Innova JC Preliminary Examination H2 Chemistry
Paper 2 Mark Scheme

1(a) E_{cell} betw Cu & VO_3^- = +1.00 – (+0.34) = +0.66V >0
(energetically feasible)
E_{cell} betw Cu & VO^{2+} = +0.34 – (+0.34) = 0V
The reaction is in equilibrium. Hence, products and reactants are in equal proportion.
Cu can reduce VO^{2+} to V^{3+}.

Colour changes from: VO_3^- (yellow) to VO^{2+} (blue) to Blue green ($VO^{2+} + V^{3+}$)

Balanced equation:
$2\,VO_3^- + 8H^+ + Cu \rightarrow 2VO^{2+} + 4H_2O + Cu^{2+}$

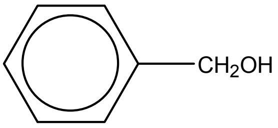
$2VO^{2+} + 4H^+ + Cu \rightarrow 2V^{3+} + 2H_2O + Cu^{2+}$

(b)(i) $CuSO_4(s)$ dissolves in water to give a blue solution containing $[Cu(H_2O)_6]^{2+}$ ions.
$Cu^{2+} + 6H_2O \rightarrow [Cu(H_2O)_6]^{2+}$

(ii) With excess $NH_3(aq)$, $CuSO_4(aq)$ gives a deep blue solution due to formation of soluble complex ion, $[Cu(NH_3)_4]^{2+}$.
$[Cu(H_2O)_6]^{2+} + 4NH_3 \Leftrightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$
Blue soln deep blue complex

NH_3 is a stronger ligand than water, so it can replace water from $[Cu(H_2O)_6]^{2+}$ to form $[Cu(NH_3)_4]^{2+}$.

(c)(i)



[1M]

(ii)
$CH_3CH_2OH + OH^- \rightarrow CH_3CH_2O^- + H_2O$ [1M]

(iii) The ✓nucleophile for compound G is OH^-.

Compound H: ✓nucleophile is $CH_3CH_2O^-$.

(iv) Test: add NaOH(aq) to each sample & heat.
Then add excess $HNO_3(aq)$, followed by $AgNO_3(aq)$.

Obs:
Compound F: white ppt of AgCl
Bromobenzene: no white ppt.

(d)(i) Reagents/conditions: PBr_3, heat
Or HBr, reflux.

(ii) Compound K: $(CH_3)_2CHCN$

Compound L: $(CH_3)_2CHCOOCH_2CH_3$

(e)(i) Discharging (using it as a galvanic cell)

Eqm (1)

$PbO_2(s) + 4H^+(aq) + 2e \Leftrightarrow Pb^{2+}(aq) + 2H_2O(l)$ +1.47V

Eqm (2)

$Pb^{2+}(aq) + 2e \Leftrightarrow Pb(s)$ –0.13V

Overall :

$PbO_2(s) + 4H^+(aq) + Pb(s) \rightarrow 2Pb^{2+}(aq) + 2H_2O(l)$

$E_{cell} = E^{\ominus}(PbO_2/Pb^{2+}) - E^{\ominus}(Pb^{2+}/Pb)$

= +1.47 – (–0.13)

= +1.60 V > 0 (energetically feasible)

(ii) $SO_4^{2-}(aq) + Pb^{2+}(aq) \rightarrow PbSO_4(s)$

The precipitation of $PbSO_4(s)$ reduced the $[Pb^{2+}(aq)]$ which caused eqm (1) to shift to the right, E_{red} (PbO_2/Pb^{2+}) is more positive than +1.47 V and eqm (2) to the left. E_{oxid} (Pb^{2+}/Pb) is more negative than –0.13 V.

As a result, the overall E_{cell} increases to 2.0 V.

