Mass Spectrometry

A Level

C C C

with focus on time-of-flight

Mass spectrometry is a technique for studying chemical substances. High resolution mass spectrometry allows us to determine relative atomic or molecular masses to a high degree of precision. Some forms of mass spectrometry can also provide structural information which is useful for structure determination.

Part A Electron ionisation

A mass spectrometer relies on the presence of ions, which it is able to separate by their mass to charge ratio. However, many samples we wish to study are neutral. The instrument therefore needs to use an ionisation technique to form these ions within the sample. We will first consider **electron ionisation (EI)**. This involves firing high energy electrons at the vaporised sample in order to remove electrons.

Which of the following equations is an accurate description of this electron ionisation process:

- $\mathrm{X\,(g) \longrightarrow X^{-}\,(g) + e^{-}}$
- $\mathrm{X\,(g) + e^{-} \longrightarrow X^{-}\,(g)}$
- $\mathrm{X\,(g) + e^{-} \longrightarrow X^{+}\,(g) + 2\,e^{-}}$
- $\mathrm{X^{+}\,(g) + e^{-} \longrightarrow X\,(g)}$

Part B Fragmentation

Electron ionisation is a hard ionisation technique, which means it often results in fragmentation of the molecular ion formed initially. As a consequence, when applied to large molecules, the mass spectrum often contains many features corresponding to these lighter ions. This can be helpful for structure determination: for a given molecular structure, we can predict likely ways in which the molecular ion might fragment (e.g. through particular bonds breaking) and check whether this is consistent with the spectrum. That said, some of the fragmentations are far more complex than simple bond breaking and involve rearrangements. This can make it difficult to account for the formation of certain ions even if we confidently know the molecular structure already.

A student was thinking about fragmentation in mass spectrometers and hypothesised that if they saw a fragment feature 15 mass units lighter than the molecular ion, they should also see a feature due to an ion with mass 15. However, consulting some real spectra, they found that it is in fact common not to see ion pairs that "complement" each other like this. By carefully considering a single, simple fragmentation process occurring on a molecular ion, suggest why this might be.

Part C Electrospray ionisation

A softer ionisation technique, resulting in far less fragmentation than electron ionisation, is **electrospray ionisation**. There are a number of variations of this, but in one type, the neutral atom or molecule bonds to a proton (hydrogen ion).

Select the correct equation describing this process for sodium:

- $\mathrm{Na\,(g) + H^+\,(g) \longrightarrow Mg^+\,(g)}$
- $\mathrm{Na\,(g) + H^-\,(g) \longrightarrow [Na + H]^-\,(g)}$
- $\mathrm{Na\,(g) + H^+\,(g) \longrightarrow Ne^+\,(g)}$
- $\mathrm{Na\,(g) + H^-\,(g) \longrightarrow Ne^-\,(g)}$
- $\mathrm{Na\,(g) + H^-\,(g) \longrightarrow Mg^-\,(g)}$
- $\mathrm{Na\,(g) + H^+\,(g) \longrightarrow [Na + H]^+\,(g)}$

Part D Time-of-flight expression

In a time-of-flight (TOF) mass spectrometer, the ions formed are accelerated through a potential so that all singly-charged ions have the same kinetic energy, E. These ions then travel along a flight tube of length d before reaching the detector. The delay is a function of the mass of a given ion, m.

Derive a formula for the time it takes an ion to travel along the flight tube (the time of flight) as a function of E, d and m. Assume that all quantities are provided in SI units, so your formula does not need to take into account any conversion factors.

The following symbols may be useful: `E, d, m`

Part E Calculating molecular mass

Based on the above formula, ions of different mass take different amounts of time to travel through the spectrometer. Calculate, in kg, the mass of an ion X^+ that takes $7.55 \times 10^{-6}\,\mathrm{s}$ to travel through the $2.00\,\mathrm{m}$ drift region, assuming it was previously accelerated to a kinetic energy of $5.83 \times 10^{-15}\,\mathrm{J}$.

Part F Converting to atomic mass units

Convert the above mass of X^+ in kg to atomic mass units (amu) in which you more typically express the mass of atoms, molecules and ions in chemistry.

Part G Electron mass

To obtain the mass of the neutral species, X, we would actually need to add on the mass of an electron. Why is this not a particularly meaningful calculation for the above quantities?

