CHEMISTRY
2009 National Qualifying Examination

TO BE COMPLETED BY THE STUDENT USE CAPITAL LETTERS

School Name: ……………………………………………………………………...State: …………

Student Name: …………………………………………………………………………………….

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E-Mail: …………………………………………………….... Date of Birth: …..../…..../…....

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

Students competing in the 2009 National Qualifying Examinations must be in Year 11 or an earlier year in 2009.

The Australian Olympiad teams in Biology, Chemistry and Physics will be selected from students participating in the Science Summer School. To be eligible for selection in one of the teams, students must have been schooled in Australia for the last two years, or hold an Australian passport.

Students who have finished their school examinations in the year of the competition can be members of the team as long as they have not commenced their university studies. Students must be under the age of twenty on 30 June of the year of the competition, and must not have started study at university as regular students.

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CHEMISTRY

2009 NATIONAL QUALIFYING EXAMINATION

Time Allowed
Reading Time: 15 minutes
Examination Time: 120 minutes

INSTRUCTIONS

- This paper is in **two** sections and you must answer each section according to the instructions.

  Section A: Answer **ALL** questions — spend no more than 30 minutes on this section.
  [This section is worth 30 marks.]
  Section B: Apportion your time equally on the questions in this section.
  Answer **ALLTHREE (3)** Questions.
  [This section is worth 90 marks.]

- All answers to Section A must be answered, using a 2B pencil, on the Multiple Choice answer sheet.
- All answers to Section B must be written in the spaces provided in the booklet.

- Use **blue** or **black** pen to write your answers; pencil is **NOT** acceptable.

- Rough working must be done only on pages 21 and 22 of this booklet.

- You are not permitted to refer to books, periodic tables or written notes.

- The only permitted aid is a non-programmable electronic calculator.

- Relevant data that may be required for a question will be found on page 2.

- Do not staple the multiple choice answer sheet to this booklet.

DATA

Avogadro constant (N)	6.02×10^{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 x 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 $K_a = [H^+][A^-]/[HA]$ $PV = nRT$ $E = h\nu$	
Molar volume of ideal gas at STP	22.7 L	$c = \nu\lambda$	
1 bar = 100 kPa		Surface area of sphere $A = 4\pi r^2$	

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES*

1	H	1.008	23	V	50.94	45	Rh	102.9	67	Ho	164.9	89	Ac	(227)
2	He	4.003	24	Cr	52.00	46	Pd	106.4	68	Er	167.3	90	Th	232.0
3	Li	6.941	25	Mn	54.94	47	Ag	107.9	69	Tm	168.9	91	Pa	(231)
4	Be	9.012	26	Fe	55.85	48	Cd	112.4	70	Yb	173.0	92	U	238.0
5	B	10.81	27	Co	58.93	49	In	114.8	71	Lu	175.0	93	Np	(237)
6	C	12.01	28	Ni	58.69	50	Sn	118.7	72	Hf	178.5	94	Pu	(244)
7	N	14.01	29	Cu	63.55	51	Sb	121.8	73	Ta	180.9	95	Am	(243)
8	O	16.00	30	Zn	65.38	52	Te	127.6	74	W	183.9	96	Cm	(247)
9	F	19.00	31	Ga	69.72	53	I	126.9	75	Re	186.2	97	Bk	(247)
10	Ne	20.18	32	Ge	72.59	54	Xe	131.3	76	Os	190.2	98	Cf	(251)
11	Na	22.99	33	As	74.92	55	Cs	132.9	77	Ir	192.2	99	Es	(252)
12	Mg	24.31	34	Se	78.96	56	Ba	137.3	78	Pt	195.1	100	Fm	(257)
13	Al	26.98	35	Br	79.90	57	La	138.9	79	Au	197.0	101	Md	(258)
14	Si	28.09	36	Kr	83.80	58	Ce	140.1	80	Hg	200.6	102	No	(259)
15	P	30.97	37	Rb	85.47	59	Pr	140.9	81	Tl	204.4	103	Lw	(260)
16	S	32.07	38	Sr	87.62	60	Nd	144.2	82	Pb	207.2	104	Db	
17	Cl	35.45	39	Y	88.91	61	Pm	(145)	83	Bi	209.0	105	Jt	
18	Ar	39.95	40	Zr	91.22	62	Sm	150.4	84	Po	(209)	106	Rf	
19	K	39.10	41	Nb	92.91	63	Eu	152.0	85	At	(210)	107	Bh	
20	Ca	40.08	42	Mo	95.94	64	Gd	157.3	86	Rn	(222)	108	Hn	
21	Sc	44.96	43	Tc	(98)†	65	Tb	158.9	87	Fr	(223)	109	Mt	
22	Ti	47.88	44	Ru	101.1	66	Dy	162.5	88	Ra	226.0			

