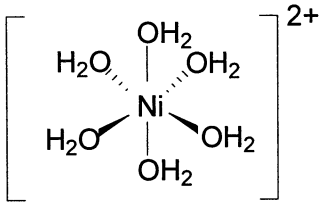
Unit Test 6245/01

1 (a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$ **(1 mark)**

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ **(1 mark)**

(b)



Shape mark
Must be 3-D ie wedges or dashes

(1)

labelled covalent between O-H *OR* arrow to H_2O and labelled covalent bond **(1)**
labelled dative covalent between O atom and ion **(1)** **(3 marks)**

(c) (i) $[Ni(H_2O)_4(OH)_2]$
ALLOW $Ni(OH)_2$ **(1 mark)**

(ii) Deprotonation **(1)**
two successive deprotonations / neutral species producing insoluble compound **(1)** **(2 marks)**

(iii) Ligand exchange **(1)**
giving (soluble) $[Ni(H_2O)_{0or\ 2}(NH_3)_{6or4}]^{2+}$ *OR in words* **(1)** **(2 marks)**

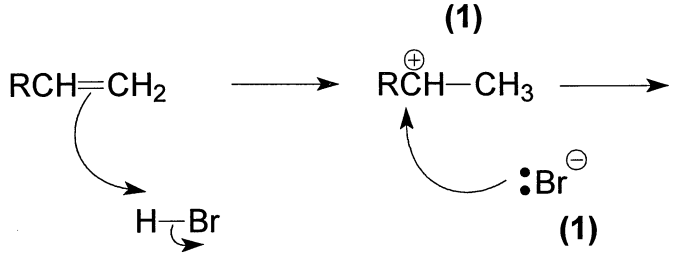
(Total 10 Marks)

---

2 (a) (i) Gas phase *or* inert solvent **(1)**
at r.t. **(1)** **(3 marks)**
$C_6H_5CH(Br)CH_3$ **(1)**

(ii)

(1)



(1)

(1) both arrows **(3 marks)**

(iii) Produced from the 2° carbocation which is more stable than the 1° **(1 mark)**

(b) (i) Nucleophilic substitution **(1 mark)**

(ii) C_6H_5COOH *NOT* $C_6H_5CO_2H$ **(1 mark)**

(iii) The product under alkaline conditions is the anion / salt and not the free acid. **(1 mark)**

(Total 11 Marks)

---

3 (a) (i) $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$
species **(1)**
balance **(1)** **(2 marks)**

(ii) starch **(1)**
blue / blue-black to colourless **(1)** **(2 marks)**

(b) double $[I_2]$ no change so zero order **(1)**
double $[Me_2CO]$ doubles rate so first order **(1)**
rate = $k[Me_2CO][H^+]$ **(1)** **(3 marks)**

(c) (i) Power to which concentration raised in rate equation
OR
the number of that species involved up to and including the rate determining step **(1 mark)**

(ii) Sum of the individual reaction orders *OR* sum of powers **(1 mark)**

(d) Iodine not involved in the rate determining step (**1**)
two **(1)***NOT* "more than 1" **(2 marks)**

(e) $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CH_3COONa + CHI_3 + 3NaI + 3H_2O$
CHI_3 **(1)**
other species **(1)**
balance **(1)** **(3 marks)**

(Total 14 Marks)

4 (a) (i) Use $E^{\ominus}$ values for reduction of Fe^{3+} to Fe^{2+} by Zn ($E^{\ominus}_{cell}$ = +1.53V)(**1**)
and Fe^{2+} to Fe by Zn ($E^{\ominus}_{cell}$ = +0.32V) **(1)**
They have positive $E^{\ominus}$ so are feasible **(1)***NOT* "will happen"
OR
ALLOW Zn^{2+}/Zn is more negative than both Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe (**1**)
so zinc is a stronger reducing agent **(1)**
so zinc reducing both is feasible **(1)** **(3 marks)**

(ii) Reduction of Fe^{2+} has high activation energy / kinetically stable **(1 mark)**

(b) (i) $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
Species **(1)**
Balance **(1)**
Any state symbols ignored. **(2 marks)**

(ii) purple colour of MnO_4^- lost **(1)**
end point when yellow / colourless solution **(1)**
becomes (permanently) pink **(1)** **(3 marks)**

(c) Amount MnO_4^- in 1st titration = 0.0182 dm^3 × 0.0200 mol dm^{-3}
= 3.64×10^{-4} mol **(1)**

Amount Fe^{2+} in original solution = 5× above value = 1.82×10^{-3} mol **(1)**

Amount Fe^{2+} in 2nd titration = amount of Fe^{2+} and Fe^{3+} original solution **(1)**

