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2002

XVIII

1583

Time allowed
64 Minutes

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/53

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%

CHEMISTRY

**Edexcel
AS & A LEVEL**

Mark Scheme

**Paper 1: Advanced Inorganic
and Physical Chemistry**

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Question Number	Acceptable Answers	Reject	Mark				
1(a)	<table border="1"><tr><td>$V^{2+}(aq) + 2e^{-} \rightleftharpoons V(s)$</td><td>-1.18 (V)</td></tr><tr><td>$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq)$</td><td>-0.26 (V)</td></tr></table> Both correct	$V^{2+}(aq) + 2e^{-} \rightleftharpoons V(s)$	-1.18 (V)	$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq)$	-0.26 (V)		(1)
$V^{2+}(aq) + 2e^{-} \rightleftharpoons V(s)$	-1.18 (V)						
$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq)$	-0.26 (V)						

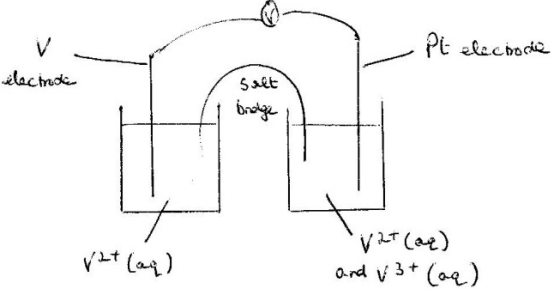
Question Number	Acceptable Answers	Reject	Mark
1(b) (i)	A (salt bridge containing saturated solution of) potassium nitrate / KNO_3 ALLOW potassium chloride / KCl / sodium chloride / $NaCl$ / sodium nitrate / $NaNO_3$ (1) B (electrode) platinum /Pt (1) C (solution containing) vanadium(II) and vanadium(III) ions / V^{2+} and V^{3+} ions ALLOW compounds of V^{2+} and V^{3+} (1) IGNORE any concentrations	KI / NaI vanadium	(3)

Question Number	Acceptable Answers	Reject	Mark
1(b) (ii)	298 K / 25°C (temperature) 1 atm / 100 kPa / 101 kPa / 1 bar (pressure) ALLOW atmospheric pressure IGNORE hydrogen / gas 1 mol dm^{-3} (all concentrations) ALLOW this if written in (b)(i) ALLOW '1 molar' / 1M / equal concentrations of V^{2+} and V^{3+} / vanadium(II) and vanadium(III) ions All 3 correct (2) Any 2 correct (1)	298°K / 273 K / 0°C / room temperature wrong pressure units eg 100 Pa wrong concentration units eg 1 mol	(2)



Question Number	Acceptable Answers	Reject	Mark
1(c)	<p>First mark – stand alone vanadium(IV) / V(IV) / (+)4 (oxidation state)</p> <p>ALLOW V^{4+} (1)</p> <p>IGNORE VO^{2+}</p> <p>Second mark E°_{cell} (= 1.00 – 0.54) = (+)0.46 (V) (1)</p> <p>Third mark $2VO_2^+ + 4H^+ + 2I^- \rightarrow 2VO^{2+} + 2H_2O + I_2$</p> <p>ALLOW multiples / \rightleftharpoons (1)</p> <p>IGNORE any working before this equation</p> <p>Fourth mark For the reduction of V (IV) to V (III) E°_{cell} (= 0.34 – 0.54) = –0.2(0) (V)</p> <p>OR E°_{cell} for the reaction between VO^{2+} and I^- is negative (so V(IV) is not reduced to V(III))</p> <p>OR I_2/I^- electrode potential / SEP / E° value is more positive than the VO^{2+}/V^{3+} value (so V(IV) is not reduced to V(III))</p> <p>OR VO^{2+}/V^{3+} electrode potential / SEP / E° value is less positive than the I_2/I^- value (so V(IV) is not reduced to V(III)) (1)</p> <p>IGNORE equation for VO^{2+} and I^-</p> <p>Fifth mark – stand alone E°_{cell} is positive / greater than 0 so (first) reaction is feasible and E°_{cell} is negative / less than 0 so (second) reaction is not feasible</p> <p>ALLOW spontaneous for feasible (1) IGNORE incorrect values provided the signs are correct</p>	<p>Mention of iodide ions reduced</p> <p>Incorrect value</p>	(5)



