STARTER FOR 10...

The electrochemical series

Good **reducing agents** (good at losing electrons)

Reduction half equation	**$E^{\ominus}$ / V**
$Li^{+}(aq) + 1\,e^{-} \rightleftharpoons Li(s)$	–3.03
$Ba^{2+}(aq) + 2\,e^{-} \rightleftharpoons Ba(s)$	–2.90
$Ca^{2+}(aq) + 2\,e^{-} \rightleftharpoons Ca(s)$	–2.87
$Al^{3+}(aq) + 2\,e^{-} \rightleftharpoons Al(s)$	–1.66
$Zn^{2+}(aq) + 2\,e^{-} \rightleftharpoons Zn(s)$	–0.76
$Fe^{2+}(aq) + 2\,e^{-} \rightleftharpoons Fe(s)$	–0.44
$Cr^{3+}(aq) + 1\,e^{-} \rightleftharpoons Cr^{2+}(aq)$	–0.41
$V^{3+}(aq) + 1\,e^{-} \rightleftharpoons V^{2+}(aq)$	–0.26
$Sn^{2+}(aq) + 2\,e^{-} \rightleftharpoons Sn(s)$	–0.14
$2\,H^{+}(aq) + 2\,e^{-} \rightleftharpoons H_2(aq)$	0.00
$Cu^{2+}(aq) + 1\,e^{-} \rightleftharpoons Cu^{+}(aq)$	+0.15
$Cu^{2+}(aq) + 2\,e^{-} \rightleftharpoons Cu(s)$	+0.34
$VO^{2+}(aq) + 2\,H^{+}(aq) + 1\,e^{-} \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$Cu^{+}(aq) + 1\,e^{-} \rightleftharpoons Cu(s)$	+0.52
$I_2(s) + 2\,e^{-} \rightleftharpoons 2\,I^{-}(aq)$	+0.54
$MnO_4^{-}(aq) + 1\,e^{-} \rightleftharpoons MnO_4^{2-}(aq)$	+0.56
$MnO_4^{2-}(aq) + 2\,H_2O(l) + 2\,e^{-} \rightleftharpoons MnO_2(s) + 4\,OH^{-}(aq)$	+0.59
$O_2(g) + 2\,H^{+}(aq) + 2\,e^{-} \rightleftharpoons H_2O_2(aq)$	+0.68
$Fe^{3+}(aq) + 1\,e^{-} \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^{+}(aq) + 1\,e^{-} \rightleftharpoons Ag(s)$	+0.80
$VO_2^{+}(aq) + 2\,H^{+}(aq) + 1\,e^{-} \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
$Br_2(g) + 2\,e^{-} \rightleftharpoons 2\,Br^{-}(aq)$	+1.07
$\frac{1}{2}\,O_2(g) + 2\,H^{+} + 2\,e^{-} \rightleftharpoons H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14\,H^{+}(aq) + 6\,e^{-} \rightleftharpoons 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$Cl_2(g) + 2\,e^{-} \rightleftharpoons 2\,Cl^{-}(aq)$	+1.36
$MnO_4^{-}(aq) + 8\,H^{+}(aq) + 5\,e^{-} \rightleftharpoons Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
$HClO(g) + H^{+}(aq) + 1\,e^{-} \rightleftharpoons \frac{1}{2}\,Cl_2(g) + H_2O(l)$	+1.59
$H_2O_2(aq) + 2\,H^{+}(aq) + 2\,e^{-} \rightleftharpoons 2\,H_2O(l)$	+1.77
$F_2(g) + 2\,e^{-} \rightleftharpoons 2\,F^{-}(aq)$	+2.87

Good **oxidising agents** (good at gaining electrons)

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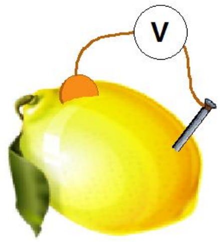
STARTER FOR 10...

12.3. Calculations involving electrochemical cells

1. For each of the electrochemical cells described below;



(i) Calculate the emf of the cell as written,

(ii) Identify the reaction occurring at the positive and negative electrodes,

(iii) Write an equation for the overall cell reaction which occurs when the electrodes are connected

Assume standard conditions. Use the table of standard electrode potentials provided at the start of this chapter for reference.

