ملزمة -2- كورس اول 2018-2017

Volumetric analysis (titration analysis):- تابع صفحة 30 موضوع

Example:- How many millilitres of 0.25 M solution of H_2SO_4 will react with 10 mL of a 0.25 M solution of NaOH.

$$\mathrm{H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O}$$

One half as many millimoles of H_2SO_4 will react one millimole NaOH

$$(\mathrm{M \times V})_{\mathrm{H_2SO_4}} = \frac{1}{2}\ (\mathrm{M \times V})_{\mathrm{NaOH}}$$

$$0.25 \times \mathrm{V} = \frac{1}{2}\ (0.25 \times 10) \qquad\qquad \mathrm{V} = 5.0\ \mathrm{mL\ H_2SO_4}$$

Example:- An approximate 0.1M hydrochloric acid solution is prepared by 120-fold dilution of concentration hydrochloric acid. It is standardized by titrating 0.1876 g of dried primary standard sodium carbonate: $\mathrm{CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2}$

The titration required 35.86 mL acid. Calculate the molar concentration of the hydrochloric acid.

Solution: Millimoles HCl equal to twice the millimoles of Na_2CO_3

$$\mathbf{(M \times V)_{HCl} = \frac{2}{1}\ (\frac{wt}{M.wt})_{Na_2CO_3}}$$

$$\mathbf{M\ \times 35.86 = 2\ (\frac{187.6\ mg}{105.99\ mg/mmol})}$$

$$\mathbf{M_{HCl} = 0.0987\ mmol/mL}$$

Example:- The iron(II)in an acidified solution is titrated with a 0.0206 M solution of potassium permanganate:$\mathrm{5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O}$

If the titration required 40.2 mL, how many milligrams iron are in the solution.

$$\mathbf{\left(\frac{wt}{M.wt}\right)_{Fe} = \frac{5}{1}\ (M \times V)_{KMnO_4}}$$

$$\mathbf{\frac{wt}{55.8} = 5\ (0.0206\ \times\ 40.2)}$$

$$\mathbf{wt = 231.0\ mg}$$

Example:- Aluminum is determined by titrating with EDTA:

$$\mathrm{Al^{3+} + H_2Y^{2-} \rightarrow AlY^- + 2H^+}$$

A 1.00 g sample requires 20.5 mL EDTA for titration. The EDTA was standardized by titrating 25.0 mL a 0.100M $CaCl_2$ solution, requiring 30.0 mL EDTA. Calculate the percent Al_2O_3 in the sample.

Solution: $\mathbf{1\ millimoles\ Ca^{2+} = 1\ millimoles\ EDTA}$

$$\mathbf{(M \times V)_{EDTA} = (M \times V)_{CaCl_2}}$$

$$\mathbf{M \times 30.0 = 0.10 \times 25.0}$$

$$\mathbf{M = 0.0833\ mmol/mL}$$

$$\mathbf{1\ millimoles\ Al_2O_3 = \frac{1}{2}\ millimoles\ EDTA}$$

$$\mathbf{(\frac{wt}{M.wt} X1000)_{Al_2O_3} = \frac{1}{2} \times (M \times V)_{EDTA}}$$

$$\mathbf{(\frac{wt}{101.96} X1000)_{Al_2O_3} = \frac{1}{2} \times (0.0833 \times 20.5)_{EDTA}}$$

$$\mathbf{wt = 0.0871\ g}$$

$$\%\ \mathbf{Al_2O_3 = \frac{wt\ component}{wt\ sample} \times 100}$$

$$= \mathbf{\frac{0.0871}{1} \times 100 = 8.71\%\ Al_2O_3}$$

Example:- In acid solution, potassium permanganate reacts with H_2O_2 to form Mn^{2+}: $5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$
In neutral solution, it reacts with $MnSO_4$ to form MnO_2:

$$3Mn^{2+} + 2MnO_4^- + 4OH^- \rightarrow 5MnO_2 + 2H_2O$$

Calculate the number of millilitres of 0.100M $KMnO_4$ that will react with 50.0mL of 0.200M H_2O_2 and with 50.0mL of 0.200 M $MnSO_4$.

Solution:

$$\mathbf{1\ millimoles\ MnO_4^- = \frac{2}{5}\ millimoles\ H_2O_2}$$

$$\mathbf{(M \times V)_{MnO_4^-} = \frac{2}{5}\ (M \times V)_{H_2O_2}}$$

$$\mathbf{(0.10 \times V)_{MnO_4^-} = \frac{2}{5}\ (0.20 \times 50.0)_{H_2O_2}}$$

$$\mathbf{V_{KMnO_4} = 40.0\ mL}$$

$$\mathbf{1\ millimoles\ MnO_4^- = \frac{2}{3}\ millimoles\ Mn^{2+}}$$

$$\mathbf{(M \times V)_{MnO_4^-} = \frac{2}{3}\ (M \times V)_{Mn^{2+}}}$$

$$\mathbf{(0.10 \times V)_{MnO_4^-} = \frac{2}{3}\ (0.20 \times 50.0)_{Mn^{2+}}}$$

$$\mathbf{V_{KMnO_4} = 66.7\ mL}$$

Example:- Oxalic acid, $H_2C_2O_4$, is a reducing agent that reacts with $KMnO_4$ as follows:

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Its two protons are also titratable with a base. How many millilitres of 0.100 M NaOH 0.100 M KMnO4 will react with 500 mg $H_2C_2O_4$?

Solution:

$$\text{millimoles NaOH} = 2\ \text{millimoles}\ H_2C_2O_4$$

$$\mathbf{(0.10 \frac{mmol}{mL} \times \mathit{x}\ mL)_{NaOH} = 2\ (\frac{500mg}{90.0 \frac{mg}{mmol}})}$$

$$x = 111\ \mathbf{mL\ NaOH}$$

$$\mathbf{millimoles\ KMnO_4} = \frac{2}{5}\ \mathbf{millimoles\ H_2C_2O_4}$$

$$(0.10 \times x\ \mathbf{mL})_{\mathbf{KMnO_4}} = \frac{2}{5}\ \left(\frac{500\mathbf{mg}}{90.0\,\frac{\mathbf{mg}}{\mathbf{mmol}}}\right)$$

$$x = 22.2\ \mathbf{mL\ KMnO_4}$$

Example:- Pure $Na_2C_2O_4$ plus $KHC_2O_4.H_2C_2O_4$ (three replaceable protons, KH_3A_2) are mixed in such a proportion that each gram of the mixture will react with equal volumes of 0.100 M $KMnO_4$ and 0.100 M NaOH. What is the proportion?

Assume 10.0 mL titrant, so there is 1.00 mmol NaOH or $KMnO_4$. The acidity is due to $KHC_2O_4.H_2C_2O_4$ (KH_3A_2):

$$\mathbf{mmol\ KH_3A_2} = \mathbf{mmol\ NaOH} \times \frac{1}{3}\ \left(\frac{\mathbf{mmol\ KH_3A_2}}{\mathbf{mmol\ OH^-}}\right)$$

$$= \left(1.0\ \text{mmol} \times \frac{1}{3}\right)_{\text{NaOH}} = 0.333\ \text{mmol}\ \text{KH}_3\text{A}_2$$

From example 5.26, each mmol $Na_2C_2O_4$ (Na_2A) reacts with 2/5 mmol $KMnO_4$:-

$$\text{mmol KMnO}_4 = \text{mmol Na}_2\text{A} \times \frac{2}{5}\left(\frac{\text{mmol MnO}_4^-}{\text{mmol Na}_2\text{A}}\right) + \text{mmol KH}_3\text{A}_2 \times \frac{4}{5}\left(\frac{\text{mmol MnO}_4^-}{\text{mmol KH}_3\text{A}_2}\right)$$

$$1.00\ \text{mmol KMnO}_4 = \text{mmol Na}_2\text{A} \times \frac{2}{5} + 0.333\ \text{mmol KH}_3\text{A}_2 \times \frac{4}{5}\ \text{mmol Na}_2\text{A}$$

$$\text{mmol Na}_2\text{A} = 1.83\ \text{mmol}$$

$$\text{The ratio is:} \frac{1.83\ \text{mmol Na}_2\text{A}}{0.333\ \text{mmol KH}_3\text{A}_2}$$

$$= \frac{5.50\ \text{mmol Na}_2\text{A}}{\text{mmol KH}_3\text{A}_2}$$

$$\text{the weight ratio is} = \frac{5.50\ \text{mmol Na}_2\text{A} \times 134\,\frac{\text{mg}}{\text{mmol}}}{218\ \text{kg}\,\frac{\text{KH}_3\text{A}_2}{\text{mmol}}}$$

$$= 3.38\ \text{g Na}_2\text{A/g KH}_3\text{A}_2$$

Example:- A 0.4671 g sample containing sodium bicarbonate (a monoacidic base) is dissolved and titrated with a standard solution of hydrochloric acid, requiring 40.72 mL. The hydrochloric acid was standardized by titrating 0.1876 gm sodium carbonate, which required 37.86 mL acid (see example 5.18 for reaction). Calculate the percent sodium bicarbonate in the sample.

