

Course Notes – Chapter 8, 10, and 11

Chapter 8

Mass balance

Let's look at a triprotic system, such as H_3PO_4

There are four different species within this system



For a 0.0500 M solution of NaHPO_4 , we can write the following mass balance equation.

$$F_{\text{NaHPO}_4} = 0.0500 = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$$

Charge balance

All solutions must be electrically neutral!!!!!!! Which means they carry a no net charge.

mole positive charges = moles negative charges

ex. A dilute solution of acetic acid, HA

What species exist in solution?



A mole of A^- carries a mole of negative charge. A mole of OH^- carries a mole of negative charge. A mole of HA carries no charge. A mole of H_3O^+ carries a mole of positive charge. Therefore,

$$[\text{H}_3\text{O}^+] = [\text{A}^-] + [\text{OH}^-]$$

charge balance eq.

Let's go back and write a charge balance for the NaHPO_4 .

One mole of H_3PO_4 carries no moles of charge

One mole of H_2PO_4^- carries one mole of charge

One mole of HPO_4^{2-} carries two moles of charge

One mole of PO_4^{3-} carries three moles of charge

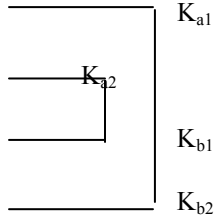
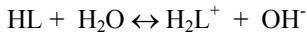
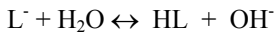
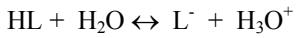
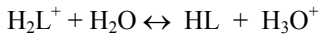
Therefore,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}]$$

In many instances when we are dealing with very complex equilibria, it is useful to use mass balance and charge balance in efforts to reduce an expression to one variable.

We will use these in chapter 11 and 12, and then again when we come back to chapter 9.

Chapter 10
Diprotic Acids



$$K_w = K_{a1} K_{b2}$$

$$K_w = K_{a2} K_{b1}$$

Zwitter ion (amino acids)

Example 1 – (diprotic system, where neutral species is the most acidic form)

Calculate the pH of 0.010 M malonic acid, H_2M , solution.

$$K_{a1} = 1.42 \cdot 10^{-3}$$

$$K_{a2} = 2.01 \cdot 10^{-6}$$



$$K_{a1} = \frac{[\text{HM}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{M}]} \approx x^2 / F_{\text{H}_2\text{M}} \rightarrow x = 3.76 \cdot 10^{-3} \text{ M, approx. 2 invalid!}$$

$$\text{Succ. Approx.} \rightarrow x = 0.006182 \text{ M, pH} = 2.21$$

This assumes that the second equilibrium is unimportant!! Is it?

$$K_{a2} = \frac{[\text{M}^{2-}][\text{H}_3\text{O}^+]}{[\text{HM}^-]}$$

$$[\text{M}^{2-}] = K_{a2} \frac{[\text{HM}^-]}{[\text{H}_3\text{O}^+]} = (2.01 \cdot 10^{-6}) \frac{0.006182}{0.006182} = 2.01 \cdot 10^{-6} \text{ M}$$

$$\alpha_2 = \frac{[\text{M}^{2-}]}{[\text{HM}^-]} = 2.01 \cdot 10^{-6} / 0.006182 = 0.000325 \text{ or } \approx 0.03 \%$$

It is unimportant!!!!

Example 2 (diprotic system, where neutral species is the most basic form)

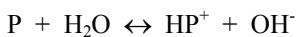
Calculate the pH of a 0.10 M piperazine (P) solution

$$K_{a1} = 4.65 \cdot 10^{-6}$$

$$K_{a2} = 1.86 \cdot 10^{-10}$$

$$K_{b1} = K_w / K_{a2} = 5.43 \cdot 10^{-5}$$

$$K_{b2} = K_w / K_{a1} = 2.79 \cdot 10^{-9}$$



$K_{b1} = [\text{HP}^+][\text{OH}^-] / [\text{P}] \approx x^2/F_P \rightarrow x = [\text{OH}^-] = 2.33 \cdot 10^{-3} \text{ M}$ approx. 2 is valid!
 Succ. Approx. $\rightarrow [\text{H}_3\text{O}^+] = 4.334 \cdot 10^{-12} \text{ M}$, pH = 11.36

This assumes that the second equilibrium is unimportant!! Is it?

$$K_{b2} = [\text{H}_2\text{P}^{2+}][\text{OH}^-]/[\text{HP}^+]$$

$$[\text{H}_2\text{P}^{2+}] = K_{b2} [\text{HP}^+]/[\text{OH}^-] = (2.79 \cdot 10^{-9})(2.33 \cdot 10^{-3})/(2.33 \cdot 10^{-3}) = 2.79 \cdot 10^{-9} \text{ M}$$

$$\alpha_2 = [\text{M}^{2-}]/[\text{HM}^-] = 2.79 \cdot 10^{-9} / 2.33 \cdot 10^{-3} \approx 1 \cdot 10^{-6}$$

The second equilibrium has a negligible effect on the pH!!!!

This is almost always the case!!!!!!..... Unless K_{a1} and K_{a2} are very close, and even then the pH will not be off by much.

For instance,

Calculate the pH of a 0.010 M H_2A , where K_{a1} and K_{a2} are $1.00 \cdot 10^{-4}$ and $3.00 \cdot 10^{-4}$, respectively.

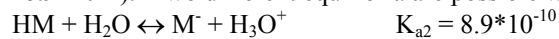
Ignoring the second equilibrium, $\rightarrow \text{pH} = 3.02$

Solving strictly (we will learn how to do this when we cover chapter 9) $\rightarrow \text{pH} = 2.93$

Example 3 (diprotic system, where neutral species is the intermediate form)

Calculate the pH of a 0.050 M solution of Methionine (HM).