2 (a)

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} \quad mol^{-1}\,dm^3$$

(b)

	$I^-(aq)$ +	$I_2(aq)$ $\rightleftharpoons$	$I_3^-(aq)$
Initial amt	**0.058**	**0.080**	**0**
Change	–0.0375	–0.0375	**+**0.0375
Eqm amt	0.0205	**0.0425**	+0.0375
Eqm conc	0.0205/0.5	0.0425 / 0.5	0.0375/0.5

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} = \frac{\left[\frac{0.0375}{0.5}\right]}{\left[\frac{0.0205}{0.5}\right]\left[\frac{0.0425}{0.5}\right]} = 21.5\ mol^{-1}\,dm^3$$

(c) (i) Amount of iodine in toluene layer = 0.0525 x 800/1000 = 0.042 mol

Amount of iodine in aqueous layer = 0.0425 – 0.042 = 5 x 10^{-4} mol

(ii)

$$\text{Partition coefficient} = \frac{[I_2 \text{ in toluene}]}{[I_2 \text{ in water}]} = \frac{(0.0525)}{\left(\frac{5\times10^{-4}}{500/1000}\right)} \text{ [1M] } = 52.5$$

(iii) Iodine is much more soluble in toluene than in water.
This is because iodine is a simple molecular compound which forms weak van der waals forces of attraction between the iodine molecules. It is able to form similar van der waals forces of attraction with the toluene molecule.

As iodine is not able to form hydrogen bonding or ion-dipole interaction with the water molecules, the solution of iodine will involve the breaking of stronger hydrogen bonding between the water molecules, hence it will be too endothermic for the reaction to occur.

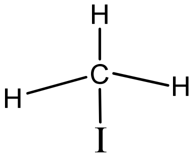
(d) (i) Pressure:
The pressure should be high to that equilibrium will shift to the right to form fewer gaseous molecules to reduce the pressure.

Temperature:
The temperature should be low so that the equilibrium will shift to the right to favour exothermic reaction, releasing the heat to increase the temperature.

(ii) Logical answers accepted e.g.:

- The products from step 1 can be easily fed into step 2 and reduce transport cost.
- The heat released from the exothermic step 2 reaction can be used to supply the heat energy required for endothermic step 1.

(e) **(i)**



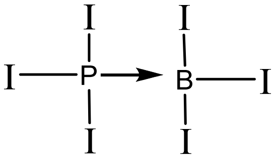
(ii)

$3CH_3OH + PI_3 \longrightarrow 3CH_3I + H_3PO_3$

To neutralise the acid, H_3PO_3 formed in the reaction.
Excess Na_2CO_3 will remain as suspension.

CH_3I will undergo nucleophilic substitution with NaOH to form back methanol.