(a) $Al(s) \mid Al^{3+}(aq) \parallel Zn^{2+}(aq) \mid Zn(s)$

$E^{\ominus}_{cell}$..

Positive electrode half equation...

Negative electrode half equation ....

Overall cell reaction...(4 marks)

(b) $Cl^{-}(aq) \mid Cl_2(g) \parallel Fe^{2+}(aq) \mid Fe(s)$

$E^{\ominus}_{cell}$..

Positive electrode half equation...

Negative electrode half equation ....

Overall cell reaction...(4 marks)

2. The electrochemical cell shown below is set up;

$$Pt \mid Mn^{2+}(aq)\text{ , }MnO_4^{-}(aq) \parallel S_2O_8^{2-}(aq), SO_4^{2-}(aq) \mid Pt,\ E^{\ominus}_{cell} = +0.50\text{ V}$$

(a) Calculate the standard electrode potential for the following half-reaction;

$$S_2O_8^{2-}(aq) + 2e^{-} \rightleftharpoons 2SO_4^{2-}(aq)$$

....

....(1 mark)

(b) For the standard electrode potentials, all ion concentrations must be 1 mol dm^{-3}.

Deduce what effect an increase in the concentration of $S_2O_8^{2-}(aq)$ ions to higher than 1 mol dm^{-3} would have on $E^{\ominus}_{cell}$.

....

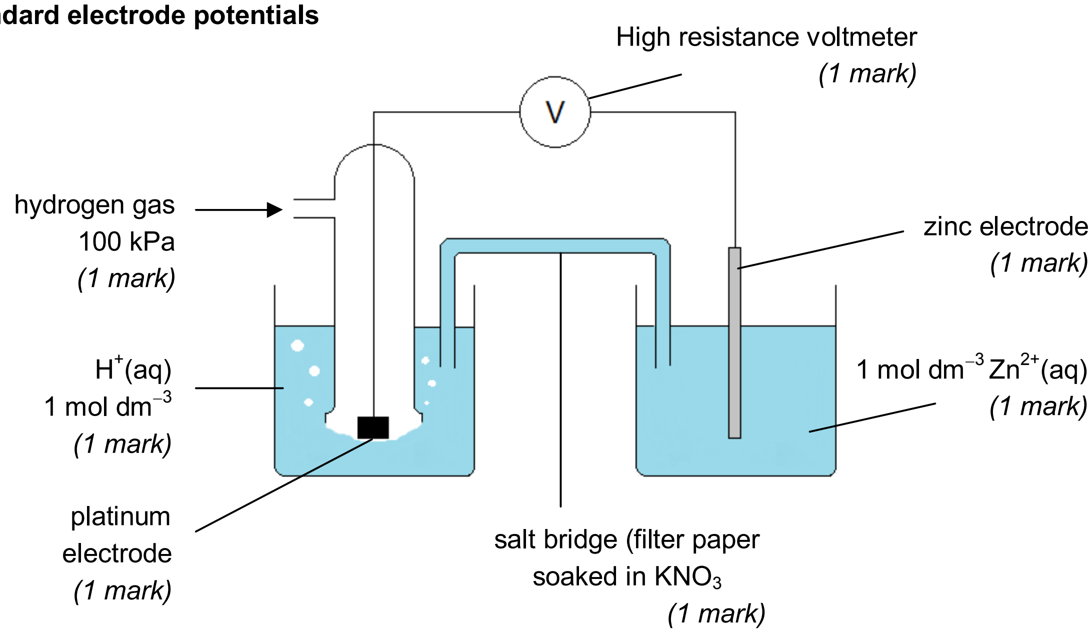
....(1 mark)

STARTER FOR 10...

12. Redox equilibria answers

12.2. Standard electrode potentials

1.