Created for isaacphysics.org by Andrea Chlebikova

Lines in Mass Spectra

A Level P P P

Part A Chlorine

Which of the following could be an excerpt from the mass spectrum of chlorine?

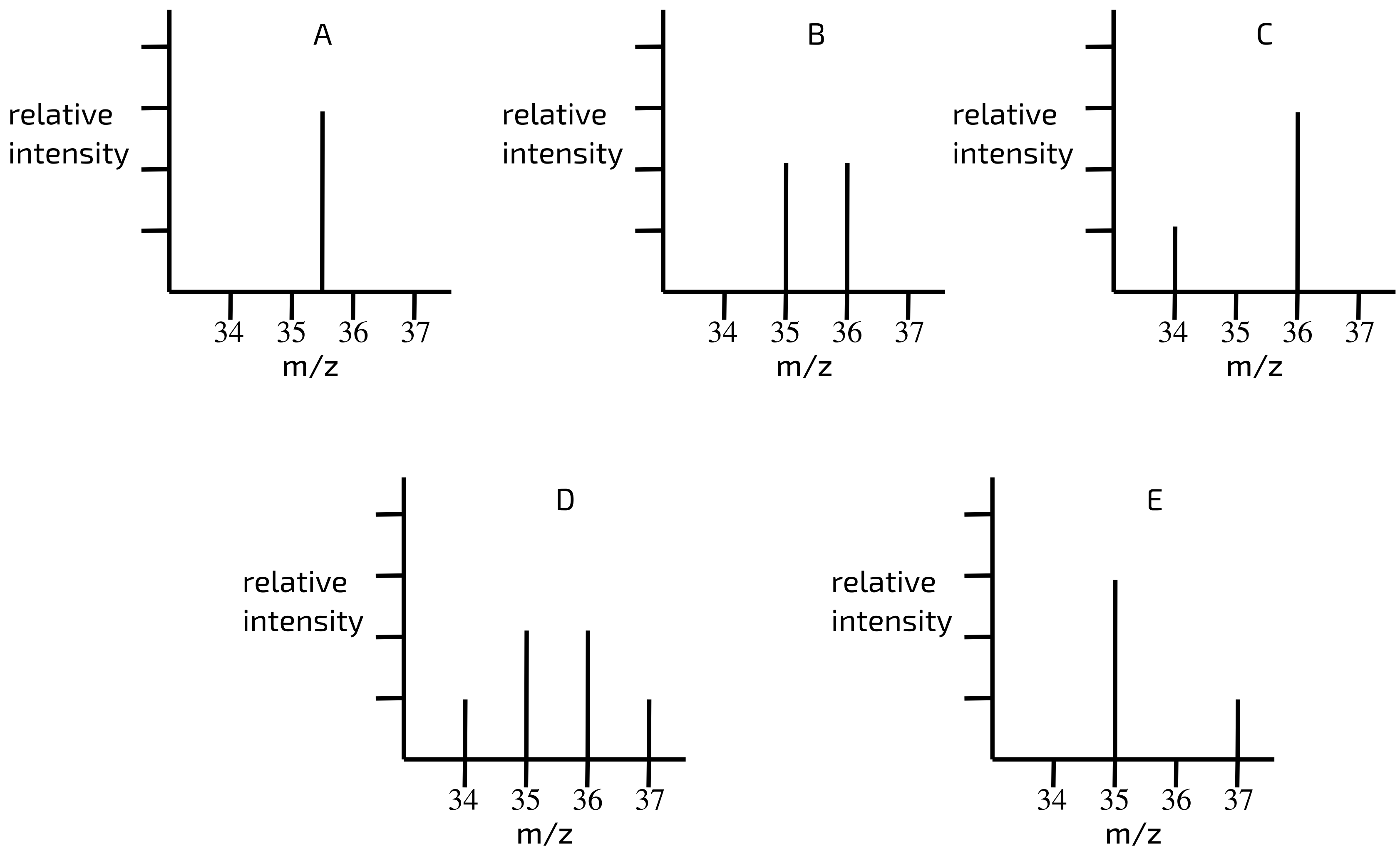

Figure 1: Mass Spectra

- A
- B
- C
- D
- E

Part B Bromine

Bromine occurs naturally as two isotopes, $^{79}\mathrm{Br}$ and $^{81}\mathrm{Br}$, in equal abundance.

