Chem Factsheet

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Titration Curves and Indicators

When an alkaline (high pH) solution (e.g., NaOH(aq)) is added to an acidic (pH low) solution (e.g., HCl(aq)) the pH of the mixture would be expected to increase. The exact pattern of pH changes can be determined experimentally and, if the pH is plotted against volume of titrant (here the NaOH(aq)), the resulting graph is called a "titration curve".

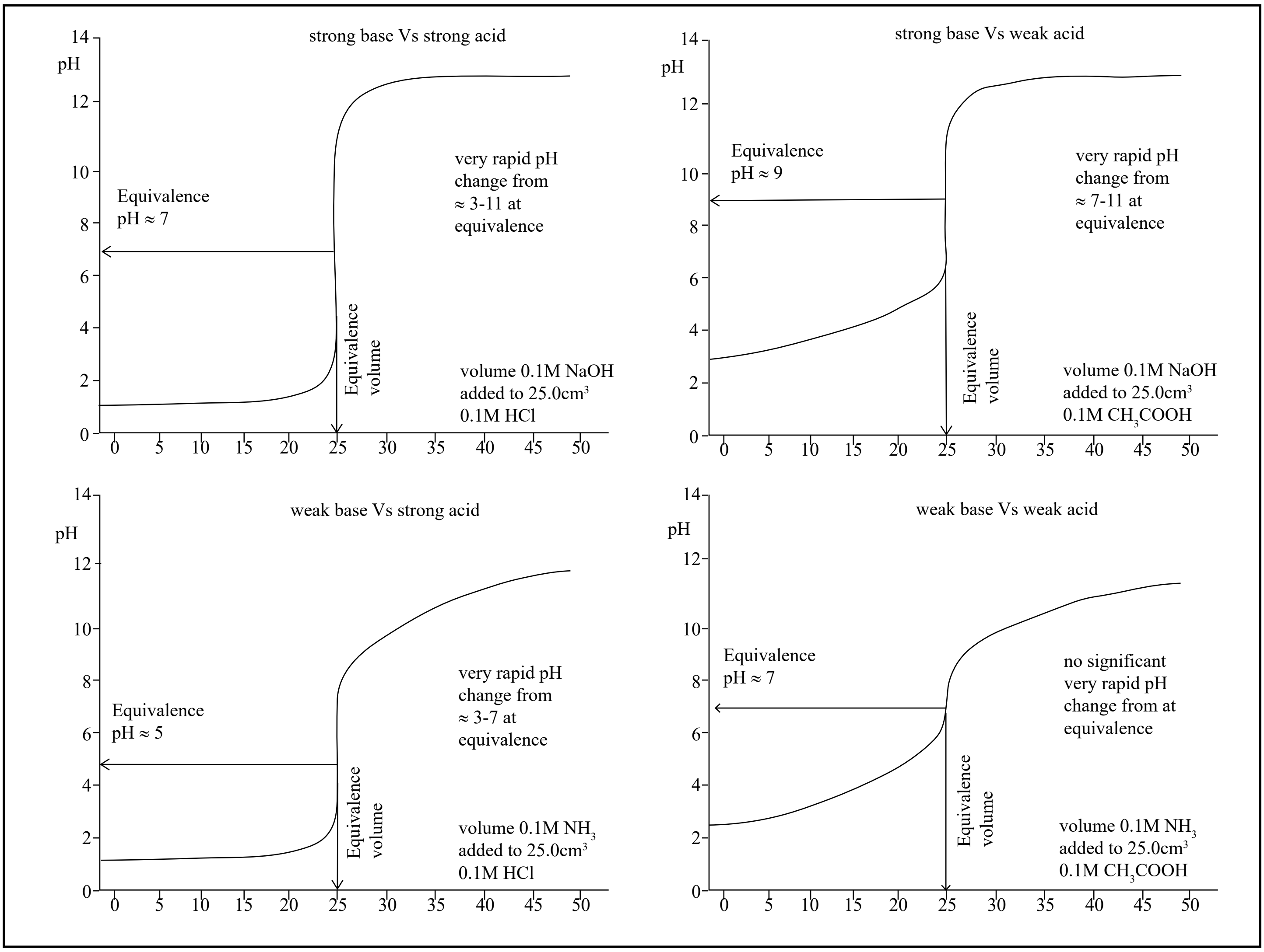
In outline, an appropriate procedure for obtaining a titration curve would be:

1. Calibrate a pH electrode and meter using two buffer solutions of different pH values – one to set the pH meter reading and one to check the calibration.
2. Prepare a graph of pH (0-14 on the y-axis) against volume of alkali added during titration (0-about 50 cm^3 on x-axis).
3. Pipette 25.0 cm^3 of a 0.10 mol dm^{-3} weak (partially ionised e.g. CH_3COOH) or strong (fully ionised e.g. HCl) acid into a 250 cm^3 beaker. Clamp the pH electrode in this solution. Measure its pH and plot the initial pH (0 cm^3 alkali added) of the acid.
4. Add a 0.10 mol dm^{-3} weak (partially ionised e.g. NH_3) or strong (fully ionised e.g. NaOH) alkali to the acid sample from a burette in 1.00 cm^3 portions, mixing the reagents thoroughly and then measuring and plotting the mixture's pH after each addition. Repeat these additions and pH measurements up to 50 cm^3.
5. Draw the best fit curve to the experimental points.

The Titration Curves

Typical titration curves derived by the previous procedure are shown in Fig. 1.

Fig. 1 Titration Curves



Discussion

The whole idea of an acid-base titration is to find the point at which the H^+ ions in an acid sample are exactly reacted with an equal number of OH^- ions from an alkali.

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

This is the "equivalence point / volume" of the reaction.
If the concentration of one of the solutions is known (standardised), the concentration of the other can be calculated from the equivalence volume.
In the examples shown in Fig. 1, the equivalence points/volumes all occur at $25.0cm^3$ because:

Moles monobasic acid added = 0.100 × 0.025 = moles monobasic alkali added.
Suppose the alkali concentration had been $0.080 \text{ mol dm}^{-3}$ instead of $0.100 \text{ mol dm}^{-3}$, then the equivalence volume would move to a higher value because more of the lower concentration solution would be needed to provide the equivalent number of moles.
In fact, it would move to $V cm^3$ where:

Moles acid = 0.100 × 25.0/1000 = 0.080 × V/1000 = Moles alkali
$\rightarrow V = 25.0 \times 0.100 / 0.080 = 31.25cm^3$.

As seen in Fig. 1, the exact shape of a titration curve is controlled by the relative strengths (weak or strong) of the reacting acid and alkali. In general, there is a sudden increase in pH at the equivalence point, but the degree of change varies. It spans about 6-8 pH units for a strong-strong titration but only about 3-4 pH units for either strong-weak combination. The weak-weak combination produces a much smaller and less sudden pH change at equivalence. These differences are central to making the correct choice of indicator during any particular titration – see later.
It is also worth noting that the strong-strong and weak-weak combinations produce more symmetrical titration curves.

The equivalence point / volume is often referred to as the "point of neutralisation" but, as seen in Fig. 1, the pH at this point is not always neutral. It occurs at about pH 7 for strong-strong and weak-weak combinations of acid and base but significantly above or below for the other two.

(a) For a STRONG ACID-STRONG BASE titration (e.g. HCl vs NaOH)
  → NaCl salt formed at equivalence
  → Na^+ and Cl^- ions in solution
  → Neither of these ions hydrolyses water
  → pH near 7

(b) For a STRONG ACID-WEAK BASE titration (e.g. NH_3 vs HCl)
  → NH_4Cl salt formed at equivalence
  → NH_4^+ and Cl^- ions in solution
  → NH_4^+ ions partially hydrolyse water; $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
  → H_3O^+ ions produced
  → pH below 7

(c) For a WEAK ACID-STRONG BASE titration (e.g. NaOH vs CH_3COOH)
  → CH_3COONa salt formed at equivalence
  → Na^+ and CH_3COO^- ions in solution
  → CH_3COO^- ions partially hydrolyse water; $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
  → OH- ions produced
  → pH above 7

(d) For a WEAK ACID-WEAK BASE titration (e.g. CH_3COOH vs NH_3)
  → CH_3COONH_4 salt present at equivalence
  → NH_4^+ and CH_3COO^- ions in solution
  → both of these ions hydrolyse water
  → $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ and $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
  → These approximately cancel
  → pH near 7

To answer many examination questions, you must be able to sketch these titration curves with reasonable precision. The starting pH (lower for strong acid, higher for a weak acid) affects the shapes of the curves before and after equivalence, the equivalence volume and the pH at equivalence will be checked.

