



St Mary's Anglican Girls' School

The Chemistry of Acids and Bases

3AB 2010

**Acids and Bases in aqueous solutions**

- Apply an understanding of the concept of an electrolyte to explain the self-ionisation of water
- Explain and apply the Arrhenius and Bronsted-Lowry models to describe acids and bases
- Apply the relationship between  $K_w$  and temperature to explain the pH value of a neutral solution at different temperatures
- Apply the relationship  $\text{pH} = -\log [\text{H}^+(\text{aq})]$  to calculate the pH of:
  - Strong acid solutions
  - Strong base solutions
  - The resulting solution when strong acid-base solutions are mixed
- Apply the Bronsted-Lowry model to the hydrolysis of salts derived from monoprotic and polyprotic acids, and bases
- Describe and explain the conjugate nature of buffer solutions

Explain using Le Chatelier's Principle how buffers respond to the addition of  $\text{H}^+$  and  $\text{OH}^-$   
Explain qualitatively the concept of buffering capacity

**Chemical Reactions****Reactions, equations and stoichiometry**

- Describe, write equations for and interpret observations for the following reaction types:
  - Neutralisation
  - Hydrolysis of salts of weak acids and weak bases
- Perform volumetric analysis using either acid-base or redox context, and:
  - Give a description of procedures used and methods for minimising experimental error
  - Describe and explain characteristics of primary standards and standard solutions
  - Demonstrate an understanding of end point and equivalence point to the selection of an appropriate indicator in an acid-base titration
  - Explain the choice of indicators (in acid-base only) or use self-indicators (redox)
- Perform calculations based on acid-base

- Determine by calculation the empirical and molecular formulae and the structure of a compound from the analysis of combustion or other data

## Acids and Bases Revision

### Reactions of acids

Acids may be neutralised by reacting with:

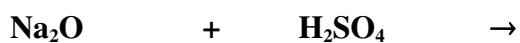
Metal oxides



Predict

Ionic equation

Observation



Predict

Ionic equation

Observation



Metal hydroxides



Predict

Ionic equation

Observation

**And generally react with carbonates**

Equation

Predict

Ionic equation

Observation

**and hydrogencarbonates**

Equation

Predict

Ionic equation

Observation

### **Acids and Bases**

1.
  - a) Why do aqueous solutions of all acids conduct electricity?
  
  
  
  
  
  
  
  
  
  
  - b) Why does a solution of an acid conduct electricity better than a more dilute solution of the same acid?
  
  
  
  
  
  
  
  
  
  
  - c) Why does a solution of a strong acid conduct better than a solution of a weak acid of the same concentration?
  
2. Acetic acid and ammonia solutions each have relatively low conductivity though greater than that of water. If the two solutions are mixed the conductivity increases sharply.
  - a) Explain, with the aid of an equation, why acetic acid solution is a poor conductor of electricity.

- b) Explain, with the aid of an equation, why ammonia is a poor conductor of electricity.
- c) Explain, with the aid of equations, why the conductivity increases when the two poorly conducting solutions are mixed.

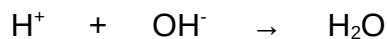
## Definitions and theories of acidity and basicity

### Arrhenius (limited application)

Acids contain free  $\text{H}^+$  ions in aqueous solution

Bases contain free  $\text{OH}^-$  ions in aqueous solution

Neutralisation involves the reaction



### Bronsted-Lowry (most applicable)

Acids donate protons

Bases accept protons

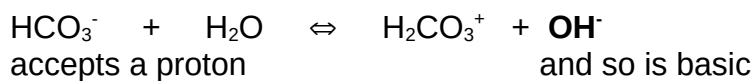
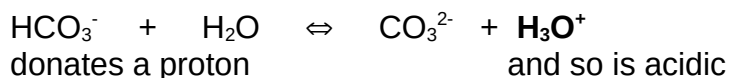
Acids and bases form conjugate pairs in solution systems



$\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  are a conjugate pair

$\text{OH}^-$  and  $\text{H}_2\text{O}$  are also a conjugate pair

A substance may be an acid in one reaction but a base in another (may be amphoteric)

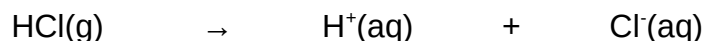


- How can we tell which reaction occurs to the greater extent?



