ACJC solutions for H2 Chemistry Prelim Paper 1 2022

1	A	**11**	A	**21**	C
2	C	**12**	C	**22**	A
3	D	**13**	D	**23**	A
4	A	**14**	C	**24**	C
5	D	**15**	B	**25**	B
6	D	**16**	D	**26**	C
7	C	**17**	B	**27**	B
8	B	**18**	B	**28**	A
9	C	**19**	D	**29**	C
10	A	**20**	B	**30**	B

1 Which species deflects the most in an electric field?

[redacted] [redacted]

B $^{24}Mg^{2+}$

C $^{32}S^{2-}$

D $^{27}Al^{3+}$

Answer: A

	$^{7}Li^{+}$	$^{24}Mg^{2+}$	$^{32}S^{2-}$	$^{27}Al^{3+}$
$\frac{\text{charge}}{\text{mass}}$	$\frac{1}{7}$	$\frac{1}{12}$	$\frac{1}{16}$	$\frac{1}{9}$

Angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$

2 The shape of each p-orbital is represented as two lobes.

How many 3d orbitals have four lobes?

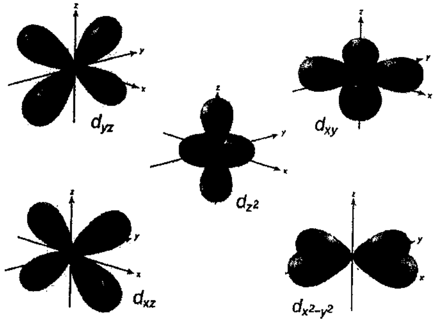
A 2

B 3

[redacted] 4

D 5

Answer: C



3 Which species has the greatest number of unpaired electrons in its ground state?

A Cu^+

B CH_3^-

C Mg

[redacted] F

Answer: D
Cu^+: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (no unpaired electrons)
CH_3^-: no unpaired electrons
Mg: $1s^2 2s^2 2p^6 3s^2$ (no unpaired electrons)
F: $1s^2 2s^2 2p^5$ (1 unpaired electron)

4 Which species contains a dative bond?

[redacted] CO

[redacted] NO_3^-

[redacted] O_3

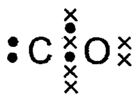
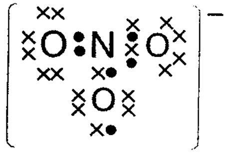
[redacted] [redacted]

B 1 and 2 only

C 1 and 3 only

D 2 only

Answer: A


5 Which option correctly describes the shape and polarity of the species?

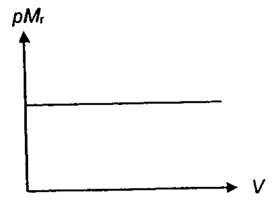
	species	shape	polarity
A	$AlCl_3$	trigonal planar	polar
B	SiF_4	square planar	non-polar
C	BrF_3	trigonal pyramidal	polar
[redacted]	$BeCl_2$	linear	non-polar

Answer: D

	species	shape	polarity
A	$AlCl_3$	trigonal planar (3 b.p.)	non-polar
B	SiF_4	tetrahedral (4 b.p.)	non-polar
C	BrF_3	T shaped (3 b.p. + 2 l.p.)	polar
D	$BeCl_2$	Linear (2 b.p.)	non-polar

6 Which graph shows the behaviour of a fixed mass of an ideal gas at a constant temperature?

[p = pressure, V = volume, M_r = molar mass, ρ = density]

A


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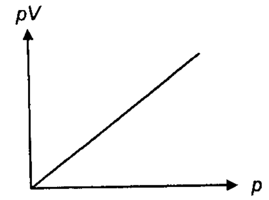
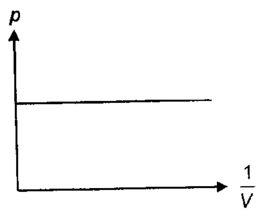
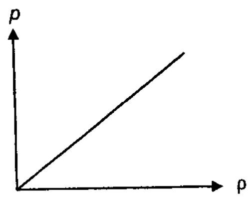
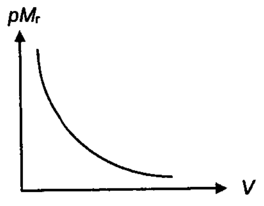


C


[redacted]


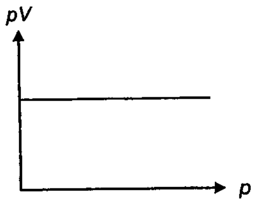
Answer: D

A


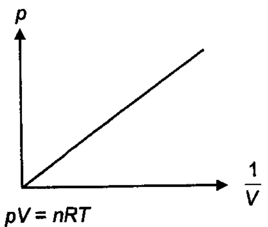
$pV = nRT$

$pV = \frac{m}{M_r}RT$

$pM_r = k\frac{m}{V}$

B


$pV = nRT$
$= k$

C


$pV = nRT$

$p = nRT\left(\frac{1}{V}\right)$

$p = k\left(\frac{1}{V}\right)$

D

$pV = \frac{m}{M_r}RT$

$p = \left(\frac{m}{V}\right)\left(\frac{RT}{M_r}\right)$

$= \rho k$

7 Which statements explain the difference in ionic radius between Na^+ and F^-?

[redacted] Outermost electrons of F^- experience weaker nuclear charge than those of Na^+.

2 Outermost electrons of Na^+ experience greater shielding effect than those of F^-.

[redacted] Outermost electrons of Na^+ are nearer to the nucleus than those of F^-.

A 3 only

B 1 and 2 only

[redacted]

D 1, 2 and 3

Answer: C
Statement 1: Correct. F^- contains fewer protons compared to Na^+.
Statement 2: Incorrect. Valence electrons of Na^+ experience the same shielding effect as those of F^- as both species contain the same number of inner shell electrons.

Statement 3: Correct. Valence electrons of Na^+ are nearer the nucleus than those of F^-, resulting in a smaller ionic radius.

8 0.1 mol of compound **X** dissolves in 1 dm^3 of water to give a solution with a pH of 1.

What is the identity of **X**?

A $AlCl_3$

■ CH_3COCl

C NH_4NO_3

D CH_3COOH

Answer: B

$AlCl_3$: $AlCl_3(g) \rightarrow Al^{3+}(aq) + 3Cl^-(aq)$
$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$ (pH > 1)
$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$
HCl dissociates completely to give a $[H^+]$ of 0.1 $moldm^{-3}$. CH_3COOH contributes negligible H^+ to the solution as it is a weak acid and its dissociation is suppressed by the strong acid. pH = 1
$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$
NH_4NO_3 dissolves in water to give NH_4^+ and NO_3^-. NH_4^+ hydrolyses in water
$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ (pH > 1)

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ (pH > 1)

9 Wüstite, containing both Fe^{2+} and Fe^{3+} ions, has the formula $Fe_{20}O_x$. Fe^{2+} constitutes 90% of the iron ions present in the compound.

What is the value of x?

A 18

B 19

■ 21

D 22

Answer: C

Total charge on iron ions:
$(18 \times 2) + (2 \times 3) = +42$
Total charge on iron ions = Total charge on oxide ions
$42 = 2x$
$x = 21$

10 Which option involves a positive entropy change?

■ The homolytic fission of gaseous chlorine.

B The lattice energy of sodium chloride.

C The contraction of an ideal gas at a constant temperature.

D Cooling a copper strip from 373 K to 273 K.

Answer: A

A: There is an increase in the number of gaseous particles as the reaction proceeds.
$Cl_2(g) \rightarrow 2Cl(g)$

B: $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$
There is a decrease in the number of gaseous particles.

C: Gas particles have fewer ways of arrangement with a smaller volume.

D: Cooling a metal results in less disorder as the particles vibrate less. In addition, there are fewer energy quanta available for distribution so there are fewer ways to distribute them in the metal.

11 The reaction between NO and Br_2 is proposed to proceed via the following mechanism:

Step 1: $NO + Br_2 \rightleftharpoons NOBr_2$ (fast)

Step 2: $NOBr_2 + NO \longrightarrow 2NOBr$ (slow)

Which statements are correct?

■ $NOBr_2$ is a radical.

■ The rate equation for this reaction is rate = $k[Br_2][NO]^2$.

3 $NOBr_2$ is a transition state.

■ 1 and 2 only

B 1, 2 and 3

C 1 and 3 only

D 2 and 3 only

Answer: A

Statement 1: Correct. There is one unpaired electron on the N atom in the molecule.
Statement 2: Correct.
From the slow step,
Rate = $k[NOBr_2][NO]$ --- (1)
From step 1, $K_c = \dfrac{[NOBr_2]}{[NO][Br_2]}$
$[NOBr] = K_c[NO][Br_2]$ --- (2)
Sub. (2) into (1), Rate = $k(K_c[NO][Br_2])[NO]$
$= k'[NO]^2[Br_2]$
Statement 3: Incorrect. $NOBr_2$ is an intermediate as it appears in the reaction mechanism but does not appear in the overall equation.

12 Which statement regarding catalysts is correct?

A Catalysts change the ΔH value of a reaction.

B Catalysts increase the yield of product in a reaction.

■ Catalysts provide a different mechanism for a reaction.

D Catalysts change the K_c value of a reaction.

Answer: C

A: Catalysts do not change the reactants and products of a reaction. Hence the ΔH value remains unchanged.
B: Catalysts do not change in the position of equilibrium in a reaction. Hence the yield of the product does not change.
C: Catalysts reduce the activation energy of a reaction by providing an alternative mechanism for the reaction to proceed by.
D: The rate constant values of both the forward and backward reaction are changed to the same extent by a catalyst. Hence the K_c value of a reaction remains unchanged.

13 In aqueous solution, an equilibrium is established between chromate, CrO_4^{2-} (yellow) and dichromate ions, $Cr_2O_7^{2-}$ (orange).

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Which statement regarding the ions and the equilibrium is correct?

A The oxidation number of chromium in both chromium-containing ions is different.

B The difference in colour between CrO_4^{2-} and $Cr_2O_7^{2-}$ is due to a difference in energy gap between the 3d orbitals.

C The K_c expression for the equilibrium is $K_c = \dfrac{[Cr_2O_7^{2-}][H_2O]}{[CrO_4^{2-}]^2[H^+]^2}$.

■ Increasing the pH turns the solution yellow.

Answer: D

A: Cr is in the same oxidation number of +6 for both species.
Let x be the oxidation number of Cr.
$x + 4(-2) = -2$
$x = +6$ (CrO_4^{2-})

$2x + 7(-2) = -2$
$x = +6$ ($Cr_2O_7^{2-}$)

B: There are no electrons in the 3d subshell for both chromium-containing species. Hence the difference in colour is not due to the difference in energy gap between the 3d orbitals.

C: The K_c expression for the equilibrium is $K_c = \dfrac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2}$. $[H_2O]$ is not included in the expression as it is a solvent and its concentration remains constant.

D: Increasing the pH results in a decrease in $[H^+]$. Position of equilibrium shifts to the left and the major species in solution is CrO_4^{2-}.

14 Nitrogen dioxide dimerises in a closed system and establishes the following equilibrium:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

When 46.0 g of NO_2 was introduced into an evacuated rigid vessel with an initial pressure 2 atm at constant temperature, the apparent M_r value of the equilibrium mixture is 64.4.

What is the K_p value of this equilibrium?

A 0.281

B 0.556

■ 0.778

D 1.11

Answer: C

Amount of $NO_2 = \dfrac{46}{46} = 1$ mol

Let x be the mole fraction of NO_2.
$46x + 92(1-x) = 64.4$
$x = 0.6$

	$2NO_2(g)$	$\rightleftharpoons$	$N_2O_4(g)$
I / mol	1		0
C / mol	−2y		+y
E / mol	1−2y		y

$n_T = 1-y$

$\dfrac{1-2y}{1-y} = 0.6$

$y = 0.2857$

$n_T = 1 - 0.2857 = 0.7143$

$\dfrac{p_1}{n_1} = \dfrac{p_2}{n_2}$

$\dfrac{2}{1} = \dfrac{p_2}{0.7143}$

$p_2 = 1.429$

$K_p = \dfrac{0.4 \times 1.429}{(0.6 \times 1.429)^2} = 0.778$

15 Which solution will solid silver phosphate, Ag_3PO_4, be the least soluble in, at 25 °C?

The numerical value of $K_{sp}(Ag_3PO_4)$ is 8.89×10^{-17}.

A pure water

■ 2.0 mol dm^{-3} $AgNO_3(aq)$

C 2.0 mol dm^{-3} $NH_3(aq)$

D 2.0 mol dm^{-3} $K_3PO_4(aq)$

Answer: B

Let the solubility of Ag_3PO_4 be s mol dm^{-3}

$K_{sp} = [Ag^+]^3[PO_4^{3-}]$

A : $K_{sp} = (3s)^3(s) \Rightarrow 27s^4 = K_{sp}$

$s = \sqrt[4]{\frac{K_{sp}}{27}} = 4.26 \times 10^{-5}$

B : $K_{sp} = (3s+2)^3(s) \approx 2^3 s$

$s = \frac{K_{sp}}{8} = 1.11 \times 10^{-17}$

C : $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$

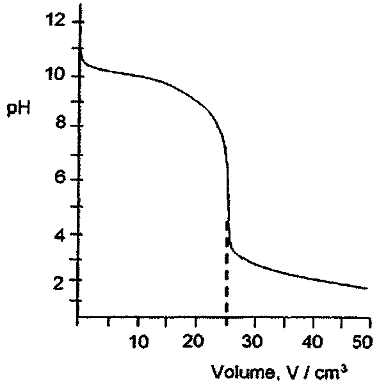
Formation of complex increases solubility of Ag_3PO_4 as the concentration of Ag^+ decreases.

D : $K_{sp} = (3s)^3(s+2) \approx (3s)^3 2$

$s = \sqrt[3]{\frac{K_{sp}}{54}} = 1.18 \times 10^{-6}$

16 In an acid-base titration, 0.10 mol dm^{-3} solution of an acid is added to 25 cm^3 of 0.10 mol dm^{-3} solution of a base.

The pH value of the solution is plotted against the volume, V, of acid added as shown in the diagram.



Which statement is **incorrect**?

A Maximum buffering capacity occurs at V = 12.5 cm^3.

B The pair of solutions could have been HC*l*(aq) and CH_3NH_2(aq).

C Methyl orange is a suitable indicator for the above titration.

■ When concentration of acid is doubled, the pH at equivalence point remains unchanged.

Answer: D

A: pH at equivalence point < 7; implies presence of acidic salt. Hence strong acid-weak base titration has occurred. When a strong acid is added to the weak base, an acidic salt is formed (conjugate acid of the weak base). As the conjugate acid is present together with the weak base in the solution, a buffer is formed. The solution is at its maximum buffering capacity at half the volume needed for complete neutralisation of the base. Option A is correct.

B: 25 cm^3 of base required 25 cm^3 of acid at equivalence point. As the concentrations of both solutions are the same, it indicates that the stoichiometry of acid:base is 1:1, hence the solutions involved should be a monoprotic base and a monobasic acid.

Since the equivalence point occurs at pH < 7, it indicates that the salt is acidic and that the base is used in the titration is a weak base. Option B is correct.

C: For strong acid-weak base titration, methyl orange is a suitable indicator as the equivalence point lies below 7 and coincides with the working range of the indicator (approximately 3 to 4). Option C is correct.

D: When the concentration of the acid is doubled, the amount of salt formed at equivalence point is the same, though total volume of the solution is now lower.

Compared to $[salt]_{original} = 25.0 \times 0.1 / (25 + 25) = 0.05$ mol dm^{-3}

$[salt]_{new} = 12.5 \times 0.2 / (12.5 + 25) = 0.0667$ mol dm^{-3}

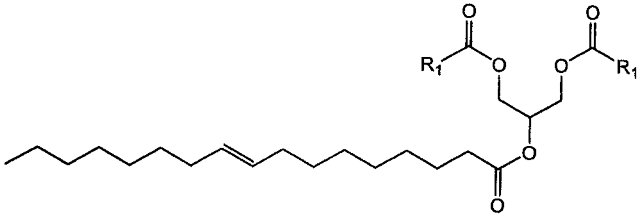
So $[H^+] = \sqrt{K_a \times [salt]}$

when [salt] is higher, new [H$^+$] be higher, hence new equivalence pH will decrease.

