Reactions and Applications of Transition Metals

Mark Scheme 3

Level	International A Level
Subject	Chemistry
Exam Board	Edexcel
Topic	Transition Metals & Organic Nitrogen Chemistry
Sub Topic	Reactions and Applications of Transition Metals
Booklet	Mark Scheme 3

Time Allowed: **71 minutes**

Score: **/59**

Percentage: **/100**

Grade Boundaries:

A*	A	B	C	D	E	U
>85%	'77.5%	70%	62.5%	57.5%	45%	<45%

Question Number	Acceptable Answers	Reject	Mark
1(a)(i)	Penalise omission of charge on NO_3^- only once in (a)(i) and (a)(ii) Penalise an incorrect coefficient in (a)(i) and (a)(ii) once only $Cu^{2+} + 2e^{(-)} \rightarrow Cu$ ($E^\ominus$ = +0.34 V) **(1)** $2NO_3^- + 4H^+ + 2e^{(-)} \rightarrow N_2O_4 + 2H_2O$ ($E^\ominus$ = +0.80 V) ALLOW multiples equations reversed reversible / double-headed arrows 2 NO_2 for N_2O_4 **(1)** IGNORE $E^\ominus$ at this point State symbols even if incorrect	Alternative nitrate(V) reductions	2

Question Number	Acceptable Answers	Reject	Mark
1(a)(ii)	$Cu + 2NO_3^- + 4H^+ \rightarrow Cu^{2+} + N_2O_4 + 2H_2O$ ALLOW multiples reversible / double-headed arrows 2 NO_2 for N_2O_4 **(1)** No TE for equation from incorrect half-equations $E^\ominus_{cell}$ (= +0.80 − 0.34) = (+)0.46 (V) **(1)** TE for $E^\ominus_{cell}$ value on incorrect selection of half-equations IGNORE State symbols even if incorrect	uncancelled electrons	2

Question Number	Acceptable Answer	Reject	Mark
1(a)(iii)	Brown fumes / gas OR Green solution ALLOW (pale) yellow fumes / gas OR effervescence / bubbling / fizzing OR blue solution IGNORE modifiers of blue IGNORE References to copper dissolving	Colourless gas bubbles	1

Question Number	Acceptable Answer	Reject	Mark
1(b)(i)	In (b)(i) and (b)(ii) penalise (correct) non-ionic equations once. $Cu^{2+} + 2I^- \rightarrow CuI + ½I_2$ OR $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$ ALLOW $Cu^{2+} + I^- \rightarrow Cu^+ + ½I_2$ OR $2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2$ OR Multiples IGNORE State symbols even if incorrect	$Cu(NO_3)_2 + 2KI \rightarrow CuI + ½I_2 + 2KNO_3$	1

Question Number	Acceptable Answer	Reject	Mark
1(b)(ii)	$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ OR Multiples	$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2KI$	1

Question Number	Acceptable Answer	Reject	Mark
1(b)(iii)	2 mol Cu^{2+} forms 1 mol I_2 which reacts with 2 mol $S_2O_3^{2-}$ OR Multiples in this explanation OR Any clear explanation in words No TE on incorrect equations in (b)(i) and (b)ii)	**Just** re-writing the equations.	1

Question Number	Acceptable Answer	Reject	Mark
1(b)(iv)	mol $S_2O_3^{2-}$ in 25 cm^3 = 0.0505 x 26.35 /1000 = 1.330675 x 10^{-3} ans* **(1)** mol Cu^{2+} in 250 cm^3 = mol Cu in sample = 10 x ans* **(1)** = 1.330675 x 10^{-2} ans** mass Cu = ans** x 63.5 = 1.330675 x 10^{-2} x 63.5 **(1)** = 0.84498 (g) ans*** % copper in rivet brass = 100 x ans***/ 1.35 = 62.591/ 62.6 % **(1)** Correct answer with no working scores 4 If incorrect ratio used then max 3 Answers >100% max 3 IGNORE SF except one Do not penalise correct intermediate rounding		4

Question Number	Acceptable Answer	Reject	Mark
1(c)(i)	More iodine would be formed **(1)** (Titre / volume of thiosulfate would be larger) so (calculated) % copper would be higher **(1)** Second mark dependent on first		2

