Q1.

6	**(a)**	**(i)**	$1s^2 2s^2 2p^6 3s^2 3p^6\ 4s^2 3d^2$ *or* $[Ar]\ 4s^2 3d^2$ (*or* vice versa)	[1]
		(ii)	**two** of $TiCl_2$, $TiCl_3$, $TiCl_4$	[1]
				2
	(b)	**(i)**	blue solution is formed	[1]
			containing $[Cu(H_2O)_6]^{2+}$	[1]
		(ii)	NH_3 **replaces** H_2O ligands *or* forms $[Cu(NH_3)_4]^{2+}$ (*or* $[Cu(NH_3)_4(H_20)_2]^{2+}$	[1]
			which is **deep blue/purple**	[1]
				4
				Total 6

Q2.

4	(a)	(i)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ **or** [Ar] $3d^6 4s^2$	[1]
		(ii)	Coloured compounds/ions/solutions/ppts; paramagnetic; variable oxidation state/valency/more than one ion; dense metals; high melting point metals; are catalysts; form complexes	**(ANY 2) [1] + [1]**
				Part (a): [3]
	(b)	(i)	$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$	[1]
			$E^\ominus = 1.52 - 0.77 = 0.75V$ (allow e.c.f. 0.90V for MnO_2	[1]
		(ii)	MnO_4^- is purple/**highly** coloured	[1]
			End point is **first** (permanent) pink colour **or** colourless-to-pink (Allow yellow-to-pink but **not** purple-to-pink)	[1]
				Part (b): [4]
	(c)		Water molecules are ligands, in that they coordinate/form **dative bonds** (to the Fe ion) with their (lone) **pairs** of electrons **or** lone pairs are donated.	[1]
			A complex ion is an ion/Fe^{3+} surrounded by/joined to ligands **or** $[Fe(H_2O)_6]^{3+}$	[1]
				Part (c): [2]
	(d)	(i)	Haemoglobin transports oxygen in the **blood or** from **lungs** (to tissues)	[1]
		(ii)	CO forms stronger bonds to Hb/Fe^{2+} than does O_2 **or** CO has higher affinity **or** bonds irreversibly **or** forms more stable complex	[1]
				Part (d): [2]
	(e)		Reagent: $I_2 + OH^-$	[1]
			Observations - ethanol: yellow **ppt.**/antiseptic smell; methanol: no change	[1]
				Part (e): [2]
				Total: [13]

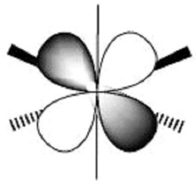
Q3.

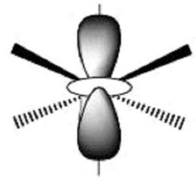
3	(a)	(i)	+2, +3, +4, +5 (ignore 0 and +1)	*all four* [1]	
		(ii)	$[Ar]3d^2$	[1]	
					[2]
	(b)	(i)	take a fixed amount/aliquot/pipette-full of the Fe^{2+} solution	[1]	
			titrate with $KMnO_4$ in **the burette**	[1]	
			until the first permanent pink colour (*or* change from colourless to pink)	[1]	
			repeat until two titres are within 0.1 cm^3	[1]	
			$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ (*or* molecular equn.)	[1]	
		(ii)	$n(MnO_4^-) = 0.02 \times 14/1000 = 2.8 \times 10^{-4}$ moles	[1]	
			$n(Fe^{2+})$ in 25 cm^3 = $2.8 \times 10^{-4} \times 5$ (= 1.4×10^{-3} moles)	*(x 5)* [1]	
			$n(Fe^{2+})$ in 100 cm^3 = $1.4 \times 10^{-3} \times 4$ (= 5.6×10^{-3} moles) mass of Fe in 2.0 g ore = $5.6 \times 10^{-3} \times 55.8$ = 0.31 g	*(x 4)* [1]	
			percentage = 100 x 0.31/2 = **15.6%** *(use of 55.8 or 56 and %)*	[1]	
					[9]
	(c)	(i)	$Cu^{2+}(aq)$ or $[Cu(H_2O)_6]^{2+}$	[1]	
		(ii)	**pale blue ppt**. (of $Cu(OH)_2(s)$) *[ignore any refs. to iron hydroxides]* (which dissolves to give....)	[1]	
			a **deep blue solution**	[1]	
			which contains $[Cu(NH_3)_4]^{2+}$ ions *(can be read into equn, below)*	[1]	
			formed by ligand displacement *or* an equation such as $Cu(OH)_2 + 4NH_3 \longrightarrow [Cu(H_2O)_4]^{2+} + 2OH^-$ *or* $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(H_2O)_4]^{2+} + 6H_2O$	[1]	
					[5]

[Total: 16 max 14]

Q4.

