



RIVER VALLEY HIGH SCHOOL
JC2 H2 CHEMISTRY 9729 PRELIMINARY EXAMINATION
SUGGESTED SOLUTIONS

Paper 1

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

- 1 A^{2+} has the highest third ionisation energy
 \rightarrow 3rd electron is removed from the inner principal quantum shell
 \rightarrow Electronic configuration of A^{2+} is $1s^22s^22p^6$
 \rightarrow Electronic configuration of A is $1s^22s^22p^63s^2$ (Period 3 Group 2)
 \rightarrow Electronic configuration of I is $1s^22s^22p^63s^23p^44s^2$ (Period 4 Group 2)

Option A is incorrect.
 Electronic configuration of B^{2+} is $1s^22s^22p^63s^1$
 Electronic configuration of C^{2+} is $1s^22s^22p^63s^2$
 Since B and C has the same number of inner principal quantum shells, shielding effect provided on the valence electrons is the approximately the same. Since C has greater number of protons than B, the ionic size of C^{2+} is smaller than that of B^{2+} .

Option B is incorrect.
 H is in Group 1, I is in Group 2.
 Since angle of deflection is directly proportional to charge/mass, H^+ will be deflected to a larger extent.

Option C:
 \rightarrow Electronic configuration of C^{2+} is $1s^22s^22p^63s^2$
 \rightarrow Electronic configuration of D^{2+} is $1s^22s^22p^63s^23p^1$
 Less energy is needed to remove an electron from D^{2+} as 3p electron is of higher energy than 3s electron.

Option D: Correct
 Answer: D

2

2 No. of moles of $MnO_4^{2-} = \frac{50}{1000} \times 0.300$
 $= 0.0150$ mol

No. of moles of $MnO_4^- = \frac{45}{1000} \times 0.200$
 $= 0.00900$ mol

0.00900 mol MnO_4^- is reduced to Mn^{2+} by gaining 0.0450 mol of electrons.
 0.0150 mol MnO_4^{2-} is oxidised to MnO_4^- by removing 0.0450 mol of electrons.

1 mol MnO_4^{2-} is oxidised to MnO_4^- by removing 3 mol of electrons

Let the oxidation state of Mn in MnO_4^{2-} be y.

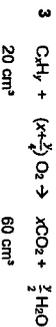


$+3 = y - 3$

$y = +6$

$+6 - 2x = -2$, solving $x = 4$

Answer: D



KOH absorbs $CO_2 \Rightarrow V_{CO_2} = 60$ cm³

Thus, $x = 60/20 = 3$

$V_{C_2H_4} + V_{initial\ O_2} = 20 + 120$ cm³ = 140 cm³

After combustion, $V_{excess\ O_2} + V_{CO_2} = 140 - 50 = 90$ cm³

$V_{excess\ O_2} = 90 - 60 = 30$ cm³

$V_{O_2\ consumed\ during\ combustion} = 120 - 30 = 90$ cm³

$x + \frac{1}{2} = \frac{90}{20} = 4.5$

$y = 6$

Answer: C

- 4 BF_3 : 3 bond pair 0 lone pair \Rightarrow 120°
 SF_4 : 4 bond pair 0 lone pair \Rightarrow 109.5°
 SF_6 : 2 bond pair 2 lone pair \Rightarrow less than 109.5° (actual 98.3°)
 BF_3 : 5 bond pair 1 lone pair \Rightarrow less than 90° (actual 85°-90°)
 Answer: D

- 12 The oxidation state of sulfur increases from 0 to +6 in SF_6 , +2 in SCl_2 and +1 in SBr_2 . Hence this shows that the oxidising ability of F_2 is the highest, followed by Cl_2 then Br_2 .

Answer: D

- 13 The reaction gives higher methanol yield at lower T \Rightarrow forward reaction is exothermic $\Rightarrow \Delta H < 0$.
Decrease in disorder as number of moles of gas molecules decreases from 3 to 1 $\Rightarrow \Delta S < 0$

Since $\Delta G = \Delta H - T\Delta S$, the gradient of ΔG against T graph gives $-\Delta S$.

With $\Delta S < 0$, the gradient is positive. (Options B and D eliminated)

With the y-intercept as ΔH , and $\Delta H < 0$, the line starts below zero at the y-axis.

At low temperature, $|-T\Delta S| < |\Delta H|$, $\Delta G < 0$, reaction is spontaneous.

As temperature increases, $|-T\Delta S| > |\Delta H|$, ΔG becomes positive. Reaction is non-spontaneous.

Hence, answer is C.

- 14 Option A is incorrect.

Initial amount / mol	$\text{NiO}_4(\text{g})$	\rightleftharpoons	$2\text{NiO}_2(\text{g})$
	1		0.2
Change in amount / mol	-0.24		+0.48
Eqm amount / mol	0.76		0.68

Option B is incorrect.

$$K_c = \frac{[\text{NiO}_2]^2}{[\text{NiO}_4]}$$

$$= \frac{(0.68)^2}{(0.76)}$$

$$= \frac{0.4624}{0.76}$$

Since the volume of the reaction vessel is not known, it is not possible to calculate the value of K_c .

Option C is incorrect.

Since V and T are constant, pressure is directly proportional to amount.

As the total number of moles of gas increased from 1.2 mol to 1.44 mol, the total pressure in the vessel at equilibrium should also increase.

Answer: D

- 15 Option A is incorrect.
O-H bonds are broken.



Position of equilibrium shifts to absorb heat when T increases. Since K_w increases, forward reaction is favoured. The ionic dissociation process is endothermic.

Option B is incorrect.

The ionic dissociation of water increases ten-fold.

Option C is incorrect as concentration of H^+ is the same as the concentration of OH^- in water.

$$\text{pH} = -\lg [\text{H}^+]$$

$$[\text{H}^+] = [\text{OH}^-] = (K_w)^{1/2}$$

Option D is correct.

