Transition metal chemistry

Transition metals recap

C	P	Y	Q	J	M	L	D	K	B	N	N	R	Z	I
Z	A	S	Q	E	J	U	E	V	X	J	I	D	M	T
R	L	T	B	B	Z	M	I	H	K	Z	C	K	Z	G
A	L	W	B	O	Q	N	Y	N	Y	R	K	C	C	V
K	A	H	V	Z	X	Y	M	K	A	Y	E	H	O	E
S	D	M	U	N	I	T	A	L	P	T	L	V	I	N
V	I	H	C	W	N	V	U	M	D	J	I	R	H	J
R	U	D	C	O	Y	Z	A	K	M	D	O	T	O	H
I	M	T	R	L	P	N	S	N	U	N	A	O	C	M
J	N	G	S	S	G	P	K	D	I	X	B	T	U	F
O	S	E	Z	A	F	W	E	T	M	P	S	I	T	F
A	A	G	N	N	X	J	R	R	O	J	D	I	J	R
G	M	E	R	C	U	R	Y	C	R	O	Y	Q	S	Z
U	S	B	T	I	S	L	K	F	H	V	F	X	G	E
E	C	V	F	O	M	J	O	R	C	O	I	I	K	A

Find in the word search above, the answers to each of the questions below to gain the mark(s);

1. The catalyst in the Haber process used to make ammonia

(1 mark)

2. 3 Common catalysts found in the catalytic converter

(3 marks)

3. The aqueous solution of this metal sulphate is blue

(1 mark)

4. This metal has a melting point of −38.3 °C

(1 mark)

5. These two transition metals are found in the smart alloy, nitinol.

(2 marks)

6. These two metals when in oxidation states +6 and +7 respectively and combined with oxygen are common oxidising agents used in organic chemistry.
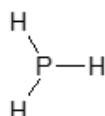
(2 marks)

Transition metal complexes

A transition metal complex consists of a central metal ion surrounded by ligands. A **ligand** is an ion or molecule with a lone pair of electrons that forms a coordinate bond with a transition metal ion.

1. For each of the ligands below, **mark** on any lone pairs which are able to form coordinate bonds, and **identify** the ligand as *unidentate* (can form one coordinate bond), *bidentate* (can form two coordinate bonds) or *multidentate* (can form three or more coordinate bonds).
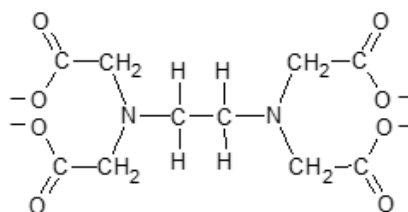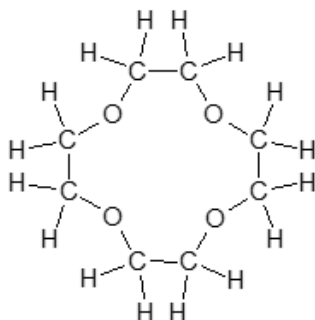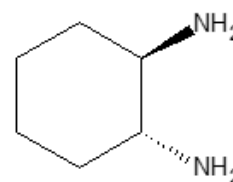
(4 marks)

(a)

....

(b)

....

(c)

....

(d)

....

2. For each of the complexes listed (a)-(c) below, draw a 3-dimensional representation of its structure, and identify the name given to its shape.
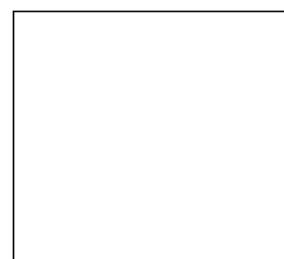
(a) $[CoCl_4]^{2-}$

(b) $[Fe(en)_3]^{2+}$
(en = $H_2NCH_2CH_2NH_2$)

(c) $[PtCl_2(NH_3)_2]$

....