$$(\mathbf{N} \times \mathbf{V})_{\mathbf{HCl}} = \left(\frac{\mathbf{wt}}{\mathbf{Eq.\,wt}}\right)_{\mathbf{Na_2CO_3}}$$

$$\mathbf{N} \times 37.86\ \mathbf{mL} = \left(\frac{0.1876\ \times 1000}{\frac{105.99}{2}}\right)_{\mathbf{Na_2CO_3}}$$

$$\mathbf{N = 0.0935\ \left(\frac{meq}{mL}\right) HCl}$$

$$\mathbf{(N \times V)_{HCl} = (\frac{wt}{Eq.wt})_{NaHCO_3}}$$

$$\mathbf{(0.0935 \times 40.72) = \frac{wt}{\frac{84.01}{1}}}$$

$$\mathbf{wt = 0.319\ gm}$$

$$\mathbf{\%NaHCO_3 = \frac{wt}{wt\ sample} \times 100}$$

$$\mathbf{= \frac{0.319}{0.467} \times 100 = 67.18\%\ NaHCO_3\ in\ sample}$$

Example:- The organic matter in a 3.776 g sample of amercuric ointment was decomposed with HNO_3. After dilution, the Hg^{2+} was titrated with 21.30 mL of a 0.1144 M solution of NH_4SCN. Calculate the percent Hg in ointment.

$$Hg^{2+} + 2SCN^- \rightarrow Hg(SCN)_{2(aq)}$$

$$\text{mmol } Hg^{2+} = \text{mmol } NH_4SCN \times \frac{1 \text{ mmol } Hg^{2+}}{2 \text{ mmol } NH_4SCN}$$

$$\mathbf{(\frac{wt}{Awt} \times 1000)_{Hg^{2+}} = (M \times V \times \frac{1}{2})_{NH_4SCN}}$$

$$\mathbf{(\frac{wt}{200.59} \times 1000)_{Hg^{2+}} = 0.1144 \times 21.30 \times \frac{1}{2}}$$

$$\mathbf{\frac{wt \times 1000}{200.59} = 1.218 \quad , \quad wt_{Hg^{2+}} = 0.2443\ g}$$

$$\mathbf{Hg^{2+}\% = \frac{wt\ Hg^{2+}}{wt\ sample} \times 100 \quad = \frac{0.2443}{3.776} \times 100 = 6.47\%}$$

Example:- Calculate the normality of an I_2 solution if 37.34mL were needed to titrate 0.2040 g of primary standard As_2O_3.

Reaction: $I_2 + H_2AsO_3^- + H_2O \rightarrow 2I^- + H_2AsO_4^- + 2H^+$

At equivalence point: $\text{meq } I_2 = \text{meq } As_2O_3$

$$\mathbf{(N \times V)_{I_2} = \frac{wt\ As_2O_3}{Eq\ wt\ As_2O_3} \times 1000}$$

Arsenic is oxidized from the +3 to +5 state in this reaction. Since two atoms of As are contained in each As_2O_3:- $As_2O_3 \equiv 2H_2AsO_3^- \equiv 2I_2 \equiv 4e$

$$\mathbf{(N \times 37.34)_{I_2} = (\frac{0.204}{\frac{197.8}{4}} \times 1000)_{As_2O_3}}$$

$$\mathbf{N = 0.1105 \frac{Eq}{L} = 0.1105 \frac{meq}{mL}}$$

.In back-titration, a known number of millimoles of reaction it is taken, in excess of the analyte. The unreacted portion is titrated.

mmol reagent reacted = mmol taken – mmol backtitrted

mg analyte = mmol reagent reacted x factor (mmol analyte/mmol reagent)

Example:- A 0.50 g sample containing Na_2CO_3 plus inert matter in analyzed by adding 50.0mL of 0.1M HCl, a slight excess, boiling to remove CO_2, and then back-titrating the excess acid with 0.1M NaOH. If 5.6mL of NaOH is required for the back-titration, what is the percent Na_2CO_3 in the sample.

Solution:

$$\mathbf{mmol\ Na_2CO_3 = \left(mmol\ HCl \times \frac{1mmol\ Na_2CO_3}{2\ mmol\ HCl}\right) - mmol\ NaOH}$$

$$\mathbf{\left(\frac{wt}{M.wt} X1000\right)_{Na_2CO_3} = \left(M \times V \times \frac{1}{2}\right)_{HCl} - (M \times V)_{NaOH}}$$

$$\mathbf{\left(\frac{wt}{106} \times 1000\right) = \left(0.1 \times 50 \times \frac{1}{2}\right) - (0.1 \times 5.6)}$$

$$\mathbf{wt_{Na_2CO_3} = 0.205\ g}$$

$$\%\mathbf{Na_2CO_3 = \frac{wt\ Na_2CO_3}{wt\ sample} \times 100}$$

$$\mathbf{= \frac{0.205}{0.500} \times 100 = 41.128\%}$$

Example:- Chromium (III) is slow to react with EDTA (H_4Y) and is therefore determined by back-titration. A pharmaceutical preparation containing chromium (III) is analyzed by treating a 2.63 gm sample with 5.00 mL of 0.0103M EDTA. Following reaction, the unreacted EDTA is back-titrated with 1.32 mL of 0.0122M zinc solution. What is the percent chromium chloride in the pharmaceutical preparation?

Solution:

$$\mathbf{mmol\ CrCl_3 = mmol\ EDTA - mmol\ Zn^{2+}}$$

$$\mathbf{\left(\frac{wt}{M.wt} X1000\right)_{CrCl_3} = (M \times V)_{EDTA} - (M \times V)_{Zn^{2+}}}$$

$$\mathbf{\left(\frac{wt}{158.4} X1000\right) = (0.0103 \times 5) - (0.0122 \times 1.32)}$$

$$\mathbf{\frac{wt}{158.4} X1000 = 0.0515 - 0.016}$$

$$\mathbf{\frac{wt}{158.4} X1000 = 0.0355 \quad , \quad wt = 0.0058\ g\ CrCl_3}$$

$$\%\ \mathbf{CrCl_3 = \frac{0.0058}{2.63} \times 100 = 0.221\%\ CrCl_3}$$

Example:- A 0.200 gm sample of pyrolusite is analyzed for manganese content as follows. Add 50.0 mL of a 0.100M solution of ferrous ammonium sulphate to reduce the MnO_2 to Mn^{2+}. After reduction is complete, the excess ferrous ion is titrated in acid solution with 0.0200M $KMnO_4$, requiring 15.0mL. Calculate the percent manganese in the sample as Mn_3O_4 (only part or none of the manganese may exist in this form, but we can make the calculations on the assumption that it does).

Solution: $\mathbf{mmol\ Fe^{2+}\ reacted = mmol\ Fe^{2+} - 5 \times mmol\ KMnO_4}$

$$\mathbf{mmol\ Fe^{2+}\ reacted = (M \times V)_{Fe^{2+}} - 5 \times (M \times V)_{KMnO_4}}$$

$$\mathbf{= (50 \times 0.10) - 5 \times (0.02 \times 15) = 5 - 1.5 = 3.5}$$

$$\mathbf{mmol\ MnO_2 = 3.5\ mmol\ Fe^{2+} \times \frac{1}{2}\ (mmol\ MnO_2/mmol\ Fe^{2+}) = 1.75\ mmol}$$

$$\mathbf{mmol\ Mn_3O_4 = 1.75\ mmol\ MnO_2 \times \frac{1}{3}\ (mmol\ Mn_3O_4/mmol\ MnO_2)}$$

$$\mathbf{= 0.583\ mmol}$$

$$\mathbf{wt_{Mn_3O_4} = 0.583\ mmol \times 228.8\ mg/mmol = 133.390\ mg}$$

$$\mathbf{\%\ Mn_3O_4 = \frac{133.390}{200} \times 100 = 66.7\%\ Mn_3O_4}$$

Acid-Base Equilibria تابع صفحة 33 موضوع

Note: if the concentration of an acid or base is much less than 10^{-7} M, then its contribution to the acidity or basicity will be negligible compared with the contribution from water. The pH of a 10^{-8} M sodium hydroxide solution would therefore not differ significantly from 7. If the concentration of the acid or base is around 10^{-7} M, then its contribution is not negligible and neither is that from water, hence the sum of the two contributions must be taken.

