

## Chapter 10 & Section 6 – 7

### Polyprotic acids and bases

We'll bounce around in the book a little: Start with part of Section 6 – 7 p. 112 – 114.

HA = Monoprotic acid

H<sub>2</sub>A = Diprotic acid

H<sub>3</sub>A = Triprotic acid

etc.

For the diprotic case, K<sub>a</sub> reactions and expressions for H<sub>2</sub>CO<sub>3</sub> (carbonic acid)

For the triprotic case, K<sub>a</sub> reactions and expressions for H<sub>3</sub>PO<sub>4</sub> (phosphoric acid)

Now Section 10 – 2 to finish off buffers discussion.

A diprotic acid can buffer around two different pH values depending on the pK<sub>a</sub>s of the diprotic acid.

H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup> are conjugates

$\text{HCO}_3^-/\text{CO}_3^{2-}$  are conjugates

A triprotic acid can buffer around three different pH values depending on the  $\text{pK}_{\text{a}}$ s of the triprotic acid.

$\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$  are conjugates

$\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  are conjugates

$\text{HPO}_4^{2-}/\text{PO}_4^{3-}$  are conjugates

A diprotic buffer example: How many mL of 0.8 M KOH should be added to 3.38 g of oxalic acid (90 mg/mmol,  $\text{H}_2\text{A}$ ) to give a pH of 4.4?

$$\text{pK}_{\text{a}1} = 1.25$$

$$\text{pK}_{\text{a}2} = 4.27$$

The desired pH >  $\text{pK}_{\text{a}2}$  so need a mixture of  $\text{HA}^-/\text{A}^{2-}$

1. Add enough base to convert all  $\text{H}_2\text{A} \rightarrow \text{HA}^-$
2. Add more base to convert some  $\text{HA}^- \rightarrow \text{A}^{2-}$  until pH = 4.4

To do the first part:

To do the second part:

Now to finish Section 6 – 7

For a monoprotic acid  $K_a \times K_b = K_w$

Similar relationships can be derived for polyprotic systems,  
a little more tricky.

For a diprotic system:  $H_2A$ ,  $HA^-$ ,  $A^{2-}$  may exist

Most acidic =  $K_{a1}$ :

Most basic =  $K_{b1}$ :

$HA^-$  as acid =  $K_{a2}$ :

$HA^-$  as base =  $K_{b2}$ :

Now that these are defined, can do analogous derivations as  
the monoprotic system.

Triprotic system is now readily derived in the same way.  
For a triprotic system:  $\text{H}_3\text{A}$ ,  $\text{H}_2\text{A}^-$ ,  $\text{HA}^{2-}$ ,  $\text{A}^{3-}$  may exist.

$K_{a1}$ :  $K_{b1}$ :

$K_{a2}$ :  $K_{b2}$ :

$K_{a3}$ :  $K_{b3}$ :

Putting these together:

Tetraprotic, pentaprotic, hexaprotic, etc. – same process.

Back to beginning of Chapter 10, Section 10 – 1.  
Find the pH of diprotic solutions, easily extended to  
polyprotic systems.

Maleic acid is diprotic ( $\text{H}_2\text{A}$ ) – Harris uses the amino acid  
leucine starting on p. 181 for his example.

The reactions, K expressions, and K values:

There are 3 different calculations for this system.

1. Find the pH of a 0.05 M  $\text{H}_2\text{A}$  solution.
2. Find the pH of a 0.05 M  $\text{Na}_2\text{A}$  solution.
3. Find the pH of a 0.05 M  $\text{NaHA}$  solution.

The first 2 are not all that bad if everything works out.  
Number 1 – Find the pH of a 0.05 M  $\text{H}_2\text{A}$  solution.

Recognize that  $\text{H}_2\text{A}$  is a weak acid - partially dissociates.

$\text{HA}^-$  is weaker, and what little is present from  $\text{H}_2\text{A}$  dissociation will dissociate even less.

So to avoid having to solve an extremely unpleasant problem – hope  $\text{H}_2\text{A}$  behaves like a monoprotic acid with  $K_a = K_{a1}$ .

And also hope that  $[\text{H}^+]$  from  $\text{H}_2\text{A} \gg [\text{H}^+]$  from water.

If both of these hopes come true, it reduces to a regular weak acid problem.

Further hope that  $x \ll 0.05$  so

Certainly  $[\text{H}^+]$  from  $\text{H}_2\text{A} \gg [\text{H}^+]$  from water  
We have checked 2 assumptions, what about the third? Is the  $[\text{H}^+]$  from  $\text{H}_2\text{A} \gg [\text{H}^+]$  from  $\text{HA}^-$ ? (The monoprotic assumption)

For most polyprotic acids  $K_{a1} \gg K_{a2}$ .