4 (a)





(between axes) [1]

(or $d_{x^2} - d_{y^2}$ i.e. along axes) [1]

[2]

(b) ligands have (lone) pairs (of electrons) [1]
(d)-electrons in orbitals pointing towards ligands are repelled/have higher energy [1]
so these electrons (i.e. the 2-orbital group, or those in d_{z^2} *or* $d_{x^2} - d_{y^2}$ have higher energy (*or* in diagram)
[*or* the 3-orbital group has the *lower* energy] [1] [3]

(c) (i) **C** = red **D** = blue [1] + [1]

(ii) **C**, because absorption is at lower wavelength/higher frequency [1] [3]

[Total: 8]

Q5.

3 (a) a (d-block) element forming stable ions/compounds/oxidation states with incomplete/ partially filled [NOT empty] d-orbitals [1] **[1]**

(b) (i) ($1s^2\ 2s^2\ 2p^6$) $3s^2\ 3p^6\ 3d^3\ 4s^2$ [1]

(ii) ($1s^2\ 2s^2\ 2p^6$) $3s^2\ 3p^6\ 3d^9$ [1] **[2]**

(c) (+)2, (+)3, (+)4, (+)5 *or* II, III, IV, V [1] **[1]**

(d) (pale blue solution ⇒) blue/cyan **solid/ppt.** (*or* (s) in the formula) [1]

(blue ppt. is) $Cu(OH)_2$ *or* copper hydroxide [1]

(then produces a) deep blue *or* purple **solution** [1]

which contains $[Cu(NH_3)_4]^{2+}$ *or* $[Cu(NH_3)_4(H_2O)_2]^{2+}$ [1]

formed by ligand replacement [1] **[5]**

(e) $2VO_3^- + 8H^+ + Cu \longrightarrow 2VO^{2+} + 4H_2O + Cu^{2+}$
or $2VO_2^+ + 4H^+ + Cu \longrightarrow 2VO^{2+} + 2H_2O + Cu^{2+}$
correct species [1]
balancing [1]
(award only [1] for just the two half-equations) **[2]**

[Total: 11]

Q6.

7 (a) *For each element, award [1] mark for each column in one particular line in the table below. The [2] marks awardable for each element are not conditional on each other, but don't take the location from one line and the role from another.*

element	location	role
iron	**red blood cells**/haemoglobin	to bind to/carry/transfer oxygen (to cells) *or* CO_2 (away from cells)
	muscle (cells)/myoglobin	to bind to/carry/transfer oxygen (to muscles) *or* CO_2 (away from muscles)
	in mitochondria/cytochromes	to aid redox reactions *or* to help oxidise NADH etc
	in iron-sulphide proteins	to aid redox reactions
	in ferrodoxin	to aid redox reactions
sodium	in nerve cells/nerves/nervous system/neurones *or* in cell membranes/phospholipid bilayers	Na^+/K^+ pump *or* ion pump *or* active transport *or* transmission/regulation of nerve impulses
	in kidneys	to help re-absorb glucose
zinc	**in blood** ("cells" not needed, but "plasma" negates) *or* carbonic anhydrase	as an enzyme co-factor/prosthetic group *or* to help the hydration/removal of CO_2 *or* production of H_2CO_3/HCO_3^-
	in the gut/carboxypeptidase	as an enzyme co-factor/prosthetic group *or* to help hydrolyse polypeptides
	in the liver/alcohol dehydrogenase	as an enzyme co-factor/prosthetic group *or* to help oxidise/break down alcohol
	[1] +	[1] for each element **[6]**

(b) (i) manufacture of NaOH *or* manufacture of batteries *or* manufacture of felt *or* gold extraction
or (mercury) fungicides *or* (mercury) compounds used in timber preservation [1]

(ii) ***In each case below, a balanced equation is worth [2] marks***
breaks disulphide bonds/linkages *or* Hg bonds to S-H groups (*or* in an unbalanced equation) [1]

