

## An Experimental Research on The Chemical Nature of Rusting

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### Abstract

Corrosion of iron occurs by rusting. Rust is a form of hydrated oxide(s) of iron formed as a result of chemical reactions of iron with atmosphere. This '*atmospheric rust formation*' is a slow process. Iron is a chemically '*active*' element and posses the tendency to react with other reagents spontaneously. Artificially '*rusting*' may be induced readily by the use of suitable chemicals and little energy input. Such reactions and methods help us to study the rusting process in a vivid manner. This technique relies on mainly usage of acids and electricity. Experiments were carried out to study the ionization of iron and its subsequent oxidation in to higher oxidation states with suitable conditions and have been elaborated in this paper.

**Keywords:** Rust; Acid; Complex; pH; Precipitate.

**Introduction:** Iron is one of the most useful metals known to mankind. Owing to its strength and ability to blend with other elements like carbon, chromium, to name a few, it finds numerous applications ranging from tiny springs to large ships, wagons, beams, etc. But even this so strong and useful iron is susceptible to rusting followed by consequent corrosion. This, in turn, makes the element brittle with the lapse of time. Now before proceeding further an insight in to what we call '*rust*' is necessary.

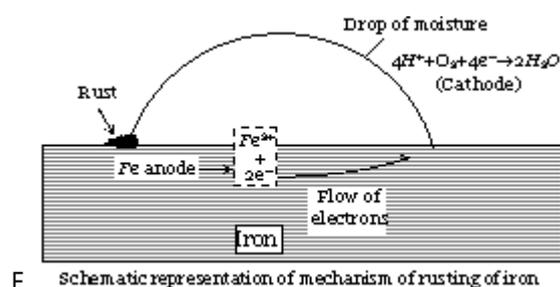
To describe the physical properties first, rust is an orange-brown (or sometimes brown) granular mass often encountered on the surface of iron that lies exposed to the atmosphere. This granular mass is brittle and is attracted by the poles of a magnet. It has an appreciable electrical resistivity thereby making it a poor conductor of electricity. This may be checked by scrapping of some rust from a rusted iron article e.g. a nail and testing the sample with a multimeter.

Chemically rust is an iron oxide formed as a result of a *redox* reaction between iron and oxygen in the presence of moisture. Rust is mainly composed of hydrated iron [III] oxide and iron [III] oxide-hydroxide. The most essential agent for induction of rusting is the presence of moisture. Rusting may be described as a redox reaction.

At anode:



Thus metal atoms in the lattice pass in to the solution as ferrous ions leaving electrons on the metal itself. At the cathode reduction of  $\text{H}^{+}$  in to  $\text{H}_2$  occurs. The hydrogen atoms on the iron surface reduce dissolved oxygen in to water.  $4\text{H}^{+} + \text{O}_2 + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}$ .



E Schematic representation of mechanism of rusting of iron

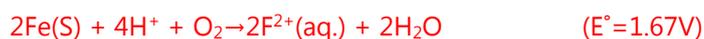
Oxidation half cell reaction:



Reduction half cell reaction:



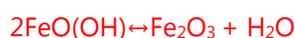
Overall cell reaction:



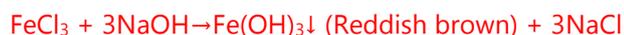
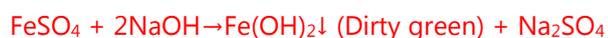
The ferrous ions are oxidized further by atmospheric oxygen to form rust.



The dehydration equilibrium may be given as:

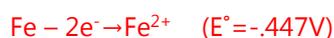


Addition of sodium or ammonium hydroxide to  $\text{Fe}^{2+}$  salts e.g. ferrous sulfate readily precipitates insoluble ferrous hydroxide. In case of  $\text{Fe}^{3+}$  ferric hydroxide is precipitated.



Both are examples of *double displacement* reactions where  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  is already present in aqueous state.

In rusting iron in non-ionised state is present. So the most crucial step towards rust formation is the *ionization of iron* in to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions i.e.