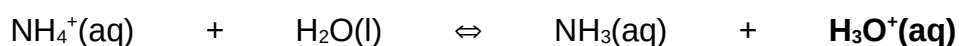
## Acids and bases

**Acids** are substances that produce hydrogen ions in aqueous solution. This may be achieved by ionisation of molecules

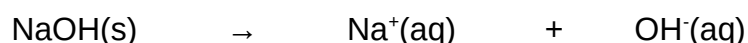


Sometimes it is useful to think of the hydrogen ion being attached to a water molecule forming the **hydronium ion**  $\text{H}_3\text{O}^+$ .

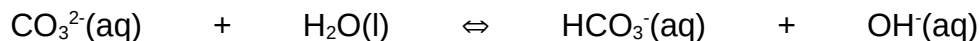
Substances may be acidic if they react with water to produce this ion.



**Bases** are substances that produce hydroxide ions in aqueous solution. This may be achieved by the dissociation of ions from an ionic hydroxide.

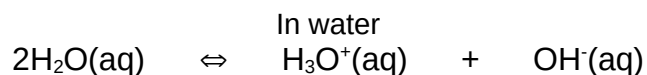


Sometimes ionisation occurs by reaction of a substance with water.



Such reactions with water are called **hydrolysis reactions** and account for the acid-base nature of some salts.

Review exercise 7.1 questions: 2, 4, 5, 6, 7, 9a



$$\text{and } K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$\text{In neutral solutions } [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7}$$

pH is defined as  $-\log_{10} [\text{H}_3\text{O}^+]$

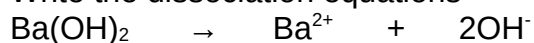
For acidic solutions  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$   
and the pH is less than 7

For basic solutions  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$   
and the pH is greater than 7

Example

Calculate the pH of a sample of  $1 \times 10^{-2} \text{ mole L}^{-1} \text{ Ba}(\text{OH})_2$  solution.

Write the dissociation equations



Determine the concentration of the  $\text{OH}^-$  ion



Determine the  $[\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{\text{OH}^-}$$

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

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

$$\text{pH} =$$

### pH and temperature

In neutral solutions  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ , that is why they are neutral.  
The pH is only 7 at  $25^\circ\text{C}$

**pH calculations**

1. Determine the pH of
  - a) 0.100M nitric acid
  - b) 0.001M sodium chloride
  - c) 0.214 sulfuric acid
  - d) 0.00125M KOH
2. If 25mL of 0.100 M HCl is diluted to 250mL what is the pH of the resulting solution?
3. If 25mL of HCl of pH = 2 is added to 50mL of HCl of pH = 4, what is the pH of the final solution?
4. If 125mL of 2.00 M KOH is added to 125mL of 0.800 M HCl what is the pH of the final mixture?
5. Three solutions X, Y and Z have the following composition  
X is 6.40g of NaOH in 200mL of solution  
Y is 1120mL of HCl gas (at STP) in 500mL of solution  
Z is 0.100 M sulfuric acid

Calculate the pH of a mixture of X and Y

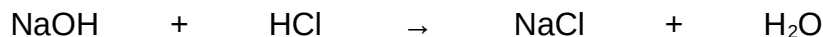
Calculate the volume of Z that would be needed to neutralise the X/Y mixture.

Review exercise 7.3 questions:1, 2, 3, 4, 5

STAWA Set 16 page 123

### Acid-base properties of salts

A salt is a compound made by the reaction between an acid and a base. We have been accustomed to thinking of salts being neutral ( $\text{pH} = 7$ ) as they are produced by neutralisation reactions.



Similarly for sodium sulfate, potassium nitrate etc.

**For many salts this is not the case.**

The salts produced by the neutralisation of strong acids by strong bases are neutral.

