Discussion Exercise 1 Key

Problem 1: What is the pH of a 1 mM solution of HCl? What is the pH of a 1 x 10^{-5} M solution of HCl? What is the pH of a 1 x 10^{-8} M solution of HCl? (Hint—it is NOT pH 8—you added an acid. What assumption do you make in problems like these?)

* 1 millimolar = 10^{-3} molar $\quad pH = -\log[H^+] = -\log[10^{-3}] = 3$

* $pH = -\log[10^{-5}] = 5$

* Assumption that we made above: All hydronium comes from added HCl. This is not true - some comes from autoionization. We can usually ignore it because it is so small in concentration, but we cannot ignore it in this last part.

Total $[H_3O^+]$ = $[H_3O^+]$ from autoionization + $[H_3O^+]$ from HCl

$= 1\times10^{-7} M + 1\times10^{-8} M = 1.1\times10^{-7} M \quad pH = -\log(1.1\times10^{-7}) = 6.96$

Problem 2: What is the pH of a 750 μM solution of NaOH?

μM = micromolar = 10^{-6}

$[^-OH] = 750\times10^{-6} M$

$[H_3O^+] = \frac{K_w}{[^-OH]} = \frac{10^{-14}}{750\times10^{-6}} = 1.3\times10^{-11}$

$pH = -\log(1.3\times10^{-11}) = \boxed{10.9}$

Problem 3: A solution of 2.67g of pyridine was adjusted with HCl until the pyridine was 78% in its protonated (conjugate acid) state. Pyridinium has a pKa of 5.25. What is the pH of the solution?

The absolute # grams of pyridine doesn't matter - only the ratio!

HA = .78

A^- = .22

$pH = pK_a + \log\frac{[A^-]}{[HA]}$

$= 5.25 + \log\frac{.22}{.78} = \boxed{4.7}$

Problem 4: A common biological buffer is Tris(hydroxymethyl)aminomethane. (Tris for short.) Tris has a pKa of 8.30. What % of Tris molecules are protonated in a solution of pH 7.6?

First, solve for ratio.

$pH = pK_a + \log\frac{A^-}{HA}$

$7.6 = 8.3 + \log\frac{A^-}{HA}$

$0.20 = \frac{A^-}{HA}$

Second, transform to %

Notice: relative amount of HA is 1.0

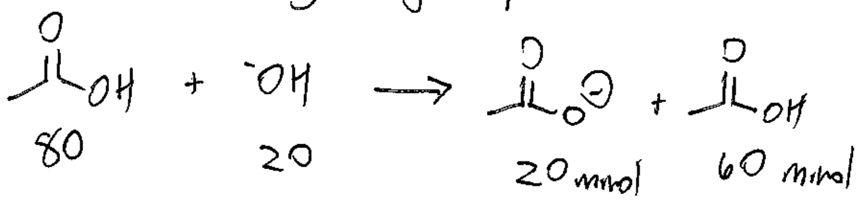
$\frac{A^-}{HA} = \frac{.20}{1}$

$\% HA = \frac{HA}{total} = \frac{1.0}{0.2+1.0} = \boxed{83\%}$

Problem 5. If a solution with 80.0 mmol of acetic acid is treated with 20 mmol of NaOH, then 20 mmol of acetic acid will react to form the conjugate base. How many mmol remain in the conjugate acid form of acetic acid?

* All the rest remains in HA form: $\boxed{60 \text{ mmol.}}$

* This is a limiting reagent problem. The strong base totally reacts



Problem 6. Refer to problem 5. Where is this point on the titration graph above? Based on the graph, what is the pH of this solution? Now solve this using the Henderson-Hasselbalch equation. Did you get the same pH value?

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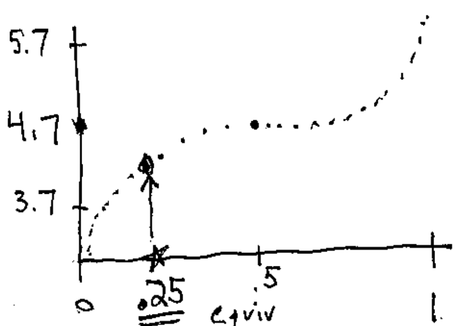


Adding 20 mmol is 0.25 equivalents. According to the graph, this pH should be a little above pH 4.

* Using H-H, $pH = pK_a + \log \frac{A^-}{HA}$

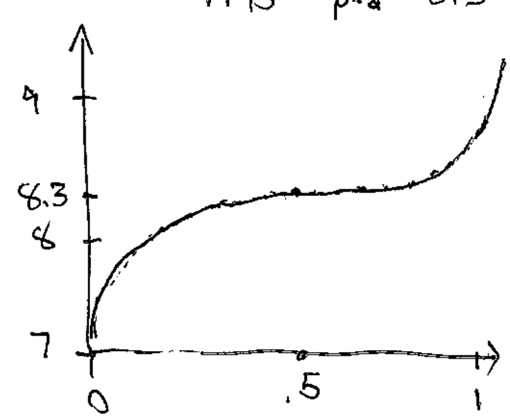
$= 4.7 + \log \frac{20}{60} = \boxed{4.2}$

This matches the graph, as it should!

