d elevote

## YEAR 12

## CHEMISTRY

## MODULE 6

## LESSON SEVEN

## THEORY

## TITRATIONS II

## Titration curves continued...

Interestingly, the titration curve can tell us more than just the pH at the equivalence point.

When a weak acid or base is involved, we may use the curve, and the equivalence point pH to determine the $K_{a}$ and/or $K_{b}$ values.

See the example question below:

## EXAMPLE QUESTION

See the question below in which a 25.00 mL sample of acetic acid of unknown concentration was titrated with 50.0 mL of 0.100 M sodium hydroxide.

a. Write a balanced chemical equation for the neutralisation reaction that occurs.
b. What is the pH at equivalence point?
c. What is the volume of titre required to reach equivalence point?
d. The point at which half the moles required to reach equivalence point is added is known as the "half-equivalence point". What is the half-equivalence point volume?

## THEORY

e. What is the pH at half equivalence point?
f. Using the Henderson-Hasselbalch equation, calculate the $K_{a}$ of acetic acid.
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NB: The accuracy of the method above is entirely dependent on the accuracy of the pH values determined from the curve.

## THEORY

## POLYPROTIC ACIDS

In addition to the content above, it is important to note that such acids and bases will have multiple equivalence points.

See the example of citric acid being titrated with sodium hydroxide and label the three equivalence points approximately.


## BACK TITRATIONS

In certain circumstances, it will not help to directly titrate one substance against another. These include situations when:

- The substance is insoluble in water but does react with an acid/base
- The substance is unreactive or occurs too slowly and there is no clearly defined endpoint.
- The endpoint is hard to determine (e.g. Weak acid/weak base titration)
- The substance is toxic or volatile in aqueous solution

In these situations, we will prefer to perform a back titration which in other words is essentially an indirect titration.

For example, we may want to analyse the chemical composition of aspirin tablets which contain acetylsalicylic acid (ASA).

acetylsalicylic acid

## THEORY

ASA is not very soluble in water, so a traditional titration will not help. Instead, we opt to:

1. Crush a tablet
2. React with an excess volume of standardised base solution (e.g. NaOH )
3. Titrate the solution from above with a standardised acid solution (e.g. HCl ) to determine the excess moles of NaOH
4. Subtract this excess amount from the original number of moles of NaOH added in step 2
5. Calculate the concentration of ASA in the original tablet.

See the example question below:

## EXAMPLE QUESTION

The concentration of acetylsalicylic acid in aspirin is to be determined in units of \%(w/w).
a. Given that acetylsalicylic acid is a diprotic acid, write an equation for its neutralisation with sodium hydroxide. Represent the acid as $\mathrm{H}_{2} \mathrm{~A}$
b. Suppose a 0.4567 g tablet was crushed and reacted with 20.00 mL of 0.100 M NaOH and then back titrated with 0.05000 M HCl . The titres for the back titration are shown below.

| Titre | Volume (mL) |
| :---: | :---: |
| 1 | 15.90 |
| 2 | 15.54 |
| 3 | 15.45 |
| 4 | 15.63 |

Calculate the number of excess moles of NaOH in the mixture.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$

## THEORY

c. By calculating the original number of moles of NaOH present, calculate the number of moles of NaOH that reacted with acetylsalicylic acid.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
d. Determine the concentration of acetylsalicylic acid in the aspirin tablet in $\%(\mathrm{w} / \mathrm{w})$ if its molecular formula is $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{4}$.
$\qquad$
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## CONDUCTOMETRIC TITRATIONS

Addressing regular titrations again, we may wish to measure how the total conductivity changes (as opposed to pH ) with volume of titrant added.

For this, we must carry out the titration with a conductivity meter submerged within the solution.


## THEORY

In aqueous solutions, several factors pertaining to the constituent ions will impact the conductivity of the solution, and these include:

- Concentration
- Charge
- Size
- Identity

NB: an implication of this is that not all ions are equally conductive. For example, the ammonium ion $\left(\mathrm{NH}_{4}^{+}\right)$is bulkier and more resistant to flow and as such, less conductive than the hydride ion $\left(H^{+}\right)$.

Recall that when pH was measured, the graph would look different if:

- A base (in burette) was titrated against an acid (in conical flask)
- An acid (in burette) was titrated against a base (in conical flask)

See below:


However, in the case of conductivity, the shape of the curve is irrespective of whether acid or base are in the conical flask and burette but rather depends on the strength of the substance only.