The mass spectrum for $^{12}\mathrm{C}_2{}^1\mathrm{H}_4\mathrm{Br}_2$ is obtained. Select which of these resembles the mass spectrum for m/z values above 184 (the vertical axis should in each case be treated as relative intensity).

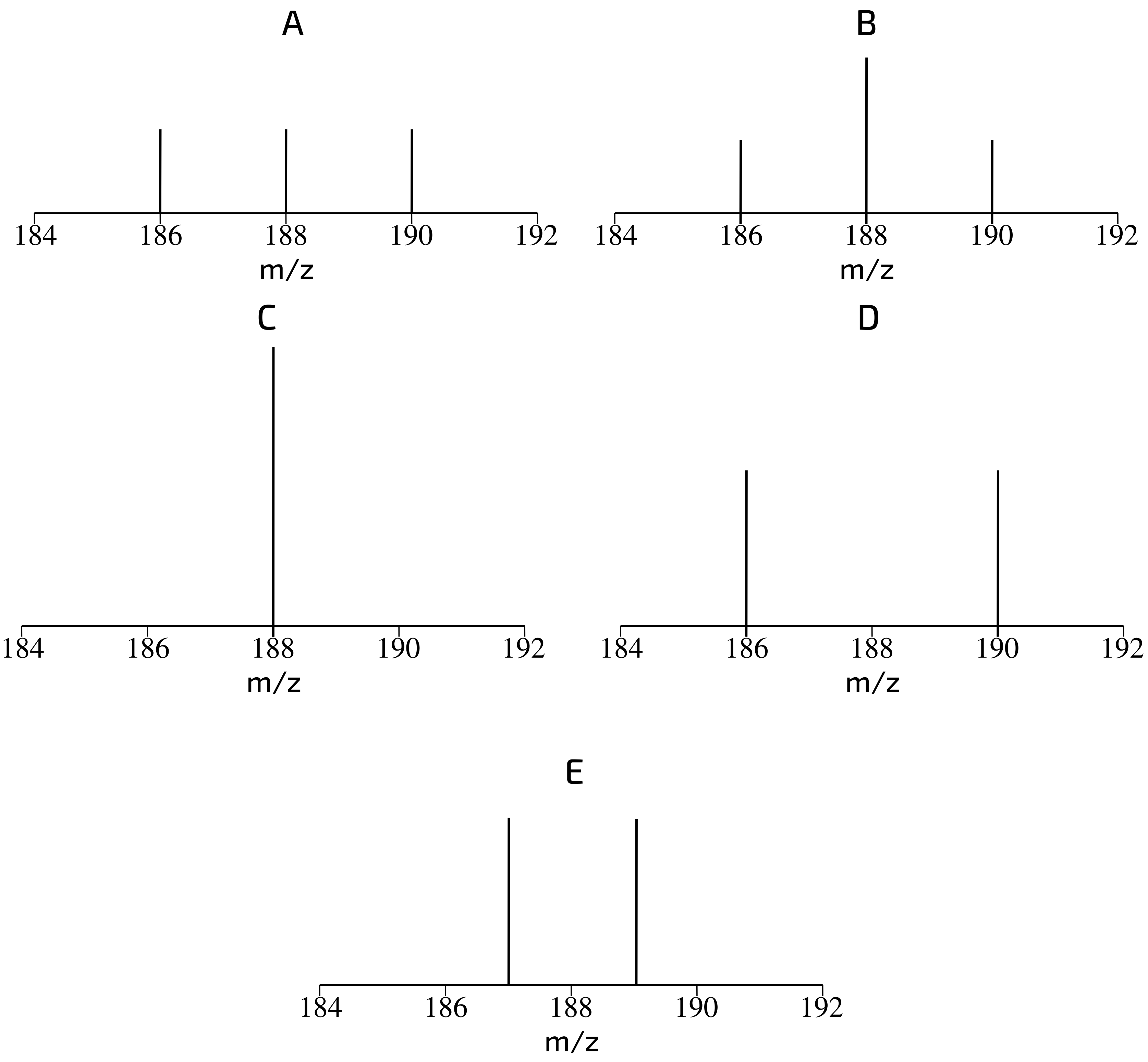

Figure 2: Mass spectra

- A
- B
- C
- D
- E

Part C Unknown

Select which of the following gives the complete mass spectrum illustrated.

