Colorful Iron Complexes

Transition Metal Complex Ions

Introduction

Easily distinguish between solutions of iron(II) and iron(III) ions by performing re-dox reactions between iron's two oxidation states. Simply add various complex ions to solutions of iron(II) or iron(III)—observe formation of the beautifully-colored Prussian blue precipitate or of the deep blood-red complex, the confirming test for iron(III).

Concepts

- Complex ions
- Oxidation numbers
- Oxidation–reduction
- Transition metals

Materials

Iron(III) chloride solution, 0.02 M, $FeCl_3 \cdot 6H_2O$, 60 mL
Iron(II) sulfate solution, 0.02 M, $FeSO_4 \cdot 7H_2O$, 60 mL
Potassium ferricyanide solution, 0.1 M, $K_3Fe(CN)_6$, 10 drops
Potassium ferrocyanide solution, 0.1 M, $K_4Fe(CN)_6 \cdot 3H_2O$, 10 drops
Potassium thiocyanate solution, 0.1 M, KSCN, 10 drops
Water, distilled or deionized, 120 mL
Colorful Iron Complexes Worksheet
Graduated cylinder, 25-mL
Stoppers to fit tubes, 6
Test tubes, 25 × 150 mm, 6
Test tube rack

Safety Precautions

This activity requires the use of hazardous components and/or has the potential for hazardous reactions. Potassium ferricyanide, potassium ferrocyanide, and potassium thiocyanate are dangerous if heated or in contact with concentrated acids since toxic hydrogen cyanide gas may be liberated. Potassium thiocyanate is moderately toxic by ingestion. Potassium ferricyanide, potassium ferrocyanide, and ferrous sulfate are slightly toxic by ingestion. Iron(II) sulfate is corrosive to skin, eyes, and mucous membranes. Iron(III) chloride may be a skin and tissue irritant. Avoid body contact with all chemicals. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information. Wash hands thoroughly with soap and water before leaving the laboratory.

Pre-Demonstration Activity

1. Copy enough worksheets for the class using the provided Colorful Iron Complexes Worksheet master.
2. Before performing the demonstration, write the chemical formulas for each of the five solutions on the chalkboard.
3. Have students determine the oxidation number of the iron atom in each compound using rules for assigning oxidation numbers in any standard chemistry text.

Procedure

1. Place six test tubes in a test tube rack. Label the tubes 1–6 and then label tubes 1–3 as Fe^{2+} and tubes 4–6 as Fe^{3+}.
2. Add approximately 20 mL of 0.02 M iron(II) sulfate solution and 20 mL of distilled or deionized water to test tubes 1–3. Stopper the tubes and invert to mix.
3. Add approximately 20 mL of 0.02 M iron(III) chloride solution and 20 mL of distilled or deionized water to test tubes 4–6. Stopper the tubes and invert to mix.

Part A. Ferrocyanide ions, $Fe(CN)_6^{4-}$ [Iron in the +2 oxidation state]

4. Add 5 drops of 0.1 *M* potassium ferrocyanide solution to Tube 1. Since both sources of iron are in the +2 state, the notable deep-blue precipitate does not form. Instead a light blue precipitate of potassium iron(II) hexacyanoferrate(II), $K_2Fe[Fe(CN)_6]$, forms according to Equation 1.

$$Fe^{2+} + 2K^{+} + [Fe(CN)_6]^{4-} \rightarrow \underset{\textit{Light blue ppt}}{K_2Fe[Fe(CN)_6](s)} \qquad \textit{Equation 1}$$

5. Add 5 drops of 0.1 *M* potassium ferrocyanide solution to Tube 4. A deep-blue precipitate will form according to equation 2, due to the presence of both iron(II) and iron(III) ions. This resulting deep blue precipitate is iron(III) hexacyanoferrate(II), $Fe_4[Fe(CN)_6]_3$, or Prussian blue. Have students determine the oxidation number of each iron atom in the complexes in Equations 1 and 2.

$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow \underset{\textit{Prussian blue}}{Fe_4[Fe(CN)_6]_3} \qquad \textit{Equation 2}$$

Upon standing for 5–10 minutes, the solution in Tube 1 will turn darker blue as the iron(II) is slowly oxidized to iron(III) by atmospheric oxygen to form the same Prussian blue precipitate as in equation 2.