Methionine is an amino acid. Its neutral form is the intermediate species, HM, of a diprotic system ($K_{a1} = 6.3 \cdot 10^{-3}$ and $K_{a2} = 8.9 \cdot 10^{-10}$). Two different equilibria are possible with HM in water.



Both will occur, and in fact based on LeChatlier's principle they will drive one another, since H_3O^+ reacts rapidly with OH^- .

Charge balance:

$$[\text{OH}^-] + [\text{M}^-] = [\text{H}_3\text{O}^+] + [\text{H}_2\text{M}^+]$$

make substitutions from K_{a2} and K_{b2} expressions!!!

$$K_{a2} = [\text{M}^-][\text{H}_3\text{O}^+]/[\text{HM}] \rightarrow [\text{M}^-] = K_{a2} [\text{HM}]/[\text{H}_3\text{O}^+]$$

$$K_{b2} = [\text{H}_2\text{M}^+][\text{OH}^-]/[\text{HM}] \rightarrow [\text{H}_2\text{M}^+] = K_{b2} [\text{HM}]/[\text{OH}^-]$$

$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+]$$

$$[\text{OH}^-] + K_{a2} [\text{HM}]/[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+] + K_{b2} [\text{HM}]/[\text{OH}^-]$$

$$K_w / [\text{H}_3\text{O}^+] + K_{a2} [\text{HM}]/[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+] + K_{b2} [\text{HM}][\text{H}_3\text{O}^+]/K_w$$

$$K_w + K_{a2} [\text{HM}] = [\text{H}_3\text{O}^+]^2 + K_{b2} [\text{HM}][\text{H}_3\text{O}^+]^2/K_w$$

$$(K_w + K_{a2} [HM]) = [H_3O^+]^2 (1 + K_{b2} [HM] / K_w)$$

$$(K_w + K_{a2} [HM]) / (1 + K_{b2} [HM] / K_w) = [H_3O^+]^2$$

$$[H_3O^+] = [(K_w + K_{a2} [HM]) / (1 + K_{b2} [HM] / K_w)]^{1/2}$$

simplify

$$[H_3O^+] = [(K_w + K_{a2} [HM]) / (1 + [HM] / K_{a1})]^{1/2}$$

$$[H_3O^+] = [K_{a1}(K_w + K_{a2} [HM]) / (K_{a1} + [HM])]^{1/2}$$

$$[H_3O^+] = [K_{a1}K_w + K_{a1}K_{a2} [HM]) / (K_{a1} + [HM])]^{1/2}$$

Now, K_{a2} and K_{b2} are small, so you can make the following approximation.

$$F_{HM} \approx [HM], \text{ and therefore, } \rightarrow [H_3O^+] = [K_{a1}K_w + K_{a1}K_{a2} F_{HM} / (K_{a1} + F_{HM})]^{1/2}$$

So, $[H_3O^+] =$

$$[(6.3 \times 10^{-3})(1.01 \times 10^{-14}) + (6.3 \times 10^{-3})(8.9 \times 10^{-10})(0.050) / (6.3 \times 10^{-3} + 0.050)]^{1/2}$$

$$2.23 \times 10^{-6} \text{ M}$$

$$\text{pH} = 5.65$$

Is the approximation a good one?

$$K_{b2} = [H_2M^+] [OH^-] / [HM] \rightarrow$$

$$[H_2M^+] = K_{b2} [HM] / [OH^-] = (1.6 \times 10^{-12})(0.050) / (4.53 \times 10^{-9}) = 1.8 \times 10^{-5} \text{ M}$$

$$K_{a2} = [M^-] [H_3O^+] / [HM] \rightarrow$$

$$[M^-] = K_{a2} [HM] / [H_3O^+] = (8.9 \times 10^{-10})(0.050) / (2.23 \times 10^{-6}) = 2.0 \times 10^{-5} \text{ M}$$

Approximation was valid!! Note that $[H_2M^+] \approx [M^-]$. This is the case even though K_{a2} is greater than K_{b2} by almost three orders of magnitude!!!

Polyprotic systems



Polyprotic buffers
Problem 11.18

Which is the Principle Species?

Histidine

$$pK_{a1} = 1.7$$

$$pK_{a2} = 6.02$$

$$pK_{a3} = 9.08$$

Alpha Fractions

Monoprotic systems (HA or B)

Monoprotic acid

$$\alpha_{HA} = [HA]/F_{HA}, \text{ where } F_{HA} = [HA] + [A^-], \text{ or } [HA] / ([HA] + [A^-])$$

$$\alpha_{A^-} = [A^-]/F_{HA}, \text{ where } F_{HA} = [HA] + [A^-], \text{ or } [A^-] / ([HA] + [A^-])$$

Monoprotic base

$$\alpha_B = [B]/F_B, \text{ where } F_B = [B] + [HB^+], \text{ or } [B] / ([B] + [HB^+])$$

$$\alpha_{HB^+} = [HB^+]/F_B, \text{ where } F_B = [B] + [HB^+], \text{ or } [HB^+] / ([B] + [HB^+])$$