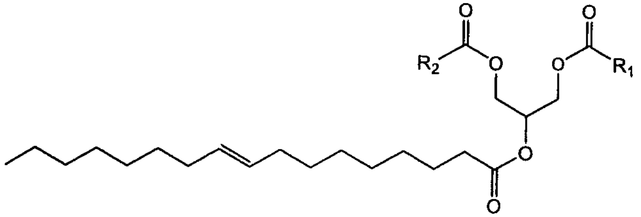
17 Some vegetable oils contain 'trans fats' that are associated with undesirable increases in the amount of cholesterol in the blood. In the structures below, R_1 and R_2 are different hydrocarbon chains.

Which structure correctly illustrates an optically active 'trans fat'?

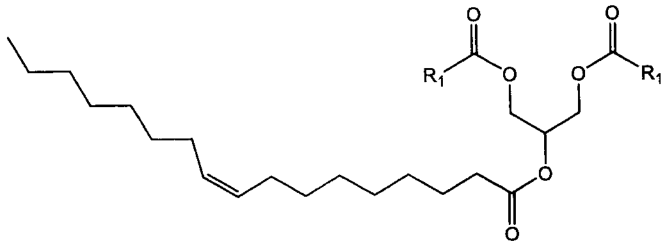
A



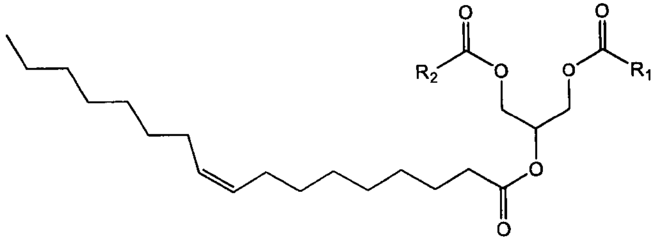
■



C

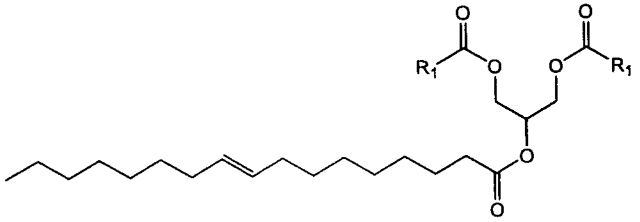


D



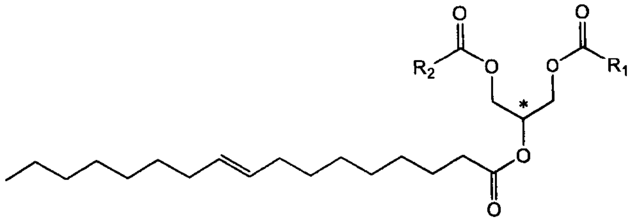
Answer: B

A



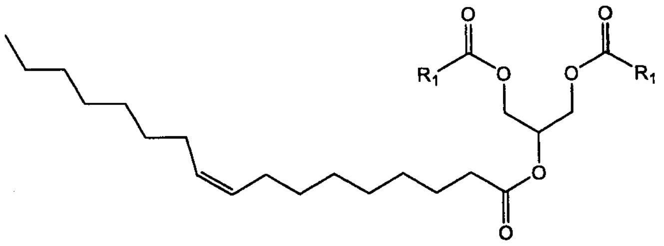
trans but no chiral carbon

B



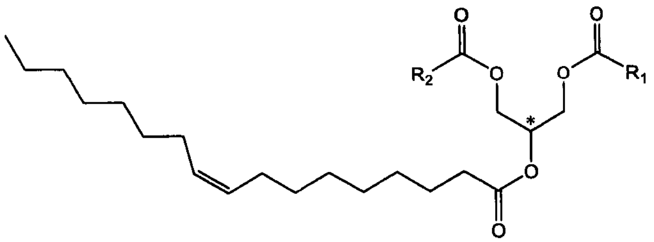
trans with one chiral carbon (correct)

C



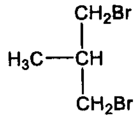
cis with no chiral carbon

D



cis with one chiral carbon

18 A hydrocarbon reacted with bromine under suitable conditions to give the following product.



$$H_3C-CH(CH_2Br)_2$$

What type of reaction occurred between the hydrocarbon and bromine?

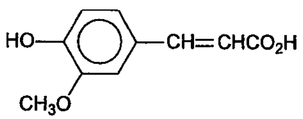
A Electrophilic addition
■ Free radical substitution
C Electrophilic substitution
D Nucleophilic addition

Answer: B
A hydrocarbon can react with bromine via free radical substitution (alkane), electrophilic addition (alkene) or electrophilic substitution (typically occurs on the benzene ring). Nucleophilic addition is not possible as it typically occurs across the carbonyl functional group.

Given that the position of Br atoms are on carbon atoms numbered 1 and 3 relative to each other, this cannot be electrophilic addition as the Br atoms are added across the C=C bond such that they are bonded to carbon atoms numbered 1 and 2 relative to each other.

19 Ferulic acid is an antioxidant that occurs widely in plants.

Assume that CH_3O- group is inert.



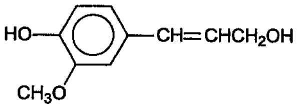
ferulic acid

Which statements about ferulic acid are true?

[redacted] It decolourises aqueous bromine.

[redacted] It is not very soluble in water but dissolves in aqueous NaOH.

[redacted] It can be prepared from



using hot acidified $K_2Cr_2O_7(aq)$.

A 1 only B 1 and 2 only C 2 and 3 only [redacted] 1, 2 and 3

Answer: D

1 The alkene functional group in ferulic acid undergoes electrophilic addition with aqueous bromine while the phenol group undergoes electrophilic substitution with aqueous bromine to give a white precipitate.

2 Although ferulic acid forms hydrogen bonding with water, it is not very soluble in water due to the benzene ring which is only able to form id – id interactions with water.
The $-COOH$ group undergoes acid-base with NaOH(aq) to form $-COO^-$ which increases the compounds solubility in water due to the formation of more favourable ion–dipole interactions with water. Similarly, the phenol group undergoes acid–base reaction with NaOH(aq) to give the phenoxide ion with forms ion-dipole interactions with water.

3 Primary alcohol will be oxidised to the carboxylic acid functional group.

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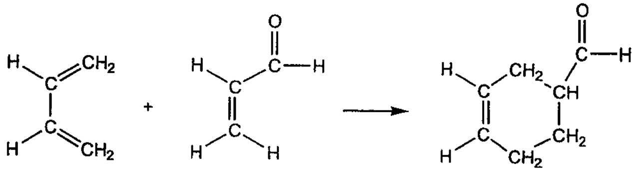
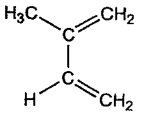
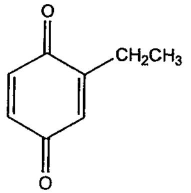
20 Unsaturated carbonyl compounds can undergo a useful reaction known as the Diels-Alder reaction with a diene. An example is shown below.



A student reacted the following diene and carbonyl compound together in a Diels-Alder reaction.

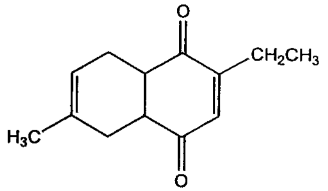


and

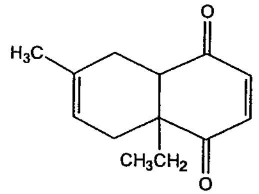


Which product will not be formed?

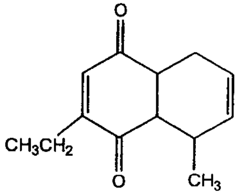
A



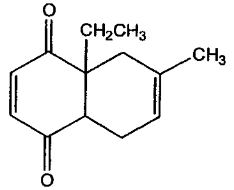
C



[redacted]

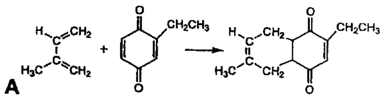


D

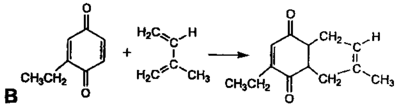


Answer: B

A

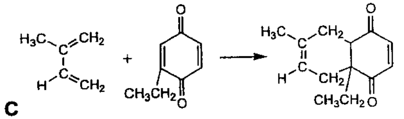


B

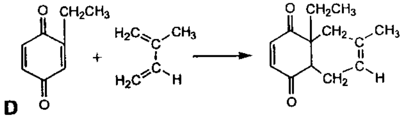


(note the position of the methyl group)

C

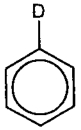


D

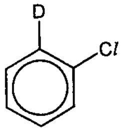


21 Deuterium, D, is a heavy isotope of hydrogen. Deuteriobenzene reacts with chlorine and $AlCl_3$ under controlled condition so that only monochlorination takes place.

Assuming that the carbon-deuterium bond is broken as easily as a carbon-hydrogen bond, what is the proportion of 2-chlorodeuteriobenzene in the mono-chlorinated products?



deuteriobenzene

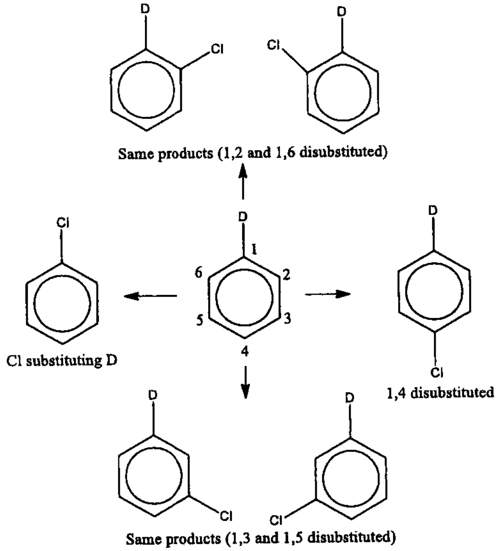


2-chlorodeuteriobenzene

A 16% **B** 20% [redacted] 33% **D** 40%

Answer: C

The Cl^+ electrophile can be substituted at the H atoms or the D atom.
Thus it can be at the 2nd position with respect to D or 3rd position with respect to D or the 4th position with respect to D



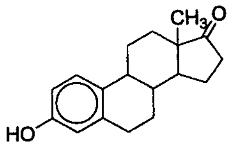
Substituting at position 2 and 6 wrt D will give the same 1,2 product and substitution at 3 and 5 wrt D will give the same 1,3 product

Substituting at position 4 will give the 1,4 product.

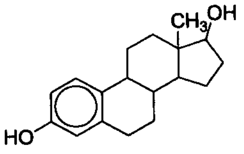
Since deuterium atom D can also be substituted (as C-D bond is equally likely to break as stated in the question), chlorobenzene can also be obtained as a product.

Since there is a total of 6 carbons that can be substituted and 2 out of the 6 carbons substituted gives 2-chlorodeuteriobenzene, the % of 2-chlorodeuteriobenzene is 2/6 x 100 = 33.3%

22 Two female sex hormones are oestrone and oestradiol.



oestrone



oestradiol

Which reagents could be used to distinguish between the two hormones?

[redacted] $SOCl_2$

[redacted] 2,4-dinitrophenylhydrazine

3 $LiAlH_4$ in dry ether

[redacted] [redacted] **B** 1 only **C** 2 and 3 only **D** 1, 2 and 3

Answer: A

Option 1 (Correct)
$SOCl_2$ reacts with the secondary alcohol group in oestradiol to give white fumes of HCl. Oestrone does react with $SOCl_2$.

Option 2 (Correct)
Ketone group in oestrone reacts with 2,4-DNPH to form an orange ppt. Oestradiol will not react.

Option 3 (Wrong)
While $LiAlH_4$ reacts with the ketone group in oestrone and not with oestradiol, there are no visible changes occurring during the reaction which allow for both compounds to be distinguished.

23 Many different compounds have been used in aerosol sprays, refrigerators and in making foamed plastics. Which compound will cause the most ozone depletion?

■ CCl_3F

B $CH_2FCHClF$

C $CH_3CH_2CH_2CH_3$

D $CH_2{=}CHCl$

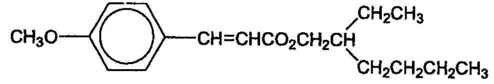
Answer: A

Ozone depletion is caused by CFCs (i.e. compounds which contain Cl and F) Options C is eliminated.

C-Cl bonds are weaker than C-F bonds. Hence Option A will form more Cl radicals than Option B, and cause more ozone depletion.

For Option D, the C-Cl bond is very strong as the p orbital of the Cl will overlap with the pi electron cloud of the C=C bond. Hence the Cl radical will not be produced.

24 Which reagent reacts with the following organic compound to give **only** one organic product?
Assume that CH_3O- group is inert.



A hot NaOH(aq)

B hot acidified $K_2Cr_2O_7$(aq)

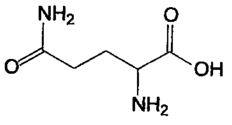
C H_2(g), Pt

D HCl(g)

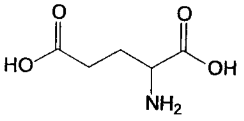
Answer: C

A	hot NaOH(aq) hydrolyses the ester to give two organic products.	B	hot acidified potassium dichromate(VI) Acid is present. It hydrolyses the ester to give two organic products. The primary alcohol fragment undergoes further oxidation to give carboxylic acid
C	hydrogen in platinum add H_2 across C=C (reduction) to give only one organic product	D	HCl(g) HCl is added across the C=C double bond to form 2 possible products.

25 The amino acids glutamine and glutamic acid can react with each other to form amide linkages.



glutamine



glutamic acid

What is the maximum number of different compounds that can be formed from one molecule of glutamine and one molecule of glutamic acid?

A 2 ■ 3 **C** 4 **D** 5

Answer: B

Possible combinations:

Glutamine / Glutamic acid	$-NH_2$	$-CO_2H$
$-NH_2$	×	√
$-CO_2H$ (1)	√	×
$-CO_2H$ (2)	√	×

∴ **3** different compounds can be formed

BP~92

26 0.01 mol of KIO_n reacts with 0.05 mol of KI stoichiometrically to produce I_2 under acidic conditions.
In this reaction, all the iodine containing reactants were converted to I_2(aq).

What is the value of n?

A 1

B 2

■ 3

D 4

Answer: C

IO_n^-: I^-

1 : 5

[O]: $2I^- \longrightarrow I_2 + 2e^-$

$5I^- \longrightarrow \frac{5}{2}I_2 + 5e^-$

[R]: $IO_n^- + 2nH^+ + (2n-1)e^- \longrightarrow I_2 + nH_2O$

$2n-1 = 5$

$n = 3$

27 Use of the *Data Booklet* is relevant to this question.

By considering relevant E° values, which metal will not dissolved in 1 mol dm^{-3} HC*l*(aq)?

A V ■ Ag **C** Mg **D** Sn

Answer: B

$2H^+ + 2e^- \rightarrow H_2$ $E_{red}^\ominus = 0.00V$

To determine whether metal will not dissolve in HC*l*(aq), $E_{cell}^\ominus$ <0. This will indicate the reaction is non-spontaneous.

Equation	$E_{oxi}^\ominus$	Overall equation	$E_{cell}^\ominus$<0
$V^{2+} + 2e^- \rightarrow V$	-1.20	$V + 2H^+ \rightarrow H_2 + V^{2+}$	+1.20
$Ag^+ + e^- \rightarrow Ag$	+0.80	$Ag + 2H^+ \rightarrow H_2 + Ag^+$	-0.80
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.38	$Mg + 2H^+ \rightarrow H_2 + Mg^{2+}$	+2.38
$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14	$Sn + 2H^+ \rightarrow H_2 + Sn^{2+}$	+0.14

Hence, Ag cannot dissolve in HC*l*(aq).

