Theory of Neutralization Titrations 3

Neutralization reactions

Neutralization reaction refers to acid and base reaction producing salt and water. The equivalent amounts of acid react with base to form equivalent amounts of salt and water. When the reaction is complete, acid and base are said to neutralize each other. Since water is produced, neutralization reaction is also referred as “**water forming reaction”.**

$$\text{acid+ base} \longrightarrow \text{salt + water}$$

Consider reaction like:

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

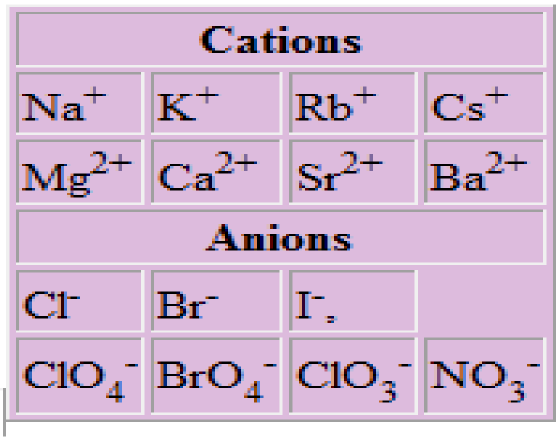
We can rewrite the reaction in ionic form as:

$$Na^+_{(aq)} + OH^{-1}_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O$$

The ionic salt formed from the reaction of strong acid [H_2SO_4, HCl, HNO_3, H_3PO_4] and strong base [NaOH, KOH, $Mg(OH)_2$, $Ca(OH)_2$] are pH neutral. Also, water is pH neutral. As such, strong acid and strong base reaction yields neutral products. In this case, equivalence and neutral points are same.

- The reason why a strong acid [HCl] and a strong base [NaOH] can make water and pH = 7. This is because a neutral salt was also made [NaCl]
- Neutral salts are like spectator ions, they move around in solution but don’t affect the pH. They are neutral.
- Any salt made from the following ions are neutral

Ions of Neutral Salts



Cations			
Na^+	K^+	Rb^+	Cs^+
Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Anions			
Cl^-	Br^-	I^-,	
ClO_4^-	BrO_4^-	ClO_3^-	NO_3^-

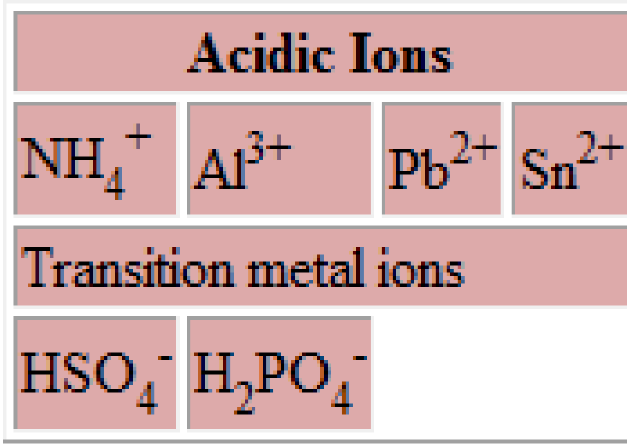
But, salts formed with other combinations like “strong acid - weak base” and “weak acid - strong base” are not neutral. They produce salts, which are either **acidic** or **basic** in nature. As such, pH of the product solution is not 7. Here, equivalence point is not same as neutral point. For example;

H_2SO_4 (strong acid)+$2NH_4OH$(weak base) $\longrightarrow$ $(NH_4)_2SO_4$ (acidic salt) +$2H_2O$

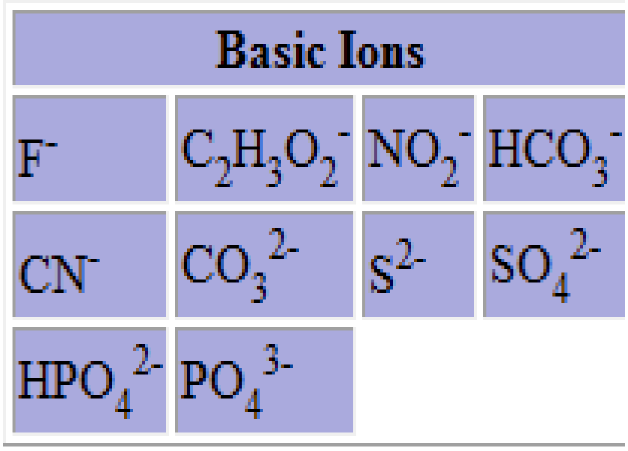
CH_3COOH (weak acid)+ NaOH(strong base) $\rightarrow$ CH_3COONa(basic salt) +H_2O

We refer acid-base reaction as neutralization reaction even though products are not neutral (pH=7). As a matter of fact, product solution is acidic (pH<7) for **strong acid -weak base reaction**. We need to add more of base solution beyond equivalence volume to make the product solution neutral.
Similarly, product solution is basic (pH>7) **for weak acid-strong base reaction**. Here, we need to add more acid beyond equivalence volume to make the product solution neutral.

- A salt formed between a strong acid and a weak base is an acid salt, for example NH_4Cl.
- A salt formed between a weak acid and a strong base is a basic salt, for example CH_3COONa.