(6 marks)

Colours of complex ions

1. Despite being a d-block element, zinc is not considered a transition element. Explain why.
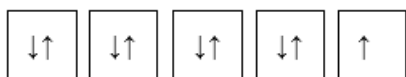
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(2 marks)

2. Anhydrous solid copper (II) sulfate is white but once hydrated, copper(II) sulfate solution is blue.
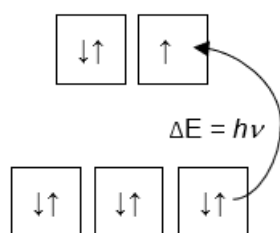Use the diagrams below to help you explain why.
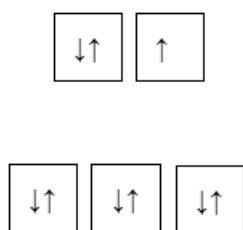Decide on the best order for the diagrams and then add a few words of explanation to each.

(8 marks)

Order

$\Delta E = h\nu$

Colorimetry

1. Nick is trying to determine the formula of the complex formed between Cu^{2+} ions and NH_3. He mixes different volumes of solutions containing the two ions and measures the absorbance of the resulting solution. His results are shown in the table opposite.
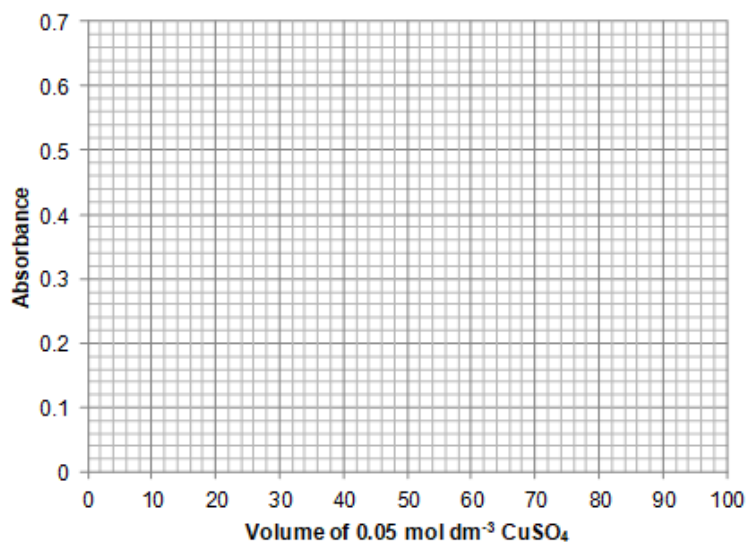
(a) Plot Nick's results on the graph paper below.

(1 mark)

(b) Use the graph to;

(i) Determine the stoichiometry of the Cu^{2+} : NH_3 complex,

(ii) Suggest a formula for the complex ion formed.

(4 marks)

Vol of 0.05 mol dm^{-3} CuSO$_4$ / cm^3	Vol of 0.10 mol dm^{-3} NH$_3$/ cm^3	Absorbance
0	100	0.0
10	90	0.2
20	80	0.4
30	70	0.6
40	60	0.6
50	50	0.5
60	40	0.4
70	30	0.3
80	20	0.2
90	10	0.1
100	0	0.0

Calculations: ....

....

....

....

....

....

....

2. In a different experiment, Nick wishes to determine the concentration of the blue dye, E133 (Blue no. 1) in a new sports drink, "*Go Go Go.*"

Outline the experiment Nick could perform in order to determine the concentration of the blue dye in "*Go Go Go.*" You can assume he has access to a solution of E133 of known concentration (0.20 mol dm^{-3}) and a sample of the sports drink as well as access to common laboratory equipment.

(5 marks)

Redox titrations

The pharmacists have had an accident and managed to mix up all their iron tablets. They have three foils of tablets (labelled A-C) which they know must have come from one of the bottles below;

FeRICH Contains 52% by mass of iron	**IRON TO GO** Contains 0.82 g of $FeSO_4$ per tablet	**Fe4U** Contains $\approx$1 g of $FeSO_4.7H_2O$ per tablet

Help the pharmacists work out which tablets are which by interpreting the results of their analyses below.