2. (a)

|	Shows a salt bridge
‖	Indicates a phase boundary

(1 mark)

(b) (i) Pt | H_2(g) | H^+(aq) ‖ Fe^{2+}(aq) | Fe(s) *(1 mark)*

(ii) Pt | H_2(g) | H^+(aq) ‖ MnO_4^-(aq), MnO_4^{2-}(aq) | Pt *(1 mark)*

12.3. Calculations involving electrochemical cells

1. (a) $E^\ominus_{cell}$ = –0.76 – (–1.66) = <u>+0.90 V</u> *(1 mark)*

Positive electrode: $Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$ × 3 *(1 mark)*

Negative electrode: $Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-$ × 2 *(1 mark)*

Overall cell reaction: $3\ Zn^{2+}(aq) + 2\ Al(s) \rightarrow 3\ Zn(s) + 2\ Al^{3+}(aq)$ *(1 mark)*

(b) $E^\ominus_{cell}$ = –0.44 – (+1.36) = <u>–1.80 V</u> *(1 mark)*

Positive electrode: $Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)$ *(1 mark)*

Negative electrode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$ *(1 mark)*

Overall cell reaction: $Cl_2(g) + Fe(s) \rightarrow 2\ Cl^-(aq) + Fe^{2+}(aq)$ *(1 mark)*

2. (a) +0.50 V = $E^\ominus_{RHS}$ – (+1.51 V), ∴ <u>$E^\ominus_{RHS}$ = +2.01 V</u> *(1 mark)*

STARTER FOR 10...

12. Redox equilibria answers

(b) According to Le Chatelier's principle, an increase in the concentration of $S_2O_8^{2-}$(aq) ions causes the equilibrium to shift to the right (using up electrons) and therefore $E^\ominus_{RHS}$ will become more positive. Since $E^\ominus_{cell} = E^\ominus_{RHS} - E^\ominus_{LHS}$, the more positive $E^\ominus_{RHS}$ the more positive $E^\ominus_{cell}$. Therefore $E^\ominus_{cell}$ <u>will increase / become more positive.</u> *(1 mark)*

12.4. Using E*m*$_{sat}$ values to predict reactions

1. (a) (i) $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34$ V, so $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

$Br_2(g) + 2e^- \rightleftharpoons 2Br^-(aq)$ $E^\ominus = +1.07$ V, so $Br_2(g) + 2e^- \rightarrow 2Br^-(aq)$

Hence the reaction, $Cu^{2+}(aq) + 2Br^-(aq) \rightarrow Cu(s) + Br_2(g)$ is <u>not feasible</u> *(1 mark)*

(ii) $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ $E^\ominus = -0.44$ V, so $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34$ V, so $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

Hence the reaction, $Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$ <u>is feasible</u> *(1 mark)*

(b) $Fe^{3+}(aq) + 1e^- \rightleftharpoons Fe^{2+}(aq)$ $E^\ominus = +0.77$ V

$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$ $E^\ominus = +2.87$ V

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36$ V

$Br_2(g) + 2e^- \rightleftharpoons 2Br^-(aq)$ $E^\ominus = +1.07$ V

$I_2(g) + 2e^- \rightleftharpoons 2I^-(aq)$ $E^\ominus = +0.54$ V

For the halogen to oxidise the Fe^{3+} ions, <u>+0.77 V must be the more negative reduction potential</u>. Therefore any of <u>fluorine, chlorine or bromine</u> would be a suitable oxidising agent. *(2 marks)*

(c) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ $E^\ominus = +1.33$ V

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ $E^\ominus = +1.51$ V

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36$ V

Comparing initially at the reduction potentials for MnO_4^-/Mn^{2+} and Cl_2/Cl^-, the latter has the more negative value and hence the chloride ions in the hydrochloric acid will be oxidised by the MnO_4^- to produce chlorine gas which is toxic. Hence a solution of MnO_4^- cannot be acidified by HCl. *(1 mark)*

Comparing now at the reduction potentials for $Cr_2O_7^{2-}/Cr^{3+}$ and Cl_2/Cl^-, the formed now has the more positive value and hence the chloride ions cannot be oxidised by $Cr_2O_7^{2-}$ (this of course assumes standard conditions). *(1 mark)*

2. (a) $Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ $E^\ominus = -0.14$ V

$V^{3+}(aq) + 1e^- \rightleftharpoons V^{2+}(aq)$ $E^\ominus = -0.26$ V