Acidic Ions			
NH_4^+	Al^{3+}	Pb^{2+}	Sn^{2+}
Transition metal ions			
HSO_4^-	$H_2PO_4^-$		



Basic Ions			
F^-	$C_2H_3O_2^-$	NO_2^-	HCO_3^-
CN^-	CO_3^{2-}	S^{2-}	SO_4^{2-}
HPO_4^{2-}	PO_4^{3-}		

Analyzing neutralization reaction

We treat neutralization reaction on similar footing as other reactions. Generally, it involves reaction between two solutions of certain concentrations. Clearly, it is helpful to describe analysis in terms of molarity or normality. For a generic consideration:

$$mA_1 + nA_2 \longrightarrow pA_3 + qA_4$$

In terms of moles, we have:

$$m \text{ moles of} A_1 \equiv n \text{ moles of} A_2 \equiv p \text{ moles of} A_3 \equiv q \text{ moles of} A_4$$

$$mM_1V_1 \equiv nM_2V_2 \equiv pM_3V_3 \equiv qM_4V_4$$

Consideration in molarity gives a relation that needs to be analyzed using unitary method. It is important to realize that this is not a relation which are not connected with "equal to (=)" sign. In terms of gram equivalents (geq), we have:

$$\text{geq of} A_1 = \text{geq of} A_2 = \text{geq of} A_3 = \text{geq of} A_4$$

$$N_1V_1 = N_2V_2 = N_3V_3 = N_4V_4$$

Consideration in normality gives a relation that are connected with "equal to (=)" sign. It is so because constituents react in the proportion of equivalent weights. As such, gram equivalents are equal. Clearly, analysis involving normality is relatively easier to handle.

Example 1: A 25 ml of nitric acid taken from a stock volume of 1 litre neutralizes 50 ml of 0 .1N NaOH solution. Determine the mass of nitric acid in the stock volume.

<u>Solution:</u> Let us denote nitric acid and sodium hydroxide by subscripts "1" and "2" respectively. Applying neutralization equation,

$$\Longrightarrow N_1V_1 = N_2V_2$$

$$\Longrightarrow N_1 X 25 = 0.1 X 50$$

$$N_1 = 5/25 = 0.2$$

The normality of sample and the stock volume is same. Hence, normality of 1 litre stock volume is 0.2N. Using formula,

$$\Longrightarrow \text{geq} = NV = 0.2 X 1 = 0.2$$

Valence factor of nitric acid is 1 as it has one furnishable hydrogen. Therefore,

$$\Longrightarrow \text{Wt (g)} = 0.2 M.W/x = 0.2\ (1+14+3X16)/\ 1 = 12.6\text{gm}$$

Theory of Neutralization Titrations of Simple Systems

Acid-base equilibria: pH calculations

Calculation of pH and pOH requires a numerical value for the equilibrium constant for the reaction of weak acid or base with water (consult course one ,lectures 3,4,5,6). Here, we will summarize the relationships which connect between the equilibrium constants and pH calculations that would be useful for neutralization titrations:

1- Calculation of pH of solution of weak monoprotic acids;

$$[H^+] = \sqrt{K_a C_{HA}}$$

$$pH = \tfrac{1}{2}(pK_a - \log C_{HA})$$

2- Calculation of pH of the solutions of weak bases;

$$[OH^-] = \sqrt{K_b C_B}$$

$$\frac{K_w}{[H^+]} = \sqrt{K_b C_b}$$

$$[H^+] = \frac{K_w}{\sqrt{K_b C_b}}$$

$$pH = pK_w - \tfrac{1}{2} pK_b + \tfrac{1}{2}\log C_b$$

3- Calculation of pH of the solutions containing salts of weak acid and strong base.

$$[OH^-] = \sqrt{\frac{K_w C_s}{K_a}}$$

$$[H^+] = \sqrt{\frac{K_w K_a}{C_s}}$$

$$pH = \frac{1}{2}(pK_w + pK_a + \log C_s)$$

4-Calculation of pH of the solutions containing salts of weak base and strong acid

$$[H^+] = \sqrt{\frac{K_w C_s}{K_b}}$$

$$pH = \frac{1}{2}(pK_w - pK_b - \log C_s)$$

5- Calculation of pH of the solutions containing salts of weak base and weak acid

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

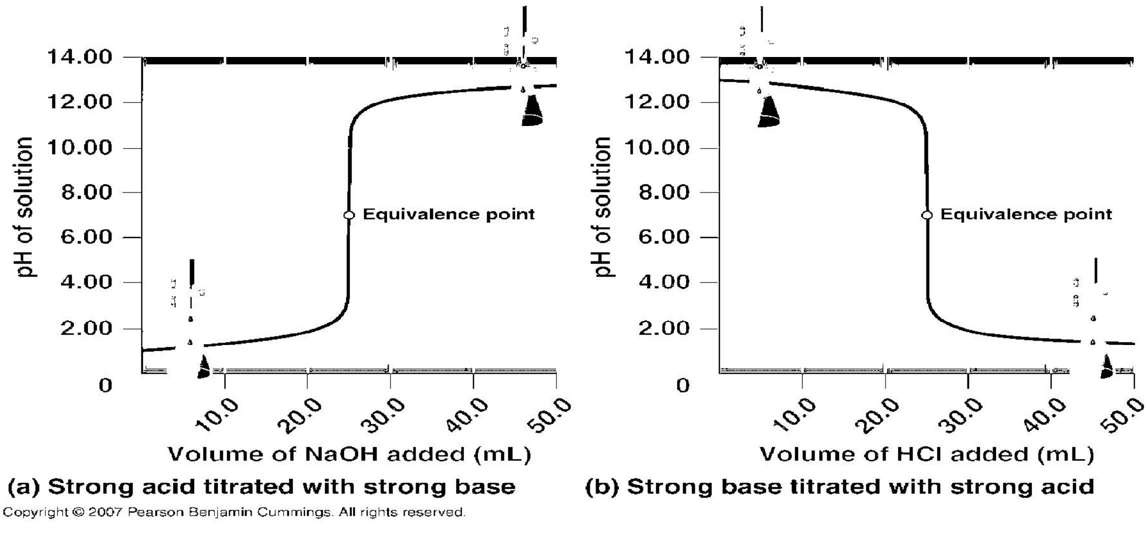
Titration Curves

A titration curve is a graph showing the pH of an acid or base solution as a function of the volume of titrant (base or acid solution) added.

It may be linear-segment curve or a sigmoidal curve depending on what is plotted on the y-axis

- **The X-axis** units are always reagent or titrant volume.
- **The Y-axis** may be in increments of analyte reacted or product formed (linear segment curve) or a p-function such as pH (s-curve).
- **The equivalence point** is characterized by large changes in the relative concentrations of the reagent and analyte.

