

CHEM 206 section 01

LECTURE #23

Wed. April 02, 2008

LECTURE TOPICS:

TODAY'S CLASS: finish Ch.17

NEXT CLASS: start Ch.18 (18.3 first)

(1)

Thinking about pK_a
will help us understand
the behaviour of **polyprotic acids...**

(2)

17.8 Polyprotic acids and bases

Many biologically important molecules have several groups on them that can exist in different "protonation states" *i.e.*, in protonated acidic form vs. deprotonated basic form

How many protons can an acid lose per molecule?

- 1 \Rightarrow "monoprotic" HCl, HNO₃, CH₃COOH...
- 2 \Rightarrow "diprotic" H₂SO₄, H₂CO₃, Vitamin C...
- 3 \Rightarrow "triprotic" H₃PO₄

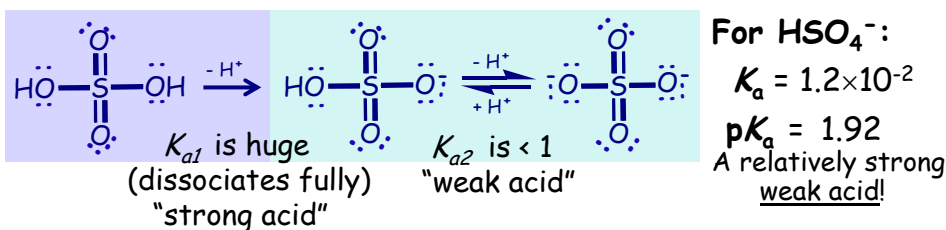
A practical question: How would we determine the pH of a solution of a polyprotic acid? Will all H⁺s dissociate?

H⁺ lost in step-wise manner to produce conjugate base

- Loss of each H⁺ is an eqm (many molecules present...)
- Loss of 1st H⁺ $\Rightarrow K_{a1}$
- Loss of 2nd H⁺ $\Rightarrow K_{a2}$
- etc...

Always easiest to lose 1st H⁺
& more difficult to next one(s):
i.e., $K_{a1} > K_{a2} > K_{a3}...$

(3)



Calculating pH for polyprotic species ("H_nA"):

Full calculation would be very complicated...so we break it into two steps, based on a reasonable assumption:

the reaction with largest eqm constant K dominates...

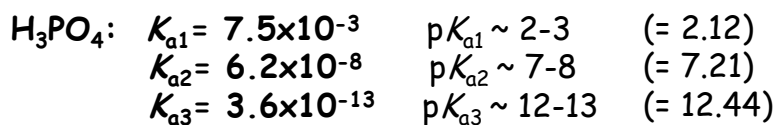
1. Calculate pH as if ONLY 1st proton loss occurs (ignore K_{a2}'s step)
 - If H_nA is a strong acid: $[\text{H}_3\text{O}^+]_{\text{eqm}} = [\text{H}_n\text{A}]_{\text{initial}}$
 - If H_nA is a weak acid: do eqm calculation using K_{a1}...

THEN
2. Start with pH produced by step1
 - Now worry about 2nd proton loss ONLY (ignore K_{a1}'s step)
 - Will be a weak acid: do eqm calculation using K_{a2}...

If 1st H⁺ loss is NOT quantitative: subsequent H⁺ losses usually insignificant.

EX: Determining the pH of a solution of a polyprotic acid

If we make a solution of 0.250M H_3PO_4 , what would be a good estimate of the pH?



A great tool for figuring out which step dominates

- Consider successive H^+ losses, starting in pure H_2O .
- Using logic (think about pK_a s): likely only 1st step will contribute
 - When H_3PO_4 equilibrates with water, some H_3O^+ & H_2PO_4^- forms
 - H_2PO_4^- is a much weaker acid (K_a is 10000x smaller...)
 - ⇒ it remains protonated in acidic soln formed by 1st H^+ loss!

*Rough guess: $\text{pH} < 7$ (acidic), and definitely < 2.12 (pK_a of 1st acid)...
• 1st loss not product-favoured ⇒ $<$ half deprotonated ⇒ $\text{pH} < pK_a$*

See end of lecture notes for full quantitative approach ⇒ $\text{pH} = 1.40$

Back to performing reactions...

not just dissolving something in water...

