

# DEMONSTRATION 9.1

## THE OXIDATION STATES OF VANADIUM

This demonstration illustrates the colour changes associated with the change in the oxidation state of vanadium from (V) to (II).

### EQUIPMENT

- 1 L separating funnel and stopper
- four small beakers
- hot plate
- stirring rod
- 1 L conical flask and stopper
- 500 mL beaker
- light box
- 500 mL conical flask and stopper
- sealed jar

### REAGENTS



- zinc wire or pellets (20-30 mesh, 50 g)
- mercury(II) chloride,  $\text{HgCl}_2$  (1 g)
- nitric acid,  $\text{HNO}_3$  (15 M, 1 mL)
- sulfuric acid,  $\text{H}_2\text{SO}_4$  (2 M, 250 mL)
- distilled water
- sodium hydroxide,  $\text{NaOH}$  (3-4 g)
- ammonium vanadate,  $\text{NH}_4\text{VO}_3$  (5 g)

### PREPARATION

#### Prepare the zinc amalgam as follows:

- Place 1 g of mercury(II) chloride in 150 mL of water.
- Add 1 mL of the concentrated nitric acid.
- Add 50 g of zinc wire.
- Stopper the flask and shake it for a few minutes.
- Pour off the liquid and wash the amalgam thoroughly with water.
- Store the amalgam under water in a sealed jar.

Prepare the vanadium solution as follows:

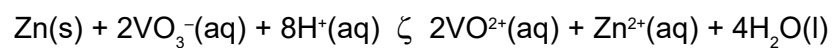
- Carefully dissolve the 3-4 g of  $\text{NaOH}$  in 100 mL of water.
- Add 5 g of ammonium vanadate (the beaker may be warmed to dissolve the solid completely), stir constantly.
- Add 250 mL of the 2 M sulfuric acid and dilute to 500 mL.
- Store in a well stoppered flask.

### PROCEDURE

- Place 50 g of zinc amalgam in the 1 L separating funnel.
- Add 100 mL of vanadium solution and stopper the flask.
- Pour a sample of the solution into a small beaker.
- Gently swirl the flask and save a sample.
- Shake the flask and save a sample.
- Shake the flask more vigorously and save a sample.
- Note the different colours of all the samples.

### RESULTS

The separating funnel initially contains a yellow solution. After gentle swirling the solution turns green. More shaking turns the solution blue. More vigorous shaking produces a violet colour. The following set of reactions explains the colour changes in terms of the oxidation states of vanadium:

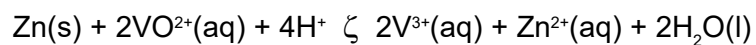


yellow

green

(oxidation state of V)

(oxidation state of IV)

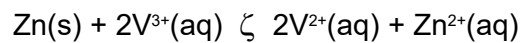


green

blue

(oxidation state of IV)

(oxidation state of III)



blue

violet

(oxidation state of III)

(oxidation state of II)

# DEMONSTRATION 9.2

## CHROMATE/DICHROMATE EQUILIBRIUM

This demonstration illustrates the effect of acid and base on the equilibrium between chromate and dichromate ions.

### EQUIPMENT

- 4 x 1 L flasks with corks (labelled 1 to 4)

### REAGENTS



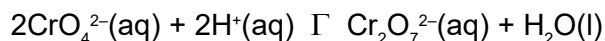
- potassium chromate,  $\text{K}_2\text{CrO}_4$  (4 g)
- potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$  (6 g)
- hydrochloric acid,  $\text{HCl}$  (3 M, 500 mL)
- sodium hydroxide,  $\text{NaOH}$  (3 M, 500 mL)

### PREPARATION

- Dissolve 4 g of  $\text{K}_2\text{CrO}_4$  in 1 L of water.
- Dissolve 6 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1 L of water.
- In the flasks labelled 1 and 2 place half of the  $\text{K}_2\text{CrO}_4$  solution, and in flasks 3 and 4 place half of the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.
- To flasks 1 and 3 add 250 mL of  $\text{HCl}$  (3 M) and to flasks 2 and 4 add 250 mL of  $\text{NaOH}$  (3 M) solution.

