## SECTION 4

Because of the prevalence and importance of acids, they Have been used and studied for hundreds of years. Over time, the definitions of acid and base have been refined.

Outline the historical development of ideas about acids including those of:

- Lavoisier
- Davy
- Arrhenius


## HISTORICAL DEVELOPMENT OF IDEAS ABOUT ACIDS

## LAVOISIER (1776)

Definition: He defined an acid as a non-metal compound containing oxygen.
Advantage: Recognised that acidic properties were a result of the composition of the substance.

Disadvantage: There are many acidic compounds that do not meet this definition (e.g. HCl) and many non-acidic compound that do meet it ( CO and $\mathrm{N}_{2} \mathrm{O}$ are not acids)

## DAVY (1810)

Definition: He defined acids as substances containing 'replaceable hydrogen'.
Advantage: Recognised that hydrogen was important to the activity of acids.
Disadvantage: However, some substances contained replaceable hydrogen but were not acids. For example, sugar reacts with metals and bases to form $\mathrm{H}_{2}$ but is not an acid.

## ARRHENIUS (1884)

## Definition:

- Acids ionise in solution to produce $\mathrm{H}^{+}$.
- Base is a substance producing $\mathrm{OH}^{-}$
$\mathrm{HCl}_{(\mathrm{g})} \rightarrow \mathrm{H}^{+}{ }_{(\mathrm{aq})}+\mathrm{Cl}_{(\mathrm{aq})}$
Advantage: Explained why acidic solutions conduct electricity and explained the range of acids we can observe.

Disadvantage: Definition requires that water be a solvent, so excludes some acid-base reactions, does not explain why some salts are acidic/basic (such as $\mathrm{NaCH}_{3} \mathrm{COO}$ and metal oxides such as MgO ), $\mathrm{H}^{+}$is a proton and sub atomic particles are not stable in solution.

## BRÖNSTED-LOWRY (1923):

- An acid is a proton donor.
- A base is a proton acceptor.

This theory removed the difficulty of having protons free in solution, as in water an acid will donate a proton directly to water.
$\mathrm{HCl}_{(\mathrm{g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}+\mathrm{Cl}_{(\mathrm{aq})}$
Also demonstrated that reactions did not require water specifically
$\mathrm{HCl}_{(\mathrm{g})}+\mathrm{NH}_{3(\mathrm{~g})} \rightarrow \mathrm{NH}_{4}{ }_{(\mathrm{s})}+\mathrm{Cl}_{(\mathrm{s})}^{-}$

## OUTLINE THE BRÖNSTED-LOWRY THEORY OF ACIDS AND BASES

Gather and process information from secondary sources to trace developments in understanding and describing acid/base reactions.

According to the Brönsted-Lowry theory, if a substance has greater tendency to give up protons than the solvent, then it is an acid in the solvent. If the substance has greater tendency to accept protons than the solvent, it is a base in the solvent.

QUESTION 31 (HSC 2002:7)
What did the Brönsted-Lowry definition of acids identify that made it a significant improvement over earlier definitions?

A Acids contain hydrogen.
B Acids are proton donors.
C Acids contain oxygen.
D Acids are electron-pair acceptors.
QUESTION 32 (HSC 2004:5)
Which statement best represents Davy's definition of an acid?
A Acids contain oxygen.
B Acids are proton donors.
C Acids contain replaceable hydrogen.
D Acids ionise in solution to form hydrogen ions.

## QUESTION 33 (HSC 2006:11)

In 1884, Svante Arrhenius proposed a definition for acids. His definition was soon accepted as superior to that put forward by earlier chemists.

Why was Arrhenius' definition seen as a major improvement?
A It explained why some acids do not contain oxygen.
B It showed how the solvent can affect the strength of an acid.
C It showed the relationship between pH and the concentration of $\mathrm{H}^{+}$ions.
D It could be used to explain why some acids are strong and others are weak.

