Iron

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La *	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac **															

^{26}Fe

*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

25-02-2016 Cobalt 1

Iron

Pyrite formed under reducing conditions

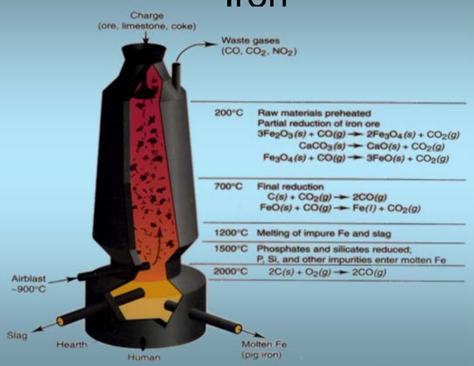
Burn in air $4FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2$

Magnetite

and

Hematite α-Fe_2O_3 formed under oxidising conditions

Iron



Iron

Fe: [[18]Ar]3$d^6$4s^2

+ 2HCl → Fe^{2+} + H_2 + 2Cl^-

Fe^{2+} d^6 as $FeCl_2(H_2O)_4$ pale green

$Fe(H_2O)_6^{2+}$ pale blue-green

readily oxidised in air to

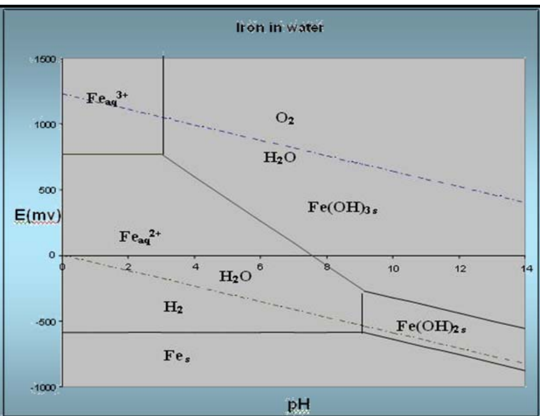
Fe^{3+} d^5 as $Fe(H_2O)_6^{3+}$ very little coloured (pale red-violet)

Tri- or divalent metal ion?

M^{3+}	E° (3+/2+) /V
Sc	very negative
Ti	-0.37
V	-0.25
Cr	-0.41
Mn	1,54
Fe	0.77
Co	1.84
Ni	large
Cu	2.4
Zn	

$M(H_2O)_6^{3+}$ and $M(H_2O)_6^{2+}$

From "Notes" p. 4



Iron i water

Reaction	E^0 / logK	E - pH equation	
1 $Fe^{2+}_{(aq)} + 2e^- \leftrightarrows Fe(s)$	-440 mV	$E = -440 + (59.2)/2 \cdot \log [Fe^{2+}]$	E
2 $Fe(OH)_{2(s)} + 2H^+ \leftrightarrows Fe^{2+}_{(aq)} + 2H_2O$	12.9	$\log[Fe^{2+}] = 12.9 - 2pH$	pH
3 $Fe^{3+}_{(aq)} + e^- \leftrightarrows Fe^{2+}_{(aq)}$	770 mV	$E = 770 + 59.2 \cdot \log([Fe^{3+}]/[Fe^{2+}])$	E
4 $Fe(OH)_{3(s)} + 3H^+ \leftrightarrows Fe^{3+}_{(aq)} + 3H_2O$	3.9	$\log[Fe^{3+}] = 3.9 - 3pH$	pH
5 $Fe(OH)_{2(s)} + 2H^+ + 2e^- \leftrightarrows Fe(s) + 2H_2O$	-47 mV	$E = -47 - 59.2pH$	E.pH
$Fe(OH)_{3(s)} + e^- + H^+ \leftrightarrows Fe(OH)_{2(s)} + H_2O$	270 mV	$E = 270 - 59.2pH$	E.pH
$Fe(OH)_{3(s)} + e^- + 3H^+ \leftrightarrows Fe^{2+}_{(aq)} + 3H_2O$	1060 mV	$E = 1060 - 3 \cdot 59.2pH - 59.2\log[Fe^{2+}]$	E.pH

Iron(II)

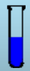
$Fe(H_2O)_6^{2+} \leftrightarrow Fe(OH)(H_2O)_5^{+} + H^+$ pK~ 10 

