RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION

H2 CHEMISTRY 9647/03

Paper 3 Free Response

Suggested Answers

1ai ΔH_r = BE(bonds broken) – BE(bonds form)

= [12BE(N-H) + 3BE(O=O)] – [2(NΞN) + 12(O-H)]

= [12(+390) + 3(+496)] – [2(+994)+12(+460)]

= –1340 kJ mol^{-1}

1aii The calculated value differs from the theoretical value because the **bond energies given in the Data Booklet are only average energies.**

1aiii ΔS is expected to be **positive** as the reaction proceeds with an increase in disorder due to **increase in the number of gaseous molecules.**

ΔG = ΔH–TΔS, since **ΔS is positive and ΔH is negative, ΔG will always be a negative value.** Hence we can conclude that the given reaction is **spontaneous**.

1aiv **Increasing deviation: $N_2 < O_2 < NH_3 < H_2O$**

Deviation from ideal behaviour depends on the strength of intermolecular forces and number of electrons in the molecule. **Weak instantaneous dipole-induced dipole/van der Waals' forces exist between nitrogen molecules and between oxygen molecules. Strong hydrogen bonds exist between ammonia molecules and water molecules**.

Water shows more extensive hydrogen bonding than ammonia while oxygen has a larger electron cloud, and therefore stronger instantaneous dipole-induced dipole/van der Waals' forces than nitrogen.

1bi Haemoglobin consists of **four protein chain subunits: two α-chain subunits and two β-chain subunits, held by** non-covalent interactions between R groups: **ionic interactions, van der Waals' forces and hydrogen bonds.**

1bii Assuming oxygen is an ideal gas,

pV = nRT

$(98.7 \times 10^3)(3.06 \times 10^{-6}) = n(8.314)(37+273)$

$n = 1.172 \times 10^{-4}$ mol

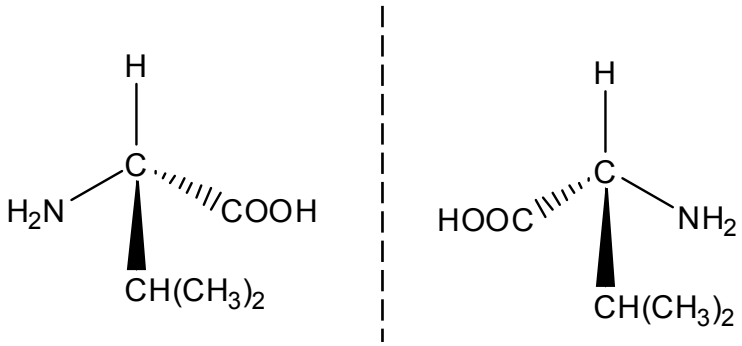
Amount of haemoglobin = n/4 = 2.930 x 10^{-5} mol

Molar mass of haemoglobin = 2.00/2.930 x 10^{-5} = 6.83 x 10^{4} g mol^{-1}

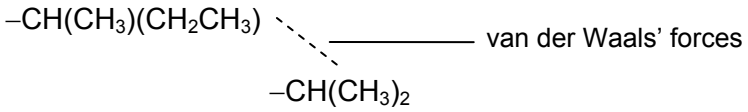
1biii **Oxygen is not an ideal gas.**

Intermolecular forces of attraction are present between oxygen molecules.

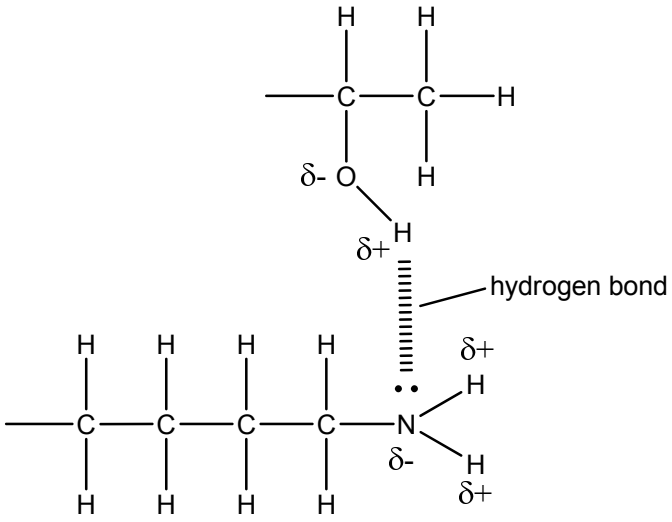
1ci Valine exhibits **optical isomerism.**



