**LABORATORY REPORT**

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| LOWER OXIDATION OF VANADIUM |
| |  |  | | --- | --- | | Name: | Kwansa Victor | | Index Number: | 2841708 | | Class: | I.1.2.3 | | Demonstrator: | Abdul Tijani Rahman | | Date: | 13th April, 2009 | |
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| **AIMS/OBJECTIVES:**   * How to estimate the lower oxidation states of vanadium quantitatively. * To study how the oxidation state of vanadium reduces. * To study the various methods by which vanadium of lower oxidation states is prepared. |
| **INTRODUCTION/THEORY:**  Vanadium is a hard grey metal with atomic number of 23. Vanadium is one of the hardest 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 is a d-transition metal found 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 coloured 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. A French chemist named Collett-Desotils disputed his claim of discovering a new element insisting that his new element was nothing more than impure chromium. Del Rio, believing he was incorrect, withdrew his claim of discovery. 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 Scandinavian goddess of beauty, Vanadis, because of its varied beautiful, multicolored compounds.  [Vanadium](http://www.mii.org/Minerals/photovan.html) naturally occurs in about 65 different minerals, including vanadinite, the ore of lead and vanadium,  In the U.S. it is most commonly found in sandstones which are rich in uranium ores. Vanadium is also found carbon-rich deposits such as coal, oil shale, crude oil, and tar sands. While minor amounts of vanadium are found in the human body, its biological purpose is unknowns.  Vanadium is used in making specialty steels, rust resistant and high speed tools. 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 State | Ion | Colour | | +5 | VO3- or VO2+ | Yellow | | +4 | VO2+ | Blue | | +3 | V3+ | Green | | +2 | V2+ | Violet |   Vanadium dissolves readily in aqua regia, in a mixture of concentrated nitric acid and hydrogen fluoride.  Vanadium may have oxidation states of +2, +3, +4, +5 and +7, among these +5 and +4 occur more frequently.  Vanadates contain pentavalent vanadium; these are analogous to phosphates. Vanadic acids like phosphoric acids exist in the form of meta-, pyro- and ortho-compounds (HVO3, H4V2O7, and H3VO4 respectively). Unlike the salts of phosphoric acids, the metavanadates are the most stable and ortho vandates are the least stable. The solution of an ortho vanadate, on boiling turns into the metavanadate, the pyro-salt being formed immediately. In strongly acidic solutions, dioxovanadium (V) cations VO2+ are present in quadrivalent form; vanadium is usually present as vandyl ion, VO2+.  In this experiment, the lower oxidation state of vanadium would be investigated through a series of oxidation and reduction redox reactions. |
| **CHEMICALS & EQUIPMENT:**  1.Vanadate solution  2.Sulphuric acid  3.KMnO4  4.NaOH solid  5.Solid Sodium sulphate  6.Pipette  7.Conical flask  8.Filter funnel  9.Beaker  10.Burette |
| **PROCEEDURE:**   |  |  | | --- | --- | | **PROCEDURE** | **OBSERVATIONS** | | 1. 2.5g of the ammonium metavanadate (empirical formula NH4VO3) was weighed and dissolved in 25cm3of 2moldm-3 of sodium hydroxide | Colour change from colourless to orange. | | 1. The solution was stirred thoroughly and 75ml of 2moldm-3 sulphuric acid was added to it. It was then topped up to the 250cm3 mark in a volumetric flask with water | Colour change from orange to yellow | | 1. 25cm3 of the prepared vanadate (V) solution was pipette 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. | Colour change from yellow to green.  There was evolution of sulphur dioxide  Whiles heating, the solution changed colour from green to blue. | | 1. The solution was cooled to 60oC and titrated with standard 0.02moldm-3 KMnO4. | The first change from blue to green and then turned yellow.  The solution finally turned pink at the endpoint. | |
