AIM

To study methods by which vanadium in low oxidation states may be prepared and how these states are quantitatively estimated.

**INTRODUCTION**

Vanadium is a d-transition metal found in Group VA of the Periodic Table. Vanadium was first discovered by the Spanish Mineralogist Andres Manuel del Rio in 1801 while experimenting with a mineral obtained from a mine near Hidalgo in Northern Mexico. He prepared a number of colored salts from this "brown lead" which were similar to salts of chromium. He named his new element erythronium which means red after observing that most of his salts turned red upon heating. Del Rio, believing he was incorrect, withdrew his claim of discovery because he was insisting that his new element was nothing more than impure chromium.

Thirty years later, the Swedish chemist Nils Sefström isolated a new oxide while experimenting with some iron ores. He named this new element Vanadium in honor of the Scandanavian goddess of beauty, Vanadis, because of its varied beautiful, multicolored compounds.

Vanadium is a hard grey metal with atomic number of 23 and melts at 1900oC. Vanadium takes a high polish and is one of the hardest of all metals. It is never found in the pure state, but occurs in combination with various minerals such as oxygen, chlorine and sulphur. It boils at about 3380° C (about 6116° F), and has a relative density of 5.96. The atomic weight of vanadium is 50.941.

Vanadium's ground state electron configuration is [Ar] 3d34s2. When transition elements ionize, they lose their valence s electrons before losing their d electrons. Vanadium has 5 valence electrons that can be lost. One of the characteristics of transition metal is their ability to adopt multiple oxidation states. Vanadium exhibits four common oxidation states +5, +4, +3, and +2 each of which can be distinguished by its color.

|  |  |  |
| --- | --- | --- |
| **Oxidation** | **Ion** | **Colour** |
| +5 | VO3- or VO2+ | Yellow |
| +4 | VO2+ | Blue |
| +3 | V3+ | Green |
| +2 | V2+ | Violet |

In this experiment, the lower oxidation state of vanadium would be investigated through a series of oxidation and reduction redox reactions.

**CHEMICALS AND APPARATUS**

1. Vanadate solution
2. Sulphuric acid
3. KMnO4
4. NaOH solid
5. Sodium sulphate
6. Pipette
7. Conical flask
8. Filter funnel
9. Beaker
10. Burette
11. Bunsen burner
12. Beam balance

PROCEDURE AND OBSERVATIONS

|  |  |
| --- | --- |
| **TEST** | **OBSERVATION** |
| 1. 25cm3 of the already prepared vanadate solution was added to 25cm3 of 2M sulphuric acid. | Yellow colour observed. |
| 1. 1g of solid sodium sulphate was added to the solution/mixture containing 25cm3 of the prepared vanadte solution and 25cm3 of 2M sulphuric acid. | Blue colour was observed. |
| 1. The resulting solution was boiled and cooled to 60oC. | Effervescence of a colourless gas with a choking smell.  Green colour was observed. |
| 1. 0.02M KMnO4  titrated against the cooled solution. | Colour changed from green to pink-orange. |

**TABLE OF VALUES**

|  |  |  |  |
| --- | --- | --- | --- |
| **TITRATION** | **1** | **2** | **3** |
| **FINAL** | 20.40 | 42.40 | 20.50 |
| **INITIAL** | 0.00 | 20.40 | 0.00 |
| **TITRE** | 20.40 | 22.00 | 20.50 |

Average Titre =

Average Titre = 20.97 cm3

Titration reactions

NH4VO3 + NaOH + H2SO4 → VO3+ + SO3 + H2O + NH4+ ------ (1)

VO3+ + SO32- → V5-n + SO42- + SO2 -------- (2)

(Oxidation reaction)

**CALCULATION**

M (NH4VO3) = 14 + 4 + 50.9 + 48 = 116.9gmol-1

n( NH4VO3) = m/M

= 2.5/116.9

= 0.0214mol

n (NaOH) = [NaOH] x V(NaOH),

n (NaOH) = 2 x 25/1000 = 0.05mol

Also

[H2SO4] = 2M and V(H2SO4) = 75ml

Hence n (H2SO4) = 2 x 75/1000 = 0.15mol

From equation (1), n(NH4VO3) = n(NaOH) = n(H2SO4)

But amount of available NH4VO3 = 0.0214mol

NaOH = 0.05mol and H2SO4 = 0.15mol

Therefore NH4VO3 is the limiting reagent and hence the formation VO3+ depends on the amount of NH4VO3 available.

