Chem Factsheet

September 2002 Number 37

Redox Equilibria I: Standard Electrode Potentials and Cells

To succeed with this topic you need to:
- be familiar with the concept of equilibrium (Factsheet 09);
- be able to assign oxidation numbers to elements (Factsheet 11).

After working through this Factsheet you will:
- understand the link between cells and oxidising and reducing powers (redox reactions);
- have met the Standard Hydrogen Electrode and why it is needed;
- know the definition for Standard Electrode Potential (SEP) and its symbol $E^{\ominus}$;
- be able to use SEP values to find values for different cells;
- know how SEP values affect reducing and oxiding powers.

Examination questions and techniques on SEPs and cells are covered separately in Factsheet 41.

Redox – revision

When a piece of zinc is placed in a copper salt solution the copper ions are **displaced** – zinc is more reactive than copper ions:

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

You will recognise this from the **reactivity series of metals** at GCSE level.

If we now apply oxidation numbers to the same equation:

oxidation *reduction*

$$\begin{array}{lccccccc} & \mathrm{Zn} & + & \mathrm{Cu^{2+}} & \rightarrow & \mathrm{Zn^{2+}} & + & \mathrm{Cu} \\ \text{O.N.} & 0 & & +2 & & +2 & & 0 \end{array}$$

reducing agent *oxidising agent*

ie. Zn is being oxidised by the Cu^{2+} which is the oxidant (oxidising agent). Cu^{2+} is being reduced by the Zn which is the reductant (reducing agent).

We can now separate the **half equations** from the full equation to show the transfer of electrons:

$Zn \rightarrow Zn^{2+} + 2e^-$ **oxidation** – loss of electrons (increase in ON)

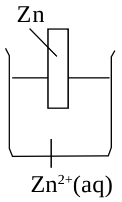
$Cu^{2+} + 2e^- \rightarrow Cu$ **reduction** – gain of electrons (decrease in ON)

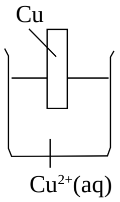
Cells

Let us stay with the zinc and copper solution displacement reaction.

The full equation shows zinc is more reactive than copper (displacement method) but doesn't tell us **how much** more reactive – this is where **cells** come into the work.

When a metal is placed into a solution of its own ions an equilibrium is set up.



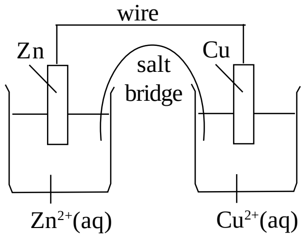


$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$ $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

You will recognise the half equations – the diagrams show the **half cells.**

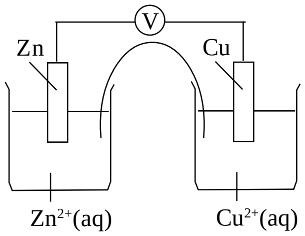
NB: In this work, half equations are always shown with electrons on the **left**.

If these two half cells are connected then the same reaction takes place as when a piece of zinc is put into a copper solution:



Electrons move from the zinc cell to the copper cell and so the zinc electrode will dissolve and the copper electrode will increase in size – this is called **short-circuiting** the cell.

However, if a **high-resistance voltmeter** is connected so electrons cannot flow through, the voltmeter gives a reading – it measures the difference in **electrode potential** between the zinc and copper cells.

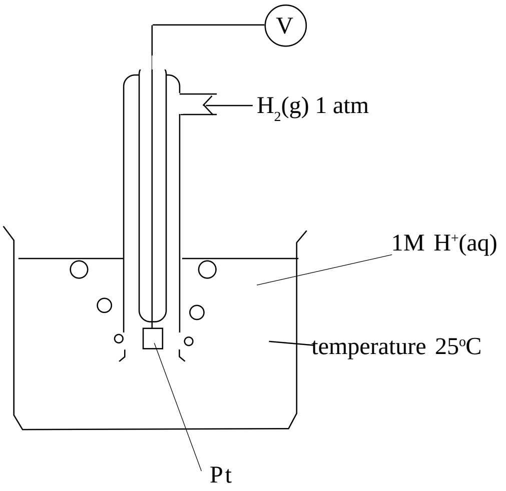


*The **salt bridge** used to connect the two half cells is a piece of filter paper soaked in **saturated potassium nitrate solution**.*
- *The salt bridge is needed to complete the circuit*
- *Potassium nitrate is chosen to **prevent preciptiation of salts** when it is dipped in the solution (nitrates are soluble). If precipitation occurred, the concentrations of the solutions would decrease, altering the electrode potentials.*

