Electrochemistry Cheat Sheet

E°_{cell}; reduction and oxidizing agent; cell potential; reduction or oxidation; anode; cathode; salt bridge; electron flow; voltage; electromotive force; galvanic/voltaic; electrode; battery; current; amps; time; grams (mass); plate/deposit; electroplating; identity of metal; coulombs of charge

Galvanic or Voltaic Cell Relationships

Cathode is + galvanic cells	OIL RIG – oxidation is loss of e^-; reduction is gain
"the more positive reduction potential gets to be reduced"	FATCAT – e^- from the anode to the cathode
ANOX – oxidation at the anode	REDCAT – reduction at the cathode
Be able to… label the parts of a galvanic cell; such as the anode; cathode; salt bridge; electron flow; half reactions; overall reaction; direction of ions from salt bridge	The cathode will gain mass because it is the site of reduction; the anode will lose mass because it is the site of oxidation. (only true when electrodes are metals – not true of inert electrodes)
$E^\circ_{cell} = +$; thermodynamically favored $\Delta G = (-)$; $K>1$	$E^\circ_{cell} = -$; non thermodynamically favored $\Delta G = (+)$; $K<1$
Salt Bridge – provides ions to balance the charge in each ½ cell; contains a neutral salt that is very soluble (avoids precipitation issues). The salt cations flow into the cathode and the salt anions flow into the anode.	Be able to explain whether E_{cell} increases or decreases or remains the same when the concentrations of ions change from 1*M* solutions. Justify by describing which direction is more thermodynamically favorable (OR USE the Nernst equation.
For the Nernst Equation you MUST be able to relate how the sign of log Q affects the overall cell potential. If Q is greater than 1 then the log of Q is positive; thus $E^\circ_{cell} - (+)$ decreases the E_{cell} If Q is greater less 1 then the log of Q is negative; thus $E^\circ_{cell} - (-)$ increases the E_{cell}	The Nernst Equation – NOT required for the EXAM but it is very helpful in solving for cell potential under non-standard conditions $E_{cell} = E^\circ_{cell} - \frac{RT}{n\Im}\ln Q$

Connections

Thermo and Equilibrium	Stoichiometry
Connects EQUILIBRIUM to ELECTRO and THERMO $E^\circ_{cell} = 0$ at equilibrium thus $\Delta G = 0$	Connects THERMO to ELECTRO $\Delta G^\circ = -n\Im E^\circ$
Use this to connect EQUILIBRIUM to THERMO (and then THERMO to ELECTRO $\Delta G^\circ = -RT \ln K$	

Potential Pitfalls

Watch signs on voltages!!	BE SURE units cancel out in your calculations.
Balancing overall reactions – make sure # of electrons is the same in both half reactions.	Units on E° are volts

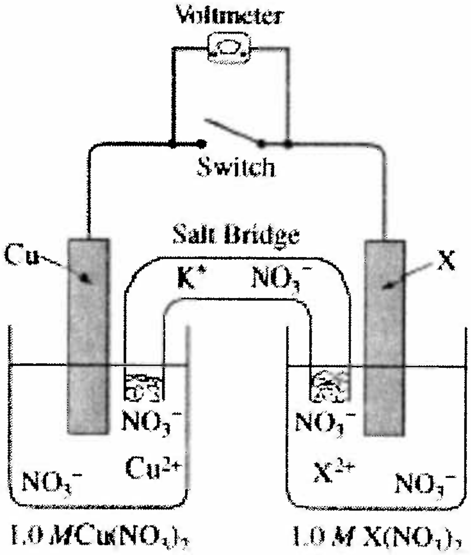
NMSI SUPER PROBLEM

Answer the questions below, which relate to reactions involving copper, Cu and copper(II) ion, Cu^{2+}.

A standard voltaic cell is constructed using copper and metal X. The standard reduction potential for Cu is given below.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E° = 0.34$ V

Immediately after closing the switch, the Voltmeter shows a reading of 0.47 V. Several minutes later it was noted that small flakes were adhering to the Cu electrode.



(a) Which metal, Cu or X, is the anode? Justify your answer.

