

Do now:

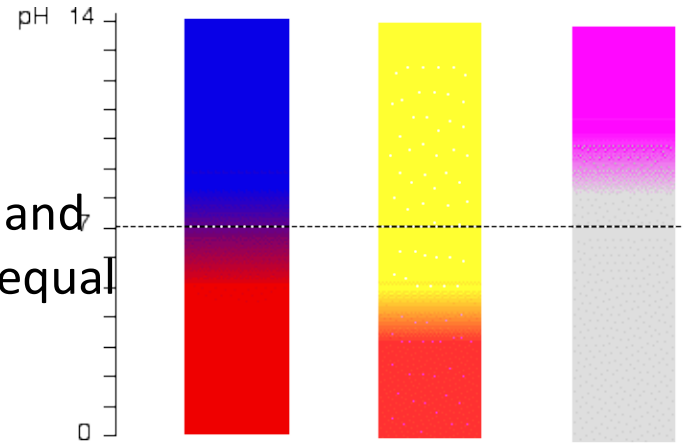
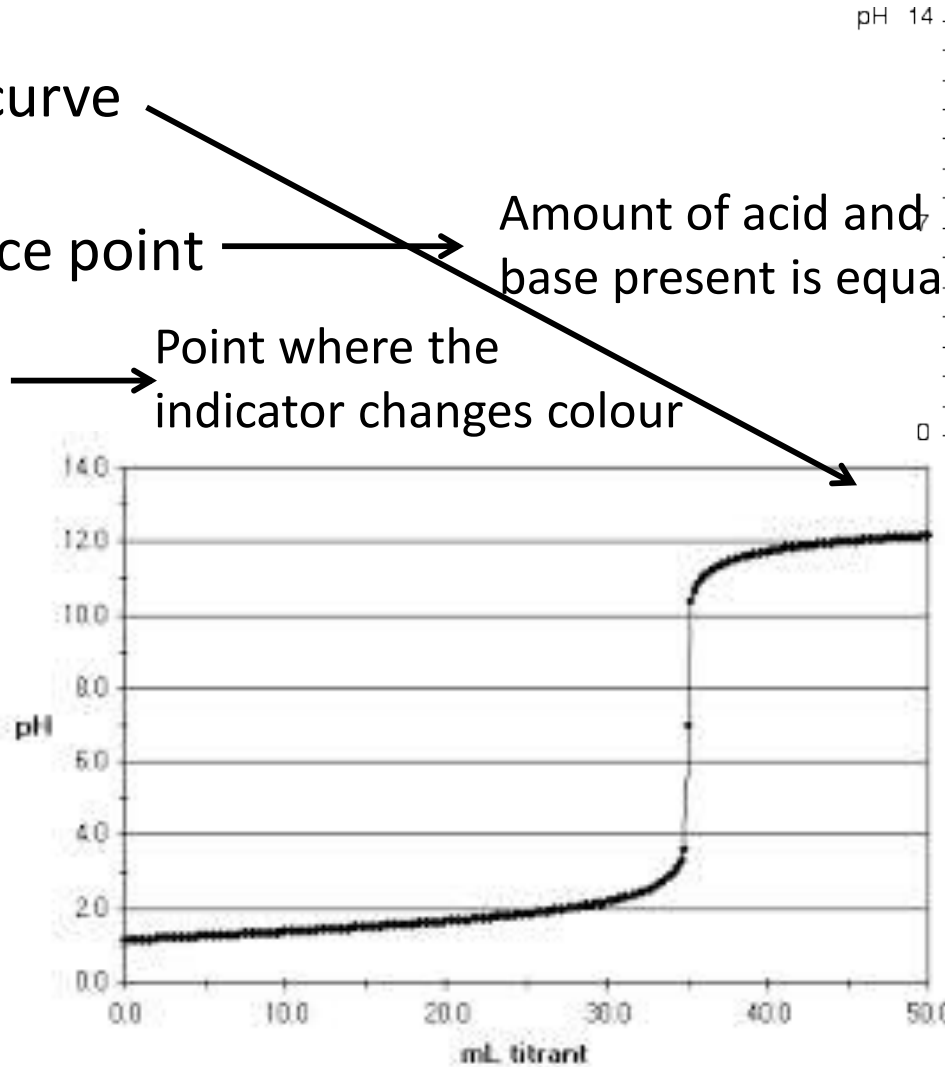
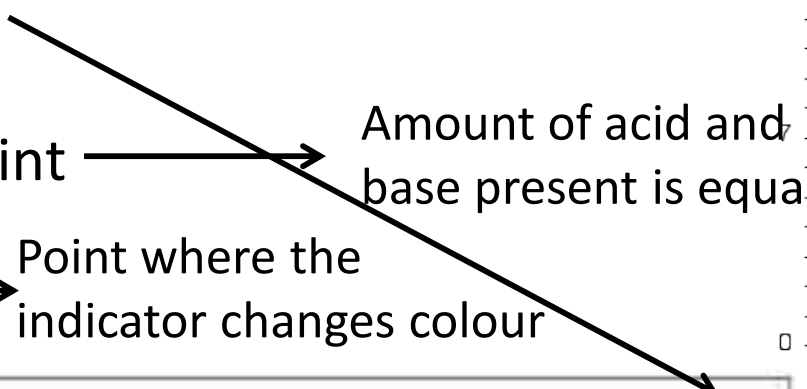
What do you think the following words mean?

