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## ACID-BASE IONIC DISTRIBUTION

### Objectives

1. To get a feel for the concentration distribution of the ions of acids and their conjugate bases as a function of pH.
2. To be able to identify the principal species present in solutions of mono- and polyprotic acids and bases at a given pH.

You can find alternative treatments of this material in Harris chapter 11, sections 1 and 4. You don't have to know or have read any of that to do this activity.

Ordinarily we think of an acid like acetic acid as something that makes a solution acidic. You walk up to this aqueous solution and dump in some acetic acid and the pH of the solution screams for the basement. For purposes of this activity let's consider things a little differently. What if we add just a small amount of acetic acid to a solution that contains other ions, some of them acids or bases, as well? The pH of such a solution is dictated by some conglomerate of the acid-base character of everything in there. Under some conditions adding a little acetic acid might not even change the pH very much at all. But there's still acetic acid and/or acetate ion in that solution because we put it in there. It's the goal of this activity to develop an understanding of just what happens to it, hopefully as simply and independently of everything else in there as possible.

Suppose that we prepare a bunch of 0.1M non-acetate buffers having various pH values. To 99.00mL, of each of these buffers suppose that we add 1.00 mL of 0.100M acetic acid. Of course we'll expect to see the equilibrium take place to which we've become accustomed:



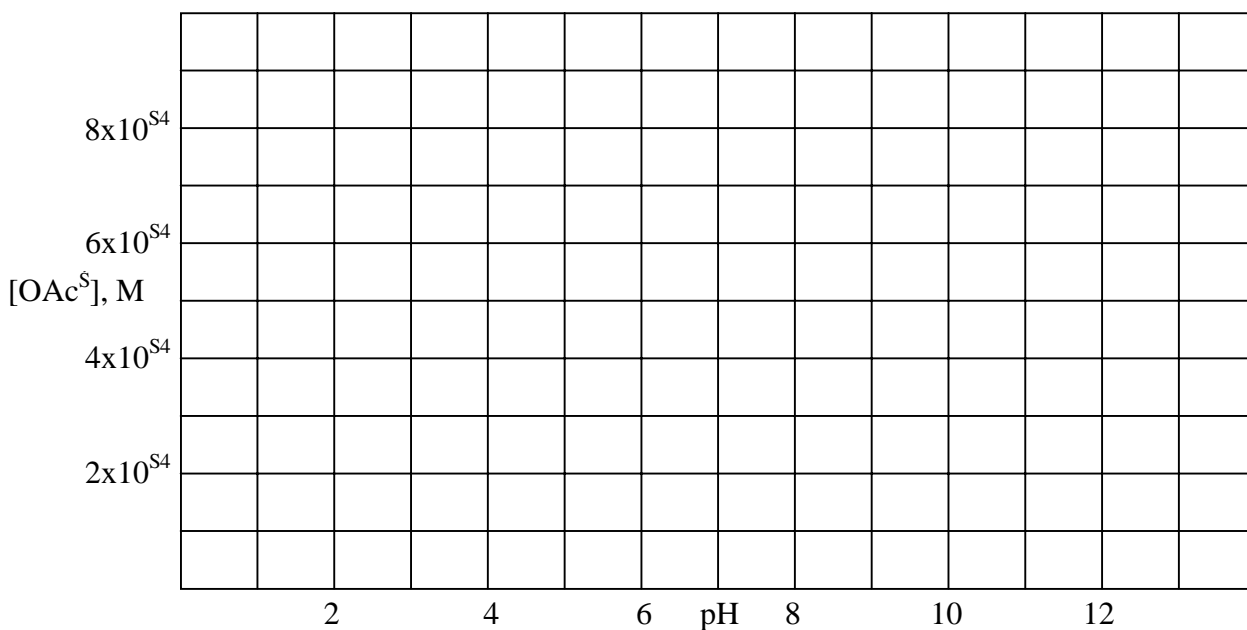
1. Calculate the formal concentration,  $C_{\text{HOAc}}$ , in each of the resulting solutions.
  
  
  
  
  
  
  
  
  
  
2. Assuming that the  $pK_a$  of each buffer is close to its nominal pH, will these buffers have sufficient capacity to deal with the  $\text{H}^+$  if all the acetic acid dissociates?