X is the anode. X must be the anode because flakes forming on the Cu electrode indicate reduction and reduction occurs at the cathode.	**1 point** for X is the anode with justification

(b) In the diagram of the cell shown above, label the

i. cathode

ii. direction of electron flow

The Cu electrode should be labeled as the cathode and arrows should be drawn showing the electrons flowing along the wire from the X electrode to the Cu electrode	**1 point** for correct cathode **1 point** for correct direction of electron flow

(c) Which substance is being oxidized, Cu or X? Explain

X is anode so it is being oxidized.	**1 point** for correct answer with explanation

(d) Determine the standard ***reduction potential*** for the X^{2+}/X half-cell.

Oxidation + Reduction = Cell Potential (X) + (0.34 V) = +0.47 V Oxidation Potential for X = 0.13 V Reduction Potential for X = –0.13 V or $X^{2+}(aq) + 2e^- \rightarrow X(s) \quad E^\circ = -0.13$ V	**1 point** for correct ***reduction*** potential

(e) Using the information provided, select the ***metal*** that was used for the X electrode. Explain your choice.

$Ag^+(aq) + e^- \rightarrow Ag(s)$	$E^\circ = 0.80$ V
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	$E^\circ = -0.13$ V
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	$E^\circ = -0.14$ V

Pb is the correct electrode – it's standard reduction potential is the same as the one for X.	**1 point** for correct ***metal*** with explanation

(f) Write a balanced net ionic equation for this electrochemical cell.

$Cu^{2+} + Pb \rightarrow Pb^{2+} + Cu$	**1 point** for correctly balanced equation

(g) This galvanic cell has a salt bridge that is filled with a saturated solution of KNO_3.

i. As the cell operates, describe what happens in the salt bridge.

The potassium ions (K^+) will move into the cathode half-cell – the one with the Cu electrode. The anion, NO_3^- ions, will move into the half-cell with the X (Pb) electrode.	**1 point** for correct salt with explanation

ii. Describe what you would observe in the anode half-cell if the salt bridge contained a saturated solution of KCl instead of KNO_3.

The Cl^- ions will move into the half-cell with the X (Pb) electrode, which also contains Pb^{2+} ions. You would observe a precipitate of $PbCl_2$ forming in the anode half-cell.	**1 point** for stating a precipitate would form because of the mixture of Pb^{2+} ions and Cl^- ions.

(h) In the original galvanic cell, if the [Cu^{2+}] is changed from 1.0 *M* to 0.1 *M*, would the new cell potential, E_{cell}, at 25°C, increase, decrease, or remain the same. Justify your answer.

Only the concentration of the Cu^{2+} was changed from standard conditions (from 1 *M* to 0.1 *M*). The decrease in Cu^{2+} ion concentration increases the ratio of X^{2+}:Cu^{2+} ions in the cells compared to standard conditions, thus the REVERSE reaction is thermodynamically favored and E_{cell} will DECREASE	**1 point** for the correct answer **1 point** for a correct justification

(i) For the original reaction in the galvanic cell above, indicate whether

i. ΔG is positive or negative. Justify your choice.

ΔG is negative since the cell potential, E°, is positive the reaction is thermodynamically favored ($-\Delta G$)	**1 point** for correct answer with justification

ii. the equilibrium constant, *K*, is greater than one or less than one. Justify your choice.

K is greater than one since E° is positive and the forward reaction is thermodynamically favored	**1 point** for correct answer with justification

In another experiment, a 1.019 gram piece of Cu was cut from the electrode used above and added to 250. mL of 0.25 *M* nitric acid, HNO_3. An oxidation-reduction reaction between the copper and the nitrate ion occurs as indicated below.

$$Cu + NO_3^- \rightarrow Cu^{2+} + NO$$

(j) Write a complete and balanced net ionic equation for this redox reaction. Show work to support your answer.

