ACID-BASE EQUILIBRIUM
4: ACID BASE TITRATIONS

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ACID BASE TITRATION - INTRODUCTION

Titration is the addition of a solution of known concentration to a solution of unknown concentration until end point.

- Titrations help us to determine initial or final concentration of solutions.
- We can use titrations to determine the concentration of unknown acid or base solutions.
- We can determine the pH of the final solution or at any point during the titration.
- pH curves can be drawn of titrations to help understand nature of solutions.

TERMS USED IN TITRATIONS

Some key terms of an acid base titration are:

- **Standard solution** - Solution with known concentration.
- **Titrant** – The solution placed in the burette.
- **Equivalence point** – The point when stoichiometrically equivalent amounts of acid-base have been added.
- **End point** – The point at which titration is finished (usually determined with the help of an indicator).
- **Indicator** – A chemical that changes color at the end point at a specific pH range. Indicator is chosen either using a pH curve or by knowing the acid-base strength. (In some acid base titrations end point is the same as equivalence point).

TYPES OF ACID BASE TITRATIONS

Depending on the type of acids and bases used in the titration, the pH can be different at the "end point"; however, at equivalence point the pH will be 7. Titration graphs can help us find exact equivalence points.

- Strong acid – strong base

  $$HCl + NaOH \longrightarrow NaCl + H_2O$$

  final products are neutral (pH = 7)

  adding one drop more of the titrant will drastically change the pH.

- Weak acid – strong base

  $$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

  final products are basic (pH > 7)

- Strong acid – weak base

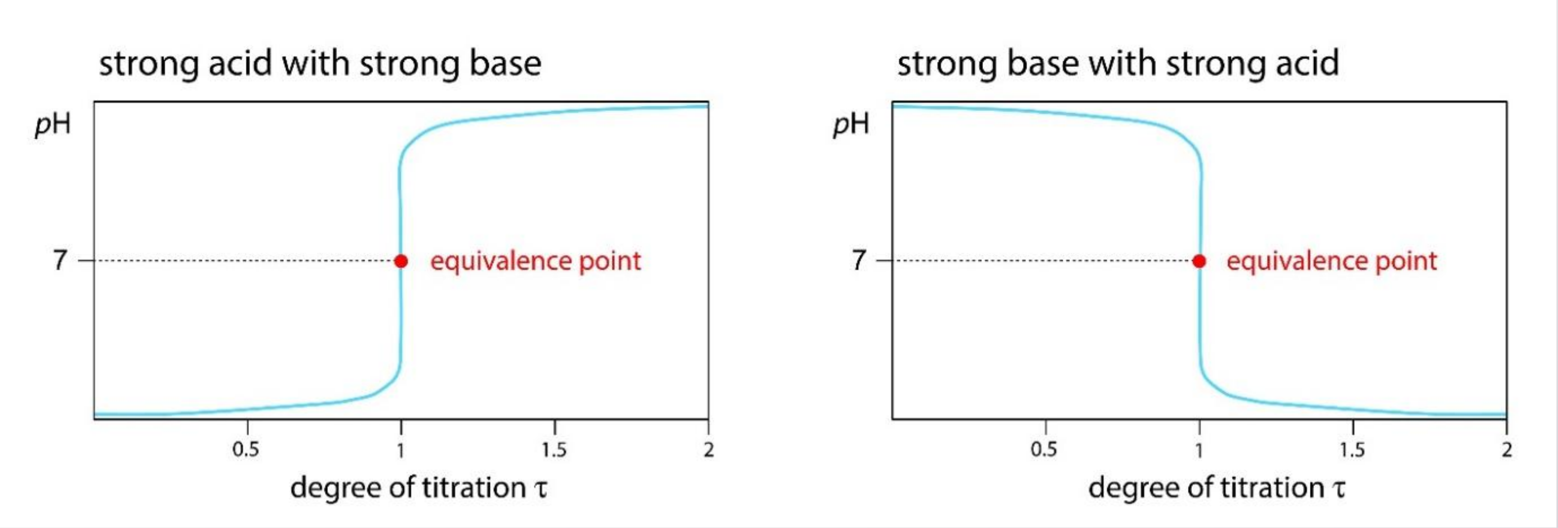
  $$HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$$

  final products are acidic (pH < 7)

TITRATION GRAPH: SA + SB

Strong acid base titration graphs are simple. The graph starts with either low pH (adding base to acid) or high pH (adding acid to base), and at the equivalence point the graph is a straight line. This straight line part of the curve is large because the pH can change drastically with the addition of a drop of acid or base.

