Acids-Base equilibria

Application of Le Châtelier's principle to acid-base equilibria: **Common-ion effect**

$HF_{(aq)} + H_2O \leftrightarrow H_3O^+_{(aq)} + F^-_{(aq)}$

$NaF_{(aq)} \rightarrow Na^+_{(aq)} + F^-_{(aq)}$

Net result: $[H^+]$; pH

The system will respond by reacting in the reverse direction until it goes back to equilibrium

This shift in equilibrium position occurs because of the addition of ion already involved in the equilibrium is called the common ion effect

$NH_{3(aq)} + H_2O \leftrightarrow NH_4^+{}_{(aq)} + OH^-_{(aq)}$ $K_b = 1.8 \times 10^{-5}$

$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)}$

Net result: [OH-] ; pH

Calculate the pH and the percent dissociation of HF in a solution containing 1.0M HF (K_a = 7.2 x10^{-4}) and 1.0 NaF.

Compare to the pH of solution in the absence of NaF

Buffer solutions (Buffers)

A buffer solution is any solution that maintains an approximately constant pH despite small addition of acid or base

A buffer contains:

1. A weak acid and a weak base that are conjugate to one another

   EX:

   HF/NaF
   $HCN/NaCN$
   CH_3COOH/CH_3COONa
   $HCOOH/HCOONa$

   NH_4Cl/NH_3
   CH_3NH_3Cl/CH_3NH_2

2. Both components have to be in approximately equal amounts (i.e., their concentration should be similar)
3. Should be in substantial amounts (i.e., high concentrations)

$HA_{(aq)} + H_2O \leftrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$ K_a

$[H_3O^+]_{(aq)} = K_a \frac{[HA]_{eq}}{[A^-]_{eq}}$

If $\frac{[HA]_{eq}}{[A^-]_{eq}}$ is not altered too much, $[H_3O^+]$ will remain unchanged

$-\log([H_3O^+]_{(aq)}) = -\log(K_a) + \left(-\log\left(\frac{[HA]_{eq}}{[A^-]_{eq}}\right)\right)$

$pH = pK_a - \log\left(\frac{[HA]_{eq}}{[A^-]_{eq}}\right)$ Henderson-Hasselbalch eq

How does a buffer work ?

If 0.01M HCl is added into water, what is the pH of the solution?
If 0.01M HCl is added into buffer (1M HA and 1M A^-, K_a for HA = 1.77×10^{-4}) , what is the pH of the solution?

(a) Suppose 1.0 mole of HCOOH and 0.5 mol HCOONa are added to water and diluted to 1.0L, calculate the pH of the solution. ($K_a = 1.77 \times 10^{-4}$)

(b) Suppose 0.1 mole HCl is added into the above HCOOH/HCOONa solution, calculate the pH of the resulting solution.

Designing Buffer at specific pH values

Designing a Buffer at pH = 4.6

$$\text{pH} = \text{p}K_a - \log\left(\frac{[HA]_{eq}}{[A^-]_{eq}}\right)$$

1. Pick the acid-conjugate base pair with $\text{p}K_a$ close to 4.6

2. Adjust the relative ratio between acid and its conjugate base

Possible choices: $[CH_3COOH]$ $[CH_3COO^-]$

Buffer capacity: ability of a buffer to withstand added acids or bases (without being swamped)

Dissociation Constants of Some Acids at 25 °C[a]

