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2016 AUSTRALIAN SCIENCE OLYMPIAD EXAM

CHEMISTRY – SECTIONS A & B

TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS

Student Name:	
Home Address:	
..... Post Code:	
Telephone: (.....)	Mobile:
E-Mail: Date of Birth:/...../.....	
<input type="checkbox"/> Male <input type="checkbox"/> Female <input type="checkbox"/> Unspecified <input type="checkbox"/> Year 10 <input type="checkbox"/> Year 11 <input type="checkbox"/> Other:	

Name of School:	State:
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To be eligible for selection for the Australian Science Olympiad Summer School, students must be able to hold an Australian passport by the time of team selection (March 2017).

The Australian Olympiad teams in Biology, Chemistry, Earth and Environmental Sciences and Physics will be selected from students participating in the Australian Science Olympiad Science Summer School.

Please note - students in Yr12 in 2016 are not eligible to attend the 2017 Australian Science Olympiad Science Summer School

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CHEMISTRY

2016 Australian Science Olympiad Exam

Time Allowed:

Reading Time: 10 minutes

Examination Time: 120 minutes

INSTRUCTIONS

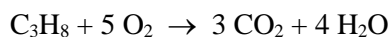
- Attempt ALL questions in ALL sections of this paper.
- Permitted materials: Non-programmable non-graphical calculator, pens, pencils, erasers and a ruler.
- Answer SECTION A on the Multiple Choice Answer Sheet provided. Use a pencil.
- Answer SECTION B in the spaces provided in this paper. Write in pen and use a pencil only for graphs.
- Ensure that your diagrams are clear and labelled.
- All numerical answers must have correct units.
- Marks will not be deducted for incorrect answers.
- Rough working must be done only on pages 26 to 28 of this booklet.
- Relevant data that may be required for a question will be found on page 3.
- Do not staple the multiple choice answer sheet to this booklet.

MARKS

SECTION A	15 multiple choice questions	30 marks
SECTION B	3 short answer questions	30 marks each
	Total marks for the paper	120 marks

SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

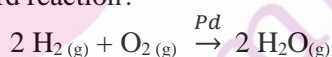
1. The combustion of propane (C_3H_8) in the presence of a stoichiometric amount of oxygen (O_2) results in the formation of carbon dioxide (CO_2) and water (H_2O). If 2.2 kg of propane fully reacted, how many moles of oxygen were used?



- (a) 0.020
(b) 0.10
(c) 0.25
(d) 50
(e) 250
2. 2.00 g of a mixture containing $NaNO_3$ and $NaCl$ was dissolved in 250 mL of water. This solution was then titrated against $0.050 \text{ mol L}^{-1} AgNO_3$, requiring 20.00 mL to fully precipitate the chloride ions as silver chloride. What was the percentage by mass of $NaCl$ in the sample?

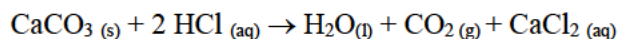
- (a) 1.77%
(b) 2.92%
(c) 5.84%
(d) 7.17%
(e) 11.7%

3. For the following reaction in a closed vessel, which of the following changes would cause an increase in the rate of the forward reaction?



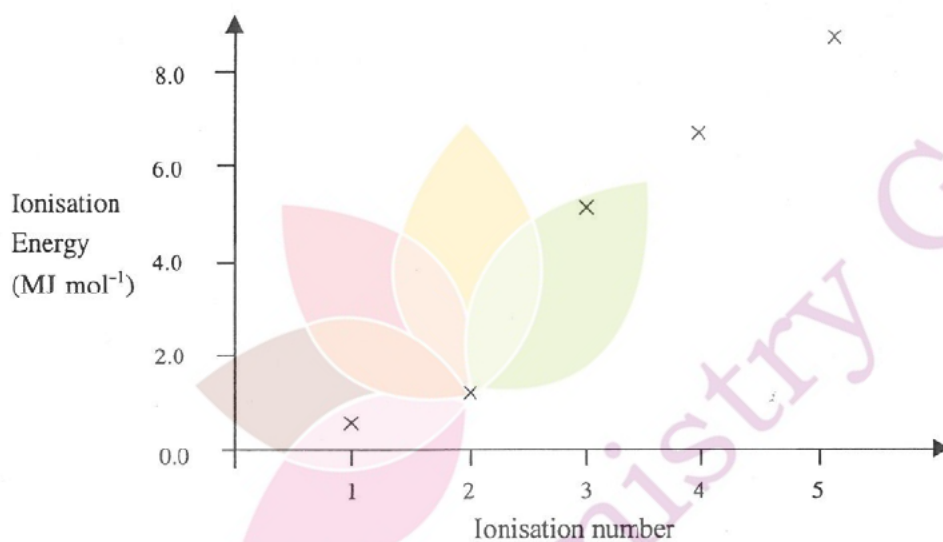
- (a) Decreasing the pressure of $H_2(g)$
(b) Increasing the pressure of $H_2O(g)$
(c) Increasing the pressure of $O_2(g)$
(d) Decreasing the pressure of $H_2O(g)$
(e) Decreasing the surface area of the palladium catalyst
4. Which of the following covalent bonds is most polar?
- (a) C – F
(b) N – F
(c) O – F
(d) N – O
(e) F – F

5. A solid sample of calcium carbonate was placed into a solution of hydrochloric acid. Which of the following options shows the correct change in concentration of each species over time, as the reaction proceeds?



