# 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).
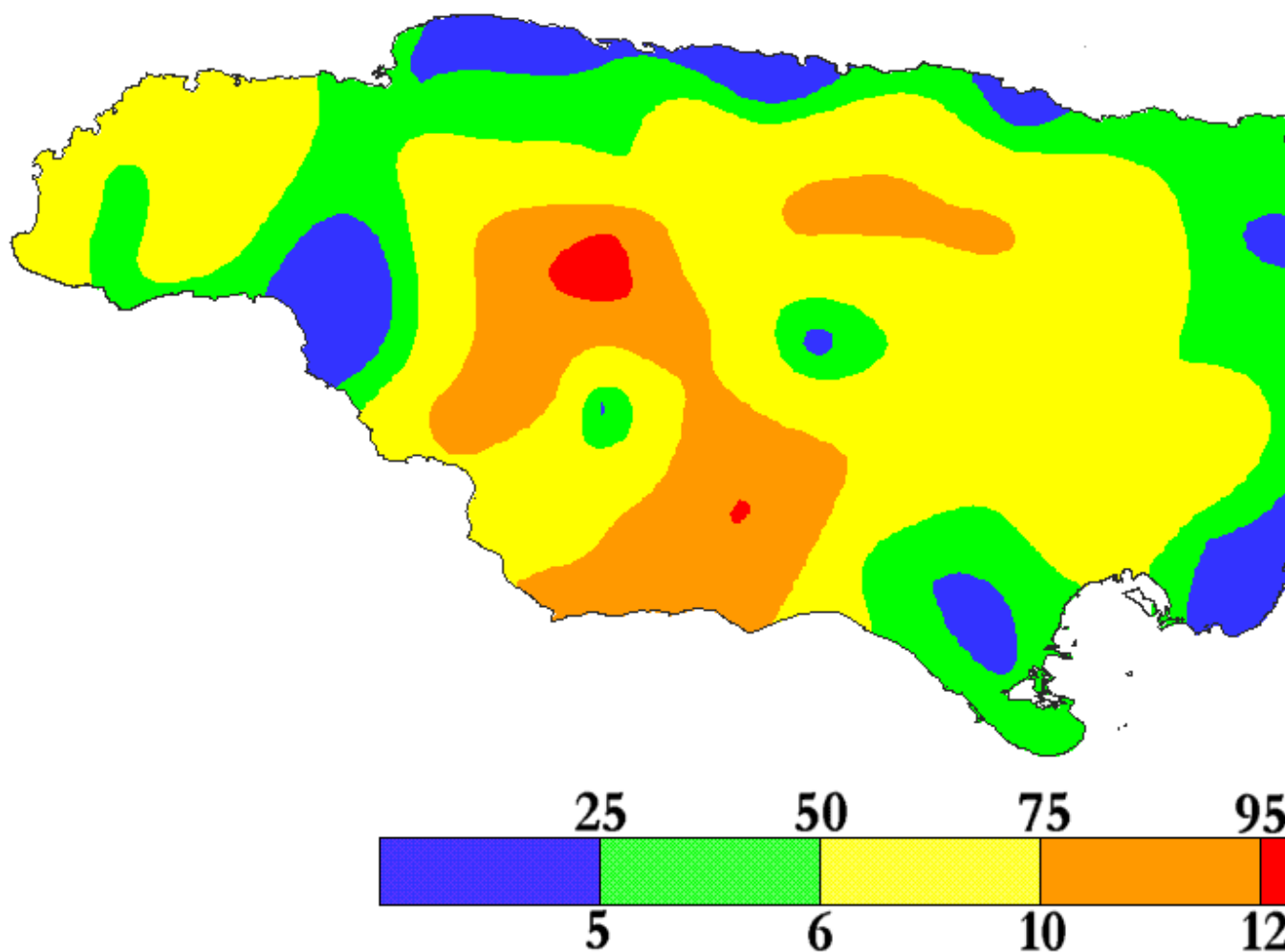
Properties of iron

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 <u>Blast furnace</u>.

Iron Halides

Iron(III) halides

Formula	Colour	MP	Structure
FeF_3	green	1000 sublimes	
$FeCl_3$	black	306 sublimes	<u>BiI_3</u>
$FeBr_3$	dark-red-brown	decomposes above 200°C	<u>BiI_3</u>

Preparations:

Prepared by reaction of $Fe + X_2 \rightarrow FeX_3$.
Note that $FeBr_3.aq$ when boiled gives $FeBr_2$.