QUESTION 34 (HSC 2011:29a)
Justify the continued use of the Arrhenius definition of acids and bases, despite the development of the more sophisticated Brönsted-Lowry definition. (3 marks)

## Solution

## DESCRIBE THE RELATIONSHIP BETWEEN AN ACID AND ITS CONJUGATE BASE AND A BASE AND ITS CONJUGATE ACID

An acid gives up a proton to form its conjugate base.
A base accepts a proton to form its conjugate acid.
For example consider: $\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})} \rightleftharpoons \quad \mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{OH}_{(\mathrm{aq})}^{-}$

- $\mathrm{H}_{2} \mathrm{O}$ acts as an acid (proton donor) with $\mathrm{OH}^{-}$its conjugate base.
- $\mathrm{CH}_{3} \mathrm{COOH}$ is an acid with $\mathrm{CH}_{3} \mathrm{COO}^{-}$its conjugate base.

The conjugate of a weak substance is weak, and the conjugate of a strong substance is too weak to react with the solvent, this is a general statement NOT a law.

When Brönsted and Lowry proposed their theories they established a relationship between acids, bases and their conjugate pairs. This definition recognised the important role of the solvent in determining acidity or basicity. Acids ionise in water due to interaction with water molecules. The acidic proton is donated to the water molecule (a base) to form the hydronium ion (the conjugate base).

## IDENTIFY CONJUGATE ACID/BASE PAIRS

## CONJUGATE BASE:

Acid + water $\rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+$conjugate base
$\mathrm{HCl}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Cl}$
$\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{CH}_{3} \mathrm{COO}$

## CONJUGATE ACID:

Base + water $\rightarrow$ conjugate acid + OH-
$\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{4}++\mathrm{OH}$
$\mathrm{CO}_{3}{ }^{2-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCO}_{3}{ }^{-}+\mathrm{OH}^{-}$

## IDENTIFY AMPHIPROTIC SUBSTANCES AND CONSTRUCT EQUATIONS TO DESCRIBE THEIR BEHAVIOUR IN ACIDIC AND BASIC SOLUTIONS

Amphiprotic substances are a sub-group of amphoteric (substances which can behave as acids or bases) and can act as both a proton donor, and as a proton acceptor. (In basic conditions they tend to act as acids and vice-versa.)

An example of this is:

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\(\mathrm{HSO}_{4}^{-(\mathrm{aq})}{ }^{( }+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq)}) \rightleftharpoons \quad \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})^{+}}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}\)
\(\mathrm{HSO}_{4(\mathrm{aq})}^{-}+\mathrm{OH}_{(\mathrm{aq})} \rightleftharpoons \mathrm{SO}_{4}{ }^{2-}{ }_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{I})}\)
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Water and $\mathrm{HPO}_{4}^{-2}$ are also amphiprotic. Amphoteric substances are those that react with both acids and bases.

QUESTION 35 (HSC 2002:6)
Which is amphiprotic?
A $\mathrm{H}_{2} \mathrm{SO}_{4}$
B $\mathrm{NH}_{4}^{+}$
C $\mathrm{HCO}_{3}^{-}$
D $\mathrm{SO}_{4}^{2-}$

QUESTION 36 (HSC 2009:7)
What is the conjugate base of $\mathrm{HSO}_{4}{ }^{-}$?
A $\quad \mathrm{SO}_{3}{ }^{2-}$
B $\mathrm{SO}_{4}{ }^{2-}$
C $\mathrm{H}_{2} \mathrm{SO}_{4}$
D $\mathrm{HSO}_{3}{ }^{-}$

## QUESTION 37

Write an equation that shows the amphiprotic nature of:
(a) Water
(b) $\mathrm{HPO}_{4}^{2}$

## Solution

## IDENTIFY A RANGE OF SALTS WHICH FORM ACIDIC, BASIC OR NEUTRAL SOLUTIONS AND EXPLAIN THEIR ACIDIC, NEUTRAL OR BASIC NATURE

## ACIDIC SALTS

When a strong acid and weak base react to form a salt, the anion conjugate acid of the weak base acts as an acid (while the acid's conjugate is too weak) and thus the salt is acidic.
$\mathrm{NH}_{4}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \quad \rightleftharpoons \quad \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}$

## BASIC SALTS

The salt formed by a weak acid and a strong base is basic.
$\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{OH}_{(\mathrm{aq})}^{-}$

## NEUTRAL SALTS

If both the acid and base are strong, the resulting salt is neutral.