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

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section on the multiple choice answer sheet, using a 2B pencil. Only one choice is allowed per question. If you make a mistake **make sure that your incorrect answer is completely erased.**
Please note the following:
• **It is recommended that you first record your answer on this question paper by circling ONE of the letters A, B, C, D or E.**
• **Then transfer these answers on to the computer sheet which will be computer marked for assessment.**

Q1   What is the concentration of a NaOH solution, 25.0 mL of which completely reacts with 35.7 mL of a 0.126 mol L^{-1} H_2SO_4 solution?

   A   0.088 mol L^{-1}

   B   0.126 mol L^{-1}

   C   0.176 mol L^{-1}

   D   0.180 mol L^{-1}

   E   0.360 mol L^{-1}

Q2   When 1.27 g samples of the following substances are all treated with excess dilute hydrochloric acid, all give off carbon dioxide. Which gives off the greatest mass of carbon dioxide?

   A   lithium carbonate

   B   beryllium carbonate

   C   sodium carbonate

   D   magnesium carbonate

   E   potassium carbonate

Q3   There are many well-documented periodic trends including ionisation energy, electronegativity and atomic radius. Through analysis of each of these trends, we can derive secondary trends. Polarisability is a measure of the tendency for an atom or molecule's electron cloud to be distorted by an external electric field. Large atoms with diffuse electron clouds (especially in d and f orbitals) are highly polarisable. Which of the following statements is true?

   A   Polarisability increases going across a period.

   B   Polarisability increases going down a group.

   C   Polarisability increases going down a group and across a period.

   D   Polarisability increases going up a group and across a period.

   E   Polarisability increases with increasing electronegativity.

Q4   Which of the following species does NOT have eight electrons around the central atom?

       A CCl_4 molecule

       B BCl_3 molecule

       C NH_3 molecule

       D NH_4^+ ion

       E CO_2 molecule

Q5   What is the oxidation state of molybdenum in the ion $[Mo_2O_4(NCS)_6]^{4-}$?

       A   +I

       B   +III

       C   +IV

       D   +V

       E   +VI

Q6   The following is a list of selected standard reduction potentials:

$$Cd^{2+}\ (aq) + 2e^- \longrightarrow Cd\ (s) \quad E^o = -0.40\ V$$

$$Zn^{2+}\ (aq) + 2e^- \longrightarrow Zn\ (s) \quad E^o = -0.76\ V$$

$$Ni^{2+}\ (aq) + 2e^- \longrightarrow Ni\ (s) \quad E^o = -0.23\ V$$

By referring to the standard reduction potentials above, which of the following species is the best oxidizing agent?

       A $Cd\ (s)$

       B $Zn^{2+}\ (aq)$

       C $Ni^{2+}\ (aq)$

       D $Zn\ (s)$

       E $Ni\ (s)$

Q7   1 mL of 1 mol L^{-1} hydrochloric acid was diluted to 100 mL with deionised water. 10 mL of this solution was diluted to 100 mL again using deionised water. What is the pH of the final solution?

       A   0

       B   1

       C   2

       D   3

       E   4

Q8   It is known that carbon monoxide reacts exothermically with hydrogen gas to form methanol at $400\,^{\circ}C$, in the presence of a catalyst.

$$CO_{(g)} + 2H_{2\,(g)} \rightleftharpoons CH_3OH_{(g)} + heat$$
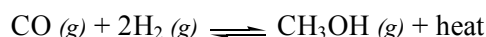
A mixture of carbon monoxide, hydrogen gas and methanol placed under conditions described above achieves equilibrium in a closed container. If the reaction temperature is changed to $450\,^{\circ}C$, which of the following statements is correct?

    A   The total number of molecules in the container decreases.

    B   The reaction rates of both the forward and reverse reactions remain constant.

    C   The average molecular mass of the gaseous mixture decreases.

    D   Rate of formation of hydrogen decreases while the rate of decomposition of methanol increases.

    E   Total pressure within the container decreases.

Q9   Magnesium oxide has a solubility of 0.0086 g/100 mL. What pH will a saturated solution of magnesium oxide have?

    A   2.37

    B   3.37

    C   10.63

    D   11.33

    E   11.63

Q10   Consider the following three scenarios:

(i)   2.3 g of pure Na_2CO_3 reacts completely with a certain volume, **V1**, of 0.1 mol L^{-1} hydrochloric acid to give sodium chloride, carbon dioxide and water.