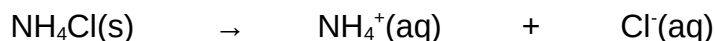
**The salts produced by the neutralisation of a strong species by a weak one are not neutral.**

Ions originating from weak bases and acids react with water in aqueous solutions to form acidic and basic salts.

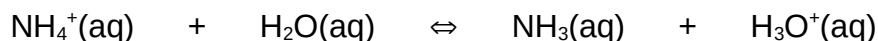
Experiments show

**ammonium salts are acidic**

ammonium chloride is a salt. As a salt it is a strong electrolyte (it totally dissociates in aqueous solution).



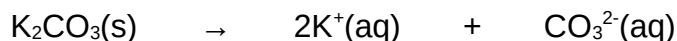
In solution, hydrolysis of the weak species occurs.



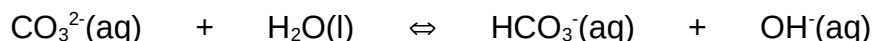
This causes the ammonium chloride solution to be acidic.  
(The chloride ion does not hydrolyse.)

**carbonates are basic**

Potassium carbonate is a salt. As a salt it is a strong electrolyte (it totally dissociates in aqueous solution).



In solution, hydrolysis of the weak species occurs.



This causes the potassium carbonate to be basic.  
(The potassium ion does not hydrolyse.)

**Acid-base properties of salts of weak diprotic acids**

Multiprotic acids like sulphuric, phosphoric can produce more than one negative ion when they lose a proton. -  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and so on. It is not possible to assign a general rule about whether these ions donate or accept protons. We rely on pH information to recognise which process has occurred.

$\text{H}_2\text{PO}_4^-$  - acidic

$\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  are basic.

Equations to explain this are:

Review exercise 7.2 questions: 1, 3, 4

STAWA Experiment 10 page 93

STAWA Set 13 hydrolysis page 115

### Acids and Bases

- Which one of the following compounds is a diprotic acid?
  - sulfuric acid
  - ethanoic acid
  - nitric acid
  - phosphoric acid
- Sodium carbonate solution is
  - basic because carbonate hydrolyses to give  $\text{HCO}_3^-$  and  $\text{OH}^-$
  - basic because sodium hydrolyses to form  $\text{OH}^-$
  - neutral because it is formed by the neutralisation of a strong acid by a strong base.
  - acidic because sodium ions hydrolyse to form  $\text{H}_3\text{O}^+$
- The pH of  $0.001 \text{ mol L}^{-1}$  barium hydroxide is
  - 2
  - 2.7
  - 12
  - 12.7
  - 11.3
- For each of the following equations identify the acid-base conjugate pairs.
  - $\text{OH}^- + \text{CH}_3\text{COOH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3\text{COO}^-$
  - $\text{HCO}_3^- + \text{Cl}^- \rightleftharpoons \text{CO}_3^{2-} + \text{HCl}$
  - $\text{HI} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{I}^-$
- Write an equation for the hydrolysis that occurs when each of the following ions dissolves in water.
  - $\text{CO}_3^{2-}$
  - $\text{ClO}^-$
  - $\text{NH}_4^+$
  - $\text{CH}_3\text{COO}^-$
- Classify each of the following as acidic, basic or neutral.
 

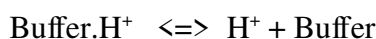
$\text{NaNO}_3$ ,     $\text{KF}$ ,     $\text{Al}_2(\text{SO}_4)_3$ ,     $\text{NaOCl}$ ,     $\text{KHSO}_4$

## The chemistry of buffer solutions

[http://www.science.smith.edu/departments/Biochem/Biochem\\_353/Buffer\\_Theory.html](http://www.science.smith.edu/departments/Biochem/Biochem_353/Buffer_Theory.html)

### Buffer Theory

Most biological systems will function only within a quite narrow range of conditions, and their activity can vary widely within that range. The acidity of the environment is an important parameter. To prevent the pH of a solution from changing, compounds can be added to a solution that "buffer" or minimize such changes. A compound will act as pH buffer if it limits changes in pH by binding protons when the pH of the solution decreases and releasing bound protons when the pH increases.