One of **Tablet A** (1.05 g) was dissolved in excess sulfuric acid and made up to 250 cm^3 in a volumetric flask. A 25.00 cm^3 aliquot of this solution required 21.65 cm^3 of a 0.005 mol dm^{-3} solution of $KMnO_4$ for complete oxidation.

Tablet A is from

(3 marks)

2.10 g of **Tablet B** (2 tablets) were dissolved in excess sulfuric acid and made up to 500 cm^3 in a volumetric flask. A 25.00 cm^3 aliquot of this solution required 19.45 cm^3 of a 0.010 mol dm^{-3} solution of $KMnO_4$ for complete oxidation.

Tablet B is from

(3 marks)

One of **Tablet C** (1.21 g) was dissolved in excess sulfuric acid and made up to 500 cm^3 in a volumetric flask. A 20.00 cm^3 aliquot of this solution required 10.5 cm^3 of a 0.0022 mol dm^{-3} solution of $K_2Cr_2O_7$ for complete oxidation.

Tablet C is from

(3 marks)

BONUS MARK How could you check that all of the iron in the **FeRICH** tablets is in the form of iron(II) and not iron(III)?

(1 mark)

# Redox chemistry of transition metals

One of the important properties of transition metals is that they can exist in a range of oxidation states in their compounds. The different oxidation states can be readily inter-converted.

1. Vanadium has an extensive redox chemistry.

(a) Complete the diagram by;

(i) Identifying the oxidation state of vanadium in each of the vanadium containing species

(ii) Adding labels to indicate if the change shown by the arrows is oxidation or reduction.

VO_2^+ VO^{2+} V^{3+} V^{2+}

Oxid^n state
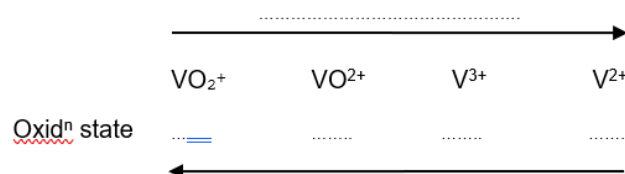
(2 marks)

(b) Use the electrode potentials in the table to explain the following;

(i) Nitric acid will oxidise V^{2+} to VO^{2+} but no further.

(2 marks)

(ii) Zinc will reduce VO_2^+ to V^{2+}.

(2 marks)

2. Write two half equations and combine to give a full redox equation for the following oxidations;

(a) The oxidation of $[Cr(OH)_6]^{3-}$ to CrO_4^{2-} using hydrogen peroxide under alkaline conditions.

(2 marks)

(b) The oxidation of $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ by oxygen in the air under alkaline conditions.
(HINT: O_2 is reduced to OH^- ions under these conditions)

(2 marks)

Transition metals as catalysts

A phase is defined as a distinct form of matter with uniform properties throughout, that is separated by its surface from other forms. Catalysts can be referred to as either;

Heterogeneous if the catalyst is present in the reaction in a different phase to the reactants, or

Homogeneous if the catalyst is present in the reaction in the same phase as the reactants.

1. For each of the reactions (a)-(g) below, identify the transition metal catalyst and state whether it is an example of a heterogeneous catalyst or a homogeneous catalyst. (7 marks)

(a) Hydrogenation of ethene to make ethane;   *Catalyst =*

$$CH_2=CH_2 + H_2 \rightarrow CH_3CH_3$$ homogeneous / heterogenous

(b) The Haber process to make ammonia;   *Catalyst =*

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$ homogeneous / heterogenous

(c) The Contact process   *Catalyst =*

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$$ homogeneous / heterogenous

(d) A catalytic converter   *Catalyst =*

$$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2$$ homogeneous / heterogenous

(e) The oxidation of iodide by peroxodisulfate ions *Catalyst =*

$$S_2O_8^{2-} + 2\,I^- \rightarrow 2\,SO_4^{2-} + I_2$$ homogeneous / heterogenous

