

Electrode Potentials part 2

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As was mentioned in part 1, all the half-equations to show the electrode potential values are written as reductions, but we also need an oxidation half-equation to do a redox reaction. We can't just use two equations as they are written as they would both be reductions, and that would be a bit silly.

What I am saying is, something on the **left of one equation** must **react** with something on the **right of another equation**.

This means we have to:

turn around one of the half-equations so it is written as an oxidation

The big question....(drum roll).....which one do you turn around?

- ✓ In the CGP guides they often talk about the 'anti-clockwise' rule. I find this confusing and overly complicated. My advice is to ignore it completely. Instead.....use a very simple rule when looking at two half equations:

reverse the equation with the more **negative** E^\ominus value

So why the more negative equation? This is simply using the theory we talked about in part 1 when looking at the best oxidising and reducing agents.

We are turning around the equation where oxidation is most likely i.e. the one with the more negative value

Redox system	Equation	E^\ominus/V
1	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.51
2	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
3	$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.09
4	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
5	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
6	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76

- ✓ How examiners word these questions varies quite a bit. But you are following the above rule more or less every single time.

Example

Predict the species that will react with Br₂ but not with Fe³⁺?

If you look at the half-equations above, both Br₂ and Fe³⁺ are on the left hand side i.e. reactants. We are looking for something that can **reduce Br₂ but not Fe³⁺**. So again we are turning an equation around but which one?

Br₂

The Br₂ equation has an E° value of **+1.09 V**. We therefore need something on the **right hand side** with a **more negative** E° value to react with Br₂.

This means *any* species on the right hand side with a value less than +1.09 will work. So suitable reducing agents would be **Ag, Fe²⁺ or Zn**.

Fe³⁺

Fe³⁺ has an E° value of **+0.77 V** but **we don't want it to react**. So we have to reverse our logic. We need a species on the right hand side of an equation with a **more positive** E° value than +0.77 so that it **won't reduce** the Fe³⁺.

The answer

We have already selected Ag, Fe²⁺ and Zn as possibilities to react with Br₂ so we need to use one of these. It has to reduce Br₂ but **not** Fe³⁺.....the only one that fits this is **Ag** as it is **inbetween +1.09 and +0.77**.

Always finish the question by writing out the EMF value. For the reaction between Ag and Br₂, we can simply use:

$$\text{EMF} = E^\ominus \text{ of the more positive value} - E^\ominus \text{ of the more negative value}$$

$$\text{EMF} = 1.09 - 0.77 = +0.32\text{V (always put in the + sign and V)}$$

- ✓ Remember that the positive value indicates that the reaction should occur.
- ✓ Something I haven't mentioned is combining half-equations. You have done this at AS by cancelling electrons and adding the two equations together. This still applies here. But remember not to multiply the electrode potential value....ever. Even if you have had to multiply an equation, let's say x2 to cancel electrons, you still simply subtract the electrode potential values.

Reactions that do not occur

For the above Ag and Fe³⁺ reaction we cannot use the usual EMF equation as it **always** gives a positive value. From our theory, the reaction should not occur. Therefore we need a **negative EMF value** to show that the reaction is not happening.

The easiest way to do this is just reverse the above rule:

$$\text{EMF} = E^\ominus \text{ more negative} - E^\ominus \text{ more positive}$$

$$\text{EMF} = +0.77 - 0.80 = -0.03\text{V}$$

However, this relies upon students understanding the theory and realising the reaction does not occur **before** they calculate EMF.

Or calculate EMF as normal and then change the sign at the end. As long as you are aware of what is going on it doesn't matter how you do it.

An alternative that covers all examples and allows you to **predict** if a reaction occurs is to use the following:

$$\text{EMF} = E^\ominus \text{ of the species being reduced} - E^\ominus \text{ of the species being oxidised}$$

✓ from our example above, we are *trying* to reduce Fe^{3+} . Even though the reaction does not happen, we still call this the reduced species to fit the equation.

Be very careful with the wording of questions as they may give you a redox equation where they have already turned one of the equations around. Occasionally they deliberately turn around the **wrong equation** i.e. the one with the more **positive value**.....just to see if you're awake, just to see if you actually know how to do this topic. So always always check which equation they have turned round.