When T increases, K_w increases, $[\text{H}^+] = [\text{OH}^-]$ increases. pH decreases. But water remains neutral because at all temperatures, $[\text{OH}^-] = [\text{H}^+]$

Answer: D

- 16 $K_a(\text{C}_6\text{H}_5\text{COOH}) > K_a(\text{C}_6\text{H}_4\text{COOH})$. $\text{C}_6\text{H}_5\text{COOH}$ is a stronger acid.

Option 1 is incorrect.

Since both acids are monoprotic, and as a stronger acid, $\text{C}_6\text{H}_5\text{COOH}$ dissociates to a larger extent to give H^+ ions. The pH of $\text{C}_6\text{H}_5\text{COOH}$ should be lower.

Option 2 is incorrect.

$$K_a = \frac{(\alpha C)^2}{(1-\alpha)C}$$

$$K_a = \frac{\alpha^2 C}{1-\alpha}$$

Option 3 is correct.

Since $\text{C}_6\text{H}_5\text{COOH}$ is a stronger acid than CH_3COCOOH , the conjugate base of $\text{C}_6\text{H}_5\text{COOH}$ is weaker than that of CH_3COCOOH . Hence, $\text{p}K_b$ of $\text{C}_6\text{H}_5\text{COO}^-$ is larger.

Answer: D

- 17 Option C is incorrect. H_2PO_4^- and HPO_4^{2-} is not a conjugate acid-base pair, thus they do not form a buffer.

H_3PO_4	H_2PO_4^-	HPO_4^{2-}	PO_4^{3-}
-H ⁺	-H ⁺	-H ⁺	-H ⁺

Option A, B & D are correct.
 In decreasing order of acidity (thus, magnitude of K_a)
 H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}
 In increasing order of basicity (thus, magnitude of K_b)
 PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4
 Answer: C

- 18 For precipitation, I.P. = K_{sp}
 $[\text{Cr}^{3+}][\text{OH}^-]^3 = 6.3 \times 10^{-31}$
 $[\text{OH}^-] = \sqrt[3]{\frac{6.3 \times 10^{-31}}{1.5 \times 10^{-16}}} = 7.499 \times 10^{-6}$
 $\text{pH} = 14 - \text{pOH} = 14 - (-\lg 7.499 \times 10^{-6}) = 8.87$
 Answer: D

- 19 Equation 1 $\text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightleftharpoons \text{PbSO}_4(\text{s})$
 Equation 2 $\text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightleftharpoons \text{PbCrO}_4(\text{s})$

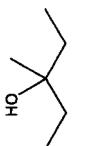
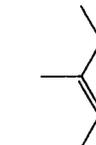
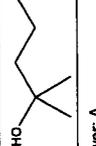
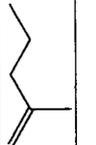
Option 1 is correct.
 Option 2 is correct.
 For the first student's experiment,
 When K_2SO_4 and $\text{Pb}(\text{NO}_3)_2$ are mixed, white ppt, PbSO_4 is formed.
 When CrO_4^{2-} ions are added, position of equilibrium of equation 2 shifts right, PbCrO_4 is formed (yellow ppt). In the process, $[\text{Pb}^{2+}]$ decreases.
 I.P. < K_{sp} (PbSO_4). Thus, position of equilibrium of equation 1 shifts left, white ppt, $\text{PbSO}_4(\text{s})$, dissolves.

For the second student's experiment,
 When Na_2CrO_4 and $\text{Pb}(\text{NO}_3)_2$ are mixed, yellow ppt, PbCrO_4 is formed.
 When SO_4^{2-} ions are added, position of equilibrium of equation 2 shifts right. However, the decrease in $[\text{Pb}^{2+}]$ is not sufficient. I.P. > K_{sp} (PbCrO_4). Thus, yellow ppt remains.

$K_{sp}(\text{PbCrO}_4) < K_{sp}(\text{PbSO}_4)$, lead(II) sulfate is more soluble than lead(II) chromate
 Option 3 is incorrect. This isn't a redox reaction.

Answer: A

20

Reactant	Product
	
	

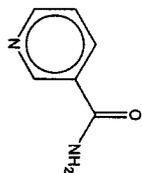
Answer: A

21 Oxidative cleavage results in formation of

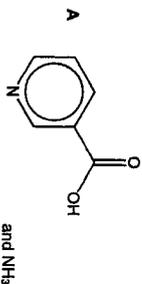
- (1) $\text{HOOCCH}_2\text{C}(\text{CH}_3)_2\text{COOH}$
 $\rightleftharpoons \text{HOOCCH}_2\text{C}(\text{CH}_3)_2\text{COCOOH}$ undergoes decarboxylation
 (2) CH_3COCOOH
 (3) CO_2 (not organic product)

Answer: A

22 Nicotthamide is marketed as nicotine substitute which hydrolysed by aqueous sodium hydroxide.



What are the products of this hydrolysis reaction?



22 Answer: C

Alkaline hydrolysis forms salt of carboxylic acid (RCOO^-) and ammonia (NH_3)

23 $2\text{-COOH} \rightarrow 2$ (45)
 $\text{C}=\text{C} \rightarrow 2$ (12)

M_r ($\text{HOOCCH}_2\text{COOH}$) = 116

Answer: B

24 Chlorobenzene is deactivated

Phenol is activated.

Answer is C

25 Carbon with methyl group make a more stable carbocation and thus -OH group is attached at carbon 2.
 Answer: C

26 α -tetrone undergo reduction and lose its carbonyl functional groups while retaining its alkene functional group.
 Answer: C

27 Option 1:

In CH_3COCl , carbon bonded to chlorine is also bonded to electronegative oxygen, making it very electron deficient.

In $\text{CH}_3\text{CH}_2\text{Cl}$, carbon bonded to chlorine is only bonded to one electronegative atom, making it electron deficient but less electron deficient than the carbon in ethanoyl chloride, less susceptible to nucleophilic attack.

In CH_2CHCl , carbon bonded to chlorine is in $\text{C}=\text{C}$, the $\text{C}-\text{Cl}$ bond is strengthened by the partial double bond character arising from the sideways overlap of π electron cloud of $\text{C}=\text{C}$ with p orbital of adjacent carbon. Thus making the carbon bonded to chlorine less electron deficient, $\text{C}-\text{Cl}$ bond harder to break, least susceptible to nucleophilic attack.