Titration curve

Equivalence point

End point

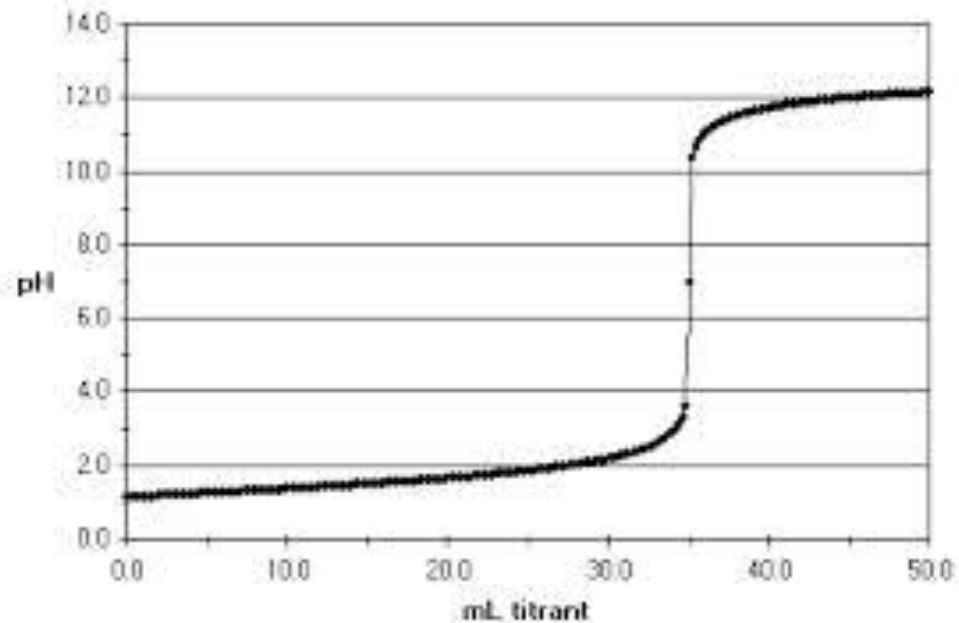
Indicator



Titrations

What do we need to be able to do?

- Discuss reasons for the pH of titrated solution at key points
- Discuss changes in concentrations of species in solution
- Calculate pH at key points on graph
- Choosing indicators



Titration curves

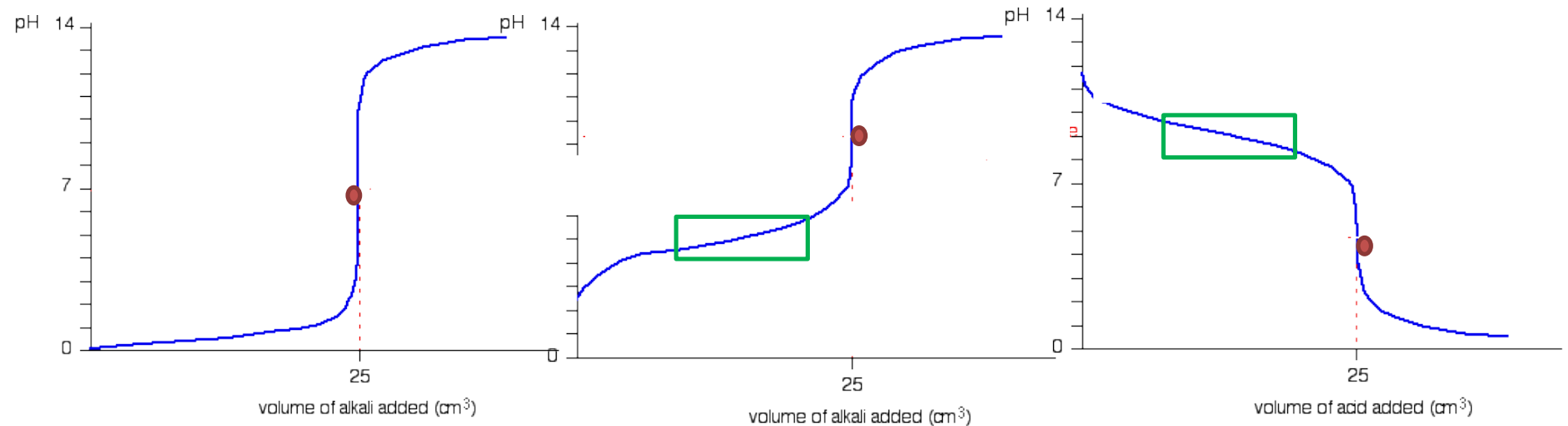
pH v volume

3 types

Strong acid
Strong base

Weak acid
Strong base

Strong acid
Weak base



Where is the equivalence point?

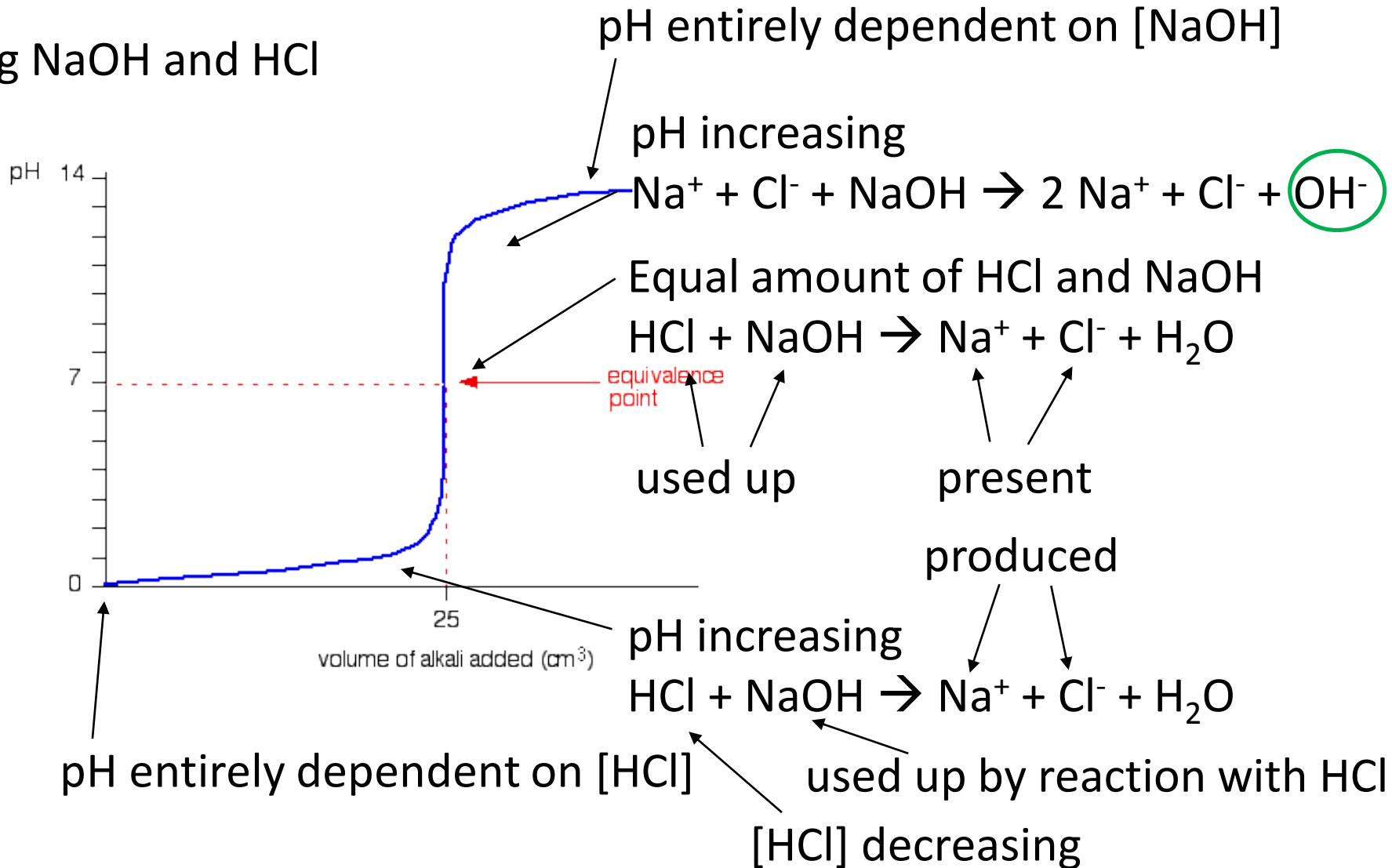
Do now:

What is the equivalence point of a titration?

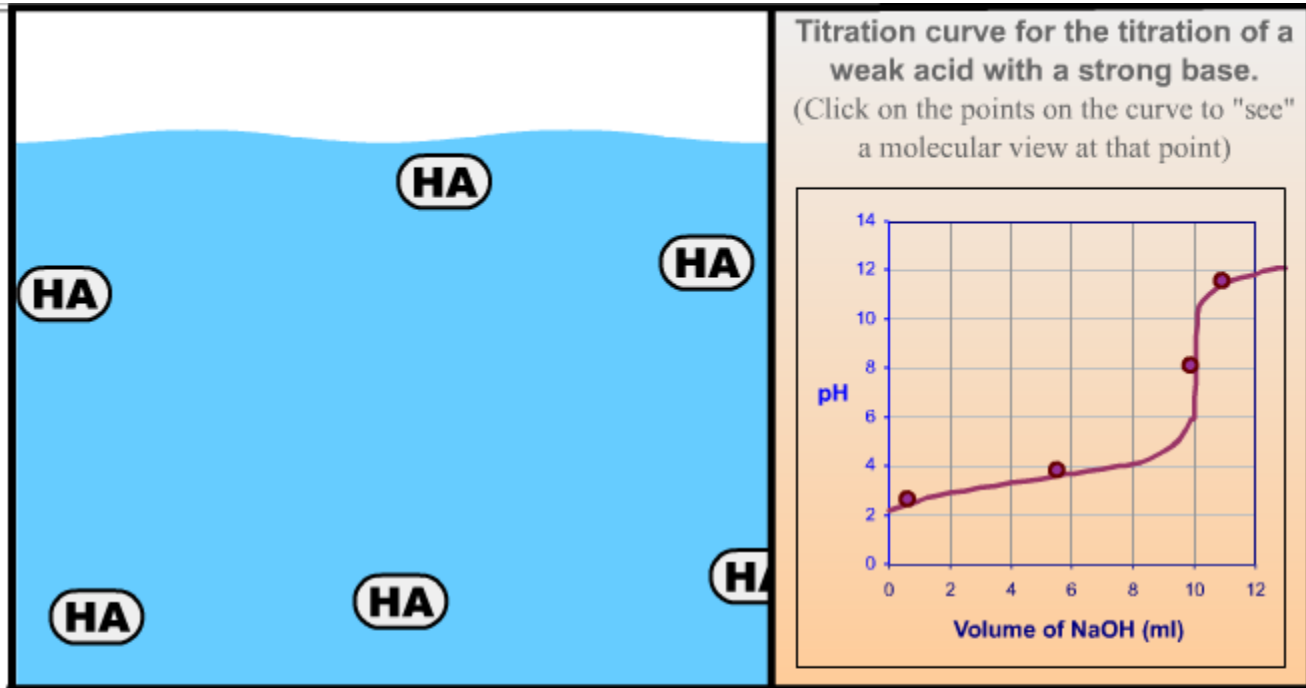
Why do titrations between strong acids and weak bases OR strong bases and weak acids have buffer zones?

Strong acid strong base titration

eg NaOH and HCl



Weak acid strong base titration



In this animation, we will show various stages of the titration of a weak acid, HA, with a strong base, NaOH.

As you may remember from the "Weak Acid" and "Buffer" animations, only a small fraction of weak acid molecules dissociates to hydronium ion, H_3O^+ , and the conjugate base A^- , when dissolved in water.

In this animation we will show HA only in its non-dissociated form because it is the dominant species in solution.

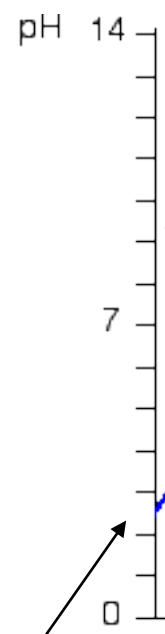


Weak acid strong base titration

eg NaOH and HCOOH

pH entirely dependent on [NaOH]