(ii) 2.3 g of a sample containing Na_2CO_3 but also contaminated with some K_2CO_3, similarly reacts completely with a certain volume, **V2**, of 0.1 mol L^{-1} hydrochloric acid.

(iii) 2.3 g of a sample containing Na_2CO_3 but contaminated with some NaOH, similarly reacts completely with a certain volume, **V3**, of 0.1 mol L^{-1} hydrochloric acid.

What is the relationship between the volumes **V1**, **V2** and **V3**?

    A   V3>V1>V2

    B   V1>V2>V3

    C   V3>V2>V1

    D   V1>V3>V2

    E   V2>V3>V1

Q11   Which of the following groups of ions can coexist in significant quantities in aqueous solution without reacting with each other?

   A HSO_4^-, K^+, Na^+, HCO_3^-

   B K^+, CO_3^{2-}, $C\ell^-$, $A\ell^{3+}$

   C K^+, Ba^{2+}, NO_3^-, OH^-

   D Na^+, Ba^{2+}, H^+, SO_4^{2-}

   E Ca^{2+}, K^+, CO_3^{2-}, $C\ell^-$

Q12   A gaseous mixture containing ethane and methane underwent complete combustion to produce 5.28 g of carbon dioxide and 3.78 g of water. What is the volume ratio of ethane to methane in the original mixture?

   A   1:1

   B   1:2

   C   2:1

   D   1:4

   E   4:1

Q13   Kravatz the Klown wishes to fill a 5.8 L balloon with nitrogen gas. Searching for cheap and effective methods to quickly produce the nitrogen gas necessary, he discovered that azide (N_3^-) salts, although highly toxic, are often used to produce nitrogen gas. Sodium azide, commonly used in car airbags, decomposes to sodium and nitrogen gas. What mass of sodium azide would Kravatz need to produce 5.80 L of nitrogen gas when measured at 25°C and 103 kPa?

   A   5.22 g

   B   10.1 g

   C   10.4 g

   D   15.2 g

   E   15.7 g

Q14   Given the following table of electronegativities, which of the following bonds is most polar?

Element	P	C	S	N	$C\ell$
Electronegativity	2.19	2.55	2.58	3.04	3.16

   A   P-S

   B   P-C

   C   S-$C\ell$

   D   C-$C\ell$

   E   S-N

Q15 A mixture containing both ethene and propene can undergo polymerisation under various different reaction conditions. Which of the following segments of polymer could potentially be formed from such a mixture?

(i)   —CH$_2$-CH$_2$-CH$_2$-CH$_2$—

(ii)   —CH$_2$-CH$_2$-CH—CH$_2$—
                            |
                            CH$_3$

(iii)   —CH$_2$-CH—CH$_2$-CH—
                      | |
                      CH$_3$ CH$_3$

(iv)   —CH—CH$_2$-CH$_2$-CH—
                 | |
                 CH$_3$ CH$_3$

(v)   —CH$_2$-CH—CH—CH$_2$—
                       | |
                       H$_3$C   CH$_3$
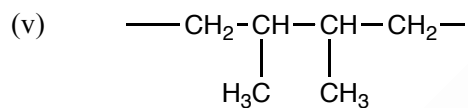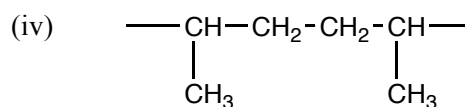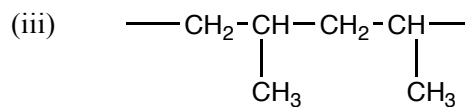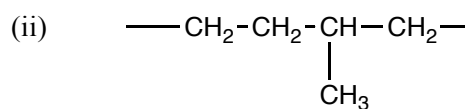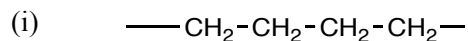
    A   Structure (ii) only

    B   Structures (i) and (iii) only

    C   Structures (i), (ii) and (iii) only

    D   Structures (i), (ii), (iii) and (iv) only

    E   Structures (i), (ii), (iii), (iv) and (v)

SECTION B

Marks will be deducted for incorrect use of significant figures. You are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.
Answer ALL three of the questions in this section.