Question Number	Acceptable Answer	Reject	Mark
1(c)(ii)	**MP1 and MP2 are stand alone** **Marking Point 1** Percentage difference in the titres is (approximately) 100 x 0.25/26.35 = 0.94877 / 0.95% **(1)** **Marking Point 2** This MP should only be awarded if the candidate appreciates that the addition of urea **improves** experimental accuracy. The percentage error in the burette reading is (±)100 x 0.1/26.35 = (±)0.3795% **and** so change is a significant improvement OR Difference in titres is greater than uncertainty / error in burette reading OR Calculation any other **specific** apparatus uncertainty **and** use of urea has a significant effect OR Error without urea is significant when compared with the typical apparatus uncertainty (so the addition of urea improves accuracy) **(1)**	1.9% Total apparatus error greater than effect of urea	2

Question Number	Acceptable Answer	Reject	Mark
1(d)(i)	(When the electronic structure is built up according to the *aufbau* rules) the last electron goes into the (3)d-subshell / one of the d-orbitals / the d-orbitals	Just 'electrons present in (3)d-subshell outer / valence electrons are in d-subshell shell for subshell	1

Question Number	Acceptable Answer	Reject	Mark
1(d)(ii)	copper forms (one or more stable) ions having partially filled (3)d orbitals / subshell (but zinc does not) OR Zinc does not form an ion with a partially filled 3(d) orbital/subshell (but copper does)	3d shell Just 'zinc only forms an ion with a full 3d subshell'	1

Question Number	Acceptable Answer	Reject	Mark
1(d)*(iii)	Penalise use of orbital (singular) once only in (d)(iii) and (d)(iv) (3)d orbitals / (3)d subshell split (by the attached ligands) **(1)** Electrons are promoted (from lower to higher energy d orbital(s) / levels) OR Electrons move from lower to higher energy d orbital(s) / levels ALLOW d—d transitions occur **(1)** Absorbing energy /photons of a certain frequency (in the visible region) ALLOW Absorbing light **(1)** Reflected / transmitted / remaining light is coloured / yellow / in the visible region ALLOW Complementary colour seen Reflected / transmitted / remaining light / frequency is seen **(1)** No mention of (3)d then max 3 IGNORE reference to electrons relaxing / dropping to the ground state	Orbital / shell is split d-d splitting emitted	4

Question Number	Acceptable Answer	Reject	Mark
1(d)(iv)	(3)d subshell / (all) (3)d orbitals of zinc(II) are full (so electron transitions are not possible) Ignore No unpaired electrons	(3)d orbital full Full 3d subshell is not split	1

Total for Question 1 = 23 marks

Question Number	Acceptable Answer	Reject	Mark
2(a)(i)	$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$ OR $Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$ OR ionic equations including sulfate ions OR multiples		1

Question Number	Acceptable Answer	Reject	Mark
2(a)(ii)	Otherwise the Fe^{2+} formed will oxidize ALLOW So air / oxygen cannot enter the flask To prevent reaction with air /oxygen **(1)** Hydrogen can escape through the slit OR So pressure does not build up **(1)** IGNORE Acid spray	Iron/steel oxidized	2

Question Number	Acceptable Answer	Reject	Mark
2(a)(iii)	Transfer the reaction mixture to a ($250\ cm^3$) **volumetric**/**graduated** flask ALLOW standard flask **(1)** (Rinse conical flask and) add washings to the volumetric flask **(1)** Make solution up to the mark (with distilled water/sulfuric acid) **and then** mix ALLOW any indication of mixing **(1)** IGNORE Filtration	Using other liquids	3

Question Number	Acceptable Answer	Reject	Mark
2(a)(iv)	$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ OR multiples Ignore state symbols even if incorrect		1

