

Strong acid with strong base

The hydronium ions in an aqueous solution of a strong acid have two sources:

- (1) the reaction of the acid with water and
- (2) the dissociation of water

In all but the most dilute solutions, however, the contribution from the strong acid far exceeds that from the solvent.

Strong acid with strong base

Stages:

1st step – before beginning titration: the solution contains only strong acid and water, the pH being determined by the dissociation of the strong acid.

2nd step – before the equivalence-point: in the preequivalence stage, we compute the concentration of the acid from its starting concentration and the amount of base added.

3rd step – at the equivalence-point: at the equivalence-point, the hydronium and hydroxide ions are present in equal concentrations, and the hydronium ion concentration is derived directly from the ion-product constant for water.

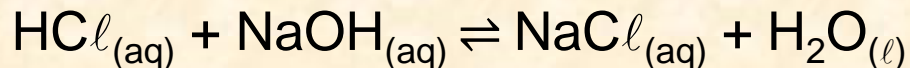
4th step – after equivalence-point: in the postequivalence stage, the analytical concentration of the excess base is computed, and the hydroxide ion concentration will be equal to (or multiple of) the analytical concentration.

Example - stoichiometry

Derive a curve for the titration of 100.0 mL of 0.100 mol L⁻¹ HCl with 0.100 mol L⁻¹ NaOH.

Initial questions:

1. Reaction?



2. Volume of NaOH at equivalence-point?

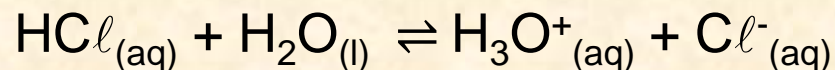
$$n^{\circ} \text{ mol NaOH} = n^{\circ} \text{ mol HCl}$$

$$0.100 \times V_{\text{NaOH}} = 0.100 \times 100$$

$$V_{\text{NaOH}} = 100 \text{ mL}$$

Initial point

At the outset, the solution is 0.100 mol L^{-1} in H_3O^+ , and



$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 1.00$$

After addition of 1.00 mL of reagent

The hydronium ion concentration decreases as a result of both reaction with the base and dilution.

$$V_{\text{NaOH}} = 1.00 \text{ mL} \Rightarrow n^\circ \text{ mol NaOH} = 0.100 \times 0.00100 = 0.000100 \text{ mol}$$

Initial	0.0100	-	-	-
Added	-	0.000100	-	-
Final	0.0099	-	0.000100	0.000100

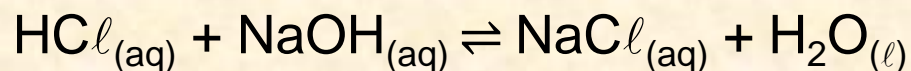
$$V_{\text{final}} = V_{\text{HCl}} + V_{\text{NaOH}} = 100.0 + 1.00 = 101.0 \text{ mL}$$

$$[\text{H}_3\text{O}^+] = 0.0099 / 0.1010 = 0.098 \text{ mol L}^{-1} \Rightarrow \text{pH} = 1.01$$

$$V_{\text{NaOH}} = 50.00 \text{ mL?}$$

Equivalence-point

At the equivalence-point, neither HCl nor NaOH is in excess, and so the concentrations of hydronium and hydroxide ions must be equal. Substituting this equality into the ion-product constant for water yields



Initial	0.0100	-	-	-
Added	-	0.0100	-	-
Final	-	-	0.0100	0.0100

$$pH = -\log[H_3O^+] = 7.00$$

After addition of 102.00 mL of reagent

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

$$V_{\text{NaOH}} = 102.00 \text{ mL} \Rightarrow n^{\circ} \text{ mol NaOH} = 0.100 \times 0.120 = 0.01020 \text{ mol}$$

	$\text{HC}\ell_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightleftharpoons \text{NaC}\ell_{(\text{aq})} + \text{H}_2\text{O}_{(\ell)}$			
Initial	0.0100	-	-	-
Added	-	0.01020	-	-
Final	-	0.00020	0.0100	0.0100

Volume final = 202.00 mL

$$[\text{OH}^-] = \frac{0.0020}{0.2020} = 9.90 \times 10^{-4} \text{ mol L}^{-1}$$

$$p\text{OH} = 3.0$$

$$p\text{H} = 11.0$$

Example – the charge-balance equation

Derive a curve for the titration of 100.0 mL of 0.100 mol L⁻¹ HCl with 0.100 mol L⁻¹ NaOH.

The charge-balance equation is given by:

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

where the sodium and chloride ion concentrations are given by

$$[\text{Na}^+] = \frac{V_{\text{NaOH}}c_{\text{NaOH}}}{V_{\text{NaOH}}+V_{\text{HCl}}} \text{ and } [\text{Cl}^-] = \frac{V_{\text{HCl}}c_{\text{HCl}}}{V_{\text{NaOH}}+V_{\text{HCl}}}$$

For volumes of NaOH short of the equivalence-point $[\text{OH}^-] \ll [\text{Cl}^-]$:

$$[\text{H}_3\text{O}^+] = [\text{Cl}^-] - [\text{Na}^+] = \frac{V_{\text{HCl}}c_{\text{HCl}}}{V_{\text{NaOH}}+V_{\text{HCl}}} - \frac{V_{\text{NaOH}}c_{\text{NaOH}}}{V_{\text{NaOH}}+V_{\text{HCl}}}$$

At the equivalence-point, $[\text{Na}^+] = [\text{Cl}^-]$ and

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

Beyond the equivalence-point, $[\text{H}_3\text{O}^+] \ll [\text{Na}^+]$, and the original equation rearranges to

$$[\text{OH}^-] = [\text{Na}^+] - [\text{Cl}^-] = \frac{V_{\text{NaOH}}c_{\text{NaOH}}}{V_{\text{NaOH}}+V_{\text{HCl}}} - \frac{V_{\text{HCl}}c_{\text{HCl}}}{V_{\text{NaOH}}+V_{\text{HCl}}}$$

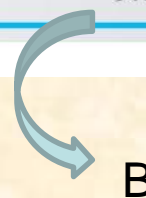
The effect of concentration

TABLE 14-2

Changes in pH during the Titration of a Strong Acid with a Strong Base

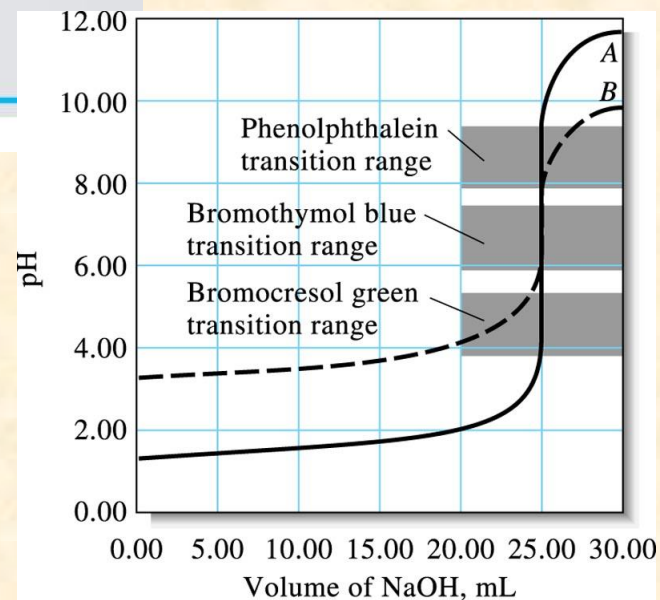
Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.100 M NaOH	50.00 mL of 0.000500 M HCl with 0.00100 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

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With 0.1 mol L⁻¹ NaOH as the titrant (curve A), the change in pH in the equivalence-point region is large.

With 0.001 mol L⁻¹ NaOH, the change is markedly less but still pronounced.



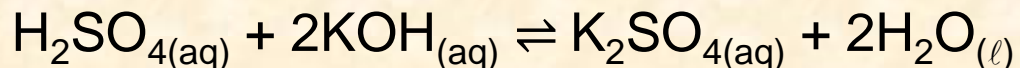
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Example

Derive a curve for the titration of 100.0 mL of 0.100 mol L⁻¹ H₂SO₄ with 0.100 mol L⁻¹ KOH.

