1 (a) Energy/heat change **(1)** *ALLOW* Enthalpy change
when gaseous ions **(1)** *NOT* "one mole of gaseous ions"
form 1 mole of solid/crystal/lattice **(1)** *NOT* "form one mole of an ionic compound" *without physical state*

OR
Energy change etc per mole **(1)**
Suitable equation **(1)**
State symbols **(1)**

If from its elements 0 (out of 3) **(3 marks)**

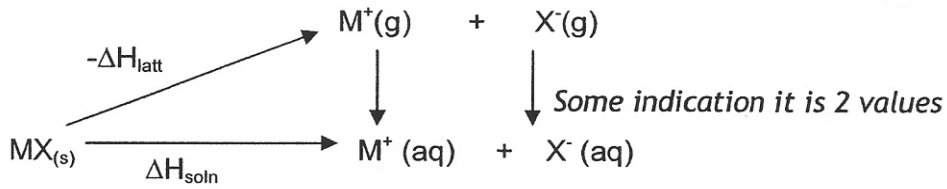
(b) (i) $-161 - 122 - 519 + 349 - 409 = -862$ (kJ mol^{-1})
working **(1)**
answer **(1)**
Correct answer with no working **(2)**
+ 862 with working **(1)**
Wrong answer with only one error **(1)** **(2 marks)**

(ii) Less endothermic due to weaker (metallic) bonding **(1)**
Li/Li^+ is smaller *OR vice versa in terms of potassium* **(1)** **(2 marks)**

(c) (i) (Ionic) charge **(1)**
Size/radius **(1)**
Charge density unexplained **(max 1)** **(2 marks)**

(ii) covalent character /"not 100 % ionic"/ "not purely ionic" **(1)**
due to polarisation/distortion of **anion** / Ag^+ is **highly** polarising **(1)** **(2 marks)**

(d) (i)



OR
energy level diagram

Species including state symbols **(1)** *ALLOW 2+/2-ions*
Arrows correctly labelled **(1)**
If L.E. arrow ↑, must be shown as -LE
ALLOW a specific example eg NaCl **(2 marks)**

(ii) $\Delta H_{solution}$ = - Lattice energy + (Σ) hydration enthalpies
ALLOW balance between lattice energy and hydration enthalpies **(1)**
the more exothermic $\Delta H_{solution}$ the more likely the compound is to dissolve **(1)** - *stand alone*

OR
If (Σ) hydration enthalpies are greater than lattice energy **(1)**
The compound (is likely to) dissolve. **(1)** **(2 marks)**

(iii) (From $CaSO_4$ to $BaSO_4$) the lattice energy changes by less than the hydration enthalpy / lattice energy changes by 106, hydration by 290 KJ moi^{-1} **(1)**
so enthalpy of solution process is more endothermic/less exothermic so solubility falls **(1)** - *dependent on the 1st mark* **(2 marks)**

Total 17 marks

2 (a) (i) *ACCEPT multiples and halves IGNORE state symbols*

$Na_2O + H_2O \rightarrow 2NaOH/2Na^+ + 2OH^-$ **(1)**

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ /$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$ **(1)**
NOT Al_2Cl_6

$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4$ / $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
OR $Al(OH)_3 + 3NaOH \rightarrow Na_3Al(OH)_6$ / $Al(OH)_3 + 3NaOH \rightarrow Al(OH)_6^{3-}$
ALLOW $Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$ **(1)**

$SO_3 + H_2O \rightarrow H_2SO_4/2H^+ + SO_4^{2-}$ **(1)** **(4 marks)**

(ii) acidic oxide - non metal **(1)**
basic oxide - metal **(1)**
If oxide omitted twice **(max 1)** **(2 marks)**

(iii) Metallic to non-metallic/decrease in metallic character **because** oxides change from basic to acidic/decrease in basic character

OR

Metallic to non-metallic/decrease in metallic character with reference to at least two reactions **(1 mark)**

(b) (Metallic character) increases (down the group) (1)

C/Si are non-metals and Sn/Pb are metals (1)
ALLOW explanation in terms of IE etc OR properties of non-metal/metals or compounds - *dependent on 1st mark*
(2 marks)

IGNORE a comment on conductivity of carbon

(c) (i) $PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2$
Species **(1)**
balance **(1)** - *dependent on 1st mark*
ALLOW multiples **(2 marks)**

(ii) It/lead(II)/Pb^{2+}/$PbCl_2$ is more/most stable (than lead(IV)/Pb^{4+}/$PbCl_4$)
ALLOW +2 is the stable oxidation state of lead
OR
$PbCl_4$ would **oxidise** the HCl.