<http://www.chemistry.wustl.edu/~edudev/LabTutorials/Buffer/Buffer.html>

### How Buffers Work: A Quantitative View

The kidneys and the lungs work together to help maintain a blood pH of 7.4 by affecting the components of the buffers in the blood. Therefore, to understand how these organs help control the pH of the blood, we must first discuss how buffers work in solution.

Acid-base buffers confer resistance to a change in the pH of a solution when hydrogen ions (protons) or hydroxide ions are added or removed. An acid-base buffer typically consists of a weak acid, and its conjugate base (salt).

Buffers work because the concentrations of the weak acid and its salt are large compared to the amount of protons or hydroxide ions added or removed.

When protons are added to the solution from an external source, some of the base component of the buffer is converted to the weak-acid component (thus using up most of the protons added).

When hydroxide ions are added to the solution protons are dissociated from some of the weak-acid molecules of the buffer, converting them to the base of the buffer (and thus replenishing most of the protons removed). However, the change in acid and base concentrations is small relative to the amounts of these species present in solution. Hence, the ratio of acid to base changes only slightly.

### The Carbonic Acid-Bicarbonate Buffer in the Blood

By far the most important buffer for maintaining acid-base balance in the blood is the carbonic acid-bicarbonate buffer.

Carbonic acid ( $\text{H}_2\text{CO}_3$ ) is the acid and the conjugate base for  $\text{H}_2\text{CO}_3$  is  $\text{HCO}_3^-$  (bicarbonate ion).

Carbonic acid also dissociates rapidly to produce water and carbon dioxide.

This second process is not an acid-base reaction, but it is important to the blood's buffering capacity.

The pH of the buffered solution (i.e., the blood) is dependent only on the ratio of the amount of  $\text{CO}_2$  present in the blood to the amount of  $\text{HCO}_3^-$  (bicarbonate ion) present in the blood (at a given temperature, so that pK remains constant).

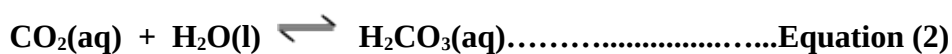
This ratio remains relatively constant, because the concentrations of both buffer components ( $\text{HCO}_3^-$  and  $\text{CO}_2$ ) are very large, compared to the amount of  $\text{H}^+$  added to the blood during normal activities and moderate exercise. When  $\text{H}^+$  is added to the blood as a result of metabolic processes, the amount of  $\text{HCO}_3^-$  (relative to the amount of  $\text{CO}_2$ ) decreases; however, the amount of the change is tiny compared to the amount of  $\text{HCO}_3^-$  present in the blood. This optimal buffering occurs when the pH is within approximately 1 pH unit from the pK value for the buffering system, i.e., when the pH is between 5.1 and 7.1.

The three related equilibrium reactions which help to regulate blood pH are as follows:

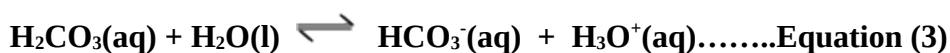
- (i) Gaseous carbon dioxide in the lungs is in equilibrium with dissolved carbon dioxide in the blood:



- (ii) The dissolved carbon dioxide reacts with water in the blood forming Carbonic acid:



- (iii) The weak acid carbonic acid is also in equilibrium with hydrogencarbonate ion and hydronium ion:



Review exercise 7.4 questions: 1, 2, 3,

Questions page 229: 3, 4, 5, 7, 9, 10, 14, 17, 20,

STAWA Experiment 12 page 98

STAWA Set 17 page 127



## Acid – Base Titration (Volumetric Analysis)

A means of determining the concentration of an unknown solution by reaction with a solution of known concentration. (A standard solution.)

### Procedure

1. A Primary Standard is usually prepared as the basic for comparison.

For acid-base titrations a good primary standard is sodium carbonate. Sodium carbonate has a high value for its atomic weight, can be obtained in pure form, is extremely soluble in water and is neither **efflorescent nor deliquescent**.