Since the reading on the voltmeter would change depending on the two half cells involved and the concentrations, we need to define standard conditions to ensure comparability:

The standard hydrogen electrode

All half cells are compared to this cell to give the voltmeter reading.



Exam Hint: - *Recall of the hydrogen electrode is commonly tested. All details of the diagram need to be learnt thoroughly.*

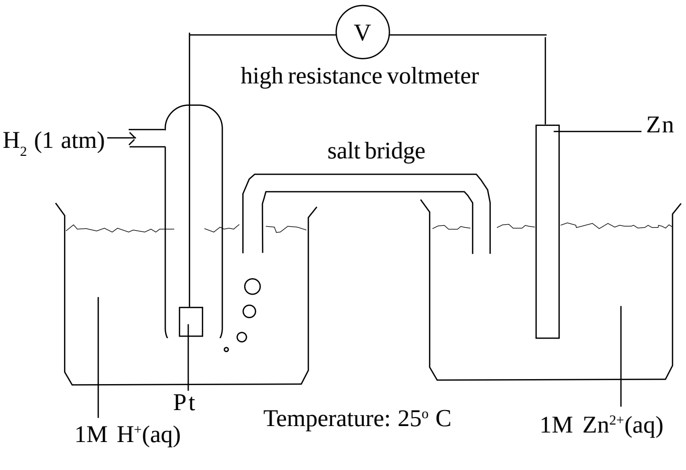
Standard electrode potential (SEP) $E^\ominus$

The E stands for EMF (electromotive force) and is the electric potential between standard cells (hence the use of $^\ominus$). It is measured in volts (V).

The hydrogen electrode is **defined** as having a standard electrode potential of 0.00 V.

*The standard electrode potential $E^\ominus$ for a half cell is when a **standard half cell** (1 mol dm^{-3}, 25°C) is connected to a **standard hydrogen electrode** (1 mol dm^{-3}H^+, 25°C, 1 atmosphere pressure) using a **high resistance voltmeter**.*

The diagram shows how this definition translates into the practical set-up for a standard zinc cell:



The reading on the voltmeter would be –0.76V. This is shown as:

$$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^\ominus = -0.76V.$$

Every half-cell has its own SEP.

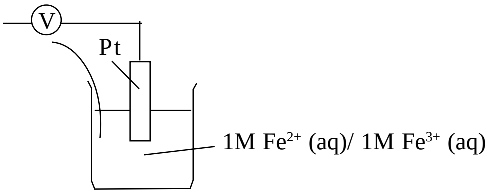
e.g. $Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus = +0.34V$

NB. (1) Electrons shown on the **left** of the half equations
(2) You do **not** need to learn $E^\ominus$ values, except that the value for the standard hydrogen electrode is 0.00V
(3) $E^\ominus$ values may be positive or negative. Always put the sign on!

Half cells without a solid metal

Half cells also exist for non-metals (eg $I_2 + 2e^- \rightleftharpoons 2I^-$) and for equilibria between two different aqueous ions (eg $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$).

A standard half cell for $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ is shown below:
Note the 1mol dm^{-3} of **both** solutions at 25°C.



Notation: Standard half cells are often written in the form
Fe^{2+} | Fe

Combining half cells

When two half cells are combined, one electrode becomes the **anode** (positive electrode), and one the **cathode** (negative electrode).

- At the **anode**, the reaction goes in the **forward** direction - **reduction** takes place.
- At the **cathode**, the reaction goes in the **reverse** direction - **oxidation** takes place.

So when looking at a cell,

- the species that is more readily **reduced**- the stronger **oxidising agent** - will be the **anode**,
- the species that is more readily **oxidised** - the stronger **reducing agent** - will be the **cathode**.