Monoprotic acid

$$K_a = [H_3O^+][A^-]/[HA] = [H_3O^+](F_{HA} - [HA])/[HA]$$

A little algebra

$$[HA] K_a + [H_3O^+][HA] = [H_3O^+]F_{HA}$$

$$[HA] (K_a + [H_3O^+]) = [H_3O^+]F_{HA}$$

$$[HA] / F_{HA} = [H_3O^+] / (K_a + [H_3O^+])$$

$$\alpha_{HA} = [HA]/F_{HA} = [H_3O^+] / (K_a + [H_3O^+])$$

similarly, you can derive

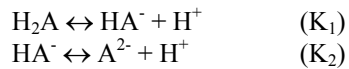
$$\alpha_{A^-} = [A^-]/F_{HA} = K_a / (K_a + [H_3O^+])$$

or for a monoprotic base,

$$\alpha_B = [B]/F_B = K_a / (K_a + [H_3O^+])$$

$$\alpha_{HB^+} = [HB^+]/F_B = [H_3O^+] / (K_a + [H_3O^+])$$

alpha fractions for a Diprotic System



$$\begin{aligned} \text{K}_1 = [\text{H}^+][\text{HA}^-]/[\text{H}_2\text{A}] &\rightarrow [\text{HA}^-] = [\text{H}_2\text{A}]\{\text{K}_1/[\text{H}^+]\} && (1) \\ \text{K}_2 = [\text{H}^+][\text{A}^{2-}]/[\text{HA}^-] &\rightarrow [\text{A}^{2-}] = [\text{HA}^-]\{\text{K}_2/[\text{H}^+]\} && (2) \end{aligned}$$

Mass balance equation

$$F = [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]$$

First solve for the $\alpha_{\text{H}_2\text{A}}$. To do these we need to write expression that put the three other species in terms of H_2A .

We already have eq 1

$$[\text{HA}^-] = [\text{H}_2\text{A}]\text{K}_1/[\text{H}^+]$$

Now substitute this into eq 2 to get

$$[\text{A}^{2-}] = [\text{H}_2\text{A}]\text{K}_1\text{K}_2/[\text{H}^+]^2$$

Substitute these three new equations into the mass balance equation

$$F = [\text{H}_2\text{A}] + [\text{H}_2\text{A}]\text{K}_1/[\text{H}^+] + [\text{H}_2\text{A}]\text{K}_1\text{K}_2/[\text{H}^+]^2$$

$$F = [\text{H}_2\text{A}] (1 + \text{K}_1/[\text{H}^+] + \text{K}_1\text{K}_2/[\text{H}^+]^2)$$

$$F/[\text{H}_2\text{A}] = 1 + \text{K}_1/[\text{H}^+] + \text{K}_1\text{K}_2/[\text{H}^+]^2$$

Get a common denominator

$$F/[\text{H}_2\text{A}] = ([\text{H}^+]^2 + [\text{H}^+]\text{K}_1 + \text{K}_1\text{K}_2) / [\text{H}^+]^2$$

Flip the numerator and denominator on both sides

$$\alpha_{\text{H}_2\text{A}} = [\text{H}_2\text{A}]/F = [\text{H}^+]^2/([\text{H}^+]^2 + [\text{H}^+]\text{K}_1 + \text{K}_1\text{K}_2)$$

Next I will solve for α_{HA^-} . To do these we need to write expression that put the three other species in terms of HA^- .

rearranging eq 1 we get

$$[\text{H}_2\text{A}] = [\text{HA}^-][\text{H}^+]/\text{K}_1$$

eq 2 gives us the expression for A^{2-}

$$[\text{A}^{2-}] = [\text{HA}^-]\text{K}_2/[\text{H}^+]$$

Substitute these into the mass balance equation

$$F = [\text{HA}^-][\text{H}^+]/\text{K}_1 + [\text{HA}^-] + [\text{HA}^-]\text{K}_2/[\text{H}^+]$$

$$F = [\text{HA}^-] ([\text{H}^+]/\text{K}_1 + 1 + \text{K}_2/[\text{H}^+])$$

$$F/[\text{HA}^-] = [\text{H}^+]/\text{K}_1 + 1 + \text{K}_2/[\text{H}^+]$$

Get a common denominator

$$F/[\text{HA}^-] = ([\text{H}^+]^2 + [\text{H}^+]\text{K}_1 + \text{K}_1\text{K}_2) / \text{K}_1[\text{H}^+]$$

Flip the numerator and denominator on both sides

$$\alpha_{\text{HA}^-} = [\text{HA}^-]/F = (\text{K}_1[\text{H}^+]) / ([\text{H}^+]^2 + [\text{H}^+]\text{K}_1 + \text{K}_1\text{K}_2 + \text{K}_1\text{K}_2)$$

Next I will solve for $\alpha_{\text{A}^{2-}}$. To do these we need to write expression that put the three other species in terms of A^{2-} .

Eq 2 gives us an expression for A^{2-} $[\text{HA}^-] = [\text{A}^{2-}][\text{H}^+]/\text{K}_2$

Rearrange eq 1 to get $[\text{H}_2\text{A}] = [\text{HA}^-][\text{H}^+]/\text{K}_1$

Rearrange eq 1 and substitute $[\text{H}_2\text{A}] = [\text{A}^{2-}][\text{H}^+]^2/\text{K}_1\text{K}_2$

$$F = [\text{A}^{2-}][\text{H}^+]^2/\text{K}_1\text{K}_2 + [\text{A}^{2-}][\text{H}^+]/\text{K}_2 + [\text{A}^{2-}]$$

$$F = [\text{A}^{2-}] ([\text{H}^+]^2/\text{K}_1\text{K}_2 + [\text{H}^+]/\text{K}_2 + 1)$$

$$F/[\text{A}^{2-}] = [\text{H}^+]^2/\text{K}_1\text{K}_2 + [\text{H}^+]/\text{K}_2 + 1$$

Get a common denominator

$$F/[\text{A}^{2-}] = ([\text{H}^+]^2 + [\text{H}^+]\text{K}_1 + \text{K}_1\text{K}_2) / \text{K}_1\text{K}_2$$

Flip the numerator and denominator on both sides

$$\alpha_{\text{A}^{2-}} = [\text{A}^{2-}]/F = (\text{K}_1\text{K}_2) / ([\text{H}^+]^2 + [\text{H}^+]\text{K}_1 + \text{K}_1\text{K}_2)$$

Isoelectric point and electrophoresis

Chapter 11 Titrations

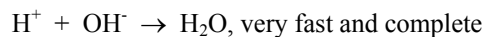
Strong acid with strong base

Titrate 25.00 ml of a 0.100 M HCl solution with 0.0500 M NaOH.

