Vanadium redox and variable oxidation states

AQA Chemistry (7405) · Full A level

Show your working where needed. Check the worked answers when you finish.

Name _____ Date _____

1. Read the species

Give the vanadium oxidation state and solution colour for VO_2^+, VO^{2+}, V^{3+} and V^{2+} in acid. Explain the difference between the first two formulae.

2. Combine with zinc

In acidic solution VO^{2+} is reduced to V^{3+} by zinc. Write a balanced vanadium half-equation and combine it with the zinc half-equation to give the ionic equation.

3. Change one condition

In acid the reduction half-equation is $VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$.

Predict how increasing the pH changes the tendency for reduction, with the concentrations of the vanadium ions held fixed. Explain using the half-equation.

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4. Where does reduction stop?

E° values in V are VO_2^+/VO^{2+} +1.00, VO^{2+}/V^{3+} +0.34, V^{3+}/V^{2+} −0.26 and Sn^{4+}/Sn^{2+} +0.15.

What is the lowest V oxidation state predicted with excess Sn^{2+}? Show the deciding E°cell values.

5. Calculate a minimum mass

An acidified sample contains 2.40×10^{-3} mol of vanadium in oxidation state +5. Calculate the minimum mass of zinc needed to reduce all the vanadium to +2, assuming no side reactions. $A_r(Zn) = 65.4$.

6. A sample exposed to air

Can dissolved O_2 oxidise V^{2+} to V^{3+} in acid under standard conditions? Use $E°(V^{3+}/V^{2+}) = -0.26$ V and $E°(O_2/H_2O) = +1.23$ V. Write the ionic equation.

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7. Change the ligand

At fixed pH, the metal(III)/metal(II) potential is +0.82 V with L and +0.48 V with M. The Fe^{3+}/Fe^{2+} potential is +0.77 V. Which ligand allows reduction by Fe^{2+}? Explain the ligand effect.

8. An ethanedioate determination

An acidified 25.0 cm^3 sample of $C_2O_4^{2-}$ reacts with 16.25 cm^3 of 0.0160 mol dm^{-3} MnO_4^-. Manganese goes from +7 to +2 and the carbon forms CO_2. Find the mole ratio and concentration of $C_2O_4^{2-}$.

9. Extra challenge · Work out a mixture from electron transfer

20.00 cm^3 contains V^{3+} and VO^{2+}, with total vanadium concentration 0.0750 mol dm^{-3}. In acid, 24.00 cm^3 of 0.0200 mol dm^{-3} MnO_4^- oxidises all vanadium to VO_2^+. Each MnO_4^- accepts five electrons.

Find the percentage of vanadium initially at oxidation state +3. Explain why the average number of electrons transferred per vanadium ion is between one and two.

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Worked answers

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1. Read the species

VO_2^+ is +5 and yellow. Two oxygen atoms contribute −4. VO^{2+} is +4 and blue. One oxygen atom contributes −2. The subscript counts oxygen atoms and the superscript gives the ion's charge.

V^{3+} is +3 and green. V^{2+} is +2 and purple. These colours refer to the individual species in acidic aqueous solution.

2. Combine with zinc

$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$

$Zn \rightarrow Zn^{2+} + 2e^-$

Double the vanadium half-equation. The overall equation is $2VO^{2+} + 4H^+ + Zn \rightarrow 2V^{3+} + 2H_2O + Zn^{2+}$.

3. Change one condition

A higher pH means a lower H^+ concentration. Removing a reactant favours the reverse direction, so the tendency for VO_2^+ to be reduced falls and the reduction potential becomes less positive.

4. Where does reduction stop?

The +5 to +4 step is favourable (+0.85 V). The +4 to +3 step gives +0.34 − (+0.15) = +0.19 V.

The +3 to +2 step gives −0.26 − (+0.15) = −0.41 V. The lowest state predicted under standard conditions is +3. Sn^{2+} is oxidised to Sn^{4+}.

5. Calculate a minimum mass

Each vanadium atom gains three electrons, requiring 7.20×10^{-3} mol of electrons.

Zinc loses two electrons per atom. Amount of zinc = 3.60×10^{-3} mol. Mass = $3.60 \times 10^{-3} \times 65.4$ = 0.235 g to three significant figures.

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Worked answers

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6. A sample exposed to air

E°cell = +1.23 − (−0.26) = +1.49 V, so the change is feasible under standard conditions.

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$. Combine it with four times $V^{2+} \rightarrow V^{3+} + e^-$: $4V^{2+} + O_2 + 4H^+ \rightarrow 4V^{3+} + 2H_2O$.

7. Change the ligand

The predicted cell potentials are +0.05 V with L and −0.29 V with M. Only the reaction with L is predicted to be feasible under these conditions.

Ligands can stabilise the two oxidation states by different amounts. Changing the ligand changes the energy difference for the reduction and can change the potential.

8. An ethanedioate determination

Manganese gains five electrons. Each carbon changes from +3 to +4, so a $C_2O_4^{2-}$ ion loses two electrons. The ratio MnO_4^- to $C_2O_4^{2-}$ is 2:5.

Amount of MnO_4^- = 0.0160 × 0.01625 = 2.60×10^{-4} mol. Amount of $C_2O_4^{2-}$ = 6.50×10^{-4} mol. Concentration = $6.50 \times 10^{-4} \div 0.0250 = 0.0260$ mol dm^{-3}.

9. Extra challenge · Work out a mixture from electron transfer

Total vanadium = 0.02000 × 0.0750 = 0.00150 mol. V(III) loses two electrons. V(IV) in VO^{2+} loses one.

Amount of MnO_4^- = 0.02400 × 0.0200 = 0.000480 mol, so 0.00240 mol electrons are transferred.

With x mol V(III), 2x + (0.00150 − x) = 0.00240. Thus x = 0.000900 mol, or 60.0% of the vanadium. The average is 0.00240 ÷ 0.00150 = 1.60 electrons per ion because the sample contains both starting ions.

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