ANDERSON SERANGOON JUNIOR COLLEGE
2025 JC2 PRELIMINARY EXAMINATION Paper 1 Solutions

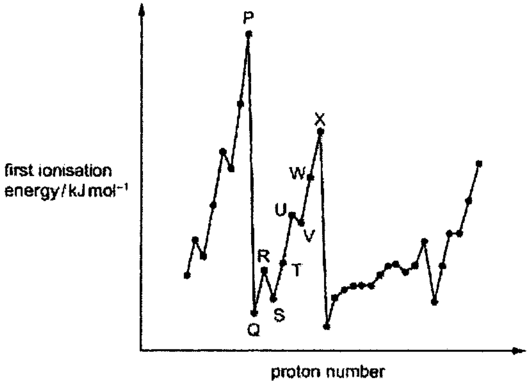
1 Sodium azide, NaN_3 is an explosive used to inflate airbags in cars when they crash. It consists of positive sodium ions and negative azide ions.

What are the number of electrons in the sodium ion and the azide ion?

	sodium ion	azide ion
A	10	20
B	10	22
C	12	20
D	12	22

Ans: B
Na^+ (11 – 1 = 10) and N_3^- (7 x 3 + 1 = 22)

2 The graph shows the variation of the first ionisation energy with proton number for some elements. The letters used are not the actual symbols for the elements.



Which statement about the elements is correct?

A P and X are in the same period in the Periodic Table.

B The general increase from Q to X is due to increasing atomic radius.

C The small decrease from R to S is due to decreased shielding.

D The small decrease from U to V is due to repulsion between paired electrons.

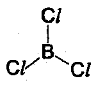
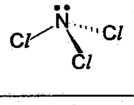
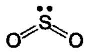
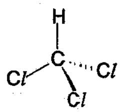
Ans: D
A – same Group
B – increasing nuclear charge (and relatively constant shielding effect)
C – higher energy level (ns^2 vs np^1)

3 The table identifies the shape and polarity of four molecules.

Which row is correct?

	molecule	molecular shape	polarity
A	boron trichloride	trigonal pyramidal	polar
B	nitrogen trichloride	trigonal planar	non-polar
C	sulfur dioxide	bent	polar
D	trichloromethane	tetrahedral	non-polar

Ans: C

	BCl_3	NCl_3	SO_2	$CHCl_3$
No. of bp, lp on central atom	3 bp, 0 lp	3 bp , 1 lp	2 bp, 1 lp	4 bp, 0 lp
Molecular shape	trigonal planar 	trigonal pyramidal 	bent 	tetrahedral 
polarity	non–polar	polar	polar	polar

4 The element tin exists in two forms, grey tin and white tin.

Some properties of grey tin and white tin are shown.

	grey tin	white tin
boiling point	2543 °C	2533 °C
electricial conductivity	none in solid or liquid	good in solid and liquid
malleability	brittle	malleable

Which structural change might take place when grey tin changes to white tin?

A giant covalent to giant ionic

B giant covalent to giant metallic

C giant ionic to giant covalent

D giant ionic to giant metallic

Ans: B

White tin must have giant metallic structure as it conducts electricity in solid and liquid state and its malleable.

Grey tin cannot have giant ionic structure as it does not conduct electricity when in liquid state, thus, it has to be giant covalent structure.

BP-187

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5 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.

What is the value of n?

A 1

B 2

C 3

D 4

Ans: C

Let the oxidation state of iodine in KIO_n be I^{n+}
(this approach allow you to focus on the species that is undergoing Redox.)
Reduction: $(2n)\,e + 2\,I^{n+} \rightarrow I_2$ x 2
Oxidation: $2I^- \rightarrow I_2 + 2e$ x 2n
Overall equation: $4I^{n+} + (4n)I^- \rightarrow 2I_2 + (2n)I_2$

Comparing mole ratio $\frac{\text{amt of } I^{n+}}{\text{amt of } I^-} = \frac{4}{4n} = \frac{0.01}{0.05}$,

solving n = 5
Since IO_n^-, considering the oxidation number and overall charges of the ion,
+5 + n(-2) = −1
n = 3

OR

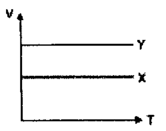
IO_n^-: I^-
1 : 5
oxidation: $2I^- \rightarrow I_2 + 2e^-$
$5I^- \rightarrow \frac{5}{2}I_2 + 5e^-$
[R]: $2IO_n^- + 4nH^+ + (4n-2)e^- \rightarrow I_2 + 2nH_2O$
2n −1 = 5
n = 3

[Turn over

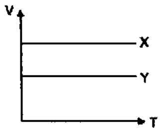
6 X and Y are two different samples of the same ideal gas.

Given that X contains a higher mass than Y, which graph shows the correct ideal gas relationship for the two samples of gas? (*T* is measured in K.)

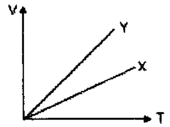
A



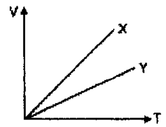
B



C



D



Ans: D
Manipulation of ideal gas equation would give
- $V = \frac{mR}{pM}(T) \Rightarrow$ graph of V against T gives a straight line passing thru the origin. [*option D*]

Since X has a larger mass, the line for X has a steeper gradient.

7 A student mixes 25.0 cm^3 of 0.350 mol dm^{-3} sodium hydroxide solution with 25.0 cm^3 of 0.350 mol dm^{-3} hydrochloric acid. The temperature increases by 2.5°C. No heat is lost to the surroundings.

The final mixture has a specific heat capacity of 4.2 J g^{-1} K^{-1}.

What is the molar enthalpy change for the reaction?

A −150 kJ mol^{-1}

B −60 kJ mol^{-1}

C −30 kJ mol^{-1}

D −0.15 kJ mol^{-1}

Ans: B
Limiting reagent is hydrochloric acid = (0.35 x 0.025) = 0.00875 mol
q = (25.0 + 25.0)(4.2)(2.5) = 525 J
$\Delta H = -(525)/(0.00875)$
$= -60$ kJ mol^{-1}

8 Silane, SiH_4, exists as a gas at standard temperature and pressure. Hess' Law can be used to calculate the average Si–H bond energy in gaseous SiH_4. Which information is needed to perform the calculation?

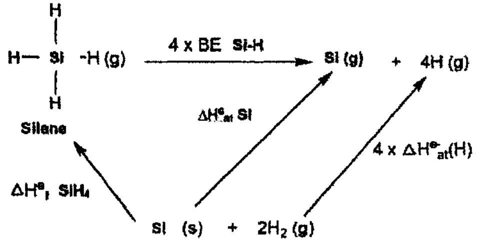
A $\Delta H^\circ_{formation}(SiH_4)$, $\Delta H^\circ_{atomisation}(Si)$, $\Delta H^\circ_{combustion}(H_2)$

B $\Delta H^\circ_{atomisation}(Si)$, $\Delta H^\circ_{atomisation}(H)$, $\Delta H^\circ_{formation}(SiH_4)$

C $\Delta H^\circ_{atomisation}(H)$, $\Delta H^\circ_{combustion}(Si)$, $\Delta H^\circ_{combustion}(SiH_4)$

D $\Delta H^\circ_{combustion}(Si)$, $\Delta H^\circ_{combustion}(H_2)$, $\Delta H^\circ_{formation}(SiH_4)$

Ans: B



9 Group 2 hydroxides undergo thermal decomposition in a similar fashion to Group 2 carbonates.

Barium hydroxide undergoes decomposition as shown in the equation below:

$$Ba(OH)_2(s) \rightarrow BaO(s) + H_2O(g) \qquad \Delta H > 0$$

Which statements about this reaction are correct?

1 The Gibbs free energy change can be positive or negative depending on the temperature.

2 The decomposition is spontaneous only at high temperature.

3 The entropy change is negative.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

Ans: A

ΔS is expected to be positive since there is formation of gaseous H_2O, thus statement 3 is wrong.
ΔG can be positive or negative depending on the temperature.
For reactions to be spontaneous, ΔG needs to be negative. As ΔG = ΔH – TΔS, T has to be high so that |TΔS| > ΔH. Thus statement 2 is correct.

10 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?

1 $NOBr_2$ is a radical.

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

3 $NOBr_2$ is formed at the transition state.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

Ans: B

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, rate of forward reaction = rate of reverse reaction
$k_f[NO][Br_2] = k_r[NOBr_2]$

$$\frac{k_f}{k_r} = \frac{[NOBr_2]}{[NO][Br_2]}$$

$$K_c = \frac{[NOBr_2]}{[NO][Br_2]}$$

$[NOBr] = K_c[NO][Br_2]$ — (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.

11 The kinetics of the following reaction is investigated, and the experimental data is given in the table below.

$$2R + 2S \longrightarrow T + U$$

$[R]$ / mol dm^{-3}	$[S]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
0.015	0.010	5.10×10^{-4}
0.030	0.020	4.08×10^{-3}
0.045	0.010	1.53×10^{-3}

What is the numerical value of the rate constant for this reaction?

A 0.00294 **B** 3.40 **C** 227 **D** 340

Ans: D

Comparing the first and third experiments,
When $[R] \times 3$ while keeping $[S]$ constant, initial rate × 3 $\Rightarrow$ rate α $[R]$.
Hence, order of reaction with respect to R is 1.

Comparing the first and second experiments,
When $[R] \times 2$ and $[S] \times 2$, initial rate × 8.
Since the order of reaction with respect to R is 1, rate α $[S]^2$.
Hence, order of reaction with respect to S is 2.

The rate equation is: rate = $k[R][S]^2$

Using data from the first experiment,
$k = 5.10 \times 10^{-4} \div (0.015 \times 0.010^2)$ = <u>340</u> mol^{-2} dm^6 s^{-1}

12 Ethanol is produced industrially by reacting ethene and steam.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \qquad \Delta H = -50.3 \text{ kJ mol}^{-1}$$

K_p has a value of 1.8×10^{-5} and the partial pressures of the reactants at equilibrium are shown.

reactant	partial pressure / x 10^6 Pa
ethene	4.8
steam	2.8

Which statement is correct?

A Adding a catalyst increases the value of K_p for the reaction at equilibrium.

B The overall process is a nucleophilic addition reaction.

C Increasing the temperature will increase the K_p for the reaction.

D Partial pressure of ethanol at equilibrium is 242 x 10^6 Pa.

Ans: D

A is incorrect as K_p is only dependent on temperature.

B is incorrect, as the overall process is an electrophilic addition reaction.

C is incorrect. Increasing the temperature will result in POE shifting left favoring the endothermic reaction. Thus, K_p will decrease.

D is correct.

$$K_p = \frac{P_{C_2H_5OH}}{P_{C_2H_4}P_{H_2O}}$$

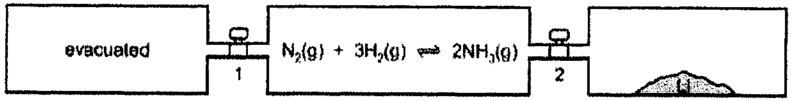
$$1.8 \times 10^{-5} = \frac{P_{C_2H_5OH}}{4.8 \times 10^6 (2.8 \times 10^6)}$$

$$P_{C_2H_5OH} = 242 \times 10^6 Pa$$

Exam tips: If you know your content knowledge, you will know that A, B and C are wrong and D must be correct. There is no need to perform the calculation

13 Lithium reacts with nitrogen at room temperature to form solid Li_3N.

Three vessels of equal volume are connected by taps 1 and 2 as shown.



At the start, taps 1 and 2 are closed, the left-hand vessel is evacuated, the middle vessel has the indicated reaction at equilibrium and the right-hand vessel contains lithium only.

Which action would allow the equilibrium mixture to contain the **most** ammonia?

A Keep both taps 1 and 2 closed.
B Open both taps 1 and 2.
C Open tap 1 only.
D Open tap 2 only.

Ans: A

Tap 2 must be closed as $N_2(g)$ can react with Li. This will cause the equilibrium position to shift left resulting in lower yield of $NH_3(g)$.

Tap 1 must be closed. This is because if tap 1 is open, the total pressure will decrease and the equilibrium position will shift left to the side with more moles of gas particles resulting in lower yield of ammonia

14 The table below describes some indicators.

indicator	colour in acid	colour in alkali	pK_a	range of pH for colour change
methyl orange	red	yellow	3.7	3.2 – 4.4
thymol blue	yellow	blue	8.9	8.0 – 9.6

For the titration of NaOH(aq) against HCOOH(aq), which row shows the most suitable indicator and the corresponding colour change?

	indicator	colour change
A	methyl orange	red to orange
B	methyl orange	yellow to orange
C	thymol blue	yellow to green
D	thymol blue	blue to green

Ans: D

The titration is between a strong base and weak acid. Hence the equivalence point pH > 7 as a basic salt is produced. Thymol blue will be a suitable indicator.
Since NaOH(aq) is in the conical flask, thymol blue will turn from blue to green.

15 In this question, Q represents an atom of chlorine, bromine or iodine.

Which statement about their atoms, molecules or halide ions is correct?

A Down the Group, permanent dipole–permanent dipole forces between halogen molecules become stronger.
B The first ionisation energy $Q(g) \rightarrow Q^+(g) + e^-$ decreases.
C Q_2 reactivity as oxidising agent increases down the group.
D The enthalpy change of formation of hydrogen halides becomes more exothermic.

Ans: B
Option A should be: Down the Group, instantaneous dipole–induced dipole forces between halogen molecules become stronger.
Option B is correct: The first ionisation energy $Q(g) \rightarrow Q^+(g) + e^-$ decreases. By referring to Data Booklet: First IE are Cl: 1260 kJ mol^{-1} Br: 1140 kJ mol^{-1} I: 1010 kJ mol^{-1}
Option C is incorrect as Q_2 oxidising strength decreases down the group.

