

# QUALITATIVE CHEMISTRY OF THE FIRST ROW

## TRANSITION METALS

There are eight sections, each part requiring about one hour and the students are required to do any 2 elements. They can often be fitted in during the programme when other experiments have slack time. The students will benefit most from these experiments if demonstrators continually question the students on the meaning of their observations.

Useful references:-

Comprehensive Inorganic Chemistry

Kolthoff and Elving - Treatise on Analytical Chemistry.

### Answers to Questions and Mark Schemes:

**Equations are essential.**

#### 1.1 **Titanium**

- i) ilmenite  $\text{FeTiO}_3$  rutile  $\text{TiO}_2$
- ii) accumulated in marine species but of unknown function
- iii) Alloys, metal pigments in paint, plastic, paper and rubber industry as  $\text{TiO}_2$ , catalysts as other complexes
- iv) nothing observable in either case  
$$\text{TiO}_2 \quad \rightarrow \quad \text{TiO}(\text{SO}_4)$$

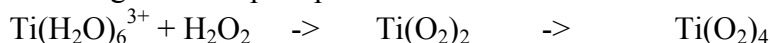


An amphoteric oxide. If they test their solutions with  $\text{H}_2\text{O}_2$  then the tests will be positive justifying the above equations.

- v) The purple solution yields a black precipitate, which gradually lightens to blue and then white  
$$\text{Ti}(\text{H}_2\text{O})_6^{3+} + \text{OH}^- \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO}_2$$

Dark violet                      white

- vi) On addition of  $\text{H}_2\text{O}_2$  a deep red colour forms. This goes yellow on addition of  $\text{OH}^-$  and on adding excess  $\text{OH}^-$  a white gelatinous precipitate forms.



which goes to  $\text{TiO}_2$  in excess  $\text{OH}^-$ .

- vii) The same observations as for (v) indicating that an ammine complex is not involved.
- viii) The white precipitate dissolves to give a clear solution. This indicates that a freshly prepared sample of rutile is more reactive than an aged sample. Reaction as in (iv)
- ix) The solution turns a light purple with evolution of a gas.  
$$\text{TiO}^{2+} + \text{Zn} \rightarrow \text{Ti}(\text{H}_2\text{O})_6^{3+} + \text{Zn}^{++}$$

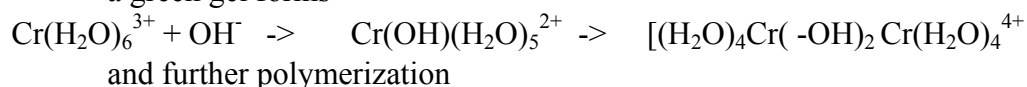


iv) The orange solid dissolves to give an orange solution which goes yellow on adding base. It goes orange again on adding acid.  
 $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{CrO}_4^{2-} + 2\text{H}^+$

v) No precipitate with acidified  $\text{Cr}_2\text{O}_7^{2-}$ . A yellow precipitate with  $\text{CrO}_4^{2-}$   
 $\text{CrO}_4^{2-} + \text{Ba}^{2+} \rightarrow \text{BaCrO}_4$

vi) Red fumes are given off, a red liquid forms, a white solid is produced.  
 $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{KCl} + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{CrO}_2\text{Cl}_2 + 3\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$   
 This is a test for chloride ions.

vii) The blue solution which results from the blue/violet chrome alum solid goes green on adding base and finally a green gel forms

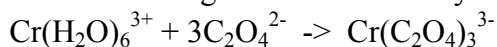


Olation - polymerization through hydroxyl bridges.

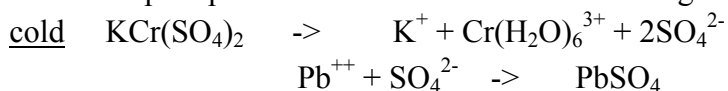
Oxalation - conversion of hydroxyl bridges to oxo bridges on heating.

