

Variable OXIDATION STATES

VARIABLE OXIDATION STATES

Transition metals have variable oxidation states, meaning that they can form ions with different charges.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
0	[Ar] 3d ² 4s ²	[Ar] 3d ³ 4s ²	[Ar] 3d ⁵ 4s ¹	[Ar] 3d ⁵ 4s ²	[Ar] 3d ⁶ 4s ²	[Ar] 3d ⁷ 4s ²	[Ar] 3d ⁸ 4s ²	[Ar] 3d ¹⁰ 4s ¹
+1			[Ar] 3d ⁵ 4s ⁰					[Ar] 3d ¹⁰ 4s ⁰
+2	[Ar] 3d ² 4s ⁰	[Ar] 3d ³ 4s ⁰	[Ar] 3d ⁴ 4s ⁰	[Ar] 3d ⁵ 4s ⁰	[Ar] 3d ⁶ 4s ⁰	[Ar] 3d ⁷ 4s ⁰	[Ar] 3d ⁸ 4s ⁰	[Ar] 3d ⁹ 4s ⁰
+3	[Ar] 3d ¹ 4s ⁰	[Ar] 3d ² 4s ⁰	[Ar] 3d ³ 4s ⁰	[Ar] 3d ⁴ 4s ⁰	[Ar] 3d ⁵ 4s ⁰	[Ar] 3d ⁶ 4s ⁰	[Ar] 3d ⁷ 4s ⁰	[Ar] 3d ⁸ 4s ⁰
+4	[Ar] 3d ⁰ 4s ⁰	[Ar] 3d ¹ 4s ⁰	[Ar] 3d ² 4s ⁰	[Ar] 3d ³ 4s ⁰	[Ar] 3d ⁴ 4s ⁰	[Ar] 3d ⁵ 4s ⁰	[Ar] 3d ⁶ 4s ⁰	[Ar] 3d ⁷ 4s ⁰
+5		[Ar] 3d ⁰ 4s ⁰	[Ar] 3d ¹ 4s ⁰	[Ar] 3d ² 4s ⁰	[Ar] 3d ³ 4s ⁰	[Ar] 3d ⁴ 4s ⁰	[Ar] 3d ⁵ 4s ⁰	
+6			[Ar] 3d ⁰ 4s ⁰	[Ar] 3d ¹ 4s ⁰	[Ar] 3d ² 4s ⁰	[Ar] 3d ³ 4s ⁰		
+7				[Ar] 3d ⁰ 4s ⁰				

VANADIUM

Vanadium can form various ions. These can each be made by reducing aqueous vanadium(V) using zinc in acid.

	VO ₂ ⁺	VO ²⁺	V ³⁺	V ²⁺
ox. state	V	IV	III	II
colour	yellow	blue	green	mauve

WRITING HALF-EQUATIONS

- Write the species being oxidised or reduced.
 $\text{VO}^{2+} \rightarrow \text{V}^{3+}$
- Add electrons depending on the change in oxidation state. V is reduced from V(V) to V(III).
 $\text{VO}^{2+} + e^- \rightarrow \text{V}^{3+}$
- Add H₂O to balance the oxygen atoms.
 $\text{VO}^{2+} + e^- \rightarrow \text{V}^{3+} + \text{H}_2\text{O}$
- Add H⁺ to complete the balanced equation.
 $\text{VO}^{2+} + 2\text{H}^+ + e^- \rightarrow \text{V}^{3+} + \text{H}_2\text{O}$

HALF-EQUATIONS

For each reduction step of vanadium, a balanced half-equation can be written.

$\text{VO}_2^+ + 2\text{H}^+ + e^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	E° (V)
$\text{VO}^{2+} + 2\text{H}^+ + e^- \rightarrow \text{V}^{3+} + \text{H}_2\text{O}$	+1.00 V
$\text{V}^{3+} + e^- \rightarrow \text{V}^{2+}$	+0.34 V
$\text{V}^{2+} + e^- \rightarrow \text{V}$	-0.26 V

TOLLENS' REAGENT

Tollens' reagent is a complex of silver with the formula $[\text{Ag}(\text{NH}_3)_2]^+$. It can be used to tell the difference between aldehydes and ketones.



In the reaction, the aldehyde is oxidised, and the silver is reduced, producing metallic silver.



REDOX POTENTIALS

A redox potential is a measure of how strong a species is at oxidising or reducing other species.

Redox potentials at standard conditions are represented as E°. If a species has a high E° value, it means that:

- its own reduction (gain of electrons) is more likely
- it will oxidise (loss of electrons) other things

pH AND REDOX POTENTIAL

pH can affect the reduction potential of a reaction. This is because pH affects the concentration of H⁺ ions in solution. Many reduction potentials also have H⁺ in the reaction. An increased [H⁺] can make the forwards or backwards reaction more favourable, resulting in a different reduction potential.

REDOX TITRATIONS

Redox titrations use redox reactions to find the amount (moles) of a species. Once the amount (moles) of a reactant has been calculated, it is often possible to find:

- the concentration of the reactant
- the mass of the reactant
- the purity of the reactant
- the percentage by mass of the reactant in a salt
- the M_r of a salt

POTASSIUM PERMANGANATE

Potassium permanganate, KMnO₄, is often used as an oxidising agent in redox titrations because:

- It has a **high reduction potential**. This means that it can oxidise many other species.
- It can act as its own indicator. MnO₄⁻ changes from clear to pink when it is reduced.

BACK TITRATIONS

Back titrations involve:

- Performing a reaction between A and B
- Using a redox titration between B and C to calculate the amount (moles) of B left over
- Calculating the amount (moles) of A used up in the first reaction
- Calculating the amount of A that reacted

WORKED CALCULATION

'A soluble iron(II) salt was dissolved in 250 cm³ water, and 25.0 cm³ aliquots were taken and titrated with 0.150 mol dm⁻³ MnO₄⁻ solution. The titres recorded were 34.55, 34.50 and 34.70 cm³.



- a) Calculate the value of the volume of MnO₄⁻ in cm³ which should be used in a titration calculation.

$$\text{vol MnO}_4^- = \frac{34.55 + 34.50}{2}$$

$$= 34.53 \text{ cm}^3$$

- b) Calculate the moles of MnO₄⁻ used in the titration.

$$\text{mol MnO}_4^- = 0.150 \times \frac{34.53}{1000}$$

$$= 5.180 \times 10^{-3} \text{ mol}$$

- c) Calculate the moles of Fe²⁺ titrated.

$$1:5 \text{ ratio MnO}_4^- : \text{Fe}^{2+}$$

$$\text{so mol Fe} = 5 \times 5.180 \times 10^{-3}$$

$$= 0.02590 \text{ mol}$$

- d) Calculate the mass of Fe²⁺ titrated.

$$\text{mass Fe} = 0.02590 \times 55.8$$

$$= 1.445 \text{ g}$$

- e) Calculate the total mass of iron in the original Fe²⁺ salt.

$$\text{mass of Fe} = 1.445 \times \frac{250}{25} = 14.5 \text{ g}$$

FIND THE OVERALL EQUATION

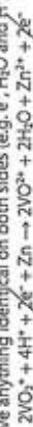
Double the numbers in front of each reactant in the first equation.



Add them together:



Remove anything identical on both sides (e.g. e⁻, H₂O and H⁺).



Overall equation:



The reaction has an overall positive charge so is feasible.

EXAMPLE

Zn(II) has a reduction potential:



VO₂⁺ has a higher (more positive) reduction potential than Zn. When Zn is added to a solution of VO₂⁺ ions, the following half-equations occur:



Note that reversing the equation changes the sign of E°.