$-CH_2\text{-}S\text{-}S\text{-}CH_2\text{-} + 4Hg^+ \rightarrow 2\ -CH_2\text{-}S\text{–}Hg + 2Hg^{2+}$
or $R\text{-}S\text{-}S\text{-}R + 4Hg^+ \rightarrow 2\ R\text{-}S\text{-}Hg + 2Hg^{2+}$ *or* $R\text{-}S\text{-}S\text{-}R + Hg^+ \rightarrow 2\ R\text{-}S\text{-}Hg^+$
or $R\text{-}SH + Hg^+ \rightarrow R\text{-}SHg + H^+$ *or* $R\text{-}SH + Hg^{2+} \rightarrow R\text{-}S\text{-}Hg^+ + H^+$
or $2\ R\text{-}SH + Hg^{2+} \rightarrow (R\text{-}S)_2Hg + 2\ H^+$ etc [1]

bonds to carboxyl side chains (in amino acids) (*or* in an unbalanced equation) [1]

$-CO_2H + Hg^+ \rightarrow -CO_2Hg + H^+$ *or* $2\ RCO_2H + Hg^{2+} \rightarrow (RCO_2)_2Hg + 2H^+$ [1]

[5]

[11 max 10]

Q7.

2	**(a)** coloured ions / compounds	(1)	
	variable oxidation states	(1)	
	formation of complexes	(1)	
	catalytic activity	(4 max 3)	[3]
	(b) (green is $[Ni(H_2O)_6]^{2+}$)		
	ppt is $Ni(OH)_2$	(1)	
	blue solution is $[Ni(NH_3)_6]^{2+}$ *or* $[Ni(NH_3)_4]^{2+}$ *or* $[Ni(NH_3)_4(H_2O)_2]^{2+}$	(1)	
	formed by ligand exchange	(1)	
	$Ni^{2+} + 2OH^- \longrightarrow Ni(OH)_2$	(1)	
	$Ni(OH)_2 + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 2OH^-$	(1) (5 max 4)	[4]
	(c) M_r = 58.7 + 48 + 6 + 28 + 32 = **172.7** (173)	(1)	
	n(Ni) = 4.00 / 172.7 = **0.0232** mol	(1)	
	mass(Ni) = 0.0232 × 58.7 = 1.36g		
	percentage = 100 × 1.36 / 3.4 = **40.0%**	(1)	[3]
			[Total: 10]

Q8.

4	**(a)** Cr^{3+}: $1s^22s^22p^6$... $\mathbf{3s^23p^63d^3}$	(1)	
	Mn^{2+}: $1s^22s^22p^6$... $\mathbf{3s^23p^63d^5}$	(1)	
	(allow (1) out of (2) for $3s^23p^64s^23d^1$ **and** $3s^23p^64s^23d^3$)		[2]
	(b) **(i)** **any three** of the following points: • initial (pale) green (solution) • fades to (almost) colourless (allow yellow) • then (permanent faint) pink • finally (deep) purple	(3)	
	(ii) $MnO_4^- + 8H^+ + 5Fe^{2+} (+ 5e^-) \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+} (+ 5e^-)$	(1)	[4]
	(c) $E^\ominus$ values: $O_2 + 4H^+/2H_2O$ = +1.23V Fe^{3+}/Fe^{2+} = +0.77 V $O_2 + 2H_2O/4OH^-$ = +0.40V $Fe(OH)_3/Fe(OH)_2$ = –0.56V	(2)	
	$\mathbf{E^\ominus_{cell}}$ = +0.46V (allow –0.37) in acid, but +0.96V in alkali *or* $E^\ominus(OH^-) > E^\ominus(H^+)$	(1)	
	If $\mathbf{E_{cell}}$ is more positive it means a greater likelihood of reaction	(1)	[4]

Q9.

(c) **(i)** $4NH_3 + CuS + 2O_2 \rightarrow [Cu(NH_3)_4]SO_4$ [1]

(ii) deep/dark/royal blue *or* purple [NOT violet] [1]

(iii) deep blue colour would change to light blue [NOT intensity of colour decreases] [1]
$\Rightarrow$ hexaquocopper(II) ion *or* $[Cu(H_2O)_6]^{2+}$ *or* $[Cu(H_2O)_n(NH_3)_{a-n}]^{2+}$, where a = 4 or 6
or ligand exchange (of NH_3) by H_2O [1]
[4]

(d) ligand exchange/substitution/displacement/replacement [IN WORDS] [1]
(use of named ligands are OK instead of 'ligand'. e.g. "water is displaced by chloride")

formula of anion (see below for possibilities) [1]
balanced equation. e.g. $[Cu(H_2O)_6]^{2+} + nCl^- \rightarrow [Cu(H_2O)_{6-n}Cl_n]^{2-n} + nH_2O$ [1]

(Allow n=1 up to n=6. Also allow $[CuCl_n]^{2-n}$ as product. Examples from many possible are:
$[Cu(H_2O)_6]^{2+} + 2Cl^- \rightarrow [Cu(H_2O)_4Cl_2] + 2H_2O$
$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$
equation could include HC*l* on the LHS, for example:
$[Cu(H_2O)_6]^{2+} + 4HCl \rightarrow H_2CuCl_4 + 2H^+ + 6H_2O$ *or* $\rightarrow CuCl_4^{2-} + 4H^+ + 6H_2O$ **[3]**

Q10.