Bottom line: A solution of the fully acidic form of a polyprotic acid behaves like a solution of a monoprotic acid with  $K_a = K_{a1}$ .

Number 2 – Find the pH of a 0.05 M  $\text{Na}_2\text{A}$  solution.

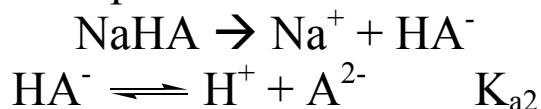
$\text{A}^{2-}$  is a weak base that partially hydrolyzes in water.  $\text{HA}^-$  is a weaker base, and little should be in solution anyway. So to avoid solving a very unpleasant problem, hope  $\text{A}^{2-}$  behaves like a monobasic compound with  $K_b = K_{b1}$ .

And – hope the  $[\text{OH}^-]$  from  $\text{A}^{2-} \gg [\text{OH}^-]$  from water.

If both of these hopes come true – then you have a regular weak base problem.

For most polyprotic systems  $K_{b1} \gg K_{b2}$  so  
Bottom line: A solution of the fully basic form of a polyprotic system behaves like a monobasic species with  $K_b = K_{b1}$ .

Number 3 – Find the pH of a 0.05 M NaHA solution.



and



This is trouble,  $\text{HA}^-$  is amphiprotic

Ignore  $K_{b2}$  since it is much less than  $K_{a2}$ ?

No can do, these equilibria are coupled.

$\text{H}^+$  from  $K_{a2} + \text{OH}^-$  from  $K_{b2} \rightarrow \text{H}_2\text{O}$  driving  $K_{b2}$  reaction to the right, more important than the  $K_{b2}$  value suggests.

Bite the bullet – set up using systematic approach. Will simplify later, so don't get lost in the forest.



Species in solution:  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{A}$ ,  $\text{HA}^-$ ,  $\text{A}^{2-}$ ,  $\text{Na}^+$   
 5 species in solution, need 5 equations to solve:

1.  $K_{a2} =$

2.  $K_{b2} =$

3.  $K_w =$

4. Charge balance:

5. Mass balance:

Go through lots of algebra, many substitutions

$[\text{H}^+] =$

Don't know the  $[\text{HA}^-]$ , but  $K_{a2}$  and  $K_{b2}$  are very small so the simplifying process begins: hope  $[\text{HA}^-] = F = 0.05 \text{ M}$  in this problem.

$[\text{H}^+] =$

Put in values for all  $\Rightarrow \text{pH} = 4.17$

Always check to see if hope came true, find  $[\text{H}_2\text{A}]$ ,  $[\text{A}^{2-}]$

It is worth noting that  $[A^{2-}] \approx [H_2A]$  even though  $K_{a2} \gg K_{b2}$ . These reactions are coupled!

In any case the concentrations of these 2 species are small, relative to 0.05 (F) anyway, so our hope did come true.

Continuing to simplify the equation used above to calculate pH: usually  $K_{a1}K_w \ll K_{a1}K_{a2}F$  so the equation simplifies to

$$[H^+] =$$

One more simplification. Often  $K_{a1} \ll F$  so

Take  $-\log$  of both sides:

Bottom Line: the pH of an amphiprotic (intermediate) species is the average of the  $pK_a$ s.

**Diprotic summary:**

- 1)  $H_2A$ : Treat as monoprotic with  $K_a = K_{a1}$
- 2)  $A^{2-}$ : Treat as monobasic with  $K_b = K_{b1}$
- 3)  $HA^-$ : Take the average of the  $pK_a$ s

**This is readily extended to triprotic systems and beyond (Section 10 – 3).**

- 1)  $H_3A$ : Treat as monoprotic with  $K_a = K_{a1}$
- 2)  $H_2A^-$ : Treat as amphiprotic with  $pH =$

3)  $\text{HA}^{2-}$ : Treat as amphiprotic with  $\text{pH} =$

4)  $\text{A}^{3-}$ : Treat as monobasic with  $K_b = K_{b1}$ .

### Section 10 – 4 Principal species

First monoprotic, then polyprotic

A. Monoprotic. The question is, at a given pH what is the majority species?

For an acid/conjugate base system is it HA or  $\text{A}^-$ ?

For a base/conjugate acid system is it B or  $\text{BH}^+$ ?

