

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, HNO<sub>3</sub>, CH<sub>3</sub>COOH...
- 2  $\Rightarrow$  "diprotic"        H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>CO<sub>3</sub>, Vitamin C...
- 3  $\Rightarrow$  "triprotic"        H<sub>3</sub>PO<sub>4</sub>

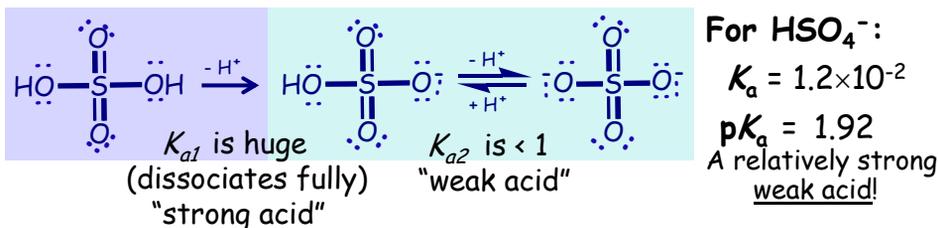
A practical question: How would we determine the pH of a solution of a polyprotic acid? Will all H<sup>+</sup>s dissociate?

H<sup>+</sup> lost in step-wise manner to produce conjugate base

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

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

(3)



**Calculating pH for polyprotic species ("H<sub>n</sub>A"):**

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...*

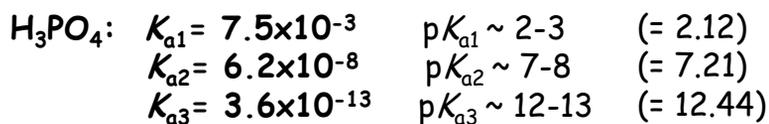
1. Calculate pH as if ONLY 1<sup>st</sup> proton loss occurs (ignore  $K_{a2}$ 's step)
  - If H<sub>n</sub>A is a strong acid:  $[\text{H}_3\text{O}^+]_{\text{eqm}} = [\text{H}_n\text{A}]_{\text{initial}}$
  - If H<sub>n</sub>A is a weak acid: do eqm calculation using  $K_{a1}$ ...

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

If 1<sup>st</sup> H<sup>+</sup> loss is NOT quantitative: subsequent H<sup>+</sup> losses usually insignificant.

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

If we make a solution of 0.250M  $\text{H}_3\text{PO}_4$ , what would be a good estimate of the pH?



A great tool for figuring out which step dominates

- Consider successive  $\text{H}^+$  losses, starting in pure  $\text{H}_2\text{O}$ .
- Using logic (think about  $pK_a$ s): likely only 1<sup>st</sup> step will contribute
  - When  $\text{H}_3\text{PO}_4$  equilibrates with water, some  $\text{H}_3\text{O}^+$  &  $\text{H}_2\text{PO}_4^-$  forms
  - $\text{H}_2\text{PO}_4^-$  is a much weaker acid ( $K_a$  is 10000x smaller...)
    - ⇒ it remains protonated in acidic soln formed by 1<sup>st</sup>  $\text{H}^+$  loss!

*Rough guess:  $\text{pH} < 7$  (acidic), and definitely  $< 2.12$  ( $pK_a$  of 1<sup>st</sup> acid)...  
• 1<sup>st</sup> 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<sup>+</sup>:

- stronger base "B<sub>s</sub>" has more reactive lone pair than weaker base "B<sub>w</sub>"
- bonding to H<sup>+</sup> produces more stable product
- effect is greater for stronger base

⇒ **ATEQM**:  $\Delta G^\circ_{\text{rxn}}$  determines exact ratio of "B<sub>s</sub>-H & B<sub>w</sub>" to "B<sub>s</sub> & B<sub>w</sub>-H"

⇒ **THE NET RESULT:**

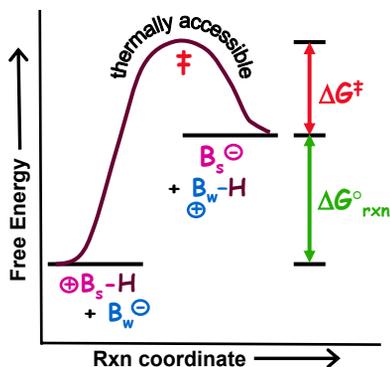
the stronger base ends up bonded to the H<sup>+</sup> more often