Example:- Calculate the pH and pOH of a 1.0×10^{-7} solution HCl ?

$$\mathbf{HCl \rightarrow H^+ + Cl^-}$$

$$\mathbf{H_2O \leftrightarrow H^+ + OH^-}$$

$$\mathbf{[H^+][OH^-] = 1.0 \times 10^{-14}}$$

$$\mathbf{[H^+]_{H_2Odiss.} = [OH^-]_{H_2Odiss.} = X}$$

Since the H^+ contributed from the ionization of water are not negligible compared to the HCl added.

$$\mathbf{[H^+] = C_{HCl} + [H^+]_{H_2O\ diss.}}$$

$$\mathbf{[H^+][OH^-] = 1.0 \times 10^{-14}}$$

$$\mathbf{(1.0 \times 10^{-7} + X)(X) = 1.0 \times 10^{-14}}$$

$$\mathbf{X^2 + 1.0 \times 10^{-7} + 1.0 \times 10^{-14} = 0}$$

Using the quadratic equation to solve:-

$$\mathbf{X = \frac{-B \pm \sqrt{B^2 - 4\,AC}}{2A}}$$

$$\mathbf{= \frac{-1.0 \times 10^{-7} \pm \sqrt{(1.0 \times 10^{-7})^2 - 4\,(1.0 \times 10^{-14})}}{2} = 6.2 \times 10^{-8}}$$

$\mathbf{, therefore\ the\ total\ concentration\ H^+ = 1.0 \times 10^{-7} + 6.2 \times 10^{-8} = 1.62 \times 10^{-7}\ M}$

$$\mathbf{pH = -\log 1.62 \times 10^{-7} = 7 - 0.21 = 6.79}$$

$$\mathbf{pOH = 14 - 6.79 = 7.21}$$

Example:- Calculate the pH and pOH of a 1.0×10^{-3} M solution acetic acid, K_a = 1.75×10^{-5} ?

	$\mathbf{HOAc}$	↔	$\mathbf{H^+}$	+	$\mathbf{OAc^-}$
Initial	$\mathbf{1.0 \times 10^{-3}}$		$\mathbf{0}$	+	$\mathbf{0}$
Equilibrium	$\mathbf{1.0 \times 10^{-3} - x}$		$\mathbf{x}$	+	$\mathbf{x}$

$$\mathbf{K_a = \frac{[H^+][OAc^-]}{[HOAc]}}$$

$$\mathbf{1.75 \times 10^{-5} = \frac{x.x}{1.0 \times 10^{-3} - x}}$$

If $C_{HA} > 100\ K_a$, x can be neglected compared to C_{HA}

$$\mathbf{1.75 \times 10^{-5} = \frac{x^2}{1.0 \times 10^{-3}}}$$

$$x = 1.32 \times 10^{-4} M = [H^+]$$

$$pH = -\log[H^+] = -\log 1.32 \times 10^{-4} = 4 - 0.12 = 3.88$$

$$\mathbf{pH + pOH = 14}$$

$$\mathbf{pOH = 14 - pH = 14 - 3.88 = 10.12}$$

$$\text{General law to calculate } [H^+] \text{for weak acids: } \mathbf{[H^+] = \sqrt{K_a C_{acid}}}$$

Example:- The basicity constant k_b for ammonia is 1.75×10^{-5} at 25°C, (H is only coincidental that this is equal to K_a for acetic acid). Calculate the pH and pOH for a 1.0×10^{-3} M solution of ammonia ? $\mathrm{NH_3 \ + \ H_2O \leftrightarrow NH_4^+ + OH^-}$

$$\text{Equilibrium} \quad 1.0\times10^{-3} - x \qquad\qquad x \qquad x$$

$$\mathbf{K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}}$$

$$\mathbf{1.75\times10^{-5} = \frac{x.x}{1.0\times10^{-3}}}$$

$$\mathbf{x = \sqrt{1.7\times10^{-5}\times1.0\times10^{-3}} = 1.32\times10^{-4}M = [OH^-]}$$

$$\mathbf{pOH = -\log\ [OH^-] = -\log 1.32\times10^{-4} = 3.88}$$

$$\mathbf{pH = 14 - pOH = 14 - 3.88 = 10.12}$$

General law to calculate [OH⁻] for weak bases:- $[\mathrm{OH^-}] = \sqrt{\mathrm{K_b C_{base}}}$

Salts:any compound that produce from reaction of acid with base, and can be classified to**:**

Salts of weak acids and bases:-

Example:- Calculate the pH of a 0.1M solution of CH3COONa, $k_a=1.75\times10^{-5}$?

$$\mathbf{(ionization) \qquad NaOAc \ \rightarrow Na^+ \ + OAc^-}$$

$$\mathbf{(hydrolysis) \quad OAc^- + H_2O \leftrightarrow HOAc + OH^-}$$

$$\mathbf{K_w = K_aK_b \qquad , K_b = \frac{[HOAc][OH^-]}{[OAc^-]}}$$

$$\mathbf{k_b = \frac{K_w}{K_a} = \frac{x^2}{0.1} \qquad C_{A^-} > 100\ K_b \rightarrow x\ can\ be\ neglected}$$

$$\mathbf{\frac{1\times10^{-14}}{1.75\times10^{-5}} = \frac{x^2}{0.1}}$$

$$\mathbf{x = OH^- = 7.6\times10^{-6}}$$

$$\mathbf{[H^+] = \frac{1\times10^{-14}}{7.6\times10^{-6}} = 1.3\times10^{-9}\ M}$$

$$\mathbf{pH = -\log[H^+] = -\log 1.3\times10^{-9} = 8.89}$$

For salt of weak acids: $[\mathbf{OH^-}] = \sqrt{\frac{\mathbf{K_w}}{\mathbf{K_a}}.\mathbf{C_{A^-}}} = \sqrt{\mathbf{K_b C_{A^-}}}$

Example:- Calculate the pH of a 0.25M solution of ammonium chloride NH_4Cl ? $(\mathbf{ionization}) \quad \mathbf{NH_4Cl} \rightarrow \mathbf{NH_4^+} + \mathbf{Cl^-}$

$$(\mathbf{hydrolysis}) \quad \mathbf{NH_4^+ + H_2O \leftrightarrow NH_4OH + H^+}$$

$$\mathbf{NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+}$$

$$\mathbf{K_a = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{x^2}{0.25} = \frac{1\times10^{-14}}{1.75\times10^{-5}} = \frac{x^2}{0.25}}$$

$$\mathbf{x = H^+ = 1.2\times10^{-5}\ M}$$

$$\mathbf{pH = -\log 1.2\times10^{-5} = 4.92}$$

For salt of weak bases: $[\mathbf{H^+}] = \sqrt{\frac{\mathbf{K_w}}{\mathbf{K_b}}.\mathbf{C_{BH^+}}}$

Buffer solution:- تابع صفحة 35 موضوع

The amount of acid or base that can be added without causing a large change in pH is governed by the buffering capacity (B), the buffering capacity increases with the concentration of the buffering species. The buffering capacity is maximum at pH=pK_a.

Example:- A buffer solution is 0.2M of acetic acid and sodium acetate. Calculate the change in pH upon adding 1.0mL of 0.1M hydrochloric acid to 10mL of this solution ?

$$\mathbf{pH = pK_a + \log\frac{[salt] - [adding\ acid]}{[acid] + [adding\ acid]}}$$

$$\mathbf{(pH)_1 = 4.76 + \log\frac{[0.2\times10] - [0.1\times1]}{[0.2\times10] + [0.1\times1]} = 4.71}$$

$$\mathbf{(pH)_2 = 4.76 + \log\frac{[0.2]}{[0.2]} = 4.76}$$

$$\mathbf{\Delta pH = (pH)_1 - (pH)_2 = 4.71 - 4.76 = -0.05}$$

The change in pH is -0.05. This is rather small especially if we consider that had the HCl been added to unbuffered neutral solution the final concentration would have been approximately 10^{-2}M, and the pH would be 2.0.

Polyprotic acids and their salts:-

$$\mathbf{H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-} \qquad \mathbf{K_{a1} = 1.1 \times 10^{-2} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}}$$

$$\mathbf{H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}} \qquad \mathbf{K_{a2} = 7.5 \times 10^{-8} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}}$$

$$\mathbf{HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}} \qquad \mathbf{K_{a3} = 4.8 \times 10^{-13} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}}$$

$$\mathbf{H_3PO_4 \leftrightarrow 3H^+ + PO_4^{3-}\ K_a = K_{a1} \times K_{a2} \times K_{a3} = 4.0 \times 10^{-22} = \frac{[H^+]3[PO_4^{3-}]}{[H_3PO_4]}}$$

The stepwise K_a values of polyprotic acids get progressively smaller as the increased negative charge makes dissociation of the next proton more difficult. We can titrate the first two protons of H_3PO_4 separately. The third is too weak to titrate.