## CHOOSE EQUIPMENT AND PERFORM A FIRST-HAND INVESTIGATION TO IDENTIFY THE PH OF A RANGE OF SALT SOLUTIONS

pH of $0.25 \mathrm{~mol} / \mathrm{L}$ solutions of some common salts:

| Salt | $\mathbf{p H}$ | Salt | $\mathbf{p H}$ |
| :--- | :---: | :--- | :---: |
| Sodium Chloride, NaCl | 7.0 | Potassium nitrate, $\mathrm{KNO}_{2}$ | 8.3 |
| Potassium Nitrate, $\mathrm{KNO}_{3}$ | 7.0 | Sodium acetate, $\mathrm{CH}_{3} \mathrm{COONa}$ | 9.1 |
| Sodium Sulfate, $\mathrm{Na}_{2} \mathrm{SO}_{4}$ | 7.0 | Potassium cyanide, KCN | 11.3 |
| Sodium hydrogen sulfate, $\mathrm{NaHSO}_{4}$ | 1.3 | Sodium carbonate, $\mathrm{Na}_{2} \mathrm{CO}_{3}$ | 11.8 |
| Potassium hydrogen oxalate, <br> $\mathrm{KHC}_{2} \mathrm{O}_{4}$ | 2.4 | Ammonium Nitrate, $\mathrm{NH}_{4} \mathrm{NO}_{3}$ | 4.8 |

## Note:

To establish the likely nature of a salt either identify the nature of the parent acid/base or identify the likelihood of ions reacting with water:

QUESTION 38 (HSC 2006:21)
You performed a first-hand investigation to identify the pH of a range of salt solutions.
(a) Identify an acidic salt you used.
(b) Explain the acidic nature of the salt you selected. Include a balanced chemical equation in your answer.

QUESTION 39 (HSC 2010:18)
Chromate and dichromate ions form an equilibrium according to the following equation.

$$
2 \mathrm{CrO}_{4}{ }^{2-}(\mathrm{aq})+2 \mathrm{H}^{+}(a q) \rightleftharpoons \mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}(a q)+\mathrm{H}_{2} \mathrm{O}(\Lambda)
$$

Which solution would increase the concentration of the chromate ion $\left(\mathrm{CrO}_{4}{ }^{2-}\right)$ when added to the equilibrium mixture?

A Sodium nitrate
B Sodium chloride
C Sodium acetate
D Ammonium chloride

## BUFFERS

## QUALITATIVELY DESCRIBE THE EFFECT OF BUFFERS WITH REFERENCE TO A SPECIFIC EXAMPLE IN A NATURAL SYSTEM.

A buffer is a solution composed of roughly equal molar amounts of a weak acid and its conjugate base. Usually this is made by mixing a weak acid (e.g. acetic acid) with its salt (e.g. sodium acetate).

Buffer solutions are able to absorb the addition of acid or base without altering the pH of the solution. Each buffer solution keeps the pH at a particular level and a different buffer system is required if a different pH is desired.

## A common buffer solution in a natural system is the $\mathrm{H}_{2} \mathrm{CO}_{3}$ and the $\mathrm{HCO}_{3}{ }^{-}$ion in blood.

The relevant equations are:
$\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{2} \mathrm{CO}_{3}$ This occurs as $\mathrm{CO}_{2}$ from the air dissolves in blood.
$\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCO}_{3}{ }^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
As there is approximately equal molar amounts of $\mathrm{H}_{2} \mathrm{CO}_{3}$ and $\mathrm{HCO}_{3}{ }^{-}$a buffer system is established. This system is then able to absorb the addition of acid or base, keeping the pH of blood approximately constant and allowing the enzymes and metabolic processes in blood to have stable pH conditions.

- Adding acid shifts the equilibrium to the left to absorb excess $\mathrm{H}_{3} \mathrm{O}^{+}$.
- Adding base $\left(\mathrm{OH}^{-}\right)$effectively removes $\mathrm{H}_{3} \mathrm{O}^{+}$and the equilibrium shifts right to replace it, keeping the pH constant.


