

# Qualitative inorganic analysis

Part (I)  
Anions  
(Direct anions)

Dr. Mai Ramadan

# Classification of anions

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**Anions are classified in two groups:**

Direct analysis of anions

Indirect analysis of anions (Soda extraction)

# Classification of anions

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## **Direct analysis of anions:**

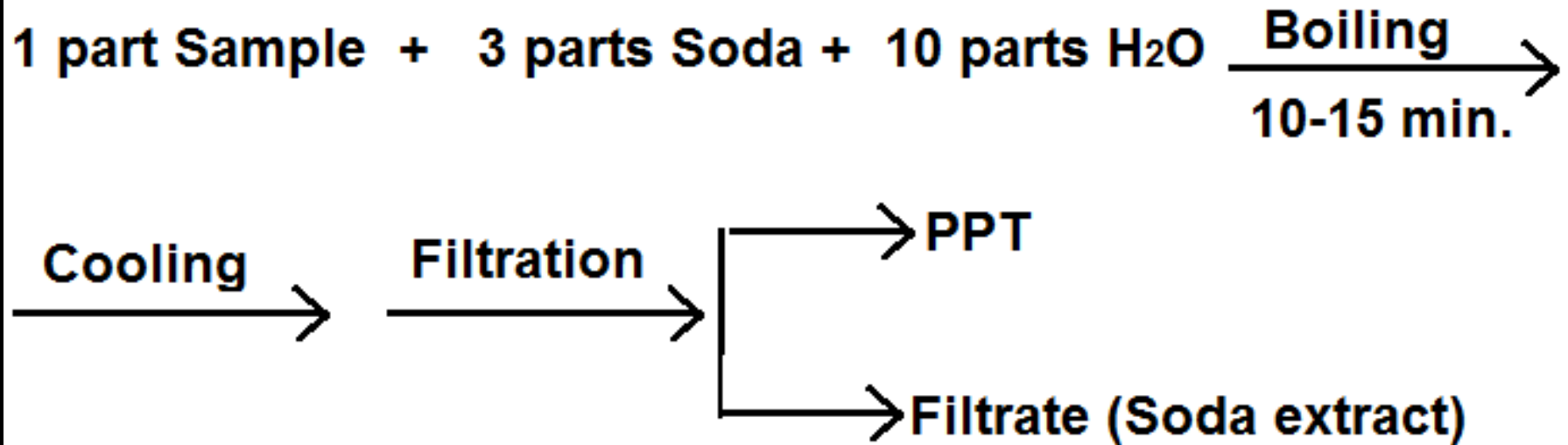
Perform detection test using the sample directly as the test described in book.

## **Indirect analysis of anions (Soda extraction):**

Perform detection test using soda extract (prepared from sample) as described in book

# Classification of anions

## Soda extraction:



Soda extract contains soluble anions accompanied with sodium cation, excess of soda ( $\text{Na}_2\text{CO}_3$ ). The solution is basic.

# Classification of anions

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## **Aim of soda extraction:**

Removal of heavy metal cations in the sample by precipitating them through boiling with soda ( $\text{Na}_2\text{CO}_3$ ).

Cations precipitated as carbonate, hydroxide, and or oxide which are separated by filtration. While anions remain soluble in soda extract accompanied with sodium cation.

# Classification of anions

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## **Soda extraction:**

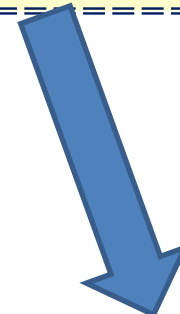
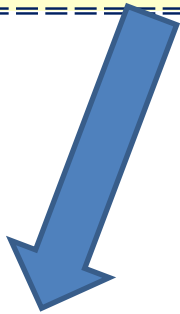
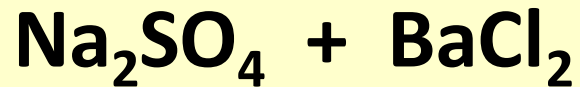
**Why should cations be removed from the sample before performing detection test of anions????**

**What is the problem caused by a cation??**

# Classification of anions

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Suppose you have unknown sample to detect sulfate anions. The sample in fact contains



**Direct analysis**

**No sulfate (Why?)**

Test is done using the sample

**Indirect analysis**

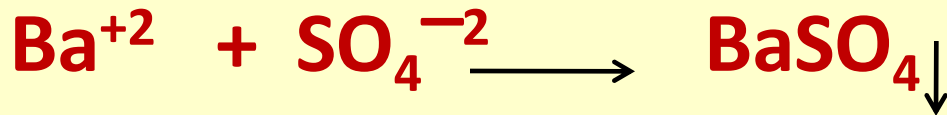
**Sulfate is present**

The test is done using soda extract.

# Classification of anions

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**Direct analysis**  
**No sulfate (Why??)**



Cation in the sample ( $\text{Ba}^{+2}$ ) reacts with sulfate -anion to be detected- to form a precipitate.

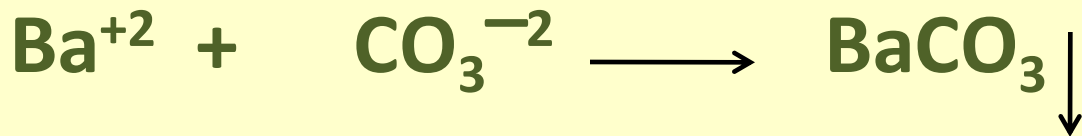


# Classification of anions

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**Indirect analysis  
Sulfate is present**

**Ba<sup>+2</sup> interferes with detection test of SO<sub>4</sub><sup>-2</sup>. It should be removed by soda extraction and sulfate is detectable in soda extract.**

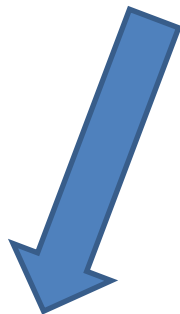


**Ba<sup>+2</sup> ion is precipitated by reacting with soda as carbonate salt.**

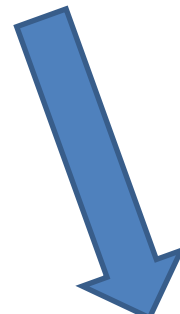
# Classification of anions

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Suppose you have unknown sample to detect cyanide anion. The sample in fact contains  
 $\text{KCN} + \text{FeCl}_3$



**Direct analysis**  
**No cyanide (Why?)**  
Test is done using the  
sample

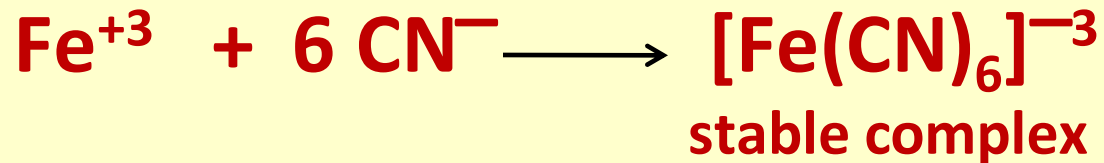


**Indirect analysis**  
**cyanide is present**  
The test is done using  
soda extract.

# Classification of anions

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**Direct analysis**  
**No cyanide (Why?)**

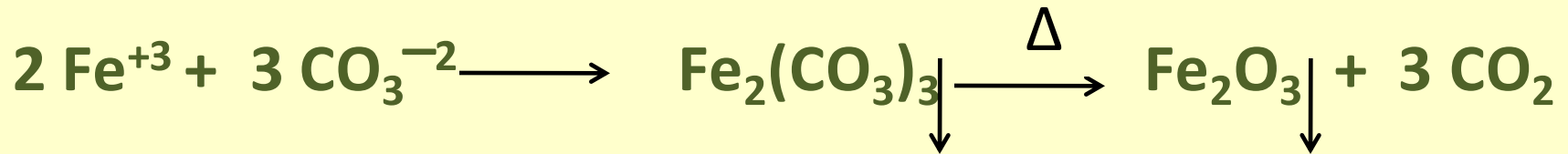


Cation in the sample ( $\text{Fe}^{+3}$ ) reacts with cyanide - anion to be detected- to form a stable complex.

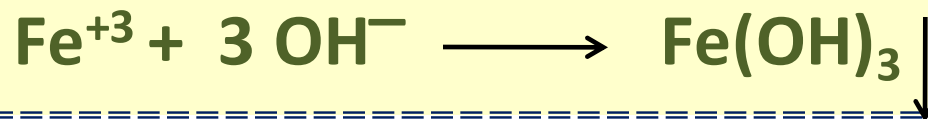
# Classification of anions

**Indirect analysis  
cyanide is present**

**$\text{Fe}^{+3}$  interferes with detection test of  $\text{CN}^-$ . It should be removed by soda extraction (precipitate as hydroxide and oxide).  $\text{CN}^-$  is detectable in soda extract.**



**Soda is basic (why???)**



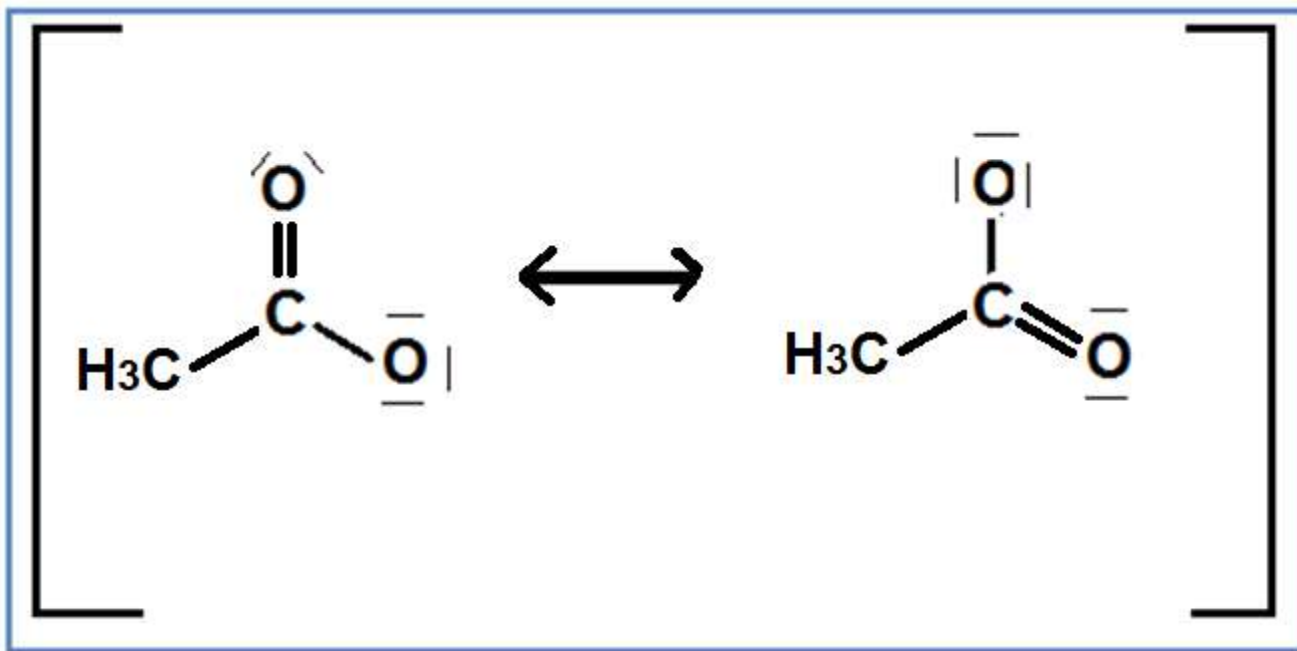
# **Direct Analysis of Anions**

**This group includes anions like:  
Acetate, carbonate, fluoride, silicate,  
borate, ----- etc**

## Acetate ion ( $\text{CH}_3\text{COO}^-$ )

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Acetate is used in preparation of acetate [buffer](#), pharmacy industry, acetic acid main component of vinegar.

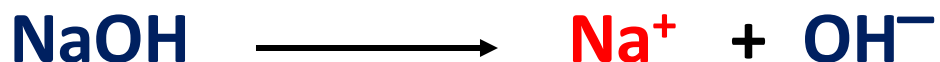
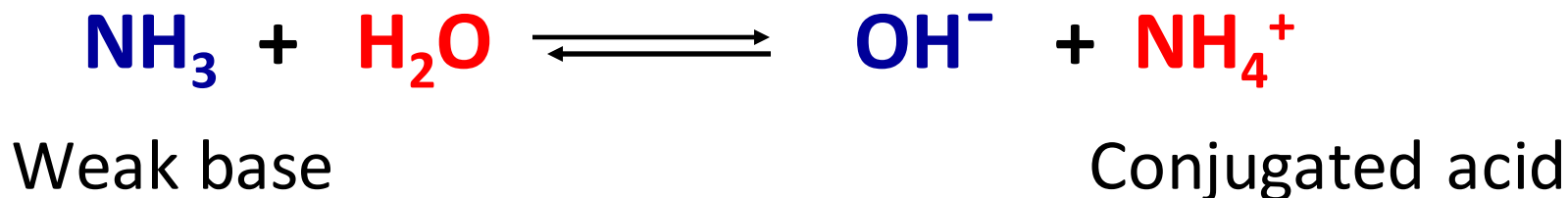
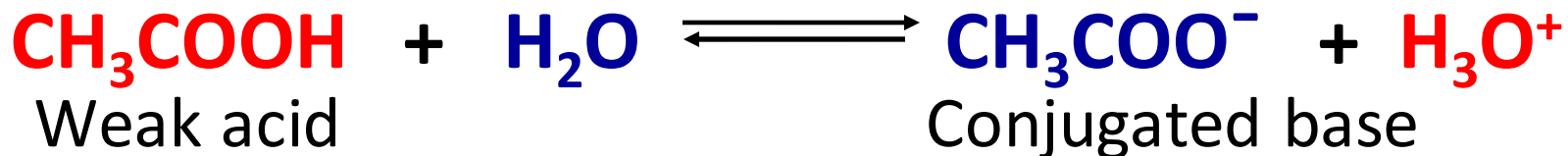


### Define:

Strong acid, Strong base, Weak acid, Weak base, buffer, Brønsted-lowery acid, lewis acid, lewis base, amphoteric

## Acetate ion $\text{CH}_3\text{COO}^-$

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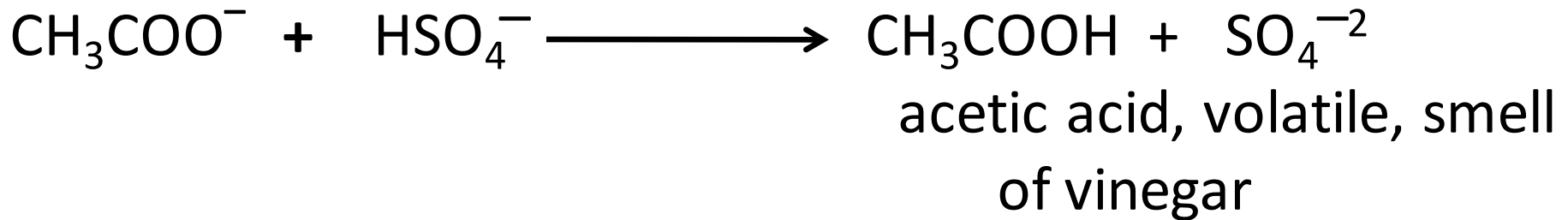


# Acetate ion $\text{CH}_3\text{COO}^-$

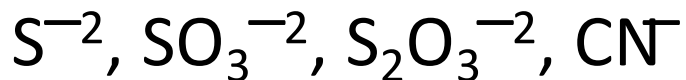
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## Test:

Sample(s) +  $\text{KHSO}_4$  (s) pulverize  $\rightarrow$  Smell of vinegar



## Malfunctions of test:

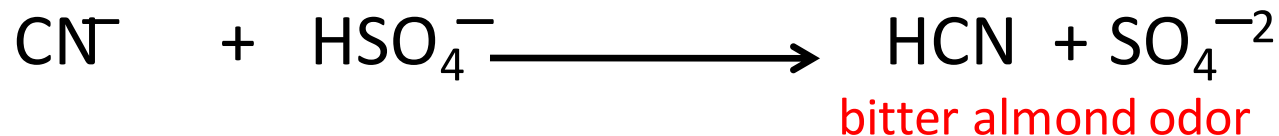
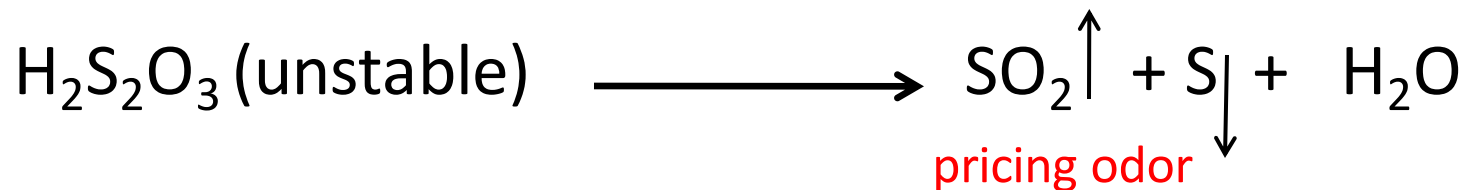
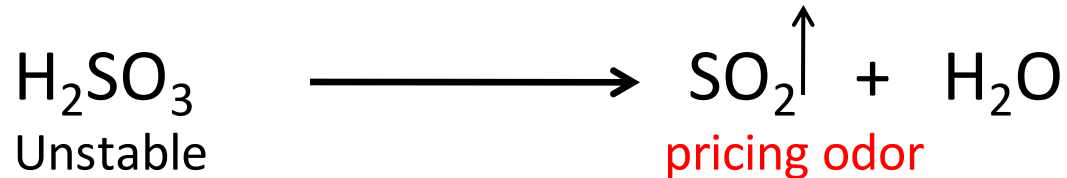
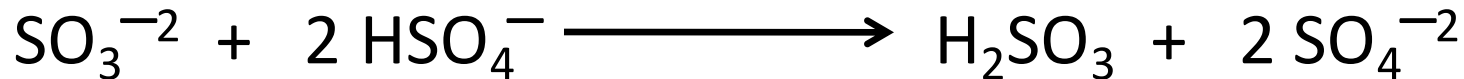
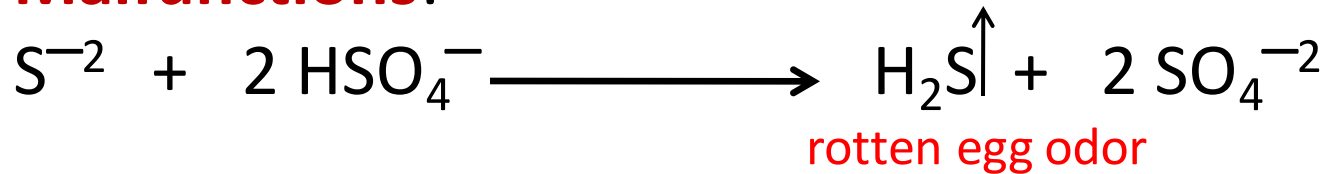




# Acetate ion $\text{CH}_3\text{COO}^-$

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## Malfunctions:



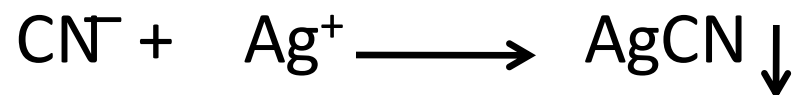
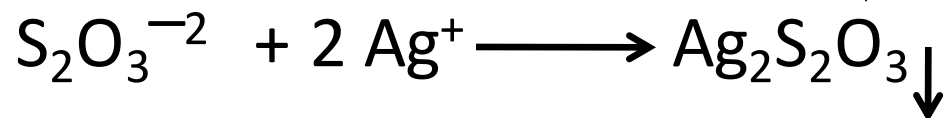
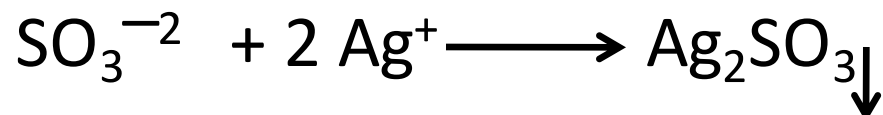
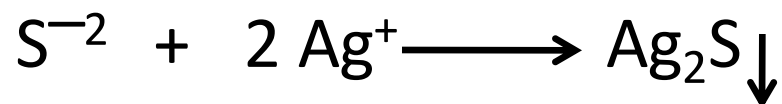
# Acetate ion $\text{CH}_3\text{COO}^-$

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## Removal of malfunctions:

Sample(s) + Silver salt ( $\text{Ag}_2\text{SO}_4$ )  $\xrightarrow{\text{pulverize}}$  +  $\text{KHSO}_4$  (s)  
 $\xrightarrow{\text{pulverize}}$  Smell of vinegar

Malfunctions react with  $\text{Ag}^+$ , forming **stable salts** which do not interfere with acetate test.



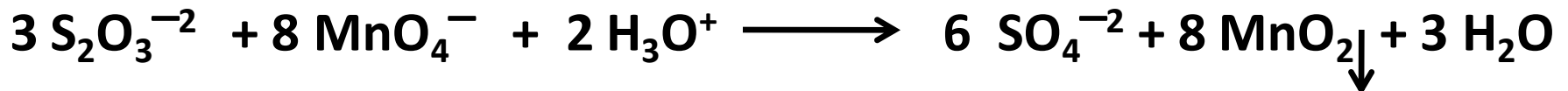
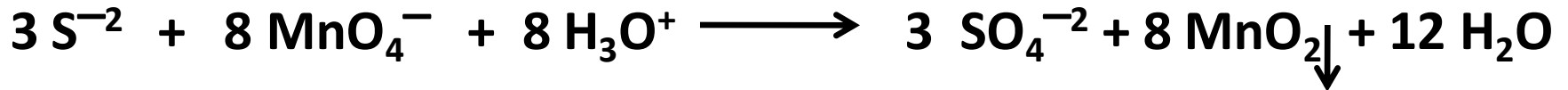
# Acetate ion $\text{CH}_3\text{COO}^-$

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## Removal of malfunctions:

Sample(s) +  $\text{KMnO}_4$  (s)  $\xrightarrow{\text{pulverize}}$  +  $\text{KHSO}_4$  (s)  $\xrightarrow{\text{pulverize}}$   $\xrightarrow{\text{pulverize}}$   
Smell of vinegar

Malfunctions ( $\text{S}^{-2}$ ,  $\text{SO}_3^{-2}$ ,  $\text{S}_2\text{O}_3^{-2}$ ) react with  $\text{KMnO}_4$  in a redox reaction forming  $\text{SO}_4^{-2}$ , which is **not malfunction**.