Example:- The pH of blood is 7.40. What is the ratio of $[HPO_4^{2-}]/[H_2PO_4^-]$ in the blood (assume 25°C) ?

$$\mathbf{pH = pK_a + \log\frac{[proton\ accepter]}{[proton\ donor]} = pK_a + \log\frac{[HPO_4^{-2}]}{[H_2PO_4^-]}}$$

$$\mathbf{7.40 = -\log 7.5 \times 10^{8-} + \log\frac{[HPO_4^{-2}]}{[H_2PO_4^-]}}$$

$$\mathbf{7.40 = 7.12 + \log\frac{[HPO_4^{-2}]}{[H_2PO_4^-]}}$$

$$\mathbf{7.40 - 7.12 = \log\frac{[HPO_4^{-2}]}{[H_2PO_4^-]}}$$

$$\mathbf{10^{0.28} = \frac{[HPO_4^{-2}]}{[H_2PO_4^-]} = \frac{1.9}{1}}$$

Example:- Calculate the pH of a 0.1M H_3PO_4 solution? Note (treat H_3PO_4 as a monoprotic acid) ? $\quad H_3PO_4 \quad \leftrightarrow \quad H^+ \quad + \quad H_2PO_4^-$

Equilibrium $\quad 0.1 - x \qquad x \qquad x$

$$\mathbf{K_{a1} = \frac{x.x}{0.1 - x} = 1.1 \times 10^{2-}}$$

In order to neglect x, C should be ≥ 100 K_a, here, it is only 10 times as large. Therefore, use the quadratic equation to solve:- $x^2 + 0.011x - 1.1 \times 10^{3-} = 0$

$$\mathbf{X = \frac{-B \pm \sqrt{B^2 - 4\,AC}}{2A} = \frac{-0.011 \pm \sqrt{(0.011)^2 - 4\,(-1.1 \times 10^{3-})}}{2} = 0.028\,M = [H^+]}$$

$$\mathbf{pH = -\log[H^+] = -\log 0.028 = -0.45 = 1.55}$$

Example:- Calculate the equilibrium concentration of the different species in a 0.10M phosphoric acid solution at pH=3.0 ? $[H^+] = 1.0 \times 10^{3-}$

$$\mathbf{\propto_\circ = \frac{1}{\left(\frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3}\right) + \left(\frac{K_{a1}K_{a2}}{[H^+]^2}\right) + \left(\frac{K_{a1}}{[H^+]}\right) + 1}}$$

$$\mathbf{= \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}}$$

$$\mathbf{= \frac{(1.0 \times 10^{3-})^3}{(1.0 \times 10^{3-})^3 + (1.1 \times 10^{2-})(1.0 \times 10^{3-})^2 + (1.1 \times 10^{2-})(7.5 \times 10^{8-})(1.0 \times 10^{3-}) +}}$$

$$\mathbf{\propto_\circ = \frac{1.0 \times 10^{9-}}{1.2 \times 10^{8-}} = 8.3 \times 10^{2-}}$$

$$\mathbf{[H_3PO_4] = C_{H_3PO_4} \propto_\circ = 0.1 \times 8.3 \times 10^{2-} = 8.3 \times 10^{3-}\ M}$$

$$\mathbf{\propto_1 = \frac{K_{a1}[H^+]^2}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} = 0.92}$$

$$\mathbf{[H_2PO_4^-] = C_{H_3PO_4} \propto_1 = 0.1 \times 0.92 = 9.2 \times 10^{2-}\ M}$$

$$\mathbf{\propto_2 = \frac{K_{a1}K_{a2}[H^+]}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} = 6.9 \times 10^{5-}}$$

$$\mathbf{\left[HPO_4^{2-}\right] = C_{H_3PO_4} \propto_2 = 0.1 \times 6.9 \times 10^{5-} = 6.9 \times 10^{6-}\ M}$$

$$\mathbf{\propto_3 = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} = 3.3 \times 10^{14-}}$$

$$\mathbf{\left[PO_4^{3-}\right] = C_{H_3PO_4} \propto_3 = 0.1 \times 3.3 \times 10^{14-} = 3.3 \times 10^{15-}\ M}$$

We see that at pH=3.0, the majority (91%) of the phosphoric acid exists as $H_2PO_4^-$ and 8.3% exists as H_3PO_4, only $3.3{\times}10^{12-}$% exists as PO_4^{3-}.

Salts of polyprotic (acids or bases):-

1. Amphoteric salts:-$H_2PO_4^-$ possesses both acidic and basic properties. That is, it is amphoteric. It ionizes as a weak acid and it also is a Bronsted base that hydrolyzes:-

$$\mathbf{H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} \qquad K_{a2} = 7.5 \times 10^{-8} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}}$$

$$\mathbf{H_2PO_4^- + H_2O \leftrightarrow H_3PO_4 + OH^- \qquad K_b = \frac{K_w}{K_{a1}} = \frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]} = 9.1 \times 10^{-10}}$$

2. Unprotonated salt in a fairly strong Bronsted base in solution and ionizes as follows:- $\mathbf{PO_4^{3-} + H_2O \leftrightarrow HPO_4^{2-} + OH^-}$ $\mathbf{K_b = \frac{K_w}{K_{a3}}}$

Example:- Calculate the pH of 0.1M Na_3PO_4 ?

$$\mathbf{PO_4^{3-} \ + \ H_2O \ \leftrightarrow \ HPO_4^{2-} + \ OH^-}$$

$$\mathbf{Equilibrium \quad 0.1 - x \qquad\qquad x \qquad x}$$

$$\mathbf{K_b = \frac{K_w}{K_{a3}} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 0.02 = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]} = 0.02 = \frac{x^2}{0.1 - x}}$$

$$\mathbf{x^2 + \ 0.02x - 2.0 \times 10^{3-} = 0}$$

$$\mathbf{X = \frac{-0.2 \ \pm \ \sqrt{(0.02)^2 - 4\,(-2.0 \times 10^{3-})}}{2} = 0.036\ M = [OH^-]}$$

$$\mathbf{pOH = 1.44 \quad , \quad pH = 12.56}$$

Example:- EDTA is a polyprotic acid with four protons (H_4Y). Calculate the hydrogen ion concentration of a 0.01M solution Na_2EDTA (Na_2H_2Y) ?

$$\mathbf{H_2Y^{2-} + H_2O \leftrightarrow H_3Y^- + OH^- \qquad K_b = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{2.2 \times 10^{-3}}}$$

$$\mathbf{H_2Y^{2-} \leftrightarrow H^+ + Y^{3-} \qquad K_{a3} = 6.9 \times 10^{-7}}$$

Note (H_2Y^{2-} is the equivalent of HA^- and H_3Y^- is the equivalent of H_2A. The equilibrium constants involved are Ka_2 and Ka_3, the former conjugate acid H_3Y^- of the hydrolyzed salt).

Thus:-$\mathbf{[H^+] = \sqrt{K_{a2}K_{a3}} = \sqrt{(2.2 \times 10^{3-})(6.9 \times 10^{7-})} = 3.9 \times 10^{5-}\ M}$

Physiological Buffers (they keep you alive):-

The pH of the blood in healthy individual remains remarkably constant at (7.35-7.45). this is because the blood contains a number of buffers that protect against pH change due to the presence of acidic or basic metabolites. From a physiological viewpoint, a change of ± 0.3 pH unit is extreme. An important diagnostic analysis is the CO_2/HCO_3^- balance in blood. This ratio is related to the pH of the blood by the Henderson-Hassellatch equation (pH = 6.10 + log $[HCO_3^-]/[H_2CO_3]$ where H_2CO_3 can be considered equal to the concentration of dissolved CO_2 in blood, 6.10 is pKa1 of carbonic acid in blood at body temperature (37°C).

Example:- The total carbon dioxide content (HCO_3^- + CO_2) in a blood sample is determined by acidifying the sample and measuring the volume of CO_2 evolved with a VanSlyke manomertric apparatus. The total concentration was determined to be 28.5mmol/L. The blood pH at 37°C was determined to be 7.48. What are the concentration of HCO_3^- and CO_2 in the blood?

$$\mathbf{pH = pK_{a1} + \log\frac{[HCO_3^-]}{[CO_2]}}$$

$$\mathbf{7.48 = 6.10 + \log\frac{[HCO_3^-]}{[CO_2]} = 1.38 = \log\frac{[HCO_3^-]}{[CO_2]}}$$

$$\mathbf{10^{1.38} = \log\frac{[HCO_3^-]}{[CO_2]} \Rightarrow \frac{[HCO_3^-]}{[CO_2]} = 24}$$

$$\mathbf{[HCO_3^-] = 24[CO_2]}$$

$$\mathbf{But\ [HCO_3^-] + [CO_2] = 28.5mmol/L}$$

$$\mathbf{24[CO_2] + [CO_2] = 28.5}$$

$$\mathbf{25[CO_2] = 28.5 \Rightarrow [CO_2] = \frac{28.5}{25} = 1.14mmol/L}$$

$$\mathbf{[HCO_3^-] = 28.5 - 1.14 = 27.4mmol/L}$$

Buffers for Biological and Clinical Measurements:-

Many biological reactions of interest occur in the pH range (6-8). A number, particularly specific enzyme reactions that might be used for analyses, may occur in the pH range (4-10). One useful series of buffers are phosphate buffers ($H_3PO_4/H_2PO_4^-$) or ($H_2PO_4^-/HPO_4^{-2}$) or (HPO_{4-2}/PO_4^{-3}).

