Chem Factsheet

January 2003 Number 45

Standard Electrode Potentials & The Feasibility of Reactions

To succeed with this topic you need to:
- ensure you are **fully** able to write equations for cells and work of $E^\ominus$ cell values (covered in Factsheets No.37 & 41).

After working through this Factsheet you will:
- understand the concepts of 'feasibility' of a chemical reaction and 'spontaneous change';
- be able to use $E^\ominus$ data to decide if a chemical reaction is 'feasible' or not;
- have met the concept of the 'anti-clockwise rule' as one way of assessing if a reaction is 'feasible';
- be able to write balanced chemical equations from half equations using the 'electron balance method;
- have met the concept of 'disproportionation';
- understand how 'non-standard' conditions affect the 'feasibility' of a reaction.

Introduction

We need to pick out some **key points** from earlier work before we start:

1. **REDOX** means reduction and oxidation
2. **OXIDATION NUMBERS** define whether reduction or oxidation is taking place
3. **HALF EQUATIONS** are equilibria and relate oxidised and reduced forms
4. **SEP ($E^\ominus$) VALUES (+/-)** show the tendency for oxidation or reduction for a particular half equation
5. **THE TABLE OF $E^\ominus$ VALUES** below shows the **trend** in oxidising/reducing power for particular half equations
6. **COMBINING HALF EQUATIONS** based on reduction and oxidation using $E^\ominus$values (+/-) gives the BALANCED CHEMICAL EQUATION

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
$Fe^{2+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

You must keep these ideas at the forefront of your thinking as you work through this Factsheet because all we are doing is putting them together in a slightly different way to answer these key questions:

1. Will **this** substance react with **that** substance?
2. **If** they **do** react what is the final balanced chemical equation?
3. If they **do not** react – why not?
4. What could be done to **make** them react?

'Feasibility' - will these two substances react or not?

$E^\ominus$ Values and Feasibility

The best example you can use to help you look at these key questions is the cell made by combining zinc and copper.

The Data

(a) $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V

Using the data

(b) Zn/Zn^{2+} is **above** Cu/Cu^{2+} in the table i.e. zinc will be the **cathode** i.e. the electron provider so needs to be written the other way round

$Zn \rightarrow Zn^{2+} + 2e$ i.e. **oxidation**

O.N. 0 → +2

(Zn is the **reducing agent** because it is **oxidised**)

Copper is the **anode** i.e. the electron acceptor so stays in the same order as in the table

$Cu^{2+} + 2e \rightarrow Cu$ i.e. **reduction**

+2 → 0

(Cu is the **oxidising agent** because it is **reduced**)

Writing the overall equation (the cell reaction)

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

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

NB. there are $2e^-$ on each side - so on addition they are 'cancelled out' and do not appear in the final equation.

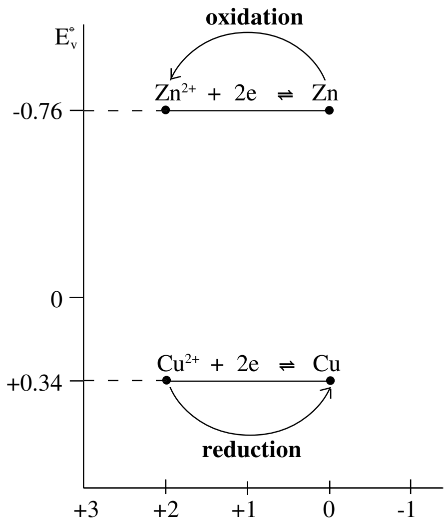
Let us look at this cell and $E^\ominus$values again if you were asked the question:
Q. Will zinc react when put into copper sulphate solution?

i.e. What is the **feasibility** of a reaction between Zn(s) and Cu^{2+}(aq)?

Before you go any further– can **you** answer the question: will Zn(s) react with Cu^{2+}(aq)?
Not sure? Go back again – there is no other way. Sorry!

The Anti-Clockwise Rule

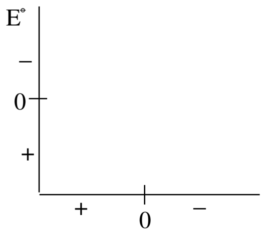
Study the following way of showing what has been talked about with the Zn/Zn^{2+} and Cu/Cu^{2+} example.



i.e. bottom line left (Cu^{2+}) reacts with top line right (Zn)

These are the key points that you need to note:

1. the anti-clockwise rule is just another way of presenting the answer to the questions 'Will Zn(s) react with Cu^{2+}(aq)?'
2. the axes can be easily remembered:



Write it on your examination paper once given the instruction to 'start' to help you remember it.

3. It's called the Anti-clockwise rule because **if** the 'graph' is presented like this ($E^{\ominus}$/-/+ and ONs +/-) then: **bottom left** reacts with **top right**

   If the graph is written on your paper according to these guidelines you can use the data in a question on the paper (i.e. $E^{\ominus}$ data are given – **over** +, **and** ions on left, metal on right (like $Zn^{2+} + 2e^- \rightleftharpoons Zn$)
   You can then say **'bottom left** with **top right**' will work.