Option D
$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$, $\Delta H_f = \frac{1}{2}(436) + \frac{1}{2}(244) - 431 = -91$ kJ mol^{-1}
$\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightarrow HBr(g)$, $\Delta H_f = \frac{1}{2}(436) + \frac{1}{2}(193) - 366 = -52$ kJ mol^{-1}
$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightarrow HI(g)$, $\Delta H_f = \frac{1}{2}(436) + \frac{1}{2}(151) - 299 = -5.5$ kJ mol^{-1}
The enthalpy change of formation of hydrogen halides becomes more endothermic not exothermic

16 Magnesium, aluminium, silicon and phosphorus are consecutive elements in Period 3 of the Periodic Table.
Which of the following properties generally decreases from magnesium to phosphorus?

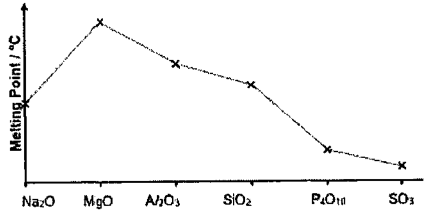
- **A** electrical conductivity
- **B** ionic radius
- **C** melting point of their oxides
- **D** electronegativity

Ans: C

Electrical conductivity increases from Mg to A*l* due to more delocalised electrons in A*l* in its sea of delocalised electron. Hence incorrect.

The ionic radius of P, being an anion, is larger than the other 3 which are cations. Hence incorrect. (You can check them out from the *Data Booklet*).

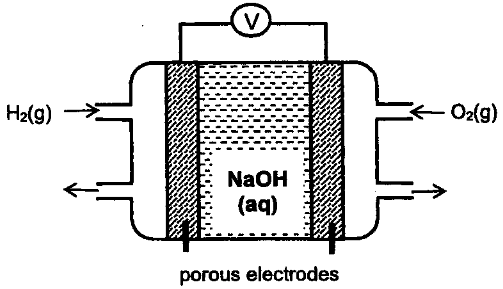
Their structure of their oxides transit from ionic (for Mg) to ionic with covalent character (for A*l*) to giant covalent (for Si) to simple covalent (for P). Hence their melting point decreases and correct.



Electronegativity increases across the Period.

[Turn over

17 A hydrogen-oxygen fuel cell is constructed using 1.00 mol dm^{-3} sodium hydroxide as the electrolyte. What is the change in pH of the solution around each electrode when the current is flowing?



	Cathode	Anode
A	increase	increase
B	increase	decrease
C	decrease	increase
D	decrease	decrease

Ans: B

Half equations from *Data Booklet for analysis*

Anode (anion will migrate towards anode, H_2O is present as well)

$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ +1.23 V

$O_2 + 2H_2O + 4e \rightleftharpoons \underline{4OH^-}$ + 0.40 V (less positive, will happen)

Cathode (Cation will migrate towards cathode, H_2O is present as well)

$\underline{2H_2O} + 2e \rightleftharpoons H_2 + 2OH^-$ −0.83 V (more positive, will happen

$Na^+ + e \rightleftharpoons Na$ −2.71 V

At cathode, H_2O will undergo reduction to OH^-. Thus, $[OH^-]$ should increase resulting in increase in pH. (Note that Na^+ will not be reduced to Na at the cathode as the E° value is too negative.)

At anode, OH^- will undergo oxidation, this causes $[OH^-]$ to decrease and pH should decrease.

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

In the electrolysis of molten aluminium oxide. 0.27 g of aluminium is liberated when 2904 coulombs of electricity is passed through molten aluminium oxide.

Which value of Avogadro's constant do **these figures** give?

A 6.02×10^{23}

B 6.05×10^{23}

C 1.82×10^{24}

D 2.02×10^{23}

Ans: B

The **Avogadro's number (L) is the number of particles in one mole.**
In this question, it would be the number of electrons present in 1 mole of electrons.
1 Faraday (F) is the charge on 1 mole of electrons.
1 Faraday (F) = Avogadro's number (L) × Charge on 1 e^- (e)

In this question, since we must solve for the Avogadro's number, we cannot use 1 Faraday as 96500C mol^{-1} (which is obtained when we take Avogadro's number to be 6.02×10^{23}).

How to solve:
$n(Al) = 0.27g \div 27.0 = 0.01$ mol
$n(e^-)$ required to deposit 1 mol of $Al = 0.01 \times 3 = 0.03$ mol

Using $Q = n_eF$,
$F = Q \div n_e = 2904 \div 0.03 = 96800$
$F = L \times e$
Taking the value of e from the *Data Booklet*,
$96800 = L \times 1.60 \times 10^{-19}$
$L = \underline{6.05 \times 10^{23}}$

OR
Use the following 2 formulas:

$\text{Amt} = \frac{I \times t}{n \times F}$ and $F = L \times e$

Substitute F into the first formula and since $Q = I \times t$ we have

$$\text{Amt} = \frac{Q}{n \times L \times e}$$

$$\frac{\text{mass}}{M_R} = \frac{Q}{n \times L \times e}$$

$$\frac{0.27}{27.0} = \frac{2904}{3 \times L \times 1.60 \times 10^{-19}}$$ (n = 3, since $Al^{3+} + 3e \rightarrow Al$, hence 3 Faradays is required)

Solving, $L = 6.05 \times 10^{23}$

19 10 cm^3 of an organic substance Z burns completely with exactly 75 cm^3 of oxygen to produce 50 cm^3 of carbon dioxide. All the volume are measured at the same temperature and pressure.

Which statements about the organic substance are correct?

1 Z may be an alcohol.

2 Z may be cycloalkane.

3 Z may decolorise aqueous bromine in the dark

A 1, 2 and 3

B 1 and 2 only

C 1 and 3 only

D 3 only

Ans: A

If X is a hydrocarbon,

$C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + y/2\ H_2O$
10 75 50
$x = 5, y = 10$
Z can be alkene which can decolourise bromine in the dark and it can also be cycloalkane.

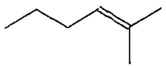
If X is an alcohol
$C_xH_yO_z + (x + y/4 - z/2)O_2 \rightarrow xCO_2 + y/2\ H_2O$
10 75 50
$x = 5$
assuming x is pentan-1-ol,
$C_5H_{12}O + 15/2\ O_2 \rightarrow 5CO_2 + 6H_2O$
10 75 50
Thus, Z can be alcohol.

BP-194

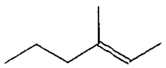
20 Which compound has the greatest number of stereoisomers?

- **A** 2-methylhex-2-ene
- **B** 3-methylhex-2-ene
- **C** 4-methylhex-2-ene
- **D** 5-methylhex-2-ene

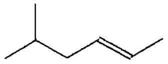
Ans: C



(2-methylhex-2-ene) do not exhibit stereoisomerism

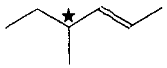


(3-methylhex-2-ene) and



(5-methylhex-2-ene)

These alkenes have only cis and trans isomers, number of stereoisomers = 2^1



4-methylhex-2-ene has $2^2 = 4$ stereoisomers

21 Which statement about methylbenzene and its properties is correct?

- **A** Methylbenzene undergoes nucleophilic substitution and free radical substitution reactions with Br_2 in the presence of $AlBr_3$.
- **B** The methylbenzene molecule is planar so hydrogen can easily undergo addition reactions with it without the use of a catalyst.
- **C** The π electrons in the benzene ring are able to donate an electron pair to attack a carbocation to form a bond.
- **D** The sideways overlap of p orbitals in benzene means the C–C bonds alternate between long, single bonds and short, double bonds.

Ans: C

Statement A is incorrect.
Methylbenzene undergoes **electrophilic substitution** reactions in the presence of $AlBr_3$ and Br_2. $AlBr_3$ being a Lewis acid will generate a Br^+ electrophile which will attack the benzene ring.

Statement B is incorrect.
Methylbenzene is resistant to addition reactions as it will **destroy the extra stability brought about by the delocalisation of the π electrons in the benzene ring.** Hydrogenation of benzene to cyclohexane, for example, requires a catalyst and high pressures. Methylbenzene is not a planar structure.

Statement C is correct.
The π electrons in benzene can donate an electron pair to attack a carbocation and form a bond. An example of this is when benzene donates its electron pair to CH_3^+ during a Friedel-Crafts alkylation reaction.

Statement D is incorrect.
The sideways overlap of p orbitals in benzene means the **C–C bonds in benzene are of equal length**, and they do not alternate between single and double bonds; instead, they have an intermediate C–C partial double bond character.

22 Which pair of reagents react together in a redox reaction?

A $CH_3CHCH_2 + Br_2$

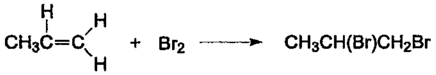
B $CH_3CH_2CH_2OH$ + concentrated H_3PO_4

C $CH_3COCH_3 + HCN$

D $HCO_2C_2H_5$ + dilute H_2SO_4

Ans: A

Option A:



$$CH_3\overset{H}{C}{=}C\begin{smallmatrix}H\\H\end{smallmatrix} + Br_2 \longrightarrow CH_3CH(Br)CH_2Br$$

Oxidation number of carbon: -3 -1 -2 -3 0 -1

Thus, oxidation number of carbon change from -1 to 0 and -2 to -1.

Oxidation number of bromine changes from 0 in Br_2 to -1 in $CH_3CH(Br)CH_2Br$.

Option B:

$$CH_3CH_2CH_2OH \longrightarrow CH_3CHCH_2 + H_2O$$

Oxidation number of carbon: -3 -2 -1 -3 -1 -2

There is no change in oxidation number of the carbon, hydrogen and oxygen.

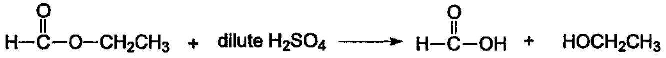
$$CH_3COCH_3 + HCN \longrightarrow CH_3-\underset{CN}{\overset{OH}{C}}-CH_3$$

Option C:

Oxidation number of carbon: 3 +2 -3 +2 -3 +2 -3

There is no change in oxidation number of the carbon, hydrogen, oxygen and nitrogen.

Option D:

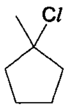


$$H-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + \text{dilute } H_2SO_4 \longrightarrow H-\overset{O}{\overset{\|}{C}}-OH + HOCH_2CH_3$$

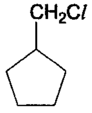
O.N of C: +3 -2 -3 +3 -2 -3

There is no change in oxidation number of the carbon, hydrogen and oxygen.

23 Methylcyclopentane can react with chlorine via free radical substitution to produce A and B as shown below.



A



B

Given the relative rate of substitution of tertiary and primary hydrogen atoms follows a 5 : 1 ratio.

What is the likely ratio of compound A and B formed?

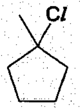
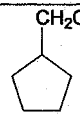
A 1 : 15

B 1 : 3

C 3 : 5

D 5 : 3

Ans: D

	
1 H each with reactivity of 5 = 1 x 5 = **5**	3 H each with reactivity of 1 = 3 x 1 = **3**

24 K_a values for two acids are given.

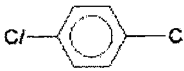
acid	K_a
$CH_3CH_2CO_2H$	1.34×10^{-5}
$C_6H_5CO_2H$	6.46×10^{-5}

Which statement is correct?

A The K_a of $CH_3C_6H_4OH$ is larger than 1.34×10^{-5}.

B The K_a of $CH_3CH(Cl)CO_2H$ is larger than 1.34×10^{-5}, but smaller than the K_a of $CH_2(Cl)\,CH_2CO_2H$.

C In a mixture containing equal concentrations of $CH_3CH_2CO_2H$ and $C_6H_5CO_2H$, $[CH_3CH_2CO_2^-] = [C_6H_5CO_2^-]$.

D In two separate solutions of  CO_2H and $C_6H_5CO_2H$, which have the same pH, there is a greater concentration of $C_6H_5CO_2H$ in mol dm^{-3}.

Ans: D
Statement A is incorrect.
Methyl-phenol is less acidic than carboxylic acids thus the K_a is smaller.

Statement B is incorrect.
The presence of more electron-withdrawing *Cl* atom disperses the negative charge on anion $CH_3CH(Cl)CO_2^-$ and stabilises it. Hence, $CH_3CH(Cl)CO_2H$ is more acidic than $CH_3CH_2CO_2H$ and has a larger K_a value. When compared with $CH_2(Cl)\,CH_2CO_2H$, $CH_3CH(Cl)CO_2H$ will have a larger K_a (not smaller K_a as stated in the statement) as the *Cl* group is closer to the negative charge on anion $CH_3CH(Cl)CO_2^-$.

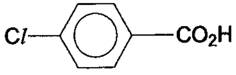
Statement C is incorrect.
Since $CH_3CH_2CO_2H$ has a lower K_a value, it is less acidic than C_6H_5COOH . Thus, at equal concentration of acids, $CH_3CH_2CO_2H$ will dissociate to a lesser extent.

.
Statement D is correct.
The presence of electron-withdrawing *Cl* atom disperses the negative charge on conjugate base of 4-*chlorobenzoic acid* and stabilises it. Hence, 4-chlorobenzoic acid is more acidic than C_6H_5COOH and able to dissociate to a greater extent to produce more H$^+$ ions .