From equation (1), the mole ratio of VO3+ to NH4VO3 is 1:1

Thus, n(VO3+) = n(NH4VO3)

Therefore n (VO3+) = 0.0214mol, but this amount is contained in 250ml

Hence 25ml of the solution will contain (25 x 0.0214)/250 = 0.00214mol

From equation (2) Na2SO3 is oxidized to V5-n and SO2.

VO3+ + SO32- → V5-n + SO42- + SO2

1mol of VO3+ produces 1mol of V+(5-n). This implies n( V (5-n)+ ) = 0.00214mol.

**Calcultions involving Redox reactions**

VO3+ + MnO4 → V+(5-n) + Mn2+ ----------(3)

VO3+ is oxidized to V (5-n)+

Oxidation half reaction: 5V(5-n)+ + 10H2O → 5VO2+ + 5e- + 2OH-

MnO4 is reduced to Mn2+

Reduction half reaction: MnO4- + 8H+ + 5e- → Mn2+ + 4H2O

(4)x 1 5V+(5-n) + 10H2O→ 5VO2+ + 5e- + 2OH-

(3)x n nMnO4- + 8nH+ + 5ne- → nMn2+ + 4nH2O

(4) + (3)

5V+(5-n) + nMnO4- + (10-4n)H2O → nMn2+ + 5VO3+ + H+ + (5-5n)e-

From (3) n (VO3+) = n (V+(5-n) ) = 0.00214mol

From equation (1), the mole ratio of V+ (5-n) to MnO4- is 5:1

n (V+(5-n) ) /n (MnO4-) = 5/n = 0.00214

n (MnO4-) = 20.97/1000 x 0.02 = 4.194 x10-4mol

From the balanced redox equation,

n( V+(5-n) ) /n(MnO4) = 5/n

n = [ 5 x [ MnO4-] /n(V+(5-n) )]

= (5 x 4.194 x 10-4)/0.00214

= 0.98 ≈ 1.0

Therefore total oxidation state of vanadium = V(5-1) = 5-1= +4

**DISCUSSION**

The solution of vanadate already prepared from ammonium metavanadate and sodium hydroxide had a colour of yellow indicating the presence of V5+.

The colour change from yellow to blue upon addition of H2SO4 indicated the presence of V4+ and the colour change to green after heating and cooling indicated the presence of V3+. This shows that the +5 oxidation state of vanadium was reduced to +4 and then to +3.

Finally there was a reduction in the oxidation state when KMnO4 of +3 oxidation state of vanadium in the vanadate solution to +4 and finally to the +5 oxidation when titrated against the vanadium. The colour change observed in the process was from yellow to pink at the end point. This colour change shows that the KMnO4 oxidized the vanadium.

It was also observed during the heating process that a pungent smelling gas was evolved. The evolution of this gas gave opportunity for the clear appearance of the blue solution which indicated the presence of the V3+ oxidation state of vanadium. The gas was SO2.

**PRECAUTIONS**

* All beakers and test-tubes were washed thoroughly before performing the experiments.
* All the apparatus were handled with care to avoid any breakages.
* All precautions such as wearing of lab coats and goggles were observed

**CONCLUSION**

It can be concluded that V2O5 Vanadium is soluble in sulphuric acid.

The +5 oxidation state of vanadium is easily reduced to the +4 oxidation state in redox reactions. Therefore it can be concluded that the +4 oxidation state of vanadium is the most stable oxidation state.

**EXERCISES**