

Electrode Potentials part 2

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. It's very repetitive.

Example

Predict the species that will react with Br_2 but not with Fe^{3+} ?

Looking at Br₂ first. From the wording in the question, they are telling us that Br₂ is a reactant. Therefore, we must keep this equation as it is. But we need something to reduce Br₂, so we have to turn around an equation. But which one?

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.

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.

Now for the Fe³⁺...The question tells us that Fe³⁺ is a reactant but is **not reacting**. So we have to reverse our logic. We need a species on the right hand side of an equation but with a **more positive** E° value than +0.77. From our shortlist of Ag, Fe²⁺ and Zn, 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 E_{cell} value. For the reaction between Ag and Br₂, we can simply use:

$$E_{\text{cell}} = E^{\circ} \text{ of the more positive value} - E^{\circ} \text{ of the more negative value}$$

$$E_{\text{cell}} = 1.09 - 0.8 = +0.29\text{V (always put in the + sign and V)}$$

- ✓ 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 E_{cell} equation (more positive value minus the more negative) as it will **always** give a positive value. We said above that the reaction should not occur as Ag has a more positive value than Fe³⁺. Therefore, we need a **negative E_{cell} value** to show that the reaction is not happening.

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

$$E^{\circ} \text{ more negative} - E^{\circ} \text{ more positive}$$

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

Or calculate E_{cell} 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:

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

- ✓ from our example above, we are *trying* to reduce Fe^{3+} . Even though the reaction does not happen, we 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

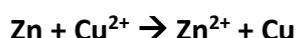
Remember that all the E^{\ominus} values are measured under **standard** pressure, temperature and concentrations. If any of those conditions are changed then the E^{\ominus} values change. And therefore the E_{cell} value must also change. Any change in the conditions are called **non- standard conditions**.

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 E_{cell} 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 E_{cell} value?

- ✓ when answering these questions it is best to refer to the reduction half equations (as shown above) as otherwise 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:

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

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):

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

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 (rate) can also have an influence on whether a reaction occurs or not.

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

In this scenario, we have to talk about our old friend kinetics and specifically.... **activation energy**.

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

This is very similar to the theory in the [entropy topic](#).