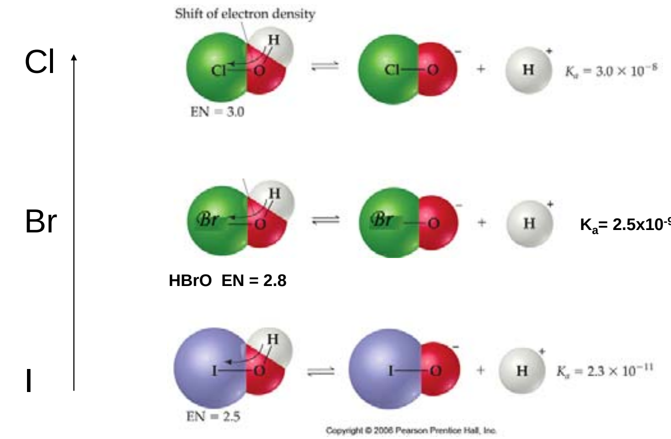
A	water	K_a
HSO_4^-		Huge
NO_2^-		4×10^{-4}
CH_3COO^-		1.8×10^{-5}
NH_3		5.6×10^{-10}



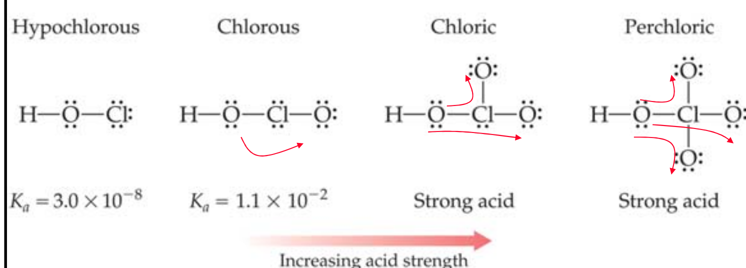
What do you observe? How does K_a change with structure?

This kind of question WILL be on exam

Electronegativity



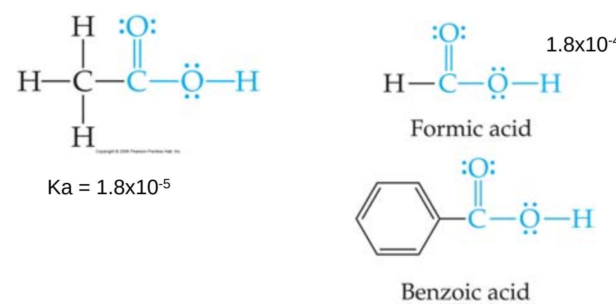
What do you observe?



Additional O pull e from Cl which in turn pulls e from OH group

Acid-Base Behavior and Chemical Structure

Which is strongest acid and why?



Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

Increasing acid strength ↑

*The units of K_a are mol/L but are customarily omitted.

$$HA_{aq} \rightleftarrows A^-_{aq} + H_3O^+_{aq} \qquad K_{Acid\ Disociation} = K_A = \frac{[A^-][H^+]}{[HA]}$$

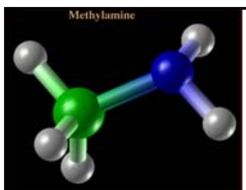
Values of K_b for Some Common weak bases

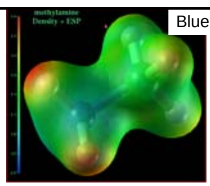
Formula	Name	Value of K_b*
SO_4^-	sulfate ion	1.0×10^{-12}
F-	fluoride	1.4×10^{-11}
NO2-	Nitrite	1.7×10^{-11}
C2H3O2-	Acetate	5.6×10^{-10}
OCl-		3.6×10^{-7}
CN	cyanide	1.7×10^{-5}
NH_3	Ammonia	1.8×10^{-5}
CO32-	carbonate	2.1×10^{-4}
PO423	phosphate	2.2×10^{-2}

Increasing basic strength ↓

*The units of K_b are mol/L but are customarily omitted.

$$A^-_{aq} + H_2O_\ell \rightleftarrows HA_{aq} + OH^-_{aq} \qquad K_{base} = \frac{[HA][OH^-]}{[A^-_{aq}]}$$



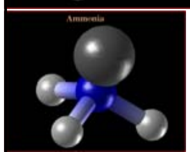


Blue is high electron density

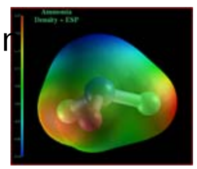
4.38x10^{-4}

CH_3NH_2

$$CH_3NH_2 + H_2O \rightleftarrows CH_3NH_3^+ + OH^-$$



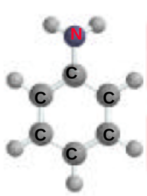
Explain This trend

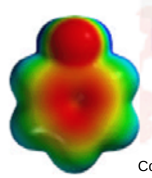


Color change to red

NH_3 **1.8x10^{-5}**

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$





$(C_6H_5)NH_2$

3.8x10^{-10}

$$(C_6H_5)NH_2 + H_2O \rightleftarrows (C_6H_5)NH_3^+ + OH^-$$

Color change (red=electrons)
Electrons can get "shoved" back onto molecule

"A" students work (without solutions manual)
~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

Office Hours Th&F 2-3:30 pm

Module #17A: Acid BaseVisualization

Polyprotic acids

Polyprotic acids can supply more than 1 proton

$$H_2CO_{3,aq} \rightleftarrows H^+_{aq} + HCO^-_{3aq}$$

$$HCO^-_{3aq} \rightleftarrows H^+_{aq} + CO^{2-}_{3aq}$$

Commonly: $K_{a1} >>> K_{a2}$
which means commonly (but not always!) only the first one makes the proton contribution.