Part B. Ferricyanide ions, $Fe(CN)_6^{3-}$ [Iron in the +3 oxidation state]

6. Add 5 drops of 0.1 *M* potassium ferricyanide solution to Tube 2. A deep-blue precipitate will form with the iron(III) sulfate. In this reaction, the ferricyanide ions, $[Fe(CN)_6]^{3-}$, oxidize iron(II) to iron(III) forming ferrocyanide ions, $[Fe(CN)_6]^{4-}$, according to Equation 3:

$$Fe^{2+} + [Fe(CN)_6]^{3-} \rightarrow Fe^{3+} + [Fe(CN)_6]^{4-} \qquad \textit{Equation 3}$$

The products of equation 3, the iron(III) ions and ferrocyanide ions, then combine to form iron(III) hexacyanoferrate(II) or Prussian blue, according to equation 2 above.

7. Add 5 drops of 0.1 *M* potassium ferricyanide solution to Tube 5. A brown solution is observed, indicating no reaction since both iron sources are in the +3 oxidation state, as shown below:

$$Fe^{3+} + [Fe(CN)_6]^{3-} \rightarrow \textit{No Reaction}$$

Part C. Thiocyanate ions, SCN^-

8. Add 5 drops of 0.1 *M* potassium thiocyanate solution to Tube 3. Some light red-brown coloring may appear due to slight oxidation of Fe^{2+} to Fe^{3+}, but no visible reaction is observed.

$$Fe^{2+} + 3SCN^{-} \rightarrow \textit{No Reaction}$$

9. Add 5 drops of 0.1 *M* potassium thiocyanate solution to Tube 6. A deep-red complex will form with the iron(III) sample according to Equation 4. This is a positive indicator test for the iron(III) ion.

$$Fe^{3+} + 3SCN^{-} \rightarrow \underset{\textit{Blood-red complex}}{Fe(SCN)_3} \qquad \textit{Equation 4}$$

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. Dispose of the solutions in the test tubes down the drain with excess water according to Flinn Suggested Disposal Method #26b. Flush any excess potassium thiocyanate, iron(II) sulfate, or iron(III) chloride solution down the drain according to Flinn Suggested Disposal Method #26b. Dispose of excess ferricyanide and ferrocyanide solution according to Flinn Suggested Disposal Method #14.

Tips

- It is very helpful to write Fe^{2+} and Fe^{3+} on the appropriate test tubes and to have the students fill in the provided worksheet as the demonstration is performed. Even the most skilled students (and teachers) may find it hard to keep track of which form of iron is in the tube and which is being added. The demo will have the greatest effect if this confusion is removed.
- Use this demonstration during the oxidation–reduction unit when teaching students about oxidation numbers. Have students perform the pre-demonstration activity to assure that they can determine the oxidation number for iron in each compound.
- After performing the demonstration, you may wish to use the tests to determine if an "unknown" contains iron(II) or iron(III) ions. You can use a few milliliters of either the iron(II) sulfate solution or the iron(III) chloride solution as the unknown. Or you can test any iron solution in your chemical stockroom. Enough of the testing reagents are provided for testing unknowns in each class.

Discussion

Many transition metals exhibit the ability to exist as relatively stable ions in different oxidation states. Iron can be found as the Fe^{2+} ion [iron(II)] in some compounds. Iron is also found as the Fe^{3+} ion [iron(III)] in other compounds.

The variable valence states can be explained by looking at the electron configuration of iron, which is $[Ar]4s^23d^6$. When transition metal atoms form positive ions, the outer s electrons are lost first because the inner d sublevels are lower in energy (more stable) than the outer s sublevels. In the iron(II) ion, the two 4s electrons have been lost, leaving $[Ar]3d^6$. In the iron(III) ion, the two 4s electrons and one 3d electron have been removed, leaving $[Ar]3d^5$. The iron(III) ion is more stable than the iron(II) ion since its d orbital is half-filled, containing five electrons, while that of iron(II) is one more than half-filled. Half-filled orbitals (and filled orbitals) have been shown to have greater stability. Therefore, a compound or a solution containing the iron(II) ion will slowly oxidize to the iron(III) state on exposure to air due the greater stability of the Fe^{3+} ion.

In order to distinguish between iron(II) and iron(III) ions, potassium ferrocyanide [$K_4Fe(CN)_6{\cdot}3H_2O$] and potassium ferricyanide [$K_3Fe(CN)_6$] complexes are used in this experiment. The cyano group in each complex has a charge of –1 and potassium has a charge of +1. Thus, the complex ferrocyanide, $Fe(CN)_6^{4-}$, contains iron in the +2 oxidation state while the complex ferricyanide, $Fe(CN)_6^{3-}$, contains iron in the +3 oxidation state.