$Fe(H_2O)_6^{2+} + OH^- \rightarrow Fe(OH)_2$ (almost white)

$Fe(H_2O)_6^{2+} + OH^- + O_2H^- \rightarrow Fe_2O_3$ $(Fe(OH)_3)$

$Fe(H_2O)_6^{2+} + CN^- \rightarrow Fe(CN)_6^{4-}$ (yellow - low spin)

$+ Fe(CN)_6^{4-} \rightarrow K_2Fe[Fe(CN)_6]$ (almost white)

$Fe(CN)_6^{4-} + Fe(H_2O)_6^{3+} \rightarrow Fe\,Fe(CN)_6^-$ 

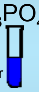
$Fe(H_2O)_6^{2+} + HNO_3 \rightarrow Fe(H_2O)_6^{3+} + NO_2$

Iron(III)

$Fe(H_2O)_6^{3+} \leftrightarrow Fe(OH)(H_2O)_5^{2+} + H^+$ pK~ 2 

$Fe(OH)(H_2O)_5^{2+} + H_2PO_4^- \rightarrow$ "$FePO_4$"$_{(s)}$ pH~3

$FePO_4 + 3H^+ \leftrightarrow Fe(H_2O)_6^{3+} + H_3PO_4$

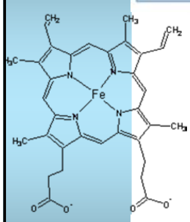
$Fe(CN)_6^{3-} + Fe^{2+} \rightarrow Fe\,Fe(CN)_6^-$ 

Low spin (**red**) Charge transfer

$Fe^{3+} + nSCN^- \leftrightarrow Fe(SCN)_n^{(3-n)+}$ (red)

2 drops of 1 M KSCN to a dilute (colourless) solution of $Fe(H_2O)_6^{3+}$

Heme (+ cytochromes)



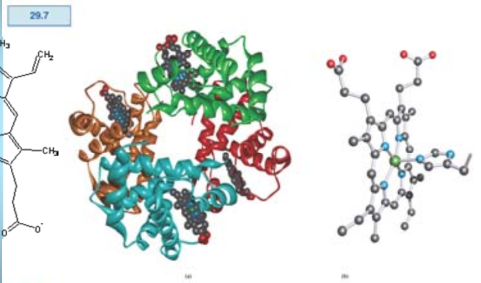
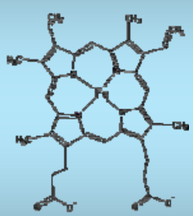
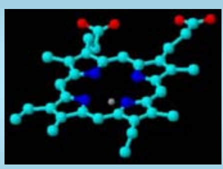
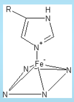


Fig. 29.7 (a) The structure of haemoglobin shown in a ribbon representation. The four sub-units, each containing a hae unit, are shown in different colours. (b) The structure of the haem unit in its rest state. The Fe(II) centre is coordinated by a protoporphyrin IX ligand and a histidine residue; the non-terminated stick represents the connection to the protein backbone. Hydrogen atoms are omitted for clarity. Colour code: Fe, green; C, grey; N, blue; O, red.

