Section A (Multiple Choice)

Question #	Answer	Question #	Answer	Question #	Answer
Q1	E	Q6	C	Q11	C
Q2	B	Q7	D	Q12	B
Q3	B	Q8	C	Q13	C
Q4	B	Q9	E	Q14	D
Q5	D	Q10	A	Q15	E

Question 16

a) Need to know no. of moles in 2.500 g in order to calculate mass of one mole.

No of mmoles in 20.00 mL is five times no. of mmol permanganate in 12.75 mL 0.0200 mmol mL^{-1} permanganate

$= 5 \times 12.75 \times 0.0200 = 1.275$ mmol in in 20.00/100.0 of 2500 = 500 mg mg **A**

∴ 1 mmol weighs $500/1.275 = 392.2$ mg. **Ans 392 g mol^{-1}**

(b) For 1 mol **A** (392.2 g), the precipitate weighs 119.05% of 392.2 = 446.9 g $BaSO_4 = 446.9/233.4 = 2$ mol (whole number).

Thus 1 mol **A** contains 2 mole sulphate: **Ans: y = 2**

(c) No. of mmoles NaOH added to 1.000 g **A** = $20.00 \times 1.00 = 20.0$

No. of mmoles NaOH remaining = 200.0/20.00 of $9.80 \times 0.0500 \times 2$ = 9.80

∴ No. of mmoles NaOH consumed = $20.0 - 9.8 = 10.2$

1.000 g is $1000/392.2 = 2.550$ mmoles and consumes 10.2 mmoles NaOH

∴ 1 mmol **A** consumes 4 mmol OH^- **Ans: 4 moles**

(d) NH_3

(e) NH_4^+

(f) $NH_4^+ + OH^- \ \square \ NH_3(g) + H_2O$

(g)   **GL$_x$(SO$_4$)$_2$.zH$_2$O**

Question states in the formula of the salt that 1 mole **A** contains 1 mole **G**

Let valency of **G** be *a*

Let aw of **G** be X

mw of **G**(OH)$_a$ = X + 17.016 a

No. of mmoles **G**(OH)$_a$ from 1000 mg **G** = 1000/392.2 = 2.550 mmoles **G**

Mass   of **G**(OH)$_a$ = 229 mg (from (c))

∴ mw of **G**(OH)$_a$ = 229/2.550 = 89.8

∴ aw of **G** = 89.8 − 17.016 a .

a can be 1,2 or 3 (not 4 as this would mean no NH_4^+)

[a, aw of **G**]:   [1, 72.8]   [2, 55.8]   [3, 38.8]

55.8 corresponds to Fe. ∴ a = 2, the formula is **Fe^{2+}**

(h) MnO_4^- + 5 Fe^{2+} + 8 H^+ Mn^{2+} + 5 Fe^{3+} + 4 H_2O
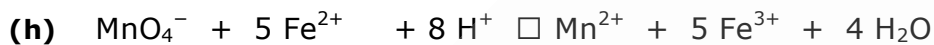
(i)   For total cation charge of +4, x must be 2

mw of salt = 392.2 of which $Fe(NH_4)_2(SO_4)_2$ contributes 55.8 + 2 × 17.06 + 2 × 96.06 =   282.0

∴ water contributes 392.2 − 282.0 = 110.2

∴ z = 110.2/18.016 = 6.11. Nearest whole number is **6**.

(j) $Fe(OH)_2$

(k) $Fe(NH_4)_2(SO_4)_2.6 H_2O$
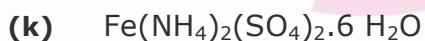
(l) $Fe(OH)_2$ is rapidly oxidised in air to $Fe(OH)_3$.
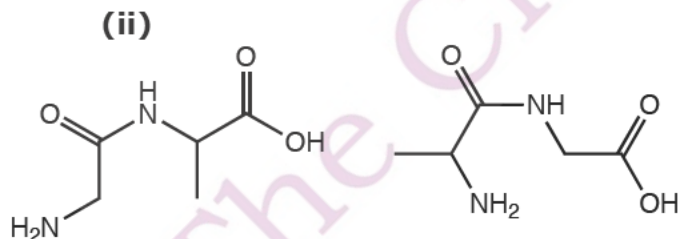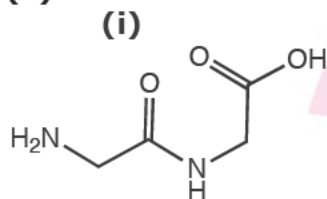
Question 17

(a) **(i)** amine and ester
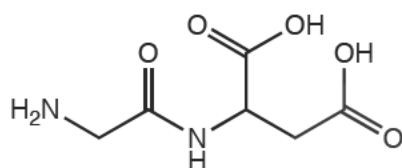**(ii)** carboxylic acid, ketone and alcohol
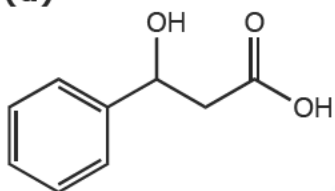**(iii)** aldehyde, amide

