School ID

2015 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:** ……/…..../...….

☐ **Male** ☐ **Female** **Year 10** ☐ **Year 11** ☐ **Other:** …….

Name of School: …….……..**State:** ……...

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 2016).

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 2015 are not eligible to attend the 2016 Australian Science Olympiad Science Summer School

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CHEMISTRY

2015 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 27 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	90 marks
	Total marks for the paper	120 marks

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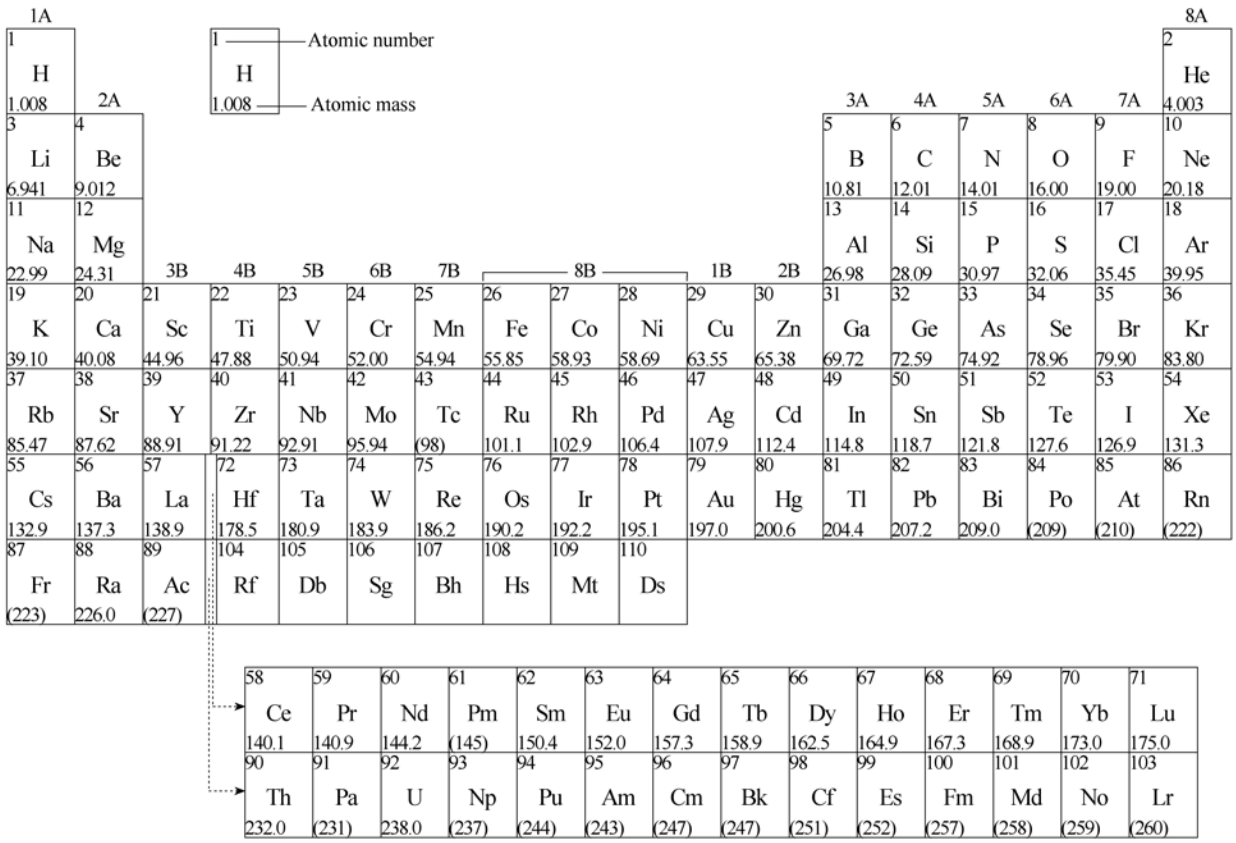
DATA

Avogadro constant (N) 6.022×10^{23} mol^{-1}	Velocity of light (c) 2.998×10^{8} m s^{-1}
1 faraday 96,486 coulombs	Density of water at 25°C 0.9971 g cm^{-3}
1 coulomb 1 A s^{-1}	Acceleration due to gravity 9.81 m s^{-2}
Universal gas constant (R) 8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}	1 newton (N) 1 kg m s^{-2}
Planck's constant (h) 6.626×10^{-34} J s	1 pascal (Pa) 1 N m^{-2}
Standard temperature and pressure (STP) 273 K and 100 kPa 0˚C and 100 kPa 0˚C and 1 bar 0˚C and 750 mm Hg	$pH = -\log_{10}[H^+]$ $pH + pOH = 14.00$ at 25˚C $K_a = \{[H^+][A^-]\} / [HA]$ $pH = pK_a + \log_{10}\{[A^-] / [HA]\}$ PV = nRT E = hν
Molar volume of ideal gas at STP 22.71 L	c = νλ
1 bar = 100 kPa	Surface area of sphere A = 4πr^2

Periodic table of the Elements



Atomic mass values given here are to four significant figures. A value given in parentheses denotes the mass of the longest-lived isotope.