Acid[b]	HA	A^-	K_a	pK_a
Perchloric	$HClO_4$	ClO_4^-	$\sim 10^{+8}$	~ -8
Permanganic	$HMnO_4$	MnO_4^-	$\sim 10^{+8}$	~ -8
Chloric	$HClO_3$	ClO_3^-	$\sim 10^{+3}$	~ -3
Nitric	HNO_3	NO_3^-		
Hydrobromic	HBr	Br^-		
Hydrochloric	HCl	Cl^-		
Sulfuric (1)	H_2SO_4	HSO_4^-		
Hydrated proton or protonated solvent	H^+	H_2O(solvent)	1.00	0.00
Trichloroacetic	CCl_3COOH	CCl_3COO^-	2×10^{-1}	0.70
Oxalic (1)	HOOC—COOH	$HOOC—COO^-$	5.9×10^{-2}	1.23
Dichloroacetic	$CHCl_2COOH$	$CHCl_2COO^-$	3.32×10^{-2}	1.48
Sulfurous (1)	H_2SO_3	HSO_3^-	1.54×10^{-2}	1.81
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.20×10^{-2}	1.92
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}	2.12
Bromoacetic	$CH_2BrCOOH$	CH_2BrCOO^-	2.05×10^{-3}	2.69
Malonic (1)	$HOOC—CH_2—COOH$	$HOOC—CH_2—COO^-$	1.49×10^{-3}	2.83
Chloroacetic	$CH_2ClCOOH$	CH_2ClCOO^-	1.40×10^{-3}	2.85
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Hydrofluoric	HF	F^-	3.53×10^{-4}	3.45
Formic	HCOOH	$HCOO^-$	1.77×10^{-4}	3.75
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.46×10^{-5}	4.19
Oxalic (2)	$HOOC—COO^-$	$^-OOC—COO^-$	6.4×10^{-5}	4.19
Acetic	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.75
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.34×10^{-5}	4.87
Malonic (2)	$HOOC—CH_2—COO^-$	$^-OCC—CH_2—COO^-$	2.03×10^{-6}	5.69
Carbonic (1)	$CO_2 + H_2O$	HCO_3^-	4.3×10^{-7}	6.37
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.02×10^{-7}	6.91
Hydrogen sulfide (1)	H_2S	HS^-	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}	7.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Hydrocyanic	HCN	CN^-	4.93×10^{-10}	9.31
Silver ion	$Ag^+ + H_2O$	AgOH	9.1×10^{-11}	10.04
Carbonic (2)	HCO_3^-	CO_3^{2-}	5.61×10^{-11}	10.25
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Hydrogen sulfide (2)	HS^-	S^{2-}	1.1×10^{-12}	11.96
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.67
Water[c]	H_2O	OH^-	1 X 10^{-14}	14

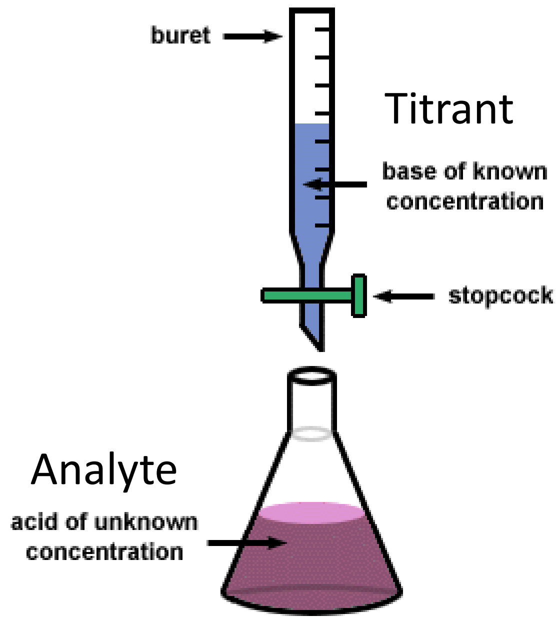
pH calculation summary

$K_a \times K_b = K_W$

				pH	% dissociation
Strong acid	$HA + H_2O \rightarrow H_3O^+ + A^-$	$K_a = \frac{[H_3O^+][A^-]}{[HA]0}$	$[H_3O^+] = [HA]_0$	$-\log([HA]_0)$	100%
Weak acid			$\mathbf{[H_3O^+] = \sqrt{[HA]0\ xK_a}}$	$-\log(\sqrt{[HA]0\ xK_a})$	$\sqrt{\frac{K_a}{[HA]0}}$
	Biprotic acid (H_2A)	K_{a1}, K_{a2}	$[H_3O^+] = [HA^-]= \sqrt{[HA]0\ xK_{a1}}$ $[A^{2-}]=K_{a2}$	$-\log(\sqrt{[HA]0\ xK_a})$	$\sqrt{\frac{K_a}{[HA]0}}$
Strong base	$BOH + H_2O \rightarrow OH^- + B^+$	$K_b = \frac{[B^+][OH^-]}{[BOH]_0}$	$[OH^-] = [BOH]_0$	$14 + \log([BOH]_0)$	100%
Weak base			$\mathbf{[OH^-] = \sqrt{[BOH]_0\ xK_b}}$	$14 + \log(\sqrt{[BOH]_0\ xK_b})$	$\sqrt{\frac{K_b}{[BOH]_0}}$
buffer	HA/A^-			**pH = pKa –log** $\mathbf{(\frac{[HA]_0}{[A^-]_0})}$	
	Add in acid	$H_3O^+ + A^- \rightarrow HA$	Recal $[HA]_{eq}, [A^-]_{eq}$	pH = pKa –log $(\frac{[HA]_{eq}}{[A^-]_{eq}})$	
	Add in base	$OH^- + HA \rightarrow A^-$			