Exam Hint:- *To test your understanding of this difficult concept the examination question will often give you the data in the following way:*
*(1) $E^{\ominus}$ data with the (+) values **over** the (–) values*
*(2) ions on **right, not** the left.*

The Zn/Zn^{2+} and Cu/Cu^{2+} example would look like this:
$Cu \rightleftharpoons Cu^{2+} + 2e^-$ $E^{\ominus} = +0.34$ V
$Zn \rightleftharpoons Zn^{2+} + 2e^-$ $E^{\ominus} = -0.76$ V

Find a blank part of the paper and put it in a format you can use to answer the question and re-write.
*(a) ions (oxidised from on the **left**)*
*(b) put $E^{\ominus}$ (-) **over** $E^{\ominus}$ (+)*

Using Electrons to Balance Equations

We combine the half equations to give the chemical equation – we use the electrons to **balance** the equation.

These two examples show the principle involved:

Example 1

Will manganese react with tin (II) solutions?
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$ $E^{\ominus} = -1.19$ V
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ $E^{\ominus} = -0.14$ V

(Method – arranged like this i.e. electrons on the left and more negative $E^{\ominus}$ over the less negative half cell we can say 'yes' – top right, Mn(s), with bottom left, Sn^{2+}(aq))

$Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$ (reversed)
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

$\boxed{Mn(s) + Sn^{2+}(aq) \rightarrow Mn^{2+}(aq) + Sn(s)}$ (add – electrons cancel out)

Example 2

Will Cu(s) react with Ag^+(aq)?
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^{\ominus} = +0.34$ V
$Ag^+(aq) + e \rightleftharpoons Ag(s)$ $E^{\ominus} = +0.80$ V

The answer is **yes**. (Can you explain why? Remind yourself of the method shown in Example 1.)

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (reversed)
$Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ (doubled to get $2e^-$ as for copper equation)

$\boxed{Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)}$ (add – electrons cancelled)

Disproportionation

The use of $E^{\ominus}$ values explains this term.

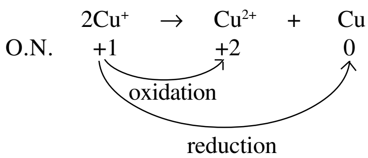
Disproportionation is when the same species is simultaneously oxidised and reduced

The best example to remember is **copper**:
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$ $E^{\ominus} = +0.15$ V
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$ $E^{\ominus} = +0.53$ V

Using the method,
$Cu^+ \rightarrow Cu^{2+} + e^-$ (reversed)
$Cu^+ + e^- \rightarrow Cu$

$\boxed{2Cu^+ \rightarrow Cu^{2+} + Cu}$ (add – cancel electrons)

The Cu^+ has been oxidised to Cu^{2+} and reduced to Cu:



Non-Standard Conditions and Feasibility

You need to keep in mind what $E^{\ominus}$ means! It is **standard conditions** i.e. 298K (25°C) and 1 mol dm^{-3} concentration.

1. If you change the **temperature** or the **concentration** you change the $E^{\ominus}$ values so reactions that normally would not react (i.e. do not obey the anti-clockwise rule) may react because their relative positions would change.

2. If the $E^{\ominus}$ values of the two half equations are not very different then they may **not** react even if they obey the rule. There is not enough difference in $E^{\ominus}$ values.

> ***Exam Hint**:- These concepts are examined in two types of questions.*
> 1. *You are given two half equations with $E^{\ominus}$ values. The question asks you if they are feasible – the answer will be 'no'.*
>   *The questions tells you they **will** react if 2M acid (or a higher temperature) is used and asks you to explain. You explain that **non-standard conditions** are being used so $E^{\ominus}$ values change so they may obey the anti-clockwise rule and so react.*
> 2. *You are give two half equations with $E^{\ominus}$ values and asked if they are feasible – the answer will be 'yes'. The question tells you they do not react – explain. You will say there is not enough difference between the $E^{\ominus}$ values for feasibility.*

Questions

To answer these questions you need to use the data from the $E^{\ominus}$ table and the additional half-equations given below:

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
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$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

$Mn^{2+} + 2e \rightleftharpoons Mn$ $E^{\ominus} = +0.15v$

$Sn^{2+} + 2e \rightleftharpoons Sn$ $E^{\ominus} = -0.14v$

$Cu^{2+} + e \rightleftharpoons Cu^+$ $E^{\ominus} = +0.15v$

$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$ $E^{\ominus} = +1.70v$

Are the following reactions feasible?

1. Cu^+ with Sn
2. Sn^{2+} with Mn
3. Sn^{2+} with Zn
4. Cu^+ with Ag^+
5. Cl^- with Ni^{2+}
6. V with I_2
7. Cl_2 with Zn^{2+}
8. Cu^{2+}/Cu^+ with Fe
9. Al^{3+} with Cu^{2+}/Cu
10. Sn^{2+} with Mg

Answers

1. ✗
2. ✓
3. ✓
4. ✓
5. ✗
6. ✓
7. ✗
8. ✓
9. ✗
10. ✓

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