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SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

1. What is the concentration (in mol L^{-1}) of Na^+ ions in a solution prepared by diluting 250.0 mL of 0.550 mol L^{-1} Na_2SO_4 to 1250 mL?

(a) 0.110 mol L^{-1}
(b) 0.138 mol L^{-1}
(c) 0.220 mol L^{-1}
(d) 0.275 mol L^{-1}
(e) 0.550 mol L^{-1}

2. Which compound contains the highest percentage by mass of magnesium (Mg)?

(a) $MgNH_4PO_4$
(b) $Mg(H_2PO_4)_2$
(c) $Mg_2P_4O_7$
(d) $Mg_3(PO_4)_2$
(e) $MgHPO_4$

3. Which one of the following is **not** assumed by the kinetic theory of gases?

(a) Gases are composed of particles in random motion.
(b) Gas particles do not attract or repel each other.
(c) Gas particles constantly collide with each other.
(d) The size of gas particles is negligible compared to the size of the container.
(e) When gas particles collide, kinetic energy is lost.

4. The formula for terbium phosphate is $TbPO_4$. What is the formula for terbium sulfate?

(a) Tb_2SO_4
(b) $TbSO_4$
(c) $Tb_2(SO_4)_3$
(d) $Tb(SO_4)_2$
(e) $Tb_3(SO_4)_2$

5. The molecular compound BH_3 has three bonding pairs of electrons and no lone pairs of electrons around the central boron atom. What is the shape of BH_3?

(a) bent
(b) linear
(c) tetrahedral
(d) triangular (trigonal) planar
(e) triangular (trigonal) pyramidal

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6 A student dissolves solid calcium carbonate in an excess of 0.01 mol L^{-1} nitric acid while stirring, and is looking for ways to make this reaction faster. Which of the following actions would increase the rate of reaction?

(a) Adding distilled water to the solution while stirring.
(b) Cooling the nitric acid before adding the calcium carbonate.
(c) Decreasing the concentration of nitric acid.
(d) Heating the nitric acid before adding the calcium carbonate.
(e) Increasing the volume of nitric acid.

7. Which list below gives non-metals that can be found in their elemental form in nature?

(a) neon, phosphorus, fluorine
(b) helium, hydrogen, iodine
(c) helium, carbon, fluorine
(d) nitrogen, chlorine, sulfur
(e) oxygen, chlorine, phosphorus

8. Solid silver was added to a solution of copper(II) nitrate at standard conditions. Given that silver is a less reactive metal than copper, which of the following observations would be most likely?

(a) A blue precipitate forms on the silvery solid and the solution turns colourless.
(b) The blue solid dissolves in the colourless solution and a silvery precipitate is formed.
(c) The silvery solid dissolves and a blue precipitate forms; the blue colour of the solution fades.
(d) The silvery solid dissolves into the blue solution, and an odourless gas is evolved.
(e) No visible reaction.

9. 25.00 mL of each of the following solutions is added to 20 g of solid $MgCO_3$. After the reactions are complete, which of the solutions will produce the largest volume of CO_2 at room temperature and pressure?

(a) 1 mol L^{-1} H_2SO_4
(b) 2 mol L^{-1} $HC\ell$
(c) 2 mol L^{-1} HNO_3
(d) 2 mol L^{-1} H_2SO_4
(e) 3 mol L^{-1} $HC\ell$

10. Which of the following compounds contains polar covalent bonds, but has no net dipole moment?

(a) CO_2
(b) H_2O
(c) HCN
(d) N_2
(e) $NaC\ell$

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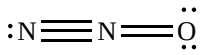
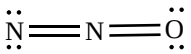
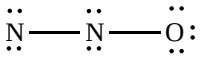
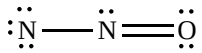
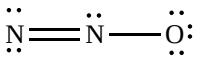
11. What is the correct Lewis (electron dot) structure for N_2O ?

(a) 

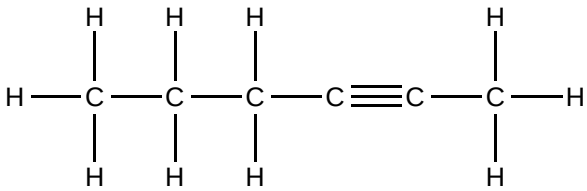
(b) 

(c) 

(d) 

(e) 

12. Which one of the following responses is the correct name for the structure below?



(a) hex-2-yne
(b) hex-4-yne
(c) hept-2-yne
(d) hept-4-yne
(e) hex-2-ene

13. Which of the following is true of elements as one moves from left to right across a period of the periodic table?

(a) electronegativity increases, atomic radius increases
(b) electronegativity decreases, atomic radius increases
(c) electronegativity increases, atomic radius does not change
(d) electronegativity increases, atomic radius decreases
(e) electronegativity decreases, atomic radius decreases

14. How is the structure and bonding in diamond best described?

(a) covalent molecular
(b) covalent network
(c) metallic
(d) molecular
(e) polymeric

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15. Which of these pairs of compounds could be separated on the basis of their solubility in water?