Q16

A double salt is a salt that crystallises from a water solution containing two different cations other than H^+. The mineral dolomite ($CaMg(CO_3)_2$), for example, is a double salt that crystallises from a solution containing both calcium and magnesium ions. The colourless, efflorescent crystalline compound potassium sodium tartrate, $KNaC_4H_4O_6 \cdot 4H_2O$, is another example of a double salt. It is used in making mirrors, in electronics, and has been used medicinally as a laxative. It is also called *Rochelle salt*. Double salts exist only in the solid state. When dissolved they act as a mixture of the two separate salts.

Consider the double salt **A** which contains two types of cation, **G** and **L**, and has the general formula $GL_x(SO_4)_y \cdot zH_2O$. The aim of the question is to identify the values of **x, y** and **z** and to determine the identity of cations **G** and **L**.

Cation **G** reacts in a 5:1 molar ratio with a solution containing $KMnO_4$ and dilute sulfuric acid. When 2.500 g of **A** was dissolved in water and made up to 100.0 mL with water, it was found that 20.00 mL samples required 12.75 mL of 0.0200 mol L^{-1} $KMnO_4$ acidified with dilute sulfuric acid.

(a) What is the molar mass of **A**?

When a solution of **A** is treated with an excess of $BaCl_2$ (which has been acidified with dilute HNO_3), the precipitate formed weighs 19.05% more than the mass of **A** used.

(b) What is the value of **y** in the formula?

Both cation **G** and cation **L** react, when boiled for a few minutes in an open vessel, with dilute NaOH. **G** produces a coloured solid whilst **L** forms a gas.

When 1.000 g of **A** was boiled with 20.00 mL of 1.00 mol L^{-1} NaOH (an excess) and then rapidly filtered, the residue after washing and drying had a mass of 0.229 g. The filtrate was diluted to 200.0 mL. 20.00 mL samples of the diluted solution required 9.80 mL of 0.0500 mol L^{-1} H_2SO_4 for complete neutralisation.

(c) How many moles of NaOH react with 1 mol of **A**?

(d) What gas is evolved during the experiment?

(e) What is the identity of cation **L**?

(f) Write an equation for the reaction of cation **L** with dilute NaOH. Omit spectator ions.

(g) What is the molar mass and formula of **G**?

(h) Write an equation for the reaction of **G** with a solution containing $KMnO_4$ and dilute sulfuric acid. Omit spectator ions.

(i) What is the value of both of **x** and **z** in the formula?

(j) What is the formula of the coloured residue?

(k) What is the formula of **A?**

(l) Why must the filtration be rapid?

Q17

Functional groups are a group of atoms arranged in a particular way that is constant between all molecules. Functional groups will behave in a similar way across molecules regardless of the size of the molecule of which it is a part. One molecule can contain a variety of functional groups.

A common list of organic functional groups and what they look like is shown in **Table 1**. Note that R is used to symbolise further bonding to other carbon atoms that may contain further functionality, but will not affect the identification of the functional group.

Table 1. Common Functional Groups

Functional Group Name	Atom arrangement	Visualisation
carboxylic acid	–COOH	
ester	–COOR	
ether	ROR	
amide	–CONH$_2$	
aldehyde	–CHO	
ketone	R$_2$CO	
alcohol	–OH	R——OH
amine	–NH$_2$	R——NH$_2$

Carbon atoms and the implicit hydrogen atoms on carbon atoms are not drawn, so that

 is identical to
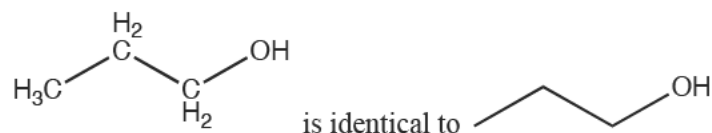
(a)   Using the information in Table 1 above, name the functional groups present in each of the following molecules.

(i)
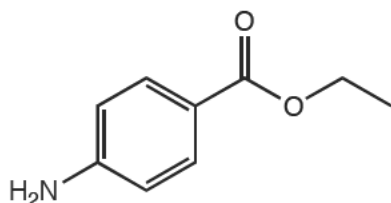
(ii)
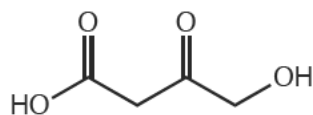
(iii)
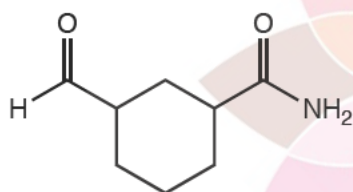
Two interesting functional groups in chemistry are the amide and the ester. Although these two groups have somewhat limited reactivity, they are both formed by condensation reactions: Amides are formed by the reaction of a carboxylic acid group with an amine, and esters are formed by the reaction of a carboxylic acid group with an alcohol, with both reactions producing water. With amides and amines, they remain the same functional group if the nitrogen atom is bonded to carbon atoms instead of hydrogen atoms.