Determining the concentration of the primary standard

Calculate the number of moles of sodium carbonate  $n = m/M$

Calculate the solution concentration  $c = n/V$

2. The primary standard solution is reacted quantitatively with the unknown acid and the volumes of each solution used form the basis of the calculation of concentration of the acid.



$$n(\text{HCl}) = 2n(\text{Na}_2\text{CO}_3)$$

$$n(\text{HCl}) = 2 \times cV(\text{Na}_2\text{CO}_3)$$

$$c(\text{HCl}) = n/V$$

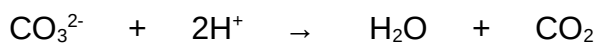
This reaction is the neutralisation of a **strong acid by a weak base**.

The solution at the **equivalence point is acidic**. Thus an indicator with an end point in the acidic pH range is used in the titration.

Such an indicator is **methyl orange** that changes colour from yellow to red as the solution's pH drops to around 3 or 4.

### Equivalence Point And The Choice Of Indicator

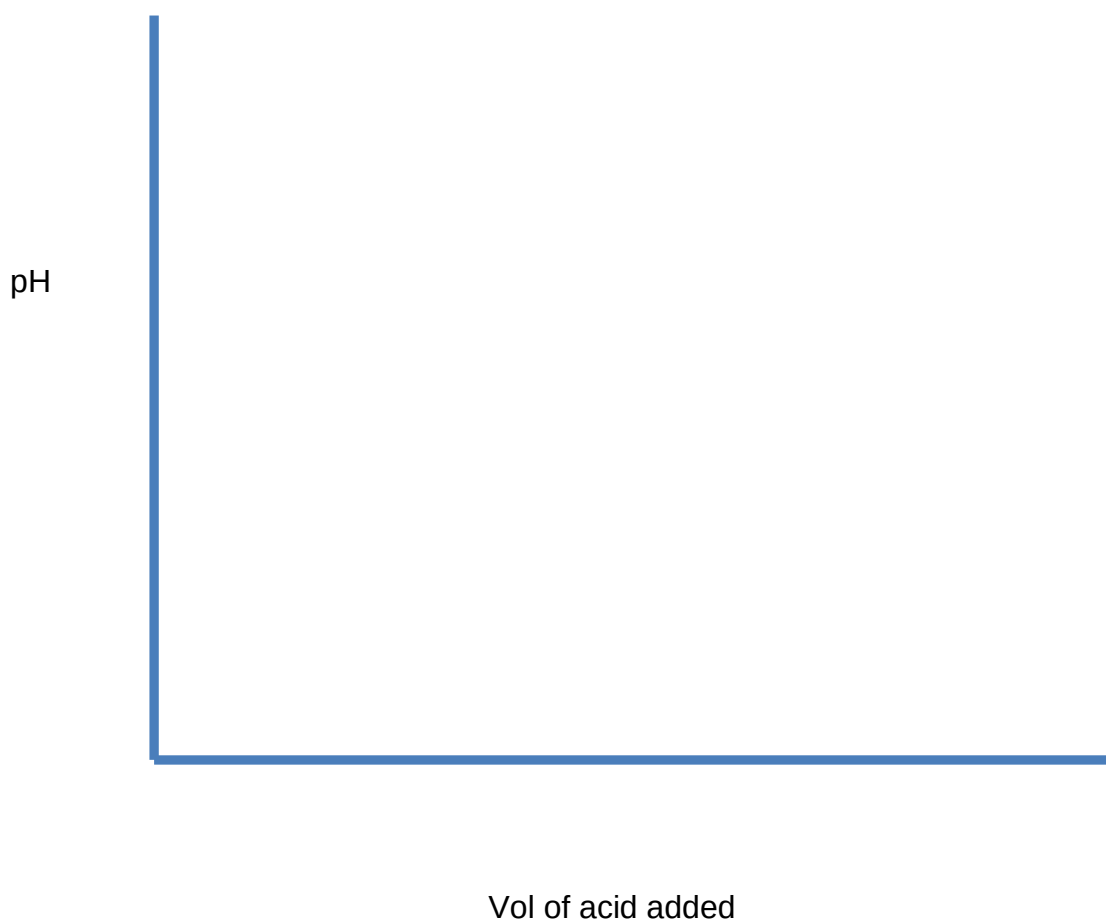
The equivalence point of a titration is the point at which chemically equivalent amounts of acid and base are present.