Calculate the pH at 0.00 ml NaOH added

$$\text{pH} = -\log(0.100) = 1.000$$

Calculate the pH at 5.00 ml NaOH added.



$$\text{mmol of OH}^- \text{ added} = (5.00\text{ml})(0.0500) = 0.250 \text{ mmol}$$

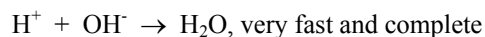
$$\text{initial mmol H}^+ = (25.00\text{ml})(0.100) = 2.50 \text{ mmol}$$

$$\text{final mmol H}^+ = 2.50 - 0.250 = 2.25 \text{ mmol}$$

$$[\text{H}^+] = (2.25 \text{ mmol})(25.00 + 5.00) = 0.0750 \text{ M}$$

$$\text{pH} = 1.125$$

Calculate the pH at 15.00 ml NaOH added.



$$\text{mmol of OH}^- \text{ added} = (15.00\text{ml})(0.0500) = 0.750 \text{ mmol}$$

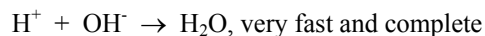
$$\text{initial mmol H}^+ = (25.00\text{ml})(0.100) = 2.50 \text{ mmol}$$

$$\text{final mmol H}^+ = 2.50 - 0.750 = 1.75 \text{ mmol}$$

$$[\text{H}^+] = (1.75 \text{ mmol})(25.00 + 15.00) = 0.0750 \text{ M}$$

$$\text{pH} = 1.359$$

Calculate the pH at 40.00 ml NaOH added.



$$\text{mmol of OH}^- \text{ added} = (40.00\text{ml})(0.0500) = 2.00 \text{ mmol}$$

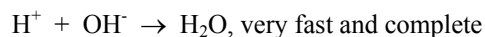
$$\text{initial mmol H}^+ = (25.00\text{ml})(0.100) = 2.50 \text{ mmol}$$

$$\text{final mmol H}^+ = 2.50 - 2.00 = 0.50 \text{ mmol}$$

$$[\text{H}^+] = (0.50 \text{ mmol})(25.00 + 40.00) = 0.0750 \text{ M}$$

$$\text{pH} = 2.11$$

Calculate the pH at 49.50 ml NaOH added.



$$\text{mmol of OH}^- \text{ added} = (49.50\text{ml})(0.0500) = 2.475 \text{ mmol}$$

$$\text{initial mmol H}^+ = (25.00\text{ml})(0.100) = 2.50 \text{ mmol}$$

$$\text{final mmol H}^+ = 2.50 - 2.475 = 0.025 \text{ mmol}$$

$$[\text{H}^+] = (0.025 \text{ mmol}) / (25.00 + 49.50) = 0.0750 \text{ M}$$

$$\text{pH} = 3.5$$

Calculate the pH at 50.00 ml NaOH added.

This is the equivalence pt, the point in the titration where you have added precisely enough base to react with the acid. The product of the reaction is water. Thus, the pH = 7

Calculate the pH at 50.50 ml NaOH added.

After the equivalence point, the excess OH⁻ determines the pH.

$$\text{mmoles of excess OH}^- = \text{mole OH}^-(\text{added}) - \text{mol OH}^-(\text{equiv})$$

$$= 50.50(0.0500) - 50.00(0.0500) = 0.025 \text{ mmol OH}^-$$

$$[\text{OH}^-] = (0.025 \text{ mmol}) / (25.00\text{ml} + 50.50\text{ml}) = 3.3 \times 10^{-4} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 3.1 \times 10^{-11} \text{ M, pH} = 10.52$$

Calculate the pH at 60.00 ml NaOH added.

After the equivalence point, the excess OH⁻ determines the pH.

$$\text{mmoles of excess OH}^- = \text{mole OH}^-(\text{added}) - \text{mol OH}^-(\text{equiv})$$

$$= 60.00(0.0500) - 50.00(0.0500) = 0.500 \text{ mmol OH}^-$$

$$[\text{OH}^-] = (0.500 \text{ mmol}) / (25.00\text{ml} + 60.00\text{ml}) = 5.88 \times 10^{-4} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 1.72 \times 10^{-12} \text{ M, pH} = 11.765$$

Strong base with strong acid

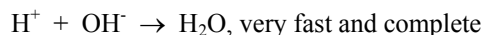
Titrate 50.00 ml of a 0.100 M NaOH solution with 0.200 M HBr.