(f) The decomposition of hydrogen peroxide   *Catalyst =*

$$2\,H_2O_2 \rightarrow 2\,H_2 + O_2$$ homogeneous / heterogenous

(g) The oxidation of ethanedioic acid by MnO_4^- ions   *Catalyst =*

$$2\,MnO_4^- + 16\,H^+ + 5\,C_2O_4^{2-} \rightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2$$ homogeneous / heterogenous

2. The reaction in **1.** (g) is an example of *autocatalysis*.

(a)   Explain what is meant by *autocatalysis*

(1 mark)

(b) By writing balanced symbol equations for the stages involved in the reaction, explain how *autocatalysis* in this case works.

(2 marks)

Transition metal chemistry – Answers
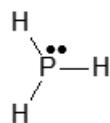
Transition metals recap

C	P	Y	Q	J	M	L	D	K	B	N	N	R	Z	I
Z	A	S	Q	E	J	U	E	V	X	J	I	D	M	T
R	L	T	B	B	Z	M	I	H	K	Z	C	K	Z	G
A	L	W	B	O	Q	N	Y	N	Y	R	K	C	C	V
K	A	H	V	Z	X	Y	M	K	A	Y	E	H	O	E
S	D	M	U	N	I	T	A	L	P	T	L	V	D	N
V	I	H	C	W	N	V	U	M	D	J	I	R	H	J
R	U	D	C	O	Y	Z	A	K	M	D	O	T	O	H
I	M	T	R	L	P	N	S	N	U	N	A	O	C	M
J	N	G	S	S	G	P	K	D	I	X	B	T	U	F
O	S	E	Z	A	F	W	E	T	M	P	S	I	T	F
A	A	G	N	N	X	J	R	R	O	J	D	I	J	R
G	M	E	R	C	U	R	Y	C	R	O	Y	Q	S	Z
U	S	B	T	I	S	L	K	F	H	V	F	X	G	E
E	C	V	F	O	M	J	O	R	C	O	I	I	K	A

Coordinates are for the first letter of each answer.

1. iron (14 across, 6 down) *(1 mark)*
2. platinum (10 across, 6 down), rhodium (9 across, 15 down) or palladium (2 across, 1 down) *(3 marks)*
3. copper (4 across, 7 down) *(1 mark)*
4. mercury (2 across, 13 down)   *(1 mark)*
5. nickel (12 across, 1 down) and titanium (13 across, 8 down)   *(2 marks)*
6. chromium (10 across, 15 down) and manganese (9 across, 7 down)   *(2 marks)*
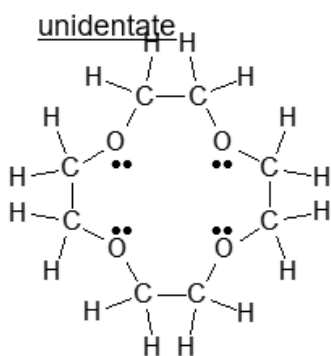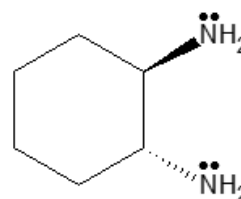
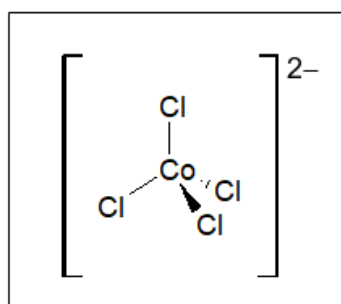# Transition metal complexes
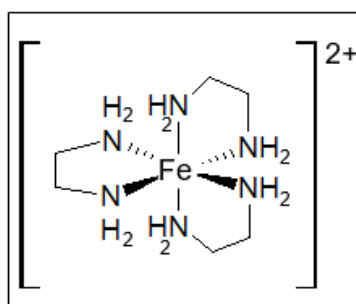
1. (a)