(b)   The antibiotic Penicillin G is shown below. Circle each functional group that it contains and name the groups that you have identified.
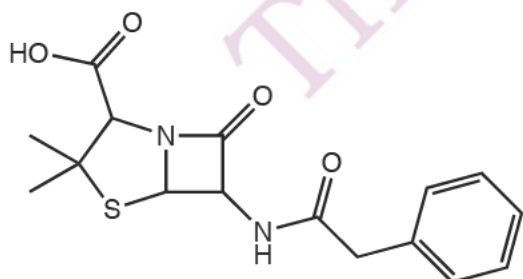
Penicillin G

Often in organic chemistry, more than one product may be formed in a specific reaction.

(c)   Draw all possible products in each of (i), (ii) and (iii) that may form when the following two molecules are allowed to react:
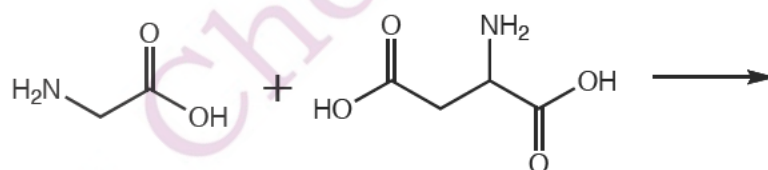
(i)
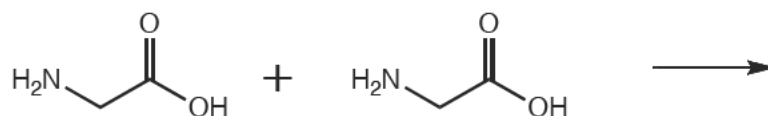
(ii)
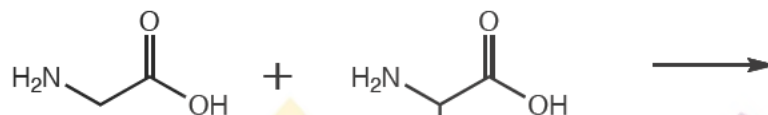

(iii)

To obtain a single product, sometimes "protections" are employed to "mask" certain functional groups to prevent them from taking part in a reaction. Some of these protections include converting reactive amines, alcohols, aldehydes and carboxylic acids into relatively unreactive esters, ethers and amides. These protecting groups can then be removed selectively through a deprotection step.

(d) Compound **A** normally has an alcohol and a carboxylic acid as functional groups but it is shown below in its protected form as an ether and ester respectively. Draw compound **A** as it would appear without either of the protecting groups.
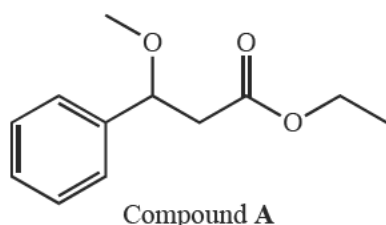
Compound **A**

(e) In compound **B**, all reactive functional groups but one is protected. Circle the protecting groups and identify the functional groups that they are masking. Identify the functional group which remains unprotected.

Compound **B**
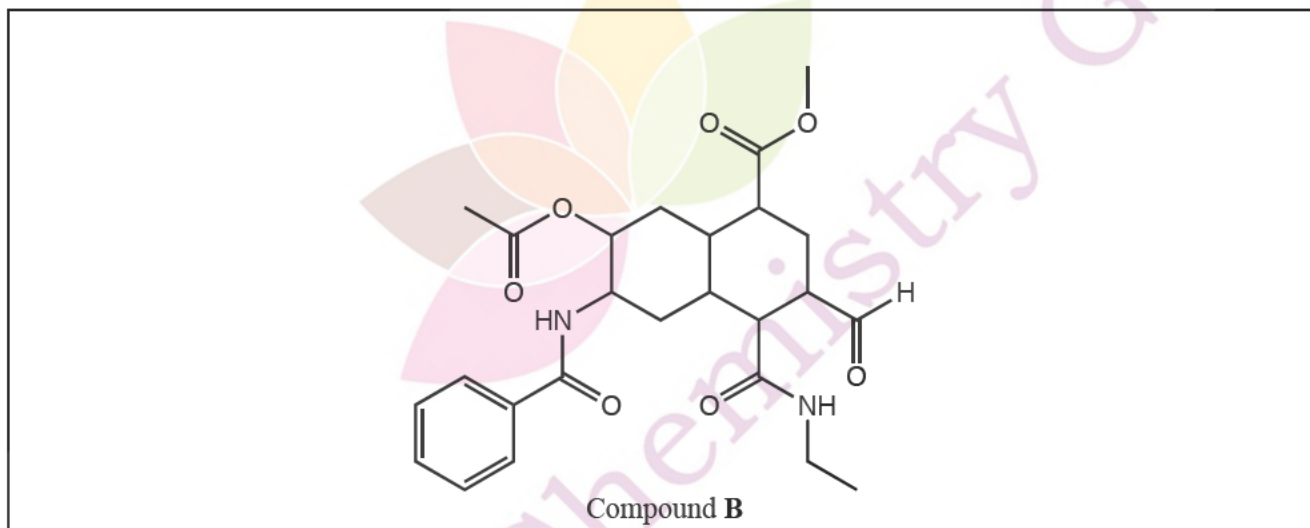
When more than one protecting group is used, they need to be orthogonal to each other. That is, each protecting group needs to be added and removed under conditions independent to one another. See **Table 2** for conditions.