NOT "prefers +2" **(1 mark)**

(Total 12 marks)

3 (a) (i) A→B

KCN/NaCN **(1)** *OR name*

IGNORE reference to HCN if given with KCN/NaCN

(aqueous) ethanol/alcohol **and** heat (under reflux) / reflux/warm**(1)**

If HCN given as the reagent, condition mark can still be given

B→C

$LiAlH_4$ **(1)** or name

Dry ether/ ethoxyethane **(1)**

OR

H_2 **(1)** Ni **(1)**

OR

Na **(1)** ethanol **(1)**

(4 marks)

(ii) Mg in dry ether **(1)**

C_4H_9MgBr **(1)** *IGNORE charges NOT* C_4H_9BrMg

CO_2 / dry ice **(1)**

Dilute acid / $H^+(aq)$ / H_2O**(1)** *these must not be added at the same time as* CO_2

ALLOW acidify

ALLOW HCl / HCl(g)/conc HCl NOT H_2SO_4 *or conc* H_2SO_4

OR

Mg in dry ether **(1)**

C_4H_9MgBr **(1)** *IGNORE charges NOT* C_4H_9BrMg

Methanal **(1)**

(hydrolyse and oxidise with) acidified (potassium) dichromate ions **(1)**

(4 marks)

(b) (i) Weak acid is dissociated to a small extent/slightly dissociated/ionised/few molecules dissociate

ALLOW partial dissociation

NOT 'not fully dissociated'.

(1 mark)

(ii) $Ka = \dfrac{[H^+][C_4H_9COO^-]}{[C_4H_9COOH]}$ *OR* $[H_3O^+]$ for $[H^+]$

(1 mark)

(iii) $Ka = [H_3O^+]^2$ / [acid] *OR* $[H_3O^+] = \sqrt{Ka[acid]}$ **(1)**

$[H_3O^+] = 1.23 \times 10^{-3}$ **(1)** - *dependent on 1st mark*

pH = 2.91/2.92 **(1)** *ACCEPT* 2.9 1 or 2 d.p.

Correct answer with working **(3)**

Correct answer with no working **(1)**

ALLOW TE only if pH below 7

(3 marks)

(iv) starting pH 2.9 *ALLOW starting in 2nd or 3rd boxes above pH 2* **(1)**
consequential on (iii)

pH range vertical max 6 to 12 min 7-10 **(1)**

Equivalence point at $25cm^3$ **(1)**

General shape of curve **and** finish at pH between 12-13 **(1)** - *and end in 1st three boxes above 12, extending to 40-50 cm^3*

If drawn wrong way round ***2 max*** *ie equivalence point* **(1)** *and vertical drop* **(1)** *marks can be awarded* **(4 marks)**

(v) Thymol blue **(1)** - *Consequential on (iv)*
(Completely) changes colour within vertical portion/the working range of the indicator is within the vertical portion / $pK_{ind} \pm 1$ in vertical position / pK_{ind} in centre of vertical position **(1)** **(2 marks)**

Total 19 marks

4 (a) (i) $K_c = \frac{[CH_3CH(NH_2)COOC_2H_5][H_2O]}{[CH_3CH(NH_2)COOH][C_2H_5OH]}$ *IGNORE minor slip in formulae*

(1 mark)

(ii) Bonds broken: O–H and C–O
Bonds made: C–O and O–H **(1)**

Notes that there is no change (and therefore ΔH is zero) **(1)**

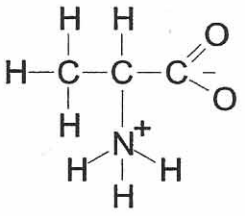
OR
Bonds broken + (464 + 358) = (+) 822
And bonds made – (358 + 464) = (–) 822 **(1)**
therefore ΔH = 0 *OR correct signs* **(1)**

(2 marks)

(iii) No effect **(1)**
Increases **(1)**

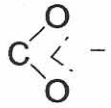
(2 marks)

(b) (i)



Do not accept +ve charge on covalently bonded H in NH_3^+ but OK if dative covalent bond to H^+

OR

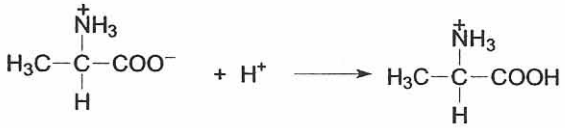


ALLOW $CH_3CH(NH_3^+)COO^-$ / $CH_3CH(NH_3^+)CO_2^-$ *brackets can be omitted*

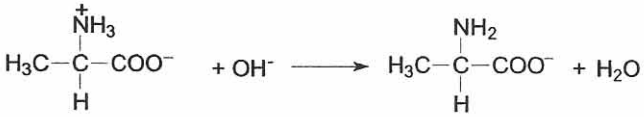
(1 mark)

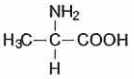
(ii) Attraction between (ionic) charges on **different** ions/zwitterions (is strong) **(1 mark)**

(iii)



$(H_3CCH(NH_3)COOH)^+$ ✓
$H_3CCH(NH_3)COOH^+$ ✗



ACCEPT variations starting with 

MUST be balanced equations
Can use NaOH or HCl etc

(2 marks)

(c) (i) Non-superimposable on its mirror image
OR has no plane of symmetry / it has an asymmetric carbon atom
NOT "4 different groups on a C atom" *on its own*

(1 mark)

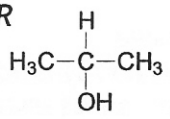
(ii) One diagram correct and 3D **(1)**
Mirror image **(1)** - *can be awarded if 1st mark not given because of a nearly correct structure eg ester*

(2 marks)

(iii) Rotation of the plane of (plane)-polarised light in opposite directions **(1 mark)**

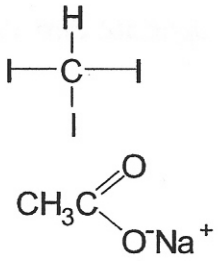
Total 13 marks

5 (a) (i) $CH_3CH(OH)CH_3$ *OR*



(1 mark)