# Acetate ion $\text{CH}_3\text{COO}^-$

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$\text{KMnO}_4$  is a strong oxidizing agent

Define:

Redox RXN

Oxidation

Reduction

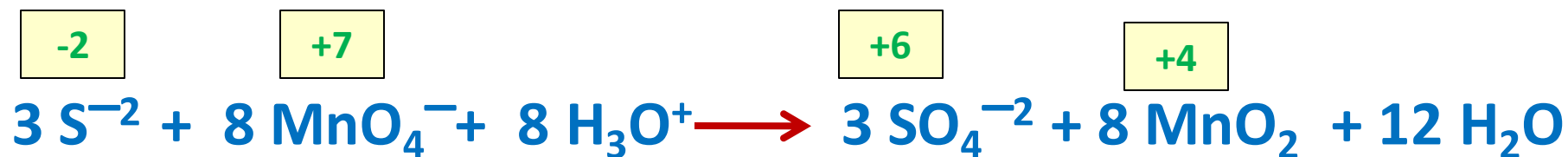
Oxidizing agent

Reducing agent

# Acetate ion $\text{CH}_3\text{COO}^-$

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$\text{KMnO}_4$  is a strong oxidizing agent



Reducing  
agent

Oxidizing  
agent

Balance of redox RXN is subject of next lecture

# Carbonate ion $\text{CO}_3^{2-}$

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Carbonate used in preparation of carbonate buffer, effervescent tablet, carbonate beverages, food industry

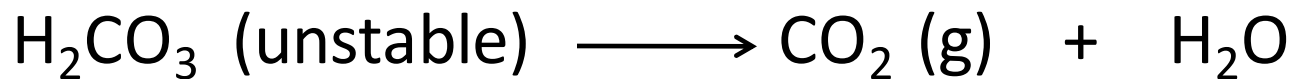
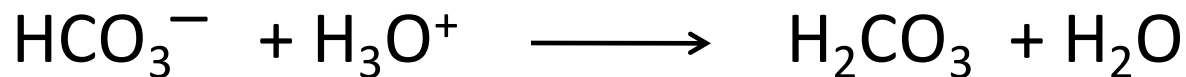
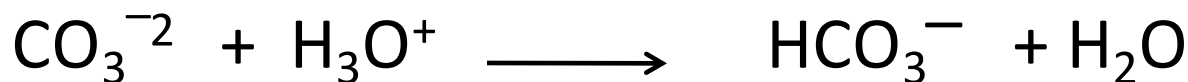
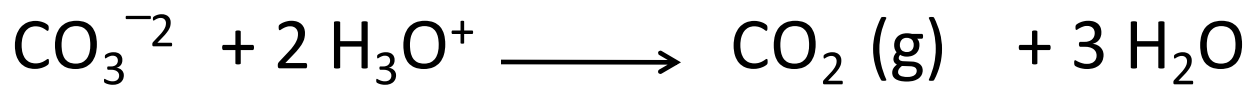
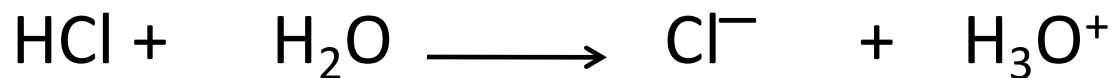
Carbonate is a weak base

## **Test :**

Sample (s) in watch glass + HCl (dil)  $\longrightarrow$  Effervescence due to development of  $\text{CO}_2$  gas ( it has no physical characters e.g. no color, no odour)

# Carbonate ion $\text{CO}_3^{-2}$

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Malfunctions:  $\text{S}^{-2}$ ,  $\text{SO}_3^{-2}$ ,  $\text{S}_2\text{O}_3^{-2}$ ,  $\text{CN}^-$ ,  $\text{F}^-$  (write the reactions)

# Carbonate ion $\text{CO}_3^{-2}$

---

Specify and detect  $\text{CO}_2$  by chemical reaction

Put sample in test tube 1, add HCl (dil) and close tightly. Tube 1 is connected through a U glass tube with a clear solution of  $\text{Ba}(\text{OH})_2$

When  $\text{CO}_2$  ( non polar, acidic gas ) passes into  $\text{Ba}(\text{OH})_2$  solution , turbidity will appears due to formation of insoluble  $\text{BaCO}_3$

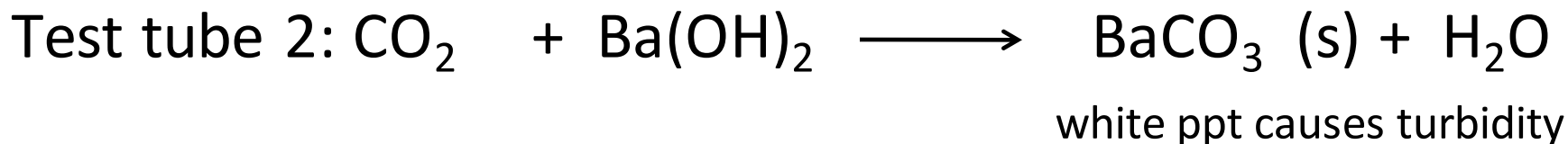
Malfunction: Excess of  $\text{CO}_2$  gas



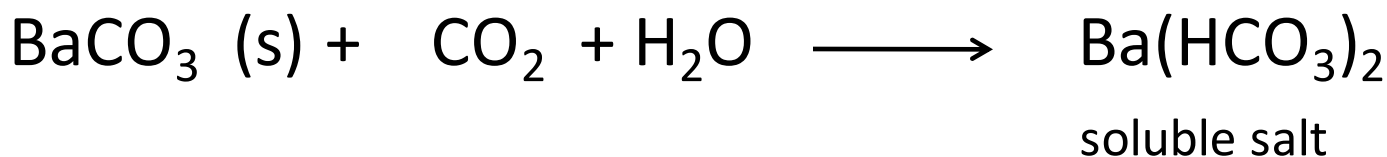
# Carbonate ion $\text{CO}_3^{-2}$

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Specify and detect  $\text{CO}_2$  by chemical reaction

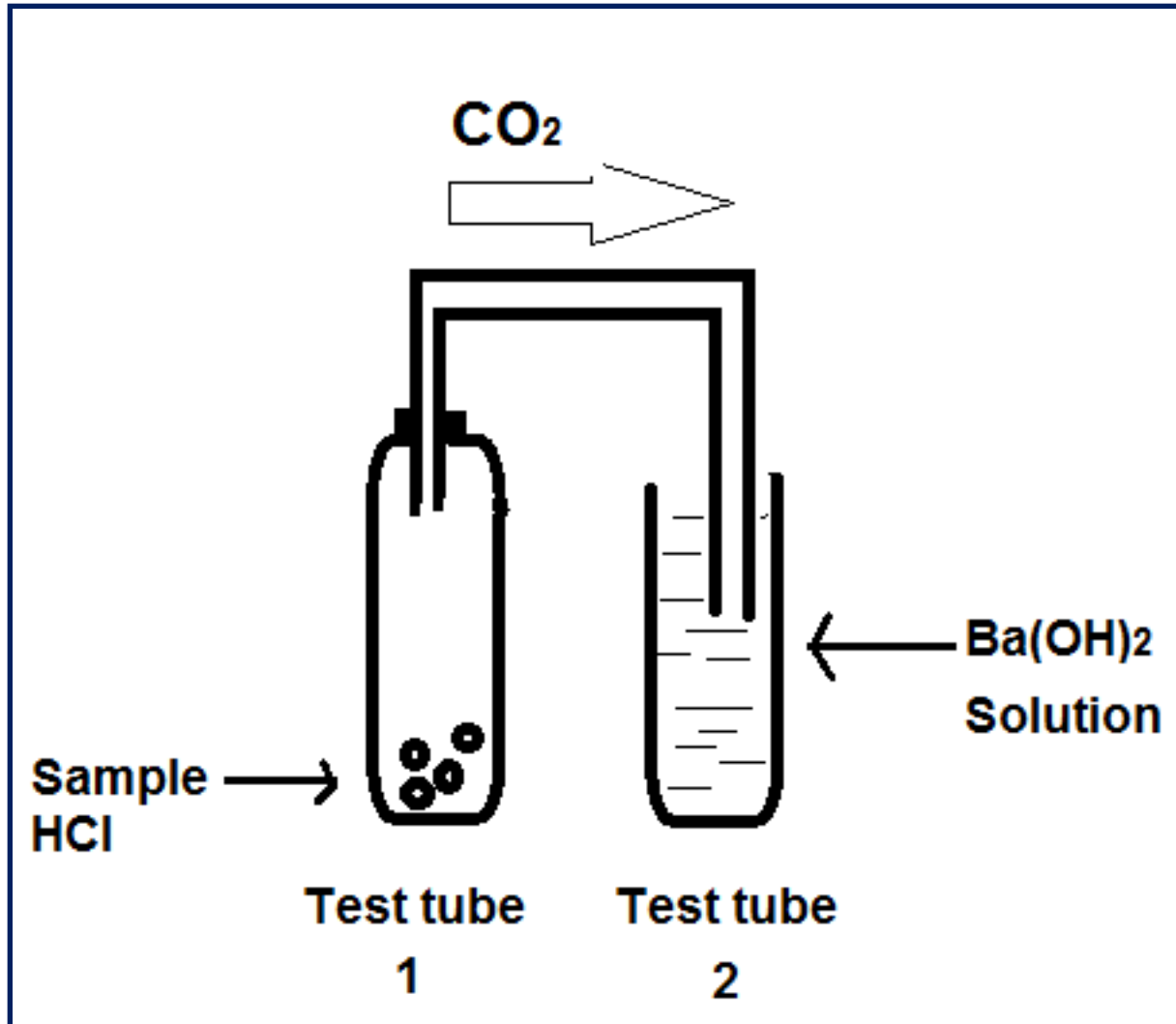


Malfunction:



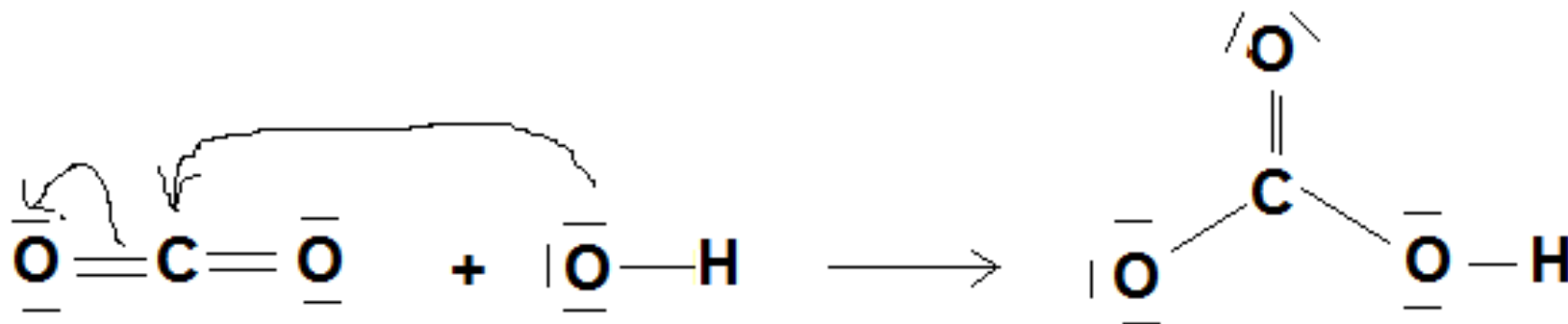
# Carbonate ion $\text{CO}_3^{2-}$

Specify and detect  $\text{CO}_2$  by chemical reaction



# Carbonate ion $\text{CO}_3^{-2}$

Specify and detect  $\text{CO}_2$  by chemical reaction



**Lewis Acid**

**Lewis Base**

$\text{HCO}_3^-$

$\text{HCO}_3^-$

+

$\text{O}-\text{H}$

$\longrightarrow$

$\text{CO}_3^{-2}$

+  $\text{H}_2\text{O}$

**Acid**

**Base**

$\text{Ba}^{+2}$

+

$\text{CO}_3^{-2}$

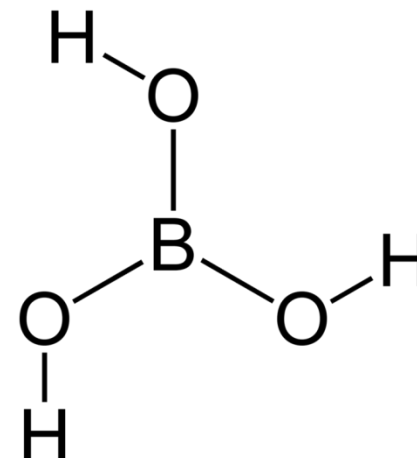
$\longrightarrow$

$\text{BaCO}_3 \downarrow$

White ppt

## Boric acid

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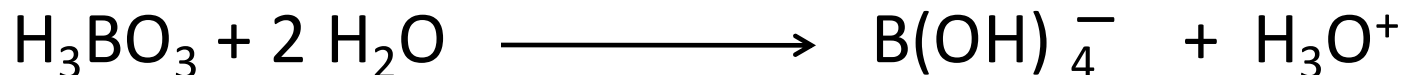
Boric acid, ortho-boric acid



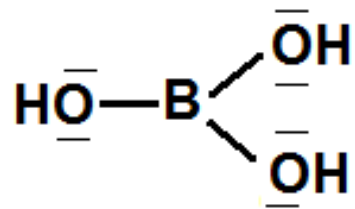
is used as antiseptic in ear drops and as insecticide.

Boron has valence electron = 3 that it has an incomplete octet

Boric acid is a weak monoprotic lewis acid

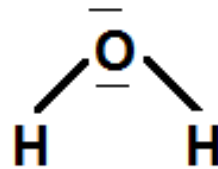


# Boric acid

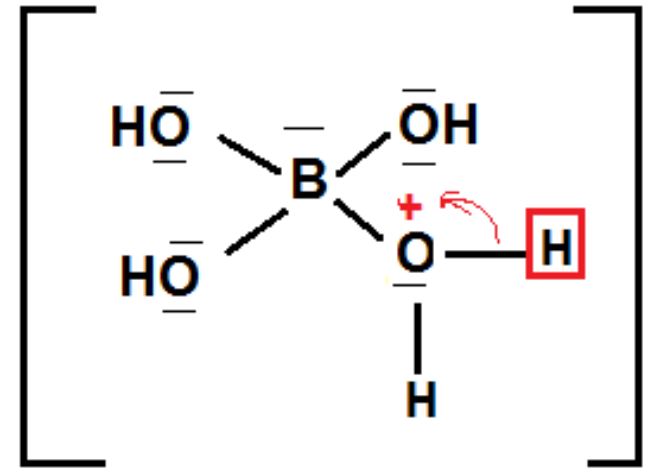
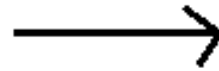


Lewis acid

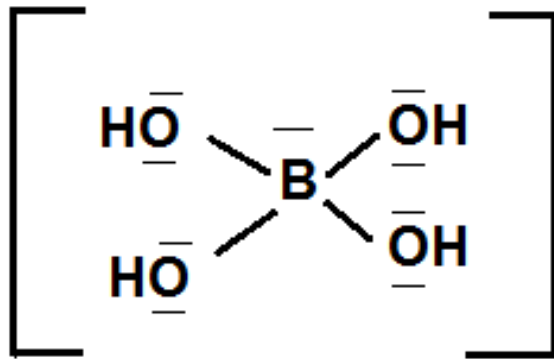
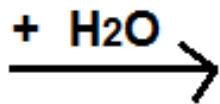
+



Lewis base



+ H<sub>2</sub>O



$\text{B}(\text{OH})_4^{\ominus}$

+ H<sub>3</sub>O<sup>+</sup>

# Detection of borate

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Borates ion  $\text{BO}_3^{-3}$ ,  $\text{B}_4\text{O}_7^{-2}$ ,  $\text{BO}_2^{-}$

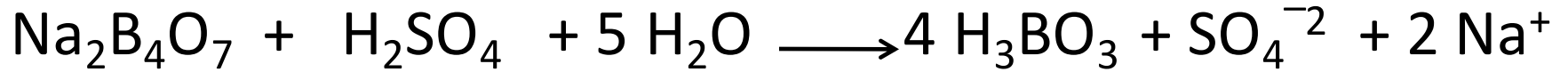
The salt used in test is **borax** (sodium tetraborate decahydrate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  )

**Test:** with sulphuric acid and alcohol (Flame test)

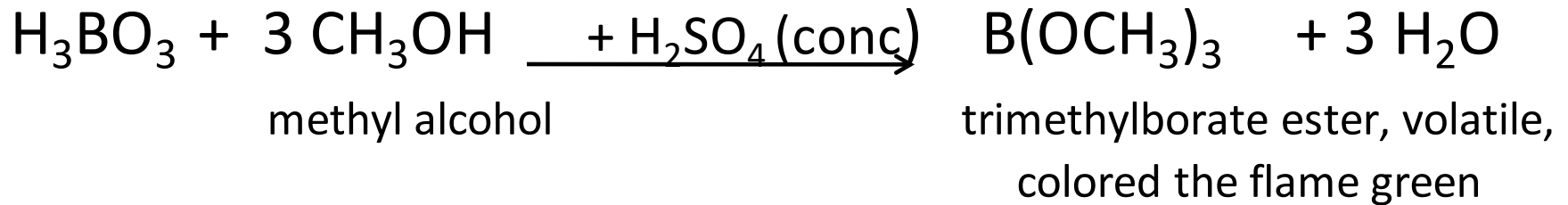
Sample + 1 mL  $\text{H}_2\text{SO}_4$  (Conc) + 5 mL  $\text{CH}_3\text{OH}$  heat in water bath, then direct the upper edge of test tube to the bunsen flame, the flame colored green

# Detection of borate

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**Acid + alcohol**  $\longleftrightarrow$  **Ester + water**

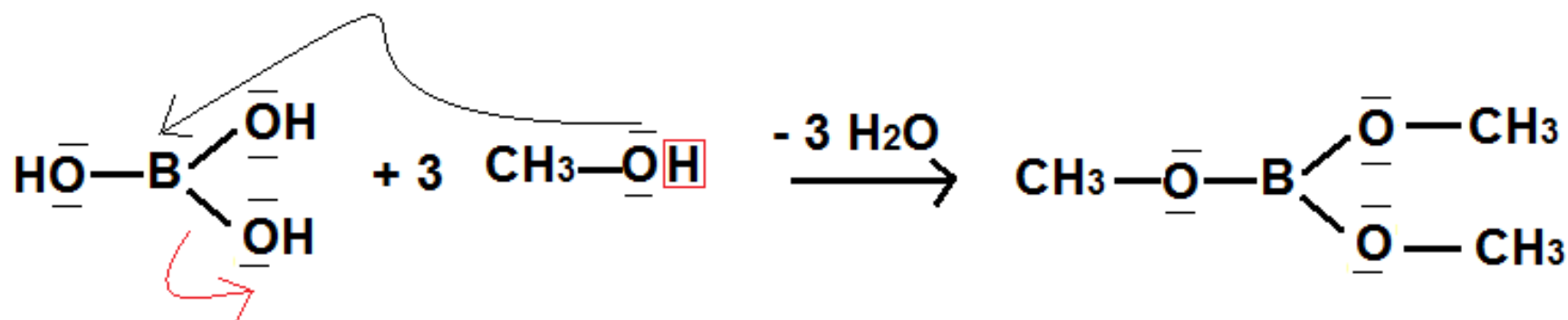


Water hydrolyzed ester back to its component

$\text{H}_2\text{SO}_4(\text{conc})$  is hygroscopic, it adsorbs water resulted in reaction and prevent hydrolysis.

# Detection of borate

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**Methylester of boric acid**

**Trimethylborate ester**

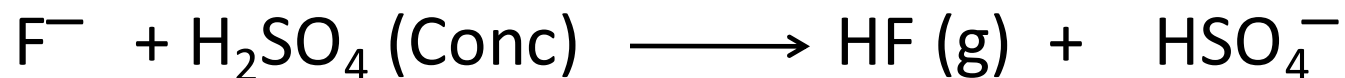


# Flouride ion

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## Bubble test:

Sample + H<sub>2</sub>SO<sub>4</sub> (Conc.) warm in water bath small bubbles are formed which collect to form larger bubbles



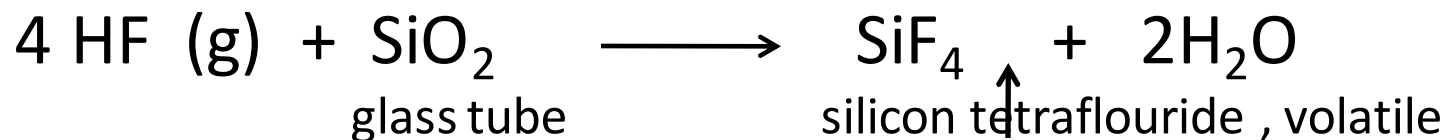
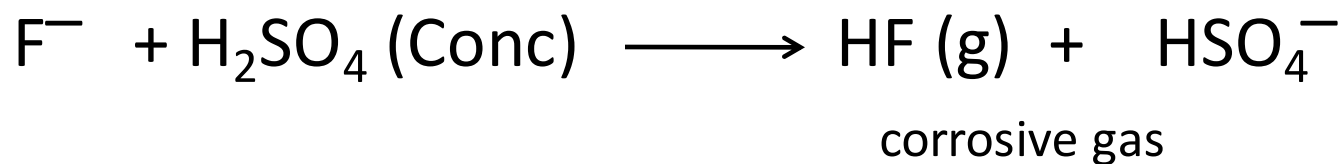
H<sub>2</sub>SO<sub>4</sub> (Conc.) is viscous

# Flouride ion

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## Etching test:

Sample + H<sub>2</sub>SO<sub>4</sub> (Conc) in new test tube, warm in water bath, then move sulphuric acid out of the test tube, put water in tube then move it out. Sulphuric acid move like water on oil and particles of water remain attached to the inner surface of test tube because it is rough.



# Silicate ion $\text{SiO}_3^{-2}$

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Test of silicate **can not be performed** in glass test tube.  
(Why?)

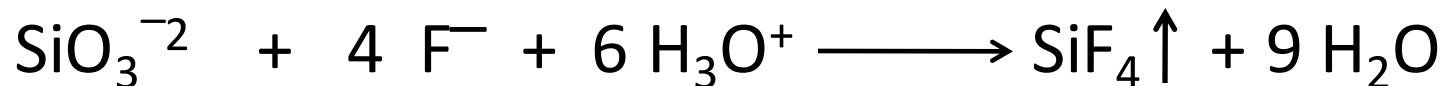
Importance: Silica gel in chromatography, glass industry,  
Cosmetic, ----

## Test:

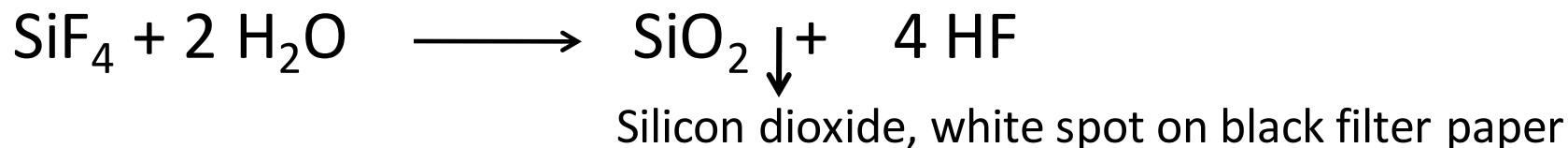
Sample is put in platin or lead crucible followed by  $\text{H}_2\text{SO}_4$   
(Conc) and NaF and put on the upper edge of crucible black  
Filter paper saturated (soaked) with water then warm in a  
water bath  $\longrightarrow$  a white spot appears on the filter  
paper ( $\text{SiO}_2$ )

## Silicate ion $\text{SiO}_3^{-2}$

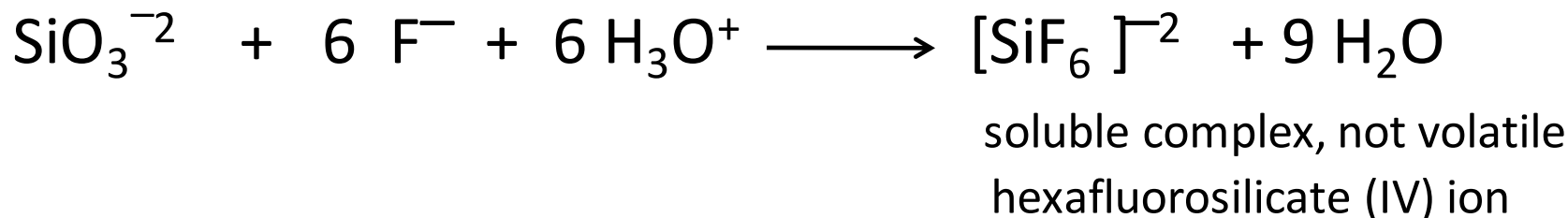
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$\text{SiF}_4$  is volatile and reaches the filter paper, where the following reaction takes place



Malfunction: Excess of Fluoride



## Questions of this week

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$\text{SiO}_2$  is not like  $\text{CO}_2$ . It is a polymer what is the structure?

How can you keep a solution of fluoride or hydrofluoric acid since it attacks glass container?

