Chem Factsheet

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Vanadium Chemistry

To succeed in this topic you should:
- Be familiar with the characteristics of Transition Metals.
- Be familiar with electronic configurations (Lewis structures).
- Be familiar with how to work out oxidation states.
- Be familiar with the basic principles of redox equilibria and electrode potentials.

After working through this Factsheet you will:
- Be aware of the variety of oxidation states exhibited by Vanadium.
- Know the main redox reactions involved in interconversions between these oxidation states.
- Understand how V_2O_5 acts as a heterogeneous catalyst.
- Understand why complex ions of vanadium are coloured.

The key characteristics of transition metals are usually considered to be:
- Variable oxidation state,
- Catalytic behaviour,
- Formation of coloured ions,
- Formation of complex ions.

The main A Level syllabuses typically use vanadium to illustrate the first three of these characteristics; its variable oxidation states, the interconversion between oxidation states +2, +3 , +4 and +5—especially in terms of reduction with zinc—and the observations of the accompanying colour changes, and the use of V_2O_5 as a catalyst for the Contact Process.

Vanadium is both a d-block element (which is the block of elements in the Periodic Table that lies between Group 2 and Group 3 (or 13) and a transition metal (an element that forms at least one stable ion with an incompletely filled d-subshell).

Its isolated atom in the ground state has the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$, which is often abbreviated to $[Ar]\ 3d^3\ 4s^2$.

The electronic configuration of vanadium is often written as $[Ar]\ 4s^2\ 3d^3$ as a result of using The Aufbau Principle, to work out electronic configurations. The problem is that although The Aufbau Principle gives correct electronic configurations for all the elements up to calcium and for most transition metals, it does not actually correctly describe the way in which transition metal configurations are 'built up'. The reasons for this are complicated but, in simple terms, although the 4s orbital is at a slightly lower energy level than the 3d in potassium and calcium (which is why the 4s 'fills first') this is not the case from scandium onwards where the 3d is actually at a lower energy level than the 4s.

This then leads to the question of why scandium is not $[Ar]\ 3d^3 4s^0$, but that can be explained by the fact that the 3d orbitals are quite compact, so introducing a second and third electron into the 3d orbitals would create repulsion forces that make it a less stable alternative than introducing those electrons into the slightly higher energy 4s orbital.

Overall, at A Level, the more advanced considerations are not needed and The Aufbau Principle can safely be used to predict most electronic configurations (but watch out for chromium and copper!).

However, it is very important to remember that the 4s electrons in a d-block element are the outer, higher energy electrons and so they are the ones that are lost first during ion formation.

The Oxidation States of Vanadium

Vanadium commonly exhibits oxidation states of +5, +4, +3 and +2 in its compounds.

+5 oxidation state

In solution, the commonest representation of an ion containing vanadium in oxidation state +5 is $[VO_2]^+$, but the precise nature of the ion actually varies with pH and this is an abbreviation for $[VO_2(H_2O)_4]^+$.

VO_2^+ is actually the ion that exists in strongly acidic solution while, in a strongly alkaline environment, it is $[VO_4]^{3-}$. At intermediate pHs, a range of ions such as $[VO_3(OH)]^{2-}$, $[VO_2(OH)_2]^-$, as well as various polyvanadates, exist. The ion present in alkaline solution is also sometimes represented as $[VO_3]^-$, which is the ion found in ammonium metavanadate, NH_4VO_3.

The +5 oxidation state is also found in V_2O_5, which is used as a catalyst in the Contact Process and is amphoteric:

$V_2O_5 + 6OH^- \rightarrow 2VO_4^{3-} + 3H_2O$

$V_2O_5 + 2H^+ \rightarrow 2VO_2^+ + H_2O$

+4 oxidation state

Vanadium(IV) oxide, VO_2 is also amphoteric:

$VO_2 + 4OH^- \rightarrow VO_4^{4-} + 2H_2O$

$VO_2 + 2H^+ \rightarrow VO^{2+} + H_2O$

The oxide can be obtained by reduction of V_2O_5 with SO_2 and it readily oxidises back to V_2O_5 when heated in air.

In solution, vanadium(IV) is most commonly represented as VO^{2+}.