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

Iron(II) halides

Formula	Colour	MP	BP	Structure
FeF_2	white	1000	1100	<u>rutile</u>
$FeCl_2$	pale yellow-grey	670-674	-	<u>$CdCl_2$</u>
$FeBr_2$	yellow-green	684	-	<u>CdI_2</u>
FeI_2	grey	red heat	-	<u>CdI_2</u>

Preparations:

$Fe + HX$ at red heat $\rightarrow FeX_2$ for X=F,Cl and Br
$Fe + I_2 \rightarrow FeI_2$

Iron Oxides and Aqueous Chemistry

Iron oxides

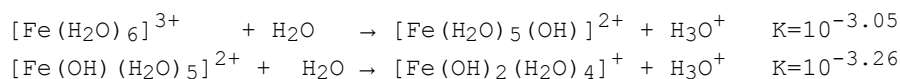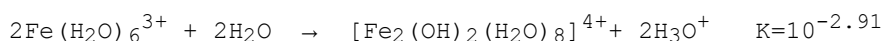| Formula	Colour	Oxidation State	MP	Structure / comments
Fe_2O_3	red brown	Fe^{3+}	1560d	α-form Haematite, β-form used in cassettes
Fe_3O_4	black	$Fe^{2+/3+}$	1538d	magnetite/lodestone
FeO	black	Fe^{2+}	1380	pyrophoric

Preparations:
α-Fe_2O_3 is obtained by heating alkaline solutions of Fe(III) and dehydrating the solid formed.
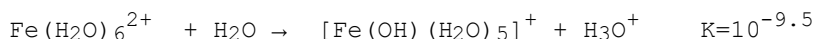
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FeO,Fe3O4, γ-Fe2O3 ccp
α-Fe2O3   hcp
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The Fe(III) ion is strongly acidic:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(H_2O)_5(OH)]^{2+} + H_3O^+ \quad K=10^{-3.05}$$
$$[Fe(OH)(H_2O)_5]^{2+} + H_2O \rightarrow [Fe(OH)_2(H_2O)_4]^+ + H_3O^+ \quad K=10^{-3.26}$$

olation

$$2Fe(H_2O)_6^{3+} + 2H_2O \rightarrow [Fe_2(OH)_2(H_2O)_8]^{4+} + 2H_3O^+ \quad K=10^{-2.91}$$

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

$$Fe(H_2O)_6^{2+} + H_2O \rightarrow [Fe(OH)(H_2O)_5]^+ + H_3O^+ \quad K=10^{-9.5}$$

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: $Fe \rightarrow Fe^{2+} + 2e^-$

and the cathodic reduction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

i.e. overall: $Fe + 2H_2O \rightarrow H_2 + Fe^{2+} + 2OH^-$

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: $2Fe \rightarrow 2Fe^{2+} + 4e^-$

and the cathodic reduction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

i.e. overall: $2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$ with limited O_2, magnetite is formed (Fe_3O_4), otherwise the familiar red-brown
Fe_2O_3 H_2O "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.
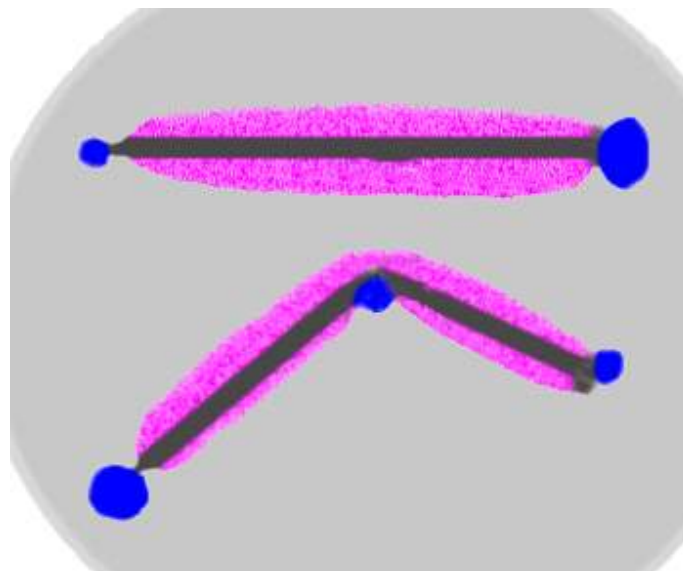
The illustration above shows 2 nails immersed in an agar gel containing phenolphthalein and $[Fe(CN)_6]^{3-}$. The nails can be seen to have started to corrode since the Prussian blue formation indicates the formation of Fe(II) (the Anodic sites which correspond to the end of the nails and the bend in 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 Fe_2O_3. 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. Zn^{2+} 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/Sn^{2+} 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.

