

CHEM 191
Module 1
**Chemical Reactions in Aqueous
Solution**

Lecture 8

Acid/Base Titrations

Chapter 18.3, 29.2 Brown

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Module 1 Lecture 8

Learning Objectives:

- Recognise the characteristic shapes of different types of acid-base titration curves
- Understand the chemical reactions occurring at different points during a titration
- Understand how the acid-base chemistry of an amino acid leads to the characteristic shape of its titration curve.

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Titration

- A titration is an experimental technique that allows the determination of the concentration of a solution of some compound A through reaction with a solution of known concentration of a second compound B.
- Need to know the reaction stoichiometry – mole ratio between A and B
- Used extensively in all of chemistry
 - determination of metal ions in body fluids
 - determination of CO₂ in seawater
 - determination of contaminants in industrial/food products
 - analysis of wastewater



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Acid/base titration curves

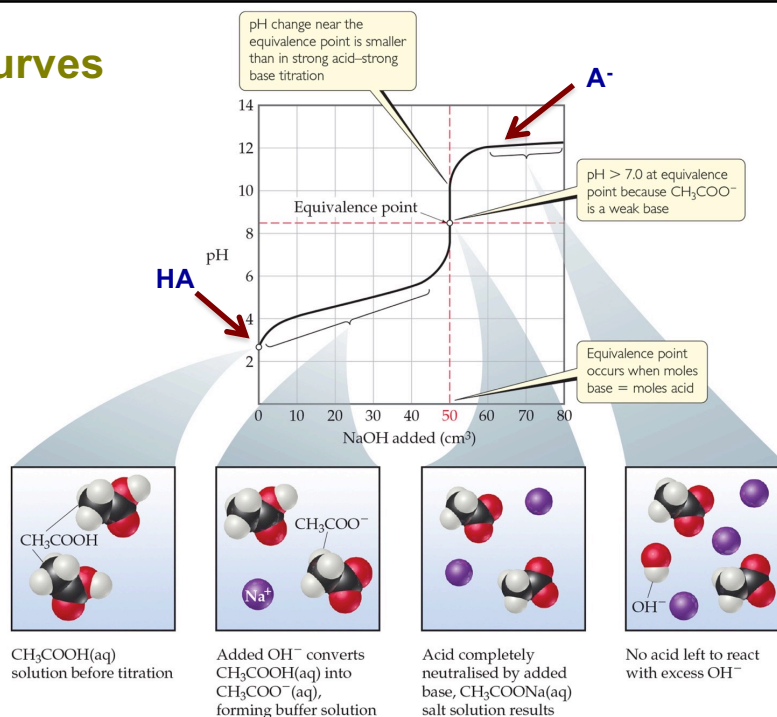
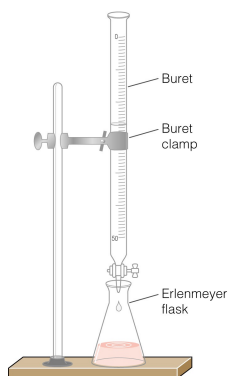
- We stated in the last lecture that a buffer solution could be prepared by adding NaOH(aq) to a solution of CH₃COOH(aq). How does the pH change during this process?
- Can monitor the pH of the weak acid solution as known volumes of NaOH(aq) are added. This process is called an acid/base titration.
- The behaviour of weak and strong acids in titrations with NaOH(aq) are different. Consider each in turn. In each case, however, the essential reaction is



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Acid/base titration curves

50.00 mL of 0.100 mol L⁻¹
CH₃COOH(aq) with
0.100 mol L⁻¹ NaOH(aq)



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The regions

Initial pH:

- Have a 0.100 mol L⁻¹ solution of CH₃COOH. pK_a = 4.74, so pH can be calculated as 2.89 (lecture 6).

