UNIT 04

Acid

Base

ACID-BASE CHEMISTRY

Student Learning Outcomes (SLOs)

- State that pH $=-\log[H^+_{aq}]$ and $[H^+]$ = 10(to the power)-pH.
- State that change of one pH unit represents a 10 -fold change in the hydrogen ion concentration $[H^+]$.
- Use the ionic product constant, $K_w=[H^+][OH^-]=10^{-14}$ at 298 k to solve problems.
- Sketch the pH titration curves of titrations using combinations of strong and weak acids with strong and weak alkalis.

Acid-base chemistry is a fundamental aspect of chemical science. It describes the concepts of acids and bases as well as their interactions in aqueous solutions. Acid-base reactions are essential in various chemical processes, from biological systems to industrial applications, and are often visualized through pH of solutions.

4.1 The pH

The pH scale was originally introduced by the Danish biochemist S.P.L. Sorenson in 1909 and used the symbol of pH. The letter p is derived from the German word potenz meaning power or exponent of, in this case, 10. In 1909, S.P.L. Sorenson published a paper in Biochem Z in which he discussed the effect of H^+ ions on the activity of enzymes. In the paper, he invented the term pH (purported to mean pond us hydrogen ii in Latin) to describe this effect and defined it as the $-\log[H^+]$. In 1924, Sorenson realized that the pH of a solution is a function of the "activity" of the H^+ ion and not the concentration. Thus, he published a second paper on the subject. A better definition would be.

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

where a{H^+} denotes the activity(an effective concentration) of the H^+ ions. The activity of an ion is a function of many variables of which concentration is one. Concentration is abbreviated by using square brackets, e.g., [H_3O^+]is the concentration of hydronium ion in solution. Activity is abbreviated by using "a" with curly brackets.

The concentration of Hydrogen ions in aqueous solution can be expressed in terms of the pH scale. The pH of a solution is the logarithm to base 10 of the reciprocals of the numerical value of the hydrogen ion concentration.

$$pH = \log \frac{1}{[H_3O^+]}$$

$$= -\log [H_3O^+] \qquad \text{OR} \qquad = -\log [H^+]$$

pH values of bases

The concentration of hydroxide ions in a solution can be expressed in terms of pOH. This is given by:

$$pOH = -\log[OH^-]$$

It is possible to write an expression relating pH and pOH as $pK_w = pH + pOH$

At 25°C: $pH + pOH = 14$

4.2 The pH Scale

The pH scale is a numerical scale that shows acidic or alkaline strength of solution. The values on the pH scale go from 0-14 (extremely acidic substances have values of below 1). All acids have pH values less than 7. The lower the pH, the more acidic the solution is. The higher the pH, the more alkaline the solution is.

pH is an indication of concentration of H^+. For example, at a pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar. Typically, the concentrations of H^+ in water in most solutions fall between a range of 1 M (pH=0) and 10^{-14} M (pH=14). Figure 1.1 depicts the pH scale with common solutions and where they are on the scale.

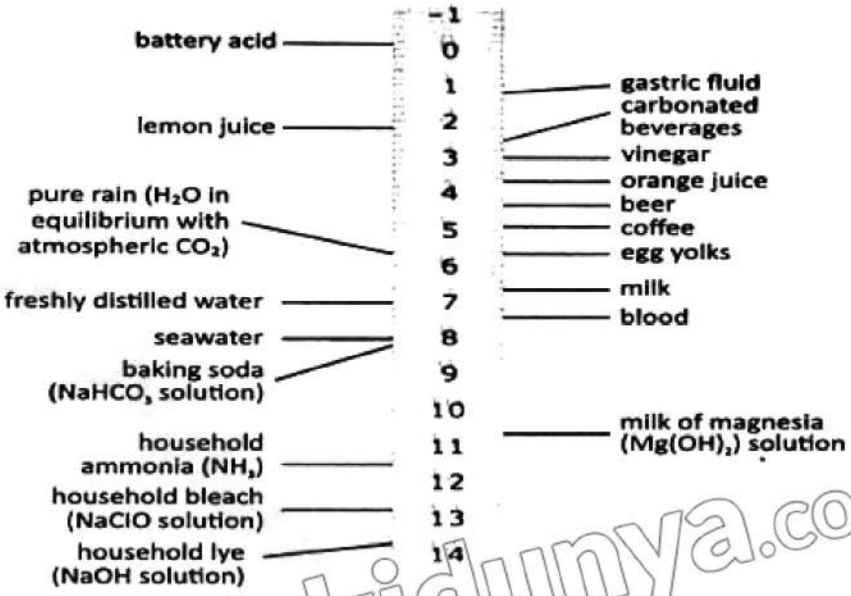


Fig 4.1: Solutions and the placement of them on pH scale

Example: 4.1

Find the pH of a solution of 0.002 M of HCl.