(ii) CHI_3 **(1)**
CH_3COONa **(1)**
OR



Penalise a covalent bond between O and Na
Either no charges or both charges needed

(2 marks)

(b) (i) HCN (+ base)
OR KCN + acid
OR HCN + KCN
OR either HCN or KCN pH 5-8 - *or any no. or range within 5-8*
ACCEPT names

(1 mark)

(ii) (hydrolysis with) dilute acid /H^+(aq) **(1)**
ALLOW NaOH(aq) / OH^-(aq) / dilute alkali followed by acid [*if acid <u>not</u> added still carry on marking forwards*]

to $(CH_3)_2C(OH)COOH$/ $(CH_3)_2C(OH)CO_2H$ **(1)**

PCl_5 / PCl_3 / $SOCl_2$ *or names* **(1)** *OR* *any alcohol*

to $(CH_3)_2C(Cl)COCl$ **(1)** *ALLOW* $(CH_3)_2C(OH)COCl$ *correct formula of ester from that alcohol*

(Aqueous) NH_3/ ammonia **(1)**
IGNORE attempt to hydrolyse Cl

OR
(hydrolysis with) dilute acid /H^+(aq) **(1)**

to $(CH_3)_2C(OH)COOH$/ $(CH_3)_2C(OH)CO_2H$ **(1)**

ammonia / ammonium carbonate **(1)**

to $(CH_3)_2C(OH)COONH_4$ **(1)**

heat **(1)**

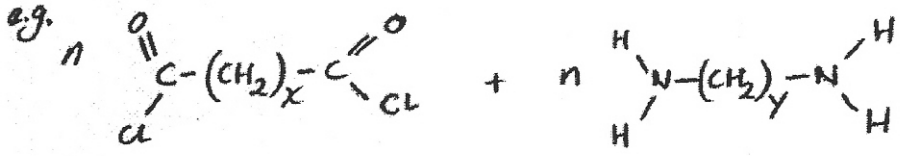
OR
State/imply partial hydrolysis **(1)**
NaOH **(1)** aq **(1)** *or names*
Warm **(1)** *ACCEPT temperatures 40-60 °C* *NOT* heat / boil
H_2O_2 / stopped to prevent further/complete hydrolysis (to acid) **(1)**

OR
State/imply partial hydrolysis **(1)**
HCl **(1)** aq **(1)** *or names*
Warm **(1)** *ACCEPT temperatures 40-60 °C* *NOT* heat / boil
H_2O_2 / stopped to prevent further/complete hydrolysis (to acid) **(1)**

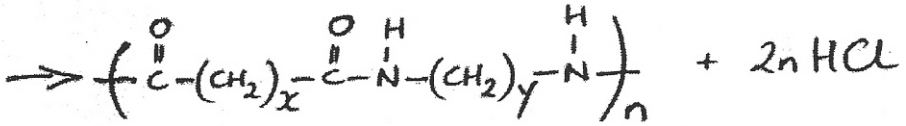
OR
Any other alternative correct route **(5 marks)**

(iii) Bromine/ Br_2 **(1)** *NOT* Br
(aqueous) sodium / potassium hydroxide / NaOH / KOH **(1)** **(2 marks)**

(c) e.g.



(1) (1)



(1)

IGNORE n, x, y values, 2n HCl and ( ) in polymer

ALLOW
Any amino acid OR
Any amino acyl chloride for first 2 marks **(3 marks)**

Total 14 marks

Unit Test 6245/01

1 (a) (i) One $t_{½}$ = 17 ± 1 s **(1)**
Another half life = 17 ± 1 s **(1)**
As they are constant **(1)**
Reaction is 1st order **(1)** **(4 marks)**

(ii) The reaction must take place in two (or more) steps **(1)**

Any one of the following for a second mark **(1)**
- Only 1 molecule of N_2O_5 appears in the mechanism (up to and) in the rate determining step
- 1 molecule of N_2O_5 appears in the mechanism after r.d.s
- if 1 step, then as there are 2 N_2O_5 molecules on LHS of equation, the order would be 2 *consequential on first mark*

(2 marks)

(iii) (The activation energy) is small **(1 mark)**

(b) Graph:
Two curves of correct shape drawn and labelled hot and cold with peak of hotter curve to right and lower than peak of colder curve **(1)**

One activation energy marked to the right of both peaks **(1)**

Explanation:
Q W C Area under curve to the right of E_a is less for the colder curve than for the hotter curve, **(1)**
therefore fewer molecules have $E \geq E_a$, **(1)**
so fewer successful collisions. **(1)**

Note: fully correct explanation of hotter therefore rate faster scores max 2 ex 3.