Titration Curves for Dibasic Acids and Alkalis

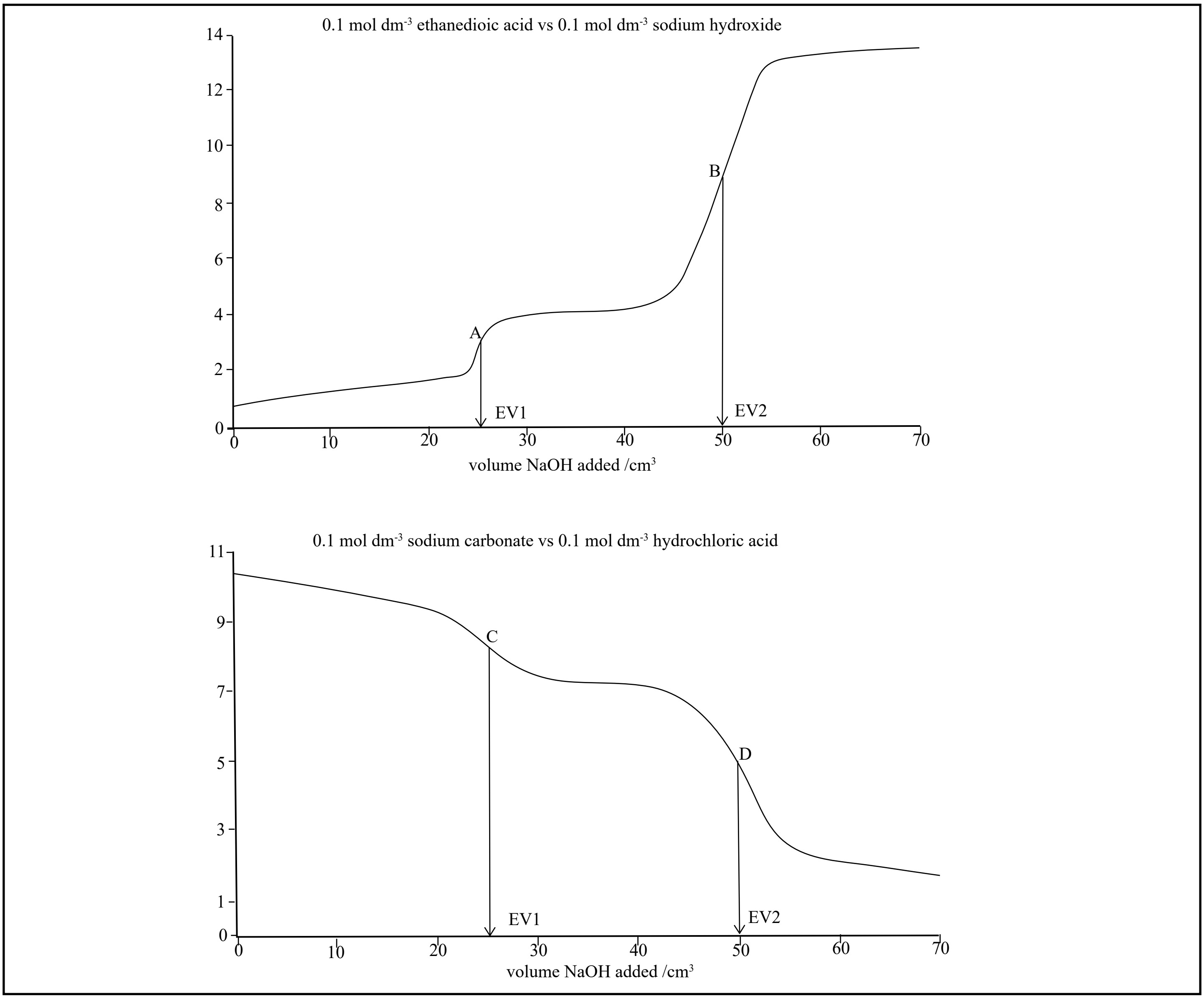
Typically these would be titrations such as:
(a) Ethanedioic acid against sodium hydroxide,
(b) Sodium carbonate against hydrochloric acid.