See below:

## THEORY

6.3.2 Investigate titration curves and conductivity graphs to analyse data to indicate characterisitic reaction profiles, for example strong acid/strong base, strong acid/weak base, weak acid/strong base (PART 2)

## STRONG ACID + STRONG BASE



Volume of titre ( $m L$ )

Consider a titration where the strong base NaOH is titrated into the strong acid HCl .

Initially the conductivity is high as the strong acid dissociates completely and liberates abundant $\mathrm{H}^{+}$and $\mathrm{Cl}^{-}$ions. As NaOH is added progressively, neutralisation occurs as shown below:

$$
\mathrm{HCl}_{(a q)}+\mathrm{NaOH}_{(a q)} \rightarrow \mathrm{NaCl}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)}
$$

The net ionic reaction for this is:

$$
\mathrm{H}_{(a q)}^{+}+\mathrm{OH}_{(a q)}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(l)}
$$

The $\mathrm{OH}^{-}$reacts with the $\mathrm{H}^{+}$ions and the conductivity decreases linearly.
NB: whilst there are $\mathrm{Na}^{+}$ions introduced in the salt, these are bulkier than $\mathrm{H}^{+}$so overall conductivity still decreases.

## THEORY

The lowest point of the graph represents the equivalence point where $\mathrm{OH}^{-}$have reacted with all $H^{+}$ions.

The solution now only contains $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$ions. After this point, as more NaOH is added, conductivity again increases linearly as the strong base dissociates completely and liberates $\mathrm{OH}^{-}$and $\mathrm{Na}^{+}$ions.

Note that the curve would look the same if we started with base and acid were added instead.

## STRONG ACID/BASE (CONICAL FLASK) + WEAK ACID/BASE (BURETTE)



An example of this reaction is the addition of hydrochloric acid into a solution of the weak base ammonia:

Initially the conductivity is high as the strong acid dissociates completely and liberates abundant $\mathrm{H}^{+}$and $\mathrm{Cl}^{-}$ions.

As ammonia is added, it reacts with the $\mathrm{H}^{+}$to produce the bulkier and less conductive $\mathrm{NH}_{4}^{+}$ ions, lowering the conductivity steadily.

$$
\mathrm{HCl}_{(a q)}+\mathrm{NH}_{3(a q)} \rightarrow \mathrm{NH}_{4} \mathrm{Cl}_{(a q)} \rightarrow \mathrm{NH}_{4(a q)}^{+}+\mathrm{Cl}_{(a q)}^{-}
$$

The lowest point of the graph represents the equivalence point where all $H^{+}$ions have been reacted with only $\mathrm{NH}_{4}^{+}$and $\mathrm{Cl}^{-}$ions exist at this point.

After this point, as more $\mathrm{NH}_{3}$ is added, the conductivity doesn't change very much as the weak base ionises to a very small extent.

## THEORY

Note that the equivalence point is curved as opposed to sharp as in the previous graph. This is due to the hydrolysis of salts at the equivalence points which creates a chemical equilibrium and facilitates a smooth change.

## WEAK ACID/BASE (CONICAL FLASK) + STRONG BASE/ACID (BURETTE)



An example of this reaction is the addition of the weak acetic acid into a solution of the strong base sodium hydroxide:

Initially the conductivity is low as the weak acid dissociates incompletely and liberates few ions.

As strong base is added, there is a quick but fleeting decrease in conductivity until the relatively few $\mathrm{H}^{+}$ions are reacted with:

$$
\mathrm{H}_{(a q)}^{+}+\mathrm{OH}_{(a q)}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(l)}
$$

After this point, as more NaOH is added, neutralisation occurs as follows:

This process liberates $\mathrm{Na}^{+}$and $\mathrm{CH}_{3} \mathrm{COO}^{-}$ions steadily as the salt is produced and the conductivity will increase steadily.

The equivalence point occurs when the gradient of the line suddenly becomes steeper. This is representative of the point where excess NaOH is added which liberates $\mathrm{OH}^{-}$ions which have relatively high conductivity.

## THEORY

Note that the equivalence point is curved as opposed to sharp as in the 'strong-strong' graph. This is due to the hydrolysis of salts at the equivalence points which creates a chemical equilibrium and facilitates a smooth change.

## WEAK ACID + WEAK BASE



An example of this reaction is the addition of the weak base ammonia into a solution of the weak acetic acid:

Initially the conductivity is low as the weak acid dissociates incompletely and liberates few $H^{+}$ions.