A simple titration curves are shown in the following figure;



(a) Strong acid titrated with strong base (b) Strong base titrated with strong acid

Titration Curves for Strong Acid vs. Strong Base

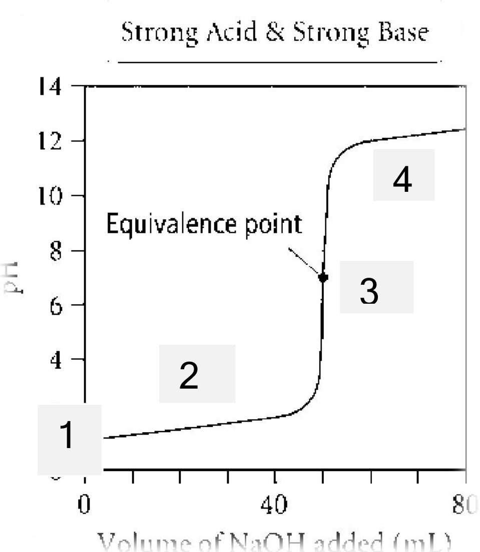
In this titration curve, a strong acid (HCl) is titrated with a strong base (NaOH).

(1) Initial pH: Before any NaOH has been added, the pH is low because all that is present is H_3O^+ from a strong acid.

Thus, pH = -log [H_3O^+].

(2) pH before equivalence point (pre-equivalent point) :

The pH gradually increases as HCl is neutralized by NaOH. The pH increase more sharply closer to the equivalence point.



- The number of moles of OH^- added equals the number of moles of H_3O^+ which have reacted.
- Subtract the number of moles of H_3O^+ reacted from the initial moles of H_3O^+.
- Divide the moles of H_3O^+ by the total solution volume to obtain [H_3O^+]; determine the pH

$$[H_3O^+] = \frac{\text{moles of } [H_3O^+] - \text{moles of } [OH^-]}{V_{acid} + V_{base}}$$

$$\mathbf{pH = -\log [H_3O^+]}$$

(3) pH at the equivalence point:

At the equivalence point, the same number of moles of NaOH has been added as there were moles of HCl initially. The solution contains only neutral ions (cations of strong bases and anions of strong acids) and H_2O, and is therefore neutral:

$$\mathbf{[H_3O^+] = 1.0\times10^{-7}\ M;\ pH = 7.00.}$$

(4) pH after the equivalence point (post-equivalent point) :

The pH continues to increase sharply at first, then more slowly as more NaOH is added. All of the H_3O^+ has been neutralized, so the amount of OH^- in excess must be determined.

- Subtract the initial number of moles of H_3O^+ from the number of moles of OH^- added.
- Divide the moles of OH^- by the total solution volume to obtain [OH-];
- Determine the pOH and pH.

$$[OH^-] = \frac{Kw}{[H_3O^+]} = \frac{\text{moles of } [OH^-]_{added} - [H_3O^+]}{V_{acid} + V_{base}}$$

Example 2: Derive a curve for the titration of 50 mL of 0.05 M HCl with 0.1M NaOH at (a) start (b) 10 mL (c) equivalent point (d) 25.10mL addition of NaOH

<u>**Solution**</u>:

(a) Initial point (start or 0.0 mL addition of NaOH)

- at the outset, the solution is 0.05 M in H_3O^+ and,

$$pH = -\log[H^+] = -\log 0.05 = \mathbf{1.30}$$

(b) After addition of 10 mL of NaOH

The hydronium ion concentration decreases as a result of both reaction with the base and dilution .Thus the analytical concentration of HCl is;

$$C_{HCl} = \frac{\text{No. mmol HCl remaining after addition of NaOH}}{\text{total volume}}$$

solution

$$= \frac{\text{original no. Mmol HCl} - \text{no. Mmol NaOH added}}{\text{Total volume solution}}$$

$$= \frac{(50\ x0.05) - (10x0.1)}{50+10} = 2.5\ x10^{-2}\ M$$

$[H_3O^+] = 2.5\ x10^{-2}\ M$

$$pH = -\log[H^+] = -\log 2.5x10^{-2} = 1.602$$

Addition points defining the curve in the region before the equinalence point are obtained in the same way.The results of such calculations are shown in the second column of Table.

(c) At equivalent point

At the equivalence point , neither HCl or NaOH is in excess, and so the concentration of H_3O^+ and OH^- ions must be equal . substituting this equality into the ion-product constant for water yields;

$$[H_3O^+] = \sqrt{Kw} = \sqrt{1.0x10^{-14}} = 1.0\ x10^{-7}$$

$$pH = 7$$

(d) After addition of 25.10 mL of NaOH

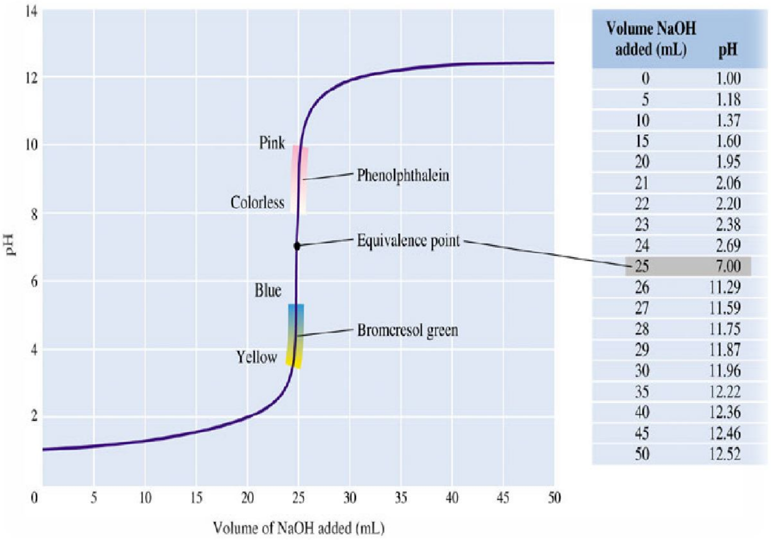
The solution now contains an excess of NaOH , and we can write;