+3 oxidation state

Reduction of V_2O_5 by heating in a stream of hydrogen produces the basic oxide V_2O_3.

$V_2O_3 + 6H^+ \rightarrow 2V^{3+} + 3H_2O$

Like other transition metal ions in aqueous solution the V^{3+} ion exists as an aquo complex, so this should, more correctly, be written as:

$V_2O_3 + 6H^+ + 3H_2O \rightarrow 2[V(H_2O)_6]^{3+}$

Solutions containing $V^{3+}(aq)$ ions are oxidised on standing to give $VO^{2+}(aq)$ ions.

+2 oxidation state

Reduction of a solution of ammonium metavanadate, NH_4VO_3, with zinc, in the presence of sulfuric acid, produces $[V(H_2O)_6]^{2+}(aq)$, which is a powerful reducing agent and, in the absence of a more powerful reducing agent such as Zn/H^+, reacts with water forming hydrogen gas.

In the laboratory, the ready interconversion between these oxidations states can be demonstrated in solution using different reducing agents, starting with a solution of ammonium metavanadate, NH_4VO_3.

An explanation of these processes involves the use of standard electrode potentials and those needed for this discussion are listed:

1. $VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$ $E^\ominus = +1.00\,V$
2. $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^\ominus = +0.77\,V$
3. $VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$ $E^\ominus = +0.34\,V$
4. $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $E^\ominus = -0.14\,V$
5. $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$ $E^\ominus = -0.26\,V$
6. $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^\ominus = -0.76\,V$

There are many different methods for working out overall reactions using electrode potentials but one method is based on the fact that electrons have a negative charge. So, whenever we consider a combination of two half equations, the one with the more negative value for its electrode potential will end up 'going' in the direction that produces electrons, i.e., oxidation. For standard electrode potentials, the half equations are typically written as reductions and so the more negative one will 'go backwards'.

We will use this idea to decide what will happen if solid zinc is added to an acidified solution containing $VO_2^+(aq)$ ions.

Comparing half-equations 1 and 6, 6 clearly has a more negative $E^\ominus$ (-0.76 V), which allows us to conclude that 6 will go in the direction of producing electrons, i.e., zinc will be oxidised to Zn^{2+}.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$
Overall:
$Zn(s) + 2VO_2^+(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + 2VO^{2+}(aq) + 2H_2O(l)$

We would therefore expect Zn to reduce $VO_2^+(aq)$ to form $VO^{2+}(aq)$. However, half-equation 6 also has a more negative $E^\ominus$ than 3 so Zn will also reduce $VO^{2+}(aq)$ to V^{3+}.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$
Overall: $Zn(s) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$

And, as 6 is also more negative than 5, it will also reduce the $V^{3+}(aq)$ to $V^{2+}(aq)$.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$
Overall: $Zn(s) + 2V^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2V^{2+}(aq)$

Thus, if powdered zinc is added to an acidified solution of ammonium metavanadate, the yellow solution of $VO_2^+(aq)$ will turn blue as $VO^{2+}(aq)$ forms (via an intermediate green colour due to a mixture of the yellow and blue ions). On standing for longer the green colour of $V^{3+}(aq)$ is seen and then, finally, the violet colour of $V^{2+}(aq)$.

If this violet solution is decanted off from the solid zinc then the process can be reversed by careful, drop-wise addition of acidified manganate(VII) solution, MnO_4^-.

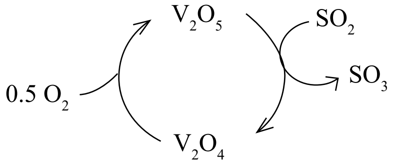
If the reduction is carried out with tin instead of zinc then the electrode potentials show that the tin can reduce the $VO_2^+(aq)$ to $VO^{2+}(aq)$ and further to $V^{3+}(aq)$, but not to $V^{2+}(aq)$, so the reaction would stop at the green solution.

With $Fe^{2+}(aq)$ the reduction only proceeds as far as $VO^{2+}(aq)$ (but here the colour observations are complicated by the colour of the iron ions in solution).