As ammonia is added, the conductivity experiences a steep but fleeting decrease as the following neutralisation reaction takes place:

$$
H_{(a q)}^{+}+N H_{3(a q)} \rightarrow N H_{4(a q)}^{+}
$$

This is because this process produces the bulky $\mathbf{N H}_{4}^{+}$ions as ammonia reacts with $H^{+}$ions.

Once the $\mathrm{H}^{+}$ions in solution have all been reacted with, the neutralisation reaction continues to occur, and the conductivity rises steadily as the salt produced $\left(\mathrm{NH}_{4} \mathrm{CH}_{3} \mathrm{COO}_{(a q)}\right)$ liberates more $\mathrm{NH}_{4}^{+}$and $\mathrm{CH}_{3} \mathrm{COO}^{-}$ions.

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{NH}_{3(a q)} \rightarrow \mathrm{NH}_{4} \mathrm{CH}_{3} \mathrm{COO}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)}
$$

After the equivalence point, the graph flattens out and only rises very slightly as the further addition of weak base (which dissociates minimally) does not change conductivity substantially.

## THEORY

Note that the equivalence point is curved as opposed to sharp as in the 'strong-strong' graph. This is due to the hydrolysis of salts at the equivalence points which creates a chemical equilibrium and facilitates a smooth change.

### 6.3.6 Conduct a chemical analysis of a common household substance for its acidity or basicity, for example: soft drink, wine, juice, medicine

Aim: To determine the acid content of orange juice

## Materials:

- 100 mL orange juice
- 200 mL of standardised 0.1 M NaOH solution
- Calibrated pH meter
- 50 mL burette
- Retort stand
- Burette clamp
- 25 mL Bulb pipette
- $3 \times 250 \mathrm{~mL}$ conical flask
- Wash bottle with 100 mL of distilled water
- Electronic balance
- Filter funnel
- Safety glasses


## Background:

It is not advisable to use acid-base indicators for this practical as the colour of orange juice will interfere with that of the indicator and make it difficult to observe the endpoint.

Rather we will use a pH probe and computer software to create a titration curve. From here, the equivalence point will be determined by finding the bisection of the vertical portion of the graph.

## Method:

1. Rinse burette three times with distilled water and then three times with sodium hydroxide before filling it with standardised sodium hydroxide
2. Rinse bulb pipette with three times with distilled water and then three times with orange juice before filling it with the orange juice (analyte).
3. Rinse conical flask three times with distilled water and transfer a 25.00 mL aliquot of orange juice from the bulb pipette.
4. Set up equipment as shown in the diagram below
5. Titrate with sodium hydroxide and repeat steps $1-4$ THREE times.
6. Analyse titration curves provided by the software to determine equivalence points.

## THEORY

## Diagram:



### 6.3.5 Explore acid/base analysis techniques that are applied: in industries, by Aboriginal and Torres Strait Islander Peoples, using digital probes and equipment

## FOOD INDUSTRY

Acid/base analysis techniques are highly prevalent in the food industry and in particular, the manufacturing of wine.

Whilst the ethanol concentration of wines is an important consideration in determining the alcohol content, the acidity of wine is one of the main factors that contributes to its taste.

There are more than 40 weak organic acids in wine, of which tartaric acid is the main component. For convenience the total acid content of wine is reported in terms of percentage content of tartaric acid in wine. This assumes that all acidity in wine is due to the presence of tartaric acid.

Often a titration with a strong base such as NaOH will help ascertain this acid content.

$$
\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{6(a q)}+2 \mathrm{NaOH}_{(a q)} \rightarrow \mathrm{Na}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6(a q)}+2 \mathrm{H}_{2} \mathrm{O}_{(l)}
$$

As seen above, tartaric acid is a diprotic acid and its content in wine is closely monitored to ensure the taste is optimised to an industry standard.

## THEORY

## MEDICINE

As explored earlier, one of the best examples of acid/base monitoring in medicine is in the monitoring of acetylsalicylic acid (ASA) content in aspirin tablets. This is crucially important as ASA is one of the main active ingredients and its levels must be tightly regulated as per the Therapeutic Goods Association (TGA) guidelines.

Furthermore, antacid tablets will contain insoluble substances such as $\mathrm{CaCO}_{3}$ and are used to treat gastric reflux by neutralising excess or regurgitated stomach acid ( HCl ). Both aspirin and antacid tablets contain insoluble active ingredients and as such, are best monitored using back titrations.

## ABORIGINAL AND TORRES-STRAIT ISLANDER PEOPLES

Australia's indigenous peoples were highly resourceful and had a great many purposes for natural substances. Whilst perhaps not aware, they were in many situations, utilising acid/base reactions to their advantage!