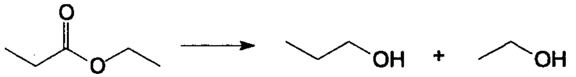
$$\text{using } [H^+] = \sqrt{K_a \times [acid]}$$

$$[acid] = \frac{[H^+]^2}{K_a}$$

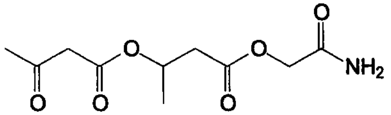
when pH are similar, [H$^+$] is the same, thus stronger the acid, greater K_a, the lower the [acid]

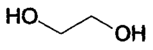
since $C_6H_5CO_2H$ is a weaker acid than  , concentration of $C_6H_5CO_2H$ will be greater.

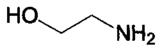
25 Esters can be reduced by $LiAlH_4$ in dry ether to give two alcohols as shown below.

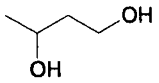


What are the possible products formed when the following compound is reacted with $LiAlH_4$ in dry ether?



1 

2 

3 

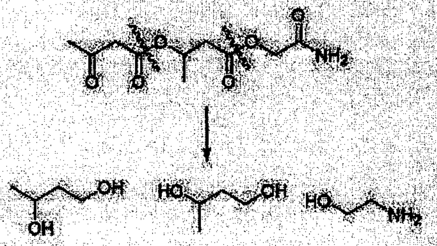
A 1 only

B 1 and 2 only

C 2 and 3 only

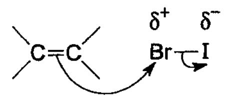
D 1, 2 and 3

Ans: C
Apply the same pattern of reduction across the ester bonds to alcohols, bearing in mind that ketones are also reduced to secondary alcohols and amides are reduced to amines. Hence a total of three fragments are produced after the reaction.

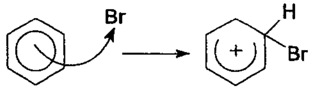


26 Which of the following shows the most likely first step in the mechanism of a reaction?

A

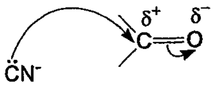


B



C

D

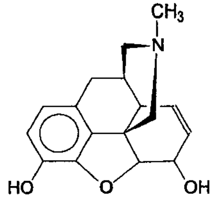


Ans: D
Option A is incorrect as bromine is more electronegative than iodine.

Option B is incorrect. Br^+ electrophile is required.

Option C is incorrect. Lone pair of electrons should be on C and not N. No doubt CN^- is an ambident nucleophile, it is not a likely step as N is more electronegative than C and thus will not share its electrons in a covalent bond. The C being less electronegative than C will share its electrons with the carbon in C=O to form a covalent bond.

27 Morphine and codeine are both effective painkillers.



morphine

Which observation will be given by morphine?

1 the decolourisation of liquid bromine

2 the evolution of hydrogen with metallic sodium

3 the formation of green Cr^{3+} ions from an acidified solution of $Cr_2O_7^{2-}$

A 3 only

B 1 and 2 only

C 2 and 3 only

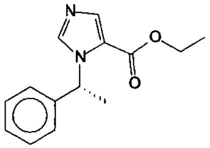
D 1, 2 and 3

Ans: D

1. Presence of C=C, which decolourises orange $Br_2(aq)$.
2. Presence of alcohol, which can react with Na(s) to produce $H_2(g)$.
3. Presence of 2° alcohol, which can be oxidised by $Cr_2O_7^{2-}/H^+$ (reduced to Cr^{3+})

BP~198

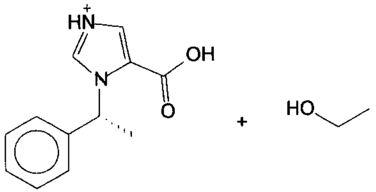
28 Etomidate is an anaesthetic agent that has been found in e-vapoorisers. It will soon be listed by Singapore as a Class C drug under the Misuse of Drugs Act.



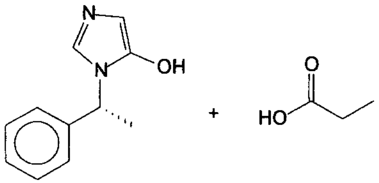
etomidate

What are the products when etomidate is hydrolysed by heating with a dilute acid?

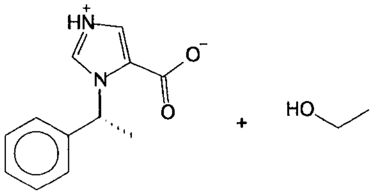
A



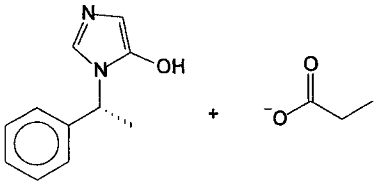
B



C



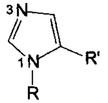
D



Ans: A

Etomidate contains an ester group (*hydrolysis*) and a basic nitrogen compound (*acid-base*) which will react with the dilute acid. Hydrolysis of the ester in etomidate gives ethanol (options **A** and **C**) and a carboxylic acid (option **A**) as products.

Teaching points for the acid-base reaction
Etomidate contains two aromatic rings – phenyl group and substituted imidazole (a planar, 5-membered ring). Both N atoms in the imidazole ring are sp^2 hybridised; one of the N atoms is basic while the other is neutral.
Similar to how the lone pair on the N atom in a pyrrole molecule is delocalised (**N24/III/1c,d,e**), the lone pair in N1 forms part of the six π electrons in the aromatic ring and is not available in accepting a proton while the lone pair on N3 resides in a sp^2 hybrid orbital and is able to accept a proton. It is a weaker base than a sp^3 hybridised N atom though (sp^2 – more s-character and lone pair is closer to the nucleus and less available).

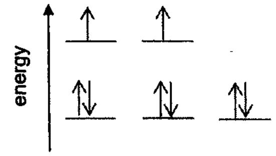


[Turn over

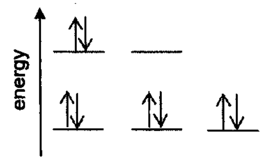
29 In a 'high spin' state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

Which energy diagram shows the electron arrangement in the 3d orbitals for a nickel in the +2 oxidation state in an octahedral complex in a 'high spin' state.

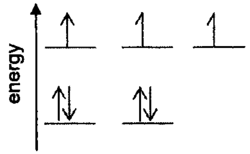
A



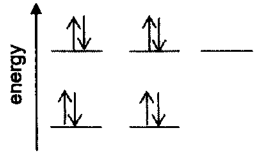
B



C



D



Ans: A

Ni^{2+} electronic configuration is $1s^22s^22p^63s^23p^63d^8$
Since it is an octahedral complex, the 3d orbital will split with 3 at the lower energy and 2 at the higher energy. Since high spin state is expected, electrons should occupy the d-orbital singly first before pairing up in the lower energy d-orbitals.

30 The rate of reaction between peroxodisulfate(VI) and iodide ions is increased by the presence of small concentrations of Fe^{2+}(aq).

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

Which property of iron allows it to act as a homogeneous catalyst?

A partially filled d subshell

B variable oxidation states

C low activation energy

D high charge density

Ans: B

A homogeneous catalyst operates in the same phase as the reactants. Iron exhibits variable oxidation states which allows it to perform its role.

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$ $E^\ominus_{cell} = 2.01 - 0.77 = +1.24$ V
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ $E^\ominus_{cell} = 0.77 - 0.54 = +0.23$ V

END

ANDERSON SERANGOON JUNIOR COLLEGE

2025 JC 2 PRELIMINARY EXAMINATION
PAPER 2 SUGGESTED SOLUTIONS

NAME:________________________ (   )   **CLASS:** 25 / ____

(a) Mild steel is an alloy that contains iron and carbon. A sample of mild steel was analysed, and four different types of atoms were identified; **A**, **B**, **C** and **D**. Table 1.1 shows information about the four types of atoms found in the sample.

Table 1.1

atom	relative mass	relative % abundance
A	12.00	0.238
B	13.00	0.012
C	53.94	5.79
D	55.93	93.96

(i) Calculate the relative atomic mass of carbon in this sample to four significant figures. Show your working. [1]

Relative atomic mass of carbon

$= \frac{12\times0.238+13\times0.012}{0.238+0.012} = \underline{\mathbf{12.05}}$ [1]

(ii) In an experimental set-up, beams of particles travelling at the same speed from different sources are subjected to an electric field as shown in Fig. 1.1.

A beam of protons with an angle of deflection of 60° has already been drawn.

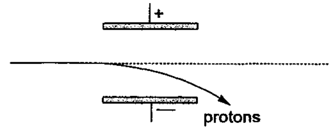
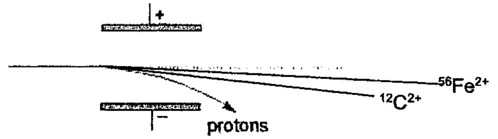


Fig. 1.1

Under identical conditions, beams of particles $^{12}C^{2+}$ and $^{56}Fe^{2+}$ were subjected to the same electric field.
Calculate the angle of deflection of $^{12}C^{2+}$ and $^{56}Fe^{2+}$ particles under the electric field and sketch the beams of $^{12}C^{2+}$ and $^{56}Fe^{2+}$ on Fig. 1.1. Label the beams clearly. [2]

Angle of $^{12}C^{2+}$ $= \frac{2}{12} \times 60° = \underline{\mathbf{+10.0°}}$ Angle of $^{56}Fe^{2+}$ $= \frac{2}{56} \times 60 = \underline{\mathbf{+2.14°}}$ [1] for both



[1] for both beams

(b) The compound C_6H_6 has many possible structural isomers. Three suggested structures of C_6H_6 are shown in Fig. 1.2.

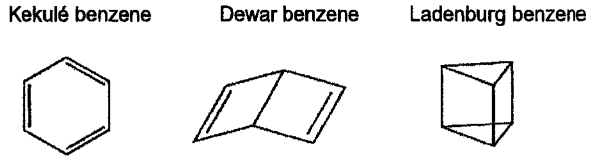


Fig. 1.2

(i) Using Fig. 1.2, complete Table 1.2 to predict the number of carbon atoms that have sp, sp^2 and sp^3 hybridisation in Kekulé benzene, Dewar benzene and Ladenburg benzene.

Table 1.2

C_6H_6 structure	sp hybridised	sp^2 hybridised	sp^3 hybridised
Kekulé benzene			
Dewar benzene			
Ladenburg benzene			

[2]

	sp	sp^2	sp^3
Kekulé benzene	0	6	0
Dewar benzene	0	4	2
Ladenburg benzene	0	0	6

[1] row 1 and 2 correct; [1] row 3 correct

(ii) Dewar benzene contains both σ bonds and π bonds.
By reference to the hybridisation of the carbon atoms and orbital overlap, describe the covalent bonding in Dewar benzene. [2]

σ bonds: [1]
- Head-on overlap of the sp^2 orbital of C with sp^2 orbital of adjacent C
- Head-on overlap of sp^3 orbital of C with sp^3 orbital of adjacent C
- Head-on overlap of sp^2 orbital of C with sp^3 orbital of adjacent C

- Head-on overlap of the sp^2 orbital of C with the s orbital of H
- Head-on overlap of the sp^3 orbital of C with the s orbital of H

π bonds: [1]
- Side-way overlap of two unhybridised 2p orbital of sp^2 C

(iv) Suggest why Dewar benzene and Ladenburg benzene are unstable isomers of C_6H_6. [1]

Bond strain or ring strain [1]

[Total: 8]

BP-199

BP-200

2 Aluminum is the most abundant metal in the earth's crust and has been produced commercially since 1888. It is now the second most used metal in the world after iron.

Approximately 75% of aluminum ever produced is still in use today, as it can be recycled endlessly without compromising any of its unique properties or quality.

(a) Aluminum objects that have had the aluminum oxide layer removed may be anodised.

(i) Complete Table 2.1 to show the relevant half-equations, during the anodisation of an aluminum object.

Table 2.1

	half-equation
anode	..... Al + ... $H_2O \rightarrow$ ..... Al_2O_3 + ... H^+ + ...e
cathode	

[2]

Table 2.1

	half-equation
anode	$2Al + 3H_2O \rightarrow Al_2O_3(s) + 6H^+ + 6e^-$ [1]
cathode	$2H^+ + 2e^- \rightarrow H_2$ [1]

(ii) During the anodisation of an aluminum object, 3.50 g of a protective layer aluminum oxide is formed in 2 hours.
Calculate the value of the current used. [2]

Amount of $Al_2O_3 = \dfrac{3.50}{2\times27.0+3\times16.0} = 0.034313$ mol

Amount of electrons passed = 0.034313 x 6
= 0.2059 mol [1]

$n_e \times F = I \times t$

$0.20588 \times 96500 = I \times (2\times60\times60)$

$I = 2.76A$
[1]

(b) Fig. 2.1 shows an **incomplete** energy cycle involving aluminium oxide, Al_2O_3.

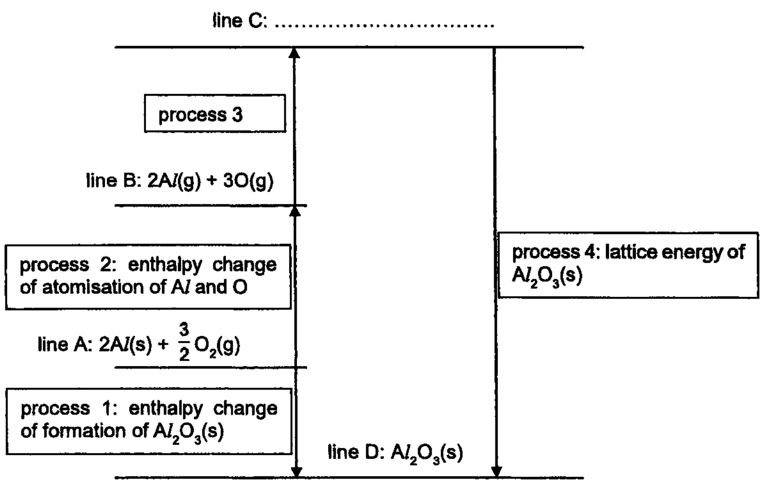


Fig. 2.1

(i) Complete line C. Include state symbols. [1]

$2Al^{3+}(g) + 3O^{2-}(g)$ [1]

[Turn over

(ii) Using Fig 2.1, the data in Table 2.2, together with data from the *Data Booklet*, to calculate the lattice energy of $Al_2O_3(s)$.