Question Number	Acceptable Answer	Reject	Mark
2(a)(v)	Amount MnO_4^- = 22.15 x 0.0195 /1000 **(1)** = 4.31925×10^{-4} ans* Amount Fe^{2+} = 5 x ans* **(1)** = 2.159625×10^{-3} ans** Mass of iron in wire = 10 x ** x 55.8 **(1)** = 1.20507 (g) ans*** % purity = 100 x ans*** / 1.25 = 96.40566 = 96.4 % **(1)** Ignore rounding errors until final answer Correct answer (96.4%) with or without working scores 4 ALLOW Use of Ar(Fe) = 56 when Amount MnO_4^- = 22.15 x 0.0195 /1000 **(1)** = 4.31925×10^{-4} ans* Amount Fe^{2+} = 5 x ans* **(1)** = 2.159625×10^{-3} ans** Mass of iron in wire = 10 x ** x 56 **(1)** Mass of iron in wire = 1.20939 % purity = 96.7512 = 96.8 % **(1)** Ignore intermediate rounding until final answer Correct answer (96.8%) with or without working scores 4 TE on each stage in the calculation % purity > 100 scores max 2	Answer not to 3 SF Answer not to 3 SF	4

Question Number	Acceptable Answer	Reject	Mark
2(a)(vi)	Colourless / pale yellow to (pale) pink / first permanent pink	Purple Just '(pale) pink'	1

Question Number	Acceptable Answer	Reject	Mark
2(a)(vii)	(More manganate(VII) is needed to oxidize Fe^{2+}, so) titre will be larger **(1)** Stand alone mark Because the Mn oxidation number changes from 7 to 4 (rather than 2) OR Mn accepts fewer electrons per mole **(1)** (Brown precipitate is) manganese(IV) oxide / MnO_2 ALLOW $Mn(OH)_4$ **(1)** IGNORE References to inaccurate / inconsistent titre values	$Mn(OH)_2$	3

Question Number	Acceptable Answer	Reject	Mark
2(b)(i)	Anodic area: $Fe^{2+} + 2e(^-) \rightleftharpoons Fe$ ($E^\ominus = -0.44$ V) OR $Fe \rightleftharpoons Fe^{2+} + 2e(^-)$ **(1)** Cathodic area: $O_2 + 2H_2O + 4e(^-) \rightleftharpoons 4OH^-$ ($E^\ominus = +0.40$ V) **(1)** ALLOW $½O_2 + 2H^+ + 2e(^-) \rightleftharpoons H_2O$ ($E^\ominus = +1.23$ V) Penalise omission of electrons or use of cell diagrams once only Anode and cathode reversed max 1. IGNORE State symbols even if incorrect Single arrow in equations		2

Question Number	Acceptable Answer	Reject	Mark
2(b)(ii)	$E^{\ominus}_{cell}$ = (+)0.40 – (−0.44) = (+)0.84 (V) ALLOW $E^{\ominus}_{cell}$ = (+)1.23 – (−0.44) = (+)1.67 (V) Correct answer with no working scores 1		1

Question Number	Acceptable Answer	Reject	Mark
2(b)(iii)	Dissolved salt makes the **water** a better conductor (of ions) OR The **solution** acts like a salt bridge OR Makes it an (effective) electrolyte OR Improves the flow of ions through the **solution** ALLOW Improves the flow of electrons through the **metal**	Improves the flow of ions through the metal Improves the flow of electrons through the solution	1

Question Number	Acceptable Answer	Reject	Mark
2(b)(iv)	Magnesium has a more negative $E^{\ominus}$ (allow more reactive) **and** so reduces the Fe^{2+} OR suppresses the oxidation of iron OR forces the iron (in the absence of oxygen) to act as the cathode ALLOW Mg corrodes / oxidizes in preference to / faster than (the Fe / steel) OR Magnesium acts as a sacrificial anode	Just 'sacrificial protection'	1

Total for Question 2 = 20 marks

Question Number	Acceptable Answers	Reject	Mark
3(a)(i)	<table><tr><th>Ion</th><th>Oxidation number of vanadium</th></tr><tr><td>$V(H_2O)_6^{2+}$</td><td>+2</td></tr><tr><td>$V(H_2O)_6^{3+}$</td><td>+3</td></tr><tr><td>VO^{2+}</td><td>+4</td></tr><tr><td>VO_2^{+}</td><td>(+5)</td></tr></table> All three correct **(1)** IGNORE omission of '+'		1