(a)	$AgNO_3$	$CaBr_2$
(b)	$CC\ell_4$	C_6H_{14}
(c)	$PbCO_3$	$CaCO_3$
(d)	SiO_2	$BaSO_4$
(e)	$ZnSO_4$	$AgC\ell$

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ANSWER IN THE SPACES PROVIDED

Question 16

Atomic absorption spectrophotometry (AAS) is a simple and rapid method for the quantitative determination of metals in solution. In this technique, the solution is sprayed into a flame; the metal atoms then absorb light from a beam passing through the flame. The measured absorbance is directly proportional to the concentration of the metal in the solution.

Before a sample containing an unknown concentration of metal can be determined, a standard curve needs to be generated by measuring the absorbance of known concentrations of metal. In this question we will examine the analysis of steel for iron and other elements. For our standard, iron(III) oxide will be dissolved in nitric acid.

(a) Write a balanced equation for the reaction of iron(III) oxide with nitric acid.

(b) Calculate the molar mass of iron(III) oxide (Fe_2O_3).

0.1292 g iron(III) oxide is dissolved in nitric acid and made up to 250.0 mL in a volumetric flask.

(c) Calculate the chemical amount (in mol or mmol) of iron(III) oxide dissolved **per litre of solution**.

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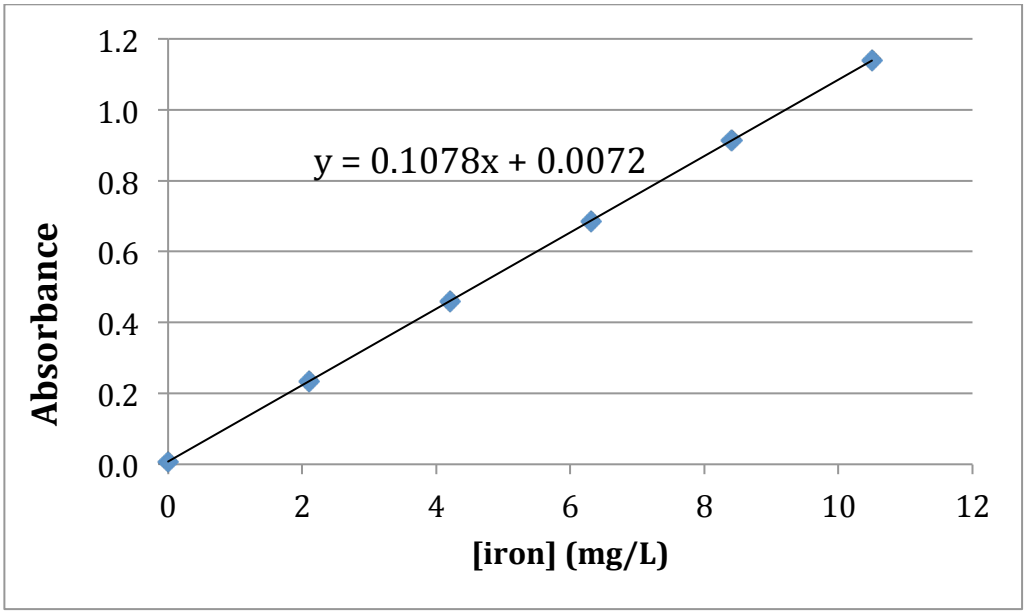
It is normal in AAS to express solution concentrations in terms of the concentration of metal ions present.

(d) Calculate the concentration of iron(III) ions in the solution (in mol L^{-1}).

The concentration range used in iron AAS is typically 2-10 mg of iron per litre. Dilutions were performed as necessary to generate a standard curve. The linear fit was good and the equation of the line of best fit was y = 0.1078x + 0.0072, with y representing absorbance and x representing mg of iron per litre.



A steel sample of mass 0.1082 g was digested in concentrated nitric acid, cooled, filtered and made up to 500.0 mL volumetric flask (this procedure converts all iron in the steel sample to Fe^{3+}). A 10.00 mL sample of this solution were taken and made up to 500.0 mL in a volumetric flask. The solution was analysed on the same AAS machine as the standard curve, with the absorbance measured to be 0.4207.

(e) Calculate the percentage by mass of iron in the steel.