These reactions occur in two stages.
For (a) $HOOC\text{-}COOH + OH^- \rightarrow HOOC\text{-}COO^- + H_2O$ -----------------(1)
then $HOOC\text{-}COO^- + OH^- \rightarrow {}^-OOC\text{-}COO^- + H_2O$ -----------------(2)
Hence, by adding these together, the overall reaction is $HOOC\text{-}COOH + 2OH^- \rightarrow {}^-OOC\text{-}COO^- + 2H_2O$

For (b) $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ -----------------(3)
then $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ -----------------(4)
Hence, by adding these together, the overall reaction is
$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

If the technique outlined earlier is applied to these reactions the titration curves obtained are as shown in Fig. 2.

Fig. 2



Unlike the curves for monobasic acids and bases seen in Fig. 1, these curves both show two regions of sharper pH changes – A with B and C with D – and hence 2 equivalence points per reaction (EV1 and EV2).

These correspond to the completion of the reaction stages discussed above.
At A, reaction 1 is complete.
At B, reaction 2 is complete.
At C, reaction 3 is complete.
At D, reaction 4 is complete.

This means that bubbles of carbon dioxide will be seen *only* between points C and D for the carbonate-acid titration.

Indicators

Equivalence volumes can be determined directly from titration curves but, rather than measuring pH changes throughout the reaction, it is more convenient to detect just the larger and sharper pH change associated with the equivalence point by adding a colour indicator. This shows when the equivalence point has been reached by producing a sudden and distinct colour change at that point.

Most acid-base indicators are weak acids and are traditionally represented by HIn. Crucially they have just two distinct colours for the molecular form (HIn – colour A) and the ionised form (In^- - colour B).

COLOUR A $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$ COLOUR B

Methyl orange and phenolphthalein are probably two of the most commonly encountered indicators at A-level.

Methyl orange is red in acid solution but yellow in alkaline solution. Hence the molecular form is red but the ionised form is yellow.

Since indicators are weak acids, the equilibrium can be described by a K_a value (see FactSheet 208).

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

$$Ka = \frac{[H^+] \times [In^-]}{[HIn]}$$

Suppose that a particular indicator has $K_a = 1 \times 10^{-6}$.

> *Note that K_a is quoted as a dimensionless quantity. In other words, it has no units. This is true for ALL equilibrium constants but you should check your specification to see if units in terms of mol dm^{-3} are expected. Strictly speaking, each molar concentration in a K expression should be replaced by concentration x "activity coefficient". The latter is assumed to be 1 in most A-level specifications. Having units of 1/concentration, this cancels all units.*

This can be rearranged to give an expression for the ratio of HIn to In- for this indicator, which is what determines the visible colour.

$$\begin{matrix}\text{Colour A} \rightarrow \\ \text{Colour B} \rightarrow\end{matrix} \quad \frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_a} = \frac{[H^+]}{1.0 \times 10^{-6}}$$

As shown in the following table, consider placing this indicator in separate samples of solutions of increasing pH (row 1). The pH for each sample can be converted to $[H^+]$ (row2) which can then be used to calculate the [HIn]:[In-] ratio (row 3). This ratio will then indicate the visible colour, but it must be noted that the human eye cannot distinguish the colours caused by the ratios in the 10:1 to 1:10 range.

pH of solution	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
$[H^+]$ / mol dm^{-3}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}
[HIn]:[In-]	10^4	10^3	10^2	10^1	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
Visible colour	A	A	A	INDISTINCT			B	B	B