How is AgF differs from other silver halides e.g. AgCl?  
(Hint : p 180, 174 in Vogel's qualitative inorganic analysis)

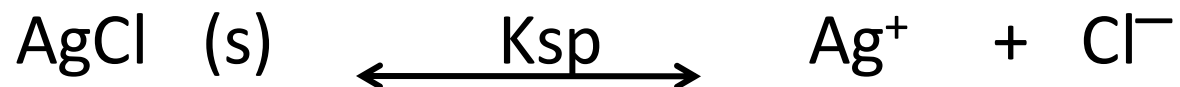
What is lime water and baryta water chemically ?  
(hint p 150)

What should happen if  $\text{CO}_2$  passes into lime water?

## Questions of this week

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The following are sparingly soluble salts. which solubility (as you expect) is improved by changing pH acidic with explanation? AgCl, AgBr, CaC<sub>2</sub>O<sub>4</sub>, BaCO<sub>3</sub>, CaCO<sub>3</sub>, CuS, Ag<sub>3</sub>PO<sub>4</sub>

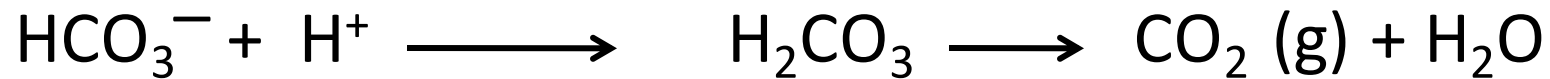
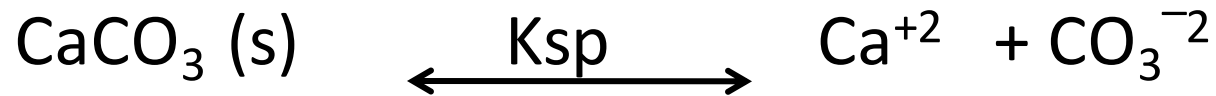


because Cl<sup>-</sup> is extremely weak base, that it can not be consumed in the second reaction with acidic media and accepts proton

**AgCl is not dissolved in acidic pH**

## Questions of this week

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CaCO<sub>3</sub> solubility is improved in acidic pH

Carbonate of the first equilibrium is a base which starts reaction with acidic media

# **Qualitative inorganic analysis**

## **Part (I)**

**Anions  
(Indirect anions)**



# Indirect analysis of anions

**The anions should be detected in soda extract**

Chloride, iodide, bromide, sulfide, sulfite, sulfate, nitrate, nitrite, phosphate, cyanide, -----

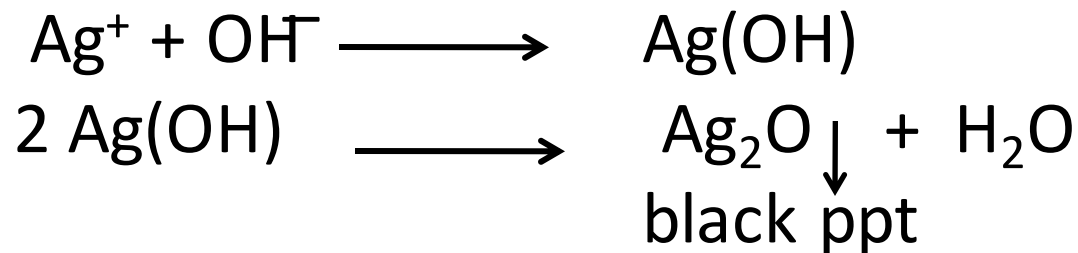
Dr. Mai Ramadan

# Chloride ion

## With AgNO<sub>3</sub> Solution:

Soda extract + acidify with HNO<sub>3</sub> (dil) + then add AgNO<sub>3</sub> Solution  $\longrightarrow$  white ppt, insoluble in HNO<sub>3</sub> (conc.), soluble in NH<sub>3</sub> (dil.)

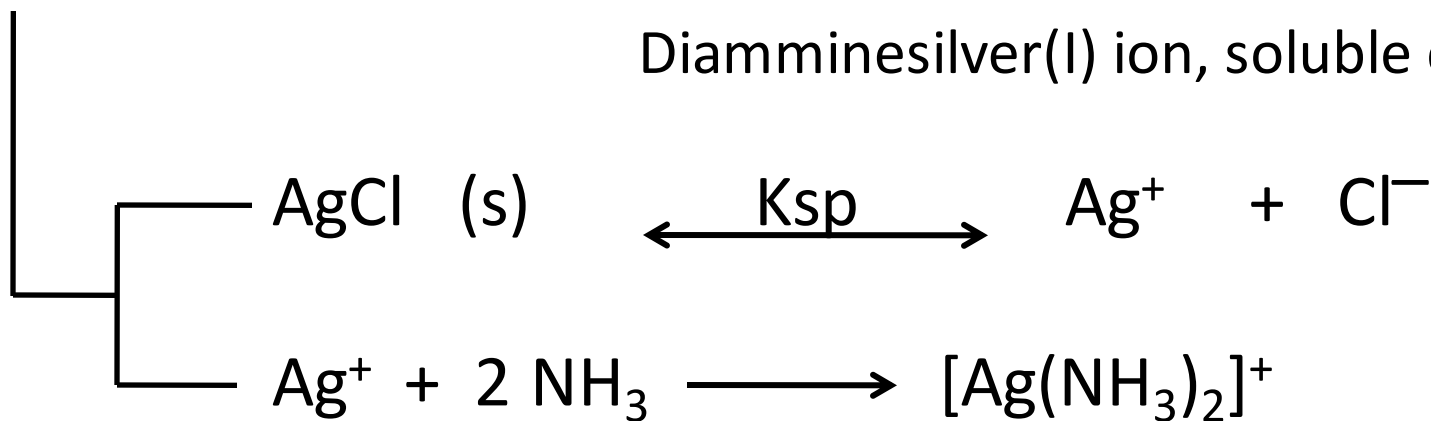
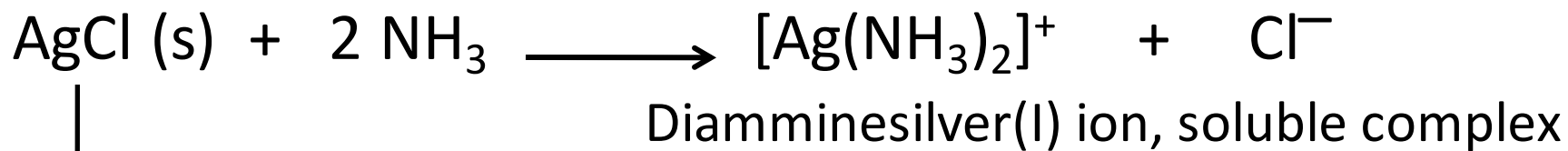
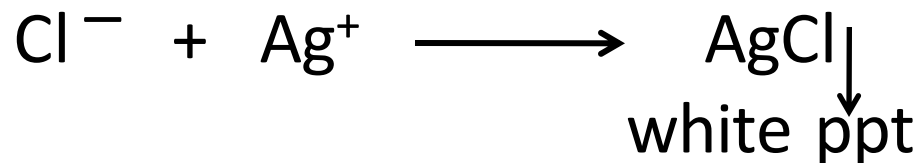
Soda extract had basic pH, it should be acidified before adding Ag<sup>+</sup> reagent to prevent its precipitation as Ag<sub>2</sub>O



(Can you acidify with HCl? Explain)

# Chloride ion

Reactions:



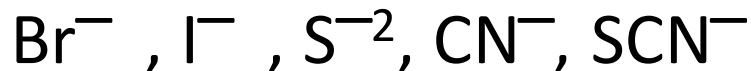
# Chloride ion

## Question:

when  $\text{HNO}_3$  (dil) is added after dissolution of  $\text{AgCl}$  in ammonia, the precipitate is reformed (hint: p 66, 174)



## Malfunction:



$\text{Ag}^+$  + ions mentioned previously  $\longrightarrow$  give ppt. of different colors

# Chloride ion

## Potassium dichromate and sulphuric acid: (Chromyl chloride test)

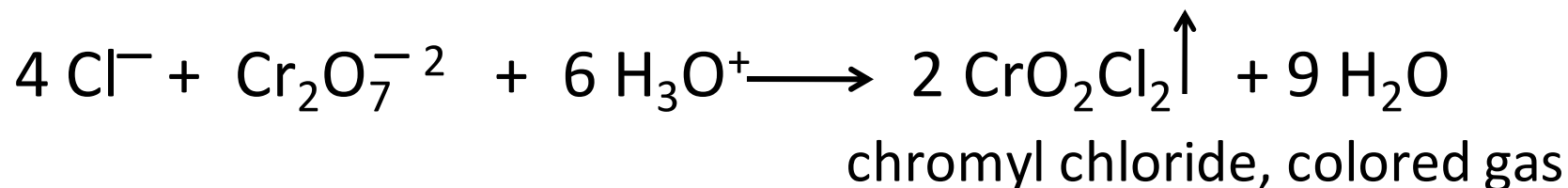
Soda extract +  $K_2Cr_2O_7$  +  $H_2SO_4$  (Conc.) warm gently in water bath  $\longrightarrow$  a colored gas is evolved ( $CrO_2Cl_2$ ), this gas is identified by a filter paper soaked with NaOH/ Diphenylcarbazide solution (colorless), the filter paper turns violet due to formation of diphenylcarbazone.

There are 3 reactions one in the test tube and the next two on filter paper

# Chloride ion

## Chromyl chloride test:

1] In the test tube:



Note:

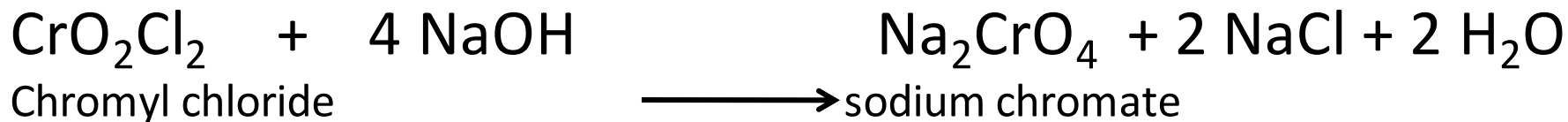
This reaction is **not a redox**

The oxidation number of **Cr** in  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_2\text{Cl}_2$  is +6

## Chloride ion

**Chromyl chloride test:**

2] on the filter paper



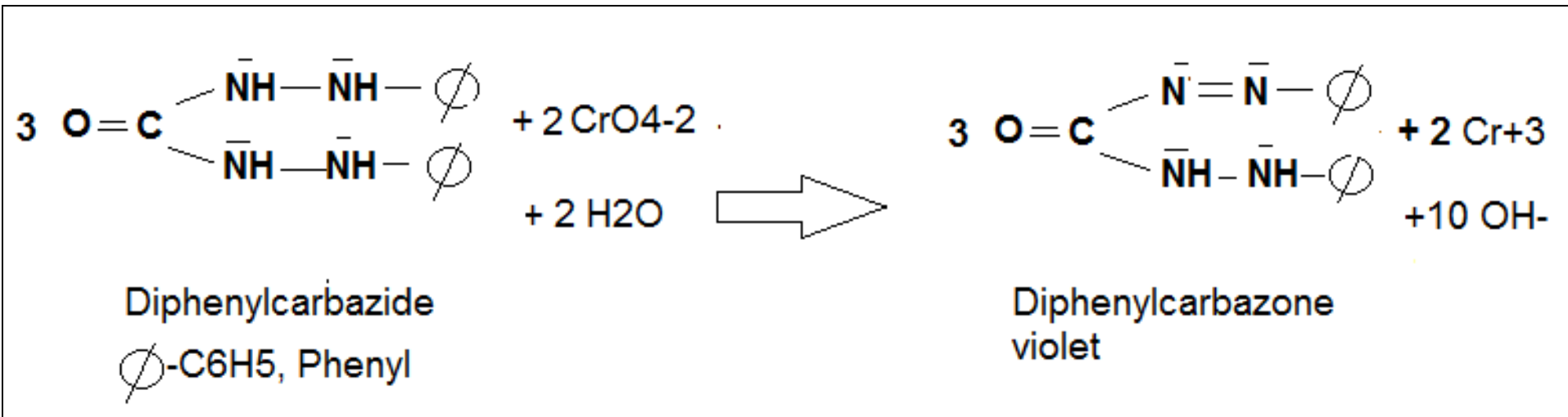
Note:

Remember chromate, dichromate and permanganate are strong oxidizing agent

# Chloride ion

## Chromyl chloride test:

3] On the filter paper



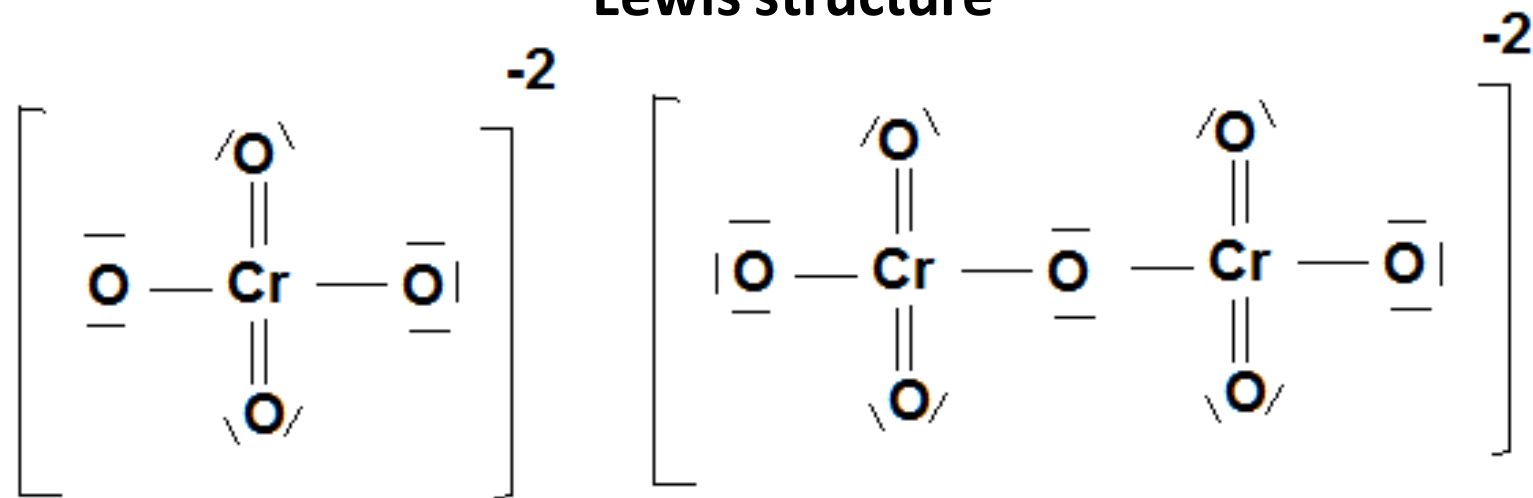
Note:

**Redox reaction:** Diphenylcarbazide (colorless) is oxidized by chromate to diphenylcarbazone (violet color)



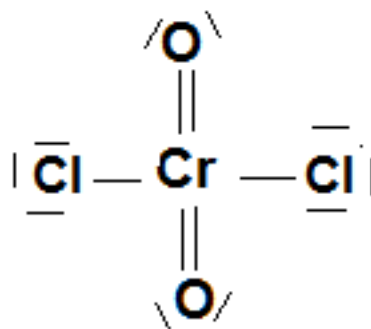
# Chloride ion

Lewis structure



$\text{CrO}_4^{2-}$

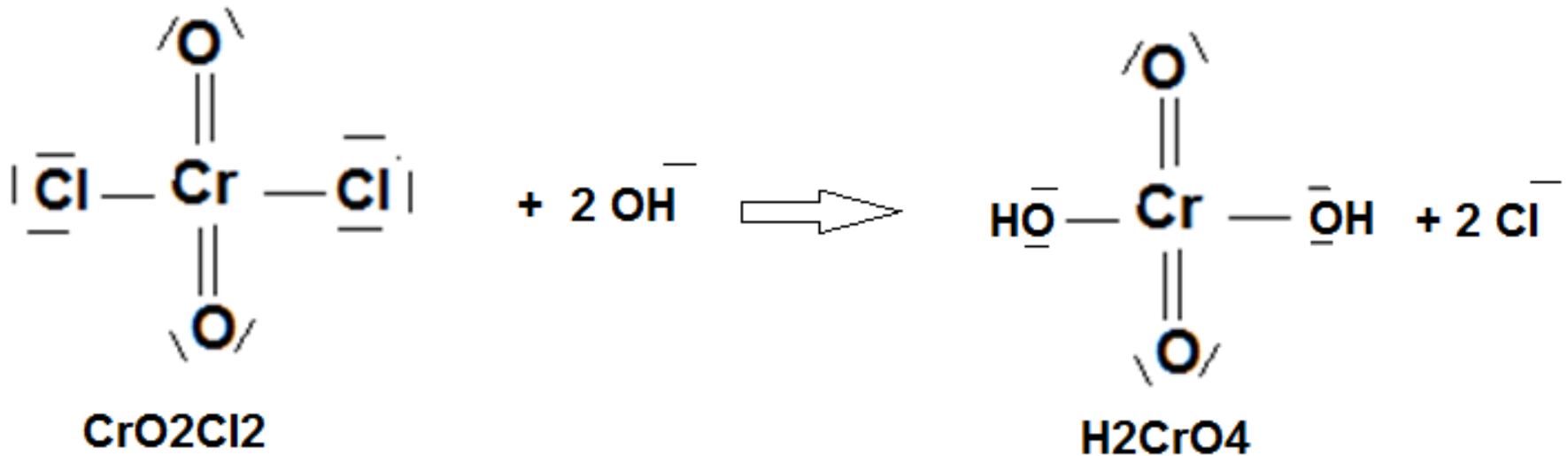
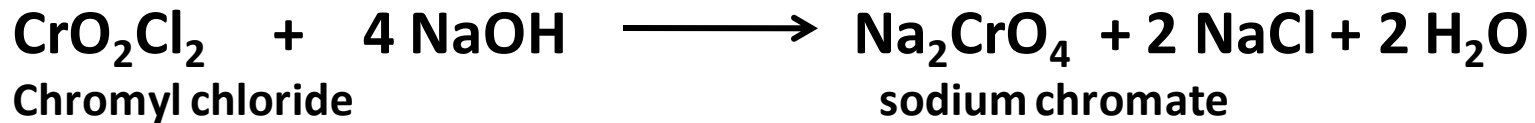
$\text{Cr}_2\text{O}_7^{2-}$



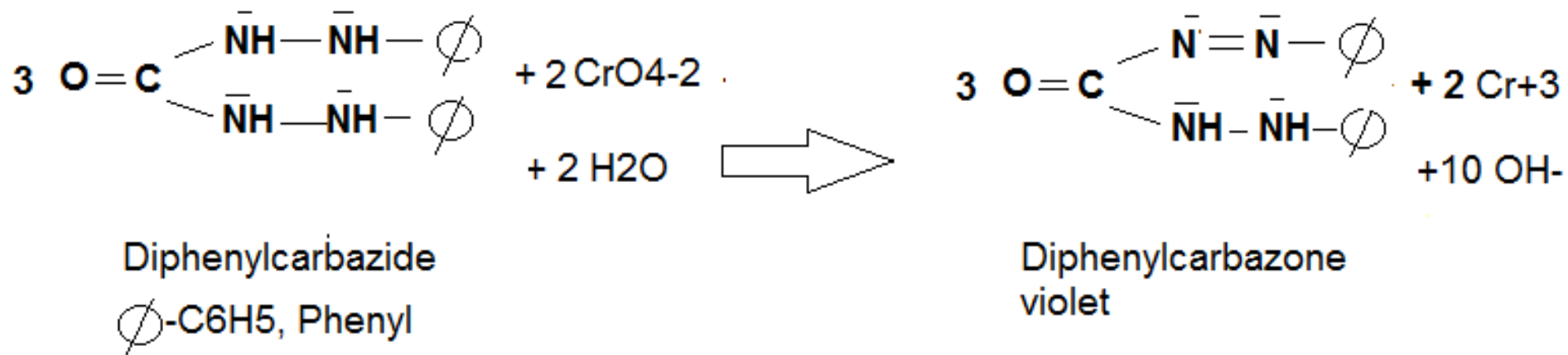
$\text{CrO}_2\text{Cl}_2$

# Chloride ion

## Chromyl chloride test in details

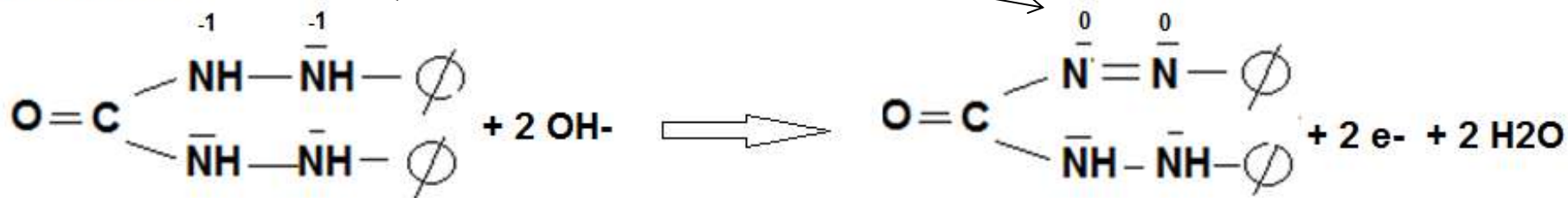


# Chloride ion



Oxd half RXN:

Oxidation number



Red half RXN:



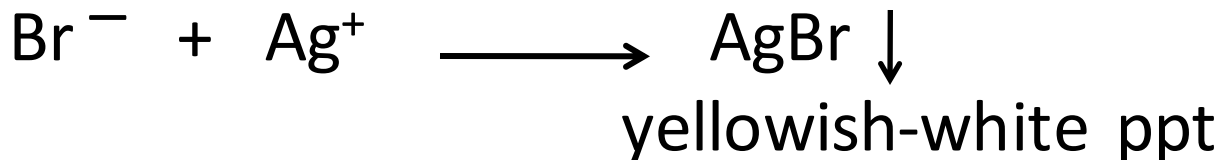
# Bromide ion

## With $\text{AgNO}_3$ Solution:

Soda extract + acidify with  $\text{HNO}_3$  (dil) + then add  $\text{AgNO}_3$  Solution  $\longrightarrow$  yellowish-white ppt, insoluble in  $\text{HNO}_3$  (conc.), insoluble in  $\text{NH}_3$  (dil.), soluble in  $\text{NH}_3$  (conc.)