Iron being above hydrogen in the electrochemical series is capable of displacing  $\text{H}^+$  from acids. Hence as regards to ionization iron itself can react with dilute acids giving  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  ions as the case may be. It is known that iron reacts with steam viz.  $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \uparrow$ . But what if a piece of iron is placed in neutral water at S.T.P? Under such a condition no apparent reaction is visible. In order to start the reaction an external input of energy is required. This may be easily accomplished by maintaining the iron piece at a higher potential relative to water. If the positive pole of a battery is connected to the iron piece dipped in water while the negative pole being connected to a metallic wire also dipped in the same water, ionization of iron occurs. This is the same as the arrangement of electrolysis. Under this condition iron readily ionizes in to  $\text{Fe}^{2+}$  ions. If the pH of the solution is made lower by the addition of  $\text{H}^+$ , the tendency to ionize increases. But if a piece of iron is placed in an acid solution (without passage of any current) will the entire iron be converted in to the respective salt? Since iron

can displace hydrogen from acids, ideally this *should* be the case. For e.g. if iron is made to react with HCl, the entire mass should be converted in to soluble chloride viz.  $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$ . Precipitation in any form is unexpected unless the solution is saturated with  $\text{FeCl}_2$ . Identical results are expected in other acids like sulfuric acid and acetic acid. Therefore if an *iron piece is placed in dilute acid solution, there should be no question of rusting*. But experiments conducted in this regard have yielded contradictory results as will be dealt in the subsequent sections.

Removal of rust is also crucial. Two chemicals often used as '*rust removers*' are oxalic acid and sodium bicarbonate. The former is said to convert rust in to a soluble complex that may be washed with water. But does this imply that use of sodium bicarbonate or oxalic acid will prevent rusting? Experiments were carried out to test this.

#### **Apparatus and chemicals:**

1. 5V D.C source
2.  $\text{KMnO}_4$  crystals
3. Oxalic acid crystals
4. Acetic acid (50%)
5. HCl (5M)
6.  $\text{H}_2\text{SO}_4$  (4N)
7. Sodium Chloride crystals
8. Stannous chloride dihydrate
9. Lead acetate trihydrate crystals
10. Barium hydroxide octahydrate crystals
11. Copper chloride dihydrate crystals
12. Sodium bisulfate crystals
13. pH paper
14. Table sugar
15. Hydrogen Peroxide (6%)
16. Boric acid
17. Sodium bicarbonate crystals
18. Sodium carbonate decahydrate crystals

#### **Experimental:**

As mentioned earlier water is essential rust inducing agent. So far as oxygen is concerned, it may be found dissolved in water itself. Using these facts a basic experiment was tried. A clean piece of iron, a nail, was

immersed in 100ml. clean water (free from any impurity) for 7 days at room temperature. After the expiry of the said period, the nail was taken out and observed carefully under a magnifying lens of focal length 25mm so as not to let the even minutest details escape. Not the slightest trace of rust could be encountered. The same experiment was repeated using brine and table sugar i.e. sucrose solution in turn. No variation was noticed i.e. there was no rust formation.

### **Experiment no. 1**

A piece of iron (a nail) was immersed in 100ml. 5M HCl solution. After a few seconds bubbles were seen evolving from its surface. The solution continued to remain colorless even after the expiry of a few hours. The set up was left undisturbed at room temperature for another 24 hours. After this it was observed that though the solution remained colorless, yet the intensity of bubbles from the iron surface had decreased. Evidently the nail had become thinner. The iron nail was fished out and the solution was divided in to two parts, 50ml. each and labeled SOLUTION A and SOLUTION B respectively. As for the iron nail, it was kept in the open for a day without washing. After this period bright orange crystals became visible on its surface. As time passed, the thickness of the orange layer increased, indicating the formation of more crystals. These orange red crystals were scrapped off and were added to SOLUTION A. After a day, yellow insoluble mass settled at the bottom of SOLUTION A. This appeared to be insoluble on the addition of excess HCl. To this 5ml. of 5M H<sub>2</sub>SO<sub>4</sub> was added. After about half an hour, the particles dissolved completely and the colorless solution reappeared. To SOLUTION B excess sodium carbonate was added. Dirty green mass precipitated at the bottom. The solution had evidently become alkaline indicated by a pH paper. It was allowed to stand for a day and no change in the color of the ppt. was observed. Addition of excess H<sub>2</sub>SO<sub>4</sub> was able to dissolve the entire mass and a colorless solution was obtained.