Initial questions:

1. Reaction?



2. Volume of NaOH at equivalence-point?

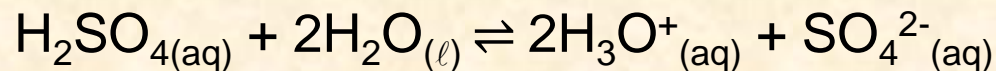
$$n^\circ \text{ mol KOH} = 2x n^\circ \text{ mol H}_2\text{SO}_4$$

$$0.100xV_{\text{KOH}} = 2x0.100x100$$

$$V_{\text{KOH}} = 200\text{mL}$$

Initial point

At the outset, the solution is 0.200 mol L^{-1} in H_3O^+ , and



$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.200) = 0.70$$

After addition of 10.00 mL of reagent

The hydronium ion concentration decreases as a result of both reaction with the base and dilution.

$$V_{\text{KOH}} = 10.00 \text{ mL} \Rightarrow n^\circ \text{ mol KOH} = 0.100 \times 0.00100 = 0.00100 \text{ mol}$$

	$\text{H}_2\text{SO}_{4(\text{aq})}$	$+ 2\text{KOH}_{(\text{aq})}$	$\rightleftharpoons \text{K}_2\text{SO}_{4(\text{aq})}$	$+ 2\text{H}_2\text{O}_{(\ell)}$
Initial	0.0100	-	-	-
Added	-	0.00100	-	-
Final	0.0095	-	0.000500	0.00100

$$V_{\text{final}} = V_{\text{H}_2\text{SO}_4} + V_{\text{KOH}} = 100.0 + 10.00 = 110.0 \text{ mL}$$

$$V_{\text{KOH}} = 50.00 \text{ mL?}$$

$$[\text{H}_3\text{O}^+] = 2 \times (0.0095 / 0.1100) = 0.173 \text{ mol L}^{-1} \Rightarrow \text{pH} = 0.76$$

Equivalence-point

At the equivalence-point, neither H_2SO_4 nor KOH is in excess, and so the concentrations of hydronium and hydroxide ions must be equal. Substituting this equality into the ion-product constant for water yields

	$\text{H}_2\text{SO}_{4(\text{aq})}$	$+ 2\text{KOH}_{(\text{aq})}$	$\rightleftharpoons \text{K}_2\text{SO}_{4(\text{aq})}$	$+ 2\text{H}_2\text{O}_{(\ell)}$
Initial	0.0100	-	-	-
Added	-	0.0200	-	-
Final	-	-	0.0100	0.0200

$$pH = -\log[H_3O^+] = 7.00$$

After addition of 210.00 mL of reagent

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

$$V_{\text{KOH}} = 210.00 \text{ mL} \Rightarrow n^{\circ} \text{ mol KOH} = 0.100 \times 0.210 = 0.0210 \text{ mol}$$

Initial	0.0100	-	-	-
Added	-	0.0210	-	-
Final	-	0.0010	0.0100	0.0200

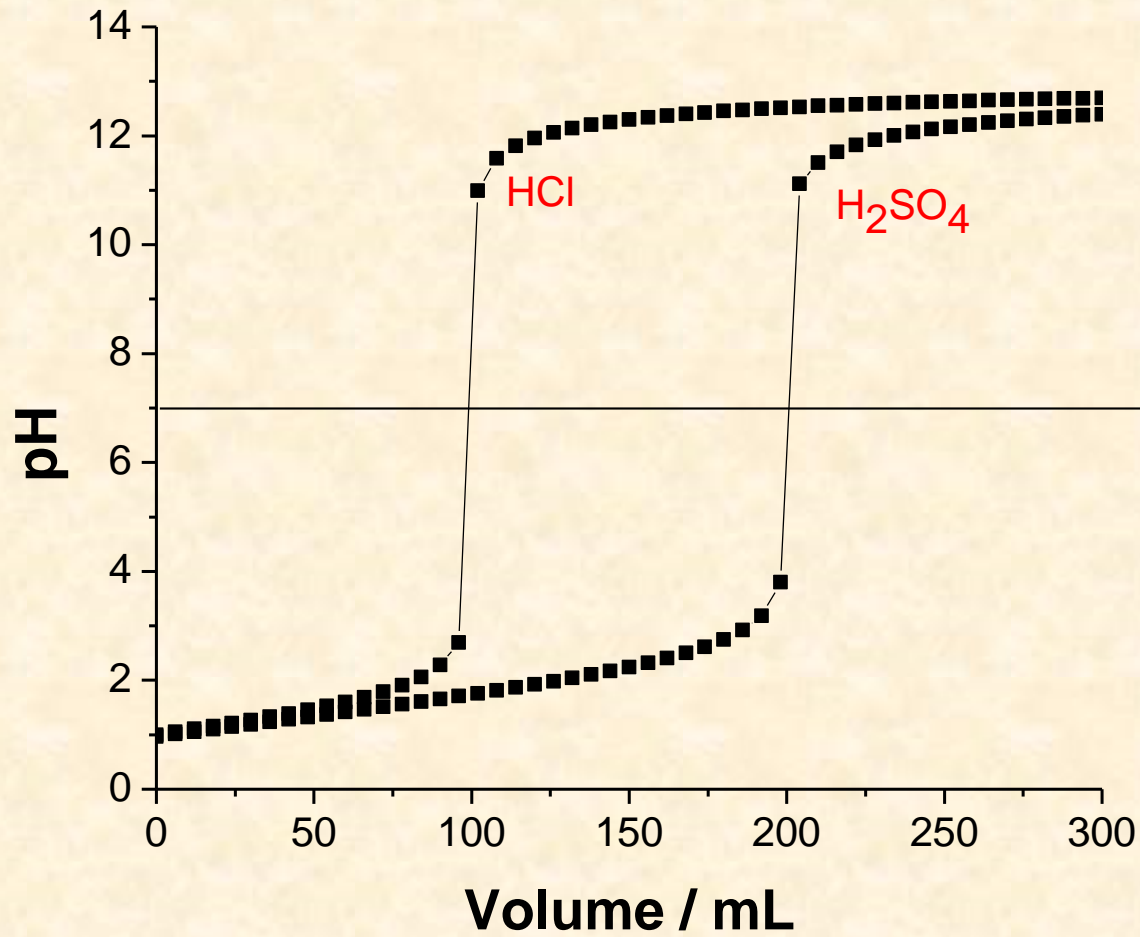
$$V_{\text{final}} = 310.0 \text{ mL}$$

$$[\text{OH}^-] = \frac{0.0010}{0.310} = 3.22 \times 10^{-3} \text{ mol L}^{-1}$$

$$p\text{OH} = 2.49$$

$$p\text{H} = 11.51$$

Curve



Weak acid/base with strong base/acid

1st step – before beginning titration: at the beginning, the solution contains only the solute acid or base, and the pH is calculated from the concentration of that solute and its dissociation constant.

2nd step – before the equivalence-point: after various increments of titrant have been added (in quantities up to, but not including, an equivalent amount), the solution consists of a series of buffers.

3rd step – at the equivalence-point: the solution contains only the conjugate of the weak acid or base being titrated (that is, a salt), and the pH is calculated from the concentration of this product.

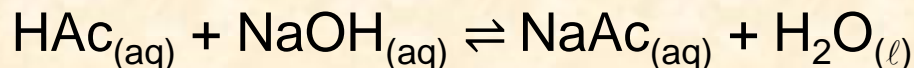
4th step – after equivalence-point: the excess of strong acid or base titrant represses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.

