

Chapter 9 – Monoprotic Acid/Base Equilibria

By Section

1. Strong acids/bases + shortened Sections 8.4/8.5
2. Weak acids/bases – repeat of Section 6-7 – skip
3. Weak acid equilibria + shortened Sections 8.4/8.5
4. Weak base equilibria + shortened Sections 8.4/8.5
5. Buffers

9-1 Strong acids/bases (Know table 6.2, p. 108)

Simple – find pH of a 0.05 M HCl solution.

Find pH of a 0.05 M NaOH solution.

A third problem: Find pH of a 10^{-8} M HCl solution.

Do this problem right – using techniques from Sections 8.4 and 8.5. Write down in equation form everything we know:

- 1) The reactions occurring and, if appropriate, the K expressions.

- 2) Any solution has zero net charge. In other words the sum of the positive charges in solution must equal the sum of the negative charges in solution. The result is a charge balance equation.

- 3) Matter must be conserved. What you put in must remain. In this problem it is trivial.

Add up equations and unknowns – hopefully at least as many equations as unknowns.

This answer is rigorously correct (ignoring activities, oh well). In every equilibrium problem done in your life, you have made assumptions without knowing it. Most of the time they are OK...

Now we will do weak acid (9-3) and weak base (9-4) problems to review how to do them and what assumptions are being made when you do them as learned.

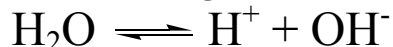
Section 9 – 3 (Skipped 9 – 2 since it repeats 6 – 7)

A typical weak acid problem – calculate the pH and pOH of a 6.6×10^{-2} M formic acid solution ($K_a = 1.8 \times 10^{-4}$)

Let formic acid = HA



To do this problem “right” we know in water



We also know that the sum of the charges must be balanced

And matter must be conserved. We put in 6.6×10^{-2} M HA, and all of that must still be there in some form (Formal concentration, F)

Gather together equations and unknowns:

<u>Unknowns</u>	<u>Equations</u>
[HA]	K_a
[A ⁻]	K_w
[H ⁺]	F
[OH ⁻]	C.B.

With 4 equations and 4 unknowns this can be solved, but it will be difficult because a cubic equation will result.

A key insight: For any “respectable” acid solution, that is one with a sufficiently large K_a and high enough concentration, H^+ contributed from HA \gg H^+ contributed from H_2O .

which means $[H^+] \approx [A^-]$ (i.e. ignore OH^- in charge balance equation)

$$\begin{aligned} \text{Set } [H^+] &= x, \text{ so } [A^-] = x \\ \text{Since } F &= 6.6 \times 10^{-2} = [HA] + [A^-] \\ &\text{rearrange} \end{aligned}$$

$$[\text{HA}] = F - [\text{A}^-] = F - x = 6.6 \times 10^{-2} - x$$

Now using the K_a expression

Since earlier it was reasoned that $[\text{H}^+] \approx [\text{A}^-]$
In general for any “respectable” acid solution

This result is identical to an ICE table perhaps seen in gen
chem..

But an assumption was made:
 $[\text{H}^+] \text{ from } \text{H}_2\text{O} \ll [\text{H}^+] \text{ from HA}$
For very dilute solutions or very weak acids this is not true.

Now go forward and solve the problem.

The bottom line: for any “respectable” weak acid solution:

Section 9 – 4 Weak base equilibria

Use the identical set of arguments as for weak acids

First set up using the systematic treatment (sections 8 – 4, 8 – 5)

For any “respectable” base solution, $[\text{OH}^-]$ from the base is $\gg [\text{OH}^-]$ from H_2O .

Result is the same as ICE table with the assumption that $[\text{OH}^-]$ from the base $\gg [\text{OH}^-]$ from water.

Just as for weak acids the bottom line:

Ex. K_b for cocaine = 2.6×10^{-6} . Calculate the pH of a 1.5×10^{-2} M solution.

2 more examples set up to illustrate the thinking through pH of salt solutions – set up but unsolved.

1) Calculate the pH of 6.6×10^{-2} M sodium formate solution.

$K_b = x^2/F - x$; $F = 6.6 \times 10^{-2}$, Find K_b as shown in Ch. 6 notes

2) Calculate the pH of a 0.05 M NH_4Cl solution.

Section 9-5 Buffers p. 167 – 175 = Conjugate acid/base mixtures

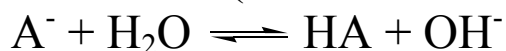
Buffers resist pH changes when strong acids or bases are added, or diluted.

a) “What you mix is what you get”. No equilibria involved. Strangely buffers are easier to deal with than their components.