The acidic region, $v < v_e$:

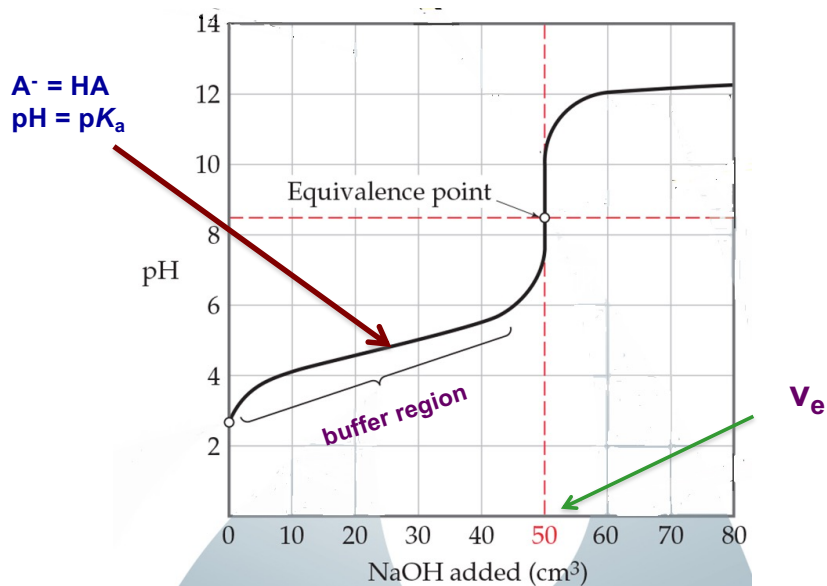
- Reaction occurs between CH₃COOH and NaOH to give CH₃COO⁻. pH controlled by dissociation of CH₃COOH in the presence of increasing amounts of CH₃COO⁻. In this region the solution is a **buffer solution**. When exactly 25 mL of NaOH(aq) has been added, [CH₃COOH] = [CH₃COO⁻], and from the Henderson-Hasselbalch equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

this means that pH = pK_a = 4.74 at this point.

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Buffer region



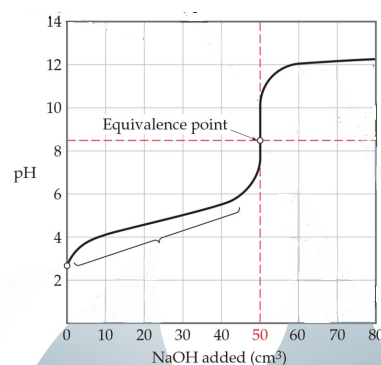
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The regions

The equivalence point; $nNaOH_{added} = nCH_3COOH_{initial}$; $v = v_e$

- The reaction between CH_3COOH and $NaOH$ has gone to completion. Have a solution of CH_3COO^- and Na^+ at this point.
- The pH is basic (8.34). This is **always** the case in such titrations, due to the reaction of the conjugate base with water to give OH^- .

In this case, the reaction is



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pH at the equivalence point

Initially, $n(\text{CH}_3\text{COOH}) = 0.100 \text{ mol L}^{-1} \times 0.050 \text{ L} = 0.005 \text{ mol}$

There will therefore be 0.005 mol of CH_3COO^- formed when the equivalence point is reached.

The total volume of solution at the equivalence point will be

$$50 \text{ mL (initial acid solution)} + 50 \text{ mL (added base solution)} = 100 \text{ mL}$$

Therefore $[\text{CH}_3\text{COO}^-] = 0.005 \text{ mol} / 0.100 \text{ L} = 0.05 \text{ mol L}^{-1}$