unidentate

(b)
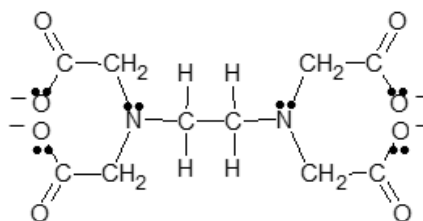
multidentate

(c)
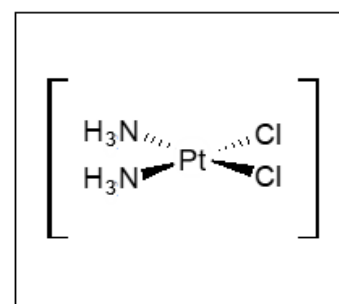
multidentate

(d)

bidentate *(4 marks)*

2. (a) $[CoCl_4]^{2-}$

tetrahedral

(b) $[Fe(en)_3]^{2+}$

octahedral

(c) $[PtCl_2(NH_3)_2]$

square planar

*(one mark for each correct **3D** drawing, one mark for each correct name)*

Colours of complex ions

1. The formal definition of a transition metal is '*an element that forms at least one stable ion with a partially full d-shell*.' Zinc forms only one stable ion, Zn^{2+} which has an electronic configuration of [Ar] $4s^o$ $3d^{10}$ i.e. has a full d shell.
(1 mark for definition, 1 mark for full explanation of why zinc does not meet the criteria)

NOTE IUPAC gives the definition of a transition element as '*An element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell*.' Elemental zinc does not contain an incomplete d sub-shell either ([Ar] $4s^2$ $3d^{10}$) so can also be ruled out on the basis of this criteria.

2.
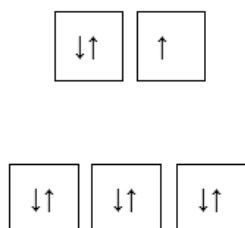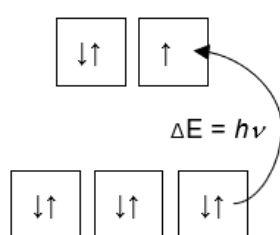

(1) ⬆⬇ ⬆⬇ ⬆⬇ ⬆⬇ ⬆
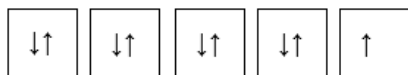
Copper(II) has an electronic configuration of [Ar] $4s^03d^9$. In the solid form, the 3d orbitals all have the same energy.

(2) ⬆⬇ ⬆

⬆⬇ ⬆⬇ ⬆⬇

On addition to water, the complex $[Cu(H_2O)_6]^{2+}(aq)$ is formed. Complexation with the water ligands, raises the energy of the copper(II) 3d orbitals by different amounts, splitting them into two groups.

(3) ⬆⬇ ⬆

$\Delta E = hv$

⬆⬇ ⬆⬇ ⬆⬇

When white light passes through the solution, some of the white light is absorbed and its energy is used to promote an electron from the lower set of orbitals to the higher set. The frequency of the light absorbed is dependent on the size of the energy gap between the two sets of orbitals as shown by the equation;

$$E = hv$$

E = energy gap
h = Planck's constant
v = the frequency

(4)

The light that passes through the solution and out the other side contains white light with, in this case yellow/orange light removed. This produces a blue/cyan colour. The colour of light produced when one colour of light is removed, is known as **complementary colours** and is often shown in a colour wheel.

(8 marks, 1 mark for each diagram placed in the correct order, 1 mark for each explanation)

Colorimetry

1. (a)
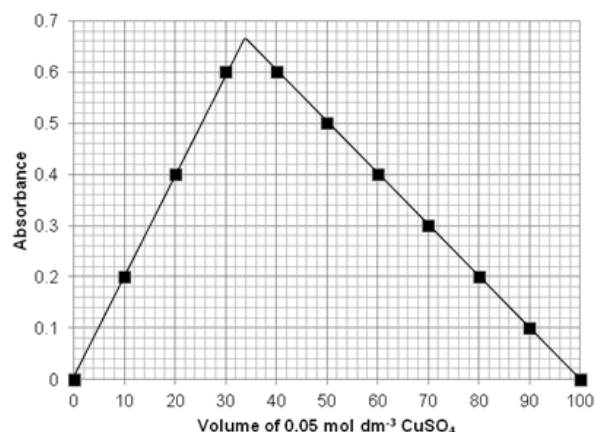
(1 mark for correctly plotting points)