Indigenous Australians were well known for their use of clays and ochres. Ochres are natural clay earth pigments and common ochres include:

- Red Ochre $-\mathrm{Fe}_{2} \mathrm{O}_{3}$
- Yellow Ochre - $\mathrm{FeO}(\mathrm{OH}) . n \mathrm{H}_{2} \mathrm{O}$
- Kaolin $-\mathrm{Al}_{2}\left(\mathrm{Si}_{2} \mathrm{O}_{5}\right)(\mathrm{OH})_{5}$

Aboriginal people were known to ingest these substances to treat gastric illnesses such as gastroesophageal reflux disease as it is known today. This is largely due to the alkaline nature of the clays which could be used to neutralise the excess stomach acid.

In addition, Indigenous Australians were known to use plants to treat various types of stings and other medical problems.

See the summary table below.
NB: analgesia refers to pain relief whilst anaesthesia brings on a period of insensitivity to pain.

| Use | Plant name | Plant <br> common <br> name | Property | Use |
| :---: | :---: | :---: | :---: | :---: |
| Jellyfish <br> stings | Carpobratus glaucescens | Pig face |  |  |
| Stingray <br> stings | Ipomea pes - caprae | Goat's foot | Contain <br> alkaloids | Anaesthetic |
|  <br> insect <br> stings | Capparis lasiantha | Nipan |  |  |
| Headaches <br> muscle <br> aches, <br> tooth <br> aches | Alphitonia excelsa | Soap tree | Contains <br> saponins <br> which are <br> weakly acidic | Analgesia |

## PRACTICE OUESTIONS

1. The graph below shows how the pH of a weak polyprotic acid changes, as strong base NaOH is added to it. Choose the option that best describes this acid.

a. A triprotic acid with $\mathrm{pKa}_{1}=2.5, \mathrm{pKa}_{2}=10$ and $\mathrm{pKa}_{3}=12$
b. A triprotic acid with $\mathrm{pKa}_{1}=5, \mathrm{pKa}_{2}=10$ and $\mathrm{pKa}_{3}=13$
c. A diprotic acid with $\mathrm{pKa}_{1}=5, \mathrm{pKa}_{2}=10$
d. A diprotic acid with $\mathrm{pKa}_{1}=2.5, \mathrm{pKa}_{2}=7.5$
2. Two titrations are carried out between equimolar acids and bases:


## PRACTICE OUESTIONS

Select the statement which is most correct
a. The volume of base required to reach equivalence point is greater for the strong acid than the weak acid
b. The volume of base required to reach equivalence point is greater for the weak acid than the strong acid
c. The volume of base required to reach equivalence point is identical for both acids as all solutions are equimolar
d. The volume of base required to reach equivalence point depends on the actual identity of the acid and in particular, its own acid dissociation constant.
3. Which of the following statements is INCORRECT?
a. Nipan was used by the Aborignal people as anaesthestic due to containing alkaloids
b. Pig's foot was use by Aborignial peoples due its basic properties caused by having hydroxide in its structure
c. Back titrations are used in the monitoring of ASA in aspirin tablets
d. Tartaric acid is monitored in wine due to its influence on taste
4. Conductivity graphs are affected by:
a. Strength of acid
b. Apparatus holding the acid
c. Size of ions
d. All of the above
5. Which indicator is appropriate for titration between HF and $\mathrm{NH}_{3}$ ?
a. Phenolphthalein
b. Methyl orange
c. Bromothymol blue
d. None of the above

## PRACTICE OUESTIONS

6. A student uses a pH probe connected to a data logger to determine the concentration of a 25.00 mL aliquot of monoprotic weak acid titrated with a 0.05 M solution of KOH .

a. Write a balanced chemical equation for this reaction
(1 mark)
b. Draw a diagram of the experimental setup used.

## PRACTICE QUESTIO@S

c. Use the graph to calculate the concentration of the acid
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d. Using the graph determine the identity of the acid. Explain your reasoning.
(2 marks)

| Acid | $\mathbf{p K}_{\mathbf{a}}$ |
| :---: | :---: |
| $\alpha$ | 8.5 |
| $\beta$ | 4.7 |
| $\gamma$ | 3.2 |

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7. A scientist wanted to measure the calcium carbonate content in a shell she found at the beach. The shell, which weighed 5.654 g was placed in a beaker containing 10 mL of 5 M hydrochloric acid.
a. Write a balanced chemical equation for the reaction between hydrochloric acid and calcium carbonate.