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pH at the equivalence point

Remember that, since CH_3COOH and CH_3COO^- are a conjugate acid-base pair,

$$\text{p}K_{\text{a}}(\text{CH}_3\text{COOH}) + \text{p}K_{\text{b}}(\text{CH}_3\text{COO}^-) = 14$$

$$\text{So } \text{p}K_{\text{b}}(\text{CH}_3\text{COO}^-) = 14 - 4.74 = 9.26$$

$$\text{and } K_{\text{b}} = 10^{-9.26} = 5.5 \times 10^{-10}$$

Now, calculate the pH of a weak base solution as in Lecture 6

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pH at the equivalence point

$$K_b = \frac{[\text{CH}_3\text{COOH}]_e [\text{OH}^-]_e}{[\text{CH}_3\text{COO}^-]_e} = \frac{[\text{OH}^-]_e^2}{[\text{CH}_3\text{COO}^-]_{\text{initial}}}$$

$$[\text{OH}^-]_e = \sqrt{K_b \times [\text{CH}_3\text{COO}^-]_{\text{initial}}} = \sqrt{5.5 \times 10^{-10} \times 0.050} = 5.2 \times 10^{-6}$$

$$\text{pOH} = -\log(5.2 \times 10^{-6}) = 5.28$$

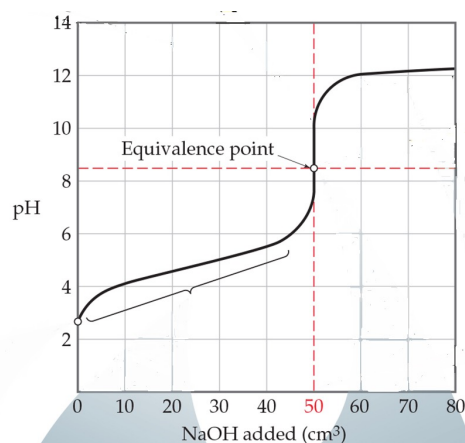
$$\text{pH} = 14 - 5.28 = 8.72$$

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The regions

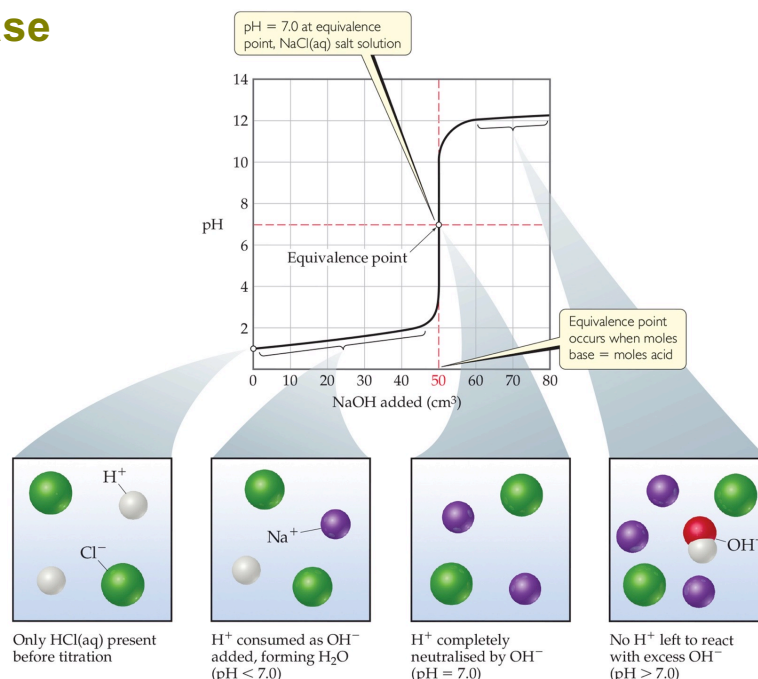
The alkaline region, $v > v_e$:

- The pH is now determined solely by the amount of excess OH^- ions added to the solution after the equivalence point has been reached.