pH increasing
More OH⁻ added



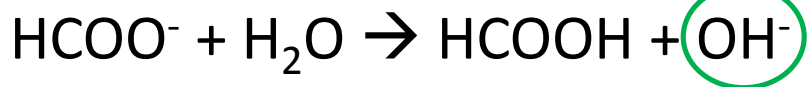
HCOOH, HCOO⁻
present:
buffer zone

Equal amount of HCOOH and NaOH
HCOOH + NaOH → Na⁺ + HCOO⁻ + H₂O

equivalence point

used up

present



produced

pH increasing



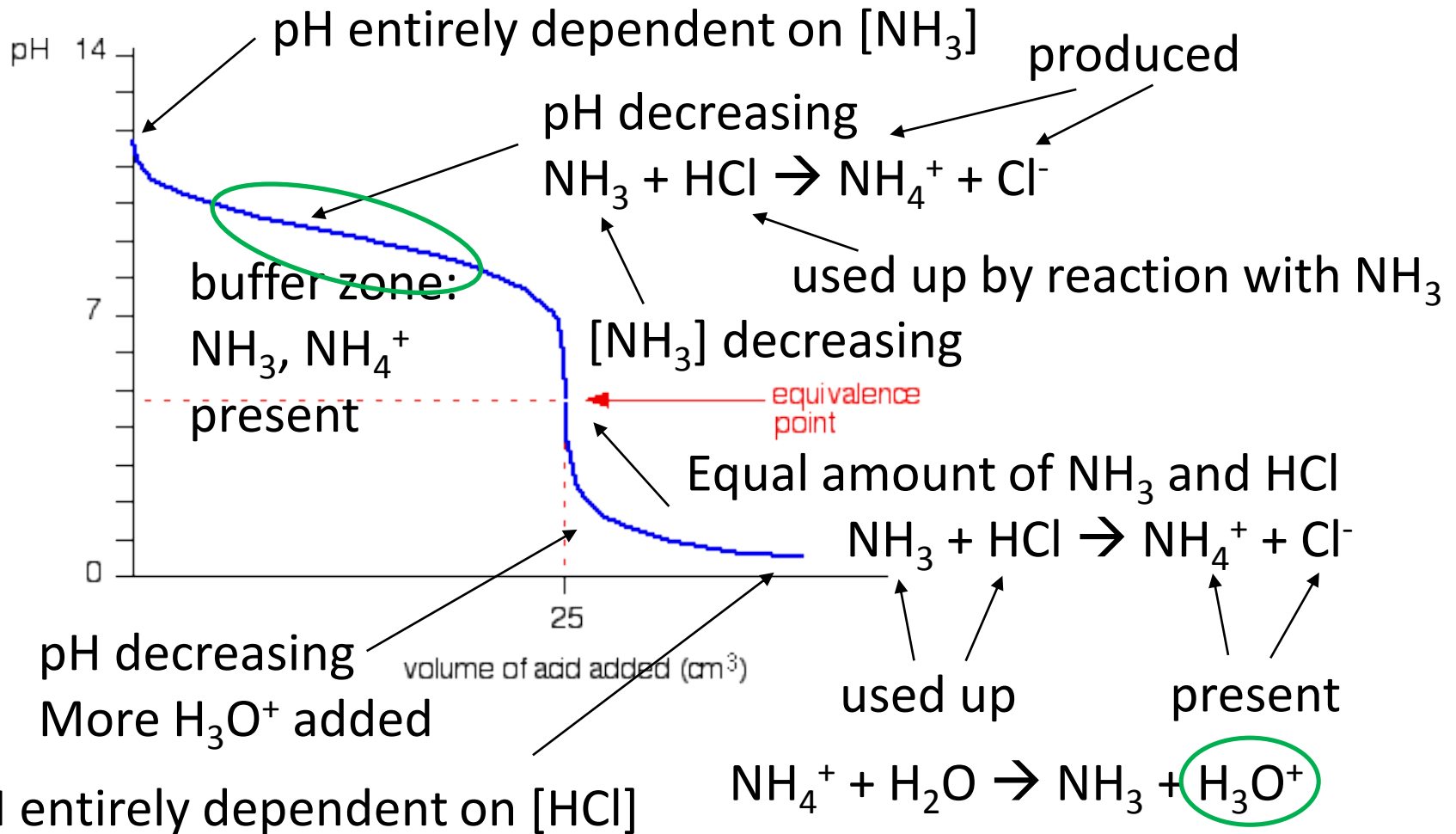
pH entirely dependent on [HCOOH]

used up by reaction with HCOOH

[HCOOH] decreasing

Strong acid weak base titration

eg NH_3 and HCl



Buffer zones

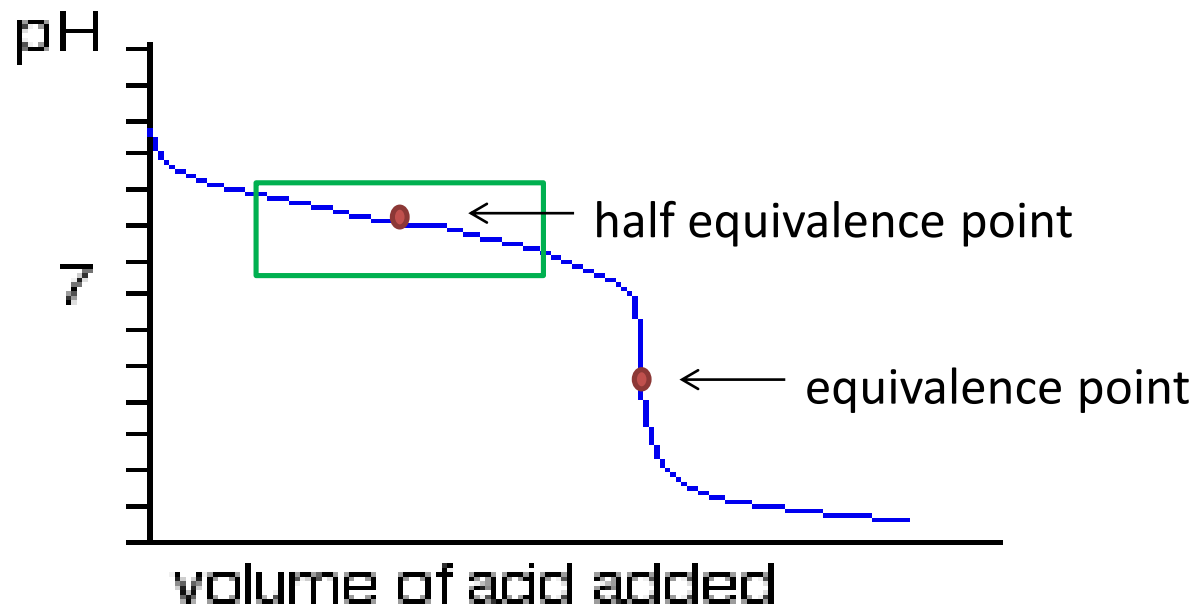
Recap: What is a buffer solution?