Table 2.2

	$\Delta H^{\ominus}$ / kJ mol^{-1}
1st electron affinity of oxygen, $O(g) + e^- \rightarrow O^-(g)$	–141
2nd electron affinity of oxygen, $O^-(g) + e^- \rightarrow O^{2-}(g)$	+790
standard enthalpy change of atomisation of $Al(s)$	+326
standard enthalpy change of formation of $Al_2O_3(s)$	–1676

[2]

$\Delta H_f^{\ominus} = 326 \times 2 + 3/2 \times 496 + 2(577+1820+2740) + 3 \times (-141) + 3 \times 790 + LE$ [1]
$= -1676$
LE = -15293 kJ mol^{-1}[1]

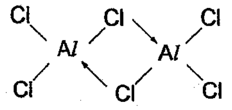
(iii) Explain why the first electron affinity of oxygen is exothermic, but the second electron affinity is endothermic. [2]
First EA is exothermic as **energy is released when an electron is attracted to the neutral oxygen atom by its nucleus.** [1]

Second EA is endothermic as **energy is required to overcome the repulsion between the added electron and the negatively charged O^- ion.** [1]

(c) When aluminum reacts with dry chlorine, aluminum chloride, $AlCl_3$, is formed.

(i) $AlCl_3$ can undergo dimerisation to form Al_2Cl_6.

With the aid of a diagram, name the type of bond formed during dimerisation and explain why this bond is formed. [2]



[1]

In forming the Al_2Cl_6 dimer, two $AlCl_3$ molecules are joined by **dative bonds.**
Reason: **Al is electron deficient** and can **accept lone pair of electron from chlorine** forming octet structure [1] name and reason

(ii) When $AlCl_3$ is dissolved in water, a solution of pH 3.0 is formed.

Explain with the aid of a balanced equation why the solution has a pH of 3.0. [2]

$AlCl_3(s)$ dissolves in water to form hydrated $[Al(H_2O)_6]^{3+}(aq)$.

Due to **high charge density of Al^{3+}**, it is able to **polarise** the neighbouring **water molecule**, which **further breaks the O-H bonds, thereby producing H^+** in the solution. Hence, $AlCl_3$ undergoes hydrolysis in water to form an acidic solution. [1]

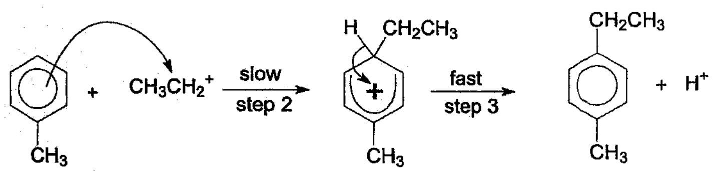
$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$ [1]

(iii) $AlCl_3$ can be used as a catalyst in the reaction of methylbenzene with chloroethane to form 4-ethylmethylbenzene.

Describe the mechanism of this reaction. [3]

Electrophilic Substitution

Step 1: $CH_3CH_2Cl + AlCl_3 \longrightarrow CH_3CH_2^+ + AlCl_4^-$



Step 4: $H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$

[1] name of mechanism
[1] for correct intermediates (carbocation and H^+) and regeneration of catalyst
[1] for correct arrows and charges

[Total: 16]

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BP~202

3 (a) The acid strength of a carboxylic acid is measured by its pK_a value.
Table 3.1 shows pK_a of ethanoic acid, chloroethanoic acid and fluoroethanoic acid.

Table 3.1

carboxylic acid	pK_a
ethanoic acid, CH_3COOH	4.76
chloroethanoic acid, $ClCH_2COOH$	2.87
fluoroethanoic acid, FCH_2COOH	2.60

(i) Explain the difference in pK_a values for ethanoic acid, chloroethanoic acid and fluoroethanoic acid. [3]

pKa in the order:

$CH_3COOH > ClCH_2COOH > FCH_2COOH$
hence acid strength in the order:

ethanoic acid < chloroethanoic acid < fluoroethanoic acid.

- CH_3 group is electron-donating, intensifies the negative charge on the carboxylate group ($-COO^-$) destabilises the anion, ethanoic acid is the weakest acid. [1]
- Cl is electron-withdrawing, disperses the negative charge on the carboxylate group ($-COO^-$), stabilises the ion to a greater extent, chloroethanoic acid is **stronger** than ethanoic acid. [1]
- F is more electronegative than Cl, stronger electron-withdrawing effect on the carboxylate ion, greater negative charge dispersal leading to greater stabilisation of the ion, fluoroethanoic acid is the strongest acid. [1]

(ii) Calculate the $\frac{[\text{anion}]}{[\text{acid}]}$ ratio for each of the following acids when it is placed in a buffer solution kept at pH 3.8. Give your answer to **three** significant figures. [1]

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

For CH_3CO_2H:

$$\frac{[A^-]}{[HA]} = \frac{10^{-4.76}}{10^{-3.8}}$$

$$\frac{[A^-]}{[HA]} = 0.110$$

For $ClCH_2CO_2H$:

$$\frac{[A^-]}{[HA]} = \frac{10^{-2.87}}{10^{-3.8}}$$

$$\frac{[A^-]}{[HA]} = 8.51$$

[1] for both values

(iii) Hence, using your answer from **(a)(ii)**, explain if ethanoic acid or chloroethanoic acid, and its conjugate base forms a more effective buffer in removing the small amount of H^+ added at pH 3.8. [1]

At pH 3.8, the ratio of $[A^-]$ to $[HA]$ for chloroethanoic acid is much greater (8.51) than for ethanoic acid (0.110).

This means a higher concentration of conjugate base ($ClCH_2COO^-$) is present to remove added H^+, so chloroethanoic acid forms a buffer with a greater capacity to resist pH change. [1]

[Turn over

(b) Both ethanoic acid, CH_3COOH, and lactic acid, $CH_3CH(OH)CO_2H$, can be synthesised from ethanol, C_2H_5OH, in the laboratory via different routes, as shown in Fig. 3.1.

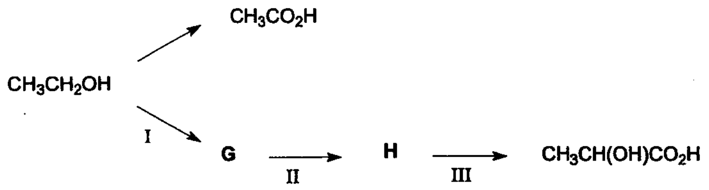


Fig. 3.1

(i) Suggest structures for compounds **G** and **H**. [2]

CH_3CHO **G**	$CH_3CH(OH)CN$ **H**

(ii) Suggest reagents and conditions for each of the steps I and II.

step I ....

step II .... [2]

step I $K_2Cr_2O_7$, dilute H_2SO_4, warm/heat with (immediate) distillation
(accept acidified $K_2Cr_2O_7$ but not $KMnO_4$)

step II HCN, KCN (as catalyst), cold
(accept trace of NaOH(aq) as catalyst or KCN, dilute acid, cold)

(iii) It is found that lactic acid synthesised in the lab do not rotate plane polarised light while naturally occurring lactic acid found in goat milk exhibits optical activity. Explain why such observation is made. [2]

In the synthesis, the carbonyl carbon is trigonal planar, so nucleophilic attack occurs from the top and bottom with equal probability. This produces a racemic mixture/ equal amounts of both enantiomers. The enantiomers cancel each other's optical activity, so the product is optically inactive

Naturally occurring lactic acid exists as a pure enantiomer. Its central carbon is chiral, bonded to four different substituent groups and lacking an internal plane of symmetry, hence it exhibits optical activity. [1]

(c) Lactic acid reacts in the presence of hot, concentrated sulfuric acid to form two different compounds, **J** and **K**.

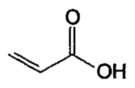
- **J** has a molecular mass 72.0 g mol^{-1}
- **K** is a cyclic compound and has a molecular formula $C_6H_8O_4$.

Draw the skeletal formula of **J** and **K**.

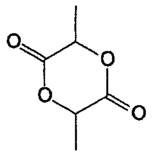
J

K

[2]



J [1]



K [1]

(d) Table 3.2 shows the solubility of various calcium salts in water.

Table 3.2

calcium salt	solubility / mol dm^{-3}	colour
CaC_2O_4	4.8×10^{-5}	white
$Ca_3(PO_4)_2$	1.6×10^{-7}	white
$CaCrO_4$	2.7×10^{-2}	bright yellow

(i) Write an expression for the solubility product of $Ca_3(PO_4)_2$. [1]

K_{sp}= $[Ca^{2+}]^3\ [PO_4^{3-}]^2$ [1]

(ii) Calculate the solubility product, K_{sp}, for $Ca_3(PO_4)_2$, giving its units. [1]

$K_{sp} = [Ca^{2+}]^3\ [PO_4^{3-}]^2$
$= (3 \times 1.6 \times 10^{-7})^3 (2 \times 1.6 \times 10^{-7})^2$
$= \underline{\mathbf{1.13 \times 10^{-32}\ mol^5\ dm^{-15}}}$ [1] including units

(iii) Describe what you would observe if equal volumes of saturated solutions of CaC_2O_4 and $CaCrO_4$ were mixed. Explain your answer using calculations. [3]

$$\begin{array}{lcccc} & CaC_2O_4 & \rightleftharpoons & Ca^{2+}(aq) & + & C_2O_4^{2-}(aq) \\ \text{Eqm (mol dm}^{-3}) & & & 4.8 \times 10^{-5} & & 4.8 \times 10^{-5} \end{array}$$

$$\begin{array}{lcccc} & CaCrO_4 & \rightleftharpoons & Ca^{2+}(aq) & + & CrO_4^{2-}(aq) \\ \text{Eqm (mol dm}^{-3}) & & & 2.7 \times 10^{-2} & & 2.7 \times 10^{-2} \end{array}$$

When **equal volumes** of the 2 saturated solutions are mixed, **concentration** in mol dm^{-3} of all ions will be **halved**:

$$\left.\begin{array}{l} [Ca^{2+}]_{total} = \frac{1}{2}(4.8 \times 10^{-5} + 2.7 \times 10^{-2}) \\ \quad = 0.013524 \\ [C_2O_4^{2-}] = \frac{1}{2}(4.8 \times 10^{-5}) = 2.4 \times 10^{-5} \\ [CrO_4^{2-}] = \frac{1}{2}(2.7 \times 10^{-2}) = 0.0135 \end{array}\right\} \text{[1] for correct concentrations of all ions after mixing}$$

$$\left.\begin{array}{l} \text{Ionic product of } CaC_2O_4 = [Ca^{2+}][C_2O_4^{2-}] \\ \quad = (0.013524) \times (2.4 \times 10^{-5}) = 3.246 \times 10^{-7} \\ \quad > K_{sp} \text{ of } CaC_2O_4 \\ \text{Ionic product of } CaCrO_4 = [Ca^{2+}][CrO_4^{2-}] \\ \quad = (0.013524) \times (0.0135) = 1.826 \times 10^{-4} \\ \quad < K_{sp} \text{ of } CaCrO_4 \end{array}\right\} \text{[1] for correct IP calculations for both}$$

Hence, a <u>**white precipitate**</u> of CaC_2O_4 would be observed. [1] ecf based on IP calculation (no calculation no marks)

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(e) An iodometric titration can be used to determine the percentage purity of calcium oxalate crystals, CaC_2O_4.

A 3.20 g impure sample of CaC_2O_4 is shaken with 100.0 cm^3 of 0.10 mol dm^{-3} aqueous acidified MnO_4^- ions. One of the products of this reaction is CO_2.

The remaining MnO_4^- is reacted with an excess of iodide solution to liberate $I_2(aq)$.

$$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$$

A 25.0 cm^3 aliquot requires 24.50 cm^3 of 0.2 mol dm^{-3} $S_2O_3^{2-}$ for this titration.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

(i) Construct an equation for the reaction between MnO_4^- ions and $C_2O_4^{2-}$ ions. [1]

Reduction: $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ -----(1)
Oxidation: $C_2O_4^{2-} \rightarrow 2CO_2 + 2e$ -----(2)

Overall: [(1) x 2] + [(2) x 5]
$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$ [1]

(ii) Calculate the percentage purity of the sample of CaC_2O_4. [3]

amount of $S_2O_3^{2-}$ required $= \frac{24.50}{1000} \times 0.20$
$= 4.90 \times 10^{-3}$ mol

$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

amount of I_2 that reacted with $S_2O_3^{2-} = \frac{1}{2} \times 4.90 \times 10^{-3}$
$= 2.45 \times 10^{-3}$ mol

$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$

amount of remaining $MnO_4^- = \frac{2}{5} \times 2.45 \times 10^{-3}$
$= 9.80 \times 10^{-4}$ mol [1]

Amount of remaining MnO_4^- in 100 cm^3 of solution $= 9.80 \times 10^{-4} \times 100/25$
$= 0.00392$ mol

initial amount of $MnO_4^- = \frac{100.0}{1000} \times 0.10$
$= 0.0100$ mol

amount of MnO_4^- that reacted with $C_2O_4^{2-} = 0.0100 - 0.00392$
$= 0.00608$ mol [1]

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

amount of $C_2O_4^{2-}$ in sample = amount of CaC_2O_4 in sample
$= \frac{5}{2} \times 0.00608$
$= 0.0152$ mol

mass of pure $CaC_2O_4 = 0.0152 \times [40.1 + 2(12.0) + 4(16.0)]$
$= 1.95$ g

Percentage by mass of $CaC_2O_4 = \frac{1.95}{3.20} \times 100\%$
$= 60.9$ % [1]

(f) The trend in the thermal stability of Group 2 oxalates, MC_2O_4, is similar to that of Group 2 carbonates.