3 **(a)** **(i)** density = mass per unit volume [1]

(ii) mass per atom *or* A_r is larger (for Fe)
Or
Fe 55.8 **and** Ca 40.1 [1]

Fe radii/volume of atom/ion is smaller
or
R_{Fe} = 0.116 nm whereas R_{Ca} = 0.197 nm [1]
[3]

(b)

reaction	acid-base	ligand exchange	precipitation	redox
$[Cu(H_2O)_6]^{2+}$ + $4NH_3$ → $[Cu(NH_3)_4]^{2+}$ + $6H_2O$		✓		
$[Cu(H_2O)_6]^{2+}$ + 4HCl → $[CuCl_4]^{2-}$ + $4H^+$ + $6H_2O$		✓		
$2FeCl_2$ + Cl_2 → $2FeCl_3$				✓
$[Fe(H_2O)_6]^{2+}$ + $2OH^-$ → $Fe(OH)_2$ + $6H_2O$	✓		✓	
$2Fe(OH)_2$ + ½O_2 + H_2O → $2Fe(OH)_3$				✓
CrO_3 + 2HCl → CrO_2Cl_2 + H_2O	✓	✓		
$Cr(H_2O)_3(OH)_3$ + OH^- → $[Cr(H_2O)_2(OH)_4]^-$ + H_2O	✓	✓		
$[Cr(OH)_4]^-$ + 1½H_2O_2 + OH^- → CrO_4^{2-} + $4H_2O$		✓		✓

(Where more than one tick appears on a line in the table above – these are alternatives – but allow the mark if both are given).

[8]

(c) $n(H_2)$ = 8/24 = 0.33 mol [1]

from equation, this is produced from 0.22 mol of Al ecf (× 2/3) [1]

A_r(Al) = 27 thus mass of Al = 27 × 0.22 = 5.9 – 6 g hence 5.9–6.0% ecf (× 27) [1]
[3]

[Total: 14]

Q11.

4. **(a)** **(i)** Many electrons of similar energy in a valence-shell orbital

or

successive ionisation energies rise steadily (no big jumps)

or

ability to form bonds with ligands can stabilise very low or very high oxidation states

or

4s + 3d orbitals/shells/energy levels have similar / same energies

[1]

(ii) VO_2^{+}: +5

CrF_6^{2-}: +4

MnO_4^{2-}: +6 [3 × 1]

[4]

(b)

- (colour due to) absorption of light/photons/frequencies/wavelengths
  or
  colour seen is complement of colour absorbed.
- d-orbitals/d-subshell split (by ligand field)
- (when photon is absorbed), electron is promoted *or* moves (from lower) to higher (d–)orbital
- energy difference/gap *or* ΔE *or* splitting corresponds to photon/frequency/wavelength in visible region
- in s-block elements the energy gap is too large (to be able to absorb visible light)

[any four 4 × 1]

[4]

(c) **(i)** $2MnO_4^{-} + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^{+}$ [1]

(ii) solution will go from purple [1]

to colourless [1]

[3]

(d) (pale) blue solution [1]

gives a (pale) blue ppt. [1]

which re-dissolves, *or* forms a solution, which is dark/deep blue *or* purple [1]

[3]

[Total: 14]

Q12.

4 (a) **Both** (m.pt. and density) of Fe are higher than those for Ca [1]
m.pt.: (due to:) stronger lattice/bonding *or* more delocalised electrons [1]
density:(due to:) heavier atoms/larger A_r but (roughly) the same/smaller radius/size *or* closer packing **[both mass and size need to be referred to]** [1]

3

(b) The third IE is not much greater than the second IE for iron,
or for Ca the third IE is much greater than the second IE
or Fe can use/ionise d-electrons as well as 4s electrons
or d and s electrons/orbitals are of similar energies [1]

1

(c) (i) $CaCO_3 \longrightarrow CaO + CO_2$ [1]

(ii) $2\,FeCO_3 + \frac{1}{2}O_2 \longrightarrow Fe_2O_3 + 2CO_2$ [1]

