Some chemistry of Iron

History

For some background information on the origin and history of Iron see the Rossell Forge Site in Andorra

Introduction

Iron is the most abundant transition metal on Earth (62000 ppm).

The International Centre for Environmental and Nuclear Sciences (ICENS) has an on-going programme of mapping the geochemical content of Jamaica. 'A Geochemical Atlas of Jamaica' was published in 1995 and is available from Amazon or ICENS. The results found for Iron are shown below (courtesy of Prof G.C. Lalor).

Properties of iron

An excellent site for finding the properties of the elements, including iron, is at

webElements periodic table
Extraction of Iron

Iron is generally extracted in a Blast furnace.

Iron Halides

<table>
<thead>
<tr>
<th>Formula</th>
<th>Colour</th>
<th>MP</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeF₃</td>
<td>green</td>
<td>1000 sublimes</td>
<td></td>
</tr>
<tr>
<td>FeCl₃</td>
<td>black</td>
<td>306 sublimes</td>
<td>BiI₃</td>
</tr>
<tr>
<td>FeBr₃</td>
<td>dark-red-brown</td>
<td>decomposes above 200°C</td>
<td>BiI₃</td>
</tr>
</tbody>
</table>

Preparations:

Prepared by reaction of Fe + X₂ → FeX₃.
Note that FeBr₃.aq when boiled gives FeBr₂.

An important application of the chloride is as an etching material for copper electrical printed circuits.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Colour</th>
<th>MP</th>
<th>BP</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeF₂</td>
<td>white</td>
<td>1000</td>
<td>1100</td>
<td>rutile</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>pale yellow-grey</td>
<td>670-674</td>
<td>-</td>
<td>CdCl₂</td>
</tr>
<tr>
<td>FeBr₂</td>
<td>yellow-green</td>
<td>684</td>
<td>-</td>
<td>CdI₂</td>
</tr>
<tr>
<td>FeI₂</td>
<td>grey</td>
<td>red heat</td>
<td>-</td>
<td>CdI₂</td>
</tr>
</tbody>
</table>

Preparations:

Fe + HX at red heat → FeX₂ for X=F,Cl and Br
Fe + I₂ → FeI₂

Iron Oxides and Aqueous Chemistry

<table>
<thead>
<tr>
<th>Formula</th>
<th>Colour</th>
<th>Oxidation State</th>
<th>MP</th>
<th>Structure / comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>red brown</td>
<td>Fe³⁺</td>
<td>1560d</td>
<td>α-form Haematite, β-form used in cassettes</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>black</td>
<td>Fe²⁺/³⁺</td>
<td>1538d</td>
<td>magnetite/lodestone</td>
</tr>
<tr>
<td>FeO</td>
<td>black</td>
<td>Fe²⁺</td>
<td>1380</td>
<td>pyrophoric</td>
</tr>
</tbody>
</table>

Preparations:
α-Fe₂O₃ is obtained by heating alkaline solutions of Fe(III) and dehydrating the solid formed.
The Fe(III) ion is strongly acidic:

\[
[\text{Fe(H}_2\text{O)_6}]^{3+} + \text{H}_2\text{O} \rightarrow [\text{Fe(H}_2\text{O)_5(OH)}]^2+ + \text{H}_3\text{O}^+ \quad \text{K}=10^{-3.05}
\]

\[
[\text{Fe(OH)(H}_2\text{O)_5}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Fe(OH)_2(H}_2\text{O)_4}]^+ + \text{H}_3\text{O}^+ \quad \text{K}=10^{-3.26}
\]

The Fe\(^{2+}\) ion is barely acidic:

\[
[\text{Fe(OH)(H}_2\text{O)_5}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Fe(OH)_2(H}_2\text{O)_4}]^+ + \text{H}_3\text{O}^+ \quad \text{K}=10^{-9.5}
\]

**Rusting of Iron**

The economic importance of rusting is such that it has been estimated that the cost of corrosion is over 1\% of the world's economy. (25\% of the annual steel production in the USA goes towards replacement of material that has corroded.)

Rusting of iron consists of the formation of hydrated oxide, Fe(OH)\(_3\) or FeO(OH), and is an electrochemical process which requires the presence of water, oxygen and an electrolyte - in the absence of any one of these rusting does not occur to any significant extent. In air, a relative humidity of over 50\% provides the necessary amount of water and at 80\% corrosion is severe.