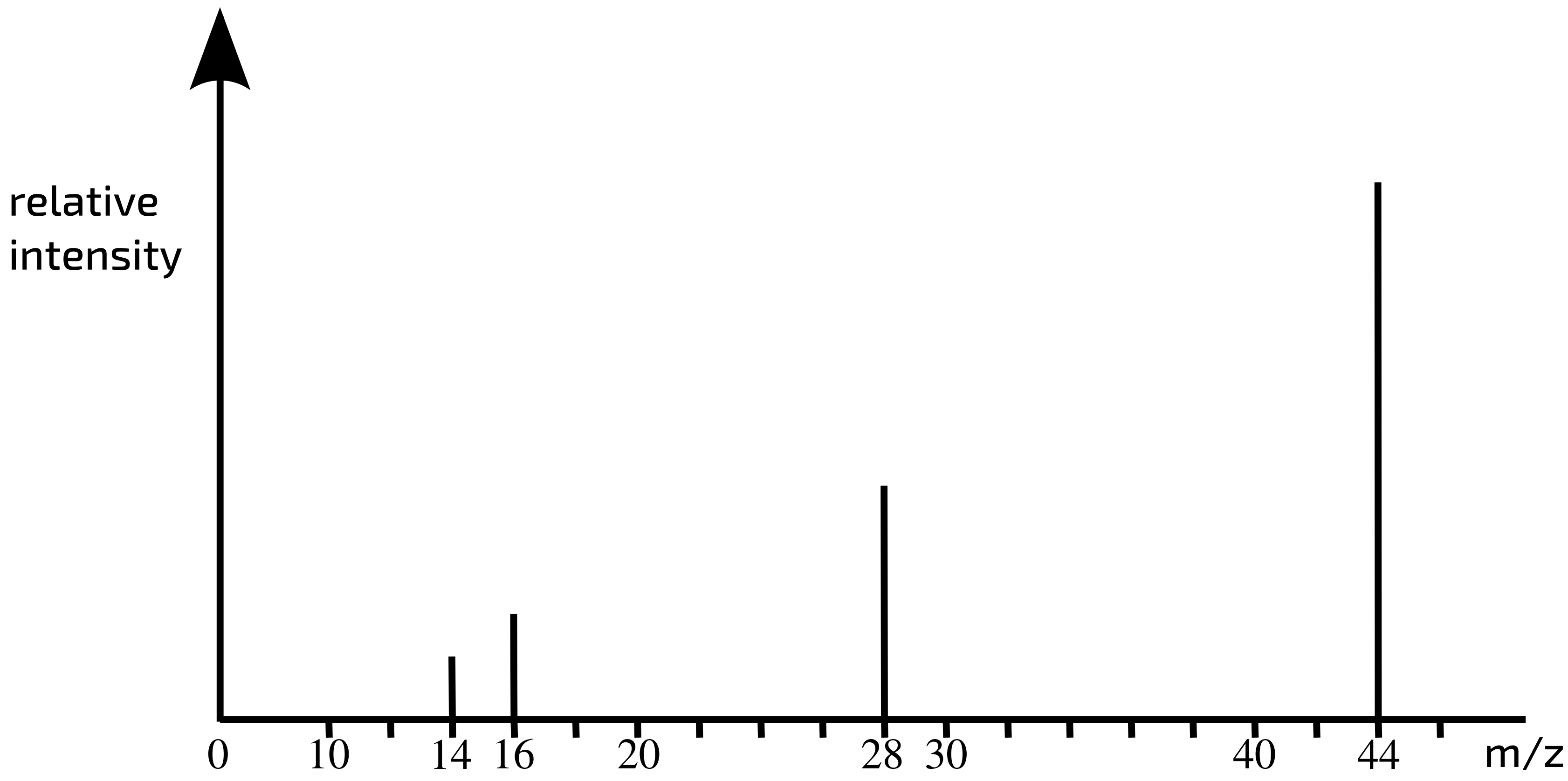

Figure 3: Mass spectrum

- CO_2
- C_3H_8
- N_2O
- a mixture of CH_4 and N_2

Adapted with permission from UCLES, A Level Chemistry, 1988, Paper 3, Question 3; November 1993, Paper 4, Question 5 and June 1994, Paper 4, Question 1

Gameboard:

STEM SMART Chemistry Week 14

Higher-charged Ions

(in mass spectrometry)

A Level

C C C

A small proportion of ions with higher charge can form during the ionisation process in a mass spectrometer. If a given potential accelerates a singly-charged ion to have a kinetic energy of E, a doubly-charged ion will instead acquire a kinetic energy of $2E$, a triply-charged ion a kinetic energy of $3E$, $\ldots$ and an ion with charge z a kinetic energy of zE. (If you are interested in the physics behind this, you may wish to read more about Electric fields and complete a physics question on accelerating charged particles.)