Acid-base titration curves

In acid-base titration, the completion of the reaction is signaled by a sudden jump in pH



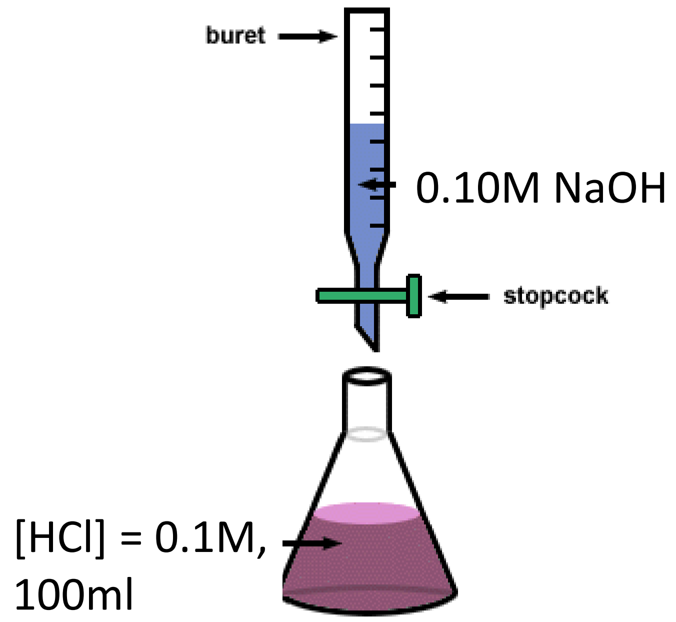
The pH dependence as titrant is added to the analyte, a plot of the pH of the analyte as a function of the volume of titrant added is called a titration curve

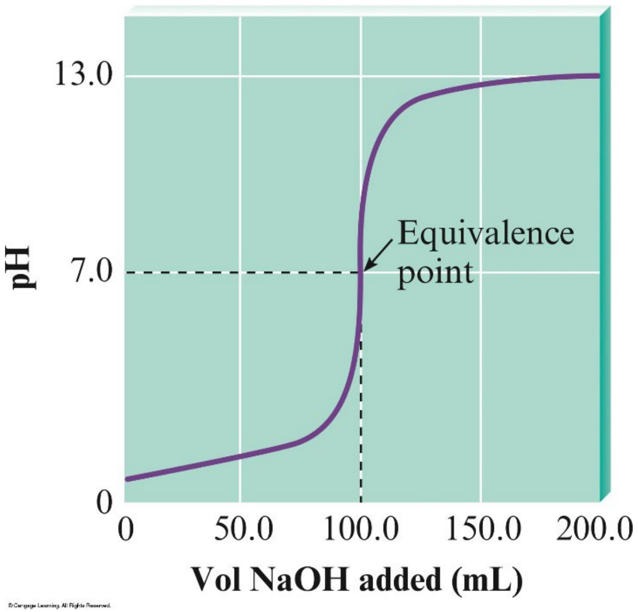
Acid base titrations can be of 3 types:

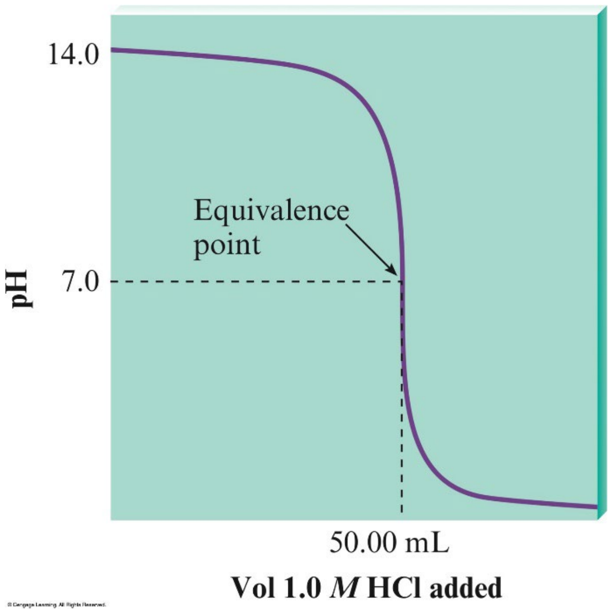
1. Strong acid vs strong base
2. Weak acid vs strong base
3. Weak base vs strong acid

<u>Strong acid vs strong base</u>

EX: HCl vs NaOH







Complete ionic eq:

net ionic eq:

(a) Before adding in any titrant

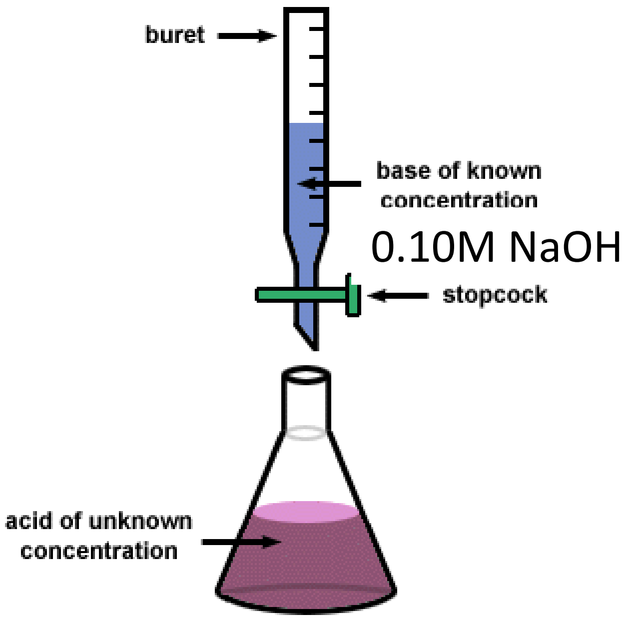
(b) Before equivalence point adding 30 ml NaOH

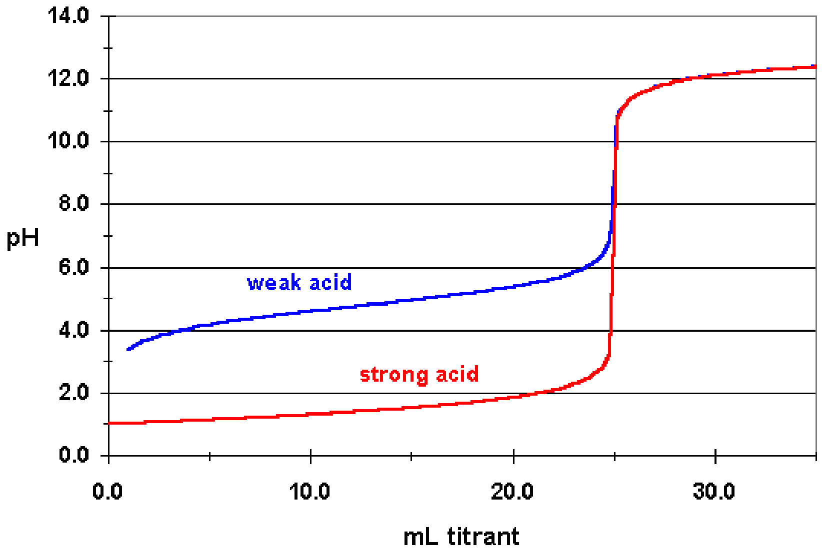
(c) At equivalence point adding 100 ml NaOH