$Cu \rightarrow Cu^{2+}$ $Cu \rightarrow Cu^{2+} + 2e^-$ $NO_3^- \rightarrow NO$ $NO_3^- \rightarrow NO + 2\,H_2O$ $4H^+ + NO_3^- \rightarrow NO + 2\,H_2O$ $3e^- + 4H^+ + NO_3^- \rightarrow NO + 2\,H_2O$ $3(Cu \rightarrow Cu^{2+} + 2e^-)$ $2\,(3e^- + 4H^+ + NO_3^- \rightarrow NO + 2\,H_2O)$ $3\,Cu + 8\,H^+ + 2\,NO_3^- \rightarrow 3\,Cu^{2+} + 2\,NO + 4\,H_2O$	**2 points** for the correctly balanced redox reaction with acceptable work. **1 point** can be earned if the complete reaction is incorrect but the work shows a correctly balanced reduction half reaction

(k) Identify the limiting reactant. Show work to support your answer.

amount 1.019g 0.25M 0.25M *reaction* $3\ Cu + 8\ H^+ + 2\ NO_3^- \rightarrow 3\ Cu^{2+} + 2\ NO + 4\ H_2O$ *conversion* 63.55g 0.250 mL 0.250 mL mol$_{present}$ 0.01600 0.063 0.063 if Cu limiting multiply by $\frac{8}{3}$ $\frac{2}{3}$ mol$_{reacted}$ 0.01600 0.043 0.043 mol$_{excess}$ 0 0.020 0.052 therefore Cu is limiting	**1 point** for the correct number of moles of ***all*** reactants present. **1 point** for the identifying Cu as the limiting reactant with proper mathematical justification.

(l) On the basis of the limiting reactant identified above, calculate the value of the concentration of Cu^{2+} ions after the reaction is complete.

0.0160 mol Cu : 0.0160 mol of Cu^{2+} $\frac{0.0160\text{ mol}}{0.250\text{ L}} = 0.0640M\ Cu^{2+}$	**1 point** for the correct number of moles of Cu^{2+} consistent with the previous part. **1 point** for the concentration of Cu^{2+}

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Question 6
(9 points)

In a laboratory experiment, Pb and an unknown metal Q were immersed in solutions containing aqueous ions of unknown metals Q and X. The following reactions summarize the observations.

Observation 1: $\text{Pb}(s) + \text{X}^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{X}(s)$
Observation 2: $\text{Q}(s) + \text{X}^{2+}(aq) \rightarrow$ no reaction
Observation 3: $\text{Pb}(s) + \text{Q}^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{Q}(s)$

(a) On the basis of the reactions indicated above, arrange the three metals, Pb, Q, and X, in order from least reactive to most reactive on the lines provided below.

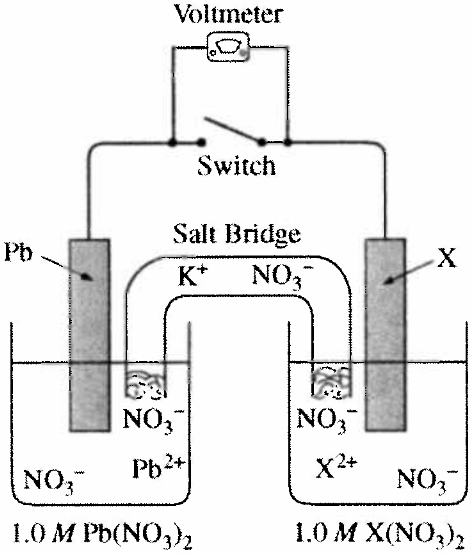
____Q____ , ____X____ , ____Pb____

least reactive metal | most reactive metal

Q, X, Pb	2 points are earned for the correctly ordered relationship. (1 point earned for Q, Pb, X or X, Q, Pb)

Question 6 (continued)

The diagram below shows an electrochemical cell that is constructed with a Pb electrode immersed in 100. mL of 1.0 *M* $Pb(NO_3)_2(aq)$ and an electrode made of metal X immersed in 100. mL of 1.0 *M* $X(NO_3)_2(aq)$. A salt bridge containing saturated aqueous KNO_3 connects the anode compartment to the cathode compartment. The electrodes are connected to an external circuit containing a switch, which is open. When a voltmeter is connected to the circuit as shown, the reading on the voltmeter is 0.47 V. When the switch is closed, electrons flow through the switch from the Pb electrode toward the X electrode.



(b) Write the equation for the half-reaction that occurs at the anode.

$Pb(s) \rightarrow Pb^{2+}(aq) + 2\,e^-$	1 point is earned for the correct equation.

(c) The value of the standard potential for the cell, $E°$, is 0.47 V.

(i) Determine the standard reduction potential for the half-reaction that occurs at the cathode.