At equivalent point, the pH is 7, which is also the center of the straight line on graph, which is also the end point (change of color of indicator).



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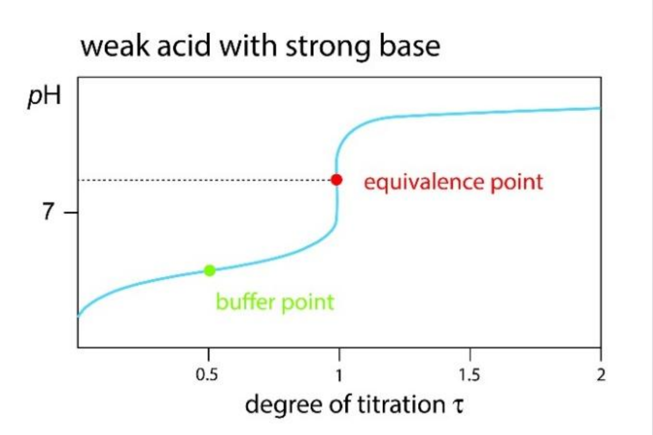
TITRATION GRAPH: WA+SB AND SA+WB

In these titrations the end point may not be equivalence point which may not be pH 7 as weak acids give strong conjugate base (pH > 7) and weak bases give strong conjugate acids (pH < 7).

<u>Weak Acid + Strong Base</u>: In this case (graph on the right), pH starts low and changes slowly as the base is added, until the pH does not change which is the equivalence point. The center of that straight line has a pH > 7 because of the strong conjugate base formed.



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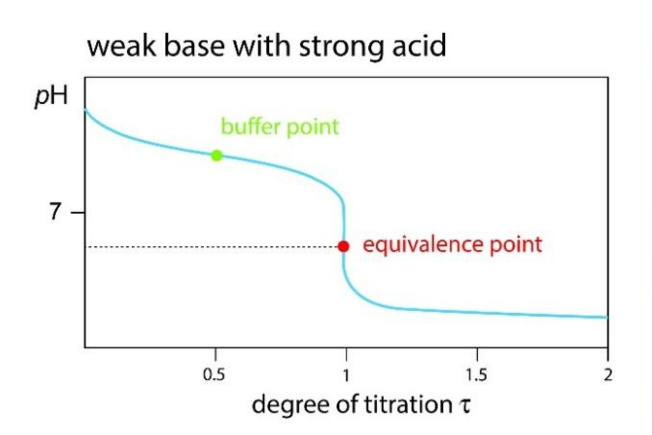
<u>Weak Base + Strong Acid</u>: In this case (graph on the right), pH starts high and changes slowly as the acid is added, until the pH does not change, which is the equivalence point. The center of that straight line has a pH < 7 because of the strong conjugate acid formed.



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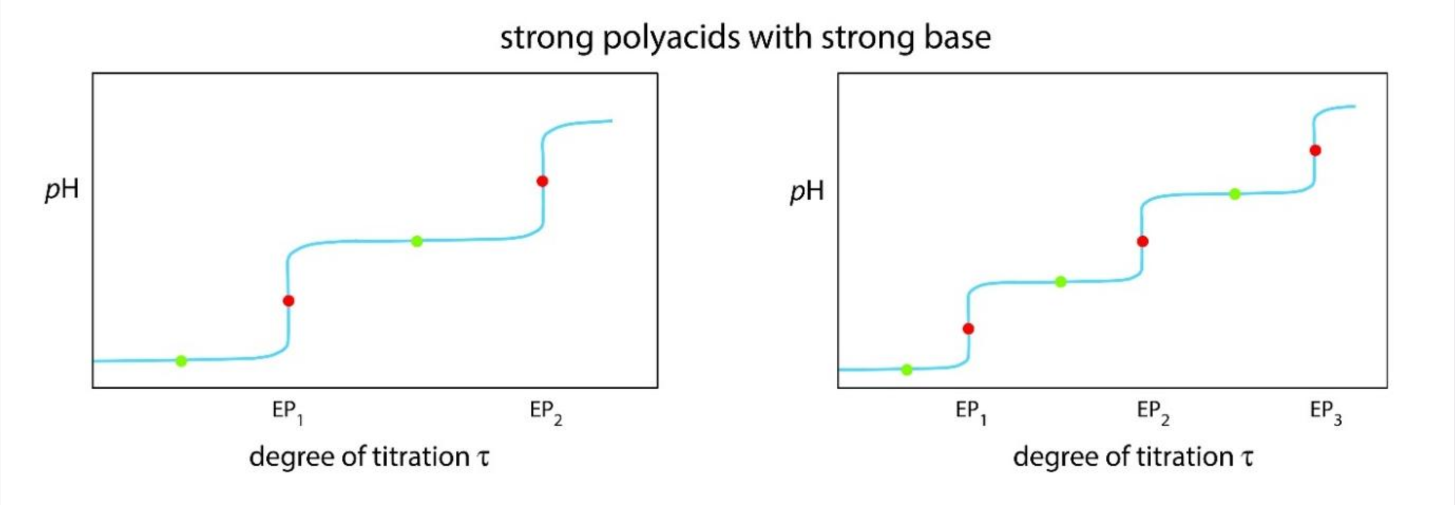
TITRATION GRAPH: POLYPROTIC ACIDS