### RESULTS

The equilibrium between chromate and dichromate ions is:



Addition of acid shifts the equilibrium to the right causing the orange dimeric dichromate ion to dominate. The addition of hydroxide removes protons from the equilibrium causing a shift to the left and the yellow chromate ion dominates.

### CAUTION



**Chromium(VI) is carcinogenic.**

# DEMONSTRATION 9.3

## THE OXIDATION STATES OF MANGANESE

A solution of potassium permanganate is sequentially reduced from oxidation state VII through to VI, then from VI to IV, and finally from IV to oxidation state II.

### EQUIPMENT

- 1 L conical flask with stopper
- 3 x 10 mL measuring cylinders
- 1 x 50 mL measuring cylinder
- 4 reagent bottles
- light box

### REAGENTS



- potassium permanganate,  $\text{KMnO}_4$  (a few crystals)
- sodium hydroxide,  $\text{NaOH}$  (1 M, 10 mL)
- sulfuric acid,  $\text{H}_2\text{SO}_4$  (5 M, 10 mL) + (2 M, 50 mL)
- iron(II) sulfate-7-water,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (13.9 g)
- cyclohexene,  $\text{C}_6\text{H}_{10}$  (10 mL)
- deionised water

### PREPARATION

- Prepare 50 mL aqueous 1 M iron(II) sulfate in 2 M sulfuric acid by dissolving 13.9 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 50 mL 2 M sulfuric acid.
- Provide the reagents in stoppered, labelled reagent bottles and place them alongside the appropriate measuring cylinders.
- Fill the flask with 400 mL of water and place it on the light box.
- Switch on the light and add sufficient crystals of permanganate to produce a solution that is strongly coloured.

### PROCEDURE

- Add the reagents to the flask in the following sequence:
- 10 mL of sodium hydroxide solution.
- 10 mL of cyclohexene. This will form a layer over the surface of the permanganate solution. Swirl the flask for 1 minute.

### CAUTION



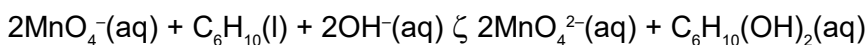
**Cyclohexene is a recognised carcinogen. Provide adequate ventilation during demonstration and disposal. The flask should be stoppered as soon as the demonstration is completed until safe disposal can be effected.**

- Add 5 to 10 mL of the sulfuric-acid solution.
- Add 25 to 30 mL of the iron(II) sulfate solution. Swirl the flask.

### RESULTS

The reactions are, sequentially:

**Reduction** of permanganate ( $\text{Mn(VII)}$ ) to manganate ( $\text{Mn(VI)}$ )



purple

green

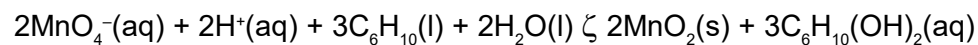
**Disproportionation** ( $\text{Mn(VI)}$  to  $\text{Mn(VII)}$  and  $\text{Mn(IV)}$ ).



purple                  brown

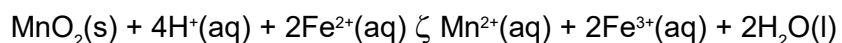
The starting material is now in acidic conditions.

**Reduction** of permanganate to manganese dioxide (Mn(VII) to Mn(IV)) is now possible.



brown

**Reduction** of manganese dioxide to manganese ions (Mn(IV) to Mn(II)).



colourless/pale pink

### High Risk Demonstration:

**1- Refer to HIRAC**

**2- Set up in Red Tray**

## IRON COMPLEXES

## EQUIPMENT

- ## REAGENTS

- 

## PREPARATION

- 

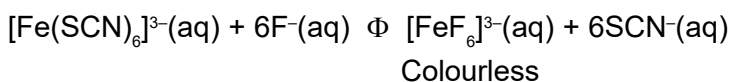
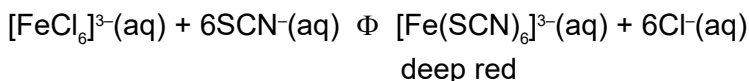
## PROCEDURE

- Transfer 300 mL of the pale-yellow iron(III) nitrate solution to the flask.
- Add 30 mL hydrochloric acid.
- Add 30 mL thiocyanate solution.
- Add 300mL fluoride solution.