Calculate the pH at 0.00 ml NaOH added

$$[\text{H}_3\text{O}^+] = K_w / 0.100 = 1.00 \times 10^{-13} \text{ M}$$

$$\text{pH} = -\log(1.00 \times 10^{-13}) = 13.000$$

Calculate the pH at 5.00 ml HBr added.



$$\text{mmol of H}^+ \text{ added} = (5.00\text{ml})(0.200) = 1.00 \text{ mmol}$$

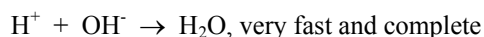
$$\text{initial mmol OH}^- = (50.00\text{ml})(0.100) = 5.00 \text{ mmol}$$

$$\text{final mmol H}^+ = 5.00 - 1.00 = 4.00 \text{ mmol}$$

$$[\text{OH}^-] = (4.00 \text{ mmol}) / (50.00 + 5.00) = 0.0727 \text{ M}$$

$$\text{pH} = 12.857$$

Calculate the pH at 15.00 ml HBr added.



$$\text{mmol of H}^+ \text{ added} = (15.00\text{ml})(0.200) = 3.00 \text{ mmol}$$

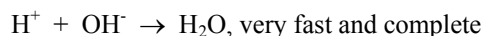
$$\text{initial mmol OH}^- = (50.00\text{ml})(0.100) = 5.00 \text{ mmol}$$

$$\text{final mmol H}^+ = 5.00 - 3.00 = 2.00 \text{ mmol}$$

$$[\text{OH}^-] = (2.00 \text{ mmol}) / (50.00 + 15.00) = 0.0308 \text{ M}$$

$$\text{pH} = 12.483$$

Calculate the pH at 24.50 ml HBr added.



$$\text{mmol of H}^+ \text{ added} = (24.50\text{ml})(0.200) = 4.90 \text{ mmol}$$

$$\text{initial mmol OH}^- = (50.00\text{ml})(0.100) = 5.00 \text{ mmol}$$

$$\text{final mmol H}^+ = 5.00 - 4.90 = 0.10 \text{ mmol}$$

$$[\text{OH}^-] = (0.10 \text{ mmol}) / (50.00 + 24.5) = 0.0013 \text{ M}$$

$$\text{pH} = 11.12$$

Calculate the pH at 25.00 ml HBr added.

This is the equivalence pt, the point in the titration where you have added precisely enough base to react with the acid. The product of the reaction is water. Thus, the pH = 7

Calculate the pH at 25.50 ml HBr added.

After the equivalence point, the excess H^+ determines the pH.

$$\text{mmoles of excess H}^+ = \text{mole H}^+(\text{added}) - \text{mol H}^+(\text{equiv})$$

$$= 25.50(0.200) - 25.00(0.200) = 0.10 \text{ mmol H}^+$$

$$[\text{H}^+] = (0.10 \text{ mmol}) / (50.00\text{ml} + 25.50\text{ml}) = 1.3 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.88$$

Calculate the pH at 30.00 ml HBr added.

After the equivalence point, the excess H^+ determines the pH.

$$\text{mmoles of excess H}^+ = \text{mole H}^+(\text{added}) - \text{mol H}^+(\text{equiv})$$

$$= 30.00(0.200) - 25.00(0.200) = 1.00 \text{ mmol H}^+$$

$$[\text{H}^+] = (1.00 \text{ mmol}) / (50.00\text{ml} + 30.00\text{ml}) = 1.25 \times 10^{-2} \text{ M}$$

$$\text{pH} = 1.903$$

Weak acid titrations

12-6

100.0 ml of a solution of 0.100 M weak acid, HA, is titrated with 1.00 M KOH. ($K_a = 1.0 \times 10^{-5}$)

@ 0 ml added

$$K_a = [H^+]^2/0.1 = 1.0 \times 10^{-5}$$
$$[H^+] = 1.0 \times 10^{-3}$$
$$pH = 3.00$$

@ 1.00 ml added

$$OH^- \text{ added} = (1.00 \text{ M}) \cdot (1.00 \text{ ml}) = 1.00 \text{ mmol } OH^-$$
$$HA + OH^- \rightarrow A^- + H_2O \text{ (to completion/or near to)}$$
$$pH = pK_a + \log(\text{mol } A^- / \text{mol } HA)$$
$$\text{mol } A^- = 1.00 \text{ mmol}$$
$$\text{mol } HA = (100.0 \text{ ml} \cdot 0.100 \text{ M}) - 1.00 \text{ mol} = 9.00 \text{ mmol}$$
$$pH = 5.00 + \log(1/9) = 4.05$$

@ 5.00 ml added

$$OH^- \text{ added} = (1.00 \text{ M}) \cdot (5.00 \text{ ml}) = 5.00 \text{ mmol } OH^-$$
$$HA + OH^- \rightarrow A^- + H_2O \text{ (to completion/or near to)}$$
$$pH = pK_a + \log(\text{mol } A^- / \text{mol } HA)$$
$$\text{mol } A^- = 5.00 \text{ mmol}$$
$$\text{mol } HA = (100.0 \text{ ml} \cdot 0.500 \text{ M}) - 5.00 \text{ mol} = 5.00 \text{ mmol}$$
$$pH = 5.00 + \log(5/5) = 5.00$$

@ 9.00 ml added

$$OH^- \text{ added} = (1.00 \text{ M}) \cdot (9.00 \text{ ml}) = 9.00 \text{ mmol } OH^-$$
$$HA + OH^- \rightarrow A^- + H_2O \text{ (to completion/or near to)}$$
$$pH = pK_a + \log(\text{mol } A^- / \text{mol } HA)$$
$$\text{mol } A^- = 9.00 \text{ mmol}$$
$$\text{mol } HA = (100.0 \text{ ml} \cdot 0.500 \text{ M}) - 9.00 \text{ mol} = 1.00 \text{ mmol}$$
$$pH = 5.00 + \log(9/1) = 5.95$$

@ 9.90 ml added

$$OH^- \text{ added} = (1.00 \text{ M}) \cdot (9.90 \text{ ml}) = 9.90 \text{ mmol } OH^-$$
$$HA + OH^- \rightarrow A^- + H_2O \text{ (to completion/or near to)}$$
$$pH = pK_a + \log(\text{mol } A^- / \text{mol } HA)$$
$$\text{mol } A^- = 9.90 \text{ mmol}$$
$$\text{mol } HA = (100.0 \text{ ml} \cdot 0.500 \text{ M}) - 9.90 \text{ mol} = 0.10 \text{ mmol}$$
$$pH = 5.00 + \log(9.9/.1) = 7.00$$