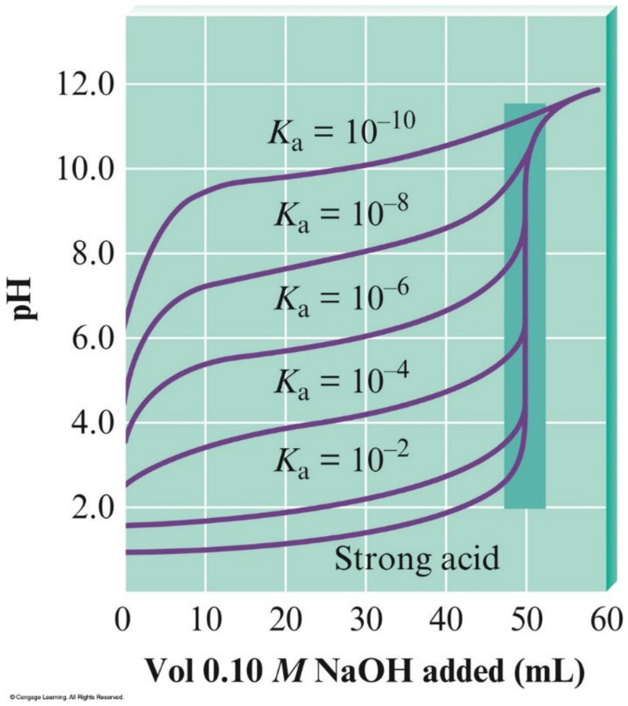
(d) After equivalence point adding 100.05 ml NaOH

<u>Weak acid vs strong base</u>

EX: CH_3COOH vs NaOH







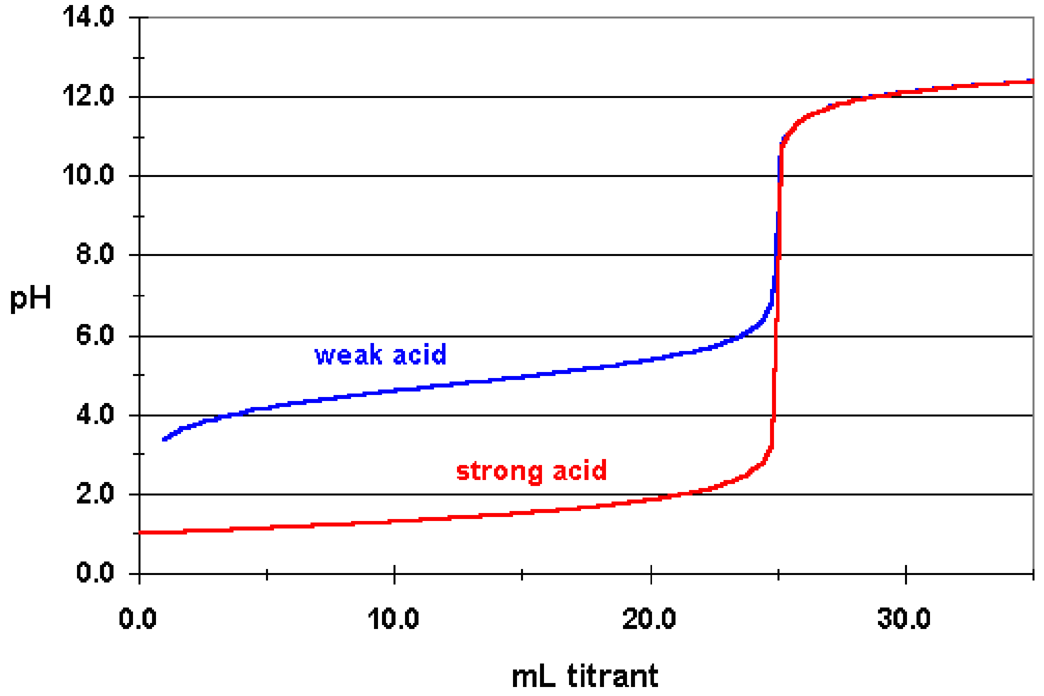
$[CH_3CO_2H]$ = 0.1M, 100ml

$K_a = 1.76 \times 10^{-5}$

Complete ionic eq:

net ionic eq:

HA (analyte) with Strong base (titrant)



On the curve, indicate the points that correspond to the following:

1. The stoichiometric (equivalence) point
2. The region with maximum buffering
3. pH = pK_a
4. pH depends only on $[HA]_0$
5. pH depends only on A^-
6. pH depends only on the amount of excess strong base added