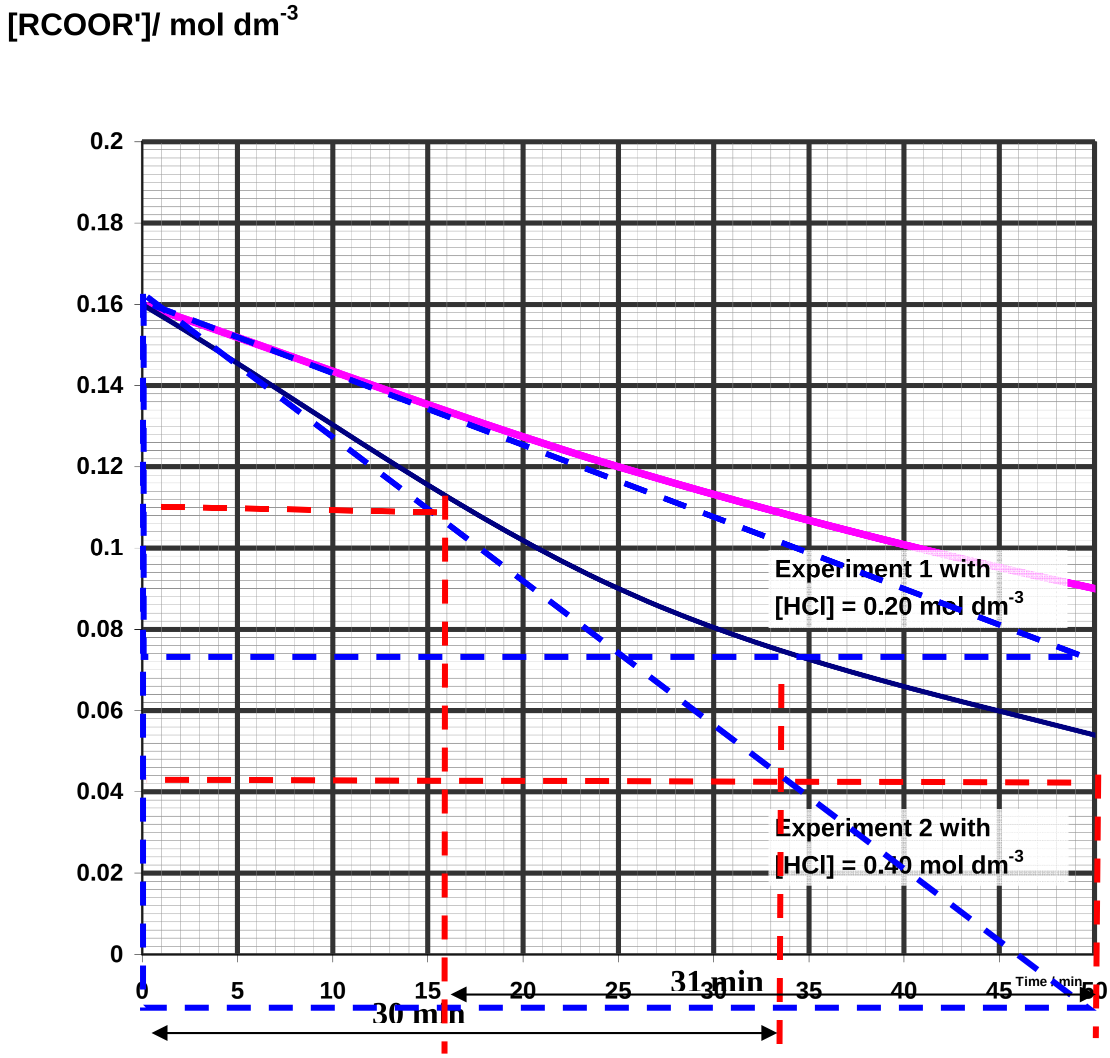
(ii)



[1M]

Tetrahedral about phosphorus atom.
A dative bond is formed between P and B atom. [½M]

3 (a)



(b) **(i)** Since the half lives for the hydrolysis of ester are relatively constant, 30 min and 31 min respectively, the reaction is first order with respect to RCOOR'

(ii) hydrochloric acid, HCl
Initial rate when [HCl] is 0.20 mol dm^{-3} = 1.777 x 10^{-3} mol dm^{-3} min^{-1}
Initial rate when [HCl] is 0.40 mol dm^{-3} = 3.556 x 10^{-3} mol dm^{-3} min^{-1}
When concentration of HCl doubles, initial rate of reaction increase by approximately 2 times, $\frac{3.556 \times 10^{-3}}{1.777 \times 10^{-3}}$.
Hence the reaction is first order with respect to HCl.

(iii)

Rate = k[RCOOR'][HCl]

using [H^{+}] = 0.20 mol dm^{-3}
k = 5.49 x 10^{-2} mol^{-1} dm^{3} min^{-1}

(c) The <u>hydrolysis of ester is a reversible process</u>, hence not 100% of the carboxylic acid is formed when the system reaches equilibrium.

(d)
- Lowers the activation energy (E_a) of the reaction. Hence, more reactant particles obtain energy > E_a. The frequency of effective collisions increases, hence the rate increases.
- The rate constant increases with arrhenius equation, $k = Ae^{-\frac{E_a}{RT}}$.