28 The Kolbe reaction involves decarboxylative dimerisation of carboxylate ions by electrolysis. When an aqueous solution of sodium carboxylate is electrolysed, the overall equation is as follows:

$$2RCO_2Na + 2H_2O \rightarrow R\text{–}R + 2CO_2 + 2NaOH + H_2$$

where R = CH_3, C_2H_5 etc.

Which statements about the anode and cathode are correct?

	anode	cathode
■	The solution around the anode turns moist blue litmus red.	The solution around the cathode turns moist red litmus blue.
2	RCO_2Na is oxidised to R–R at the positive terminal.	H_2O is reduced to H_2 at the negative terminal.
3	The standard electrode potential involving H_2O is the least positive.	The standard electrode potential involving H_2O is the most positive.

■ 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3

Answer: A

Option 1 (correct)
Anode: CO_2 produced at the anode is acidic in solution and will turn moist blue litmus red.
Cathode: OH^- produced at the cathode is basic and will turn moist red litmus blue.

Option 2 (Incorrect)
Anode: R<u>C</u>O$_2$Na (oxidation number is +3) is oxidised to <u>C</u>O$_2$ (oxidation number is +4) at the anode, not to R–R where the oxidation number of C is +3 as well.
Cathode: <u>H</u>$_2$O (oxidation number is +1) is reduced to <u>H</u>$_2$ (oxidation number is 0) at the cathode.

Option 3 (Incorrect)
$E(O_2/H_2O) > E(RCO_2^-/CO_2)$.
Thus RCO_2^- is selectively oxidised at the anode.
$E(H_2O/H_2) > E(Na^+/Na)$.
Thus H_2O is selectively reduced at the cathode.

29 15.7 g of the metal gadolinium (Gd) was deposited in electrolysis by a current of 5.0 A for 96.5 minutes.

What is the formula of the gadolinium ion? [A_r of Gd = 157]

A Gd^+ **B** Gd^{2+} ■ Gd^{3+} **D** Gd^{4+}

Answer: C

Q = It = (5)(60)(96.5) = 28950C
= (28950/96500) F = 0.3F
No. of moles of Gd = 15.7/157 = 0.1
$Gd^{n+} + n\,e^- \rightarrow Gd$
Quantity of electricity required to deposit 0.1 mol of Gd = 0.3F
no. of mol of electrons: no. of mol of Gd = 0.3: 0.1
n = 3
Thus, formula of Gd ion is Gd^{3+}.

30 **X** is a transition metal. Under a high concentration of Cl^-, the cation of **X** forms a coloured complex ion, **[XCl_4]$^{2-}$**. When **[XCl_4]$^{2-}$** is reduced to **[XCl_2]$^-$**, the solution turns colourless.

What is the ground state electronic configuration of **X**?

A [Ar] $3d^5\ 4s^1$ ■ [Ar] $3d^{10}\ 4s^1$ **C** [Ar] $3d^5\ 4s^2$ **D** [Ar] $3d^9\ 4s^2$

Answer: B

Solution turns colourless ⇒ no d-d transition took place, electronic configuration of d subshell is either d^0 or d^{10}.

In [XCl_4]$^{2-}$, oxidation number of X is +2. In [XCl_2]$^-$, oxidation number of X is +1. Since X^+ is [Ar]$3d^{10}$ (cannot be $3d^0$ because if X^+ is [Ar], then X is [Ar]$3d^1$, Sc, which is not a transition metal), X is [Ar]$3d^{10}4s^1$.

ACJC solutions for H2 Chemistry Prelim Paper 2 2022

1 **(a)** Table 1.1 shows the solubility of two organic molecules at 25 °C.

Table 1.1

	solubility in water / g dm^{-3}
propanone	miscible
chloromethane	5.04

(i) Identify the type of intermolecular force present between the molecules.

propanone: .... permanent dipole -permanent dipole ....

chloromethane:............permanent dipole -permanent dipole ....[1]

(ii) Give a reason for the difference in their solubilities in water

Propanone is able to form hydrogen bonds with water but chloromethane is unable to.

(b) The boiling point of three ligands are shown in Table 1.2.

Table 1.2

ligand	formula	boiling point / °C
water	H_2O	100
ammonia	NH_3	–33.3
hydrazine	N_2H_4	114

(i) Explain what is meant by the term *ligand*.

A ligand is a neutral molecule or anion species that has a lone pair of electrons to form a dative bond with a central metal atom or ion.

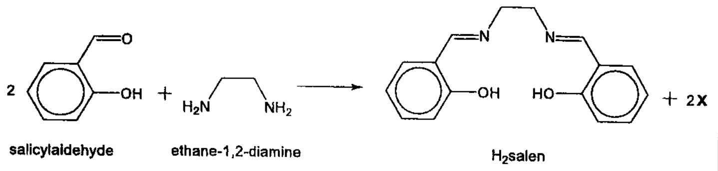
(ii) Explain the difference in the boiling points of the three ligands.

Hydrazine has the highest boiling point as it has the largest/most polarisable electron cloud size has strongest instantaneous dipole-induced dipole.

Water form more extensive hydrogen bonds than ammonia and hence it has a higher boiling point.

(c) Polydentate ligands are ligands which form more than one bond with the metal atom or ion.

Salicylaldehyde, ethane-1,2-diamine and H_2salen are examples of such ligands. H_2salen can be synthesised from salicylaldehyde and ethane-1,2-diamine.

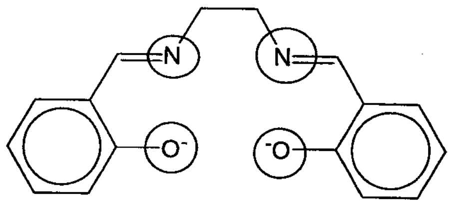


When the phenolic groups of H_2salen are deprotonated, salen^{2-} acts as a ligand. It has a high affinity for Co^{2+} ions and forms a planar complex Co(salen).

(i) Suggest the identity of molecule **X**.

H_2O

(ii) Draw the structure of a salen^{2-} ligand and circle the atoms which are used to coordinate to a Co^{2+} ion.



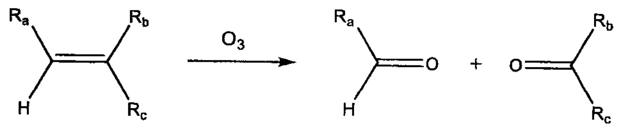
salen^{2-}

[2]

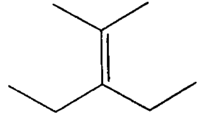
(iii) State the coordination number of the Co^{2+} ion in Co(salen).

Four

(d) Ozonolysis is a method to oxidatively cleave alkenes using ozone, O_3, to form carbonyl compounds.

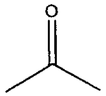


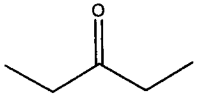
(i)



2-methyl-3-ethylpent-2-ene

Draw the structure of the organic products when 2-methyl-3-ethylpent-2-ene undergoes ozonolysis.





[2]

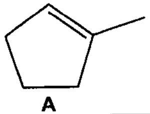
(ii) Ozonolysis of **A**,C_6H_{10}, gives a single compound, **B**,$C_6H_{10}O_2$.
B gives a yellow precipitate when treated with alkaline aqueous iodine and forms a red-brown precipitate when treated with Fehling's solution.

Draw the structures of the compounds **A** and **B**.

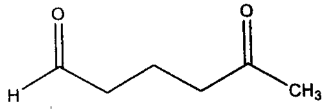
A

B

[2]



A



B

[Total: 13]

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2 Chromium is a transition metal that is values for its high resistance to corrosion and is added to steel to form stainless steel.
While chromium can exist in various oxidation states, the most common oxidation state is the +3 state.

(a) Hydrated chromium (III) chloride exists as isomers, with the general formula of $CrCl_3.6H_2O$. One such isomer is $[CrCl_2(H_2O)_4]Cl.2H_2O$ and it appears dark green.

Suggest the formula of two other isomers of hydrated chromium (III) chloride.

isomer 1: ....

isomer 2: ....[2]

$[CrCl_3(H_2O)_3].3H_2O$
$[CrCl(H_2O)_5]Cl_2.H_2O$
$[Cr(H_2O)_6]Cl_3$

(b) When a sample of hydrated chromium (III) chloride is added to excess water, a green solution of $CrCl_3(aq)$ is obtained. Fig. 2.1 shows the reactions that aqueous $CrCl_3$ can undergo.

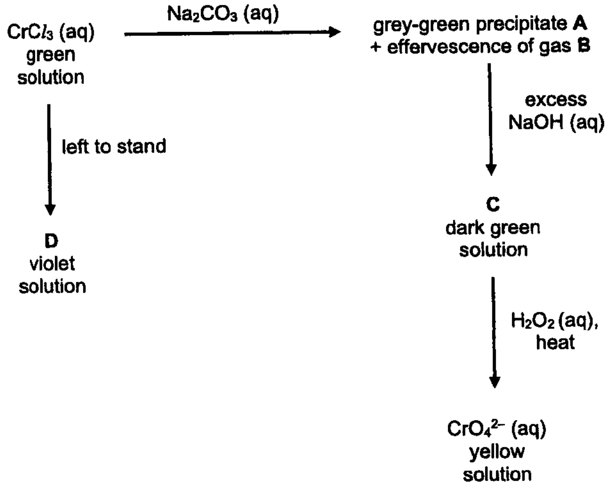


Fig. 2.1

(i) Identify precipitate **A** and gas **B**.

precipitate **A**: ....

gas **B**: ....[2]

A: $Cr(OH)_3$ or $Cr(OH)_3(H_2O)_3$ or chromium(III) hydroxide,

B: CO_2 or carbon dioxide

(ii) Suggest the formula of compound **C**.

....[1]

$Na_3[Cr(OH)_6]$

(iii) Explain why solutions of transition metal compounds are often coloured.

The d orbitals are partially filled.

In the presence of **ligands,** the **degenerate d-orbitals/d-subshell are split into two groups of different energy levels**.

An electron in the **lower energy level orbital** can **absorb energy** equivalent to the **energy gap** which corresponds to a certain wavelength of **light from the visible region** of the electromagnetic spectrum and be **promoted to the higher energy level orbital**.

The **colour seen is complementary to the colour absorbed**.

(iv) Given that the oxidation state of chromium in compound **D** is still +3, suggest what happened that caused the colour change from green to violet.

Ligand exchange occurred.
The energy gap between lower energy level d orbitals and the higher energy level d orbitals changed and hence a different wavelength of visible light is absorbed.

(v) State the role of H_2O_2 (aq).

....[1]

oxidising agent

Comments:

- Students need to recognise that the oxidation state increased from +3 to +6 and hence H_2O_2 acted as an oxidising agent.
- This question was well answered.

(vi) Write a balanced equation for the formation of CrO_4^{2-} from **C**.

....[1]

$2[(Cr(OH)_6)]^{3-} + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 2\ OH^- + 8\ H_2O$
OR

$2Na_3[(Cr(OH)_6)] + 3H_2O_2 \rightarrow 2Na_2CrO_4 + 2\ NaOH + 8\ H_2O$

(c) Fig. 2.2 shows the first seven ionisation energies of calcium and chromium.

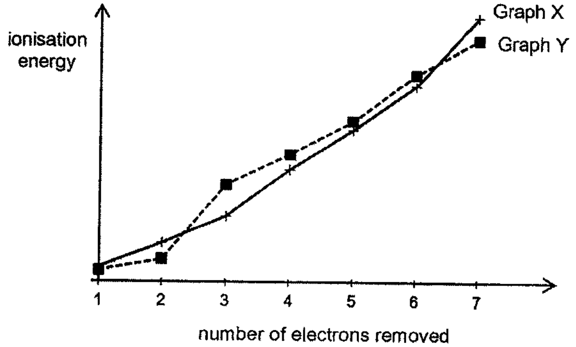


Fig. 2.2

State and explain which graph shows the successive ionisation energies for calcium.

Graph Y showed the variation in successive ionisation energies (IE) for Ca.
This is because there is a large jump between the 2nd and 3rd IE showing that the 3rd electron is removed from an inner shell and the atom has 2 valence electrons.

[Total: 14]

BP~98

3 **(a)** The variation of the volume with temperature of a fixed mass of an ideal gas at constant pressure may be represented by a relationship known as Charles's law,

$$V = kT$$

where V is the volume of a gas, T is the temperature in Kelvin and k is a constant.

An experiment was carried out to attempt to verify this law using a gas, phosphine, PH_3.
The experiment was repeated several times at different temperatures.
Fig. 3.1 was plotted to determine the relationship between the volume of the gas and its temperature.

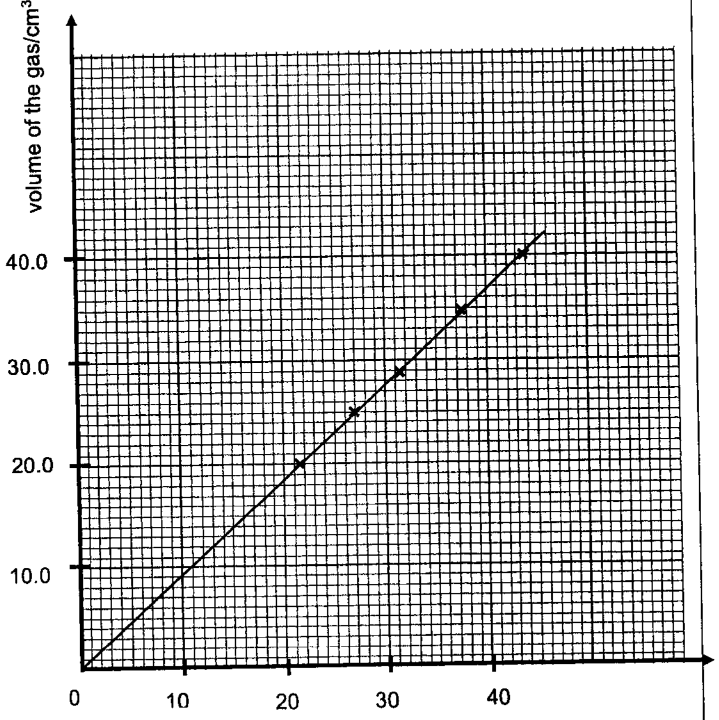


Fig. 3.1

(i) Based on Fig. 3.1, state whether the result is consistent with Charles's law. Give a reason for your answer.

Charles's law is confirmed because a straight line passing through the origin with a positive gradient (direct proportionality) is obtained.

(ii) State the **two** properties of a gas necessary for it to approach ideal behaviour.

The gas must have negligible intermolecular forces of attraction.

There is negligible size/volume of the gaseous molecules/particles compared to the size of the container/volume of gas.

(b) Orange street lamps contain sodium with a small amount of neon. The light is produced when gaseous atoms are ionised in an electric field. When it is first turned on, the lamps emit a red glow characteristic of neon, but after some time, the orange glow of sodium predominates.

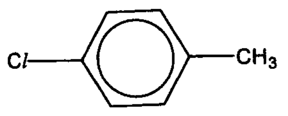
Explain the order for the appearance of the colours. Use relevant data from the *Data Booklet* in your answer. [2]

The ionisation energy of Na is 494 $kJmol^{-1}$ which is smaller than Ne which has an ionisation energy of 2080 $kJmol^{-1}$.

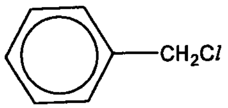
However, Na is a solid at room temperature needs to be vapourised to Na(g) before ionization. OR
Ne is already a gas at room temperature can be ionised immediately.

Since time is required to vapourise the Na prior to ionisation, red glow of Ne is observed before the orange glow of sodium.

(c) 4–chloromethylbenzene and (chloromethyl)benzene are isomers.



4-chloromethylbenzene



(chloromethyl)benzene

(i) Explain the difference in their reactivities towards hot aqueous sodium hydroxide.

(Chloromethyl)benzene undergoes nucleophilic substitution with hot NaOH(aq) readily while 4–chloromethylbenzene requires vigorous conditions (or does not react). OR
Chloromethyl)benzene is more reactive than 4-chloromethylbenzene (or any other form of comparison of reactivity).