## QUESTION 40 (HSC 2005:9)

Which of the following pairs would form a buffer solution?
A $\mathrm{HCl}_{(a q)} / \mathrm{Cl}_{(a q)}^{-}$
B $\quad \mathrm{H}_{2} \mathrm{PO}_{4(a q)}^{-} / \mathrm{PO}_{4(a q)}^{3-}$
C $\mathrm{H}_{2} \mathrm{SO}_{4(a q)} / \mathrm{HSO}_{4(a q)}^{-}$
D $\mathrm{CH}_{3} \mathrm{COOH}_{(a q)} / \mathrm{CH}_{3} \mathrm{COO}_{(a q)}^{-}$

QUESTION 41 (HSC 2011:25)
Explain the role of the conjugate acid/base pair, $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-} / \mathrm{HPO}_{4}{ }^{2-}$, in maintaining the pH of living cells. Include chemical equations in your answer. (3 marks)

## Solution

## IDENTIFY NEUTRALISATION AS A PROTON TRANSFER REACTION WHICH IS EXOTHERMIC

Neutralisation is a proton transfer reaction (protons are transferred from one species to another to form a salt). All neutralisation reactions are exothermic.

Acid + base $\rightarrow$ water + salt ( $H$ )
e.g. In the neutralisation of ammonia by nitric acid:

$$
\mathrm{HNO}_{3(\mathrm{aq})}+\mathbf{N H}_{3(\mathrm{aq})} \rightarrow \mathbf{N H}_{4^{+}}{ }_{(\mathrm{aq})}+\mathbf{N O}_{3^{-}(\mathrm{aq})} \quad(\quad H)
$$

The acid transfers a proton to ammonia (to form the $\mathrm{NH}_{4}{ }^{+}$ion).
Neutralisation is a proton transfer reaction in which an acid and a base react to form a salt and water. Neutralisation reactions are exothermic. The amount of heat liberated when neutralisation occurs depends on the strengths of the acid and the base.

The amount of heat released can be calculated using calorimetry measurements and the $\Delta \mathrm{H}$ $=\mathrm{mc} \Delta \mathrm{T}$ equation (similar to finding heat of combustion as done earlier).

QUESTION 42 (HSC 2011:29b)
Why does the neutralisation of any strong acid in an aqueous solution by any strong base always result in a heat of reaction of approximately $-57 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ?

## Solutions

## ANALYSE INFORMATION FROM SECONDARY SOURCES TO ASSESS THE USE OF NEUTRALISATION REACTIONS AS A SAFETY MEASURE OR TO MINIMISE DAMAGE IN ACCIDENTS OR CHEMICAL SPILLS

- Neutralisation can be used as a safety measure or to minimise damage in spills but only weak acids or bases should be used.
- Sodium hydrogencarbonate $\left(\mathrm{NaHCO}_{3}\right)$ is used to clean up industrial acid spills because it contains the amphiprotic ion $\mathrm{HCO}_{3}$.


## ADVANTAGES OF $\mathrm{NaHCO}_{3}$

1. Can react with an acid or a base, so it is not necessary to know precise nature of the spill in advance.
with acid:
$\mathrm{NaHCO}_{3(\mathrm{~s})}+\mathrm{H}^{+}{ }_{(\text {(qq) }} \rightarrow \mathrm{Na}^{+}{ }_{(\text {aq })}+\mathrm{CO}_{2(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$
with base: $\quad \mathrm{NaHCO}_{3(\mathrm{~s})}+\mathrm{OH}^{-}{ }_{(\mathrm{aq})} \rightarrow \mathrm{Na}^{+}\left(\mathrm{aq)}+\mathrm{CO}_{3}{ }^{2-}\left(\mathrm{aq)}+\mathrm{H}_{2} \mathrm{O}_{(l)}\right.\right.$
2. Cheap, so easy to store in large quantities.
3. Solid and relatively stable so can be stored for long periods of time.
4. Can be used in excess, as adding extra solid will not make a spill worse.
5. Non-hazardous, so will not make a spill more dangerous .

## DISADVANTAGES OF NaHCO

1. If the spill is acidic, $\mathrm{CO}_{2}$ can build up if the area is not ventilated, and it can cause asphyxiation.
2. Reactions with acids and bases are exothermic, there is potential for large amounts of heat to build up.

Before acidic waste can be discharged from factories into waterways it needs to be neutralised and diluted. This ensures that excessive heat does not build up in the waterways (neutralisation is exothermic) and that a high concentration of ions is not discharged.