Option 2:

Water is a nucleophile. Refer to explanation for option 1.

Option 3:

Acidity of ethanoyl chloride is irrelevant to the rate of reaction.

Answer: B

28 Option A:

Changing the size of the metal electrode has no effect on the standard electrode potential, hence the reading on the voltmeter does not change.

Option B:

Adding water dilutes the concentration of the Fe^{2+} ions, the equilibrium $\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$ favours the reverse reaction, and the electrode potential of Fe^{2+}/Fe becomes more negative, so the voltmeter would register a more positive reading.

Option C:

Adding aqueous AgNO_3 decreases the concentration of Cl^- ions due to precipitation of AgCl . The equilibrium $\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Cl}^-$ favours the forward reaction, making the electrode potential of Cl_2/Cl^- more positive, causing the voltmeter reading to become more positive.

Option D is correct.

Answer: D

11

- 29 Amount of $\text{Ni}^{2+} = 3 \times 10^{-3} \times (4/1000) = 1.2 \times 10^{-5}$ mol
 Amount of $\text{X} = 4 \times 10^{-3} \times (6/1000) = 2.4 \times 10^{-5}$ mol
 Ratio of Ni^{2+} to $\text{X} = 1 : 2$

Hence the formula of the nickel complex is NiX_2 , and the ionic charge on it is 0.

Answer: B

- 30 Check for the oxidation state of the transition metal.
 Option A: Cu is in +1 oxidation state. [Range of available O.S. for Cu = +1 to +3]
 Option B: Cr is in +3 oxidation state. [Range of available O.S. for Cr = +1 to +6]
 Option C: Mn is in +8 oxidation state. [Range of available O.S. for Mn = +1 to +7]
 Option D: V is in +4 oxidation state. [Range of available O.S. for V = +1 to +5]

Answer: C

Paper 2

- 1 (a) (i) There is an increase in successive ionisation energies as the electron is removed from an ion/species of increasing positive charge. [1]
 Accept: Number of electrons decrease, nuclear charge remains the same, stronger electrostatic forces of attraction between nucleus and remaining electrons, more energy required.
 (ii) There is a large increase from 4th to 5th ionisation energies. This means that the 4th electron is the last electron to be removed from the outermost principal quantum shell. 5th electron is removed from an inner principal quantum shell which is closer to the nucleus and hence experiences stronger attraction to the nucleus. [1]
 Element A has 4 valence electrons and is likely to be in Group 14. [2]
 (b) Nuclear charge is higher for scandium than calcium, while shielding effect by inner shells of electrons remains relatively constant as 3d electrons provide relatively poor shielding effect / 3d electrons provide only slightly increased shielding effect. [2]
 Hence, effective nuclear charge is higher for scandium than for calcium. Attraction between the valence electrons and nucleus is stronger in scandium than calcium resulting in smaller atomic radii for nickel. [2]
 (c) (i) $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$ [1]
 (ii) Nickel(II) hydroxide would decompose at a lower temperature than calcium hydroxide. [1]
 Ni^{2+} has a smaller ionic radius and higher charge density than Ca^{2+} . As a result, Ni^{2+} has a greater polarising power than Ca^{2+} / OH^- anions are polarised to a greater extent by Ni^{2+} . It weakens the O-H bond [2]

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[Turn over]

12

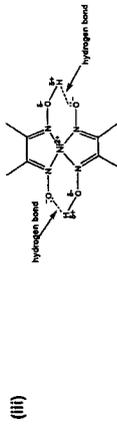
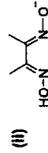
in OH^- anion to a greater extent, hence Ni(OH)_2 is less thermally stable.

- (d) (i) Ammonia acts as either

Bronsted-Lowry base / proton acceptor

or

Lewis base / electron pair acceptor



- (iv) $3d^8s^2$ [2]

- 2 (a) A Lewis base is a substance that can donate a pair of electrons to an acid to form a dative bond, i.e. electron pair/lone pair donor. [1]

- (b) (i) $\text{Nicotine} + 2\text{H}^+ \rightarrow \text{NicotineH}_2^{2+}$

$$n(\text{HCl}) = 0.100 \times 49/1000 = 0.00490 \text{ mol}$$

$$n(\text{nicotine}) = 0.00490 \text{ mol} / 2 = 0.002450 \text{ mol}$$

$$[\text{NicotineH}_2^{2+}] \text{ at } 2^{\text{nd}} \text{ equivalence point} = 0.002450 \text{ mol} / [(49 + 25)/1000]$$

$$= 0.03311 \text{ mol dm}^{-3}$$

$$= 0.0331 \text{ mol dm}^{-3}$$

- (ii) Salt hydrolysis: $\text{NicotineH}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NicotineH}^+ + \text{H}_3\text{O}^+$

$$K_a \text{ of } \text{NicotineH}_2^{2+} = 10^{-(14-11.0)} = 10^{-3.0} = 0.001 \text{ mol dm}^{-3}$$

$$[\text{H}^+] = \sqrt{0.001 \times 0.03311} = 0.005754$$

$$\text{pH} = -\lg [\text{H}^+] = 2.24$$

- (iii) $[\text{nicotine}] = \frac{0.002450}{25} = 0.0980 \text{ mol dm}^{-3}$

$$K_b = \frac{[\text{OH}^-][\text{nicotineH}^+]}{[\text{nicotine}]}$$

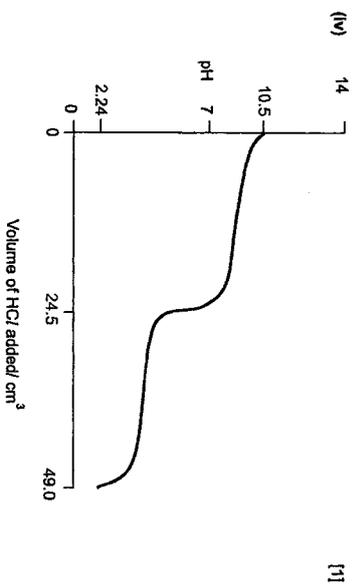
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$$[\text{OH}^-] = \sqrt{10^{-14} \times 0.09800} = 0.0003130 \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log 0.0003130 = 3.504$$

$$\text{pH} = 14 - 3.504 = 10.5$$



(iv) [1]

(c) **Z** is the least basic. The p orbital of nitrogen atom overlaps with the π electron cloud of the neighbouring C=O group. The lone pair of electrons on nitrogen atom is effectively delocalised into C=O, hence not available for protonation.