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ $E^\circ_{cathode} = E^\circ_{cell} + E^\circ_{anode}$ $E^\circ_{cathode} = 0.47 + (-0.13) = 0.34$ V	1 point is earned for the calculated reduction potential with mathematical justification.

Question 6 (continued)

(ii) Determine the identity of metal X.

The metal is copper.	1 point is earned for identification of the metal.

(d) Describe what happens to the mass of each electrode as the cell operates.

The mass of the Pb electrode decreases and the mass of the Cu electrode increases.	1 point is earned for both descriptions.

(e) During a laboratory session, students set up the electrochemical cell shown above. For each of the following three scenarios, choose the correct value of the cell voltage and justify your choice.

(i) A student bumps the cell setup, resulting in the salt bridge losing contact with the solution in the cathode compartment. Is V equal to 0.47 or is V equal to 0? Justify your choice.

V = 0 V. The transfer of ions through the salt bridge will stop. A charge imbalance between the half-cells will prevent electrons from flowing through the wire.	1 point is earned for the correct choice with an appropriate explanation.

(ii) A student spills a small amount of 0.5 M $Na_2SO_4(aq)$ into the compartment with the Pb electrode, resulting in the formation of a precipitate. Is V less than 0.47 or is V greater than 0.47 ? Justify your choice.

V > 0.47 V. The sulfate ion will react with the Pb^{2+} ion to form a precipitate. This results in a thermodynamically favored anode half-cell reaction and hence a larger potential difference. The choice may also be justified using the Nernst equation. $E_{cell} = E^\circ_{cell} - \left(\frac{RT}{nF}\right)\ln\frac{[Pb^{2+}]}{[Cu^{2+}]}$ Decreasing the $[Pb^{2+}]$ will increase the cell voltage.	1 point is earned for the correct choice with an appropriate explanation.

(iii) After the laboratory session is over, a student leaves the switch closed. The next day, the student opens the switch and reads the voltmeter. Is V less than 0.47 or is V equal to 0.47? Justify your choice.

V < 0.47 V. Over time, $[Pb^{2+}]$ increases and $[Cu^{2+}]$ decreases, making both half-cell reactions less thermodynamically favorable. The choice may also be justified using the Nernst equation. Increasing $[Pb^{2+}]$ and decreasing $[Cu^{2+}]$ decreases the cell voltage. The choice may also be justified by stating that the voltage is zero as a result of the establishment of equilibrium.	1 point is earned for the correct choice with an appropriate explanation.

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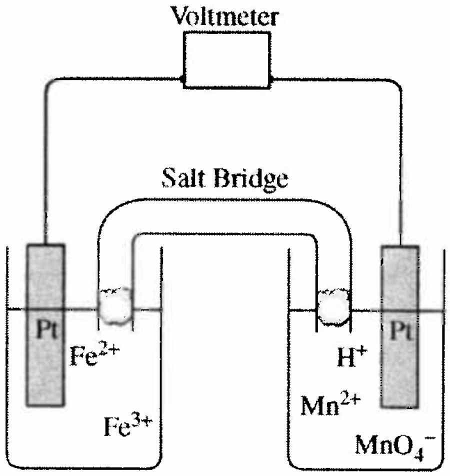
Question 2
(10 points)



$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

A galvanic cell and the balanced equation for the spontaneous cell reaction are shown above. The two reduction half-reactions for the overall reaction that occurs in the cell are shown in the table below.

Half-Reaction	$E°$ (V) at 298 K
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$	+1.49

(a) On the diagram, clearly label the cathode.

The electrode in the beaker on the right should be labeled.	One point is earned for correct identification of the cathode.

(b) Calculate the value of the standard potential, $E°$, for the spontaneous cell reaction.

$E_{cell} = 1.49 - 0.77 = 0.72$ V	One point is earned for the correct numerical answer.

(c) How many moles of electrons are transferred when 1.0 mol of $MnO_4^-(aq)$ is consumed in the overall cell reaction?

5.0 moles of electrons are transferred.	One point is earned for the correct numerical answer.

Question 2 (continued)

(d) Calculate the value of the equilibrium constant, K_{eq}, for the cell reaction at 25°C. Explain what the magnitude of K_{eq} tells you about the extent of the reaction.

