Mass and charge balance   When you have complex equilibria

① write down all the unknowns

② create $\#$ of equations = $\#$ of unknowns from
      K value and mass/charge balance.

③ back substitute and solve

Example.   HA in H_2O makes H^+, OH^-, HA, A^-
so need 4 equations.

① $Kw = [H^+][OH^-]$ ② $Ka = \dfrac{[H^+][A^-]}{[HA]}$ ⟩ from These

Plus ③ charge balance $\overset{\oplus}{[H^+]} = \overset{\ominus}{[A^-]} + [OH^-]$

④ mass balance (take from known mass of starting material)

here $C_{HA} = [HA] + [A^-]$
      known acid to start   all the forms at equilibrium

Equilibria Calculations: dilute solutions

   If a solution is dilute the approximations don't
hold. Typically 10^{-5} m ~ less. Why? Kw
produces 10^{-7} M H^+ and OH^-.

What to do with dilute solutions?
   Solve the complex case as above.
Dilute strong acid ≡ makes quadratic ⎫ stick Ca
Dilute weak acid ≡ makes cubic ⎬ in and solve
   ⎭ for exact answer

OR recognize that dilute acid or base makes
      pH close to neutral H_2O (around 7)
   so 10^{-9} M HA ≈ 7 (actually a little less)
      10^{-8} M NaOH ≈ 7 (actually a little more)

Equilibrium Calculations: weak polyprotic acids (amphiprotic case)

There are two forms of polyprotic acids:

Diprotic (H_2A) $H_2A \overset{Ka_1}{\rightleftharpoons} HA^- \overset{Ka_2}{\rightleftharpoons} A^=$

Triprotic (H_3A) $H_3A \overset{Ka_1}{\rightleftharpoons} H_2A^- \overset{Ka_2}{\rightleftharpoons} HA^{-2} \overset{Ka_3}{\rightleftharpoons} A^{-3}$
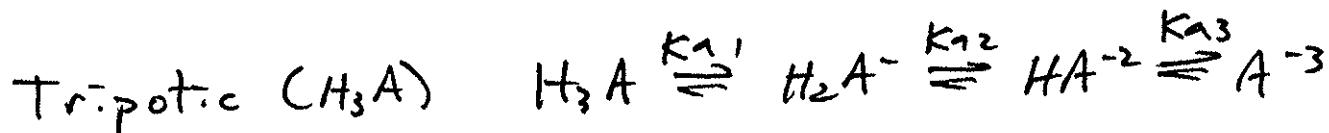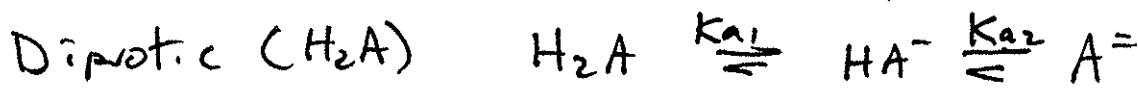
You can make buckets showing the possible calculation cases for each in which protons are removed by OH^-

adding OH^- →

Diprotic

$\boxed{\begin{array}{c}H_2A\\H_2A\end{array}}$	$\boxed{\begin{array}{c}H_2A\\HA^-\end{array}}$	$\boxed{\begin{array}{c}HA^-\\HA^-\end{array}}$	$\boxed{\begin{array}{c}HA^=\\A^=\end{array}}$	$\boxed{\begin{array}{c}A^=\\A^=\end{array}}$
weak acid Ka_1	buffer Ka_1	amphprotic Ka_1Ka_2	buffer Ka_2	weak base Kb_1 from Ka_2

So if you know the kind of solution, you can crank out a pH.

Amphiprotic is easy. $H^+=(Ka_1Ka_2)^{1/2}$ $H^+=(Ka_2Ka_3)^{1/2}$ $H^+=(Ka_1Ka$
diprotic   triprotic

what is pH of 0.2?
$NaHCO_3$ of pK= 3,9
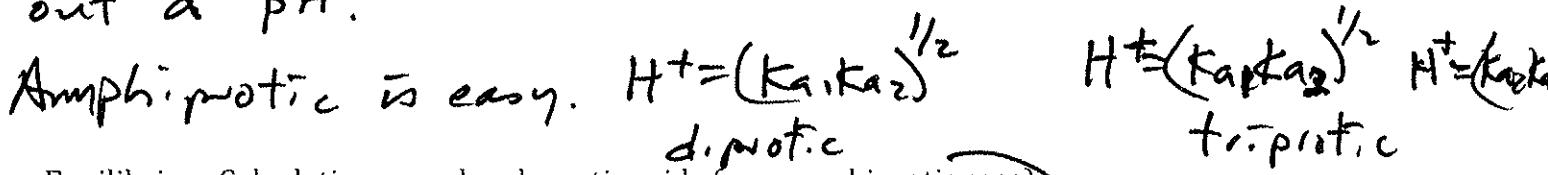
Equilibrium Calculations: weak polyprotic acids (non-amphiprotic case)

Note that if the Ks are far apart, polyprotic acid calculations become simple A/B calculations just like monoprotic case.