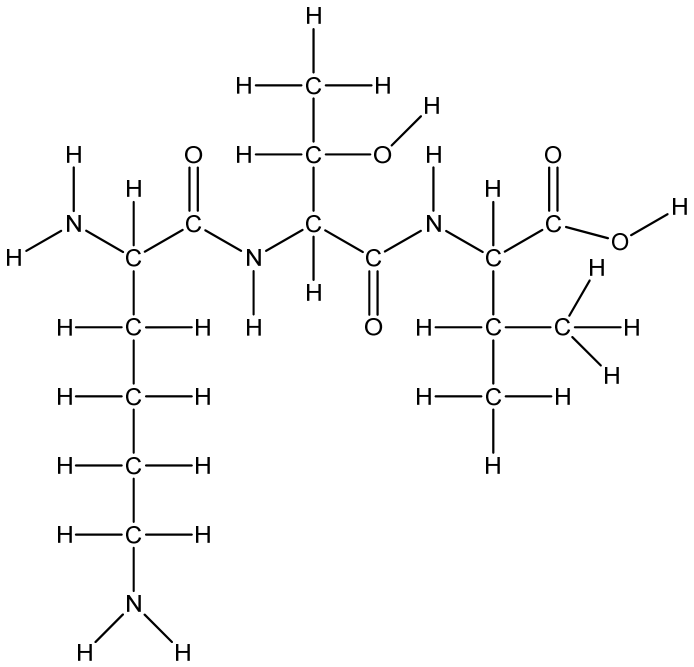
1cii **Van der Waals' forces** between ile, leu, met, phe, val (any two).



Hydrogen bonds between lys, thr, trp (any two).



1ciii



2a A is not soluble in acid : A is not basic. [✓]

Acid hydrolysis [✓] of A took place to give B and C. A is likely to be an ester [✓] while B is likely to be an alcohol. [✓]

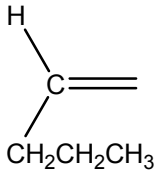
B rotates plane-polarized light. B has at least 1 chiral C. [✓]

B is oxidized [✓] by hot acidified $KMnO_4$ to give D, with the removal of 2 H in D. D is a ketone [✓] while B is a secondary alcohol. [✓]

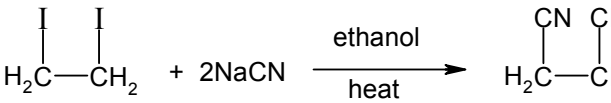
D gives a positive iodoform test [✓] with alkaline I_2: D is a methyl ketone [✓] while B is a methyl alcohol. [✓]

B undergoes dehydration [✓] with Al_2O_3 to give alkene E. [✓]

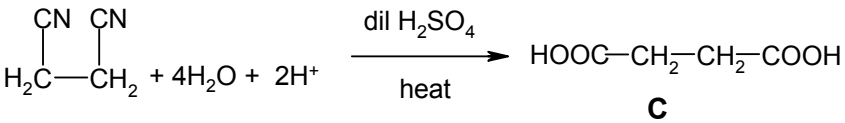
E undergoes oxidative cleavage to give butanoic acid. E contains a fragment with structure.



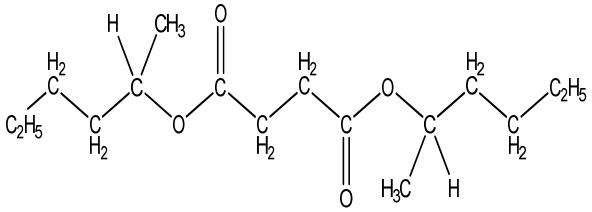
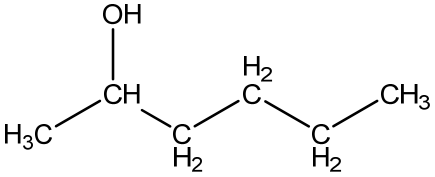
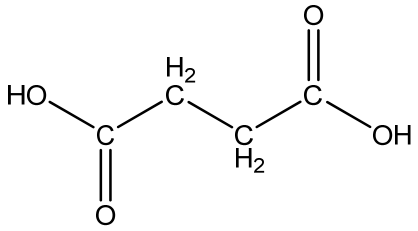
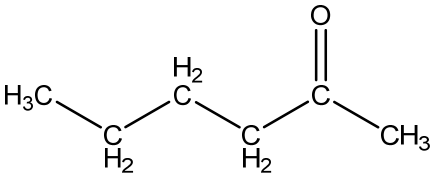
[✓]