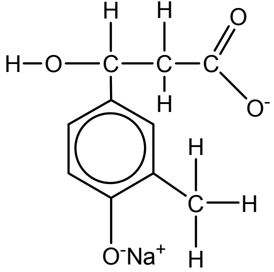
(e) **(i)** CH_3^+

(ii) Step II
Reagent: Br_2 in CCl_4
Condition: *uv l*ight

Step III
Reagent: $K_2Cr_2O_7$, Dilute H_2SO_4
Condition: Heat with distillation

Step IV
Reagent: Concentrated H_2SO_4
Condition: 170°C.

(iii) **Compound R**



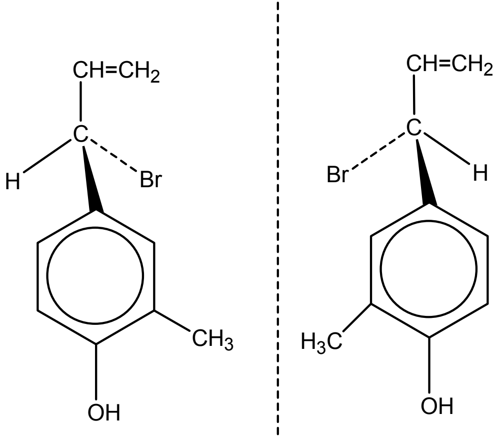
(iv) Free radical substitution

This reaction is not specific or very difficult to control the position of Br as it can be substituted to two different C atoms

In addition, other side products can be formed.
It can give rise to a mixture of mono-, di- or tri- substituted products from free radical sub **or**, electrophilic substitution is also possible with phenol.

(v) Test: add NaOH(aq) to each sample & heat.
Then add excess HNO_3(aq), followed by $AgNO_3$(aq).
Obs:
Compound Q: cream ppt of AgBr
Compound P: no cream ppt.

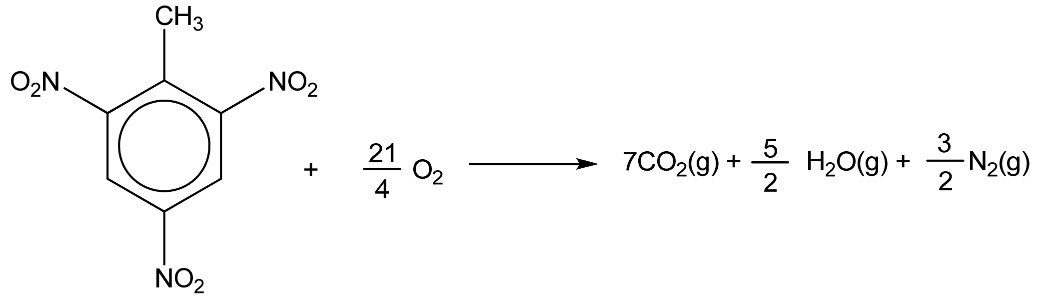
(vi)



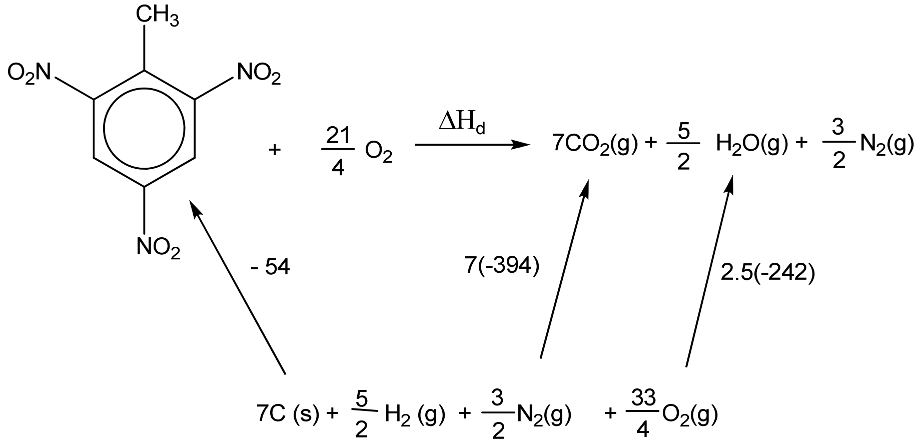
Optical isomerism

4 **(a)** Hess's law states that because enthalpy is a state function, the enthalpy change of a reaction is the same regardless of what pathway is taken to achieve the product.