(b)
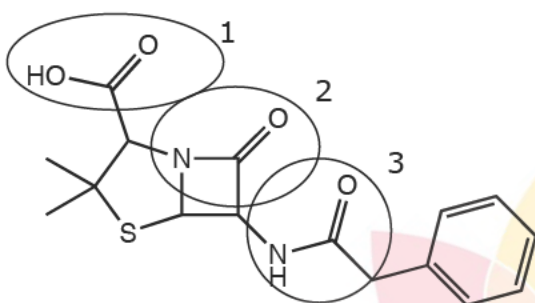
1) Carboxylic acid
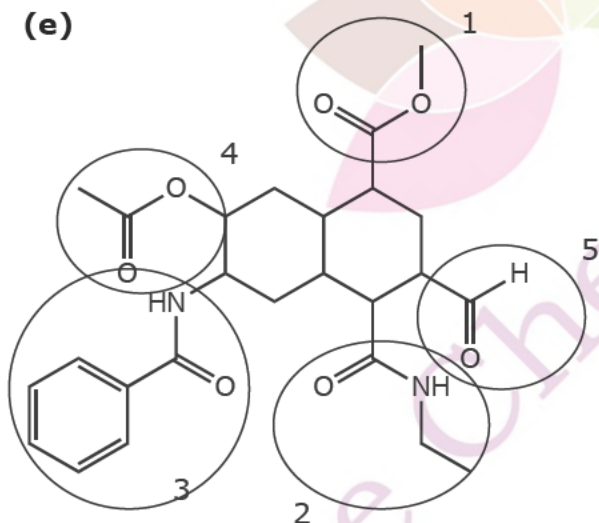2) amide
3) amide

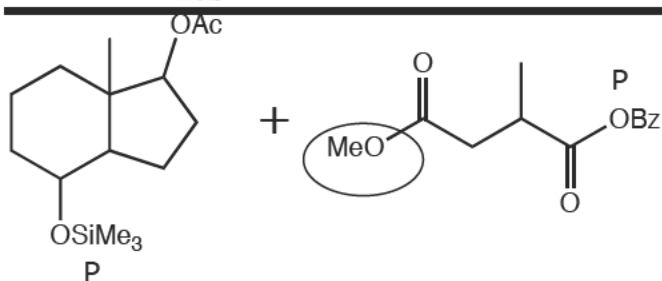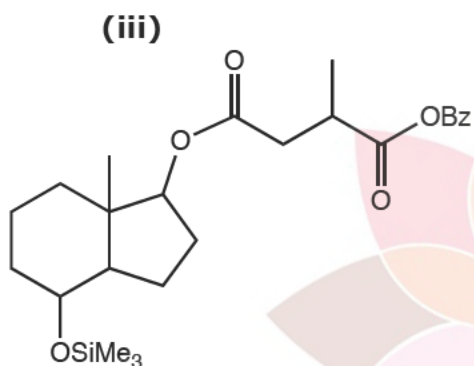**(c)**

(i)

(ii)

(iii)
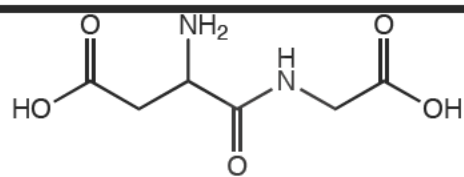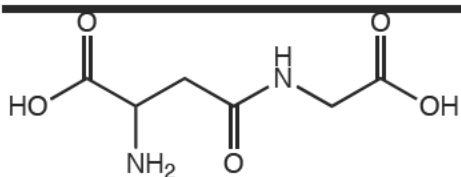
(d)

(e)

1) carboxylic acid
2) carboxylic acid
3) amine
4) alcohol
5) aldehyde – unprotected

(f)   **(i)**

(ii)
HCl for OAc and LiOH for OMe

(iii)

K_2CO_3 could be used to deprotect in one step.
This might cause the newly formed ester to break

(g) **(i)**

(ii)

P
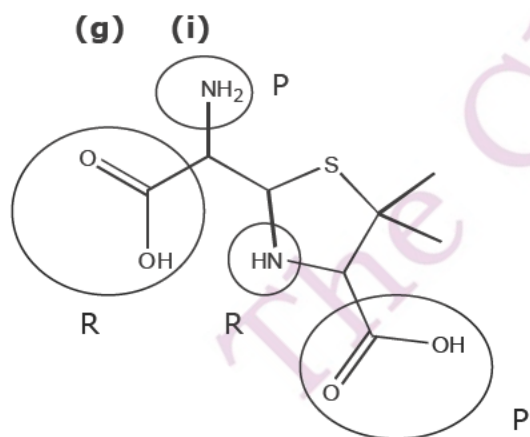
P
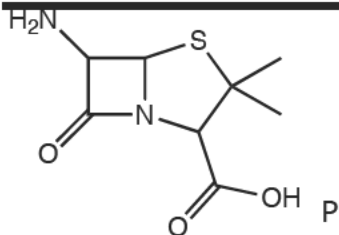
(iii)
The other amine may can react with the other carboxylic acid