Example – weak acid

Derive a curve for the titration of 100.0 mL of 0.100 mol L⁻¹ acetic acid with 0.100 mol L⁻¹ NaOH. $K_a = 1,8 \times 10^{-5}$

Initial questions:

1. Reaction?



2. Volume of NaOH at equivalence-point?

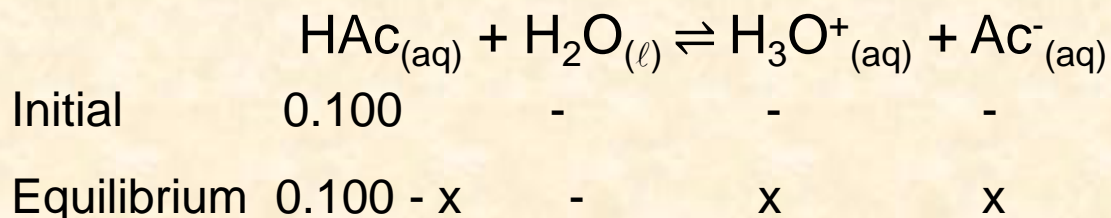
$$n^{\circ} \text{ mol NaOH} = n^{\circ} \text{ mol HAc}$$

$$0.100xV_{\text{NaOH}} = 0.100x100$$

$$V_{\text{NaOH}} = 100\text{mL}$$

Initial point

We must calculate the pH of a 0.100 mol L⁻¹ solution of HAc



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]}$$

$$[\text{H}_3\text{O}^+] = 1.33 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = 2.88$$

After addition of 10.00 mL of reagent

A buffer solution consisting of NaAc and HAc has now been produced. The analytical concentrations of the two constituents are

$$V_{\text{NaOH}} = 10.00 \text{ mL} \Rightarrow n^{\circ} \text{ mol NaOH} = 0.100 \times 0.0100 = 0.00100 \text{ mol}$$

	$\text{HAc}_{(\text{aq})}$	$+$	$\text{NaOH}_{(\text{aq})}$	\rightleftharpoons	$\text{NaAc}_{(\text{aq})}$	$+$	$\text{H}_2\text{O}_{(\ell)}$
Initial	0.0100		-		-		-
Added	-		0.01000		-		-
Final	0.00900		-		0.00100		0.00100

Volume final = 110.00 mL

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]}$$

$$[\text{H}_3\text{O}^+] = 1.62 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{pH} = 3.79$$

Equivalence-point

All of the acetic acid has been converted to sodium acetate \Rightarrow Hydrolysis

$$V_{\text{NaOH}} = 100.0 \text{ mL} \Rightarrow n^{\circ} \text{ mol NaOH} = 0.100 \times 0.100 = 0.0100 \text{ mol}$$

	$\text{HAc}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightleftharpoons \text{NaAc}_{(\text{aq})} + \text{H}_2\text{O}_{(\ell)}$			
Initial	0.0100	-	-	-
Added	-	0.0100	-	-
Final	-	-	0.0100	0.0100

	$\text{Ac}^{-}_{(\text{aq})} + \text{H}_2\text{O}_{(\ell)} \rightleftharpoons \text{OH}^{-}_{(\text{aq})} + \text{HAc}_{(\text{aq})}$			
Initial	0.050	-	-	-
Equilibrium	0.050-x	-	x	x

$$V_{\text{final}} = 200.0 \text{ mL}$$

$$K_h = \frac{K_w}{K_a} = \frac{[\text{HAc}][\text{OH}^{-}]}{[\text{Ac}^{-}]} \quad \Longrightarrow \quad [\text{OH}^{-}] = 5.27 \times 10^{-6} \text{ mol L}^{-1}$$

$p\text{OH} = 5.28$
$p\text{H} = 8.72$

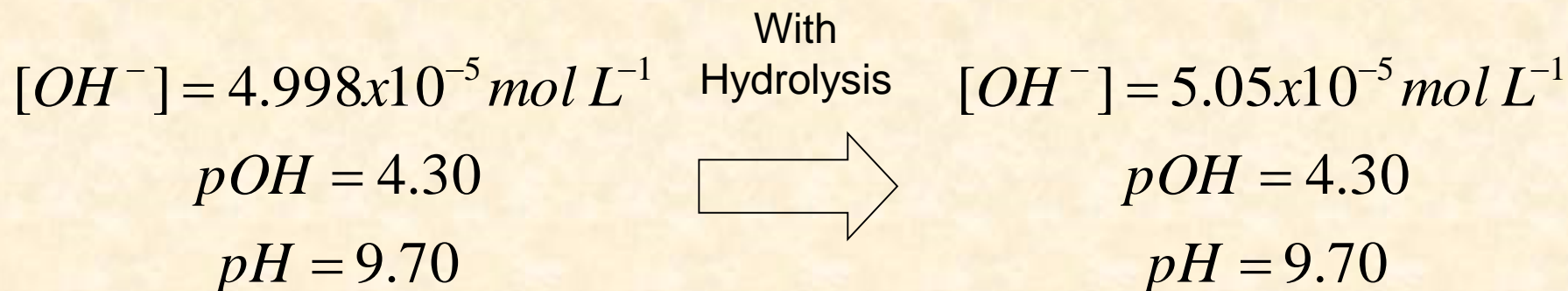
After addition of 100.1 mL of base

Both excess base and the acetate ion are sources of hydroxide ion. The contribution of later is small, however, because the excess of strong base represses the reaction.

$$V_{\text{NaOH}} = 100.1 \text{ mL} \Rightarrow \text{no mol NaOH} = 0.100 \times 0.1001 = 0.01001 \text{ mol}$$

	$\text{HAc}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightleftharpoons \text{NaAc}_{(\text{aq})} + \text{H}_2\text{O}_{(\ell)}$			
Initial	0.0100	-	-	-
Added	-	0.01001	-	-
Final	-	0.00001	0.0100	0.0100

$$V_{\text{final}} = 200.1 \text{ mL}$$



Problem – weak base

Derive a curve for the titration of 100.0 mL of 0.100 mol L⁻¹ NH₄OH with 0.100 mol L⁻¹ HCl. $K_b = 1.8 \times 10^{-5}$

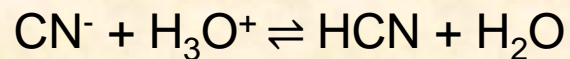
Initial questions:

1. Reaction?
2. Volume of NaOH at equivalence-point?

Problem

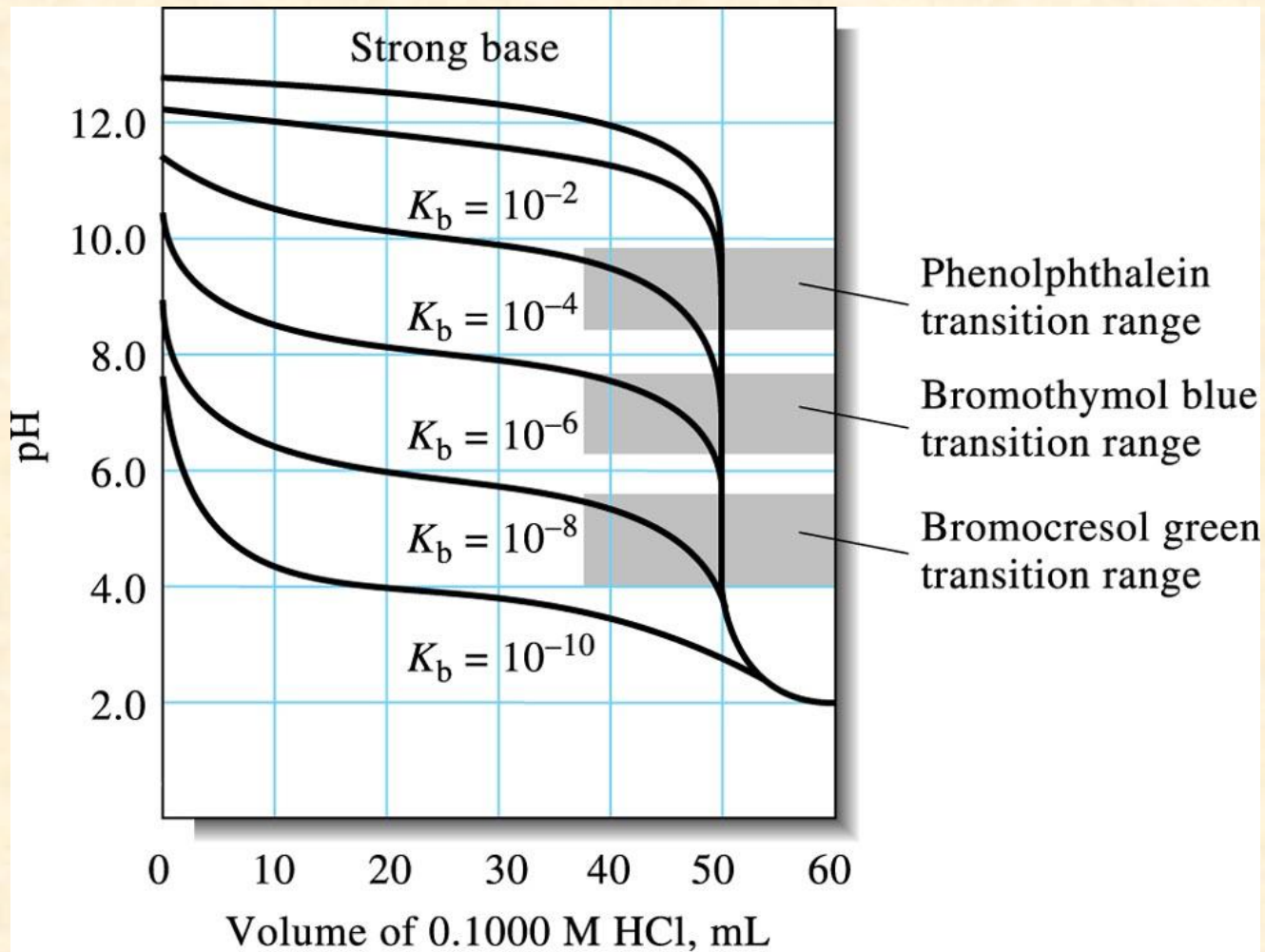
A 50.00 mL aliquot of 0.0500 mol L⁻¹ NaCN is titrated with 0.100 mol L⁻¹ HCl

