

# E - pH diagrams.

Just like the acidity of an aqueous solution can be regulated by adding a certain amount of acid or base, the electrochemical potentials of a solution can be regulated - if not designed - by adding an oxidising agent or a reducing agent. Acidity and electrochemical potential are thus parameters of a solution which can be experimentally set and measured (pH and E). Some chemical reactions are almost instantaneous, whereas some are quite slow, but when equilibrium has been reached, equilibrium constants in a quantitative thermodynamic treatment can be used to predict the speciation of the system.

E - pH diagrams are useful for that purpose, and any equilibrium - e.g. precipitation, acid-base, redox, complex formation - can be involved.

Aqueous solutions exist only under conditions where water itself is not reduced to hydrogen gas  $H_2$  or oxidised to oxygen gas,  $O_2$ , if strong reducing or oxidising agents are added. There are, therefore, limits to how reducing or oxidising an aqueous solution (measured as an electrochemical potential) can be in equilibrium.

The relevant reaction scheme for the oxidation of water can be expressed by



which at 25 °C has the half cell potential  $E = E^0 + \frac{59.2}{4} \log \frac{pO_2 \cdot a_{H^+}^4}{a_{H_2O}^2}$ .

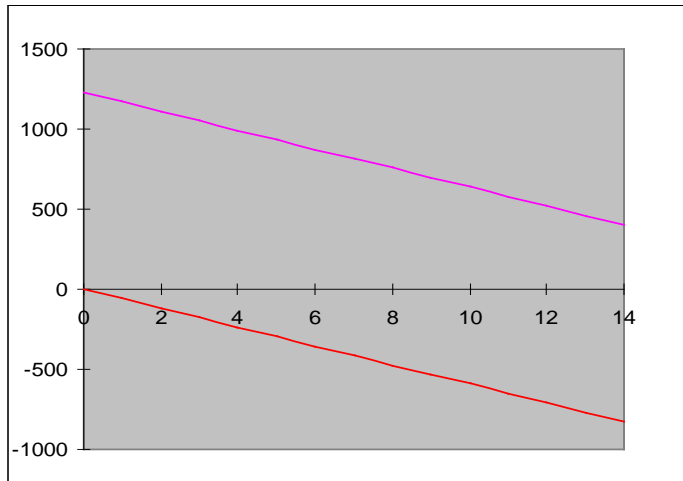
In aqueous solutions the activity of water is 1 and if  $pO_2$  is 1 atm. - which means that the oxygen bubbles up with a partial pressure of 1 atm. - then we have defined the limit for water existing in equilibrium with free oxygen (1 atm.) If the potential is kept at a value larger than  $E^0 + 59.2 \cdot \log [H^+]$  (the proton activity is set to the concentration) - the formation of free oxygen will proceed until there is no more water. The limit  $E^0 + 59.2 \cdot \log [H^+]$  can be written as  $1230 - 59.2 \cdot \text{pH}$ , from which it can be seen that at higher pH a lower potential can result in the water being oxidised to free oxygen. This limit is apparently pH-dependant.

A similar treatment of the reduction of water to free hydrogen gives



The corresponding half cell potential is  $E = E^0 + \frac{59.2}{2} \log \frac{a_{H^+}^2}{pH_2}$

If the limiting pressure of hydrogen is set to 1 atm. the pH-dependant limit potential is  $E = -59.2 \cdot \text{pH}$ . If the potential is kept at a value smaller than  $-59.2 \cdot \log [H^+]$  the water will be reduced to free hydrogen until there is no more water left.



Notice, that the two pH-dependencies have the same slope.

If we are only dealing with water, the E - pH diagram looks like the diagram to the left. Above the upper line  $pO_2$  has a value of 1 atm., and only below that line water exists. Likewise, below the lower line  $pH_2$  is 1 atm. and only above that line water exists.

If we now introduce iron into the system several fairly simple reactions may happen depending on pH and redox potential.