In Table 1 are shown the results we'd get if we measured the molar concentration of acetate ion in each buffer using, for example, an electrode sensitive to acetate ion (you can make one of these from a piece of copper wire in a few hours in the lab). It should be noted that such an electrode actually responds to the activity of acetate which is somewhat different from its molar concentration under these conditions. For clarity, the activities so obtained have already been divided by the appropriate activity coefficient to give molar concentrations. Be aware of this if you attempt to compare these results with some you might calculate ignoring activity:

**Table 1**

pH	[OAc <sup>-</sup> ], M
1.00	$2.26 \times 10^{-7}$
2.00	$2.25 \times 10^{-6}$
3.00	$2.21 \times 10^{-5}$
4.00	$1.84 \times 10^{-4}$
5.00	$6.93 \times 10^{-4}$
6.00	$9.58 \times 10^{-4}$
7.00	$9.96 \times 10^{-4}$
8.00	$1.00 \times 10^{-3}$
9.00	$1.00 \times 10^{-3}$
11.00	$1.00 \times 10^{-3}$
13.00	$1.00 \times 10^{-3}$

3. Draw a graph below showing how acetate ion concentration changes with pH.



4. According to the suppositions on the first page none of the buffers were to contain any acetate and we only put acetic acid in each solution. Yet in the pH 5 solution it looks as though there's nearly 0.0007M acetate present. So where did all this acetate ion come from?
5. What is the molar concentration of acetic acid, [HOAc], in that pH 5 solution?
6. For each of the buffer solutions calculate [HOAc] and plot those on the graph on the previous page too. Label the two lines with [OAc<sup>-</sup>] and [HOAc] so that you know which is which.

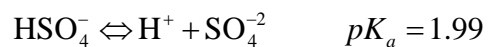
**Table 2**

pH	[OAc <sup>-</sup> ], M	[HOAc], M
1.00	$2.26 \times 10^{-7}$	
2.00	$2.25 \times 10^{-6}$	

3.00	$2.21 \times 10^{-5}$	
4.00	$1.84 \times 10^{-4}$	
5.00	$6.93 \times 10^{-4}$	
6.00	$9.58 \times 10^{-4}$	
7.00	$9.96 \times 10^{-4}$	
8.00	$1.00 \times 10^{-3}$	
9.00	$1.00 \times 10^{-3}$	
11.00	$1.00 \times 10^{-3}$	
13.00	$1.00 \times 10^{-3}$	

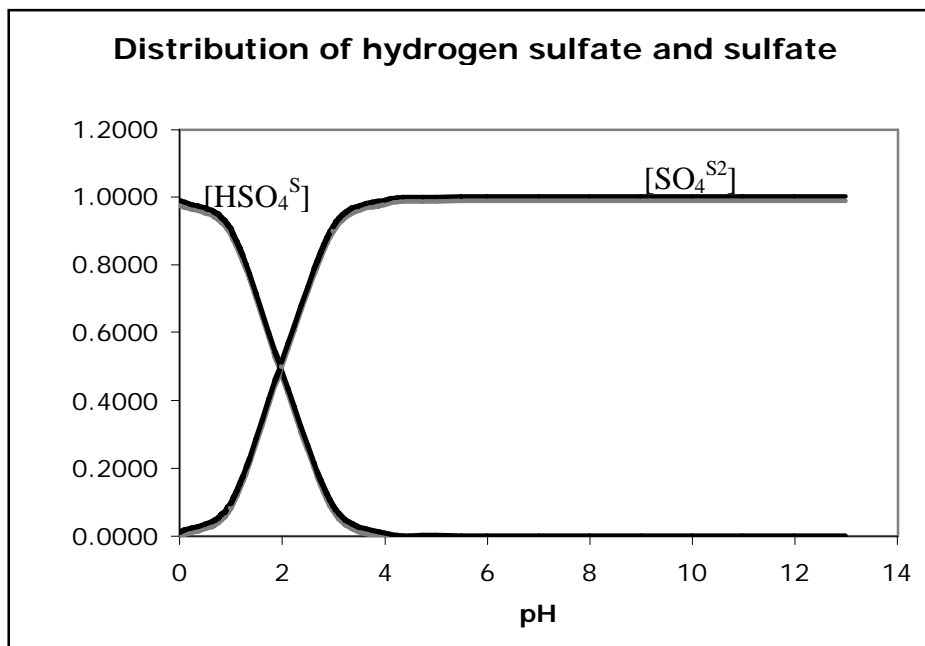
7. At what pH do the lines cross?