The reaction is



Calculate the pH after the addition of (a) 0.00; (b) 10.00; (c) 25.00; and (d) 26.00 mL of acid. $K_a = 6.2 \times 10^{-10}$

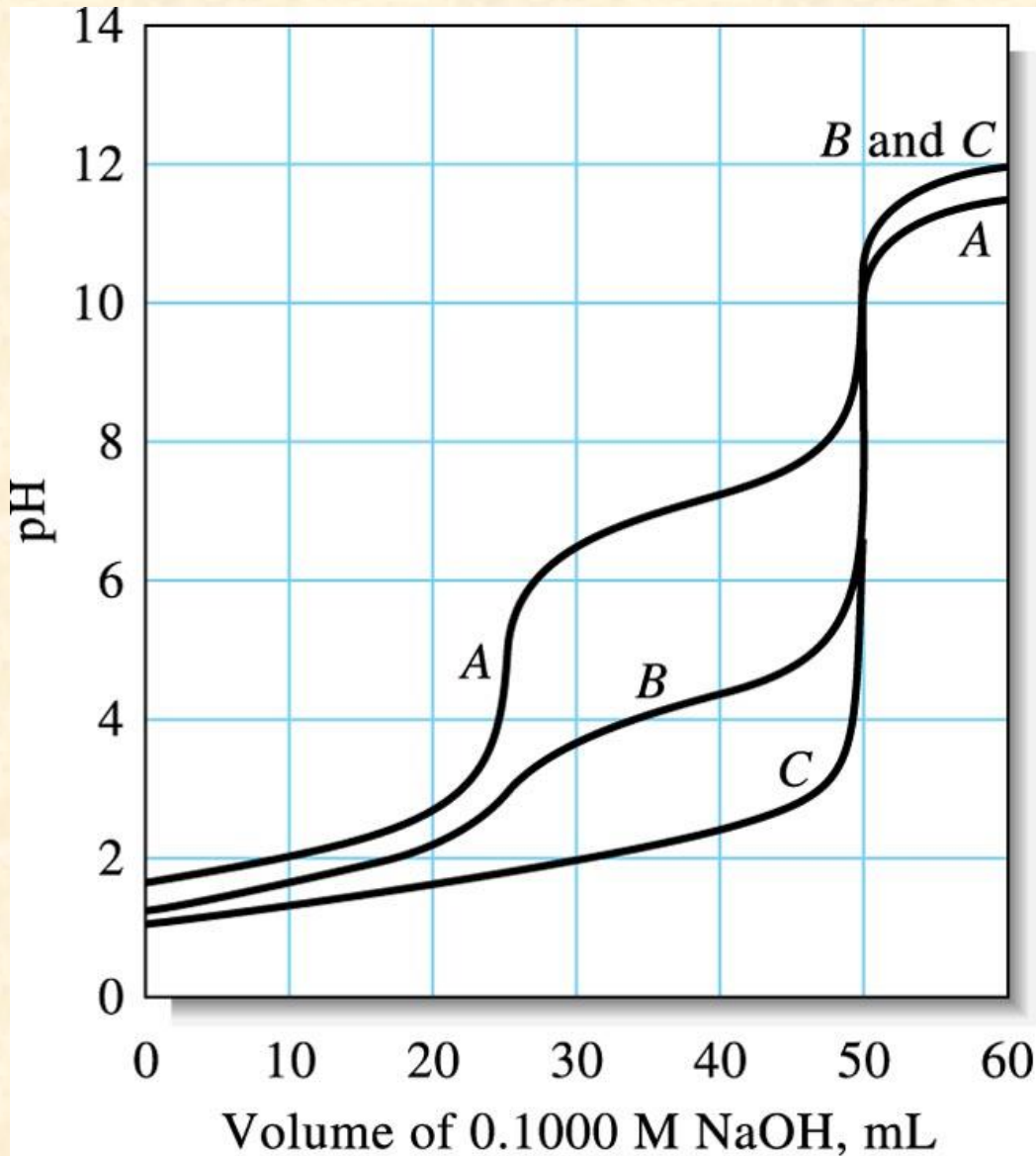
Curves - base strength



Weak acid with weak base

- Important characteristic: gradual change of the pH close to equivalence-point, which incidentally occurs along the entire neutralization curve.
- There is no sudden change in pH, so a clear end point with simple indicators is not achieved.
- It is sometimes possible to find a suitable mixed indicator with sharp color change over a very narrow pH range.

Polyprotic acids



A – 25.00 mL of 0.1000 mol L⁻¹ H₃PO₄

B – 25.00 mL of 0.1000 mol L⁻¹ H₂C₂O₄

C – 25.00 mL of 0.1000 mol L⁻¹ H₂SO₄

Polyprotic acids with strong base

- The shape of the titration curve depends on the relative magnitude of the various dissociation constants (i.e., it may exhibit 2 or more end points).
- $K_{a1} / K_{a2} > 10^3 \rightarrow$ simple monoprotic weak acids
- Assuming a diprotic acid H_2A with dissociation constant $K_{a1} = 1.00 \times 10^{-3}$ and $K_{a2} = 1.00 \times 10^{-7}$.

Initial pH (A): we treat the system as if it contained a single monoprotic acid with a dissociation constant of K_{a1} .