Heme







Iron – sulphur proteins

Redox reactive enzymes
e.g. in aconitase

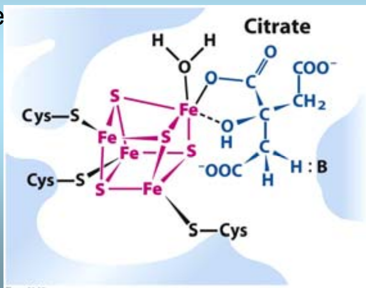


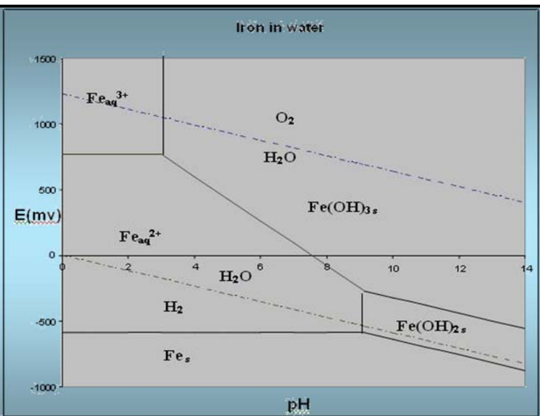
Figure 16-10

Synthesis 1

$Fe + H_2SO_4 \rightarrow FeSO_4{\cdot}7H_2O + H_2(g)$

Isolate as $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$

purity check $+SCN^-$



Synthesis 2

$3Fe(H_2O)_6^{2+} + HNO_3 + 3H^+ \rightarrow 3Fe(H_2O)_6^{3+} + NO + 2H_2O$

$Fe(H_2O)_6^{2+} + NO \rightarrow FeNO(H_2O)_5^{2+}$ (intensely brown)

Isolate as $(NH_4)Fe(SO_4)_2{\cdot}12H_2O$

purity check $+ Fe(CN)_6^{3-}$

$Fe\,Fe(CN)_6^-$ only if Fe(II) present

Ligand influence on potential

M | M^{n+} (C_m) ‖ L, M^{n+} (C_m) | M

$\Delta E = E_r - E_l = (RT\ln 10/nF)\mathbf{log}([M^{n+}]/C_m) < 0$

$[M^{n+}]/C_m < 1$ because of the formation of ML_x^{n+}
Hence ΔE becomes negative upon addition of L

Nernst

$aA + hH^+ + ze^- \rightarrow bB$ (balanced !)

$E = E^0 + (RT\ln 10/zF)\mathbf{log}([A]^a \cdot [H^+]^h/[B]^b)$

R = 8.314 5J/mol ·K; ln10 = 2.3026… ;F = 96485.3 C/mol

RTln10/F: nernst-factor (n-f)

0.1984 ·(t°C+273.15)

t	20	21	22	23	24	25
n-f/mV	58.16	58.36	58.56	58.76	58.96	59.16

Fe(III)/Fe(II)

E measured at a electron conducting wire pure Au or Pt

$E = E^0 + (n\text{-}f)\mathbf{log}([Fe^{3+}]/[Fe^{2+}]) - E_{ref}$

$E - E^0 + E_{ref} = (n\text{-}f) \cdot \log([Fe^{3+}]/[Fe^{2+}])$

Potential differences!

- Reference electrodes:

- Ag/AgCl in KCl_{sat} E=0.244 V
- Hg/Hg_2SO_4 in K_2SO_{4sat} E=0.64 V
- Hg/Hg_2Cl_2 in KCl_{sat} E=0.199 V

Ligand influence on potential

Fe^{3+} and Fe^{2+} in same solution , add bipy:
4 reactions

1. Fe^{3+} + xbipy ↔ $Febipy_x^{3+}$ $\quad {}^3\beta_x$
2. Fe^{2+} + xbipy ↔ $Febipy_x^{2+}$ $\quad {}^2\beta_x$

3. $Fe^{3+} + (3\text{-}2)e^- \leftrightarrow Fe^{2+}$ $\quad E^0\,(Feaq_6^{3/2+})$
4. $Febipy_x^{3+} + e^- \leftrightarrow Febipy_x^{2+}$ $\quad E^0\,(Febipy_x^{3/2+})$

Reactions rearranged

Fe^{3+} **+(3-2)e$^-$**	+ xbipy	⟷ ${}^3\beta_x$	$Febipy_x^{3+}$ **+(3-2)e$^-$**	
↕ $E^0\,(Feaq_6^{3/2+})$			↕ $E^0\,(Febipy_x^{3/2+})$	
Fe^{2+}	+ xbipy	⟷ ${}^2\beta_x$	$Febipy_x^{2+}$	

$-\Delta G^0(\text{red } Feaq_6) - \Delta G^0(\text{form } Febipy_x^{2+}) =$
$\qquad - \Delta G^0(\text{form } Febipy_x^{3+}) - \Delta G^0(\text{red } Febipy_x)$

$1 \cdot F \cdot E^0\,(Feaq_6^{3/2+}) + RT\ln {}^2\beta_x = RT\ln {}^3\beta_x + 1 \cdot F \cdot E^0\,(Febipy_x^{3/2+})$