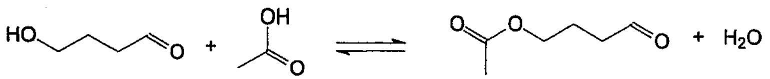
Suggest if MgC_2O_4 or CaC_2O_4 undergoes thermal decomposition at a lower temperature. Explain your answer. [3]

MgC_2O_4 decomposes at a lower temperature [1].

- ionic radius of Mg^{2+} is smaller so the charge density of the Mg^{2+} is larger and Mg^{2+} is more polarising. [1]
- The electron cloud of $C_2O_4^{2-}$ anion is more polarised / distorted [1]
- so the C-C / C-O covalent bond within the anion is weakened for MgC_2O_4.

[Total: 25]

4 (a) 4-hydroxybutanal can undergo an esterification reaction with a carboxylic acid. In a controlled experiment, 4-hydroxybutanal and ethanoic acid were heated under reflux with a small amount of concentrated sulfuric acid as a catalyst.



The following information was recorded from the experiment at 298 K.

- initial amount of 4-hydroxybutanal: 0.500 mol
- initial amount of ethanoic acid: 0.400 mol
- total volume of solution: 2.00 dm³
- at equilibrium, 60% of 4-hydroxybutanal has reacted

(i) Write the expression for the equilibrium constant, K_c, for this reaction. Use your expression to calculate the value of K_c for this reaction. [3]

				
Initial (mol)	0.50	0.40	0	0
Change (mol)	$-(\frac{60}{100}\times 0.50 = 0.30)$	-0.30	+0.30	+0.30
Eqm (mol)	0.20	0.10	0.30	0.30
Conc (mol dm⁻³)	$\frac{0.20}{2}=0.10$	$\frac{0.10}{2}=0.05$	$\frac{0.30}{2}=0.15$	$\frac{0.30}{2}=0.15$

Working for correct concentration [1]

$$K_c = \frac{[\text{ester}][H_2O]}{[\text{4-hydroxybutanal}][\text{ethanoic acid}]} \quad [1]$$

$$K_c = \frac{(0.15)(0.15)}{(0.05)(0.10)} = 4.5 \; [1]$$

(ii) Aqueous potassium hydroxide was added to the equilibrium mixture at 298 K. Suggest how the position of equilibrium might change and if the K_c will be affected. [2]

KOH undergoes acid-base reaction with CH_3COOH.

Adding KOH(aq) results in a decrease in [CH_3COOH]. Position of equilibrium of esterification reaction will shift left to increase the [CH_3COOH]. [1]

K_c will not change as it is temperature dependent. [1]

(b) 4-hydroxybutanal can form a cyclic hemiacetal in the presence of an acid catalyst as shown in Fig. 4.1.

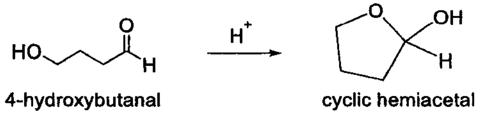
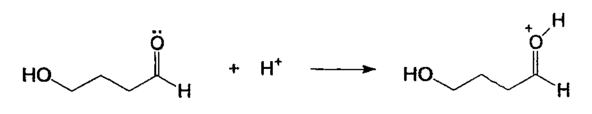
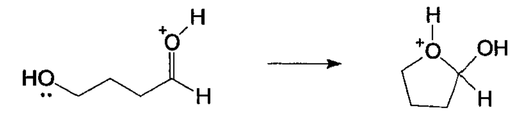
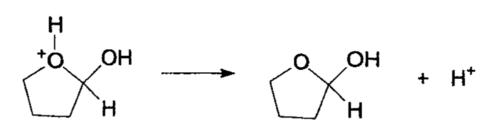
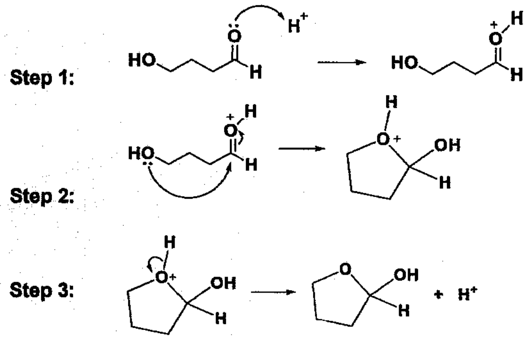


Fig. 4.1

(i) The mechanism for the reaction in Fig. 4.1 is shown in Table 4.1. Draw **four** curly arrows to complete the mechanism shown in Table 4.1. [2]

Table 4.1

Step 1: The aldehyde is protonated by the acid catalyst to form a non-cyclic intermediate.	
Step 2: Nucleophilic attack by the alcohol to form a cyclic intermediate.	
Step 3: Deprotonation of the cyclic intermediate to form the product.	



[1]: 1 curly arrow in step **1 and** 3 each [1]: 2 curly arrows in step 2

(ii) The reaction to form cyclic hemiacetal is completed when all the 4-hydroxybutanal is used up. Describe a chemical test to check the completion of the reaction.

Include the reagents and conditions for the test. Explain how the observations will be used to determine if the reaction has been completed. [3]

Add 2,4-DNPH to a sample of the reaction mixture. [1] for test
Students can propose Tollen's reagent and Felding reagent
Do not accept test involving cyclic hemiacetal (e.g. PCl_3, PCl_5, $SOCl_2$, Na)

If traces of 4-hydroxybutanal is presence, an orange/yellow ppt. is observed [1] for observation from the test

The reaction will be completed when no orange ppt is observed in the sample of reaction mixture. [1] showing idea of how to ensure reaction has been completed.

(c) Koch reaction uses carbon monoxide to manufacture tertiary carboxylic acids as shown in Fig. 4.2.

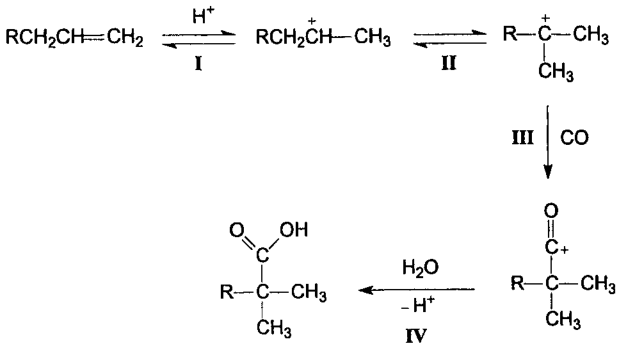


Fig. 4.2

(i) Step **II** is known as a rearrangement reaction. With reference to the stability of the species involve, suggest a reason why such a reaction occurs. [1]

The 3° carbocation formed after step **II** is more stable the 2° carbocation [1]

(ii) Draw the "dot–and–cross" diagram for carbon monoxide, CO. [1]

[1]

(iii) Hence, state the role of carbon monoxide, CO, in the mechanism of step **III**. [1]

Carbon monoxide acts as a **nucleophile** ***or*** **Lewis base** (due to the presence of a lone pair of electrons on the carbon atom. This lone pair of electrons is donated to an electron-deficient carbon in the carbocation) [1]

(iv) Acidic hydrolysis of an ester can be explained in terms of nucleophilic acyl substitution.

Besides electronic effect, suggest another reason why esters synthesised from tertiary carboxylic acids are stable when heated in the presence of acids. [1]

The steric hindrance due to the 3 bulky R groups present in 3° carboxylic acid prevents the attack of the nucleophile on the carbonyl carbon during the hydrolysis reaction. [1]

(do not accept: electron–donating effect of alkyl groups making the carbonyl carbon less electron deficient and hence less susceptible to nucleophilic attack by water as question already mentioned "beside electronic effect").

For your information.
Under neutral conditions, the carbonyl carbon in esters is not reactive enough for water to attack efficiently.

Protonating the carbonyl oxygen with H⁺ increases the electrophilicity of the carbonyl carbon, making nucleophilic attack more favourable. Thus, when 3 bulky R groups are present, beside electronic factor, steric factor is also considered.

3. Step-by-Step Mechanism (Nucleophilic Acyl Substitution)

1. *Activation of the electrophile*
   - *H⁺ protonates the carbonyl oxygen of the ester.*
   - *This makes the C=O more positively polarised, increasing the δ⁺ charge on the carbon.*
2. *Nucleophilic attack*
   - *Water acts as the nucleophile, attacking the carbonyl carbon.*
   - *This forms a tetrahedral intermediate.*
3. *Proton transfers*
   - *Within the tetrahedral intermediate, proton transfers occur to prepare the alkoxy group (–OR') for departure.*
   - *One common path is protonating the –OR' oxygen so it becomes a better leaving group (–OH+R').*
4. *Elimination of leaving group*
   - *The C–OR' bond breaks, reforming the C=O and ejecting the alcohol.*
5. *Deprotonation of product*
   - *The protonated carboxylic acid loses a proton, regenerating the acid catalyst and yielding the neutral carboxylic acid.*

[Total: 14]

5 **(a)** Volatile Organic Compounds (VOCs) are a group of organic chemicals that easily vaporise at room temperature. They are released by a wide range of products and processes, both indoors and outdoors.

Some VOCs can contribute to the formation of secondary pollutants like ozone and have adverse health effects. They are usually released from sources like vehicle exhaust, paint and solvents.

In the presence of sunlight, photochemical reaction is triggered between nitrogen oxides (NO and NO_2) and VOCs. The five stages of the reaction between formaldehyde, one of the common VOCs, with NO in the presence of sunlight leading to the formation of ozone, O_3, are described in Table 5.1.

Table 5.1

stage	description of stage	equation
1	*photolysis of formaldehyde	$HCHO \rightarrow \bullet H + \bullet CHO$
2	oxidation of formyl radical	$\bullet CHO + O_2 \rightarrow CO + \bullet HO_2$
3	oxidation of NO(g)	$\bullet HO_2 + NO \rightarrow NO_2 + \bullet OH$
4	photolysis of NO_2(g)	
5	formation of O_3(g)	

* photolysis is the decomposition of a molecule by the action of light.

After stage 3, NO_2 is photolysed by sunlight to generate NO and O atoms. The O atom formed then reacts with the oxygen gas in the air to form ozone.

(i) Explain why the hydrogen atom produced in step 1 is described as a *free radical*. [1]

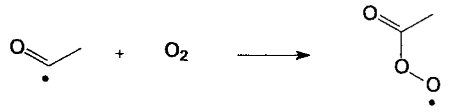
An hydrogen atom has one unpaired electron making them highly reactive. [1]

(ii) Complete Table 5.1 by adding the two equations to represent stages 4 and 5. [1]

$NO_2 \rightarrow NO + O$ (not necessary to put $h\nu$)
$O + O_2 \rightarrow O_3$ Two equations [1]

(iii) Propanone, CH_3COCH_3, undergoes a similar reaction to that shown for stages 1 to 3 in Table 5.1.
Complete Table 5.2 by adding the equations to represent stage 1 and 3.

Table 5.2

stage	description of stage	equation
1	photolysis of CH_3COCH_3 to generate two radicals, $CH_3CO\bullet$ being one of them	
2	oxidation of $CH_3CO\bullet$ radical to form peroxyacetyl radical	
3	oxidation of NO(g) by peroxyacetyl radical to form brown gas	

[2]

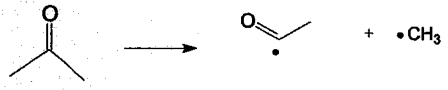
Stage 1: $\mathbf{CH_3COCH_3 \rightarrow \bullet CH_3 + CH_3CO\bullet}$ [1]

Stage 2: $CH_3CO\bullet + O_2 \rightarrow CH_3C(O)OO\bullet$ (FYI not required)

Stage 3: $\mathbf{CH_3C(O)OO\bullet + NO \rightarrow CH_3C(O)O\bullet + NO_2}$ [1]
(brown gas)

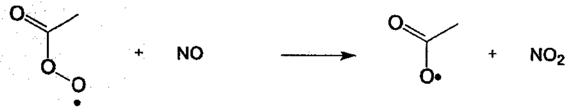
Or

Stage 1:



Stage 2: $CH_3CO\bullet + O_2 \rightarrow CH_3C(O)OO\bullet$ (FYI not required)

Stage 3:



(b) In recent years, there is an increasing concern about the post renovation air quality in buildings. In 2018, the death of a flat-dweller in Beijing has been attributed to formaldehyde, a carcinogenic substance widely used in wood products due to its strong adhesive, preservative and binding properties. Similarly, homeowners in Singapore have also been seeking help as they experienced stinging sensation in their nose and eyes due to VOCs released from furniture in their newly-renovated houses.

The air quality of a newly renovated office with limited ventilation was studied over the course of one week. Table 5.3 shows the average concentrations, in parts per billion (ppb), of selected VOCs detected.