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A stainless steel sample is known to contain iron (83.54% by mass, determined by AAS as described previously) as well as chromium, manganese, carbon, silicon and oxygen. A 0.3647 g sample of this stainless steel was digested in concentrated nitric acid, cooled, filtered and made up to 100.0 mL in a volumetric flask. This procedure converts all iron in the stainless steel sample to Fe^{3+}, chromium to Cr^{3+} and manganese to Mn^{2+}.

(f) Calculate the mass of iron present in the 0.3647 g sample.

(g) Calculate the chemical amount (in mol or mmol) of Fe^{3+} present in a 10.00 mL sample of the digested stainless steel solution.

EDTA is a complexing agent that reacts in a 1:1 mole ratio with many metal ions including Fe^{3+}, Cr^{3+}, Mn^{2+} and Zn^{2+}. For example Zn^{2+} reacts as follows:

$$Zn^{2+} + EDTA^{4-} \rightarrow [Zn(EDTA)]^{2-}$$

50.00 mL of 0.02143 M EDTA was added to a 10.00 mL sample of the digested stainless steel solution and the resulting solution heated for 15 minutes. The excess EDTA required on average 20.53 mL of 0.02005 M Zn^{2+} for complete reaction.

(h) Calculate the chemical amount (in mol or mmol) of Zn^{2+} required for reaction with the excess EDTA.

(i) Calculate the chemical amount (in mol or mmol) of EDTA that reacted with the Fe^{3+}, Cr^{3+} and Mn^{2+} ions present in the 10.00 mL sample of the digested stainless steel solution.

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(j) Calculate the sum of the chemical amounts of Cr^{3+} and Mn^{2+} ions (in mol or mmol) present in the 10.00 mL sample of the digested stainless steel solution.

(k) Calculate the sum of the chemical amounts of Cr^{3+} and Mn^{2+} (in mol or mmol) present in the original 0.3647 g stainless steel sample (**n.b. if you do not get an answer to this part of the question you may use $n(Cr^{3+}) + n(Mn^{2+})$ in the 0.3647 g sample = 1.200×10^{-3} mol for subsequent parts of the question**).

In a separate experiment, 0.1848 g of the same stainless steel dissolved in HNO_3 and heated. The resulting solution is treated with potassium peroxydisulfate ($K_2S_2O_8$), which oxidises Cr^{3+} to $Cr_2O_7^{2-}$ and Mn^{2+} to MnO_4^-.

(l) Write a balanced equation for the oxidation of Cr^{3+} to $Cr_2O_7^{2-}$ by peroxydisulfate, given the following half equations:

$$S_2O_8^{2-} + 2\ e^- \rightarrow 2\ SO_4^{2-}$$

$$2\ Cr^{3+} + 7\ H_2O \rightarrow Cr_2O_7^{2-} + 14\ H^+ + 6\ e^-$$

Following boiling (to decompose any excess peroxydisulfate), cooling and filtration, the solution required 34.70 mL of standard 0.05683 M Fe^{2+} to completely react with all of the $Cr_2O_7^{2-}$ and MnO_4^- present.

(m) Calculate the chemical amount (in mol or mmol) of Fe^{2+} required in this reaction.

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The equations for the reduction of $Cr_2O_7^{2-}$ and MnO_4^- by Fe^{2+} are as follows:

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 2\ Cr^{3+} + 7\ H_2O + 6\ Fe^{3+}$$

$$MnO_4^- + 8\ H^+ + 5\ Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5\ Fe^{3+}$$

(n) Calculate the percentage by mass of chromium in the stainless steel sample.

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Question 17

Polymers are an extremely important class of molecules, which comprise of small repeating units called monomers. There are a wide variety of polymers and polymerisation methods, however two of the most important are radical polymerisation and condensation polymerisation.

In organic chemistry, we use skeletal structures to represent organic molecules. We do not draw the carbon atoms or hydrogen atoms which are attached to carbon atoms.

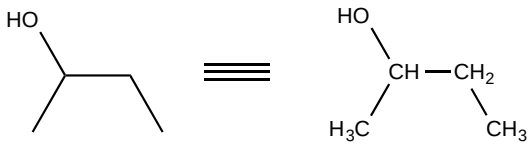
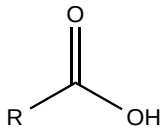
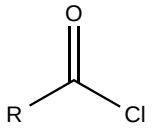
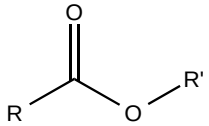
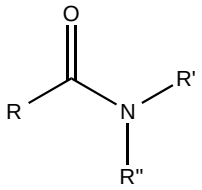
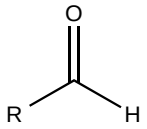
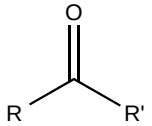
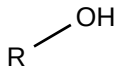
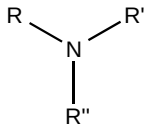
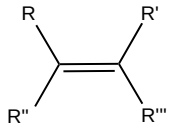
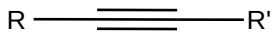