For this titration the **equivalence point** occurs when

**the number of moles of  $\text{H}^+$  = twice the number of moles of  $\text{CO}_3^{2-}$**

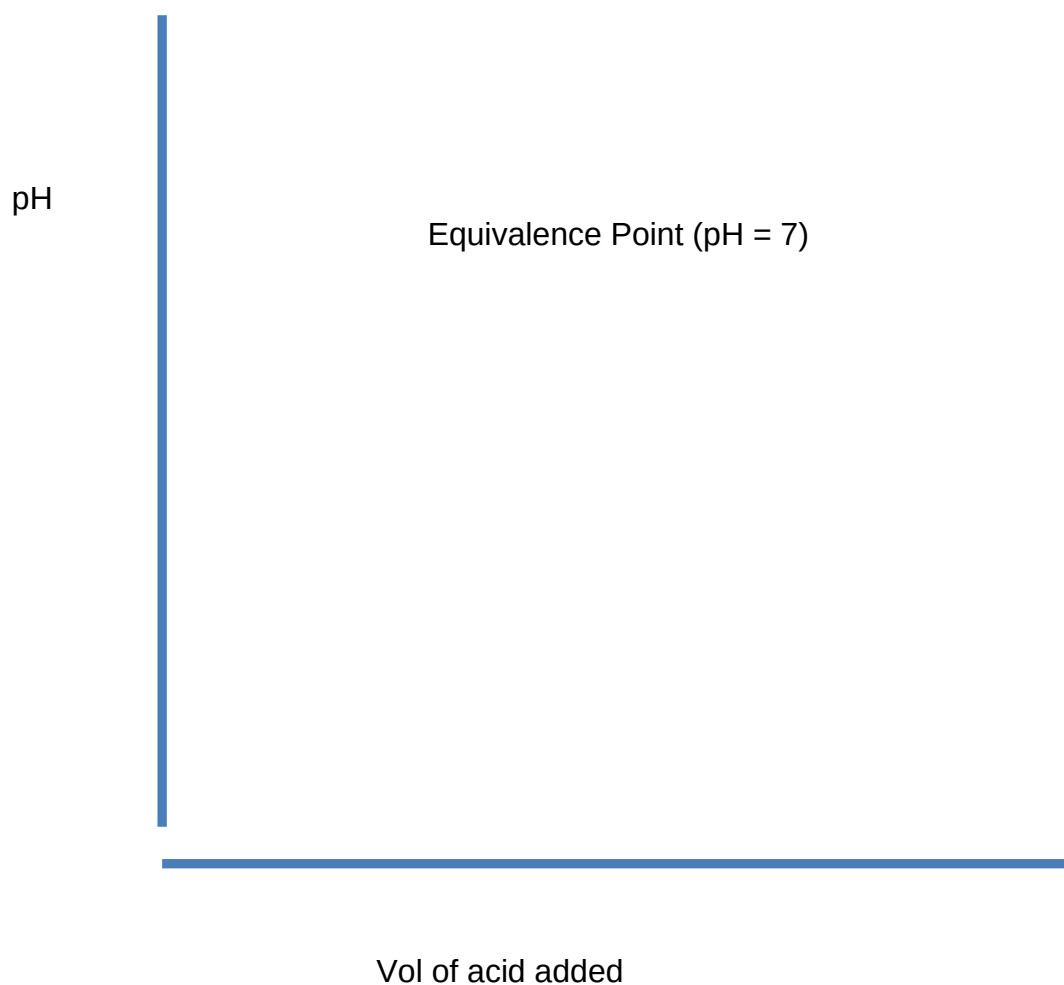
Consider this graph which plots pH change during the titration. It shows that the pH changes rapidly around the equivalence point.



Appropriate indicators for this titration have **end point** colour changes at pH values that are within the vertical portion of the graph.