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Strong acid/strong base titration curve

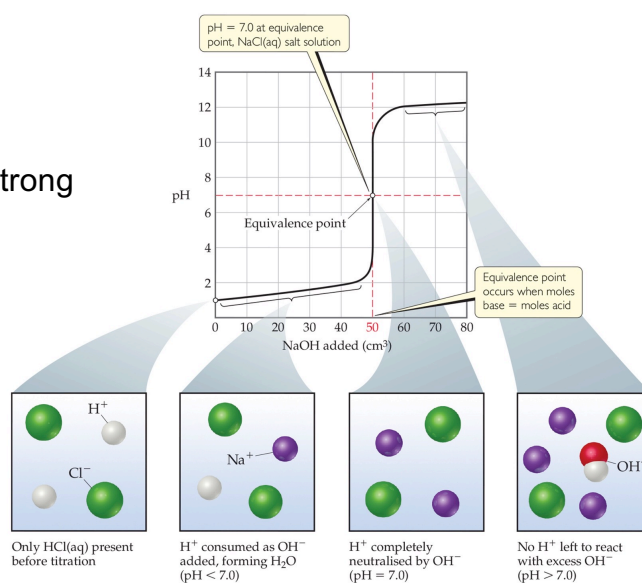


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Strong acid/strong base titration curve

Why is there no buffer region in a strong acid/strong base titration?

The pH must not change on reasonable dilution. This is not a buffer solution.

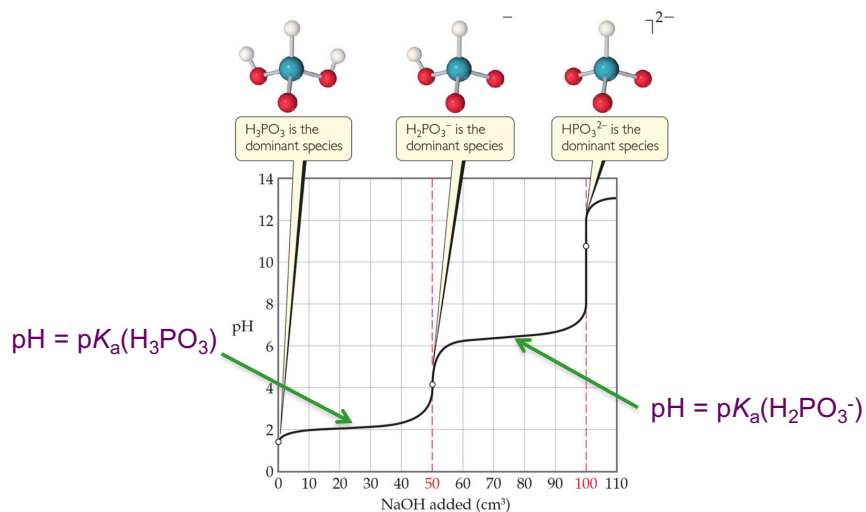


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Diprotic Acids

If the acid has two protons that it can donate, then it will do so **one at a time**.

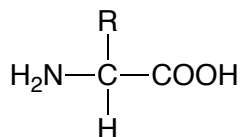
eg H_3PO_3



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Amino acids

- Amino acids are biological molecules which are necessary for life. At least 20 naturally occurring amino acids are known.
- All amino acids have both a **weak acid** and a **weak base** within the same molecule.

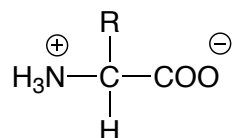


- They differ in the nature of the R group attached to the carbon atom.

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Zwitterions

- Neutral amino acids exist primarily as **zwitterions**. This means they contain both a positive and a negative charge, but the overall molecule is neutral.

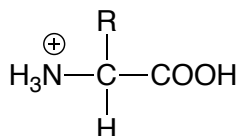


- This can be thought of in terms of the acidic $-\text{COOH}$ proton protonating the basic $-\text{NH}_2$ centre.
- Zwitterions behave like ionic salts rather than organic molecules – they are generally involatile solids, they have high melting points, they are water-soluble and they are insoluble in nonpolar solvents.

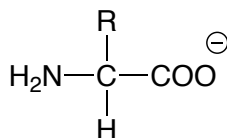
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Zwitterions

- Under **very acidic** conditions, both the $-\text{COOH}$ and the $-\text{NH}_3^+$ groups will be protonated.