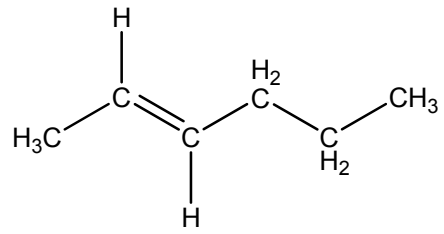


[✓]



C [✓]

	
A	B
	
C	D



E

2bi Concentration of $(R_3NH)^+$ = 0.20 mol dm^{-3}

$R_3NH^+ \rightleftharpoons R_3NH + H^+$

Let concentration of H^+ at eqm be x mol dm^{-3}

$x^2 / (0.20 - x) = K_w / 1.62 \times 10^{-6}$

Solving, $x = 3.514 \times 10^{-5}$ mol dm^{-3}

pH = -lg x = 4.45

2bii At equivalence point, only R_3N is present.

$R_3N + H_2O \rightleftharpoons R_3NH + OH^-$

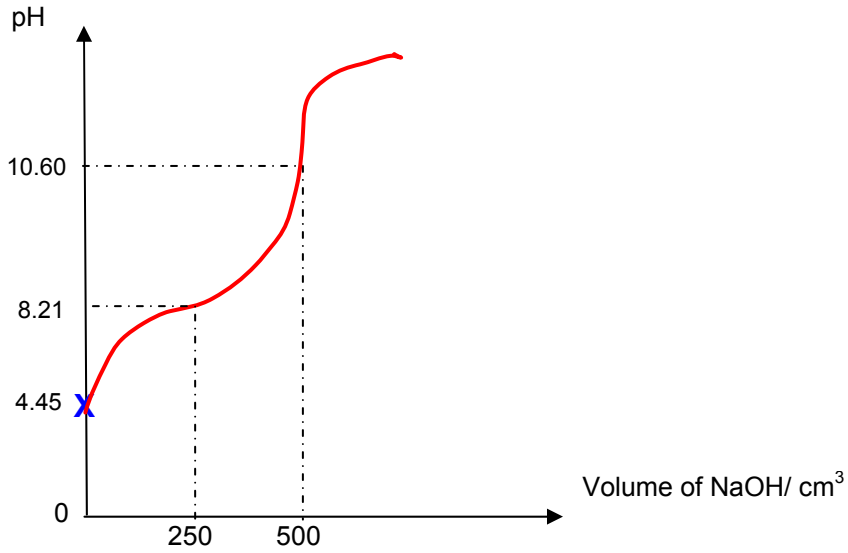
Let concentration of OH^- at eqm be y mol dm^{-3}

$y^2 / (0.1 - y) = 1.62 \times 10^{-6}$

Solving, $y = 4.025 \times 10^{-4}$ mol dm^{-3}

pOH = -lg y = 3.40, pH = 14.0 – 3.40 = 10.60

2biii

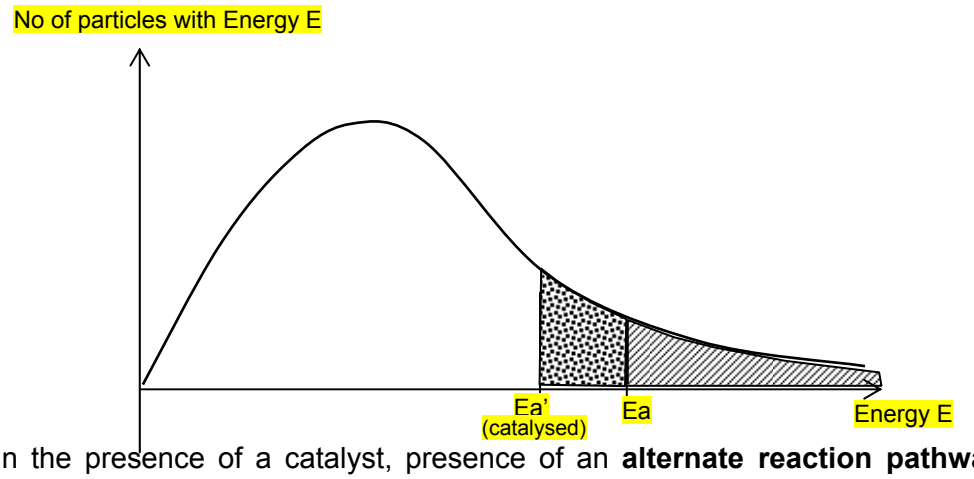


1 mark for correct shape with correctly labeled axes.