QUESTION 43 (HSC 2007:25)
Sodium hydrogen carbonate, $\mathrm{NaHCO}_{3}$, is commonly used to neutralise chemical spills that are a potential hazard to the environment. Assess the effectiveness of $\mathrm{NaHCO}_{3}$ in this role, with reference to its chemical properties. (5 marks)

## Solution

## VOLUMETRIC ANALYSIS

Volumetric analysis is a quantitative technique that involves reactions in solution. It requires the determination of the volume of a standardised solution that reacts with the substance (or 'unknown') being analysed. A technique called titration which is used in the analysis. In acid-base analysis the reaction involves a neutralisation reaction.

Volumetric analysis requires that one solution must have an accurately known concentration. This solution is called the standard solution. The standard solution may be either a primary standard or a secondary standard. The preparation of primary standards is discussed below.

## DESCRIBE THE CORRECT TECHNIQUE FOR CONDUCTING TITRATIONS AND PREPARATION OF STANDARD SOLUTIONS

In preparing a standard solution of definite concentration the chemical to be used (the 'Primary standard') must satisfy the following criteria:
(a) It must be a water-soluble solid.
(b) It must have high purity.
(c) It must not lose or gain water or react with oxygen or carbon dioxide in the air.
(d) It must have a high molecular mass (reducing the effect of measurement errors).

The most common substances to be used as Primary standards included sodium carbonate $\left(\mathrm{Na}_{2} \mathrm{CO}_{3}\right)$ and oxalic acid $\left(\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}\right)$.

Sodium Hydroxide is NEVER used as a primary standard. This is because it undergoes two reactions when exposed to air, both of which affect the mass of the sodium hydroxide. Firstly, sodium hydroxide is deliquescent, which means it absorbs water from the air. Secondly, sodium hydroxide reacts with carbon dioxide in the air.

## WHAT IS A STANDARD SOLUTION?

- It is a solution whose concentration is accurately known and is therefore able to be used in titrations to determine an unknown solution concentration.
- It is a solution made using a primary standard or one whose concentration has been accurately determined by reaction against another standard solution.


## PREPARING A STANDARD SOLUTION.

1. Rinse volumetric flask with distilled H 2 O .
2. Weigh PRIMARY STANDARD in a small beaker.
3. Dissolve PRIMARY STANDARD in small volume of distilled $\mathrm{H}_{2} \mathrm{O}$.
4. Pour solution into volumetric flask.
i. Use filter funnel.
ii. Rinse beaker and funnel several times with distilled $\mathrm{H}_{2} \mathrm{O}$ and add rinsings to flask.
iii. Invert to mix the solution, until all solid is dissolved.
5. Add distilled $\mathrm{H}_{2} \mathrm{O}$ until bottom of meniscus reaches calibration line. Place lid on and invert to mix solution.

## EXPLAIN THE PROCESS OF TITRATING

In this process the concentration of a solution is accurately determined by measuring exactly how much of the standard solution is required to neutralise a known volume of it. This is because neutralisation occurs when the number of moles of acid is stoichiometrically equal to the number of moles of base. This is called the EQUIVALENCE POINT.

The problem is that acid solutions are colourless, base solutions are colourless and so is the product solution. How can we tell when the reaction has reached the equivalence point? The answer is to use an appropriate indicator. The indicator should be chosen so that it changes colour at the pH of the equivalence point. The point when the indicator changes colour is called the END POINT. The goal is the choose an indicator where the end point will be same as the equivalence point.

| Indicator | Colour Change at different pH levels |
| :--- | :--- |
| Methyl orange | Red below 3.1 - Yellow above 4.4 |
| Bromothymol Blue | Yellow below 6.2 - Green around 7-Blue above 7.6 |
| Phenolphthalein | Colourless below 8.3 - Red above 10.0 |

NOTE: pH meters improve accuracy, but appropriate indicators are a very useful alternative which do not need to be calibrated or checked.