Polyprotic acids start as strong acids but get weaker by the second and third proton ionization. In these titrations there are multiple curves in the graph that mark the different equivalence points. The center of each straight line is the equivalent point which can vary as the of the strong conjugate base formed.

The graphs below are of polyprotic acid titrated with a strong base.



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TITRATION CALCULATIONS

Strong Acid + Strong Base: In this titration, all of the acid or base is neutralized since there is no equilibrium. We can calculate mols of each chemical, find the excess mols, divide by total volume to find new concentration and finally calculate pH (or pOH or pH), depending on whether the acid or base was in excess. We have also used the equation on the right to calculate unknown concentrations in titrations.

$$\boxed{\frac{M_a V_a}{n_a} = \frac{M_b V_b}{n_b}}$$

Strong Acid + Weak Base and Weak Acid + Strong Base: In these titrations there is equilibrium. Mols of acid or base are subtracted and added to either side of the equilibrium. Using the new concentrations, pH or pOH can be calculated.

In these titrations there are a few things to help with pH calculations:

1) For small acid base additions, use the Henderson Hasselback equation.
2) For halfway point half [acid] has been neutralized to give equal concentration of [base]), so pH = pKa. (*Easiest calculation to do!*)
3) For equivalence point, all acid or base has been converted to the corresponding acidic or basic salt. We calculate pH of the salt. (*Which we have done in section 4 of Acids and Bases*).

EXAMPLE 1: SA-SB TITRATION

Calculate the pH of a solution in which 10.0 mL of 0.100 M HCl is added to 25.0 mL of 0.100 M NaOH.

Answer:

a) Calculate the mols of HCl and NaOH, b) then subtract the two to find excess mols; c) add the volumes; d) determine the new concentration and e) determine pH.

The overall reaction is: $HCl_{(aq)} + NaOH_{(aq)} \longrightarrow H_2O_{(l)} + NaCl_{(aq)}$

a) Moles HCl = (0.100 M)(10.0×10^{-3} L) = 1.00×10^{-3} mol (less mols)

Moles NaOH = (0.100 M)(25.0×10^{-3} L) = 2.50×10^{-3} mol

b) All of the HCl reacts, ($2.5 \times 10^{-3} - 1.00 \times 10^{-3}$) = 1.50×10^{-3} mol NaOH.

c) New volume is 10.0 mL + 25.0 mL = 35.0 mL = 0.0350 L

d) New conc of [OH-]

$$[\mathrm{OH^-}] = \frac{1.50 \times 10^{-3}\ \mathrm{mol}}{35.0 \times 10^{-3}\ \mathrm{L}} = 4.29 \times 10^{-2}\ \mathrm{M}$$

$$\mathrm{pOH} = -\log(4.29 \times 10^{-2}) = 1.36$$

e) pH

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.368 = \boxed{12.6}$$

EXAMPLE 2: WA + SB TITRATION

What is the $[OH^-]$ and the pH at equivalence point in the titration of a 500.0 mL 0.100 M propionic acid (HPr) and 0.050 M $Ca(OH)_2$. $K_a = 1.3 \times 10^{-5}$

Answer: At equivalence point all of acid is neutralized to give only conjugate base in the solution. Eventually this is a calculation of salt solution (as in section 16-2). a) Calculate mols of propionic acid; b) find volume of $Ca(OH)_2$ needed for titration; c) find new volume; d) use ICE method to find pH.