No mark for lower collision frequency

(5 marks)

Total 12 marks

2 (a) (i) Electrophilic addition **(1 mark)**

QWC

(ii) The pair of electrons in the (π) bond in ethene **(1)**

forms a (covalent) bond with one bromine atom **(1)**

The bond pair in the Br_2 molecule moves to the other bromine atom. **(1)** **(3 marks)**

(iii) Electrophilic substitution **(1 mark)**

(iv) Anhydrous **(1)**
iron (III) chloride/bromide/aluminium chloride/iron **(1)**

(2 marks)

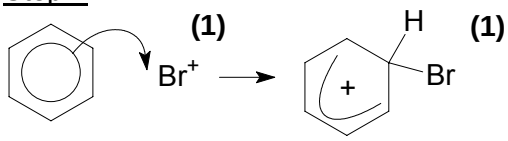
ACCEPT words or formulae

(v)

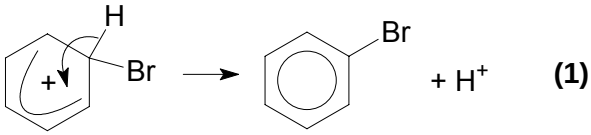
Step 1

$Br_2 + FeBr_3 \longrightarrow / \rightleftharpoons Br^+ FeBr4^-$ **(1)**

Step 2



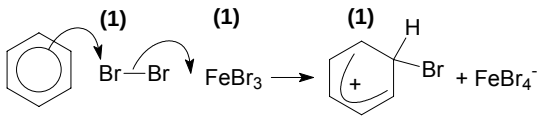
Step 3



(1)

OR

Step 1



Step 2 as Step 3 above **(4 marks)**

	(vi)	Delocalisation in benzene <u>or</u> no delocalisation in ethene	**(1)**		
Q W C		Loss of H^+ (or 'substitution') regains delocalisation/stabilisation	**(1)**		
		Substitution energetically favourable in benzene/or addition energetically favourable in ethene (If no mention of ethene **max 2**)	**(1)**		**(3 marks)**
(b)	**(i)**	1,2-dibromoethane would give 1 peak	**(1)**		
		1,1- dibromoethane would have 2 peaks	**(1)**		**(2 marks)**
	(ii)	Areas / peaks in the ratio of 3:1			**(1 mark)**

Total 17 marks

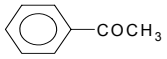
3 **(a)** **(i)** ethanoic acid / CH_3COOH/CH_3CO_2H **(1 mark)**

(ii) Reagents: potassium dichromate(VI) and sulphuric acid. **(1)**

OR full formulae or potassium manganate(VII) + sulphuric acid
Conditions: heat **(1)** **(2 marks)**

(iii) PCl_5 /PCl_3/$SOCl_2$ or names **(1 mark)**

(b) $C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$

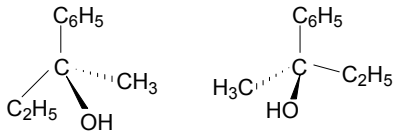
OR  *OR*  **(1 mark)**

(c) **(i)** Red-orange/orange/orange-yellow/yellow Precipitate **(1 mark)**

(ii) Blue solution remaining /no red ppt/no change **(1 mark)**

(iii) A (pale) yellow or cream precipitate **(1 mark)**

(d) **(i)**



Any One 3D formula **(1)**

Object and mirror image **(1)** **(2 marks)**

(ii) No effect **(1)**
because equal amounts of each optical isomer produced / racemic mixture produced / planar carbonyl can be attacked from either side **(1)** **(2 marks)**

(e) **(i)** The peak at 120 is caused by the moleculer ion/ both have same molar mass/both have same formula **(1)**
105 due to $(C_6H_5CO)^+$ **(1)** **(2 marks)**

(ii) No line in the IR spectrum due to C=O / at around 1700 cm^{-1} **(1 mark)**

Total 15 marks

4 **(a)** **(i)** Amount of $C_2O_4^{2-}$ = 0.0450 mol dm^{-3} x 0.0250 dm^3
= 0.001125 mol (0.00113) **(1)**
amount of MnO_4^- = 0.0200 mol dm^{-3} x 0.0225 dm^3
= 0.000450 mol **(1)**
ratio $C_2O_4^{2-}$: MnO_4^- = 2.5 : 1 or 5 : 2 / or ecf from above **(1)** **(3 marks)**

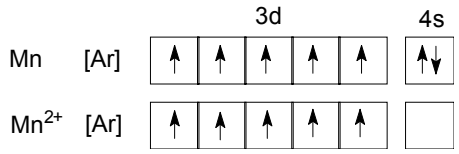
(ii) $5C_2O_4^{2-} + 16H^+ + 2MnO_4^- \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$
species **(1)**
balance **(1)** **(2 marks)**

(iii) Mn goes down by 5 per atom **(1)**
= 10 in total, so the 10 carbon atoms go up by 10
Each up by 1 **(1)**

OR

Oxidation number per carbon is $C_2O_4^{2-}$ is +3 **(1)**
And in CO_2 is +4 (therefore up by 1) **(1)** **(2 marks)**

(b)



(1)
(1) **(2 marks)**

(c) **(i)** The hydrated cation is **deprotonated** **(1)**
equation or indentification of ppt
i.e. $Mn(H_2O)_4(OH)_2$ / $Mn(OH)_2$ / manganese(II)hydroxide **(1)**
(The hydrated manganese(II) hydroxide is) **oxidised** (by the air) **(1)**
to MnO_2 **(1)** **(4 marks)**

(ii) Variable oxidation state **(1)**
Coloured ions (*NOT* compounds) } Max(2) **(1)**
Complex formation **(1)** **(2 marks)**

Total 15 marks

5 **(a)** **(i)** Adding the $E^{\ominus}$ of FeO_4^{2-}/Fe^{3+} equation to the H_2O_2/O_2 gives **(1)**
+1.52V **(1)**
and adding the $E^{\ominus}$ of Fe^{3+}/Fe^{2+} to H_2O_2/O_2 gives +0.09V **(1)**
positive means feasible **(3 marks)**