The p–orbital of C*l* in 4–chloromethylbenzene can overlap with the π electron cloud/p orbitals of the benzene ring, thus lone pairs of electrons of Cl delocalizes into benzene ring resulting in partial double bond between C and C*l* and strengthening it. Hence, the C–C*l* bond does not undergo nucleophilic substitution with NaOH(aq) easily.

(ii) Alkyl halides can undergo nucleophilic substitution, with the simplified general mechanism as shown below:

The mechanism involves the heterolytic fission of the C–X bond, resulting in X leaving with a pair of electrons as X^-. X^- is called the leaving group. When alkyl halide undergoes nucleophilic substitution, one factor that affects its reactivity is the basicity of X^-. In general, when X^- is a stronger base, it is a poorer leaving group. This results in the alkyl halide being less reactive towards nucleophilic substitution.

Using the data given in Table 3.1 and relevant data from the *Data Booklet*, suggest **two** reasons to explain why (iodomethyl)benzene reacts much faster than (chloromethyl)benzene.

Table 3.1

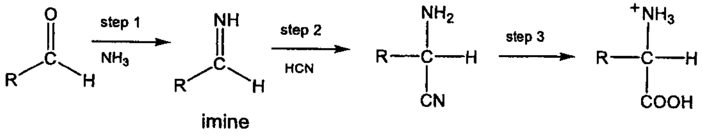
halide	pK_b
Cl^-	21.0
I^-	24.0

(Iodomethyl)benzene reacts much faster than (chloromethyl)benzene due to the weaker C–X bond and more stable X^- formed.

BE(C–I) 340 kJ mol^{-1} is smaller than BE(C–Cl) 240 kJ mol^{-1}. C–I bond is weaker than C–Cl, hence (iodomethyl)benzene tends to react much faster than (chloromethyl)benzene.

From the larger pK_b (or smaller K_b), I^- is a weaker base making it a good leaving group, I^- is a more stable conjugate base. Hence, I^- is formed more readily and hence (iodomethyl)benzene tends to react much faster than (chloromethyl)benzene.

(d) The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker.



(i) Name the type of reaction in step 1.

....[1]

Condensation

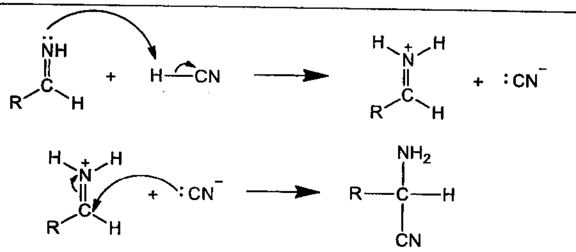
Comments:

- This reaction resembles <u>condensation</u> reaction between carbonyl and 2,4 DNPH.

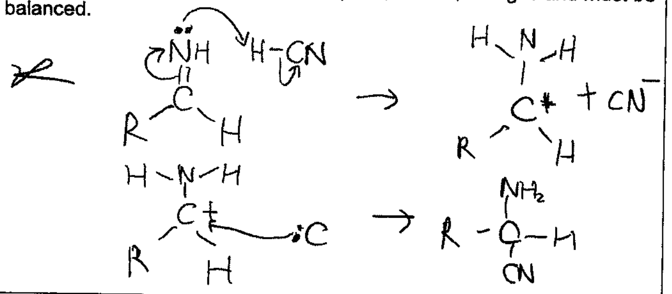
(ii) In step 2, the reaction proceeds via two stages:

(I) acid-base reaction between the N atom in imine and HCN
(II) nucleophilic attack on C atom by CN^-

Draw the step 2 for this mechanism. Show all relevant charges, dipoles, lone pairs and curly arrows. [2]



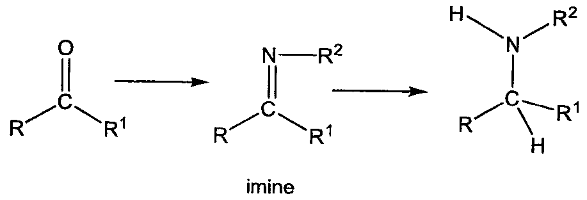
All steps must have appropriate lone pairs, arrows, charges and must be balanced.



Comments:

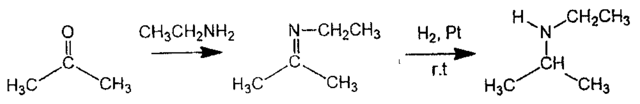
- Dipoles should not be drawn for polar bonds in polyatomic ions as the electron distribution within the ion may not be the same as that depicted by the polarity of the bond.

(iii) An imine intermediate is also formed in preparing secondary amines from ketones.



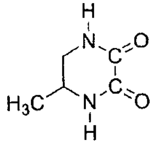
Suggest the synthetic route by giving all the reagents, conditions and intermediate for the preparation of $(CH_3)_2CHNH(CH_2CH_3)$.

[4]



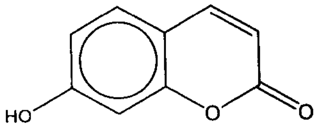
Alternative Ans: LiA/H₄ in dry ether, r.t. as reducing agent in second step

(iv) Another amine **X**, $CH_3CH(NH_2)CH_2NH_2$ reacts with ethanedioyl dichloride $(COCl)_2$ to produce compound **Y** with molecular formula $C_5H_8N_2O_2$. Suggest the structure for compound **Y**. [1]



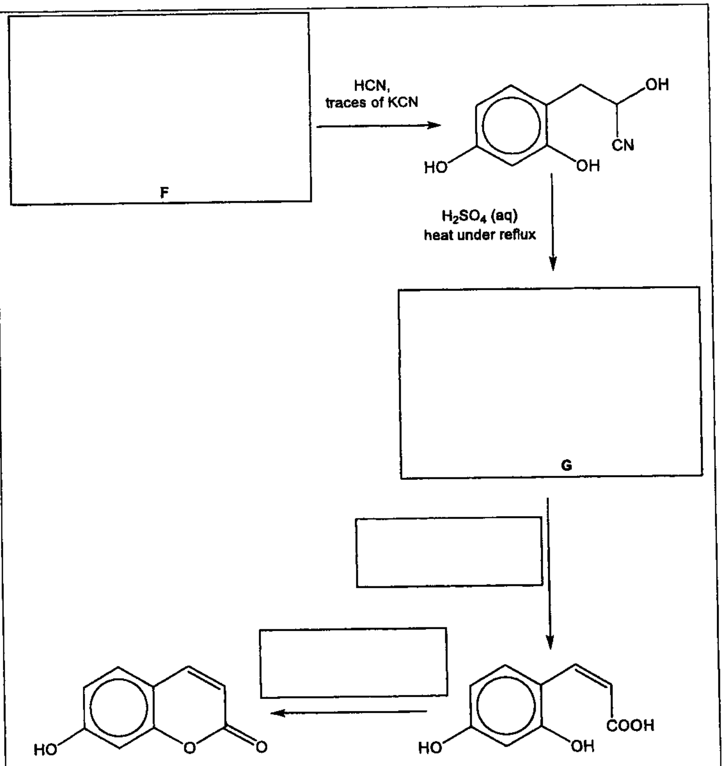
[Total: 16]

4 **(a)** Umbelliferone is a yellowish-white crystalline solid occurring naturally in carrots and is used as a sunscreen agent. It has the structure shown below:

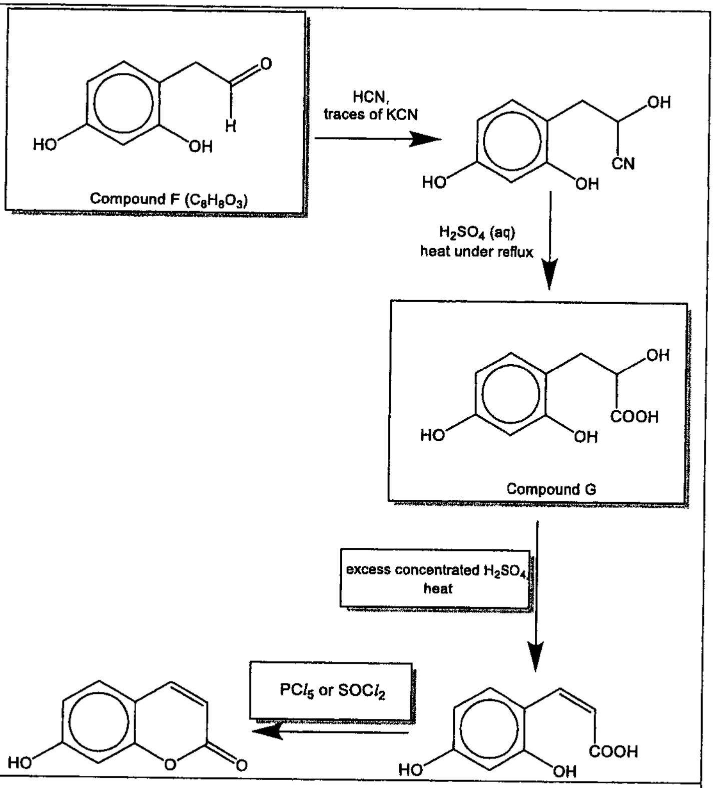


The following reaction scheme shows how umbelliferone may be synthesised from compound **F**, which has a molecular formula of $C_8H_8O_3$.

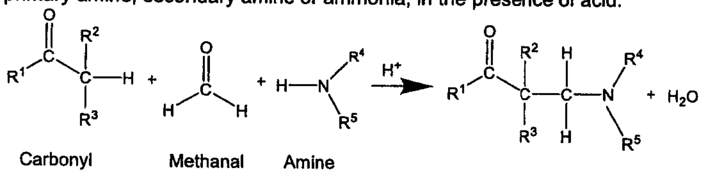
In the boxes provided, fill in the missing
- reagents and conditions,
- structures of compounds **F** and **G**.



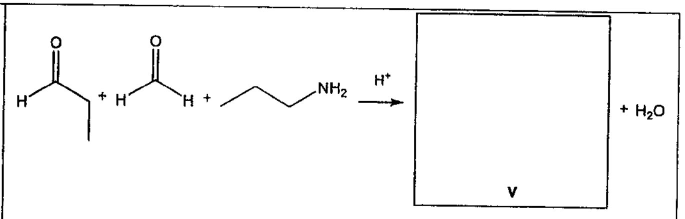
[4]



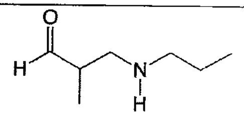
(b) Mannich reaction is an organic reaction which consists of an amino alkylation of the hydrogen atom adjacent to a carbonyl functional group, by methanal and a primary amine, secondary amine or ammonia, in the presence of acid.



(i) Predict the structure of **V** for each of the following Mannich reactions.



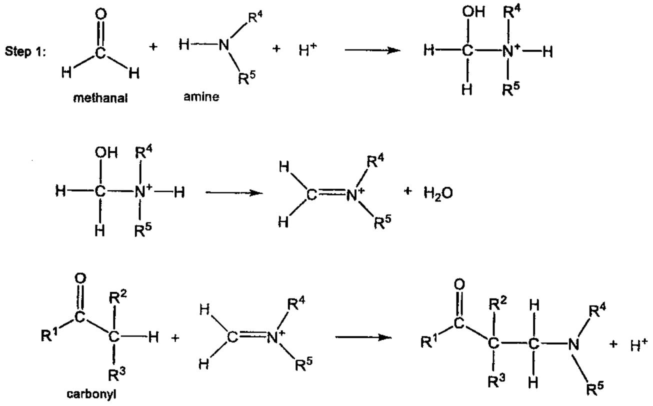
[1]



[1]

V ($C_7H_{15}NO$)

(ii) The proposed mechanism for Mannich reaction is as follows:



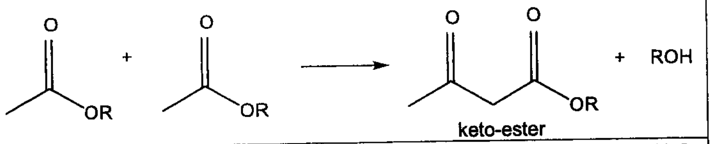
Suggest the types of reaction that occurred in Step 1 and 2.

Step 1 ……………………………………………………………………………

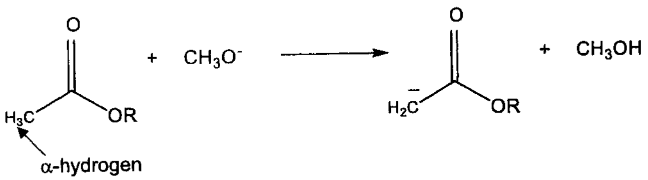
Step 2 …………………………………………………………………………… [2]

Step 1: Nucleophilic addition
Step 2: Elimination

(c) The Claisen condensation of esters involves the formation of a new carbon-carbon bond between two esters. The products are a keto-ester and an alcohol. The reaction takes place in the presence of a strong base e.g. CH_3O^-.



(i) The first step in Claisen condensation involves the strong base CH_3O^- removing an α-hydrogen atom (i.e. the hydrogen atom bonded to the carbon atom next to the carbonyl carbon atom) in an acid-base reaction as shown below.



Suggest a reason why the α-hydrogen atom of the ester is acidic.

....

....[1]

The conjugate base of the ester is stabilised as the negative charge can be dispersed by delocalisation into the adjacent C=O group.

(ii) With reference to the acid-base reaction mentioned in **(c)(i)**, suggest why each of the following reactions does not take place in the presence of CH_3O^-.

(1) $CH_3CH_3 \longrightarrow {}^-CH_2CH_3$
(2) $CH_3COOH \longrightarrow {}^-CH_2COOH$

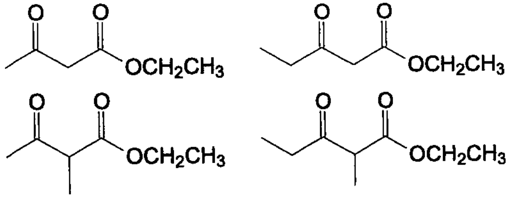
....[2]

(1) The conjugate base of ethane is unstable as the electron-donating methyl group will intensify the negative charge.
OR
CH_3O^- is a more stable base than $CH_3CH_2^-$ as the negative charge is stabilized by electronegative O atom in CH_3O^-

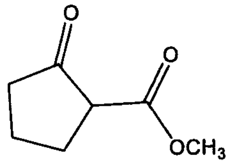
(2) The conjugate base formed $-COO^-$ in deprotonating -COOH is more stable as negative charge is delocalised over 2 electronegative O atoms.
OR
O is more electronegative than C, hence stabilised negative charge more.

(iii) Draw **two** possible structures of all the keto-esters formed when a mixture of $CH_3CO_2CH_2CH_3$ and $CH_3CH_2CO_2CH_2CH_3$ undergo the Claisen condensation.

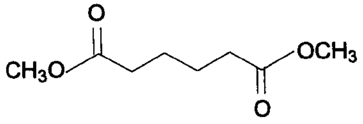
[2]



(iv) Draw the structure of the reactant that can be used to prepare the following compound by the Claisen condensation.



[1]



[Total: 13]

5 Hydrogen fuel cells use hydrogen gas with oxygen gas to form water and generate electricity. Two types of hydrogen fuel cells have been used to power vehicles. **Alkaline fuel cells (AFCs)** use an aqueous solution of potassium hydroxide as the electrolyte. In recent years, novel AFCs that use an alkaline polymer membrane as the electrolyte have been developed. Fig. 5.1 shows the diagram of an AFC.

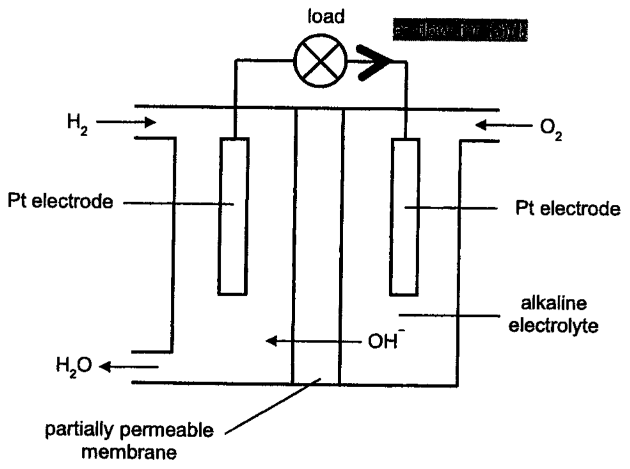


Fig. 5.1

Proton exchange membrane (PEM) fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum or platinum alloy catalyst. It has the same overall reaction as the AFC but uses an acidic electrolyte.