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

$$\text{p}K_a = \text{pH} - \log_{10} \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

When $\text{A}^- = \text{HA}$
then $\text{p}K_a = \text{pH}$

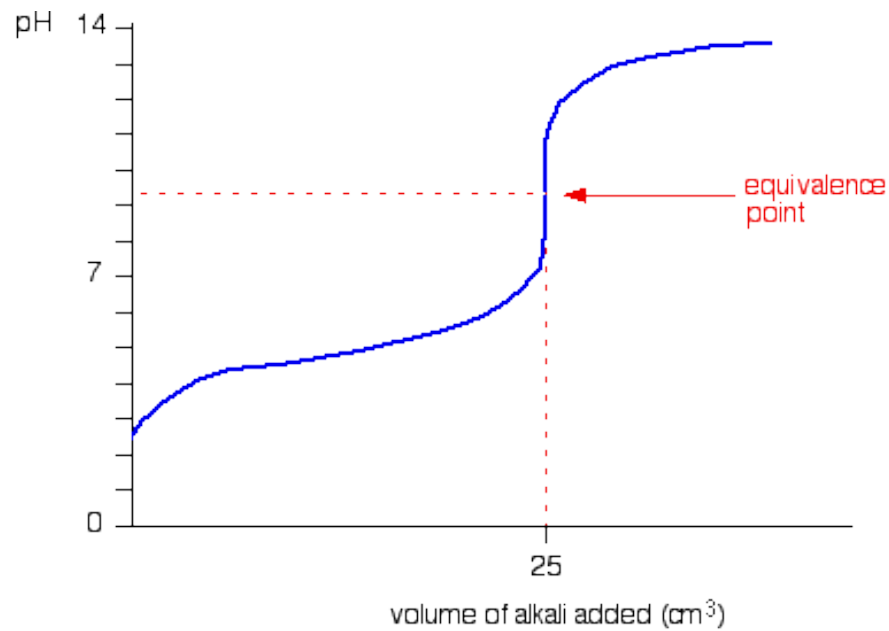
strong acid - weak base



Key points

In exams you are usually asked to:

- Discuss the buffer zone
- Discuss the equivalence point and its pH and/or calculate its pH
- Discuss the change in the concentration of species in solution as the titration progresses
- Calculate initial pH of weak acid/base solution



2013 Exam Q3 b

20.0 mL of $0.0896 \text{ mol L}^{-1}$ ethanoic acid is titrated with 0.100 mol L^{-1} sodium hydroxide.

$$pK_a(\text{CH}_3\text{COOH}) = 4.76$$

(b) Halfway to the equivalence point of the titration, the $\text{pH} = pK_a$ of the ethanoic acid.

Discuss the reason for this.

What would be the A answer?

- Recognises that there are equimolar quantities of ethanoic acid and sodium ethanoate.

What would be the M answer?

- Relates equation correctly to explanation.

Halfway to equivalence point, half of the ethanoic acid has been used up. There are now equimolar quantities of ethanoic acid and sodium ethanoate.

$$\text{As } K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

According to the equation when $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$
then $K_a = [\text{H}_3\text{O}^+]$
So $pK_a = \text{pH}$.

- (c) (i) Discuss the change in the concentration of species in solution, as the first 5.00 mL of NaOH is added to the 20.0 mL of ethanoic acid.

Your answer should include chemical equations.

No calculations are required.

What is happening when NaOH is added?

What key things is the examiner looking for?

- | | | |
|---|--|---|
| • Correct equation <i>minor error</i> . | Correct equation and correctly describes the change in concentration of 2 species. | • Correct equation.
AND
Correctly describes the change in concentration of the 4 species. |
| • Correct statement relating to change in concentration of 1 species. | | |



$[\text{CH}_3\text{COO}^-]$ increases as it is formed in reaction (1).

$[\text{Na}^+]$ increases as NaOH is added (1).

$[\text{CH}_3\text{COOH}]$ decreases as it reacts with NaOH (1).

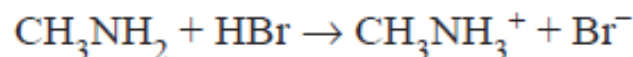
$[\text{H}_3\text{O}^+]$ decreases because $[\text{CH}_3\text{COO}^-] / [\text{CH}_3\text{COOH}]$ increases and K_a is a constant.

$[\text{OH}^-]$ increases because $[\text{H}_3\text{O}^+]$ decreases and $[\text{H}_3\text{O}^+][\text{OH}^-]$ is constant.

2014 Exam Q3 a

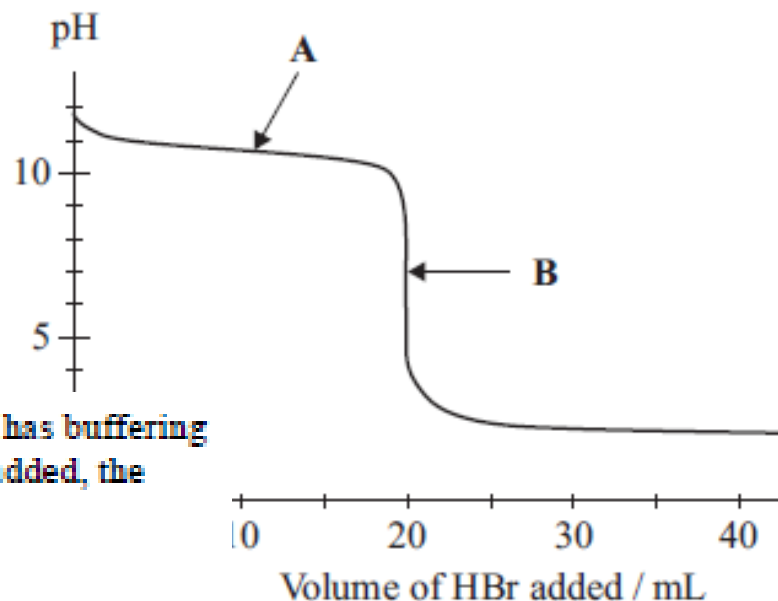
A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH_3NH_2 , solution.

The equation for the reaction is:



$$K_a(\text{CH}_3\text{NH}_3^+) = 2.29 \times 10^{-11}$$

The curve for this titration is given below:



At point A, $[\text{CH}_3\text{NH}_2] \approx [\text{CH}_3\text{NH}_3^+]$. So the solution has buffering properties in the proximity of point A. When HBr is added, the H_3O^+ is consumed:



Since the H_3O^+ is removed from the solution (neutralised), the pH does not change significantly.

- (a) Explain why the pH does not change significantly between the addition of 5 to 15 mL of HBr (around point A on the curve).

Include any relevant equation(s) in your answer.