Table 1: Common functional groups

Functional Group Name	Name	Structure
Carboxylic acid	-oic acid	
Acid chloride	-oyl chloride	
Ester	-yl -oate	
Amide	-yl -amide	
Aldehyde	-al	
Ketone	-one	
Alcohol	-ol	
Amine	-amine	
Alkene	-ene	
Alkyne	-yne	

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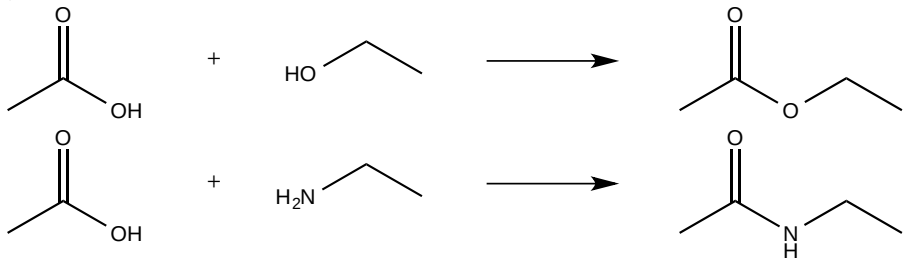
Note that R here can be a hydrogen or a carbon chain, except where when R being a hydrogen would change the name of the group, e.g. aldehydes and ketones. For alkenes and alkynes only, R can be another type of atom.

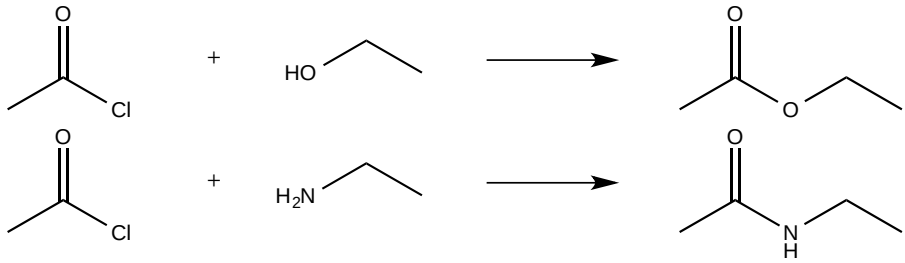
Before we start examining polymers, let us start by looking at some smaller molecules with the same functional groups. We are mostly interested in esters and amides for condensation polymerisation. We can use a wide variety of functional groups to make esters and amides, but the reaction is similar.

(a) What is the other product for these esterification and amidation reactions?

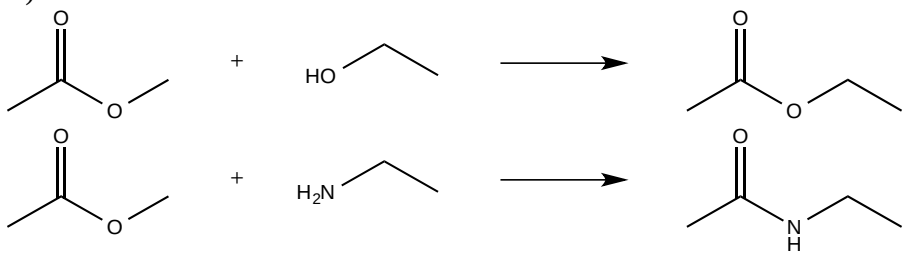
i)



ii)

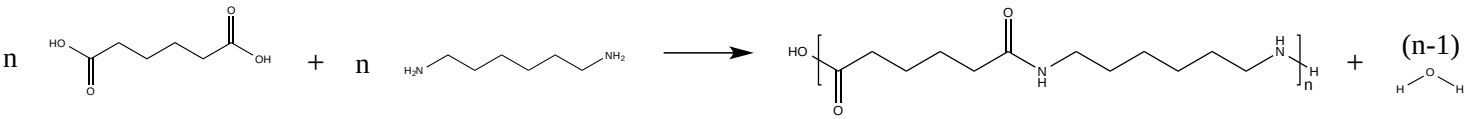


iii)



The nylons are a familiar group of polymers to many people as they are used widely in clothing.

Some can synthesised by using a diamine and a dicarboxylic acid. For example, Nylon 6,6 is synthesised as below. The 6,6 indicates the number of carbons in the diamine and the number of carbons in the dicarboxylic acid respectively.



(b) i) What is the structure of the polymer for Nylon 4,4?