A deep-blue (Prussian blue) precipitate results when either complex ion combines with iron in a different oxidation state from that present in the complex. The deep-blue color of the precipitate is due to the presence of iron in both oxidation states in the cyano complex. This provides a means of identifying either iron ion. Thus, when a solution of iron(II) is mixed with ferricyanide [iron(III)], a deep-blue precipitate is formed; likewise, when a solution of iron(III) is mixed with ferrocyanide [iron(II)], a deep-blue precipitate is formed.

The deep-blue precipitate, Prussian blue, has the composition of $Fe_4[Fe(CN)_6]_3$. Prussian blue has been used as a pigment in printing inks, paints, cosmetics (eye shadow), artist colors, carbon paper, and typewriter ribbons.

The thiocyanate ion, SCN^-, provides an excellent confirming test for the Fe^{3+} ion. The soluble, blood-red $Fe(SCN)_3$ complex is formed from the Fe^{3+} ion, while no complex is formed with the Fe^{2+} ion.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Systems, order, and organization
Evidence, models, and explanation
Content Standards: Grades 9–12
Content Standard B: Physical Science, structure and properties of matter, chemical reactions

Answers to Colorful Iron Complexes Worksheet

Test Tube	Solution #1 (Name & Formula)	Oxidation # of Iron	Solution #2 (Name & Formula)	Oxidation # of Iron	Observations	Reaction
1	Iron(II) sulfate $FeSO_4$	+2	Potassium ferrocyanide $K_4Fe(CN)_6$	+2	Blue ppt	$Fe^{2+} + 2K^{+} + [Fe(CN)_6]^{4-} \rightarrow K_2Fe[Fe(CN)_6]$
2	Iron(II) sulfate $FeSO_4$	+2	Potassium ferricyanide $K_3Fe(CN)_6$	+3	Deep-blue ppt (Prussian blue)	$Fe^{2+} + [Fe(CN)_6]^{3-} \rightarrow Fe^{3+} + [Fe(CN)_6]^{4-}$ $4Fe^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3$
3	Iron(II) sulfate $FeSO_4$	+2	Potassium thiocyanate KSCN	—	Lt. red-brown solution	$Fe^{2+} + 3SCN^{-} \rightarrow$ NR
4	Iron(III) chlo-ride $FeCl_3$	+3	Potassium ferrocyanide $K_4Fe(CN)_6$	+2	Deep-blue ppt (Prussian blue)	$4Fe^{3+} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_6]_3$
5	Iron(III) chlo-ride $FeCl_3$	+3	Potassium ferrocyanide $K_3Fe(CN)_6$	+3	Deep reddish-brown solution	$Fe^{3+} + [Fe(CN)_6]^{3-} \rightarrow$ NR
6	Iron(III) chlo-ride $FeCl_3$	+3	Potassium thiocyanate KSCN	—	Deep-red solution	$Fe^{3+} + 3SCN^{-} \rightarrow Fe(SCN)_3$

NR = No Reaction

References

Bilash, B.; Gross, G.; Koob, J. *A Demo A Day: Another Year of Chemical Demonstrations, Vol 2;* Flinn Scientific: Batavia, IL, 1998; pp 244–246.

Tzimopoulos, N. D.; Metcalfe, H. C.; Williams, J. E.; Castka, J. F. *Modern Chemistry Laboratory Experiments;* Holt, Rinehart and Winston: New York, 1990; p 63.

Flinn Scientific—Teaching Chemistry™ eLearning Video Series

A video of the *Colorful Iron Complexes* activity, presented by Peg Convery, is available in *Transition Metal Complex Ions* and in *Oxidation States*, part of the Flinn Scientific—Teaching Chemistry eLearning Video Series.

Materials for *Colorful Iron Complexes* are available from Flinn Scientific, Inc.

Materials required to perform this activity are available in the *Colorful Iron Complexes—Chemical Demonstration Kit* available from Flinn Scientific. Materials may also be purchased separately.

Catalog No.	Description
AP5946	Colorful Iron Complexes—Chemical Demonstration Kit
F0069	Iron(III) Chloride Solution, 1.0 M, 100 mL
F0016	Iron(II) Sulfate, 500 g
P0165	Potassium Ferricyanide Solution, 0.1 M, 500 mL
P0220	Potassium Ferrocyanide Solution, 0.1 M, 500 mL
P0178	Potassium Thiocyanate Solution, 0.1 M, 500 mL

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.

Colorful Iron Complexes Worksheet

Test Tube	Solution #1 (Name & Formula)	Oxidation # of Iron	Solution #2 (Name & Formula)	Oxidation # of Iron	Observations	Reaction
1						
2						
3						
4						
5						
6						