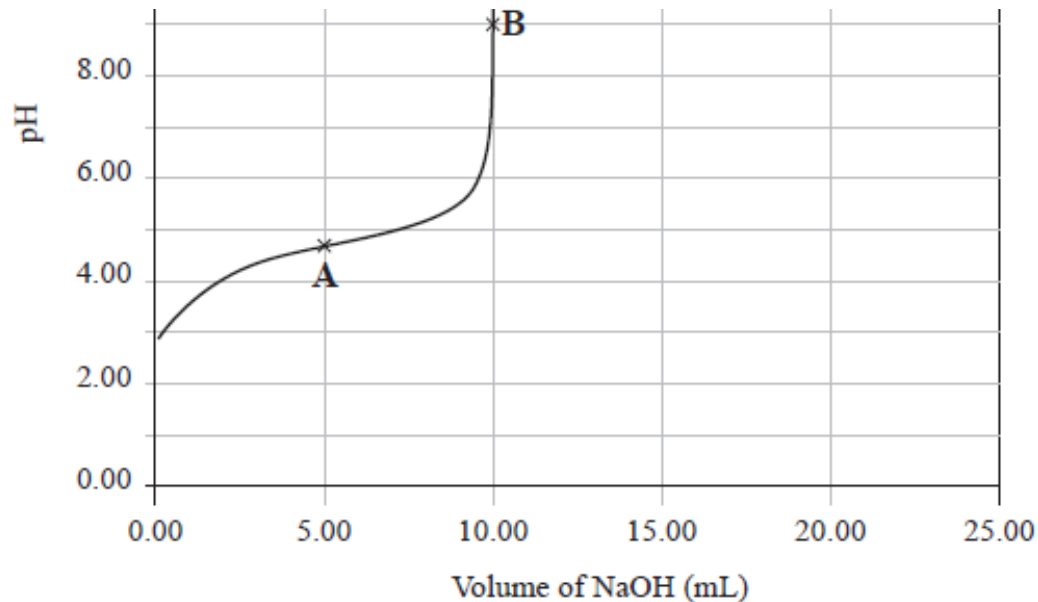
2011 Exam Q4

QUESTION FOUR

- (a) With reference to the point marked A on the graph, discuss:
- the species present, and their relative concentrations
 - an estimate of the pK_a value for ethanoic acid
 - the effect of adding small amounts of strong acid or strong base to the solution.

Include relevant equations in your answer.

No calculations are necessary.



2011 Exam Q4

ONE of:

- Recognises that at point A there is a buffer solution.
- States that equimolar amounts of acid / base conjugate are present at A.
- States that pH will not change when small amounts of acid or base are added.
- Correct pK_a / K_a

Describes how a buffer works (for when both acid AND base are added) by:

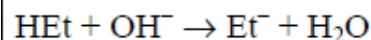
EITHER

- Giving equations for the specific buffer
- OR
- Writing about how a buffer works in general terms
- OR
- Links that due to equimolar HEt and Et^- thus $pK_a = pH$

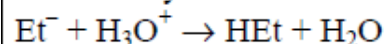
Shows recognition of equimolar HEt and Et^- thus $pK_a = pH$ and discusses how the buffer solution works and links to equations.

A

At point A, there is an equi-molar mixture of HEt and Et^- . On addition of OH^- ions, the acid part of the buffer neutralises the OH^- ions, by donating a proton. The acid reacts with the base:



On addition of H_3O^+ , the ethanoate will accept a proton from the hydronium ion:



Candidate may discuss equilibrium shift.

$pK_a = pH = 4.76$ (accept 4.5 – 4.9)

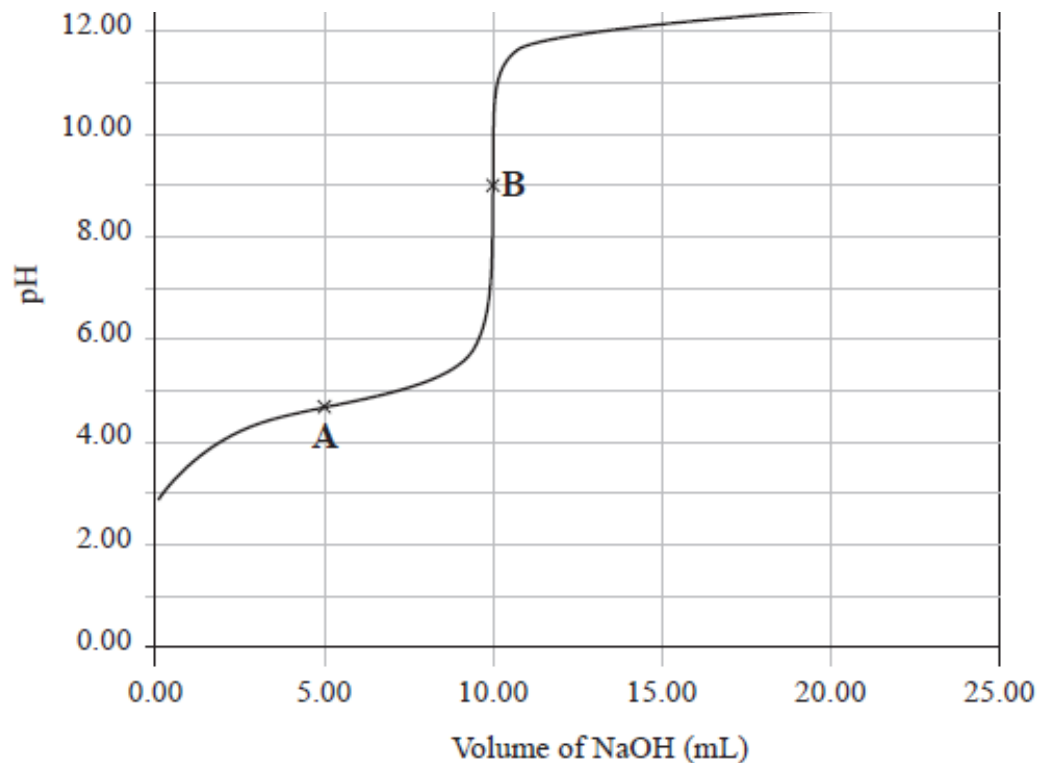
2011 Exam Q4

QUESTION FOUR

- (b) With reference to the point marked **B** on the graph, discuss the species present, and their effect on the pH at the equivalence point.