$$C_{NaOH} = \frac{(25.1\ x0.1\ ) - (50x0.05)}{50+\ 25.1} = 1.33\ x10^{-4}\ M$$

$$[OH-] = C_{NaOH} = 1.33\ x10^{-4}\ M$$

$$pOH = -\log 1.33\ x10^{-4} = 3.88$$

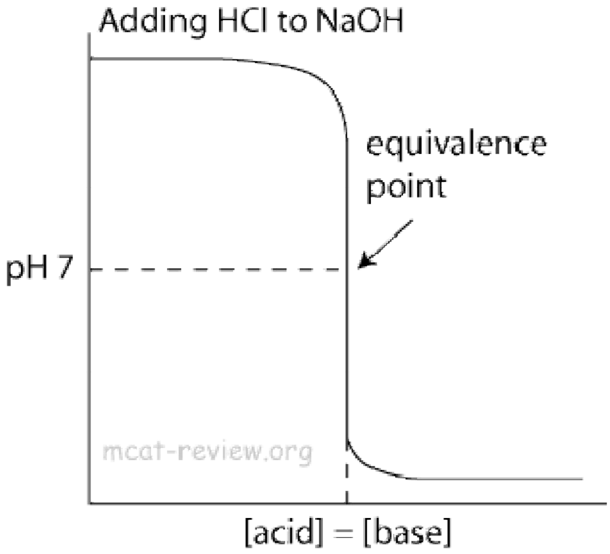
$$pH = 14 - 3.88 = 10.12$$



Volume NaOH added (mL)	pH
0	1.00
5	1.18
10	1.37
15	1.60
20	1.95
21	2.06
22	2.20
23	2.38
24	2.69
25	7.00
26	11.29
27	11.59
28	11.75
29	11.87
30	11.96
35	12.22
40	12.36
45	12.46
50	12.52

Titration Curve for Strong Base vs. Strong Acid

In this titration curve, a strong base (NaOH) is titrated with a strong acid (HCl). Calculating the pH along this curve is similar to a strong acid-strong base curve, except that the solution starts out basic, and becomes more acidic as the titrant is added.



- Preequivalence: calculate the concentration of the base from is starting concentration and the amount of acid that has been added, the concentration of the base is equal to the concentration of the hydronium ion and you can calculate pOH from the concentration, and then the pH
- Equivalence: the hydronium and hydroxide ions are present in equal concentrations, so the pH is 7
- Postequivalence: the concentration of the excess acid is calculated and the hydronium ion concentration is the same as the concentration of the acid, and the pH can be calculated

Example 3: Caculate the pH during the titration of 50 mL of 0.05 M NaOH with 0.1M HCl after addition of the following volumes of HCl (a)24.50 mL(b) 25 mL(c) 25.5 mL

Solution:

(a) At 24.5 mL added, $[H_3O^+]$ is very small and cannot be computed from stoichiometric considerations but $[OH^-]$ can be obtained readily;

$$[OH^-] = C_{NaOH} = \frac{\text{original no. mmol NaOH - no. mmol HCl added}}{\text{Total volume solution}}$$

$$= \frac{(50\text{x}0.05) - 24.5\text{x}0.1}{50+24.5} = 6.71\text{x}10^{-4}\text{ M}$$

$$[H_3O^+] = K_w / 6.71\text{x}10^{-4} = 1.0\text{x}10^{-14} / 6.71\text{x}10^{-4} = 1.49\text{x}10^{-11}$$

pH= -log(1.49x10^{-11})= 10.83

(b) This is the equivalence point where $[H_3O^+] = [OH^-]$

$$[H_3O^+] = \sqrt{Kw} = \sqrt{1.0\text{x}10^{-14}} = 1.0\text{x}10^{-7}\text{ M}$$

pH =7

(c)

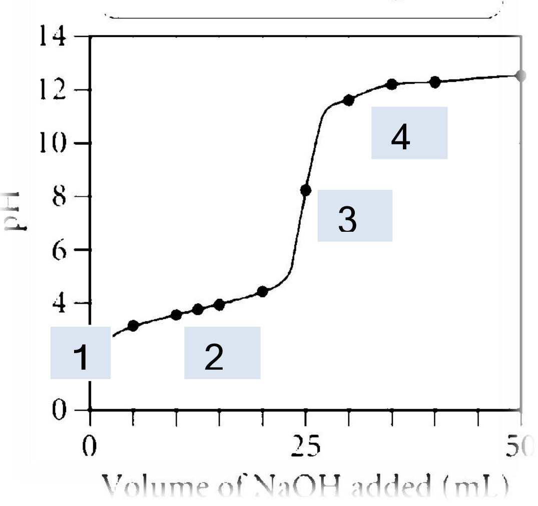
$$[H_3O^+] = C_{HCl} = \frac{(25.5\text{ x}0.1)-(50\text{x}0.05)}{75.5} = 6.62\text{x}10^{-4}\text{ M}$$

pH= 3.18

Titration Curve for Weak acid vs. Strong Base

Titration Curves for Weak Acids: Four types of calculations are needed to derive the titration curve for a weak acid, these are;

1) Before the addition of base
2) Before the equivalence point (buffer region 1)
3) At the equivalence point
4) After the equivalence point



1) Initial pH:

The initial pH is higher than for the strong acid titration, since a weak acid dissociates less than a strong acid at the same concentration (less H_3O^+, higher pH).