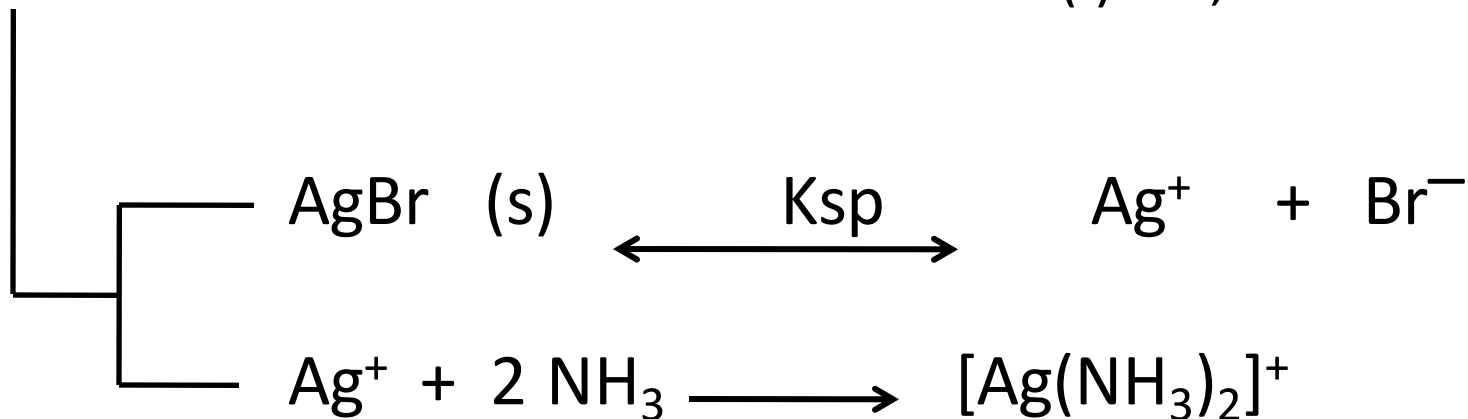
Soda extract had basic pH, it should be acidified before adding  $\text{Ag}^+$  reagent to prevent its precipitation as  $\text{Ag}_2\text{O}$  (discussed before)

Reactions:



# Bromide ion

Reactions:



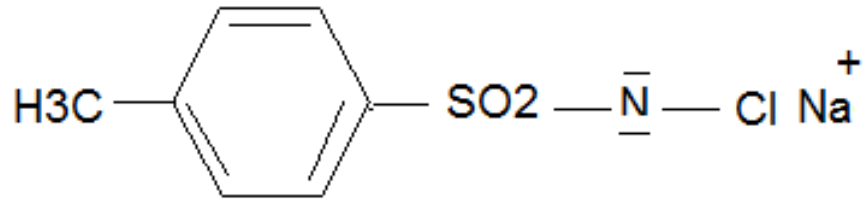
# Bromide ion

## With Chloramine-T solution:

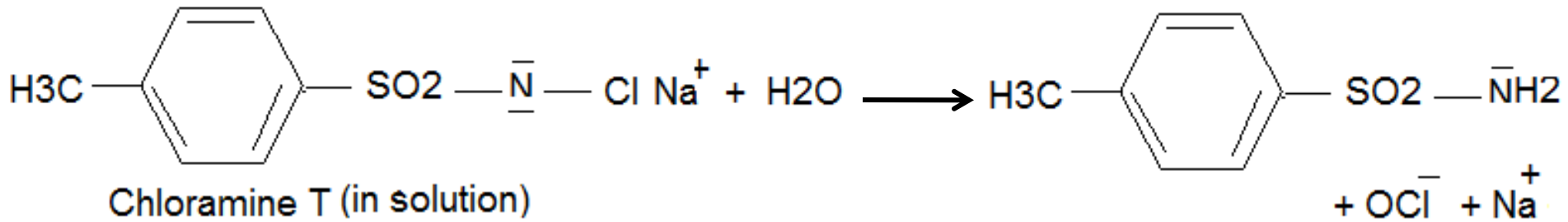
Soda extract + acidify with HCl + 3-4 ml  $\text{CHCl}_3$  or  $\text{CCl}_4$  (two immiscible phases are formed) then add drop wise freshly prepared chloramine T (dil.)  $\longrightarrow$  the organic phase ( $\text{CHCl}_3$  or  $\text{CCl}_4$ ) is colored brown  $\longrightarrow$  when excess chloramine T reagent is added the organic phase is colored yellow.

# Bromide ion

Reactions:



Chloramine T (solid state)



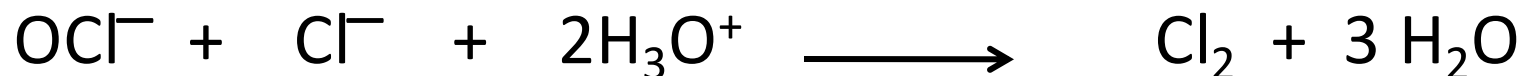
Chloramine T (in solution)

+ OCl<sup>-</sup> + Na<sup>+</sup>

OCl<sup>-</sup> : hypochlorite ion

## Bromide ion

Reactions:



Note:

This reaction is **synproportionation** reaction (Redox, Auto-oxidation reaction).

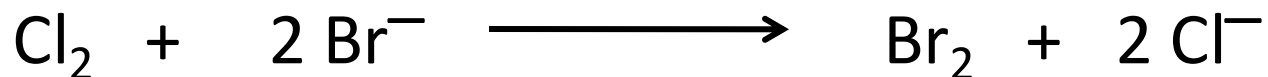
Cl atom in hypochlorite has oxidation number +1, in chloride ion is -1. The product chlorine (halogen) has oxidation number of 0.

$\text{Cl}^-$ ,  $\text{H}_3\text{O}^+$  originate from HCl. Do not use another acid in test



## Bromide ion

Reactions:



$\text{Br}_2$  (bromine , non polar molecule) dissolves in organic phase with brown color.

**Excess chloramine T solution is added:**



$\text{BrCl}$  dissolves in organic phase with yellow color

# Do you remember?

## Halogens



Chlorine

$\text{Cl}_2(\text{g})$

Bromine

$\text{Br}_2(\text{l})$

Iodine

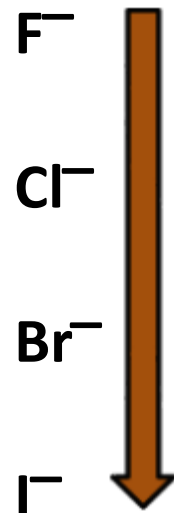
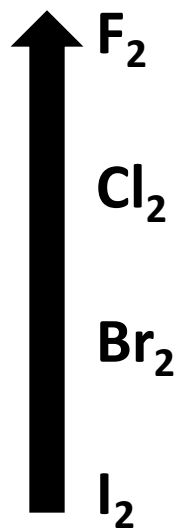
$\text{I}_2(\text{s})$

Increasing molecular weight →

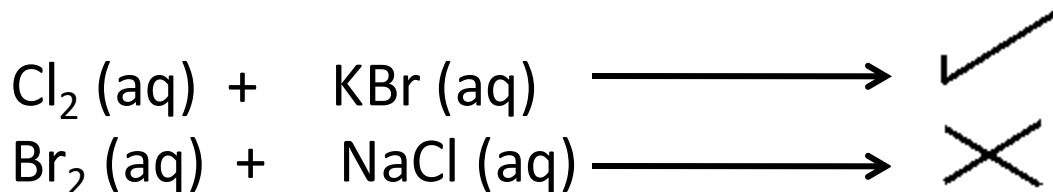
# Do you remember?

Oxidizing agent

Reducing agent



Which reaction occurs spontaneously?



# Bromide ion

## With potassium dichromate and sulphuric acid:

Soda extract +  $K_2Cr_2O_7$  +  $H_2SO_4$  (Conc.) warm gently in water bath  $\longrightarrow$   $Br_2$  is produced (reddish brown vapor)

To identify the vapor put a filter paper soaked with fluorescein solution (yellow)  $\longrightarrow$  the filter paper acquires red color (Eosin).

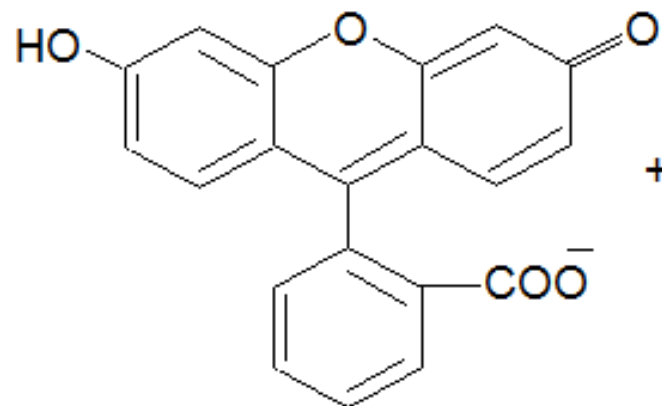
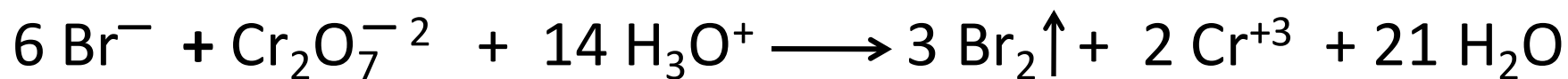
## Malfunction:

$I^-$  produces  $I_2$  turns the filter paper to red-brown color (tetraiodofluorescein).

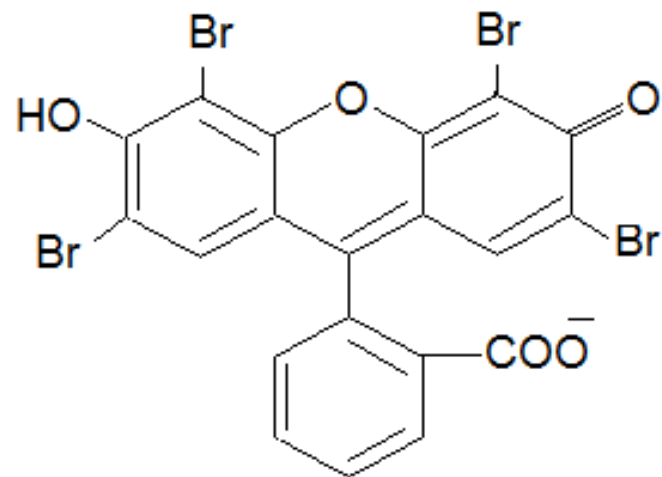
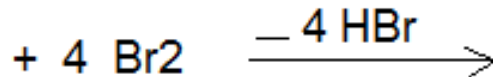
# Bromide ion

With potassium dichromate and sulphuric acid:

Reaction:



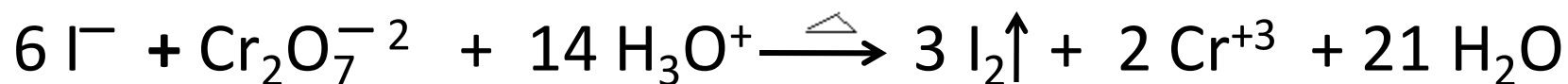
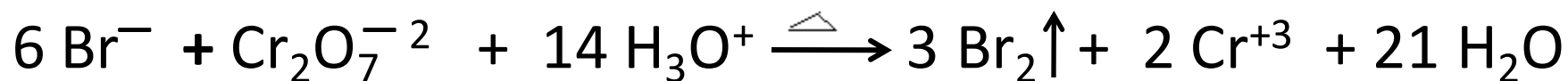
Fluorescein (Yellow)



Eosin (violet-red)

# Bromide ion

**Remember:**



**Halides**  $\text{Br}^-$ ,  $\text{I}^-$  are oxidized by dichromate to corresponding halogen(Redox).

$\text{Br}_2$  is liquid and volatile,  $\text{I}_2$  is solid and sublimate

$\text{Cl}^-$  reacts with dichromate to produce chromyl chloride (Not redox).



# Questions

Name the following oxoanions and their corresponding acids:

$\text{ClO}^-$  : *hypochlorite* ion

$\text{HClO}$ : *hypochlorous acid*

$\text{ClO}_2^-$  : chlor*ite* ion

$\text{HClO}_2$ : chlor*ous acid*

$\text{ClO}_3^-$  : chlor*ate* ion

$\text{HClO}_3$ : chlor*ic acid*

$\text{ClO}_4^-$  : *perchlorate* ion

$\text{HClO}_4$ : *perchloric acid*

***Remember:***

$\text{NO}_3^-$  : nitr*ate* ion

$\text{NO}_2^-$  : nitr*ite* ion

# Questions

Name the following:

$\text{IO}^-$  ,  $\text{HIO}_3$ ,  $\text{ClO}_2^-$  ,  $\text{BrO}_2^-$  ,  $\text{HBrO}_3$  ,  $\text{IO}_4^-$  ,  $\text{PO}_4^{3-}$  ,  $\text{SO}_4^{2-}$  ,  $\text{SO}_3^{2-}$  ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ .

Define Synproportionation and disproportionation reaction.  
Give example per each one?

What is the oxidation number of Cl atom in the following  
 $\text{Cl}_2$ ,  $\text{ClO}^-$  ,  $\text{CrO}_2\text{Cl}_2$ ,  $\text{HClO}_4$  ,  $\text{NaCl}$

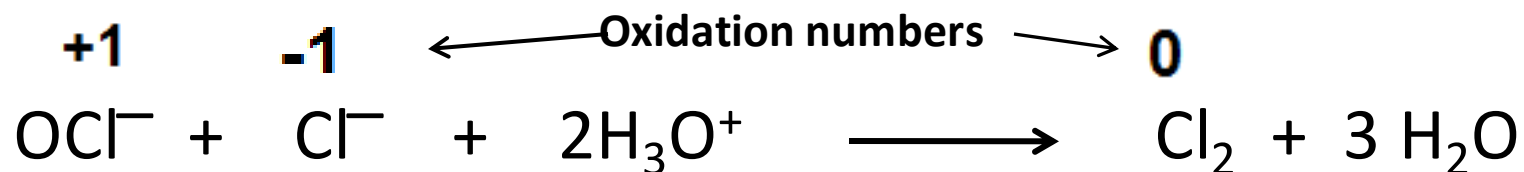
What is chlorine water, how can it be replaced with a more convenient reagent in laboratory ( Hint: p 176)?



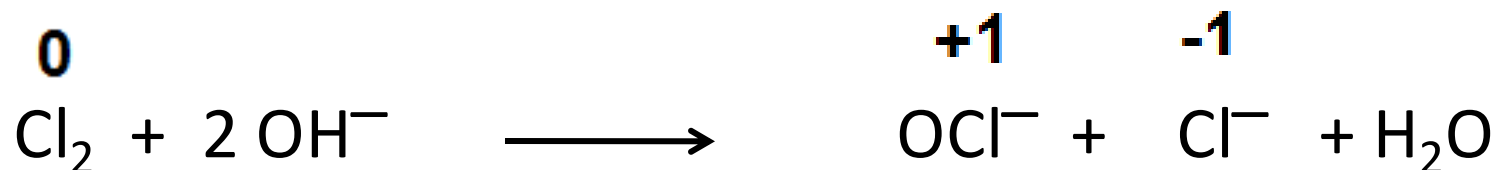
# Questions

## Synproportionation vs Disproportionation

### Synproportionation



### Disproportionation



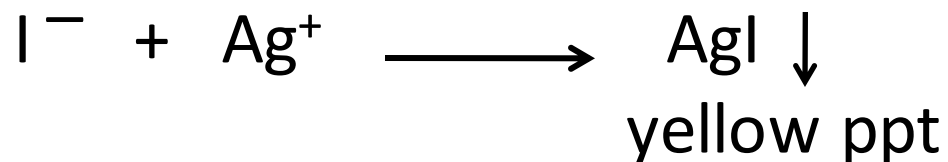
# Iodide ion

## With $\text{AgNO}_3$ Solution:

Soda extract + acidify with  $\text{HNO}_3$  (dil) + then add  $\text{AgNO}_3$  Solution  $\longrightarrow$  yellow ppt, insoluble in  $\text{HNO}_3$  (conc.), insoluble in  $\text{NH}_3$  (dil.), insoluble in  $\text{NH}_3$  (conc.)

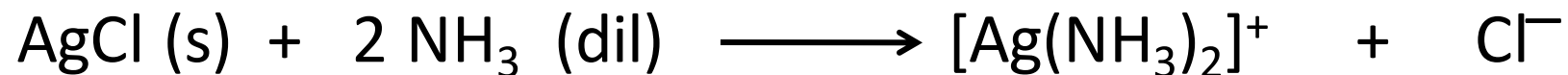
Soda extract had basic pH, it should be acidified before adding  $\text{Ag}^+$  reagent to prevent its precipitation as  $\text{Ag}_2\text{O}$  (discussed before)

Reactions:



# Iodide ion

**With AgNO<sub>3</sub> Solution:**

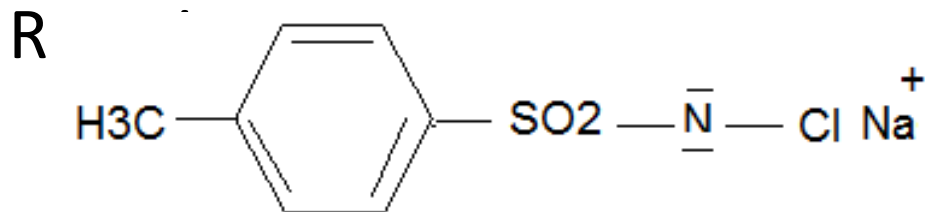


***K<sub>sp</sub>: AgCl > AgBr > AgI***

# Iodide ion

## With Chloramine-T solution:

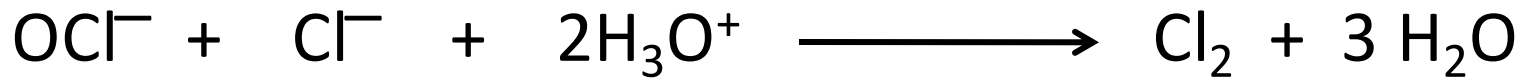
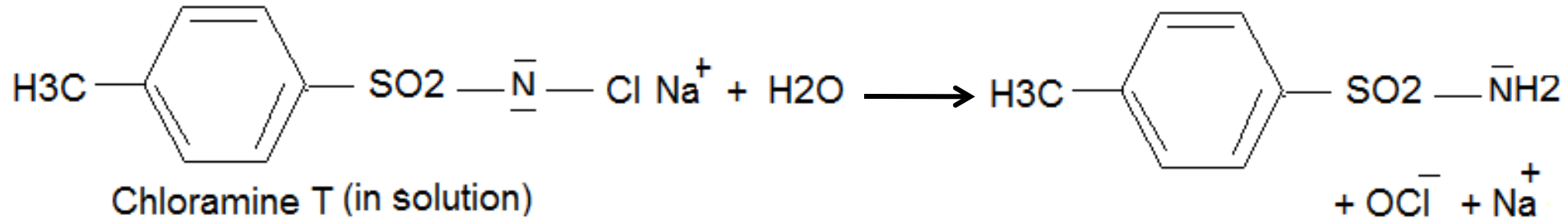
Soda extract + acidify with HCl + 3-4 ml  $\text{CHCl}_3$  or  $\text{CCl}_4$  (two immiscible phases are formed) then add drop wise freshly prepared chloramine T (dil.)  $\longrightarrow$  the organic phase ( $\text{CHCl}_3$  or  $\text{CCl}_4$ ) is colored violet  $\longrightarrow$  with excess of reagent the color disappear.



Chloramine T (solid state)

# Iodide ion

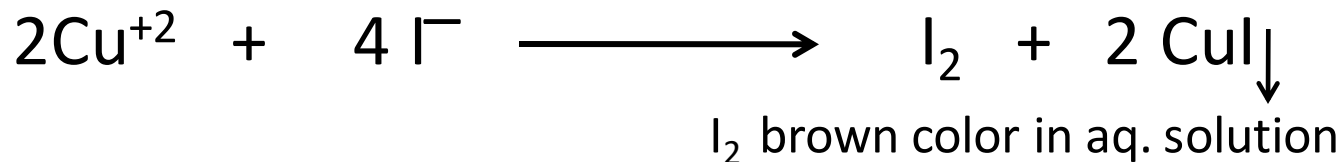
Reactions:



$\text{I}_2$  (Iodine , non polar molecule) dissolves in organic phase with violet color.

# Iodide ion

With copper (II) solution:



With iron (III) solution:



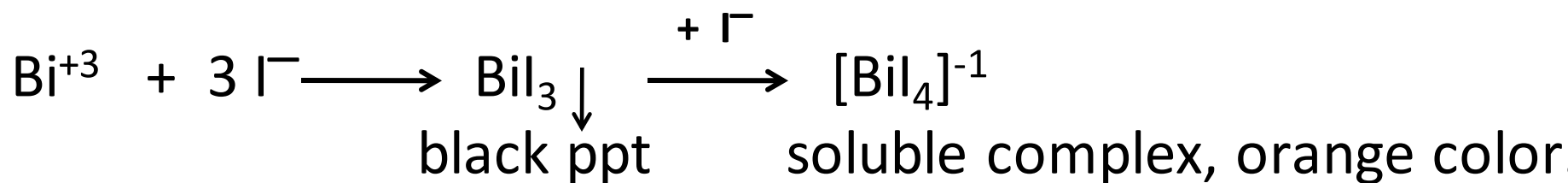
$\text{I}_2$  has brown color in aq. solution

$\text{I}_2$  is identified by deep blue coloration of starch solution



# Iodide ion

With Bismuth (III) solution:

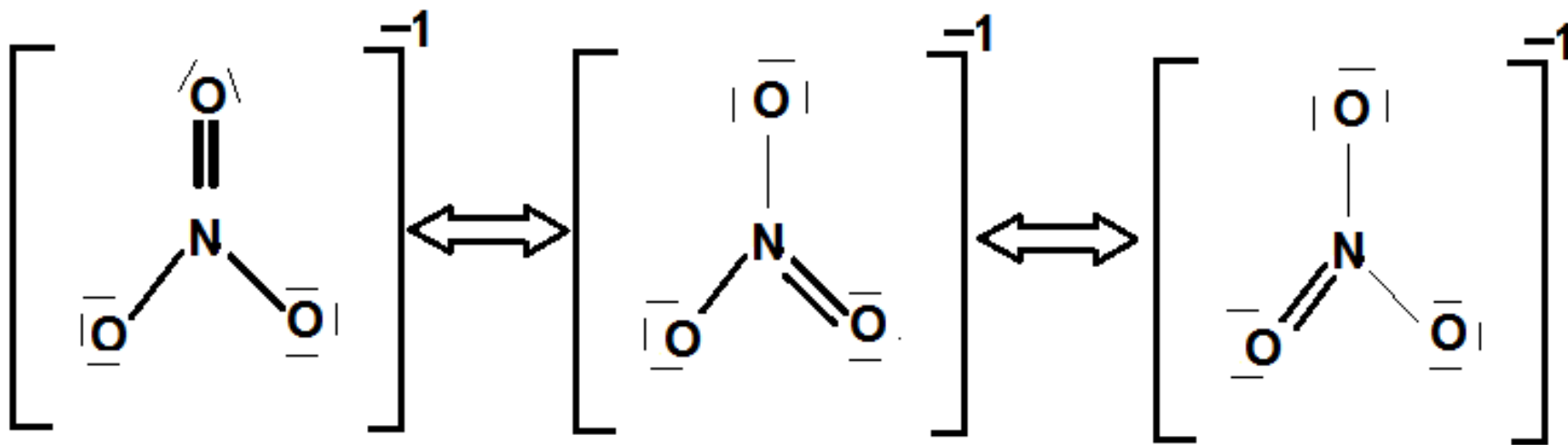


$[\text{BiI}_4]^{-1}$  : Dragendorf's reagent, tetraiodobismuthate(III) ion



# nitrate ion

Lewis structure:  $\text{NO}_3^-$



# nitrate ion

Ring test:

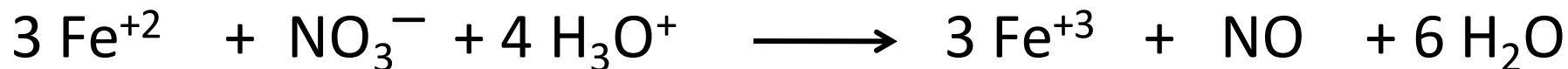
Soda extract + acidify  $\text{H}_2\text{SO}_4$  (dil)+  $\text{FeSO}_4$  solution then add  $\text{H}_2\text{SO}_4$  (Conc.) on the inner edge of test tube slowly **without shaking**  $\longrightarrow$  two layers are formed (aqueous layer and sulphuric acid conc. layer due to difference in density, but they are miscible)  $\longrightarrow$  brown ring will be formed between two layers.



# nitrate ion

Ring test:

Reactions:



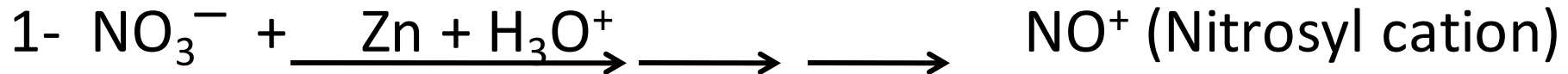
The brown color is concentrated on the upper surface of Sulphuric acid (Conc.), because  $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$  is adsorbed on  $\text{H}_2\text{SO}_4$  (Conc.) the hygroscopic layer.