(a) (i) On Fig. 5.1, draw the direction of electron flow. [1]

(ii) When adjusted for standard conditions, an AFC is known to generate 1.23 V of electromotive force. With reference to the *Data Booklet*, write the half equation for each electrode and the overall equation.

anode:... $H_2 + 2OH^- \rightarrow 2H_2O + 2e$ ....

cathode:... $O_2 + 2H_2O + 4e \rightarrow 4OH^-$..

overall:... $2H_2 + O_2 \rightarrow 2H_2O$ .... [2]

(iii) Using information from **(a)(ii)**, calculate the Gibbs free energy change per mol of water generated in the AFC. [1]

$\Delta G = -nFE_{cell} = -(2)(96500)(1.23)$
$= -237390 \text{ J mol}^{-1} = -237 \text{ kJ mol}^{-1}$ (3 s.f.)

(iv) Calculate the $E_{cell}^\ominus$ of the PEM fuel cell. [2]

$E_{cell}^\ominus = E_{cathode}^\ominus - E_{anode}^\ominus$
$= 1.23 - 0.00$
$= +1.23 \text{ V}$

(v) Comment on the voltages generated by the AFC and PEM fuel cell. [1]

They have the same voltage because they undergo the same overall chemical reaction, which possesses the same chemical energy.

(b) The disadvantage of transporting hydrogen gas is one of the factors limiting the use of hydrogen fuel cells. More recently, liquid organic hydrogen carriers **(LOHC)** such as the methylbenzene / methylcyclohexane system have been used to transport hydrogen safely over long distances.

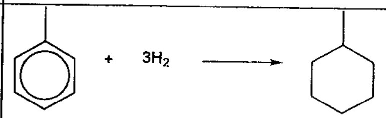
At its source, hydrogen is 'loaded' on the LOHC by reacting hydrogen with methylbenzene in the presence of platinum catalyst to produce methylcyclohexane. Hydrogen is 'unloaded' from the LOHC by reacting methylcyclohexane with the catalyst to regenerate methylbenzene.

Table 5.1 contains information about methylbenzene and methylcyclohexane.

Table 5.1

liquids	density under conditions for transportation / kg m^{-3}	boiling point at 1 atm / °C	flammability
hydrogen	71	–252.9	very high
methylcyclohexane	770	101	high

(i) Write a balanced equation for the loading of hydrogen on the LOHC.



(ii) State the type of catalyst used in the loading of the LOHC. Describe how it catalyses the reaction.
.... [3]

Heterogeneous catalyst.

- Hydrogen gas and methylbenzene adsorb on the surface of the platinum catalyst by forming weak bonds with the catalyst.
- Intramolecular covalent bonds are weakened, hence E_a is lowered when the reactants bond to the catalyst, allowing the reaction to occur more easily.
- Reactant molecules are brought into close contact at the catalyst surface. The surface concentration of the reactants increases, so the rate of reaction increases.

- Methylcyclohexane desorb from the surface of the catalyst, allowing more reactants to occupy the site.

(iii) Calculate the mass of H_2 transported per m^3 of methylcyclohexane. [2]

Amount of methylcyclohexane per m^3
$= 770\ 000\ g\ m^{-3} \div 98\ g\ mol^{-1} = 7857\ mol$

Amount of hydrogen per m^3 of methylcyclohexane
$= 7857 \times 3 = 23571\ mol$

Mass of hydrogen per m^3 of methylcyclohexane
$= 23571\ mol\ m^3 \times 2\ g\ mol^{-1}$
$= 47142\ g\ m^{-3} = 47.1\ kg\ m^{-3}$ (3 s.f.)

(iv) Suggest whether it is advantageous for the transport of hydrogen to be changed from liquid hydrogen to the use of LOHC.

.... [1]

This change is advantageous as LOHC is less flammable / less explosive than hydrogen. OR

This change is advantageous because LOHC has a higher boiling point / it is in the liquid state at room conditions, so it can be transported without cooling OR high pressure unlike H_2. OR

This change is not advantageous as LOHC has a lower mass (or less) of hydrogen gas transported per unit volume.

(c) The hydrogen supply for fuel cells have been classified according to its impact on the environment. Green hydrogen refers to the gas that is produced using renewable energy, without greenhouse gas emissions. For example, electrolysis of water powered by solar, wind or geothermal energy produces green hydrogen.

(i) Currently the most common method for generating hydrogen gas involves two successive reactions:

1) steam-methane reformation
2) water-gas shift reaction

Using this method, methane reacts with steam to form four times the amount of hydrogen gas along with a side product.

Write the overall balanced equation for the above method.

.... [1]

$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$

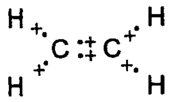
(ii) Hence suggest whether the method in **(c)(i)** is a source of green hydrogen.

.... [1]

It is not a source of green hydrogen as the greenhouse gas CO_2 is formed.

(iii) Hydrogen produced by steam-methane reformation may contain trace contaminants such as ethene.
Draw the dot-and-cross diagram of ethene. State the bond angle and shape around the carbon atom.

Bond angle: 120°
Shape: Trigonal planar



[2]

(d) Electric vehicles (EVs) have been known as a greener form of transportation than petrol powered vehicles because greenhouse gases are not emitted from EVs.

By considering the source of the electrical energy, comment on the validity of this claim.

.... [1]

The claim is valid because using renewable sources of energy such as solar, wind or geothermal energy to generate electricity does not release greenhouse gases.

OR

The claim is not valid since the burning of fossil fuels / fuels / coal to generate electricity releases greenhouse gases.

Further information about electric vehicles:
- Watch CNA Insider 'Switching To Electric Car: Is It Worth It?' **https://youtu.be/cc9iYjPLnFM?t=693**

[Total: 19]

ACJC solutions for H2 Chemistry Prelim Paper 3 2022

Section A

1 **(a)** Explain what is meant by the term *Lewis acid.* [1]

Lewis acid is a substance that accepts an electron pair from a base via a dative covalent bond (i.e. an electron-pair acceptor)

(b) The water molecule can react in various ways: as an acid, as a base, as a nucleophile, as an oxidising agent and as a reducing agent.

Study the following reactions and decide in which way water is reacting in each case.

Explain your answers fully. [5]

(i) $2F_2 + 2H_2O \rightarrow 4HF + O_2$

Reducing agent as itself is being oxidised. The oxidation number of O increases from –2 in H_2O to 0 in O_2.

Or water reduces F_2 to HF as the oxidation number of F decreases from 0 in F_2 to –1 in HF.

(ii) $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$

Nucleophile. The carbon of the acyl chloride functional group is electron deficient and is susceptible to nucleophilic attack by water, which has a lone pair of electrons on its oxygen atom.

(iii) $H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$

Base. H_2O accepts a proton from $H_2PO_4^-$ to form H_3O^+ and HPO_4^{2-}.

(iv) $Li + H_2O \rightarrow LiOH + ½ H_2$

Oxidising agent. Water oxidises Li to Li^+ as the oxidation number of Li increases from 0 in Li to +1 in LiOH

(v) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

Acid. H_2O donates a proton to NO_2^- to form OH^- and HNO_2.

(c) The pK_a values of three acids are listed in the Table 1.1 below:

Table 1.1

acid	formula	pK_a
1	CH_3CH_2COOH	4.9
2	$CH_3CHClCOOH$	2.8
3	CH_2ClCH_2COOH	z

(i) Explain the difference in pK_a values between acid 1 and acid 2. [2]

The presence of the electron withdrawing chlorine group in acid 2 disperses the negative charge on the conjugate base, $CH_3CHClCOO^-$, hence making it a more stable conjugate base than $CH_3CH_2COO^-$.

Therefore, acid 2 has a lower pK_a as this increases the acid strength of $CH_3CHClCOOH$.

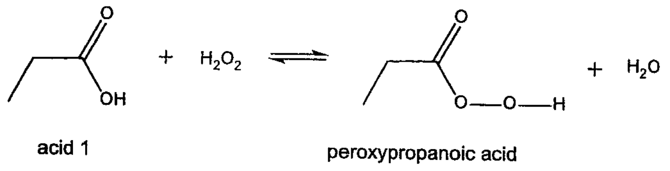
(ii) Suggest a value for z and explain your answer. [1]

4.0 (accept any value between 2.8 and 4.9)

As the distance between the –COOH group and the Cl atom increases, the negative charge on the conjugate base is less dispersed. The conjugate base becomes less stable and hence acid strength decreases.

However, acid 3 should still be more acidic than acid 1 due to the presence of the electron withdrawing Cl group.

(iii) Peroxyacids are weak acids. One way to prepare peroxypropanoic acid is to treat the corresponding carboxylic acid with hydrogen peroxide.



acid 1 peroxypropanoic acid

Suggest why the pK_a of peroxypropanoic acid is higher than that of acid 1. [1]

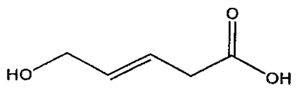
$CH_3CH_2CO_3H$ is less acidic than CH_3COOH as $CH_3CH_2CO_3^-$ is less stable than $CH_3CH_2CO_2^-$ because the negative charge on $CH_3CH_2CO_3^-$ cannot be delocalised over the C=O group due to the additional oxygen atom, hence the resonance stabilisation of the conjugate base is lost.

(d) **A**, **B** and **C** are isomers with the molecular formula $C_5H_6O_2$. All three compounds decolourise bromine water in the dark.

A produces effervescence in the presence of $Na_2CO_3(aq)$ whereas **B** and **C** do not. **A** also reacts with hot acidified $KMnO_4$ to form **D**, $C_3H_2O_5$.

B forms a brick-red precipitate when heated with Fehling's solution.

C reacts with hot aqueous sodium hydroxide. Upon acidification, it forms $C_5H_8O_3$.

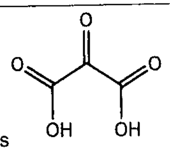


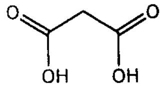
$C_5H_8O_3$

When **B** and **C** are separately reacted with hot acidified $KMnO_4$, they form the same mixture of **E** $C_3H_4O_4$ and **F** $C_2H_2O_4$. **F** undergoes further oxidation to give effervescence.

(i) Draw the structures of **D**, **E** and **F**. [3]

BP-105

D is 

E is 

F is HOOC–COOH

(ii) Deduce the structures of **A**, **B** and **C** with reasoning. [7]

A, **B** and **C** have 3 degrees of unsaturation.

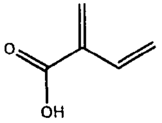
A, **B** and **C** have alkene functional group that undergoes electrophilic addition with bromine water.

A, **B** and **C** undergoes vigorous oxidation / oxidative cleavage of the alkene functional group.

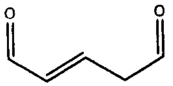
A has the carboxylic acid functional group that undergoes acid-carbonate / acid-base reaction with carbonate.

B has the aldehyde functional group that undergoes oxidation in the presence of Fehling's solution.

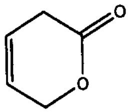
C undergoes alkaline hydrolysis, so it has an ester functional group.



A



B



C

[Total: 20]

2 (a) The acid-base behaviour of aluminium oxide, Al_2O_3, shows similarities to that of magnesium oxide, MgO, on the one hand, and sulfur trioxide, SO_3, on the other.

Describe what these similarities are, and explain why aluminium oxide occupies this in-between position.

Write equations for all the reactions you choose to illustrate your answer. [5]

MgO is an ionic oxide. Hence it is basic and is able to react with acids.

$MgO + 2HCl \rightarrow MgCl_2 + H_2O$ or $MgO + 2H^+ \rightarrow Mg^{2+} + H_2O$

SO_3 is a covalent oxide, hence it is acidic and is able to react with bases.

$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$ or $SO_3 + 2OH^- \rightarrow SO_4^{2-} + H_2O$ or
$SO_3 + H_2O \rightarrow H_2SO_4$

Al_2O_3: amphoteric oxide hence it react with both acids and bases.

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ or $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$
$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$ or $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$

Al^{3+} has high charge density/polarizing power which is able to polarise the electron cloud of O^{2-}/anion, hence giving the oxide some covalent character.

Therefore, Al_2O_3 has a giant ionic lattice structure with covalent character, making it an amphoteric oxide that reacts with both acids and alkalis.

(b) (i) Explain what is meant by the term *standard enthalpy change of atomisation of magnesium.* [1]

Standard enthalpy change of atomisation of magnesium is the energy absorbed/required/taken in when one mole of gaseous Mg atom/Mg(g) is formed from Mg at 298 K and 1 bar.

(ii) An experiment was carried out by adding 0.05 g of magnesium ribbon to 50 cm³ of excess hydrochloric acid solution. The increase in temperature was 4.5 °C.

The reaction is represented by the ionic equation as shown:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g) \qquad \Delta H_1^\circ$$

Use data from the *Data Booklet* to calculate ΔH_1°, the standard enthalpy change of this reaction. [2]

Heat released = $mc\Delta T$
= 50 x 4.18 x 4.5
= 940.5 J

$\Delta H_1^\circ = -[940.5 / (0.05 / 24.3)]$
$= -457\ kJ\ mol^{-1}$

(iii) Besides using an experimental method, another way to determine ΔH_1°, the standard enthalpy change of the above reaction, is to construct an energy cycle.

Use the data in Table 2.1, together with data from the *Data Booklet*, to calculate another value of ΔH_1°. [4]

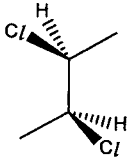
Table 2.1

	ΔH° / kJ mol^{-1}
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of hydration of Mg^{2+}(g)	−1921
standard enthalpy change of hydration of H^+(g)	−1090

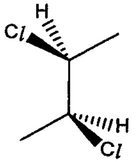
$$\begin{tikzcd}
Mg(s) + \arrow[d, "\Delta H_{atom}^\ominus"'] & 2H^+(aq) \arrow[r, "\Delta H_1^\ominus"] \arrow[d, "-2 \times \Delta H_{hyd}^\ominus \text{ of } H^+(g)"] & Mg^{2+}(aq) + H_2(g) \\
Mg(g) + \arrow[d, "1^{st} \text{ IE of Mg}"'] & 2H^+(g) \arrow[d, "-2 \times 1^{st} \text{ IE of } H(g)"] & \\
Mg^+(g) + \arrow[d, "2^{nd} \text{ IE of Mg}"'] & 2H(g) \arrow[d, "-BE\ (H\text{–}H)"] & \\
Mg^{2+}(g) + & H_2(g) \arrow[uuur, "\Delta H_{hyd}^\ominus \text{ of } Mg^{2+}(g)"'] &
\end{tikzcd}$$

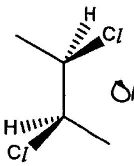
$\Delta H_1^\ominus = \Delta H_{atom}^\ominus + 1^{st}$ IE of Mg + 2^{nd} IE of Mg + $(-2 \times \Delta H_{hyd}^\ominus$ of $H^+(g))$ +
$(-2 \times 1^{st}$ IE of $H(g))$ + $(-BE\ (H\text{–}H))$ + $\Delta H_{hyd}^\ominus$ of $Mg^{2+}(g)$
$= +148 + 736 + 1450 + (-2 \times -1090) + (-2 \times 1310) + (-436) + (-1921)$
$= -463$ kJ mol^{-1} [1]

(c) 2,3-dichlorobutane exhibits stereoisomerism, one of which is enantiomerism. One enantiomer of 2,3-dichlorobutane is shown below.

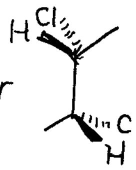


(i) Draw the other enantiomer. [1]



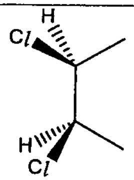


or



(ii) A molecule with n chiral centres can have a maximum of 2^n stereoisomers. 2,3-dichlorobutane has two chiral centres but it only has three stereoisomers.