	[H ⁺]	[Ca ²⁺]	[Cl ⁻]
(a)	decreases	increases	increases
(b)	decreases	increases	no change
(c)	decreases	no change	increases
(d)	no change	increases	increases
(e)	no change	no change	no change

6. An element has the first five successive ionisation energies as shown on the graph below.



Which one of the following could this element be?

- (a) aluminium
- (b) boron
- (c) carbon
- (d) calcium
- (e) sodium

7. A chemist wishes to make a fertiliser solution containing ions that will act as a source of nitrogen, phosphorus and potassium. Which one of the following mixtures of solids will completely dissolve to give such a solution?

- | | | | |
|-----|--------------------------|------------------------------|--------------------------|
| (a) | NaNO_3 | $\text{Ca}_3(\text{PO}_4)_2$ | KCl |
| (b) | K_2CO_3 | Na_3PO_4 | AgNO_3 |
| (c) | NH_4NO_3 | Na_3PO_4 | KCl |
| (d) | NH_4Cl | K_3PO_4 | CaCl_2 |
| (e) | KNO_3 | $\text{Ca}(\text{NO}_3)_2$ | Na_3PO_4 |

8. A sample of water from a stream was analysed for the presence of metal ions. The results of some tests on the water are recorded in the table.

Test Result

Add dilute HCl	No reaction
Add Na_2CO_3 solution	White precipitate formed
Add Na_2SO_4 solution	No reaction

Which metal is most likely to be present in the water?

- (a) Ba^{2+}
(b) Mg^{2+}
(c) Cu^{2+}
(d) Fe^{3+}
(e) Li^+
9. Which of the following best describes the most likely pathway for the K^- ion to achieve a noble gas electron configuration?
- (a) lose two electrons
(b) gain two electrons
(c) lose one electron
(d) gain one electron
(e) nothing is required, it already has a noble gas electron configuration
10. The relative atomic mass of thallium, which consists of the isotopes ^{203}Tl and ^{205}Tl , is 204.4. What is the percentage of ^{203}Tl atoms in the isotopic mixture?
- (a) 3.3%
(b) 7.0%
(c) 30%
(d) 70%
(e) 81%

11. Each of the following species is composed of molecules in the gas phase. Which of the following molecules does **not** have eight electrons around the central atom?
- (a) CCl_4
 - (b) CS_2
 - (c) H_2S
 - (d) F_2O
 - (e) AlF_3

12. Which of the following compounds have the same molecular geometry?

I. NH_3 **II.** BF_3 **III.** SCl_2 **IV.** H_2O **V.** CO_2 **VI.** CH_4

- (a) I and II
 - (b) I and VI
 - (c) III, IV and V
 - (d) III and IV
 - (e) III and V
13. Why is the boiling point of methane (CH_4) greater than that of neon (Ne)?
- (a) The covalent bonds within CH_4 are stronger than the dispersion forces between Ne atoms.
 - (b) The dispersion forces between CH_4 molecules are stronger than those between Ne atoms.
 - (c) A molecule of CH_4 has more electrons than an atom of Ne.
 - (d) Molecules of CH_4 form hydrogen bonds, but atoms of Ne do not.
 - (e) Methane is a compound whereas neon is an element.
14. The atomic number for four different nuclei are given in the table below. Which two have the same number of neutrons?

	Atomic Number	Mass Number
I.	101	258
II.	102	258
III.	102	260
IV.	103	259

- (a) I and II
- (b) I and III
- (c) II and III
- (d) II and IV
- (e) III and IV

15. Which pair of substances is listed in **increasing** order of the property given?
- (a) First ionisation energy: O, S
 - (b) Radius: Mg, Mg²⁺
 - (c) Boiling point: I₂, Br₂
 - (d) Covalent character: HI, HBr
 - (e) Electronegativity: O, F

**END OF SECTION A
SECTION B COMMENCES OVERLEAF**



SECTION B
ANSWER IN THE SPACES PROVIDED

Question 16

In 1809, Joseph Louis Gay-Lussac published “Memoir on the Combination of Gaseous Substances with Each Other”, in which he presented evidence that gaseous substances react with each other in simple ratios by volume (when measured at the same temperature and pressure). For example, one volume of ammonia reacts with an identical volume of hydrogen chloride to give ammonium chloride, or with an identical volume of hydrogen cyanide to give ammonium cyanide.

Such ratios were not always 1:1 however, for example:

- decomposing 2 volumes of ammonia gave one volume of azote (nitrogen) and three of hydrogen
- two volumes of steam can be produced from the reaction of two volumes of hydrogen and one of oxygen.

(a) If 100 mL of ammonia is decomposed, what volume of hydrogen gas is produced (both of these volumes are measured at 20 °C and 101.3 kPa)?

