ELECTROCHEMISTRY

REDOX
Reduction gain of electrons \( \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \)
Oxidation removal of electrons \( \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \)

HALF CELLS
- these are systems involving oxidation or reduction
- there are several types

METALS IN CONTACT WITH SOLUTIONS OF THEIR IONS

| Reaction | \( \text{Cu}^{2+}(aq) + 2e^- \leftrightarrow \text{Cu}(s) \) |
| Electrode | copper |
| Solution | \( \text{Cu}^{2+}(aq) (1M) \) - 1M copper sulphate solution |
| Potential | + 0.34V |

| Reaction | \( \text{Zn}^{2+}(aq) + 2e^- \leftrightarrow \text{Zn}(s) \) |
| Electrode | zinc |
| Solution | \( \text{Zn}^{2+}(aq) (1M) \) - 1M zinc sulphate solution |
| Potential | - 0.76V |

GASES IN CONTACT WITH SOLUTIONS OF THEIR IONS

| Reaction | \( 2\text{H}^+(aq) + 2e^- \leftrightarrow \text{H}_2(g) \) |
| Electrode | platinum - you need a metal to get electrons in and out |
| Solution | \( \text{H}^+(aq) (1M) \) - 1M hydrochloric acid or 0.5M sulphuric |
| Gas | hydrogen at 100kPa (1 atm) pressure |
| Potential | 0.00V |

IMPORTANCE This half cell is known as... THE STANDARD HYDROGEN ELECTRODE

SOLUTIONS OF IONS IN TWO DIFFERENT OXIDATION STATES

| Reaction | \( \text{Fe}^{3+}(aq) + e^- \leftrightarrow \text{Fe}^{2+}(aq) \) |
| Electrode | platinum - you need a metal to get electrons in and out |
| Solution | \( \text{Fe}^{3+}(aq) (1M) \) and \( \text{Fe}^{2+}(aq) (1M) \) |
| Potential | + 0.77 V |

SOLUTIONS OF OXIDISING AGENTS IN ACID SOLUTION

| Reaction | \( \text{MnO}_4^- (aq) + 8\text{H}^+(aq) + 5e^- \leftrightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}(l) \) |
| Electrode | platinum - you need a metal to get electrons in and out |
| Solution | \( \text{MnO}_4^- (aq) (1M) \) and \( \text{Mn}^{2+}(aq) (1M) \) and \( \text{H}^+(aq) \) |
| Potential | + 1.52 V |
CELL POTENTIAL
- each electrode / electrolyte combination has its own half-reaction

Measurement
- it is impossible to measure the potential of a single electrode BUT...
- you can measure the potential difference between two electrodes
- value is measured relative to a reference cell under standard conditions

STANDARD ELECTRODE POTENTIAL
The potential difference of a cell when the electrode is connected to the standard hydrogen electrode under standard conditions

The value is affected by...
- temperature
- pressure of any gases
- solution concentration

The ultimate reference is the STANDARD HYDROGEN ELECTRODE.

![Diagram of standard hydrogen electrode](https://example.com/diagram)

**CONDITIONS**
- temperature: 298K
- solution conc: 1 mol dm⁻³ with respect to H⁺ hydrogen
- pressure: 100 kPa (1 atm)

**WHY USE PLATINUM?**
- you need an inert metal to get the electrons in / out

Standard hydrogen electrode

\[ E^\circ = 0.00V \]

However, as it is difficult to set up, secondary standards are used.

Secondary standards
- The standard hydrogen electrode (SHE) is hard to set up so it is easier to use a more convenient secondary standard which has been calibrated against the SHE.

Calomel
- the calomel electrode contains Hg₂Cl₂
- it has a standard electrode potential of +0.27V
- is used as the left hand electrode to determine the potential of an unknown
- to obtain the \( E^\circ \) value of the unknown cell ADD 0.27V to the measured potential
Experimental determination of $E^\circ$

In the diagram below the standard hydrogen electrode is shown coupled up to a zinc half cell. The voltmeter reading gives the standard electrode potential of the zinc cell.

The species with the more positive potential ($E^\circ$ value) will oxidise one (i.e. reverse the equation) with a lower $E^\circ$ value.