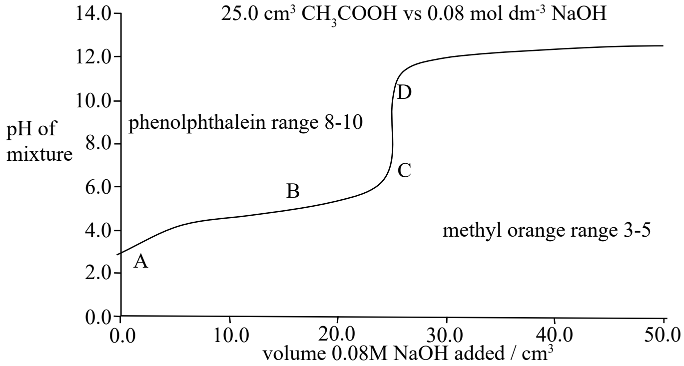
This means that the indicator is seen to change colour over a range of 2 pH units, one on either side of the pK_a (= $-\log_{10} K_a$) value of the indicator. Consequently, because different indicators have different K_a values, they have different end-point ranges but all cover about 2 pH units. This is illustrated in the following table for the two indicators already considered.

Indicator	K_a	pK_a	End-point Range
Methyl orange	2.0×10^{-4}	3.7	2.7 – 4.7 (≈ 3 – 5)
Phenolphthalein	5.0×10^{-10}	9.3	8.3 – 10.3 (≈ 8 – 10)

> *If the equivalence point of an acid-base titration is to be detected accurately, an indicator must be chosen such that its end-point range fits into sharp pH change for that particular titration. In other words, the indicator pH range must include the equivalence pH of the titration.*

Fig. 3 shows a titration curve for a strong acid (e.g. HCl) and weak base (e.g. NH_3) with the end-point ranges of methyl orange and phenolphthalein superimposed.

Fig. 3



As the titration reaches the equivalence point, the pH increases rapidly from C to D. This includes the end-point range of phenolphthalein, which means that the indicator will change colour rapidly *at the same time* as the reaction reaches equivalence. Hence, phenolphthalein is appropriate for this titration.

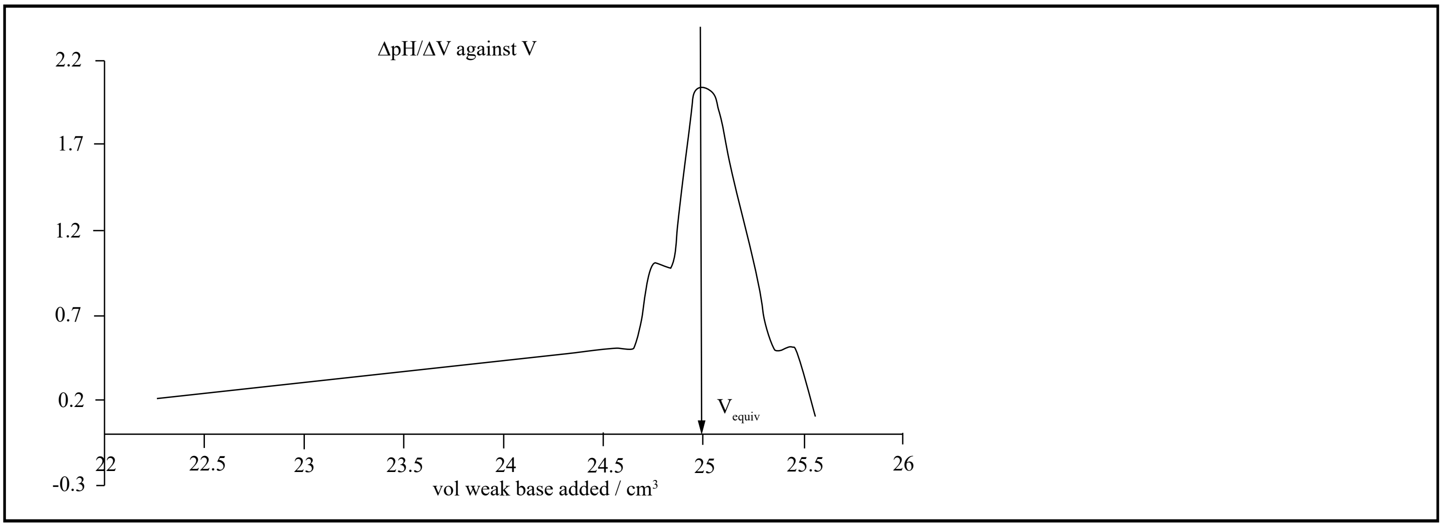
However, methyl orange will change colour well before equivalence is reached (at B) and the colour change will be very gradual from A to B. Hence, methyl orange is not appropriate for this titration.