So of pKa = 3 and 9
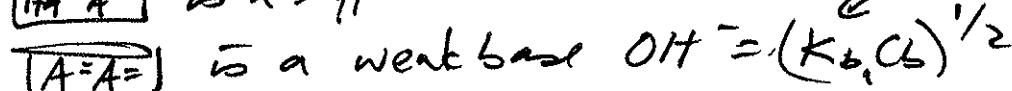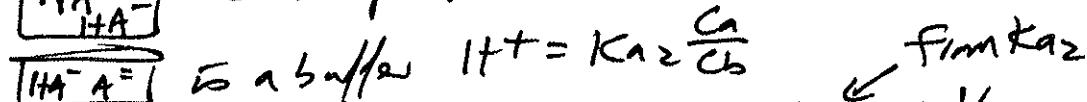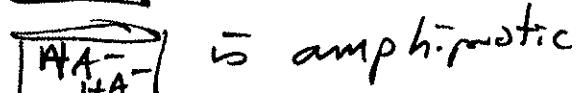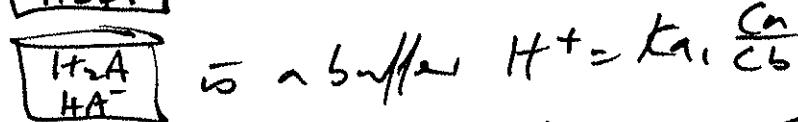
Answer:
$H^+=(Ka_1K_2)^{1/2}$
$H^+=(10^{-3} \times 10^{-9})^{1/2}=10^{-6}$
$pH = 6$

Then

$\boxed{\begin{array}{c}H_2A\\H_2A\end{array}}$ is a weak acid $H^+=(K_aC_a)^{1/2}$

$\boxed{\begin{array}{c}H_2A\\HA^-\end{array}}$ is a buffer $H^+=Ka_1\dfrac{C_a}{C_b}$

$\boxed{\begin{array}{c}HA^-\\HA^-\end{array}}$ is amphiprotic

$\boxed{\begin{array}{c}HA^-\ A^=\end{array}}$ is a buffer $H^+=Ka_2\dfrac{C_a}{C_b}$

$\boxed{\begin{array}{c}A^=A^=\end{array}}$ is a weak base $OH^-=(K_bC_b)^{1/2}$ from Ka_2

Polyprotic acid calculations (estimates using alpha diagrams)

α- diagrams make it possible to quickly order the relative concentration of species at equilibrium in solution. This is especially true of polyprotic acids

creating α diagram
1. create pH scale   2. make dots where pH = pk   3. swoop

Example: draw the α diagram of H_3A where $pka = 3, 7, 11$
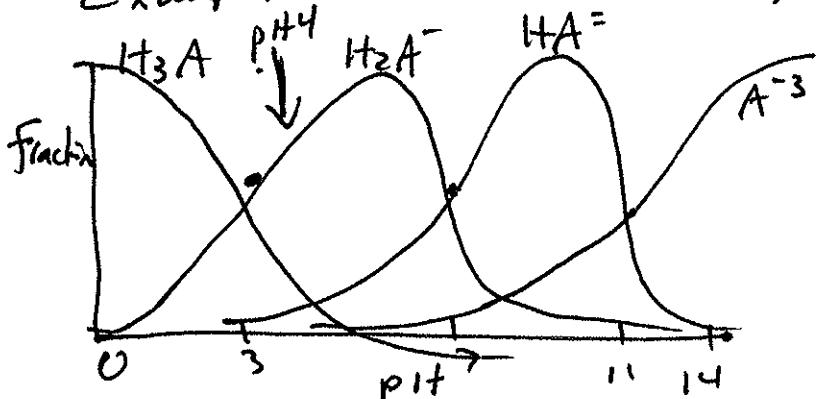
What is relative concentration of H_3A species at pH 4?