Consider a 1M solution of  $\text{NaHSO}_4$ .  $\text{HSO}_4^-$  is a weak acid that dissociates to form sulfate:



(recall that the first proton of  $\text{H}_2\text{SO}_4$  is strong in water, leading to its total dissociation into  $\text{H}^+$  and  $\text{HSO}_4^-$ . Consequently, in aqueous solutions of  $\text{HSO}_4^-$  such as this one we won't expect to see the formation of any  $\text{H}_2\text{SO}_4$ )

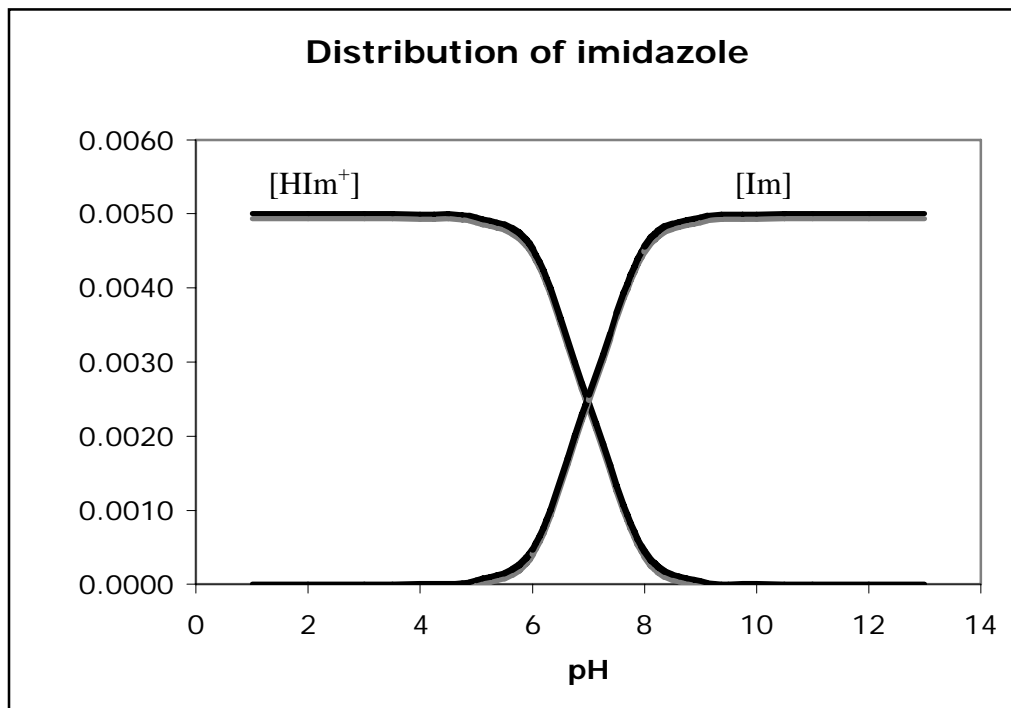
Here's what happens to the equilibrium concentrations of sulfate-containing ions as we adjust the pH with some pretty concentrated reagents.



8. At what pH do the lines cross in this case?
9. What is the mathematical relationship between  $[\text{HSO}_4^-]$  and  $[\text{SO}_4^{2-}]$  at the pH where the lines cross?
10. Which of  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  is most abundant (the principal species) at pH 4?

Here's the distribution of 0.005M imidazole, call it simply Im, which undergoes the aqueous equilibrium