## PRACTICE OUESTIONS

b. After the shell had completely dissolved in the beaker, the existing solution was made up to 25.00 mL and titrated against 0.78 M NaOH . Given the titres below, calculate the moles of HCl which reacted with the calcium carbonate in the shell.

| Titre | Volume (mL) |
| :---: | :---: |
| 1 | 12.95 |
| 2 | 12.35 |
| 3 | 12.45 |
| 4 | 12.25 |

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c. Using the information from above, calculate the percentage by weight of calcium carbonate in the shell $\%(w / w)$.
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## HOMEWORK

1. Johnathan conducted a titration between a nitric acid and potassium hydroxide and then between hydrochloric acid and aqueous ammonia. In both titrations, the acid starts in the conical flask and base is delivered via burette. Explain the differences in:
a. How the pH varies between both titrations.
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b. How the conductivity varies between both titrations
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## HOMEWORK

c. The pH of the salt produced at equivalence point:
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2. Oven cleaner is often called 'caustic soda'. Its active ingredient is in fact, the strong base sodium hydroxide. See the label of a household oven cleaner below:

## Dusty Rusty's Oven cleaner

## Ingredients:

$\mathrm{NaOH}=125 \mathrm{gL}^{-1}$
CAUTION

## KEEP OUT OF REACH OF CHILDREN

A 50.0 mL sample of this oven cleaner was made up to a volume of 250.0 mL in a volumetric flask. A $\mathbf{2 5 . 0 0} \mathrm{mL}$ aliquot of this was titrated against a 1 M hydrochloric acid solution. The following results were obtained:

| Titre | Initial burette reading <br> $(\mathrm{mL})$ | Final burette reading <br> $(\mathrm{mL})$ |
| :---: | :---: | :---: |
| 1 | 0 | 20.30 |
| 2 | 20.05 | 40.15 |
| 3 | 0 | 19.95 |
| 4 | 19.95 | 39.95 |

a. Explain why the solution was diluted prior to titration
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## HOMEWORK

b. Using the results shown above, evaluate the accuracy of the label.
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3. Dry ice is the solid form of carbon dioxide and is used primarily as a cooling agent. A sample is contaminated during manufacture and its percentage purity by mass must be determined.
a. A 0.55 g sample of dry ice was reacted with 50.00 mL of 0.97 M potassium hydroxide solution to produce potassium carbonate and water. Write a balanced chemical equation for this reaction.
b. Knowing that the potassium hydroxide was added in excess, the resulting solution from part a was titrated against 1.00M hydrochloric acid and an average titre of 25.60 mL was recorded. Calculate the purity of the dry ice sample in \%(w/w).
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## HOMEWORK

4. Outline the use of acids and bases by Aboriginal peoples, with reference to TWO examples.
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5. See the statement below:
"Acid/base analysis techniques are fundamental to the functioning of society today"

Assess the accuracy of the statement above, making reference to specific examples to support your claim.
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## HOMEWORK

6. Most commercially available antacids are combinations of aluminum and magnesium hydroxide.

A chemist conducted a complexometric titration with ethylenediaminetetraacetic acid (EDTA) to determine the percentage composition of $\mathrm{Al}(\mathrm{OH})_{3}$ in an antacid.

The formation of a stable coloured complex with $\mathrm{Al}^{3+}$ is outlined in the following equations.
$\underset{\text { Analyte }}{\mathrm{Al}^{3+}(a q)} \underset{\text { Excess EDTA }}{+} \underset{\text { pH } 10}{ } \mathrm{HY}^{3-}(a q) \underset{\text { Al-EDTA complex }}{\Leftrightarrow} \underset{\text { Unreacted EDTA }}{\Leftrightarrow}(a q)$


A 0.25 gram sample of of antacid was dissolved in 50.00 mL of 0.1050 $\mathrm{mol} / \mathrm{L}$ excess EDTA. The solution was treated to ensure that the remainder consisted only of unreacted EDTA. This remainder was diluted to 125 mL . A 25.0 mL sample of this diluted solution was reacted with $\mathrm{Zn}^{2+}$ to form a colourless metal complex. The solution turned dark red once 23.85 mL of $0.065 \mathrm{~mol} / \mathrm{L} \mathrm{Zn}^{2+}$ was added.
a. Determine the number of moles of $\mathrm{Al}^{3+}$ in the antacid.
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## HOMEUORK

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b. Hence, determine the percentage composition of $\mathrm{Al}(\mathrm{OH})_{3}$ in the antacid if it is known to contain $\mathrm{Al}(\mathrm{OH})_{3}$ and $\mathrm{Mg}(\mathrm{OH})_{2}$
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7. A chemistry class is tasked with determining the concentration of ascorbic acid, $C_{6} H_{8} O_{6}$ in a sample of orange juice.