@ 10.00 ml added

$$OH^- \text{ added} = (1.00 \text{ M}) \cdot (10.00 \text{ ml}) = 10.00 \text{ mmol } OH^-$$
$$HA + OH^- \rightarrow A^- + H_2O \text{ (to completion/or near to)}$$
$$pH = pK_a + \log(\text{mol } A^- / \text{mol } HA)$$
$$\text{mol } A^- = 10.00 \text{ mmol}$$
$$\text{mol } HA = (100.0 \text{ ml} \cdot 0.500 \text{ M}) - 10.0 \text{ mol} = 0 \text{ mmol}$$

This is the equivalence point. The appropriate equilibrium is the K_b reaction for A^- .



$$F_{A^-} = (10.00 \text{ mmol}) / (110.0 \text{ ml}) = 0.0909 \text{ M}$$
$$K_b = K_w / K_a = 1.00 \times 10^{-9} = [HA][OH^-] / (F_{A^-} - [HA])$$

Assume $[OH^-] = [HA]$, and let $[HA] = x$

Assume $F_{A^-} \cong [A^-]$

$$\begin{aligned}1.00 \cdot 10^{-9} &= x^2 / (0.0909) \\x &= [OH^-] = 9.53 \cdot 10^{-5} \text{ M} \\[H_3O]^+ &= 1.05 \cdot 10^{-9} \\pH &= 8.98\end{aligned}$$

@ 10.10 ml After the equiv. point the excess OH^- is what controls the pH.

$$\begin{aligned}[OH^-] &= [(10.10 \text{ ml KOH})(1.00 \text{ M KOH}) - (\text{mmol } HA_{\text{initial}})] / V_t \\&= [10.10 - 10.0] / (110.10) = 9 \cdot 10^{-4} \text{ M} \\pH &= 11.0\end{aligned}$$

@ 12.00 ml After the equiv. point the excess OH^- is what controls the pH.

$$\begin{aligned}[OH^-] &= [(12.00 \text{ ml KOH})(1.00 \text{ M } OH^-) - (\text{mmol } HA_{\text{initial}})] / V_t \\&= [12.00 - 10.0] / (112.00) = 1.80 \cdot 10^{-2} \text{ M} \\pH &= 12.25\end{aligned}$$

Weak base titration

20.0 ml of a solution of 0.200 M weak base, B, is titrated with 0.0500 M HClO. ($K_a(HB^+) = 1.00 \cdot 10^{-5}$)

@ 0 ml added

$$\begin{aligned}K_b &= [OH^-]^2 / 0.200 = 1.00 \cdot 10^{-9} \\[OH^-] &= 4.47 \cdot 10^{-5} \text{ M}, [H^+] = 2.26 \cdot 10^{-10} \text{ M} \\pH &= 9.646\end{aligned}$$

@ 5.00 ml added

$$\begin{aligned}H^+ \text{ added} &= (0.0500 \text{ M}) \cdot (5.00 \text{ ml}) = 0.250 \text{ mmol } H^+ \\B + H^+ &\rightarrow BH^+ \text{ (to completion/or near to)} \\pH &= pK_a + \log(\text{mol B} / \text{mol } BH^+) \\&\quad \text{mol } BH^+ = 0.250 \text{ mmol} \\&\quad \text{mol B} = (20.0 \text{ ml} \cdot 0.200 \text{ M}) - 0.250 \text{ mol} = 3.75 \text{ mmol} \\pH &= 5.000 + \log(3.75 / 0.250) = 6.176\end{aligned}$$

@ 20.00 ml added

$$\begin{aligned}H^+ \text{ added} &= (0.0500 \text{ M}) \cdot (20.00 \text{ ml}) = 1.00 \text{ mmol } H^+ \\B + H^+ &\rightarrow BH^+ \text{ (to completion/or near to)} \\pH &= pK_a + \log(\text{mol B} / \text{mol } BH^+) \\&\quad \text{mol } BH^+ = 1.00 \text{ mmol} \\&\quad \text{mol B} = (20.0 \text{ ml} \cdot 0.200 \text{ M}) - 1.00 \text{ mol} = 3.00 \text{ mmol} \\pH &= 5.000 + \log(3 / 1) = 5.477\end{aligned}$$

@ 40.00 ml added (1/2 way)

$$\begin{aligned}H^+ \text{ added} &= (0.0500 \text{ M}) \cdot (40.00 \text{ ml}) = 2.00 \text{ mmol } H^+ \\B + H^+ &\rightarrow BH^+ \text{ (to completion/or near to)} \\pH &= pK_a + \log(\text{mol B} / \text{mol } BH^+) \\&\quad \text{mol } BH^+ = 2.00 \text{ mmol} \\&\quad \text{mol B} = (20.0 \text{ ml} \cdot 0.200 \text{ M}) - 2.00 \text{ mol} = 2.00 \text{ mmol} \\pH &= 5.000 + \log(2 / 2) = 5.000\end{aligned}$$

@ 60.00 ml added

$$\begin{aligned}H^+ \text{ added} &= (0.0500 \text{ M}) \cdot (60.00 \text{ ml}) = 3.00 \text{ mmol } H^+ \\B + H^+ &\rightarrow BH^+ \text{ (to completion/or near to)}\end{aligned}$$

