Explore the nitrogen oxides: unexpected equilibrium

These notes accompany the video demonstration **Unexpected equilibrium** from *Education in Chemistry* which you can view at: rsc.li/4ostPIG.

You can use the syringe of nitrogen dioxide, NO_2, produced using the Avogadro's law revisited demonstration to explore a counterintuitive example of equilibria chemistry (rsc.li/4oAF81x).

Use this experiment in your 14–16 and post-16 lessons on the nitrogen oxides and equilibrium.

Kit

- 60 cm^3 syringe loaded with nitrogen dioxide
- 60 cm^3 syringe loaded with nitrogen monoxide
- Syringe caps
- Kettle and container for a hot water bath
- Access to freezer or salted ice bath
- Approximately 3 cm silicone tubing with a 4 mm internal diameter
- 50 cm^3 stop bath of 0.4 M sodium hydroxide

Health, safety and disposal

- Read our standard health and safety guidance, available from rsc.li/47WtYhs, and carry out a risk assessment before running any live practical.
- Wear eye protection.
- Work in an efficiently running fume cupboard.
- Nitrogen dioxide and nitrogen monoxide are toxic, corrosive and oxidising – avoid skin contact and inhalation. CLEAPSS members should consult HC068B: bit.ly/47mZhk3.
- 0.4 M sodium hydroxide is an irritant to skin and eyes. Dilute the contents of the stop bath and dispose of down a foul-water drain.

Preparation

Make a capped syringe of NO_2 using the technique in part 1 (rsc.li/4oAF81x). You can use a syringe left over from the previous demonstration or make a fresh sample. Eject 10 cm^3 (leaving 30 cm^3) into a stop bath of 0.4 M sodium hydroxide, $NaOH$, in a fume cupboard to allow you to move the syringe's plunger.

In front of the class and teaching goal

The syringe of NO_2 contains a mixture of NO_2 (red-brown) with dinitrogen tetroxide, N_2O_4 (colourless), according to the equilibrium in the equation below.

Equation 1: $2NO_2(g) \rightleftharpoons N_2O4(g)$

The equilibrium is exothermic as written (ΔH = -57 kJ) and lies to the right at room temperature with a K_c of 215 at 25°C.

Students should predict that depressing the plunger will cause the equilibrium to shift right, leading to a paler colour. Holding a finger over the syringe cap to secure it, depress the plunger and show that, counterintuitively, the colour darkens briefly before paling once more to a similar colour seen at the start. Show the opposite effect by retracting the plunger. This happens because the NO_2, which causes the red-brown colour, is contained in a smaller volume and it takes a few seconds for the chemistry to catch up.

Make a hot water bath using the kettle (up to 80°C, above which the plastic may weaken) and an ice bath. Placing the syringe in the ice bath causes the gas to contract slightly while getting substantially paler. When left in the hot water, the colour darkens significantly even though the volume increases slightly.

You can demonstrate a second equilibrium if you have time. Working in a fume cupboard, connect the syringe of NO_2 (and N_2O_4) to a syringe of NO and draw 30 cm^3 of the colourless gas. Leave the 60 cm^3 syringe either in the freezer or in a salted ice bath for 10 minutes. A blue liquid will form.

Equation 2: $NO(g) + NO_2(g) \rightleftharpoons N_2O_3(l)$

Either keep the NO_2 syringe when finished or bubble the gaseous contents through a stop bath of 0.4 M $NaOH$. When I am finished with a syringe, I demonstrate the reaction of NO_2 with water and the neutralisation of the resulting acid. If you add a few drops of universal indicator to the stop bath and draw up 5 cm^3 into the syringe, the colour will change as the gas dissolves into and reacts with the $NaOH$ solution, demonstrating the formation and neutralisation of nitric acid.