Include relevant equations in your answer.

No calculations are necessary.



2011 Exam Q4

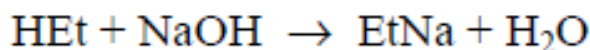
ONE of:

- Recognises that all the HEt has been used up at B.
 - That the pH of equivalence point is greater than 7. (must have clearly indicated that point B is the equivalence point)
- Recognises that none of the original HEt remains as it has all reacted with NaOH
 - OR
 - That the pH of equivalence point is greater than 7 with a valid reason.

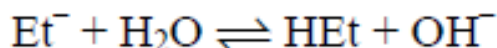
Uses two equations to explain why the pH is above 7. (One equation may be implied in the candidate's written answer.)

B

At the equivalence point all the HEt has been neutralised by NaOH.



The Et^- reacts further to a small extent with water.



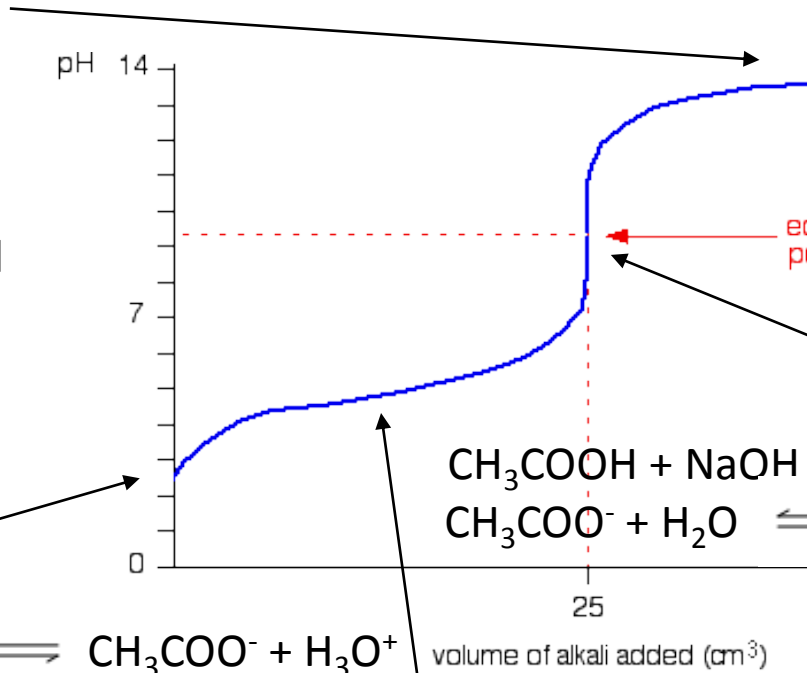
Thus the pH of the equivalence point is above 7 due to presence of OH^- .

Titration curve pH calculations

final pH

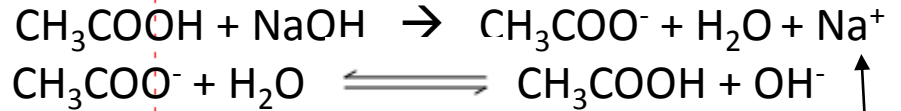
$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

need to recalculate concentrations as volume has changed



need to recalculate concentrations as volume has changed

equivalence point



$$K_b = \frac{[\text{OH}^-][\text{A}^-]}{[\text{A}^-]}$$

initial pH



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

½ equivalence



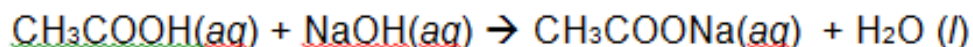
$$\text{pH} = \text{p}K_a \text{ as } [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$$

only CH_3COO^- , H_2O and Na^+ present in solution

2013 Sample Exam Q3 b i

QUESTION THREE

20.00 mL of 0.125 mol L⁻¹ ethanoic acid is titrated with 0.125 mol L⁻¹ sodium hydroxide solution. The equation for this reaction is:



The titration curve for the reaction is given below and the buffer region is marked on the graph.

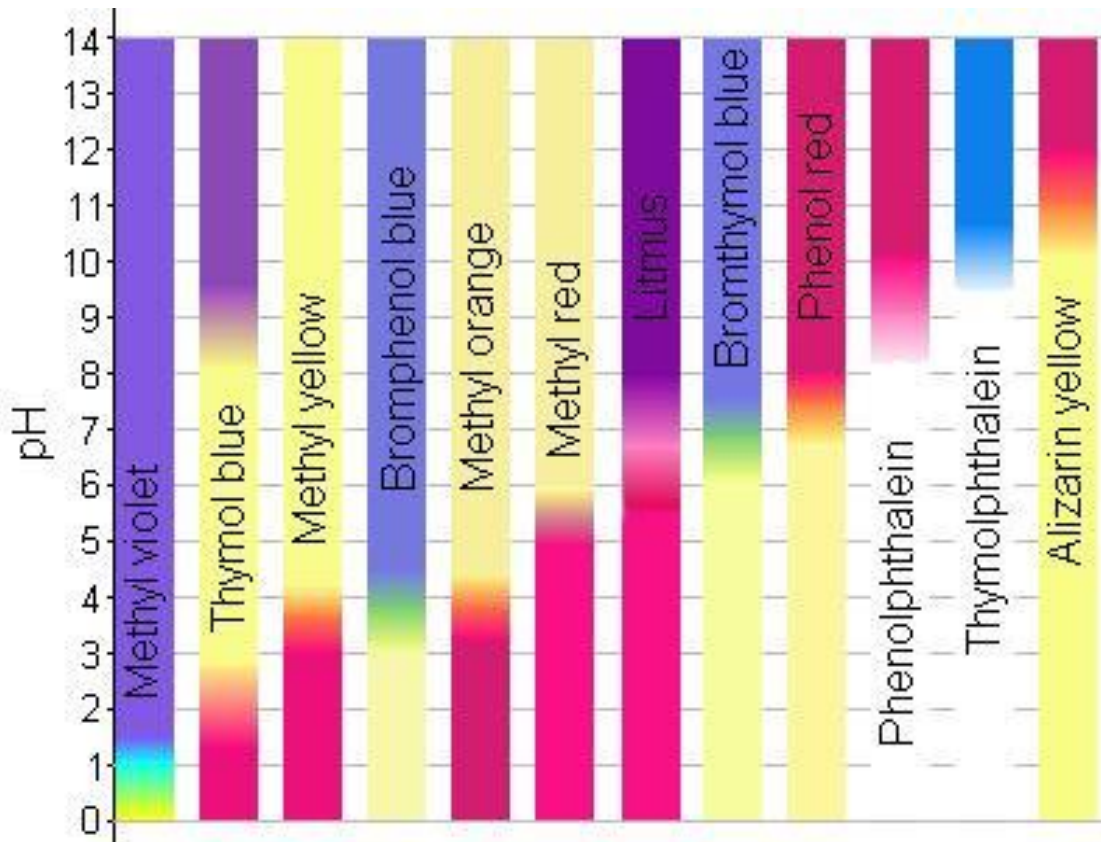


- (b) (i) Show that the pH at the equivalence point for this titration is 8.78.