Mols propionic acid = (0.10 *M*)($500. \times 10^{-3}$ L) = 0.050 mol HPr

$2HPr + Ca(OH)_2 \rightarrow Ca(Pr)_2 + 2H_2O$ *(write equation for mol ratio!)*

Mols $Ca(OH)_2$ =

$$0.050\text{ mol HPr} \times \frac{1\text{ mol Ca(OH)}_2}{2\text{ mol HPr}} = \mathbf{0.025\ \boldsymbol{mol\ Ca(OH)_2}}$$

$$\text{Volume Ca(OH)}_2 = \frac{0.025\text{ mol}}{0.050\ \frac{\text{mol}}{\text{L}}} = \mathbf{0.50\ \boldsymbol{L}}$$

The new volume is 0.50 L + 0.50 L = **1.00 L**

The mols of conjugate base Pr^- formed is 0.050 mol (from initial HPr conc.)

New conc. of

$$[\text{Pr}^-] = \frac{0.050\text{ mol}}{1.0\text{ L}} = 5.0 \times 10^{-2}\text{ M} = \mathbf{0.050\ \boldsymbol{M}}$$

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EXAMPLE 1: WA + SB TITRATION CONTD…

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Reaction: $Pr^-_{(aq)} + H_2O_{(aq)} \rightleftharpoons HPr_{(aq)} + OH^-_{(aq)}$

Initial	0.050		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.050 - x$		x	x

Since K_a was given, we have to calculate K_b, because there is only conjugate base present at equivalent point giving OH^- in solution

$\boxed{K_w = K_a \times K_b}$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}$$

$$K_b = \frac{[HPr]\,[OH^-]}{[Pr^-]} \qquad 7.7 \times 10^{-10} = \frac{x^2}{(0.050 - x)} = \frac{x^2}{0.050}$$

$$x = \sqrt{(7.7 \times 10^{-10})(0.05)} = 6.20 \times 10^{-6}\ M$$

$$[OH^-] = x = 6.20 \times 10^{-6}\ M$$

$\boxed{pOH = 5.21}$

$\boxed{pH = 8.79}$

EXAMPLE 2: TITRATION WA + SB

Calculate the pH in the titration of 50.0 mL of 0.100 M HCN acid with 0.150 M NaOH, when a) 6.00 mL NaOH is added, b) at halfway point and c) at equivalence point. ($K_a = 6.2 \times 10^{-10}$)

Answer:

a) We will calculate it two ways; using K_a constant and also using the Hendersen-Hasselback equation, like a buffer solution. (*I like the second one*).

b) This is when half HCN is neutralized and thus equal amount of conj base is formed.

c) At eq. point is when all acid is neutralized and all conj base is present. This is weak salt calculation, but we need the total volume of solution to know the new conc. of the conj. base.

EXAMPLE 2: TITRATION WA + SB – PART A

a) 6.00 mL NaOH is added

$$HCN_{(aq)} + OH^-_{(aq)} \rightleftharpoons CN^-_{(aq)} + H_2O_{(l)}$$

Initial	50 mL × 0.1 M = 5 mmol	6 L × 0.15 M = 0.9 mmol	0
Change	5 – 0.9 mmol	-0.9 mmol	+ 0.9 mmol
Eq. conc	4.1 mmol ÷ (50 + 6 mL) = 0.0732 M	0	0.9 mmol ÷ (50 + 6 mL) = 0.01607 M

$$HCN_{(aq)} + H_2O_{(aq)} \rightleftharpoons CN^-_{(aq)} + H_3O^+_{(aq)}$$

0.0732 M 0.01607 x

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

$$6.2 \times 10^{-10} = \frac{x\,(0.01607)}{(0.0732 - x)} = \frac{x}{0.0732}$$

Ignore x

$$[H_3O^+] = x = \frac{6.20 \times 10^{-10} \times 0.0732\ \text{M}}{0.01607\ M} = 2.72 \times 10^{-9}$$

$$pH = -\log\left(2.72 \times 10^{-9}\right) = \boxed{8.56}$$

Second way: Use the new concentrations of acid and conj. base and the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$pH = -\log 6.2 \times 10^{-10} + \log\frac{[0.01607\ M]}{[0.0732\ M]}$$

$$pH = 9.21 + (-0.64) = \boxed{8.56}$$

EXAMPLE 2: TITRATION WA + SB – PART B

b) pH at halfway point.

$$HCN_{(aq)} + OH^-_{(aq)} \rightleftharpoons CN^-_{(aq)} + H_2O_{(aq)}$$

Half of HCN is neutralized and equal amount of CN^- is formed.

$[HCN] = [CN^-]$

$$\boxed{K_a = \frac{[H_3O^+]\,\cancel{[A^-]}}{\cancel{[HA]}}}$$

$K_a = [H_3O^+]$; pH = -log 6.2×10^{-10} = $\boxed{9.21}$

Side note:

At halfway point mols of HCN neutralized are 50 mL × 0.1 M ÷ 2 = 2.5 mmol

This means 2.5 mmol of NaOH have been added. The volume of NaOH added will be 2.5 mmol ÷ 0.15 M = 16.7 mL.