# nitrate ion

## Azo-test:

Soda extract + acidify with HCl (dil) + Zn (powder) then add sulfanilic acid +  $\alpha$ -naphthylamine  $\longrightarrow$  red color (azo compound)

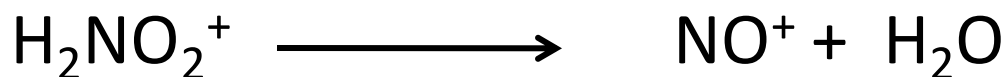
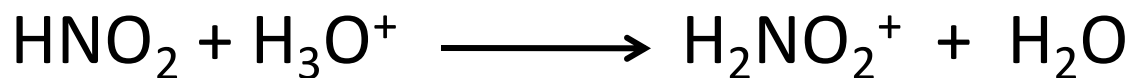
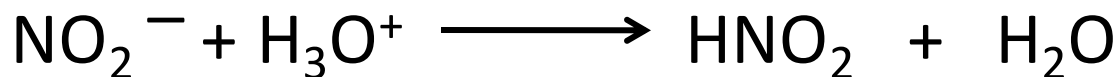
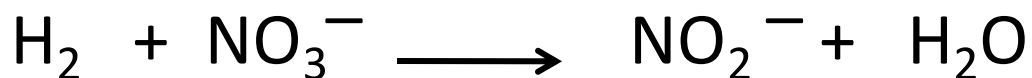
## Reactions:



# nitrate ion

## Azo-test:

### Reaction:



(Nitrosyl cation, lewis acid , reactive

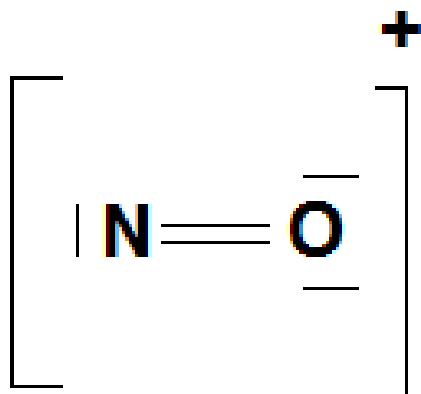
species)

# nitrate ion

Azo-test:

Reaction:

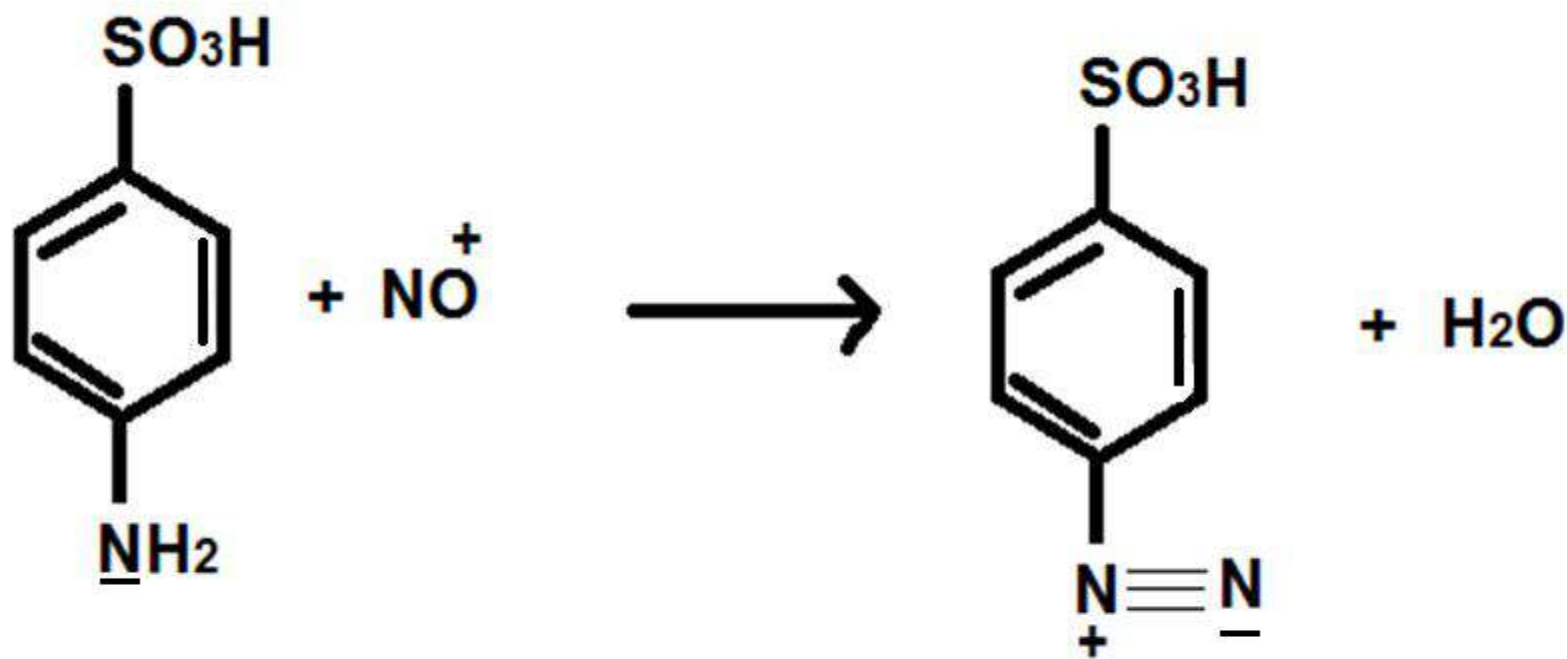
**Lewis structure of NO<sup>+</sup>**



$$\text{VE} = 5 + 6 - 1 = 10e$$

**N atom is surrounded only with 6 e**

# nitrate ion



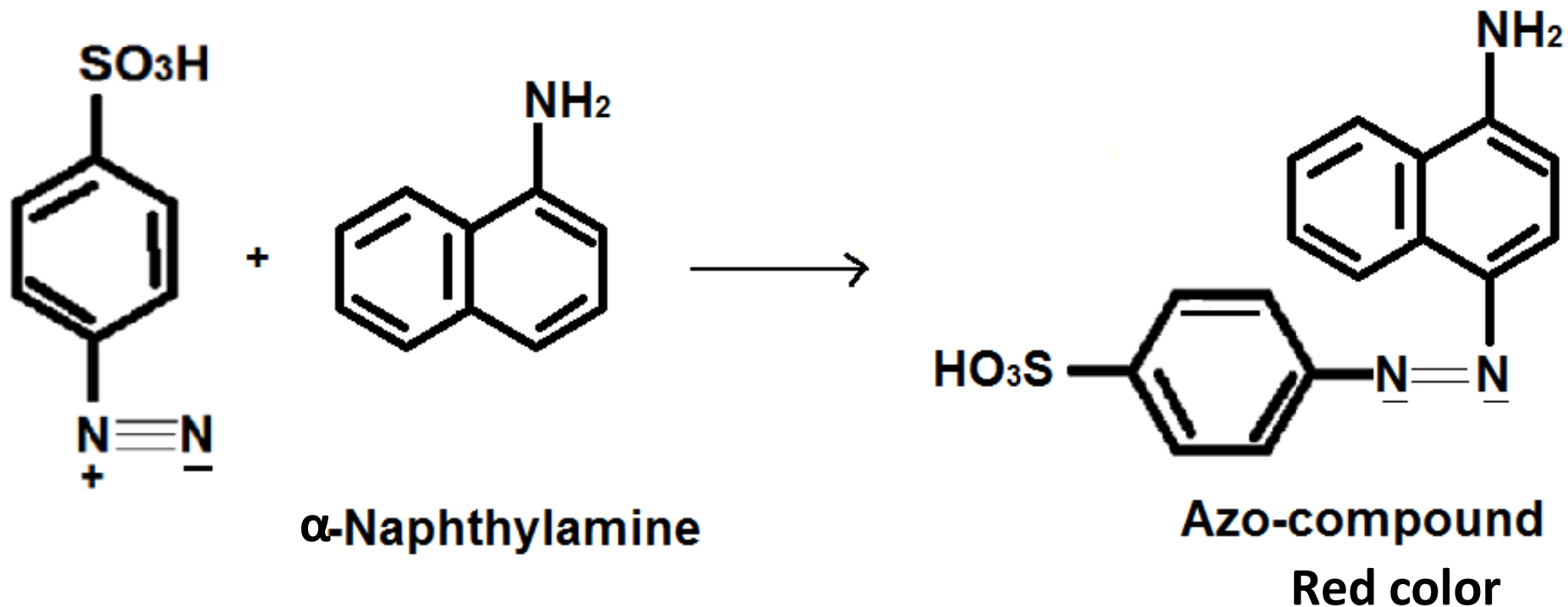
Sulfanilic acid

Diazonium salt

# nitrate ion

## Azo-test:

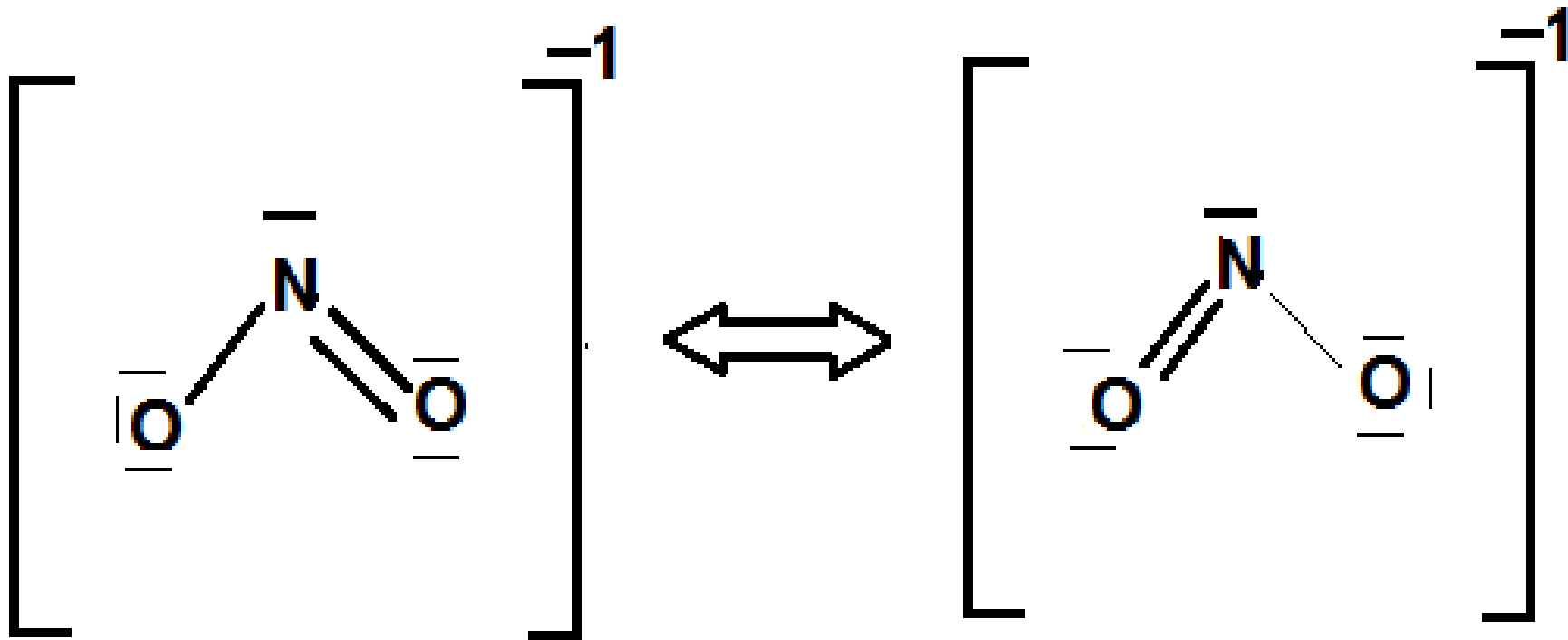
Reaction:





# nitrite ion

Lewis structure:  $\text{NO}_2^-$

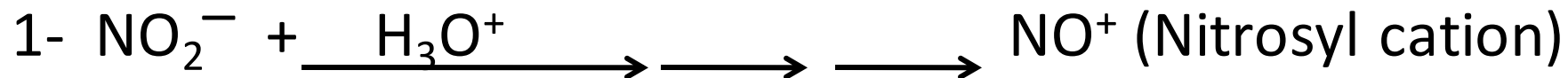


# nitrite ion

## Azo-test:

Soda extract + acidify with HCl (dil) **[Without Zn powder]**  
then add sulfanilic acid +  $\alpha$ - naphthylamine  $\longrightarrow$  red  
color (azo compound)

Reactions: **[discussed before]**

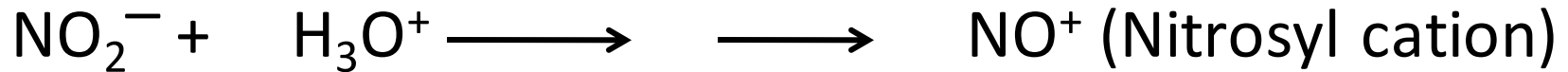


# nitrite ion

**With Antipyrine:**

**Soda extract + HCl (dil) + antipyrine  $\longrightarrow$  green color**

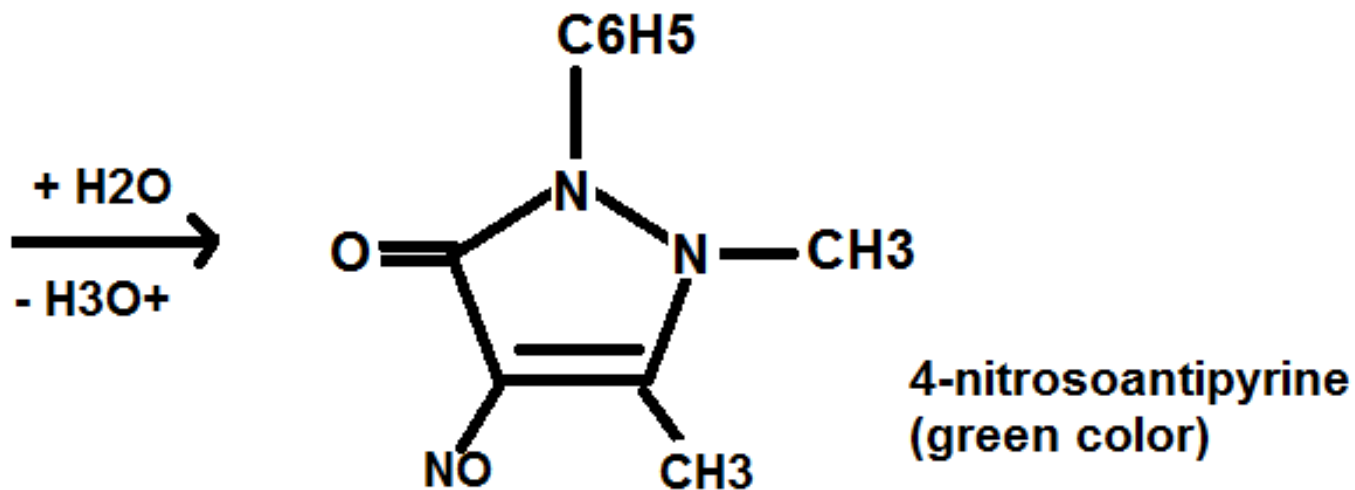
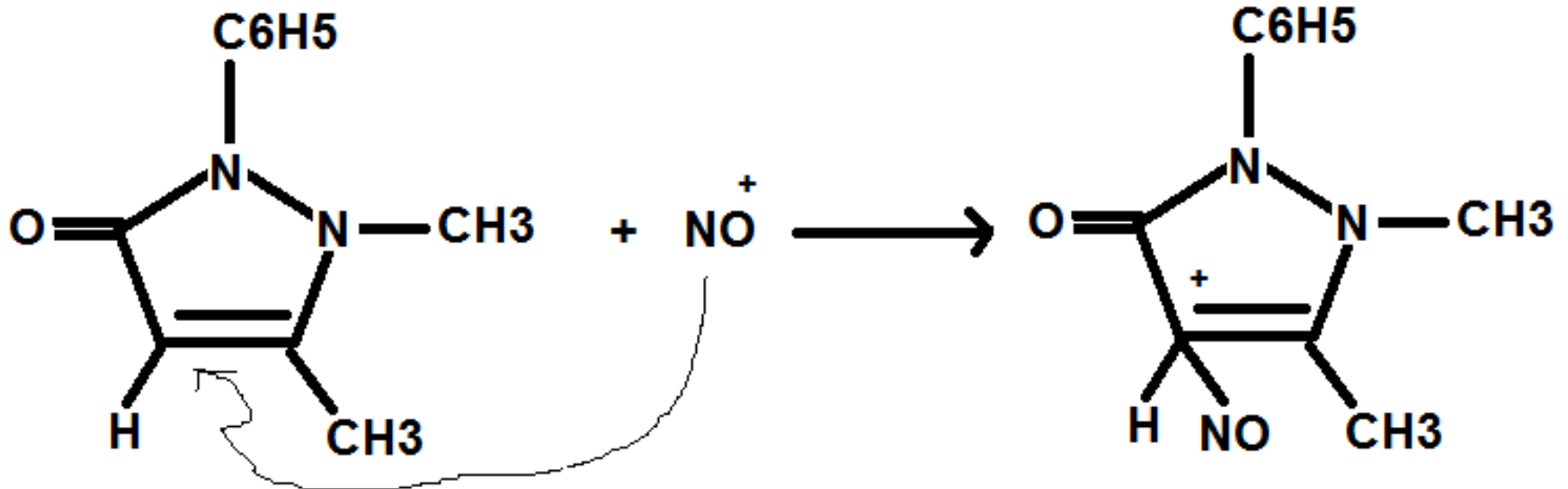
**Reactions:**



**Nitrosyl cation is a lewis acid reacts with antipyrine to produce 4-nitrosoantipyrine (green color)**

# nitrite ion

With Antipyrine:  
Reactions:



## **nitrite ion**

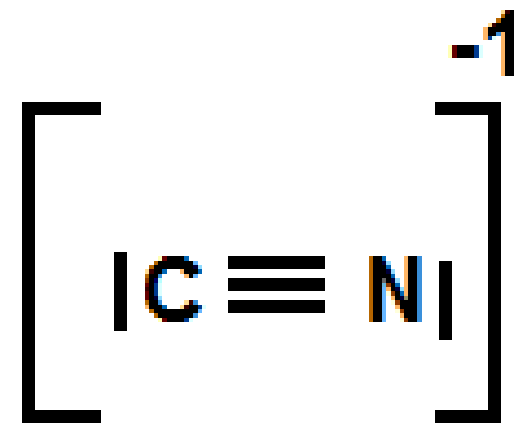
**How to remove nitrite from a sample before detection of nitrate???**

**By addition of one of these compounds: urea, sulfamic acid or ammonium chloride.**

**These compounds reacts with nitrite in syn-proportionation reactions to eliminate nitrogen of both substances as nitrogen gas.**

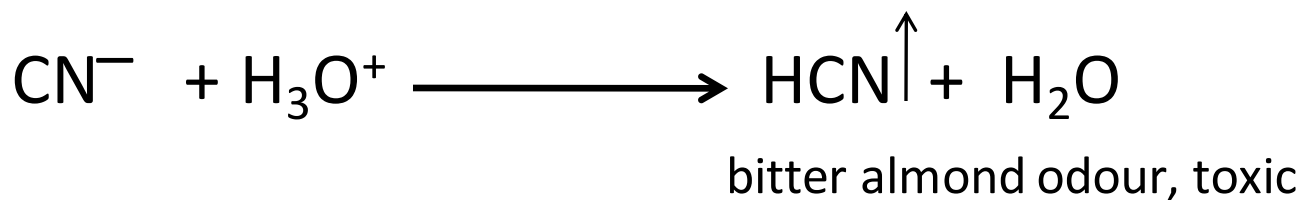
# cyanide ion

Lewis structure of  $\text{CN}^-$ :



With HCl (dil):

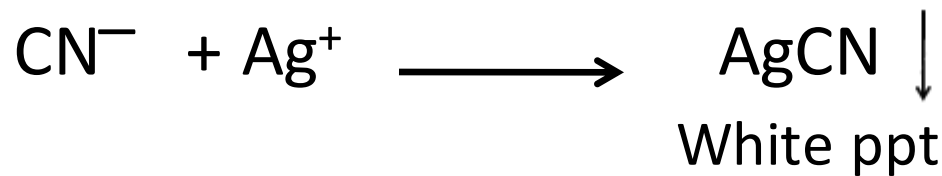
Soda extract + HCl (dil)  $\longrightarrow$  bitter almond odour, toxic



## cyanide ion

With  $\text{AgNO}_3$  solution:

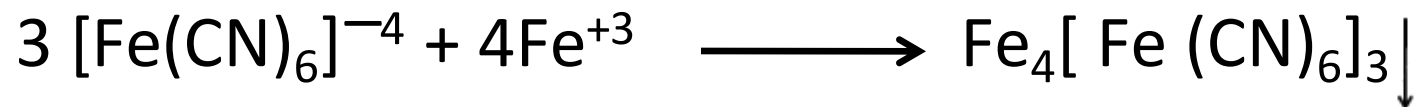
Soda extract +  $\text{AgNO}_3 \longrightarrow$  white ppt, soluble by excess of cyanide



# cyanide ion

Prussian blue test:

Soda extract in basic solution + add FeSO<sub>4</sub> → then acidify and add FeCl<sub>3</sub> → Blue ppt is formed (Prussian or Berliner blue)



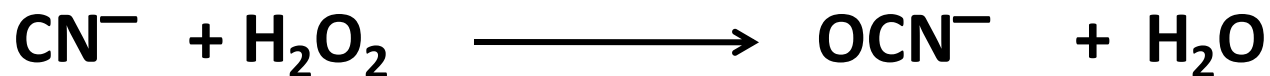
Prussian (Berliner) blue  
blue ppt



# cyanide ion

How could you eliminate a toxic solution of cyanide from laboratory???????

To a strong alkali solution of cyanide add  $\text{H}_2\text{O}_2$ . cyanide is oxidized to cyanate ion, which is non-toxic.



$\text{OCN}^-$  : cyanate ion, nontoxic, since it dissolved in water and produces carbonate and ammonium ions



# Sulfate ion



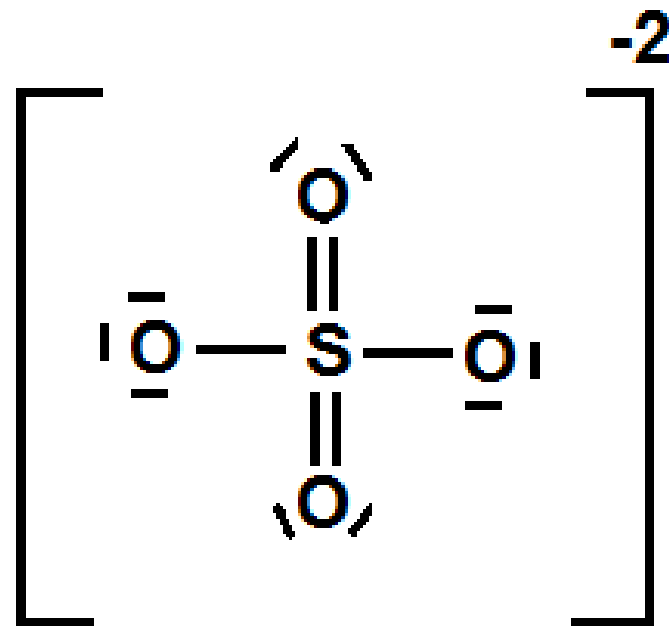
**What is hybridization state and molecular geometry of sulfate ion?**

MgSO<sub>4</sub> is English salt.

Bone fracture.

Salts of drugs.