(iii) $FeCO_3 = 55.8 + 12 + 48 = 115.8$

$Fe_2O_3 = 2\,(55.8) + 48 = 159.6$ **(both M_r values)** [1]

$2 \times 115.8 \longrightarrow 159.6$

$\therefore$ 10 tonnes $\longrightarrow 10 \times 159.6/(2 \times 115.8)$

= **6.89** (tonnes) **(2 or more sig figs. allow ecf from wrong M_r values)** [1]

[if candidates think iron carbonate is $Fe_2(CO_3)_3$ or $Fe(CO_3)_2$, they lose the mark for (ii), but can be awarded ecf marks in (iii) as follows: for $Fe_2(CO_3)_3$, M_r = 291.6 and mass = 5.47 tonnes,
for $Fe(CO_3)_2$ M_r = 175.8 and mass = 4.54 tonnes]

[no units required, but if answer is given as 6890, kg must be specified; or 6.89×10^6 g]

4

Total: 8

Q13.

Total: 10

3 (a) (i) $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ (1) + (1)
[*or* $MnO_4^- + 4H^+ + 3Fe^{2+} \rightarrow MnO_2 + 3Fe^{3+} + 2H_2O$]
(reactants + products) + balancing

(ii) $Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ (1) + (1) **[4]**

(or molecular equations including the counter ions K^+ and SO_4^{2-})

(b) (i) purple (1)

(ii) the first (permanent) pink colour (from a colourless solution) (1)

$n(MnO_4^-) = 0.01 \times 14/1000 \quad = 1.4 \times 10^{-4}$ (1)

$n(Fe^{2+}) = 5 \times 1.4 \times 10^{-4} \quad = 7 \times 10^{-4}$

$FeSO_4 = 55.8 + 32.1 + 64 \quad = 151.9$ (1)

so mass = $151.9 \times 7 \times 10^{-4}$ = **0.106** g (1) **[5]**

(c) (i) to carry O_2 from lungs to muscles/tissues

the O_2 molecule is a ligand attached to the Fe atom/F^{e2}+ ion in haemoglobin (1)

(ii) CO exchanges with O_2 and forms a **stronger ligand bond**. [1] **[3]**

Total: 12 max 11

Q14.

4 (a) an element forming one or more ions with a partially filled/incomplete d-shell **[1] 1**

(b) (i) almost no change (allow *slight* increase or *slight* decrease) **[1]**

(ii) density should increase **[1]**

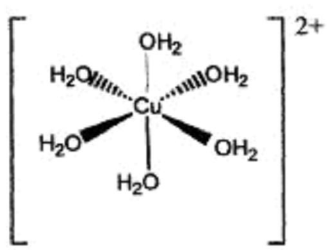
because A_r is increasing but size/volume/radius stays the same **[1]**

(allow partial ecf from **b (i)**) **3**

(c) ....$3d^9$ **[1] 1**

(d) (i) an ion formed when a ligand (datively) bonds to a (central metal) cation **[1]**

(ii)



[1] 2

(e) (i) dark/deep/navy/royal/Oxford blue *or* purple [NOT Prussian blue or lilac or mauve] **[1]**

(ii) $4NH_3 + [Cu(H_2O)_6]^{2+} \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

or $\longrightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$ **[1]** **2**

(f) $CuCl_4^{2-}$ is produced **[1]**

the equilibrium is **reversible** *or* $\rightleftharpoons$ in equation **[1]**

Cl^- ligands **replace/exchange** with H_2O ligands (in words) **[1]**

(the following equation is worth the first two marks)

$[Cu(H_2O)6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$ **3**

Total 12

Q15.

10 **(a)** Iron is higher in the reactivity series than copper (owtte)/allow use of $E^{\ominus}$ [1]

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$ [1]
If conversion to Fe^{3+} given, E_{cell} is –0.38 **[2]**

(b) It does not require investment in machinery/labour [1]

It requires little energy [1]

accept it produces little/no pollution/noise [1]
Do <u>not</u> accept comparison with electrolytic method **[max 2]**

(c) The process takes a long time/requires smaller workforce [1]
[1]

(d) **(i)** 0.75% is 7.5 kg in every tonne of ore

Hence 150,000 tonnes of ore yield $\frac{7.5 \times 150000}{1000}$ tonnes

or 1,125 tonnes Cu

1125 x 0.6 = 675 tonnes (accept 680) [1]

(ii) 450 x 0.17 = 76.5 tonnes (accept 77) [1]
or 1125 x 0.17 = 191.25 tonnes (accept 191) – this is an ecf if 675 not in **(i)** **[2]**

(e) Aluminium is too high in the reactivity series/very reactive/aluminium forms bonds with oxygen which are too strong/aluminium ore doesn't exist as sulphide /Fe unable to displace A*l* [1]
[1]

(f) Control the pH (*greater* than pH 6.0) [1]
Bioremediation/growth of special plants (to remove heavy metals)
Other reasonable suggestions such as displacement by a more reactive metal/ precipitation/ion exchange [1]
[2]
[Total: 9]

Q16.