(ii) $FeO_4^{2-} + 2H_2O_2 + 4H^+ \rightarrow Fe^{2+} + 2O_2 + 4H_2O$
ALLOW $8H^+$ on left with $4H^+$ on right
ALLOW $\rightleftharpoons$ *OR* $\rightarrow$

OR
$2FeO_4^{2-} + 3H_2O_2 + 10H^+ \rightarrow 2Fe^{3+} + 3O_2 + 8H_2O$
ALLOW $16H^+$ on left with $6H^+$ on right

Species **(1)** *IGNORE state symbols*
Balance **(1)** **(2 marks)**

(b) **(i)** Ligand exchange / ligand substitution **(1 mark)**

(ii) The ion is octahedral **(1)**
It has 6 bonds around the Fe (ion) **(1)**
The electron pairs repel to a position of minimum repulsion / maximum separation **(1)** **(3 marks)**

(iii) The *d*-orbitals in the iron are split by the ligands **(1)**
Q light is **absorbed** **(1)**
W And an electron promoted to a higher *d*-orbital. **(1)** **(3 marks)**
C *If any hint of emission of light, only the 1st mark can be scored.*

(c) **(i)** The iron is oxidised / loss of electrons (or show e^- loss in an equation) **(1)**
To Fe^{2+} **(1)**
Then to Fe^{3+} **(1)** **(3 marks)**

(ii) The oxygen is reduced to OH^- ions
or equation $\frac{1}{2}O_2+H_2O+2e^- \rightarrow 2OH^-$ **(1 mark)**

Total 16 marks

Unit Test 6246/01A (Practical)

1. (a)

Observation	Inference
Steamy fumes/white fumes/misty fumes [not white smoke] **(1)** Blue litmus turns red **(1)**	HCl **(1) hydrogen chloride** NOT hydrochloric acid -OH *OR* carboxylic acid, alcohol – *both needed* **(1)** *NOT* carboxylic acid NOT OH^-

(4 marks)

(b)

Observation	Inference
No reaction/No change/red stays red and blue stays blue **(1)**	Alcohol **(1)** do not allow "carboxylic acid absent"

(2 marks)

(c)

Observation	Inference
Yellow / orange ppt **(1)**	C=O / carbonyl /aldehyde, ketone – *both needed* **(1)**

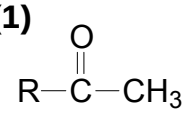
(2 marks)

(d)

Observation	Inference
No change **(1)** *OR* Stays Orange (1) allow "no reaction"	Ketone *OR* not aldehyde**(1)** Tertiary alcohol **(1)** (stand alone marks)

(3 marks)

(e)

Observation	Inference
[Pale] yellow/cream ppt **(1)** not "off white"	CHI_3/triiodomethane/iodoform **(1)**  (1) allow methyl ketone *NOT* alcohol

(3 marks)

(f)

Wavenumber (cm^{-1})	Functional group
3400-3500	OH / hydroxyl /hydroxy
1700	C=O /carbonyl

Only look for O-H and C=O

1700 **and** C=O/ketone/carbonyl **[1]**

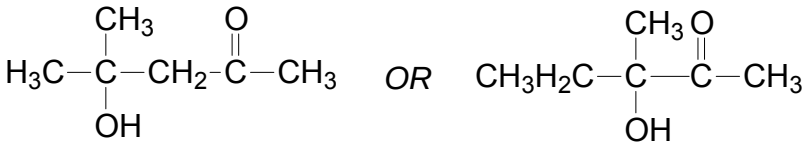
Any single wavenumber between 3400 and 3500 **and** O-H/hydroxyl [alcohol] **[1]**

If a range is given [ie copied from table] then **horizontally [0]**

If 2 ranges are given then **vertically [0]** but award **[1]** for correct assignment

(2 marks)

(g)



(1 mark)

Total 17 marks

2 (a)

Observation	Inference
Pale green solid / solution **(1)**	Transition metal ion/ compound/ Ni^{2+}/ Cr^{3+}/Fe^{2+}/Cu^{2+} any TWO ions needed**(1) NOT** just "transition metal"

(2 marks)

(b)

Observation	Inference
[Pale] green ppt **(1)** Gas: red litmus turns blue **(1)** "smell of ammonia" gets the 2nd inf mark	$Ni(OH)_2$ / Ni^{2+}**(1)** Ammonia/NH_3 **(1)** NH_4^+ /ammonium [ion]**(1)** Allow ammonium without reference to ammonia if litmus test is positive

(5marks)

(c)

Observation	Inference
Green ppt **(1) NOT "blue"** allow "blue/green" Blue solution **(1)**	$[Ni(NH_3)_6]^{2+}$ / $Ni(OH)_2$ ppt /Ni^{2+}**(1)**

(3 marks)

(d)

Observation	Inference
White ppt **(1)**	SO_4^{2-}, CO_3^{2-} Cl^- Br^- any **three(1)**

(2 marks)

(e)

Observation	Inference
White ppt **(1)** Insoluble in acid [not "no change"]**(1)**	SO_4^{2-} ONLY **(1)** *only awarded if "insoluble in acid" mark given ignore bisulphate* Any ppt [0] insoluble [1] allow sulphate inf [1]

