

REDOX CHEMISTRY OF CHROMIUM

1. Preliminary Exercises

Consult F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Edition for a list of the oxidation states of chromium.

2. Reactions with Hydrogen Peroxide

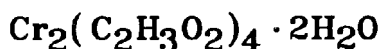
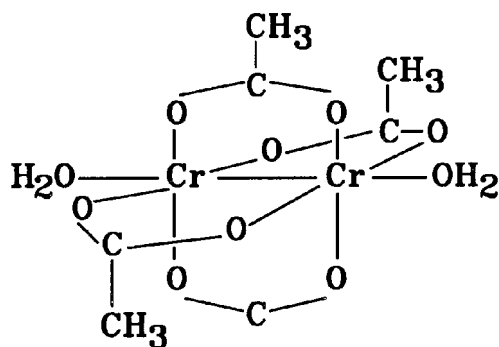
Carry out the following tests. Record your observations and explain them on the basis of the information gleaned from the preliminary exercises.

- (a) Dissolve 25 mg of chromium(III) sulfate in 2 ml of water. Divide the solution into 2 parts. To one add 1 ml 2M-sulfuric acid, to the other add 1 ml 2M sodium hydroxide solution. Then to each add 1 ml hydrogen peroxide (6% solution).
After observing any initial reaction warm the solution.
- (b) Dissolve 25 mg of potassium chromate in 2 ml of water. Divide the solution into 2 parts and repeat the test described in (a).

3. Preparation of Chromium(II) Acetate

Chromous acetate as a dimeric, relatively insoluble material is a relatively stable chromium(II) compound, the rate of oxidation being sufficiently slow to enable it to be prepared without the elaborate precautions of oxygen, which other chromous preparations demand.

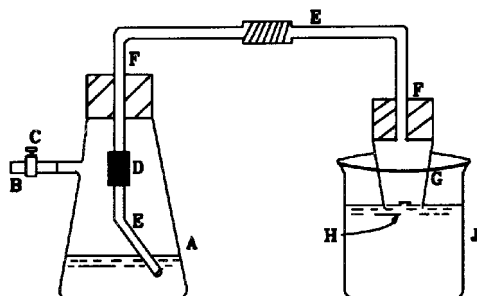
Each chromium ion in the dimer has six octahedral bonds, four to the oxygen atoms of the acetate groups (which act as bridging ligands between the two chromium ions), one to a water molecule and the sixth a mutual chromium-chromium bond.



The acetate is of interest in that it is diamagnetic. The 3d electrons have 'paired-up' in forming the dimer (evidence for a weak chromium-chromium bond).

Weigh 10 g of potassium dichromate into a 250 ml beaker and add 50 ml of concentrated hydrochloric acid. Place the beaker near a fume extraction vent and simmer gently for about 30 minutes. Allow to cool.

During this time assemble the apparatus shown in the diagram below:



- A = filter flask (500 ml)
- B, D = rubber tubing connections
- C = screw clip
- E = glass tubing (3 sections)
- F = rubber bungs
- G = Gooch crucible
- H = glass wool pad
- J = beaker (600 ml)

Weigh 30g of mossy Zn into flask A. Weigh 50g of sodium acetate into 600 ml beaker J, then add 150 ml of water. Cool the solution and add a few pieces of dry ice to remove oxygen, then warm gently to dissolve the salt.

Add a similar quantity of carbon dioxide to a 400 ml beaker containing 300 ml of water. Cover this beaker with a watchglass, and add more carbon dioxide as required to maintain an

inert atmosphere over the water. This is to provide oxygen-free water to wash the chromous acetate.

Transfer the prepared chromic chloride solution to flask A. Ensure that clip C is open. Add* 50 ml of concentrated hydrochloric acid to A and fit the bung carrying tube E firmly into place. Place beaker J containing sodium acetate solution with the end of the Gooch crucible just immersed in the solution.

Allow the reaction in A to continue until the solution has a clear sky-blue color. Then close C so that the solution is forced through E and H into J. The chromous acetate precipitates immediately as a red-brown solid.

The product needs to be protected from oxygen while you are working it up. A simple way is to add a few small pieces of dry ice to the Büchner funnel in which you are filtering off the precipitate. This will generate an atmosphere of CO₂ over the solution, and the sample. After filtering off the solid wash it with oxygen free water, then finally with acetone. Dry the product in a vacuum desiccator.

5. Analysis of the Chromium(II) Compound

The chromium content is determined by conversion to CrO₄²⁻, and the measurement of the intensity of the yellow color using the spectrophotometer.

A weighed sample of the compound** is dissolved in dilute nitric acid to give a solution of various Cr^{III} ions. Make the solution up to 100 ml in a volumetric flask, take a 5.0 ml aliquot and place it in a 250 ml Erlenmeyer flask. Add enough 2.0 M NaOH to neutralize the free acid, and then add 10.0 ml more NaOH. Add about 5-10 drops of 30% hydrogen peroxide, then heat on a steambath for a few minutes until oxygen evolution ceases. Cool to room temperature and make up to 250 ml. A duplicate determination should be made, and also in this case a blank solution (*same reagents and procedure but no Cr*).

Measure the absorbance of both solutions and blank in a 1 cm path length cell at 374 nm and calculate the concentration of chromate ion from the relationship:

* The reaction of conc. HCl with zinc can be quite violent. It would seem wise to add the acid portionwise to the Cr(III) chloride solution in the reaction flask, and to mix it by swirling to avoid the concentrated acid forming a dense lower layer in contact with the zinc, without dilution.

** Calculate the weight required by assuming $\ell = 1$, $A = 0.5$ in the formula below.

$$\epsilon = \frac{A}{Cl}$$

ϵ = molar extinction coefficient = 4820 L mol⁻¹ cm⁻¹ at 374 nm

A = absorbance - measured by experiment

c = molar concentration - calculated from measured value of A

ℓ = path length of cell - 1 cm

Remember the dilution step when calculating chromium content of the original sample.

Post-lab Questions

1. Draw the structure of the chromium(II) acetate molecule, pointing out with notes any special features it might have.
2. Write a balanced chemical equation for the oxidation of Cr(III) to chromate(VI) by hydrogen peroxide in alkaline solution.
3. Calculate the Cr content (mass %) of a sample of a complex given the following: 0.10 g of the sample was dissolved in dilute nitric acid, and made up to 100 mL. 50 mL of this solution was taken, and the Cr(III) converted to chromate by the addition of sodium hydroxide and hydrogen peroxide. The solution was made up to 250 mL and its absorbance was measured at 374 nm in a 1 cm pathlength cell. A = 0.5; ϵ = 4820 L mol⁻¹ cm⁻¹.