(b) (i) Cu = 57.7/63.5 = 0.91 ratios correct scores [1]
O = 36.2/16 = 2.26
C = 5.4/12 = 0.45
H = 0.9/1 = 0.90 hence $Cu_2O_5CH_2$ [1]

(ii) Cu^{2+}(aq) *or* $[Cu(H_2O)_6]^{2+}$ NOT $[Cu(H_2O)_4]^{2+}$ [1]

(iii) **D** is CuO / copper(II) oxide [1]

$Cu_2O_5CH_2 \longrightarrow 2CuO + CO_2 + H_2O$ [1]
$221 \longrightarrow 159$ (M_rs) [1]

$\therefore 10 \longrightarrow 10 \times 159/221 = 7.2$ g (7.19)

if candidate thinks only CO_2 is lost, answer will be 8.0g [1]

(iv) **E** is copper; **F** is Fe^{2+} / Fe SO_4 [1]
$Fe + Cu^{2+} \longrightarrow Fe^{2+} + Cu$ (or molecular) [1]

(v) redox/displacement [1]

(vi) blue ppt./solid formed [1]
(dissolves to give) dark blue/purple colour [1]
blue ppt. is $Cu(OH)_2$(s) [1]
deep blue is $[Cu(NH_3)_4]^{2+}$ (allow $[Cu(NH_3)_4(H_2O)_2]^{2+}$ NOT $[Cu(NH_3)_6]^{2+}$ [1]

Q17.

3 (a) d-orbitals split into two / different levels
light is absorbed
electron is promoted from a lower to a higher level
colour observed is the complement of the colour absorbed
E = hf any 3 points [3]
[3]

(b) (i) $[Cu(H_2O)_6]^{2+}$ is pale blue [1]
$[Cu(NH_3)_4(H_2O)_2]^{2+}$ is deep / dark blue *or* purple [1]

(ii) because it has a larger absorbance peak *or* a larger ε_o value [1]
because λ_{max} is in the visible region (hence more visible light is absorbed) [1]

(iii) curve will have λ_{max} between >600 nm and 800 nm [1]
with maximum ε_o in between the other two [1]
[6]

(c) (i) $K_c = [CuCl_4^{2-}]/([Cu^{2+}][Cl^-]^4)$ units are $mol^{-4}\ dm^{12}$ [1] + [1]

(ii) $[CuCl_4^{2-}]/[Cu^{2+}] = K_c[Cl^-]^4 = 672$ (no units) [1]
[3]

[Total: 12]

Q18.

9 (a) **Length of DNA** **nanosphere diameter** **cell diameter**

Length of DNA	nanosphere diameter	cell diameter
3	1	2

Both marks for correct sequence, [1] for cell smaller than DNA **[2]**

(b) (i) Gaps in structure of shaft much smaller, hence less prone to fracture / more flexible [1]

(ii) Composites and carbon nanotubes less dense than metal (of comparable strength) [1] **[2]**

(c) Wavelength of infrared energy is longer than that of light [1]
Gaps between nano-sized particles allow light to pass through, but reflect infrared energy [1] **[2]**

(d) (i) Resistance to corrosion / reaction [1]

(ii) Ability to kill bacteria / prevent bacteria multiplying [1]

(iii) Very much larger surface area means they dissolve more readily [1] **[3]**

[Total: 9]

Q19.

2 (a) (i) A ligand is a species that contains a lone pair of electrons, *or* that can form a dative bond (to a transition element) (1)

(ii)

species	can be a ligand	cannot be a ligand
OH^-	✓	
NH_4^+		✓
CH_3OH	✓	
CH_3NH_2	✓	

(4 × ½) **[3]**

(b) (i) **C** is $[Cu(NH_3)_6]^{2+}$ SO_4^{2-} (allow $[Cu(NH_3)_4]^{2+}$ SO_4^{2-} (1)
D is CuO (1)
E is Na_2SO_4 (1)
F is $BaSO_4$ (1)

(ii) acid-base *or* neutralisation (1) **[5]**

(c) (i) any **two** from:
brown fumes or vapour evolved / gas relights glowing splint / black solid formed (2)

(ii) $2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$ (1) **[3]**

[Total: 11 max 10]

Q20.