Part A Time of flight

Derive an expression for the time taken to travel through the drift region of length d by an ion with mass m and charge z, if it has a kinetic energy of zE.

The following symbols may be useful: `E, d, m, z`

Part B Isotopic clusters

Ions containing atoms with several stable isotopes form characteristic so-called "isotopic clusters". For example, the molecular ion HCl^+ would be expected to give rise to two lines in the mass spectrum due to the two **isotopologues** $\mathrm{H}^{35}\mathrm{Cl}^+$ and $\mathrm{H}^{37}\mathrm{Cl}^+$. The lines would be expected to appear in a 3:1 ratio due to this being the ratio of abundances of the respective chlorine isotopes.

At what (integer) m/z value would you expect the lighter of the two ions above to appear?

At what (integer) m/z value would you expect the heavier of the two ions above to appear?

Part C Doubly positive

Now consider the two possible isotopologues for HCl^{2+} which has formed in the ionisation stage.

At what (integer) m/z value would you expect the lighter of the two ions above to appear?

At what (integer) m/z value would you expect the heavier of the two ions above to appear?

Part D More generally

If you know that a compound contains one chlorine atom, how can you identify the charge of the ion responsible for a particular ion cluster (assuming the ion contains the chlorine atom present in the original molecule)?

If you know that a compound contains chlorine, you can relatively easily identify the charge of the ion responsible for a particular isotopic cluster containing at least one chlorine atom. Give an expression for how many units apart individual, neighbouring lines in the isotopic cluster (corresponding to the different isotopologues) will appear on the mass spectrum, as a function of the charge on the ion, z.

The following symbols may be useful: z

Created for isaacphysics.org by Andrea Chlebikova

Gameboard:

STEM SMART Chemistry Week 14

Gases 5

GCSE C C C A Level P P P

Essential Pre-Uni Chemistry B3.5

RTP = room temperature and pressure.

Any gas occupies $24\,\mathrm{dm}^3$ per mole at RTP.

Avogadro's number, $N_\mathrm{A} = 6.02 \times 10^{23}$.

Part A (a)

Calculate the mass of $1.0\,\mathrm{m}^3$ of neon at RTP.

Part B (b)

Calculate the mass of $20\,\mathrm{cm}^3$ of $(\mathrm{CH_3})_2\mathrm{O}$ at RTP.

Part C (c)

Calculate the mass of $420\,\mathrm{cm}^3$ of ammonia at RTP. Give your answer to 2 significant figures.

Solutions 2

Essential Pre-Uni Chemistry B5.2

GCSE C C C A Level P P P

Calculate the mass of solute in grams of each of the following:

Part A (a)

$500\,\text{ml}$ of $0.010\,\text{mol}\,\text{dm}^{-3}$ NaOH

Part B (b)

$150\,\text{ml}$ of $4.0\,\text{mol}\,\text{dm}^{-3}$ HCl

Part C (c)

$1.00\,\text{ml}$ of $10.0\,\text{mol}\,\text{dm}^{-3}$ H_2SO_4

Part D (d)

$25.0\,\text{ml}$ of $0.50\,\text{mol}\,\text{dm}^{-3}$ $FeSO_4$

Part E (e)

$21.8\,\mathrm{ml}$ of $0.0050\,\mathrm{mol\,dm^{-3}}\ \mathrm{KMnO_4}$

Part F (f)

$2.0\,\mathrm{dm^3}$ of $0.10\,\mathrm{mol\,dm^{-3}}\ \mathrm{NaCl}$

Part G (g)

$100\,\mathrm{ml}$ of limewater with a concentration of $0.00020\,\mathrm{mol\,dm^{-3}}$

Gameboard:

STEM SMART Chemistry Week 14

Reactions 3

Essential Pre-Uni Chemistry B6.3

GCSE C C C A Level P P P

Consider the equation for each reaction and hence calculate the amount of acid required for complete reaction in each of the following cases.