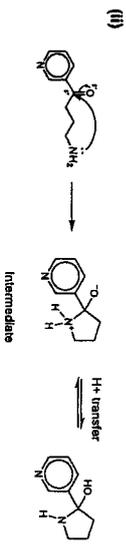
Y is less basic than **X**. The p orbital of the nitrogen atom overlaps with the π electron cloud of the (aromatic) ring. The lone pair of electrons on nitrogen atom is delocalised into the (aromatic) ring, making it less available for protonation.

X is the most basic as the electron-donating alkyl group makes the lone pair of electrons on nitrogen atom most available for protonation.

[3]

(d) (i) Nucleophilic addition

[1]



[2]

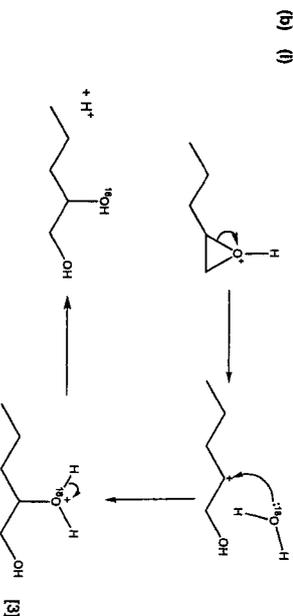
(iii) Limited ethanolic methyl chloride/ bromide/ iodide, heat

[1]

3 (a) The bond angle in the ring is 60° .

[2]

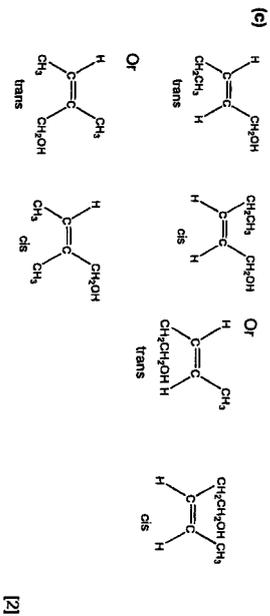
Each C is sp^3 hybridised / has a tetrahedral shape with a bond angle of 109.5° . However, the C in epoxides is only 60° and faces ring strain/ angle strain/ torsional strain.



(ii) The other C-O bond was broken instead, forming a primary carbocation intermediate, which is stabilised by only 1 electron-donating alkyl group. H_2^{18}O was then able to attack the primary carbocation to form isotopic isomer A.

The primary carbocation formed is more unstable than the secondary carbocation. The reaction mechanism is therefore much less likely to proceed to form A.

[2]



4 (a)				
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Alternatives: side-chains in different positions [4]

- (b) Phenol functional group undergoes acid-base reaction with NaOH (aq). Energy produced from ion-dipole interactions between phenoxide ions and water molecules is enough to overcome the hydrogen bonds between water molecules. [2]
- (c) (i) Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ [2]
 Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ [2]
 (ii) (Left to right in the external wire.) [1]
 (d) (i) $E_{cell}^{\circ} = +1.23 - (-0.61) = +1.84V$ [1]
 (ii) The value of the cell emf becomes less positive. When pressure of CO_2 is increased, the position of equilibrium for $CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH$ shifts to the right and electrode potential of reducing CO_2 becomes more positive/less negative. Since $E_{cell} = E(O_2/H^+(aq)) - E(CO_2(g)/HCOOH(aq))$, E_{cell} becomes less positive. [2]
- (e) (i) The particles of an ideal gas have negligible volume compared to the volume of the container. The gas particles exert negligible attractive forces on one another. The collisions between particles of an ideal gas are perfectly elastic. [3]
 (ii) SO_2 deviates more from ideal gas behaviour as compared to CO_2 . SO_2 is a polar molecule while CO_2 is a non-polar molecule. Hence, there is permanent dipole-permanent dipole attractions between SO_2 molecules as compared to weaker id-id attractions between CO_2 molecules. [1]

OR
 SO_2 deviates more from ideal gas behaviour as compared to CO_2 . SO_2 is a larger molecule and has a larger and more polarisable electron cloud / more electrons in the molecules.

Hence, there is stronger instantaneous dipole-induced dipole (id-id) attractions between SO_2 molecules than between CO_2 molecules.

- 5 (a) ΔH° per mol of NH_4NO_3
 $= \frac{1}{4} [2\Delta H^{\circ}(N_2) + \Delta H^{\circ}(O_2) + 4\Delta H^{\circ}(H_2O)] - [2(\Delta H^{\circ}(NH_4NO_3))]$
 $= \frac{1}{4} [0 + 0 + 4(-242)] - [2(-365)]$
 $= \frac{1}{4} [(-968) - (-730)]$
 $= \frac{1}{4} (-238)$
 $= -119 \text{ kJ mol}^{-1}$ [1]
- (b) $\Delta S^{\circ} = \frac{1}{4} [2(192) + 206 + 4(189)] - [2(151)]$
 $= \frac{1}{4} (1044)$
 $= +522 \text{ J mol}^{-1} \text{ K}^{-1}$ [1]
- (c) $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$
 $= - (238 / 2) - 298(521.5/1000)$
 $= -274.56 \text{ kJ mol}^{-1}$
 $= -275 \text{ kJ mol}^{-1}$ (3 s.f.) [1]
- Since $\Delta G^{\circ} < 0$, the decomposition reaction is energetically feasible/spontaneous. [1]
- (d) There is high activation energy due to the stability of NH_4NO_3 , thus heat or an external shock will be required to overcome the energy barrier to start the reaction. [1]
- (e) (i) Note: 2750 tonnes = $2750 \times 10^6 \text{ g} = 2.75 \times 10^9 \text{ g}$
 Amount of ammonium nitrate decomposed
 $= 2.75 \times 10^8 + 80.0$
 $= 3.4375 \times 10^7 \text{ mol}$
 Energy released
 $= 3.4375 \times 10^7 \text{ mol} \times 119$
 $= 4.09 \times 10^9 \text{ kJ}$
 $= 4.09 \times 10^6 \text{ MJ}$ [2]

$$\begin{aligned} \text{(ii) Total amount of gases produced} \\ = 3.4375 \times 10^7 \times \frac{1}{2} = 1.2031 \times 10^8 \text{ mol} \\ PV = nRT \\ (101325)V = (1.2031 \times 10^8)(8.31)(298) \\ V = 2.94 \times 10^8 \text{ m}^3 \text{ (3 s.f.)} \end{aligned}$$