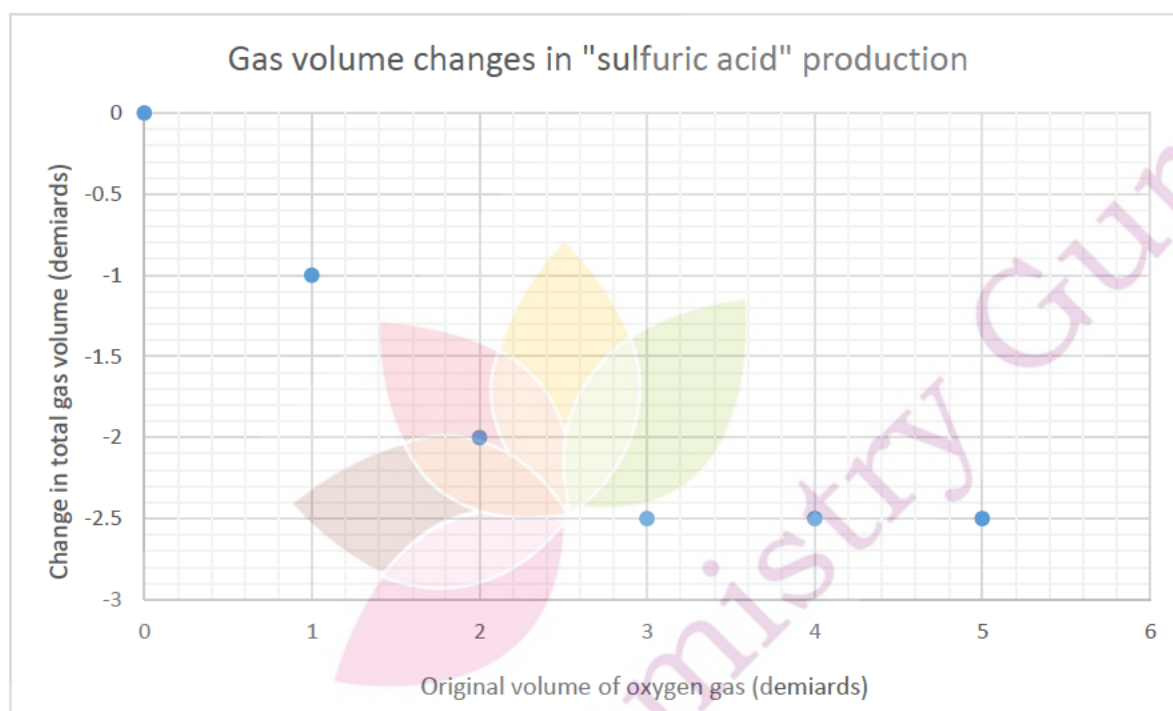
(b) This volume of hydrogen has its temperature raised to 100 °C, which increases its volume at 101.3 kPa to 191 mL. If it is then combusted with excess oxygen, what volume of water vapour is produced (when measured at 100 °C and 101.3 kPa)?

(c) When 191 mL of hydrogen gas reacts 191 mL of oxygen gas, what volume of oxygen gas remains (all of these gas volumes being measured at the same temperature and pressure)?

Many reactions of hydrogen and oxygen with other gases were investigated thoroughly during this period of history. The change in gas volume, if any, in such reactions was of some academic curiosity and could be investigated by comparing gas volumes before and after a chemical reaction.

Gay-Lussac reported the combination of "sulphurous gas" with oxygen to form "sulfuric acid" (the quotation marks are used because these do not correspond to the current names for these compounds). Data from an experiment investigating this reaction is plotted below. The gas volumes are expressed in demiards, an old French unit of volume approximately equal to 238 mL, and all volumes are measured at the same temperature and pressure.

In each reaction, 5.00 demiards of sulphurous gas were mixed with a different volume of oxygen gas and allowed to react. The change in total gas volume was then calculated by subtracting the total gas volume after reaction from the total gas volume before the reaction. This is plotted below, against the original volume of oxygen gas.



(d) Predict the change in total gas volume if the experiment was repeated with 5.00 demiards of sulphurous gas and 6.00 demiards of oxygen gas.

(e) Predict the change in total gas volume if the experiment was repeated with 5.00 demiards of sulphurous gas and 0.75 demiards of oxygen gas.

(f) In what ratio by volume does sulphurous gas combine with oxygen gas? Express your answer in terms of volume(s) of sulphurous gas to volume(s) of oxygen gas.

_____ volume(s) of sulphurous gas to _____ volume(s) of oxygen gas

(g) Predict the change in total gas volume if the experiment was repeated with 10.00 demiarads of sulphurous gas and 6.00 demiarads of oxygen gas.

(h) Predict the change in total gas volume if the experiment was repeated with 8.00 demiarads of sulphurous gas and 3.00 demiarads of oxygen gas.

We now know (as Avogadro correctly hypothesised) that Gay-Lussac's law of combining volumes holds because identical volumes of gases at the same temperature and pressure contain identical numbers of molecules (or atoms in the case of monatomic gases) and that atoms combine with each other in simple integer ratios.