Part A (a)

$0.10\,\mathrm{mol}\ \mathrm{NaOH}$ reacting with $\mathrm{H_2SO_4}$. Give your answer to 2 significant figures.

Part B (b)

HCl reacting with $20\,\mathrm{g}$ of $\mathrm{CaCO_3}$. Give your answer to 2 significant figures.

Part C (c)

$24\,\mathrm{g}\ \mathrm{CuO}$ reacting with $\mathrm{HNO_3}$. Give your answer to 2 significant figures.

Part D (d)

$5.6\,\mathrm{g}\ \mathrm{Fe}$ reacting with HCl. Give your answer to 2 significant figures.

Part E (e)

$14.8\,\mathrm{g}$ of calcium hydroxide reacting with H_2SO_4. Give your answer to 3 significant figures.

Part F (f)

$10\,\mathrm{g}$ of magnesium oxide reacting with nitric acid. Give your answer to 2 significant figures.

Gameboard:

STEM SMART Chemistry Week 14

Titration 2

Essential Pre-Uni Chemistry B7.2

GCSE C C C A Level P P P

$2.50\,\mathrm{g}$ of an unknown carbonate were dissolved in $100\,\mathrm{cm}^3$ of $1.00\,\mathrm{mol\,dm^{-3}}$ hydrochloric acid (an excess). The resulting solution was made up to $250\,\mathrm{cm}^3$ in a volumetric flask. $25.00\,\mathrm{cm}^3$ aliquots of this solution were titrated against $0.250\,\mathrm{mol\,dm^{-3}}$ sodium hydroxide. Some of the results are shown below. Fill in the gaps in the table (Parts A-D), and then calculate the quantities in Parts E-L to identify the cation (Part M).

Titration	Initial burette reading / cm^3	Final burette reading / cm^3	Titre / cm^3
Rough	0.60	25.10	**Part A**
1	0.15	**Part B**	24.10
2	**Part C**	25.25	24.45
3	1.35	25.45	**Part D**

Part A Rough, Titre/cm^3

Give your answer to 4 significant figures.

Part B 1, Final burette reading/cm^3

Give your answer to 4 significant figures.

Part C 2, Initial burette reading/cm^3

Give your answer to 2 significant figures.

Part D 3, Titre/cm^3

Give your answer to 4 significant figures.

Part E Average concordant titre

Calculate the average concordant titre. Give your answer to 4 significant figures.

Part F Amount of sodium hydroxide

Calculate the amount of sodium hydroxide in that volume. Give your answer to 3 significant figures.

Part G Amount of hydrochloric acid

The amount of hydrochloric acid in each aliquot. Give your answer to 3 significant figures.

Part H Initial amount of HCl

Calculate the initial amount of hydrochloric acid added to the carbonate. Give your answer to 3 significant figures.

Part I Final amount of HCl

Calculate the amount of hydrochloric acid remaining after reaction. Give your answer to 3 significant figures.

Part J Amount of HCl used

Calculate the amount of hydrochloric acid used in reaction with the carbonate. Give your answer to 3 significant figures.

Part K Amount of carbonate

Calculate the amount of carbonate in $2.50\,g$. Give your answer to 3 significant figures.

Part L Molar mass of carbonate

Calculate the molar mass of the carbonate. Give your answer to 3 significant figures.

Part M Identity of cation

Identify the cation in the carbonate.

Gameboard:

STEM SMART Chemistry Week 14

Titrating Sulfur Dioxide

A Level

P P P

Sulfur dioxide is a by-product of the combustion of coal in power stations. It can react with oxygen and water vapour in the air to form sulfuric acid, $\mathrm{H_2SO_4}$. This is one of the causes of acid rain.

The amount of sulfur dioxide in the air may be determined by bubbling a sample of the air through sodium hydroxide solution, where it reacts according to the equation below:

$$\mathrm{SO_2\,(g) + 2\,NaOH\,(aq) \longrightarrow Na_2SO_3\,(aq) + H_2O\,(l)}$$

The concentration of the unreacted sodium hydroxide can be determined by titration against a standard solution of hydrochloric acid.

$1000\,\mathrm{dm^3}$ of air were bubbled through $200\,\mathrm{cm^3}$ of a $1.00\,\mathrm{mol\,dm^{-3}}$ solution of sodium hydroxide. The remaining solution was diluted to $1000\,\mathrm{cm^3}$ with water, and $25.0\,\mathrm{cm^3}$ of this solution was neutralised by $20.4\,\mathrm{cm^3}$ of a $0.100\,\mathrm{mol\,dm^{-3}}$ solution of hydrochloric acid.