Solution

The equation for pH is -log $[H^+]$

$$[H^+] = 2.0\times 10^{-3}M$$

$$pH = -\log[2.0\times 10^{-3}] = 2.70$$

Example: 4.2

If moist soil has a pH of 7.84, what is the H^+ concentration of the soil solution?

Solution

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

$$7.84 = -\log[H^+]$$

$$[H^+] = 1.45\times 10^{-8}M$$

Hint

Place −7.84 in your calculator and take the antilog (often inverse log or 10^x) = 1.45×10^{-8}M

Concept Assessment Exercise 4.1

1. What is the pH of a solution of 2g pure H_3PO_4 per dm^3 of solution?
2. Calculate the concentration of hydrogen ion(H^+) in a solution of sulphuric acid having pH of 1.5.

4.3 Ionic Product of Water and Calculation of pH and pOH

Recall that the product of the concentration of H^+ and OH^- ions in pure water at room temperature (298 k).

$$K_w = [H_3O^+][OH^-]$$

Where K_w is the ionic product or dissociation constant of water.

Unit of K_w is mol^2dm^{-6}.

In pure water, the concentration of H^+ and OH^- ions are equal i.e 1.0×10^{-7}. So, value of K_w at room temperature is 1.0×10^{-14}.

$$pK_w = -\log K_w$$

As value of K_w is 1.0×10^{-14} so $\quad pK_w = -\log 1.0 \times 10^{-14} = 14$

The ionic product of water is related to the dissociation constants pKa and pKb of an acid and its conjugate base respectively.

$$pK_a + pK_b = pK_w = 14 \text{ (at 298 K)}$$

OR

$$pH + pOH = pK_w = 14 \text{ (at 298 K)}$$

Thus, if the pK_a value of an acid is known, the pK_b value of its conjugate base can be found.

Example: 4.3

If the concentration of NaOH in a solution is 2.5×10^{-4} M, what is the concentration of H_3O^+ ion at 25 °C?

Solution

Data:

$$[OH^-] = 2.5 \times 10^{-4}\ M$$

We can assume room temperature, so

$$1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

to find the concentration of H_3O^+, solve for the $[H_3O^+]$.

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-4}}$$

$$= 4.0 \times 10^{-11} M$$

Example: 4.4

Calculate the pH value of 0.001 $moldm^{-3}$ solution of NaOH at 25°C.

Solution

Data:

$$[OH^-] = 0.001\ moldm^3$$

$$\text{As } K_w = [H_3O^+][OH^-]$$

value of K_w at 298 k is $1.0 \times 10^{-14} mol^2dm^{-6}$

$$1.0 \times 10^{-14} = [H_3O^+][0.001]$$

$$[H_3O^+] = \frac{1.0\times10^{-14}}{0.001} = 1.0 \times 10^{-11} \text{mol dm}^{-3}$$

$$pH = -\log[H_3O^+]$$

$$pH = -\log[1 \times 10^{-11}] = 11$$

Example: 4.5

Calculate the pH of $5.0\times 10^{-5} M$ solution of sodium hydroxide.

Solution

The equation for pOH is

$$pOH = -\log [OH^-]$$

$$[OH^-] = 5.0\times 10^{-5} M$$

$$pOH = -\log [5.0\times 10^{-5}] = 4.30$$

$$14 = PH + pOH$$

$$pH = 14 - pOH$$

$$pH = 14 - 4.30 = 9.70$$

Concept Assessment Exercise 4.2

1. The concentration of hydroxide ion in given solution of slaked lime ($Ca(OH)_2$) is 0.001M. Calculate the concentartion of hydrogen ion in it.
2. An aqueous solution contain 2×10^{-3} M of hydrogen ions (H^+). Calculate pOH of this solution.