(3 marks)

(f) $Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$
OR
$[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow [Ni(OH)_2(H_2O)_4] + 2H_2O$
OR
$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$
OR
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$
OR $[Ni(H_2O)_4(OH)_2] + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 2OH^- + 4\ H_2O$

(1mark)

(g) $(NH_4)_2SO_4.NiSO_4$ allow alternative assembly of correct ions in formula **(1 mark)**

Total 17 marks

3. **(a)** **WRITE S/V falling temperature on scripts** and compare to candidate's falling temperature

for recording two temperatures **(1)**
difference between two temperatures $\leq 5^{o}C$ **(1)**
for falling temperature +/- 2 **(3)** +/- 3 **(2)** +/- 4 **(1)** **(5 marks)**

(b) ✓O observation problems – can't see temperature and bubbles together/ difficult to judge flow of bubbles **(1)**
✓H heating problems - too rapid / difficult to control **(1)**
✓S stirring not enough **(1)**
✓C conductivity water poor conductor / temperature of liquid different from that recorded on thermometer **(1)** **(3 marks)**

ANY THREE

(c) Melting temperature **(1)**
more widely spread / significant difference/boiling temperatures too close/boiling temperatures dependent on pressure **(1)** "m pt" with NO reason **[0]** **(2 marks)**

Total 10 marks

4. ✓**V** Add known volume **(1)**
✓**K** Of oxidising agent solution to *excess* **(1)** KI (aq)
✓**T** Titrate liberated iodine against (standardised) sodium thiosulphate [if name and formula given ignore incorrect one]**(1)**
✓**S** To starch end point [colour change must be stated]**(1)**
✓**R** Repeat with second solution **(1)**
✓**C** Capable of oxidising more iodide ions **(1)**

OR

✓**V** Known volume **(1)**
✓**K** Excess KI **(1)**
✓**C** Colorimeter **(1)**
✓**M** Measure colour density **(1)**
✓**R** Repeat with 2nd solution **(1)**
✓**D** Darkest is best **(1)**

If candidate assumes identity of oxidising solutions then ignore and mark appropriately **(6 marks)**

Total 6 marks

Materials required for this practical test

Materials

Each candidate will require:

(a) 5 cm^3 of a 50:50 by volume mixture of propanone and 2-methylpropan-2-ol. This must be labelled **S**. Its identity must **not** be revealed to candidates
(b) access to solid phosphorus pentachloride
(c) 3 cm^3 of 2,4-dinitrophenylhydrazine reagent prepared by dissolving 0.25 g of solid reagent in 50 cm^3 of concentrated HCl with 50 cm^3 of water then diluting to 250 cm^3
(d) 3 cm^3 of aqueous potassium dichromate(VI); concentration 0.2 mol dm^{-3}
(e) 5 cm^3 of aqueous sulphuric acid; concentration 2 mol dm^{-3}
(f) 10 cm^3 of aqueous sodium hydroxide; concentration 2 mol dm^{-3}
(g) 5 cm^3 of aqueous iodine, prepared by mixing 12.7 g solid iodine with 20 g of solid potassium iodide, dissolved in 40 cm^3 of water and then diluted to 1 dm^3
(h) 5 cm^3 of **freshly prepared** aqueous ammonia; concentration 2 mol dm^{-3}
(i) 1 cm^3 of aqueous barium nitrate; concentration 0.5 mol dm^{-3}
(j) 2 cm^3 of aqueous lead(II) nitrate; concentration 0.1 mol dm^{-3}
(k) 5 cm^3 of butanone, labelled **T**. The identity of this must **not** be revealed to candidates
(l) red and blue litmus paper
(m) 0.5 g of solid ammonium nickel(II) sulphate, labelled **X**. The identity of this must **not** be revealed to candidates
(n) 2 cm^3 of dilute nitric acid; concentration 2 mol dm^{-3}.

Unit Test 6246/02

1 (a) (i) Amount NaOH =0 .0243 x 0.100 = 0.00243 mol = amount of HCl in 25 cm^3 portion **(1)**
Amount HCl in excess = 0.00243 x 4 = 0.00972 mol **(1)**
Amount HCl at start = 0.100 x 0.225 = 0.0225 mol **(1)**
Amount HCl reacted with NH_3 = 0.0225 – 0.00972 = 0.01278 mol **(1)**
Amount of ammonia produced = 0.01278 mol **(1)**

Alternative route via 25 cm^3 possible

If x 4 not included mark consequentially **(5 marks)**

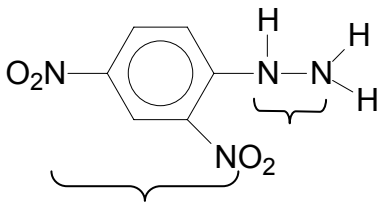
(ii) Mass of nitrogen in sample = 14 x 0.01278 = 0.1789 g **(1)**

% nitrogen in **X** = 0.1789 x 100 / 1.19 = 15.0% **(1)** **(2 marks)**

(b) (i) N 28.3 ÷ 14 = 2.02
C 36.4 ÷ 12 = 3.03
H 3.0 ÷ 1 = 3.0 **(1)**
O 32.3 ÷ 16 = 2.02
Empirical formula is $C_3H_3N_2O_2$ **(1)** **(2 marks)**