### **Experiment no. 2**

This was a replica of the previous experiment except for the fact that 5M sulfuric acid was used instead of 5M HCl. To colorless solutions labeled SOLUTION A and SOLUTION B respectively were obtained. The reddish orange mass formed as a result of exposing the iron to air was scrapped off and the crystals dissolved in A. Excess sodium carbonate was added to SOLUTION A and SOLUTION B. Dirty green ppt. was obtained. It showed no change in color after a day and promptly dissolved on addition of excess sulfuric acid.

### **Experiment no. 3**

Iron fillings were immersed in 5ml. 6% H<sub>2</sub>O<sub>2</sub> in a clean dry test tube. In no time bubbles were evolved from the iron surface. A brown insoluble mass precipitated at the bottom of the test tube. The ppt. dissolved on the addition of a few drops of H<sub>2</sub>SO<sub>4</sub> resulting in a colorless solution. After a few days the yellow ppt. reappeared. Again a few drops of H<sub>2</sub>SO<sub>4</sub> resulted in the clear solution as before.

### **Experiment no. 4**

An old rusted iron nail was immersed in 100ml. 5M HCl solution. For a few minutes no reaction was visible. It seemed as if the rust coating had rendered the iron surface inert resulting in no reaction. Gradually a yellow insoluble mass could be observed as a result of a relatively slow reaction. Continuous bubbles were observed on the iron piece. The yellow insoluble particles are insoluble in excess HCl but are readily soluble in H<sub>2</sub>SO<sub>4</sub> resulting in the formation of a colorless solution. This was divided in to two equal parts 50ml. each and labeled SOLUTION A and SOLUTION B respectively. Excess NaOH on being added to SOLUTION A gave a yellowish brown ppt. To solution B excess sodium carbonate was added. A dirty green ppt was obtained. The pH of this solution was 10. The yellowish brown ppt did not dissolve in HCl or H<sub>2</sub>SO<sub>4</sub> but the dirty green ppt dissolved in H<sub>2</sub>SO<sub>4</sub>. The same experiment on being repeated with 5M H<sub>2</sub>SO<sub>4</sub>, a lot of 'fizzing' could be observed. A gas was evolved with a pungent odour. Sooty black insoluble particles remain suspended in the solution. These are insoluble in excess HCl as well as H<sub>2</sub>SO<sub>4</sub>.

**Experiment no.5**

Oxalic acid can remove rust following the formation of soluble complexes. With this, in view a rusted piece of iron was immersed in 100ml. oxalic acid solution for several hours. A lime green solution was obtained. The iron piece was fished out, and the solution was left undisturbed for another 24 hours at room temperature. No change of color was perceived. This solution was divided into two parts 50ml. each and labeled SOLUTION A and SOLUTION B respectively. To SOLUTION A  $\text{KMnO}_4$  acidified with HCl and to SOLUTION B  $\text{KMnO}_4$  acidified with  $\text{H}_2\text{SO}_4$  was added. A retained the purple hue of potassium permanganate but SOLUTION B turned completely colorless. To the colorless solution excess sodium carbonate was added so as to make the solution completely alkaline. Dirty green ppt. was obtained. The ppt. dissolved in excess  $\text{H}_2\text{SO}_4$  and a clear colorless solution was obtained.

The above mentioned experiments were conducted with out input of external energy i.e. iron (or rust) was allowed to react on its own. The reaction being spontaneous proceeded without difficulty. In the succeeding experiments energy input in the form of electricity was given so as to see whether the reactions and consequent products alter in any way and also to find out how electricity would affect rust formation.