11. Which of  $\text{HIm}^+$  and  $\text{Im}$  is the principal species present at pH 4?

12. What is the principal species at pH 9?

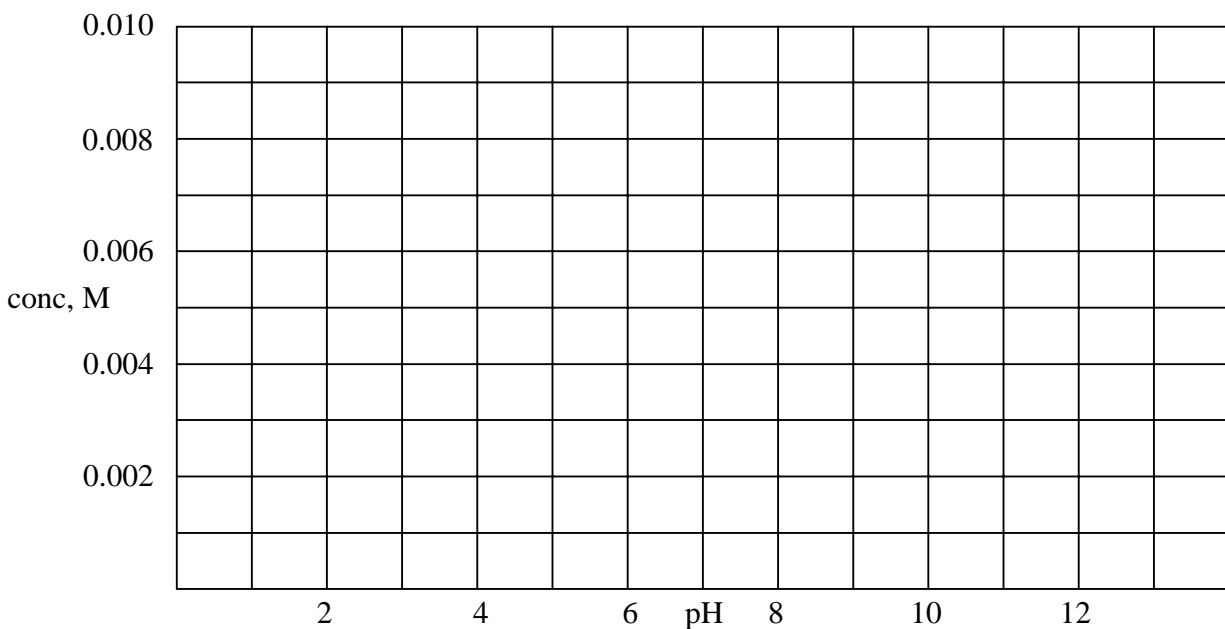
13. At what pH do the lines cross?

14. How might one predict the pH where the lines will cross for any given weak acid?

Chloroacetic acid ( $\text{HOClAc}$ ) undergoes an equilibrium analogous to acetic acid



15. Sketch the distribution graph you'd expect for the two species above as a function of pH in 0.01F chloroacetic acid. No, don't do any calculations. Just sketch it. Label the two lines with their respective species so you can tell which is which.

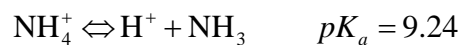


16. What is the principal species present in solution at pH 1?

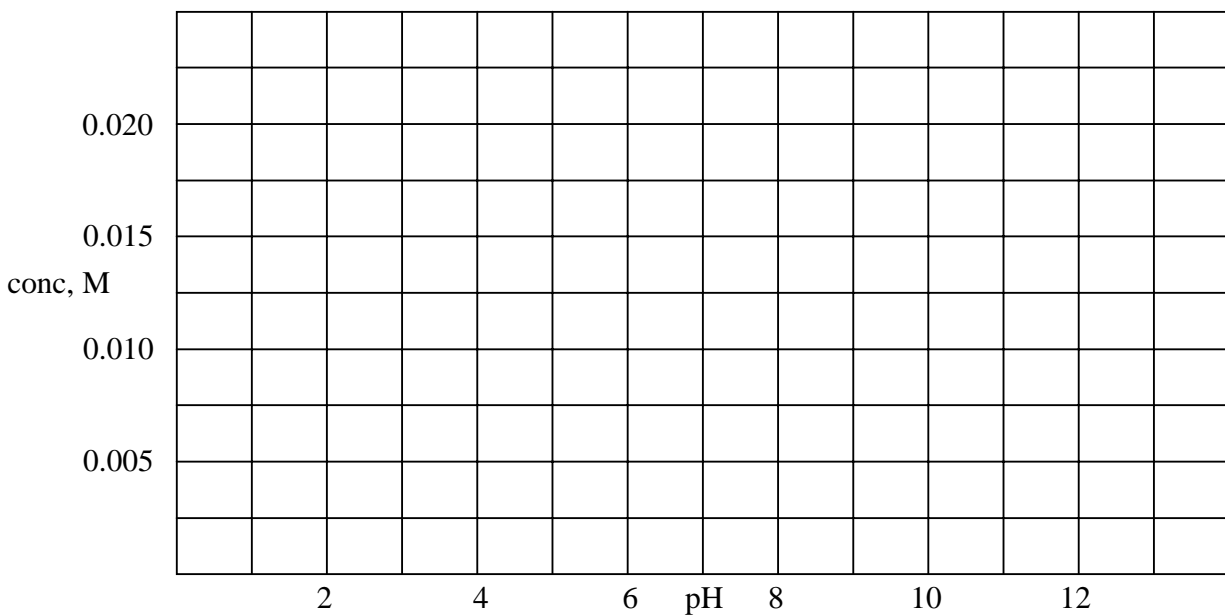
17. What is the principal species at pH 4?