Considering the copper and zinc example from page 1: we know zinc is the stronger reducing agent, so it will be the cathode, making copper the anode.

The table of $E^\ominus$ values below can be used to determine which will be the anode and which the cathode in a cell - and hence which species is oxidised and which reduced.

Table of $E^\ominus$ values

Half Equation	$E^\ominus$/V
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.37
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$V^{2+} + 2e^- \rightleftharpoons V$	-0.26
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0.25
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

Using $E^\ominus$ Values

1. Identifying the cathode and the anode

When two half cells are combined, the one with the smaller (= more negative or less positive) SEP value is the cathode.

eg $Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^\ominus = -0.76V$
$Fe^{2+} + 2e^- \rightleftharpoons Fe \qquad E^\ominus = -0.44V$

Zn is therefore the cathode.

2. Finding the overall reaction

Once we know which is the cathode and which the anode, we know in which direction each reaction is proceding.

The reaction at the anode goes in the forward direction - so we have:

$Fe^{2+} + 2e^- \rightarrow Fe$

The reaction at the cathode goes in the reverse direction, so we have:

$Zn \rightarrow Zn^{2+} + 2e^-$

Combining these two gives the **overall cell reaction**:

$Zn + Fe^{2+} \rightarrow Fe + Zn^{2+}$

3. Calculating $E^\ominus$ cell

The difference in values between two electrodes (half cells) gives the $E^\ominus$ of the cell i.e. the reading you would see on the high resistance voltmeter.

The equation is:

$E^\ominus$ cell = E (reactant being reduced) – E (reactant being oxidised)

e.g. $Zn^{2+} | Zn \quad E = -0.76V$

$Cu^{2+} | Cu \quad E = +0.34$

Zn — cathode is OXIDISED
Cu^{2+} — anode is REDUCED

$E^\ominus$cell $= +0.34 - (-0.76)$
$= +0.34 + 0.76 = +1.10V$

4. Oxidising/ Reducing Power

- *The more positive the $E^\ominus$ value, the stronger the oxidising agent.*
- *The more negative the $E^\ominus$ value, the stronger the reducing agent.*

Questions

1. (a) Explain why the salt bridge is necessary in an electrochemical cell.

   (b) Explain why potassium nitrate is used in this bridge

2. Define standard electrode potential.

3. A cell is produced by combining these two half cells.
   $Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus = +0.34V$
   $Ag^+ + e^- \rightleftharpoons Ag \qquad E^\ominus = +0.80V$

   (a) State which is the anode

   (b) Write down the half-equations for the reaction taking place at the anode and the cathode, stating clearly which is which.

   (c) Find the overall reaction taking place in the cell

   (d) Calculate $E^\ominus$ cell

4. Use the table of $E^\ominus$ values on page 2 to answer the following questions:

   (a) Which is the stronger reducing agent, vanadium or nickel?

   (b) A student looked up $F_2 + 2e^- \rightleftharpoons 2F^-$ in a table of $E^\ominus$ values.
   He wrote down the value +1.20 V.
   Explain why this cannot be correct.

Answers

1. (a) To complete the circuit

   (b) To prevent salts being precipitated (as nitrates are soluble)

2. The standard electrode potential $E^\ominus$ for a half cell is when a standard half cell (1 mol dm^{-3}, 25°C) is connected to a standard hydrogen electorde (1 mol dm^{-3} H^+, 25°C, 1 atmosphere pressure) using a high resistance voltmeter.

3. (a) Silver

   (b) Anode: $Ag^+ + e^- \rightarrow Ag$
   Cathode: $Cu \rightarrow Cu^{2+} + 2e^-$

   (c) $2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$

   (b) 0.46V

4. (a) Vanadium

   (b) Fluorine is the strongest oxidising agent
   So its $E^\ominus$ value must be the most positive.
   This value is less than that for chlorine.

Acknowledgements:
This Factsheet was researched and written by Sam Goodman
Curriculum Press, Unit 305B, The Big Peg, 120 Vyse Street, Birmingham, B18 6NF

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