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log(\text{mol B/mol BH}^+) \\ \text{mol BH}^+ &= 3.00 \text{ mmol} \\ \text{mol B} &= (20.0 \text{ ml} \cdot 0.200 \text{ M}) - 3.00 \text{ mol} = 1.00 \text{ mmol} \\ \text{pH} &= 5.000 + \log(1/3) = 4.523 \end{aligned}$$

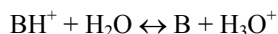
@ 70.00 ml added

$$\begin{aligned} \text{H}^+ \text{ added} &= (0.0500\text{M}) \cdot (70.00 \text{ ml}) = 3.50 \text{ mmol H}^+ \\ \text{B} + \text{H}^+ &\rightarrow \text{BH}^+ \text{ (to completion/or near to)} \\ \text{pH} &= \text{pK}_a + \log(\text{mol B/mol BH}^+) \\ \text{mol BH}^+ &= 3.50 \text{ mmol} \\ \text{mol B} &= (20.0 \text{ ml} \cdot 0.200 \text{ M}) - 3.50 \text{ mol} = 0.50 \text{ mmol} \\ \text{pH} &= 5.000 + \log(0.50/3.50) = 4.16 \end{aligned}$$

@ 79.50 ml added

$$\begin{aligned} \text{H}^+ \text{ added} &= (0.0500\text{M}) \cdot (79.50 \text{ ml}) = 3.98 \text{ mmol H}^+ \\ \text{B} + \text{H}^+ &\rightarrow \text{BH}^+ \text{ (to completion/or near to)} \\ \text{pH} &= \text{pK}_a + \log(\text{mol B/mol BH}^+) \\ \text{mol BH}^+ &= 3.98 \text{ mmol} \\ \text{mol B} &= (20.0 \text{ ml} \cdot 0.200 \text{ M}) - 3.98 \text{ mol} = 0.02 \text{ mmol} \\ \text{pH} &= 5.000 + \log(0.02/3.98) = 2.7 \end{aligned}$$

@ 80.00 ml added
This is the equivalence point. The appropriate equilibrium is the K_a reaction for BH^+ .



$$\begin{aligned} F_{\text{BH}^+} &= (4.000 \text{ mmol}) / (100.0 \text{ ml}) = 0.0400 \text{ M} \\ K_a &= 1.00 \cdot 10^{-5} = [\text{B}][\text{H}_3\text{O}^+] / (F_{\text{BH}^+} - [\text{B}]) \\ \text{Assume } [\text{H}_3\text{O}^+] &= [\text{B}], \text{ and let } [\text{B}] = x \\ \text{Assume } F_{\text{BH}^+} &\cong [\text{BH}^+] \\ 1.000 \cdot 10^{-5} &= x^2 / (0.04000) \\ x = [\text{H}_3\text{O}^+] &= 6.325 \cdot 10^{-4} \text{ M} \\ \text{pH} &= 3.199 \end{aligned}$$

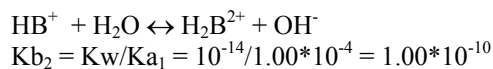
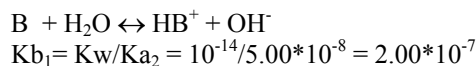
Why is the pH higher than what we calculated at 79.50 ml added?

@ 90.00 ml After the equiv. point the excess H^+ is what controls the pH.

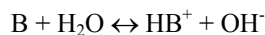
$$\begin{aligned} [\text{H}^+] &= [(10.0 \text{ ml HOCl})(0.0500 \text{ M HOCl}) / V_t \\ &= [(0.500) / (110.00)] = 4.556 \cdot 10^{-3} \text{ M} \\ \text{pH} &= 2.34 \end{aligned}$$

Polyprotics titrations

Titrate 40.0 ml of a 0.100 M diprotic base (B) solution with 0.100 M HCl ($K_{a1} = 1.00 \cdot 10^{-4}$ and $K_{a2} = 5.00 \cdot 10^{-8}$)



@ 0 ml added



$$F_B = 0.100 \text{ M}$$

Assume $[\text{OH}^-] = [\text{HB}^+]$, and let $[\text{HB}^+] = x$

$$\text{Assume } F_A \cong [\text{B}] = 0.100 \text{ M}$$

$$2.00 \times 10^{-7} = x^2/(0.100)$$

$$x = [\text{OH}^-] = 1.41 \times 10^{-4} \text{ M}, \alpha_{\text{BH}^+} = 0.0014 \text{ (apprx. valid)}$$

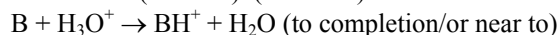
$$[\text{H}_3\text{O}^+] = 7.16 \times 10^{-11} \text{ M}$$

$$\text{pH} = 10.15$$

@ 10.00 ml added

$$\text{p}K_{a2} = 7.301$$

$$\text{H}^+ \text{ added} = (0.100 \text{ M}) \times (10.00 \text{ ml}) = 1.00 \text{ mmol H}^+$$



$$\text{pH} = \text{p}K_a + \log(\text{mol P/mol HP}^+)$$

$$\text{mol BH}^+ = 1.00 \text{ mmol}$$

$$\begin{aligned} \text{mol B} &= (40.0 \text{ ml} \times 0.100 \text{ M}) - 1.00 \text{ mol} \\ &= 3.00 \text{ mmol} \end{aligned}$$

$$\text{pH} = 7.301 + \log(3/1) = 7.778$$

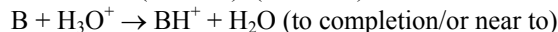
@ 20 ml we are half way to the first equivalence point

$$\text{pH} = \text{p}K_{a2} = 7.301$$

@ 30 ml added

$$\text{p}K_{a2} = 7.301$$

$$\text{H}^+ \text{ added} = (0.100 \text{ M}) \times (30.00 \text{ ml}) = 3.00 \text{ mmol H}^+$$