This is the basis of the use of Cr(III) in the tanning industry.

viii) In the presence of oxalate no colour changes occur. The oxalate coordinates to the Cr(III) and hydrolysis is very slow illustrating the kinetic stability of Cr(III).



ix) Cold solution - an initial blue solution gives a white precipitate on addition of  $\text{Pb}^{2+}$ . Warm solution - the initial blue solution goes green on warming and gives very much less precipitate than the cold solution of adding Pb(II)



Warm  $\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{SO}_4^{2-} \rightarrow [\text{Cr}(\text{SO}_4)(\text{H}_2\text{O})_4]^+$   
 and thus less sulphate available for precipitation.  
 This again shows the slow reaction of Cr(III)

## 1.4 Manganese

- i) Pyrolusite,  $\text{MnO}_2$   
 Psilomelane  $\text{MnO}_2$
- ii) An essential trace element in both plant and animal life, essential in photosynthesis and other enzyme processes
- iii) Alloys (as metal)

In electrical batteries, glasses, fertilizers, pesticides, fungicides, petrol additive (as compounds)

- iv) On adding a drop of  $\text{KMnO}_4$  a pink colour develops which disappears on heating  
Pink colour - unreacted  $\text{KMnO}_4$   
 $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$   
Reaction is slow at room temperature,  $\text{Mn}^{2+}$  catalyses the reaction
- v) On adding  $\text{KMnO}_4$  the colour is immediately lost. On further addition a brown colour develops about the point of entry. This may or may not remain, depending on the concentration of the acid.  
brown:-  $2\text{MnO}_4^- + 3\text{C}_2\text{O}_4^{2-} + 4\text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 6\text{CO}_2 + 8\text{OH}^-$
- vi) The initially colourless solution goes Cherry red on addition of  $\text{KMnO}_4$   
 $\text{MnO}_4^- + 4\text{Mn}^{2+} + 8\text{H}^+ \rightarrow 5\text{Mn}^{3+} + 4\text{H}_2\text{O}$
- vii) a) A yellow/green gas, irritating, is given off  
 $2\text{MnO}_4^- + 16\text{HCl} \rightarrow 2\text{MnCl}_2 + 2\text{KCl} + 5\text{Cl}_2 + 8\text{H}_2\text{O}$   
b) as above  
 $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
- viii) The initially clear solution goes yellow and then a white precipitate forms on adding base. On the surface of the solution a brown precipitate forms:-  
 $\text{Mn}(\text{H}_2\text{O})_6^{2+} + 2\text{OH}^- \rightarrow \text{Mn}(\text{OH})_2 \rightarrow \text{MnO}_2$   
white brown

## 1.5 Iron

- i) Magnetite,  $\text{Fe}_3\text{O}_4$ ; Hematite,  $\text{Fe}_2\text{O}_3$ ;  
Limonite,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; Siderite  $\text{FeCO}_3$ ;  
Iron pyrite  $\text{FeS}_2$
- ii) Important constituent of blood and tissues of animals, present in porphyrins or haemproteins (haemoglobin), myoglobin and heme enzymes also present as nonheme proteins (transferrin, ferritin, hemosiderin)
- iii) Steel industry  
Catalysis
- iv) a)  $\text{Fe}(\text{III}) + \text{SCN}^- \rightarrow$  red solution  
 $\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{SCN}^- \rightarrow \text{Fe}(\text{H}_2\text{O})_5(\text{SCN})^{2+}$   
b) A deep green solution  
Berlin green " $\text{Fe}[\text{Fe}(\text{CN})_6]$ "  
c) A deep blue solution and precipitate  
 $4\text{Fe}(\text{III}) + 3\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}_4\{\text{Fe}[\text{Fe}(\text{CN})_6]\}^3$

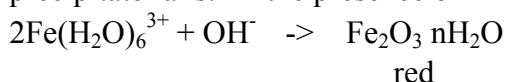
(Turnbull's blue or Prussian Blue)

- v) a) no reaction (unless Fe(III) present)  
b) a deep blue solution and precipitate  
(Turnbull's blue, as above)  
c) a white precipitate (possibly light blue)  
$$2\text{K}^+ + \text{Fe(II)} + \text{Fe(CN)}_6^{4-} \rightarrow \text{K}_2\text{Fe[Fe(CN)}_6]$$