Example:- What weights of NaH_2PO_4 and Na_2HPO_4 would be required to prepare (1L) of a buffer solution of pH7.45 that has an ionic strength of 0.10 ?

Let x=[Na_2HPO_4] and y=[NaH_2PO_4]. There are two unknowns, and two equations are needed (remember there must be the same number as unknowns to solve) our first equation is the ionic strength equation:-

$$\mu = \frac{1}{2}\sum C_i(Z_i)^2 \qquad \mu = \text{ionic strength}, C_i = \text{molar conc.}, Z_i = \text{equavelent}$$

$$0.1 = \frac{1}{2}[Na^+](1)^2 + [HPO_4^{2-}](2)^2 + [H_2PO_4^-](1)^2$$

$$0.1 = \frac{1}{2}[(2x + y)(1)^2 + x(2)^2 + y(1)^2]$$

$$0.1 = 3x + y \ldots\ldots\ldots (1)$$

$$pH = pK_{a2} + \log\frac{[HPO_4^{-2}]}{[H_2PO_4^-]}$$

$$7.45 = 7.12 + \log\frac{x}{y}$$

$$10^{0.33} = \frac{x}{y}$$

$$2.14y = x \qquad \text{subsitute in } (1)$$

$$0.1 = 3(2.14)y + y$$

$$0.0135\ M = y = [NaH_2PO_4] \quad \text{Substitute in (2)}$$

$$x = (2.14)(0.0135) = 0.0289\ M = [Na_2HPO_4]$$

$$g\ NaH_2PO_4 = 0.0135\ mol/L \times 120 g/mol = 1.62 g/L$$

$$g\ Na_2HPO_4 = 0.0289\ mol/L \times 142 g/mol = 4.10 g/L$$

A buffer that is widely used in the clinical laboratory and in biochemical studies in the physiological pH range is that prepared from tris(hydroxymethyl)aminomethane [$(HOCH_2)_3CNH_2$, Tris, or THAM] and its conjugate acid (the amino group is protonated).

Acid-Base Titrations

An Acid-Base titration involves a neutralization reaction in which an acid is reacted with an equivalent amount of base at equivalence point or endpoint.

The titration is always a strong acid or strong base

A) Titration of strong acid versus strong base.

$$\mathbf{H^+Cl^- + Na^+OH^- \rightarrow Na^+Cl^+ + H_2O}$$

$$\mathbf{HCl + NaOH \rightarrow NaCl + H_2O}$$

The equivalence point is where the reaction is theoretically complete while the endpoint where the colour of indicator were changed.

Detection of the endpoint and equivalence point (selection indicators):

***Example*:-** Calculate the pH at 0, 10, 90, 100, 110% titration of 50.0mL of 0.10M HCl with 0.10M NaOH?

(1) At 0% titration: before addition of 0.1M NaOH

$$\mathbf{pH = -\log[H^+] = -\log 0.1 = 1.0}$$

(2) At 10% titration: before equivalence point

$$\mathbf{50mL \times \frac{10}{100} = 5mL\ NaOH\ added}$$

$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 5 = 0.5}$$

$$\mathbf{mmol\ HCl\ = M \times V = 0.1 \times 50 = 50}$$

$$\mathbf{mmol\ HCl\ remaining = mmol\ HCl\ total - mmol\ NaOH\ added}$$

$$\mathbf{= 5.0 - 0.5 = 4.5}$$

$$\mathbf{M_{HCl} = \frac{mmol}{V} = \frac{4.5}{50+5} = 0.0818M}$$

$$\mathbf{pH = -\log 0.0818 = 1.09}$$

(3) At 90% titration: before equivalence point

$$\mathbf{50mL \times \frac{90}{100} = 45mL\ NaOH\ added}$$

$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 45 = 4.5}$$

$$\mathbf{mmol\ HCl\ remaining\ (unreacted) = 5.0 - 4.5 = 0.5}$$

$$\mathbf{M_{HCl} = \frac{mmol}{V} = \frac{0.5}{50+45} = 0.00526M}$$

$$\mathbf{pH = -\log 0.00526 = 2.88}$$

(4) At 100% titration: equivalence point

$$\mathbf{50mL \times \frac{100}{100} = 50mL\ NaOH\ added}$$

$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 50 = 5}$$

$$\mathbf{mmol\ NaOH\ added\ (5.0) = mmol\ HCl\ (5.0)}$$

$$\mathbf{2H_2O \leftrightarrow H_3O^+ + OH^-}$$

$$\mathbf{Kw = 1 \times 10^{-14} = [H^+][OH^-]}$$

$$\mathbf{\sqrt{1 \times 10^{-14}} = [H^+] = [OH^-] = 1 \times 10^{-7}M}$$

$$\mathbf{pH = -\log 10^{-7} = 7\ (neutrilization\ step)}$$

(5) At 110% titration: after equivalence point

$$\mathbf{50mL \times \frac{110}{100} = 55mL\ NaOH\ added}$$

$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 55 = 5.5}$$

$$\mathbf{mmol\ NaOH\ remaining\ (excess) = 5.0 - 4.5 = 0.5}$$

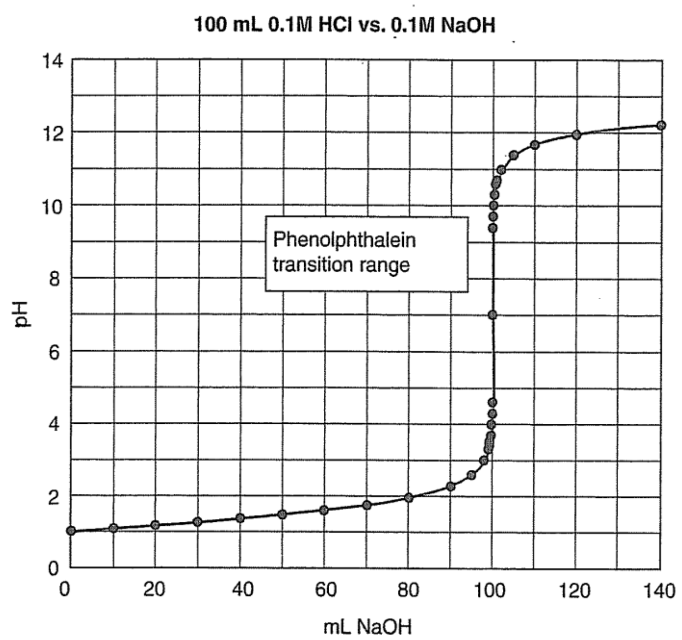
$$\mathbf{M_{NaOH} = \frac{mmol}{V} = \frac{0.5}{50+55} = 0.00476M}$$

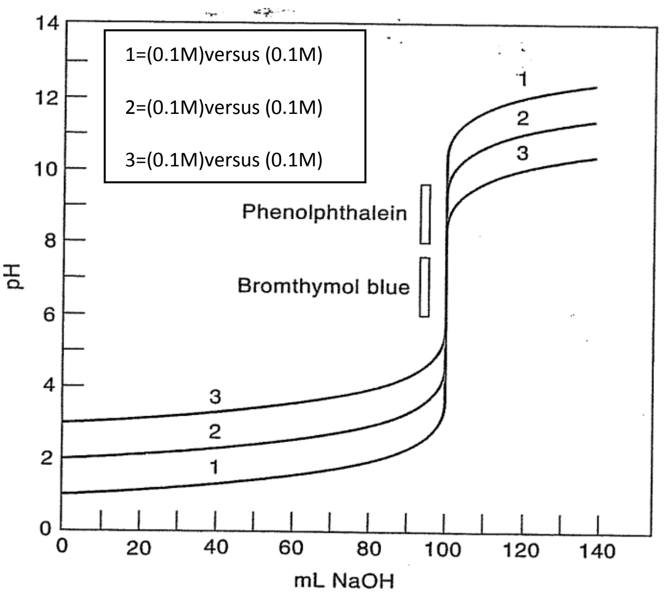
$$\mathbf{pOH = -\log 0.00476 = 2.32}$$

$$\mathbf{pH = 14 - 2.32 = 11.68}$$

Construction (plot) titration curve of strong acid versus strong base:-

The relationship between pH calculated for HCl remaining or unreacted (excess) or NaOH on Y axis and the volume of titrant (0.1M NaOH) added on X axis, this curve called titration curve. This curve used for estimation the equivalence point (theoretically) and selection of the indicator for detecting the endpoint reaction by the colour change of the indicator.