18. Estimate the molar concentration of the chloroacetate ion at pH 8.

Consider a 0.02F solution of ammonia



You can draw the distribution graph below if you wish.



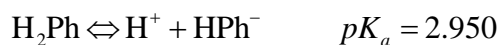
19. Of ammonia and the ammonium ion, which is the principle species at pH 7?

20. What is the principal species at pH 11?

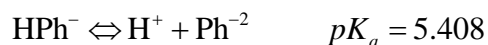
21. What is the principal species at pH 10?

22. What is the principal species at pH 9.20?

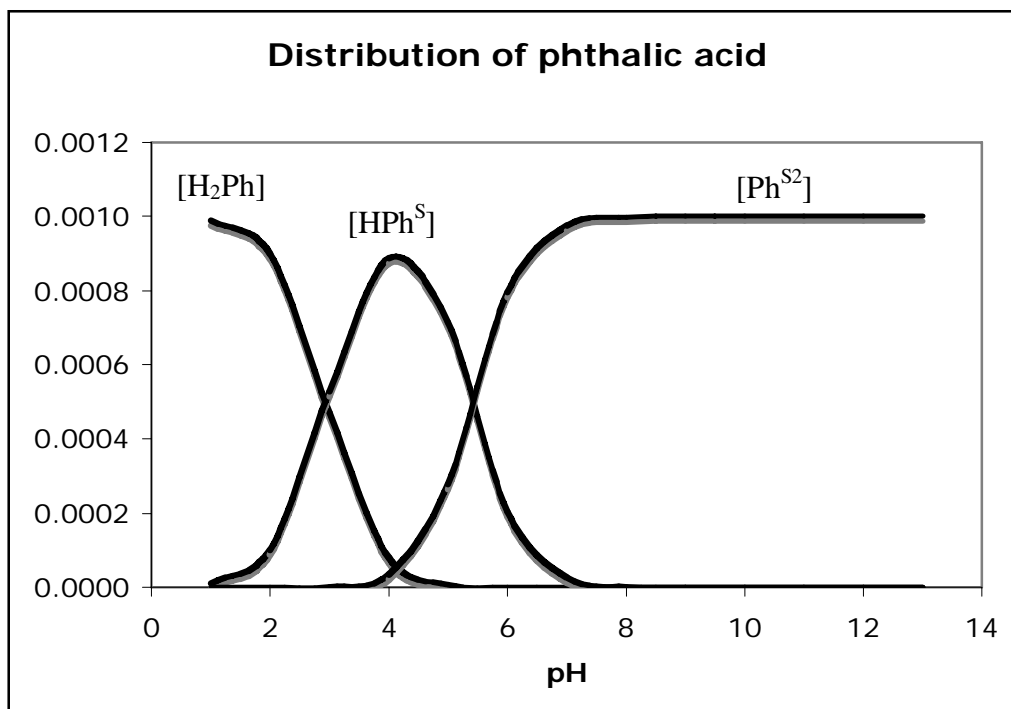
Some weak acids exhibit more than one acidic proton. Consider, for example, phthalic acid, which looks much like benzoic acid except that it has two carboxylic acid functions right next to each other on the ring. For simplicity, we'll represent phthalic acid as  $\text{H}_2\text{Ph}$ .



Once that first proton is gone to form  $\text{HPh}^-$  there's still another that can be lost, but as you might imagine it's a lot tougher to pull that second one off (we'd say that the naked  $\text{Ph}^{-2}$  anion is a pretty good base)



This means that we can have as many as three species floating around in solution all at once:  $\text{H}_2\text{Ph}$ ,  $\text{HPh}^-$  and  $\text{Ph}^{-2}$ . Here's how they distribute in a 0.001F phthalic acid solution



23. Notice the pH at which the  $\text{H}_2\text{Ph}$  and the  $\text{HPh}^-$  lines cross. Is that where you'd expect the crossing to be? Why?

