ELECTROCHEMISTRY

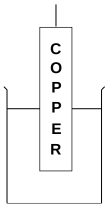
REDOX

Reduction	**gain** of electrons	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
Oxidation	**removal** of electrons	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

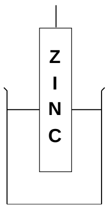
HALF CELLS

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

METALS IN CONTACT WITH SOLUTIONS OF THEIR IONS

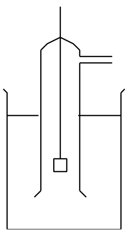


Reaction $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
Electrode **copper**
Solution $Cu^{2+}(aq)$ **(1M)** - 1M copper sulphate solution
Potential **+ 0.34V**



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

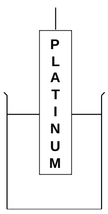
GASES IN CONTACT WITH SOLUTIONS OF THEIR IONS



Reaction $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$
Electrode **platinum** - *you need a metal to get electrons in and out*
Solution $H^+(aq)$ **(1M)** - 1M hydrochloric acid or 0.5M sulphuric

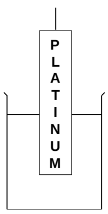
Gas **hydrogen at 100kPa (1 atm) pressure**
Potential **0.00V**
IMPORTANCE **This half cell is known as...** **THE STANDARD HYDROGEN ELECTRODE**

SOLUTIONS OF IONS IN TWO DIFFERENT OXIDATION STATES



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

SOLUTIONS OF OXIDISING AGENTS IN ACID SOLUTION



Reaction $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$
Electrode **platinum** - *you need a metal to get electrons in and out*
Solution $MnO_4^-(aq)$ **(1M)** and $Mn^{2+}(aq)$ **(1M)** and $H^+(aq)$
Potential **+ 1.52 V**

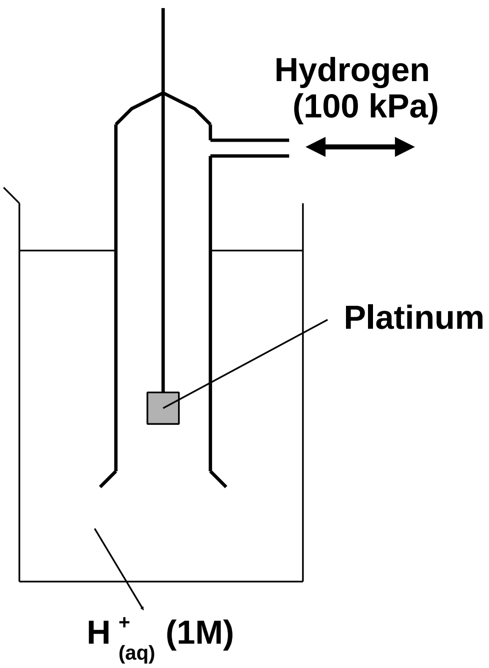
CELL POTENTIAL
- each electrode / electrolyte combination has its own half-reaction

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 refernce 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.**



CONDITIONS

temperature	**298K**
solution conc	**1 mol dm^{-3} with respect to H^+**
hydrogen	**100 kPa (1 atm) pressure**

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

Standard hydrogen electrode

E° = 0.00V

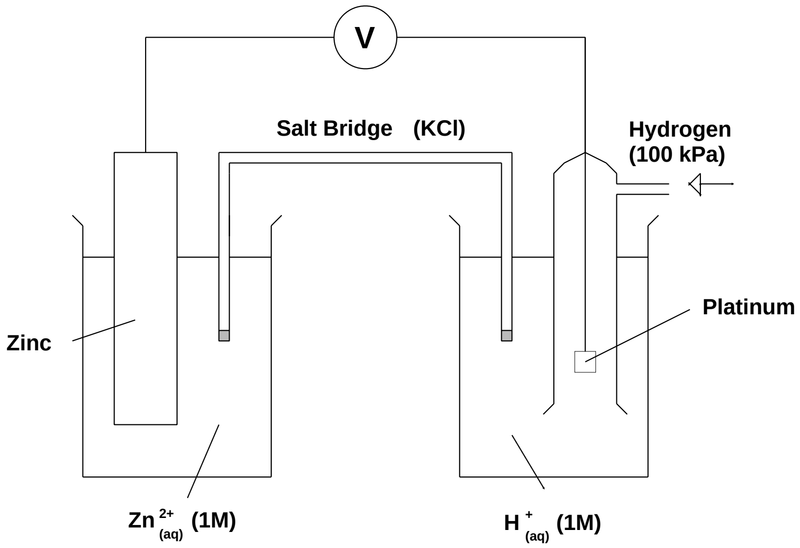
However, as it is difficult to set up, **secondary standards** are used.