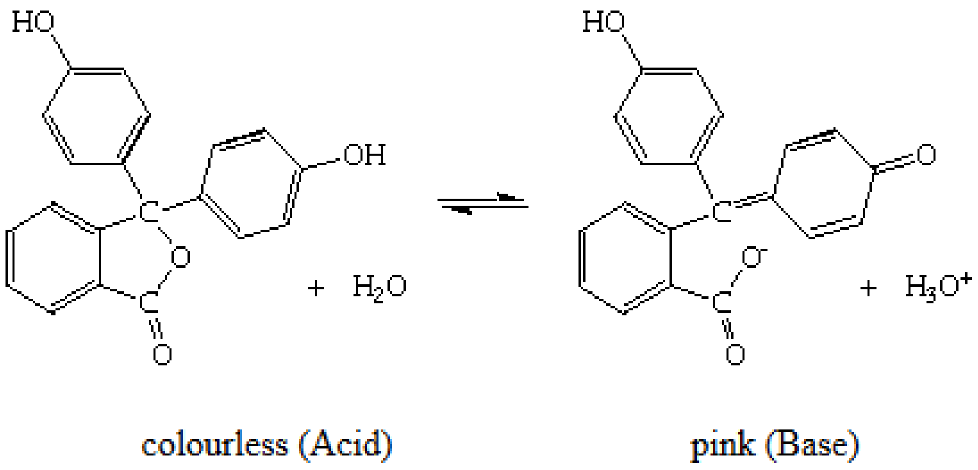


Note: The selection of the indicator become more critical as the solution become more dilute and the sharpness endpoint decrease as the concentration.

The point at which the reaction is observed to be complete at the indicator colour where changed is called endpoint.

Acid-Base indicators (also known as pH indicators):- are substances which change colour with change pH. They are usually weak acids or bases, which when dissolved in water dissociate slightly and form ions.

Phenolphthalein is a colourless, weak acid which dissociates in water forming pink anions. Under acidic conditions, the equilibrium is to the left, and the concentration of the anions is too low for the pink colour to be observed. However, under alkaline conditions, the equilibrium is to the right, and the concentration of the anion becomes sufficient for the pink colour to be observed.



Acid–base titration is performed with a phenolphthalein indicator, when it is a strong acid – strong base titration, a bromthymol blue indicator in weak acid – strong base reactions, and a methyl orange indicator for strong acid – weak base reactions. If the base is off the scale, i.e. a pH of >13.5, and the acid has a pH >5.5, then an Alizarine yellow indicator may be used. On the other hand, if the acid is off the scale, i.e. a pH of <0.5, and the base has a pH <8.5, then a Thymol Blue indicator may be used.

Common Acid – Base Indicators

Indicator	Approximate pH Range for Color Change	Color Change
Methyl Orange	3.2-4.4	Red to yellow
Bromthymol blue	6.0-7.6	Yellow to blue
Phenolphthalein	8.2-10	Colorless to pink
Litmus	5.5-8.2	Red to blue
Bromcresol green	3.8-5.4	Yellow to blue
Thymol blue	8.0-9.6	Yellow to blue

Assume the indicator is a weak acid designated HIn, and assume that the nonionized form is red while the ionized form is blue and designated In^-.

$$\mathbf{HIn} \leftrightarrow \mathbf{H^+ + In^-} \quad , \quad \mathbf{Ka} = \frac{[\mathbf{H^+}][\mathbf{In^-}]}{[\mathbf{HIn}]}$$

Acidic (nonionized form), red color Basic (ionized form), blue color

We can write a Henderson–Hasselbalch equation for this just like other weak acids:

$$\mathbf{pH = pKa + log\frac{[In^-]}{[HIn]}}$$

Your eyes can generally discern only one color if it is 10 times as intense as the other.

When only the color of the nonionized form is seen:

$$\mathbf{pH = pKa + log\frac{1}{10} = pKa - 1}$$

When only the color of the ionized form is observed:

$$\mathbf{pH = pKa + log\frac{10}{1} = pKa + 1}$$

So, the pH is going from one color to the other has changed from pKa-1 to pKa+1. This is a pH change of 2 units, and most indicators require a transition range of about two pH units. Choose an indicator with a pKa near the equivalence point.

Two drops (0.1mL) of 0.01m indicator (0.1% solution with Fwt=100) is equal to 0.01mL of 0.1M titrant.

B) Titration of weak acid versus strong base:-Acetic acid with sodium hydroxide

$$\mathbf{HOAc + Na^+OH^- \leftrightarrow Na^+OAc^- + H_2O}$$

***Example*:-** Calculate the pH at 0, 10, 25, 50, and 60mL titrant in the titration of 50mL of 0.1M acetic acid ($Ka=1.75\times10^{-5}$) with 0.10M NaOH?

(1) At 0mL titrant (0.1M NaOH): HOAc solution only

$$\mathbf{[H^+] = \sqrt{K_aC_{HA}} = \sqrt{1.75\times10^{-5}\times0.1} = 1.32\times10^{-3}M}$$

$$\mathbf{pH = -log[H^+] = -log1.23\times10^{-3} = 2.88}$$

(2)At 10mL titrant (0.1M NaOH):before equivalence point (buffer formation region)

$$HOAc + Na^+OH^- \leftrightarrow Na^+OAc^- + H_2O$$

$$\text{mmol NaOH added} = \text{M} \times \text{V} = 0.1 \times 10 = 1.0 = \text{mmol of NaOAc (salt) formed}$$

$$\text{mmol of HOAc (total)} = \text{M} \times \text{V} = 0.1 \times 50 = 5.0$$

$$\text{mmol of HOAc remaining (unreacted)} = 5.0 - 1.0 = 4.0$$

$$\mathbf{pH = pKa + \log\frac{[Salt]}{[Acid]} = 4.76 + \log\frac{1.0}{4.0} = 4.16}$$

(3) At 25mL titrant (0.1M NaOH): before equivalence point (buffer formation region)

$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 25 = 2.5mmol}$$
$$\mathbf{= mmol\ of\ NaOAc\ (salt)\ formed}$$

$$\mathbf{mmol\ of\ HOAc\ remaining\ (unreacted) = 5.0 - 2.5 = 2.5mmol}$$

$$\mathbf{pH = pKa + \log\frac{[Salt]}{[Acid]} = 4.76 + \log\frac{2.5}{2.5} = 4.76}$$

$$\mathbf{pH = pKa\ (mid - point)}$$

(4) At 50mL titrant (0.1M NaOH): equivalence point

$$\text{mmol NaOH added} = \text{M} \times \text{V} = 0.1 \times 50 = 5.0 = \text{mmol of NaOAc (salt) formed}$$

All NaOH reacted with all HOAc and converted it to its salt sodium acetate.

$$\text{OAc}^- + \text{H}_2\text{O} \leftrightarrow \text{HOAc} + \text{OH}^-$$

$$[\text{OH}^-] = \sqrt{\text{K}_\text{b}\text{C}_{\text{OAc}^-}} = \sqrt{\frac{\text{K}_\text{w}}{\text{K}_\text{a}}\text{C}_{\text{OAc}^-}} = \sqrt{\frac{10^{-14}}{1.75 \times 10^{-5}} \times 0.05} = 5.35 \times 10^{-6}\text{M}$$

$$\mathbf{pOH = -\log[OH^-] = -\log 5.35 \times 10^{-6} = 5.27}$$

$$\mathbf{pH = 14 - 5.27 = 8.73}$$

(5) At 60mL titrant (0.1M NaOH): after equivalence point (NaOH solution alone)

