KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF ENGINEERING
DEPARTMENT OF CHEMICAL ENGINEERING

TITLE: LOWER OXIDATION OF VANADIUM

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Aims and Objectives:

- To To study the various methods by which vanadium of lower oxidation states is prepared.
- How to estimate the lower oxidation states of vanadium quantitatively.

INTRODUCTION

Vanadium, symbol V, silver-white metallic element with an atomic number of 23. Vanadium is one of the transition elements of the periodic table. It was discovered in 1801 in Mexico by Andrés Manuel del Rio.

PROPERTIES AND OCCURRENCE

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 melts at about 1890° C (about 3434° F), 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 is soluble in nitric and sulphuric acids and insoluble in hydrochloric acid, dilute sodium hydroxide, and dilute alcohol. Vanadium forms several acidic oxides, the most important of which are the dark green trioxide, V_2O_3, and the orange pentoxide, V_2O_5. Other important compounds include vanadium monosulphide, VS; vanadium trisulphide, V_2S_3; vanadium dichloride, VCI_2; vanadium trichloride, VCI_3; vanadium dihydroxide, $V(OH)_2$; and metavanadic acid, HVO_3.

Vanadium in the form of V^{4+} (e.g. as in VO_2) is most stable compared to the other forms in which vanadium can exist. As a result, V^{5+} compounds are easily reduced to V^{4+} compounds in chemical reactions. For example when V_2O_5 is dissolved in HCL, vanadium (IV) is produced.

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

CHEMICALS AND APPARATUS

- Vanadate solution
- Sulphuric acid
- $KMnO_4$
- NaOH solid
- Sodium sulphite
- Pipette
- Conical flask
- Filter funnel
- Beaker
- Burette

PROCEDURE AND OBSERVATIONS

PROCEDURE	OBSERVATIONS

2.5g of the ammonium metavanadate (empirical formula NH_4VO_3) was weighed and dissolved in $25cm^3$ of $2moldm^{-3}$ of sodium hydroxide	A brick-red solution was formed
The solution was stirred thoroughly and 75ml of $2moldm^{-3}$ sulphuric acid was added to it. It was then topped up to the $250cm^3$ mark in a volumetric flask with water	The brick-red solution turned yellow, indication the presence of V_2O_5.
$25cm^3$ of the prepared vanadate (V) solution was pipetted into 25ml of $2moldm^{-3}$ sulphuric acid. 1g of solid sodium sulphite was added and the solution was boiled until the evolution of sulphur dioxide ceased.	There was effervescence, SO_2 gas was evolved. The yellowish solution turned blue after heating.
The solution was cooled to 60^oC and titrated with standard $0.02moldm^{-3}$ $KMnO_4$.	The blue solution turned pink-orange at the endpoint.

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TABLE OF VALUES

Burette reading/ml	**I**	**II**	**III**
Final	21.10	21.30	21.20
Initial	0.00	0.00	0.00
Titre	21.10	21.30	21.20

Average titre = 15.50ml

Titration reactions

$NH_4VO_3 + NaOH + H_2SO_4$ $VO_3^+ + SO_3 + H_2O + NH_4^+$ ------ (1)

$VO_3^+ + SO_3^{2-}$ V^{5-n} $+ SO_4^{2-} + SO_2$ -------- (2)

(Oxidation reaction)

CALCULATION

M (NH_4VO_3) = 14 + 4 + 50.9 + 48 = 116.9gmol^{-1}

n(NH_4VO_3) = m/M

= 1/116.9

= 0.0086mol

n (NaOH) = [NaOH] x V(NaOH), but V(NaOH) = 10ml and [NaOH] = 2M

Hence n (NaOH) = 2 x 10/1000 = 0.02mol

Also

[H_2SO_4] = 2M. and V(H_2SO_4) = 30ml

Hence n (H_2SO_4) = 2 x 30/1000 = 0.06mol

From equation (1), n(NH_4VO_3) = n(NaOH) = n(H_2SO_4)

But amount of available NH_4VO_3 = 0.0086mol

NaOH = 0.02mol

H_2SO_4 = 0.06mol

Therefore NH_4VO_3 is the limiting reagent and hence the formation VO_3^+ depends on the amount of NH_4VO_3 available.

From equation (1), n(VO_3^+) = n(NH_4VO_3)

Therefore n (VO_3^+) = 0.0086mol, but this amount is contained in 100ml

Hence 25ml of the solution will contain (10 x 0.0086)/100 = 0.00086mol

From equation (2) Na_2SO_3 is oxidized to V^{5-n} and SO_2.

$$VO_3^+ + SO_3^{2-} \text{ ----> } V^{5-n} + SO_4^{2-} + SO_2$$

1mol of VO_3^+ produces 1mol of $V^{+(5-n)}$. This implies n($V^{(5-n)+}$) = 0.00086mol.