As the volume of base is increasing, pH is also increasing.

EXAMPLE 2: TITRATION WA + SB – PART C

c) pH at eq. point. $HCN_{(aq)} + OH^-_{(aq)} \rightleftharpoons CN^-_{(aq)} + H_2O_{(aq)}$

Only conj. base, CN-, will be present at this point. Calculate the [CN^-] by finding total volume. Mols is the same as HCN (5 mmol).

1. Initial mols of HCN = 5 mmol; 5 mmol of NaOH must have been added at eq. pt.
2. Volume of NaOH = 5 mmol ÷ 0.15mol/L NaOH = 33.3 mL
3. Total volume of solution = 50 mL HCN + 33.3 mL NaOH = 83.3 mL
4. [CN^-] = 5 mmol ÷ 83.3 mL =0.060 M
5. To set this up quickly remember that CN^- will now be the reactant as it is conj base, so we are going to be using K_b (not K_a). $HCN + H_2O \rightleftharpoons CN^- + H_3O^+$

$$K_b = \frac{1 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

$$\boxed{K_b = \frac{[HB^+][OH^-]}{[B]}} \quad 1.61 \times 10^{-5} = \frac{x^2}{0.060 - x}$$

$$x = \sqrt{(1.61 \times 10^{-5})(0.060)} = 9.84 \times 10^{-4}\ \text{M}$$

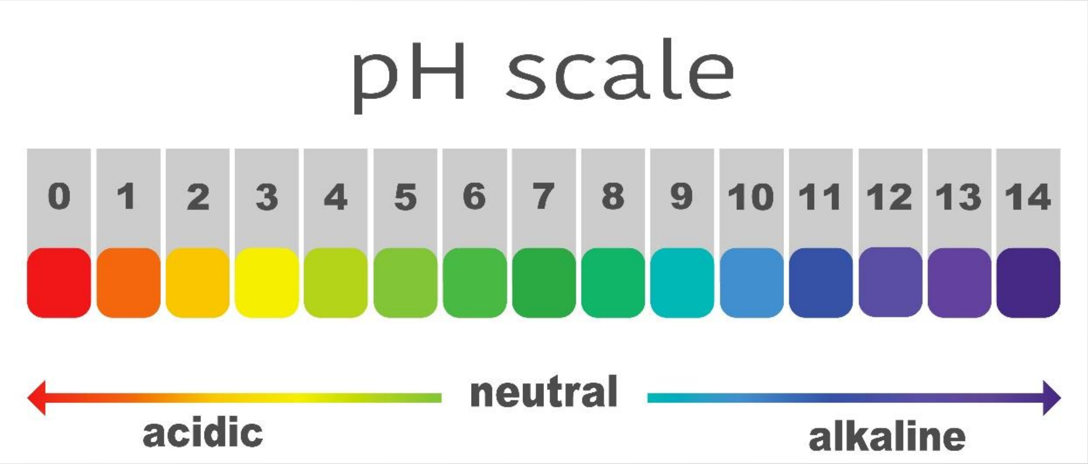
$$\text{pOH} = -\log(9.84 \times 10^{-4}) = 3.01$$

$$\text{pH} = 14 - \text{pOH} = 14 - 3.01 = 10.99 = \boxed{11.0}$$

INDICATORS

Indicators are weak acids or bases that ionize in acidic or basic conditions and change colors with ionizations.

- pH range can be different for different indicators (see next slide)
- Indicators are key in identifying the end point of a titration.
- The equivalence point must fall in the pH range of the indicator.
- Cabbage juice indicator (shown below) has a variety of colors at the different pH levels.



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INDICATORS

pH range and colors of common indicators.

	Color		
Indicator	**Acid**	**Base**	**pH Range**
Thymol blue	Red	Yellow	1.2-2.8
Bromophenol blue	Yellow	Blue purple	3.0-4.6
Methyl orange	Orange	Yellow	3.1-4.4
Methyl red	Red	Yellow	4.2-6.3
Chlorophenol blue	Yellow	Red	4.8-6.4
Bromothymol blue	Yellow	Blue	6.0-7.6
Cresol red	Yellow	Red	7.2-8.8
Phenolphthalein	Colorless	Reddish pink	8.3-10.0

KEY CONCEPTS

- Interpret titration graphs and identify type of titrations.
- Calculate pH of a strong acid-base titration.
- Calculate pH of strong/weak acid-strong/weak base titration.