## METHOD FOR TITRATION

1. Pour standard solution into a clean burette using a clean funnel. Ensure solution goes above 0 mL line.
2. Run excess solution out of the burette and discard (ensure new level is 0 mL ).
3. Rinse a clean conical flask with distilled water.
4. Add the unknown solution to the flask by careful measurement using a pipette (previously rinsed with the unknown solution) and place it under the burette.
5. Add 2-5 drops of an appropriate indicator.
6. Slowly add the standard solution in the burette to the flask, swirling continuously until the indicator just changes colour (end point, and hopefully the equivalence point).
7. Read volume of burette.
8. Repeat three times. Calculate average. Calculate required concentration of unknown.

QUESTION 44 (HSC 2006:9)
Which statement best describes the equivalence point in a titration between a strong acid and a strong base?

A The point at which the first sign of a colour change occurs.
B The point at which equal moles of acid and base have been added together.
C The point at which equal moles of $\mathrm{H}^{+}$ions and $\mathrm{OH}^{-}$ions have been added together.
D The point at which the rate of the forward reaction equals the rate of the reverse reaction.

QUESTION 45 (HSC 2002:8)
In a titration, an acid of known concentration is placed in a burette and reacted with a base that has been pipetted into a conical flask.


What should each piece of glassware be rinsed with immediately before the titration?

| Burette | Pipette | Conical Flask |  |
| :--- | :--- | :--- | :--- |
| A | Acid | Base | Water |
| B | Water | Water | Water |
| C | Acid | Base | Base |
|  | Water | Water | Base |
|  |  |  |  |

QUESTION 46 (HSC 2003:14)
In a titration of a strong base with a strong acid, the following procedure was used:

1. A burette was rinsed with water and then filled with the standard acid.
2. A pipette was rinsed with some base solution.
3. A conical flask was rinsed with some base solution.
4. A pipette was used to transfer a measured volume of base solution into the conical flask.
5. Indicator was added to the base sample and it was titrated to the endpoint with the acid.

Which statement is correct?
A The calculated base concentration will be correct.
B The calculated base concentration will be too low.
C The calculated base concentration will be too high.
D No definite conclusion can be reached about the base concentration.

## 4 STEPS TO SUCCESS WITH TITRATION CALCULATIONS

1. Find the moles used of the known solution (moles $=$ conc. x volume).
2. Find the ratio of reactants (usually using a balanced chemical equation).
3. Use this ratio to find the moles of the unknown.
4. Calculate the concentration of the unknown solution (conc. = mole / volume).

The formula to use: ( $\mathrm{C}=$ concentration in $\mathrm{mol}^{-1}, \mathrm{n}=$ number of moles, $\mathrm{V}=$ volume in L )


Remember The formula to use if dilutions are involved: $\mathrm{C}_{1} \mathrm{~V}_{1}=\mathrm{C}_{2} \mathrm{~V}_{2}$

Sometimes the formula $\mathrm{C}_{\mathrm{A}} \mathrm{V}_{\mathrm{A}} / \mathrm{a}=\mathrm{C}_{\mathrm{B}} \mathrm{V}_{\mathrm{B}} / \mathrm{b}$ is taught. However, it is preferable to use the four steps outlined above, especially for back titrations.

QUESTION 47 (HSC 2008:28)
A standard solution was prepared by dissolving 1.314 g of sodium carbonate in water.
The solution was made up to a final volume of 250.0 mL .
(a) Calculate the concentration of the sodium carbonate solution. (2 marks)

This solution was used to determine the concentration of a solution of hydrochloric acid. Four 25.00 mL samples of the acid were titrated with the sodium carbonate solution. The average titration volume required to reach the end point was 23.45 mL .
(b) Write a balanced equation for the titration reaction. (1 mark)
(c) Calculate the concentration of the hydrochloric acid solution. (3 marks)

QUESTION 48 (HSC 2010:28)
The flowchart shown outlines the sequence of steps used to determine the concentration of an unknown hydrochloric acid solution.