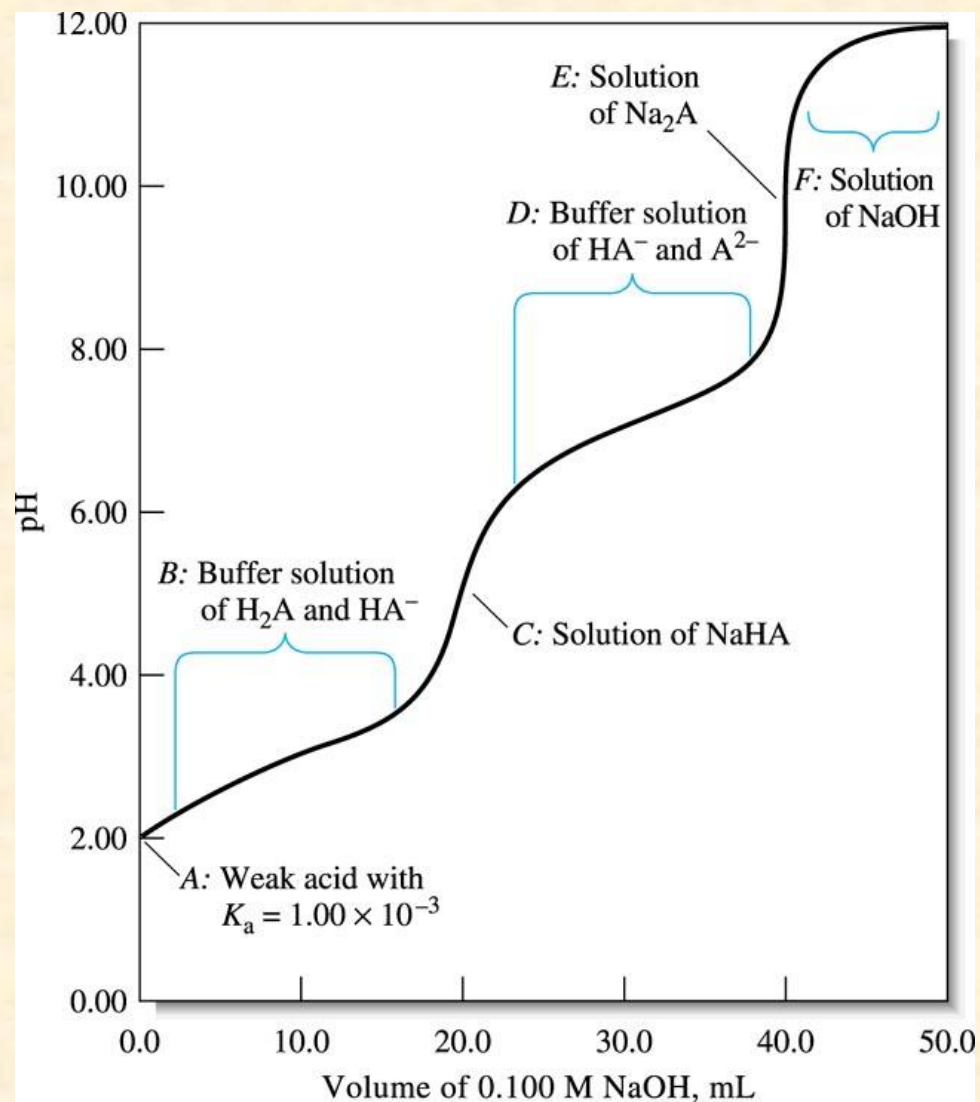
Region B: we have the equivalent of a simple buffer solution consisting of the weak acid H_2A and its conjugate base $NaHA$. (assume $[A^{2-}]$ is negligible)

Equivalence-point (C): we have a solution of an acid salt.

Region D: we have a second buffer consisting of a weak acid HA^- and its conjugate base Na_2A , and we calculate the pH employing the second dissociation constant K_{a2} .

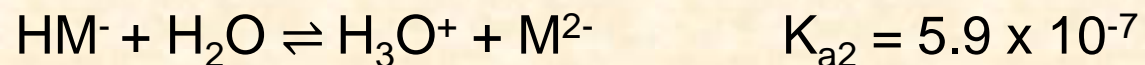
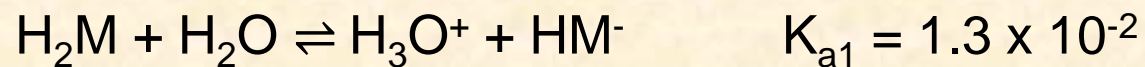
Point E: the solution contains the conjugate base of a weak acid with a dissociation constant of K_{a2} .

Region F: we compute the hydroxide concentration from the molarity of the excess $NaOH$.



Example

Derive a curve for the titration of 25.00 mL of 0.1000 mol L⁻¹ maleic acid, HOOC-CH=CH-COOH, with 0.1000 mol L⁻¹ NaOH.



$$K_{a1} / K_{a2} > 10^3$$

Initial pH

Only the first dissociation makes an appreciable contribution to $[H_3O^+]$;
thus,

$$[H_3O^+] \approx [HM^-]$$

Mass balance requires that

$$[H_2M] + [HM^-] \approx 0.1000 \text{ or } [H_2M] = 0.1000 - [HM^-] = 0.1000 - [H_3O^+]$$

$$K_{a1} = \frac{[H_3O^+]^2}{0.1000 - [H_3O^+]} = 1.3 \times 10^{-2}$$

$$[H_3O^+] = 3.01 \times 10^{-2} \text{ mol L}^{-1}$$

$$pH = 1.52$$

1st 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^- . Assuming $[M^{2-}]$ negligible:

$$c_{NaHM} \approx [HM^-] = \frac{5.00 \times 0.1000}{30.00} = 1.67 \times 10^{-2} \text{ mol L}^{-1}$$

$$c_{H_2M} = \frac{25.00 \times 0.1000 - 5.00 \times 0.1000}{30.00} = 6.67 \times 10^{-2} \text{ mol L}^{-1}$$

$$[HM^-] = c_{NaHM} + [H_3O^+] - [OH^-]$$

$$[H_2M] = c_{H_2M} - [H_3O^+] + [OH^-]$$

$$K_{a1} = \frac{[H_3O^+][HM^-]}{[H_2M]} = 1.3 \times 10^{-2}$$

$$[H_3O^+] = 1.81 \times 10^{-2} \text{ mol L}^{-1}$$

$$pH = 1.74$$

Just before the 1st equivalence-point

The $[H_2M]$ is so small that it becomes comparable to $[M^{2-}]$ and the second equilibrium also needs to be considered.

$$V_{\text{added}} = 24.90 \text{ mL}$$

$$c_{H_2M} = \frac{25.00 \times 0.1000 - 24.90 \times 0.1000}{49.90} = 2.00 \times 10^{-4} \text{ mol L}^{-1}$$

$$c_{NaHM} \approx [HM^-] = \frac{24.90 \times 0.1000}{49.90} = 4.99 \times 10^{-2} \text{ mol L}^{-1}$$

$$MB : c_{H_2M} + c_{NaHM} = [H_2M] + [HM^-] + [M^{2-}]$$

$$CB : [H_3O^+] + [Na^+] = [HM^-] + 2[M^{2-}] + [OH^-]$$



c_{NaHM}



negligible

$$c_{NaHM} = [HM^-] + 2[M^{2-}] - [H_3O^+]$$

$$c_{NaHM} = [H_2M] + [HM^-] + [M^{2-}] - c_{H_2M}$$

$$[H_3O^+] = c_{H_2M} + [M^{2-}] - [H_2M]$$

$$K_{a1} = \frac{[H_3O^+][HM^-]}{[H_2M]}$$

$$K_{a2} = \frac{[H_3O^+][M^{2-}]}{[HM^-]}$$

$$[H_3O^+] = c_{H_2M} + \frac{K_{a2}[HM^-]}{[H_3O^+]} - \frac{[H_3O^+][HM^-]}{K_{a1}} = 1.014 \times 10^{-4} \text{ mol L}^{-1}$$

$$pH = 3.99$$

1st equivalence-point

$$c_{NaHM} \approx [HM^-] = \frac{25.00 \times 0.1000}{50.00} = 5.00 \times 10^{-2} \text{ mol L}^{-1}$$

$$MB : c_{NaHM} = [H_2M] + [HM^-] + [M^{2-}]$$

$$CB : [H_3O^+] + c_{NaHM} = [HM^-] + 2[M^{2-}] + [OH^-]$$

$$[H_3O^+] = [M^{2-}] + [OH^-] + [H_2M]$$

$$[HM^-] \approx c_{HM^-}$$

$$[H_3O^+] = \frac{K_{a2}[HM^-]}{[H_3O^+]} + \frac{K_w}{[H_3O^+]} - \frac{[H_3O^+][HM^-]}{K_{a1}} = 7.80 \times 10^{-5} \text{ mol L}^{-1}$$

$$pH = 4.11$$

$$pH = \frac{1}{2} (pK_{a1} + pK_{a2})$$

Shortly after 1st equivalence-point

$$V_{\text{added}} = 25.01 \text{ mL}$$

In this region, the solution consists basically of HM^- with some M^{2-} formed.