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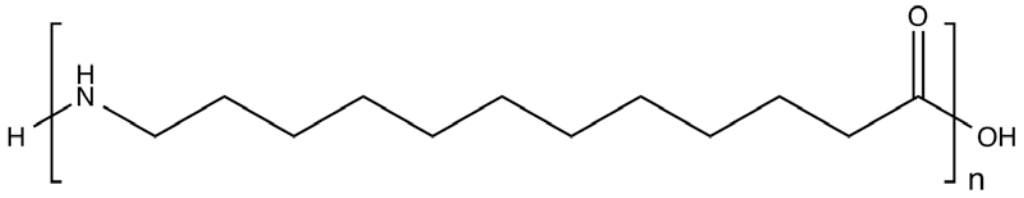
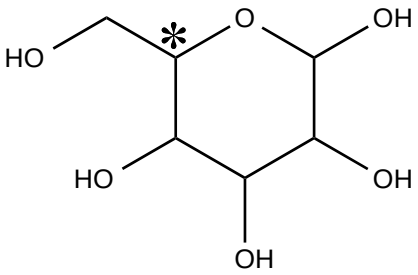
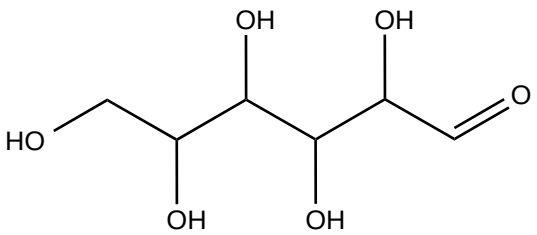
ii) Nylon 12 is produced using a different monomer than that used in Nylon 4,4 or 6,6. What is the structure of the monomer given the polymer?



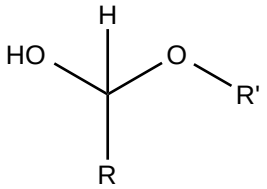
A biologically important class of polymers are the starches, which are familiar from food. We first examine glucose, which is the monomer of starch. It can exist in open-chain and cyclic isomers (compounds with the same formula). This process of interconversion between the open-chain and cyclic forms is called tautomerism, as there is an equilibrium between two isomers. Glucose, however, is almost completely found in the cyclic form.

(c) i) Label which carbon atom of the open-chain form is the starred (*) carbon atom of the cyclic form.



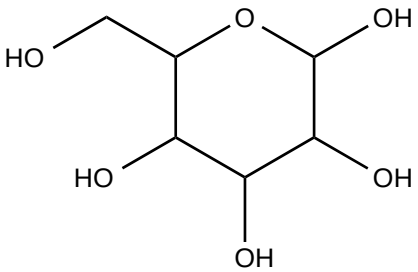


Another functional group, the hemiacetal, which is shown below, is formed in the cyclic form.



hemiacetal functional group

ii) **Circle** the hemiacetal group in the cyclic form shown below.



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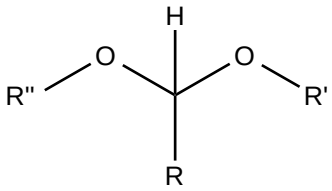
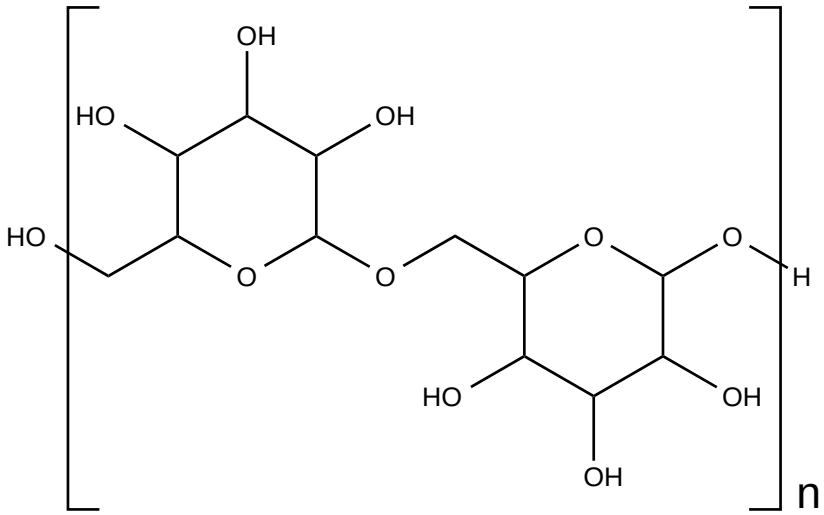
In starch, units are linked by acetal groups, condensing out water. The acetal group is shown below.



iii) Circle the acetal groups in the segment of starch drawn below.



iv) Name two functional groups that react to form a hemiacetal.

v) Name two functional groups that react to form an acetal.