- vi) The initial yellow/red solution goes colourless on adding F<sup>-</sup> and no reaction is evident with SCN<sup>-</sup>

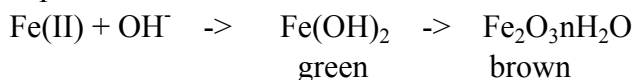
$$\text{Fe(H}_2\text{O)}_6^{3+} + 6\text{F}^- \rightarrow [\text{FeF}_6]^{3-}$$
 and the hexafluoride is very inert and thus no reaction with thiocyanate.

- vii) The initial yellow/red solution becomes deeper yellow on adding OH<sup>-</sup> and finally a brown precipitate falls. In the presence of F<sup>-</sup> no reaction occurs with OH<sup>-</sup>

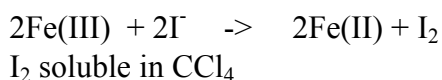


See (vi) above for F<sup>-</sup> explanation.

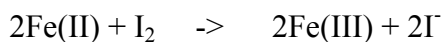
- viii) A green precipitate forms on adding OH<sup>-</sup> to Fe(II). In the presence of F<sup>-</sup> a similar result but the formation of the precipitate is slower. The precipitate goes brown on exposure to air.



- ix) The initially green/yellow solution reacts with I<sup>-</sup> to give a deep red colour. CCl<sub>4</sub> goes red.

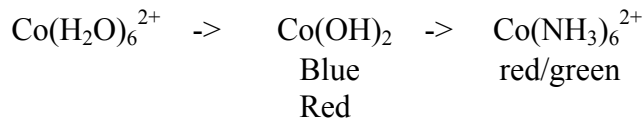


- x) Decolourization of the I<sub>3</sub><sup>-</sup> solution occurs slowly, on adding CCl<sub>4</sub> the organic layer does not become coloured.

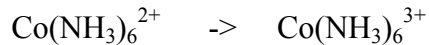


## 1.6 Cobalt

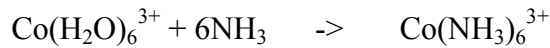
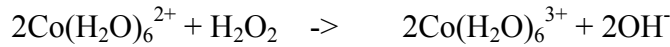
- i) Smallite CoAs<sub>2</sub>; Skutterudite (Co, Ni)As<sub>3</sub>  
Cerrollite CuS.Co<sub>2</sub>S<sub>3</sub>; Linnaeite Co<sub>3</sub>S<sub>4</sub>  
Cattierite CoS<sub>2</sub>
- ii) A vital trace element in animal nutrition. Vitamin B<sub>12</sub> contains Co<sup>3+</sup> in a porphyrin type environment
- iii) Alloying, electroplating (as metal) catalysis, Drying agents, glasses, adhesives [as compounds]
- iv) The initially pink solution yields a blue precipitate on adding NH<sub>3</sub> which dissolves to give a red/green solution on adding excess NH<sub>3</sub>.



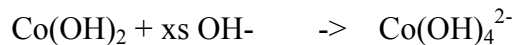
v) On adding H<sub>2</sub>O<sub>2</sub> a deep/solution results (clearly not simply dilution)



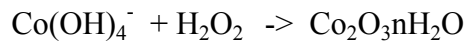
vi) the light pink solution goes to an orange/red colour but the change is only slight. On adding NH<sub>3</sub> a deep red colour results



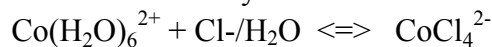
vii) The light pink solution gives initially a blue precipitate which slowly turns pink. On adding solid NaOH a deep blue solution results.



viii) On adding H<sub>2</sub>O<sub>2</sub> a black solid results. A similar precipitate results on reversing the order of addition of H<sub>2</sub>O<sub>2</sub> and NaOH.



ix) On adding HCl a deep blue solution forms which goes pink on diluting. This should also happen with NaCl but H<sup>+</sup> is necessary.