First, the ascorbic acid is oxidised to dehydroascorbic acid, $C_{6} H_{6} O_{6}$ using excess triiodide, $I_{3}^{-}$:

$$
\mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{6(a q)}+I_{3(a q)}^{-} \rightarrow 3 I_{(a q)}^{-}+\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{O}_{6(a q)}+2 \mathrm{H}_{(a q)}^{+}
$$

The remaining triiodide ions are then titrated with a solution of sodium thiosulfate, $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ :

$$
I_{3(a q)}^{-}+2 S_{2} O_{3(a q)}^{2-} \rightarrow S_{4} O_{6(a q)}^{2-}+3 I_{(a q)}^{-}
$$

A 25.00 mL sample of orange juice is diluted to 125.0 mL .50 .00 mL of 0.01023 M potassium triiodide, $\mathrm{KI}_{3}$ was added to a 25.00 mL aliquot of the diluted solution. This solution was then titrated with $0.07203 \mathrm{M} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ until the endpoint of a starch indicator was reached. The following results were obtained.

## HOMEWORK

| Titre | Volume $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}(\mathrm{~mL}):$ |
| :---: | :---: |
| 1 | 14.68 |
| 2 | 13.78 |
| 3 | 13.86 |
| 4 | 13.82 |

a. Explain why traditional methods of acid-base titration may be inappropriate in determining the ascorbic acid content of orange juice.
(2 marks)
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$\qquad$
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$\qquad$
$\qquad$
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$\qquad$
b. Calculate the ascorbic acid content of the orange juice in $\mathrm{mg} / \mathrm{L}$.
(6 marks)
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## HOMEWORK

8. A 30 mL solution of sulfurous acid (H2SO3) acid is titrated against 0.25 M sodium hydroxide. The titration curve is given below.

a. Write out the reactions occurring during the titration and which part of the graph they occur in.
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b. Calculate the concentration of the sulfurous acid solution.
(3 marks)
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## HOMEWORK

## HW AnSWERS

## Module 6 Lesson 6

$1 a$.

| 1 | $\mathrm{Na}_{2} \mathrm{CO}_{3}(a q) \rightarrow 2 \mathrm{Na}^{+}(a q)+\mathrm{CO}_{3}^{2-}(a q)$ <br> Explains that $\mathrm{Na}_{2} \mathrm{CO}_{3}$ dissociates to give: <br> - $\mathrm{CO}_{3}^{2-}$, which is the conjugate base formed from the ionisation of weak bicarbonate ion $\left(\mathrm{HCO}_{3}^{-}\right)$ <br> - Stronger base than water and so will react with water as a base: $\mathrm{CO}_{3}^{2-}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{OH}^{-}(a q)+\mathrm{HCO}_{3}^{-}(a q)$ <br> - $\quad N a^{+}$is a spectator ion and will not react with water |
| :---: | :---: |
| 1 | Identifies salt is basic |

$$
\mathrm{KHSO}_{4}(\mathrm{aq}) \rightarrow \mathrm{K}^{+}(a q)+\mathrm{HSO}_{4}^{-}(a q)
$$

Explains that $\mathrm{KHSO}_{4}$ dissociates to give:

- $\mathrm{HSO}_{4}^{-}$, which is the conjugate base formed from the ionisation of strong diprotic sulfuric acid
b.

1

- Being diprotic, $\mathrm{HSO}_{4}^{-}$undergoes a further ionisation in water as an acid:

$$
\mathrm{HSO}_{4}^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{SO}_{4}^{2-}(a q)
$$

- $K^{+}$is a spectator ion and will not react with water

1 Identifies salt is acidic

| 1 | $\mathrm{Ca}_{3} \mathrm{PO}_{4}(\mathrm{aq}) \rightarrow 3 \mathrm{Ca}^{2+}(\mathrm{aq})+\mathrm{PO}_{4}^{3-}(\mathrm{aq})$ <br> Explains that $\mathrm{Ca}_{3} \mathrm{PO}_{4}$ dissociates to give: <br> - $\mathrm{PO}_{4}^{3-}$, which is the conjugate base formed from the weak $3^{\text {rd }}$ ionisation of phosphoric acid <br> - Relatively strong conjugate base and will react with water as a base: $\mathrm{PO}_{4}^{3-}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{OH}^{-}(a q)+\mathrm{HPO}_{4}^{2-}(a q)$ <br> - $\quad \mathrm{Ca}^{2+}$ is a spectator ion and will not react with water |
| :---: | :---: |
| 1 | Identifies salt is basic |

