Acid-Base Titrations

The Titration

- One of the most important lab procedures involving acids and bases is the titration.
- A titration is an analytical procedure that allows for the measurement of the amount of one solution that is required to exactly react with the contents of another solution.
- In acid-base terms, you add one solution to the other until the equivalence point is reached.
- The use of a pH meter will produce a pH curve (titration curve), so you can specifically calculate at what pH your solutions have been neutralized.

Titration Types

1. acid-base

 $HCI + NaOH \rightarrow H_2O + NaCI$

2. redox

 $5NaC_2O_4 + 2 KMnO_4 + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

3. precipitation

 $Ag^+ + X^- \rightarrow AgX(s)$

4. complex formation (EDTA)

ethylenediaminetetraacetic acid



*Equivalence Point*The point at which there are stoichiometric equivalent amounts of

- a cid and base. $[H^+] = [OH^-]$
- Determined by...
 - indicator color change
 - dramatically change in pH





General Many indicators are weak acids and partially dissociate in aqueous solution

 $Hin_{(aq)} \iff H^+_{(aq)} + In_{(aq)}$

The un-ionised form (HIn) is a different colour to the anionic form (In).

General Many indicators are weak acids and partially dissociate in aqueous solution Hln_(aq) ⇐ H⁺_(aq) + In⁻_(aq) The un-ionised form (Hln) is a different colour to the anionic form (In⁻). Apply Le Chatelier's Principle to predict any colour change In acid - increase of [H⁺]

- equilibrium moves to the left to give red undissociated form
- In alkali increase of [OH]
 - OH⁻ ions remove H⁺ ions to form water; H⁺(aq) + OH⁻(aq) \implies H₂O(I)
 - equilibrium will move to the right to produce a blue colour

 General
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 Hln(aq)
 H⁺(aq)

 Hn(aq)
 H⁺(aq)

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 Apply Le Chatelier's Principle to predict any colour change

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 - increase of [H⁺]

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Summary

In acidic solution

$$HIn_{(aq)} \iff H^+_{(aq)} + In_{(aq)}$$

In alkaline solution

Must have an easily observed colour change. Must change immediately in the required pH range over the addition of 'half' a drop of reagent.

COLOUR CHANGES OF SOME COMMON INDICATORS

рН	1	2	3	4	5	6	7	8	9	10	11	12	13	14
METHYL ORANGE			С	HANG	BE									
LITMUS						C	HANC	E						
PHENOLPHTHALEIN								C	HANG	GE				

The pH range of indictors

Indictors dose not change colour sharply at one particular pH, they change over a narrow range of pH

indctors	pKind	рН
litmus	6.5	5-8
methylorange	3.7	3.1-4.4
phenophthaline	9.3	8.3-10.0



Phenolphthalein

 is a <u>chemical compound</u> with the <u>formula C20H14O4</u> (often written as "HIn" or "phph"). Often used in <u>titrations</u>, it turns colorless in <u>acidic</u> solutions and pink in <u>basic</u> solutions



Species	In	H ₂ In	In ²⁻	In(OH) ³⁻
Structure	ajo	HO COH		° Hor
Model	, the second		The second	No.
рН	< 0	0-8.2	8.2-12.0	>12.0
Conditions	strongly acidic	acidic or near-neutral	basic	strongly basic
Color	orange	colorless	pink to fuchsia	colorless
lmage			100 m	

Must have an easily observed colour change. Must change immediately in the required pH range over the addition of 'half' a drop of reagent.

To be useful, an indicator must change over the "vertical" section of the curve where there is a large change in pH for the addition of a very small volume of alkali.

The indicator used depends on the pH changes around the end point - the indicator must change during the 'vertical' portion of the curve.

In the example, the only suitable indicator is PHENOLPHTHALEIN.



pH curves

Types There are four types of acid-base titration; each has a characteristic curve.

strong acid (HCI) v. strong base (NaOH) weak acid (CH₃COOH) v. strong alkali (NaOH) strong acid (HCI) v. weak base (NH₃) weak acid (CH₃COOH) v. weak base (NH₃)

In the following examples, alkali (0.1M) is added to 25cm³ of acid (0.1M)

End points need not be "neutral' due to the phenomenon of salt hydrolysis

Strong Acid-Strong Base



- This diagram shows the change in pH as a solution of strong acid is slowly added to a solution of strong base.
- Strong acid-strong base titrations usually have an equivalence point around 7.
- This is due to the fact that in solution, strong acids and strong bases will both completely dissociate, so there is an approximate 1:1 ratio of moles of acid to moles of base at the equivalence point.