= 0.0253 dm^3 × 0.0200 mol dm^3 × 5 = 2.53×10^{-3} mol

Amount of Fe^{3+} in original solution = 0.00253 – 0.00182 = 7.10×10^{-4} mol **(1)**

Amount zinc needed to reduce Fe^{3+} = ½ ×0.000710 = 0.000355 mol
Mass of zinc = 0.000355 mol × 65.4 g mol^{-1} = 0.0232 g (1) 2,3 or 4 SF
Consequential on their moles iron

The marks are for the following processes:

Either volume of MnO_4^- to moles of MnO_4^- **(1)**

Convert to moles of Fe^{2+} by multiplying either moles of MnO_4^- by 5 **(1)**

Realising that 2nd titration measures total number of moles of iron **(1))**

Subtracting to get original moles Fe^{3+} **(1)**

Going to moles Zn then mass Zn **(1)**

OR
Volume MnO_4^- for Fe^{3+} which has been reduced by zinc **(1)**3rd point

= 25.3 cm^3 – 18.2 cm^3 = 0.0253 dm^3 – 0.0182 dm^3 = 0.0071 dm^3 **(1)** 4th point

Amount of MnO_4^- = 0.0071 dm^3 × 0.0200 mol dm^{-3} = 1.42×10^{-4} mol **(1)**1st point

Amount Fe^{3+} reduced by zinc = 5× above value = 7.10×10^{-4} mol **(1)**2nd point

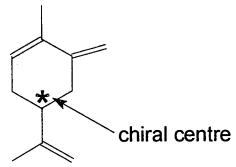
Amount zinc needed = ½ × 7.10×10^{-4} = 3.55×10^{-4} mol
mass of zinc needed = 3.55×10^{-4} mol × 65.4 g mol^{-1} = 0.00232 g **(1)**5th point **(5 marks)**

(d) (i) $[Fe(H_2O)_6]^{2+} + H_2O \rightarrow [Fe(H_2O)_5OH]^+ + H_3O^+$
H_3O^+ in equation **(1)**
other ion in equation **(1)**
(Fe^{2+}) polarises the O-H bond in ligand **(1)** **(3 marks)**

(ii) $[Fe(H_2O)_6]^{3+}$ more acidic than $[Fe(H_2O)_6]^{2+}$ **(1)**
Fe^{3+} higher charge density than Fe^{2+} **(1)**
Fe^{3+} ion if more polarising **(1)** **(3 marks)**
(Total 15 Marks)

---

5 (a) (i)

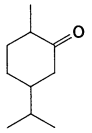


(1 mark)

(ii) rotation of plane of polarisation (of plane) polarised (monochromatic) light **(1 mark)**

(b) 2,4-dinitrophenylhydrazine (**1**) orange / red / yellow ppt **(1)**
NOT "DNP" *OR* "DNPH"
Warm ammoniacal silver nitrate / Fehlings / Benedicts / $K_2Cr_2O_7 + H_2SO_4$
(1)no silver mirror / red ppt *OR* stays blue / stays orange **(1)** **(4 marks)**

(c) Amount of carvone used
= 2.70g/150 g mol^{-1} = 0.018 mol **(1)**
amount of hydrogen used
= 0.864dm^3/24 dm^3mol^{-1} = 0.036 mol **(1)**
Ratio carvone : hydrogen is 1:2 **(1)**
therefore two / π / double / both C=C bonds reduced per molecule **(1)**
and so the structure is



(1) **(5 marks)**

(d) (i) Dry **(1)**ethoxyethane **(1)** **(2 marks)**

(ii) Attack by H^- / AlH_4^- / or by nucleophilic addition **(1)**
C=O polar, C=C non-polar **(1)** **(2 marks)**

(iii) Carvone shows peak near 1700 cm^{-1} **(1)**
characteristic of C=O / because it is a ketone **(1)**
Z shows (broad) peak around 3300 cm^{-1} due to O–H group (from reduction of C=O) **(1)** **(3 marks)**

(e) Several possibilities:
NaOH (1) $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$ (1) ethanol no reaction (**1**);
OR
(aqueous) bromine (**1**)
$C_6H_5OH + 3Br_2 \rightarrow C_6H_3Br_3OH + 3HBr$ (ignore substitution pattern if structural formulae are used) (**1**) ethanol no reaction (**1**)
OR conc sulphuric acid
nitration
R-halogen (Friedel-Crafts)
Phosphorus(V) chloride
Potassium dichromate(VI) / sulphuric acid
ethanoic acid (+ conc H_2SO_4) **(3 marks)**

(Total 21 marks)