2a.
$\square$
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{NaCH}_{3} \mathrm{COO}(\mathrm{aq})$

## HW AnSWERS

b.

| 1 | Calculates moles of sodium hydroxide delivered |
| :---: | :---: |
| $n(\mathrm{NaOH})=0.0176 \times 0.1=0.00176$ |  |
| 1 | Determines moles of acetic acid <br> 1 |
| $n(\mathrm{NaOH})=n\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=0.00176$ <br> 1 | $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=\frac{0.00176}{0.025}=0.0704 \mathrm{M}$ |

c.

| $\mathbf{1}$ | Identifies salt formed from the reaction between a weak acid and strong base is a <br> basic salt |
| :---: | :--- |
| $\mathbf{1}$ | Identifies phenolphthalein as the appropriate indicator |

$3 a$.

| $\mathbf{1}$ | Identifies error is the rinsing of the conical flask with acid solution in step 3 |
| :---: | :--- |
| $\mathbf{1}$ | Suggests that the conical flask should only be rinsed with distilled water |

b.

Explains that rinsing the conical flask with acid introduces EXTRA moles of acid 1 into the reaction, resulting in more moles of base being needed for complete neutralisation

1
Identifies that there is a resultant overestimation of acid concentration

| 1 | Writes a generalised equation of the reaction AND calculates the moles of <br> ammonia delivered: |
| :--- | :--- |
|  | $H_{3} X(a q)+3 N H_{3}(a q) \rightarrow\left(N H_{4}\right)_{3} X(a q)$ <br> $n\left(N H_{3}\right)=0.035 \times 0.105=0.003675$ |
| 1 | Calculates the concentration of triprotic acid <br> $n($ triprotic $a c i d)=\frac{n\left(N H_{3}\right)}{3}=\frac{0.003675}{3}=0.001225$ <br> $[$ triprotic $a c i d]=\frac{0.001225}{0.023}=0.05326 \ldots \approx 0.053(2 s f)$ |


| $\mathbf{1}$ | Identifies curve represents titration between weak base and strong acids |
| :---: | :--- |
| $\mathbf{1}$ | Explains that pH starts moderately high due to the weak base in the conical flask, <br> and that as acid is added and neutralisation occurs, there is a steep but fleeting <br> drop in pH which is stabilised as a buffer forms with the weak base and its <br> conjugate acid |
| $\mathbf{1}$ | Explains that as acid continues to be added, the pH will decrease rapidly once the <br> reaction reaches the equivalence point due to pH being a logarithmic function, <br> meaning any small amount of acid creates a large change in pH immediately after <br> the equivalence point |
| $\mathbf{1}$ | Explains that as more strong acid is added the pH flattens out at a very low value <br> and does not change substantially |

## HW AnSWERS

6. 

| 1 | Calculates moles of $\mathrm{NaOH}{ }_{n(\mathrm{NaOH})=0.01 \times 0.01=0.0001}$ |
| :---: | :---: |
| $\mathbf{1}$ | Calculates the moles of sulfuric acid <br> $2 \mathrm{NaOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+\mathrm{Na}_{2} \mathrm{SO}_{4}(a q)$ <br> $n\left(\mathrm{H}_{2} \mathrm{SO}_{4}\right)=\frac{(\mathrm{NaOH})}{2}=0.0005$ |
| $\mathbf{1}$ | Calculates volume of average titre <br> $V\left(\mathrm{H}_{2} \mathrm{SO}_{4}\right)=\frac{0.00005}{0.05}=0.001$ <br> $\therefore 1 \mathrm{~mL}$ |

7. 

| $\mathbf{1}$ | Identifies A is distilled water |
| :---: | :--- |
| $\mathbf{1}$ | Explains A is distilled water as pH just changes purely logarithmically |
| $\mathbf{1}$ | Identifies B is an ACIDIC buffer solution |
| $\mathbf{1}$ | Explains B is an acidic buffer solution as the pH remains relatively constant <br> throughout and is likely a weak acid/conjugate base buffer as its initial buffer pH <br> is acidic |
| $\mathbf{1}$ | Identifies C is a strong base |
| $\mathbf{1}$ | Explains that C is titration curve between a strong acid and strong base, with base <br> in conical flask, as the pH starts relatively high and there is no 'steep but fleeting' <br> drop in pH in the beginning |

8. 

a.