## RESULTS

$$\text{[Fe(H}_2\text{O)}_6\text{]}^{3+}(\text{aq}) + 6\text{HCl(aq)} \rightleftharpoons \text{[FeCl}_6\text{]}^{3-}(\text{aq}) + 6\text{H}_3\text{O}^+(\text{aq})$$

pale yellow                      intense yellow



## High Risk Demonstration:

- 1- Refer to HIRAC                      2- Set up in Red Tray**



# DEMONSTRATION 9.5

## THE COLOUR OF TRANSITION METAL COMPLEXES

The colour of iron complexes depends on the oxidation state of the iron and the ligands in the complex.

### EQUIPMENT

- spray bottle
- absorbent paper
- paint brush

### REAGENTS



- iron(III) chloride,  $\text{FeCl}_3$  (10 g)
- hydrochloric acid,  $\text{HCl}$  (3 M, 200 mL)
- potassium thiocyanate,  $\text{KSCN}$  (saturated)
- potassium hexacyanoferrate(II),  $\text{K}_4\text{Fe}(\text{CN})_6$  (10%)

### PROCEDURE



- Paint a message such as “transition metal complexes are coloured” on blotting paper using potassium thiocyanate.
- Paint a separate message using 10% potassium hexacyanoferrate(II).
- Allow to dry (or use a hair-drier).
- Show the colours by spraying with  $\text{FeCl}_3$  (10 g) in dilute  $\text{HCl}$  (3 M, 200 mL).

### RESULTS

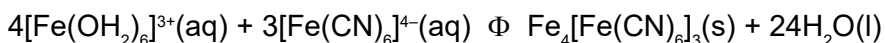
The saturated potassium thiocyanate produces a red colour.

The 10% potassium hexacyanoferrate(II) produces a blue colour.

The addition of iron(III) ions to thiocyanate ions results in the formation of a red coloured iron(III) thiocyanate complex:



The addition of iron(III) ions to potassium hexacyanoferrate(II) results in the formation of an intensely blue coloured precipitate commonly known as Prussian blue:



### High Risk Demonstration:

**1- Refer to HIRAC**

**2- Set up in Red Tray**



# DEMONSTRATION 9.6

## TEMPERATURE CHANGES AND COBALT COMPLEXES

The effect of temperature on equilibrium can be demonstrated using cobalt complexes.

### EQUIPMENT

- 250 mL beaker
- 3 x 50 mL beakers
- large beaker filled with ice
- hot plate
- scales
- spatula

### REAGENTS



- cobalt(II) chloride-6-water,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.4 M)
- hydrochloric acid,  $\text{HCl}$  (10 M)

### CAUTION

**Cobalt(II) chloride is toxic.**

### PREPARATION

- Dissolve 5.2 g of cobalt(II) chloride-6-water in 100 mL of distilled water.
- Place the solution in the 250 mL beaker.

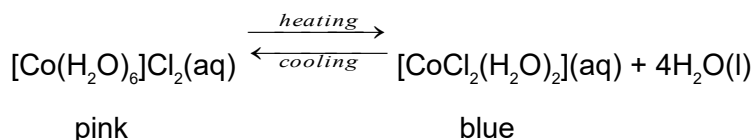
### PROCEDURE



- Add hydrochloric acid to the  $\text{CoCl}_2$  solution until the solution changes from pink to blue-purple. Excess hydrochloric acid (10 M) is required to get the formation of the blue complex.
- Divide the solution evenly amongst the three smaller beakers and treat them as follows:
  - Place one beaker on a hot plate.
  - Place one beaker in an ice bath.
  - Leave one beaker at room temperature as a standard.
- After a few minutes, show that the heated sample has turned a darker blue and the cooled sample has turned a light pink.