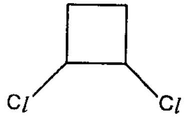
Draw the third stereoisomer of 2,3-dichlorobutane and explain why it has only three stereoisomers. [2]



The diastereomer of 2,3-dichlorobutane is a meso compound which has an internal plane of symmetry.

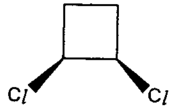
Hence, 2,3-dichlorobutane has a pair of enantiomers and only one diastereomer.

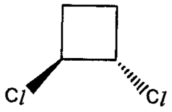
(iii) Suggest why 1,2-dichlorocyclobutane can exhibit cis–trans isomerism and draw the pair of cis–trans isomers. [2]



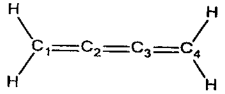
There is restricted rotation about the C–C bond that is bonded to the 2 Cl groups due to the presence of a ring structure. There are also two different groups bonded to each of the two adjacent carbon atoms with restricted rotation.

Thus, 1,2-dichlorocyclobutane can exhibit cis–trans isomerism.





(iv) A cumulene is a hydrocarbon with three or more consecutive double bonds. The simplest molecule in this class is butatriene, C_4H_4.

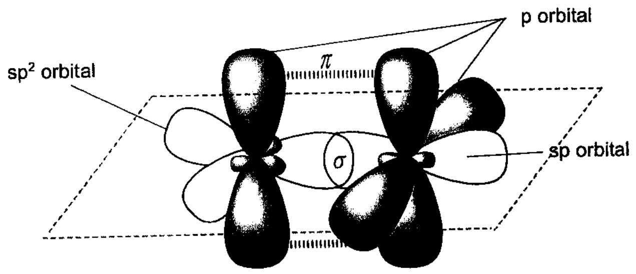


With the aid of a labelled diagram, describe the orbitals that form the C_1=C_2 bond in butatriene, and state the type of hybridisation involved. [3]

In butatriene, the double bond of C=C is made of one σ bond and one π bond.

C-C σ bond: Formed by head-on overlap of the sp^2 hybrid orbitals of C_1 atom and sp hybrid orbitals of C_2 atom.

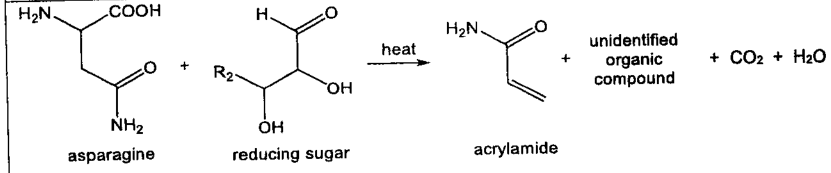
C-C π bond: Formed by sideways overlap of the two unhybridised p orbitals, forming an electron cloud above and below the plane.



[Total: 20]

3 **(a)** The Maillard reaction is an important process that occurs between sugars with amino acids during cooking. Its occurrence is responsible for the golden brown colouration and crispy texture that makes food appealing and tasty.

In 2002, it was discovered that Maillard reaction involving asparagine, an amino acid, forms acrylamide, a known carcinogen. Reaction **1** shows the chemical equation for the formation of acrylamide.



reaction **1**

To determine the kinetics of reaction **1**, three experiments were carried out and the results are shown in Table 3.1.

Table 3.1

experiment	concentration / mol dm^{-3}		initial rate / 10^{-3} mol dm^{-3} s^{-1}
	asparagine	reducing sugar	
1	0.100	0.500	2.46
2	0.100	0.625	3.08
3	0.200	0.750	3.69

(i) Deduce the order of reaction with respect to asparagine and the reducing sugar. Hence write the rate equation. [3]

Comparing Experiment 1 and 2,

When [reducing sugar] was increased 1.25x while keeping [asparagine] constant, rate of reaction was increased 1.25x.

Order of reaction with respect to the reducing sugar is 1.

Comparing Experiment 1 and 3,
Let the rate equation be rate = k[reducing sugar] [asparagine]^m

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k\,(0.750)(0.200)^m}{k\,(0.500)(0.100)^m}$$

$$\frac{0.00369}{0.00246} = \frac{k\,(0.750)(0.200)^m}{k\,(0.500)(0.100)^m}$$

m = 0
Order of reaction with respect to asparagine is 0.

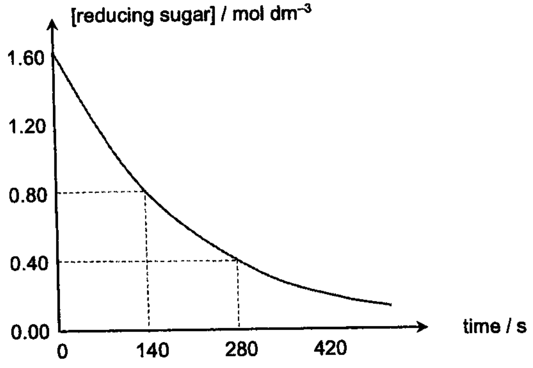
OR
Comparing Experiment 1 and 3,
When [reducing sugar] x1.5 while keeping the rest constant, rate of reaction x1.5.

Since observed rate of reaction was increased 1.5 times when [asparagine] was doubled, it implies that doubling [asparagine] has no effect on the rate.
Order of reaction with respect to asparagine is 0.

Rate = k [reducing sugar]

(ii) The reducing sugar is at an initial concentration of 1.60 mol dm^{-3} and its half-life is 140 s.

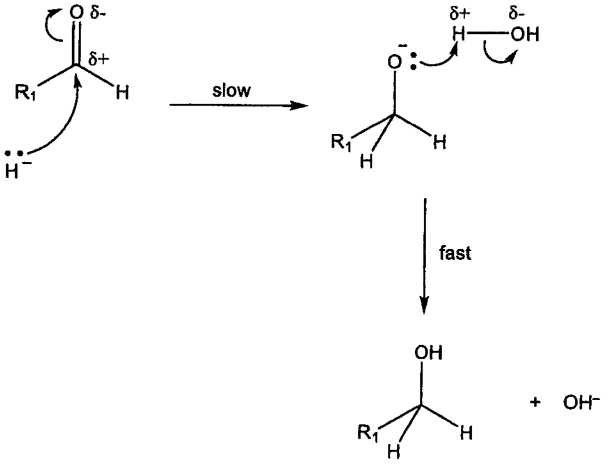
Sketch a graph of concentration of the reducing sugar against time for reaction **1**. [2]

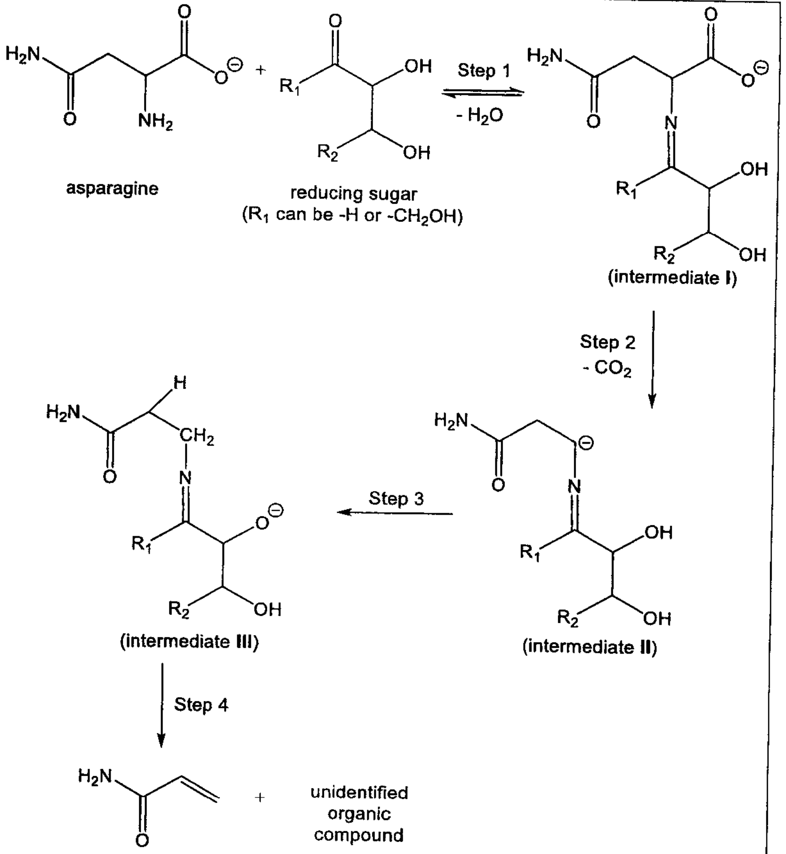


(iii) Determine the rate constant, *k*, for reaction **1**. [1]

$t_{½}$ = ln 2 ÷ k
k = ln 2 ÷ $t_{½}$ = ln 2 ÷ 140 = 0.00495 s^{-1}

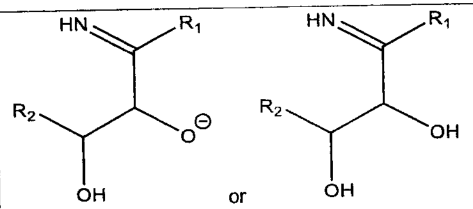
OR
Using experiment 1,

		Rate = k [reducing sugar] 0.00246 = k 0.500 k = 0.00492 s^{-1}
	(b)	The reaction between the reducing sugar and aqueous sodium borohydride is a nucleophilic addition reaction. Draw the mechanism for this reaction, assuming that sodium borohydride produces the hydride ion, :H^-, as the reacting species. In your answer, you may represent the reducing sugar as RCHO. [3]
		
	(c)	The following mechanism in figure 3.1 has been proposed for the Maillard reaction involving asparagine.

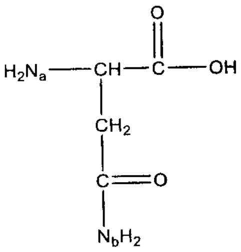
			 **Fig. 3.1**
		(i)	State the role of asparagine in step 1. [1]
			Nucleophile
		(ii)	Suggest and explain the effect on the rate of step 1 when R_1 is changed from –H to –CH_2OH. [1]
			The electron-donating alkyl (or –CH_2OH) group causes the carbonyl carbon to be less electron deficient. Hence there is a slower rate of nucleophilic addition. OR The –CH_2OH group poses greater steric hindrance to the nucleophile, so there is a slower rate of nucleophilic addition. OR The electron-withdrawing –CH_2OH group causes the carbonyl carbon to be more electron deficient. Hence there is a faster rate of nucleophilic addition.

BP-110

(iii) Draw the structure of the unidentified product of the above mechanism. [1]



(d) Compare and explain the base strength of the atoms N_a and N_b in asparagine.



$H_2N_a{-}CH(CH_2C(=O)N_bH_2){-}C(=O){-}OH$

asparagine

[2]

N_b is less basic than N_a.

The amide functional group at N_b is neutral / not basic. This is because the lone pair of electron on N_b delocalises to the electron withdrawing C=O group, making it unavailable to accept protons/H^+ / coordinate to protons / protonation.

OR

The amine functional group at N_a is a stronger base. It is bonded to an electron-donating alkyl group that increases electron density at the N_a atom. This makes the lone pair of electrons on N_a more available to accept protons.

(e) In the 2020 Olympic Games, winners received medals made from recycled gold, silver and bronze. These metals were from recycled from electronic waste collected throughout Japan. In the recycling process, metal parts are physically removed from the plastics, and the metals are sorted by elements and levels of purity.

Low purity silver is refined using electrolysis to remove metal impurities such as gold and copper.

(i) The electrode potential for Au^+/Au is given below.

$$Au^+ + e^- \rightleftharpoons Au \qquad E^\circ = +1.83\text{ V}$$

Define the term *standard electrode potential of Au^+/Au.* [1]

Standard Electrode (Redox) Potential, E° is defined as the potential difference between a standard hydrogen electrode OR H^+/H_2 half cell and the Au^+/Au half cell under standard conditions at 1 mol dm^{-3}, 25 °C / 298K and 1 bar.

(ii) Describe the electrode reactions that take place during this electrolysis and explain in detail how each of the two impurity metals is removed from the silver. [3]

At the anode:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e$ and $Ag(s) \rightarrow Ag^+(aq) + e$

Since the $E^\circ_{Cu2+/Cu}$ is more negative than $E^\circ_{Ag+/Ag}$, Cu is oxidised to Cu^{2+} ions at the anode, followed by Ag.

Since the $E^\circ_{Au+/Au}$ is more positive than $E^\circ_{Ag+/Ag}$, Au will not be oxidised to Au^+ ions at the anode but will drop just off at the anode as anodic sludge.

At the cathode: $Ag^+(aq) + 2e \rightarrow Ag(s)$

Since $E^\circ_{Ag+/Ag}$ is more positive than $E^\circ_{Cu2+/Cu}$, Cu^{2+} will remain in the solution as Ag^+ is preferentially reduced over Cu^{2+}.
Thus, both Cu and Au are removed from the silver.

(iii) The electrolytic refining of silver was carried out for 90 minutes using a current of 10.2 A.

Using data from the *Data Booklet*, calculate the expected mass of silver deposited in this process. [2]

Q = (90 × 60) × 10.2 = 55080 C
n(e) = 55080 ÷ 96500 = 0.5707 mol
n(Ag) deposited = 0.5707 mol
Mass of silver deposited = 0.5707 × 107.9 = 61.6 g

[Total: 20]

Section B

Answer **one** question from this section.

4 (a) (i) A glass rod was heated in a Bunsen burner flame and placed into a sample of hydrogen chloride gas.

The experiment was repeated using a sample of hydrogen iodide gas.

Use data from the *Data Booklet* to explain why a colour change was observed for hydrogen iodide but not hydrogen chloride. [2]

The bond energy of H-I is 299 kJ mol^{-1} while bond energy of H-C*l* is 431 kJ mol^{-1}.

Less energy is required to break the weaker H-I bond than H-C*l*, hence purple fumes of I_2 will be obtained for HI but no colour change for HCl [1]

OR

The heat energy in a Bunsen burner flame is sufficient to break H-I bond but not H-C*l* bond.

$2HI(g) \rightarrow H_2(g) + I_2(g)$

A purple vapour I_2 will be seen in the sample of hydrogen iodide gas.

(ii) Hydrogen chloride can be oxidised to chlorine and water in the presence of Cu*Cl*.

Likewise, hydrogen cyanide can be oxidised to cyanogen and water in the presence of Cu according to the following equation.

$$2HCN + \tfrac{1}{2}O_2 \rightarrow (CN)_2 + H_2O$$

Describe the change in oxidation state of carbon which occurs during this reaction. [1]

C in HCN is oxidised from +2 to +3 in $(CN)_2$

(iii) Cyanogen can be converted to ethanedioic acid by heating with aqueous acid. State the type of reaction for this conversion. [1]

Acid hydrolysis

To determine the solubility product, K_{sp}, of calcium ethanedioate, CaC_2O_4, at 20 °C, an excess of solid calcium ethanedioate was shaken with 6.25×10^{-5} mol dm^{-3} of sodium ethanedioate.

The resulting mixture was allowed to equilibrate at 20 °C in a water bath and then the mixture was filtered to obtain the filtrate, Solution **A**, which contains a saturated solution of calcium ethanedioate.

25.0 cm^3 of Solution **A** was titrated with 5.0×10^{-5} mol dm^{-3} of acidified potassium manganate(VII). 16.60 cm^3 of potassium manganate(VII) was required for complete reaction.

The reaction of ethanedioate ions and acidified manganate(VII) ions is shown below.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(b) **(i)** The reaction between ethanedioate ions and acidified potassium manganate(VII) has a high activation energy, hence solution **A** was heated to 60 °C before titration.

Explain why the reaction has a high activation energy. [1]

There is repulsion between two anions MnO_4^- and $C_2O_4^{2-}$ thus energy is required to overcome the repulsion.