(b)



(i)



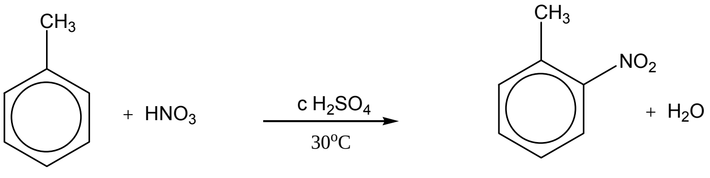
$\Delta H_d = 54 + 7(-394) + 2.5(-242) = -3310 \text{ kJ mol}^{-1}$

(ii) Heat lost to surrounding.

(iii) The number of gaseous molecules has increased after the reaction; the system has become more disordered. Thus entropy has increased and thus the sign of ΔS is positive. $\Delta G = \Delta H - T\Delta S$. Since ΔH is negative, and the term $-T\Delta S$ is negative thus ΔG is always negative. i.e. the reaction is always spontaneous.

(iv) The forward reaction is highly exothermic because the products are all stable molecules and thus have lesser energy than TNT.

(c) **(i)** Electrophilic Substitution.



Balanced equation

(ii) The reactivity of the ring decreases for every nitro group added. This is because $-NO_2$ group is an electron withdrawing group / deactivating group and will decrease the electron density of the benzene ring which makes it less susceptible to electrophilic attacks of subsequent $-NO_2$ groups.

(iii) Sn, conc HCl, reflux, followed by NaOH (aq)

(d) **(i)** $MCO_3 \rightarrow MO + CO_2$, where M is a Gp II element

Due to the smaller size of Mg^{2+} as compared to Ba^{2+}, Mg^{2+} has a higher charge density. The electron cloud of CO_3^{2-} ion is polarized to a greater extent by Mg^{2+}. Hence, the C–O bond in CO_3^{2-} is weaken and thus decomposes with greater ease and thus less energy is needed to decompose it.

(ii) Mg has no reaction with cold water. It reacts with steam to form oxide. MgO is not very soluble in water; hence it will only give weakly alkaline solution.

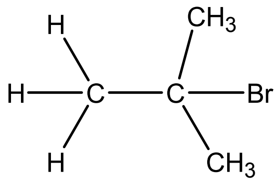
$Mg (s) + H_2O (g) \rightarrow MgO (s) + H_2(g)$

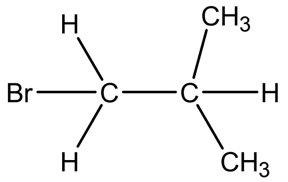
$MgO (s) + H_2O (l) \rightleftharpoons Mg(OH)_2 (s)$

Ca reacts vigorously with cold water to give hydroxides._Hence solution of $Ca(OH)_2$ is <u>more alkaline</u> than that of $Mg(OH)_2$ or illustrated by giving pH values.

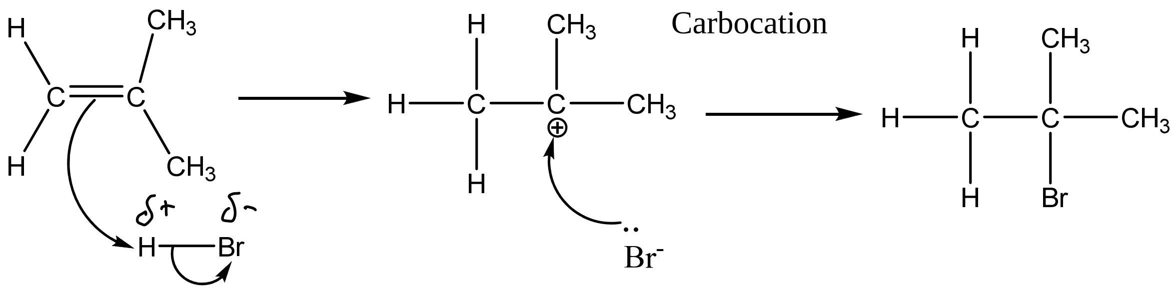
$Ca (s) + 2H_2O (l) \rightarrow Ca(OH)_2 (aq) + H_2 (g)$