$$c_{\text{HM}^-} = \frac{n_{\text{NaHMform}} - (n_{\text{NaOHadic}} - n_{\text{NaHMform}})}{V_{\text{total}}} = 0.04997 \text{ mol L}^{-1}$$

$$c_{\text{M}^{2-}} = \frac{(n_{\text{NaOHadic}} - n_{\text{NaHMform}})}{V_{\text{total}}} = 1.996 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{MB} : c_{\text{Na}_2\text{M}} + c_{\text{NaHM}} = [\text{H}_2\text{M}] + [\text{HM}^-] + [\text{M}^{2-}] = 0.49999 \text{ mol L}^{-1}$$

$$\text{CB} : [\text{H}_3\text{O}^+] + [\text{Na}^+] = [\text{HM}^-] + 2[\text{M}^{2-}] + [\text{OH}^-]$$

$$[H_3O^+] + [Na^+] = 2[M^{2-}] + [OH^-] - [H_2M] - [M^{2-}]$$

$$[H_3O^+] = [M^{2-}] - [H_2M] - [Na^+] + [OH^-]$$

$$\frac{K_{a2}[HM^-]}{[H_3O^+]}$$

$$\frac{[H_3O^+][HM^-]}{K_{a1}}$$

$$\frac{(n_{NaOHadic} - n_{NaHMform})}{V_{total}}$$

negligible

$$[H_3O^+] = 7.40 \times 10^{-5} \text{ mol L}^{-1}$$

$$pH = 4.13$$

2nd buffer region

Addition of 25.50 mL of base resulted in the formation of a weak acid buffer

HM^- and its conjugate base M^{2-}

$$[M^{2-}] \approx c_{Na_2M} \approx \frac{(n_{NaOHadic} - n_{Na_2Mform})}{V_{total}}$$

$$[HM^-] \approx c_{NaHM} \approx \frac{n_{Na_2Mform} - (n_{NaOHadic} - n_{Na_2Mform})}{V_{total}}$$

$$K_{a2} = \frac{[H_3O^+][M^{2-}]}{[HM^-]}$$

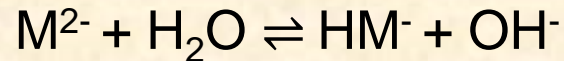
$$[H_3O^+] = 2.89 \times 10^{-5} \text{ mol L}^{-1}$$

$$pH = 4.54$$

Just before the 2nd equivalence-point

$$V_{\text{added}} = 49.90 \text{ mL}$$

In this region, the ratio M^{2-} / HM^- becomes large and the equation for the simple buffers is no longer applied.



$$[M^{2-}] \approx c_{Na_2M} \approx \frac{(n_{NaOH_{adic}} - n_{Na_2M_{form}})}{V_{total}}$$

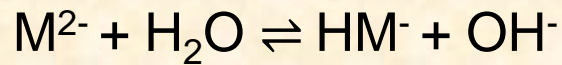
$$[HM^-] \approx c_{NaHM} \approx \frac{n_{Na_2M_{form}} - (n_{NaOH_{adic}} - n_{Na_2M_{form}})}{V_{total}}$$

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{[OH^-][HM^-]}{[M^{2-}]} = \frac{[OH^-](c_{HM^-} - [OH^-])}{c_{M^{2-}} - [OH^-]}$$

$$pH = 8.61$$

2nd equivalence-point

After the addition of 50.00 mL of 0.1000 mol L⁻¹ sodium hydroxide, the solution is 0.0333 mol L⁻¹ in Na₂M. Reaction of the base M²⁻ with water is the predominant equilibrium in the system and the only one that we need to take into account. Thus,



$$[M^{2-}] \approx c_{Na_2M} \approx \frac{(n_{NaOHadic} - n_{Na_2Mform})}{V_{total}} = \frac{(50 - 25) \times 0.1000}{75} = 0.0333 \text{ mol L}^{-1}$$

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

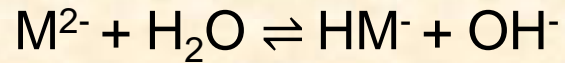
$$[OH^-] \approx [HM^-]$$

$$[M^{2-}] = c_{Na_2M} - [OH^-]$$

$$pH = 9.38$$

Shortly after the 2nd equivalence-point

$$V_{\text{added}} = 50.01 \text{ mL}$$



$$c_{M^{2-}} \approx \frac{n_{M^{2-}} \text{ produced}}{V_{\text{total}}}$$

$$[OH^-]_{\text{excess}} = [OH^-]_{\text{added}} - [OH^-]_{\text{reacted}}$$

$$[M^{2-}] = c_{M^{2-}} - [HM^-]$$

$$[OH^-] = [OH^-]_{\text{excess}} + [HM^-]$$

$$pH = 10.14$$

Beyond the 2nd equivalence-point

$$V_{\text{added}} = 51.00 \text{ mL}$$

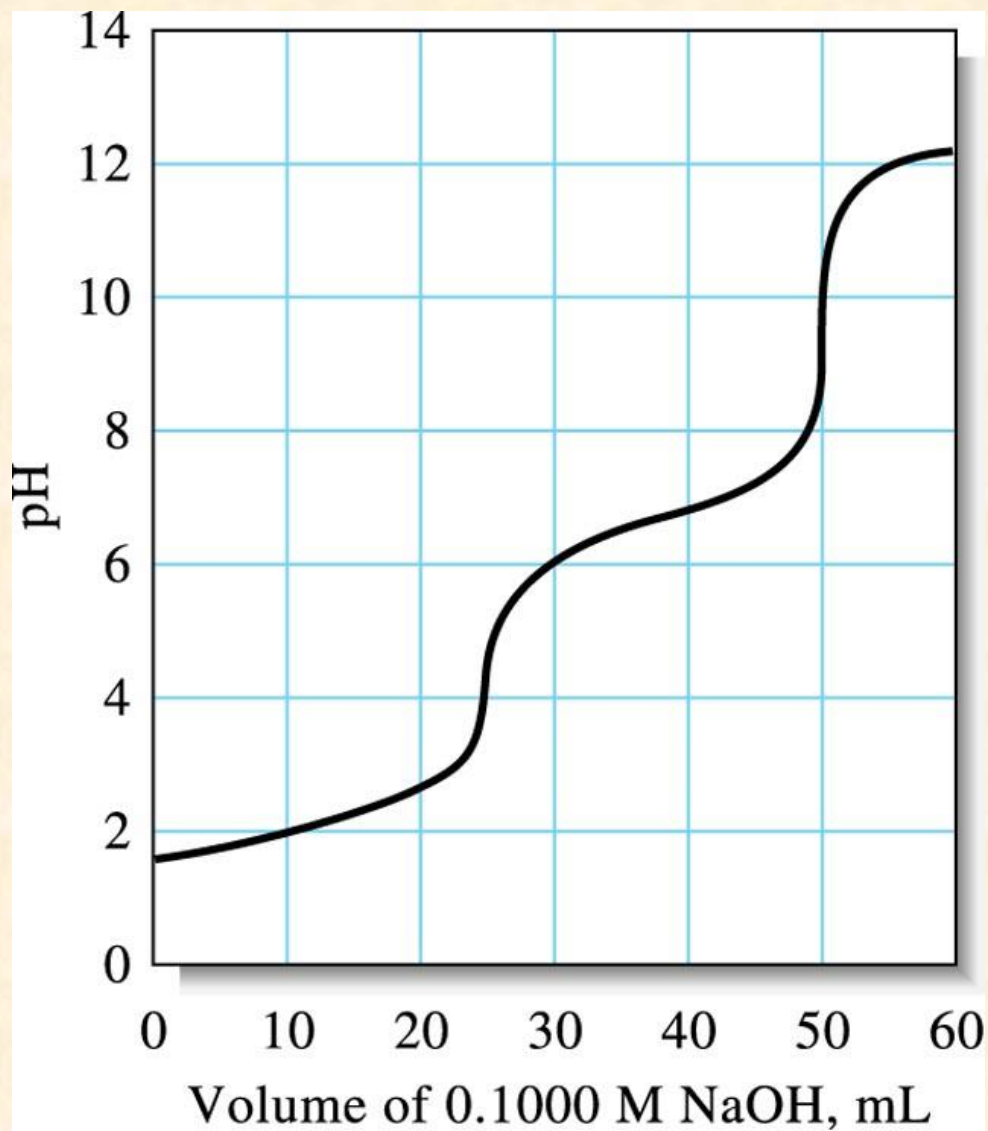
Further additions of sodium hydroxide repress the basic dissociation of M^{2-} .

The pH is calculated from the concentration of NaOH added in excess of that required for the complete neutralization of H_2M .