(ii) Calculate the amount of ethanedioate ions in 25.0 cm^3 of Solution **A**. [2]

Amount of MnO_4^- = $5.0 \times 10^{-5} \times \frac{16.60}{1000}$
= 8.30×10^{-7} mol

Amount of ethanedioate ions in 25.0 cm^3 of Solution A = $\frac{5}{2} \times 8.30 \times 10^{-7}$
= 2.08×10^{-6} mol

(iii) Calculate the concentration of ethanedioate ions in Solution **A**. [1]

[ethanedioate ions] in 25.0 cm^3 of Solution **A** = $\frac{1000}{25} \times 2.075 \times 10^{-6}$
= 8.30×10^{-5} mol dm^{-3}

(iv) Calculate the concentration of calcium ions in solution **A**. [1]

[ethanedioate ions] from CaC_2O_4 = $8.30 \times 10^{-5} - 6.25 \times 10^{-5}$
= 2.05×10^{-5} mol dm^{-3}

$[Ca^{2+}] = 2.05 \times 10^{-5}$ mol dm^{-3} since $[Ca^{2+}] = [C_2O_4^{2-}]$ from CaC_2O_4

(v) Write an expression for the solubility product, K_{sp}, of calcium ethanedioate and calculate its value at 20 °C, stating the units clearly in your answer. [3]

$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$
$= (2.05 \times 10^{-5})(8.30 \times 10^{-5})$
$= 1.70 \times 10^{-9}$ mol^2 dm^{-6}

(c) When a precipitate of calcium ethanedioate is formed, ΔG°_{ppt} in J mol^{-1}, is given by the following expression.

$$\Delta G^\circ_{ppt} = RT\ln K_{sp}$$

(i) Given that the K_{sp} value of calcium ethanedioate at 25 °C is 2.70×10^{-9} mol^{2}dm^{-6}, calculate the ΔG°_{ppt} of calcium ethanedioate. [1]

$\Delta G^\circ_{ppt} = RT\ln K_{sp}$
$= 8.31 \times 298 \times \ln(2.70 \times 10^{-9})$
$= -48859$ J mol^{-1}
$= -48.9$ kJ mol^{-1}

(ii) The standard entropy change of the precipitation of calcium ethanedioate, ΔS°_{ppt} is +93.2 J mol^{-1} K^{-1}.

Calculate the standard enthalpy change of precipitation of calcium ethanedioate, ΔH°_{ppt}. [1]

$-48859 = \Delta H^\circ_{ppt} - 298(+93.2)$
$\Delta H^\circ_{ppt} = -21.1$ kJ mol^{-1}

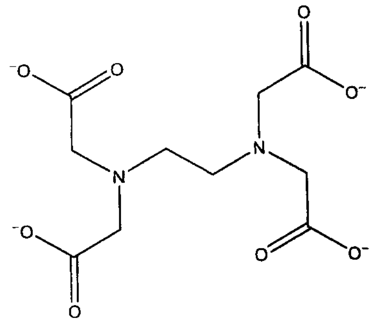
(d) The precipitation of calcium ethanedioate is one of the reasons for the formation of kidney stones.

Given that the stomach has a pH of about 2.0 while the kidney has a pH of about 6.5, explain why stones are not formed in the stomach but stones can be formed in the kidney. [2]

At pH 2.0 in the stomach, $[H^+]$ is higher than at pH 6.5 in the kidney.
The high $[H^+]$ in the stomach reacts with $C_2O_4^{2-}$ to form $H_2C_2O_4$ (or $HC_2O_4^-$), hence $[C_2O_4^{2-}]$ is much lower in the stomach than kidney.

Thus the ionic product of calcium ethanedioate remains below K_{sp} in the stomach but can rise above K_{sp} in the kidney.

(e) Ethylenediaminetetraacetate, also known as EDTA has the structure shown below.



Suggest a reason why EDTA can be used as a treatment for kidney stones. [2]

EDTA can form a complex / chelates/ binds via a dative bond with Ca^{2+}, thus $[Ca^{2+}]$ decreases.

Ionic product in the kidney can fall below K_{sp} thus the calcium ethanedioate precipitate will not form. (or is soluble)

OR

$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$ OR make reference to earlier part's equation.

POE shifts right as $[Ca^{2+}]$ decreases, thus calcium ethanedioate dissolves.

(f) Calcium ethanedioate decomposes at a temperature of 400 °C according to the equation shown below.

$$CaC_2O_4(s) \rightarrow CaO(s) + CO_2(g) + CO(g)$$

Explain why magnesium ethanedioate decomposes at a lower temperature than calcium ethanedioate. [2]

Mg^{2+} has a higher charge density/polarising power than Ca^{2+}.
The electron cloud of $C_2O_4^{2-}$ in MgC_2O_4 is distorted to a greater extent hence the bonds in anion are weakened more than in CaC_2O_4.
Less energy is required to break the bonds in MgC_2O_4.

[Total: 20]

---

5 (a) The equilibrium constant, K_p, of the following reaction is 1.64 at a certain temperature.

equation 1

$$I_2(s) + Br_2(g) \rightleftharpoons 2IBr(g) \qquad \Delta H < 0$$

In a study, some bromine gas was introduced into a vessel with excess solid iodine at the same temperature and the reaction was allowed to take place until equilibrium was reached. The partial pressure of IBr(g) at equilibrium was found to be 0.80 atm. Assume that all the bromine is in the gaseous state and that the vapour pressure of iodine is negligible.

(i) State the K_p expression for equation 1.

Hence, calculate the partial pressure of Br_2 at equilibrium. [2]

$K_p = \frac{(P_{IBr})^2}{(P_{Br2})}$

$1.64 = \frac{0.8^2}{(P_{Br2})}$

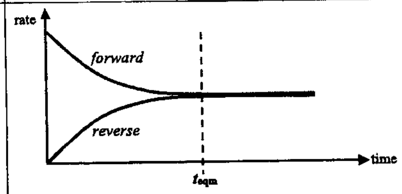
$P_{Br2} = \frac{0.8^2}{1.64} = 0.39024 = 0.390$ atm

(ii) Hence calculate the initial pressure of Br_2 in the container. [1]

	$I_2(s)$	+ $Br_2(g)$	$\rightleftharpoons$	$2IBr(g)$
Initial / atm	-	x + 0.4		0
Change / atm	-	−0.4		+0.80
Equilibrium / atm	-	x		0.80

Initial pressure = 0.390 + 0.4 = 0.790 atm

(iii) Sketch a graph of rate against time, showing how the rates of the forward and reverse reactions change with time, from the point of mixing to the point after equilibrium is established. Label your graphs clearly. [2]



(iv) State and explain the effect on the rate of production and yield of IBr when temperature is decreased. [3]

As temperature is decreased, the system would favour the forward, exothermic reaction to release heat. POE shifts to the right.

Frequency of effective collision decreases as fewer particles have kinetic energy greater than activation energy.

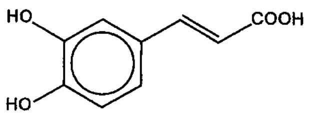
The yield of IBr increases and rate of production of IBr decreases.

(v) State and explain the effect on the equilibrium partial pressure of Br_2 when the pressure of the system is halved at constant temperature. [2]

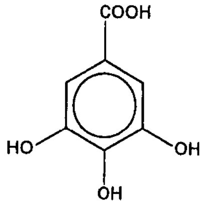
When the pressure of the system is halved, the system will respond by increasing the number of gaseous particles present, to increase pressure.

This favours the forward reaction for the position of equilibrium to shift to the right and the partial pressure of Br_2 will decrease.

b Caffeic acid and gallic acid are organic compounds that can be found in coffee and tea leaves respectively.



caffeic acid



gallic acid

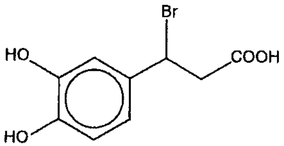
(i) Describe a chemical test to distinguish the above two compounds and state the expected observations. [2]

Add $KMnO_4$, $H_2SO_4(aq)$ to both compounds and heat

For caffeic acid, purple $KMnO_4$ will decolorise. Colourless, odourless gas (CO_2) produced will form white ppt with limewater. For gallic acid, purple $KMnO_4$ will remain.

Or add $KMnO_4$ in NaOH
For caffeic acid, purple $KMnO_4$ will decolorise and brown ppt form while for gallic acid, purple $KMnO_4$ will remain.
Or $KMnO_4$, $H_2SO_4(aq)$
For caffeic acid, purple $KMnO_4$ will decolorise while for gallic acid, purple $KMnO_4$ will remain.

(ii) Draw the structure of the major product that is formed when caffeic acid reacts with HBr. [1]



(c) Buffer solutions are very important in many biological reactions as enzymes need a specific pH range to function properly. One of the most important buffer systems is the carbonic acid, H_2CO_3, and bicarbonate, HCO_3^-, buffer system in blood.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The above equilibrium has a K_a value of 7.90×10^{-7} mol dm^{-3} and is responsible for buffering the pH of the blood at 7.4.

(i) A blood buffer can be simulated by mixing 0.500 mol dm^{-3} H_2CO_3 and 2.00 mol dm^{-3} of $NaHCO_3$.

Show that the volumes of H_2CO_3 and $NaHCO_3$ required to make 200 cm^3 of this buffer solution with pH 7.4 are 34 cm^3 and 166 cm^3 respectively [3]

$pK_a = -\lg(7.90 \times 10^{-7}) = 6.102$

$$pH = pK_a + \lg\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$7.4 = -\lg(7.90 \times 10^{-7}) + \lg\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\lg\frac{[HCO_3^-]}{[H_2CO_3]} = 1.298$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 19.86$$

Since volume of H_2CO_3 + HCO_3^- = 0.200 dm^3, let the volume of HCO_3^- be A dm^3 and the volume of H_2CO_3 be (0.200 – A) dm^3.

$$\frac{\frac{A \times 2}{0.200}}{\frac{(0.200 - A) \times 0.5}{0.200}} = 19.86$$

A = 0.166 dm^3
= 166 cm^3

Volume of HCO_3^- = 166 cm^3
Volume of H_2CO_3 = 200 – 166 = 34 cm^3 for showing both volumes

(ii) With the aid of an equation, explain how the buffer solution prepared in **c(i)** helps to maintain the pH at around 7.4 when a small amount of sodium hydroxide is added. [2]

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$$

H_2CO_3 will react with hydroxide added to minimise the decrease in $[H^+]$/no significant increase in $[OH^-]$. Hence, the increase in pH of the solution is not significant.

		(iii)	Hence calculate the resultant pH of the above buffer solution when 0.003 mol of solid sodium hydroxide is added. [2]
			Amount of H_2CO_3 consumed = [(34/1000) x 0.5] – 0.003 = 0.0140 mol Amount of HCO_3^- produced = [(166/1000) x 2] + 0.003 = 0.335 mol $\mathrm{pH} = \mathrm{p}K_a + \lg\frac{[HCO_3^-]}{[H_2CO_3]} = 6.102 + \lg\frac{\frac{0.335}{0.200}}{\frac{0.0140}{0.200}} = 7.48$
			[Total: 20]

Answer **all** the questions in the spaces provided.

1 **Identification of an unknown organic acid by titration**

In this experiment, you will perform titrations to determine the relative molecular mass, M_r, of an unknown monoprotic organic acid, **FA 1**, and use it to identify the acid.

FA 1 is an aqueous solution containing 4.80 g dm^{-3} of an unknown monoprotic organic acid.

You are also provided with:
FA 2 is 0.110 mol dm^{-3} sodium hydroxide, NaOH.
thymol blue indicator

Prepare a table in the space provided below to record, to an appropriate level of precision, all your burette readings.

(a) Titration of FA 1 with FA 2

1. Fill the burette with **FA 2**.
2. Pipette 25.0 cm^3 of **FA 1** into a conical flask.
3. Add 3 to 4 drops of thymol blue indicator into the flask. The solution in the flask should turn pink.
4. Titrate **FA 1** in the conical flask with **FA 2**. The end-point is reached when the solution changes from yellow to green.
5. Record your burette readings in your table.
6. Repeat steps 2 to 5 until consistent results are obtained.

Titration Results

final burette reading / cm^3	23.50	47.50		
initial burette reading / cm^3	0.00	24.00		
volume of **FA 2** added / cm^3	23.50	23.50		

[5]

From your titrations, obtain a suitable volume of **FA 2**, to be used in your calculations. Show clearly how you obtained this volume.

average titre = ½ (23.50 + 23.50)
= 23.50 cm^3

volume of **FA 2** = ...23.50 cm^3..... [1]

(b) **(i)** Calculate the amount of sodium hydroxide present in the volume of **FA 2** that you calculated in **(a)**

amt of NaOH used = 23.50/1000 x 0.110
= 2.59 x 10^{-3} mol

amount of NaOH reacted = ...2.59 x 10^{-3} mol.....[1]

(ii) Calculate the concentration of organic acid present, in mol dm^{-3} in **FA 1**.

Concentration of organic acid = 2.585 x 10^{-3} ÷ 25/1000
= 0.103 mol

concentration of organic acid in **FA 1** = ...0.103 mol ..... [1]

(iii) Calculate the relative molecular mass, M_r, of the organic acid in **FA 1**.

M_r of organic acid = 4.80 ÷ 0.1034
= 46.4

M_r of the organic acid = ...46.4..... [1]

(iv) From another experiment, the identity of **FA 1** was narrowed down to these four acids.

CH_3COOH $HCOOH$ $CH_2=CHCO_2H$ $CH_3CH_2CO_2H$

Given that sodium hydroxide reacts only with the COOH group in the organic acid, deduce the identity of the organic acid present in **FA 1**. Explain your answer.

[A_r: H, 1.0; C, 12.0; O, 16.0; Cl, 35.5]

M_r of HCOOH = 1.0 + 12.0 + 16.0 x 2 + 1.0 = 46.0

HCOOH is the organic acid present in FA 1 as its M_r is the closest to the one calculated in b(iii). [1]

(c) This identification method uses the calculated relative molecular mass of the acid.

As the relative molecular masses of $CH_2=CHCO_2H$ and $CH_3CH_2CO_2H$ are so similar, any slight inaccuracy in the titration could lead to an incorrect conclusion.

Describe a chemical test that would enable you to distinguish between $CH_2=CHCO_2H$ and $CH_3CH_2CO_2H$.

There is **no need** to carry out this test. [2]

Test: $KMnO_4$(aq), H_2SO_4(aq), heat
Results: purple $KMnO_4$ decolourises for $CH_2=CHCO_2H$, CO_2 gas evolved forms white ppt in limewater. Purple colour remains for $CH_3CH_2CO_2H$

Or
Test: $KMnO_4$(aq), NaOH(aq),
Results: purple $KMnO_4$ decolourises for $CH_2=CHCO_2H$ and a brown ppt is formed. Purple colour remains for $CH_3CH_2CO_2H$

Or

Test: Br_2(aq)/Br_2(l)/Br_2(inert solvent like CCl_4)
Results: orange (aq)/reddish brown(liquid), orange-red(inert solvent) Br_2 decolourises for $CH_2=CHCO_2H$ while orange (aq)/reddish brown(liquid), orange-red(inert solvent) colour remains for $CH_3CH_2CO_2H$

(d) Another student was provided a solution of another unknown organic acid. It has the same concentration, in mol dm^{-3}, as that used in the titration above. However, this new unknown organic acid is a diprotic acid.

State and explain how the calculated relative molecular mass obtained will differ from that obtained in **b(iii)**. [2]

Since the new acid is diprotic, the volume of FA 2 or NaOH required will be doubled. This causes the calculated amount of acid present to be doubled and in turn, the calculated concentration of FA 1 to be doubled. Hence the calculated M_r will be halved.

[Total: 14]

2 Determination of the concentration of NaOH and the enthalpy change of neutralisation, ΔH_{neut}

You are provided with the following solutions:

FA 3 is a solution of sodium hydroxide, NaOH

FA 4 is a solution of 2.00 mol dm^{-3} hydrochloric acid, HC*l*

In this question, you are to perform a series of 6 experiments where different volumes of **FA 3** and **FA 4** are mixed together to give a total volume of 50 cm^3. The temperature change, ΔT, for each experiment will be determined and a graph of ΔT against the volume of **FA 3** will be plotted.