**Experiment no. 6**

A 250 ml. beaker was filled with 100ml. 50% acetic acid. This was electrolyzed using a 5V D.C source having iron (without rust) as anode and copper as cathode. As soon as the current was switched ON bubbles started evolving from both electrodes the vigor being higher at the cathode. Slowly the color of the solution changed to dark brown along with the formation of brown-black insoluble particles. These particles remained insoluble on the addition of excess acetic acid. Addition of excess  $\text{H}_2\text{SO}_4$  produced no significant effect either. Addition of barium hydroxide resulted in a white ppt. the dark brown solution remaining unchanged in color. The white ppt. was filtered out. On diluting with water so as to make the vol. 200ml. a brownish orange solution was obtained.

**Experiment no. 7**

100ml.  $\text{H}_2\text{SO}_4$  was electrolyzed using Fe anode and Cu cathode connected to a 5V D.C source. Bubbles were seen at both electrodes. The soln. remained colorless even after the expiry of 2 hours. The current was switched off and the setup was left undisturbed for another 24 hours. The solution had turned pale yellow during the period. 10ml. of 5M  $\text{H}_2\text{SO}_4$  was added to it and the contents were kept under bright sunlight. After an hour a clear colorless solution was obtained. Addition of excess sodium carbonate resulted in a dirty green ppt. Addition of a few drops of  $\text{H}_2\text{SO}_4$  changed the color to orange-brown. This ppt. was filtered and dried under the sun.

**Experiment no.8**

100ml. stannous chloride solution acidified with 5ml. 5M HCl was electrolyzed using Fe anode and Cu cathode supplied from a 5V D.C source. Bubbles were observed at both electrodes. Glittering ash colored particles are seen sticking to the cathode. Slowly the solution assumed a green appearance. The green hue deepened as more iron got consumed at anode. Addition of  $\text{H}_2\text{SO}_4$  brought no apparent change. Addition of M/50  $\text{KMnO}_4$  (acidified) caused immediate discoloration of the purple hue the green color remaining unaffected. Addition of excess sodium carbonate produced a dirty green ppt. which on being left for a while turned partly yellow. This ppt. was filtered and dried under the sun. Bright orange brown crystals resulted. These particles were found to be soluble in  $\text{H}_2\text{SO}_4$  (resulting in a clear colorless solution) but not in HCl, the strength of both being 5M.

**Experiment no. 9**

A solution 100ml. in volume containing a mixture of oxalic acid and a pinch ammonium sulfate (so as to increase the conductivity) was electrolyzed using iron electrodes. Bubbles were visible at both electrodes. A greenish-yellow solution was obtained. On prolonged electrolysis dirty green insoluble mass was synthesized. Bright orange crystals formed on the surface of the cathodes on exposing to atmosphere. The mass was insoluble in 50% acetic acid though a lot of 'fizzing' could be heard. These crystals were also insoluble in oxalic acid.

**Experiment no. 10**

Acidified M/100  $\text{KMnO}_4$  was electrolyzed using a Fe anode and copper cathode supplied from a 5V D.C source. Bubbles were visible at both electrodes. The color of the solution changed from purple to deep red, then to brown and finally got decolorized. On prolonged electrolysis, the solution retained its clear colorless nature. The anode reduced in volume, evidence of its dissolution in the solution. Addition of excess sodium carbonate resulted in a dirty brown ppt, which on being filtered and dried gave bright orange brown crystals. These crystals were soluble in  $\text{H}_2\text{SO}_4$ , and a clear colorless solution was obtained.

**Experiment no. 11**

Sodium bisulfate is an acid salt of sulfuric acid. Hence its solution is acidic in nature. 5g. of sodium bisulfate was dissolved in 100ml. water and the resultant pH of the solution was found to be 6. It was then electrolyzed using a rusted iron anode and copper cathode. Bubbling could be observed at both electrodes. Initially, the solution continued to remain clear and colorless. After 5 hours dirty green insoluble mass was noticed sticking at the anode surface. After a few days the solution turned pale yellow, but no significant insoluble mass was observed.