(iv)
amine

(v)

vi)

Other protecting groups could also be used which would change the answers to the following questions

(vii)
LiOH

(viii)
H_2/Pd

Question 18

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).
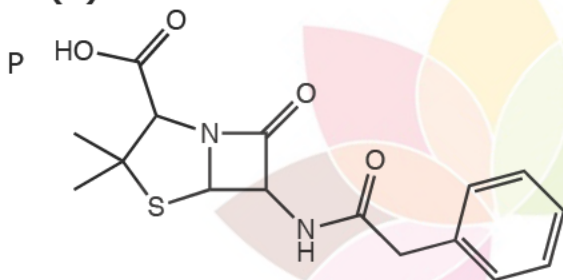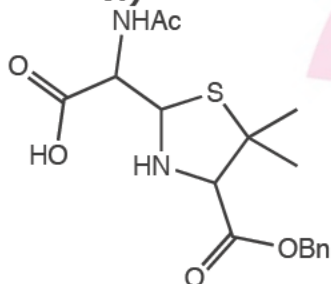
Cl ☒   CH$_3$ ☒   NO$^+$ ☐   NO$_2$ ☒

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 biomolecules such as fats, sugars and DNA. Superoxide, $O_2 \cdot^-$, 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 | -II | $O_2 \cdot^-$ | - | OH· | -I | H_2O_2 | -I |

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: $Fe^{2+} \rightarrow Fe^{3+} + e^-$
Reduction: $H_2O_2 + e^- \rightarrow OH + OH^-$
Full equation: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$

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:
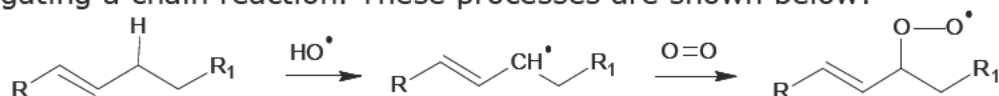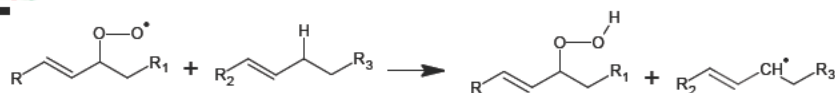
The potential for a chain reaction means the damage caused by a single OH· radical can be extensive. For this reason, the body has antioxidants to 'scavenge' for ROS. One such molecule is glutathione, a small peptide ($M_W = 307.3$ g mol^{-1}) containing a sulfur-hydrogen bond. Glutathione, written G-SH 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: 2 G-SH → G-SS-G + 2 H$^+$ + 2 e$^-$
Reduction: H_2O_2 + 2 H$^+$ + 2 e$^-$ → 2 H_2O
Full equation: 2 G-SH + H_2O_2 → G-SS-G + 2 H_2O

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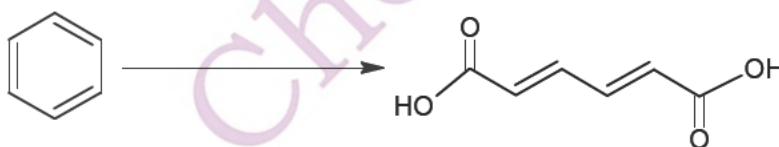
e) Write half equations and a balanced full equation to describe the clean up of benzene using OH·.

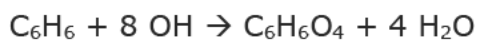Oxidation:

$$C_6H_6 + 4\ H_2O \rightarrow C_6H_6O_4 + 8\ H^+ + 8\ e^-\quad(\ x1\ )$$

Reduction:

$$OH + H^+ + e^- \rightarrow H_2O\qquad\qquad(\ x8\ )$$

Full equation:

$$C_6H_6 + 8\ OH \rightarrow C_6H_6O_4 + 4\ H_2O$$

f) 1.00 L of water containing 0.030 molL^{-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?

1 mol benzene requires 8 mol OH (from e))
8 mol of OH requires 8 mol of Fe^{2+} (from c))
therefore 8 x 30 mmol of $FeSO_4$ is required.

$m(FeSO_4)$ = 8 x 30/1000 x (55.85 + 32.07 + 4 x 16) = 36.46 g

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

Production of unwanted molecules caused by side reactions of the free radicals

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

Propagation of the free radicals similar to lipid peroxidation