Any of the indicators listed will be suitable - they all change in the 'vertical' portion

strong acid (HCI) v. weak base (NH₃)



strong acid (HCI) v. weak base (NH₃)



Only methyl orange is suitable - it is the only one to change in the 'vertical' portion

Weak Acid-Strong Base



- At the beginning, the weak acid is in equilibrium with itself. Thus, the beginning pH is higher than that of a strong acid.
- More moles of the weak acid are required to completely react with the amount of strong base present, because the acid is not entirely dissociated.
- For every mole of base, there is less than one mole of acid able to react: there is an excess of base.
- The initial change in pH is steeper because there is excess base.
- Weak acid-strong base titrations reach their equivalence point at a pH greater than 7.

weak acid (CH₃COOH) v. strong base (NaOH)



weak acid (CH₃COOH) v. strong base (NaOH)



Only phenolphthalein is suitable - it is the only one to change in the 'vertical' portion

weak acid (CH₃COOH) v. weak base (NH₃)



- Weak acid-weak base titrations are difficult because each solution is in equilibrium.
- The pH of the equivalence point is around 7.

weak acid (CH_3COOH) v. weak base (NH_3)





weak acid (CH_3COOH) v. weak base (NH_3)



There is no suitable indicator- none change in the 'vertical' portion. The end point can be detected by plotting a curve using a pH meter.

Ex. 1

What is the concentration of HCl if 30.0 mL of 0.10 M NaOH neutralizes 50.0mL HCl? NaOH + HCl \rightarrow H₂O + NaCl Use $nM_aV_a=nM_bV_b$ $M_a=$

How many moles of HCl were used? moles= M_aV_a , but convert the volume to L(50mL=0.05L).

Titration

• 42.5 mL of 1.3MKOH are required to neutralize 50.0 mL of H_2SO_4 . Find the molarity of H_2SO_4 .

 H_3O^+ OH^- nMV = n MVM = ?M = 1.3MM(50.0mL)(2)V = 50.0 mLV = 42.5 mL=(1.3M)(42.5mL)(1)n = 2n = 1 $M = 0.55M H_2SO_4$

Sample Calculation: Strong Acid-Strong Base Titration Curve

Derive the curve of the titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

Region 1. Before the equivalence point, after adding 20.0 mL of 0.100 M NaOH. (Half way to the equivalence point.)

Initial mmoles of $H_3O^+ = 0.100^* 40 \text{ ml} = 4$

mMoles of OH^{-} added =0.1*20 ml= 2

 $[H_{3}O^{+}] = \frac{\text{amount(mmol)of }H_{3}O^{+} \text{ remaining}}{\text{original volumeof acid + volumeof added base}}$ = (4-2)/60 = 0.033 $pH = -\log [H^{+}] = -\log 0.033 = 1.48$

Sample Calculation: Strong Acid-Strong Base Titration Curve

Region 2. At the equivalence point, after adding 40.0 mL of 0.100 M NaOH.

Initial mmoles of H_3O^+ 40 ml x 0.100 M = 4 mmol H_3O^+

mMoles of OH⁻ added 40ml x 0.100 M =4 mmol OH⁻

 $\left[OH^{-}\right] = \left[H^{+}\right] = \sqrt{K_{w}}$

pH =7

Sample Calculation: Strong Acid-Strong Base Titration Curve

Region 3. After the equivalence point, after adding 50.0 mL of 0.100 M NaOH. (Now calculate excess OH⁻)

Total mmoles of $OH^{-} = 50 \text{ ml } x \text{ } 0.100 \text{ M} = 5 \text{ mmol } OH^{-}$

mMoles of H_3O^+ consumed = 40 ml x 0.100 M =4 mmol amount (mmol) of OH^- remaining original volume of acid + volume of added base =5-4/90 =0.011