[2]

(iii) The actual total volume of gas is expected to be smaller. [1]
Some possible reasons: (choose any 1)

- When molecules of real gases are close together, there will be significant intermolecular forces, decreasing the total volume of gases.
- Upon release into the atmosphere, condensation of water vapour occurs as the cooler surroundings cool down the water vapour fast enough, causing a reduction in the total gas volume after the explosion.
- There may be incomplete decomposition of NH_4NO_3 , which results in the amount of gases lower than expected, thus leading to a smaller total volume of gases.

OR

The actual total volume of gas is expected to be larger. [1]

Some possible reasons: (choose any 1)

- The volume of the real gas molecules is much more significant to the volume of the container as compared to the volume of ideal gas molecules. As such, for the same amount of gases generated, the real gas molecules will take up much more space and this leads to an increase in the overall volume of gases.
- Under highly elevated temperatures, the gas molecules possess very high kinetic energy and can occupy a larger overall volume (within a short span of time).
- There is a sudden and rapid expansion of gases after ignition/detonation. Thus, intermolecular forces of attraction between gas molecules will be easily overcome by this rapid expansion and this leads to a larger total volume of gases.
- The atmosphere above gets thinner further up into the sky. As the gases from the explosion escape into the atmosphere, the gas molecules can expand much more in the upper atmosphere layers.

[2]

Turn over

6 (a) (i) At 15 km,

$$\ln \frac{0.101325}{P_2} = 0.119(15)$$

$$P_2 = 0.017002 \text{ MPa}$$

$$P_2 - P_0 = 3595 \times \ln \left(\frac{T_2}{T_0} \right)$$

$$0.017002 - 0.101325 = 3595 \times \ln \left(\frac{T_2}{273} \right)$$

$$T_2 = 272.99 = 273 \text{ K}$$

Hence, the melting temperature of ice remains relatively constant in the troposphere.

[2]

(ii) $6.5x = 31$

$$x = 4.77 \text{ km}$$

[1]

(b) (i) Structure B.

(Tetrahedral arrangement of Γ^- about each Ag^+)

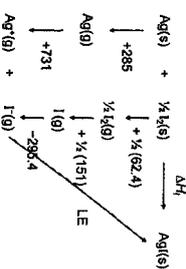
[1]

$$\text{(ii) Mass of AgI} = \frac{2}{6.02 \times 10^{23}} (107.9 + 126.9) = 7.801 \times 10^{-22} \text{ g}$$

$$\text{Density} = \frac{7.801 \times 10^{-22}}{(0.466 \times 10^{-7})^2 \times 0.755 \times 10^{-7}} = 4.758 = 4.76 \text{ g cm}^{-3}$$

[2]

(c)



$$-62 = +285 + 731 + \frac{1}{2}(62.4) + \frac{1}{2}(151) - 295.4 + \text{LE}$$

$$\text{LE} = -899.3 = -899 \text{ kJ mol}^{-1}$$

[3]

Commented [rev2]: should be rev2: 28

- (d) (i) I^- is a large anion/large electron cloud and is polarised by Ag^+ ion which results in the ionic bond in AgI having some covalent character, causing the experimental value to deviate from the theoretical value of lattice energy.

F^- ion is a small ion and is not easily polarised, hence AgF is essentially ionic (no covalent character). [1]

- (ii) Low solubility of AgI.

$$\Delta H_{hyd} = -LE + \Delta H_{hyd}$$

$$\frac{|\Delta H_{hyd}|}{LE} < \frac{|\Delta H_{hyd}|}{LE}$$

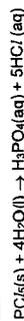
high magnitude of LE or strong electrostatic force of attraction of attraction between Ag^+ and I^- or presence of covalent character in ionic bond which causes LE to be larger in magnitude, coupled with the low magnitude of enthalpy change of hydration of I^- , causing the enthalpy change of solution of AgI is likely to be positive, making the solute less likely to dissolve at surface temperature. [2]

[Total: 12]

Paper 3

- 1 (a) $MgCl_2$ undergoes hydration/dissolve readily in water followed by slight hydrolysis because Mg^{2+} has a relatively high charge density and is able to polarise the water molecules/weaken O-H bond in water molecules, resulting in breakage of O-H bond to form H_3O^+ . The pH of the solution is 6.5.
- $$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$$
- $$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$$

PCl_5 undergoes complete hydrolysis to give a strongly acidic solution. The pH of the solution is 2.



The thermal stability of hydrogen halides decreases from HCl to HI.

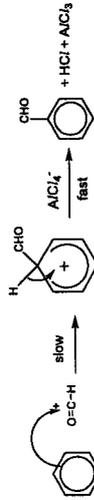
The size of the halogen atoms increases from Cl to I and their valence orbitals become more diffuse. This results in less effective overlap of the orbitals between the small H atom and the larger halogen atom and less energy is required to break the weaker H-X bond.

- (c) Substitution reaction allows the benzene ring to retain its stable delocalised π electron system. However, addition reaction will cause the benzene to lose its aromaticity.

- (d) (i) An electrophile is an electron-pair acceptor and it is electron-deficient.