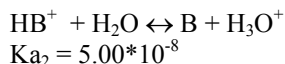
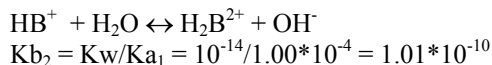
$$\text{pH} = \text{p}K_a + \log(\text{mol B/mol HB}^+)$$

$$\text{mol BH}^+ = 3.00 \text{ mmol}$$

$$\begin{aligned} \text{mol B} &= (40.0 \text{ ml} \times 0.100 \text{ M}) - 3.00 \text{ mol} \\ &= 1.00 \text{ mmol} \end{aligned}$$

$$\text{pH} = 7.301 + \log(1/3) = 6.824$$

@ 40 ml added we have reached the first equivalence point, and the dominant species is therefore BH^+ . This is an intermediate species that can act as both an acid and a base.



$$[\text{H}^+] = [(K_1 K_2 F + K_1 K_w)/(K_1 + F)]^{0.5}$$

$$F = (40 \text{ ml})(0.100)/(80 \text{ ml}) = 0.05 \text{ M}$$

$$K_1 = 1.00 \times 10^{-4}$$

$$K_2 = 5.00 \times 10^{-8}$$

$$K_w = 1.01 \cdot 10^{-14}$$

After simplifying

$$[H^+] = (K_1 K_2)^{0.5} = 2.24 \cdot 10^{-6} \text{ (strictly } \rightarrow 2.23 \cdot 10^{-6} \text{ M)}$$

$$pH = 5.651$$

@ 50.00 ml added

$$pK_{a1} = 4.000$$

$$H^+ \text{ added (after eq pt)} = (0.100M) \cdot (10.00 \text{ ml}) = 1.00 \text{ mmol}$$

$$HB^+ + H_3O^+ \rightarrow H_2B^{2+} + H_2O \text{ (to completion/or near to)}$$

$$pH = pK_{a1} + \log(\text{mol } HB^+ / \text{mol } H_2B^{2+})$$

$$\begin{aligned} \text{mol } H_2B^{2+} &= 1.00 \text{ mmol} \\ \text{mol } HB^+ &= (40.0 \text{ ml} \cdot 0.100 \text{ M}) - 1.00 \text{ mol} \\ &= 3.00 \text{ mmol} \end{aligned}$$

$$pH = 4.000 + \log(3/1) = 4.477$$

@ 60 ml we are half way to the second equivalence point

$$pH = pK_{a2} = 4.000 @ 60.00 \text{ ml added}$$

@ 70 ml added

$$pK_{a1} = 4.000$$

$$H^+ \text{ added (after eq pt)} = (0.100M) \cdot (30.00 \text{ ml}) = 3.00 \text{ mmol}$$

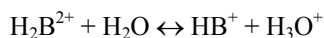
$$HB^+ + H_3O^+ \rightarrow H_2B^{2+} + H_2O \text{ (to completion/or near to)}$$

$$pH = pK_{a1} + \log(\text{mol } HB^+ / \text{mol } H_2B^{2+})$$

$$\begin{aligned} \text{mol } H_2B^{2+} &= 3.00 \text{ mmol} \\ \text{mol } HB^+ &= (40.0 \text{ ml} \cdot 0.100 \text{ M}) - 3.00 \text{ mol} \\ &= 1.00 \text{ mmol} \end{aligned}$$

$$pH = 4.000 + \log(1/3) = 3.523$$

@ 80 ml we hit the second equivalence point. The dominant species is H_2B^{2+} . We can find the pH by examining the hydrolysis of this species.



$$F_{H_2B^{2+}} = (40.0 \text{ ml} \cdot 0.100 \text{ M}) / (120.0 \text{ ml}) = 0.0333 \text{ M}$$

$$K_a = 1.00 \cdot 10^{-4} = [HB^+][H^+] / (F_{H_2B^{2+}} - [HB^+])$$

Assume $[H_3O^+] = [HB^+]$, and let $[HB^+] = x$

Assume $F_{B^+} \cong [H_2B^{2+}]$

$$1.00 \cdot 10^{-4} = x^2 / (0.0333)$$

$$x = [H_3O^+] = 1.82 \cdot 10^{-3} \text{ M (approx. failed!!!)}$$

$$pH = 2.739$$

$$1.00 \cdot 10^{-4} = x^2 / (0.0333 - x)$$

$$x = [H_3O^+] = 1.776 \cdot 10^{-3} \text{ M}$$

$$pH = 2.751$$

@ 90.0 ml

$$[H^+] = (10.0 \text{ ml}) \cdot (0.100) / (90 \text{ ml} + 40 \text{ ml})$$

$$= 7.69 \cdot 10^{-3} \text{ M}$$

$$pH = 2.114$$

@ 100.0 ml added

$$[\text{H}^+] = (20.0 \text{ ml}) \cdot (.100) / (90 \text{ ml} + 50 \text{ ml}) \\ = 1.43 \cdot 10^{-2} \text{ M} \\ \text{pH} = 1.845$$

Primary Standards

KHP

Indicators

First derivative plots (ΔpH vs. ΔV) and second derivative plots ($\Delta(\Delta\text{pH}/\Delta V)/\Delta V$)

Leveling effect

HClO_4 and HCl (in water) are both strong acids

HClO_4 and HCl (in acetic acid) are weak acids of different strengths.

$$K(\text{HClO}_4) = 1.3 \cdot 10^{-5}$$

$$K(\text{HCl}) = 2.8 \cdot 10^{-9}$$

This is because acetic acid is less basic than water

Titration Spreadsheet (Do Problem 12-66)