(ii) Mass of $C_3H_3N_2O_2$ = 99 which is ½ of 198
Molecular formula is $C_6H_6N_4O_4$ **(1)**

Z is



(1)

(1) **(2)**
Note: 2 x NO_2 in any position on the ring **(3 marks)**

Section A: Total 12 marks

2 (a) (i) $C_6H_5NH_2 + H_2O \rightarrow C_6H_5NH_3^+ + OH^-$

Or $C_6H_5NH_3OH$ **(1 mark)**

(ii) Axes labelled with **linear** pH scale **(1)**
Starting pH = 8.8 and finishing pH = 1 -2 **(1)**
Vertical at 10 cm^3 HCl **(1)**
Equivalence point pH 4 - 5 **(1)**
Vertical range: at least 3 pH units in the range 2 to 7 **(1)**
(5 marks)

Max 3 if graph drawn from low to high pH

Max 4 if poor shape

(b) (i) Phenylamine **reacts** with acids to form **ions** / forms a salt / joins with H^+ from acid as it is base/ionic equation **(1)**

which form strong (ion/dipole) attractions with / are hydrated by the water molecules / or some explanation of interaction with water. **(1)**

QWC

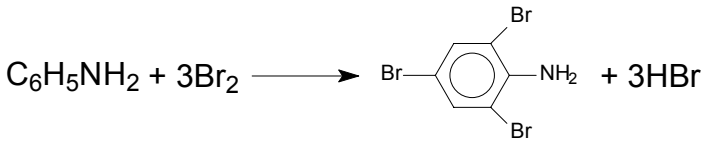
In phenylamine the hydrogen bonding between (the δ+ H in) the NH_2 group and the (δ- O in) water (causes its slight solubility) **(1)** **(4 marks)**

in spite of the large non-polar benzene ring

QWC **(ii)** There are hydrogen bonds (and van der waals' forces) between phenylamine molecules **(1)**

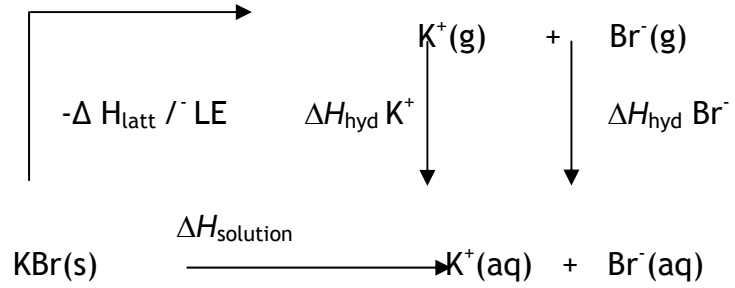
Which are stronger and so require more energy to separate than the van der waals' forces between chlorobenzene molecules. **(1)** **(2 marks)**

(c)



Correct formula of organic product with 3 Br atoms on ring in any position **(1)**
Rest of equation correct **(1)** **(2 marks)**

(d) (i)



Cycle (or as energy level diagram) drawn **(1)**
Labels **(1)**

$\Delta H_{solution} = -\Delta H_{lattice} + \Delta H_{hydration}$ of $K^+ + \Delta H_{hydration}$ of Br^- **(1)**

$= -(-670) + (-322) + (-335)$
$= +13$ kJ mol^{-1} **(1)**

Probably / yes / possible/because reaction only **slightly** endothermic. **(1)**
The mark here is for the argument.
Allow *probably not* if this is followed by a sound argument.
Do not allow *it is insoluble*.

(5 marks)

Total 19 marks

3 (a) (i) Buta-1,3-diene would have 2 nmr peaks **(1)**
One caused by the CH_2 hydrogen atoms and the other by the CH hydrogen atoms **(1)**
The peaks could be shown on an annotated diagram. **(2 marks)**

(ii)

Bond break:		Bond make	
2 x C=C	2x b.e.	2 x C-C	2 x – 348
2 x H-H	2 x +436	4 x C-H	4 x – 412
Total =	2 x b.e. + 872	total =	- 2344

(1)

2 x b.e. + 872 - 2344 = ΔH = - 237 **(1)**

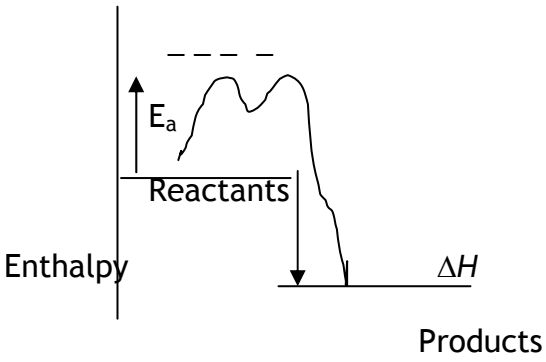
2 x b.e. = - 237 – 872 + 2344 = + 1235

b.e. = +618 kJ mol^{-1} **(1)**

If candidate chooses to break all the bonds, form all the bonds the data is 3692 and 5164.