 $pOH = -\log\left[OH^{-}\right] = 1.95$

pH = 14-1.95 = 12.05



Titration of strong base with strong acid

• In the titration of any strong base with any strong acid,

 $H^+ + OH^- \rightarrow H_2O$

there are three regions of the titration curve that require different kinds of calculations:

1. Before the equivalence point, the pH is determined by excess OH^- in the solution.

$$pOH = -\log \left[OH^{-} \right]$$

2. At the equivalence point, H^+ is just sufficient to react with all OH^- to make H_2O . The pH is determined by dissociation of water.

$$\left[OH^{-}\right] = \left[H^{+}\right] = \sqrt{K_{w}}$$

3. After the equivalence point, pH is determined by excess H⁺ in the solution.

$$pH = -\log\left[H^+\right]$$

Calculating the pH during a weak acid-strong base titration



pH before equivalence point

$$[H_{3}O^{+}] = K_{a} \times \frac{[HA]}{[A^{-}]} \quad \text{or}$$

$$pH = pK_{a} + \log \frac{[base]}{[acid]}$$

Calculating the pH during a weak acid-strong base titration

pH at the equivalence point $A^{-}(aq) + H_2O(l) \Longrightarrow HA(aq) + OH^{-}(aq)$ $[OH^{-}] = \sqrt{K_{b} \times [A^{-}]}$ where $[A^{-}] = \frac{\text{mol HA}_{\text{init}}}{V_{\text{acid}} + V_{\text{base}}}$ and $K_{\text{b}} = \frac{K_{\text{w}}}{K_{\text{a}}}$ $[H_3O^+] \approx \frac{K_w}{\sqrt{K_h \times [A^-])}} \text{ and } pH = -\log[H_3O^+]$ pH beyond the equivalence point $[OH^{-}] = \frac{\text{mol OH}^{-}_{\text{excess}}}{V_{\text{acid}} + V_{\text{base}}} \qquad [H_3O^{+}] = \frac{K_{\text{w}}}{[OH^{-}]}$

 $pH = -log[H_3O^+]$

Titration of a Weak Acid by a Strong Base

Derive the curve of the titration of 25.0 mL of 0.200 M HA (acetic acid) is titrated with 0.200 M NaOH.

 $(K_a = 1.8 \times 10^{-5})$

Determine pH in each of four regions:

(a) at the start -- before any NaOH is addedJust a simple weak acid:

$$\left[H^{+}\right] = \sqrt{C_{HA}K_{a}}$$

pH = 2.72

(b) before the equivalence point: after addition of 10.0 mL of NaOH The acid is partially neutralized by the added OH⁻ HA + OH⁻ --> H₂O + A⁻ 25x0.2 10x0.2 10x0.2 Since both HA and A⁻ are now present, the mixture is a *buffer solution* ! $pH = pK_a + \log (C_A^{-}/C_{HA})$

[HA] left = $(25 \times 0.2 - 10 \times 0.2)/35 = 0.085$ [A⁻] produced = $(10 \times 0.2)/35 = 0.057$ pH = $(-\log 1.8 \times 10^{-5}) + \log (0.057/0.085)$ pH = 4.57 (c) at the equivalence point:

The acid (HA) is completely neutralized, and only the anion A⁻ is present

 \therefore the solution is now the *salt of a weak acid*! Total volume is now 50.0 mL,

so [A⁻] = 0.10 M and pH = 8.88

(d) after the equivalence point:

All acid (HA) is gone and excess OH⁻ is present

 \therefore the pH is determined by how much OH⁻ is left after all the acid has been neutralized

e.g. after 40.0 mL of NaOH added: pH = 12.66



Finding the pH During a Weak Acid– Strong Base Titration

PROBLEM: Calculate the pH during the titration of 40.00 mL of 0.1000

 M propanoic acid (HPr; $K_a = 1.3 \times 10^{-5}$) after adding the following volumes of 0.1000 M NaOH:

 (a) 0.00 mL
 (b) 30.00 mL
 (c) 40.00 mL
 (d) 50.00 mL

PLAN: The initial pH must be calculated using the K_a value for the weak acid. We then calculate the number of moles of HPr present initially and the number of moles of OH⁻ added. Once we know the volume of base required to reach the equivalence point we can calculate the pH based on the species present in solution.