Table 5.3

VOCs detected in the air of the office	molar mass ($g\ mol^{-1}$)	concentration (ppb)
Formaldehyde, HCHO	30.0	0.0692
Toluene, $C_6H_5CH_3$	92.0	38.5
Xylene $C_6H_4(CH_3)_2$	106.0	12.7

(i) State two basic assumptions of the kinetic theory as applied to an ideal gas. [2]

The volume of the gas molecules is negligible compared to the volume of the container. [1]

The forces of attraction between the gas molecules as well as between the gas molecules and walls of the container are negligible. [1]

(ii) Explain, with reference to intermolecular forces, which VOC vapour in Table 5.3 will have the greatest deviation from ideal gas behaviour. [2]

Xylene ($C_6H_4(CH_3)_2$). [1]
Thus, it has– the most electrons and the instantaneous dipole–induced dipole between xylene molecules is the most extensive. [1]

(iii) The concentration of VOC in the air is often represented in parts per billion (ppb). 1 ppb VOC means there should be 1 mole of VOC for every 1 000 000 000 moles of air.
Calculate the concentration, in $mol\ dm^{-3}$, of toluene in the sample of office air.

[Assume the sample of air is at room temperature and pressure conditions.] [1]

38.5 ppb = 38.5 mole of toluene in 1 000 000 000 mole of air
= 38.5 mol of toluene in 1 000 000 000 x 24 dm^3 of air
$= \frac{38.5}{24\ 000\ 000\ 000}$ mol of toluene in 1 dm^3 of air

concentration of toluene at 38.5 ppb = 1.60×10^{-9} $mol\ dm^{-3}$ [1]

(iv) The indoor air quality is often measured by TVOC (Total Volatile Organic Compounds) levels. It is calculated as the sum of the concentrations of all measured VOCs, expressed in ppb.

Using Table 5.3, determine the TVOC level of the office. [1]

TVOC = 0.0692 + 38.5 + 12.7 = 51.3 ppb (3sf) [1]

(v) The World Health Organisation (WHO) recommends a target level of under 50 ppb for TVOC.

Explain if the TVOC level of the office is of concern and suggest a measure that can be taken to keep TVOC low in indoor spaces. [2]

The TVOC level in the office is 51.3 ppb, above the recommended level. Hence, it is of concern. [1]

Measure to keep TVOC level low (any of the below) [1]:
- increase ventilation by opening windows, turning on fan
- use air purifier with activated carbon
- use less/omit use of formaldehyde/toluene/xylene in furniture

[Total: 12]

END

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ANDERSON SERANGOON JUNIOR COLLEGE

2025 JC 2 PRELIMINARY EXAMINATION PAPER 3 SOLUTIONS

Section A

1 **(a)** Transition elements have characteristic physical and chemical properties.

(i) Explain what is meant by the term *transition element.* [1]

A transition element is a d block element that can form one or more stable ions with partially filled d subshells. [1]

(ii) Explain why the melting point and density of nickel is higher than that of calcium. [3]

- [A] In Ni, both the 3d and 4s electrons are available for metallic bonds since the energy level difference between the 3d and 4s orbitals is small.
  In Ca, only two 3s electrons are available for metallic bonding.
- [B] The greater number of 3d and 4s delocalised electrons available for metallic bonding in Ni results [A or B - 1m]
- in stronger electrostatic attraction between the cations and the 'sea' of delocalised electrons. More energy is required to overcome the stronger metallic bonds in transition elements as compared to Ca. [1m]

- Ni has smaller atomic radii and higher atomic mass compared to Ca.
- Also, Ni has more closely packed [1m] structure due to their stronger metallic bonding.
- Thus, transition elements are denser than Ca.

(b) **(i)** A solution containing the $[Ni(H_2O)_6]^{2+}$ complex ion is green.

When 1,2-diaminoethane, *en*, $H_2NCH_2CH_2NH_2$, is added, the colour of the solution changes to purple. This is due to the formation of the $[Ni(en)_2(H_2O)_2]^{2+}$ complex ion.

Explain why the two solutions are coloured, and why the colours are different. [3]

In the presence of the ligands, the partially filled 3d orbitals of Ni^{2+} are split into two levels with a small energy gap, ΔE *(d orbital splitting)*.

When a 3d electron absorbs energy from the visible light region corresponding to ΔE, this electron is promoted from the d orbital of a lower energy level to a d orbital of a higher energy level *(d–d transition)*.

The colour observed is the complementary of the colour absorbed.

The colours are different as different ligands split the partially filled 3d orbitals to different extents with different ΔE. Red is absorbed for $[Ni(H_2O)_6]^{2+}$ complex and yellow is absorbed for $[Ni(en)_2(H_2O)_2]^{2+}$ complex.

[1]: presence of ligand; partially filled 3d–orbital for Fe^{2+}(aq); small energy gap
[1]: d–d transition explanation; colour is the complement of the colour absorbed
[1]: different ligands, different ΔE

(ii) $[Ni(en)_2(H_2O)_2]^{2+}$ complex ion can exist in three different forms where the ions differ in the spatial arrangement of the ligands around the central metal ion.

Fig. 1.1 shows one of the isomers.

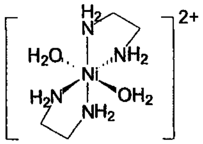
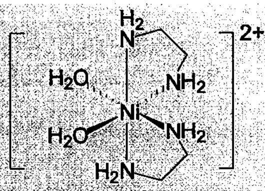


Fig. 1.1

Draw another isomer and state the type of isomerism. [2]



[1]

cis-trans isomerism [1]

BP~210

(c) When a sample of aqueous copper(II) sulfate was added to a small amount of aqueous ammonia, a blue precipitate **A** was formed. Upon adding excess aqueous ammonia, **A** dissolved, and a deep blue solution containing a complex ion, **B**, was formed.

When another sample of aqueous copper(II) sulfate was added to concentrated hydrochloric acid, a yellow-green solution was formed.

(i) Identify **A** and **B** and explain their formation. Include relevant equations. [4]

[1] correct ID of A and B
A is $Cu(OH)_2(H_2O)_4$ [accept $Cu(OH)_2$] and **B** is $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

To explain formation of A
[1] for mention of acid-base reaction with correct relevant equation

Either
In aqueous solution, the weak base NH_3 undergoes partial ionisation, producing OH^- ions.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

When a small amount of NH_3(aq) is added, the OH^-(aq) undergoes acid-base reaction with $[Cu(H_2O)_6]^{2+}$(aq) to produce a blue precipitate of $Cu(OH)_2$.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} + 2OH^-(aq) \rightleftharpoons \underset{\text{blue ppt}}{[Cu(OH)_2(H_2O)_4](s)} + 2H_2O(l) \text{ ......(1)}$$

OR
Acid-base reaction occurs
$$[Cu(H_2O)_6]^{2+}SO_4^{2-}(aq) + 2NH_3(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + (NH_4)_2SO_4\ (l) \text{ ....(1)}$$

To explain formation of B
[1] for mention of ligand exchange reaction with correct relevant equation
[1] explanation for ppt dissolving

The increasing addition of NH_3(aq) shifts the position of equilibrium (2) to the right, forming a deep blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$(aq). As the concentration of $[Cu(H_2O)_6]^{2+}$(aq) decreases, the position of equilibrium (1) shifts left, causing the blue precipitate of $Cu(OH)_2$ to dissolve.

When excess NH_3(aq) is added, ligand exchange reaction occurs and the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion is formed.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} + 4NH_3(aq) \rightleftharpoons \underset{\text{deep blue solution}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)} + 4H_2O(l) \text{ ......(2)}$$

(ii) Write an equation to explain the observation of the yellow-green solution. [1]

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$ [1]

(d) Ruthenium can form complexes with ligands like $H_2NCH_2CH_2NH_2$ (represented as *en*) and NH_3.

Three half equations involving rubidium complex ions are shown in Table 1.1.

Table 1.1

half-cell	half equation
A	$[Ru(H_2O)_6]^{3+} + e^- \rightleftharpoons [Ru(H_2O)_6]^{2+}$
B	$[Ru(NH_3)_6]^{3+} + e^- \rightleftharpoons [Ru(NH_3)_6]^{2+}$
C	$[Ru(en)_3]^{3+} + e^- \rightleftharpoons [Ru(en)_3]^{2+}$

(i) Two electrochemical cells are set up to compare the standard electrode potential, $E^⦵$, of the three half-cells. Fig 1.2 shows the relative potential of each electrode.

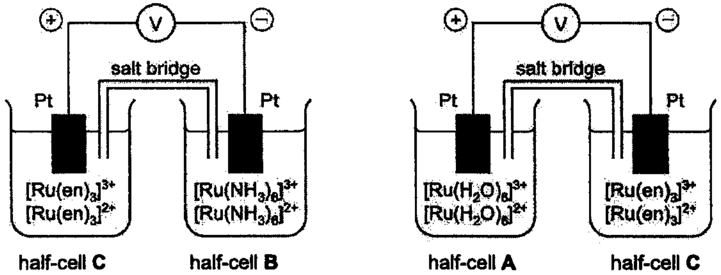


Fig 1.2

Using this information, state and explain the order of standard reduction potential, $E^⦵$, for the three half-cells from the least negative to the most negative. [2]

In the first electrochemical cell, half-cell **C** has a positive electrode (cathode) and half-cell **B** has a negative electrode (anode). Hence, reduction take place in half-cell **C** and oxidation take place in half-cell **B**. Therefore half-cell **C** will have a less negative $E^⦵$ than half-cell **B**.

In the second electrochemical cell, half-cell **A** has a positive electrode (cathode) and half-cell **C** has a negative electrode (anode). Hence, reduction take place in half-cell **A** and oxidation take place in half-cell **C**. Therefore half-cell **A** will have a less negative $E^⦵$ then half-cell **C**. [1]

Hence, from the order of $E^⦵$ from the least negative to the most negative is **A, C, B**. [1]

(ii) The standard electrode potential of the half-cell **A** is +0.25 V.

An electrochemical cell was set up using half-cell **A** and a $[Cu(NH_3)_4]^{2+}/Cu$ half cell.

Use data from the *Data Booklet* to calculate the E° cell for this cell [1]

$[Ru(H_2O)_6]^{3+} + e \rightleftharpoons [Ru(H_2O)_6]^{2+}$ +0.25V (E_{red})
$[Cu(NH_3)_4]^{2+} + 2e \rightleftharpoons Co + 4NH_3$ – 0.05 V (E_{oxd})

$E^\circ_{cell} = 0.25 - (-0.05) = \underline{+0.30\ V}$ [1]

(iii) Write the overall equation for the reaction that occurs in the cell in **(d)(ii)**.

Using the E°_{cell} you have calculated in **(d)(ii)**, calculate a value of ΔG° for the cell reaction represented by your overall equation. [2]

[R]: $[Ru(H_2O)_6]^{3+} + e \rightarrow [Ru(H_2O)_6]^{2+}$

[O]: $Cu + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2e$

$Cu + 4NH_3 + 2[Ru(H_2O)_6]^{3+} \rightarrow [Cu(NH_3)_4]^{2+} + 2[Ru(H_2O)_6]^{2+}$ [1]

$\Delta G^\circ = -nFE^\circ_{cell}$

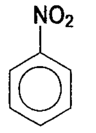
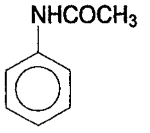
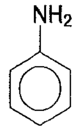
The no. of electrons exchanged in the overall balanced equation is 2. Hence, n = 2.

$\Delta G^\circ = -2 \times 96500 \times (+0.300) = \underline{-57900\ J\ mol^{-1}}$ or $\underline{-57.9\ kJ\ mol^{-1}}$ [1]

[Total: 19]

2 **(a)** The reactivity of three nitrogen-containing compounds with aqueous bromine is shown in the Table 2.1.

Table 2.1

	 nitrobenzene	 acetanilide	 phenylamine
reactivity with $Br_2(aq)$ at room temperature	no reaction	mono-substitution of benzene ring	tri-substitution of benzene ring

(i) Explain the difference in the reactivity of the three compounds with $Br_2(aq)$. [3]

Phenylamine is the most reactive as the lone pair of electrons on N can delocalise into the benzene ring due to overlap between p orbital of N and π electron cloud of benzene. This increases the electron density of the benzene ring greatly, making it most susceptible to electrophilic attack. [1]

Acetanilide is less reactive than phenylamine because delocalisation of the lone pair of electrons on N into the C=O reduces the extent of delocalisation of the lone pair into the benzene ring. Hence, the benzene ring is less electron-rich than phenylamine. [1]

Nitrobenzene is the least reactive as the $-NO_2$ withdraw electrons from the benzene ring. This decreases the electron density of the ring and electrophiles are less attracted to the benzene ring slowing down the rate the electrophilic substitution greatly. [1]

(ii) State the reagents and conditions to form acetanilide from nitrobenzene. [2]

Step 1: Sn, conc HC*l*, heat followed by NaOH [1]

Step 2: CH_3COCl [1] r.t.p.

(iii) Explain why acetanilide is effectively neutral. [1]

The orbital of the lone pair of electrons on the N atom overlaps with the π-electron cloud of the adjacent C=O group and the lone pair of electrons is delocalised and thus not available for dative bond with a proton. [1]

(iv) Phenylamine can react with hydrochloric acid to form phenylammonium chloride. Given the pK_b of phenylamine at 25 °C is 9.38, calculate the pH of the resultant mixture when 25 cm^3 of 0.25 mol dm^{-3} phenylamine is titrated with 25 cm^3 of 0.25 mol dm^{-3} of hydrochloric acid. [2]

$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$

Amt of $C_6H_5NH_3^+ = \frac{25}{1000} \times 0.25 = 0.00625$ mol

Total volume = 50 cm^3

$[C_6H_5NH_3^+] = \frac{0.00625}{50/1000} = 0.125$ mol dm^{-3} [1]

$[H^+] = \sqrt{K_a \times [\text{phenylammonium ion}]}$

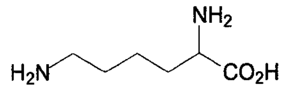
$[H^+] = \sqrt{\frac{K_w}{K_b} \times [\text{phenylammonium ion}]}$

$[H^+] = \sqrt{\frac{10^{-14}}{10^{-9.38}} \times 0.125} = 0.001732$ mol dm^{-3}

pH = $-\lg 0.001732 = 2.76$ [1]

BP-211

(b) Lysine is an α-amino acid that is used in the biosynthesis of proteins.