Describe steps A, B and C including correct techniques, equipment and appropriate calculations. Determine the concentration of the hydrochloric acid. (8 marks)

## Solution

QUESTION 49 (HSC 2004:16)
(a) Outline the procedure you would use to prepare a standard solution of sodium hydrogen carbonate from solid hydrogen carbonate. (3 marks)
(b) Calculate the mass of solid sodium hydrogen carbonate required to make 250 mL of $0.12 \mathrm{~mol} \mathrm{~L}^{-1}$ solution. (2 marks)

QUESTION 50 (HSC 2003:23)
25.0 mL of $0.12 \mathrm{~mol} \mathrm{~L}^{-1}$ standard barium hydroxide solution was titrated with nitric acid. The results are recorded in the table.

| Titration | Volume of nitric acid used (mL) |
| :---: | :---: |
| 1 | 20.4 |
| 2 | 18.1 |
| 3 | 18.2 |
| 4 | 18.1 |

(a) Write a balanced chemical equation for the reaction of barium hydroxide with nitric acid. (1 mark)
(b) Calculate the concentration of the nitric acid. (3 marks)

QUESTION 51 (HSC 2001:23)
A household cleaning agent contains a weak base of general formula NaX .1 .00 g of this compound was dissolved in 100.00 mL of water. A 20.0 mL sample of the solution was titrated with $0.1000 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acid and required 24.4 mL of the acid for neutralisation.
(a) What is the Brönsted-Lowry definition of a base? (1 mark)
(b) What is the molar mass of this base? (3 marks)

QUESTION 52 (HSC 2011:26)
A manufacturer makes lemon cordial by mixing flavouring, sugar syrup and citric acid.
The concentration of the citric acid is determined by titration with NaOH .
The sodium hydroxide solution is prepared by dissolving 4.000 g of NaOH pellets in water to give 1.000 L of solution. This solution is standardised by titrating 25.00 mL with a $0.1011 \mathrm{~mol} \mathrm{~L}^{-1}$ standardised solution of HCl . The average titration volume is found to be 24.10 mL .

To analyse the lemon cordial 50.00 mL of the cordial is diluted to 500.0 mL . Then 25.00 mL of the diluted solution is titrated with the NaOH solution to the phenolphthalein endpoint.

The following data were collected during one of the analysis runs of the lemon cordial.

| Titration \#1 volume | 26.55 mL |
| :--- | :--- |
| Titration \#2 volume | 27.25 mL |
| Titration \#3 volume | 27.30 mL |
| Titration \#4 volume | 27.20 mL |

(a) Why is the calculated concentration of the standardised NaOH solution different from the concentration calculated using the mass given, assuming no human error occurred? (2 marks)
(b) Determine the concentration of citric acid in the lemon cordial. (4 marks)

QUESTION 53 (HSC 2009:14)
Citric acid, the predominant acid in lemon juice, is a triprotic acid. A student titrated 25.0 mL samples of lemon juice with $0.550 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{NaOH}$. The mean titration volume was 29.50 mL . The molar mass of citric acid is $192.12 \mathrm{~g} \mathrm{~mol}^{-1}$.

What was the concentration of citric acid in the lemon juice?
A $\quad 1.04 \mathrm{~g} \mathrm{~L}^{-1}$
B $\quad 41.6 \mathrm{~g} \mathrm{~L}^{-1}$
C $\quad 125 \mathrm{~g} \mathrm{~L}^{-1}$
D $\quad 374 \mathrm{~g} \mathrm{~L}^{-1}$

## QUESTION 54

## Back Titration

2.479 L of ammonia gas (at $25^{\circ} \mathrm{C}, 100 \mathrm{kPa}$ ) is bubbled into a conical flask containing 200 mL of $0.500 \mathrm{molL}^{-1} \mathrm{H}_{2} \mathrm{SO}_{4}$. All the ammonia was allowed to react.
(a) Write a balanced equation for the reaction.
(b) Calculate the number of mole of $\mathrm{H}_{2} \mathrm{SO}_{4}$ that did not react.
(c) The excess $\mathrm{H}_{2} \mathrm{SO}_{4}$ was titrated with $2.0 \mathrm{molL}^{-1} \mathrm{NaOH}_{(\mathrm{aq})}$. What volume of NaOH is required to reach EP?