You will then use the data from your graph to determine the concentration of NaOH in **FA 3**, and the enthalpy change of neutralization for the reaction between aqueous sodium hydroxide and hydrochloric acid.

$$NaOH + HCl \rightarrow NaCl + H_2O \qquad \Delta H_{neut}$$

(a) Procedure

Experiment 1

1) Place one polystyrene cup inside a second polystyrene cup. Place these into a 250 cm^3 beaker to prevent them from tipping over.
2) Use a 50 cm^3 measuring cylinder to transfer 10.0 cm^3 of **FA 3** into the polystyrene cup.
3) Measure the temperature of **FA 3** in the polystyrene cup and record the initial temperature of **FA 3**, T_1, in Table 2.1 on the next page.
4) Use another 50 cm^3 measuring cylinder, transfer 40.0 cm^3 of **FA 4** into the same polystyrene cup.
5) Stir the mixture in the polystyrene cup with the thermometer. Measure and record the highest temperature, T_2 in Table 2.1 on the next page.
6) Rinse the polystyrene cup and thermometer with distilled water and dry them with paper towels.
7) Repeat steps **2** to **6** using 20.0 cm^3, 30.0 cm^3 and 40.0 cm^3 of **FA 3**, each time using appropriate volume of **FA 4**, such that the total volume of the reaction mixture is 50 cm^3.
8) Record all measurements of volume, temperature (T_1 and T_2) and temperature change, ΔT, in Table 2.1 on the next page.

(b) Results

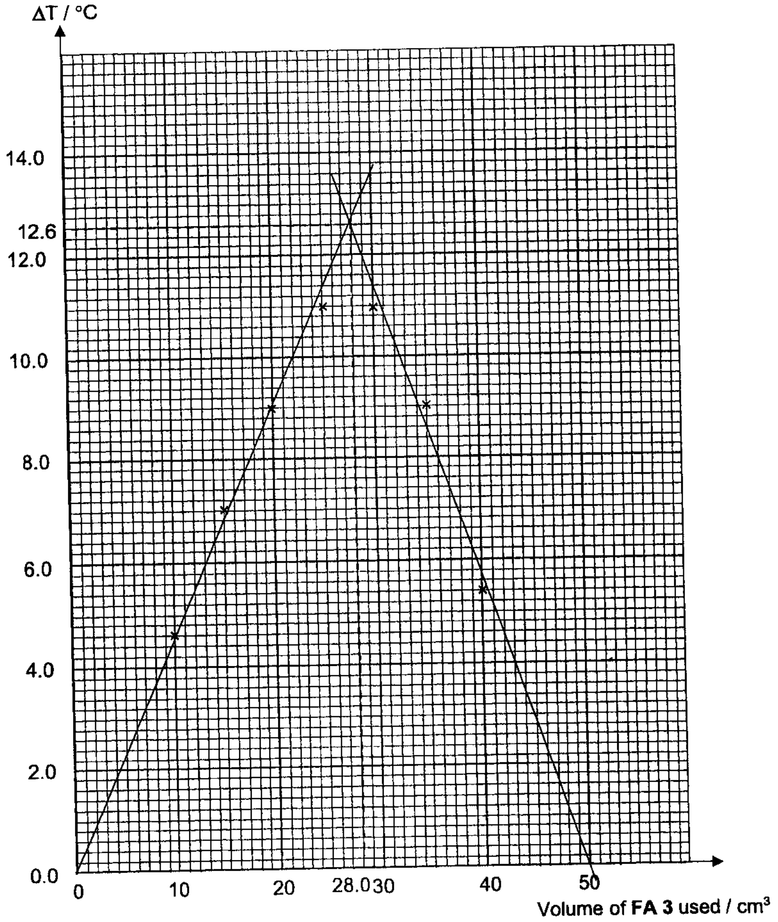
Table 2.1

	Experiment					
	1	2	3	4	5	6
Volume of **FA 3** / cm^3	10.0	20.0	30.0	40.0	25.0	35.0
Volume of **FA 4** / cm^3	40.0	30.0	20.0	10.0	25.0	15.0
Initial temperature, T_1/ °C	29.0	29.0	29.0	29.0	29.0	29.0
Final temperature, T_2/ °C	33.6	38.0	40.0	34.4	40.0	38.0
Temperature change, ΔT / °C	+4.6	+9.0	+11.0	+5.4	+11.0	+9.0

[3]

(c) (i) Plot a graph of ΔT (y–axis) against volume of **FA 3** used (x–axis) using the four experimental results that you have obtained.

The scales for both axes must be chosen to provide an origin.



By considering your plotted points, perform two additional experiments to identify the volume of **FA 3** needed to produce the maximum temperature change, ΔT_{max}.

In each experiment, ensure that the total volume of the reaction mixture is 50 cm³. You may find it helpful to plot the results from each experiment before choosing the volumes to use in the next experiment.

Record all measurements of volume, temperature (T_1 and T_2) and temperature change, ΔT, in **Table 2.1**. [2]

(ii) Draw two straight lines of best fit. The first best fit line should be drawn using the plotted points where ΔT is increasing and the second best fit line should be drawn using the plotted points where ΔT is decreasing. Extrapolate these two lines until they cross. [1]

(d) (i) **Use your graph** to determine the maximum temperature change, ΔT_{max}, as well as the volume of **FA 3**, V_{FA3}, used to obtained it.

ΔT_{max} = ...12.6...........................°C
V_{FA3} = ...28.0................cm³ [1]

(ii) Using your results in **(d)(i)**, calculate the concentration of NaOH in **FA 3**.

volume of HCl reacted = 50.0 – 28.0 = 22.0 cm³

Amount of HCl reacted = Amount of NaOH reacted = 22.0/1000 x 2.00 = 0.044 mol

Concentration of NaOH = 0.044 / (28.0/1000) = 1.57 mol dm^{-3}

concentration of NaOH in **FA 3** = ...[2]

(iii) Hence, calculate the enthalpy change of neutralisation, ΔH_{neut}.

You may assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1}, and that the density of the reaction mixture is 1.00 g cm^{-3}.

heat released = 50 x 4.18 x 12.6= 2633 J

Amount of water produced = amount of NaOH reacted = 0.044 mol

ΔH_{neut} = –2592/0.044 = –59850 J mol^{-1}
= –59.9kJmol^{-1}

ΔH_{neut} = ...[2]

(e) Predict and explain the following:

(i) the effect on ΔT_{max} when the volumes of **FA 3** and **FA 4** used in the reaction are doubled [1]

Heat evolved = $mc\Delta T_{max} = n \times \Delta H_n \Rightarrow \Delta T_{max} = \frac{n \times \Delta H_n}{m \times c}$

When volume of FA1 and FA2 are doubled, <u>both n (amount of water produced) and m (mass of solution)/volume are doubled/increased</u> (ΔH_n and c remain constant). Hence <u>ΔT_{max} is unaffected</u>.

(ii) the effect on ΔH_{neut} if the experiment was repeated with ethanoic acid, CH_3CO_2H, of the same concentration instead of hydrochloric acid. [1]

ΔH_{neut} would be less exothermic/smaller/lower as ethanoic acid is a weak acid. Energy is absorbed to ionise/dissociate the weak acid.

(f) State one significant source of error in the experiment and suggest an improvement that can be made to reduce this error. [1]

Heat is lost to the surrounding, hence a cup with lid can be used to minimise heat exchange with the surrounding air. (cannot just say use better insulated cup)

Or

Heat capacity of the styrofoam cup is not accounted for, hence the heat absorbed by the styrofoam cup can be included in the calculation of heat change.

Or

Initial temperature of **FA 4** was not accounted for, hence the weighted initial temperature can be calculated where

$$T_{\text{weighted initial}} = \frac{(\text{Volume of FA 3} \times T_{FA3}) + (\text{Volume of FA 4} \times T_{FA4})}{\text{Volume of FA 3} + \text{Volume of FA 4}}$$

[Total: 14]

---

3 Inorganic Analysis

FA 5 is a solution which contains up to two cations and one anion.

Carry out the following tests and carefully record your observations in Table 3.1.

Using the observations in Table 3.1, you will then identify the ions present in **FA 5**.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved.

Table 3.1

		test	observations
(a)	**(i)**	Place one drop of **FA 5** solution on Universal indicator paper	UI paper: orange or yellow pH = 3 or pH = 4
	(ii)	Add about 1cm^3 of dilute nitric acid to 1cm depth of **FA 5** solution.	No effervescence
		Add barium nitrate dropwise until no further change is seen.	White ppt formed.
	(iii)	Add sodium hydroxide to 1cm depth of **FA 5** until no further change is seen.	Pale blue ppt forms, insoluble in excess NaOH
		Gently warm the mixture.	Pungent gas forms and **turns moist red litmus** paper **turns blue** + Gas is **NH_3**. Blue ppt turns black

	(iv)	Add aqueous ammonia to 1cm depth of **FA 5** until no further change is seen.	Blue ppt forms soluble in excess ammonia to give a dark blue solution
	(v)	Add I^- (aq) to 1cm depth of **FA 5** until no further change. Leave mixture to stand	white/off-white/cream ppt in a brown solution.
			[5]

(b) **(i)** Identify the cation(s) and anion present in **FA 5**.

cation(s) in **FA 5** Cu^{2+}, NH_4^+

anion in **FA 5** SO_4^{2-} [3]

(ii) Write an equation to explain the observation in test **(a)(i)**.

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

[Total: 9]

---

4 Determination of oxidising strength of oxidising agents

You are provided with samples of the following four aqueous solutions.

Solution that contains bromide ions, Br^-
Solution that contains iron(III) ions, Fe^{3+}
Solution that contains iodine water, I_2
Solution that contains iodide ions, I^-

Carry out the tests in Table 4.1 to investigate possible redox reactions and rank the oxidising strength of the oxidising agents Br_2, Cl_2, Fe^{3+} and I_2.

$Br_2 + 2e^- \rightleftharpoons 2Br^-$
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
$I_2 + 2e^- \rightleftharpoons 2I^-$

Your answers should correspond to the given observations/equations/deductions. The results of the first test has been given to you and you should use it as an example.

Table 4.1

		test	Observations	Deductions
(a)	(i)	Transfer 1 cm^3 of **Br$^-$** to a test-tube. Add 1 cm^3 of **C*l*$_2$**.	Solution turns yellow	C*l*$_2$ oxidises Br$^-$ to Br$_2$ C*l*$_2$ > Br$_2$
	(ii)	Transfer 1 cm^3 of **Fe^{3+}** to a test-tube. Add 1 cm^3 of **Br$^-$**. Add aqueous NaOH dropwise until in excess.	Solution remains orange. Red brown ppt formed, insoluble in excess NaOH	Fe^{3+} cannot oxidise Br$^-$ Br$_2$ > Fe^{3+}
	(iii)	Transfer 1 cm^3 of **Fe^{3+}** to a test-tube. Add 1 cm^3 of **I$^-$** then add 5 drops of starch solution.	(orange) Solution turns brown. (brown) Solution turns blue-black with starch	Fe^{3+} oxidises I$^-$ to I$_2$ Fe^{3+} > I$_2$
	(iv)	Transfer 1 cm^3 of **I$_2$** to a test-tube. Add 1 cm^3 drops of **Br$^-$** then add 5 drops of starch solution.	Solution remains brown Solution turns blue-black with starch	I$_2$ cannot oxidise Br$^-$ Br$_2$ > I$_2$

[4]

(b) Use your information in the above completed table to rank the order of oxidising strengths of the species: Br$_2$, C*l*$_2$, Fe^{3+} and I$_2$.

Note: In some of the tests performed in part **(a)** there will have been no reaction. Such tests can still help you to deduce the relative oxidising powers of the species involved.

....[1]

C*l*$_2$ > Br$_2$ > Fe^{3+} > I$_2$ OR in any form that clearly shows the correct trend.

(c) Using your observations, explain why aqueous FeI$_3$ cannot be prepared.

....[1]

In test (a)(iii), Fe^{3+} oxidises I$^-$ to I$_2$

[Total:6]

5 Planning

When a solute is added to two immiscible solvents, A and B, some of the solute dissolves in each of the solvents and an equilibrium is set up between the two solvents. It has been shown that for dilute solutions, at equilibrium, the ratio of the two concentrations is a constant known as the partition coefficient, $K_{\text{partition}}$.

Trichloromethane, $CHCl_3$, and water separate into two immiscible layers when shaken together and allowed to stand. Ammonia can dissolve in both of these layers. The $K_{\text{partition}}$ for ammonia in these two solvents is given by:

$$K_{\text{partition}} = \frac{[NH_3]_{\text{water}}}{[NH_3]_{\text{trichloromethane}}}$$

50 cm^3 of trichloromethane and 50 cm^3 of aqueous ammonia are mixed and left to equilibrate for about an hour. Samples of the aqueous layer are obtained and the amount of ammonia present in the aqueous layer is determined by titration. The concentrations of ammonia in the separate layers can be calculated and the value of $K_{\text{partition}}$ can then be determined.

(a) Explain why ammonia is likely to be more soluble in water than in trichloromethane.

....[1]

Ammonia can form hydrogen bonds with water molecules while it can only form permanent dipole – permanent dipole interactions with trichloromethane.

(b) You are to plan a procedure that will allow you to obtain the titration results necessary to determine value of $K_{\text{partition}}$ of ammonia between water and trichloromethane at room temperature.

You are provided with the following

- trichloromethane
- 1.00 mol dm^{-3} aqueous ammonia
- 0.500 mol dm^{-3} hydrochloric acid
- methyl orange indicator
- 250 cm^3 conical flask with stopper
- 10.0 cm^3 pipette
- the laboratory apparatus normally found in a school

In your plan you should include the following:

- an outline of how you would prepare the equilibrium mixture
- practical details of how you would carry out the titration
- appropriate apparatus and their capacities

....[7]

1. Using a 50 cm^3 measuring cylinder, add 50 cm^3 of aqueous ammonia into a 250 cm^3 conical flask.
2. Using another 50 cm^3 measuring cylinder, add 50 cm^3 of trichloromethane into the same conical flask.
3. Stopper the conical flask and shake to mix well. Leave the flask at room temperature to equilibrate for 1 hour.

4. Using a 10.0 cm^3 pipette, transfer 10.0 cm^3 of the aqueous layer into another 250 cm^3 conical flask.
5. Add 2-3 drops of methyl orange.
6. Fill a 50.00 cm^3 burette with 0.500 mol dm^{-3} HCl
7. Titrate the solution against HCl in the burette, taking care to add dropwise near the end. The end point is reached when the solution in the conical flask changes from yellow to orange colour.
8. Repeat steps 4 to 7 until at least two consistent results within ±0.10 cm^3 are obtained

(c) It is unnecessary to titrate both layers of the partition. Explain why the titration is carried out on a sample of the aqueous layer rather than the trichloromethane layer.

....[1]

The concentration of ammonia is higher in aqueous layer which means the titration reading will be larger. The percentage error associated with the volume used will be lower and hence the determination of its concentration will be more accurate.

Or

Hydrochloric acid is immiscible with trichloromethane layer.

(d) A student carried out the experiment and obtained a mean titre of 19.20 cm^3.

(i) Using this mean titre value, calculate the equilibrium amounts of ammonia

1. in the aqueous layer
2. in the trichloromethane layer

amount of HCl reacted
= 19.20/1000 x 0.500
= 9.60 x 10^{-3} mol

amount of ammonia in aqueous layer
= 9.60 x 10^{-3} ÷ 10/1000 x 50/1000
= 0.0480 mol

initial amt of ammonia used = 50/1000 x 1.00 = 0.0500 mol

amt of ammonia in trichloromethane layer = 0.0500 – 0.0480 = 0.00200 mol

amount of ammonia in the aqueous layer = ...0.0480 mol ....[1]

amount of ammonia in the trichloromethane layer = ...0.00200 mol ....[1]

(ii) Hence calculate the value of the partition coefficient, $K_{partition}$.

$[NH_3]_{water} = 0.0480 \div 50/1000 = 0.960$ mol dm^{-3}

$[NH_3]_{trichloromethane} = 0.00200 \div 50/1000 = 0.0400$ mol dm^{-3}

$K_{partition} = 0.960 \div 0.0400 = 24.0$

partition coefficient, $K_{partition}$ = ...24.0...[1]
[Total: 12]