$\log K_{eq} = \frac{nE}{0.0592} = \frac{5 \times 0.72}{0.0592} = 61$ $K_{eq} = 6.5 \times 10^{60}$ Because the magnitude of K_{eq} is very large, the extent of the cell reaction is also very large and the reaction goes essentially to completion.	One point is earned for the correct substitution. One point is earned for the correct numerical answer. One point is earned for an explanation.

Three solutions, one containing $Fe^{2+}(aq)$, one containing $MnO_4^-(aq)$, and one containing $H^+(aq)$, are mixed in a beaker and allowed to react. The initial concentrations of the species in the mixture are 0.60 M $Fe^{2+}(aq)$, 0.10 M $MnO_4^-(aq)$, and 1.0 M $H^+(aq)$.

(e) When the reaction mixture has come to equilibrium, which species has the higher concentration, $Mn^{2+}(aq)$ or $MnO_4^-(aq)$? Explain.

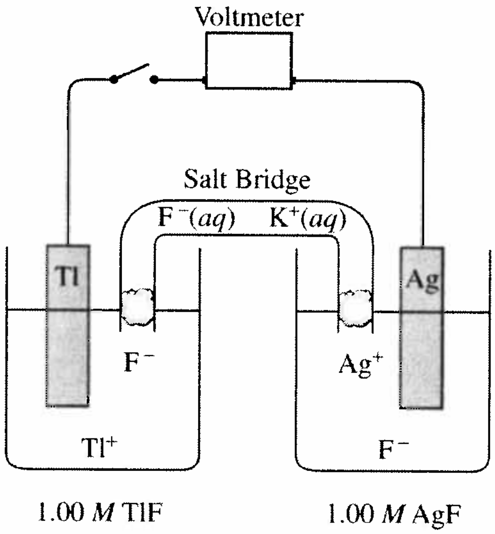
$[Mn^{2+}(aq)]$ will be greater than $[MnO_4^-(aq)]$ because: (1) as indicated in part (d), the reaction essentially goes to completion, and (2) there is more than sufficient Fe^{2+} and H^+ to react completely with the MnO_4^-. $[MnO_4^-(aq)]$ at equilibrium is essentially zero.	One point is earned for the choice of Mn^{2+} with the explanation including only item (1). One point is earned for including item (2) in the explanation.

(f) When the reaction mixture has come to equilibrium, what are the molar concentrations of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$?

At equilibrium, $[Fe^{2+}(aq)] = [Fe^{2+}(aq)]_{initial} - 5[MnO_4^-(aq)]_{reacted}$ $= 0.60 - 5(0.10) = 0.10\ M$ $[Fe^{3+}(aq)] = 5 \times [MnO_4^-(aq)]_{reacted}$ $= 5(0.10) = 0.50\ M$	One point is earned for a correct setup (including a correct setup for an equilibrium calculation). One point is earned for correct numerical answers.

Question 6 (9 points)

Answer the following questions about electrochemical cells.



It is observed that when silver metal is placed in aqueous thallium(I) fluoride, TlF, no reaction occurs. When the switch is closed in the cell represented above, the voltage reading is +1.14 V.

(a) Write the reduction half-reaction that occurs in the cell.

$Ag^+ + e^- \rightarrow Ag$	One point is earned for the correct equation.

(b) Write the equation for the overall reaction that occurs in the cell.

$Tl + Ag^+ \rightarrow Tl^+ + Ag$	One point is earned for the correct equation.

(c) Identify the anode in the cell. Justify your answer.

The anode is where oxidation occurs. In the overall reaction Tl is oxidized to Tl^+, so the anode is the Tl electrode in the left cell.	One point is earned for the correct answer with justification.

(d) On the diagram above, use an arrow to clearly indicate the direction of electron flow as the cell operates.

The arrow should show electron flow in the direction from the Tl electrode through the wire to the Ag electrode.	One point is earned for a correct arrow.

Question 6 (continued)

(e) Calculate the value of the standard reduction potential for the Tl^+/Tl half-reaction.

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$ $+1.14\text{ V} = +0.80\text{V} - E^\circ_{ox}$ $E^\circ_{ox} = \mathbf{-0.34\ V}$	One point is earned for the correct setup. One point is earned for the correct answer.

The standard reduction potential, E°, of the reaction $Pt^{2+} + 2\,e^- \rightarrow Pt$ is 1.20 V.