1 mark for initial pH and pH at equivalence point. ECF.

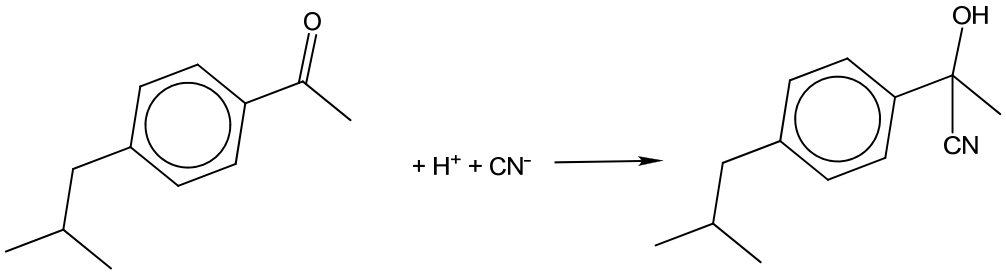
1 mark for showing pH at maximum buffer capacity at 250 cm^3 of NaOH added.

2c



In the presence of a catalyst, presence of an **alternate reaction pathway with lower Ea. [✓] Greater proportion of particles will possess the minimum amount of energy, [✓]** Ea, for a successful collision to occur. **Frequency of effective collisions increases[✓]** , rate of reaction increases.

3ai



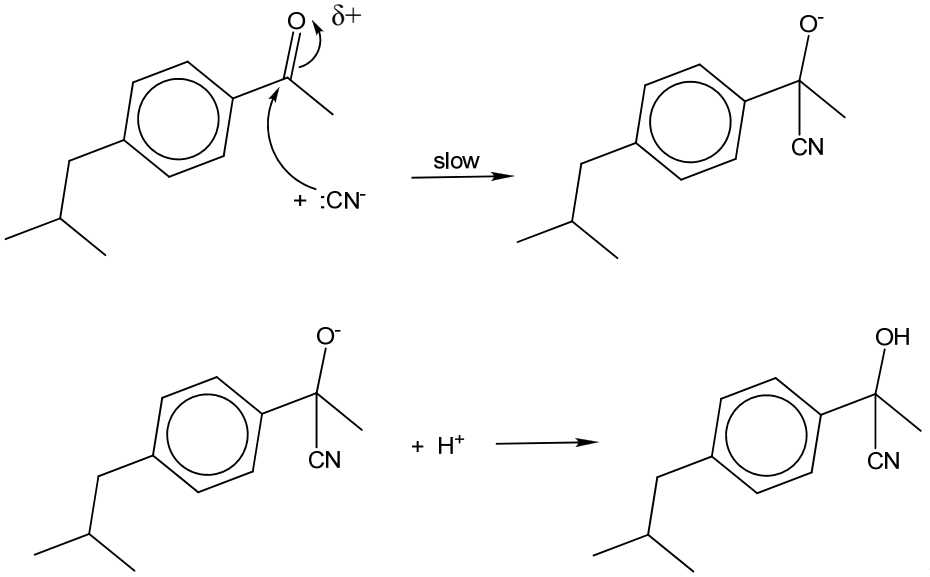
3aii Comparing Expt 1 and 3: initial rate of formation of **B** remained unchanged when only [H^+] was changed. The reaction is zero order with respect to H^+.

Comparing Expt 2 and 4: When [**A**] increased to 1.25 times while [H^+] and [CN^-] were unchanged, initial rate of formation of **B** increased to 1.25 times. The reaction is first order with respect to **A**.

Comparing Expt 2 and 3: When [CN^-] increased to 1.2 times while [H^+] and [**A**] were unchanged, initial rate of formation of **B** increased to 1.2 times. The reaction is first order with respect to CN^-.