4.4 pH Titration Curves

In order to determine the concentration of the unknown solution, the technique of titration is used in neutralisation reactions between acids and alkalis. It involves adding a titrant of known concentration from a burette into a conical flask containing the analyte of unknown concentration. An indicator is added which will change colour at the endpoint of the titration. The endpoint is the point at which equal number of moles of titrant and analyte reacts with each other. The equivalence point is halfway the vertical region of the curve.

Equivalence point → moles of alkali = moles of acid

This is also known as the equivalence point, and this is the point at which neutralisation takes place. There are different types of titration curves depending on the strength of acid or alkalis used.

a. Strong acid and strong alkali pH titration curve

In this case hydrochloric acid is taken in the conical flask. Initially, there are only H^+ ions present in the conical flask (initial pH about 1-2). As the volume of strong alkali (NaOH) added from the burette increases, the pH of the HCl solution slightly increases too as more and more H^+ ions react with the OH^- ions from the NaOH to form water. The change in pH is not that much until the volume added gets close to the equivalence point. The pH surges upwards very steeply. The equivalence point is the point at which all H^+ ions have been neutralised (therefore pH is 7 at equivalence point). Adding more NaOH will increase the pH as now there is an excess in OH^- ions (final pH about 13-14). Figure 4.2 represents the titration curve 1.0 mol dm^{-3} HCl with NaOH. Hence 25 cm^3 of titrant (NaOH) is used to neutralise 25 cm^3 of HCl.

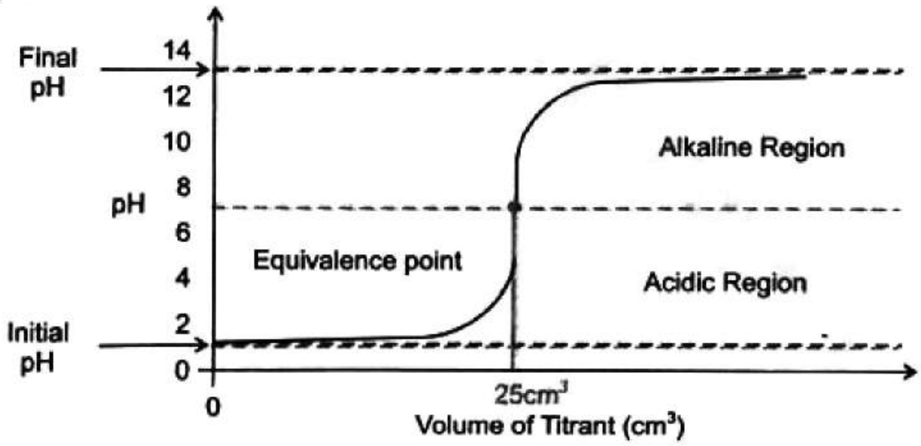


Fig 4.2: The diagram shows a pH titration curve of 1.0 mol dm^{-3} HCl (25 cm^3) with NaOH

The pH titration curve for HCl added to a NaOH has the same shape. The initial pH and final pH are the other way around. The equivalence point is still 7. Following figure represents a pH titration curve when HCl is added from a burette into the conical flask containing aqueous solution of NaOH.

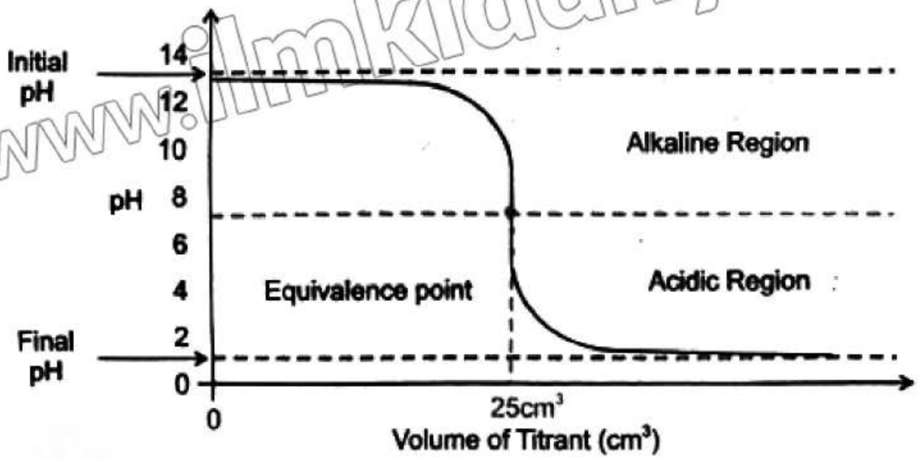


Fig 4.3: The diagram shows a pH titration curve of 1.0 mol dm^{-3} NaOH (25 cm^3) with HCl

b. Strong acid and weak alkali pH titration curve

Initially, there are only H^+ ions present in the conical flask (initial pH about 1-2). As the volume of weak alkali (NH_3) added form the burette increases, the pH of the analyte solution slightly increases too as more and more H^+ ions react with the NH_3. The change in pH is not that much until the volume added gets close to the equivalence point.