(i) If "sulfuric acid" in the previous reaction is now known as sulfur trioxide, what is "sulphurous gas" known as?

In 1815, William Prout published experimental data concerning the densities of gases and their composition. He expressed the “specific gravity” of gases relative to the specific gravity of atmospheric air, being 1.000 (these days we would call this “relative density”), for example he quoted the specific gravity of nitrogen gas as 0.9722.

Prout also stated that air consists of 80.00% nitrogen gas and 20.00% oxygen gas by volume.

(j) Assuming (as Prout did) that air is composed only of nitrogen and oxygen, calculate the relative density of oxygen gas (relative to atmospheric air being 1.000).

(k) As we saw previously, two volumes of ammonia decompose to give one volume of nitrogen gas and three volumes of hydrogen gas. If the relative density of ammonia gas is 0.5902 (relative to atmospheric air being 1.000), calculate the relative density of hydrogen gas.

In 1858, Stanislao Cannizzaro proposed that “hydrogen being the lightest gas, we may take it as the unit to which we refer the densities of other gaseous bodies”.

(l) From Prout’s data, calculate the density of oxygen gas (relative to **hydrogen gas** being 1.000).

Prout hypothesised that the atomic weights of all elements were multiples of that of hydrogen, which although not exactly correct was tremendously influential. This led to efforts to investigate the mass ratios in which substances combined.

For example:

- 1 part by mass of hydrogen reacts with 8 parts by mass of oxygen to give water
- 1 part by mass of hydrogen reacts 35.5 parts by mass of chlorine to give hydrogen chloride

The mass of a substance that combined with or displaced 1 part by mass of hydrogen was called the **equivalent weight** of that element or compound.

Therefore, oxygen has an equivalent weight of 8 and chlorine has an equivalent weight of 35.5. The mass of a substance that combined with or displaced 8 parts of oxygen or 35.5 parts of chlorine by mass is therefore an alternative definition for equivalent weight.

(m) A common oxide of osmium, containing 74.8% osmium by mass, can be prepared by the reaction of osmium metal with excess oxygen. Calculate the equivalent weight of osmium in this compound.

A problem with equivalent weights quickly emerged, which was that it seemed possible for the same element to have multiple different equivalent weights depending on reaction conditions.

(n) Treating osmium metal with excess nitric oxide at 600 °C gives of an oxide of osmium that weighs 16.8% more than the original osmium metal. Calculate the equivalent weight of osmium in this compound.

(o) Explain why the equivalent weight of osmium is different in these two compounds.

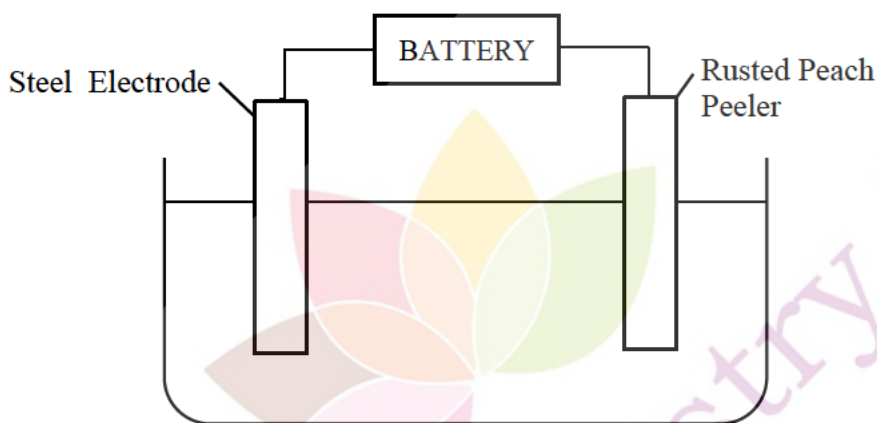
Faraday's Laws of Electrolysis state that the mass of a substance liberated at one electrode is proportional to the total electric charge passed through the electrolytic cell and to the equivalent weight of the substance produced. These two relationships can be written mathematically as follows:

$$m = \frac{Q}{F} E$$

Where:

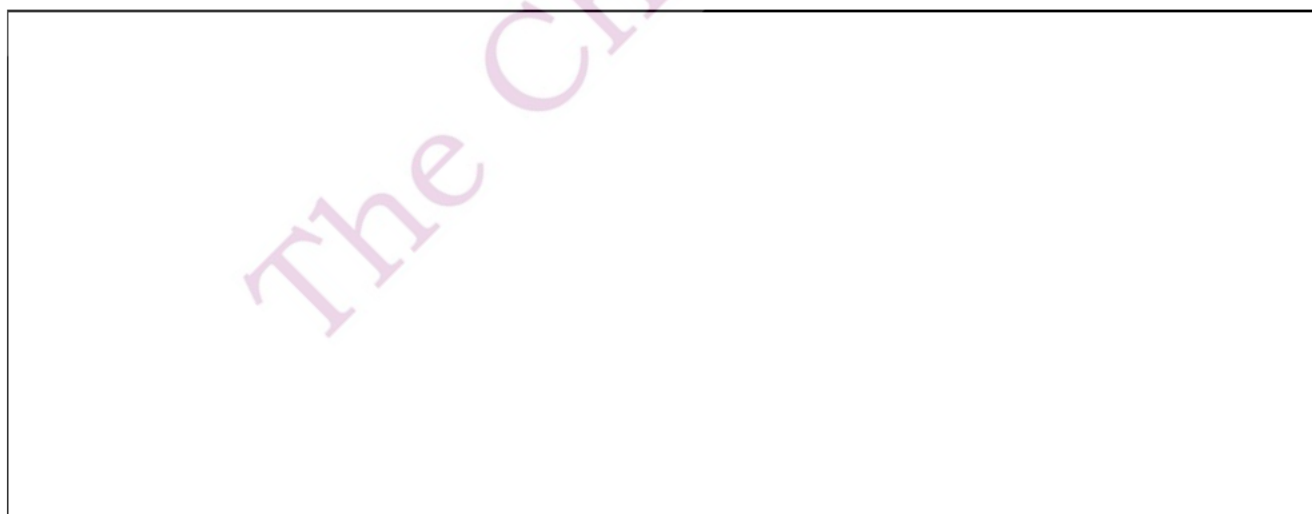
- m is the mass of the substance produced in grams (g)
- Q is the total electric charge passed through the electrolytic cell in coulombs (C)
- E is the equivalent weight of the substance
- F is Faraday's constant, with a value of $96\,485\text{ C mol}^{-1}$

Michael wishes to use electrolysis to clean the rust from his iron antique peach peeler, and sets up an electrolytic cell as in the following diagram:



As current is applied to the cell, bubbles of oxygen gas form at the steel electrode, while the rust on the peach peeler is converted into a loose layer of a dark solid that Michael identifies as iron metal. By weighing the cell before and after the electrolysis is complete, Michael finds that 6.82 g of oxygen were evolved (recall that oxygen has an equivalent weight of 8).

(p) Use Faraday's law to determine the total charge passed through the cell.



Michael then wonders whether he can use his cell to work out the equivalent weight of iron. He brushes the black solid from the peach peeler, and finds that it has a mass of 19.06 g.

(q) Calculate the equivalent weight of iron based on Michael's experiment.

Michael decides to compare this value to a table of equivalent weights. He discovers that iron actually has an equivalent weight of 18.6. Curious to work out where he went wrong, Michael researches the chemistry of electrolytic rust removal. He finds that the black solid is in fact a mixture of iron and magnetite (an oxide of iron). Looking it up in his table of equivalent weights, Michael finds that magnetite has an equivalent weight of 232.

(r) Using the correct values for the relevant equivalent weights, calculate the masses of magnetite and iron metal in the black solid. (Hint: the total charge passed through the cell will be equal to the sum of the charge passed through the magnetite and the charge passed through the iron)

Question 17

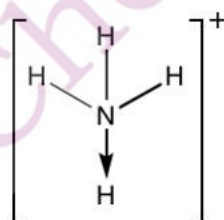
Acids and bases are ubiquitous in chemistry. Familiar to many are the acids which donate a hydrogen ion to water when they are present in aqueous solution, such as hydrochloric acid or sulfuric acid. These acids are called Brønsted-Lowry acids. A species which can accept a hydrogen ion is called a Brønsted-Lowry base. One example of this is ammonia.

(a) Write a balanced equation for the reaction of ammonia with hydrochloric acid.

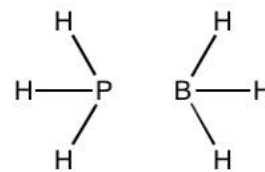
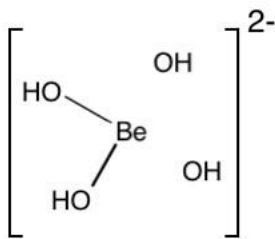
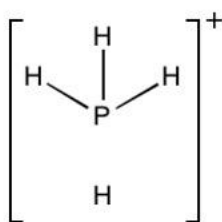
(b) Draw a Lewis dot diagram (or electron dot structure) for ammonia.

Ammonia, like many compounds, obeys the octet rule. Ammonia is a Brønsted-Lowry base because it can readily react with a hydrogen ion to form the ammonium ion. Another more general theory of acids and bases is Lewis theory. A Lewis base can donate a lone pair and a Lewis acid can accept a lone pair. Thinking about ammonia as Lewis base, it can donate a lone pair to a hydrogen ion, which makes ammonia both a Lewis and a Brønsted-Lowry base.

The product of a Lewis acid-base reaction is called a Lewis adduct. In this question, Lewis adducts will be drawn with an arrow, which represents the bond formed by the donation of a pair of electrons, as in the structure of the ammonium ion below.



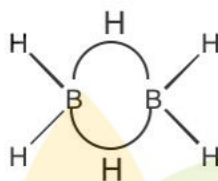
(c) Draw the missing bond(s) in the following structures of Lewis adducts.