(b) (i) Maximum absorbance at 33 cm^3 0.05 mol dm^{-3} CuSO$_4$: 67 cm^3 of 0.10 mol dm^{-3} NH$_3$ solution

In moles this is, 1.65×10^{-3} mol : 6.70×10^{-3} mol
                              Stoichiometric ratio <u>1 : 4</u>

(1 mark for reading correct volume of graph, 1 mark for mol calculations, 1 mark for stoichiometry)

(ii) Since copper is normally hexacoordinate, the formula of the complex formed must be;
                                      <u>[Cu(NH$_3$)$_4$(H$_2$O)$_2$]$^{2+}$</u>   *(1 mark)*
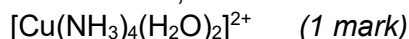
2. Key features of the experiment described include;

1. Initially the sample of E133 of known concentration must be diluted with water to produce dilute samples of known concentration. Five or more solutions must be produced. Possible dilutions would be;

Vol. of 0.20 mol dm^{-3} solution of E133 / cm^3	Vol. of water added	New conc. of solution of E133 / mol dm^{-3}	Absorbance
10	0	0.20	
8	2	0.16	
6	4	0.12	
4	6	0.08	
2	8	0.04	
0	10	0.00	

2. Measure the absorbance of each new known concentration of E133 and record these results in a suitable table.
3. Plot a calibration graph of concentration of E133 (x-axis) against absorbance (y-axis).
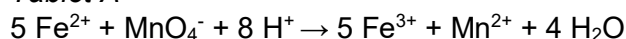4. Measure the absorbance of the sports drink '*Go, go, go*.'
5. Use the calibration graph plotted in 3. to determine the concentration of E133 in '*Go, go, go*.'

(5 marks)

Redox titrations

Tablet A
5 Fe^{2+} + MnO$_4^-$ + 8 H$^+$ → 5 Fe^{3+} + Mn^{2+} + 4 H$_2$O

No. of moles in 21.65 cm^3 of 0.005 mol dm^{-3} KMnO$_4$
= 1.08×10^{-4} mol

Therefore, no. of moles of Fe^{2+} in 25.00 cm^3 aliquot
= $(1.08 \times 10^{-4}$ mol$) \times 5 = 5.41 \times 10^{-4}$ mol

Therefore, no. of moles of Fe^{2+} in 250 cm^3 and hence in one of Tablet A
= (5.41 × 10^{-4} mol) × 10
= 5.41 × 10^{-3} mol

(1 mark)

Molar mass of $FeSO_4$ = 151.9 g mol^{-1}
Therefore mass of $FeSO_4$ per tablet = 5.41 × 10^{-3} mol × 151.9 g mol^{-1} = 0.82 g   *(1 mark)*
Therefore Tablet A comes from the ***IRON TO GO*** pack.

(1 mark)

Tablet B

5 Fe^{2+} + MnO_4^- + 8 H^+ → 5 Fe^{3+} + Mn^{2+} + 4 H_2O
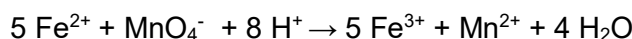
No. of moles in 19.45 cm^3 of 0.010 mol dm^{-3} $KMnO_4$
= 1.945 × 10^{-4} mol

Therefore, no. of moles of Fe^{2+} in 25.00 cm^3 aliquot
= (1.08 × 10^{-4} mol) × 5 = 9.725 × 10^{-4}mol

Therefore, no. of moles of Fe^{2+} in 500 cm^3 and hence in two of Tablet B
 = (9.725 × 10^{-4} mol) × 20
= 0.01945 mol