Example

What will happen if an $Sn_{(s)}/Sn^{2+}_{(aq)}$ cell and a $Cu_{(s)}/Cu^{2+}_{(aq)}$ cell are connected?

- Write out the appropriate equations
  
  - $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$; $E^\circ = +0.34V$
  
  - $Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)}$; $E^\circ = -0.14V$

- the half reaction with the more positive $E^\circ$ value is more likely to work
- it gets the electrons by reversing the half reaction with the lower $E^\circ$ value
- therefore $Cu^{2+}_{(aq)} \rightarrow Cu_{(s)}$ and $Sn_{(s)} \rightarrow Sn^{2+}_{(aq)}$
- the overall reaction is $Cu^{2+}_{(aq)} + Sn_{(s)} \rightarrow Sn^{2+}_{(aq)} + Cu_{(s)}$
- the cell voltage is the difference in $E^\circ$ values ... $(+0.34) - (-0.14) = +0.48V$
### THE ELECTROCHEMICAL SERIES

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Standard Reduction Potential (E°) / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2(\text{g}) + 2e^- \rightarrow 2\text{F}^- (\text{aq}) )</td>
<td>+2.87</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+ (\text{aq}) + 2e^- \rightarrow 2\text{H}_2\text{O}(\text{l}) )</td>
<td>+1.77</td>
</tr>
<tr>
<td>( \text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5e^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O}(\text{l}) )</td>
<td>+1.52</td>
</tr>
<tr>
<td>( \text{PbO}_2(\text{s}) + 4\text{H}^+ (\text{aq}) + 2e^- \rightarrow \text{Pb}^{2+} (\text{aq}) + 2\text{H}_2\text{O}(\text{l}) )</td>
<td>+1.47</td>
</tr>
<tr>
<td>( \text{Ce}^{4+} (\text{aq}) + e^- \rightarrow \text{Ce}^{3+} (\text{aq}) )</td>
<td>+1.45</td>
</tr>
<tr>
<td>( \text{Cl}_2(\text{g}) + 2e^- \rightarrow 2\text{Cl}^- (\text{aq}) )</td>
<td>+1.36</td>
</tr>
<tr>
<td>( \text{Cr}_2\text{O}_7^{2-} (\text{aq}) + 14\text{H}^+ (\text{aq}) + 6e^- \rightarrow 2\text{Cr}^{3+} (\text{aq}) + 7\text{H}_2\text{O}(\text{l}) )</td>
<td>+1.33</td>
</tr>
<tr>
<td>( \text{MnO}_2(\text{s}) + 4\text{H}^+ (\text{aq}) + 2e^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 2\text{H}_2\text{O}(\text{l}) )</td>
<td>+1.23</td>
</tr>
<tr>
<td>( \text{Br}_2(\text{l}) + 2e^- \rightarrow 2\text{Br}^- (\text{aq}) )</td>
<td>+1.07</td>
</tr>
<tr>
<td>( \text{Ag}^+ (\text{aq}) + e^- \rightarrow \text{Ag} (\text{s}) )</td>
<td>+0.80</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} (\text{aq}) + e^- \rightarrow \text{Fe}^{2+} (\text{aq}) )</td>
<td>+0.77</td>
</tr>
<tr>
<td>( \text{O}_2(\text{g}) + 2\text{H}^+ (\text{aq}) + 2e^- \rightarrow \text{H}_2\text{O}_2(\text{l}) )</td>
<td>+0.68</td>
</tr>
<tr>
<td>( \text{I}_2(\text{s}) + 2e^- \rightarrow 2\text{I}^- (\text{aq}) )</td>
<td>+0.54</td>
</tr>
<tr>
<td>( \text{Cu}^+ (\text{aq}) + e^- \rightarrow \text{Cu} (\text{s}) )</td>
<td>+0.52</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Cu} (\text{s}) )</td>
<td>+0.34</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} (\text{aq}) + e^- \rightarrow \text{Cu}^+ (\text{aq}) )</td>
<td>+0.15</td>
</tr>
<tr>
<td>( \text{Sn}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Sn}^0 (\text{s}) )</td>
<td>+0.15</td>
</tr>
<tr>
<td>( \text{H}_2(\text{g}) )</td>
<td>0.00</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Pb} (\text{s}) )</td>
<td>-0.13</td>
</tr>
<tr>
<td>( \text{Sn}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Sn} (\text{s}) )</td>
<td>-0.14</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Ni} (\text{s}) )</td>
<td>-0.25</td>
</tr>
<tr>
<td>( \text{Cr}^{3+} (\text{aq}) + e^- \rightarrow \text{Cr}^{2+} (\text{aq}) )</td>
<td>-0.41</td>
</tr>
<tr>
<td>( \text{Fe}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Fe} (\text{s}) )</td>
<td>-0.44</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Zn} (\text{s}) )</td>
<td>-0.76</td>
</tr>
<tr>
<td>( \text{Al}^{3+} (\text{aq}) + 3e^- \rightarrow \text{Al} (\text{s}) )</td>
<td>-1.66</td>
</tr>
<tr>
<td>( \text{Mg}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Mg} (\text{s}) )</td>
<td>-2.38</td>
</tr>
<tr>
<td>( \text{Na}^+ (\text{aq}) + e^- \rightarrow \text{Na} (\text{s}) )</td>
<td>-2.71</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Ca} (\text{s}) )</td>
<td>-2.87</td>
</tr>
<tr>
<td>( \text{K}^+ (\text{aq}) + e^- \rightarrow \text{K} (\text{s}) )</td>
<td>-2.92</td>
</tr>
</tbody>
</table>