Part A $\mathrm{H_2SO_4}$ formation

Construct an overall equation for the formation of sulfuric acid from sulfur dioxide (do not include state symbols). Balance it so as to use the smallest possible integer coefficients.

Part B Neutralisation reaction

Give the (net) ionic equation for the reaction of sodium hydroxide with hydrochloric acid.

Part C Unreacted moles

Find the amount, in moles, of unreacted sodium hydroxide.

Part D Sulfur dioxide moles

Find the amount, in moles, of sulfur dioxide in $1000\,\mathrm{dm}^3$ of air.

Part E Percentage by volume

Hence calculate the percentage by volume of sulfur dioxide in air. (You may assume $1\,\mathrm{mol}$ of any gas occupies $24\,\mathrm{dm}^3$ at this temperature and pressure.)

Adapted with permission from OCR, A Level Chemistry, June 1999, General and Physical Paper, Question 3

Gameboard:
STEM SMART Chemistry Week 14

Titration 4

A Level

C C C

Essential Pre-Uni Chemistry B7.4

Three students each prepare a standard solution by dissolving $10.6\,\mathrm{g}$ of solid from different bottles labelled 'sodium carbonate' in exactly $1\,\mathrm{dm}^3$ of water. They use this standard solution in a titration to determine the exact concentration of a solution of sulfuric acid at approximately $0.1\,\mathrm{mol\,dm^{-3}}$. They each use a pipette to measure out exactly $25.00\,\mathrm{cm}^3$ of the standard solution into a conical flask, they each use the same indicator and they each carry out their titrations with great care and accuracy.

The volumes of sulfuric acid solution that they each use are listed below. Only student A finds the correct concentration of the sulfuric acid. Student B is within $20\,\%$ but student C is so far out that they know something is wrong. Student C asks for help and is reminded that some solids can contain water of crystallisation. Student A uses anhydrous sodium carbonate, but what is x in the formula $\mathrm{Na_2CO_3 \cdot xH_2O\,(s)}$ for students B and C?

Student A: $23.75\,\mathrm{cm}^3$
Student B: $20.20\,\mathrm{cm}^3$
Student C: $8.80\,\mathrm{cm}^3$

Part A Acid concentration

Calculate the exact concentration of the sulfuric acid. Give your answer to 3 significant figures.

Part B $\mathrm{Na_2CO_3 \cdot xH_2O\,(s)}$

Find x in $\mathrm{Na_2CO_3 \cdot xH_2O\,(s)}$ for student B.

Find x in $\mathrm{Na_2CO_3 \cdot xH_2O\,(s)}$ for student C.

Compounds TBC

A Level
C C C

When calcium oxide is heated with carbon, an ionic compound, **D**, containing 62.5% of calcium and 37.5% of carbon (by mass), is formed. Under similar conditions, aluminium metal and carbon produce compound **E** which contains 75% of aluminium and 25% of carbon.

When treated with cold water:

- compound **D** produces a gaseous hydrocarbon **F** containing 92.3% of carbon
- compound **E** produces another gaseous hydrocarbon **G** containing 75% of carbon

Part A D

Determine the empirical formula of compound **D**.

Part B E

Determine the empirical formula of compound **E**.

Part C F

Determine the empirical formula of compound **F**.

Part D G

Determine the empirical formula of compound **G**.

Part E Reaction to form D

Write a balanced equation for the reaction of calcium oxide with carbon, using the empirical formula for **D** you have previously deduced.

$$\mathrm{CaO} + \boxed{}\,\mathrm{C} \longrightarrow \boxed{} + \mathrm{CO}$$

Items:

1 2 3 4 5 D 2D 3D 4D 5D

Part F Reaction to form E

Write a balanced equation for the reaction of aluminium metal and carbon to form **E** (do not include state symbols).

Part G Reaction of E with water

Assuming the empirical formula you deduced for **G** is also its molecular formula, write a balanced equation for the reaction when compound **E** is treated with water.

E $+ \boxed{} H_2O \longrightarrow \boxed{} Al(OH)_3 + \boxed{}$ **G**

Items:

1 2 3 4 6 8 12

Adapted with permission from UCLES, A Level Chemistry, November 1990, Special Paper, Question 5