**Experiment no. 12**

Sodium bicarbonate acts as a rust remover. To test its role in the formation of rusts an solution of the same was prepared by dissolving 2g. solute in 50ml. water to get a solution of pH 9. Electrolysis was conducted using a rusted Fe anode and a copper cathode. On switching ON the supply, nothing was observed for the first few minutes. Then bubbles became visible at cathode. It was seen with the unaided eye that a dirty green 'something' was leaving the anode and was passing in to the solution. After a few hours of passage of current a pale yellow solution along with some ppt. was observed. After a day no change in color of the solution or particles could be observed. Addition of excess  $\text{H}_2\text{SO}_4$  resulted in a clear colorless solution resembling water. To this excess sodium hydroxide pellets were added with shaking. Yellow insoluble mass was formed.

**Experiment no. 13**

It is well known that iron would displace copper from a solution containing  $\text{Cu}^{2+}$  ions. This copper should be precipitated and iron would pass in to the solution as  $\text{Fe}^{2+}$ . 100ml. copper chloride solution was prepared. 10ml.  $\text{H}_2\text{SO}_4$  (5M) was added to prevent hydrolysis and precipitation of insoluble hydroxides. The color of the solution was pale blue evidently due to the presence of  $\text{Cu}^{2+}$ . A clean piece of iron was immersed in this solution and kept under bright sunlight. After a few hours no trace of iron was to be found. The solution had turned deep greenish-blue with the precipitation of reddish mass. This was very different from the previous experiments where dissolution of iron had resulted in a colorless solution. To this sodium carbonate was added till pH=7 was reached. Precipitation of green mass was observed. A thin film of wet ppt. was applied to a glass plate and was allowed to dry under the sun. On drying the color changed to yellow.

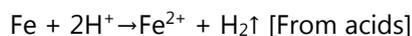
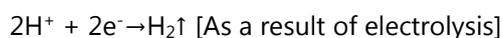
**Experiment no. 14**

A 100ml. NaCl solution was electrolyzed using Fe electrodes. Bubbles were visible at the cathode only. Dirty green insoluble mass was visible issuing from the anode. This slowly changed its hue to orange-yellow. The anode became thinner, indicating its consumption. The cathode on the other hand accumulated the orange-

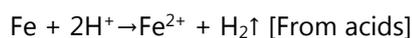
yellow mass. The cathode when exposed to air gave bright orange-brown crystals. These crystals were scrapped off and treated in turn with  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ . The particles dissolved in the former yielding a colorless clear solution while were not much soluble in the later. To the orange brown ppt.  $\text{H}_2\text{SO}_4$  was added and a clear colorless solution was obtained. This colorless solution on being treated with excess sodium carbonate resulted in a dirty green ppt.

**Observations:** Rust may be described as hydrated ferric oxide. Neutral water as well as brine (also neutral in nature) couldn't induce rust formation over a small period of time. Strong acids like  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  on the other hand dissolved iron as  $\text{Fe}^{2+}$  which in solution state remained colorless. These ions were indeed  $\text{Fe}^{2+}$ , which became evident once the pH of the solution was increased above 7 (by addition of excess sodium carbonate) resulting in the formation of dirty green insoluble mass. Under certain situations yellow hue became visible which might have been due to the partial oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  species. The iron while immersed in the acid solution did not exhibit any tendency of rust formation. However once the iron piece id taken out of the acid and exposed to air, it readily gave reddish orange crystals. It appeared as if  $\text{H}_2\text{SO}_4$  was a better solvent for these crystals compared with  $\text{HCl}$  of the same molar strength. Hydrogen peroxide appeared to be an extremely good rust inducing agent which may be attributed to its oxidizing property which readily oxidized iron in to insoluble  $\text{Fe}^{3+}$ . Organic acids like acetic acid and oxalic acid showed the tendency to form soluble  $\text{Fe}^{3+}$  (evident from the dark brown color) complexes rather than simple  $\text{Fe}^{2+}$ . However insoluble particles were obtained at the same time which depended mainly on the acid concentration. Apparently insoluble hydroxides were difficult to precipitate from these complexes.