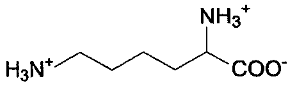
lysine

The pK_a values of lysine are given Table 2.2.

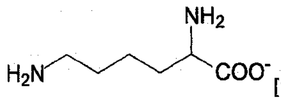
Table 2.2

functional group on lysine	pK_a value
α-carboxyl group	2.2
α-amino group	9.0
side chain	10.5

(i) Draw the structures of the major species present in solution of lysine at pH 5 and pH 12. [2]

At pH 5:


[1]

At pH 12:


[1]

(ii) Suggest a reason why the α-amino group of protonated lysine has a lower pK_a than the amino group on the side chain. [1]

Due to its closer proximity to the electron–withdrawing α–COOH group.

This decreases the availability of the lone pair of electron on N atom in the amine on α-amino group of lysine to accept a proton, resulting in a lower pK_a [1]

(c) When a 10.0 cm^3 sample of the fully protonated lysine is titrated against 0.100 mol dm^{-3} NaOH, the following titration curve is obtained.

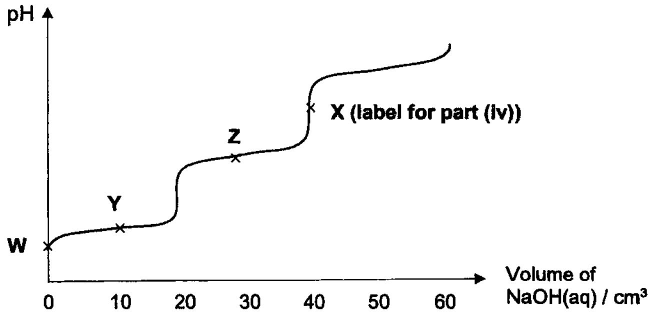


Figure 2.1

(i) Calculate the concentration of lysine in the 10.0 cm^3 sample.
Hence, calculate the pH of the solution at point **W** (ignore the effects of the second and third acid dissociations on the pH). [3]

Concentration of lysine = 0.100 × 20 ÷ 10 = 0.200 mol dm^{-3} [1]

$[H^+] = \sqrt{K_a \times [acid]}$
$= \sqrt{10^{-2.2} \times [0.100]}$
$= 0.0251$ mol dm^{-3} [1]

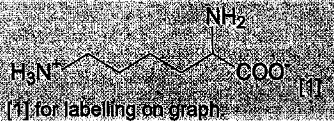
pH = - lg(0.0251)
= 1.6 [1]

Calculate [H$^+$] correctly [1] allow ecf from (c)(i)
Calculate pH correctly [1] allow ecf from [H$^+$] calculated

(ii) Determine the pH at point **Y** and **Z** [2]

pt Y = 2.2 (since pH = pK_1) [1] pt Z = 9.0 (since pH = pK_2) [1]

(iii) Suggest the structure of the zwitterion of lysine and indicate the point of the titration curve where only the zwitterion is found. Mark it with an "X". [2]



[1]

[1] for labelling on graph

[Total: 18]

3 **(a)** **(i)** Describe and explain the trend in the thermal stability of HC*l*, HBr and HI. [2]

Down the group from Cl to I
- **Valence orbital** of halogen used in bonding with hydrogen is **bigger** and **more** diffused
- **Overlap of orbitals between the H atom and halogen atom** is **less** effective
- **Bond energy:** H–C*l* > H–Br > H–I
- **Thermal stability:** HC*l* > HBr > HI

2 points for [1] must include the last point
4 points for [2]

(ii) Explain why the volatility of Group 17 hydrides decreases from HC*l*, HBr and HI. [2]

Hydrogen halides have simple molecular structures

The volatility of Group 17 hydrides decreases from HC*l*, HBr and HI, volatility inversely proportional to boiling point [1]

[1] for **HC*l* to HBr to HI** explanation
- **From HC*l* to HBr to HI**, the **number of electrons** in the hydrogen halide molecules **increases**
- **Strength** of **instantaneous dipole–induced dipole attractions** between the hydrogen halide molecules **increases**
- **Larger amount of energy** is required to overcome the **stronger** instantaneous dipole–induced dipole attractions between the hydrogen halide molecules.

(iii) Predict the colour of the solutions that would be observed when the following pairs of solution are mixed. Give equations for any reactions that occurs.
- Br_2(aq) and KI(aq)
- I_2(aq) and KBr(aq)

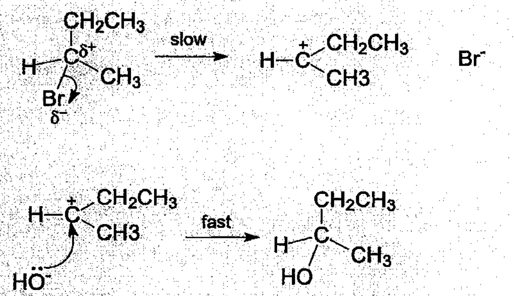
[2]

Equation	colour of solution
$Br_2 + 2I^- \rightarrow 2Br^- + I_2$ ✓	**brown** ✓
I_2 + $2Br^- \rightarrow$ no reaction ✓ Or **didn't write equations for this reaction**	**brown**✓

4✓ → [2]; 2✓ → [1]

(b) S_N1 and S_N2 are two different mechanisms for the nucleophilic substitution of halogenoalkanes.

(i) Draw a mechanism for the reaction between 2-bromobutane and OH^- via S_N1. Show relevant lone pairs of electrons, dipoles and use curly arrows to indicate the movement of electron pairs. [2]



[1] for lone pairs, dipoles, slow and fast
[1] for carbocation and arrows

(ii) Write the rate equation for the reaction in **(b)(i)**.
Suggest if the value of the rate constant, *k*, will change when concentration of 2-bromobutane is doubled. [2]

Rate = *k*[2-bromobutane] [1]

Rate constant, *k*, will not change as it is **only dependent on activation energy and temperature.** [1] (do not accept if mention independent of [reactant]

(iii) An investigation of the kinetics of the nucleophilic substitution of 2-bromobutane with OH^- is carried out. The overall rate equation of this nucleophilic substitution is found to be:

rate = *y* [2-bromobutane] + *z* [2-bromobutane][OH^-]

where *y* and *z* are rate constants.

The results of two such experiments are recorded in Table 3.2

Table 3.2

Experiment	[2-bromobutane]/ mol dm^{-3}	[OH^-]/ mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.20	8.0×10^{-7}
2	0.20	0.40	1.4×10^{-6}

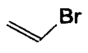
Use the results to calculate the values of *y* and *z* for the rate equation shown, stating their units. [3]

rate = *y* [2-bromobutane] + z [2-bromobutane][OH^-]
From experiment 1,
$8.0 \times 10^{-7} = y(0.2) + z(0.2)(0.2)$
From experiment 2,
$1.4 \times 10^{-6} = y(0.2) + z(0.2)(0.4)$
Both equations – [1]

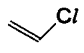
$y = 1.00 \times 10^{-6}$
units of $y = s^{-1}$
$z = 1.50 \times 10^{-5}$
units of $z = mol^{-1}\ dm^3\ s^{-1}$
Both units – [1] Both value – [1]

Can add in the explanation of mixed order in the mark scheme for further reading.

3 **(c)** Vinyl bromide and vinyl chloride are common monomers used in manufacture of addition polymers.



Vinyl bromide



Vinyl chloride

In order to differentiate vinyl bromide and vinyl chloride, the following steps are observed.

Step 1: $H_2(g)$ in the presence of solid platinum was introduced into the respective vinyl halides.

Step 2: Hot aqueous sodium hydroxide is added followed by nitric acid. The samples are then cooled before silver nitrate is added. Precipitate will be observed.

Step 3: To confirm the identity of the precipitate, dilute $NH_3(aq)$ was added to fresh sample of the precipitate.

(i) Complete Table 3.3 by stating the relevant observations for each step.

Table 3.3

compound	Name of organic substance after step 1	Colour of ppt after step 2	Solubility of precipitate	
			In dil. $NH_3(aq)$	In conc $NH_3(aq)$
Vinyl bromide	bromoethane	Cream ppt	Insoluble	Soluble
Vinyl chloride	chloroethane	White ppt	Soluble	Soluble

[2]

All correct [2] At least 2 correct [1]

(ii) Step 1 is conducted before step 2 as vinyl halides do not undergo nucleophilic substitution. Explain the unreactivity of vinyl halides towards nucleophiles. [1]

- In the halogenoalkene the p orbital of the halogen atom interact with the pi electron cloud of the C=C.
- This strengthen the C-X bond which make nucleophilic substitution not possible. [1]
- By reducing the vinyl halides into halogenoalkane, nucleophilic substitution can then occur.

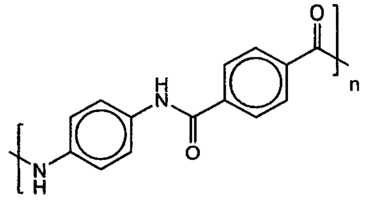
(iii) Explain why it is necessary to add nitric acid in step 2. [1]

To **react with excess acid** and **prevent the formation of ppt between Ag^+ and OH^-**, affecting the results. [1]

(iv) H_2 gas with platinum can be used to reduce C=C bond in an alkene and C=O bond in an aldehyde.
Explain why the C=C bond in an alkene is weaker than the C=O bond in an aldehyde. [2]

- oxygen is more electronegative than carbon creating a polar C=O bond which increases the electrostatic attraction between atoms, making the bond stronger. [1]
- The C=C bond in propene is non-polar and lacks the additional electrostatic attraction between atoms due to partial charges. [1]

3 **(d)** Kevlar is a lightweight and strong material, used to make tyres and bulletproof vests. Its structure is given below.



Kevlar

Upon undergoing hydrolysis, two monomers **A** and **B** are formed.

monomer **A**	$C_6H_8N_2$
monomer **B**	$C_8H_6O_4$

(i) Draw the structures of **A** and **B**. [1]

A:

B:

[1] for both

(ii) Suggest reagents and conditions required to differentiate the monomers **A** and **B**. [2]

Add anhydrous PCl_3 /$SOCl_2$/PCl_5 room temperature to **A** and **B**.
White fume will be observed for **B** but not for **A**.

Or

Add Br_2(aq) to **A** and **B**
Orange Br_2(aq) decolourised and white ppt will be observed for **A** but not for **B**.

Or

Add Na_2CO_3 / $NaHCO_3$ to **A** and **B**
Effervescence will be observed for **B** but not for **A**.

[1] for test [1] for correct observation

(iii) Kevlar can withstand a large amount of pulling force before breaking. Explain why Kevlar has such propert [1]

Presence of extensive **<u>H-bonding</u>** and instantaneous dipole-instantaneous dipole between the polymer chain require great amount of energy to overcome thus leading to high tensile strength. [1]

[Total: 23]

Section B

4 (a) (i) Sodium, magnesium and phosphrous are elements from Period 3.

Describe what you would observe when water is added to separate samples of the chlorides of these three elements.
Suggest the pH of the resulting solutions, and write equations where appropriate. [3]

NaC*l* undergoes hydration in water to form a neutral solution of pH 7. **[1]**
Hydration: NaC*l*(s) → Na^+(aq) + Cl^-(aq)

$MgCl_2$ undergoes hydration and slight hydrolysis in water to form a slightly acidic solution of pH 6.5. **[1]** with equation
$MgCl_2$(s) + $6H_2O$(l) → $[Mg(H_2O)_6]^{2+}$(aq) + $2Cl^-$(aq)
$[Mg(H_2O)_6]^{2+}$(aq) ⇌ $[Mg(H_2O)_5(OH)]^+$(aq) + H^+(aq)

PCl_5 undergoes complete hydrolysis (vigorous hydrolysis) in water to form a strongly acidic solution of pH 1. **[1]** with equation
PCl_5(s) + $4H_2O$(l) → H_3PO_4(aq) + 5HC*l*(aq)

(ii) Carbon tetrachloride, CCl_4, and silicon tetrachloride, $SiCl_4$, are both tetrachlorides of Group 14 elements. Explain why CCl_4 does not hydrolyse in water but $SiCl_4$ does. [2]

CCl_4 does not undergo hydrolysis in water because of the much smaller size of the C atom relative to the large C*l* atoms which hinders the approach of the water molecules. **[1]**

In addition, C does not have available and energetically accessible 3d orbitals to accommodate the lone pair of electrons from water unlike Si. **[1]**
(accept explanation in terms of Si)

(iii) NCl_3 and PCl_3 are both chlorides of Group 15 elements. Predict and explain the difference in bond angles between NCl_3 and PCl_3. [2]

Bond angle of NCl_3 (107°) is larger than PCl_3 (100°). **[1]**

Explanation **[1]**
N is more electronegative than P. Hence,
- bonding electrons in N–C*l* bond is drawn more towards the N atom
- more crowding of electron density around N atom
- more inter–electronic repulsion between the electron pairs around the N atom
- larger bond angle in NCl_3

(b) D-glucose exists in two forms. The α-form has an optical rotation of +113.4° and the β-form which has an optical rotation of +19.0°.

The following equilibrium exists in aqueous solution.

$$\alpha\text{-glucose(aq)} \rightleftharpoons \beta\text{-glucose(aq)} \qquad \Delta H^\circ = -2.10 \text{ kJ mol}^{-1}$$

If an aqueous solution of either form is allowed to stand, the optical rotation changes until it reaches +52.2°.