Since we have a dilute solution of a weak acid, solve for $x = [H_3O^+]$, and find the pH;

$$HA \longleftrightarrow H^+ + A^-$$

2) pH before the equivalence point:

As OH^- is added, some HA is converted to its conjugate base, A^-, slowly raising the pH of the solution. Before the equivalence point is reach, the solution is a mixture of a weakacid, HA, and its conjugate base, A^-, and is a **buffer**. The pH can be calculated from the Henderson-Hasselbalch equation. (It is not necessary to account for the change in volume, since this will cancel out in the concentration ratio.) At the midpoint of the buffer region, the pH equals the pK_a of the acid (since $[HA]=[A^-]$

3) pH at the equivalence point:
At the equivalence point, enough moles of OH^- have been added to turn *all* of the HA into A^-. The solution is no longer a buffer. The pH is greater than 7.00, since A^- is the conjugate base of a weak acid, and reacts with water to produce OH^-, yielding a basic solution. The pH is calculated from an ICE table using the base dissociation of A^-(make sure to use the *total solution volume* when calculating [A-]:

$$A^-(aq) + H_2O \longrightarrow HA(aq) + OH^-(aq)$$

4) pH after the equivalence point:
The pH continues to increase slowly as more bases is added. The pH is calculated the same way as in a strong acid-strong base titration.

Example 4: Derive the titration curve for 50 mL of 0.1 M acetic acid ($K_a=1.75x10^{-5}$) with 0.1 M NaOH, after addition of (a) 0.00, (b) 10.00 mL (c) 40 mL (d) 50 mL (e) 50.1 mL .

<u>Solution:</u>

(a) After the addition of 0.00 mL of the titrant (NaOH) , we have only a weak acid (CH_3COOH)

$$HA \overset{K_a}{\rightleftarrows} H^+ + A^-$$

$$[H^+] = \sqrt{K_a C_{HA}}$$

or

$$pH= ½(pK_a-\log C_{HA})$$

$$[H^+] = \sqrt{1.75x10^{-5}\ x0.1} = 1.32x10^{-3}$$

$$\mathbf{pH} = -\log 1.32x10^{-3} = \mathbf{2.88}$$

(b) At different additions of titrant(before equivalent point) buffer solution is formed , so after addition of 10 mL of NaOH.

$$pH = pK_a + \log \frac{C_s}{C_a}$$

$$C_a = \frac{50\ x0.1\ -10x0.1}{60} = \frac{4}{60} = 6.6x10^{-2}\ M$$

$$C_s = \frac{10x0.1}{60} = \frac{1}{60} = 1.6x10^{-2}\ M$$

$$pH = -\log(1.75x10^{-5}) + \log \frac{1.6x10^{-2}}{6.6x10^{-2}}$$

$$\mathbf{pH} = +5 -\log 1.75 \quad +(-0.59) = 5-0.24-0.59 = \mathbf{4.17}$$

(c) After the addition of 40 mL

$$pH = pK_a + \log \frac{C_s}{C_a}$$

$$C_a = \frac{50\ x0.1\ -40x0.1}{90} = \frac{1}{90}\ M$$

$$C_s = \frac{40x0.1}{90} = \frac{4}{90}\ M$$

$$\mathbf{pH} = -\log(1.75x10^{-5}) + \log \frac{4/90}{1/90} = 4.76 + 0.6 = \mathbf{5.36}$$

(d) At equivalent point : all acid is converted to sodium acetate , the solution is similar to one formed by dissolving salt of strong base in water, so after addition of 50 mL of the base; we can apply ;

$$[OH^-] = \sqrt{\frac{K_w C_s}{K_a}}$$

$$[H^+] = \sqrt{\frac{K_wK_a}{C_s}}$$

$$pH = ½(pK_w + pK_a + \log C_s)$$

$$Cs = \frac{50x0.1}{100} = 0.05\ M$$

$$[OH^-] = \sqrt{\frac{(1x10^{-14})(0.05)}{1.75x10^{-5}}} = 5.34x10^{-6}\ M$$

$$pOH = -\log(5.34x10^{-6}) = 6 - \log 5.34 = 6 - 0.72 = 5.8$$

pH= 14-5.8 = **8.4**

(e) pH after the addition of 50.1 mL of NaOH , the base is in excess;

$$[OH\text{-}] = [NaOH] = \frac{50.1x0.1 - 50x0.1}{100.1} = \frac{0.01}{100.1} = 1x10^{-4}\ M$$

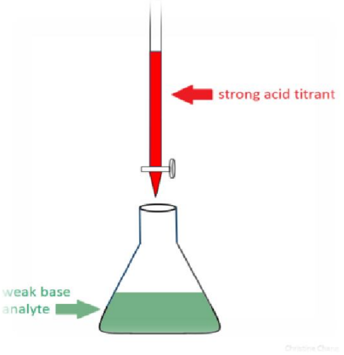
pOH= -log (1x10-4) = 4
pH = 14-4 = **10**

Homework : Calculate pH at the following volumes in the titration of 50.00 mL of 0.0750 M benzoic acid ($K_a = 6.3x10^{-5}$) ($pK_a = 4.20$) with 0.10 M NaOH, after adition of (a) 10.00 mL (b) 18.75 mL (c) 37.50 mL(d) 40.00 mL

Titration Curve for Weak base vs. Strong acid

In this titration curve, a weak base (B) is titrated with a strong acid . Calculating the pH along this curve is similar to a weak acid-strong base curve, except that the solution starts out basic, and becomes more acidic as the titrant is added. The pH at the equivalence point is less than 7, because all of the weak base B has been converted to its conjugate acid, BH.