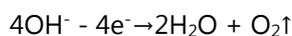
Maintaining iron positive w.r.t solution by using an electrolytic arrangement i.e. electrolysis of acid solutions caused dissolution of  $\text{Fe}$  in to  $\text{Fe}^{2+}$ , which remained in the solution. Maintaining iron negative would in no way retard the ionization of  $\text{Fe}$  in the presence of acid. In that case  $\text{H}_2$  would be evolved at cathode in two different ways viz.



Similarly, use of  $\text{Fe}$  anode also caused two different reactions viz.



A little amount of oxygen might have been liberated as a result of side reactions viz.



Usage of non ionizing cathode like  $\text{Cu}$  exhibits a tendency to attract insoluble oxide-hydroxide compounds during electrolysis. These on exposure to atmosphere readily yielded rust. These particles were soluble in  $\text{H}_2\text{SO}_4$  but not so much in  $\text{HCl}$  of the same molar strength. The observations made during electrolysis have been tabulated under:—

**Table No. 1**

Solution used	Anode used	Cathode used	Current in mA	Solution color	Precipitation agent	Ppt. color	Solubility of ppt. in H <sub>2</sub> SO <sub>4</sub>	Solubility of ppt. in HCl
HCl	Fe	Cu	50	Colorless	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	Dirty green	Soluble	Moderately soluble
H <sub>2</sub> SO <sub>4</sub>	Fe	Cu	80	Colorless	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	Dirty green	Soluble	Moderately soluble
Oxalic acid	Fe	Fe	20	Lime green	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	Almost nil	—	—
Acetic acid	Fe	Fe	25	Dark brown	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	Almost nil	—	—
NaHSO <sub>4</sub>	Rusted Fe	Cu	62	Colorless (almost)	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	Dirty green	Soluble	Soluble
Acidified KMnO <sub>4</sub>	Fe	Cu	80	Colorless	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	Dirty brown	Soluble	Almost Soluble
NaHCO <sub>3</sub>	Fe	Cu	35	Pale yellow insoluble mass	NaOH	Yellow	Soluble	Soluble
SnCl <sub>2</sub> .2H <sub>2</sub> O	Fe	Cu	75	Green	Na <sub>2</sub> CO <sub>3</sub> .10H <sub>2</sub> O	Dirty green Partly yellow	Soluble	Insoluble
NaCl	Fe	Fe	90	Yellow brown insoluble mass	—	—	Soluble	Soluble

**Results and discussions:** Iron rusts spontaneously when atmospheric conditions are 'favorable.' The essential conditions are availability of oxygen and water. Experiments show that rust can be synthesized under laboratory conditions, with or without input of energy in a very short time. In the former case Fe<sup>3+</sup> species are more easily formed, the iron having been oxidized in to Fe<sup>2+</sup> using suitable reagents. The following points are noteworthy:-

1. Mineral acids dissolve iron to give Fe<sup>2+</sup> which forms a thin film on the metal surface. This film on exposure to the atmosphere gets oxidized to Fe<sup>3+</sup> in a very short time, thereby yielding rust.
2. H<sub>2</sub>SO<sub>4</sub> is more potent in dissolving iron as Fe<sup>2+</sup> when compared with HCl bearing the same molarity.