Predict who gets the proton:

$$X^{n-}_{aq} + H_2O \rightarrow HX^{(n-1)-}_{aq} + OH^-_{aq}$$

SO_4^{2-}	HSO_4^-
CO_3^{2-}	HCO_3^-
HPO_4^{2-}	$H_2PO_4^-$
PO_4^{3-}	HPO_4^{-2}
S^{2-}	HS^-

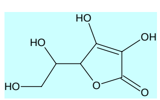
Think about

$$\frac{q_1}{r_1}$$

General Trend
K_{a1} vs K_{a2}?

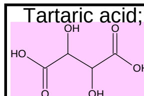
	K_{a1}		K_{a2}		
H_2SO_4	∞	HSO_4^-	$1.2x10^{-2}$	SO_4^{2-}	
H_3PO_3	$1.00x10^{-2}$	$H_2PO_3^-$	$2.6x10^{-7}$	HPO_3^{2-}	
H_2SO_3	$1.7x10^{-2}$	HSO_3^-	$6.4x10^{-8}$	SO_3^{2-}	
$H_2(COO)_2$	$5.9x10^{-2}$	$H(CO_2)_2^-$	$6.4x10^{-5}$	$(CO_2)_2^{2-}$	
$H_2C_2H_2O_2(COO)_2$	$1.0x10^{-3}$	$HC_2H_2O_2(COO)_2^-$	$4.6x10^{-5}$	$C_2H_2O_2(COO)_2^{2-}$	
H_3PO_4	$7.5x10^{-3}$	$H_2PO_4^-$	$6.2x10^{-8}$	HPO_4^{2-}	$4.2x10^{-13}$
$H_3C_3OH_5(COO)_3$	$7.4x10^{-4}$	$H_2C_3OH_5(COO)_3^-$	$1.7x10^{-5}$	$HC_3OH_5(COO)_3^{2-}$	$4.0x10^{-7}$
$H_2C_6H_6O_6$	$8.0x10^{-5}$	$HC_6H_6O_6^-$	$1.6x10^{-12}$	$C_6H_6O_6^{2-}$	
H_2CO_3	$4.45x10^{-7}$	HCO_3^-	$5.6x10^{-11}$	CO_3^{2-}	
H_2S	$5.7x10^{-8}$	HS^-	$1.x10^{-15}$		

$K_{a1}>K_{a2}>K_{a3}$

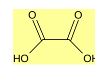


Ascorbic Acid; polar bear liver

Tartaric acid; wine



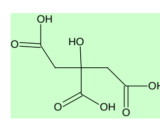
Oxalic acid; rhubard



Orders
Of magnitude
Difference Ka[1]
And Ka_2

	K_{a1}		K_{a2}		
H_2SO_4	∞	HSO_4^-	$1.2x10^{-2}$	SO_4^{2-}	
H_3PO_3	$1.00x10^{-2}$	$H_2PO_3^-$	$2.6x10^{-7}$	HPO_3^{2-}	10^5
H_2SO_3	$1.7x10^{-2}$	HSO_3^-	$6.4x10^{-8}$	SO_3^{2-}	10^4
$H_2(COO)_2$	$5.9x10^{-2}$	$H(CO_2)_2^-$	$6.4x10^{-5}$	$(CO_2)_2^{2-}$	10^3
$H_2C_2H_2O_2(COO)_2$	$1.0x10^{-3}$	$HC_2H_2O_2(COO)_2^-$	$4.6x10^{-5}$	$C_2H_2O_2(COO)_2^{2-}$	10^2
H_3PO_4	$7.5x10^{-3}$	$H_2PO_4^-$	$6.2x10^{-8}$	HPO_4^{2-}	10^5
$H_3C_3OH_5(COO)_3$	$7.4x10^{-4}$	$H_2C_3OH_5(COO)_3^-$	$1.7x10^{-5}$	$HC_3OH_5(COO)_3^{2-}$	10^1
$H_2C_6H_6O_6$	$8.0x10^{-5}$	$HC_6H_6O_6^-$	$1.6x10^{-12}$	$C_6H_6O_6^{2-}$	10^7
H_2CO_3	$4.45x10^{-7}$	HCO_3^-	$5.6x10^{-11}$	CO_3^{2-}	10^4
H_2S	$5.7x10^{-8}$	HS^-	$1.x10^{-15}$		10^7

Do you notice Anything?



Citric acid; oranges

What explains what is Happening?

"A" students work
(without solutions manual)
~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
508-3119
afitch@luc.edu

Office Hours Th&F 2-3:30 pm

Module #17A:
Acid Base Visualization