Q1 Planning

(a) Effervescence would be seen; colourless gas which forms a white ppt with Ca(OH)₂(aq) would be evolved.
The deep blue equities would discolve completely to give a blue solution.

The deep blue azurite would dissolve completely to give a blue solution.

(b) <u>Calculation of a suitable mass of powdered rock to react with about 75% of the acid in the conical flask</u>

 $Cu_3(CO_3)_2(OH)_2\equiv 3H_2SO_4$

Amt of H₂SO₄ in 50.00 cm³ = 1.00 x 50.00 x 10⁻³ = 0.0500 mol Amt of azurite that reacts with 75% of H₂SO₄ = $\frac{1}{3}$ x 0.75 x 0.0500 = 0.0125 mol Mass of azurite in 0.0125 mol = 0.0125 x 344.5 = 4.306 g Mass of powered rock to be used = $\frac{4.306}{0.90}$ = 4.78 g

<u>Dilution and Volume of unreacted sulfuric acid required for titration</u> Amt of excess H_2SO_4 in reaction mixture = 0.25 x 0.0500 = 0.0125 mol

Assume that <u>average</u> volume of NaOH required for titration is 25.00 cm³ Amt of excess H_2SO_4 used for titration = $\frac{1}{2} \times 0.100 \times 25 \times 10^{-3} = 0.00125$ mol (ie 10% of 0.0125 mol) Hence, 10% of excess H_2SO_4 is needed for titration with NaOH(aq). So, the final reaction mixture can be diluted to 250 cm³ and 25.0 cm³ (ie 10% of 250 cm³) will be pipetted for titration with NaOH.

Procedure

- 1. Using an electronic balance, weigh out accurately about 4.78 g of the powdered rock in a clean and dry weighing bottle. Record the mass of the weighing bottle and powdered rock.
- 2. Transfer the powdered rock sample into the 250 cm³ conical flask containing 50.00 cm³ of sulfuric acid and swirl the contents. Place a glass filter funnel on the mouth of the conical flask to prevent acid spray.
- 3. Reweigh the emptied weighing bottle and record its mass.
- 4. When effervescence has ended and all the powdered rock has dissolved, transfer the final reaction mixture quantitatively into a 250 cm³ graduated flask with the aid of a funnel and a glass rod. Rinse the conical flask and the glass filter funnel a few times with small volumes of deionised water each time and transfer all the washings into the graduated flask.
- 4. Fill the graduated flask to the 250 cm³ mark with more deionised water. Use a teat pipette (or dropper) to add the deionised water drop by drop when nearing the mark.
- 5. Stopper the graduated flask and shake the solution thoroughly to ensure that it is homogeneous. Label the solution **FA 3**.
- 6. Pipette 25.0 cm³ of **FA 3** into a 250 cm³ conical flask. Add 2 drops of phenolphthalein indicator.
- 7. Fill the burette with the 0.100 mol dm⁻³ NaOH(aq) provided. Titrate the solution in the conical flask with the standard dilute NaOH(aq) placed in the burette.

- 8. Stop the titration when one drop of the NaOH(aq) added changes the colour of the solution in the conical flask from blue to light purple.
- 9. Repeat the titration until at least two consistent results are obtained, i.e. the two titre volumes do not differ by more than 0.10 cm³.

Calculations

Let that the **average** values of two consistent titres be 1000b cm^3 or b dm³. and

mass of powdered rock sample and weighing bottle / g = d mass of emptied weighing bottle / g = e mass of powdered rock sample /g = d - e = c

Amt of excess sulfuric acid in 25.0 cm³ of $FA3 = \frac{1}{2} \times b \times 0.100 = 0.0500b$ mol

Amt of excess sulfuric in reaction mixture = 0.0500b x $\frac{250}{25.0}$ = 0.500b mol

Amt of sulfuric acid reacted with azurite = 0.0500 - 0.500b mol Amt of pure azurite present in the powdered rock sample = $\frac{1}{3}$ x (0.0500 - 0.500b) mol Mass of pure azurite present in the powdered rock sample = $\frac{1}{3}$ x (0.0500 - 0.500b) x 344.5 = 114.8 x (0.0500 - 0.500b) g Percentage by mass of pure azurite present in the powdered rock sample = $\frac{114.8 \times (0.0500 - 0.500b)}{c}$ x 100 %

Question 2

(a)(i) Individual fatty acids have intermolecular hydrogen bonds which are stronger than the permanent dipole-permanent dipole intermolecular forces between triester. Fatty acids have higher boiling points than triester as more energy is needed to overcome the strong hydrogen bonding between fatty acid molecules, resulting in its higher boiling point.