Question Number	Acceptable Answers	Reject	Mark
2(a) (i)	 <p>Beaker with V electrode in solution containing $V^{2+}(aq)$ AND beaker containing $V^{2+}(aq)$ and $V^{3+}(aq)$ with Pt electrode</p> <p>N.B. Both solution levels must be shown (1)</p> <p>Labelled salt bridge AND connections to voltmeter ALLOW Suitable name or formula of salt for label</p> <p>ALLOW Salts eg NaCl in salt bridge (1)</p> <p>Ion concentrations = 1 mol dm^{-3} ALLOW M for mol dm^{-3} Concentrations given in one beaker only (1)</p> <p>Beaker positions may be reversed</p> <p>Ignore references to temperature and pressure</p>	<p>Salt bridge neither dipping into nor touching solution unless penalised in MP1</p> <p>Salt bridge containing an alkali/acid</p> <p>1 mole of V^{2+} and 1 mole of V^{3+}</p>	3



Question Number	Acceptable Answers	Reject	Mark
2(a)(ii)i)	<p>1st mark $2V^{3+} + V \rightarrow 3V^{2+}$ Balanced equation, either direction ALLOW Eqm sign for \rightarrow</p> <p>IGNORE State symbol even if incorrect (1)</p> <p>Second mark Correct direction ALLOW If balancing is incorrect or e^- included in equation (1)</p>	e^- included	2

Question Number	Acceptable Answers	Reject	Mark
2b(i)	$([VO^{2+}(aq) + 2H^+(aq)], [V^{3+}(aq) + H_2O(l)] Pt)$	+0.34	1
	$([VO_2^+(aq) + 2H^+(aq)], [VO^{2+}(aq) + H_2O(l)] Pt)$	+1.00	
	Sign and value needed		



Question Number	Acceptable Answers	Reject	Mark
2(c)(iii)i	<p>final answer 92.2 scores 3 marks 33.2 scores 2 marks (ratio inverted) 55.3 scores 2 marks (ratio 1:1)</p> <p>METHOD 1 Mol V^{2+} reacting = $7.10 \times 10^{-4} \times 5/3$ = 1.18333×10^{-3} = mol VO_2^+ TE on answer to (c)(ii) (1)</p> <p>Mass NH_4VO_3 = $(1.183 \times 10^{-3} \times 116.9)$ = 0.1382927 g TE from 4.26×10^{-3} = 0.497994 (1)</p> <p>% purity = $(0.1382927 \times 100 / 0.150) =$ (92.19333) = 92.2% TE from 0.497994 = 33.2% (1)</p> <p>METHOD 2</p> <p>If 100% pure, moles of NH_4VO_3 = $0.150 / 116.9 = 1.283 \times 10^{-3}$ (1)</p> <p>Mol V^{2+} reacting = $7.10 \times 10^{-4} \times 5/3$ = 1.18333×10^{-3} = mol VO_2^+ TE on answer to (c)(ii) (1)</p> <p>% purity = = $1.18333 \times 10^{-3} \times 100 / 1.283 \times 10^{-3}$ = 92.2% (1)</p> <p>ALLOW TE at each step provided that each number used is to at least 2sf</p>	<p>x 3/5 = 4.26×10^{-4}</p>	3