Example 5: 20 mL of 0.50 M NH_4OH is diluted to 100 mL with water and titrated with 0.50 M HCl . Calculate the pH value (a) at the start (b) at equivalent point. Show the general form of the titration curve. $K_b = 1.75x10^{-5}$



Solution:

We find the concentration of NH_4OH

C_B= 20x0.5=100=0.1 M

(a) At start (0.0 mL of HCl)

$[OH^-] = \sqrt{K_b C_B} = \sqrt{1.75x10^{-5} x0.1} = 1.32x10^{-3}$ M

pOH= -log $1.32x10^{-3}$= 2.878

pH=14-2.878=**11.122**

(b) Vx 0.5 = 100x0.1 =20 mL volume of HCl needed for equivalent point

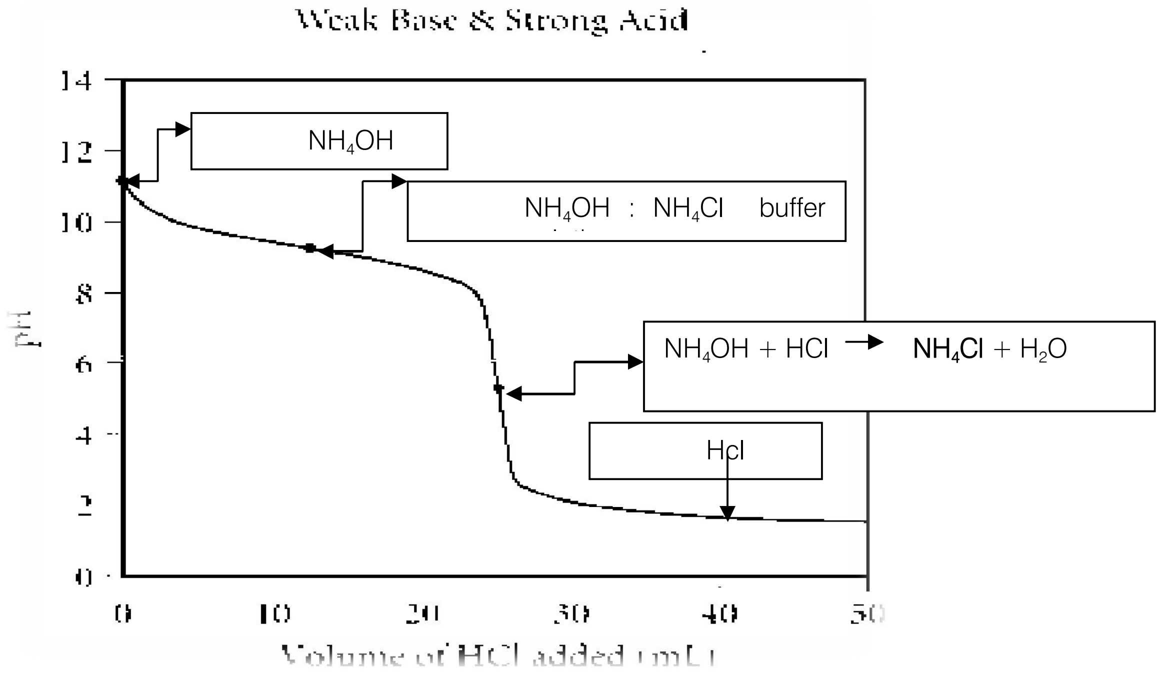
$$C_s = \frac{0.1x100}{100+20} = 0.0833 \text{ M}$$

The pH can be calculated from

pH= ½ (pK_w- pK_b-log C_s)

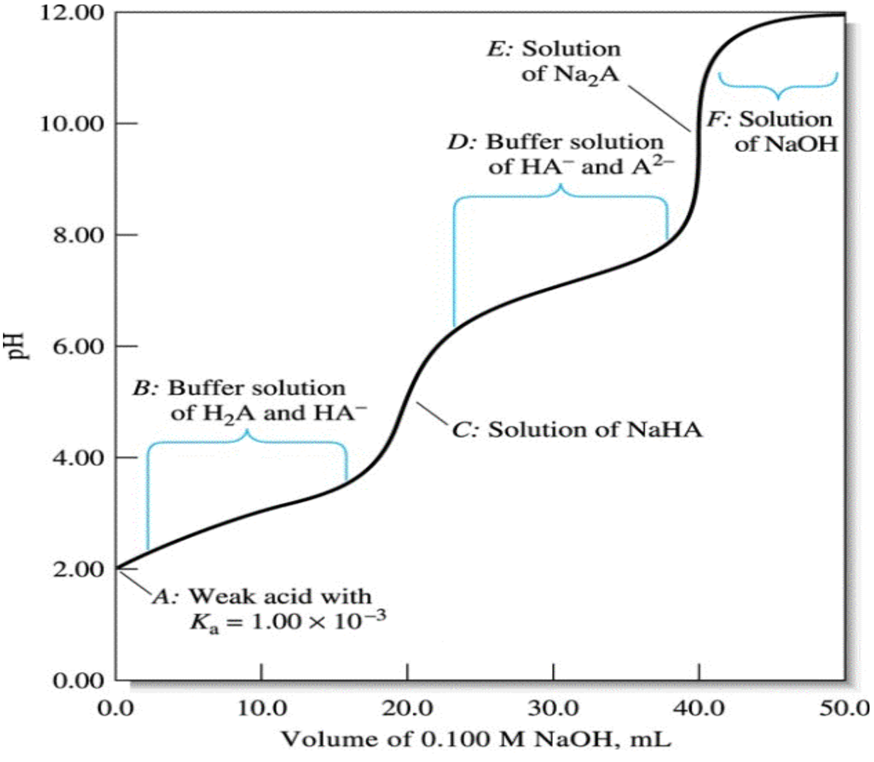
=½(14- 4.76-log 0.0833)

= ½(9.24+1.08)= **5.16**



Titration Curve for polyprotic acids

Any polytropic acid give multiple end points in a tritration , provided the functional groups differ sufficiently in strengths as acid. The following Figure show the titration curve for a polytropic acid H_2A with dissociation constants, for example of $K_{a1}= 1.0x10^{-3}$ and $_{Ka2}= 1.0x10^{-7}$, we can differentiate six regions in the titration curve of this kind of acids.