For a closer examination of Lewis acids, we'll examine borane (BH_3). The boron in borane does not obey the octet rule.

(d) Draw a Lewis dot diagram (or electron dot structure) for borane (BH_3).

At standard conditions, BH_3 exists as a dimer called diborane, B_2H_6 . It is unusual as it has what are called 3-centre-2-electron bonds over the B-H-B bonds, which have two electrons shared over three atoms rather than two. The curved bonds in the structure are used to represent these bonds.



(e) Do the borons of diborane obey the octet rule? Explain your answer.

Boron trifluoride (BF_3) is a much stronger Lewis acid than BH_3 , but is only found in the monomeric form.

(f) Draw a Lewis dot diagram (or electron dot structure) for BF_3 .

(g) Explain why BF_3 is a stronger Lewis acid than BH_3 .

Hydrofluoric acid (HF) is a weak Brønsted-Lowry acid in solution, meaning that it does not completely dissociate into ions in water. HF reacts with boron trifluoride to form another Brønsted-Lowry acid which is a strong acid, meaning it does completely dissociate into ions in water.

(h) What is the formula of this acid?

(i) Draw a Lewis dot diagram (or electron dot structure) for the anion present in this acid.

In practice however, boron trifluoride is an extremely toxic colourless gas. When a Lewis acid is required for a reaction a common choice is aluminium chloride (AlCl_3), which is a white solid.

(j) With which molecule previously mentioned in this question does aluminium chloride (AlCl_3) share a similar Lewis dot diagram? Explain your answer.

When sodium chloride melts at 801 °C, the resulting liquid is highly conductive as the sodium and chloride ions can move freely. Aluminium chloride melts at 192.4 °C and the resulting liquid is only poorly conductive.

(k) What does this indicate about the type of bonding in molten aluminium chloride?

Aluminium chloride forms a dimer (Al_2Cl_6) in the liquid phase with a structure similar to diborane. Unlike diborane however, the dimer of aluminium chloride has no 3-centre-2-electron bonds.

(l) Draw the structure of the dimer of aluminium chloride (Al_2Cl_6), indicating the correct type of bonding.



When boron trifluoride and boron trichloride are mixed as gases, a mixture of four gases forms, including some boron trifluoride and boron trichloride. The resultant mixture cannot be purified back to boron trifluoride and boron trichloride.

(m) Predict the identities of the other two gases and write a balanced chemical equation for their formation from boron trifluoride and boron trichloride.

The reaction proceeds through an intermediate with a similar structure to Al_2Cl_6 .

(n) Draw the structure of this intermediate.



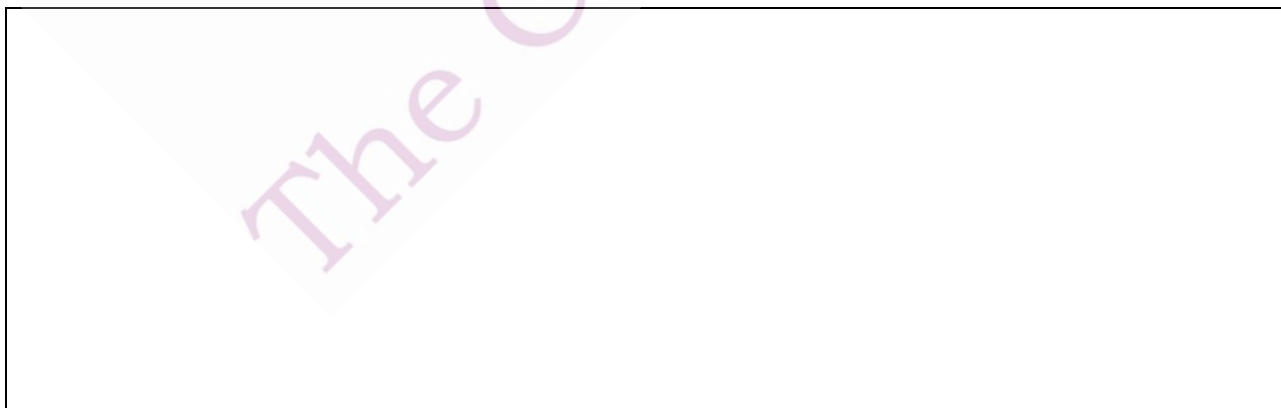
Passing BF_3 over crystalline boron at high temperature and low pressure gives rise to a mixture of products, amongst them a yellow solid with molecular formula B_8F_{12} that has a structure similar to B_2H_6 and AlCl_3 .

(o) Draw the structure of B_8F_{12} .



One molecule of B_8F_{12} can react with two PCl_3 molecules to give two molecules of a single product.

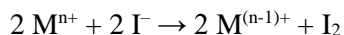
(p) Draw the structure of this product.



Question 18

An unknown salt was known to have a formula of the type $M_xA_y \cdot zH_2O$, where M^{n+} is a metal cation, A^{b-} is a polyatomic anion and x , y and z are all unknown integers.

M^{n+} reacts with I^- to form $M^{(n-1)+}$ and I_2 , according to the following balanced chemical equation:



(a) Write the oxidation and reduction half equations for this reaction.