Problem 7. Draw a titration curve like the one above for Tris. (See problem 4 for one piece of necessary information.)

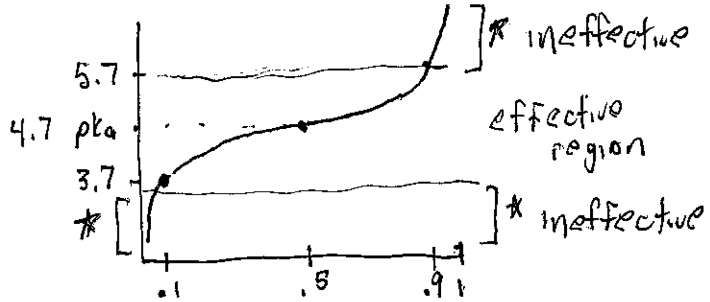
Tris $pK_a = 8.3$

The titration curve will always have the same basic shape, but will have its flat point at the $pH = pK_a$ of the acid.



Problem 8. An acetic acid/acetate buffer would only be effective on the range of 3.7 to 5.7. Explain.

Outside of these ranges, the pH rises and falls quickly with only small amounts of added acid or base



This is because the ratio of A^-/HA gets too big or small, meaning there is not enough conj acid/conj. base. (See problem 9.)

Problem 9. What is the ratio of conjugate acid to conjugate base in an acetic acid/acetate buffer at pH 3.7? What is the ratio of conjugate acid to conjugate base in an acetic acid/acetate buffer at pH 5.7? Use the Henderson-Hasselbalch equation to solve for these values.

At pH 3.7

$$pH = pK_a + \log \frac{A^-}{HA}$$

$$3.7 = 4.7 + \log \frac{A^-}{HA}$$

$$\frac{1}{10} = \frac{A^-}{HA}$$

10 out of 11 molecules are in HA form (91%)

At pH 5.7

$$pH = pK_a + \log \frac{A^-}{HA}$$

$$5.7 = 4.7 + \log \frac{A^-}{HA}$$

$$\frac{10}{1} = \frac{A^-}{HA}$$

10 out of 11 molecules are in A^- form (91%)

At pH 3.7, not enough conjugate base!

At pH 5.7, not enough conjugate acid!

Problem 10. Draw a titration curve for the acetic acid/acetate buffer, and mark the region in which the buffer is effective.

See problem 8.

Problem 11. One liter of a Tris buffer has 100 mmol of tris. If the pH of the solution is 8.0, how many mmol of tris are in the conjugate acid form, and how many are in the conjugate base form?

First, find ratio.

$$pH = pK_a + \log \frac{A^-}{HA}$$

$$8.0 = 8.3 + \log \frac{A^-}{HA}$$

$$.50 = \frac{A^-}{HA}$$

Second, find %

$$\frac{A^-}{HA} = \frac{.50}{1.0}$$

$$\% A^- = \frac{.50}{1.0 + .50} = 33\%$$

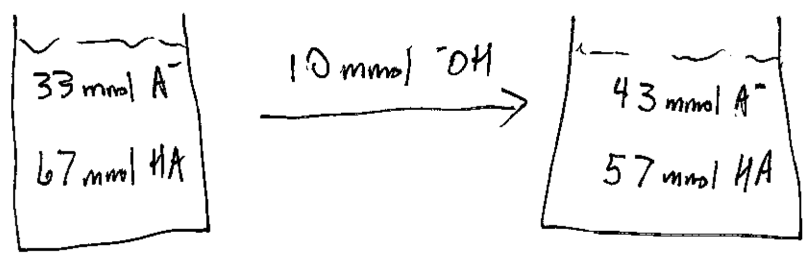
- Total tris = 100 mmol
- [CB] of tris = 33% of 100 mmol

$\boxed{33 \text{ mmol}}$

[CA] form = $\boxed{67 \text{ mmol.}}$

Problem 12. If the solution from problem 10 is treated with 10 mmol of NaOH, how many mmol of tris are now in the conjugate acid form and the conjugate base form? What is the new pH of the solution?

If treated with NaOH, the conjugate acid is transformed to A^-



New pH

$$pH = pK_a + \log \frac{A^-}{HA} =$$

$$= 8.3 + \log \frac{.43}{.57} = \boxed{8.2}$$

Adding 10 mmol ^-OH only raised the pH 0.2 units.

Adding 10 mmol to 1 L of water would have raised the pH to <u>11</u>.