Here the double bonds are delocalised and so the bond enthalpy is different. **(1)** **(4 marks)**

(iii)



Double humps with E_a marked **(1)** **(1)**
Reactants above products with ΔH marked **(1)** **(1)**

Catalyst will have no effect on ΔH **(1)** **(3 marks)**

(b) **(i)** (As there are 6 ligands around the Ni^{2+} ion,) there are 6 **bonding pairs of electrons** (and no lone pairs) **(1)**

QWC These adopt a position of minimum repulsion / repel to get as far apart as possible, which is an octahedral shape. **(1)**

The ligands cause the *d*-orbitals in the nickel ion to split into two levels **(1)**

Some frequencies of (white) light are absorbed **(1)**

the energy promotes an electron / electron jumps from the lower to the upper level (causing the ion to have the complementary colour to the light absorbed). **(1)**

If answer includes reference to emitted energy as electron falls back MAX 1 for splitting of d-orbitals **(5 marks)**

(ii) $[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Ni(OH)_2(H_2O)_4] + 2NH_4^+$ **(1)**
or
$[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow [Ni(OH)_2(H_2O)_4] + 2H_2O$

$[Ni(OH)_2(H_2O)_4] + 4NH_3 \rightarrow [Ni(NH_3)_4(H_2O)_2]^{2+} + 2OH^- + 2H_2O$ **(1)**

Allow $[Ni(NH_3)_6]^{2+}$
Allow any balanced equation that involves correct ligand exchange **(2 marks)**

(c) $Fe(s) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) + 2e^-$ **(1)**
$2NiO(OH)(s) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$
state symbols not required **(1)**

The reaction must be reversible / redox products must be solids. **(1)** **(3 marks)**

Total 19 marks

4 (a) (i) *EITHER* a catalyst provides an alternative path with a lower activation energy **(1)**

QWC

Thus a greater proportion of the molecules/ collisions has (kinetic) energy greater than or equal to the new activation energy (than to the old). **(1)**

This means that a greater fraction of the collisions will result in reaction / are successful **(1)**

OR

- Gas molecules absorbed onto (active sites) on surface of catalyst/ bonds to surface **(1)**
- This lowers E_n for reaction **(1)**
- Thus a greater proportion of the molecules/ collisions has (kinetic) energy greater than or equal to the new activation energy (than to the old) / reference to better orientation for reaction on surface **(1)** **(3 marks)**

(ii) Lowering the pressure will have no effect on K_p **(1)**

QWC

However it will cause the position of equilibrium to shift to the left **(1)**

(1)

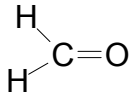
which is the side with more gas molecules. **(3 marks)**

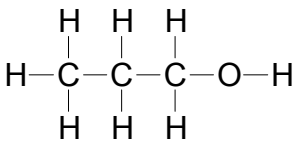
(b) (i) The functional group in **P** is an aldehyde / CHO group **(1)**

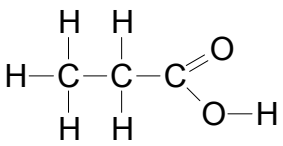
Not carbonyl

The functional group in **Q** is an alcohol / OH group **(1)**

The functional group in **R** is a (carboxylic) acid / COOH group **(1)**

P is  **(1)**

Q is  **(1)**

R is  **(1)**

(6 marks)

(ii) The reagent is ethylmagnesium bromide/chloride/iodide/ Grignard
Allow name or correct formula **(1)**

The conditions are dry ether(solution) **(1)**

followed by hydrolysis with dilute acid **(1)** **(3 marks)**

(c) **(i)** $6Cl^- \rightleftharpoons 3Cl_2 + 6e^-$ $E^\ominus = -1.36$ V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\ominus = +1.33$V **(1)**

$6Cl^- + Cr_2O_7^{2-} + 14H^+ \rightleftharpoons 3Cl_2 + 2Cr^{3+} + 7H_2O$ $E^\ominus_{cell} = -0.03$V **(1)**

which is negative so it will / should not happen/ not feasible **(1)**

OR

$Cr_2O_7^{2-}/Cr^{3+}$ is less positive than Cl_2/Cl^-, **(1)**
so $Cr_2O_7^{2-}$ is a weaker oxidising agent (than Cl_2) **(1)** therefore $Cr_2O_7^{2-}$ will / should not oxidise Cl^- **(1)**

The answer can be argued from a calculation that shows that the reaction between chromium(III) ions and chlorine molecules has a positive $E^\ominus_{cell}$ and this would mean that the reverse reaction would not be feasible. **(3 marks)**

(ii) The conditions are not standard when concentrated solutions are used / when solutions are not 1 molar/ when reaction mixture is heated.

E ($Cr_2O_7^{2-}/Cr^{3+}$) gets more positive / E (Cl^-/Cl_2) gets less negative, (so E_{cell} gets more positive) **(1 mark)**

Total 19 marks

APPENDIX A (STATISTICS)

Mark Ranges and Award of Grades

Unit/Component	Max. Mark (Raw)	Mean Mark	Standard Deviation	% Contribution to award	Number Sat
6245/01	75	39.6	17.1	100	475
6246/01A	50	29.4	8.8	50	276
6246/02	50	26.8	11.4	50	334

6245/01

Grade	Max Mark	A	B	C	D	E
Raw boundary mark	75	57	51	45	39	34
Uniform boundary mark	90	72	63	54	45	36

6246/01A + 6B

Grade	Max Mark	A	B	C	D	E
Raw boundary mark	100	76	70	64	58	53
Uniform boundary mark	120	96	84	72	60	48

January 2005

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