(ii) stearic acid has longer hydrocarbon chain (2 more carbon atoms) than palmitic acid. As the chain length of alkyl group, R, increases, the instantaneous dipole-induced dipole forces between RCO₂H molecules become stronger. More energy is needed to overcome these forces.

(iii) The presence of C=C bonds in fatty acids with the same number of carbon atoms lowers the melting point of the fatty acids. [m.p. of linolenic acid < linoleic acid < oleic acid < stearic acid]

- (b)(i) Electrophilic addition
- (b)(ii) Mass of iodine that would react with 100g of olive oil = (100/0.256) x 0.237 = **92.6 g**
- **(b)(iii)** Amt of iodine in 92.6 g = 92.6 / 254 = 0.3646 mol

Amt of C=C bonds in olive oil = 0.3646 mol Amt of olive oil in 100 g = 100/782 = 0.1279mol

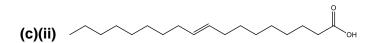
Average number of C=C bonds = 0.3646/0.1279 = **2.85**

(b)(iv) Triesters containing 3 oleic acids contain 3 C=C bonds per molecule.

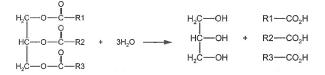
As the average number of C=C bond in each molecule of olive oil is 2.85 which is less than 3 and triesters of olive oil are mainly formed from oleic acid, olive oil should contain triesters of palmitic acid and/or stearic acid as the other significant component. Since the average Mr of olive oil is smaller than that of triester of oleic acid ($Mr = 282 \times 3 + 12 \times 3 + 2 = 884$), the other

major component of olive oil should be triester of palmitic acid which has a lower Mr than that of stearic acid.

(c)(i) H₂, Ni catalyst, heat



(d) ester undergoes hydrolysis



alkene(C=C) undergoes oxidative cleavage

 $R_1CH=CHR_2CO_2H + 4[O] \longrightarrow R_1COOH + HO_2CR_2CO_2H \text{ or}$

 $CH_{3}(CH_{2})_{7}CH=CH(CH_{2})_{7}CO_{2}H + 4[O] \longrightarrow CH_{3}(CH_{2})_{7}COOH + HO_{2}C(CH_{2})_{7}CO_{2}H$

Question 3

(a) Silicon carbide has a giant molecular structure. Each silicon atom is covalently bonded to four other carbon atoms arranged tetrahedrally around it. Each carbon atom is also covalently bonded to four other silicon atoms. This tetrahedral arrangement is repeated throughout the whole molecule. Melting requires a lot of energy to break the strong covalent bonds between all atoms, hence silicon carbride has very high melting point.

(b)(i)
$$C_xH_y + (x + \frac{y}{4}) O_2 \longrightarrow x CO_2 + \frac{y}{2} H_2O$$

(b) (ii) Heterogeneous catalyst is used, whereby the catalyst and the reactants are in different phases.

For heterogeneous catalysis to occur, the reactant molecules need to be readily adsorbed onto the catalyst surface. The adsorption of the reactant molecules at the catalyst surface increases the reaction rate because it

1. weakens the covalent bonds within the reactant molecules, thereby reducing the activation energy for the reaction.

2. increases the concentration of reactant molecules at the catalyst surface and allows the reactant molecules to come into close contact with proper orientation for reaction.

(c) (i) N(-3) in NH_3 to N(0) in N_2

N(+4) in NO_2 to N(0) in N_2

(ii) $8NH_3 + 6NO_2 \longrightarrow 7N_2 + 12H_2O$

(d) (i)NO₂ + SO₂ \longrightarrow SO₃ + NO (l)

 $NO + \frac{1}{2}O_2 \longrightarrow NO_2$ (II)

Homogeneous catalyst; oxidizes SO_2 to SO_3 , and is regenerated (II)

(ii) Cause breathing difficulties; form acid rain, corrodes buildings

(iii)
$$K_{\rm p} = \frac{P_{\rm N_2O_4}}{p_{\rm NO_2}^2} = \frac{P_{\rm N_2O_4}}{(1.5x10^{-3})^2}$$