| **CALCULATIONS:**  **TABLE OF VALUES**   |  |  |  |  | | --- | --- | --- | --- | | Burette reading/ml | I | II | III | | Final | 27.50 | 27.40 | 27.30 | | Initial | 0.00 | 0.00 | 0.00 | | Titre | 27.50 | 27.40 | 27.30 |   Average titre = 27.40 + 27.30  2  = 27.35cm3  Titration reactions  NH4VO3 + NaOH + H2SO4 → VO3+ + SO3 + H2O + NH4+ ------ (1)    VO3+ + SO32- → V5-n + SO42- + SO2 -------- (2)  (Oxidation reaction)  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  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) = 0.00214mol.  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 (MnO4-) = 0.00214/5  n (MnO4-) = 27.35/1000 x 0.02 = 5.47 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 5.47 x 10-4)/0.00214  = 1.28 ≈ 1.0  Therefore total oxidation state of vanadium = V(5-1) = 5-1= +4    EXERCISES 1 (REDUCTION)   1. V5+ reacted with NaOH during preparation of standard solution   NH4VO3+ + 2NaOH → Na2VO4 + NH4OH  VO3+ + 4OH- → VO2++ 2H2O  H2SO4 + Na2SO3 → SO2 + Na2SO4 +H2O    VO2+ + SO32- →VO2++ SO42- ----- (1)    Balancing (1) yields  VO2+ + 2H+ + e- → VO2+ + H2O ------ (2)  (2) x 2 2VO2+ + 4H+ + 2e- →2VO2+ + 2H2O    SO2 + 2H2O → SO42- + 4H+ +2e-    2VO2+ + SO2 → 2VO2+ + S042-  The VO2+ produced reacted with MnO4-    5VO2+ + H2O + MnO4- → 5VO2+ +Mn2+ + 2H+  EXERCISES 2   |  |  |  | | --- | --- | --- | | FORMULA | STEREOCHEMISTRY | COLOUR | | VO2+ Dioxovanadate (v) ion | Octahedral (VF5) | Yellow | | VO2+  Oxovanadate (IV) ion | Tetrahedral (VCL4) | Blue | | V3+ Vanadium (III) ion | Hexahydrate | Dark Green | | V2+ Vanadium (II) ion | Hexahydrate | Violet | |
| **DISCUSSION:**  From the experiment, the orange colour formation of the solution indicated the presence of +5 oxidation state of vanadium, when the NH4VO3 was added to the NaOH. The oxidation state of +5 is the most stable and most frequent oxidation state for vanadium.  The further colour change from orange to temporal green upon addition of H2SO4 and heating shows that the +5 oxidation state of vanadium was oxidized to +3.  Finally there was a reduction in the oxidation state when KMnO4 was added to the solution from +3 oxidation state of vanadium in the vanadate solution to +4.  The temporal green colour represented the +3 oxidation state which was very unstable.  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.  The evolution of the pungent gas resulted in a clear blue solution free of most of the gas which indicated the presence of the V3+ oxidation state of vanadium. The gas was SO2. |
| **ERROR ANALYSIS:**   1. Some of the water molecules which remained in the apparatus after washing could have changed the expected concentrations of the solutions which were put in after the washing. 2. A few drops more of the KMnO4 solution on reaching the end point was added thus could have altered the titre values. |
| **PRECAUTIONS:**   * It was ensured that all beakers and test-tubes were washed thoroughly before performing the experiments to prevent any impurities from contaminating the consequent solutions. * The apparatus were all handled with care to avoid any breakages. * Insulators were worn to transfer the hot beaker from the heating mantle to the work table to prevent heat burns to the skin. * Reading of the potassium permanganate titre value was read from the top of the meniscus since KMnO4 is coloured and very difficult to take its readings from below the meniscus. * It was also ensured that all or most of the SO2 gas evolved by making sure that all the pungent smell of the gas was no more smelt. |
| **CONCLUSION:**  It can be concluded that (V2O5 )Vanadium is soluble in sulphuric acid.  The +5 oxidation state of vanadium was easily oxidized by the KMnO4 to +3 and 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. |
| **REFRENCES:**   1. Vogel’s inorganic Chemistry Practical Handbook (Page 527). 2. <http://www.answers.com/topic/vanadium> 3. *The Columbia Electronic Encyclopedia*, Sixth Edition, Copyright © 2003, Columbia University Press. Licensed from Columbia University Press. |