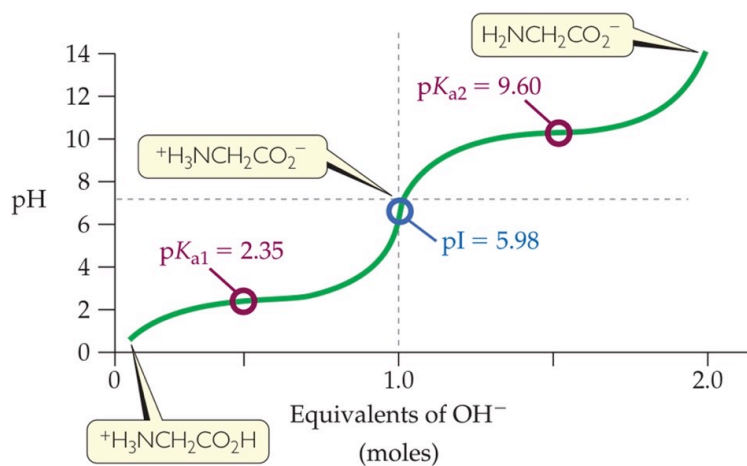


- Under **very basic** conditions, both the $-\text{COO}^-$ and the $-\text{NH}_2$ groups will be deprotonated.



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Titration curve for glycine



◀ **FIGURE 29.18** Titration of glycine with aqueous NaOH solution. $\text{pK}_{\text{a}1}$ relates to the pK_{a} of the carboxylic acid, while $\text{pK}_{\text{a}2}$ relates to the pK_{a} of the ammonium ion.

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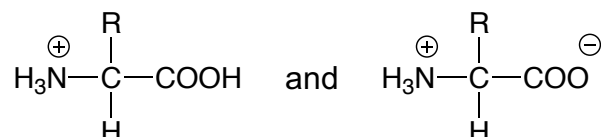
The regions

Initial pH

- More acidic than a normal weak acid as it is easier to lose a proton from a positively-charged ion than from a neutral molecule.

Region where less than one mole of OH⁻ has been added

- In this region, the more acidic $-\text{COOH}$ proton reacts (is being titrated), hence there is a mixture of both



in this region. When half an equivalent of OH⁻ has been added, the $\text{pH} = \text{pK}_{\text{a}}$ ($\text{pK}_{\text{a}1} = 2.35$)

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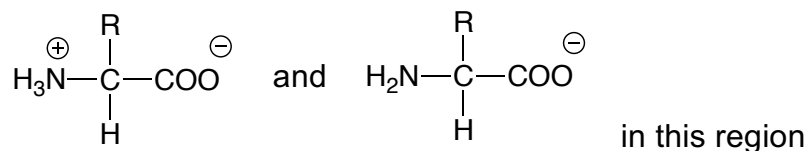
The regions

One mole of OH^- has been added.

- At this point, the $\text{pH} = \text{pI}$ (6.06) and the solution contains the zwitterion essentially exclusively. pI is called the **isoelectric point** and is the point at which most of the molecules in the solution have a net charge of zero.

Region where more than one mole of OH^- has been added

- In this region, the less acidic $-\text{NH}_3^+$ proton now reacts (is titrated), hence there is a mixture of both

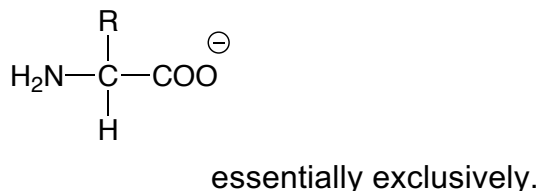


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The regions

Region where more than one mole of OH^- has been added

- When 1.5 equivalents of OH^- have been added, the $\text{pH} = \text{pK}_a$ ($\text{pK}_{a2} = 9.78$)
- The titration is complete when two equivalents of OH^- have been added. At this point, the solution contains



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*** Homework ***

Brown (15th)

Problems 17.51, 17.70, 17.74, 17.100, 17.103

some problems require K_a from Appendix D, Page 1515

Answers on Blackboard