3aiii Rate = k[**A**][CN^-]

3aiv



Since H+ does not appear in rate equation, it is not involved in slow/r.d. step. / Only 1 CN^- and 1 A is involved in the r.d.s/slow step as indicated by their order of reaction in the rate equation. [1]

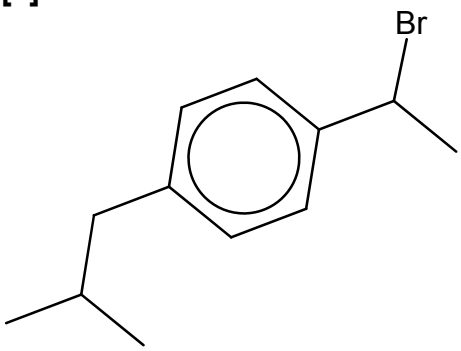
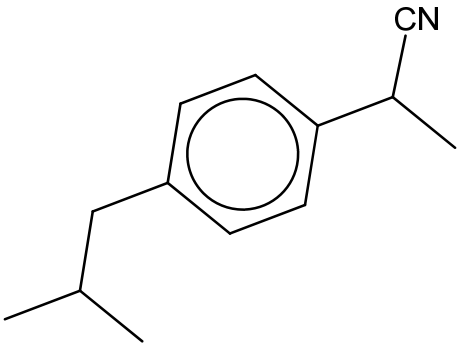
Or

Step I involve breaking of **π bond of C=O**, which involved **higher Ea** compared to Step II.

3b **Step 1**: HX(g) (X= C*l*, Br, X) **[1]**

Step 2: alcoholic KCN/ NaCN, heat (under reflux) **[1]**

Step 3: dilute H_2SO_4, heat (under reflux) **[1]**

Intermediate from step 1 **[1]**	Intermediate from step 2 **[1]**
	

3ci

	Ibuprofen	+	propanol	=	ester	+	water
Initial amt	0.00500		0.500		0		0
Change	- 0.00230		- 0.00230		+ 0.00230		+ 0.00230
Eqm amt	0.00270		0.498		0.00230		0.00230

$$K_c = \frac{(\frac{0.00230}{V})(\frac{0.00230}{V})}{(\frac{0.00270}{V})(\frac{0.498}{V})}$$

$$= 0.00393$$

3cii When temperature is increased, the proportion of ibuprofen reacted decreased. The **equilibrium position shifted to the left to absorb some of the energy**.

Since **increased in temperature favours endothermic reaction**, the forward reaction is **exothermic**.

3ciii **Propanol is very volatile/ evaporates rapidly** at higher temperature.

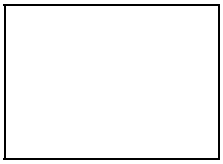
(The equilibrium position is shift to the left to replenish some of the propanol lost. Therefore, a smaller proportion of ibuprofen reacted to form ester.)

3civ **In the original experiment, t**he **equilibrium position is shift to the left to consume some of the water** added. Therefore, a smaller **proportion ibuprofen reacted** in the original experiment.

KOH (aq), an alkali, **neutralized some of the sulfuric acid which is the catalyst** for the reaction. Equilibrium is established at a **slow rate/less negative gradient** than the original.

4ai Disproportionation (Reject wrong spelling)

$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

4aii 

Trigonal pyramidal

4bi

Element	K	Br	O
Mass ratio	23.4	47.8	28.8
Mole ratio	$\frac{23.4}{39.1} = 0.598$	$\frac{47.8}{79.9} = 0.598$	$\frac{28.8}{16} = 1.8$
Simplest ratio	1	1	$\frac{1.8}{0.598} = 3.01 \approx 3$

Formula of solid is $KBrO_3$

4bii $n_{KBrO_3} = \frac{0.835}{167} = 0.00500$ mol

$n_{PbCl_2} = \frac{4.17}{278} = 0.0150$ mol

$\frac{n_{KBrO_3}}{n_{PbCl_2}} = \frac{0.00500}{0.0150} = \underline{\frac{1}{3}}$

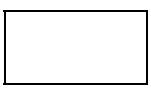
4biii $3Cl_2 + KBr + 6KOH \rightarrow 6KCl + KBrO_3 + 3H_2O$

4ci pK_a of 3-chloropropanoic acid will be <u>lower</u> than 4.87/that of propanoic acid.

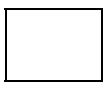
3-chloropropanoic acid is a <u>stronger acid</u> [✓] than propanoic acid because the <u>electron-withdrawing Cl atom</u> [✓] <u>disperses the negative charge on the COO^- group</u> [✓], making the <u>3-chloropropanoate ion more stable</u> [[✓] than the propanoate ion.

4cii After 20 cm^3 of NaOH added, V_{total} = 20 + 50 = 70 cm^3 = 70 × 10^{-3} dm^3

[3-chloropropanoic acid] =  = 0.257 mol dm^{-3}

[3-chloropropanoate ions] =  = 0.0286 mol dm^{-3}

Using the Henderson-Hasselbalch equation,

pH = pK_a + log  = 3.03

$pK_a = 3.03 - \log$ [ ] = 3.98

4ciii A buffer solution is one that can resist a change in pH when a small amount of acid or base is added to it.