17.5 Rxns of acids & bases & their eqm constants

Every A/B rxn involves: acid + BASE \rightleftharpoons base + ACID
 The stronger base wins (on average)...

If 2 bases competing for H⁺:

- stronger base "B_s" has more reactive lone pair than weaker base "B_w"
- bonding to H⁺ produces more stable product
- effect is greater for stronger base

⇒ **ATEQM**: $\Delta G^\circ_{\text{rxn}}$ determines exact ratio of "B_s-H & B_w" to "B_s & B_w-H"

⇒ **THE NET RESULT:**

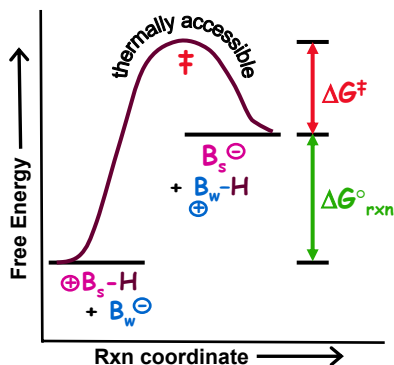
the stronger base ends up bonded to the H⁺ more often

∴ at eqm: a larger proportion* of the **stronger** base exists in its conjugate acid form (*compared to the weaker base!)

⇒ the larger the difference in base strengths, the larger $\Delta G^\circ_{\text{rxn}}$...

⇒ thus: the more obviously product or reactant favoured the rxn is

(7) (i.e., can more easily predict if rxn will go fwd when mix reactants).



17.6 Types of Acid/Base Rxns: Where will the eqm lie? Is rxn favoured, or not?

1. Strong-strong

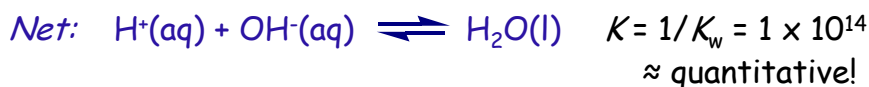
2. Strong-weak

3. Weak-weak...

1. Equal molar quantities of **strong acid & strong base** ⇒ **neutral soln**

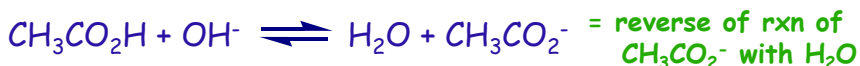
⇒ conj. base of HA & conj. acid of B are **exceptionally weak**

⇒ do not significantly affect solution's pH (☹ or, not acidic/basic at all)



(8)

2. Equal molar quantities of **weak acid & strong base** \Rightarrow **basic solution**
 \Rightarrow note: we did not add excess strong base!
 \Rightarrow acid's conjugate base = a weak base (but not exceptionally weak...)
THUS: conjugate base attacks water & releases OH^- \Rightarrow basic soln



THUS: $K = 1/K_{\text{b of acetate}} = 5.6 \times 10^4$ = highly product favoured

... OH^- is strong enough to nearly fully deprotonate CH_3COOH

2b. Mix equal molar quantities of **strong acid & weak base** \Rightarrow **acidic soln**
 \Rightarrow base's conjugate acid = a weak acid (but not exceptionally weak...)
 \Rightarrow note: we did not add excess strong acid!
THUS: conjugate acid attacks water & produces H_3O^+ \Rightarrow acidic solution



THUS: $K = 1/K_{\text{a of ammonium}} = 5.6 \times 10^4$ quite product favoured

... H_3O^+ is strong acid, so almost fully protonates NH_3

Scenario 3: find pH of a solution after an acid/base rxn
Key: solution will essentially be a "salt" solution!

If we mix 15mL of 0.035 M NaOH with 15mL of 0.035 M formic acid, what will be the pH of the resulting solution?