The equivalence point is not neutral, but the solution is still acidic (pH about 5.5). This is because all H^+ have reacted with NH_3 to form NH_4^+ which is a relatively strong acid, causing the solution to be acidic. As more of the NH_3 is added, the pH increases to above 7 but below that of a strong alkali as NH_3 is a weak alkali. Following figure represents the pH titration curve of this reaction.

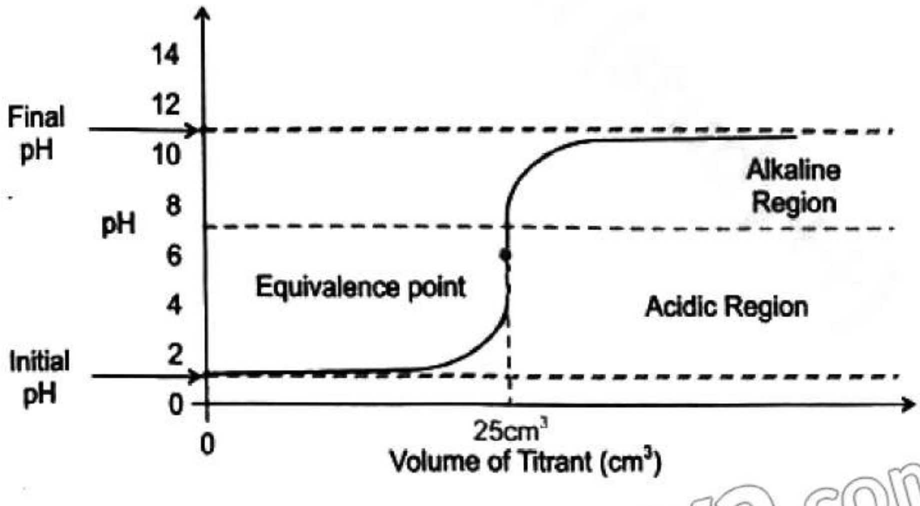


Fig 4.4: The diagram shows a pH titration curve of 1.0 mol dm^{-3} HCl (25 cm^3) with NH$_3$

The pH titration curve for strong acid added to a weak alkali has the same shape. The initial and final pH are the other way around. The equivalence point is still about 5.5.

c. Weak acid and strong alkali pH titration curve

Initially ethanoic acid (CH_3COOH), having initial pH of about 2-3 is taken in the conical flask. As the volume of strong alkali (NaOH) added from the burette increases, the pH of the ethanoic acid solution slightly increases too as more and more H^+ ions react with the OH^- from the NaOH to form water. The change in pH is not that much until the volume added gets close to the equivalence point. The pH surges upwards very steeply. The equivalence point is not neutral, but the solution is slightly basic (pH about 9). This is because all H^+ in CH_3COOH have reacted with OH^- however, CH_3COO^- is a relatively strong base, causing the solution to be basic. As more of the NaOH is added, the pH increases to about 13-14. Following figure represents the pH titration curve of this reaction.

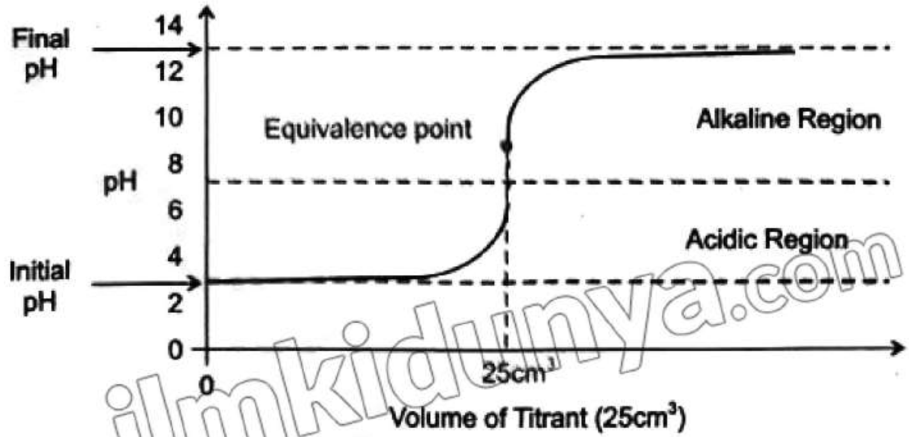


Fig 4.5: The diagram shows a pH titration curve of a weak acid with a strong base