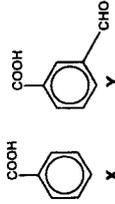
- (ii) CO: Lewis base/ Bronsted-Lowry base
 $AlCl_3$: Lewis acid

- (iii) electrophilic substitution



- (iv) Step 1 : acidified $KMnO_4$, heat under reflux

Step 2 : CH_3Br , anhydrous $AlBr_3$



- (e) $B > A > C$

B hydrolyses most rapidly as the carbonyl C atom is the most electron-deficient as it is bonded to electronegative atoms of O and Br. Hence, the δ^+ charge on this C atom will attract water molecules (nucleophile) most strongly and undergoes hydrolysis most readily.

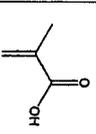
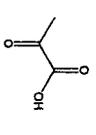
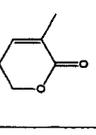
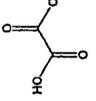
A hydrolyses less readily than **B** as there is significant steric hindrance by the methyl group/methyl group which is electron-donating will increase the electron density in benzene and reduce the δ^+ charge on this C atom on the carbonyl atom, so **A** undergoes hydrolysis less readily.

C is least easily hydrolysed as the lone pair of electrons on Br atom is delocalised into benzene ring as the p orbital on Br can overlap sideways with the π -electron cloud of benzene ring. This results in partial double bond character in C-Br bond in C_6H_5Br . Hence, C-Br bond is stronger in C_6H_5Br and is less susceptible to nucleophilic attack and hence bond cleavage of C-Br bond.

- 2 (a) MMA undergoes oxidation/oxidative cleavage [γ -1] in hot acidified $\text{KMnO}_4(\text{aq})$ to give F (only organic prod). MMA is a terminal alkene.
 G undergoes oxidation (of C=C bond) [γ -1] and acid hydrolysis (of ester linkage) when treated with hot acidic $\text{KMnO}_4(\text{aq})$ to give F. G is an ester. G is an alkene.

F undergoes oxidation with $\text{I}_2/\text{OH}^-(\text{aq})$ to give G. F has . Yellow ppt is CHI_3 .

1 mole of H undergoes acid-metal reaction/ redox with Na to give 1 mole of H_2 gas. G has 2 $-\text{COOH}$ groups.

MMA		F		G		H	
-----	--	---	--	---	--	---	--



$= -\Delta G / (n \times F)$

$= -92840 / (2 \times 9.65 \times 10^4) = -0.48 \text{ V}$

Minimum voltage = $-0.48 + 0.70 = 1.18 \text{ V}$

- (ii) The extra voltage is required for any of the following:

- Activation Energy: Reactions at the electrode surface require overcoming activation energy barriers for electron transfer and bond breaking/formation, necessitating extra voltage.
- Mass Transport: Ions need to move from the bulk solution to the electrode surface and vice versa, which can be hindered by diffusion and other factors, contributing to overvoltage.
- Concentration polarisation: The concentration of reactants near the electrode surface changes during electrolysis, creating a concentration gradient and requiring additional voltage to overcome.
- Gas evolution: If a gaseous product is formed at an electrode (e.g., during water electrolysis), overvoltage can arise from the energy needed to create gas bubbles at the interface.

Any logical answer.

- (d) (i) Amount of charge = $5.07 \times 2.0 \times 60 \times 60 = 36504 = 36500 \text{ C}$

- (ii) Amount of chromium = $\frac{6.56}{52} = 1.242 \times 10^{-1} \text{ mol}$

Amount of charge per mole of Cr = $\frac{36500}{0.1242} = 2.940 \times 10^5 \text{ C}$

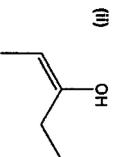
(3)(L) $(1.60 \times 10^{-19}) = 2.940 \times 10^5$

$L = 6.125 \times 10^{23} = 6.13 \times 10^{23}$

Electrode reaction	E^\ominus / V
$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	-2.38
$\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}$	-2.87
$\text{Ba}^{2+} + 2e^- \rightleftharpoons \text{Ba}$	-2.90

Down the Group, $E^\ominus(\text{M}^{2+}/\text{M})$ becomes more negative, oxidation of Group 2 metals becomes more spontaneous. Therefore, the reducing power of the Group 2 metals increases down the Group.

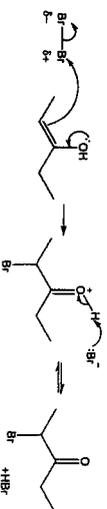
- 3 (a) (i) $\text{H}^+/\text{H}_3\text{O}^+$ provides an alternate reaction pathway with lower activation energy which speeds up the rate of reaction. It is regenerated at the end of reaction.



There is restricted rotation about the C=C bond.

- (iii) (Electrophilic) Substitution

(iv)



(b) (i) $[\text{C}_6\text{H}_5\text{CHO}] = \frac{0.212}{(12.0 \times 7 + 1.0 \times 6 + 16.0) \times 1000} = 0.0100 \text{ mol dm}^{-3}$

$[\text{NH}_4\text{Cl}] = \frac{10.7}{(14.0 + 1.0 \times 4 + 35.5) \times 1000} = 1.00 \text{ mol dm}^{-3}$

$$(ii) K_c = \frac{[\text{benzylimine}][\text{ammoniumchloride}]}{[\text{benzaldehyde}][\text{ammoniumchloride}]} \text{ mol}^{-1} \text{ dm}^3$$

	$\text{C}_6\text{H}_5\text{CHO}$	$+$	NH_4Cl	\rightleftharpoons	$\text{C}_6\text{H}_5\text{CH=NH}_2$	
I	0.01		1.00		0.00	
C	-8.80×10^{-3}		-8.80×10^{-3}		$+8.80 \times 10^{-3}$	
E	1.20×10^{-3}		0.9912		8.80×10^{-3}	

$$K_c = \frac{[\text{benzylimine}]}{[\text{benzaldehyde}][\text{ammoniumchloride}]} = \frac{0.80 \times 10^{-3}}{(1.20 \times 10^{-3})(0.9912)} = 7.398 \text{ mol}^{-1} \text{ dm}^3$$

(iii) At higher pH, $[\text{H}^+(\text{aq})]$ decrease, position of equilibrium of $\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}^+(\text{aq})$ shift to the right to increase $[\text{H}^+(\text{aq})]$. $[\text{NH}_4^+(\text{aq})]$ decrease / $\text{NH}_4^+(\text{aq})$ deprotonates to form $\text{NH}_3(\text{aq})$.
Position of equilibrium of step 1 shift to the left to increase $[\text{NH}_4^+(\text{aq})]$, yield decrease.