5 **(a)** **(i)**

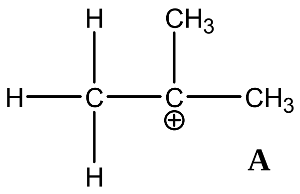




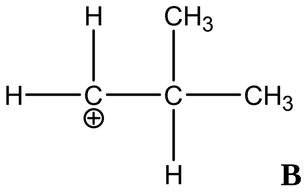
(ii) Electrophilic addition



(iii)



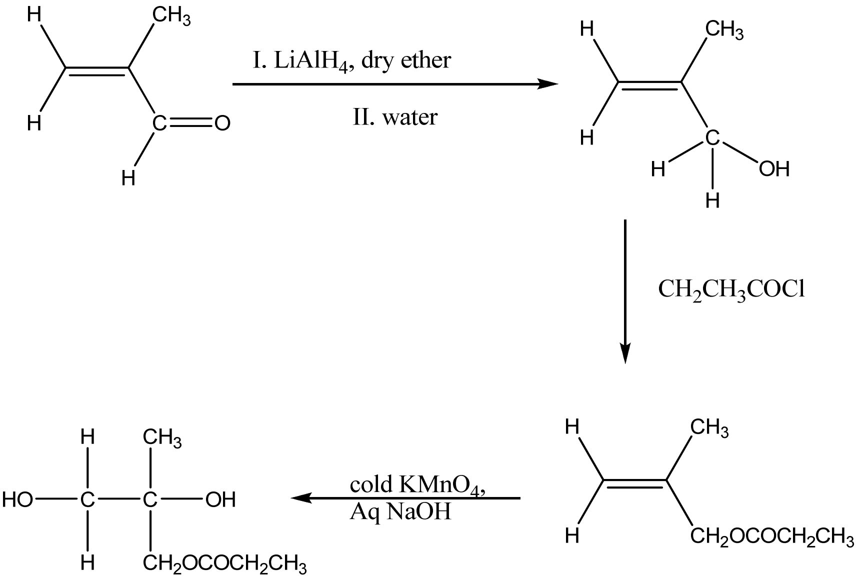
A



B

The carbocation A is more stable than carbocation B. This is because there are two electron R group ($-CH_3$) attached to the carbocation in A, OR hence deintensify the positive charge and stabilises it.

(b)



(c) **(i)** NaBr(s) + concH_2SO_4→ *HBr(g) + $NaHSO_4$(s)*

Some HBr is further oxidized:

2HBr(g) +concH_2SO_4→ *Br_2(g) +SO_2(g) +2H_2O(l)*

Orange-brown fumes of mixture of Br_2 and HBr produced

(ii) Hydrogen bromide is a stronger acid than hydrogen fluoride because the H-Br bond strength is weakerand the bond length is longer than the H-F bond. Hence, it requires less energy to overcomethe H-Br bond and dissociate into H^+ ionsin water.

(d) **(i)** SO_3 and SO_2 are simple molecules. SO_2 has permanent dipole-permanent dipole interactions whereas SO_3 has temporary induced dipole interactions. However, as SO_2 has much smaller molecular size and electron cloud than sulphur trioxide. The temporary dipole interactions outweighs the permanent dipole interactions. Hence the van der waals forces between SO_2 molecules is weaker than that of SO_3. Since less energy is needed to overcome the weaker intermolecular forces between SO_2 molecules, the melting point of SO_2 is lower.

(ii) This is because silicon chlorine is a simple molecular structure. It has weak van der waals forces as intermolecular forces of attraction between the molecules. SiO_2 is a giant covalent molecule, the atoms are held by strong and extensive covalent bonds . Less energy is needed to overcome the weaker van der waals forces, the melting point of $SiCl_4$ is lower.