Table 2. Common protecting groups and conditions required for their removal.

Functional Group	Protecting Group	Visualisation	Conditions for Removal
alcohol	$-OSiMe_3$		Option 1) Bu_4NF Option 2) K_2CO_3
alcohol	$-OAc$		Option 1) K_2CO_3 Option 2) HCl
Table 2 continues on the next page.			

amine	–NHTFA		Option 1) LiOH Option 2) K_2CO_3
amine	–NHAc		HCl
carboxylic acid	–COOMe		Option 1) LiOH Option 2) K_2CO_3
carboxylic acid	–COOBn		Option 1) H_2/Pd Option 2) K_2CO_3
carboxylic acid	–COOSiMe$_3$		Option 1) Bu_4NF Option 2) K_2CO_3

(f) (i) Consider the reaction below for the production of compound **C**:

All functional groups on the starting material for this reaction have been protected.

On the appropriate structure, circle the functional groups which need to be deprotected in order for this reaction to proceed to give the product on the right. Label with a P the protections which need to remain on during the reaction.
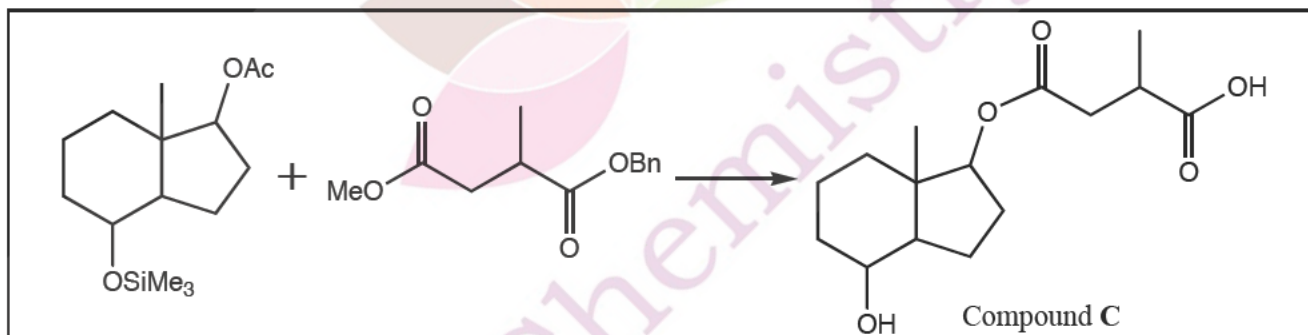
(ii) Using the information contained in **Table 2**, suggest reaction conditions that could be used to carry out the deprotections you circled above.

(iii)   Once the condensation reaction is complete, a protected version of compound **C** is obtained. Draw the structure of the protected product and using the information in **Table 2** give conditions that you would use to deprotect in one step to give compound **C**. What problem might arise using this method of deprotection?
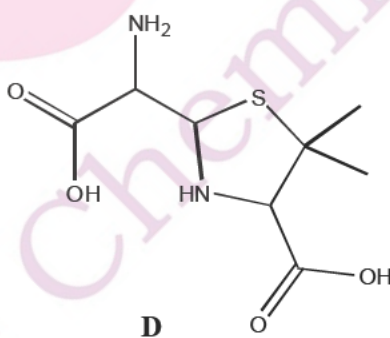
(g)   Now, let us apply these principles in the synthesis of Penicillin G.