(1 mark)

Mass of iron in two tablets of B = 0.01945 mol × 55.8 g mol^{-1} = <u>1.085 g</u>   *(1 mark)*
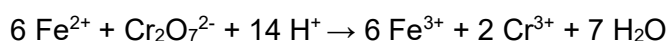Therefore the % by mass of iron in Tablet B
= (1.085 g / 2.10 g) × 100% = 51.6 %

Therefore Tablet B comes from the ***FeRICH*** tablets.   *(1 mark)*

Tablet C

6 Fe^{2+} + $Cr_2O_7^{2-}$ + 14 H^+ → 6 Fe^{3+} + 2 Cr^{3+} + 7 H_2O

No. of moles in 10.5 cm^3 of 0.0022 mol dm^{-3} $K_2Cr_2O_7$
= 2.31 × 10^{-5} mol

Therefore, no. of moles of Fe^{2+} in 20.00 cm^3 aliquot
= (2.31 × 10^{-5} mol) × 6 = 1.386 × 10^{-4} mol

Therefore, no. of moles of Fe^{2+} in 500 cm^3 and hence in one of Tablet C
= (1.386 × 10^{-4} mol / 20) × 500
= 3.465 × 10^{-3} mol

(1 mark)

Molar mass of $FeSO_4.7H_2O$ = 151.9 + (7 × 18.0) = 277.9 g mol^{-1}
Therefore mass of $FeSO_4.7H_2O$ per tablet
= 3.465 × 10^{-3} mol × 277.9 g mol^{-1} = 0.96 g   *(1 mark)*
Therefore Tablet C comes from the ***Fe4U*** tablets.   *(1 mark)*

BONUS MARK

Either

Add an excess of zinc to a 25.0 cm^3 aliquot of the original solution. This will reduce any Fe^{3+} ions to Fe^{2+} ions. Filter off the unreacted zinc and titrate the mixture against $KMnO_4$. If the titre is the same (i.e. the amount of $KmnO_4$ needed for complete oxidation has not changed) then only Fe^{2+} ions were present in the original solution. If the titre has increased (i.e. more $KmnO_4$ is needed for complete oxidation) then the original sample must have contained some Fe^{3+} ions.
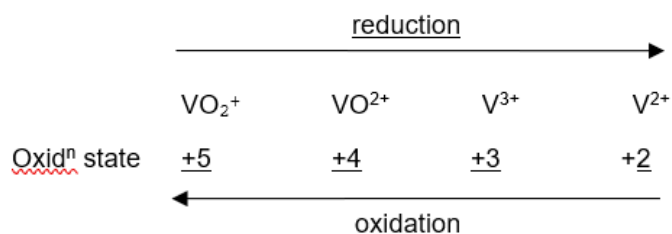
Or

Dissolve the tablet in water and add sodium hydroxide solution until present in excess. If Fe^{2+} is present a green precipitate of $[Fe(H_2O)_4(OH)_2]$ would form. Any Fe^{3+} present would form an orange/brown precipitate of $[Fe(H_2O)_3(OH)_3]$.

(1 mark for either method)

Redox chemistry of transition metals

1. (a)

*(1 mark for correct oxidation states, 1 mark for correct identification of oxidation and reduction)*

(b) (i) The electrode potentials for the V^{3+}/V^{2+} electrode and the VO^{2+}/V^{3+} electrode are each more negative that the NO_3^-/NO electrode potential. Therefore, NO_3^- will initially oxidise V^{2+} to V^{3+} which will then be oxidised further to VO^{2+}. Since the electrode potential for the VO_2^+/VO^{2+} electrode is more negative than that of the NO_3^- / NO electrode no further oxidation is possible.

*(2 marks; 1 mark for comment on electrode potentials and 1 mark for explaining comment)*

(ii) The electrode potential of the Zn^{2+}/Zn electrode is more negative than each of the VO_2^+/VO^{2+}, VO^{2+}/V^{3+} and the V^{3+}/V^{2+} electrodes. Therefore it will reduce each of the vanadium species in turn i.e. VO_2^+ will be reduced to VO^{2+} which in turn will be reduced to V^{3+} which in turn will be reduced to V^{2+}.