Finding Equivalence for a Weak Acid-Weak Base Titration

As seen, it is not possible to determine equivalence accurately for a weak acid-weak base titration using an indicator. Instead, the equivalence volume can be read from the titration curve a shown in Fig. 1. The equivalence volume corresponds to the point where the curve has its maximum gradient. This can be read with reasonable accuracy, especially if the experiment is repeated to acquire more data points in the region of the curve's inflexion.

Alternatively, the rate of change of pH with respect to volume added ($\Delta pH/\Delta V$) can be calculated.

$\Delta pH/\Delta V$ is then plotted against V_{mean} to give the following graph:

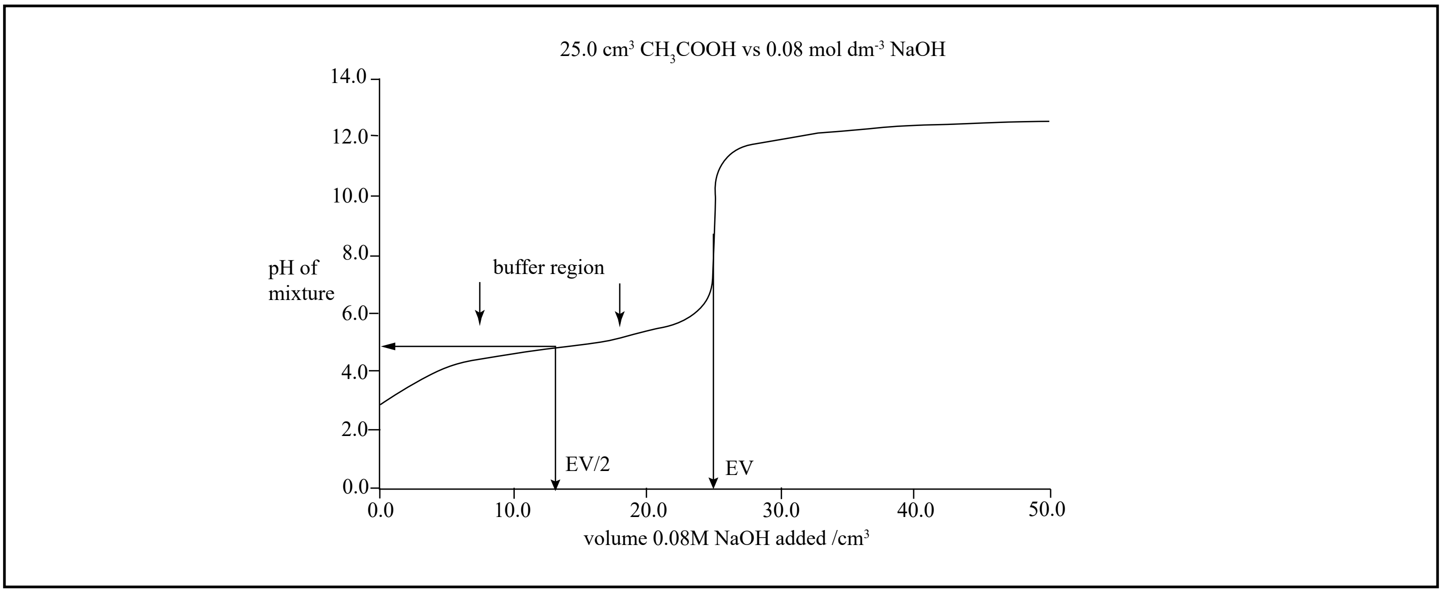


The equivalence volume is then read off at the maximum value of $\Delta pH/\Delta V$.

K_a from a Titration Curve

K_a for a weak acid can be determined using a titration curve for it being titrated against a strong alkali. This is demonstrated in Fig. 4.