The pH titration curve for weak acid added to a strong alkali has the same shape. The initial and final pH are the other way around. The equivalence point is still about 9.

d. Weak acid and weak alkali pH titration curve

Initially there are only H^+ ions present in solution from the dissociation of the weak acid (CH_3COOH, ethanoic acid) (initial pH about 2-3). In these pH titration curves, there is no vertical region. There is a 'point of inflexion' at the equivalence point. The curve does not provide much other information.

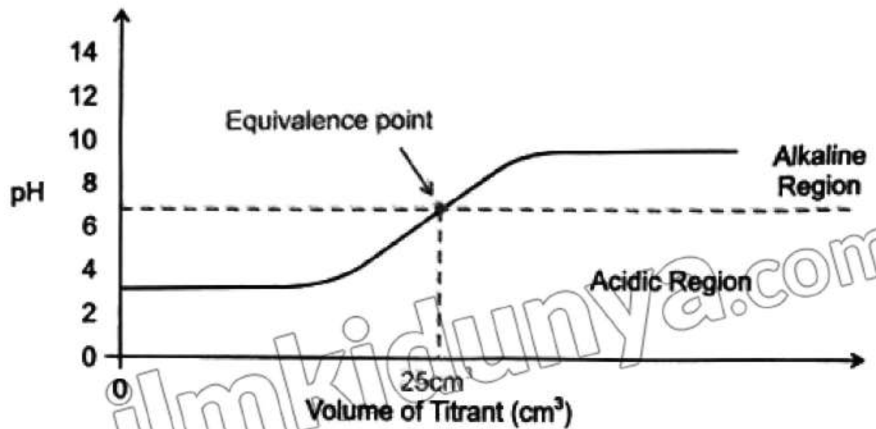


Fig 4.6: The diagram shows a pH titration curve of 1.0 mol dm^{-3} weak acid (25 cm^3) with weak alkali

Concept Assessment Exercise 4.3

1. In a titration it is found that 25 cm^3 of 0.1 M solution of NaOH is neutralised with 19 cm^3 of HCl of unknown concentration. Calculate concentration of a given HCl solution.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

2. Draw the pH titration curve when 20 cm^3 of HCl from the burette is added to 20 cm^3 of aqueous solution of ammonia present in the conical flask.

KEY POINTS

- The pH of a solution is the logarithm to base 10 of the reciprocals of the numerical value of the hydrogen ion concentration.
- pH is used to find the relative strength of acidity and alkalinity of the solution.
- The pH scale ranges from 0—14. As the pH of a given solution increases basic character increases and vice versa
- The ionic product of water is the product of the concentration of hydrogen ion and hydroxide ion.
- Value of Kw at 25 °C is 1×10^{-14} .
- Titration is a technique used in neutralisation reactions between acids and alkalis to determine the concentration of the unknown solution.
- Equivalence point is the point at which indicator changes its colour and the point at which neutralisation takes place. $H^+ + OH^- \rightarrow H_2O$

References for additional information.

- George M. Bodner and harry L. Pardue, Chemistry an Experimantal Science.
- Disha Expert- Disha NCERT Xtract errorless objective Chemistry
- Chemistry for A level by Francesca

EXERCISE

1. Multiple Choice Questions (MCQs)

i. The value of the ionic product of water

a) depends on volume of water
b) depends on temperature
c) changes by adding acid or alkali
d) always remains constant

ii. A base when dissolved in water yields a solution with a hydroxyl ion concentration of 0.05 mol dm^{-3}. The solution is

a) Basic
b) Acidic
c) Neutral
d) either b or c

iii. pH scale was introduced by

a) Arrhenius | b) Sorensen
d) Lewis | d) Lowry

iv. pH of solution is defined by expression

a) $\log[H^+]$ | b) $\log\left[\frac{1}{H^+}\right]$
c) $\frac{1}{log[H^+]}$ | d) $\frac{1}{-log[H^+]}$

v. The pH of a 10^{-3} M HCl solution at 25°C if it is diluted 1000 times, will be

a) 3 | b) zero
c) 5.98 | d) 6.02

vi. How many dm^3 of water must be added to 1 dm^3 an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?

