Electrochemical Cell (A2)

An electrochemical cell converts chemical energy to electrical energy.

It can be constructed by combining two half-cells with different $E^\ominus$ values.

The half-cell with the more +ve $E^\ominus$ value forms the +ve terminal.

The half cell with the more −ve $E^\ominus$ value forms the −ve terminal

Standard Cell Potential, $E^\ominus_{cell}$

Definition: a measure of the tendency of the electrons to flow through the external circuit when two half cells are combined, under standard conditions of 25°C, 1 atm pressure and 1 mol dm^{-3} concentration.

$E^\ominus_{cell}$ calculation:

$$\boxed{E^\ominus_{cell} = E^\ominus_{(reduction)} - E^\ominus_{(oxidation)}}$$

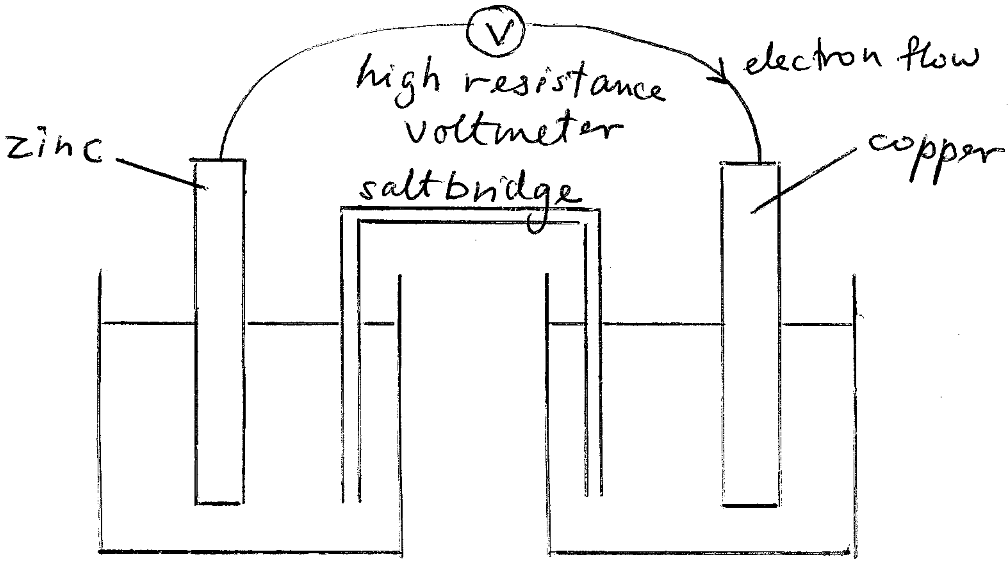
or

$$\boxed{E^\ominus_{cell} = E^\ominus_{(cathode)} - E^\ominus_{(anode)}.}$$

Daniel Cell.

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ $\quad E^\ominus = -0.76V$

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



Zinc sulfate solⁿ $[Zn^{2+}] = 1\ mol\,dm^{-3}$

Copper(II) sulfate solⁿ $[Cu^{2+}] = 1\ mol\,dm^{-3}$

$E^\ominus_{cell} = E^\ominus(\text{reduction}) - E^\ominus(\text{oxidation})$

$= +0.34 - (-0.76)$

$= +1.10\ V$

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

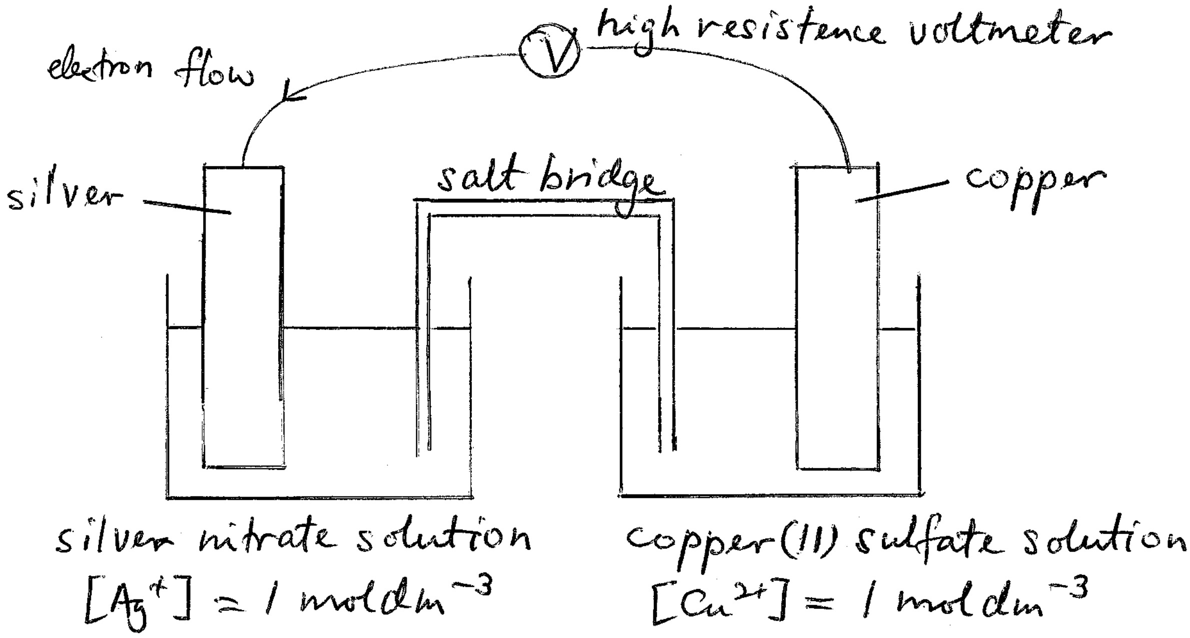
Cell diagram:

$Zn_{(s)} / Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)} / Cu_{(s)}$

A cell consisting of half cells: $Cu_{(s)}$ in $CuSO_{4(aq)}$ and $Ag_{(s)}$ in $AgNO_{3(aq)}$

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

$$2Ag^+_{(aq)} + 2e^- \rightleftharpoons 2Ag_{(s)} \qquad E^\ominus = +0.80V$$



$$E^\ominus_{cell} = E^\ominus(\text{reduction}) - E^\ominus(\text{oxidation})$$
$$= +0.80 - (+0.34)$$
$$= +0.46 \, V$$

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$
$$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$$
$$Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

Cell diagram:

$$Cu_{(s)} / Cu^{2+}_{(aq)} // Ag^+_{(aq)} / Ag_{(s)}$$

Note: Doubling an equation does not double the $E^\ominus$ value

$$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \qquad E^\ominus = +0.80V$$
$$2Ag^+_{(aq)} + 2e^- \rightleftharpoons 2Ag_{(s)} \qquad E^\ominus = +0.80V$$

Cell Diagram

V → electron flow.

Anode $Zn_{(s)} \,|\, Zn^{2+}_{(aq)} \,||\, Cu^{2+}_{(aq)} \,|\, Cu_{(s)}$ Cathode

zinc is in contact with a solution of zinc ions.

the solutions are joined by a salt bridge

the solution of copper ion is in contact with copper

These give a diagrammatic representation of what is happening in a cell.

- Place the half cell with the more positive $E^\ominus$ value on the RHS
- the cell reaction goes from left to right
- the electrons go round the external circuit from left to right.
- the cell voltage is $E^\ominus_{(RHS)} - E^\ominus_{(LHS)}$. In this way it must be positive.
- oxidation takes place at the anode, reduction at the cathode.

Conclusion : The reactions will proceed from left to right

OXidation $\quad Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ at the ANODE

REDuction $\quad Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ at the CATHODE

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

Cell reaction $\quad Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Cell voltage $\quad E^\ominus(RHS) - E^\ominus(LHS) = +0.34V - (-0.76V) = +1.10V$

Predict the feasibility of a reaction using standard cell potential

Reactions with positive $E^\ominus_{cell}$ are thermodynamically feasible under standard conditions.

Example 1, Will this reaction occur spontaneously?

$$Sn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + Cu_{(s)}$$

Method 1

- Write out the appropriate equations as reductions with their $E^\ominus$ values.

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

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

- The reaction which take place will involve the more positive one reversing the other.
  i.e. $Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)}$ and $Sn_{(s)} \longrightarrow Sn^{2+}_{(aq)}$
- The cell voltage will be the difference in $E^\ominus$ values
  $E^\ominus = +0.34 - (-0.14) = +0.48\ V$
- The value is positive, the reaction will be spontaneous
- Note: if the equation is in the opposite direction, then $E^\ominus = -0.48V$, the reaction will not be spontaneous.

Method 2

- Find the reduction equations and respective $E^\ominus$ values

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

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

$$E^\ominus_{cell} = E^\ominus(\text{reduction}) - E^\ominus(\text{oxidation})$$
$$= +0.34 - (-0.14V)$$
$$= +0.48V$$ (positive – thermodynamically feasible.

Example 2: Predict whether Zn metal can reduce Sn^{4+} ions to Sn^{2+} ions.

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^\ominus = -0.76\,V$$
$$Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)} \qquad E^\ominus = +0.15\,V$$

$$E^\ominus_{cell} = E^\ominus_{(reduction)} - E^\ominus_{(oxidation)}$$
$$= E^\ominus_{(cathode)} - E^\ominus_{(anode)}$$
$$= +0.15 - (-0.76)$$
$$= +0.91\,V$$

+ve, reaction is possible.

or

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^\ominus = -0.76\,V$$
$$Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)} \qquad E^\ominus = +0.15\,V \leftarrow \text{more positive}$$

Reduction	$Sn^{4+}_{(aq)} + 2e^- \longrightarrow Sn^{2+}_{(aq)}$	$E^\ominus = +0.15\,V$
Oxidation	$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$	$E^\ominus = +0.76\,V$
Redox	$Sn^{4+}_{(aq)} + Zn_{(s)} \longrightarrow Sn^{2+}_{(aq)} + Zn^{2+}_{(aq)}$	$E^\ominus_{cell} = +0.15 + 0.76 = +0.91\,V$

$E^\ominus_{cell}$ (+ve), reaction is possible.