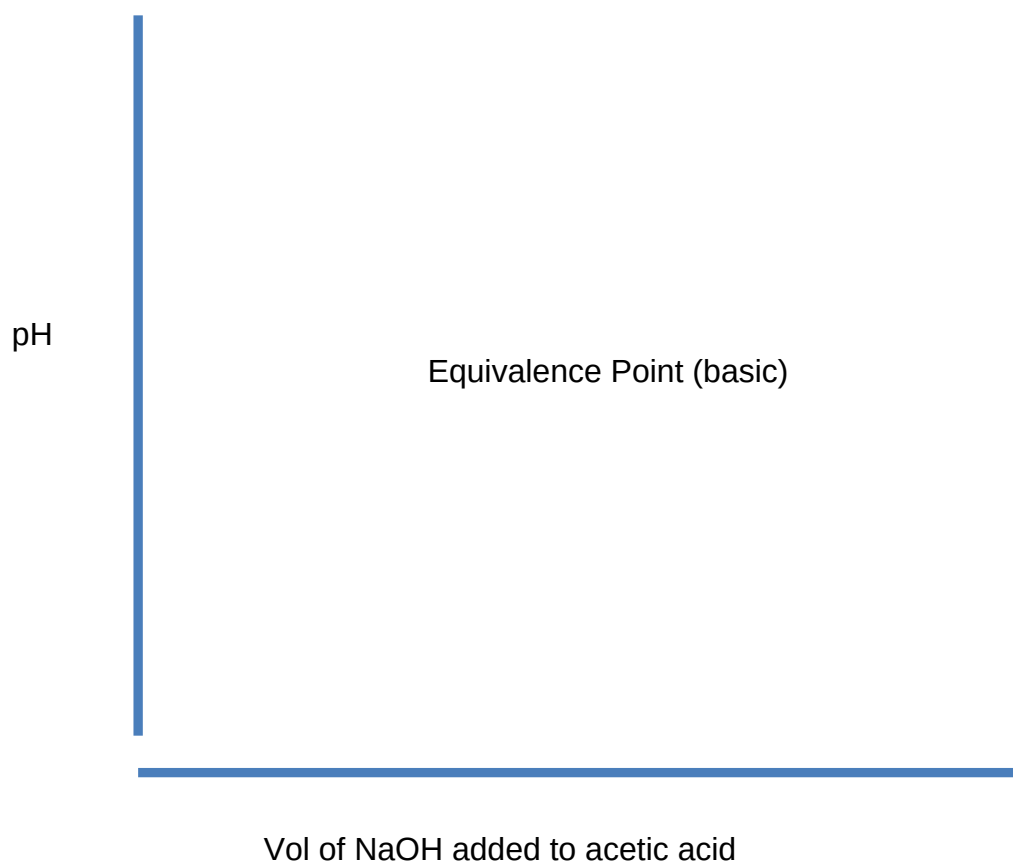
**Strong Acid – Strong Base Titration**

e.g. HCl v NaOH



For such a titration any indicator that changes colour between pH 12 and 1 would be suitable. Phenolphthalein turns pink (basic) to colourless (acidic) between pH 8.3 and pH 10.

**Weak Acid – Strong Base Titration**  
e.g. acetic acid v sodium hydroxide



**Phenolphthalein** would be the best choice of indicator.

Review exercise 8.3 questions: 1, 2, 3, 4, 6

Page 257 questions: 5, 6, 8, 9, 11, 14

STAWA Experiments 13 – 16 pages 101 to 108

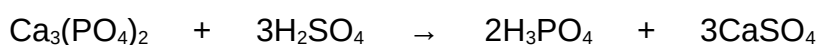
Investigation 9 page 110

STAWA Set 15 page 123

STAWA Set 18 and 19 page 129 - 132

### Percentage purity calculations based on titration data

1. The active ingredient of a drain cleaner is sodium hydroxide. A sample of this powder weighing 45.6g is dissolved in water and made up to 1L in a volumetric flask. A 20.0mL sample of the resulting solution required 18.75mL of 0.320 mol L<sup>-1</sup> sulfuric acid for complete neutralisation. Determine the percentage by weight of sodium hydroxide in the drain cleaner.
2. A 7.32g sample of a mixture of calcium carbonate and copper sulfate required 28.5mL of 0.100 mol L<sup>-1</sup> hydrochloric acid for complete neutralisation. Calculate the percentage mass of calcium carbonate in the sample.
3. The production of phosphoric acid from rock phosphate (an impure form of calcium phosphate) can be represented by the equation



What mass of rock phosphate would be required to produce 500Kg of phosphoric acid assuming the rock contains 65% by mass of calcium phosphate?