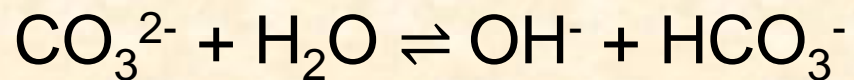
$$[OH^-]_{\text{excess}} = [OH^-]_{\text{added}} - [OH^-]_{\text{reacted}}$$

$$pH = 11.12$$

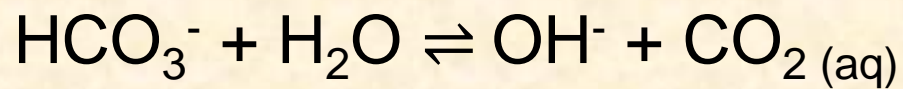
Titration curve for 25.00 mL of 0.1000 mol L⁻¹ maleic acid



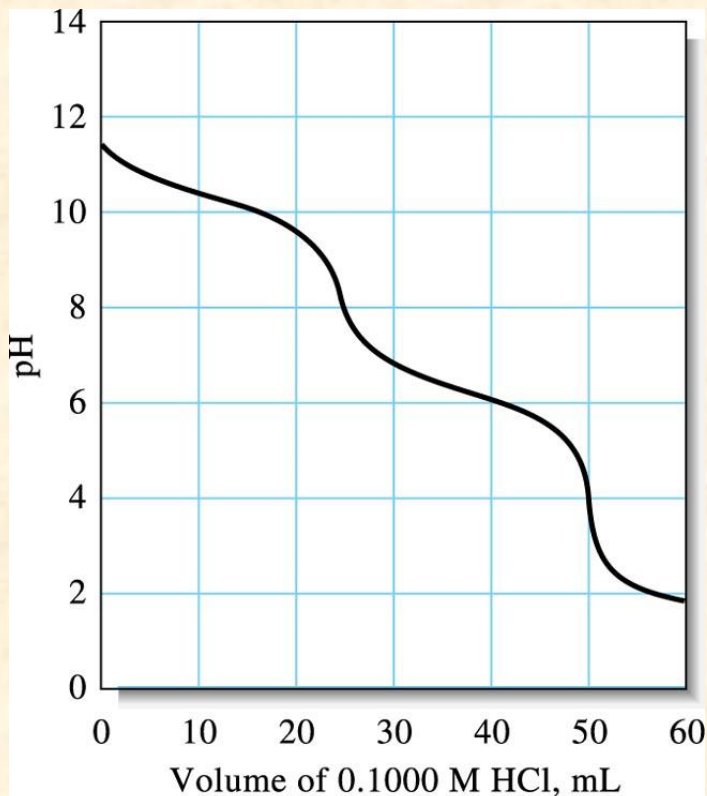
Polyprotic base with strong acid



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

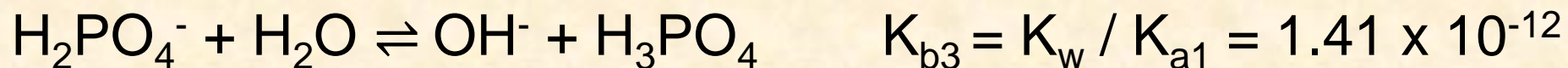
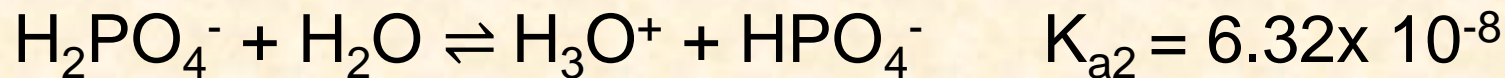


$$K_{b2} = K_w / K_{a1}$$

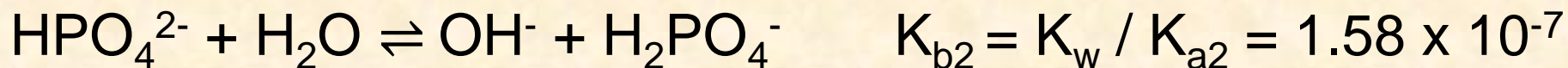


25.00 mL of 0.1000 mol L⁻¹ Na₂CO₃

Amphiprotic species



$K_{a2} \gg K_{b3} \rightarrow$ titration with base



$K_{a3} \ll K_{b2} \rightarrow$ titration with acid

Mixtures of strong and weak acids or strong and weak bases

Calculate the pH of a 25.00 mL mixture that is 0.1200 mol L⁻¹ in hydrochloric acid and 0.0800 mol L⁻¹ in the weak acid HA ($K_a = 1.00 \times 10^{-4}$) during its titration with 0.1000 mol L⁻¹ KOH. Derive data for addition of the following mL of base: (a) 0.00 and (b) 5.00.

$$V_{\text{added}} = 0.00 \text{ mL}$$

[H₃O⁺] from dissociation of HA

$$[H_3O^+] = c_{HCl} + [A^-] + [H_3O^+]_{H_2O}$$

negligibly small

CHECK!!!!

Assume that the presence of the strong acid so represses the dissociation of HA that $[A^-] \lll 0.1200 \text{ mol L}^{-1} \rightarrow \text{pH} = 0.92$

$$V_{\text{added}} = 5.00 \text{ mL}$$

$$V_{\text{mixture}} = 25.00 \text{ mL}$$

$$c_{\text{HCl}} = \frac{nH_3O^+_{\text{initial}} - nH_3O^+_{\text{reacted}}}{V_{\text{total}}}$$

$$[A^-] \lll c_{\text{HCl}} \rightarrow \text{pH} = 1.08$$

$$V_{\text{KOH}} = 29.00 \text{ mL}$$

$$c_{\text{HCl}} = \frac{nH_3O^+_{\text{HCl}} - nH_3O^+_{\text{reacted}}}{V_{\text{total}}} = \frac{25.00 \times 0.1200 - 29.00 \times 0.1000}{25.00 + 29.00} = 1.85 \times 10^{-3} \text{ mol L}^{-1}$$

$$c_{\text{HA}} = \frac{nH_3O^+_{\text{HA}}}{V_{\text{total}}} = \frac{25.00 \times 0.0800}{54.00} = 3.70 \times 10^{-2} \text{ mol L}^{-1}$$

$$[H_3O^+] = c_{\text{HCl}} + [A^-] = 1.85 \times 10^{-3} + [A^-]$$

$$[HA] = \frac{[H_3O^+][A^-]}{1.00 \times 10^{-4}}$$

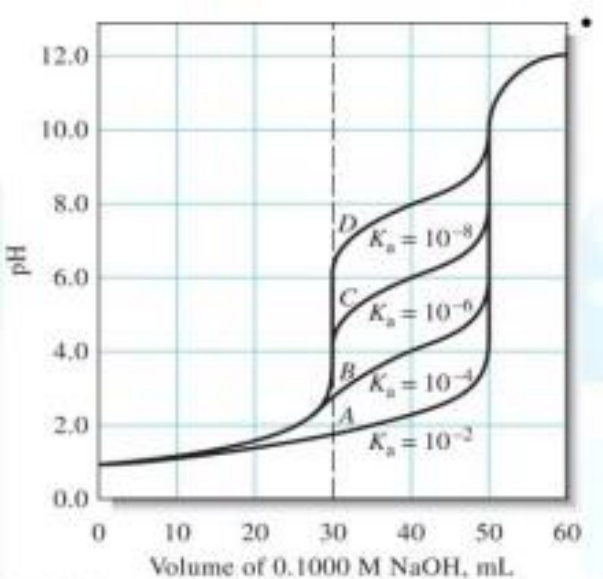
$$[HA] + [A^-] = c_{\text{HA}} = 3.70 \times 10^{-2}$$

$$\frac{[H_3O^+][A^-]}{1.00 \times 10^{-4}} + [A^-] = 3.70 \times 10^{-2} \rightarrow [A^-] = \frac{3.70 \times 10^{-6}}{[H_3O^+] + 1.00 \times 10^{-4}}$$

$$[H_3O^+] = 1.85 \times 10^{-3} + \frac{3.70 \times 10^{-6}}{[H_3O^+] + 1.00 \times 10^{-4}}$$

$$[H_3O^+] = 3.03 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = 2.52$$



The shape of the curve for a mixture of weak and strong acids, depends in large measure on the strength of the weak acid.

pH changes that occur during the titration of mixtures containing HCl and several weak acids.