a) 0.1 dm^3 | b) 0.9 dm^3
c) 2.0 dm^3 | d) 9.0 dm^3

vii. What is the approximate pH of a 1×10^{-3} M NaOH solution?

a) 3 | b) 11
c) 7 | d) 1×10^{-11}

viii. Calculate the pOH of a solution at 25°C that contains1×10^{-10} M of hydronium ions, i.e. H_3O^+

a) 4.0 | b) 9.0
c) 1.0 | d) 7.0

ix. The pH value of a 10 M solution of HCl is

a) less than 0 | b) equal to 0
c) equal to 1 | d) equal to 2

x. Which of the following has the highest pH?

a) $\frac{M}{4}$ KOH | b) $\frac{M}{4}$ $NaOH$
c) $\frac{M}{4}$ NH_4OH | d) $\frac{M}{4}$ $Ca(OH)_2$

xi. Which of the following statements are correct?

(i) $Kw = [H^+][OH^-] = 10^{-14}\ mol^2dm^{-6}$ at 298K

(ii) At 298K $[H^+] = [OH^-] = 10^{-7}$

(iii) Kw does not depend upon temperature

(iv) Molarity of pure water = 55.55 M

a) (i), (ii) and (iii) | b) (i), (ii) and (iv)
c) (i) and (iv) | d) (ii) and (iii)

2. Short Answer Questions

i. Calculate H^+ ion concentration of a solution prepared by dissolving 4 g of NaOH (Atomic weight of Na = 23 amu) in1000 cm^3 of solution?

ii. Calulate the pH of 0.005 molar solution of H_2SO_4

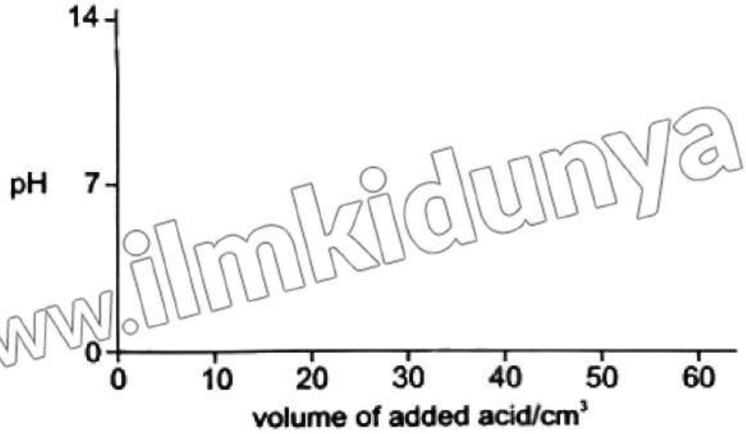
iii. Calculate the pH of the following compounds

(i) 10^{-4} M KOH (ii) 10^{-10} M HCl (iii) 10^{-10} M KOH (iv) 10^{-4} M HCl

iv. 100 cm^3 of 0.04 M HCl aqueous solution is mixed with 100 cm^3 of 0.02 M NaOH solution. Calculate the pH of the resulting solution.

v. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?

vi. A 20.0 cm^3 sample of 0.200 mol dm^{-3} $NH_3(aq)$ was titrated with 0.100 mol dm^{-3} HCl. On the following axes, sketch how the pH changes during this titration. Mark clearly where the end point occurs.



3. Long Answer Questions

i. Explain the concept of pH and its significance in acid-base chemistry. How does the pH scale relate to the concentration of hydrogen ions in a solution?

ii. Compare and contrast the titration curves for a strong acid with a strong base, a weak acid with a strong base, a strong acid with a weak base, and a weak acid with a weak base.

iii. A 50 cm^3 solution of 0.1 M acetic acid is titrated with 0.1 M sodium hydroxide. The K_a of acetic acid at 25 °C is 1.8×10^{-5} mol dm^{-3}. Calculate the pH of the solution at the equivalence point and explain the shape of the titration curve for this reaction.