$$2 \text{ Fe} + 2 \text{ Na}_2\text{CrO}_4 + 2 \text{ H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + 4 \text{ NaOH}$$
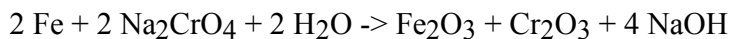
The iron oxide coating formed has been found to be impervious to water and oxygen so no further corrosion can occur.

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 E° at 25°C for some FeIII/FeII couples in acid solution

FeIII		FeII	E°/V
$[\text{Fe(phen)}_3]^{3+}$	$+ e^- \rightarrow$	$[\text{Fe(phen)}_3]^{2+}$	1.12
$[\text{Fe(bipy)}_3]^{3+}$	$+ e^- \rightarrow$	$[\text{Fe(bipy)}_3]^{2+}$	0.96
$[\text{Fe(H}_2\text{O)}_6]^{3+}$	$+ e^- \rightarrow$	$[\text{Fe(H}_2\text{O)}_6]^{2+}$	0.77
$[\text{Fe(CN)}_6]^{3-}$	$+ e^- \rightarrow$	$[\text{Fe(CN)}_6]^{4-}$	0.36
$[\text{Fe(C}_2\text{O}_4)3]^{3-}$	$+ e^- \rightarrow$	$[\text{Fe(C}_2\text{O}_4)_2]^{2-} + (\text{C}_2\text{O}_4)^{2-}$	0.02
$[\text{Fe(edta)}]^-$	$+ e^- \rightarrow$	$[\text{Fe(edta)}]^{2-}$	-0.12
$[\text{Fe(quin)}_3]$	$+ e^- \rightarrow$	$[\text{Fe(quin)}_2] + \text{quin-}$	-0.30

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 $1/2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}$, E° = 1:229 V, i.e. oxygen gas is sufficiently strong an oxidizing agent to render $[\text{Fe(H}_2\text{O)}_6]^{2+}$ (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 Fe_2O_3 (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:

$$\text{Fe(H}_2\text{O)}_6{}^{3+} + e- \rightarrow \text{Fe(H}_2\text{O)}_6{}^{2+} \quad E°=0.771V$$
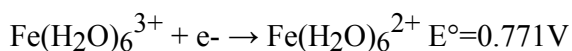
The actual potential E of the couple is given by the Nernst equation,

where 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:
$[\text{Fe(III)}][\text{OH}^-]^2 \sim 10^{-14} \text{ (mol dm}^{-3})^3$ and
$[\text{Fe(III)}][\text{OH}^-]^3 \sim 10^{-36} \text{ (mol dm}^{-3})^4$

Therefore when $[\text{OH}^-] =1 \text{ mol dm}^{-3}$; $[\text{FeII}]/[\text{FeIII}] \sim 10^{22}$

Hence E ~ 0.771 - 0.05916 $\log_{10}.(10^{22})$ = 0.771 - 1.301 = -0.530 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 μ =5.9 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:

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K3Fe(C2O4)3.3H2O          →         2Fe(C2O4)          +          2CO2          +          3K2C2O4
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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:

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Fe(phen)33+       +          e-          →          Fe(phen)32+                          E°=1.12V
blue                                                       red
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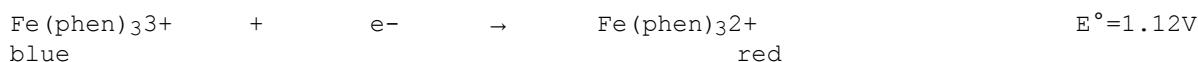
The ligand is 1,10 phenanthroline and the indicator is called ferroin.
An interesting example of how acetates can bind to metal ions is seen in what has been described as a "molecular ferric wheel".

The structure was determined in 1990 and contains $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$
see J. Amer. Chem. Soc., 1990, 112, 9629.

References:

"Complexes and First-Row Transition Elements", D. Nicholls
"Basic Inorganic Chemistry", F.A. Cotton, G. Wilkinson and P.L. Gaus
"Advanced Inorganic Chemistry", F.A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann

"Chemistry of the Elements", Greenwood and Earnshaw

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