### RESULTS

This reaction involves the following equilibrium:



Addition of heat causes shift of equilibrium toward the products, a blue solution. Cooling causes a shift to the left, a pink solution.

For an interesting variation, heat 150 mL of  $\text{CoCl}_2$  solution until it turns blue. Fill a large test tube with this solution and immerse it halfway into a beaker that contains crushed ice and salt. The bottom half of the test tube will turn pink.

### High Risk Demonstration:

**1- Refer to HIRAC**

**2- Set up in Red Tray**

# DEMONSTRATION 9.7

## NICKEL COMPLEXES

Solutions of nickel(II) chloride and 1,2-ethanediamine are prepared and added to one another in three different ratios. These additions result in three solutions with different colours.

### EQUIPMENT

- 6 x 500 mL measuring cylinders of identical make
- 3 x 1 L conical flasks
- 3 stirring rods
- light box

### REAGENTS



- 1,2-ethanediamine, ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 = \text{en}$ )
- nickel(II) chloride-6-water,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (30 g)

### PREPARATION

- Prepare a solution of 1,2-ethanediamine (7.5 g in 1 L)
- Prepare a solution of nickel(II) chloride solution by dissolving  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (30 g) in distilled water (1 L).
- Arrange the measuring cylinders in pairs and add the solutions as outlined below :

	diamine	nickel	ratio
1.	170 mL	500 mL	1:3
2.	330 mL	330 mL	1:1
3.	500 mL	170 mL	3:1

- With identical cylinders, the ratio of the volumes will become obvious.
- Place them in pairs on the light box and put one empty flask and one stirring rod with each pair.
- Variations in the purity of the 1,2-ethanediamine as well as in temperature may require some adjustments to the concentrations.

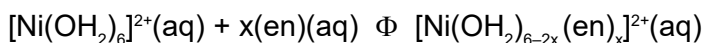
### PROCEDURE

- Combine the contents of each pair in the associated conical flask and Stir.

### RESULTS

	colour	composition	ratio
Flask 1	blue-green	$[\text{Ni}(\text{OH}_2)_6]^{2+}$ & $[\text{Ni}(\text{en})(\text{OH}_2)_4]^{2+}$	1:3
Flask 2	light blue	mainly $[\text{Ni}(\text{en})_2(\text{OH}_2)_2]^{2+}$	1:1
Flask 3	purple	mainly $[\text{Ni}(\text{en})_3]^{2+}$	3:1

The general equation for these reactions is:



# DEMONSTRATION 9.8

## COPPER COMPLEXES

A variety of coloured solids and solutions can be generated by reactions of the copper(II) aqueous ion.

### EQUIPMENT

- 8 large test tubes
- perspex test-tube rack
- 500 mL beaker
- 3 pasteur pipettes

### REAGENTS



- copper(II) chloride-2-water,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (20 g)
- hydrochloric acid,  $\text{HCl}$  (3 M, 20 mL)
- ammonia,  $\text{NH}_3$  (15 M, 20 mL)
- acetic acid,  $\text{CH}_3\text{COOH}$  (17 M, 10 mL)
- potassium hexacyanoferrate(II) solution,  $\text{K}_4[\text{Fe}(\text{CN})_6]$  (1 mL)
- sodium dithionite,  $\text{Na}_2\text{S}_2\text{O}_4$  (2 g)

### PREPARATION

- Prepare a copper(II) stock solution by adding 20 g of copper chloride-2-water to 80 mL of 3 M hydrochloric acid in the 500 mL beaker.

