

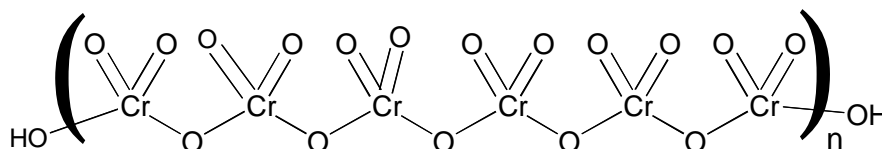
**PREPARATION AND ANALYSIS OF A PECULIAR
AND POORLY UNDERSTOOD OXIDE OF TUNGSTEN**

Introduction

The chromium group of transition metals forms a large number of oxides, the structures of which vary greatly. Some of these materials have well-understood structures and simple stoichiometries. Others, however, are poorly understood; they often have odd properties such as metallic conductance, exceptionally intense colors, and "non-stoichiometric" formulas.

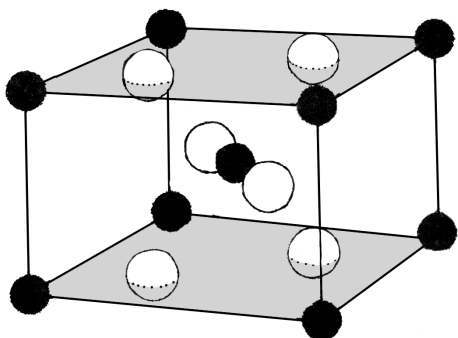
Chromium Oxides

Chromium forms three well-defined oxides. The most commonly encountered one is dark red chromium(VI) oxide, CrO_3 . In the solid state, it is a chain polymer, as illustrated below. The polymeric chain of solid CrO_3 can be broken up by various coordinating molecules such as water; this oxide thus acts as a Lewis acid. It is also a powerful oxidizing agent that is used extensively in organic chemistry.



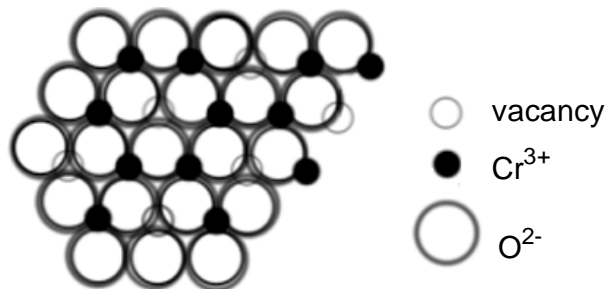
Polymeric Structure of Solid Chromium Trioxide

The two other commonly encountered chromium oxides are CrO_2 and Cr_2O_3 . Chromium(IV) oxide is brown-black, and has a three-dimensional polymeric structure of the rutile (TiO_2) type. Significant bonding occurs among the Cr atoms, leading to metallic conductivity. In addition, CrO_2 is ferromagnetic. The latter property is makes CrO_2 useful as a component of magnetic recording tapes. Chromium(III) oxide, the most stable oxide of chromium, has the corundum (Al_2O_3) structure. Its stability and green color have made it important as a pigment. The figures below illustrate the two types of crystal structures.



The Unit Cell of the Rutile (TiO_2)
Structure Assmed by CrO_2

black = chromium white = oxygen



Two Layers of a Small Section of a Crystal of Cr_2O_3 . The oxide ions form a hexagonal close-packed structure; 2/3 of the vacancies are occupied by Cr^{3+} ions

Other, less thoroughly studied, oxides of chromium are known. At least one of these, Cr_5O_{12} , is an example of a mixed valence compound: it contains chromium in both the +4 and +6 oxidation states, and is formulated as $\text{Cr}_2^{\text{III}}\text{Cr}_3^{\text{VI}}\text{O}_{12}$.

Molybdenum Oxides

Molybdenum(VI) forms a white oxide of formula MoO_3 . This oxide, in contrast to CrO_3 , is not a powerful oxidizing agent. It is insoluble in water, but dissolves in aqueous base to form molybdate. Its structure is polymeric, but different from that of CrO_3 : MoO_3 consists of layers of distorted octahedra, with each molybdenum atom coordinated to six oxygen atoms. The corners of the octahedra are shared.

Molybdenum(IV) oxide (MoO_2) is the ultimate decomposition product that is obtained by strong heating of MoO_3 under vacuum. It has a distorted rutile structure, in which edges of MoO_6 octahedra are shared. As in CrO_2 , this oxide has significant bonding interactions among the Mo atoms, leading to metallic conductivity. It is diamagnetic.

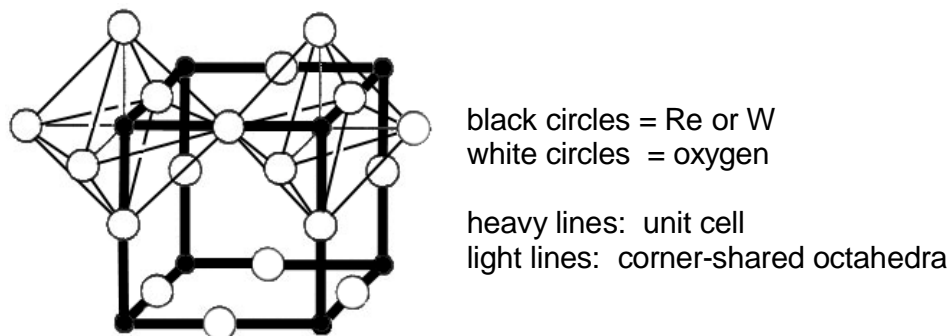
Less vigorous heating, or treatment of MoO_3 with mild reducing agents such as tin(II) or zinc in acid, yields a plethora of blue or violet oxides with formulas such as $\text{Mo}_{17}\text{O}_{47}$ (containing some pentacoordinate Mo) and Mo_4O_{11} (containing some tetrahedrally-coordinated Mo). Other materials of intermediate Mo/O ratios can also be obtained.