(a) Before adding in any titrant

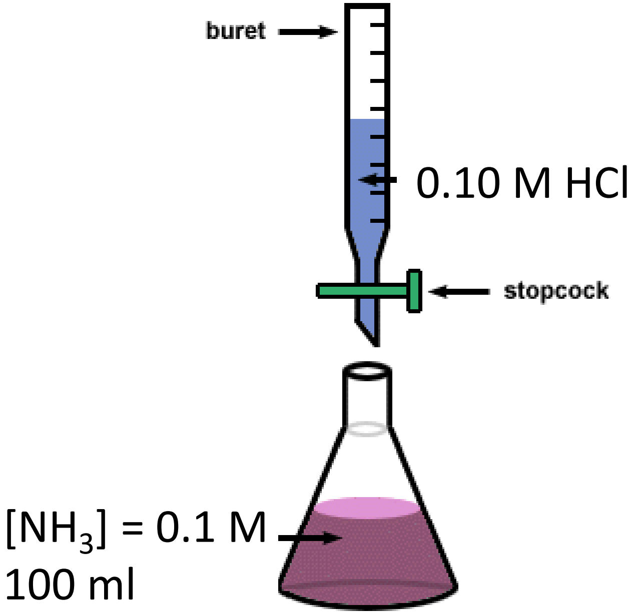
(b) Before equivalence point adding 50 ml NaOH

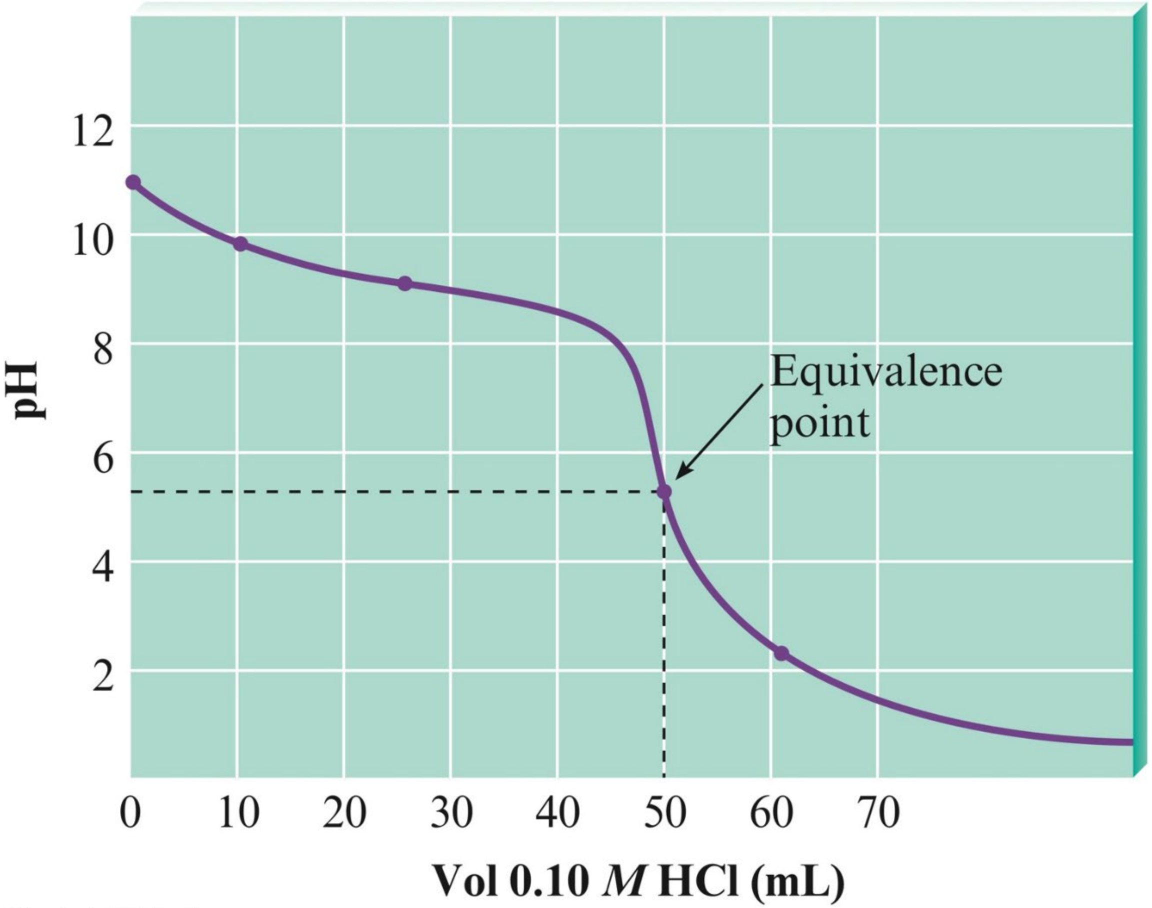
(c) At equivalence point adding 100 ml NaOH