Catalytic Behaviour

Vanadium pentoxide, V_2O_5, can be used as a catalyst in a variety of processes including the oxidation of ethanol to ethanal, and in the production of phthalic anhydride and ethanedioic acid. By far, its most familiar application is as a heterogeneous catalyst in the Contact process for the production of sulfuric acid.
This is commonly represented as a sequence of two reactions:

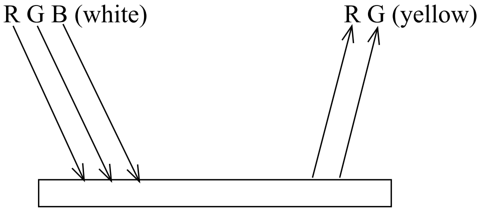
$V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$
$V_2O_4 + ½O_2 \rightarrow V_2O_5$



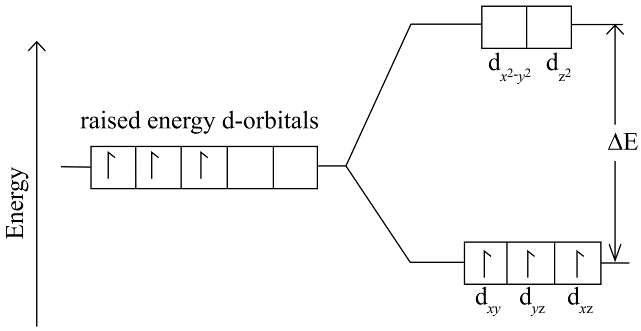
As with any heterogeneous catalysis, the process involves the adsorption of SO_2 onto the surface of the catalyst, but the mechanism is actually complex and details are not required for school-level Chemistry.

Formation of Coloured Ions

To understand the origin of the colour of transition ions in solution we need to apply the concept of 'colour subtraction'. For the sake of simplicity, we start by representing visible light (white light) as a mixture of red, green, and blue (RGB). If RGB shines onto a surface that absorbs blue, then only the red and green are reflected by the surface – our brain 'sees' this mixture of colours as yellow.



When transition metal ions form complexes in aqueous solution the interactions between the ligands (e.g., water molecules) and the central cation (e.g., V^{2+}) causes all of the d-orbitals to be raised in energy and additionally split into two groups with two orbitals being higher in energy than the other three.



For octahedral complex ions, e.g., $[V(H_2O)_6]^{2+}(aq)$, two of the five 3d orbitals are promoted to a higher energy than the remaining three. When white light shines onto the solution, photons with energy, E, corresponding to the gap between the two sets of d-orbitals are absorbed in order to promote electrons in the lower energy orbitals to the vacant, higher energy, d-orbitals. In the case of the $[V(H_2O)_6]^{2+}$ ion, the photons absorbed are in the yellow/green region of the spectrum, so the remaining wavelengths combine to appear as a violet colour.

Sample Questions

1. Write overall equations for the reactions of:
    (a) Tin with an acidic solution of VO_2^+ ions producing V^{3+} ions.
    (b) Fe^{2+} ions with an acidic solution of VO_2^+ ions producing VO^{2+} ions.

2. Explain, using an equation, what would happen if a solution of V^{2+} ions was added to an acidic solution of VO^{2+} ions.

3. What oxidation state change(s) occur to vanadium in the following reactions:
    (a) $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$
    (b) $VO_2 + 4OH^- \rightarrow VO_4^{4-} + 2H_2O$
    (c) $Zn(s) + 2VO^{2+}(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$

Answers

1 (a) $Sn(s) + VO_2^+(aq) + 4H^+(aq) \rightarrow Sn^{2+}(aq) + V^{3+}(aq) + 2H_2O(l)$
(b) $Fe^{2+}(aq) + VO_2^+(aq) + 2H^+(aq) \rightarrow Fe^{3+}(aq) + VO^{2+}(aq) + H_2O(l)$

2. V^{2+} ions would reduce VO^{2+} ions to V^{3+} ions and the V^{2+} ions would undergo oxidation to V^{3+} ions.
$V^{2+}(aq) + VO^{2+}(aq) + 2H^+(aq) \rightarrow 2V^{3+}(aq) + H_2O$

3 (a) +5 to +4
(b) No change (stays at +4)
(c) +4 to +3

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