= 6.25 x 10⁻⁵ Pa⁻¹
 $p_{\rm N_2O_4} = 1.41 \times 10^{-10}$ Pa

Question 4

(a) (i) K: 1s²2s²2p⁶3s²3p⁶4s¹ Cu: 1s²2s²2p⁶3s²3p⁶3d¹⁰4s¹

(ii) Cu²+ + 2e⁻ 🛁 Cu	<i>E</i> [⊕] = +0.34 V
K⁺ + e⁻ 🛁 K	<i>E</i> [⊕] = -2.92 V

First ionisation energy of K is +418 kJmol⁻¹ while that for Cu is +745 kJmol⁻¹. Much more energy is required to remove an electron from Cu than K. (Not in syllabus: Cu has a higher nuclear charge than K and there is a minimal increase in shielding effect from K to Cu. This causes the valence electron in Cu to be more strongly attracted to the nucleus and less easily removed.)

From both the standard reduction potential and ionisation energies, it can be seen that it

is much easier for K to lose an electron than for Cu to lose an electron. Hence Cu is much less reactive than potassium.

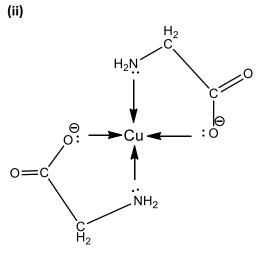
(b) (i)
$$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$$
 $E^{\ominus} = +0.34 \vee$
 $O_2 + 4H^+ + 4e^{-} \rightleftharpoons 2H_2O$ $E^{\ominus} = +1.23 \vee$
 $2H^+ + 2e^{-} \rightleftharpoons H_2$ $E^{\ominus} = 0.00 \vee$

In acid without O_2 , $E^{\Theta_{cell}} = 0 - 0.34 = -0.34V < 0$ (not spontaneous) In acid with O_2 , $E^{\Theta_{cell}} = 1.23 - 0.34 = +0.89V > 0$ (spontaneous)

(ii) Even though the reaction is spontaneous/thermodynamically feasible, the activation energy is high and hence the rate of reaction is slow.

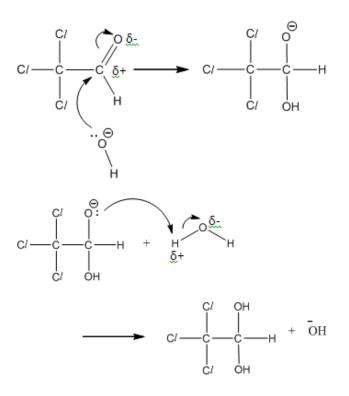
(iii) $[Cu(NH_3)_4]^{2+}+2e^- \rightleftharpoons Cu + 4NH_3 E^{\oplus}=-0.05 V$ $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- E^{\oplus} = +0.40 V$ $2Cu + 8NH_3 + O_2 + 2H_2O \rightarrow$ $2[Cu(NH_3)_4]^{2+} + 4OH^- E^{\oplus}_{cell} = +0.45 V$

(c) (i) A ligand is an ion or a molecule which contains at least one atom bearing a lone pair of electrons which can be donated into a low-lying vacant orbital of a central metal atom or ion forming a co-ordinate bond (or dative covalent bond), and resulting in the formation of a complex.



Question 5

- (a) (i) Add 2,4-dinitrophenylhydrazine to the mixture. If orange precipitate is seen, there is some remaining trichloroethanal.
 - (ii)



(iii) $CCl_3CHO + OH^- \rightarrow HCOO^- + CHCl_3$

(b) (i) The acidity of a compound depends on the relative stability of its conjugate base anion (A⁻). The more stable the conjugate base, the more acidic the compound will be. The anion may be stabilized by dispersal of negative charge.

 $CH_{3}COOH \rightleftharpoons CH_{3}COO^{-} + H^{+}$ $CCl_{3}COOH \rightleftharpoons CCl_{3}COO^{-} + H^{+}$

The conjugate base of trichloroethanoic acid is more stable than that of ethanoic acid as the negative charge can be dispersed over 3 electronegative Cl atoms which are electron withdrawing. (ii) (*Not in syllabus*) Acids disrupt ionic interactions by protonating ionic side chain R groups containing carboxylate anions:

$$\sim COO^{-} + H^{+} \longrightarrow \sim COOH$$

The protonated carboxyl groups are then unable to participate in ionic interactions with side chains containing $-NH_3^+$, bringing about denaturation of the protein.