Question Number	Acceptable Answers	Reject	Mark										
3(a)	<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Half-equation</th> <th>E^{\ominus} / V</th> </tr> </thead> <tbody> <tr> <td style="background-color: #cccccc;"> </td> <td style="background-color: #cccccc;"> </td> </tr> <tr> <td style="background-color: #cccccc;"> </td> <td style="background-color: #cccccc;"> </td> </tr> <tr> <td style="background-color: #cccccc;"> </td> <td>+0.4(0)</td> </tr> <tr> <td style="background-color: #cccccc;"> </td> <td>+1.23</td> </tr> </tbody> </table> <p>(1) for each correct value Penalise omission of + once only</p>	Half-equation	E^{\ominus} / V						+0.4(0)		+1.23	+2.46	2
Half-equation	E^{\ominus} / V												
	+0.4(0)												
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Question Number	Acceptable Answers	Reject	Mark
3(b)(i)	<p>hydrogen / H₂</p> <p>hydrogen ions / H⁺ / any strong acid</p> <p>platinum electrode</p> <p>First mark: Hydrogen / H₂(g) / H₂ (1) IGNORE Any pressure value quoted</p> <p>Second mark: Name or formula of any strong acid (e.g. HCl / H₂SO₄)</p> <p>ALLOW hydrogen ions / H⁺(aq) / H⁺ (1) IGNORE Any acid concentration value quoted IGNORE State symbols for ANY formula of hydrogen and / or acid, even if incorrect IGNORE any references to platinum</p>	<p>H(g) / H for hydrogen gas</p> <p>'HCL' / HSO₄ Just 'acidic'</p>	2



Question Number	Acceptable Answers	Reject	Mark
3(b)(ii)	<ul style="list-style-type: none">• 1 atm / 100 kPa / 101 kPa / 1 bar• 1 mol dm⁻³ ([H⁺] / [HCl]) ALLOW '1 molar' / '1M' <ul style="list-style-type: none">• 298 K / 25 °C ALLOW "°K" All THREE conditions correct = 2 marks Any TWO conditions correct = 1 mark IGNORE References to 'standard conditions' References to Pt/catalyst ALLOW 0.5 mol dm ⁻³ H ₂ SO ₄ INSTEAD of the 1 mol dm ⁻³ ([H ⁺] / [HCl])	Wrong pressure units Incorrect concentration units (eg '1 mol' / 1 mol ⁻¹ dm ³ for [H ⁺]) 273 K / 0°C / 'room temperature'	2

Question Number	Acceptable Answers	Reject	Mark
3(c)	<p>First mark: Mentions / some evidence for the use of BOTH equations 1 AND 3 from the table in any way, even if reversed or left unbalanced eg $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ AND $4OH^-(aq) + 2H_2(g) \rightarrow 4H_2O(l) + 4e^-$ (1) ALLOW \rightleftharpoons for \rightarrow</p> <p>Second mark: (Adds the above half-equations cancelling $4e^-$ to get) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ OR $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ (1) ALLOW \rightleftharpoons for \rightarrow but must have H_2 and O_2 on left</p> <p>Mark the second scoring point independently</p> <p>Award this mark if the correct equation is seen, no matter how it is derived</p> <p>ALLOW MULTIPLES OF EQUATIONS IN ALL CASES</p> <p>IGNORE any state symbols, even if incorrect</p> <p>ALLOW equilibrium sign \rightleftharpoons used in ANY of the above equations instead of the full arrows</p>	<p>Equations involving H^+</p> <p>If $e^- / OH^- / H^+$ / two surplus H_2O molecules remain in this final equation (0) for 2nd mark</p>	2



Question Number	Acceptable Answers	Reject	Mark
3(d)	$E^{\circ}_{\text{cell}} = +0.40 - (-0.83) \text{ (V)}$ $= (+)1.23 \text{ (V)}$ + sign NOT required in final answer Correct answer with or without working scores (1) No ECF from any incorrect E° values used	-1.23 (V)	1

Question Number	Acceptable Answers	Reject	Mark
3(e)	Reaction / equation is the same OR Reaction / equation for both is $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ ALLOW \rightleftharpoons for \rightarrow IGNORE state symbols even if incorrect ALLOW statements such as 'they both produce water from hydrogen and oxygen' / 'reactants and products are the same' ALLOW multiples of the equation	'Electrode potentials don't change' Just same product / water is produced Just same reactants are oxidized and reduced Same reaction but in reverse scores (0)	1

Question Number	Acceptable Answers	Reject	Mark
3(f)	To increase the surface area /to increase the number of active sites		1



