Topic 19 Redox processes (HL)

Syllabus:

19.1 Electrochemical cells

A voltaic cell generates an electromotive force (EMF) resulting in the movement of electrons from the anode to the cathode via the external circuit. The EMF is termed the cell potential (E°).

The standard hydrogen electrode (SHE) consists of an inert platinum electrode in contact with 1 mol dm^{-3} hydrogen ion and hydrogen gas at 100 kPa and 298 K. The standard electrode potential (E°) is the potential (voltage) of the reduction half-equation under standard conditions measured relative to the SHE. Solute concentration is 1 mol dm^{-3} or 100 kPa for gases. E° of the SHE is 0 V.

In the electrolysis of water, water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode.

$\Delta G° = -nFE°$. If E° is positive, ΔG° is negative and the reaction is spontaneous. If E° is negative, ΔG° is positive and the reaction is not spontaneous.

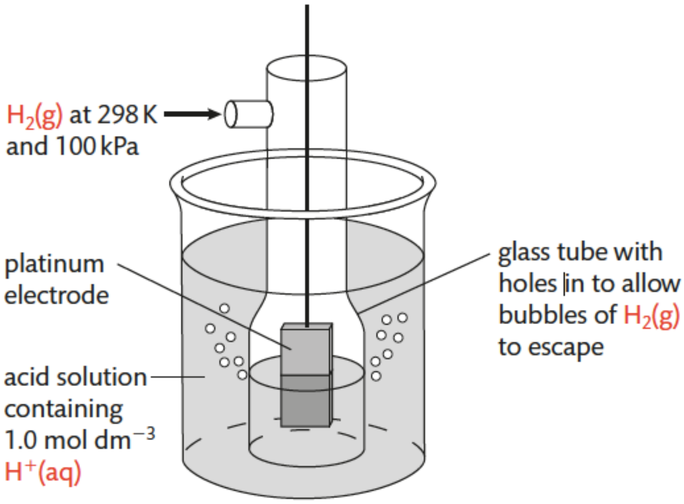
Current, duration of the electrolysis and charge on the ion affect the amount of product formed at the electrodes during electrolysis.

Electroplating involves the electrolytic coating of an object with a metallic thin layer.

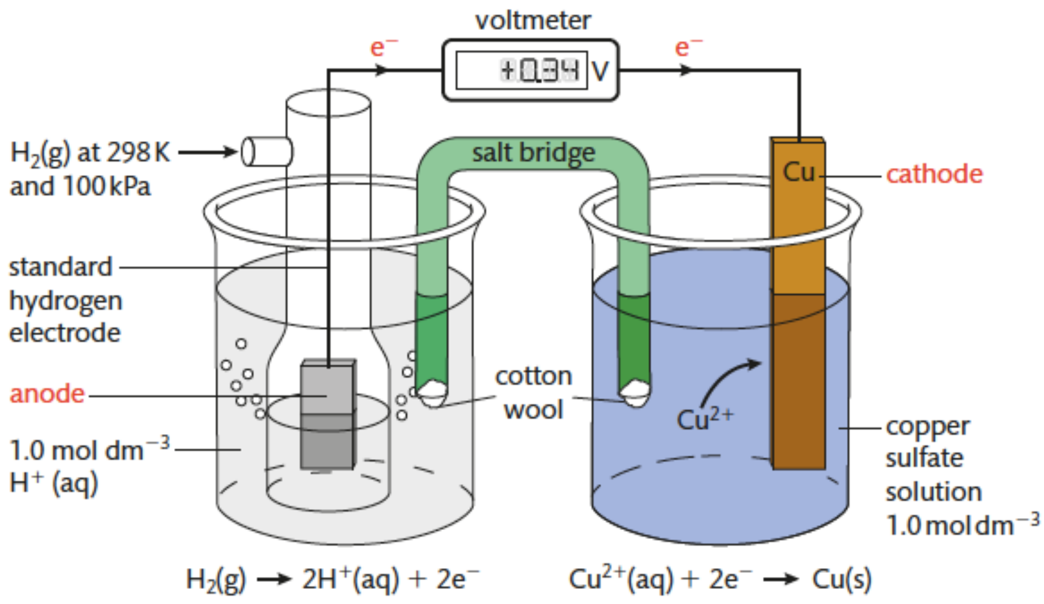
19.1 Electrochemical cells

(A) Standard Hydrogen Electrode (SHE)

- Electromotive force (EMF) is the potential difference generated by a voltaic cell.
- Each half-cell has the electrode potential value (E) which depends on the difference in tendency of the two half-cells to undergo reduction.
- The **standard electrode potential(E°)** of a half-cell can be measured by connecting to standard hydrogen electrode (SHE) which is a reference standard, by an external circuit with a high-resistance voltmeter and a salt bridge.



- Inert Platinum is used as the electrode in SHE.
- $[H^+] = 1.0$ mol dm^{-3}
- The pressure of H_2 is 100 kPa.
- 298 K
- $2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad E^\circ = 0$ V
- The half-cell with positive E° oxidizes SHE.
- The half-cell with negative E° reduces SHE.