(i) Show that the equilibrium mixture contains 35.2% of the α-form. [1]

Let the proportion of α-glucose be x and that of β-glucose be $1 - x$
x[α-glucose] + $(1-x)$[β-glucose] = $[\text{glucose}]_{eqm}$
$113.4x + (1-x)19 = 52.2$
$x = 0.352$
∴ % of α-form in equilibrium mixture = 35.2% (shown) [1] with correct working

(ii) Calculate the K_c value at 298 K. [1]

$$K_c = \frac{[\beta\text{-glucose}]}{[\alpha\text{-glucose}]} = \frac{100-35.2}{35.2} = \underline{1.84} \text{ [1]}$$

(iii) Given that $\Delta G^\circ = -\text{RT} \ln K_c$, using your answer from **(b)(ii)**, calculate the value of ΔG° and ΔS° at 298 K. [2]

$$\Delta G^\circ = -\text{RT} \ln K_c = -(8.31)(298)\ln(1.84) = \underline{-1510 \text{ J mol}^{-1}} \text{ [1]}$$

$$\Delta G^\circ = \Delta H^\circ - \text{T}\Delta S^\circ$$
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{\text{T}} = \underline{-1.98 \text{ J mol}^{-1} \text{K}^{-1}} \text{ [1]}$$

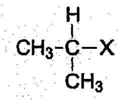
(c) The Corey–House reaction is an organic reaction that involves the reaction of a lithium dialkyl cuprate, R_2CuLi, with a halogenoalkane, R'X, to form a new alkane, an organocopper compound and a lithium halide.

The reaction is as shown.

$$R_2CuLi + R'X \rightarrow R\text{-}R' + RCu + LiX$$

(X = C*l*, Br or I)

(i) Suggest the lithium dialkyl cuprate and a secondary halogenoalkane to form $CH_3CH(CH_3)CH_2CH_2CH_3$. [1]

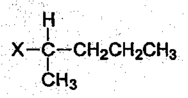


$CH_3-\overset{H}{\underset{CH_3}{C}}-X$

$(CH_3CH_2CH_2)_2CuLi$

[1] for both structures

OR

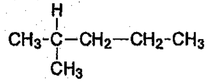


$X-\overset{H}{\underset{CH_3}{C}}-CH_2CH_2CH_3$

$(CH_3)_2CuLi$

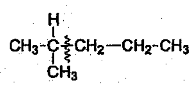
Thinking process:

Given

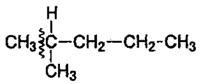


$CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$

, as stated by question, you need a secondary halogenoalkane, the only way to get is by "cutting" the structure as shown.



or



all other sites will result in primary halogenoalkane.

(ii) Suggest the type of reaction for the Corey–House reaction. [1]

Nucleophilic substitution [1]

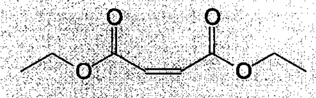
(d) Compound **T**, $C_8H_{12}O_4$, is a neutral, sweet-smelling liquid. It does not give any orange precipitate with 2,4-DNPH. One mole of compound **T** decolourised one mole of liquid Br_2.

Samples of compound **T** are reacted separately with

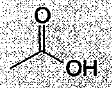
- hot aqueous KOH to form organic compound **V**, C_2H_6O, and salt **W**, $C_4O_4H_2K_2$.
- hot acidic $KMnO_4$ to form **U**, $C_2H_4O_2$, as the only organic product

Compound **V** gives a yellow precipitate with alkaline aqueous iodine.

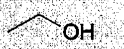
Suggest possible structures for **T**, **U**, **V** and **W**. For each reaction, state the type of reaction described and explain what the information tells you about the functional group present in each compound. [7]



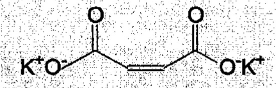
T



U

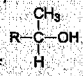


V



W

[1] for each correct structure

	Deduction
Compound T, $C_8H_{12}O_4$, is a neutral, sweet-smelling oil	Ester is present in T ✓
does not give any orange precipitate with 2,4-DNPH	No condensation ✓, no carbonyl compound ✓
compound T decolourised one mole of liquid Br_2	Electrophilic addition ✓, presence of alkene ✓
compound T reacts with hot aqueous KOH	Basic hydrolysis ✓, ester in T
compound T reacts with hot acidic $KMnO_4$ forming U, $C_2H_4O_2$, as the only organic product	Acidic hydrolysis of ester ✓; Oxidation of alkene ✓
Compound V gives a yellow precipitate with alkaline aqueous iodine	Oxidation ✓, presence of  $R-\overset{CH_3}{\underset{H}{C}}-OH$ ✓

8 to 9 ✓ ➔ [3]   6 to 7 ✓ ➔ [2]   4 to 5 ✓ ➔ [1]

[Total: 20]

BP-217

5 In aqueous solution, chlorine dioxide, ClO_2, reacts with hydroxide ions as shown.

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$$

(a) (i) Suggest how the shape and bond angle of a ClO_3^- ion is different from those of ClO_2^- ion. [2]

In ClO_3^-, there are also **three bond electron pairs and one lone pair around the central *Cl* atom.**
In ClO_2^-, there are also **two bond electron pairs and two lone pair around the central *Cl* atom.**
Lone pair-lone pair repulsion in In ClO_2^-, is stronger than lone pair-bond pair repulsion in ClO_3^-. [1]

Hence, **shape changes from trigonal pyramidal in ClO_3^- to bent in ClO_2^-. Bond angle in ClO_2^- is smaller than in ClO_3^-.** [1]

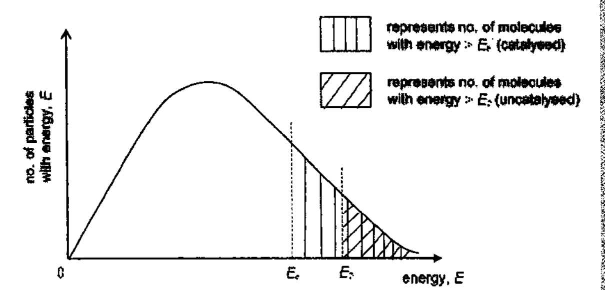
(ii) Determine the oxidation number of chlorine in ClO_2, ClO_3^- and ClO_2^-. Hence, suggest what is special about this reaction. [2]

ON of *Cl* in ClO_2: +4   ON of *Cl* in ClO_3^-: +5   ON of *Cl* in ClO_2^-: +3
ON all correct :[1]

This is a **disproportionation reaction** [1] as chlorine undergo reduction and oxidation at the same time.

(b) The reaction between chlorine dioxide and hydroxide ions can be influenced by the presence of Fe^{2+}(aq) catalyst.

Explain, with the aid of a labelled Boltzmann distribution diagram, the effect of the use of Fe^{2+}(aq) on the rate constant. [3]



[1]

- In the presence of a Fe^{2+} catalyst at a certain temperature *T*, the reaction proceeds via an alternative pathway which has lower activation energy ($E_a' < E_a$).
- As shown on the diagram, more molecules have **energies greater than or equal to the lowered activation energy E_a'** [1]
- This results in an increase in the frequency of effective collisions.
- The **rate constant, *k*, increases.** [1]

(c) **R**, **S** and **T** are oxides of Period 3 elements which are solids at room temperature.

R, **S**, and **T** are added to excess cold water, HC*l*(aq) and NaOH(aq) separately at room temperature. Table 5.1 shows the observation and reactions.

Table 5.1

	Observation on addition to water	Reaction with HC*l*(aq)	Reaction with NaOH(aq)
R	White solid did not dissolve.	Reacts to form salt.	Reacts to form complex ions.
S	Some white solid remain undissolved.	Reacts to form salt.	No reaction.
T	All white solid dissolved.	No salt formed.	Reacts to form salt.

Using Table 5.1, identify **R**, **S** and **T**. State the pH of the solution when each of the oxide is added to water. [3]

	Observations on addition of sample to water	Reaction with HCl	Reaction with NaOH	pH of solution	Identity of sample
R	White solid did not dissolve at all.	Reacts to form salt.	Reacts to form complex ions.	7 ✓	Al_2O_3 ✓
S	Some white solid remain undissolved.	Reacts to form salt.	No reaction.	10 ✓	MgO ✓
T	All of the white solid dissolved.	No salt formed.	Reacts to form salt.	2 ✓	P_4O_{10} ✓

6 ✓ → [3]   4 to 5 ✓ → [2]   2 to 3 ✓ → [1]   0 to 1 ✓ → No marks

(d) The evaporation of one mole of pure water has a standard entropy change of $\Delta S^\ominus = +110$ J mol^{-1} at 298 K.

(i) Given that the standard enthalpy change for the evaporation of one mole of pure water, $\Delta H^\ominus = +41.0$ kJ mol^{-1}, calculate the $\Delta G^\ominus$ in kJ mol^{-1} at 298 K. [1]

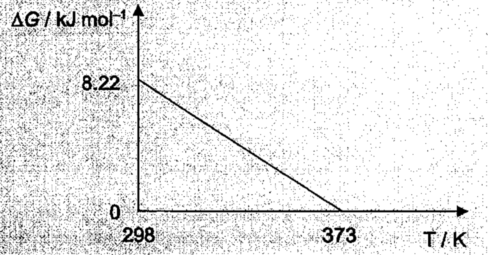
$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$\Delta G^\ominus = +41.0 - 298(\frac{+110}{1000})$

$= \underline{+8.22 \text{ kJ mol}^{-1}}$ [1]

(ii) State the ΔG of water at 373 K and sketch a clearly labelled graph of ΔG, on the y-axis, against temperature measured in Kelvin, on the x-axis, to show how ΔG changes for the evaporation process when temperature increases from 298 K to 373 K. [1]

Water boils at 373 K ∴ $\underline{\Delta G = 0 \text{ kJ mol}^{-1}}$ as an equilibrium is established between liquid water and gaseous water vapour.



[1]: well labelled sketch showing a decreasing straight line with constant gradient (from 298 K to 373 K)

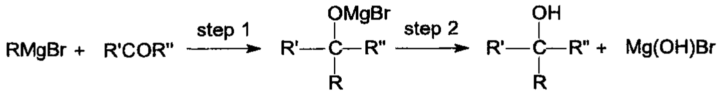
(iii) Comment on the gradient of your graph and explain how temperature affects the spontaneity of the evaporation process. [2]

As observed from the sketch,

- <u>gradient is negative</u> because gradient = –Δ*S* and <u>Δ*S* for evaporation is positive</u> (as number of ways to arrange the particles increases during a phase change from liquid to gas).
- <u>ΔG becomes more negative / less positive</u> as the <u>temperature increases</u>. Hence, the evaporation process becomes <u>more spontaneous</u>.

[1]: recognise that the gradient is negative (gradient = –Δ*S*) <u>and</u> infer the positive Δ*S* to the increase in entropy as liquid water is converted to water vapour at 373 K
[1]: use the sketch or sign of Δ*H* and Δ*S* to conclude the effect of changing T on ΔG and hence spontaneity of the process

(e) Grignard reagents, RMgBr, are excellent carbon-based nucleophiles as well as strong bases. They can add to aldehydes and ketones to form alcohols. A typical example of the use of Grignard reagent is the two-step reaction of RMgBr with a carbonyl compound to form an alcohol.



$$\text{RMgBr} + \text{R'COR''} \xrightarrow{\text{step 1}} \text{R'}-\underset{\text{R}}{\overset{\text{OMgBr}}{\text{C}}}-\text{R''} \xrightarrow{\text{step 2}} \text{R'}-\underset{\text{R}}{\overset{\text{OH}}{\text{C}}}-\text{R''} + \text{Mg(OH)Br}$$

where R = alkyl, R' and R'' = alkyl group or H.

(i) State the type of reaction in step 1. [1]

Nucleophilic addition **[1]**

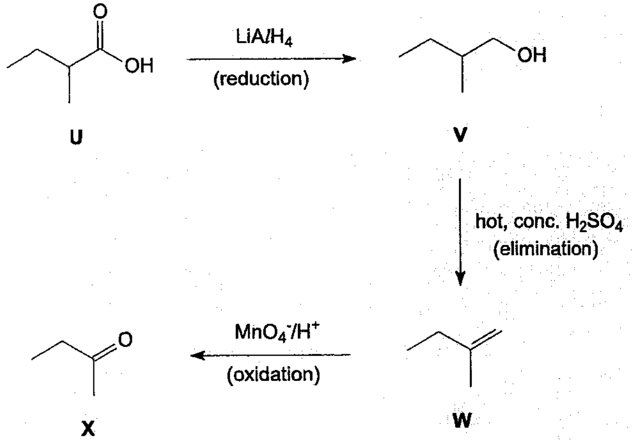
(ii) Suggest the identity of the Grignard reagent and aldehyde that is needed to form pentan-2-ol. [1]

Grignard reagent		aldehyde
CH_3MgBr	&	$CH_3CH_2CH_2CHO$
$CH_3CH_2CH_2MgBr$	&	CH_3CHO

[1] for either pair of Grignard reagent and aldehyde

(iii) The Grignard reagent $C_2H_5CH(CH_3)MgBr$ can be converted into carboxylic acid **U** by using carbon dioxide. When **U** reacted with $LiAlH_4$, **V** is produced. **W** is produced when **V** is reacted with hot concentrated sulfuric acid. When hot acidified potassium managnate(VII) is added, **X** is formed. **X** forms a yellow precipitate when reacted with alkaline aqueous iodine.

Suggest the structural formulae of **U**, **V**, **W** and **X**. [4]



[1] each structure

[Total: 20]