Oxidation half-equation:

Reduction half-equation:

This can be used to determine the amount of M^{n+} present, by iodometry. A sample of the unknown salt (0.2642 g) is dissolved in a conical flask and excess KI is added. The solution is immediately titrated with $0.03064 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$, which reacts with the liberated iodine, generating iodide ions and $\text{S}_4\text{O}_6^{2-}$ ions according to the equation:

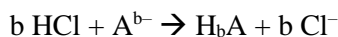


The endpoint is detected by addition of vitex indicator close to endpoint, with completion when the dark blue colour has completely faded. This requires 24.65 mL of $\text{Na}_2\text{S}_2\text{O}_3$.

(b) Calculate the chemical amount (in mol or mmol) of M^{n+} present in 0.2642 g of solid $M_xA_y \cdot zH_2O$.

(c) Determine the molar mass of the unknown salt ($M_xA_y \cdot zH_2O$) in terms of x .

The polyatomic anion A^{b-} can be determined through an acid-base titration. 1.4130 g of the unknown salt is dissolved in a 250.0 mL volumetric flask and made up to the mark. 25.00 mL aliquots are taken and titrated with a 0.07432 mol L⁻¹ HCl solution, requiring an average titre of 21.74 mL. The reaction can be considered as:



(d) Calculate the chemical amount (in mol or mmol) of A^{b-} in a **25.00 mL aliquot**, in terms of b.

(e) Determine the molar mass of the unknown salt ($M_xA_y \cdot zH_2O$) in terms of y and b.




A^{b-} can also be titrated with base. A 25.00 mL aliquot of the same unknown solution requires 26.98 mL of 0.02994 mol L⁻¹ NaOH solution, with which A^{b-} reacts in a 1:1 ratio.

(f) What does this tell us about what the anion must contain? What is the value of b?

The original unknown salt ($M_xA_y \cdot zH_2O$) is heated to $300\text{ }^\circ\text{C}$ leading to a loss of mass; heating is stopped when there is no further mass change. 0.9638 g of this new solid is dissolved and made up to the mark in a 250.0 mL volumetric flask; 25.00 mL aliquots of this solution now require 24.79 mL of the previously used $0.02994\text{ mol L}^{-1}\text{ NaOH}$.

(g) (i) What can you attribute the loss in mass to?

(ii) Calculate the mass of the original unknown salt ($M_xA_y \cdot zH_2O$) required to produce 0.9638 g of the new solid and hence calculate the mass lost when 0.9638 g of the new solid is produced.