(c) (i) Using expt 1 and 2,

$$8.40 \times 10^{-5} = \frac{(0.4)^w}{6.30 \times 10^{-5}} = \frac{(0.3)^y}{(0.3)^y}$$

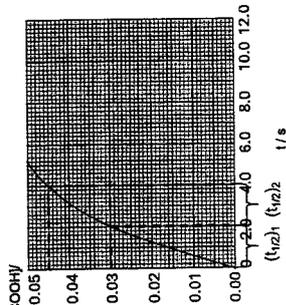
$$W = 1$$

Using expt 2 and 3,

$$6.30 \times 10^{-5} = \frac{(0.2)^z(0.3)}{2.10 \times 10^{-5}} = \frac{(0.1)^z(0.1)}{(0.1)^z(0.1)}$$

$$Z = 0$$

(ii) Since $1 \text{ C}_6\text{H}_5\text{CHO} \rightleftharpoons 1 \text{ NH}_4^+ \rightleftharpoons 1 \text{ CN}^- \rightleftharpoons 1 \text{ H}_3\text{O}^+$
 NH_4^+ is the limiting reagent
Thus, $[\text{phenylglycine}]_{\text{max}} = [\text{NH}_4^+]_{\text{initial}} = 0.0600 \text{ mol dm}^{-3}$



Constant half life where $t_{1/2} = 2s$. Working lines on graph.
Reaction is first order wrt $[\text{NH}_4^+]$

(iii) Since initial $[\text{C}_6\text{H}_5\text{CHO}]$ and initial $[\text{H}_3\text{O}^+]$ are in large excess, reaction is only dependent on $[\text{NH}_4^+]$ and $[\text{CN}^-]$. Reaction is also dependent on $[\text{NH}_4^+]$.

The reaction is a overall pseudo second order reaction / not overall first order reaction and thus half lives is not constant. The reaction is first order with respect to $[\text{NH}_4^+]$ and first order with respect to $[\text{CN}^-]$.

(iv) $k' = k [\text{C}_6\text{H}_5\text{CHO}] [\text{CN}^-]$

(v) $t_{1/2} = \ln 2 / k'$

$$k' = 0.3466$$

$$0.3466 = k (0.600)^2$$

$$k = 0.9629 \text{ mol}^2 \text{ dm}^{-3} \text{ s}^{-1}$$

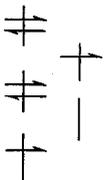
Allow calculation using initial rate with tangent drawn at $t=0s$.

(vi) Step 2.

$$\text{Rate} = k [\text{CN}^-] [\text{intermediate}]$$

$$\text{Rate} = k [\text{CN}^-] [\text{benzaldehyde}] [\text{NH}_4^+]$$

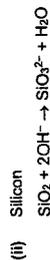
Step 2 involve one CN^- and one imine intermediate. The imine intermediate was form in step one from benzaldehyde and NH_4^+ .
This results in rate equation $\text{Rate} = k [\text{C}_6\text{H}_5\text{CHO}] [\text{CN}^-] [\text{NH}_4^+]$ which matches from the experimentally derived rate equation from (c)(i) to (v).

- 4 (a) (i) The electron configuration of Fe^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$. In the presence of H_2O or O_2 ligands, the 3d orbitals are split into 2 sets of non-degenerate orbitals with different energies. The difference in energies (ΔE) between these 2 sets of 3d orbitals is small and lies within the visible region of the electromagnetic spectrum. Radiation from the visible region of the electromagnetic spectrum is absorbed when an electron moves from a lower energy d-orbital to another unfiled/ partially-filled d orbital of higher energy. The colour observed (red) is the complement of the colours absorbed (green). Hence, haemoglobin is coloured.
- (ii) Electrons usually occupy orbitals singly to minimise/reduce repulsion between two electrons occupying the same orbital.
- (iii) The electrons would only pair up in the lower energy d-orbitals (low spin state). If the energy gap, ΔE , was larger than the energy due to electron repulsion / pairing energy. Hence, (low-spin) oxyhaemoglobin would have the larger energy gap.
- (iv) 
- Any arrangements of electrons, as long as:
for upper set - 1 half-filled orbital and 1 empty orbital
for lower set - 2 fully-filled orbital and 1 half-filled orbital
- (b) (i) Transition metal ions have energetically accessible/low-lying, vacant/empty (3d and 4s) orbitals that can accept the lone pair of electrons from the ligands to form complexes.
- (ii) Reduction involves addition of electrons. It is energetically easier to add an electron to the positively charged $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ than the negatively charged $\text{Fe}(\text{CN})_6^{2-}$ complex so that the standard reduction potential of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is higher.
OR
 CN^- is a stronger ligand than H_2O , so it will stabilise the Fe^{3+} more in the $\text{Fe}(\text{CN})_6^{2-}$ complex give rise to a more stable $\text{Fe}(\text{CN})_6^{2-}$. Reduction is less favourable, E^\ominus is less positive.
- (iii) Add aqueous potassium iodide (followed by starch) to two test-tubes, one containing $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and the other containing $\text{Fe}(\text{CN})_6^{3-}$.

