Shed new light on the two-faced reaction

These notes accompany the video demonstration **Shed new light on the two-faced reaction** from *Education in Chemistry*, available at: rsc.li/4qBduTI

Curriculum links

This variation of two-faced reaction uses methylene blue instead of thionine to make the effects easier to observe. Use this demonstration to support lessons on electrode potentials and the thermodynamics of redox reactions for your 14–16 and post-16 learners.

Kit



- 0.4 g iron(II) sulfate heptahydrate (irritating to skin and eyes)
- 0.4 g citric acid
- 0.5 cm^3 methylene blue solution, 0.1% w/v
- 50 cm^3 cell culture flask with cap
- LED work light (CLEAPSS members see PS052)
- Opaque card or similar (credit card sized) for masking the light
- Coloured filters (optional)

Health, safety and disposal

- Read our standard health and safety guidance and carry out a risk assessment before running any live practical (rsc.li/4mO9EVF).
- Wear eye protection.
- CLEAPSS members should consult HC032 and RB108 when making up the methylene blue solution, SSERC members should consult the Chemistry health and safety page, or consult your local safety authority body. The solution itself is not classified as hazardous at the concentration used in this demonstration.
- Iron(II) sulfate heptahydrate is irritating to skin and eyes.
- See CLEAPSS PS052 for safe use instructions for the LED work light or consult your local safety authority.
- Dispose of the solution down a foul water drain with plenty of water.

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Preparation

Dissolve 0.4 g of iron(II) sulfate heptahydrate and 0.4 g of citric acid in approximately 100 cm^3 of deionised water. Add about 0.5 cm^3 of 0.1% methylene blue solution. The solution is similar in hue and intensity to a 0.5 M copper sulfate solution. Fill the cell culture flask with approximately 50 cm^3 of this solution, close the cap tightly and let it settle.

In front of the class

Position the LED work light on a bench shining towards the ceiling. Use the opaque card to mask part of the light. Lay the cell culture flask on its side, with half of it on the card and half directly in the light. Position a white wall or screen behind the flask to help visualise the colour. Within a few seconds, the illuminated part of the solution will decolourise, while the shaded section will remain blue. Switch the light back off and watch the colour return to the shaded section.

Teaching goal

This demonstration supports lessons on electrode potentials and the thermodynamics of redox reactions (e.g. spontaneity). With a small extension you can also show how kinetics often overrides a prediction made using thermodynamics alone.

In this experiment, methylene blue has a coloured cationic form (MB^+) and a colourless reduced form, leucomethylene blue (LMBH). In the low pH of the citric acid solution (approximately pH 2.5), LMBH is further protonated to $LMBH_3^{2+}$.

The electrode potential for the reduction of $Fe^{3+}(aq)$ is:

$$\mathbf{Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)\ \ E = +0.77\ V}$$

At pH 0, the electrode potential for the reduction of MB^+ is:

$$\mathbf{MB^+(aq) + 2e^- + 3H^+ \rightleftharpoons LMBH_3^{2+}\ \ E = +0.53\ V}$$

By combining the half equations, we get:

$$\mathbf{\Delta E = E_{reduction} - E_{oxidation} = +0.53\ V - (+0.77\ V) = -0.24\ V}$$

The pH of the demonstration is around 2.5 rather than 0, meaning the MB^+ reduction potential is even less favourable. The Nernst equation shows that the potential at this pH ought to be closer to +0.3 V than +0.53 V.

Either way, the ΔE is negative and the dye will not spontaneously decolourise without energy being supplied to the system. In this demonstration, the energy required to nudge the dye towards spontaneity comes from light.

Methylene blue absorbs efficiently in the red end of the spectrum thanks to the delocalised π system extending over all three rings, with a λ_{max} of 664 nm.

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When MB^+ absorbs a photon, a short-lived, highly energetic excited state forms and its full two-electron reduction potential increases to +1.43 V. Now the ΔE is large and positive – the solution bleaches. You can demonstrate the importance of light at the red end of the spectrum with the use of coloured filters. Red or yellow filters allow the correct wavelengths through and the dye will bleach, while blue filters will prevent the reaction from occurring.

Once light is removed, the backward reaction wins out and the Fe^{3+} oxidises the leucomethylene blue back to its coloured form again. This happens more slowly than in the original demonstration that uses thionine, making the effect easier to observe.

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