The oxidation states of vanadium

Topic

Transition metals – the colours of different oxidation states. Redox reactions and electrode potentials.

Timing

Up to half an hour.

Level

Post-16.

Description

Zinc is used to reduce a yellow solution of ammonium vanadate(V) to a mauve solution containing vanadium(II) ions. The intermediate oxidation states of vanadium(IV) (blue) and vanadium(III) (green) are also seen.

Apparatus

- One 1 dm^3 conical flask.
- Filter funnel.
- Boiling tube.
- Dropping pipette.
- Four petri dishes (optional).
- Access to an overhead projector (optional).
- Test-tubes and rack (optional).

Chemicals

The quantities given are for one demonstration.

- 11.7 g of **ammonium metavanadate** (ammonium vanadate(V), NH_4VO_3).
- 15 g of zinc powder.
- 100 cm^3 of approximately 0.25 mol dm^{-3} **potassium permanganate** (potassium manganate(VII), $KMnO_4$) in 1 mol dm^{-3} sulfuric acid. Dissolve 4 g of potassium permanganate in 100 cm^3 of 1 mol dm^{-3} sulfuric acid.
- About 1 g of powdered tin (optional).
- About 10 cm^3 of approximately 1 mol dm^{-3} sodium thiosulphate solution (optional). Dissolve about 25 g of sodium thiosulphate-5-water in 100 cm^3 of water.
- 1 dm^3 of 1 mol dm^{-3} **sulfuric acid**.

Safety

Wear eye protection. Refer to SSERC or CLEAPSS Hazcard for each of the following chemicals;.

Ammonium metavanadate, NH_4VO_3 (s) is **Extremely toxic if inhaled, Toxic if swallowed, a skin/eye/respiratory irritant and a mutagen**.

Zinc powder, Zn (s) is P**yrophoric and water reactive and hazardous to the aquatic environment.**

Potassium permanganate, $KMnO_4$ (s) is **an Oxidiser, Harmful if swallowed and hazardous to the aquatic environment.**

Sodium thiosulfate solution, 1 mol dm^{-3} $Na_2S_2O_3$ (aq) is **Low hazard**.

Sulfuric acid, 1 mol dm^{-3} H_2SO_4(aq), is a **Skin/eye irritant**.

Method

Before the demonstration

Make up a 0.1 mol dm^{-3} solution of ammonium metavanadate by dissolving 11.7 g of solid in 900 cm^3 of 1 mol dm^{-3} sulfuric acid and making up to 1 dm^3 with deionised water. This yellow solution is usually represented as containing VO_2^+(aq) ions (dioxovanadium(V) ions) in which vanadium has an oxidation number of +5.

The demonstration

Place 500 cm^3 of the ammonium metavanadate solution in a 1 dm^3 conical flask and add about 15 g of powdered zinc. This will effervesce and give off hydrogen on reaction with the acid.

The solution will immediately start to go green and within a few seconds will turn pale blue, the colour of the VO^{2+}(aq) ion in which the vanadium has an oxidation number of +4. The short-lived green colour is a mixture of the yellow of V^{V} and the blue of V^{IV}. The blue colour of VO^{2+} is similar to that of the Cu^{2+}(aq) ion. Over a further fifteen minutes or so, the colour of the solution changes first to the green of V^{3+}(aq) ions and eventually to the mauve of V^{2+}(aq) ions. The green of V^{3+}(aq) is the most difficult to distinguish.

If desired, decant off a little of the solution at each colour stage, filter it to remove zinc and stop the reaction and place in a petri dish on the overhead projector to show the colour more clearly.

When the reaction has reached the mauve stage, filter off a little of the solution into a boiling tube and add acidified potassium permanganate solution dropwise. This will re-oxidise the vanadium through the +3 and +4 oxidation states back to V^{V}. Take care with the final few drops to avoid masking the yellow colour of vanadium(V) with the purple of permanganate ions.

Visual tips

A white background is vital if the colour changes are to be clearly seen.

If desired, prepare solutions containing V^{IV} and V^{III} beforehand for comparison. This is recommended for teachers who are not familiar with these colours. This can be done as follows.

V^{IV}: take a little of the original ammonium metavanadate solution in a test-tube and add approximately 1 mol dm^{-3} sodium thiosulphate solution dropwise until no further colour change occurs and a light blue solution is obtained. If too much thiosulphate is added, the solution will gradually go cloudy due to the formation of colloidal sulfur by reaction of the excess thiosulphate with acid but this will not affect the blue colour of V^{IV}.

V [III]: take a little of the original ammonium metavanadate solution in a test-tube and add a spatula-full of powdered tin. Leave this for about five minutes and then filter off the tin to leave a green solution containing V^{3+}(aq) ions.

Teaching tips

This demonstration can be used as an introduction to the idea that different oxidation states of transition metal ions often have different colours and that electrode potentials can be used to help predict the course of redox reactions (via the 'anticlockwise rule' or otherwise). While waiting for the reaction to go to completion, some of the reactions can be discussed.

Theory

The relevant half reactions and redox potentials are as follows:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = -0.76\ V$$

$$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq) \qquad E^\ominus = -0.26\ V$$

$$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s) \qquad E^\ominus = -0.14\ V$$

$$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons H_2O(l) + V^{3+}(aq) \qquad E^\ominus = +0.34\ V$$

$$S_4O_6^{2-}(aq) + 2e^- \rightleftharpoons 2S_2O_3^{2-}(aq) \qquad E^\ominus = +0.47\ V$$

$$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons H_2O(l) + VO^{2+}(aq) \qquad E^\ominus = +1.00\ V$$

So zinc will reduce VO_2^+(aq) to V^{2+}(aq), tin will reduce VO_2^+(aq) to V^{3+}(aq) and no further and thiosulphate ions will reduce VO_2^+(aq) to VO^{2+}(aq) and no further.

Further details

This demonstration would be a good introduction to the experiments involving the redox reactions of vanadium described in *Revised nuffield advanced science, chemistry: students' book II,* p 224. London: Longman, 1984, along with the relevant section in the Teachers' Guide (p1423) and by D. J. Redshaw in *Sch. Sci. Rev*., 1974, **193**, 753.

Credits

Health & safety checked January 2018

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