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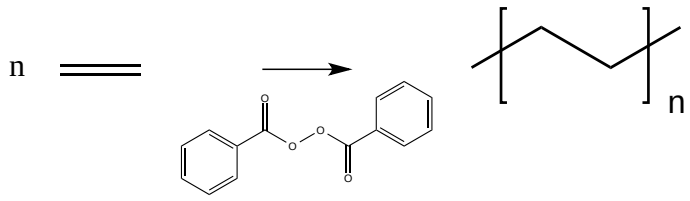
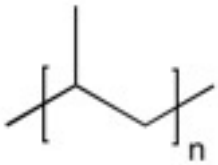
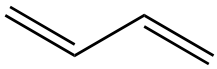
Condensation polymerisation is not the only method we have of making polymers. In radical polymerisations, we break a weaker double bond to form a stronger single bond. We also require an initiator, like potassium persulfate or benzoyl peroxide to start the reaction. One example shown below of this shown below is the polymerisation of ethene to polyethylene using benzoyl peroxide as the initiator. Behaviour at the end of the polymer chains is complicated and we need not consider the ends of the chains.



d) i) A similar polymer can also be formed and a segment is shown below. What is the monomer?



Another polymer polybutadiene is formed by the radical polymerisation of butadiene, shown below.



ii) As butadiene has two double bonds, there are two possible ways that it can polymerise. Draw a segment of polymer showing both the ways butadiene can polymerise.

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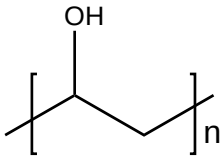
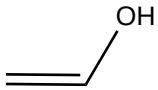
Polyvinyl alcohol is a water-soluble polymer and is used in emulsion polymerisations, which are another method of polymerisation.

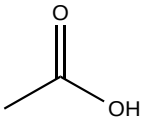
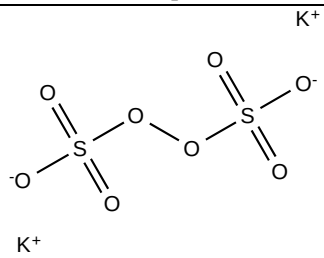
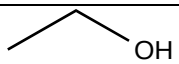
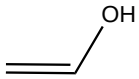
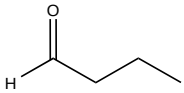
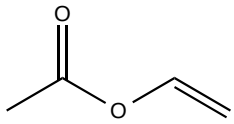


You are tasked with synthesising a sample and are provided with a number of jars of chemicals. One jar is labelled “ethenol (vinyl alcohol)” and the structure of ethenol is shown below. You however know that this label is incorrect, as ethenol, like glucose, tautomerises almost completely to another structure.



iii) What is the actual structure of the contents of the jar?

On the bench, there are jars labelled “acetic acid”, “potassium persulfate”, “ethanol”, “ethenol” “butanal” and “vinyl acetate”.

Acetic acid	Potassium persulfate	Ethanol	Ethenol	Butanal	Vinyl acetate
					

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iv) Propose the steps of a synthesis of PVA using the provided chemicals. You may like to review the reactions in part (a).

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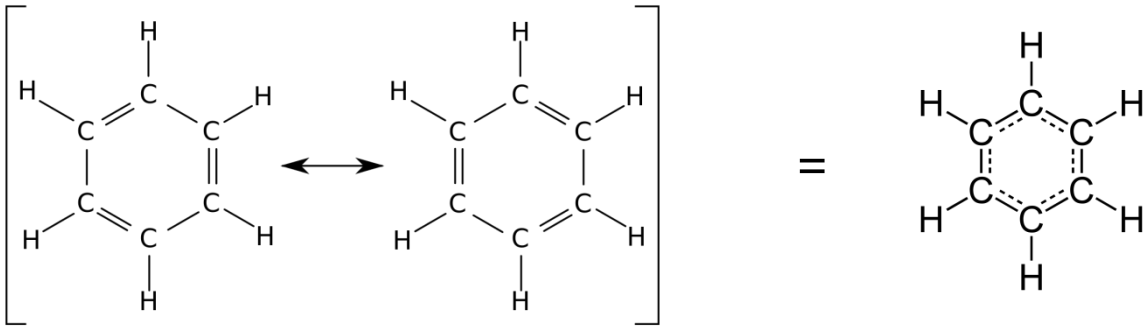
Question 18

Many students have the mistaken belief that chemical structures were correctly worked out only after modern instrumentation and analytical tools became available. It may come as a surprise that by 1910, structures were formulated for more than 200,000 unique organic compounds! One of the compounds with an interesting history is benzene (C_6H_6), whose structure is shown below. Benzene is a cyclic aromatic hydrocarbon in which <u>all the carbon-carbon bonds are equal</u>.



(a) What is the empirical formula of benzene?

The pivotal moment in the history of benzene was the announcement of its discovery by Michael Faraday to the Royal Society of Chemistry on June 16, 1825. He isolated what he then called “bicarburet of hydrogen” from a byproduct formed when producing “illuminating gas” for lights. After purifying this compound by fractional distillation and crystallisation, he performed a number of experiments to identify it.

To determine the empirical formula, Faraday analysed the products of combustion by weight by passing the vapour of benzene over heated copper(II) oxide. Copper(II) oxide can be made by heating elemental copper in pure oxygen, but this method produces some copper(I) oxide as well.

(b) Write an equation for the synthesis of copper(I) oxide and an equation for the synthesis of copper(II) oxide both from their elements.