Question Number	Acceptable Answers	Reject	Mark
3(g)	<p>Storage (problems) OR hydrogen / oxygen / the gases have to be stored under pressure OR Leakage (of hydrogen / of oxygen / of gas) OR Transport(ation) problems OR Hard to carry / lack of portability OR Hydrogen flammable / inflammable OR Hydrogen explosive OR (Fuel cell) costly / expensive OR Needs (regular) re-filling OR Needs continual replenishment of H₂ and O₂ OR Lack of availability (of hydrogen / fuel) OR Hydrogen is made from fossil fuels / hydrogen is made by electrolysis / hydrogen is made from Natural Gas / hydrogen is made from non-renewable resources</p> <p>ALLOW water is a Greenhouse gas / Fuel cell(s) have short(er) life-span / Fuel cells have to be (regularly) replaced</p> <p>IGNORE references to just 'danger' or just 'safety' or just 'hazardous'</p> <p>Any arguments in terms of voltage output</p> <p>References to cannot be recharged</p>	<p>'Fuel cell can only be used once' scores (0)</p>	1



Question Number	Acceptable Answers	Reject	Mark
4(a)	-285.8 / -286 (kJ mol ⁻¹)		1

Question Number	Acceptable Answers	Reject	Mark
4(b)(i)	$\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^{(-)} \quad (1)$ $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^{(-)} \rightarrow 4\text{OH}^-(\text{aq}) \quad (1)$ <p>For state symbols mark: Two of the four stated equations (see the two equations above and the two equations below) must be quoted even if reversed or unbalanced. All state symbols must be correct in both equations for correct species for the state symbol mark (penalise once only) (1)</p> <p>Both equations for an acid fuel cell score max 2 (1 for correct equations and 1 for states) e.g. $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^{(-)}$ OR $\text{H}_2(\text{g}) - 2\text{e}^{(-)} \rightarrow 2\text{H}^+(\text{aq})$ $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^{(-)} \rightarrow 2\text{H}_2\text{O}(\text{l})$</p> <p>ALLOW Equation multiples Equations in reverse direction Any order of equations Reversible arrows</p>		3

Question Number	Acceptable Answers	Reject	Mark
4(b) (ii)	Electrolyte / to allow the movement of ions (between electrodes) ALLOW Movement of hydrogen ions/ oxonium ions / hydroxonium ions / hydronium ions / H ⁺ / H ₃ O ⁺ / hydroxide ions / OH ⁻ (between electrodes) IGNORE References to electron transfer	Catalyst Just 'conducts electricity' Movement of other ions / charged species	1

Question Number	Acceptable Answers	Reject	Mark
4(b) (iii)	Any two of Both involve breaking / weakening bonds OR Both involve active site(s) (on the catalyst surface) OR Adsorption (2) IGNORE Lowers the activation energy Both heterogeneous References to surface area or "surface for the reaction" References to orientation of reactant molecules "Reaction pathway is similar"	Absorption	2

Question Number	Acceptable Answers	Reject	Mark
4(c) (i)	Water is the only product (at the point of use) / no oxide(s) of carbon IGNORE Reference to efficiency and/or high energy density Greener	Less oxide(s) of carbon	1



Question Number	Acceptable Answers	Reject	Mark
4(c) (ii)	Any two from: Fuel cell is more efficient / 70% efficient ALLOW Any % between 70% and 100% It produces electricity directly OR Less heat loss Releasing energy in a more controlled manner (2) IGNORE References to safety	Any mention of carbon emissions	2

Question Number	Acceptable Answers	Reject	Mark
4(c) (iii)	Either High cost / expensive OR Cost of catalyst OR Short life-span IGNORE References to liquefaction and / or storage of hydrogen / size / weight		1



Question Number	Acceptable Answers	Reject	Mark
4(c)(iv)	<p>Any two from Ethanol renewable / sustainable / carbon neutral / availability of raw materials / low(er) carbon footprint / made from natural processes e.g. fermentation or biomass</p> <p>Less explosive / less flammable / safe(r)</p> <p>Easier to store / pressure not needed for storage / easier to transfer</p> <p>Fuel tank light(er) / small(er)</p> <p>New petrol stations not required</p> <p>ALLOW Reverse arguments for hydrogen IGNORE Reference to cost References to energy density</p>		2