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1. **Region A:** At start (i.e. before addition of base) ; we treat the system as if it contained a single monotropic acid with dissociation constant of of $K_{a1}= 1.0x10^{-3}$

$$[H_3O^+] = \sqrt{K_{a1}\ C_a}$$

$$pH = ½\ pKa1 - ½ \log C_a$$

2. **Region B;** we have an equivalent of a simple buffer solution containing weak acid H_2A and its conjugate base NaHA. That is , we assum that the concentration of A^{2-} is negligible with the respect to the other two A-containing species and we emply the following equation to obtain $[H_3O^+]$

$$[H_3O^+]= K_{a1}\ x\ \frac{C_{H2A}}{C_{NaHA}}$$

$$pH= pK_{a1} + \log \frac{C_{NaHA}}{C_{H2A}}$$

4- **Region C:** the first equivalence point , we have solution containing and we use the following equation to calculate $[H_3O^+]$

5-

$$[H_3O^+]=\sqrt{\frac{K_{a2}C_{NaHA}+K_w}{1+C_{NaHA}/K_{a1}}}$$

Or one of its simplifications to compute $[H_3O^+]$

$$[H_3O^+]=\sqrt{K_{a1}\times K_{a2}}$$
$$pH=\tfrac{1}{2}(pK_{a1}+pK_{a2})$$

6- **Region D:** here we have second buffer consisting of a weak acid HA^- and its conjugated base Na_2A and we calculate the pH employing second dissociation constant (K_{a2})

$$pH=pK_{a2}+\log\frac{C_{A2-}}{C_{HA-}}$$

7- **Region E:** this is the second equivalence point , the solution consist of A^{2-} with water to form HA^- and OH^-, therefore we use the following equations to determine pH.

$$A^{2-}+H_2O \longleftrightarrow OH^-+HA^-$$

$$K_{b1}=K_w/K_{a2}=\frac{[OH^-][HA^-]}{[A^{2-}]} \qquad [OH^-]=[HA^-]$$

$$[OH^-]=\sqrt{K_{b1}C_{A2-}}$$

From $[OH^-]$, we can determine pH

8- **Region E:** just after equivalence point , the excess OH^- must also be considered.

Example 6: construct titration curve of 25 mL of 0.1 M maleic acid (HOOC-CH=CH-COOH) , with 0.1 M NaOH at (a) initial (b) first buffer region(c) first equivalence point (d)second buffer region (e) second equivalence point . $K_{a1}= 1.3x10^{-2}$ and $K_{a2}= 5.9x10^{-7}$.

Solution

Symbolizing the acid as H_2M, we can write the two dissociation equiberia as;

$$H_2M + H_2O \longleftrightarrow H_3O^+ + HM^- \qquad K_{a1}= 1.3x10^{-2}$$

$$HM^- + H_2O \longleftrightarrow H_3O^+ + M^{2-} \qquad K_{a2}= 5.9x10^{-7}$$

Because the ratio K_{a1}/K_{a2} is large (2 X 10^4), we proceed as just described.

(a) Initial pH

Only the first dissociation makes an appreciable contribution to $[H_30^+]$; thus,

Mass balance requires that;

$$[H_3O^+]= [HM^-]$$

Mass balance requires that;

$$C_{H2M} \approx [H_2M]+ [HM^-] = 0.1$$

Or

$$[H_2M] = 0.1-[HM^-]= 0.1- [H_3O^+]$$

Substituting these relationships into the expression for K_{a1} gives;

$$K_{a1} = 1.3x10^{-2}= \frac{[H_3O^+]^2}{0.1-[H_3O^+]}$$

Rearranging yields;

$$[H_3O^+]^2 + 1.3x10^{-2}[H_3O^+] -1.3x10^{-3}=0$$

Because K_{a1} for maleic acid is large, we must solve the quadratic equation exactly or by successive approximations. When we do so, we obtain;

$$[H_3O^+]= 3.01x10^{-2}$$

$$\textbf{pH}= -\log 3.01x10^{-2} = \textbf{1.52}$$

(b) First buffer region

The addition of 5.00 mL of base results in the formation of a buffer consisting of the weak acid H_2M and its conjugate base HM^-. To the extent that dissociation of HM^- to give M^{2-} is negligible, the solution can be treated as a simple buffer system. Thus we have to find the concentration of C_{NaHM} and C_{H2M}

$$C_{NaHM}=[HM^-]= \frac{50\ x0.1}{30} = 1.67x10^{-2}\ M$$

$$C_{H2M}=[\ H_2M]= \frac{(25x0.1)-(5x0.1)}{30} = 6.67x10^{-2}\ M$$

Substitution of these values into the equilibrium-constant expression for yields a tentative value of 5.2 X 10^{-2} M for $[H_30^+]$. It is clear, however, approximation $[H_3O^+] < < C_{H2M}$ or C_{HM-} is not valid; thus we apply;

$$[HM^-] = 1.67\ X\ 10^{-2} + [H_3O^+] - [OH^-]$$

$$[H_2M] = 6.67\ X\ 10^{-2} - [H_3O^+] + [OH^-]$$

Because the solution is quite acidic, the approximation that [OH-] is very small is surely justified. Substitution of these expressions into the dissociation constant relationship gives;

$$K_{a2}= \frac{[H_3O^+](1.67\ X\ 10^{-2}) + [H_3O^+]}{6.67\ X\ 10^{-2} -[H_3O^+]}=1.3x10^{-2}$$

$$[H_3O^+]^2 + (2.97\ X\ 10^{-2})\ [H_3O^+] - 8.67\ X\ 10^{-4} = 0$$

$$[H_3O^+] = 1.81\ X\ 10^{-2}\ M$$

pH= 1.74

Additional points in the first buffer region can be computed in a similar way.