Fig. 4



At EV the CH_3COOH is completely converted to CH_3COO^-.
Consequently, at EV/2 it is half converted and the ratio of $CH_3COOH:CH_3COO^-$ in the reaction mixture will be 1:1.

The equilibrium concerned is: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
Hence, $K_a = [CH_3COO^-][H^+]/[CH_3COOH] = [H^+] \times$ ratio of $CH_3COOH:CH_3COO^-$
Hence, at EV/2 only, $K_a = [H^+]$
→ pKa = pH at EV/2
→ pKa = 4.8 from the graph
→ $Ka = 10^{-4.8} = 1.59 \times 10^{-5}$ (no units).

The Buffer Region of a Weak Acid-Strong Base Titration Curve

As shown in Fig.4 there is a region on either side of half-equivalence where the pH changes very little for significant amounts of added sodium hydroxide. The reaction mixture is *buffering* the action of the added alkali.
Here, there are significant amounts of both the weak acid (unreacted so far) and the salt of the same weak acid (from the reaction with the alkali) in the same solution. Such a mixture is a classic acidic buffer with the pH varying slightly about pK_a (4.8 – see above) as the ratio of acid:salt varies.

Questions

1. When 25.0 cm^3 of $Ba(OH)_2$ is titrated against 0.075 mol dm^{-3} HCl, equivalence is achieved at 22.45 cm^3 of HCl.
   What is the molar concentration of the alkali?
2. COLOUR A $HIn(aq) \rightleftharpoons H^+(aq) + In(aq)$ COLOUR B
   When this indicator (HIn) is placed in (a) a low pH solution (b) a high pH solution, will colour A or B be seen? Explain your answer
3. Using the general curves for Fig. 1, complete the following table to decide whether methyl orange and phenolphthalein are, or are not, appropriate for each of the titration types shown.

	pH change at equivalence for this titration	Phenolphthalein (range 8-10) appropriate or not?	Methyl orange (range 3-5) appropriate or not?
Strong Acid - Strong Base			
Strong Acid - Weak Base			
Weak Acid - Weak Base			

4. For those examples in Q3, where the indicator is NOT appropriate, describe the consequences of trying to use it in terms of the sharpness of the colour change and when the colour change would occur.
5. Refer back to Fig. 2 and decide whether phenolphthalein or methyl orange can be used to carry out these titrations.
   Discuss the consequences of your choices.

Answers

1 Ba(OH)2 + 2HCl → BaCl2 + 2H2O
Moles acid = 0.075 × 22/45/1000 = 2 × Moles alkali = 2 × Concn × 25.0/1000 =
→ Concn = 0.075 × 22.45 / 2 × 25.0 = 0.0337 mol dm-3.

2 (a) At low pH, [H+] is high → equilibrium is pushed to left → ratio of HIn/In- very high → colour of HIn rather than In- is visible → colour A seen.
(b) At high pH, [OH-] is high → these react with, and remove, H+ from the indicator equilibrium → equilibrium is pulled to right → ratio of In-/HIn very high → colour of In- rather than HIn is visible → colour B seen.

3.

	pH change at equivalence for this titration	Phenolphthalein (range 8-10) appropriate or not?	Methyl orange (range 3-5) appropriate or not?
Strong Acid - Strong Base	7-11	yes	yes
Strong Acid - Weak Base	3-7	no	yes
Weak Acid - Weak Base	small	no	no

4. SA-WB : Phenolphthalein would change colour slowly and well after the equivalence point
   WA-WB : Phenolphthalein would change colour slowly and well after the equivalence point
   WA-WB : Methyl orange would change colour slowly and well before the equivalence point
5. Ethandioic acid is best titrated using phenolphthalein to detect EV2, whereas sodium carbonate is best titrated using methyl orange (also to detect EV2). This is because the pH changes are sharper and larger at EV2 and completely include the respective indicator ranges. Also, EV2 would give a smaller % error.
   Conversely, EV1 for ethandioic acid can be detected using methyl orange and EV1 for sodium carbonate can be detected using phenolphthalein but, in both cases, the end-points will be less sharp and the % errors will be larger.

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