∴ 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

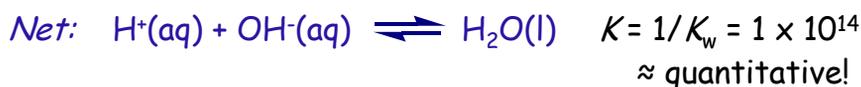
2. Strong-weak

3. Weak-weak...

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

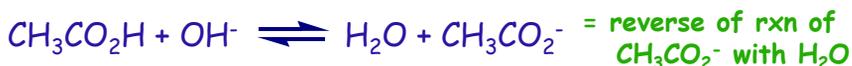
⇒ conj. base of HA & conj. acid of B are **exceptionally weak**

⇒ 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  $\text{OH}^-$   $\Rightarrow$  **basic soln**



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

... $\text{OH}^-$  is strong enough to nearly fully deprotonate  $\text{CH}_3\text{COOH}$

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  $\text{H}_3\text{O}^+$   $\Rightarrow$  **acidic solution**



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

... $\text{H}_3\text{O}^+$  is strong acid, so almost fully protonates  $\text{NH}_3$

**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,  $\text{HCO}_2\text{H}$ ,  $K_a = 1.8 \times 10^{-4}$  ...a relatively strong weak acid

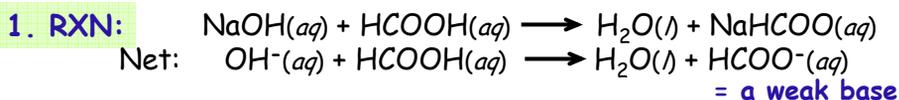
$\rightarrow$  NaOH is a strong base

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

**Strategy:** break problem into 3 smaller problems

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

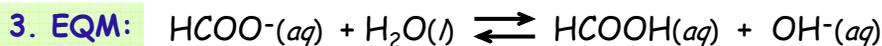
**NOTE:** same strategy used for titrations & buffers (Chapter 18)...



**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:  $x = 9.86 \times 10^{-7} \text{ M} = [\text{OH}^-]$

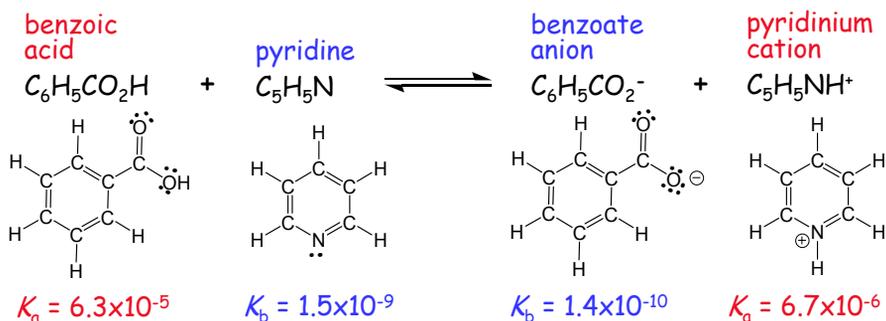
$\Rightarrow \text{pOH} = -\log(9.86 \times 10^{-7}) = 6.01$

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

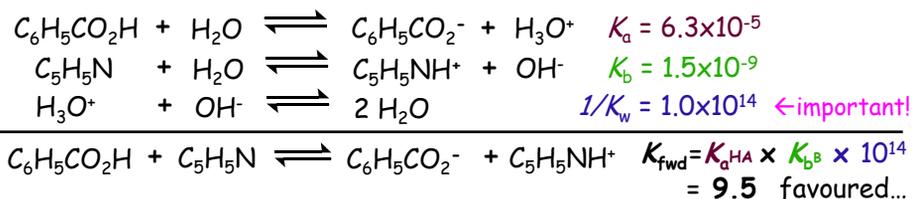
*NOTE: does not mean the rxn has a large eqm constant...*

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

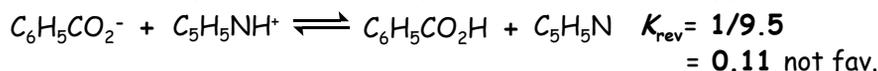
**Approach 2) Use analysis of eqm constants: be careful here...**

- 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)**

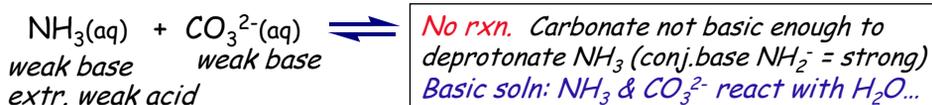
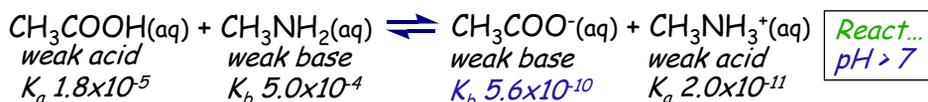