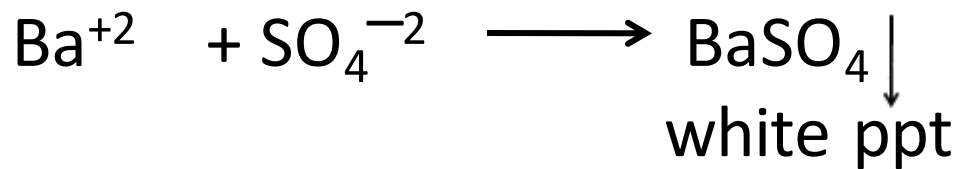
In organic chemistry to synthesize sulfonic acids (RSO<sub>3</sub>H).



# sulfate ion

## Test of $\text{SO}_4^{-2}$ :

Soda extract + acidify with HCl (Conc.) +  $\text{BaCl}_2 \longrightarrow$   
White ppt is formed which is insoluble in HCl(Conc) and  $\text{HNO}_3$ (Conc)

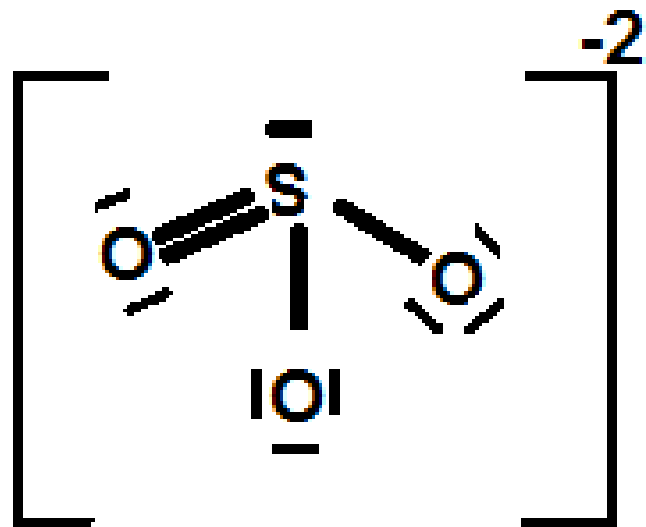


## Sulfite ion



What is hybridization state and molecular geometry of sulfite ion?

Draw lewis structure of  $\text{SO}_2$ ?



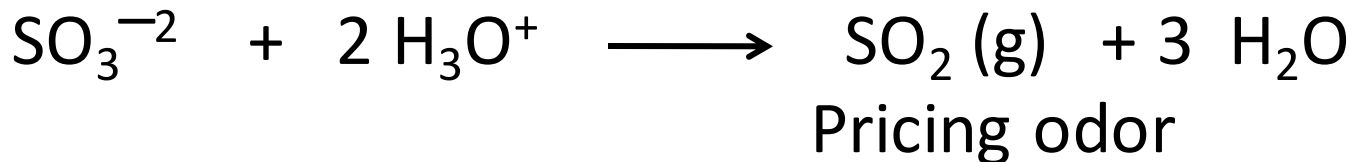
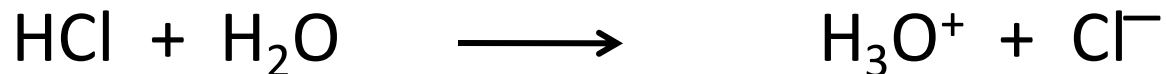
S atom in sulfate is surrounded with 12 electrons. Explain?

# sulfite ion

**Test of  $\text{SO}_3^{-2}$ :**

**With HCl(dil):**

Soda extract + acidify with HCl (dil.)  $\longrightarrow$  Pricing odor



**Note:**



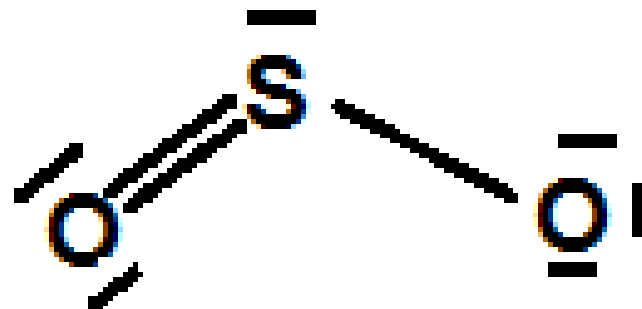
# sulfite ion

Test of  $\text{SO}_3^{-2}$ :

Note:



$\text{SO}_2$  : is acid anhydride , Lewis acid

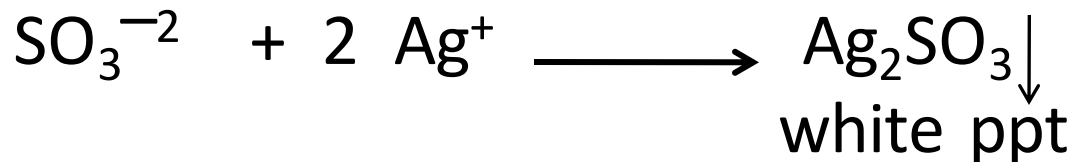


# sulfite ion

## Test of $\text{SO}_3^{-2}$ :

### With $\text{AgNO}_3$ solution:

Soda extract + acidify to be neutral or slightly acidic then add Ag-solution  $\longrightarrow$  white ppt is formed, **soluble** in hot  $\text{HNO}_3$  (dil), in  $\text{NH}_3$  solution, by excess of sulfite.

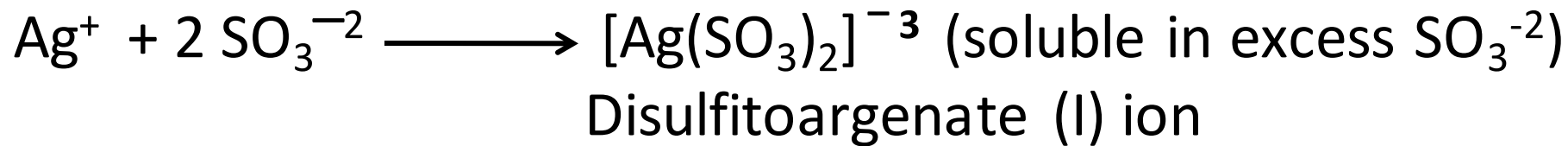
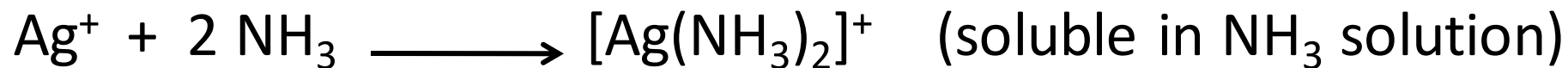
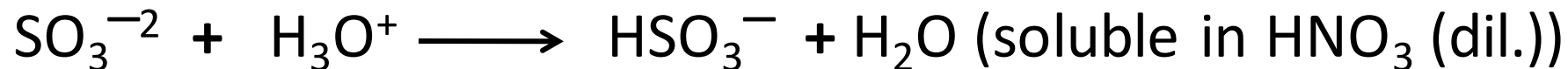
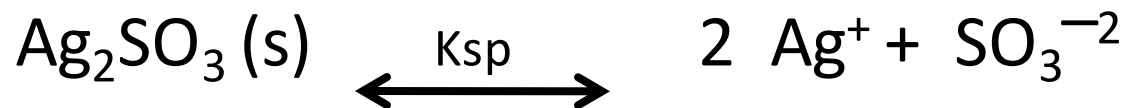


**Why acidification is restricted to be slightly acidic?**

# sulfite ion

Test of  $\text{SO}_3^{-2}$ :

**Dissolution of  $\text{Ag}_2\text{SO}_3$  (s) :**





# sulfite ion

## Test of $\text{SO}_3^{-2}$ :

### With $\text{I}_2$ solution:

Soda extract + acidify to be neutral or slightly acidic then add  $\text{I}_2$ -solution  $\longrightarrow$  Decolorization of iodine solution



$\text{I}_2$  solution is an oxidizing agent has brown color, when reduced converted to  $\text{I}^-$ , Which is colorless.

The resulted sulfate can be identified with  $\text{Ba}^{+2}$ .

**(See your book)**

# sulfite ion

## Test of $\text{SO}_3^{-2}$ :

### With malachite green:

Soda extract + acidify to be neutral or slightly acidic then add add malachite green  $\longrightarrow$  Decoloration of malachite green.

$\text{SO}_3^{-2}$  reacts with malachite green in **lewis acid lewis base** reaction.

# sulfite ion

**Test of  $\text{SO}_3^{-2}$ :**

**With malachite green:**

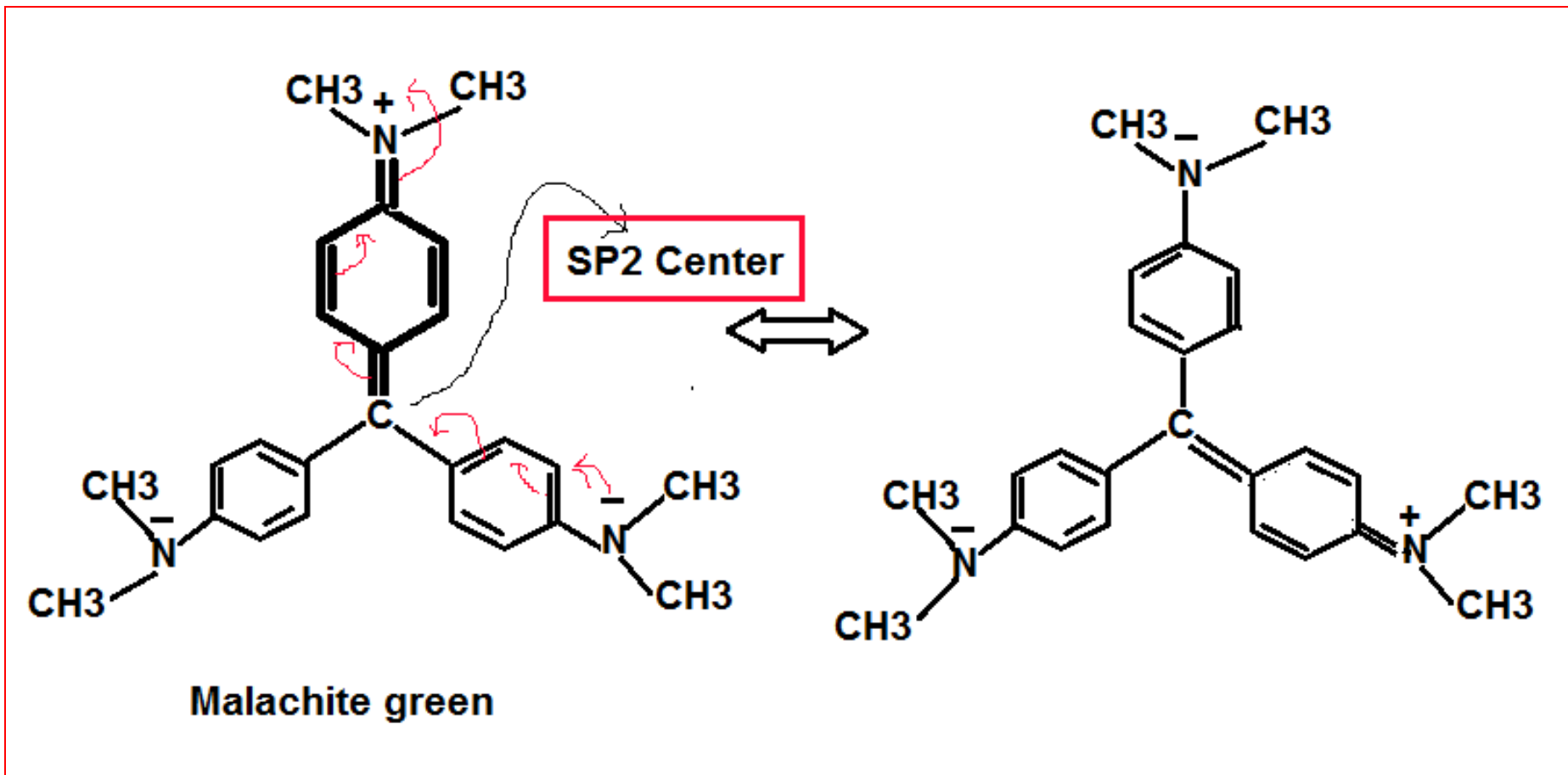
$\text{SO}_3^{-2}$  decolorize  $\text{I}_2$  solution by redox reaction but decolorization of malachite green due to a lewis acid-lewis base reaction.

Malachite green has a central carbon atom in  $\text{sp}^2$  allowing a long resonance among 3 phenolic groups. When this carbon converted to  $\text{sp}^3$  state the compound becomes colorless.

# sulfite ion

Test of  $\text{SO}_3^{-2}$ :

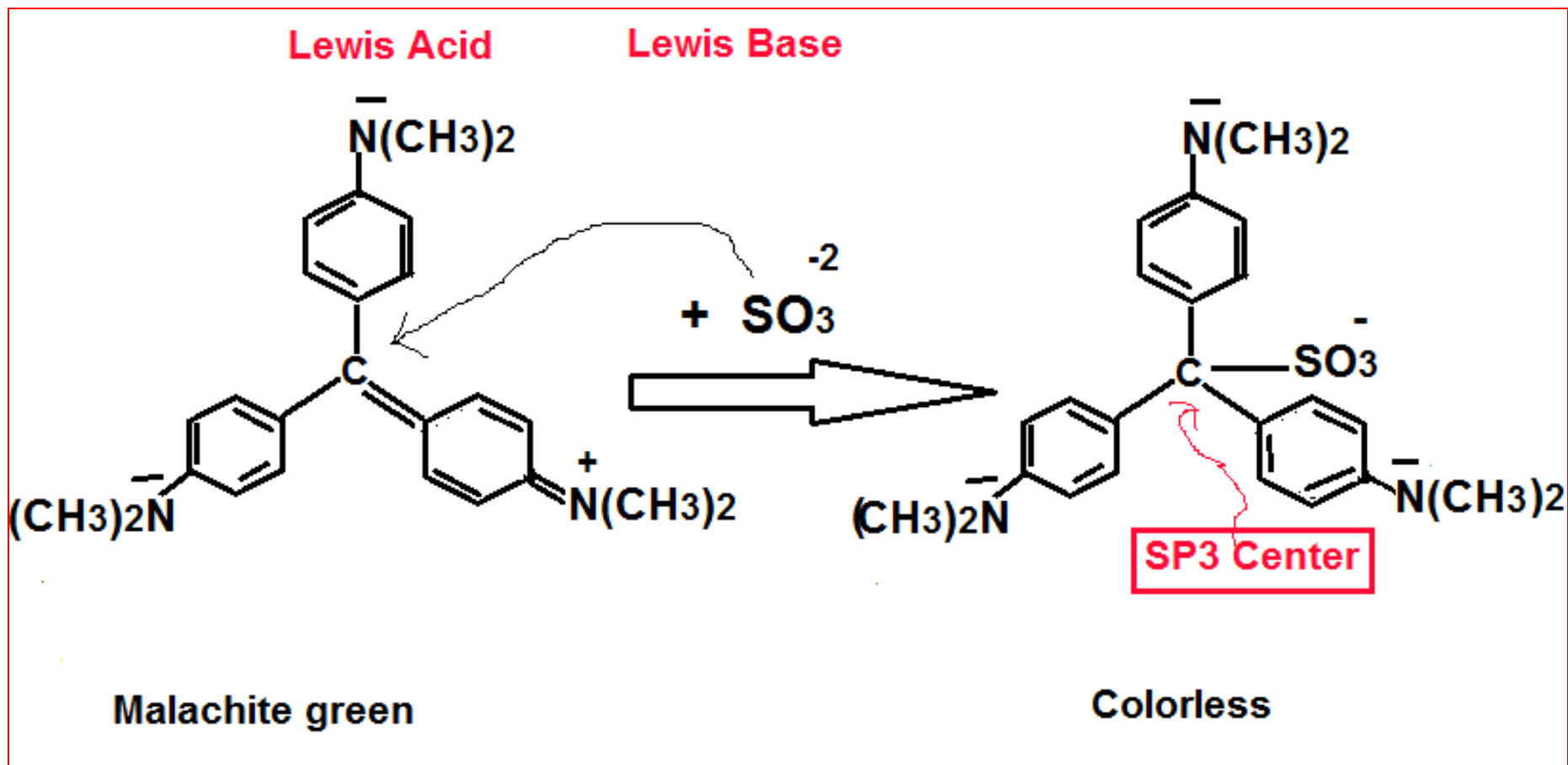
With malachite green:



# sulfite ion

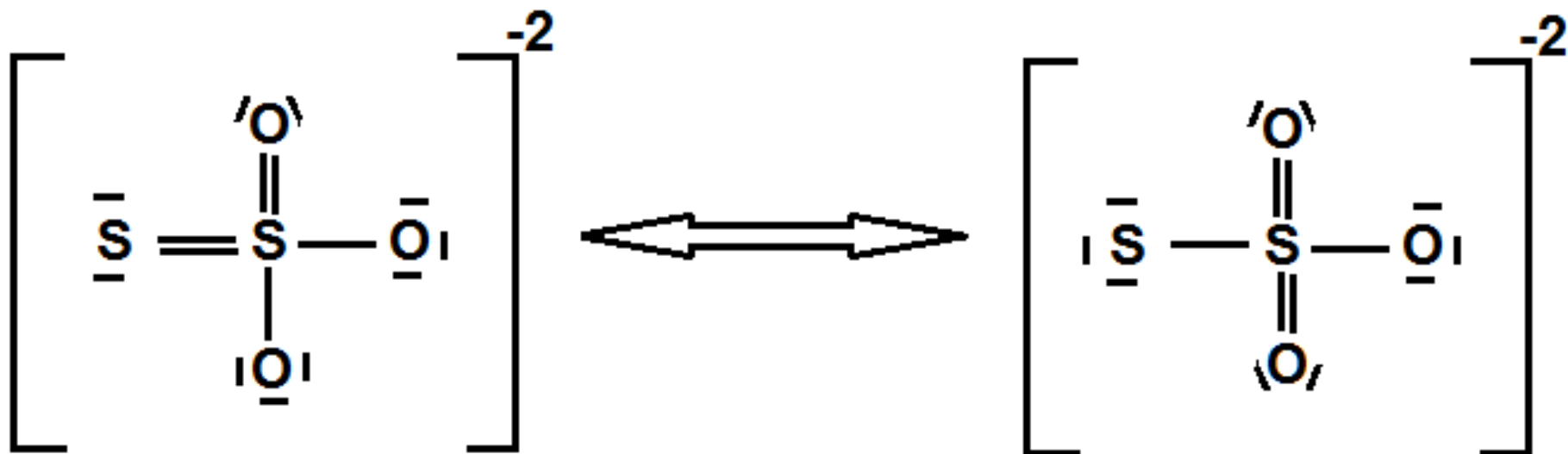
Test of  $\text{SO}_3^{-2}$ :

With malachite green:



# Thiosulfate ion

Lewis structure  $\text{S}_2\text{O}_3^{-2}$ :



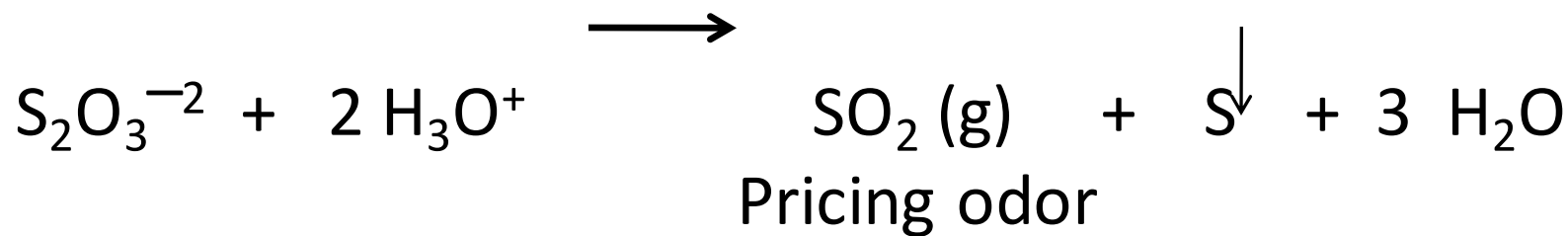
Minimum

# Thiosulfate ion

**Test of  $S_2O_3^{2-}$ :**

**With HCl (dil):**

Soda extract + HCl (dil.)  $\longrightarrow$  Pricing odour with yellow ppt

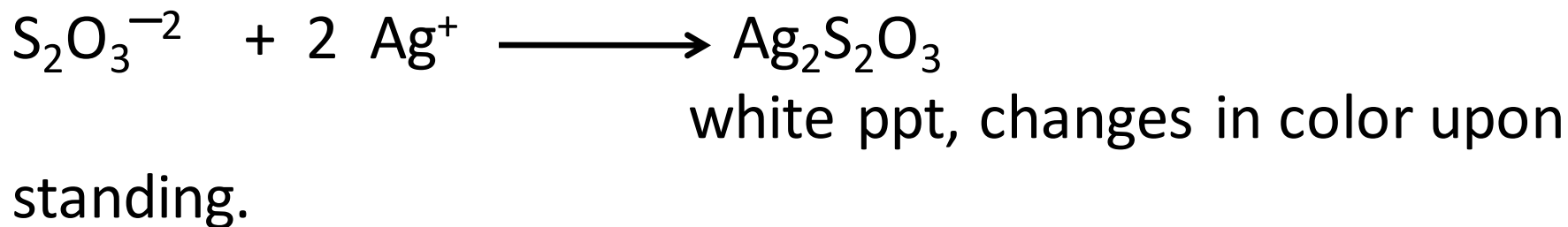


# Thiosulfate ion

**Test of  $S_2O_3^{2-}$ :**

**With  $AgNO_3$  solution: (Sunset reaction)**

Soda extract + acidify to neutral or slightly acidic then add  $Ag^+$  solution  $\longrightarrow$  white ppt which on standing the color of ppt changes to yellow  $\longrightarrow$  orange  $\longrightarrow$  brown  $\longrightarrow$  black ( $Ag_2S$ ).