(d) After equivalence point adding 100.05 ml NaOH

Weak base vs strong acid

EX: HCl vs NH_3





Complete ionic eq:

net ionic eq:

	Strong Base (T) Strong Acid (A)	Strong Acid (T) Strong Base (A)	Strong Base (T) Weak Acid (A)	Strong Acid (T) Weak Base (A)
Before titration	$[H_3O^+] = [HA]_0$	$[OH^-] = [BOH]_0$	$[H_3O^+] = \sqrt{[HA]_0 \times K_a}$	$[OH^-] = \sqrt{[BOH]_0 \times K_b}$
Before E.P.	$[H_3O^+] = \frac{C_{HA} \times V_{HA} - C_{BOH} \times V_{BOH}}{V_{HA} + V_{BOH}}$	$[OH^-] = \frac{C_{BOH} \times V_{BOH} - C_{HA} \times V_{HA}}{V_{HA} + V_{BOH}}$	$[H_3O^+] = K_a \frac{[HA]_{eq}}{[A^-]_{eq}}$	$[H_3O^+] = K_a \frac{[HA]_{eq}}{[A^-]_{eq}}$
At E.P.	pH = 7	pH = 7	$[OH^-] = \sqrt{[A^-]_{Vep} \times K_b}$	$[H_3O^+] = \sqrt{[B^+]_{Vep} \times K_a}$
After E.P.	$[OH^-] = \frac{C_{BOH} \times V_{BOH} - C_{HA} \times V_{HA}}{V_{HA} + V_{BOH}}$	$[H_3O^+] = \frac{C_{HA} \times V_{HA} - C_{BOH} \times V_{BOH}}{V_{HA} + V_{BOH}}$	$[OH^-] = \frac{C_{BOH} \times V_{BOH} - C_{HA} \times V_{HA}}{V_{HA} + V_{BOH}}$	$[H_3O^+] = \frac{C_{HA} \times V_{HA} - C_{BOH} \times V_{BOH}}{V_{HA} + V_{BOH}}$

$pH = -\log([H_3O^+])$

$pOH = -\log([OH^-])$

$pH = 14 - pOH = 14 + \log([OH^-])$

Acid-base indicator

pH meter is more accurate

indicator	Acid color	Base color	pH (color changing)	Good for
Methyl orange	Red	Yellow	3.2-4.4	Strong acid (titrant) + weak base (analyte)
Methyl red	Red	Yellow	4.2-6.5	
Bromthymole blue	Yellow	Blue	6.0-7.6	Strong acid + Strong base (titrant or analyte)
Phenol red	Yellow	Red	6.8-8.4	
Phenolphthalein	Colorless	Red	8.2-10.0	Strong base (titrant) + weak acid (analyte)
Alizarin Yellow	Yellow	Red	10.1-12.0	

Calculate the pH of a solution that results from mixing 45 mL of 0.11 M ethylamine ($C_2H_5NH_2$) with 33 mL of 0.11 M $C_2H_5NH_3Cl$. The K_b value for $C_2H_5NH_2$ is 6.5×10^{-4}.

A buffer consists of 0.29 M H_3PO_4 and 0.2 M NaH_2PO_4. Given that the K values for H_3PO_4 are, $K_{a1} = 7.2 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$, and $K_{a3} = 4.2 \times 10^{-13}$, calculate the pH for this buffer.

The pH of 0.50 M HF is 1.88. Calculate the pH difference when 0.69 g of NaF is added to 13 mL of 0.50 M HF. Ignore any changes in volume. The K_a value for HF is 3.5×10^{-4}.