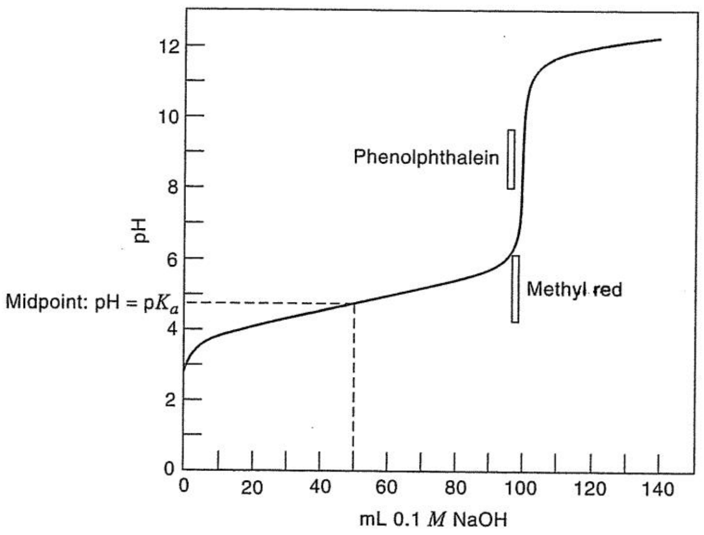
$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 60 = 6.0mmol}$$

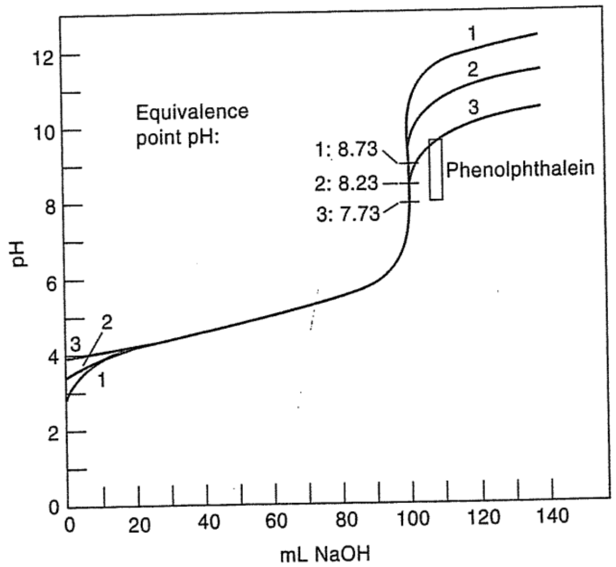
$$\mathbf{mmol\ of\ NaOH\ remaining\ (excess) = 6.0 - 5.0 = 1.0mmol}$$

$$\mathbf{pOH = -\log\frac{1.0mmol}{50mL + 60mL} = 2.04}$$

$$\mathbf{pH = 14 - 2.04 = 11.96}$$

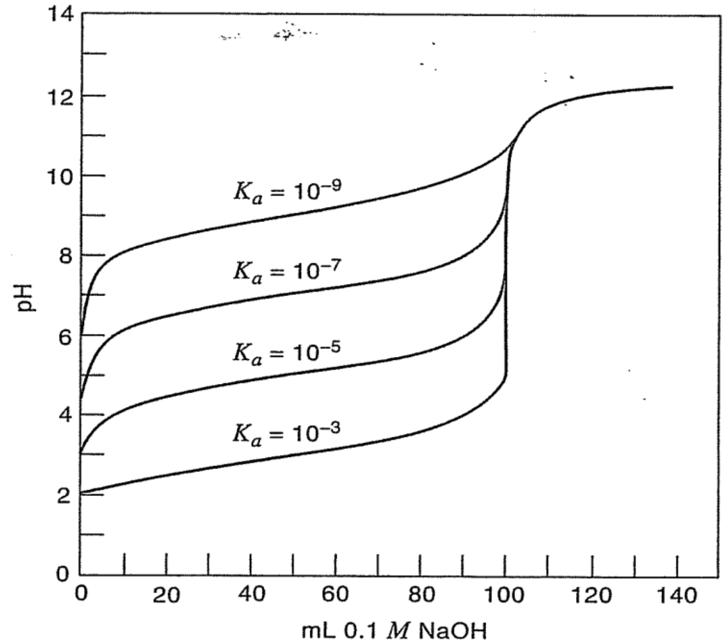
Construction (plotting) titration curve of weak acid versus strong base:-





The sharpness endpoint decreases as the concentration decreases.

Titration curves for 50mL 0.1M weak acids of different Ka value versus 0.1M NaOH.



The sharpness of the endpoint decreases as Ka decreases.

C) Titration of weak base versus strong acid:-Titration of ammonia solution versus hydrochloric acid.

***Example*:-** Calculate the pH at 0, 10, 25, 50, and 60mL of titrant of 50mL of 0.1M NH_3 (K_b=1.75×10^{-5}) with 0.1M HCl?

(1) At 0mL titrant (0.1M HCl): NH_3 solution alone

$$[\mathbf{OH^-}] = \sqrt{\mathbf{K_b C_{B^-}}} = \sqrt{\mathbf{1.75 \times 10^{-5} \times 0.1}} = \mathbf{0.00130M}$$

$$\mathbf{pOH = -\log[OH^-] = -\log 0.00130 = 2.88}$$

$$\mathbf{pH = 14 - 2.88 = 11.12}$$

(2) At 10mL titrant (0.1M HCl): before equivalence point (buffer formation region)

$$\text{mmol HCl added} = \mathrm{M \times V} = 0.1 \times 10 = 1.0 = \text{mmol of } \mathrm{NH_4Cl} \text{ (salt) formed}$$

$$\mathbf{mmol\ NH_3\ total = M \times V = 0.1 \times 50 = 5.0}$$

$$\mathbf{mmol\ NH_3\ remaining\ (unreacted) = 5.0 - 1.0 = 4.0}$$

$$\mathbf{pOH = pK_b + \log\frac{[Salt]}{[Base]} = 4.75 + \log\frac{1.0}{4.0} = 4.15}$$

$$\mathbf{pH = 14 - 4.15 = 9.85}$$

(3) At 25mL titrant (0.1M HCl): before equivalence point (buffer formation region)

$$\text{mmol HCl added} = \mathrm{M \times V} = 0.1 \times 25 = 2.5\text{mmol} = 2.5\text{mmol of } \mathrm{NH_4Cl} \text{ (salt) formed}$$

$$\text{mmol } \mathrm{NH_3} \text{ remaining (unreacted)} = 5.0 - 2.5 = 2.5$$

$$\mathrm{pOH = pK_b + \log\frac{[Salt]}{[Base]}} = 4.75 + \log\frac{2.5}{2.5} = 4.75 \qquad \mathrm{pOH = pK_b\ \ mid - point}$$

(4) At 50mL titrant (0.1M HCl): equivalence point region

$$\text{mmol HCl added} = \mathrm{M \times V} = 0.1 \times 50 = 5.0\text{mmol}$$

The all HCl added converted all NH_3 to its salt NH_4Cl

$$\mathrm{NH_4^+ + H_2O \leftrightarrow NH_4OH + H^+}$$

$$[\mathrm{H^+}] = \sqrt{\mathrm{K_a C_{BH^+}}} = \sqrt{\frac{\mathrm{K_w}}{\mathrm{K_b}}\mathrm{C_{BH^+}}} = \sqrt{\frac{10^{-14}}{1.75 \times 10^{-5}} \times 0.05} = 5.35 \times 10^{-6}\mathrm{M}$$

$$\mathrm{pH} = -\log 5.35 \times 10^{-6} = 5.27$$

(5) At 60mL titrant (0.1M HCl): after equivalence point

$$\text{mmol HCl added} = \text{M} \times \text{V} = 0.1 \times 60 = 6.0\text{mmol}$$

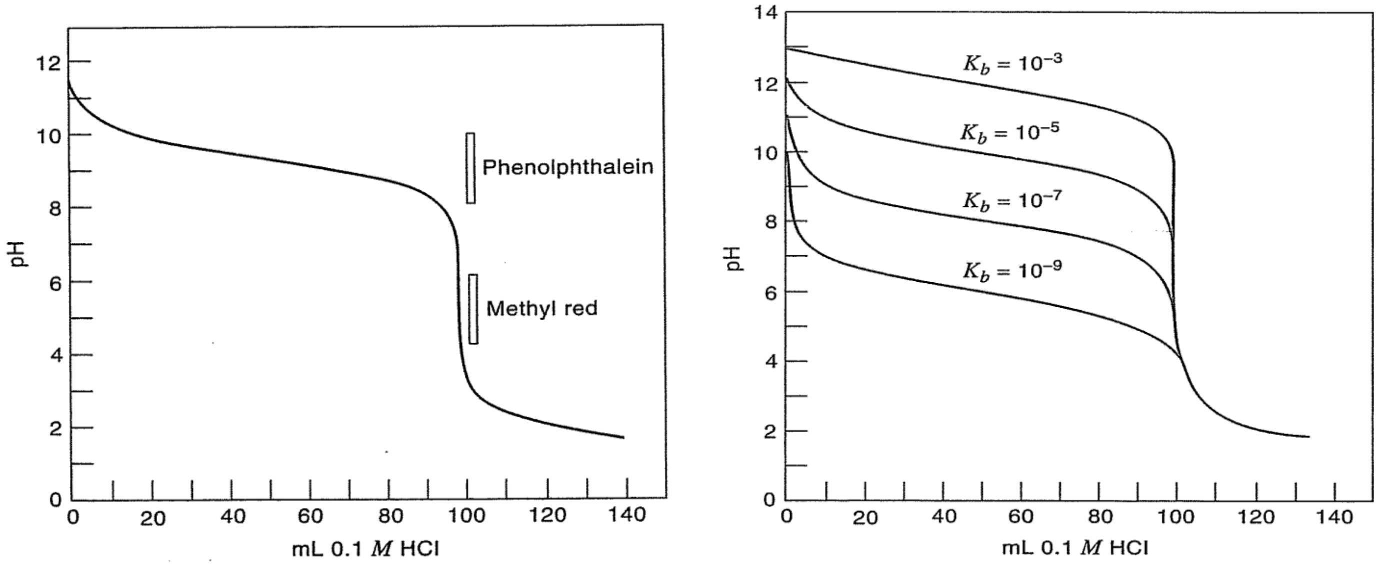
$$\mathbf{mmol\ HCl\ remaining\ (excess) = 6.0 - 5.0 = 1.0}$$