$H_2A^- > H_3A > HA^= > A^{-3}$
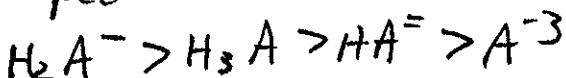
Equilibrium Calculations: sulfuric acid case

H_2SO_4 is a special case because

1. it is strong $Ka_1 \propto \infty$

2. The second K is large so the weak acid approximation doesn't work $Ka_2 = 1.1 \times 10^{-2}$

Need to work stepwise to solve.
What is $[SO_4^{2-}]$ concentration for $0.2 m H_2SO_4$?

step 1. $H_2SO_4 \rightleftharpoons H^+ + SO_4^=$
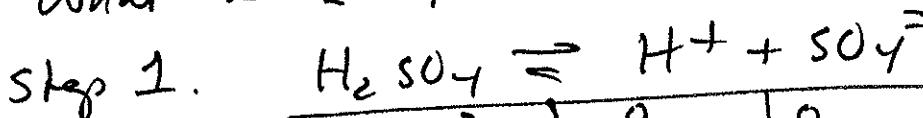
.2	0	0
-.2	+.2	+.2
0	+.2	+.2

← complete dissociation

step 2 $HSO_4^- \rightleftharpoons H^+ + SO_4^=$

.2	(.2)	0
-x	+x	+x
.2-x	.2+x	x
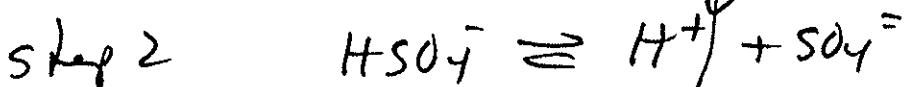
solve for x = SO_4

$\therefore Ka_2 = 1.1 \times 10^{-2} = \dfrac{(.2+x)(x)}{(.2-x)}$

Common ion calculation (Ksp)

$AgCl \rightleftharpoons Ag^+ + Cl^-$
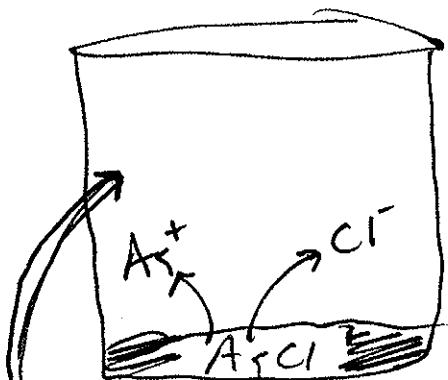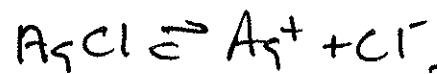
simple molar solubility problem

$AgCl \rightleftharpoons Ag^+ + Cl^-$
NaCl and $NaCl \rightleftharpoons Na^+ + Cl^-$

0.1 M Cl^-

Ag^+
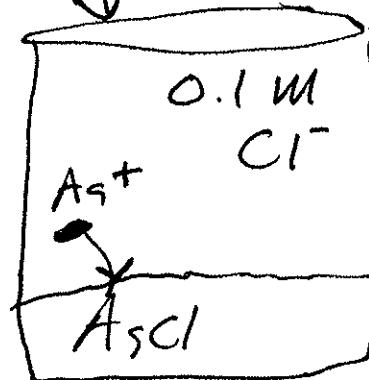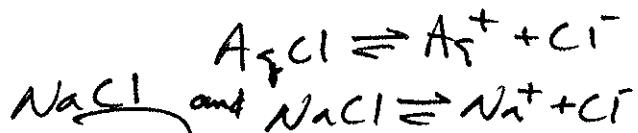
$AgCl$

common ion problem

What is the $[Ag^+]$ in solution formed from saturation of $AgCl$ in H_2O if $K_{sp} = 1 \times 10^{-10}$?

Answer $K_{sp} = 1 \times 10^{-10} = [Ag^+][Cl^-] = (1 \times 10^{-5})(1 \times 10^{-5}) = x^2$

Now add 0.1 M NaCl to that saturated solution what is new $[Ag^+]$ in saturated $AgCl$?

Answer. $AgCl \rightleftharpoons Ag^+ + Cl^-$

	Ag^+	Cl^-
	0	.1
	+x	+x
	x	.1+x

common ion

ignore

Note LeChatelier
As Cl^- speeds up Ag^+

$K_{sp} = (x)(.1 + x)$
$K_{sp} = (.1)(x)$
$x = 10^{-9}$

goes down from 10^{-5}m to 10^{-9}m

Selective precipitation (Ksp)

magic anion⊖

Ag^+ Ag^+
Cu^+ Cu^+
Na^+ Na^+

a beaker filled with mixed cations

Can I selectively remove the Ag^+ because its solubility with a magic anion⊖ is really small?

Give
$[Ag^+][anion⊖] = 10^{-12}$ for Ag^+
$[Cu^+][anion⊖] = 10^{-4}$ for Cu^+
$[Na^+][anion⊖] = 10^{-1}$ for Na^+

this says that if I add 0.1 M anion⊖, then at 10^{-11}M the Ag^+ comes out first. Then at 10^{-3}M the Cu^+ comes out, etc. An 8 order of magnitude separation of Ag^+ and Cu^+