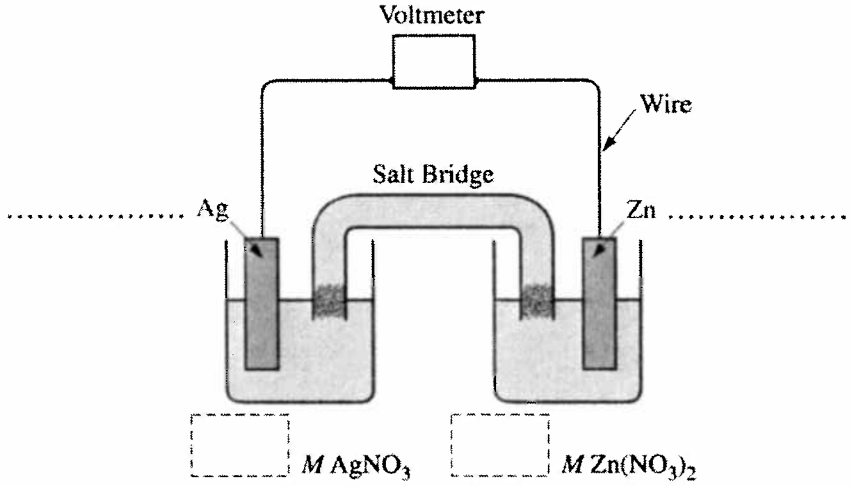
(f) Assume that electrodes of pure Pt, Ag, and Ni are available as well as 1.00 *M* solutions of their salts. Three different electrochemical cells can be constructed using these materials. Identify the two metals that when used to make an electrochemical cell would produce the cell with the largest voltage. Explain how you arrived at your answer.

E°(V) $Ni^{2+} + 2\,e^- \rightarrow Ni$ −0.25 $Ag^+ + e^- \rightarrow Ag$ 0.80 $Pt^{2+} + 2\,e^- \rightarrow Pt$ 1.20 $E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$ The two metals that yield the largest E°_{cell} are those with the biggest difference in E°, namely, Pt and Ni (see E°_{cell} calculation below). $E^\circ_{cell} = +1.20 - (-0.25) = +1.45\text{ V}$	One point is earned for the correct answer with justification.

(g) Predict whether Pt metal will react when it is placed in 1.00 *M* $AgNO_3(aq)$. Justify your answer.

When Pt metal is added to 1.00 *M* $AgNO_3$, the only redox reaction that could occur would be for Pt to become oxidized as Ag^+ is reduced. $E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox} = +0.80\text{ V} - (+1.20\text{ V}) = -0.40\text{ V}$ Because E°_{cell} for that reaction is negative, no reaction will occur.	One point is earned for comparing E° values. One point is earned for the correct interpretation.

Question 6



6. The following questions refer to the electrochemical cell shown in the diagram above.

(a) Write a balanced net ionic equation for the spontaneous reaction that takes place in the cell.

$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$ $Ag^+(aq) + e^- \rightarrow Ag(s)$ $Zn(s) + 2\,Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$	1 point for the balanced net-ionic equation 1 point for correct direction (reactants and products)

(b) Calculate the standard cell potential, $E°$, for the reaction in part (a).

$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$ $E° = -0.76$ V $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E° = +0.80$ V $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = +0.80\text{ V} - (-0.76\text{ V}) = +1.56\text{ V}$	1 point for the correct, positive E°_{cell}

(c) In the diagram above,

(i) label the anode and the cathode on the dotted lines provided, and

The anode is the zinc metal electrode, the cathode is the silver metal electrode.	1 point for the correct metal for anode and cathode

Question 6 (cont'd.)

(ii) indicate, in the boxes below the half-cells, the concentration of $AgNO_3$ and the concentration of $Zn(NO_3)_2$ that are needed to generate $E°$

$[AgNO_3] = [Zn(NO_3)_2] = 1\ M$	1 point for the correct concentration for the anodic chamber 1 point for the correct concentration for the cathodic chamber

(d) How will the cell potential be affected if KI is added to the silver half-cell? Justify your answer.

A precipitate will form as I^- ions react with Ag^+ ions in solution in cathode compartment. $[Ag^+]$ will be reduced, causing cell potential to decrease.	1 point for correctly indicating a reaction occurs 1 point for indicating the cell potential decreases