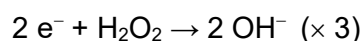*(2 marks; 1 mark for comment on electrode potentials and 1 mark for explaining comment)*

2. (a) In acid conditions the first half equation would be (this is purely a theoretical simplification, as $[Cr(OH)_6]^{3-}$ would not exist under these conditions);

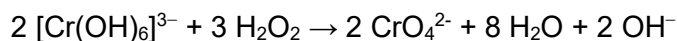$$[Cr(OH)_6]^{3-} \rightarrow CrO_4^{2-} + 2\ H_2O + 2\ H^+ + 3\ e^-$$
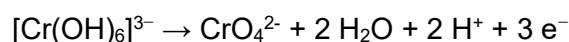
But the oxidation is in alkali conditions so it becomes (just add enough OH^- equally to both sides of the equation to remove any H+ ions);

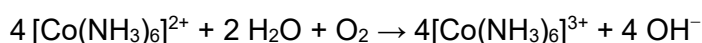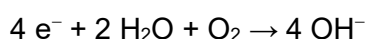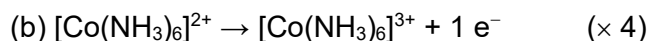$$2\ OH^- + [Cr(OH)_6]^{3-} \rightarrow CrO_4^{2-} + 4\ H_2O + 3\ e^- \qquad (\times\ 2)$$
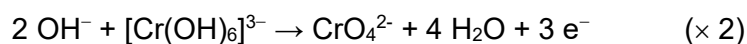
The hydrogen peroxide half equation is;

$$2\ e^- + H_2O_2 \rightarrow 2\ OH^-\ (\times 3)$$

Combining to give the full redox equation;

$$2\ [Cr(OH)_6]^{3-} + 3\ H_2O_2 \rightarrow 2\ CrO_4^{2-} + 8\ H_2O + 2\ OH^-$$

(2 marks; 1 for correct half equations, 1 for correct full redox equation)

(b) $[Co(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_6]^{3+} + 1\ e^-$ ⠀⠀(× 4)

$4\ e^- + 2\ H_2O + O_2 \rightarrow 4\ OH^-$

$4\ [Co(NH_3)_6]^{2+} + 2\ H_2O + O_2 \rightarrow 4[Co(NH_3)_6]^{3+} + 4\ OH^-$

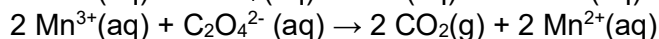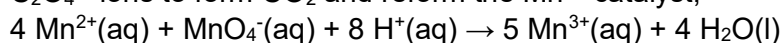*(2 marks; 1 for correct half equations, 1 for correct full redox equation)*

Transition metals as catalysts

1. (a) Nickel, heterogeneous
 (b) Iron, heterogeneous
 (c) Vanadium pentoxide (V_2O_5), heterogeneous
 (d) Platinum, palladium or rhodium, heterogeneous
 (e) Fe^{2+} ions, homogeneous
 (f) Manganese dioxide, MnO_2, heterogeneous
 (g) Mn^{2+} ions, homogeneous *(7 marks)*

2. (a) Autocatalysis is when one of the products of the reaction acts as a catalyst for the reaction.

(1 mark)

(b) Initially a little of the Mn^{2+} catalyst is made by the reaction. Once a little is made, it reacts with MnO‹ ions to form Mn^{3+} as an intermediate species. The Mn^{3+} then reacts with the $C_2O_4^{2-}$ ions to form CO_2 and reform the Mn^{2+} catalyst;
$4\ Mn^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Mn^{3+}(aq) + 4\ H_2O(l)$
$2\ Mn^{3+}(aq) + C_2O_4^{2-}\ (aq) \rightarrow 2\ CO_2(g) + 2\ Mn^{2+}(aq)$

(2 marks)