And that's all you have to do. Just keep thinking which equation do I turn around? Or which one have they turned around?

Non-Standard Conditions

Remember that all the E^\ominus values are measured under standard pressure, temperature and concentrations. If any of those conditions are changed then the E^\ominus values change. And therefore the EMF value must also change. Any change in the conditions are called **non- standard conditions**.

By changing the conditions, a reaction that was not likely to occur could become feasible or vice-versa

The questions usually ask you to predict what will happen to the EMF value if they change the conditions, which requires an equilibrium type theory to explain it.

✓ the condition they change has always been concentration. I have never seen them change temperature or pressure.....so far!

Example



We can see from the redox equation that Zn is oxidised to Zn^{2+} and Cu^{2+} is reduced to Cu.

The first thing to do is write out the two half equations as reductions:



If the Zn^{2+} concentration is increased, what happens to the EMF value?

- ✓ when answering these questions it is best to refer to the reduction half equations (as shown above) as it can get confusing.

If the Zn^{2+} concentration is **increased**, then the equilibrium would shift to the **right** to counteract the increase in concentration. The Cu half equation remains unaffected as does its E^\ominus value as we are not doing anything to the Cu half-cell. It's usually just one change that occurs.....usually 😊

Remember what the E^\ominus value tells you. The more negative the value then the more likely Zn will be oxidised to Zn^{2+} . By the equilibrium shifting to the right we are making *less* Zn^{2+} , therefore we are saying that Zn is **less likely** to be oxidised or less likely to release electrons and the E^\ominus value **increases**.

So under standard conditions:

$$\text{EMF} = +0.34 - (-0.76) = +1.10 \text{ V}$$

When the concentration of Zn^{2+} is increased we would get something like (I am just making up the changed E^\ominus value to illustrate the point):

$$\text{EMF} = +0.34 - (-0.40) = +0.74 \text{ V}$$

Similar arguments can be made for changing the concentration of Cu^{2+} .

To summarise and provide a general rule:

if the change in condition shifts the equilibrium to the **right** then the E^\ominus value **increases** (more positive)

Kinetics

Along with non-standard conditions, kinetics (rates) can also have an influence on whether a reaction occurs or not.

The classic question: *a reaction has an EMF value of +0.44V but the reaction still does not occur. Why?*

In this scenario, we can mention non-standard conditions or/and kinetics. Let's assume the conditions are standard here. Therefore we need to talk specifically about **activation energy**.

if the activation energy is too high, then the reaction will happen too slowly to be useful

Conventional Cell Representation

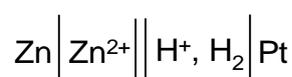
There is simply a short hand notation that shows what is being oxidised and reduced and what electrodes are used. It is the same information that a cell diagram gives but a lot quicker than drawing out the beakers and salt bridge etc!

Examples

The redox reaction between Zn and H⁺ ions:



We can see that Zn is being oxidised and H⁺ is being reduced. The conventional cell representation for this reaction is set up as follows:



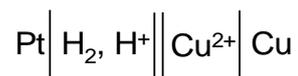
We have two half-cells that are separated by a || line, which represents the salt bridge. The single | line shows a change of state.

A few rules:

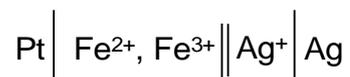
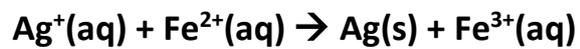
1. the more positive electrode is always placed on the **right side** (H₂ = 0 V and Zn = -0.76 V).
2. the **electrodes** are placed on the far left and far right, and the other species are placed adjacent to the vertical broken lines in the centre.

So we have a Zn electrode on the left and a Pt electrode on the right. We have Zn²⁺ in solution on the left and H⁺ and H₂ on the right.
3. on the left side (oxidation), the **lower oxidation state** is written first, and the higher oxidation state is written second.
4. on the right (reduction) the **higher oxidation state** is written first, and the lower oxidation state species is written second.

Example 2



Example 3



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