SOLUTION:

(a) $[H_3O^+] = \sqrt{K_a \times [HPr]_{init}} = \sqrt{(1.3 \times 10^{-5})(0.100)} = 1.1 \times 10^{-3} M$ pH = -log(1.1x10⁻³) = 2.96 (b) 30.00 mL of 0.1000 M NaOH has been added.

Initial amount of HPr = $0.04000 \text{ L} \times 0.1000 M = 4.000 \times 10^{-3} \text{ mol HPr}$ Amount of NaOH added = $0.03000 \text{ L} \times 0.1000 M = 3.000 \times 10^{-3} \text{ mol OH}^{-1}$

Each mol of OH⁻ reacts to form 1 mol of Pr⁻, so

Concentration (M)HPr(aq) + $OH^{-}(aq) \rightarrow$ $Pr^{-}(aq) + H_2O(N)$ Initial0.0040000.0030000-Change-0.003000-0.003000+0.003000-Equilibrium0.00100000.003000- $[H_3O^+] = K_a \times \frac{[HPr]}{[Pr]} = (1.3 \times 10^{-5}) \times \frac{0.001000}{0.003000} = 4.3 \times 10^{-6} M$ $= 4.3 \times 10^{-6} M$ pH = -log(4.3 \times 10^{-6}) = 5.37

(c) 40.00 mL of 0.1000 MNaOH has been added.

This is the equivalence point because mol of OH^- added = 0.004000 = mol of $HA_{init.}$

All the OH⁻ added has reacted with HA to form 0.004000 mol of Pr-.

$$[\Pr^{-}] = \frac{0.004000 \text{ mol}}{0.04000 \text{ L} + 0.04000 \text{ L}} = 0.05000 M$$

$$\Pr^{-} \text{ is a weak base, so we calculate } K_{b} = \frac{K_{w}}{K_{a}} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10}$$

$$[H_{3}O^{+}] \approx \frac{K_{w}}{\sqrt{K_{b} \times [A^{-}]}} = \frac{1.0 \times 10^{-14}}{\sqrt{(7.7 \times 10^{-10})(0.05000)}} = 1.6 \times 10^{-9} M$$

 $pH = -log(1.6x10^{-9}) = 8.80$

(d) 50.00 mL of 0.1000 M NaOH has been added.

Amount of OH^- added = 0.05000 L x 0.1000 M = 0.005000 mol

Excess $OH^{-} = OH^{-}_{added} - HA_{init} = 0.005000 - 0.004000 = 0.001000 mol$

$$[OH^{-}] = \frac{\text{mol OH}_{\text{excess}}}{\text{total volume}} = \frac{0.001000 \text{ mol}}{0.09000 \text{ L}} = 0.01111 M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{0.01111} = 9.0 \times 10^{-13} M$$

 $pH = -log(9.0x10^{-13}) = 12.05$

The four Major Differences Between a Strong Acid-Strong Base Titration Curve and a Weak Acid-Strong Base Titration Curve

- 1. The initial pH is higher.
- 2. A gradually rising portion of the curve, called the buffer region, appears before the steep rise to the equivalence point.
- 3. The pH at the equivalence point is greater than 7.00.
- 4. The steep rise interval is less pronounced.



Indicator	pH range	рКа	Acid Form	Base Form
methyl violet	0.0-1.6	0.8	yellow	blue
thymol blue	1.2-2.8	1.6	red	yellow
methyl yellow	2.9-4.0	3.3	red	yellow
methyl orange	3.1-4.4	4.2	red	yellow
bromocresol green	3.8-5.4	4.7	yellow	blue
methyl red	4.2-6.2	5.0	red	yellow
bromothymol blue	6.0- 7.6	7.1	yellow	blue
phenol red	6.4- 8.0	7.4	yellow	red
thymol blue	8.0-9.6	8.9	yellow	blue
phenolphthalein	8.0-9.8	9.7	colourless	red
thymolphthalein	9.3-10.5	9.9	colourless	blue
alizarin yellow R	10.1-12.0	11.0	yellow	red
indigo carmine	11.4-13.0	12.2	blue	yellow