\rightarrow Formic acid, HCO_2H , $K_{\text{a}} = 1.8 \times 10^{-4}$...a relatively strong weak acid

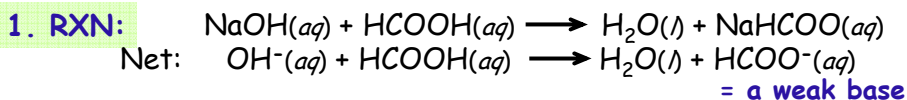
\rightarrow NaOH is a strong base

\rightarrow Both are monoprotic species, & mixed in 1:1 mole ratio!

Strategy: break problem into 3 smaller problems

- Determine what rxn will occur (**balance rxn equation**...)
 - H^+ from stronger acid \Rightarrow bonds to stronger base
- Assume it goes to 100% completion (**stoichiometry**...)
 - Perfectly reasonable if rxn involves:
strong acid + weak base *OR* weak acid + strong base
- Treat acid-base properties of products (**equilibrium**...)
 - Products of initial reaction will equilibrate with water

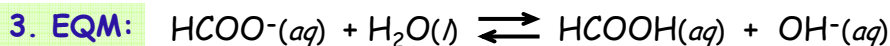
NOTE: same strategy used for titrations & buffers (Chapter 18)...



2. STOICH:

$n_{\text{OH}^-} = 0.035\text{M} \times 0.015\text{L}$ $n_{\text{HA}} = 0.035\text{M} \times 0.015\text{L}$
 $= 5.25 \times 10^{-4} \text{ mol OH}^-$ $= 5.25 \times 10^{-4} \text{ mol HA}$
 (both initially dilute sol'ns, so no great change in interactions when mixed \Rightarrow volumes add "simply"...)

1:1 rxn stoichiometry
$\Rightarrow 5.25 \times 10^{-4} \text{ mol HCOO}^-$
\Rightarrow in $V_{\text{tot}} \approx 0.0300 \text{ L}$
$\Rightarrow [\text{HCOO}^-] = 0.0175 \text{ M}$



Initial	0.0175 M	constant...	0	0
Change	- x		+ x	+ x
Eqm	0.0175 - x		x	x

$K_b = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} \Rightarrow 5.56 \times 10^{-11} = \frac{x^2}{0.0175 - x} \approx \frac{x^2}{0.0175}$

and $K_b = K_w / K_a^{\text{HCOOH}}$
 $= 10^{-14} / 1.8 \times 10^{-4}$
 $= 5.56 \times 10^{-11}$

$K \ll [A^-]_0 \Rightarrow$ use approximation...

Thus: $x^2 = (0.0175)(5.56 \times 10^{-11})$
 So: $x = 9.86 \times 10^{-7} \text{ M} = [\text{OH}^-]$

$\Rightarrow \text{pOH} = -\log(9.86 \times 10^{-7}) = 6.01$

$\Rightarrow \text{pH} = 14 - \text{pOH} = 7.99$ *slightly basic*

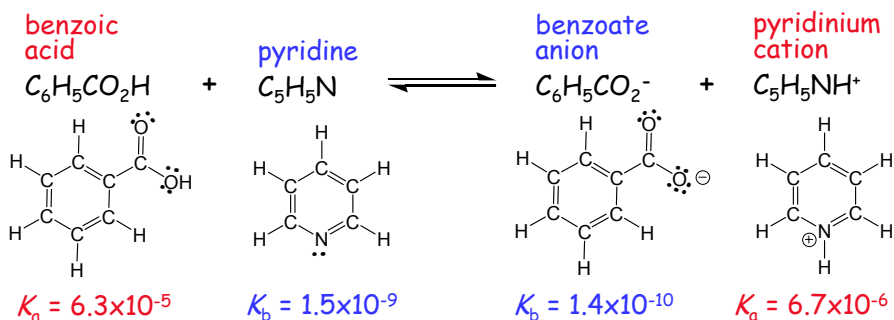
17.6 Types of Acid/Base Rxns: Where will the eqm lie? Is rxn favoured, or not?

1. Strong-strong

2. Strong-weak

3. Weak-weak...

A/B rxn type 3) WEAK ACID + WEAK BASE: Where will eqm lie?