## 1.7 Nickel

i) Pentlandite, (Ni, Fe)<sub>9</sub>S<sub>8</sub>  
Garnierite (Ni, Mg)<sub>6</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>  
Limonite (Ni, Fe)O(OH) nH<sub>2</sub>O

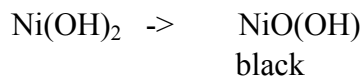
ii) Ni(II) has a considerable effect on the liver but its action and binding sites are unknown.

iii) Alloys (for high temperature alloys)  
Electroplating  
Catalysis (hydrogenation)  
Enamels (as adhesive)  
Batteries (Ni/Fe and Ni/Cd)

iv) A green gelatinous precipitate forms from the green solution. It does not dissolve in excess hydroxide



v) A black solid results



vi) The green solution gives a green gelatinous precipitate which dissolves on adding ammonia to give a blue solution  

$$\text{Ni}(\text{H}_2\text{O})_6^{2+} + \text{OH}^- \rightarrow \text{Ni}(\text{OH})_2 \rightarrow \text{Ni}(\text{NH}_3)_6^{2+}$$

vii) The blue solution shows no noticeable change on adding persulphate but on adding base, a black precipitate falls.



viii) The green solution slowly gains some yellow colour but it is not very noticeable

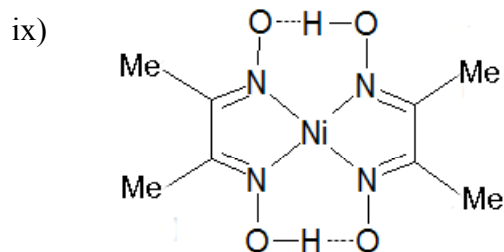


diagram of  $\text{Ni}(\text{DMG})_2$

and octahedral and square planar splitting diagrams

A reasonably common stereochemistry for  $d^8$ , especially for the heavier metals.

## 1.8 Copper

i) Chalcocite,  $\text{Cu}_2\text{S}$  Chalcopyrite  $\text{CuFeS}_2$   
 Covellite  $\text{CuS}$  terrorite  $\text{CuO}$   
 Malachite  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$   
 Cu metal can sometimes be found directly.

ii) Very important to all organisms. Constituent of many enzymes either as electron transfer or  $\text{O}_2$  transportation agents.

iii) Electrical conductor. Alloys (brass  $\text{Cu}/\text{Zn}$ ) (bronze  $\text{Cu}/\text{Sn}$ )  
 Fertilisers, Insecticides

iv) The initially blue solution goes yellow/green on adding  $\text{HCl}$   
 And then red/brown on adding  $\text{NH}_4\text{Br}$ .



Shows the lability of the ligands and the  $\text{O}_h$  to  $\text{T}_d$  interchange.

v) The light blue solution gives a white/light blue precipitate which dissolves on adding excess ammonia.



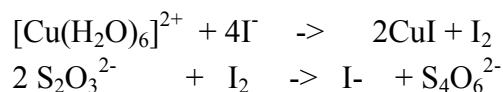
indicating the formation of complex ions and that Cu(II) often only reacts to the extent of four H<sub>2</sub>O ligands being replaced.

- vi) The light blue solution gives a blue precipitate which when heated goes through green to black.



The Cu(OH)<sub>2</sub> is slightly soluble in excess OH<sup>-</sup>

- vii) The light blue solution turns yellow/red and a white precipitate forms. The CCl<sub>4</sub> layer turns red. On adding thiosulphate the solution becomes light blue/ colourless and the precipitate appears white.



CuI is stable because it is insoluble

- viii) On adding tartaric acid and OH<sup>-</sup> a deep blue solution results. On adding glucose the solution goes green (on warming) and finally a red precipitate forms. The deep blue colour is a copper tartrate complex, and the solution is often called Fehlings solution. It is reduced by glucose, the red precipitate is Cu<sub>2</sub>O

- ix) The red precipitate dissolves to give an almost colourless solution which on addition of sodium hydroxide yields a yellow precipitate.



Yellow