$$\text{p}K_{\text{a}}(\text{CH}_3\text{COOH}) = 4.76$$

Choosing an indicator

What are we looking for when we choose an indicator for a titration?

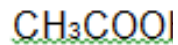


Indicators change colour when the pH of the solution = their pK_a

Choosing an indicator

QUESTION THREE

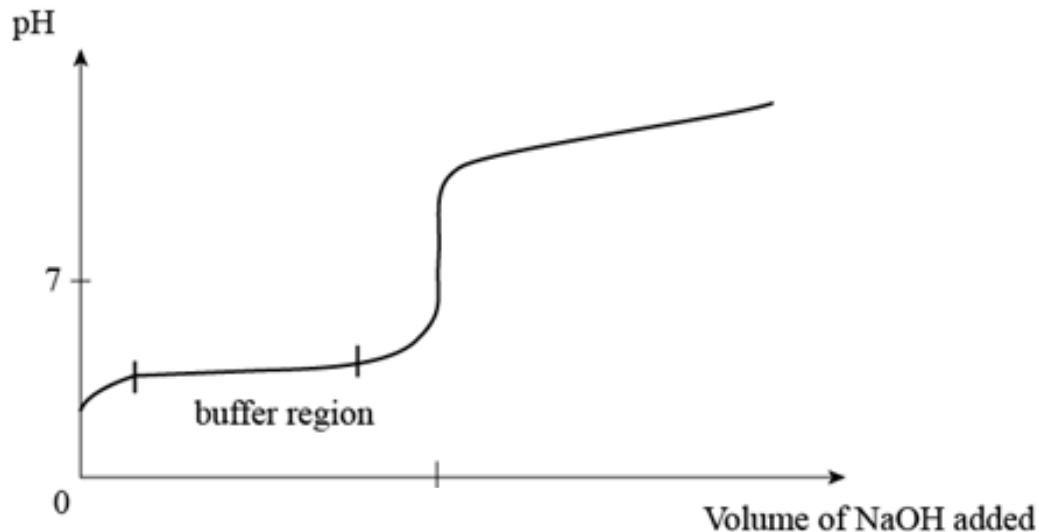
20.00 mL of 0.125 mol L⁻¹ etha
The equation for this reaction i



The titration curve for the react

- (ii) Explain why methyl orange is not a suitable indicator for this titration and why phenolphthalein is a suitable indicator for this titration.

Indicator	<u>pK_a</u>
Methyl orange	3.70
Phenolphthalein	9.60



pH calculations

Sometime you will be asked to calculate the pH at any point on the titration curve. To do this we need to keep in mind the number of moles of each species, volumes and concentrations.

The best way to do this is to use an ICE table.

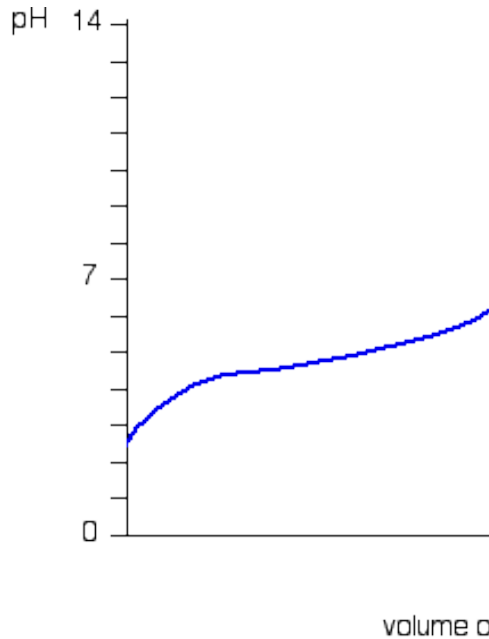
	Species in flask	Species added to flask	Species formed from reaction
I (initial)			
C (change)			
E (end)			

pH calculations

20 mL of 0.095 mol.L⁻¹ CH₃COOH is titrated with 0.110 mol.L⁻¹ NaOH.

$$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

What is the pH when 10 mL of NaOH has been added to the solution?



	Species in flask (CH ₃ COOH)	Species added to flask (NaOH)	Species formed from reaction (CH ₃ COO ⁻)
I (initial)	n = 0.0019 mol	n = 0 mol	n = 0 mol
C (change)	n = I - n(NaOH)	n = 0.0011 mol	n = n(NaOH)
E (end)	n = 0.0008 mol	n = 0 mol	n = 0.0011 mol

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$c = 0.02666 \text{ mol.L}^{-1}$$

$$c = 0.03666 \text{ mol.L}^{-1}$$

pH calculations

QUESTION THREE

20.0 mL of $0.0896 \text{ mol L}^{-1}$ ethanoic acid is titrated with 0.100 mol L^{-1} sodium hydroxide.

$$\text{p}K_{\text{a}} (\text{CH}_3\text{COOH}) = 4.76$$

(ii) Calculate the pH of the titration mixture after 5.00 mL of NaOH has been added.

	CH_3COOH	NaOH	CH_3COO^-
I (initial)	$n = 0.001792 \text{ mol}$	$n = 0 \text{ mol}$	$n = 0 \text{ mol}$
C (change)	$n = I - n(\text{NaOH})$	$n = 0.0005 \text{ mol}$	$n = n(\text{NaOH})$
E (end)	$n = 0.001292 \text{ mol}$	$n = 0 \text{ mol}$	$n = 0.0005 \text{ mol}$

$$c = 0.05168 \text{ mol.L}^{-1}$$

$$c = 0.02 \text{ mol.L}^{-1}$$

$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$