Approach 1) Use logic: compare conjugate base strengths

- K_b of pyridine > K_b of benzoate anion (by factor of 10)
 - ⇒ pyridine is stronger base than conjugate base of benzoic acid...
 - ⇒ pyridine will preferentially bond to the H^+
 - ⇒ crude estimate: equilibrium will lie slightly to the right
 - ⇒ *i.e.*, pyridine is strong enough to *deprotonate* benzoic acid

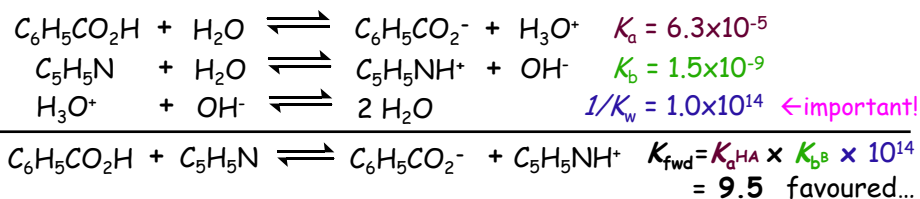
NOTE: does not mean the rxn has a large eqm constant...

(13) *just larger than the reverse reaction would have!*

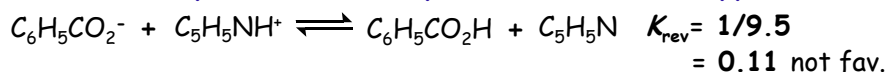
Approach 2) Use analysis of eqm constants: be careful here...

- consider rxns that define each reactant reacting with water
- MUST consider also that the released H_3O^+ and OH^- react
 - this is really what drives the rxn forward...
- desired rxn is sum of those THREE reactions
- thus: overall K_{rxn} will be product of acid's K_a & base's K_b & $1/K_w$

Consider the proposed forward reaction: (benzoate + pyridinium)

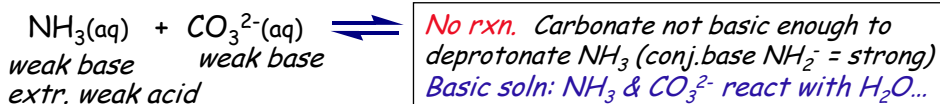
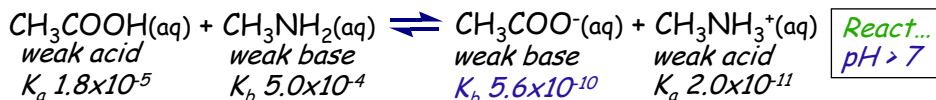


And, if we compare the reverse process: (benzoate + pyridinium)



THE LOGIC APPROACH IS SIMPLER & WORKS ⇒ CAN USE IT!

Will these substances undergo an acid-base reaction?
If mixed 1:1, what would the approx. pH be at eqm?

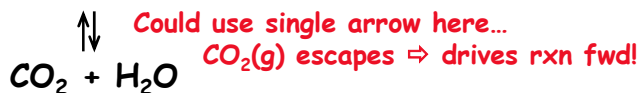
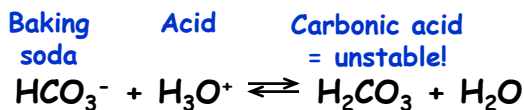


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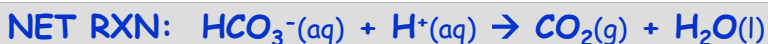
Acid-base rxns: why our baked goods rise...

Baking soda = NaHCO_3

+ A SOURCE OF ACID
stronger than bicarbonate,
to force it to act as a base:



DATA:	K_a
H_2CO_3	4.3×10^{-7}
HCO_3^-	5.6×10^{-11}
H_3PO_4	7.5×10^{-3}
H_2PO_4^-	6.2×10^{-8}
HPO_4^{2-}	4.8×10^{-13}



KITCHEN ACIDS: lemon juice, vinegar, sour milk, egg white...
& BAKING POWDER, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ a stronger acid than HCO_3^-
-- compare their $\text{p}K_a$'s!

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: rest of Ch.17

+ **WORK ON Problems from Ch.17**

BOTH calculations & conceptual Qs (explanations)

& remember:

the text's *General Questions* test you more
than the Qs that are organized by chapter section...