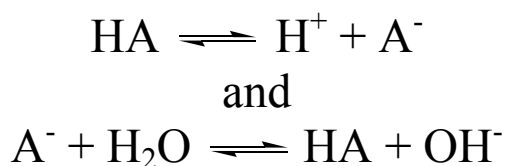
Mix 0.10 M HA ($pK_a = 4$, $K_a =$) with
0.10 M A^- ($pK_b = 10$, $K_b =$)

For HA by itself calculate α (fraction of dissociation)

For A^- by itself calculate α (fraction of association)



When the 2 are put together in the same solution here are the reactions:



So in a buffer with both HA and A^- present:

Add A^- to HA solution results in even less dissociation

Add HA to A^- solution results in even less association

Le Chatelier's Principle

Bottom Line: In a buffer solution consisting of an acid/conjugate base mixture, the concentrations of HA and A⁻ are what you put into the solution. By the same set of arguments, in a buffer solution consisting of a base/conjugate acid mixture, the concentration of B and BH⁺ are what you put into the solution.

This has implications!

b) Henderson-Hasselbach Equation (The Buffer Equation)

At Equilibrium

$$[\text{HA}] = F$$

$$[\text{A}^-] = F$$

Knowing this, that what you mix is what you get, the buffer equation is no more than a rearranged form of the K_a expression for acid/conjugate base mixtures.

Start with K_a expression

For base/conjugate acid buffers we could derive the equivalent expression starting with the K_b expression, but in general for some reason that is not done.

The buffer equation for base/conjugate acid mixtures (B/BH^+) is still in terms of pK_a of the conjugate acid.

For a B/BH^+ buffer solution

And in general

c) Buffer equation (system) properties

1. Buffer solution pH dictated by acid pK_a and the ratio of base/acid.
2. Dilution does not affect pH.
3. When: $[Base]/[Acid] = 1$, $pH = pK_a$
 $[Base]/[Acid] = 10$, $pH = pK_a + 1$
 $[Base]/[Acid] = 0.1$, $pH = pK_a - 1$

A ten-fold change in the ratio of base to acid results in a pH change of 1 unit. (It is a log function after all!)

d) How does a buffer work to resist pH changes?
 Mix a base B ($K_b = 10^{-4}$) with BH^+ ($K_a = 10^{-10}$)

Add a strong acid to this buffer, a source of H^+ .

Add a strong base to this buffer, a source of OH^- .

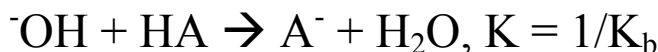
“All” free H^+ , OH^- added is reacted by the buffer.
Only the Base/Acid ratio changes as long as both the conjugate acid/base pair of the buffer are present.

For a HA/A^- buffer system:

Add H^+



Add OH^-

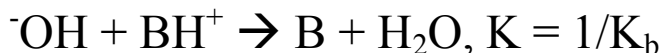


For a B/BH^+ buffer system:

Add H^+



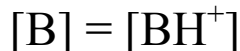
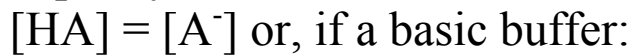
Add OH^-



e) Buffer capacity – how well a buffer solution resists pH changes.

1) Buffer capacity is increased by increasing component buffer concentrations (B/BH^+ or HA/A^-).

2) Buffer capacity is maximum when



In other words the buffer capacity is maximal when pH of the solution = pK_a of the acid component of the buffer.

- f) Choosing a buffer. Read p. 172 and understand before coming to the buffer lab – how to prepare a buffer in real life. This will save you much time, effort, and frustration in lab.

Chapter 9 Exercises C, D, F, H, I, J

Chapter 9 Problems 1 - 3, 5 - 8, 11, 13, 19 – 23, 26 – 28, 32 – 38, 40.

A few problems.

1. Plug in – no tricks.

Calculate the pH of a buffer consisting of 3g of NaOCl and 50 mL of 0.1 M HOCl. (Would you make a buffer this way? p. 172)

2. Same problem backwards – if the pH of this buffer is 8.43, find the ratio of OCl^-/HOCl .
3. Now take this original buffer, add 15 mmol strong acid, calculate the new pH.
4. Same problem backwards – how many mmol of strong acid are required to obtain a buffer pH of 7.63 from the original buffer solution?