$$\mathbf{M_{HCl} = \frac{1.0mmol}{50mL + 60mL} = 0.00909M}$$

$$\mathbf{pH = -log0.00909 = 2.05}$$

Construction (plotting) titration curve:-

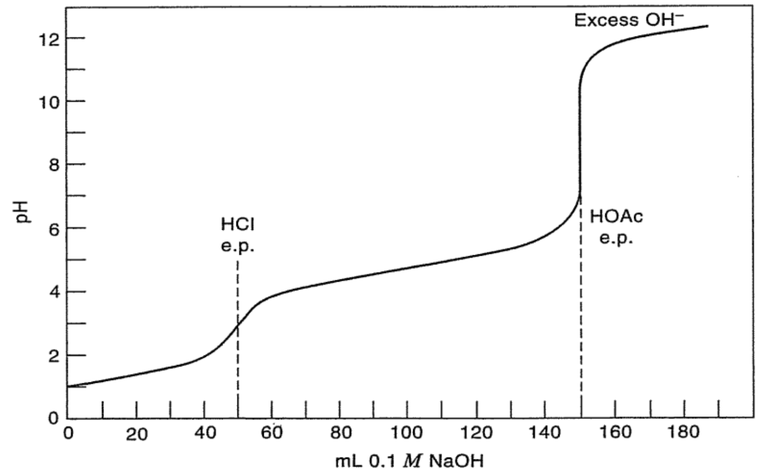
Titration curve for 50mL 0.1M weak base of different K_b values versus 0.1M HCl.



The sharpness of the endpoint decreases as K_b decreases of weak bases.

Titration of sodium hydroxide versus mixture of acids:

Mixtures of acids (or bases) can be titrated stepwise if its difference in K_a values of at least 104, unless perhaps a pH meter is used to construct the titration curve.



Note: one acid should be at least 10^4 weaker than the other to titrate separately.

***Example*:-** A mixture of HCl and H_3PO_4 is titrated with 0.1M NaOH. The first endpoint (methyl red) occurs at 35.0mL, and the second endpoint (bromothymol blue) occurs at total of 50.0mL (15.0mL after the first point). Calculate the millimoles HCl and H_3PO_4 present in the solution?

The second endpoint corresponds to that the titration of one proton of H_3PO_4 ($H_2PO_4^- \rightarrow HPO_4^{2-}$).

$$\text{mmol}\ H_3PO_4 = (M \times V)_{NaOH} = 0.1 \times 15 = 1.5\text{mmol}$$

The HCl and the first proton of H_3PO_4 titrate. A 15mL portion of base was used to titrate the first proton of H_3PO_4 (same as for the second proton), leaving 20mL used to titrate the HCl.

$$\text{mmol HCl} = (M \times V)_{NaOH} = 0.1 \times (35 - 15) = 0.1 \times 20 = 2.0\text{mmol}$$

The difference in K_b values must be at least 10^4 to titrate separately.

***Example*:-** A 0.527g sample of mixture containing Na_2CO_3 and $NaHCO_3$ and inert impurities is titrated with 0.109M HCl, requiring 15.7mL to reach the phenolphthalein endpoint and a total of 43.8mL to reach the modified methyl orange endpoint, what is the percent each of Na_2CO_3 and $NaHCO_3$ in mixture?

The phenolphthalein endpoint volume HCl equivalent for half amount of Na_2CO_3

$$\mathbf{Na_2CO_3 + 2HCl \leftrightarrow H_2CO_3 + 2NaCl}$$

$$\mathbf{mmol\ Na_2CO_3 = mmol\ HCl \times \frac{1}{2}}$$

$$\mathbf{\left(\frac{wt}{M.wt} \times 1000\right)_{Na_2CO_3} = (M \times V)_{HCl} \times \frac{1}{2}}$$

$$\mathbf{\left(\frac{wt}{106} \times 1000\right)_{Na_2CO_3} = (0.109 \times 15.7 \times 2)_{HCl} \times \frac{1}{2}}$$

$$\mathbf{wt_{Na_2CO_3} = 1.711 \times \frac{106}{1000} = 0.181g\ Na_2CO_3}$$

$$\mathbf{Na_2CO_3\% = \frac{wt_{Na_2CO_3}}{wt_{sample}} \times 100 = \frac{0.181}{0.527} \times 100 = 34.34\%}$$

The volume HCl at second endpoint (modified methyl orange) equal for second half amount of Na_2CO_3 plus the amount of $NaHCO_3$.

$$\mathbf{mmol\ NaHCO_3 = mmol\ HCl\ \times \frac{1}{1}}$$

$$\left(\frac{\mathbf{wt}}{\mathbf{M.wt}} \times \mathbf{1000}\right)_{\mathbf{NaHCO_3}} = (\mathbf{M} \times (\mathbf{V_2} - \mathbf{2V_1})_{\mathbf{HCl}} \times \frac{\mathbf{1}}{\mathbf{1}}$$

$$\left(\frac{\mathbf{wt}}{\mathbf{84}} \times \mathbf{1000}\right)_{\mathbf{NaHCO_3}} = (\mathbf{0.109} \times (\mathbf{43.8} - \mathbf{2} \times \mathbf{15.7}))_{\mathbf{HCl}}$$

$$\mathbf{wt_{NaHCO_3} = 0.113g}$$

$$\mathbf{NaHCO_3\%} = \frac{\mathbf{wt_{NaHCO_3}}}{\mathbf{wt_{sample}}} \times \mathbf{100} = \frac{\mathbf{0.113}}{\mathbf{0.527}} \times \mathbf{100} = \mathbf{21.5\%}$$

***Example*:-** Sodium hydroxide and sodium canbonate will titrate together to a phenolphthalein endpoint ($OH^- \rightarrow H_2O$, $CO_3^{2-} \rightarrow HCO_3^-$). A mixture of NaOH and Na_2CO_3 is titrated with 0.250M HCl, requiring 26.2mL for phenolphthalein endpoint and an additional 15.2mL to reach the modified methyl orange endpoint, how many milligrams NaOH and Na_2CO_3 are in the mixture.

The volume HCl at first endpoint equivalent all hydroxide and half amount of Na_2CO_3= 26.2mL. $\text{mmol NaOH} = \text{mmol HCl} \times \frac{1}{1}$

$$\left(\frac{\mathbf{wt}}{\mathbf{M.wt}}\right) = \mathbf{M} \times (\mathbf{V_1} - \mathbf{V_2})$$

$$\left(\frac{\mathbf{wt}}{\mathbf{40}}\right) = \mathbf{0.25} \times (\mathbf{26.2} - \mathbf{15.2})$$

$$\mathbf{wt_{NaOH} = 110mg}$$

The volume HCl at second endpoint equivalent the second half of Na_2CO_3=15.2

$$\mathbf{mmol\ Na_2CO_3 = mmol\ HCl\ \times \frac{1}{2}}$$

$$\left(\frac{\mathbf{wt}}{\mathbf{M.wt}} \times \mathbf{1000}\right)_{\mathbf{Na_2CO_3}} = (\mathbf{M} \times \mathbf{2V_2})_{\mathbf{HCl}} \times \frac{\mathbf{1}}{\mathbf{2}}$$

$$\frac{\mathbf{wt}}{\mathbf{106}} = \mathbf{0.250} \times \mathbf{2} \times \mathbf{15.2} \times \frac{\mathbf{1}}{\mathbf{2}}$$

$$\mathbf{wt}_{\mathbf{Na_2CO_3}} = \mathbf{7.6} \times \mathbf{106} \times \frac{\mathbf{1}}{\mathbf{2}} = \mathbf{402.8\ mg}$$