4. Strontium hydroxide is a strong base which dissociates completely in solution. 500mL of 0.00500 mol L<sup>-1</sup> Sr(OH)<sub>2</sub> was prepared.

Calculate the mass of strontium hydroxide required to make up the 500mL of solution.

Calculate the OH<sup>-</sup> concentration and hence the pH of the solution.

5. 52.0g of vinegar was diluted with 200mL of water. If 28.5mL of this diluted solution was required to neutralise 20.0mL of 0.108 M NaOH what was the % acetic acid in the original vinegar? (Assume the density of the vinegar to be 1.00g mL<sup>-1</sup>)
6. If 5.00g of commercial vinegar requires 32.0mL of 0.125 M NaOH for complete neutralisation what is the % acetic acid in the vinegar?
7. A common brand of household cleaner was analysed to find the % ammonia present.

12.2g of the cleaner was diluted to 250mL in a volumetric flask. A 20mL aliquot pipette into a conical flask and titrated against 0.204 M HCl.

An average volume of 26.4mL of acid was needed to reach the equivalence point.

- a) What materials should have been used to rinse each piece of glassware mentioned in the question?
- b) What would be a suitable indicator for use in this titration?
- c) Determine the % ammonia in the original cleaner.

### Acid-Base Revision

1. A dilute solution of nitric acid has a concentration of nitrate ions of  $0.0100 \text{ mol L}^{-1}$ .
  - a) Calculate the  $[\text{H}^+]$
  - b) Calculate the pH of the solution
2. A solution of calcium hydroxide is found to have a pH of 11.
  - a) Calculate the  $[\text{H}^+]$
  - b) Calculate the  $[\text{OH}^-]$  concentration
  - c) Calculate the concentration of the calcium hydroxide solution
3. Choose a suitable example and explain, using equations, what is meant by the term 'weak base'
4. Would you expect an aqueous solution of ammonium chloride to be acidic, basic or neutral?

Explain your answer with an appropriate equation.

5. Carefully explain the difference between the terms 'end point' and 'equivalence point'.
  
  
  
  
  
  
  
  
  
  
6. The indicator alizarin yellow changes colour between the pH values 10.1 and 12.0.
  - a) Carefully explain why this indicator would be unsuitable for use in a titration between hydrochloric acid and sodium hydroxide.
  
  
  
  
  
  
  
  
  
  
  - b) Suggest a titration that alizarin yellow may be considered appropriate for. Write equations to justify your answer.
  
  
  
  
  
  
  
  
  
  
7. Write net balanced **ionic** equations to represent the reactions that occur between a dilute acid and each of the following.

- a) iron metal
  - b) solid calcium carbonate
  - c) aqueous sodium hydrogen carbonate
  - d) aqueous potassium acetate
8. 22.1g of marble, which is mainly calcium carbonate, is put into 2200mL of 0.20 mol L<sup>-1</sup> hydrochloric acid solution.  
When the reaction was complete 22.2g of calcium chloride solid was recovered from the solution.
- a) Calculate the volume of carbon dioxide gas (at STP) produced in the same reaction.
  - b) Calculate the mass of calcium carbonate consumed in the reaction and hence the percentage purity of the marble.
9. A household ammonia solution was analysed to determine its ammonia content. 4.99g of the solution was placed in a volumetric flask and made up to 250mL of



dilute solution. 25mL of this solution required 14.8mL of  $0.110 \text{ mol L}^{-1}$  hydrochloric acid to achieve an end point with a suitable indicator. Calculate the mass of pure ammonia in the original sample of household ammonia.