Removal of oxygen in this manner introduces defects into the crystal lattice, leaving some of the molybdenum atoms with unfavorable coordination numbers. This situation causes movement of appropriate planes of atoms in the crystals in such a way as to attain edge coordination of the octahedra, thus reestablishing the octahedral coordination of molybdenum. Some of the molybdenum atoms, however, are unable to regain six-coordination, and remain in four- five- or seven-coordinate sites. In addition, these oxides contain mixed oxidation states of molybdenum, and are metallic conductors. Many of the details of the structures of the materials produced through chemical reduction are not known since they are amorphous, thus precluding analysis by X-ray diffraction.

Tungsten Oxides

The properties of tungsten oxides resemble but are even more complex than those of the molybdenum oxides. Tungsten(VI) oxide (WO_3), which has a well-defined stoichiometry, can nevertheless exist in at least seven crystalline forms. The most common form has a structure similar to that of rhenium trioxide (illustrated below), a three-dimensional polymer of corner-linked octahedra.

As with MoO_3 , strong heating of WO_3 under vacuum produces WO_2 . Milder heating or mild chemical reduction produces "non-stoichiometric" oxides of tungsten, which contain phases such as $\text{W}_{50}\text{O}_{148}$ and $\text{W}_{18}\text{O}_{49}$. The compounds, like the molybdenum analogs discussed above, are probably of mixed valence.



Structure of ReO_3 and of One Form of WO_3

Experimental Section

Background

Mild reduction of Mo(VI) or W(VI), either as MO_3 or MO_4^{2-} ($M = \text{Mo}$ or W) has long been known to yield blue oxides of an apparently nonstoichiometric nature; the exact composition varies according to the particular reducing agent and the reaction conditions. These materials can also contain hydroxy groups in addition to oxide. The materials from Mo(VI) are referred to as 'molybdenum blues'; the tungsten(VI)-derived materials are collectively known as 'mineral blue'.

The experiment that you will perform this week is based on tungsten: a solution of sodium tungstate will be reduced with zinc and acid to form mineral blue; you will then determine the empirical formula of the mineral blue by titration with standard permanganate solution. The MnO_4^- will oxidize the mineral blue to yellow WO_3 . The end point occurs when all of the blue oxide has been converted to yellow, concomitant with a persistent pink color from a slight excess of MnO_4^- in the supernatant. The reaction rate is tediously low at room temperature, so the titration will be done with the sample immersed in a boiling water bath. Heating also ensures that no unreacted zinc remains, and that all hydrogen (a by-product formed by reduction of hydronium ion) is expelled from the solution.

An alternative, high-temperature method for the production of mineral blue from WO_3 uses methane (natural gas) as the reducing agent.

Experimental Procedures¹

a. Preparation of Mineral Blue by Reduction with Zinc

Place the following materials in a 250 mL Erlenmeyer flask in the order given and at the time called for in the instructions.

Weigh 1-2 g of sodium tungstate tetrahydrate (the mass is not critical, but the particular mass that you use must be recorded accurately), then dissolve it in 25 mL of deionized water. Add 0.75 g of granulated zinc, then warm the flask to 70°C . Add 75 mL of 3 M sulfuric acid, swirl to thoroughly mix the reactants. Leave the flask to stand, with occasional swirling, until the almost all of the zinc has been consumed.

b. Titrimetric Analysis of Mineral Blue

Set up a buret for titration of the mineral blue with standard potassium permanganate solution. Record the concentration of the permanganate solution.

Near the end of the reduction reaction, heat a beaker of deionized water to the boiling point (don't forget the boiling stone), then immerse the reaction flask in the hot water bath. When the flask has been heated thoroughly, begin titration with the permanganate. The titration can be done fairly rapidly in the initial phases, with vigorous swirling. However, the end point is somewhat difficult to see; the final stages of the titration (yellow-green color) must be done slowly.

Report

Calculate the ratio of oxygen to tungsten in your samples of mineral blue. Be sure to show all of your calculations clearly.

Reference Cited: (1) Pickering, Miles; Monts, David L. *J. Chem. Educ.* **1982** 59 693.

Pre-lab Questions - Tungsten Oxides

1. Use the half-reaction method to generate a balanced equation for the oxidation of tungsten(IV) oxide to tungsten(VI) oxide by permanganate.

2. Calculate the volume of 0.020 M potassium permanganate solution needed to oxidize 1.32 g of tungsten(IV) oxide to tungsten(VI) oxide.

3. For the purpose of this problem, assume that tungsten(VI) oxide is reduced completely to tungsten(IV) oxide by high-temperature reaction with propane. Write a balanced equation for the process.