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The following is a paraphrased extract from Faraday's paper, in which he reacted the unknown substance with copper(II) oxide completely to produce only carbon dioxide and water:

> *"The following is a result obtained when it was passed in vapour over heated copper(II) oxide. 0.776 grain of the unknown substance produced 5.6 cubic inches of carbonic gas (at a temperature of 60° and a pressure of 29.98 inches); and 0.57 grain of water were collected."*

Carbonic gas is an old name for carbon dioxide, because it dissolves in water to produce carbonic acid. The grain is an old unit of weight, and its conversion to SI units is not required in this problem.

(c) What percentage of water by weight is hydrogen?

(d) How many grains of hydrogen did the substance contain originally?

The 5.6 cubic inches of gas produced in this experiment are equivalent to 0.761704 grain of carbon.

(e) What is the ratio of mass of carbon to mass of hydrogen in this sample of benzene?

(f) What is the empirical formula of benzene when determined by this method?

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Faraday also confirmed his results by detonating the benzene vapour in pure oxygen.

(g) Write an equation for complete combustion of (i) carbon, (ii) hydrogen, and (iii) benzene vapour in excess oxygen.

Faraday gives us an account of his experimental detonation of a mixture of 1 part benzene vapour with 19.6 parts oxygen gas. Not all the oxygen is used up, since the 19.6 parts of oxygen is in excess. Again, the paraphrased extract is shown below:

> *7 volumes of this mixture were detonated in a tube by an electric spark, and the total volume decreased as a result to 6.13 volumes; The resulting gas mixture was acted upon by potash to further decrease the gas volume to 4 volumes. These remaining 4 volumes were pure oxygen.*

Liquid water is formed from this reaction and not counted as gaseous volume. Potash is an old name for potassium hydroxide which reacts with carbon dioxide to form solid potassium carbonate.

(h) How many volumes of carbon dioxide were produced in the combustion process?

(i) How many volumes of oxygen were consumed in the combustion process?

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The volume of a gaseous substance is directly proportional to molar amount of the substance.

(j) What is the ratio of mass of carbon to mass of hydrogen in the unknown substance, as determined by this combustion experiment? From this ratio, what is the empirical formula of benzene?

At the time of Faraday's experiments, hydrogen was not yet known as a diatomic gas, but thought of as monoatomic. This meant that carbon was assigned a molar mass of 6.00 and oxygen had a molar mass of 8.00, relative to hydrogen, which weighed 1.00.

(k) What did Faraday calculate as the molar mass of benzene, using only the data from this combustion experiment?

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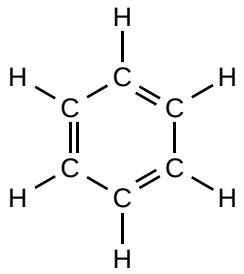
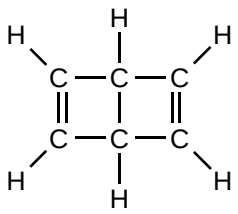
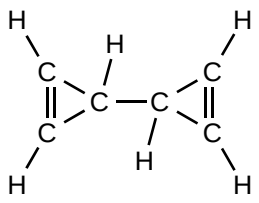
Having determined the molar mass of benzene, the next challenge for chemists was to understand the structure of benzene. Because of its highly unsaturated structure and unusual reactivity, there was a lot of debate as to the true chemical nature of benzene. Several structures were proposed for benzene, shown below, all of which satisfy the valency rules for carbon.



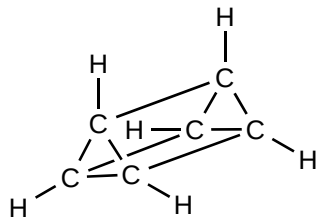
Kekulé



Dewar



Bicyclo-propenyl



Prismane
(A Triangular Prism)

(l) Draw one other structure for C_6H_6 that satisfies the valency rules for carbon.

One of the arguments for the correct structure was the number of isomers (chemically different molecules) that were produced when substituting hydrogens for chlorine atoms. It was found that substituting one of the hydrogens for chlorine in the benzene molecule produced only one new molecule. This means all hydrogen atoms in the benzene molecule are equivalent.

(m) Which of the structures above would produce only one monosubstituted product?

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Substitution of two of the hydrogen atoms with two chlorine atoms (‘disubstitution’) results in three different products. This observation meant that only the Kekulé and prismane structures could potentially be the correct structure.

(n) Draw the different three disubstituted isomers for each of the Kekulé and prismane structures.

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The correct structure that we know today, the Kekulé structure, was identified because Van't Hoff realised that one of the structures you have drawn above is optically active, and substitution of benzene does not produce optically active compounds. One way to tell an optically active compound is that it contains a carbon atom with four single bonds, each bond attached to something different.

(o) Which of the isomers you have drawn above is optically active?

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