24. Similarly, is the pH of crossing of the  $\text{HPh}^-$  and  $\text{Ph}^{-2}$  lines where you'd expect it to be?

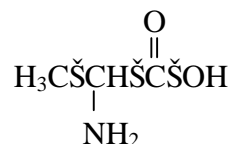
25. For phthalic acid solutions, what is the principal species present at pH 2?

26. What is the principal species at pH 4?

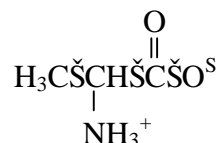
27. What is the principal species at pH 10?

28. Over what pH range is  $\text{HPh}^-$  the dominant species in phthalic acid solutions?

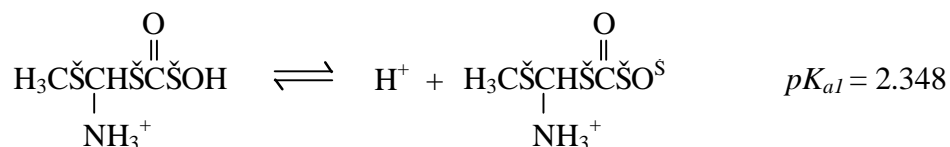
Alanine is one of the simplest of amino acids. It includes a carboxylic acid group, an amine group  $\alpha$  thereto and a methyl group. One might draw the structure:



If we do so, however, biochemists will cry foul because, they note, the  $\text{NH}_2$  function is in fact a stronger base than is the carboxylate anion, so the carboxylic acid loses out to the amine before things ever start. According to them the structure should more properly be written:

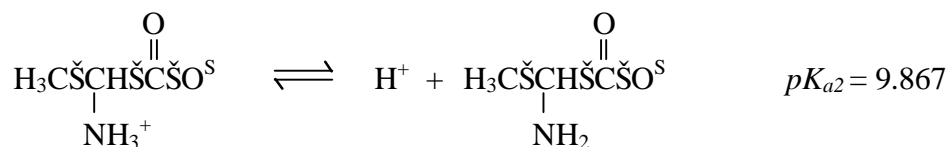


They proceed to call this a *zwitterion* (you German scholars will recognize zwitter as the root of a word meaning between). Although local charges are shown, the overall molecule is still neutral. From the point of view of the carboxylate function, however, all is not lost. If we get the pH acidic enough we can actually provide an additional  $\text{H}^+$  with which to protonate it:



This fully protonated alanine (on the left above) has a net positive charge.

Of course, those who live by the sword also die by the sword, and zwitterions are no exception. In sufficiently basic solution we can rip that extra proton off the  $\text{NH}_2$  which it so smugly stole from the carboxylate in the first place:

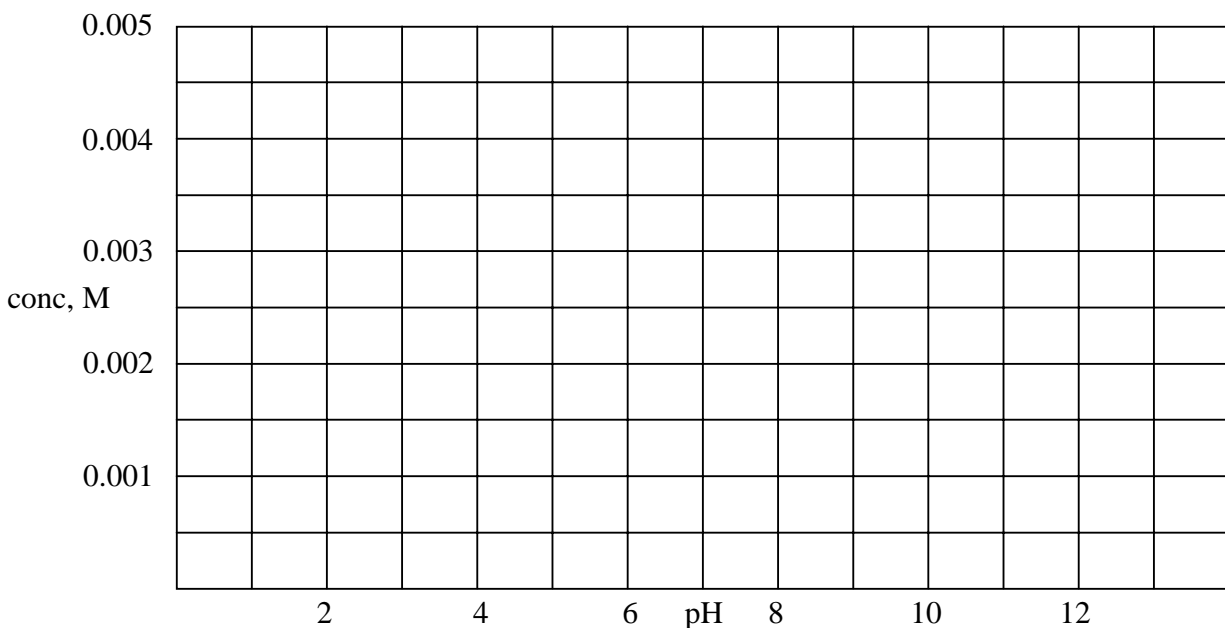


Notice that the fully deprotonated form (on the right above) exhibits a single negative charge.

Consider a 0.005 F solution of alanine in water. If we represent alanine as HA, then its fully protonated form might be written  $\text{H}_2\text{A}^+$  and it looks just like any other diprotic acid

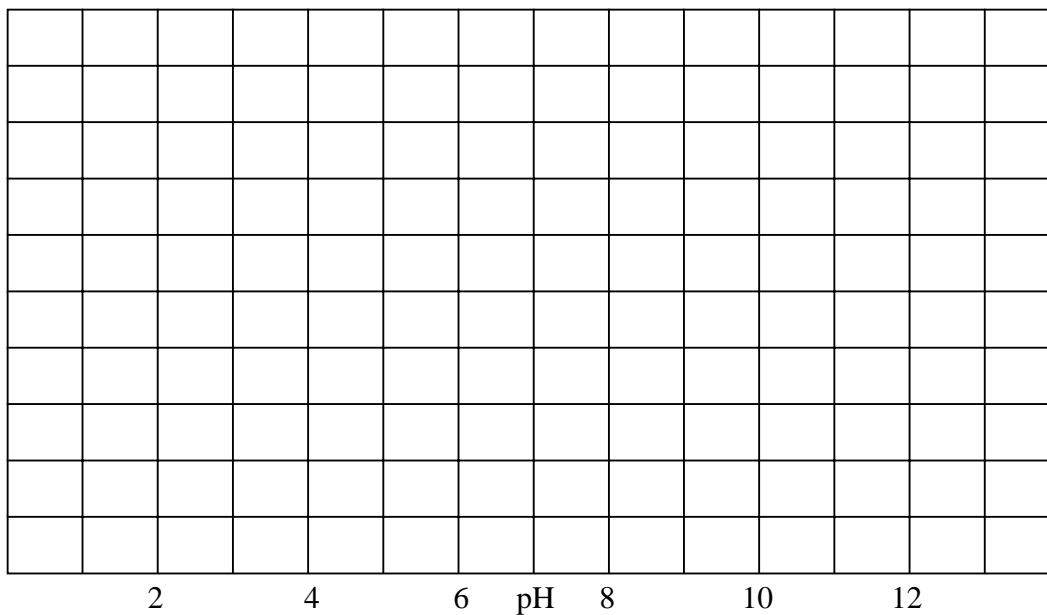
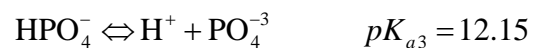
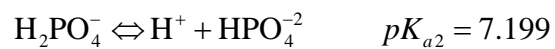


You can draw the distribution graph below if you wish.



29. What is the principal form of alanine at pH 10?
30. What is the principal species at pH 2?
31. Over what pH range is the zwitterion dominant?
32. Over what pH range would you expect alanine to move toward the positive electrode in an electric field (remember that opposite charges attract)?
33. Over what pH range would you expect alanine not to move at all in an electric field?