| 1 | Identifies that the titration is between a weak acid and weak base |
| :---: | :--- |
| 1 | The indicator chosen changes pH around 7-9. This changes colour around the flat region <br> of the titration curve prior to the equivalence point. This is another source of significant <br> deviation in the observed endpoint because a small amount of titre could change the <br> colour greatly. |
| 1 | The titration between a weak acid and a weak base does not have a steep change in pH |
| This can make it difficult to observe a change in pH and cause significant deviation from <br> when the endpoint is recorded which results in unreliability |  |
| NOTE: I think the marks should be allocated as: $3 / 3$ for 2 reasons and 2 good links to reliability, <br> $2 / 3$ for 2 reasons and 1 good link to reliability and $1 / 3$ for 1 reason and 1 link to reliability or 2 <br> reasons and no links to reliability |  |

b.

1
The titration will never be reliable no matter which indicator is used because the change in pH never occurs steeply and there will always be variation in the endpoint and hence titre recorded.

## HW AnSWERS

9. 

| 1 | The pH is initially moderately low because acetic acid is a weak acid. As the base is added, <br> the pH increases dramatically before quickly becoming less steep. This decrease in rate is <br> caused by the creation of a buffer system between $\mathrm{CH}_{3} \mathrm{COOH}$ and $\mathrm{CH}_{3} \mathrm{COO}^{-}$which resists <br> the change in pH. |
| :---: | :--- |
| 1 | After 25 mL of base has been added, the equivalence point is reached. This results in a <br> sharp change in pH because all of the $\mathrm{H}^{+}$has been used up and now $\mathrm{OH}^{-}$ions are in excess. |
| 1 | As the base is added in excess at 40 mL , the pH flattens out at a very high value and <br> does not change that much from there because any changes to [OH |
| Note: It's not necessary to identify the base as a strong base here but students probably will. |  |

10. 

| 1 | Chooses NaOH (strong base). <br> $\mathrm{Ba}(\mathrm{OH})_{2}$ does not ionise completely hence NaOH is the strongest and most likely <br> identity of the base <br> AND <br> $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ |
| :---: | :--- |
| 1 | Mol of acid reacted with base: $0.65 \times 0.02 \mathrm{LL}=0.013 \mathrm{~mol}$ <br> 0.013 mol $=$ mol base reacted |
| 1 | Concentration base $=0.013 / 0.025 \mathrm{~L}=0.52 \mathrm{~mol} / \mathrm{L} \mathrm{NaOH}$ |

11. 

a.

| 1 | $\begin{aligned} & \mathrm{Na}_{2} \mathrm{CO}_{3}(\mathrm{aq})+2 \mathrm{HCl}(\mathrm{aq}) \rightarrow 2 \mathrm{NaCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{CO}_{2}(\mathrm{~g}) \\ & \mathrm{n}\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)=2.5 \mathrm{O} / 106=0.0235 \mathrm{~mol} \mathrm{Na} \\ & 2 \\ & \mathrm{CO}_{3} \\ & 0.0235 \mathrm{~mol} \mathrm{Na}_{2} \mathrm{CO}_{3} \text { in } 250 \mathrm{~mL} \text { of solution } \end{aligned}$ <br> Therefore, <br> $0.00235 \mathrm{~mol} \mathrm{Na} 2_{2} \mathrm{CO}_{3}$ in 25 ml aliquot |
| :---: | :---: |
| 1 | $\begin{aligned} & \mathrm{Na}_{2} \mathrm{CO}_{3}: \mathrm{HCl} \\ & 1: 2 \\ & \mathrm{n}(\mathrm{HCl})=0.0047 \mathrm{~mol} \\ & \mathrm{c}(\mathrm{HCl})=0.0047 / 0.0195=0.241 \mathrm{~mol} / \mathrm{L} \end{aligned}$ |

## HW AnSWERS

b.

c.

| 1 | Matthew has read it wrong. He needs to read from the bottom of the meniscus. He would <br> obtain a reading of 19.7 mL. |
| :---: | :--- |
| 1 | This makes the titration inaccurat because he has some difference in the number of <br> significant figures to which the actual value of the concentration is known. |
| 1 | From the question, it is safe to assume he has made the same mistake 3 times. This has <br> no effect on reliability since it is consistently away from the correct reading |

d.

Matthew has been reading the burette to produce a lower titre than what is actually happening ( 19.5 mL instead of 19.7 mL ). Because the concentration of HCl is given as $\mathrm{mol} /$ volume, decreasing the volume gives a higher concentration than the actual HCl .

## HW AnSWERS

T elevote