3. Hydrogen Peroxide reacts with Fe very rapidly forming insoluble  $\text{Fe}^{3+}$ , which on drying gives rust. The same insoluble  $\text{Fe}^{3+}$  dissolves very readily in  $\text{H}_2\text{SO}_4$  giving a colorless solution.
4. Organic acids having a single carboxylic group e.g. acetic acid form soluble salt having dissolved  $\text{Fe}^{3+}$  which imparts characteristic dark brown color to the solution. In these solutions  $\text{Fe}^{3+}$  is difficult to precipitate as insoluble carbonates or hydroxides.
5. Oxalic acid forms soluble complexes with little insoluble mass which remain suspended in the solution. Exposure to atmosphere renders the iron surface rusty.
6. Application of D.C in to mineral acids rapidly dissolves iron as soluble  $\text{Fe}^{2+}$  at anode. The cathode (if iron is used) dissolves spontaneously despite the negative potential applied.
7. In the above case exposing the cathode to the atmosphere readily yields rust.
8. Neutral and alkaline solutions when electrolyzed using Fe electrodes yield insoluble  $\text{Fe}^{3+}$  at anode which remain suspended in the solution as a scummy mass. Insoluble  $\text{Fe}^{3+}$  is attracted towards the cathode and stick to it. Exposure to the atmosphere and consequent drying yields rust.
9. Acidic salt solutions on electrolysis dissolve Fe as  $\text{Fe}^{2+}$  which is precipitated using  $\text{OH}^-$  or  $\text{CO}_3^{2-}$  giving characteristic dirty green ppt.
10. Under all circumstances  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  are better precipitating agents compared with  $\text{Ba}(\text{OH})_2$  which itself forms insoluble white ppt. The following reaction occurs while using sodium carbonate:-  
$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\text{CO}_3$$
 [Due to hydrolysis of sodium Carbonate]. The  $\text{NaOH}$  so obtained supplies hydroxyl ions and precipitates insoluble hydroxides.
11.  $\text{H}_2\text{SO}_4$  is a better solvent for insolubilities compared with  $\text{HCl}$  of the same molar strength.
12. Generally  $\text{H}_2\text{SO}_4$  on dissolving precipitates gives colorless solutions containing soluble  $\text{Fe}^{2+}$  which is precipitated as a characteristic dirty green mass on increasing the pH of the solution.
13. An exception to the above case is the reaction between acidified copper chloride solution and iron wherein a greenish blue solution is obtained after precipitation of the entire  $\text{Cu}^{2+}$  contained in the solution by use of iron. On increasing the solution's pH above 8 dirty green mass is precipitated. The greenish blue solution is recovered by addition of excess  $\text{H}_2\text{SO}_4$ .
14. Acidified  $\text{KMnO}_4$  being a very strong oxidizing agent oxidizes iron in to  $\text{Fe}^{3+}$  directly. Though the solution remains colorless, addition of sodium carbonate precipitates brown  $\text{Fe}(\text{OH})_3$ .

## Conclusion

Rusting of iron is mainly the formation of insoluble oxide-hydroxide species on the iron surface. Its synthesis results from slow chemical reactions between iron and atmospheric reagents. Artificial rusting may be induced very readily by the use of mineral acids and the use of low amperage direct current electricity. Compounds which remove rusting like oxalic acid mainly form colored iron complexes rather than simple  $\text{Fe}^{2+}$  species. Mineral acid mainly oxidize iron in to soluble  $\text{Fe}^{2+}$  salts. The thin film of  $\text{Fe}^{2+}$  deposited on the iron surface under such conditions when exposed to atmosphere get oxidized to  $\text{Fe}^{3+}$  yielding rust which may be detected by the characteristic color of the layer deposited on the surface. Neutral salt solutions like  $\text{NaCl}$  and  $\text{KCl}$  when electrolyzed using Fe electrodes give insoluble  $\text{Fe}^{3+}$  species. However no apparent reaction is visible in the absence of electricity. Salts whose solutions are alkaline in nature like sodium carbonate solutions exhibit the same tendency. In this case the alkaline nature of the solution in no way hampers rust formation on the

application of electricity. Insoluble  $\text{Fe}^{3+}$  is synthesized in such a case. On the other hand solutions of salts which are acidic in nature for eg. Sodium bisulfate solution rust like mineral acids gives soluble  $\text{Fe}^{2+}$  which is precipitated as dirty green  $\text{Fe}(\text{OH})_2$  on the addition of alkalis. The metal surface on exposure to the atmosphere yields rust as usual. Organic acids give colored soluble complexes which are difficult to precipitate in the mother liquor. A small amount of iron is consumed as insoluble compounds but these do not resemble particles of rust. Sulfuric acid acts as very good solvent for insoluble compounds formed as a result of the reactions. Generally colorless solutions are obtained in maximum cases which contain soluble  $\text{Fe}^{2+}$  which may be precipitated by the addition of sodium carbonate.

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**References:**

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