# Electrochemistry

- Redox reactions in water as a solvent

Limit 1 $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ $E^0 = 1230$ mV

$$E = E^0 + \frac{59.2}{4}\log\frac{pO_2 \cdot a_{H^+}^{\ 4}}{a_{H_2O}^{\ 2}}$$ at 25 °C

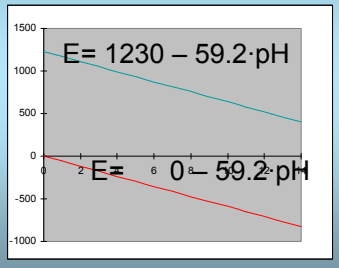
Limit 2 $2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0$ mV (pr. def.)

$$E = E^0 + \frac{59.2}{2}\log\frac{a_{H^+}^{\ 2}}{pH_2}$$ at 25 °C



# Water – aqueous solutions

- $P_{gas}$ = 1 atm → equilibrium lines

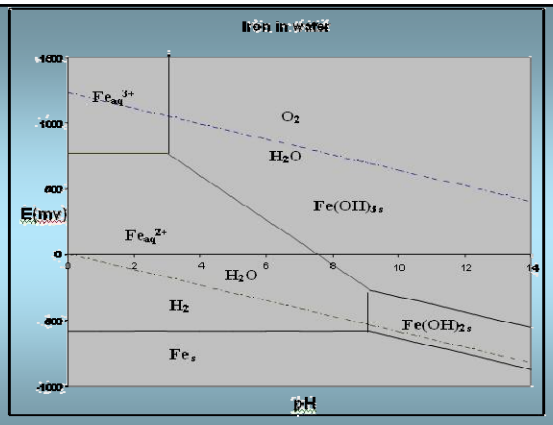



iron



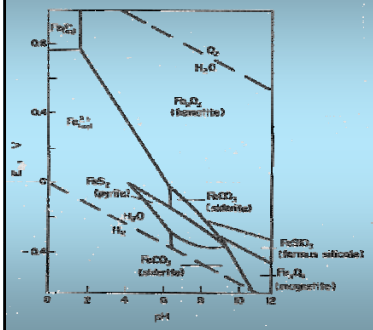
# Iron i water

| 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 | $E= -47 - 59.2pH$ | E.pH |
| $Fe(OH)_{3(s)} + e^- + H^+ \leftrightarrows Fe(OH)_{2(s)} + H_2O$ | 270 | $E= 270 - 59.2pH$ | E.pH |
| $Fe(OH)_{3(s)} + e^- + 3H^+ \leftrightarrows Fe^{2+}_{(aq)} + 3H_2O$ | 1060 | $E= 1060 - 3 \cdot 59.2pH - 59.2\log[Fe^{2+}]$ | E.pH |






## Iron speciation in the environment



Equilibria involving silicate, carbonate and sulphide and several solid states can be introduced to give an impression of conditions for mineral formation etc.



## Ligand influence on potential

$$M \mid M^{n+}(C_m) \parallel L, M^{n+}(C_m) \mid M$$

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

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

## Ligand influence on potential

$M^{n+}$ and $M^{m+}$ in same solution , add L:
4 equilibria

1. $M^{n+} + xL \leftrightarrow ML_x^{n+}$ $\quad {}^{n}\beta_x$
2. $M^{m+} + xL \leftrightarrow ML_x^{m+}$ $\quad {}^{m}\beta_x$

3. $M^{n+} + (n-m)e^- \leftrightarrow M^{m+}$ $\quad E^0\,(Maq_6^{\,n/m+})$
4. $ML_x^{n+} + (n-m)e^- \leftrightarrow ML_x^{m+}$ $\quad E^0\,(ML_x^{\,n/m+})$



## Reactions rearranged

$$\begin{array}{ccc} M^{n+} & + xL \leftrightarrow & ML_x^{n+} \\ +(n-m)e^- & {}^{n}\beta_x & +(n-m)e^- \\ \updownarrow E^0\,(Maq_6^{\,n/m+}) & & \updownarrow E^0\,(ML_x^{\,n/m+}) \\ M^{m+} & + xL \leftrightarrow & ML_x^{m+} \\ & {}^{m}\beta_x & \end{array}$$

$$-\Delta G^0(\text{red M}) - \Delta G^0(\text{form } ML_x^{m+}) = -\Delta G^0(\text{form } ML_x^{n+}) - \Delta G^0(\text{red } ML_x)$$

$$(n-m)F\cdot E^0\,(Maq_6^{\,n/m+}) + RT\ln {}^{m}\beta_x = RT\ln {}^{n}\beta_x + (n-m)F\cdot E^0\,(ML_x^{\,n/m+})$$



## Tri- or divalent metal ion?

| $M^{3+}$ | $E^o$ (3+/2+) /V |
|---|---|
| Sc | |
| 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