In either case this is most easily treated using the buffer equation which, recall, is just the rearranged form of the  $K_a$  expression.

Take benzoic acid as an example, with a  $\text{p}K_a = 4.2$ .

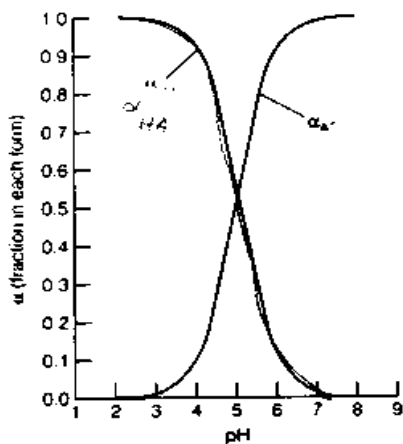
1. At  $\text{pH} = 4.2$ :

2. At  $\text{pH} = 5.2$

3. At  $\text{pH} = 3.2$

When the  $\text{pH} < \text{pK}_a$  the acidic form is in the majority (i.e. the principal species).

When the  $\text{pH} > \text{pK}_a$  the basic form is the principal species.



**Figure 11-2** Fractional composition diagram of a monoprotic system with  $\text{pK}_a = 5.00$ . Below  $\text{pH} 5$ ,  $\text{HA}$  is the dominant form, whereas above  $\text{pH} 5$ ,  $\text{A}^-$  dominates.

B. Polyprotic systems. What is the predominant species at any given  $\text{pH}$ ? Similar reasoning but  $>1$   $\text{pK}_a$ .

For phosphoric acid,  $\text{H}_3\text{A}$

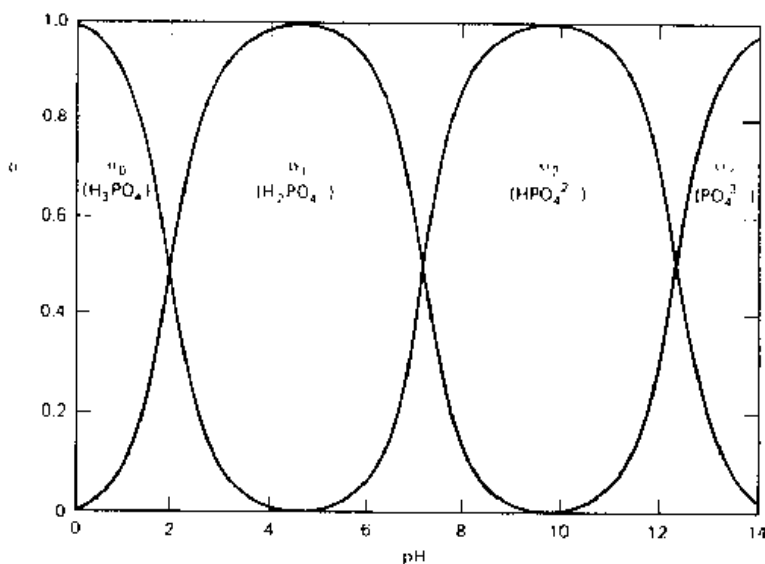


FIGURE 6.1 Fraction of  $\text{H}_3\text{PO}_4$  species as a function of pH.

The overlapping curves represent buffer regions. The pH values where  $\alpha_1$  and  $\alpha_2$  are 1 represent the end points in titrating  $\text{H}_3\text{PO}_4$ .

See Section 6.12 for a way of representing these plots as straight lines (log-log plots).

## Section 10-6. Isoelectric and Isoionic pH

Take alanine as an example:

The isoionic point is the pH obtained when the pure, neutral intermediate species (the zwitterion) is dissolved in water. Here the  $[\text{H}_2\text{A}^+] \neq [\text{A}^-]$  (but very close) since intermediate species do not dissociate much (bottom p. 184).

The isoelectric point is the pH at which  $[\text{H}_2\text{A}^+] = [\text{A}^-]$ ; where the average charge of the amino acid is zero.

The isoelectric point is important for the separation of proteins by electrophoresis using the clever technique of isoelectric focusing (Box 10-2, p. 194).

## Chapter 10

### Exercises A, B, C

Problems 1, 4, 5, 11-13, 15, 17, 18a, 22, 23

*In Chapter 10, those exercises in red and underlined are test 2 material. Remainder are for test 3. All remaining exercises and problems in Chapters 8 and 6 are for test 2, but material associated with Chapter 10.*

## Chapter 8

Exercises F, G, H

Problems 15, 17, 18, 22

## Chapter 6

Exercise I

Problems 50, 51