Note that the rise in pH at the first equivalence point is small or essentially nonexistent when the weak acid has a relatively large dissociation constant (curves A and B). For titrations such as these, only the total number of mmoles of weak and strong acid can be determined accurately.

Conversely, when the weak acid has a very small dissociation constant, only the strong acid content can be determined. For weak acids of intermediate strength (K_a somewhat less than 10^{-4} but greater than 10^{-8}), there are usually two useful end points.

Carbonates mixtures

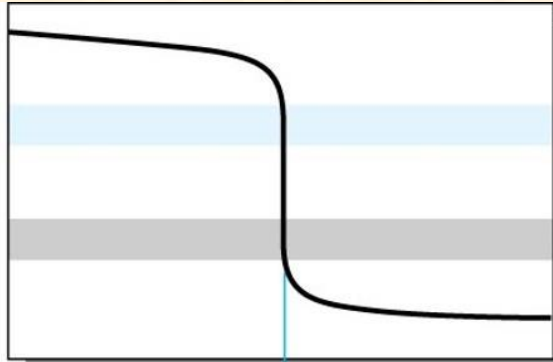
- The qualitative and the quantitative determination of the constituents in a solution containing sodium carbonate, sodium hydrogen carbonate, and sodium hydroxide, either alone or admixed, provides interesting examples of how neutralization titrations can be employed to analyse mixtures.
- The analysis of such mixtures requires two titrations: one with an alkaline-range indicator, such as phenolphthalein, and the other with an acid-range indicator, such as bromocresol green.
- The composition of the solution can then be deduced from relative volumes of acid needed to titrate equal volumes of the sample.

TABLE 16-2

Volume Relationships in the Analysis of Mixtures Containing Hydroxide, Carbonate, and Hydrogen Carbonate Ions

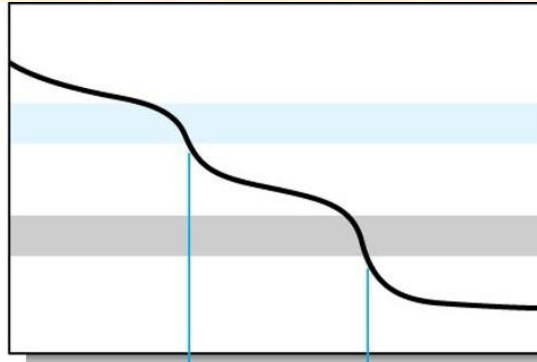
Constituents in Sample	Relationship between V_{phth} and V_{beg} in the Titration of an Equal Volume of Sample*
NaOH	$V_{\text{phth}} = V_{\text{beg}}$
Na_2CO_3	$V_{\text{phth}} = \frac{1}{2} V_{\text{beg}}$
NaHCO_3	$V_{\text{phth}} = 0; V_{\text{beg}} > 0$
NaOH, Na_2CO_3	$V_{\text{phth}} > \frac{1}{2} V_{\text{beg}}$
$\text{Na}_2\text{CO}_3, \text{NaHCO}_3$	$V_{\text{phth}} < \frac{1}{2} V_{\text{beg}}$

* V_{phth} = volume of acid needed for a phenolphthalein end point; V_{beg} = volume of acid needed for a bromocresol green end point.



V_{phth}
 V_{bcg}

NaOH



V_{phth}
 V_{bcg}

Na_2CO_3



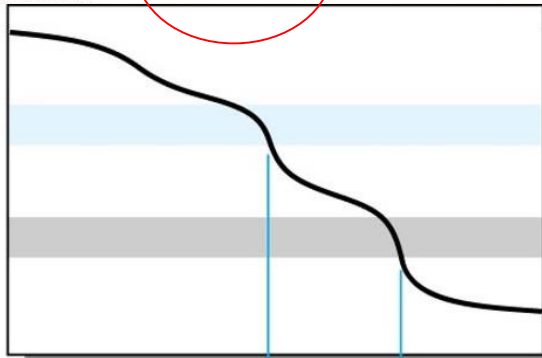
$V_{\text{phth}} = 0$
 V_{bcg}

NaHCO_3

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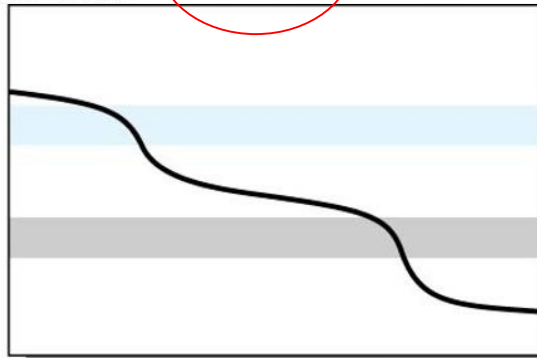
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V_{phth}
 V_{bcg}

NaOH and Na_2CO_3



V_{phth}
 V_{bcg}

NaHCO_3 and Na_2CO_3

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Phenolphthalein transition range

Bromocresol green transition range

Example

A solution contains NaHCO_3 , Na_2CO_3 , and NaOH , either alone or in a permissible combination. Titration of a 50.0 mL portion to a phenolphthalein end point requires 22.1 mL of 0.100 mol L^{-1} HCl . A second 50.0 mL aliquot requires 48.4 mL of the HCl when titrated to a bromocresol green end point. Deduce the composition, and calculate the molar solute concentrations of the original solution.

Only NaOH $\rightarrow V_{\text{phth}} = V_{\text{bcg}}$

Only Na_2CO_3 $\rightarrow 2V_{\text{phth}} = V_{\text{bcg}}$

22.1 mL (1st) less than half of 48.4 mL (2nd) $\rightarrow \text{NaHCO}_3$ in addition to Na_2CO_3

Problem

A series of solutions containing NaOH, Na₂CO₃, and NaHCO₃, alone or in compatible combination, was titrated with 0.1202 mol L⁻¹ HCl. The volumes of acid needed to titrate 25.00 mL portions of each solution to a (1) phenolphthalein and (2) bromocresol green end point are given in the table that follows. Use this information to deduce the composition of the solutions. In addition, calculate the number of milligrams of each solute per milliliter of solution. (W.M NaOH = 40 g mol⁻¹; Na₂CO₃ = 106 g mol⁻¹ and NaHCO₃ = 84 g mol⁻¹)

	(1)	(2)
(a)	22.42	22.44
(b)	15.67	42.13
(c)	29.64	36.42
(d)	16.12	32.23
(e)	0.00	33.333

Nitrogen

A 0.7121 g sample of a wheat flour was analyzed by the Kjeldahl method. The ammonia formed by addition of concentrated base after digestion with H_2SO_4 was distilled into 25.00 mL of $0.04977 \text{ mol L}^{-1} \text{ HCl}$. The excess HCl was then back-titrated with 3.97 mL of $0.04012 \text{ mol L}^{-1} \text{ NaOH}$. Calculate the percent N in the flour.

$$n_{\text{HCl}} = 1.2443 \text{ mmol}$$

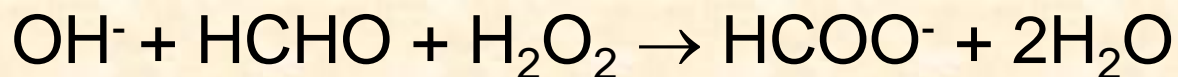
$$n_{\text{NaOH}} = 0.1593 \text{ mmol}$$

$$n_{\text{N}} = n_{\text{HCl}} - n_{\text{NaOH}} = 1.0850 \text{ mmol}$$

$$\% \text{ N} = \frac{n_{\text{N}} \times PA}{m_{\text{amostra}}} \times 100\% = 2.1341$$

Problem

The formaldehyde content of a pesticide preparation was determined by weighing 0.3124 g of the liquid sample into a flask containing 50.0 mL of 0.0996 mol L⁻¹ NaOH and 50 mL of 3% H₂O₂. Upon heating, the following reaction took place:



After cooling, the excess base was titrated with 23.3 mL of 0.05250 mol L⁻¹ H₂SO₄. Calculate the percentage of HCHO (30.026 g mol⁻¹) in the sample.