The process is complex and will depend in detail on the prevailing conditions, for example, in the presence of a small amount of O\(_2\) the anodic oxidation will be: Fe → Fe\(^{2+}\) + 2e\(^-\)

and the cathodic reduction: 2H\(_2\)O + 2e\(^-\) → H\(_2\) + 2OH\(^-\)

i.e. overall: Fe + 2H\(_2\)O → H\(_2\) + Fe\(^{2+}\) + 2OH\(^-\)

i.e Fe(OH)\(_2\) and this precipitates to form a coating that slows further corrosion.

If **both water and air are present**, then the corrosion can be severe with oxygen now as the oxidant the anodic oxidations: 2Fe → 2Fe\(^{2+}\) + 4e\(^-\)

and the cathodic reduction: O\(_2\) + 2H\(_2\)O + 4e\(^-\) → 4OH\(^-\)

i.e. overall: 2Fe + O\(_2\) + 2H\(_2\)O → 2Fe(OH)\(_2\) with limited O\(_2\), magnetite is formed (Fe\(_3\)O\(_4\)), otherwise the familiar red-brown Fe\(_2\)O\(_3\) H\(_2\)O “rust” is found.

The presence of an electrolyte is required to provide a pathway for the current and, in urban areas, this is commonly iron(II) sulfate formed as a result of attack by atmospheric SO\(_2\) but, in seaside areas, airborne particles of salt are important. The anodic oxidation of the iron is usually localized in surface pits and crevices which allow the formation of adherent rust over the remaining surface area.
The illustration above shows 2 nails immersed in an agar gel containing phenolphthalein and [Fe(CN)₆]³⁻. The nails can be seen to have started to corrode since the Prussian blue formation indicates the formation of Fe(II) (the Anodic sites which correspond to the end of the nails and the bend in the middle). The phenolphthalein (change to pink in presence of base) shows the build up of OH⁻ and shows that essentially the whole length of the nail is acting as the cathode.

 Eventually the lateral extension of the anodic area undermines the rust to produce loose flakes. Moreover, once an adherent film of rust has formed, simply painting over gives but poor protection. This is due to the presence of electrolytes such as iron(II) sulfate in the film so that painting merely seals in the ingredients for anodic oxidation. It then only requires the exposure of some other portion of the surface, where cathodic reduction can take place, for rusting beneath the paint to occur.

The protection of iron and steel against rusting takes many forms, including: simple covering with paint; coating with another metal such as zinc (galvanizing) or tin; treating with "inhibitors" such as chromate(VI) or (in the presence of air) phosphate or hydroxide, all of which produce a coherent protective film of Fe₂O₃. Another method uses sacrificial anodes, most usually Mg or Zn which, being higher than Fe in the electrochemical series, are attacked preferentially. In fact, the Zn coating on galvanized iron is actually a sacrificial anode.

**Rust prevention**

Galvanised iron is the name given to iron that has been dipped into molten zinc (at about 450°C) to form a thin covering of zinc oxide. One level of rust prevention occurs through a purely mechanical method since it is more difficult for water and oxygen to reach the iron. Even if the layer becomes somewhat worn though another reason corrosion is inhibited is that the anodic processes are affected.

The E° for zinc oxidation (0.76V) is considerably more positive that E° for iron oxidation (0.44V) so the zinc metal is oxidized before the iron. Zn²⁺ is lost to the solution and the zinc coating is called a **sacrificial anode**.

Foodstuffs are often distributed in "tin cans" and it has generally been easier to coat the iron with a layer of tin than with zinc. Another benefit is that tin is less reactive then zinc so does not react as readily with the contents. However the electrode oxidation potential for Sn/Sn²⁺ is 0.14V so once again iron becomes the anode and rust will occur once the coating is worn or punctured.

Another technique is to treat the iron surface with dichromate solution.
2 Fe + 2 Na₂CrO₄ + 2 H₂O → Fe₂O₃ + Cr₂O₃ + 4 NaOH

The iron oxide coating formed has been found to be impervious to water and oxygen so no further corrosion can occur.

The FeIII/FeII Couples

A selection of standard reduction potentials for some iron couples is given below, from which the importance of the participating ligand can be judged. Thus Fe(III), being more highly charged than Fe(II) is stabilized (relatively) by negatively charged ligands such as the anions of edta and derivatives of 8-hydroxyquinoline, whereas Fe(II) is favoured by neutral ligands which permit some charge delocalization in π-orbitals (e.g. bipy and phen).