(c) First Equivalence Point: At the first equivalence point,

$$[HM^-] \approx C_{NaHM} = \frac{25\ x0.1}{50} = 5x10^{-2}\ M$$

Our simplification of the numerator in the following equation is clearly justified.

$$[H_3O^+]= \sqrt{\frac{K_{a2}C_{NaHA}+K_w}{1+ C_{NaHA} /K_{a1}}}$$

On the other hand, the second term in the denominator is not < < 1. So,

$$[H_3O^+]= \sqrt{\frac{K_{a2}C_{NaHA}}{1+ C_{NaHA} /K_{a1}}} = \sqrt{\frac{(5.9x10^{-7})(5x10^{-2})}{1+ 5x10^{-2}/ 1.3x10^{-2}}}$$

$$= 7.8x10^{-5}\ M$$

$$pH= -\log (7.8x10^{-5})= \mathbf{4.11}$$

(d)Second buffer region:

Further additions of base to the solution create a new buffer system consisting of HM^- and M^{2-}. When enough base has been added that the reaction of HM with water to give OH^- can be neglected (a few tenths of a milliliter beyond the first equivalence point), the pH of the mixture is readily obtained from K_{a2}. When we introduce 25.50 mL of NaOH, for example,

$$[M^{2-}] \approx C_{Na2M}= \frac{(25.5 -25)(0.1)}{50.5} = \frac{0.05}{50.5} = 9.90x10^{-4}\ M$$

and the molar concentration of NaHM is,

$$[HM^-] \approx C_{NaHM}= \frac{(25.5x\ 0.1)- (25.5 -25)(0.1)}{50.5} = \frac{2.45}{50.5} = 0.04851\ M$$

Substituting these values into the expression for K_{a2} gives;

$$[H_3O^+]= \frac{K_{a2}\ x\ C_{NaHM}}{C_{Na2M}} = \frac{5.9x10^{-7}\ x\ 0.04851}{9.90x10^{-4}} = 2.89x10^{-5}\ M$$

$$pH= -\log\ 2.89x10^{-5} =\mathbf{4.54}$$

(e)Second equivalence point

After the addition of 50 mL of 0.1 M NaOH, the solution is 0.0333 Min Na_2M (2.5 mmol/75 mL) . Reaction of the base M^{2-} with ater is the predominant equilibrium in the system and the only one that we need to take into account.Thus;

$$M^{2-} + H_2O \longleftrightarrow OH^- + HM^-$$

$$K_{b1} = K_w/K_{a2} = \frac{[OH^-][HM^-]}{[M^{2-}]} = 1.69x10^{-8}$$

$[OH^-] \approx [HM^-]$

$[M^{2-}]=0.0333- [OH^-] \approx 0.0333$ M

$$K_{b1} = 1.69x10^{-8} = \frac{[OH^-]^2}{0.0333}$$

$[OH-]= 2.38x10^{-5}$ M and pOH= -log($2.38x10^{-5}$)= 4.62

pH= 14-4.62= **9.38**

Exercises No. 3

1- What are the differences between equivalent point and end point?

2- Discuss the roles of indicators in the titration of acids and bases. Explain the basis of their operation and the factors to be considered in selecting an appropriate indicator for a particular titration.

3- Which of the following has the highest pH?
   a. the endpoint of a strong acid titrated with a strong base
   b. the endpoint of a weak acid titrated with a strong base
   c. the endpoint of a weak base titrated with a strong acid
   d. the endpoint of a strong base titrated with a strong acid
   e. the endpoint of a weak acid titrated with a weak base

4- A sample of 40.0 milliliters of a 0.100 molar $HC_2H_3O_2$ solution is titrated with a 0.150 molar NaOH solution. K_a for acetic acid = $1.8x10^{-5}$.
   a. What volume of NaOH is used in the titration in order to reach the equivalence point?

b. What is the molar concentration of $C_2H_3O_2^-$ at the equivalence point?
c. What is the pH of the solution at the equivalence point?

5- A 0.682 gram sample of an unknown weak monoprotic organic acid, HA was dissolved in sufficient water to make 50 milliliters of solution and was titrated with a 0.135 molar NaOH solution. After the addition of 10.6 milliliters of base, a pH of 5.65 was recorded. Theequivalence point (end point) was reached after the addition of 27.4 milliliters of the 0.135 molar NaOH.

a. Calculate the number of moles of acid in the original sample.
b. Calculate the molecular weight of the acid HA.
c. Calculate the number of moles of unreacted HA remaining in solution when the pH was 5.65.
d. Calculate the $[H_3O^+]$ at pH = 5.65
e. Calculate the value of the ionization constant, K_a, of the acid HA.

6- The molecular weight of a monoprotic acid HX was to be determined. A sample of 15.126 grams of HX was dissolved in distilled water and the volume brought to exactly 250.00 millilitres in a volumetric flask. Several 50.00 millilitre portions of this solution were titrated against NaOH solution, requiring an average of 38.21 millilitres of NaOH. The NaOH solution was standardized against oxalic acid dihydrate, $H_2C_2O_4{\cdot}2H_2O$ (molecular weight: 126.066 gram mol^{-1}). The volume of NaOH solution required to neutralize 1.2596 grams of oxalic acid dihydrate was 41.24 millilitres.

a. Calculate the molarity of the NaOH solution.
b. Calculate the number of moles of HX in a 50.00 millilitre portion used for titration.
c. Calculate the molecular weight of HX.
d. Discuss the effect of the calculated molecular weight of HX if the sample of oxalic acid dihydrate contained a nonacidic impurity

7- In an experiment to determine the molecular weight and the ionization constant for ascorbic acid (vitamin C), a student dissolved 1.3717 grams of the acid in water to make 50.00 millilitres of solution. The entire solution solution was titrated with a 0.2211 molar NaOH solution. The pH was monitored throughout the titration. The equivalence point was reached when 35.23 millilitres of the base has been added. Under the conditions of this experiment, ascorbic acid acts as a monoprotic acid that can be represented as HA.

a. From the information above, calculate the molecular weight of ascorbic acid.
b. When 20.00 millilitres of NaOH had been added during the titration, the pH of the solution was 4.23. Calculate the acid ionization constant for ascorbic acid.
c. Calculate the equilibrium constant for the reaction of the ascorbate ion, A^-, with water.
d. Calculate the pH of the solution at the equivalence point of the titration.