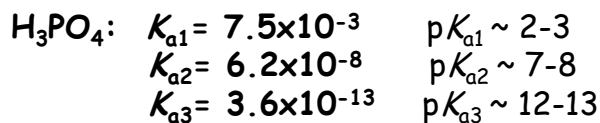
(17)

**Extra examples:
understanding polyprotic acids**

(18)

EX: Determining the pH of a solution of a polyprotic acid

If we make a solution of 0.250M H_3PO_4 , what would be a good estimate of the pH?

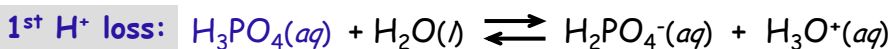
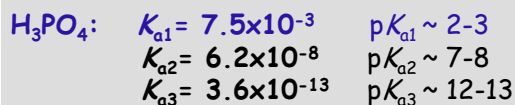


A great tool for figuring out which step dominates

- Must consider each proton loss one at a time.
- Using logic (think about pK_a s): likely only 1st step will contribute
- WHY?
 - When H_3PO_4 equilibrates with water, some H_3O^+ & H_2PO_4^- forms
 - H_2PO_4^- is a much weaker acid (K_a is 10000x smaller...)
 - ⇒ it remains protonated in acidic solns ($\text{pH} < 7 < pK_a!$)

(19)

Determining the contribution to the solution's pH by H_3PO_4 :



Initial	0.250 M	constant...	0	0
Change	- x		+ x	+ x
Eqm	0.250 - x		x	x

$$K_a = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} \quad \rightarrow \quad 7.5 \times 10^{-3} = \frac{x^2}{0.250 - x}$$

K_a is NOT $\ll [\text{H}_3\text{PO}_4]_0$
 ⇒ cannot use approximation...

Thus: $x^2 = (0.250 - x)(7.5 \times 10^{-3})$
 So: $0 = x^2 + 7.5 \times 10^{-3}x - 1.875 \times 10^{-3}$
 ⇒ $x = 3.97 \times 10^{-2} \text{ M}$ (or $-4.72 \times 10^{-2} \text{ M}$)
 ⇒ $[\text{H}_3\text{O}^+] = 3.97 \times 10^{-2} \text{ M}$
 ⇒ $\text{pH} = 1.40$ (2 SF due to K_a)
 if only the 1st H^+ loss eqm is active

The 1st H^+ loss lowers pH to well below the pK_a of H_2PO_4^- . Thus: H_2PO_4^- will remain protonated & not alter pH.

(20) But let's prove it...

Determining the contribution to the solution's pH by H_2PO_4^- :

H_3PO_4 : $K_{a1} = 7.5 \times 10^{-3}$ $pK_{a1} \sim 2-3$
 $K_{a2} = 6.2 \times 10^{-8}$ $pK_{a2} \sim 7-8$
 $K_{a3} = 3.6 \times 10^{-13}$ $pK_{a3} \sim 12-13$

2nd H^+ loss: $\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq)$

Initial	$3.97 \times 10^{-2} \text{ M}$	<i>constant...</i>	0	$3.97 \times 10^{-2} \text{ M}$
Change	- x		+ x	+ x
Eqm	$0.0397 - x$		x	$0.0397 + x$

$$K_a = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} \rightarrow 6.2 \times 10^{-8} = \frac{x(0.0397 + x)}{0.0397 - x}$$

Thus: $0.0397x \approx (0.0397)(6.2 \times 10^{-8})$

K_a is $\ll [\text{H}_2\text{PO}_4^-]_0$

\Rightarrow can use approximation...

\Rightarrow on both top & bottom of K_a expression!

$\Rightarrow x = 6.2 \times 10^{-8} \text{ M}$

= $[\text{H}_3\text{O}^+]$ contributed by 2nd H^+ loss...
 = less than 10^{-7} M provided by water!

THUS: H_3PO_4 is triprotic, but does not release all of its H^+ s in water (...all 3 H^+ are available to stronger bases...).

\Rightarrow NOTE: this depends on concentration, & identity (K_a) of acid...

For H_2SO_4 : 2nd proton loss matters...try 0.200 M (final pH = 0.67, not 0.70...)