$CH_2ClCH_2COO^- + H^+ \rightarrow CH_2ClCH_2COOH$

4cv [ ]

4cvi 2-chloropropanoic acid is a stronger acid [✓] than 3-chloropropanoic acid because the electron-withdrawing C*l* atom is closer to the COO^- group [✓] and disperses the negative charge on the COO^- group more effectively [✓], making the 2-chloropropanoate ion more stable [✓] than the 3-chloropropanoate ion.

5a Zinc does not form **stable ions with incompletely filled d orbitals.** [1]

5bi Transition metals and their compounds have a strong tendency to form complexes due to:

Presence of incomplete or vacant d orbitals to accept lone pair of electrons from a ligand

High charge density of transition metal ions to attract lone pair of electrons from the ligand which favours dative covalent bond formation.

5bii Aqueous copper (II) sulfate is a **blue solution**, $Cu(H_2O)_6^{2+}(aq)$.✓

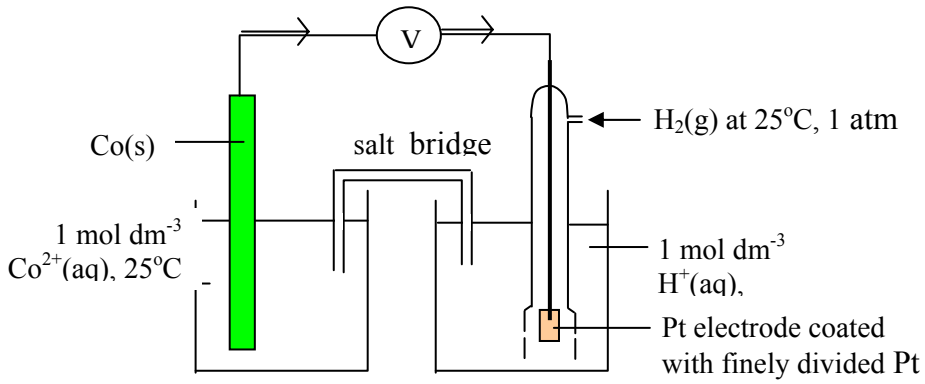
When aqueous ammonia is added to copper (II) sulfate, a pale **blue precipitate** of $Cu(OH)_2(s)$ is formed. ✓

On addition of excess ammonia, the precipitate dissolves to form a **deep blue solution,** $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$.✓

$Cu(H_2O)_6^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s) + 6H_2O(l)$

$Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq)$

5c



5d $E°(Co^{3+}/Co^{2+}) = +1.82V$

$E°(O_2/H_2O) = +1.23V$

$E°(\ C\mathit{l}_2/C\mathit{l}^-) = +1.36V$

$E_{cell} = +1.82 - 1.23 = 0.59V$ (energetically feasible)

Co^{3+} would oxidise water to oxygen.

OR

$E_{cell} = +1.82 - 1.36 = 0.46V$ (energetically feasible)

Co^{3+} would oxidise $C\mathit{l}^-$ to chlorine.

5e $E°(Co^{3+}/Co^{2+}) = +1.82V$

$E°(Co^{2+}/Co) = -0.28V$

$E°(H_2O_2/H_2O) = +1.77V$

$E°(O_2/H_2O_2) = +0.68V$

$E°(\ C\mathit{l}_2/C\mathit{l}^-) = +1.36V$

E_{cell} = +1.77 – 1.36 = 0.41V >0 (energetically feasible)

$H_2O_2(aq) + 2H^+ + 2Cl^-(aq) \rightarrow H_2O(l) + Cl_2(g)$

Yellowish-green gas Cl_2 is observed.

5fi Test

Add alkaline $I_2(aq)$ and heat. [1]

Observations

Pale yellow ppt formed for $CH_3CH(OH)CH_2CH_3$

No yellow ppt formed for $CH_3CH_2CH_2CH_2OH$ [1]

5fii Test

Add $Br_2(aq)$ [1]

Observations

Reddish brown bromine decolourised for $CH_3CH_2CH_2CH_2CH=CH_2$ but not for $CH_3CH_2CH_2CH_2CH_2CHO$ [1]

Tollens

Fehlings

2,4 DNPH

acidified potassium dichromate