## Solution

QUESTION 55 (HSC 2005:24)
An antacid tablet is known to contain calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$. To determine the mass of calcium carbonate in the tablet, the following procedure was used:

- The tablet was crushed and then placed in a beaker.
- A pipette was used to add 25.0 mL of $0.600 \mathrm{~mol} \mathrm{~L}^{-1}$ hydrochloric acid to the crushed tablet in the beaker.
- Once the reaction between the calcium carbonate and hydrochloric acid had stopped, phenolphthalein indicator was added to the reaction mixture.
- A teflon-coated burette was then used to add $0.100 \mathrm{~mol} \mathrm{~L}^{-1}$ sodium hydroxide to the beaker to neutralise the excess hydrochloric acid.
- The phenolphthalein changed from colourless to pink after 14.2 mL of the sodium hydroxide solution had been added.
(a) Write a balanced chemical equation for the reaction that occurred between the calcium carbonate in the tablet and the hydrochloric acid. (1 mark)
(b) How many moles of hydrochloric acid were added to the tablet? (1 mark)
(c) Calculate the mass of calcium carbonate in the original antacid tablet. (3 marks)


## NEUTRALISATION CURVES

A neutralisation curve describes the changes in pH that occur during an acid-base titration.
The general shape of the titration curve will depend upon which species is being added from the burette.
E.g. If the acid is being added from the burette to a base in the conical flask, the pH in the flask will decrease.


If the base is being added from the burette to an acid in the conical flask, the pH in the flask will increase.


The start and end points on the curve will depend upon the strengths of the acids and bases.

If an acid is present in the conical flask: The stronger (and more concentrated) the acid, the lower the initial pH .

If a base is present in the conical flask: The stronger (and more concentrated) the base, the higher the initial pH .

## Important Note:

To minimise the titration error (the difference in the volume between the endpoint and equivalence point of the reaction), the pH of the solution must change dramatically at the equivalence point. Furthermore, the pH must change sharply by several units across a small volume, so that the end point is sharp.


## CHOOSING AN APPROPRIATE INDICATOR

When a strong acid is used with a strong base the solution at equivalence will be neutral (a neutral salt is formed). Therefore an indicator that changes around pH 7 (bromothymol blue) is required.

When a strong acid is used with a weak base the solution at equivalence will be acidic (an acidic salt is formed). Therefore an indicator that changes below pH 7 (methyl orange) is required.

When a weak acid is used with a strong base the solution at equivalence will be basic (a basic salt is formed). Therefore an indicator that changes above pH 7 (phenolphthalein) is required.

Weak acid and weak base should not be performed. The curve is too broad for a clear end point to be seen.

QUESTION 56 (2003:15)
Which of the following graphs shows how pH will vary when dilute HCl is added to 100 ml of dilute natural buffer solution with an initial pH of 7.0 ?
(A)

(B)


(D)


QUESTION 57 (2009:21)
The graph shows changes in pH for the titrations of equal volumes of solutions of two monoprotic acids, Acid 1 and Acid 2.

(a) Explain the differences between Acid 1 and Acid 2 in terms of their relative strengths and concentrations. (3 marks)
(b) Name the salt produced by the reaction of an acid of the same type as Acid 2 with $\mathrm{KOH}(\mathrm{aq})$. (1 mark)
(c) Calculate the concentration of hydrogen ions when 20 mL of $\mathrm{KOH}(a q)$ has been added to Acid 1. (1 mark)
(d) Why would phenolphthalein be a suitable indicator for both titrations? (1 mark)

QUESTION 58 (HSC 2005:10)
A titration was conducted by adding NaOH from a teflon-coated burette to HCl in a conical flask. The pH in the flask was recorded during the titration and Curve A was produced.

Curve A


Volume of NaOH added ( mL )
The table shows appropriate indicators used to identify the equivalence point in titrations. For NaOH and HCl the appropriate indicator is bromothymol blue.

| Indicator | Acidic colour | Range of <br> colour change | Basic colour |  |
| :---: | :---: | :---: | :---: | :---: |
| Methyl orange |  | Red | $3.1-4.4$ | Yellow |
| Methyl red |  | Red | $4.4-6.2$ | Yellow |
| Bromothymol blue |  | Yellow | $6.0-7.6$ | Blue |
| Cresolphthalein |  | Colourless | $8.1-9.7$ | Red |
| Alizarin yellow |  | Yellow | $10.1-12.0$ | Red |

A second titration was conducted by adding NaOH to a different acid. The pH in the flask was recorded during the titration and Curve B was produced.


Volume of NaOH added ( mL )
What is the appropriate indicator for Curve B using the table?
A Methyl orange
B Methyl red
C Cresolphthalein
D Alizarin yellow