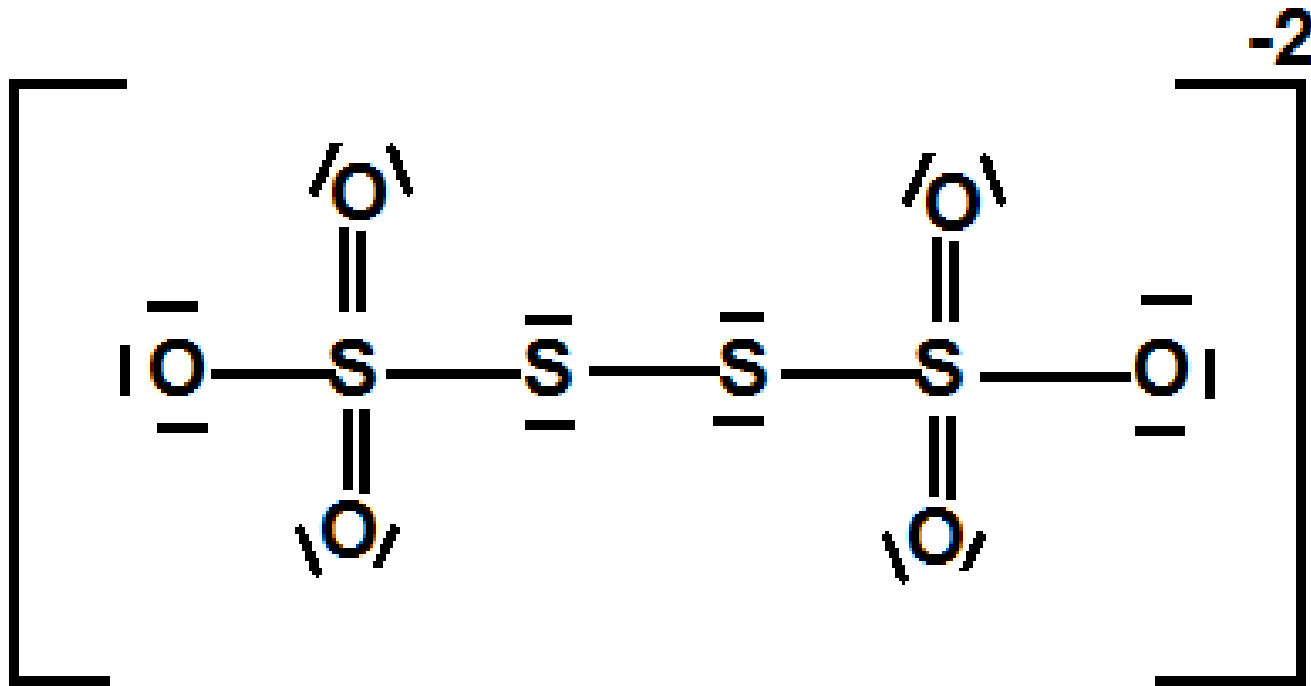




# Thiosulfate ion

Test of  $S_2O_3^{2-}$ :

With  $I_2$  Solution:

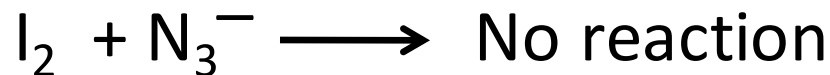


**Tetrathionate ion**

# Thiosulfate ion

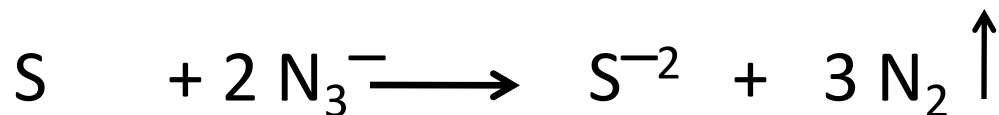
**Test of  $S_2O_3^{2-}$ :**

**With  $I_2$  – Azide Solution:**



Soda extract + acidify to neutral then add ( $I_2 + N_3^-$  - reagent)  
 $\longrightarrow$  **Development of colorless, odorless gas ( $N_2$ )**

**Reactions: ( Sulfide is a catalyst in RXN, present as impurity in thiosulfate samples)**

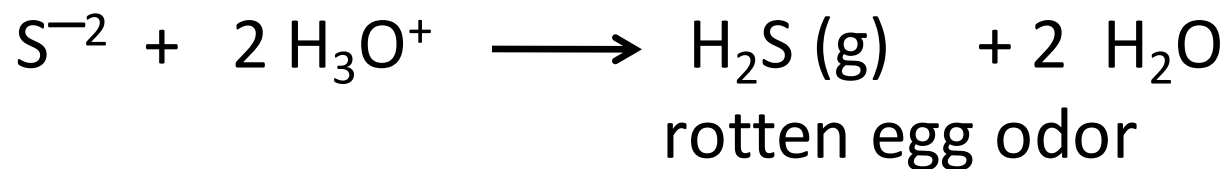


## sulfide ion

**Test of  $S^{-2}$ :**

**With HCl (dil):**

Soda extract + HCl (dil.)  $\longrightarrow$  rotten egg odor

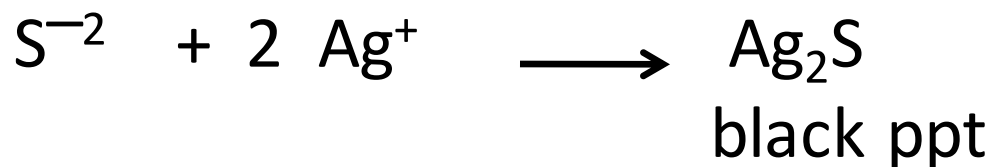


# sulfide ion

## Test of $S^{-2}$ :

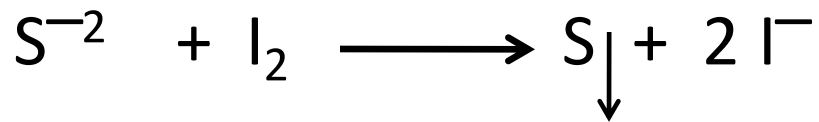
### With $AgNO_3$ solution:

Soda extract + acidify to be neutral or slightly acidic then add Ag-solution  $\longrightarrow$  black ppt is formed.



### With $I_2$ solution:

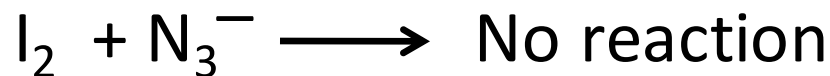
Soda extract + acidify to be neutral or slightly acidic then add  $I_2$ -solution  $\longrightarrow$  Decolorization of iodine solution



# sulfide ion

## Test of $S^{-2}$ :

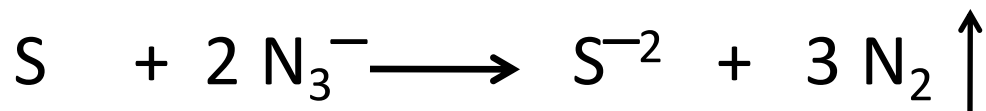
**With  $I_2$  – Azide Solution: (sulfide, thiosulfate, thiocyanate)**



Soda extract + acidify to neutral then add ( $I_2 + N_3^-$  - reagent)

**$\longrightarrow$  Development of colorless, odorless gas ( $N_2$ )**

**Reactions: ( Sulfide is a catalyst in RXN)**

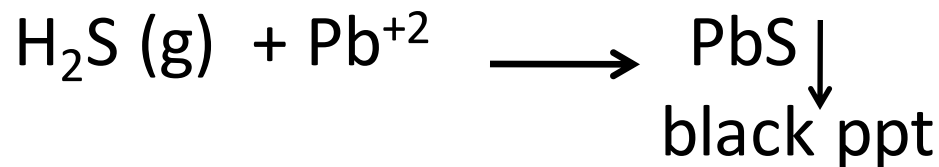
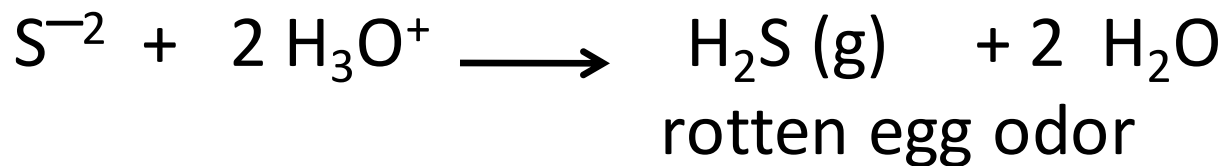


# sulfide ion

**Test of  $S^{-2}$ :**

**Specify  $H_2S$  chemically:**

Soda extract + HCl (dil.)  $\longrightarrow$  gas is evolved then put on the upper edge of test tube filter paper soaked with lead(II)acetate solution  $Pb(CH_3COO)_2 \longrightarrow$  a black ppt is formed on the filter paper.

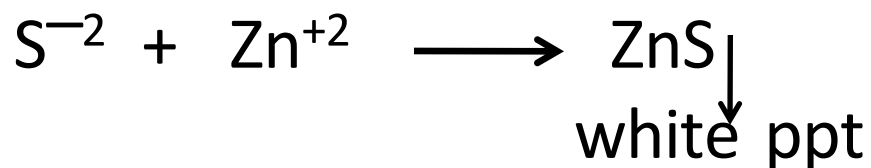


# sulfide ion

## Test of $S^{-2}$ :

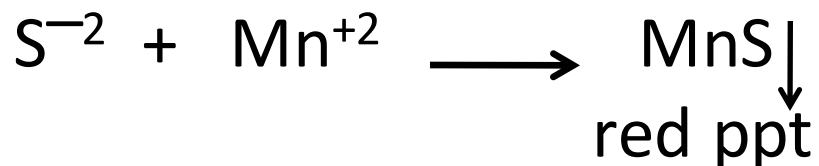
### With $Zn^{+2}$ :

Soda extract + acidify to be neutral or slightly acidic then add  $Zn^{+2}$ -solution  $\longrightarrow$  white ppt is formed.



### With $Mn^{+2}$ :

Soda extract + acidify to be neutral or slightly acidic then add  $Mn^{+2}$ -solution  $\longrightarrow$  red ppt is formed.





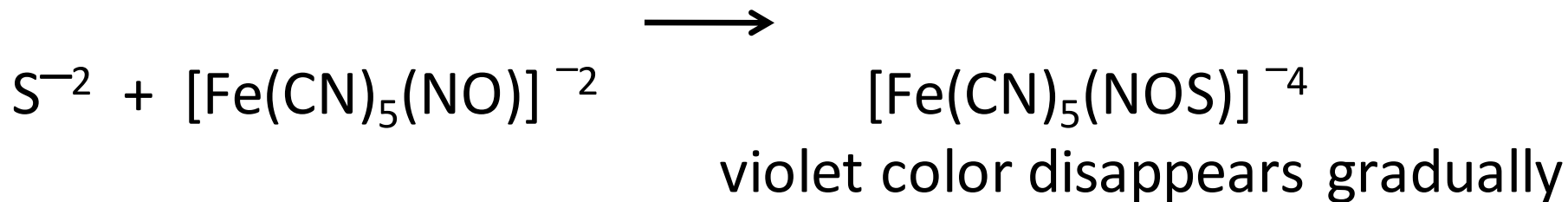
# sulfide ion

## Test of $S^{-2}$ :

### With sodium nitroprusside:

Soda extract (basic) + sodium nitroprusside  $\longrightarrow$  violet color which disappears gradually

Sodium nitroprusside is sodium pentacyanonitrosylferrate(II) dihydrate  **$Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$**

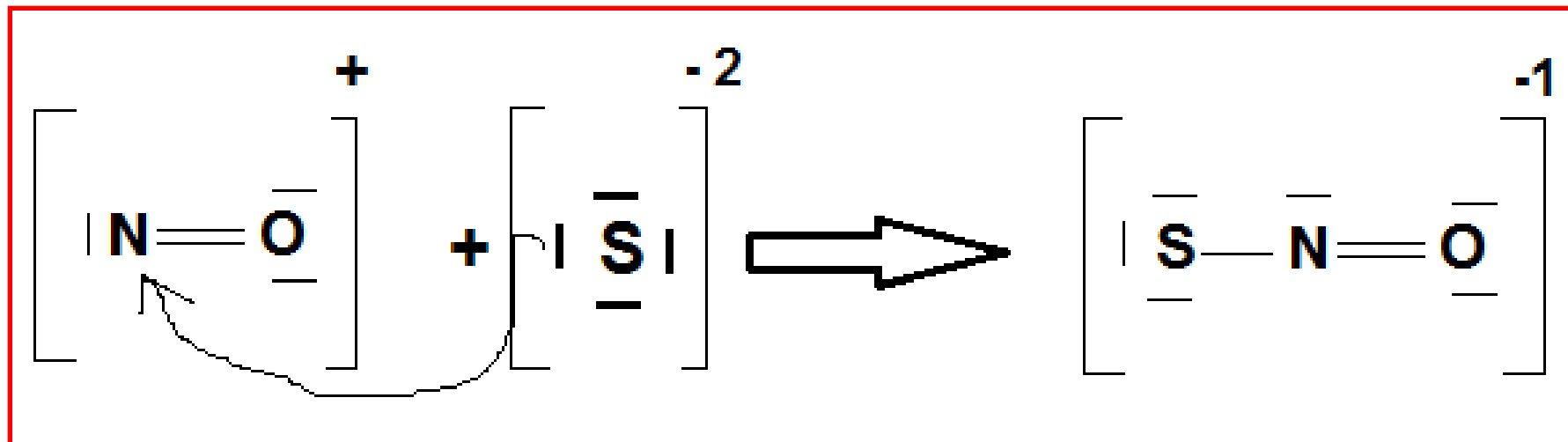


# sulfide ion

Test of  $S^{2-}$ :

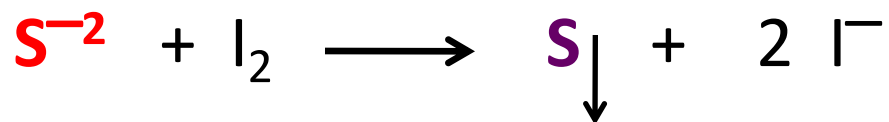
With sodium nitroprusside:

The reaction is lewis acid-lewis base



# Remember

$I_2$  is an oxidizing agent.

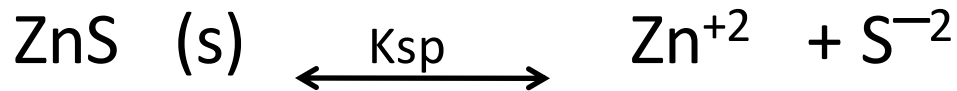


# Remember

$I_2$  should not be added to basic solution. **Why?**

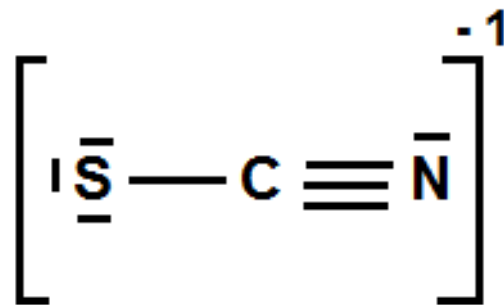


What you expect, is the solubility of ZnS improved by adding an acid . Explain?



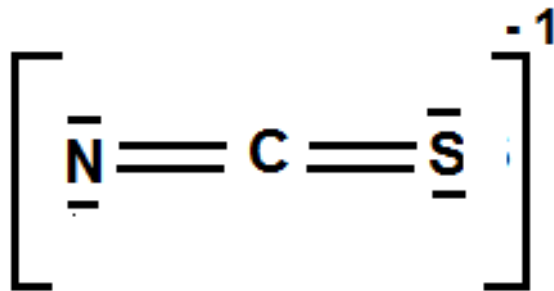
# Thiocyanate ion

Lewis structure thiocyanate  $\text{SCN}^-$  and isothiocyanate  $\text{NCS}^-$



Formal charges

-1      0      0



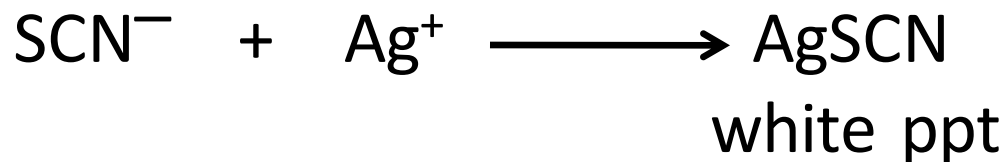
Formal charges

-1      0      0

# Thiocyanate ion

## With $\text{AgNO}_3$ solution:

Soda extract + acidify with  $\text{HNO}_3$  (dil) then add  $\text{AgNO}_3$  solution  $\longrightarrow$  white ppt is formed, **insoluble** in  $\text{HNO}_3$  (dil), **soluble** in  $\text{NH}_3$ .



# Thiocyanate ion

## With $\text{FeCl}_3$ solution:

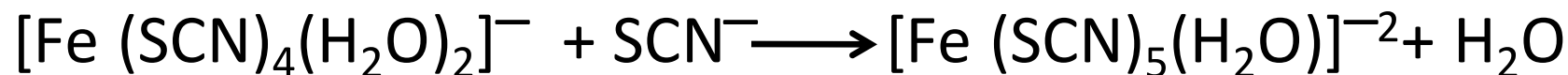
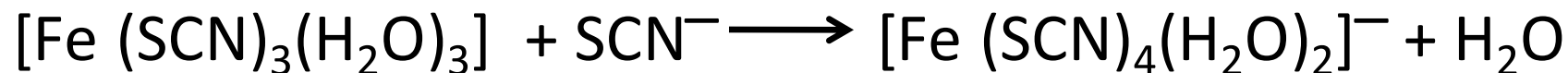
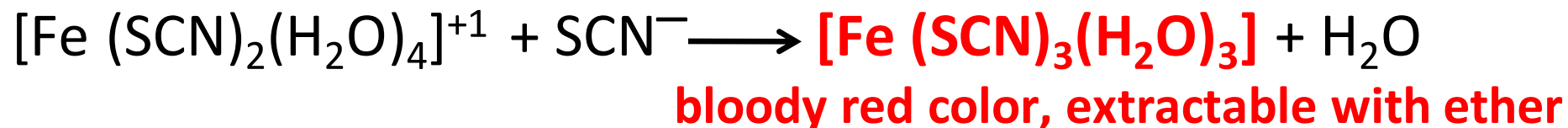
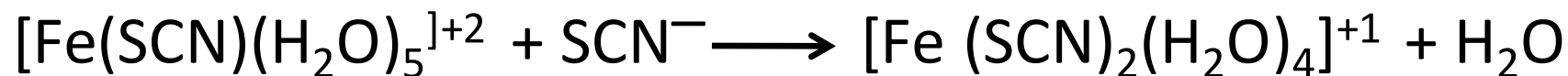
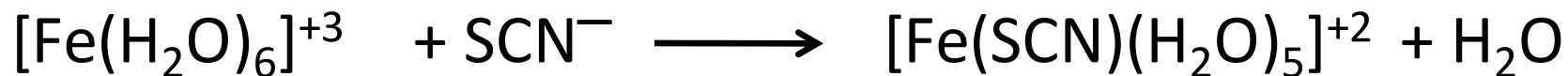
Soda extract + acidify with  $\text{HCl}$  (dil) then add  $\text{FeCl}_3$  solution  
—————→ bloody red color, which is extractable with ether

A series of complexes are formed, among which one is neutral responsible for bloody red color and extractable with ether  $[\text{Fe}(\text{SCN})_3(\text{H}_2\text{O})_3]$ , triaquatrithiocyanatoiron(III).

# Thiocyanate ion

**With FeCl<sub>3</sub> solution:**

**Reaction:**



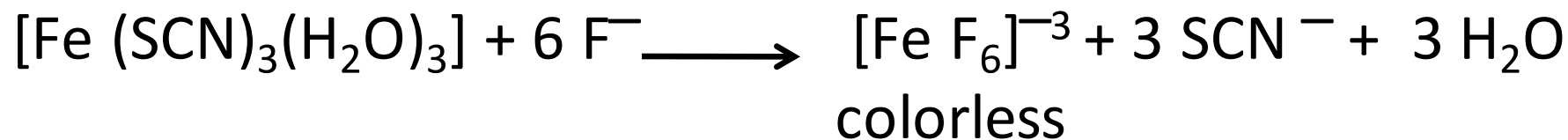


# Thiocyanate ion

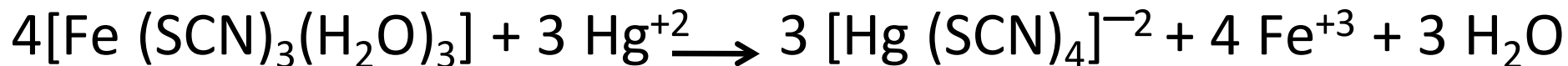
**With FeCl<sub>3</sub> solution:**

**Malfunctions of test:**

**Fluoride:**

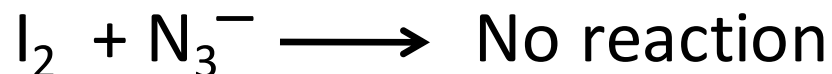


**Mercury (II):**



# Thiocyanate ion

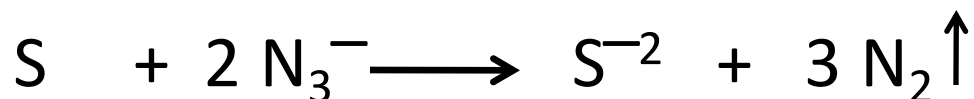
**With I<sub>2</sub> – Azide Solution: (sulfide, thiosulfate, thiocyanate)**



Soda extract + acidify to neutral then add (I<sub>2</sub>+ N<sub>3</sub><sup>-</sup> - reagent)

—————> **Development of colorless, odorless gas (N<sub>2</sub>)**

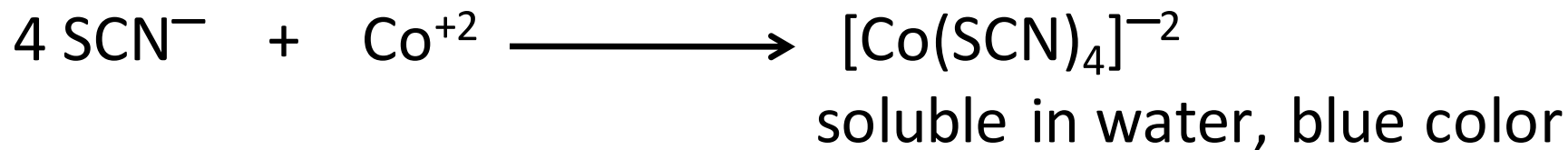
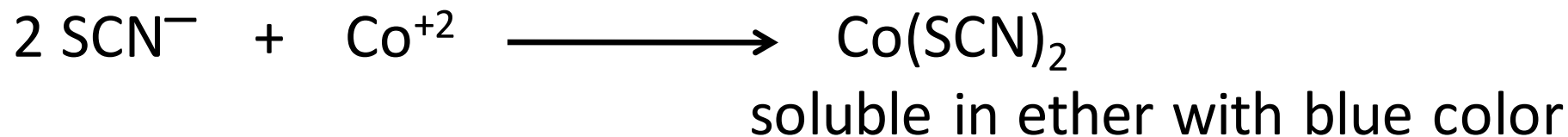
**Reactions: ( Sulfide is a catalyst in RXN)**



# Thiocyanate ion

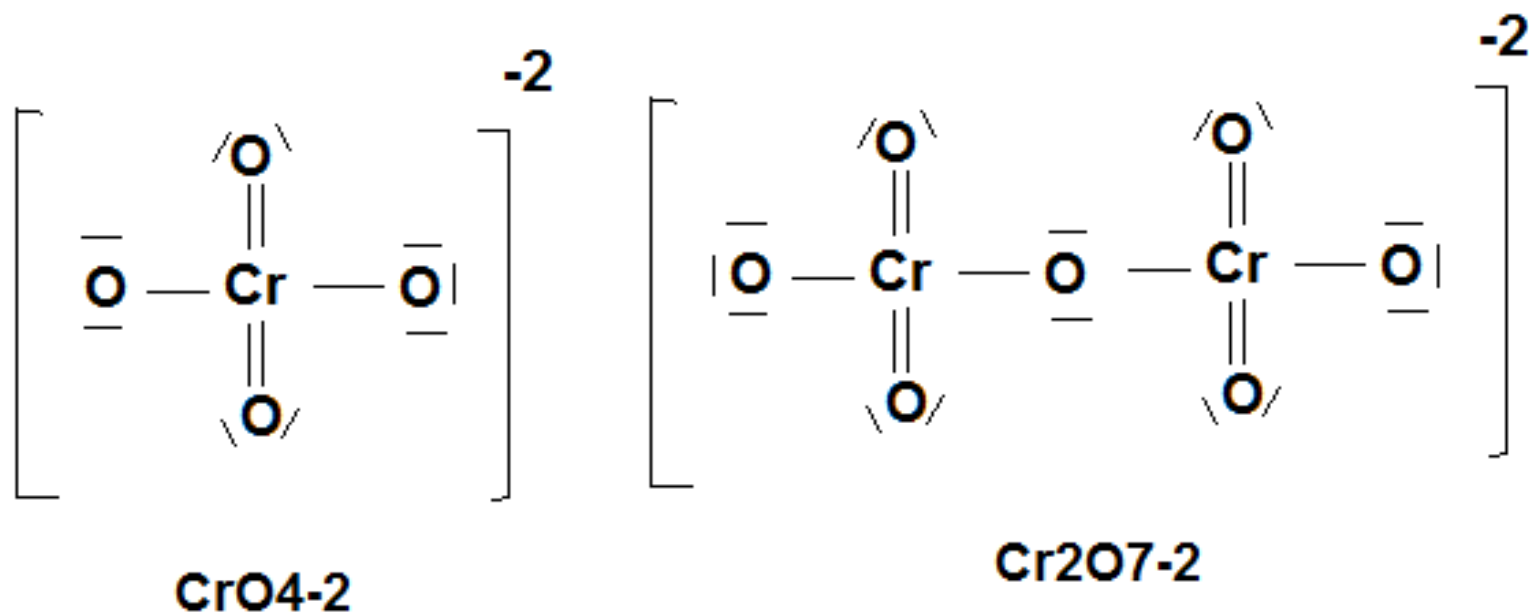
## With $\text{Co}(\text{NO}_3)_2$ solution:

Soda extract + acidify with  $\text{HNO}_3$  (dil) then add  $\text{Co}(\text{NO}_3)_2$  solution and ether  $\longrightarrow$  aqueous and ether phases are blue.