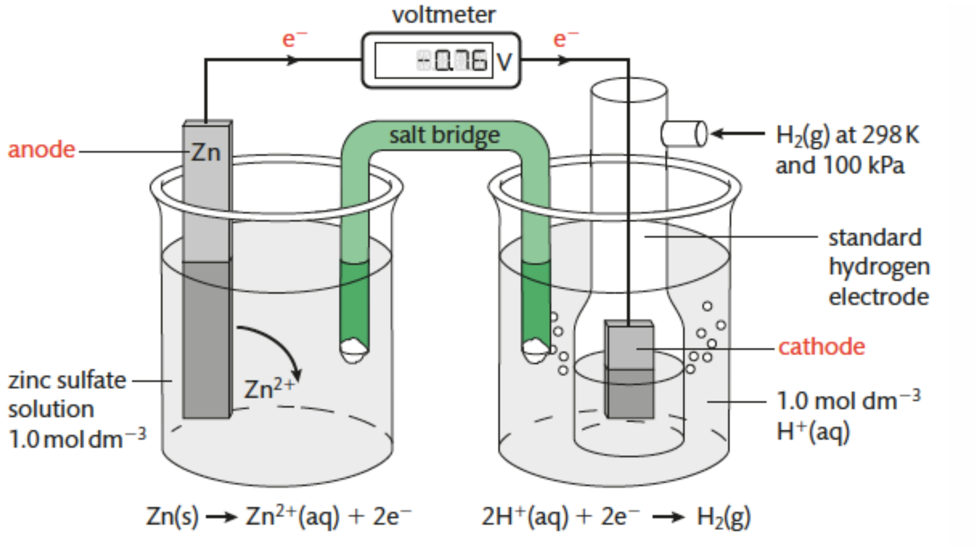


E° for $Cu^{2+}(aq)\,|\,Cu(s)$ half-cell is +0.34V.

Oxidation: $H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$

Reduction: $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

Overall: $Cu^{2+}(aq) + H_2(g) \rightleftharpoons 2H^+(aq) + Cu(s)$ $\quad E^\circ_{cell} = +0.34V$



E° for $Zn^{2+}(aq)\,|\,Zn(s)$ half-cell is −0.76V.

Oxidation: $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$

Reduction: $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

Overall: $Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$ $E^\circ_{cell} = +0.76V$

(B) Calculating the cell potential

- $E^{\circ}_{cell} = E^{\circ}_{cell}$(Reduction) – E°_{cell}(Oxidation)
- Directly copy the value from data book, DON'T change the sign.
- The half-cell with higher E° will be reduced, the half-cell with lower E° will be oxidized.
- F_2 is the strongest O.A, Li is the strongest R.A.
- Anti-Clockwise rule
- Spontaneous reaction for positive E°_{cell}
- Non-spontaneous reaction for negative E°_{cell}

24. Standard electrode potentials at 298 K

Oxidized species	$\rightleftharpoons$	Reduced species	$E^\ominus$ (V)
$Li^+(aq) + e^-$	$\rightleftharpoons$	$Li(s)$	–3.04
$K^+(aq) + e^-$	$\rightleftharpoons$	$K(s)$	–2.93
$Ca^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ca(s)$	–2.87
$Na^+(aq) + e^-$	$\rightleftharpoons$	$Na(s)$	–2.71
$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$	–2.37
$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$	–1.66
$Mn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mn(s)$	–1.18
$H_2O(l) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g) + OH^-(aq)$	–0.83
$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	–0.76
$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$	–0.45
$Ni^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ni(s)$	–0.26
$Sn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn(s)$	–0.14
$Pb^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s)$	–0.13
$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + e^-$	$\rightleftharpoons$	$Cu^+(aq)$	+0.15
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2SO_3(aq) + H_2O(l)$	+0.17
$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34
$\frac{1}{2}O_2(g) + H_2O(l) + 2e^-$	$\rightleftharpoons$	$2OH^-(aq)$	+0.40
$Cu^+(aq) + e^-$	$\rightleftharpoons$	$Cu(s)$	+0.52
$\frac{1}{2}I_2(s) + e^-$	$\rightleftharpoons$	$I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$	+0.80
$\frac{1}{2}Br_2(l) + e^-$	$\rightleftharpoons$	$Br^-(aq)$	+1.09
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\rightleftharpoons$	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$\frac{1}{2}Cl_2(g) + e^-$	$\rightleftharpoons$	$Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+} + 4H_2O(l)$	+1.51
$\frac{1}{2}F_2(g) + e^-$	$\rightleftharpoons$	$F^-(aq)$	+2.87

Question 1

Find the EMF for a voltaic cell consisting of a zinc half-cell and a copper half-cell and write the balanced redox equation for the reaction.

$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s) \qquad E^{\circ} = -0.76V$

$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s) \qquad E^{\circ} = +0.34V$

Question 2

Determine whether the reaction is spontaneous or not using E°.

$Ni(s) + Mn^{2+}(aq) \rightarrow Ni^{2+}(aq) + Mn(s)$

$Ni^{2+}(aq) + 2e^{-} \rightleftharpoons Ni(s) \qquad E^{\circ} = -0.26V$

$Mn^{2+}(aq) + 2e^{-} \rightleftharpoons Mn(s) \qquad E^{\circ} = -1.18V$