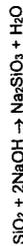
- (Without starch). A brown solution (of iodine) is formed for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ but not for $\text{Fe}(\text{CN})_6^{3-}$.
(With starch): A blue-black colouration is observed for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ but not for $\text{Fe}(\text{CN})_6^{3-}$.
 $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is strong enough an oxidising agent to oxidise iodide ions to iodine but $\text{Fe}(\text{CN})_6^{3-}$ is too weak an oxidising agent to oxidise iodide ions to iodine.
 $E^\ominus_{\text{cell}} = +0.77 - +0.54 = +0.23 \text{ V}$ for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$
 $E^\ominus_{\text{cell}} = +0.36 - +0.54 = -0.18 \text{ V}$ for $\text{Fe}(\text{CN})_6^{3-}$.
Possible alternative species: H_2O_2 ($E^\ominus(\text{O}_2/\text{H}_2\text{O}_2) = +0.68 \text{ V}$), MnO_4^{2-} ($E^\ominus(\text{MnO}_4^-/\text{MnO}_4^{2-}) = +0.56 \text{ V}$)
- (c) (i) Let the solubility of iron(II) phosphate be x.
 $\text{Fe}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3\text{Fe}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq})$
 $K_{\text{sp}} = [\text{Fe}^{2+}]^3[\text{PO}_4^{3-}]^2$
 $= (3x)^3(2x)^2$
 $= 108x^5 = 1.07 \times 10^{-29}$
Solubility of iron(II) phosphate = $6.33 \times 10^{-7} \text{ mol dm}^{-3}$
- (ii) $\text{FeS}(\text{s}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$
 $K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^{-}]^2$
 $4.87 \times 10^{-17} = [\text{Fe}^{2+}](0.200)^2$
 $[\text{Fe}^{2+}] = 1.218 \times 10^{-16} \text{ mol dm}^{-3}$
When $\text{Fe}(\text{OH})_2$ starts to precipitate, $[\text{Fe}^{2+}] = 1.218 \times 10^{-16} \text{ mol dm}^{-3}$
To find out $[\text{S}^{2-}]$ present,
 $6.00 \times 10^{-18} = 1.218 \times 10^{-16} [\text{S}^{2-}]$
 $[\text{S}^{2-}] = 4.928 \times 10^{-3} \text{ mol dm}^{-3}$
 $= 4.93 \times 10^{-3} \text{ mol dm}^{-3}$
- (iii) Add aqueous NaOH until in excess to both solutions.
While ppt of $\text{Al}(\text{OH})_3$ formed dissolves in excess NaOH to form a colourless solution and green ppt $\text{Fe}(\text{OH})_3$ remains insoluble.
 $\text{Al}(\text{OH})_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$ — equation 1
When excess OH^- is added, complex formation takes place.
 $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{Al}(\text{OH})_4^-(\text{aq})$ [1]
Addition of excess OH^- shifts the position of equilibrium of equation 1 to the right, causing the precipitate to dissolve.

27

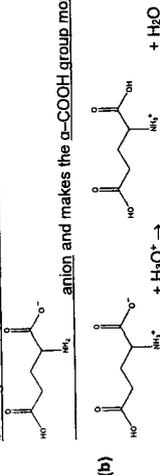
- (d) (i) Melting points increases from Na, Mg to Al.
Na, Mg and Al have giant metallic lattice structures.
As the number of delocalised valence electrons increases from Na to Al, the cationic charge increases, cationic radius decreases (charge density increases). A large amount of energy is required to overcome the stronger electrostatic attraction between the positively-charged metal ions and the sea of delocalised valence electrons (metallic bonds).
- Melting point of Si is the largest as Si has a giant covalent structure. A large amount of energy is required to overcome with strong covalent bonds between Si atoms.
- Melting point decreases sharply to P, and melting point remains low from P to Cl.
- Phosphorus, sulfur and chlorine have simple covalent structures. Sulfur exists as S₈ molecules, phosphorus as P₄ molecules and chlorine as Cl₂ molecules.
- As the number of electrons in S₈ molecule > P₄ molecule > Cl₂ molecule, the stronger instantaneous dipole-induced dipole interactions between the molecules. Therefore, melting point of S₈ molecules is the strongest, followed by that between P₄ molecules, and then that between Cl₂ molecules.



OR



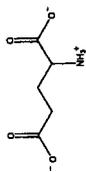
- 5 (a) The α -COOH group has the lower pK_a value as the electronegative/ electron-withdrawing N atom is closer to the COO⁻ and hence disperses the negative charge more effectively/ stabilise through intramolecular hydrogen bonding between -NH₂ and -COO⁻. Hence this stabilises the



- (b) _____ anion and makes the α -COOH group more acidic.

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- (c) (i) Species present when 40.00 cm³ of NaOH was added:



The solution at point A is a buffer consisting of

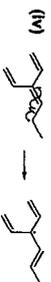
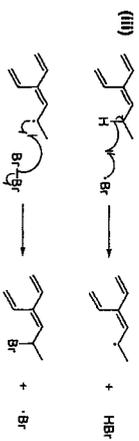


$$\begin{aligned} \text{Amount of weak acid} &= \left(\frac{10}{1000} \times 0.200\right) - \left(\frac{5}{1000} \times 0.100\right) \\ &= 1.50 \times 10^{-3} \text{ mol} \end{aligned}$$

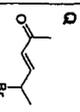
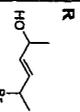
$$\text{Amount of salt} = \frac{5}{1000} \times 0.100 = 5.00 \times 10^{-4} \text{ mol}$$

$$\begin{aligned} \text{pH} &= 9.67 + \log \frac{5.00 \times 10^{-4}}{1.50 \times 10^{-3}} \\ &= 9.19 \end{aligned}$$

- (ii) Maximum buffering capacity when pH = 9.67
 Volume of NaOH at pH = 9.67 is 50.00 cm³.
 Volume of NaOH to be added = 50.00 – 45.00 = 5.00 cm³
- (d) Glutamic acid exists as zwitterions in the solid state and has a giant ionic lattice structure. Octanoic acid has a simple molecular structure.
 More energy is needed to overcome the stronger electrostatic forces of attraction between the oppositely charged groups of the zwitterions than the hydrogen bonds between the octanoic acid molecules.
- (e) (i) sp² orbital in C has a greater s character (33 %) and the orbital is closer to the nucleus and requires more energy to break the bond homolytically.
-
- (ii) Energy from the bright light is needed to start the reaction for homolytic fission of Br-Br / by forming bromine radicals.



(v) Tertiary radical formed is most stable, as the electron deficient radical is stabilised by three electron-donating alkyl groups.

(f)	Q	Step II	R	Step III
		NaBH ₄ or LiAlH ₄ in dry ether		Na