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 Hg_2Cl_2
- 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° value of the unknown cell **ADD 0.27V** to the measured potential

Experimental determination of E°

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**.



salt bridge
- **filled with saturated potassium chloride solution**
- **enables the circuit to be completed**

THE ELECTROCHEMICAL SERIES

Layout Species are arranged in order of their standard electrode potentials to get a series that tells us how good a species is (as an oxidising agent) at picking up electrons.

All equations are written as reduction processes ... i.e. gaining electrons

e.g. $Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$ $E° = -1.66V$

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

The species with the more positive potential (E° value)
will oxidise one (i.e. reverse the equation) **with a lower E° 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* $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$; $E° = +0.34V$
  $Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)}$; $E° = -0.14V$

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

THE ELECTROCHEMICAL SERIES

			E° / V
$F_{2(g)} + 2e^-$	$\rightleftharpoons$	$2F^-_{(aq}$	+2.87
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^-$	$\rightleftharpoons$	$2H_2O_{(l)}$	+1.77
$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5e^-$	$\rightleftharpoons$	$Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.52
$PbO_{2(s)} + 4H^+_{(aq)} + 2e^-$	$\rightleftharpoons$	$Pb^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.47
$Ce^{4+}{}_{(aq)} + e^-$	$\rightleftharpoons$	$Ce^{3+}{}_{(aq)}$	+1.45
$Cl_{2(g)} + 2e^-$	$\rightleftharpoons$	$2Cl^-_{(aq)}$	+1.36
$Cr_2O_7^{2-}{}_{(aq)} + I4H^+_{(aq)} + 6e^-$	$\rightleftharpoons$	$2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33
$MnO_{2(s)} + 4H^+_{(aq)} + 2e^-$	$\rightleftharpoons$	$Mn^{2+}_{(aq)} + 2H_2O_{(l)}$	+1.23
$Br_{2(l)} + 2e^-$	$\rightleftharpoons$	$2Br^-_{(aq)}$	+1.07
$Ag^+_{(aq)} + e^-$	$\rightleftharpoons$	$Ag_{(s)}$	+0.80
$Fe^{3+}_{(aq)} + e^-$	$\rightleftharpoons$	$Fe^{2+}_{(aq)}$	+0.77
$O_{2(g)} + 2H^+_{(aq)} + 2e^-$	$\rightleftharpoons$	$H_2O_{2(l)}$	+0.68
$I_{2(s)} + 2e^-$	$\rightleftharpoons$	$2I^-_{(aq)}$	+0.54
$Cu^+_{(aq)} + e^-$	$\rightleftharpoons$	$Cu_{(s)}$	+0.52
$Cu^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Cu_{(s)}$	+0.34
$Cu^{2+}_{(aq)} + e^-$	$\rightleftharpoons$	$Cu^+_{(aq)}$	+0.15
$Sn^{4+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Sn^{2+}_{(aq)}$	+0.15
$2H^+_{(aq)} + 2e^-$	$\rightleftharpoons$	**$H_{2(g)}$**	**0.00**
$Pb^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Pb_{(s)}$	-0.13
$Sn^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Sn_{(s)}$	-0.14
$Ni^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Ni_{(s)}$	-0.25
$Cr^{3+}_{(aq)} + e^-$	$\rightleftharpoons$	$Cr^{2+}_{(aq)}$	-0.41
$Fe^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Fe_{(s)}$	-0.44
$Zn^{2+}{}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Zn_{(s)}$	-0.76
$Al^{3+}_{(aq)} + 3e^-$	$\rightleftharpoons$	$Al_{(s)}$	-1.66
$Mg^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Mg_{(s)}$	-2.38
$Na^+_{(aq)} + e^-$	$\rightleftharpoons$	$Na_{(s)}$	-2.71
$Ca^{2+}_{(aq)} + 2e^-$	$\rightleftharpoons$	$Ca_{(s)}$	-2.87
$K^+_{(aq)} + e^-$	$\rightleftharpoons$	$K_{(s)}$	-2.92