2 **(a)** any **three** from:
d-orbitals / sub-shells / energy levels are split or equivalent * (1)
colour due to absorption of light (1)
when e promoted to higher orbital * (1)
$\Delta E = hf$ or $h\upsilon$ or h/λ (marks * could be in labelled diagram) (1) **[3]**

(b) blue is $[Cu(H_2O)_6]^{2+}$ (or full correct name of ion) (1)
ligand exchange/displacement/replacement (1)
($(NH_4)_2CuCl_4$ contains) $[CuCl_4]^{2-}$ (1)
$CuSO_4$ is white as it has no ligands (1) **[max 3]**

(c) n(thio) = $0.02 \times 19.5/1000 = 3.9 \times 10^{-4}$ mol (1)

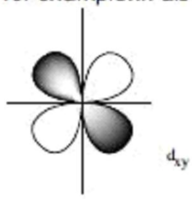
n(thio) = n(Cu^{2+}), so n(Cu^{2+}) in 50 cm^3 = 3.9×10^{-4} mol
so $[Cu^{2+}] = 3.9 \times 10^{-4} \times 1000/50$ = (**7.8×10^{-3}** (mol dm^{-3})) (1)
{*or* all-in-one-line: n(thio) = n(Cu^{2+}), so $[Cu^{2+}]$ = $0.02 \times 19.5/50$ = (**7.8×10^{-3}** mol dm^{-3})} (2)

in 100 cm^3, there will be 7.8×10^{-4} mol, which is $63.5 \times 7.8 \times 10^{-4}$ = **0.049 – 0.050%** (1) **[3]**
Allow ecf on 2nd and 3rd marks 0.5 gets 2 marks only

[Total: 9]

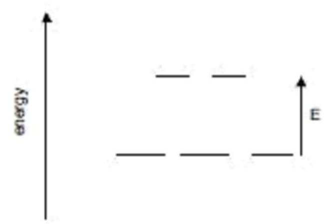
Q21.

3 **(a)** for example.... also allow d_{z^2}



shape (4 lobes) [1]
correct label e.g. d_{xy} [1]
[2]

(b) (i)



Marks are for 5 degenerate orbitals [1]
and 3:2 split [1]

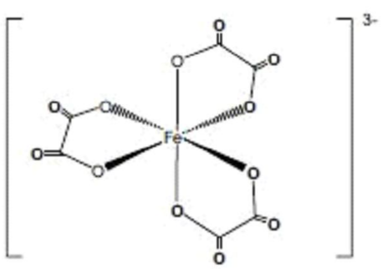
(ii) colour due to the absorption of light NOT emitted light [1]
E = hf *or* photon's energy = E in above diagram [1]
electron promoted from lower to higher orbital [1]

size of ΔE depends on the ligand [1]
as ΔE changes, so does f in E = hf [1]
[7]

(c) (i) O.N.(carbon) = +3 $(4 \times (-2) + 2x = -2$, thus $2x = +6)$ [1]

(ii) O.N. = +3 [1]

(iii)



[2]

(iv) $\underline{2}\ K_3Fe(C_2O_4)_3 \rightarrow \underline{3}\ K_2C_2O_4 + \underline{2}\ FeC_2O_4 + \underline{2}\ CO_2$ [2]
Or $K_3Fe(C_2O_4)_3 \rightarrow \underline{3/2}\ K_2C_2O_4 + FeC_2O_4 + CO_2$

[max 5]

[Total: 14]

Q22.

1 (a) Cr^{3+}: $1s^22s^22p^6$ $\mathbf{3s^2\,3p^6\,3d^3}$ [1]
Mn^{2+}: $1s^22s^22p^6$ $\mathbf{3s^2\,3p^6\,3d^5}$ [1]
[2]

(b) (i) Any two from
- H^+ is on the oxidant/L.H. side of each of the ½-equations, *or* H^+ is a reactant
- (increasing $[H^+]$) will make $E^{\ominus}$ more positive
- (increasing $[H^+]$) will drive the reaction over to the R.H./reductant side *or* forward direction

[1] + [1]

(ii) $KMnO_4$: Purple/violet to colourless (allow ***very*** pale pink) [1]
$K_2Cr_2O_7$ Orange to green [1]
[4]