# Chromate ion

## Lewis structure of $\text{CrO}_4^{2-}$

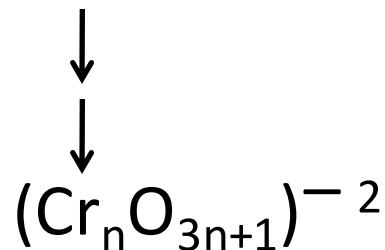
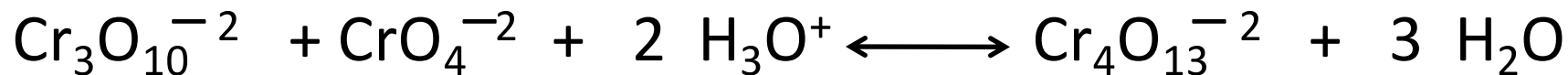
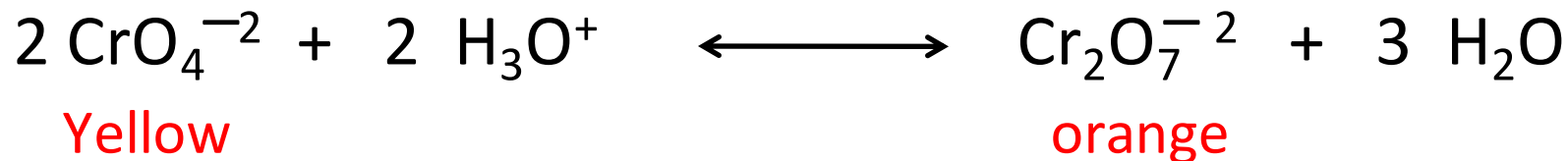


# Chromate ion

## Test of $\text{CrO}_4^{-2}$

## Chromate-dichromate equilibrium:

## In acidic solution:

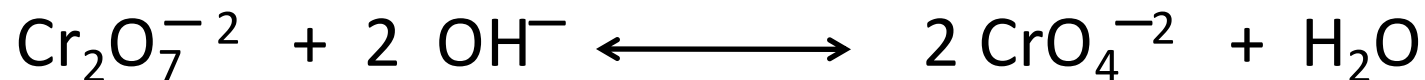


# Chromate ion

Test of  $\text{CrO}_4^{-2}$

Chromate-dichromate equilibrium:

In basic solution: The equilibrium is reversed



Orange

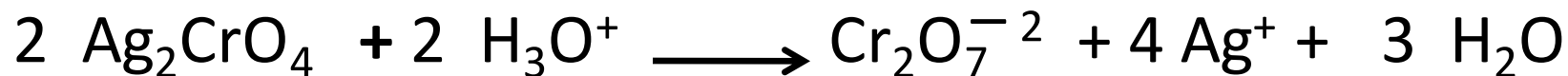
Yellow

# Chromate ion

## Test of $\text{CrO}_4^{-2}$ :

### With $\text{AgNO}_3$ solution:

Soda extract + acidify to neutral or slightly acidic then add  $\text{AgNO}_3 \longrightarrow$  a red brown ppt is formed, which is soluble in  $\text{HNO}_3$ (dil.) and  $\text{NH}_3$  (dil.).



# Chromate ion

## Test of $\text{CrO}_4^{2-}$

### With $\text{NaCl}$ & $\text{H}_2\text{SO}_4$ (Conc.):

Soda extract +  $\text{NaCl} + \text{H}_2\text{SO}_4$  (Conc.)  $\xrightarrow{\Delta}$  colored gas is evolved (chromylchloride)  $\longrightarrow$  put filter paper soaked with  $\text{NaOH}$ /Diphenylcarbazide solution  $\longrightarrow$  the filter paper colored violet due to diphenylcarbazone

**The reactions were discussed in chloride anion.**



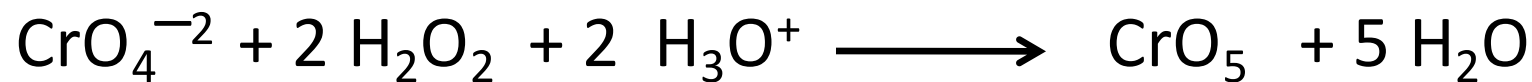
# Chromate ion

## Test of $\text{CrO}_4^{-2}$

### With $\text{H}_2\text{O}_2$ in acidic media:

Soda extract + acidify with  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  (dil.) + 2-3 mL diethyl ether then add  $\text{H}_2\text{O}_2 \longrightarrow$  a blue color in ether phase.

( $\text{CrO}_5$  is chromium pentoxide, blue color, unstable, decomposes rapidly in aq. solution) .  $\text{CrO}_5$  is extractable with diethyl ether, where it is more stable.



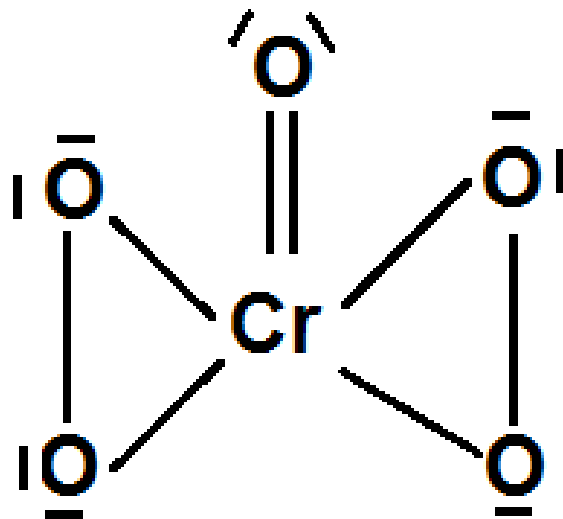
**The reaction is not a redox**

# Chromate ion

Test of  $\text{CrO}_4^{-2}$

With  $\text{H}_2\text{O}_2$  in acidic media:

The reaction is  
not  
a redox



oxidation number of Cr: +6

oxidation number of O:  $1 \times (-2)$

$4 \times (-1)$

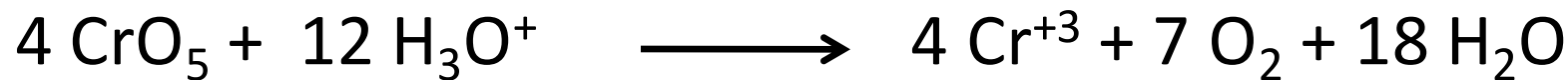
# Chromate ion

## Test of $\text{CrO}_4^{-2}$

### With $\text{H}_2\text{O}_2$ in acidic media:

$\text{CrO}_5$  is unstable in aq. Solution, decomposes to  $\text{Cr}^{+3}$  (green color) and  $\text{O}_2$  is liberated.

To increase stability put the reaction mixture in ice bath and add organic solvent like ether, which extracts  $\text{CrO}_5$  and colored blue and it is more stable in it.

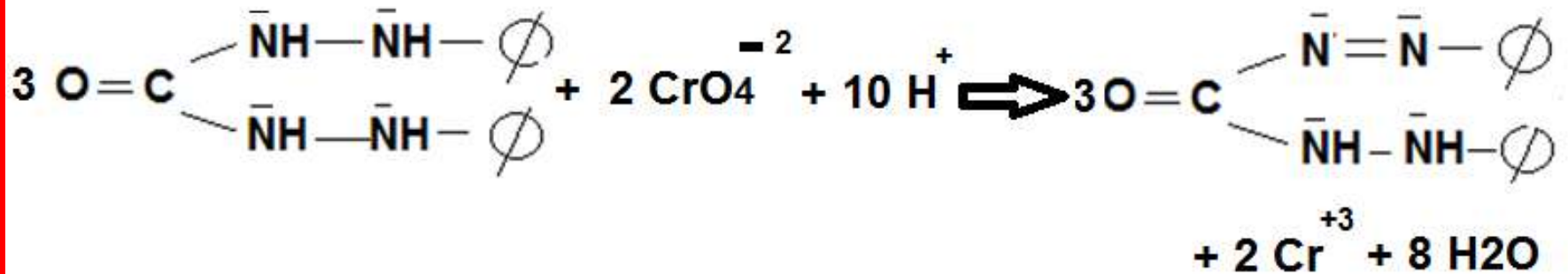


# Chromate ion

## Test of $\text{CrO}_4^{-2}$

### With diphenylcarbazide in acidic media:

Soda extract + acidify with  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  (dil.) + diphenylcarbazide solution  $\longrightarrow$  the solution colored violet (Diphenylcarbazone) **[Redox reaction]**



Diphenylcarbazone  
(Colorless)

Diphenylcarbazone  
(Violet)

# Questions

## Questions:

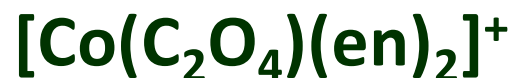
What should happen if iodide is added to chromate in acidified media?? [Hint p 209]

$\text{H}_2\text{O}_2$  is an oxidizing agent, which contains peroxides. How they are formed, how can be removed? [Hint p 208]

You have some salts in laboratory of  $\text{Ni}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Fe}^{+3}$ , which were colored. Why have these transition element cations colors?

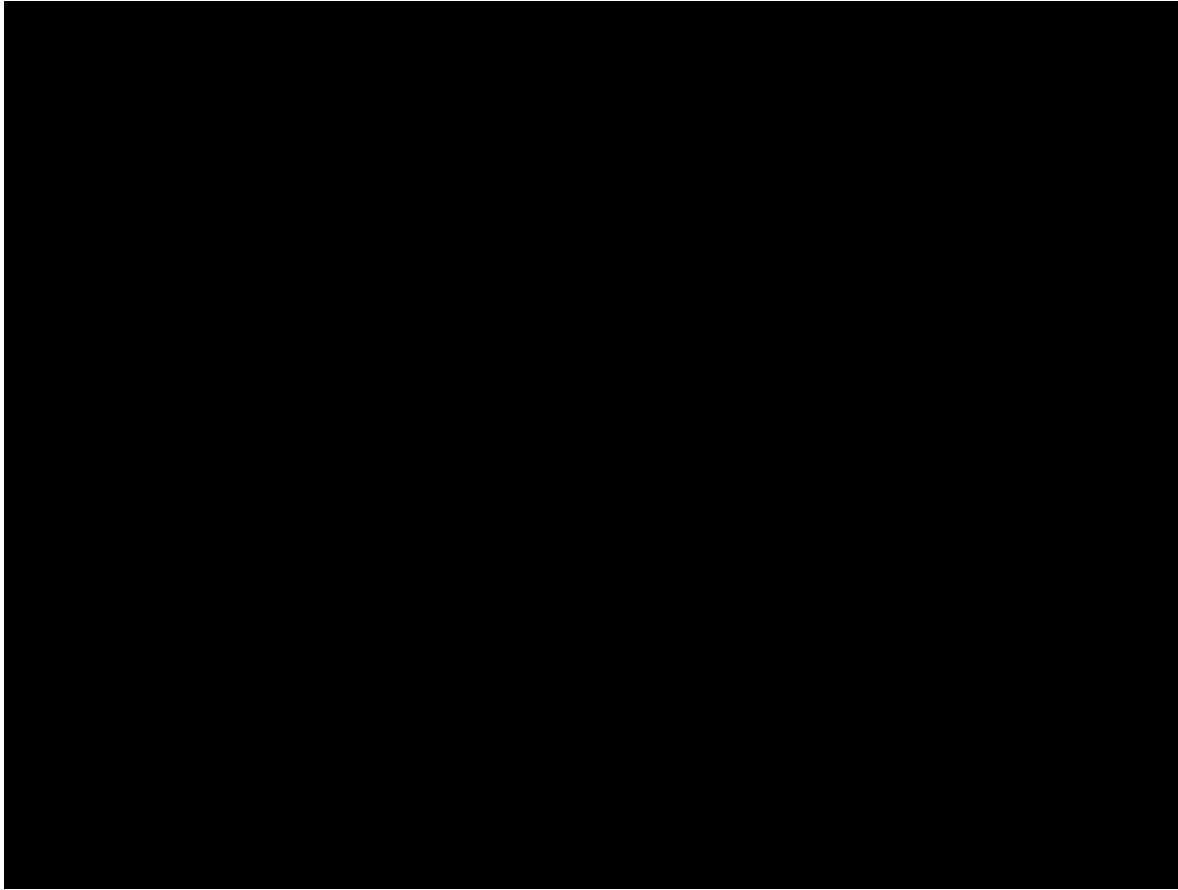
# Questions

Give the IUPAC name, Coordination and oxidation-number:



# Questions

See this video



# Questions

Write the chemical formula for the following:

**Triaquatritiocyanatoiron (III)**

**tetraflourooxocobaltate(III) ion**

**Bis(ethylenediamine)dinitroiron(III) ion**

**Bromochlorodicyanonickelate(II) ion**

**Sodium dithiosulfatoargenate(I)**

**Diaquadichlorodithiocyanatochromate(III) ion**

**Tetrahydroxozincate(II) ion**

**Hexaaquachromium (III) hexacyanoferrate (III)**

**Diamminediaquadichlorocobalt(III) ion**

**Ammonium carbonylpentacyanomanganate(II)**

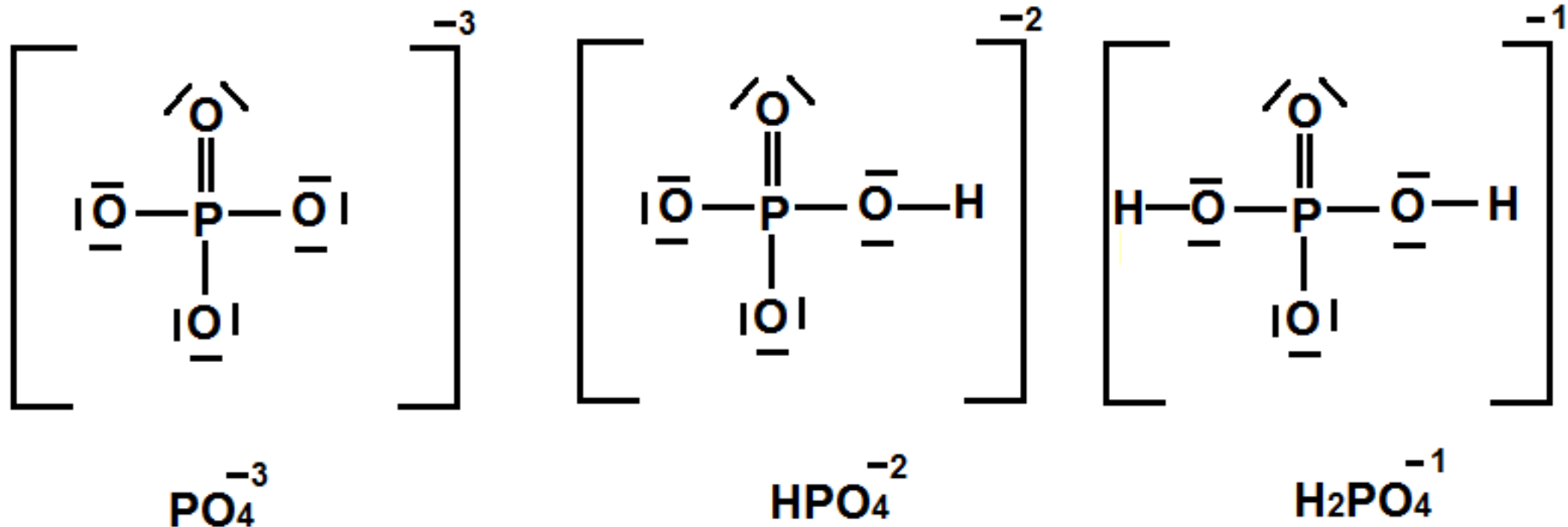
**Hexaaquanickel(II) phosphate**

**Calcium diaquatetracyanocobaltate(III)**



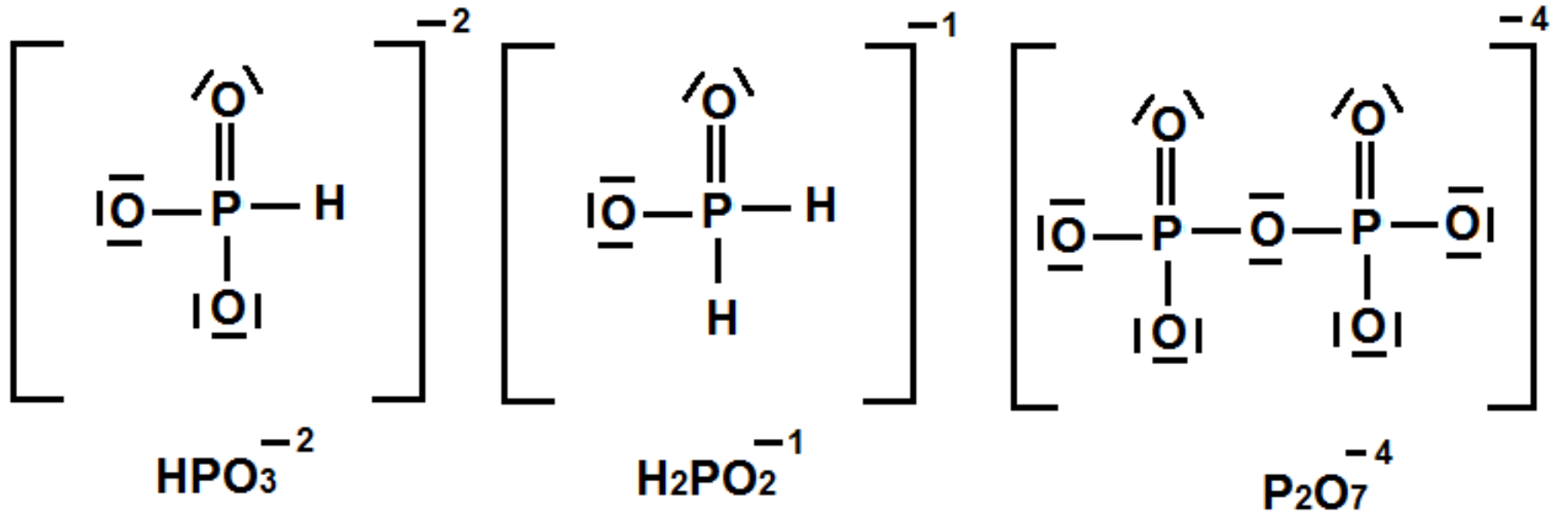
# Phosphate (Orthophosphate) ion

Lewis structure of  $\text{PO}_4^{-3}$



# Phosphate (Orthophosphate) ion

Lewis structure :



Phosphite

Hypophosphite

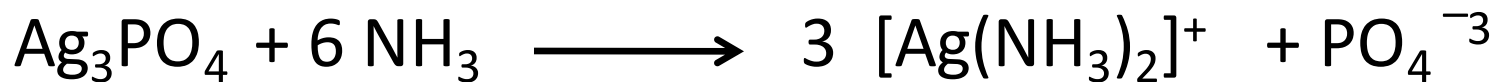
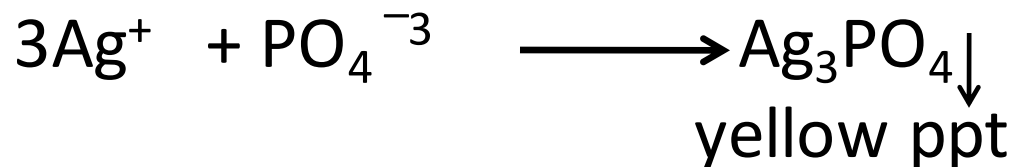
Diphosphate  
(Pyrophosphate)

# Phosphate ion

**Test of  $\text{PO}_4^{-3}$ :**

**With  $\text{AgNO}_3$  solution:**

Soda extract + acidify with  $\text{CH}_3\text{COOH}$  (dil)+  $\text{AgNO}_3$  solution  
→ yellow ppt, soluble in  $\text{NH}_3$ (dil.), in  $\text{HNO}_3$  (Conc.)

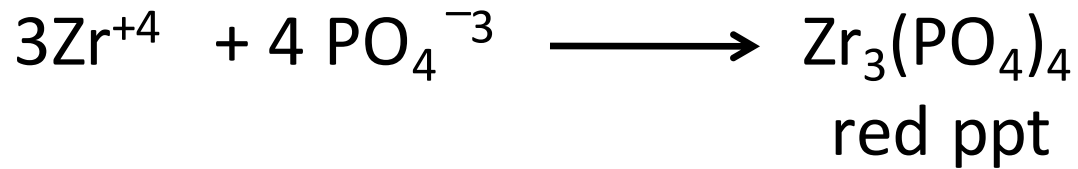


# Phosphate ion

Test of  $\text{PO}_4^{-3}$

With  $\text{Zr}(\text{NO}_3)_4$  solution:

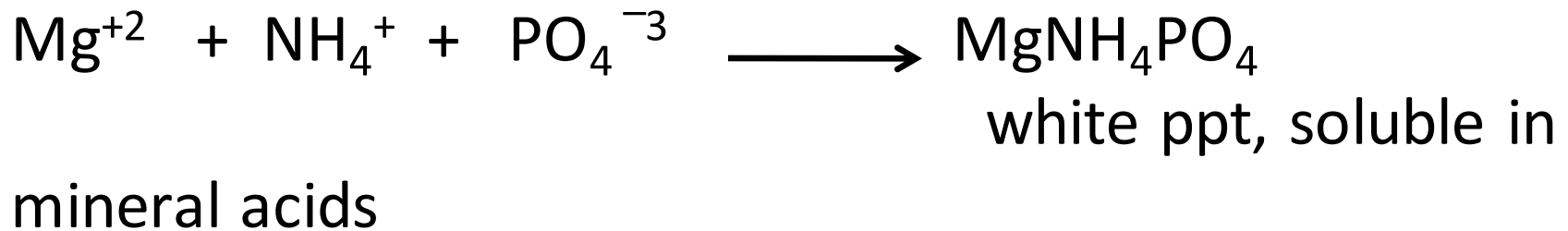
It is used to remove phosphate from a sample



# Phosphate ion

**Test of  $\text{PO}_4^{-3}$**

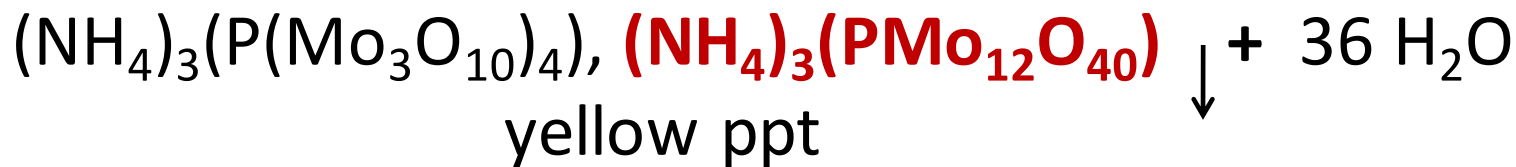
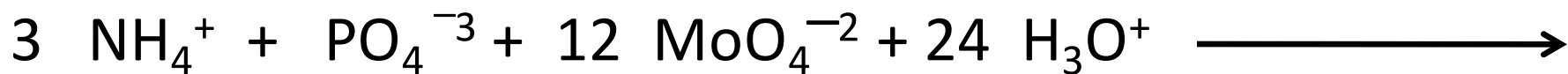
**With Magnesia mixture [ $\text{MgCl}_2$ + ammonia buffer]:**



# Phosphate ion

Test of  $\text{PO}_4^{-3}$

With  $\text{NH}_4^+$  /  $\text{MoO}_4^{-2}$  solution:



**Ammonium dodecamolybdatophosphate**

# Phosphate ion

**Question:**

**What are the main differences between white phosphorus and red phosphorus?**