reaction is more likely to go right

LH species better oxidising agents

RH species weaker reducing agents

RH species are harder to oxidise

LH species are easier to reduce

reactivity of metals decreases

reactivity of non-metals increases

Interpretation

F_2 is the best oxidising agent - *highest E° value; most feasible reaction*

K^+ is the worst oxidising agent - *lowest E° value; least feasible reaction*

K is the best reducing agent - *most feasible reverse reaction*

Use of E°

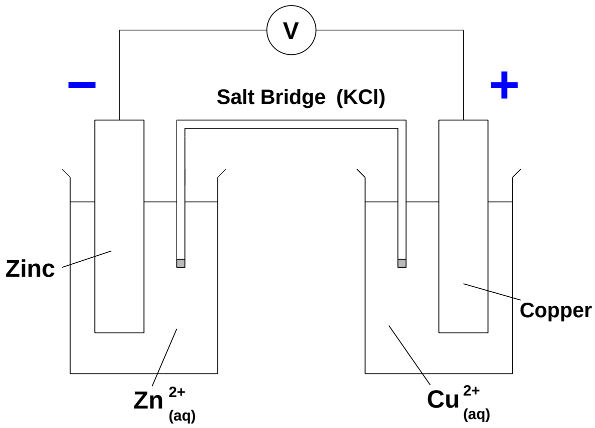
- used to **predict the feasibility (likelihood) of redox and cell reactions**
- in theory ANY REDOX REACTION WITH A POSITIVE E° VALUE WILL WORK
- **in practice, it will proceed if the E° value is greater than + 0.40V**

An equation with a more positive E° value will reverse a less positive one.

Combining half-cells

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

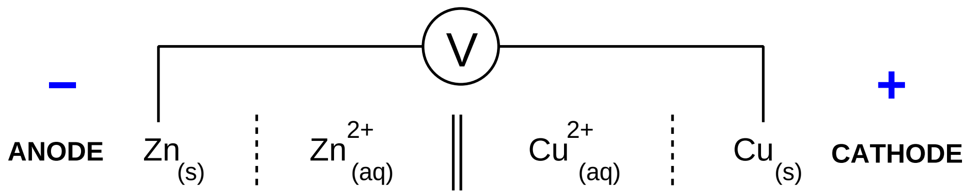
- the zinc metal is more reactive
- it dissolves to give ions
  $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$
- the electrons produced go round the external circuit to the copper
- electrons are picked up by copper ions and copper is deposited
  $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$



- The voltage of the cell is 1.10V ie (+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° value on the RHS of the diagram.



zinc 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°(RHS) - E°(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**

***OX**idation*	$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$	*at the ANODE*
***RED**uction*	$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$	*at the CATHODE*

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

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

Cell voltage **E°(RHS) - E°(LHS) = 0.34V - (- 0.76V) = 1.10V**

Example *Will this reaction be spontaneous?* $Sn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Sn^{2+}_{(aq)} + Cu_{(s)}$

Method

- *Write out the half equations* **as reductions** *with their E° values*
  $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$; $E° = +0.34V$
  $Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)}$; $E° = -0.14V$
- *The reaction which occurs involves the more positive one reversing the other therefore* $Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)}$ *and* $Sn_{(s)} \longrightarrow Sn^{2+}_{(aq)}$
- *If this is the equation you want (which it is) then it will be spontaneous*
- *The cell voltage is the difference in E° values... (+0.34V) - (-0.14V) =* ***+ 0.48V***

NOTE: DOUBLING AN EQUATION **DOES NOT** DOUBLE THE E° VALUE

$$\tfrac{1}{2}Cl_{2(g)} + e^- \rightleftharpoons Cl^-_{(aq)} \quad E° = +1.36V$$

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

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

- $Fe_{(s)} + Zn^{2+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + Zn_{(s)}$
- $Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + Sn^{2+}_{(aq)}$
- $Sn^{4+}_{(aq)} + 2I^-_{(aq)} \longrightarrow I_{2(s)} + Sn^{2+}_{(aq)}$
- $Cl_{2(g)} + 2Br^-_{(aq)} \longrightarrow Br_{2(g)} + 2Cl^-_{(aq)}$
- $I_{2(g)} + 2Br^-_{(aq)} \longrightarrow Br_{2(g)} + 2I^-_{(aq)}$
- $2H^+_{(aq)} + Zn_{(s)} \longrightarrow H_{2(s)} + Zn^{2+}_{(aq)}$

For those that work, calculate the cell voltage.

IMPORTANT WARNING

Limitation of using E° 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°

Q.2 *Explain what reactions, if any, will occur if aqueous solutions of KCl, KBr and KI are treated with;*
a) acidified $KMnO_4$
b) acidified $K_2Cr_2O_7$.

Q.3 *Using E° 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 Ni^{2+}/Ni and Zn^{2+}/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.

$$Cu^{+}_{(aq)} + e^{-} \rightleftharpoons Cu_{(s)} \qquad E° = +0.52V$$

$$Cu^{2+}_{(aq)} + e^{-} \rightleftharpoons Cu^{+}_{(aq)} \qquad E° = +0.15V$$