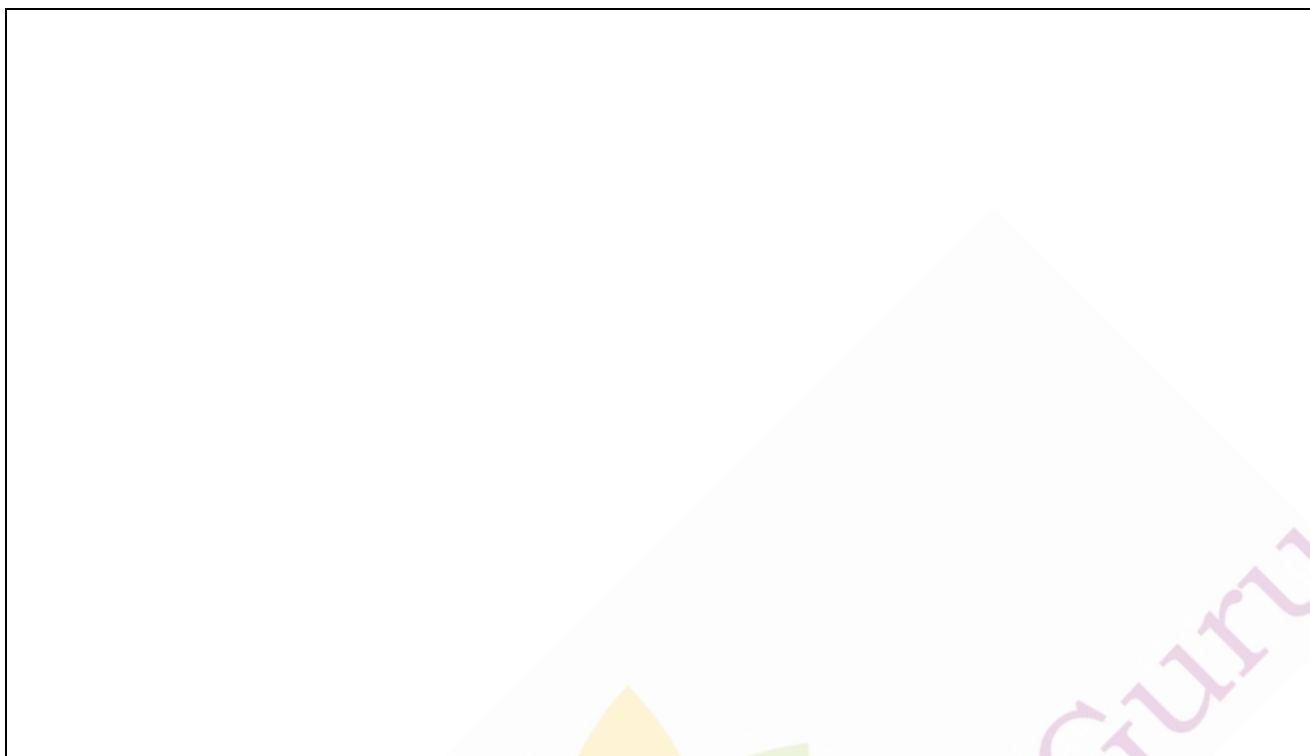
The Chemistry Guru

(h) Determine the molar mass of the original unknown salt ($M_xA_y \cdot zH_2O$) in terms of z .



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(i) Determine the values of x , y , z and the molar mass of the original unknown salt ($M_xA_y \cdot zH_2O$).



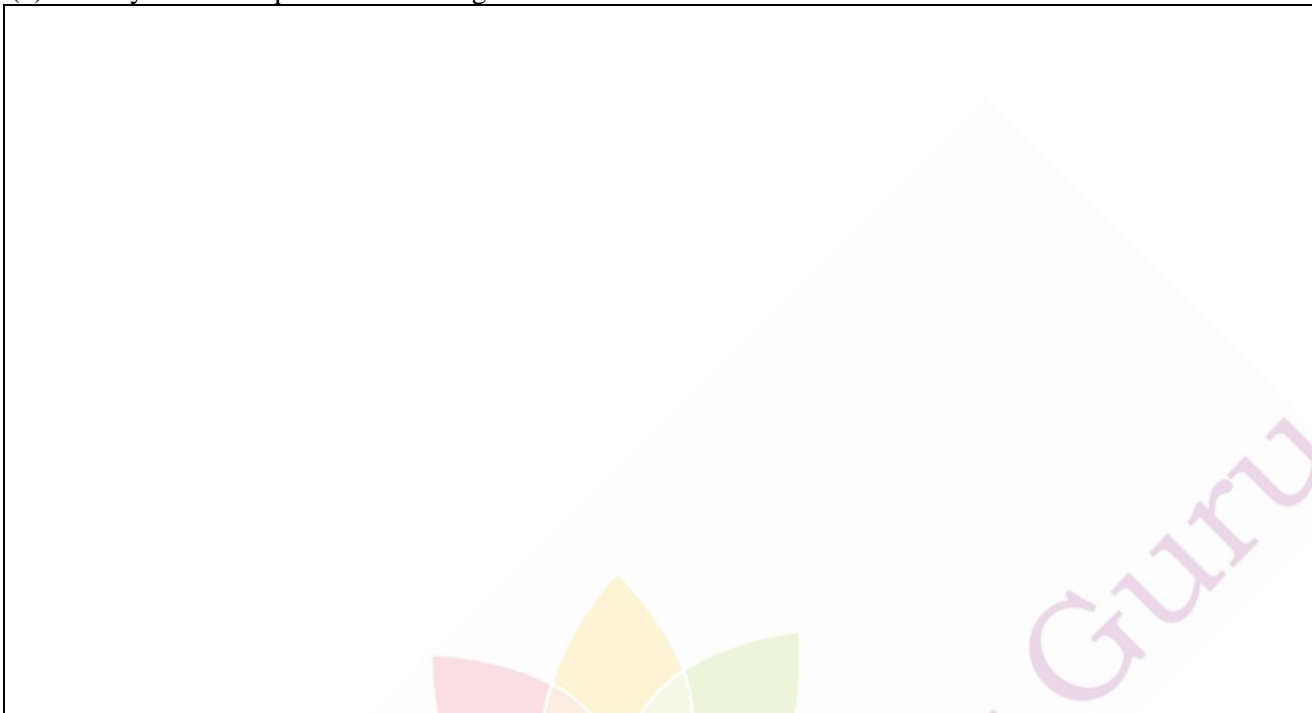
To determine the total amount of oxygen present in the sample, 1.2341 g of the original unknown salt ($M_xA_y \cdot zH_2O$) is heated to 3000 °C in a graphite crucible. The oxygen reacts with the carbon to form carbon monoxide, which is collected and has a mass of 1.0870 g.

(j) Calculate the number of oxygen atoms present per formula unit of the original unknown salt ($M_xA_y \cdot zH_2O$).



The identity of the cation can be elucidated by adding fluoride ions to a solution of the unknown salt, forming a precipitate of $\text{MF}_4 \cdot \text{H}_2\text{O}$. 2.2179 g of the original unknown salt is dissolved and NaF is added until there is no further precipitation. The solid is filtered, washed and dried, and has a mass of 1.4843 g.

(k) Identify the cation present in the original unknown salt.



The polyatomic anion A^{b-} contains only three different elements.

l) Identify the anion and hence the formula of the unknown salt.



Formula of salt:

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Integrity of Competition

If there is evidence of collusion or other academic dishonesty, students will be disqualified. Markers' decisions are final.