(c) (i) $MnO_2 + SO_2 \longrightarrow MnSO_4$ (*or* $Mn^{2+} + SO_4^{2-}$) [1]

manganese changes/is reduced from +4 to +2 [1]
sulfur changes/is oxidised from +4 to +6 [1]

(ii) **No effect**, because H^+ does not appear in the overall equation *or* its effect on the MnO_2/Mn^{2+} change is cancelled out by its effect on the SO_2/SO_4^{2-} change [1]
[4]

(d) (i) $MnO_2 + 4H^+ + Sn^{2+} \longrightarrow Mn^{2+} + 2H_2O + Sn^{4+}$ [1]

(ii) $n(MnO_4^-) = 0.02 \times 18.1/1000 = 3.62 \times 10^{-4}$ mol [1]
$n(Sn^{2+}) = 3.62 \times 10^{-4} \times 5/2 = 9.05 \times 10^{-4}$ mol [1]
$n(Sn^{2+})$ that reacted with $MnO_2 = (20 - 9.05) \times 10^{-4} = 1.095 \times 10^{-3}$ mol [1]
reaction is 1:1, so this is also $n(MnO_2)$
mass of $MnO_2 = 1.095 \times 10^{-3} \times (54.9+16+16) = 0.0952$ g [1]
$\Rightarrow$ **95% – 96%;** 2 or more s.f. [1]
[6]

[Total: 16]

Q23.

3 (a) $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^9$ [1]

[Total: 1]

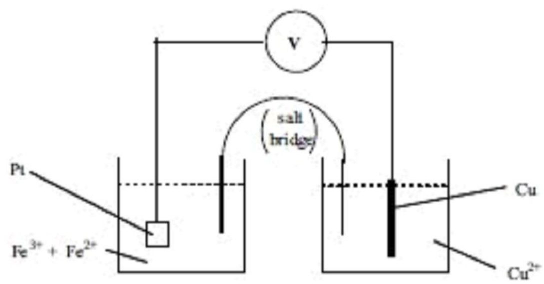
(b) (i) electron / orbitals near ligands are at a higher energy [1]
due to repulsion from ligand lone pairs [1]

(ii) when an electron moves to higher orbital / energy level **or** is promoted [1]
it absorbs a photon **or** light (mention of light being *emitted* negates this mark) [1]

(iii) (different ligands produce) different (sizes of) energy gap **or** ΔE [1]

[Total: 5]

(c)



solutions at 1 mol dm^{-3} (1 M) and 298(K)/25°C [1]
salt bridge and voltmeter [1]
platinum/carbon/graphite electrode [1]
(this mark is negated by inclusion of H_2 around the electrode)
copper electrode [1]
Fe^{3+}/Fe^{2+} mixture **and** Cu^{2+} **or** $CuSO_4$ etc [1]

[Total: 5]

(d) *Parts* **(i)** – **(iii)** *have to correspond to each other.*

	either	*or*
(i)	ligand exchange/substitution/displacement/replacement	precipitation/acid-base/deprotonation
(ii)	$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$ *or* $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$ *or* $[Cu(H_2O)_6]^{2+} + nNH_3 \rightarrow [Cu(H_2O)_{6-n}(NH_3)_n]^{2+} + nH_2O$	$Cu^{2+} + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2 + 2NH_4^+$ *or* $Cu^{2+} + 2NH_4OH \rightarrow Cu(OH)_2 + 2NH_4^+$ *or* $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$
(iii)	turns purple **or** deep/dark/royal blue	forms a pale blue ppt

[1] + [1] + [1]

(iv) $E^\ominus$ will decrease/ be less positive/more negative...
...because $[Cu^{2+}]$ decreases **or** $Cu^{2+} + 2e^- \rightleftharpoons Cu$ shifts to the LHS **or**
$E^\ominus[Cu(NH_3)_4]^{2+} = -0.05V$ **or** $[Cu(NH_3)_4]^{2+}$ is more stable. [1]

[Total: 4]

(e) (i) aldehyde [1]

(ii) red ppt./solid [1]

(iii) $2Cu^{2+} + CH_3CHO + 5OH^- \rightarrow Cu_2O + CH_3CO_2^- + 3H_2O$ [1]

[Total: 3]

(f) pH $= pK_a + \log [salt]/[acid] = -\log(9.3 \times 10^{-4}) + \log(0.8/0.5)$
$= 3.032 + 0.204 =$ **3.23/3.24** (3 or more sig. figs.) [2]

[Total: 2]

[TOTAL: 20]