**Interpretation**
- **F**₂ is the best oxidising agent: highest \( E^\circ \) value; most feasible reaction
- **K**⁺ is the worst oxidising agent: lowest \( E^\circ \) value; least feasible reaction
- **K** is the best reducing agent: most feasible reverse reaction

**Use of \( E^\circ \)**
- Used to predict the feasibility (likelihood) of redox and cell reactions
- In theory, ANY REDOX REACTION WITH A POSITIVE \( E^\circ \) VALUE WILL WORK
- In practice, it will proceed if the \( E^\circ \) value is greater than + 0.40V

An equation with a more positive \( E^\circ \) value will reverse a less positive one.
Combining half-cells

In the cell, copper has a more positive $E^\circ$ value (+0.34V) than zinc (-0.76V).

- The zinc metal is more reactive
- It dissolves to give ions
  \[
  \text{Zn}_\text{(s)} \rightarrow \text{Zn}^{2+}_\text{(aq)} + 2e^- 
  \]
- The electrons produced go round the external circuit to the copper
- Electrons are picked up by copper ions and copper is deposited
  \[
  \text{Cu}^{2+}_\text{(aq)} + 2e^- \rightarrow \text{Cu}_\text{(s)} 
  \]
- The voltage of the cell is 1.10V i.e. (+0.34V) - (-0.76V)

Cell diagrams

These give a diagrammatic representation of what is happening in a cell. Place the cell with the more positive $E^\circ$ value on the RHS of the diagram.

- Zn is in contact with a solution of zinc ions
- The solutions are joined by a salt bridge
- The solution of copper ions is in contact with copper

Drawing it out as shown indicates that ...

- The cell reaction goes from left to right
- The electrons go round the external circuit from left to right
- The cell voltage is $E^\circ$(RHS) - $E^\circ$(LHS). In this way it must be positive
- Oxidation takes place at the anode and reduction at the cathode

Conclusion

The reaction(s) will proceed from left to right

\[
\text{Oxidation} \quad \text{Zn}_\text{(s)} \rightarrow \text{Zn}^{2+}_\text{(aq)} + 2e^- \quad \text{at the ANODE}
\]

\[
\text{Reduction} \quad \text{Cu}^{2+}_\text{(aq)} + 2e^- \rightarrow \text{Cu}_\text{(s)} \quad \text{at the CATHODE}
\]

Electrons Go from the anode to the cathode via the external circuit

Cell reaction
\[
\text{Zn}_\text{(s)} + \text{Cu}^{2+}_\text{(aq)} \rightarrow \text{Zn}^{2+}_\text{(aq)} + \text{Cu}_\text{(s)}
\]