Redox reactions

$VO_3^+ + MnO_4$ ----> $V^{+(5-n)}) + Mn^{2+}$ ----------(3)

VO_3^+ is oxidized to $V^{(5-n)+}$

Oxidation half reaction: $5V^{(5-n)+} + 10H_2O$ ------> $5VO_2^+ + 5e^- + 2OH^-$

MnO_4 is reduced to $Mn2^+$

Reduction half reaction: $MnO_4^- + 8H^+ + 5e^-$ ------> $Mn^{2+} + 4H_2O$

(4)x 5 $5V^{+(5-n)} + 10H_2O$ ------> $5VO_2^+ + 5e^- + 2OH^-$

(3)x n $nMnO_4$- + $8nH^+$ + $5ne^-$ ----> nMn^{2+} + $4nH_2O$

(4) + (3)

$5V^{+(5-n)}$ + $nMnO_4^-$ + $(10-4n)H_2O$ ------> nMn^{2+} + $5VO_3^+$ + H^+ + $(5-5n)e^-$

From (3) n (VO_3^+) = n ($V^{+(5-n)}$) = 0.00086mol

n ($V^{+(5-n)}$) /n (MnO_4^-) = 5/n = 0.00086

n (MnO_4^-) = 21.20/1000 x 0.02 = 4.24 $x10^{-4}$mol

From the balanced redox equation,

n($V^{+(5-n)}$) /n(MnO_4) = 5/n

n = [5 x [MnO_4^-] /n($V^{+(5-n)}$)]

= (5 x 4.24 x 10^{-4})/0.00086

= 2.47 ≈ 3.0

Therefore total oxidation state of vanadium = $V^{(5-1)}$ = 5-3= +2

EXERCISES 1 (REDUCTION)

(1) V^{5+} reacted with NaOH during preparation of standard solution

$NH_4VO_3^+$ + 2NaOH -----> Na_2VO_4 + NH_4OH

VO_3^+ + $4OH^-$ -------> VO_2^+ + $2H_2O$

H_2SO_4 + Na_2SO_3 -----> SO_2 + Na_2SO_4 +H_2O

VO_2^+ + SO_3^{2-} --------> VO^{2+} + SO_4^{2-} ----- (1)

Balancing (1) yields

VO_2^+ + $2H^+$ + e^- ------> VO_2^+ + H2O ------(2)

(2) x 2 $2VO_2^+$ + 4H+ + 2e- ---->$2VO_2$+ + $2H_2O$

SO_2 + $2H_2O$ ----> $SO_4$2- + 4H+ +$2e^-$

$2VO_2^+$ + SO_2 -----> $2VO_2^+$ + $S0_4^{2-}$

The $VO2^+$ produced reacted with MnO_4^-

$5VO_2^+$ + H_2O + MnO_4- -----> $5VO_2^+$ +Mn^{2+} + $2H^+$

EXERCISES 2

FORMULA	STEREOCHEMISTRY	COLOUR
VO_2^+ Dioxovanadate (v) ion	Octahedral (VF_5)	Yellow
VO^{2+} Oxovanadate (IV) ion	Tetrahedral (VCL_4)	Blue

V^{3+} Vanadium (III) ion	Hexahydrate	Dark Green
V^{2+} Vanadium (II) ion	Hexahydrate	Violet

DISCUSSION

Vanadium, symbol V, silver-white metallic element with an atomic number of 23. Vanadium is one of the transition elements of the periodic table. It is never found in the pure state, but occurs in combination with various minerals such as oxygen and sulphur.

From the observations collected from the experiment and the exercise conducted,we realise that the yellow solution that was formed when the NH_4VO_3 was added to the NaOH was due to the presence of the +5 oxidation state of vanadium.

Furthermore, when the H_2SO_4 was added to the yellow solution and heated, the +5 oxidation state of vanadium was reduced to +2 as indicated by the yellow to blue colour change.

When $KMnO_4$ was titrated against the +2 oxidation state of vanadium, there was a colour change again from blue to pink-orange at the end point. This colour change shows that the $KMnO_4$ oxidized the +2 oxidation state of vanadium in the vanadate solution to +4 and finally to the +5 oxidation.

It was also observed during the heating process that a pungent smelling gas was evolved. The evolution of this gas gave chance for the clear appearance of the blue solution which indicated the presence of the V3+ oxidation state of vanadium. The gas was SO_2.

PRECAUTIONS

1. I made sure I measured the exact mass and volume needed for the experiment
2. I made sure I observed very carefully to detect whether a chemical reaction has taken place or not.
3. I also made sure that all beakers and test-tubes were washed thoroughly before performing the experiments.
4. I ensured that apparatus used were all handled with care to avoid any breakages.
5. I also ensured that the chemicals used for the experiment were spilled around.
6. Also all precautions such as wearing of lab coats and goggles were observed

CONCLUSION

- The +5 oxidation state of vanadium is easily reduced to the +2 oxidation state in redox reactions. Therefore it can be concluded that the +2 oxidation state of vanadium is the most stable oxidation state.

- Vanadium forms several acidic oxides, the most important of which are the dark green trioxide, V_2O_3, and the orange pentoxide,
- V_2O_5 Vanadium is soluble in sulphuric acid.

REFERENCE

Microsoft Encarta 2003
Vogel's inorganic Chemistry Practical Handbook.