**And, if we compare the reverse process: (benzoate + pyridinium)**



**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?

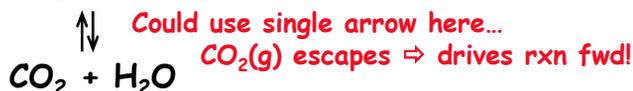
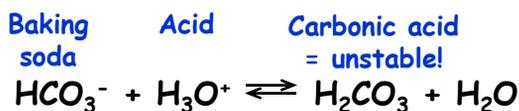


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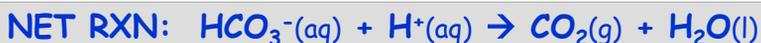
### Acid-base rxns: why our baked goods rise...

Baking soda =  $\text{NaHCO}_3$

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



DATA:	$K_a$
$\text{H}_2\text{CO}_3$	$4.3 \times 10^{-7}$
$\text{HCO}_3^-$	$5.6 \times 10^{-11}$
$\text{H}_3\text{PO}_4$	$7.5 \times 10^{-3}$
$\text{H}_2\text{PO}_4^-$	$6.2 \times 10^{-8}$
$\text{HPO}_4^{2-}$	$4.8 \times 10^{-13}$



KITCHEN ACIDS: lemon juice, vinegar, sour milk, egg white...  
& BAKING POWDER,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  a stronger acid than  $\text{HCO}_3^-$   
-- compare their  $pK_a$ '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  $\text{H}_3\text{PO}_4$ , what would be a good estimate of the pH?

$$\text{H}_3\text{PO}_4: \begin{array}{l} K_{a1} = 7.5 \times 10^{-3} \\ K_{a2} = 6.2 \times 10^{-8} \\ K_{a3} = 3.6 \times 10^{-13} \end{array} \quad \begin{array}{l} pK_{a1} \sim 2-3 \\ pK_{a2} \sim 7-8 \\ pK_{a3} \sim 12-13 \end{array}$$

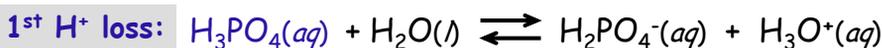
A great tool for figuring out which step dominates

- Must consider each proton loss one at a time.
- Using logic (think about  $pK_a$ s): likely only 1<sup>st</sup> step will contribute
- WHY?
  - When  $\text{H}_3\text{PO}_4$  equilibrates with water, some  $\text{H}_3\text{O}^+$  &  $\text{H}_2\text{PO}_4^-$  forms
  - $\text{H}_2\text{PO}_4^-$  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  $\text{H}_3\text{PO}_4$  :

$$\text{H}_3\text{PO}_4: \begin{array}{l} K_{a1} = 7.5 \times 10^{-3} \\ K_{a2} = 6.2 \times 10^{-8} \\ K_{a3} = 3.6 \times 10^{-13} \end{array} \quad \begin{array}{l} pK_{a1} \sim 2-3 \\ pK_{a2} \sim 7-8 \\ pK_{a3} \sim 12-13 \end{array}$$



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 1<sup>st</sup>  $\text{H}^+$  loss eqm is active

The 1<sup>st</sup>  $\text{H}^+$  loss lowers pH to well below the  $pK_a$  of  $\text{H}_2\text{PO}_4^-$ . Thus:  $\text{H}_2\text{PO}_4^-$  will remain protonated & not alter pH.

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

Determining the contribution to the solution's pH by  $\text{H}_2\text{PO}_4^-$ :

$\text{H}_3\text{PO}_4$ :  $K_{a1} = 7.5 \times 10^{-3}$   $pK_{a1} \sim 2-3$   
 $K_{a2} = 6.2 \times 10^{-8}$   $pK_{a2} \sim 7-8$   
 $K_{a3} = 3.6 \times 10^{-13}$   $pK_{a3} \sim 12-13$

2<sup>nd</sup>  $\text{H}^+$  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 2<sup>nd</sup>  $\text{H}^+$  loss...  
 = less than  $10^{-7} \text{ M}$  provided by water!

**THUS:**  $\text{H}_3\text{PO}_4$  is triprotic, but does not release all of its  $\text{H}^+$ s in water (...all 3  $\text{H}^+$  are available to stronger bases...).

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

For  $\text{H}_2\text{SO}_4$ : 2<sup>nd</sup> proton loss matters...try 0.200 M (final pH = 0.67, not 0.70...)