Penicillin G
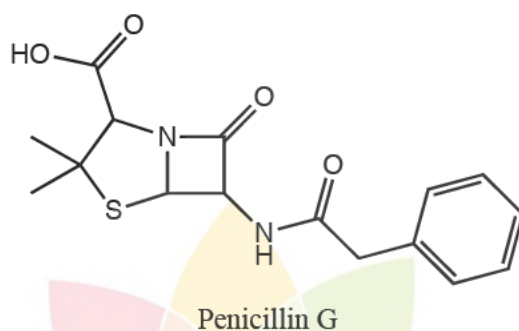
A suitably protected starting material **D** has been provided:

The first step in this synthesis is an intramolecular condensation to form an amide group.

(i)   Circle the functional groups in **D** and label as either protected (P) or reactive (R) in this step.

(ii)   Draw the structure of product **E** of this reaction.

(iii) Suggest why the product of this reaction does not readily form without the aid of protecting groups.

The second synthetic step involves the reaction of **G** (shown below) with **F**, a deprotected version of **E**:

G
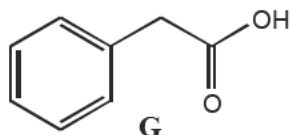
(iv) With which functional group does **G** react?

(v) Draw the structure of **H**, the product of this reaction.

To complete the synthesis, any remaining protecting groups are removed to form Penicillin G.

(vi) Considering the entire reaction scheme and using **Table 2**, draw compound **D** with appropriate protecting groups:

(vii) Give conditions for the conversion of **E** into **F**.

(viii) Give conditions for the conversion of **H** into Penicillin G.

Q18

In most stable molecules, electrons come in pairs, either as covalent bonds or lone pairs. Atoms, molecules or ions which contain unpaired electrons are called free radicals. Free radicals are often highly reactive and many examples can be found in our own biology.

(a) Which of the following species are free radicals? Tick the box(es).

Cl	CH_3	NO^+	NO_2

From now on, we will write a dot next to radical species (e.g. Na•) to represent unpaired electrons.

Reactive oxygen species (ROS) are oxygen-containing species that cause damage to biomolecules such as fats, sugars and DNA. Superoxide, O_2•⁻, and the hydroxyl radical, OH•, are both free radicals that are a part of this group. The hydrogen peroxide molecule, H_2O_2, is another ROS.

(b) What is the oxidation number of oxygen in each of the following species?

H_2O	O_2•⁻	OH•	H_2O_2

The most reactive and damaging member of the ROS family is OH•, which can be formed by the reaction of H_2O_2 with various metal ions. An example is the Fenton reaction, in which the formation of OH• occurs via the conversion of iron(II) ions into iron(III) ions.

(c) Write half equations and a balanced full equation to describe the Fenton reaction in an aqueous solution.

Oxidation:

_____

Reduction:

_____

Full equation:

One of the most documented effects of ROS is lipid peroxidation. In this process polyunsaturated fatty acids (PUFA), long-chain carboxylic acids containing several double bonds, are converted into free radicals by reaction with OH•. These PUFA free radicals then react with oxygen to form an oxygen-based free radical. Once in this form the PUFA is damaged and has the potential to react with another PUFA propagating a chain reaction. These processes are shown below:
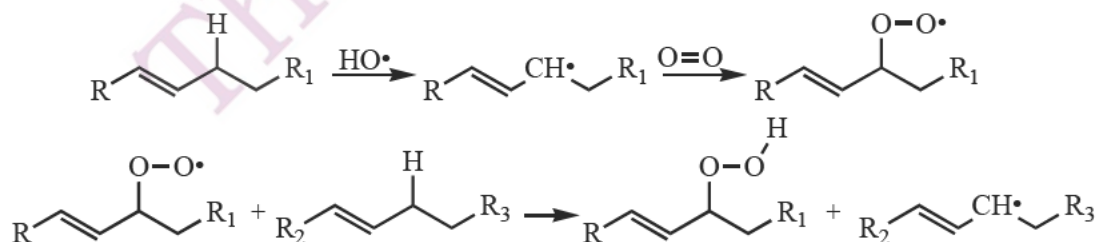
The potential for a chain reaction means the damage caused by a single OH• radical can be extensive. For this reason, the body has antioxidants to 'scavenge' for ROS. One such molecule is glutathione, a small peptide (MW =307.3 g mol^{-1}) containing a sulfur-hydrogen bond. Glutathione, written G-SH where G represents the rest of the peptide, forms a dimer linked by its sulfur atoms to give G-SS-G, and in doing so can convert H_2O_2 into H_2O.