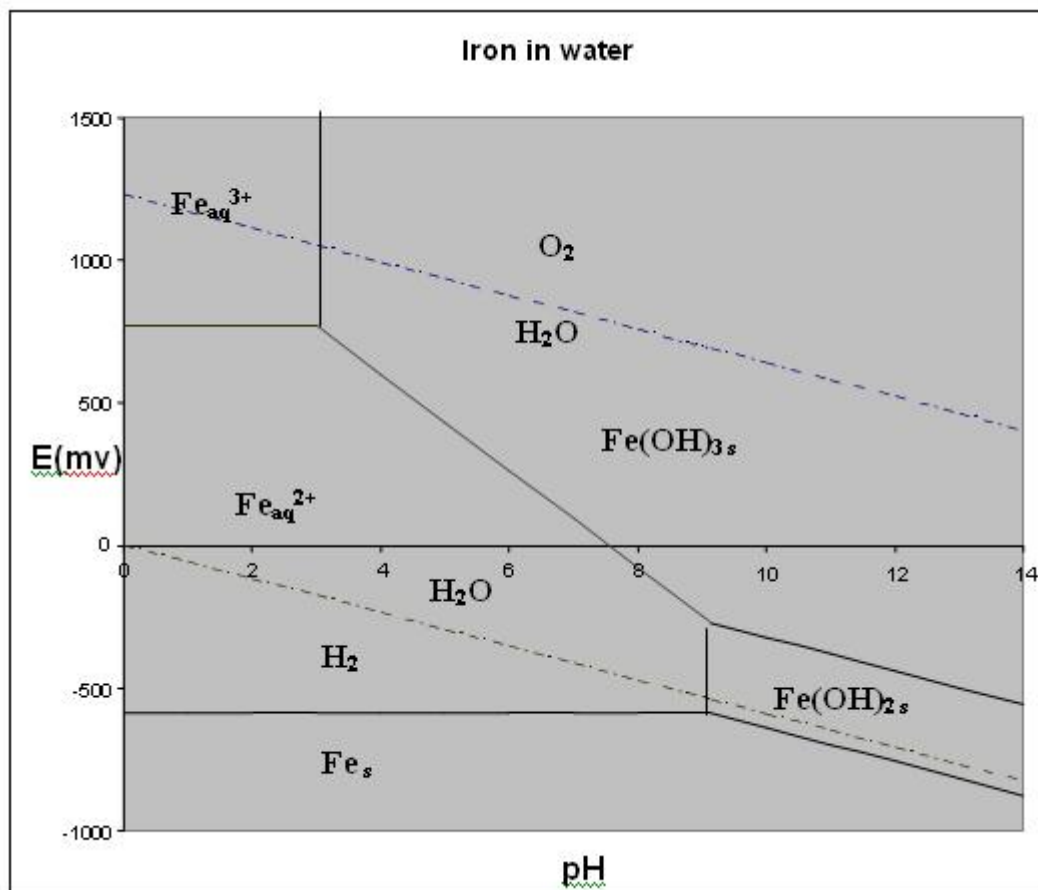
Such reactions are given below together with relevant equilibrium data

Reaction	$E^0 / \log K$	E - pH equation	
1 $Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$	-440 mV	$E = -440 + \frac{59.2}{2} \log [Fe^{2+}]$	E
2 $Fe(OH)_{2(s)} + 2H^+ \rightleftharpoons Fe^{2+} + 2H_2O$	12.9	$\log [Fe^{2+}] = 12.9 - 2pH$	pH
3 $Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	770 mV	$E = 770 + 59.2 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$	E
4 $Fe(OH)_{3(s)} + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O$	3.9	$\log [Fe^{3+}] = 3.9 - 3pH$	pH
5 $Fe(OH)_{2(s)} + 2H^+ + 2e^- \rightleftharpoons Fe_{(s)} + 2H_2O$	-47 mV	$E = -47 - 59.2pH$	E,pH
6 $Fe(OH)_{3(s)} + H^+ + e^- \rightleftharpoons Fe(OH)_{2(s)} + H_2O$	270mV	$E = 270 - 59.2pH$	E,pH
7 $Fe(OH)_{3(s)} + 3H^+ + e^- \rightleftharpoons Fe^{2+}_{(aq)} + 3H_2O$	1060mV	$E = 1060 - 3 \cdot 59.2pH - 59.2 \log [Fe^{2+}]$	E,pH

- If  $[Fe^{2+}]$  is set to  $10^{-5}$  M (arbitrarily, but corresponding to "some"  $Fe^{2+}$  in solution), then E is constant and independent of pH:  $E = (-440 + 29.6 \log(10^{-5})) = -588$  mV
- Here the concentration of dissolved  $Fe^{2+}$  is independent of the redox potential of the system, but dependent of pH. To have "some"  $Fe^{2+}$  ( $10^{-5}$  M) in equilibrium with solid  $Fe(OH)_2$  the pH is defined by  $\log 10^{-5} = 12.9 - 2pH \Rightarrow pH = \frac{1}{2} \cdot 17.9 = 8.95$
- From the Nernst-equation it is seen that if both iron(II) and iron(III) are present in some concentration (here  $10^{-5}$  M) the redox potential is constant and independent on pH:  
 $E = 770$  mV

4. With a similar argument as for the solubility of iron(II) hydroxide, the pH at which  $[\text{Fe}^{3+}] = 10^{-5} \text{ M}$  is in equilibrium with solid iron(III) hydroxide can be found through  $\log 10^{-5} = 3.9 - 3\text{pH} \Rightarrow 3\text{pH} = 8.9$  or  $\text{pH} = 2.97$
5. From this scheme it is seen that only acidity is a variable. The equation tells, that the potential will drop off when pH increases with a slope of  $-59.2 \text{ mV pr. pH-unit}$
6. The potential for this reaction is pH-dependent. Again the same number of electrons as protons is involved in the reaction, and the slope for the pH-dependence of the potential is  $-59.2 \text{ mV pr. pH-unit}$ .
7. This reaction is more complicated. As usual  $[\text{Fe}^{2+}]$  is set to  $10^{-5} \text{ M}$  which gives a pH-dependence, which is  $3 \cdot (-59.2 \text{ mV})$  per pH-unit, because 3 protons are used per electron

The condensed picture of this chemistry can be depicted in a diagram as the following, telling in which form iron will dominate, when values of potential  $E$  and acidity  $\text{pH}$  are given.



In real systems there may be more different components and this will complicate the diagram.