<table>
<thead>
<tr>
<th>Table E° at 25°C for some FeIII/FeII couples in acid solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeIII</td>
</tr>
<tr>
<td>[Fe(phen)₃]³⁺</td>
</tr>
<tr>
<td>[Fe(bipy)₃]³⁺</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]³⁺</td>
</tr>
<tr>
<td>[Fe(CN)₆]³⁻</td>
</tr>
<tr>
<td>[Fe(C₂O₄)₃]²⁻</td>
</tr>
<tr>
<td>[Fe(edta)]⁻</td>
</tr>
<tr>
<td>[Fe(quin)₃]</td>
</tr>
</tbody>
</table>

where quin⁻ = 5-methyl-8-hydroxyquinolinate,

The value of E° for the couple involving the simple aquated ions, shows that Fe(II)(aq) is thermodynamically stable with respect to hydrogen; which is to say that Fe(III)(aq) is spontaneously reduced by hydrogen gas. However, under normal circumstances, it is not hydrogen but atmospheric oxygen which is important and, for the process 1/2O₂ + 2H⁺ + 2e⁻ → H₂O, E° = 1.229 V, i.e. oxygen gas is sufficiently strong an oxidizing agent to render [Fe(H₂O)₆]²⁺ (and, indeed, all other Fe(II) species in the Table) unstable with respect to atmospheric oxidation. In practice the oxidation in acidic solutions is slow and, if the pH is increased, the potential for the Fe(III)/Fe(II) couple remains fairly constant until the solution becomes alkaline and hydrous Fe₂O₃ (considered here for convenience to be Fe(OH)₃) is precipitated. But here the change is dramatic, as explained below.

The Redox chemistry of Iron is pH dependent:

Fe(H₂O)₆³⁺ + e⁻ → Fe(H₂O)₆²⁺ E°=0.771V

The actual potential E of the couple is given by the Nernst equation,

E = E° when all activities are unity. However, once precipitation occurs, the activities of the iron species are far from unity; they are determined by the solubility products of the 2 hydroxides. These are:

[Fe(III)][OH⁻]² ~ 10⁻¹⁴ (mol dm⁻³)³ and
[Fe(III)][OH⁻]³ ~ 10⁻³⁶ (mol dm⁻³)⁴

Therefore when [OH⁻] = 1 mol dm⁻³; [FeII]/[FeIII] ~ 10²²
Hence \( E = 0.771 - 0.05916 \log_{10}(10^{22}) = 0.771 - 1.301 = -0.530 \text{ V} \)

Thus by making the solution alkaline the sign of \( E \) has been reversed and the susceptibility of Fe(II)(aq) to oxidation (i.e. its reducing power) enormously increased. In base the white, precipitated Fe(OH)_2 and FeCO_3 is a good reducing agent and samples are rapidly darkened by aerial oxidation and this explains why Fe(II) in alkaline solution will reduce nitrates to ammonia and copper(II) salts to metallic copper.

**Representative complexes**

An important Fe complex which is used in Actinometry since it is photosensitive is \( K_3[Fe(C_2O_4)_3].3H_2O \). It can be prepared from:

Fe(C_2O_4) in K_2C_2O_4 by reacting with H_2O_2 in H_2C_2O_4 to give green crystals. It is high spin \( \mu = 5.9 \text{ BM} \) at 300K and has been resolved into its two optical isomers, although they racemise in less than 1 hour.

In light the reaction is:

\[
K_3Fe(C_2O_4)_3.3H_2O \rightarrow 2Fe(C_2O_4) + 2CO_2 + 3K_2C_2O_4
\]

Another important complex is used as a redox indicator since the Fe(II) and Fe(III) complexes are both quite stable and have different colours:

\[
\text{Fe(phen)}_3^{3+} + \text{e}^- \rightarrow \text{Fe(phen)}_3^{2+} \quad \quad \text{E}^\circ=1.12\text{V}
\]

The ligand is 1,10 phenanthroline and the indicator is called ferroin.

An interesting example of how acetates can bind to metal ions is seen in what has been described as a "molecular ferric wheel".

The structure was determined in 1990 and contains \([\text{Fe(OMe)}_2(\text{O}_2\text{CCH}_2\text{Cl})]_{10}\)


**References:**

"Complexes and First-Row Transition Elements", D. Nicholls
"Chemistry of the Elements", Greenwood and Earnshaw

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