Question Number	Acceptable Answers	Reject	Mark
3(a)(ii)	Electronic configuration of V: $[Ar]3d^3 4s^2$ ALLOW $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$ $[Ar]\ 4s^2 3d^3$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$ IGNORE Additional [Ar] **(1)** 5 electrons in valence shell / available for bonding ALLOW 5 electrons in outer shell (So max ON = +5) OR Uses the 2 4s and 3 3d electrons **(1)** ALLOW Lose 5 electrons (to form Ar structure) No TE on incorrect electronic configuration except $3d^5$ ($4s^0$) IGNORE Stability of +5 oxidation state	Gives electronic structure of Ar Loss of electrons from a (single) d orbital	2

Question Number	Acceptable Answers	Reject	Mark
3(a)(iii)	(3)d orbitals / (3)d subshell split (by the attached ligands) **(1)** Electrons are promoted (from lower to higher energy d orbital(s) / levels) OR Electrons move from lower to higher energy d orbital(s) / levels) ALLOW d—d transitions occur **(1)** Absorbing energy /photons of a certain frequency (in the visible region) ALLOW Absorbing light **(1)** Reflected / transmitted / remaining light is coloured / in the visible region ALLOW Complementary colour seen Reflected / transmitted / remaining light / frequency is seen **(1)** Penalise omission of (3)d once only. Ignore reference to electrons relaxing / dropping to the ground state	Orbital / shell is split Emitted	4

Question Number	Acceptable Answers	Reject	Mark
3(a)(iv)	V^{5+} is (small &) **high**ly charged /has a (very) **high** charge density **(1)** Would polarize / distort H_2O / H_2O electron clouds / O−H bond ALLOW O-H bond weakening / breaking OR Deprotonation **(1)** IGNORE References to ionization energy of V / highly electropositive	 Just 'Polarize' Ionic bonds	2

Question Number	Acceptable Answers	Reject	Mark
3(a)(v)	No. Because V^{5+} has no d electrons / d sub-shell is empty / d orbital**s** are empty. IGNORE Any mention of 4s V^{5+} has no partially filled d orbitals		1

Question Number	Acceptable Answers	Reject	Mark
3(b)(i)	Either **Method 1 (using equations)** $4H^+ + SO_4^{2-} + 2e^- \rightarrow H_2SO_3 + H_2O$ E^o = **+**0.17 (V) $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$ E^o = **+**0.34 (V) **(1)** $2VO^{2+} + H_2SO_3 \rightarrow 2V^{3+} + SO_4^{2-} + H_2O$ **(1)** E_{cell} (SO_2) = 0.34 – 0.17 = (+)0.17 (V) AND So reduces V(IV) to V(III) / reaction is feasible **(1)** **OR** **Method 2 (using anticlockwise rule)** When half reactions are placed in order (more negative first) $4H^+ + SO_4^{2-} + 2e^- \rightarrow H_2SO_3 + H_2O$ E^o = +0.17 V $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$ E^o = +0.34 V Required reaction 'goes' in anticlockwise direction Arrows on half equations and explanation **(2)** $2VO^{2+} + H_2SO_3 \rightarrow 2V^{3+} + SO_4^{2-} + H_2O$ **(1)**	Use of thiosulphate half cell =0 Uncancelled electrons Uncancelled electrons	3

Question Number	Acceptable Answers	Reject	Mark
3(b)(ii)	$2V^{3+} + H_2O \rightarrow V^{2+} + VO^{2+} + 2H^+$ ALLOW $V(H_2O)_6^{3+}$ and $V(H_2O)_6^{2+}$		1

Question Number	Acceptable Answers	Reject	Mark
3(b)(iii)	(Relevant electrode potentials are $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$ E^o = +0.34 V $V^{3+} + e^- \rightarrow V^{2+}$ $E^o = -0.26$ V) E_{cell} (disproportionation) =(−0.26 − 0.34) = **−0.6(**0) (V) **(1)** E_{cell} negative so disproportionation not (thermodynamically) feasible. **(1)** TE for second mark only if value given		2

Total for Question 3 = 16 marks