### PROCEDURE

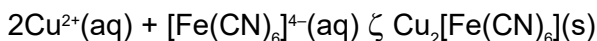


- Pour some of the copper(II) stock solution into two test tubes and keep one for comparison.
- To the other test tube, add a few drops of potassium hexacyanoferrate(II) solution.
- Dilute the remaining stock solution to 200 mL with distilled water.
- Put a test tube of this solution aside for comparison.
- Pour some of the diluted stock solution into another test tube.
- Add ammonia, a few mL at a time, until a light blue precipitate is formed.
- Put a test tube of this solution aside for comparison.
- Continue to add ammonia to the remaining test tube until a deep blue solution forms.
- Put a test tube of this solution aside for comparison.
- Slowly add acetic acid to the remaining test tube of tetraammine complex until a change occurs.
- Put a test tube of this solution aside for comparison.
- To the solution remaining from the acetic acid step, add the sodium dithionite, and stir. This solution may be heated to speed up the reaction.

**RESULTS**

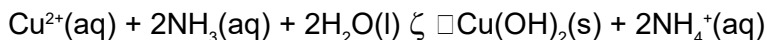
The copper(II) chloride complex is yellow and the copper(II) water complex is blue. When both the water and chloride are complexed, as in the first step, the solution will appear green.

The hexacyanoferrate(II) ion then reacts with the copper ion to produce the deep rose copper(II) hexacyanoferrate(II) precipitate.



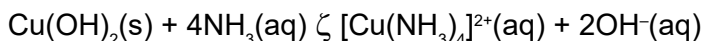
deep rose

When ammonia is added, the copper(II) aqueous ions react to produce a blue precipitate of copper(II) hydroxide.



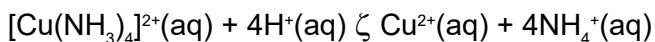
light blue

When excess ammonia is added, the copper hydroxide reacts to form the deep blue tetraammine copper(II) complex.



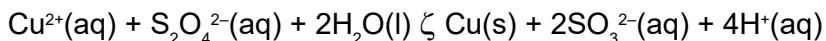
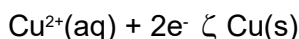
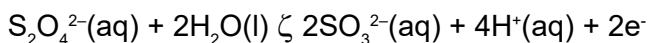
dark blue

Acetic acid added to the tetraammine complex will cause it to revert to the hydrated form.



green

Finally, addition of dithionite to the hydrated copper(II) ion reduces it to metallic copper.



### High Risk Demonstration:

1- Refer to HIRAC

2- Set up in Red Tray

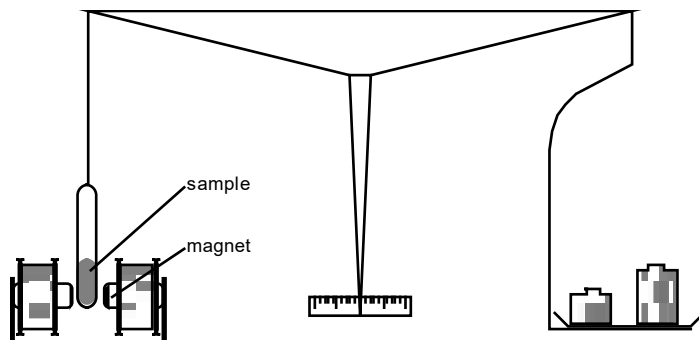
# DEMONSTRATION 9.9

## PARAMAGNETISM OF TRANSITION METAL COMPLEXES

The relationship between paramagnetism of a salt and its number of unpaired electrons is demonstrated using a Guoy balance.

### EQUIPMENT

- Guoy balance (available from Inorganic Chemistry Room 440)
- Guoy tube



### REAGENTS

- potassium chromium(III) sulfate-12-water,  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$   
(3 unpaired electrons)
- manganese(II) sulfate-4-water,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$   
(5 unpaired electrons)
- ammonium iron(III) sulfate-6-water,  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$   
(5 unpaired electrons)
- mercury(II) tetra-N-thiocyanatocobaltate(II),  $\text{HgCo}(\text{NCS})_4$   
(3 unpaired electrons)
- ammonium nickel(II) sulfate-6-water,  $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$   
(2 unpaired electrons)
- copper(II) sulfate-5-water,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
(1 unpaired electron)
- sodium chloride,  $\text{NaCl}$   
(diamagnetic)

### PROCEDURE

- Place a sample of the salt in the Guoy tube (two-thirds full).
- Place the tube into the apparatus (between the poles of the magnet).