Example 3 : Predict whether hydrogen peroxide is able to oxidise the aqueous bromide ions to bromine.

$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons 2H_2O_{(l)}$ $\quad E^\ominus = +1.77V$

$Br_{2(l)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$ $\quad E^\ominus = +1.07V$

$E^\ominus_{cell} = E^\ominus(\text{reduction}) - E^\ominus(\text{oxidation})$

$= E^\ominus(\text{cathode}) - E^\ominus(\text{anode})$

$= +1.77 - (-1.07)$

$= +0.70V$ (+ve)

reaction is possible.

Or

$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightleftharpoons 2H_2O_{(l)}$ $\quad E^\ominus = +1.77V$

$Br_{2(l)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$ $\quad E^\ominus = +1.07V$

Oxidation $\quad 2Br^-_{(aq)} \longrightarrow Br_{2(l)} + 2e^-$ $\quad E^\ominus = -1.07V$

Reduction $\quad H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \longrightarrow 2H_2O_{(l)}$ $\quad E^\ominus = +1.77V$

Redox $\quad H_2O_{2(aq)} + 2H^+_{(aq)} + 2Br^-_{(aq)} \longrightarrow 2H_2O_{(l)} + Br_{2(l)}$ $\quad E^\ominus_{cell} = -1.07 + 1.77 = +0.70V$

$E^\ominus_{cell}$ = +ve, reaction is possible

Uses of $E^{\ominus}_{cell}$

1. To predict cell voltage
2. To predict the direction of electron flow from a simple cell
3. To predict if a reaction will occur.

Limitations of predictions made using $E^{\ominus}$ values

However, the prediction of reaction is not supported by experiment because:

1. The reaction is considered energetically favourable but kinetically unfavourable (high activation energy).
2. The actual reaction conditions are not standard conditions.

Example 1

Oxidation of methanal to methanoic acid by acidified potassium dichromate(VI).

$$3HCHO + Cr_2O_7^{2-} + 8H^+ \longrightarrow 2Cr^{3+} + HCOOH + 4H_2O \quad E^{\ominus}_{cell} = +1.27$$

The reaction is predicted to be feasible.

However, in practice, there is no reaction at room temperature due to high activation energy. Heating is required for the reaction to occur.

Example 2:

Oxidation of concentrated HCl by MnO_2

$$MnO_2 + 4H^+ + 2Cl^- \xrightarrow{\Delta} Mn^{2+} + 2H_2O + Cl_2$$

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O \qquad E^\ominus = +1.23\,V$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad E^\ominus = +1.36\,V$$

$$E^\ominus_{cell} = -0.13\,V.$$

The prediction fails because $E^\ominus$ value does not apply when non-standard conditions are used

Ion concentration affecting $E^\ominus$ value

All the $E^\ominus$ values given in the Standard Electrode Potential series refer to aqueous ions of concentration 1.0 mol dm^{-3}

Example 1.

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

If $[Cu^{2+}]$ increases,

the positive of equilibrium will shift to the RHS according to Le Chatelier's principle.

This will make copper electrode more positively-charged.

Hence, the electrode potential will become more positive.

If $[Cu^{2+}]$ decreases,

The position of equilibrium will shift to the LHS according to Le Chatelier's principle.

This will make the copper electrode more negatively-charged.

Hence, the electrode potential will become more negative

The measured electrode potentials for the copper half-cell and Zinc half-cell at different concentration:

ionic concentration / $mol\,dm^{-3}$	0.1	1.0*	10.0
Cu/Cu^{2+} half-cell	+0.311	+0.340	+0.369
Zn/Zn^{2+} half-cell	-0.790	-0.760	-0.731

* standard condition.

Example 2

$$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)} \qquad E^\ominus = +1.36V$$

What happen to the $E^\ominus$ values if the concentration of the Cl^- ion is altered?

$[Cl^-]$ / $mol\,dm^{-3}$	0.1	1.0*	10.0
$E^\ominus$ / V	+1.419	+1.360	+1.301

Example 3.

Consider the following cells:

$Zn_{(s)} / Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)} / Cu_{(s)}$

The two half cells are:

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ $\quad E^\ominus = -0.76V$

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

The redox reaction:

$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

$E^\ominus_{cell} = E^\ominus_{(reduction)} - E^\ominus_{(oxidation)}$

$= +0.34 - (-0.76) = +1.10V$

case 1

If the concentration of Cu^{2+} is increased, the above redox reaction will displaced to the RHS

Hence, the $E^\ominus_{cell} > +1.10V$

case 2

If the concentration of Cu^{2+} is decreased, or the concentration of Zn^{2+} is increased, the redox reaction will be displaced to the LHS

Hence, the $E^\ominus_{cell} < +1.10V$