Orthophosphoric acid is a tri-protic acid that undergoes the following equilibria in water:

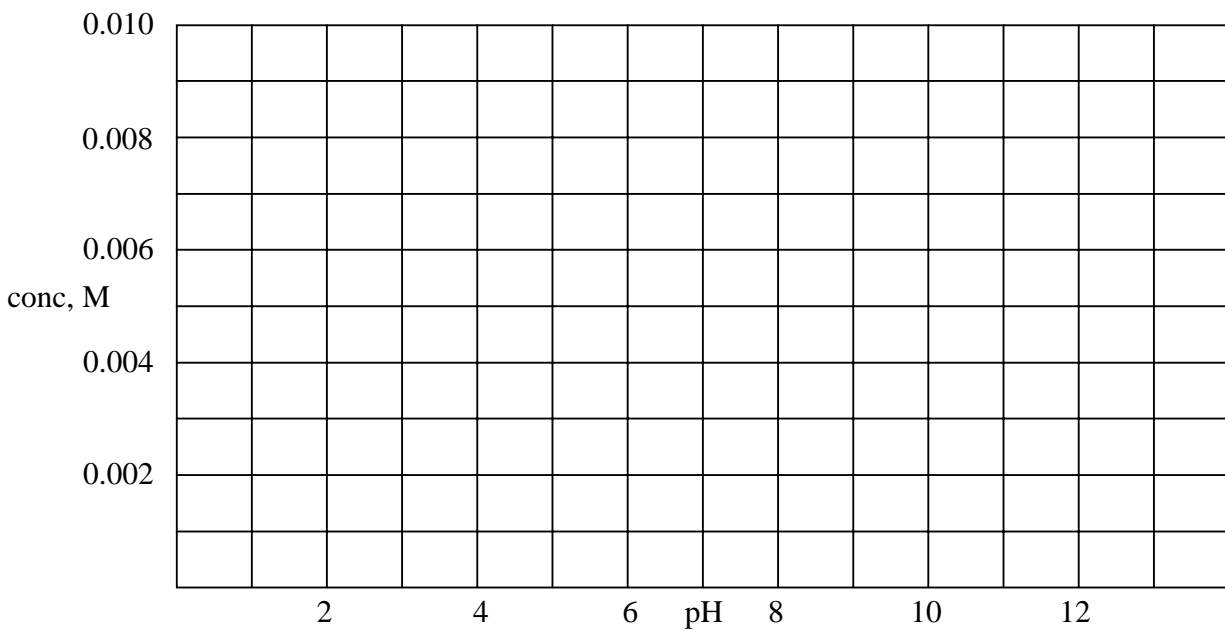


34. What is the principal phosphate-containing species at pH 10?
35. Over what pH range is the  $\text{H}_2\text{PO}_4^-$  ion dominant?
36. To what would one have to adjust the pH of a solution to be sure that most of the phosphate present was actually in the  $\text{PO}_4^{3-}$  form in water?

**Exercise 1**

Write a chemical equation showing the equilibrium between hydroxylamine,  $\text{HONH}_2$ , and the hydroxylammonium ion,  $\text{HONH}_3^+$ .

Draw the distribution graph for a 0.01 F solution of hydroxylamine.



What is the principal nitrogen-containing species at pH 7?

Over what pH range is this compound primarily present as  $\text{HONH}_2$ ?

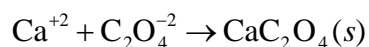
**Exercise 2**

Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is a diprotic acid in water.

Write the relevant equilibria for the dissociation of oxalic acid.

What is the principal species at pH 3?

A common application of oxalic acid is as a precipitant for the gravimetric determination of calcium:



It is convenient for this purpose because the availability of the oxalate dianion,  $\text{C}_2\text{O}_4^{-2}$ , can be readily controlled through the adjustment of pH.

It is desired to initially add a solution of oxalic acid to the analyte to form a clear solution without the precipitation of any calcium oxalate. What should the pH of the final solution be to make sure that essentially no oxalate dianion is available for precipitation?

To what value should the pH be adjusted to cause precipitation of calcium oxalate from the solution?

**Exercise 3**

Draw the three equilibria in which the amino acid glutamic acid participates (there's a nice table of amino acids at the beginning of chapter 11 in Harris).

Draw the structure of the zwitterionic form of glutamic acid.

Draw the structure of the principal glutamate-containing species at pH 7.

Over what pH range should we expect glutamic acid to move toward the negative electrode in an electric field?