### RESULTS

The transition metal compounds are attracted to the magnet. Sodium chloride (diamagnetic) is repelled.

# DEMONSTRATION 9.10

## COMPLEXES THAT CHANGE COLOUR WHEN HEATED

Transition metal complexes that have different colours at high and low temperatures.

### EQUIPMENT

- beakers
- bunsen burner
- ice bath

### REAGENTS

- copper(II) sulfate solution,  $\text{CuSO}_4$  (0.1 M, 100 mL)
- sodium chloride, NaCl.
- cobalt(II) chloride solution,  $\text{CoCl}_2$  (0.5 M, 20 mL)
- sodium chloride solution, NaCl (saturated 16 mL)
- chromium(III) nitrate,  $\text{Cr}(\text{NO}_3)_3$
- dilute nitric acid,  $\text{HNO}_3$

### PROCEDURE

#### Part A ( $\text{Cu}^{2+}$ )

- Add excess NaCl to copper(II) sulfate solution.
- Heat the solution to  $95^\circ\text{C}$ .
- Let the solution cool to room temperature.
- Observe any colour changes.

#### Part B ( $\text{Co}^{2+}$ )

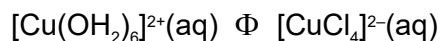
- Mix 20 mL of the 0.5 M  $\text{CoCl}_2$  solution with 16 mL of saturated NaCl solution.
- Chill the mixture.
- Heat the mixture to  $95^\circ\text{C}$ .
- Alternate heating and cooling is possible.
- Observe any colour changes.

#### Part C ( $\text{Cr}^{3+}$ )

- Prepare a solution of  $[\text{Cr}(\text{OH}_2)_6]^{3+}(\text{aq})$  by dissolving  $\text{Cr}(\text{NO}_3)_3$  in dilute  $\text{HNO}_3$  until a purple colour is obtained.
- Add excess NaCl.
- Heat to boiling and then allow to cool to room temperature.
- Observe any colour changes.

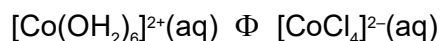
**RESULTS**

In part A the blue solution turned green when heated and returned to its original colour when cooled. In the solution there is an equilibrium between the six coordinate aqua copper(II) complex and a variety of four coordinate chloro copper (II) complexes.



blue                      green

In part B the chilled solution is pink and the heated solution is blue. The heating and cooling processes are reversible. In the solution there is an equilibrium between the six coordinate aqua cobalt(II) complex and a variety of four coordinate chloro cobalt (II) complexes.



pink                      blue

In part C the addition of the excess NaCl produces no observable colour change. Boiling the solution gives a green colour due to  $[\text{CrCl}_2(\text{OH}_2)_4]^+(\text{aq})$ . The green remains as the solution is cooled to room temperature indicating that it is stable.



purple                      green

# DEMONSTRATION 9.11

## AMPHOTERIC PROPERTIES OF HYDROXIDES

Chromium, lead and zinc hydroxides dissolve in both acid and base.