(d) Write half equations and a balanced full equation to describe this reaction (use G-SH to represent glutathione).

Oxidation:

_____
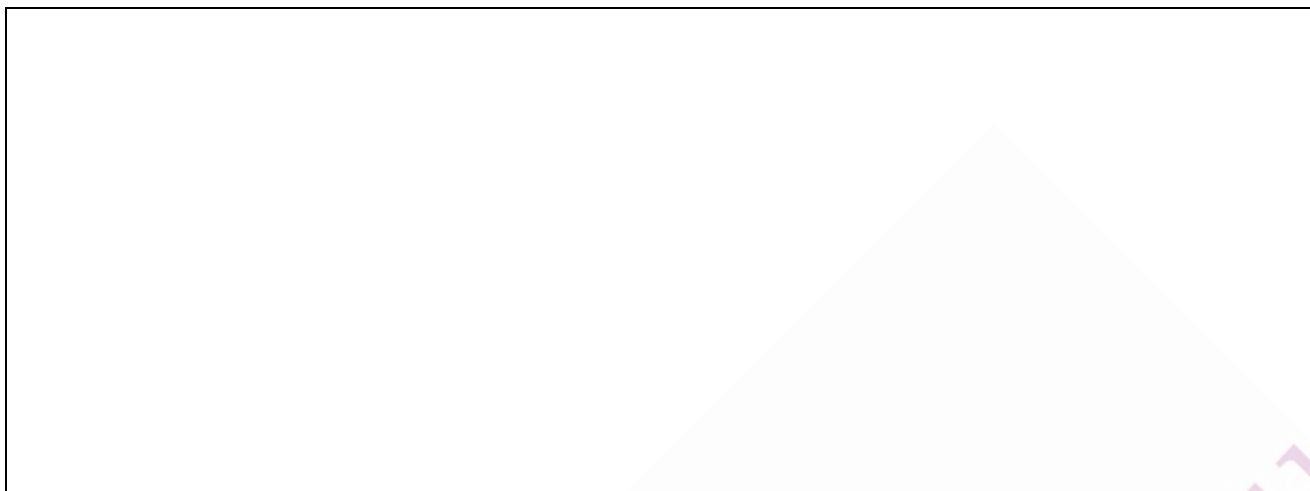
Reduction:

_____

Full equation:

Reactive oxygen species are not always bad. For example, the Fenton reaction has been used to clean up organic molecules in waste water. In such cases the OH• radical reacts with the organic molecules to produce harmless products. For example, this process would convert benzene, a toxic carcinogen, into a dicarboxylic acid:
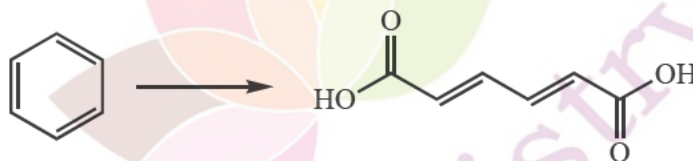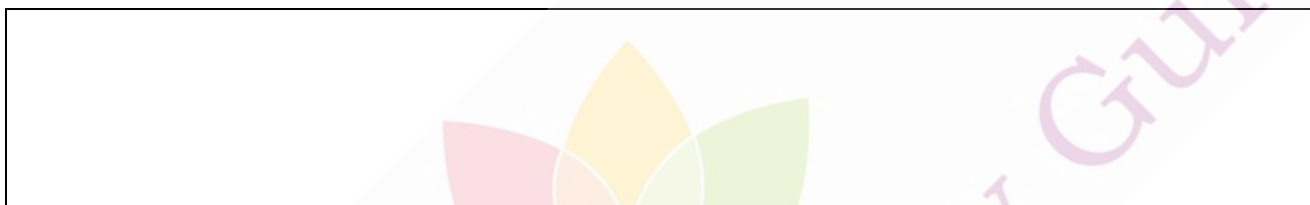

(e) Write half equations and a balanced full equation to describe the clean up of benzene using OH•.

Oxidation:

_____

Reduction:

_____

Full equation:

(f) 1.00 L of water containing 0.030 mol L^{-1} benzene as the only impurity is decontaminated using $FeSO_4$ and H_2O_2. Using the stoichiometry derived in the previous questions, what mass of $FeSO_4$ would be required assuming an excess of hydrogen peroxide was present?

(g) Give one reason why more iron(II) sulfate might be required than the amount calculated in (f).

(h) Give one reason why less iron(II) sulfate might be required than the amount calculated in (f).

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