Cell voltage
\[
E^\circ(\text{RHS}) - E^\circ(\text{LHS}) = 0.34V - (-0.76V) = 1.10V
\]
**Example**  Will this reaction be spontaneous?  \[ \text{Sn}_2(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Sn}^{2+}(aq) + \text{Cu}(s) \]

**Method**

- Write out the half equations
  \[ \text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s) ; \ E^o = +0.34V \]
  \[ \text{Sn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Sn}(s) ; \ E^o = -0.14V \]

  **as reductions with their \( E^o \) values**

  - The reaction which occurs involves the more positive one reversing the other
  - therefore  \[ \text{Cu}^{2+}(aq) \rightarrow \text{Cu}(s) \] and  \[ \text{Sn}(s) \rightarrow \text{Sn}^{2+}(aq) \]

  - If this is the equation you want (which it is) then it will be spontaneous

  - The cell voltage is the difference in \( E^o \) values...
    \[ (+0.34V) - (-0.14V) = +0.48V \]

**NOTE:**  **DOUBLING AN EQUATION DOES NOT DOUBLE THE \( E^o \) VALUE**

\[ \frac{1}{2}\text{Cl}_2(g) + e^- \rightleftharpoons \text{Cl}^-(aq) \quad E^o = +1.36V \]
\[ \text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq) \quad E^o = +1.36V \]

**Q.1**  Which of the following reactions occur spontaneously ?

- \( \text{Fe}(s) + \text{Zn}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Zn}(s) \)
- \( \text{Sn}^{4+}(aq) + 2\text{Fe}^{2+}(aq) \rightarrow 2\text{Fe}^{3+}(aq) + \text{Sn}^{2+}(aq) \)
- \( \text{Sn}^{4+}(aq) + 2\text{I}^-(aq) \rightarrow \text{I}_2(s) + \text{Sn}^{2+}(aq) \)
- \( \text{Cl}_2(g) + 2\text{Br}^-(aq) \rightarrow \text{Br}_2(g) + 2\text{Cl}^-(aq) \)
- \( \text{I}_2(g) + 2\text{Br}^- (aq) \rightarrow \text{Br}_2(g) + 2\text{I}^-(aq) \)
- \( 2\text{H}^+(aq) + \text{Zn}(s) \rightarrow \text{H}_2(s) + \text{Zn}^{2+}(aq) \)

For those that work, calculate the cell voltage.

**IMPORTANT WARNING**

**Limitation of using \( E^o \) to predict the feasibility of a reaction**

**Kinetic**

Standard electrode potentials are not always accurate in their predictions. They indicate if a reaction is possible but cannot say what the rate will be. Some reactions will not be effective as they are too slow.

**Conditions**

Because **TEMPERATURE** and **CONCENTRATION** affect the value of a standard electrode potential any variation can also affect the probability of a reaction taking place. Concentrations do change during a reaction.

*Apply le Chatelier’s principle to predict the change in \( E^o \)*
Q.2 Explain what reactions, if any, will occur if aqueous solutions of KCl, KBr and KI are treated with:
   a) acidified KMnO₄
   b) acidified K₂Cr₂O₇.

Q.3 Using $E^\circ$ values, explain why zinc reacts with dilute acids to produce hydrogen gas but silver doesn’t.

Q.4 Construct a cell diagram for a cell made up from Ni²⁺/Ni and Zn²⁺/Zn. Work out the overall reaction and calculate the potential difference of the cell.

Q.5 Why is hydrochloric acid not used to acidify potassium manganate(VII) ?

Q.6 Explain why the chemistry of copper(I) in aqueous solution is limited. The following half equations will help. Name the overall process which takes place.

\[
\begin{align*}
Cu^{+}_{(aq)} + e^- &\rightleftharpoons Cu_{(s)} \quad E^\circ = +0.52V \\
Cu^{2+}_{(aq)} + e^- &\rightleftharpoons Cu^{+}_{(aq)} \quad E^\circ = +0.15V
\end{align*}
\]