### EQUIPMENT

- 6 petri dishes

### REAGENTS



- chromium(III) sulfate,  $\text{Cr}_2(\text{SO}_4)_3$  (0.16 g)  
or chromium potassium sulfate,  $\text{CrK}(\text{SO}_4)_2$  (0.28 g)
- zinc nitrate,  $\text{Zn}(\text{NO}_3)_2$  (0.95 g)
- lead(II) nitrate,  $\text{Pb}(\text{NO}_3)_2$  (1.66 g)
- sodium hydroxide,  $\text{NaOH}$  (1 M)
- nitric acid,  $\text{HNO}_3$  (1 M, 15 mL)

### PREPARATION

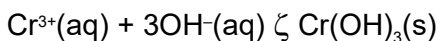
- Dissolve chromium(III) sulfate (0.16 g) or chromium potassium sulfate (0.28 g) in water (50 mL).
- Dissolve zinc nitrate (0.95 g) in water (50 mL).
- Dissolve lead nitrate (1.66 g) in water (50 mL).
- Place the petri dishes on top of the overhead projector. Into two pour chromium(III) solution (25 mL); into another two zinc solution (25 mL), and into the last two lead(II) solution (25 mL).

### PROCEDURE

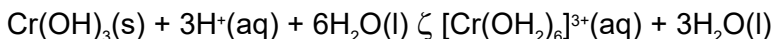
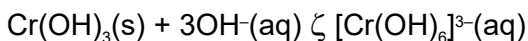
- To the chromium(III) samples, add sodium hydroxide (1 mL) and swirl.
- To the zinc and lead(II) samples, add sodium hydroxide (5 mL) and swirl.
- To one of the chromium(III) samples, add additional sodium hydroxide (2 mL) and to the other, nitric acid (2 mL) and swirl.
- To one of each of the zinc and lead(II) samples, add additional sodium hydroxide (5 mL) and to the other, nitric acid (8 mL) and mix.

### RESULTS

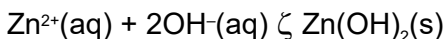
Initially a green precipitate forms:



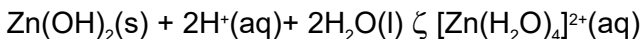
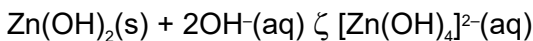
Upon the addition of excess sodium hydroxide or acid the precipitate dissolves:



A white precipitate forms:

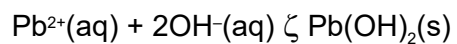


Upon the addition of excess sodium hydroxide or acid the precipitate dissolved:

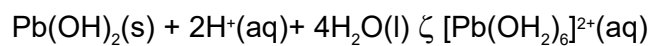
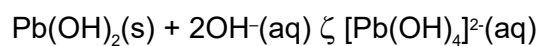




A white precipitate forms:



Upon the addition of excess sodium hydroxide or acid the precipitate dissolves:



# DEMONSTRATION 9.12

## MERCURY (II) COMPLEXES

Bright orange mercury(II) iodide is precipitated upon the mixing of mercury(II) chloride and potassium iodide. Addition of further potassium iodide removes the colour.

### EQUIPMENT

- 3 measuring cylinders: 2 x 250 mL, 1 x 1000 mL
- 1 x 2 L beaker
- stirring rod
- light box

### REAGENTS

- mercury(II) chloride,  $\text{HgCl}_2$  (0.1 M, 250 mL)
- potassium iodide, KI (0.1 M, 1000 mL)
- distilled water

### CAUTION

**Mercury (II) chloride is highly toxic and corrosive. Handle with care!**

### PREPARATION

- Dissolve mercury(II) chloride (6.79 g) in water (250 mL).
- Dissolve potassium iodide (16.6 g) in water (1000 mL).
- Place beaker, measuring cylinder, stirring rod and the two solutions in labelled reagent bottles on the light box.

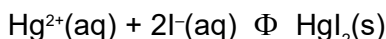
### PROCEDURE

- Place 250 mL of each solution in the beaker and stir.
- Add additional potassium iodide solution (750 mL).

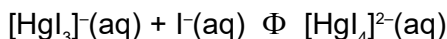
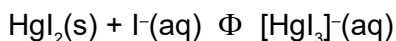
### RESULTS



A bright orange precipitate will result from the mixing of equal amounts of the two solutions.



With further addition of iodide, the solution will become clear again.



### High Risk Demonstration:

**1- Refer to HIRAC**

**2- Set up in Red Tray**