

Electrochemistry - Thermodynamics

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Summary

During the last year we have been discussing in detail many different forms and cases of corrosion in ammonia and urea. To really understand the background and fundamentals of these corrosion problems it is necessary to introduce to you the modern electrochemical theory of aqueous corrosion. Although the presentation is necessarily simplified and brief we think this theory will contribute to a better understanding of corrosion phenomena. At first in this paper we will approach thermodynamic principles. In a next paper we will discuss electrode kinetics and the application of electrochemical corrosion theory on corrosion reactions in general and in carbamate solutions specific.

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2.2 Thermodynamics (the science of energy change)

2.2.1 Change of free energy ΔG

Most metals exist in their natural state as compounds (oxides, sulfides etc.). This is their thermodynamically stable state. We dig these compounds out of the ground, extract the metal (by lifting it to a higher energy state) and then make it into useful articles. Unless we have substantially changed the metal (e.g. by alloying), the thermodynamics will not have changed. When we expose this metal article to a natural environment, it will (if not protected) revert to its natural state by corrosion. Of course, metals that exist in nature as pure elements (e.g. gold) have excellent corrosion resistance in natural environments. Corrosion is only possible if its products are more stable than the reactants. Most corrosion reactions are electrochemical and we will restrict our discussion to these.

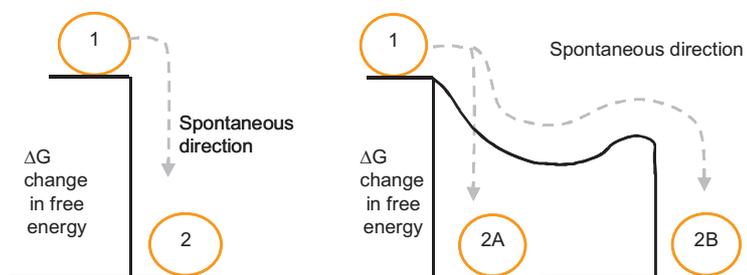
The change in free energy ΔG is a direct measure of the work capacity or maximum electric energy available from the system. If the change in free energy during transition of a system from one state to another is negative, this indicates a loss in free energy and indicates also the spontaneous reaction direction of the system. That means, if no external forces act on the system, the system will tend to transform to its lowest energy state. If the change in free energy is positive, this indicates that the transition represents an increase in energy, and this requires that additional energy be added to the system. This principle can be illustrated by a mechanical analogy as shown in figure 2.2.1.1a. If the ball moves from position 1 to position 2, this represents a decrease in free energy. The transition from position 1 to position 2 is the spontaneous direction of this particular system. The reverse transformation, from position 2 to position 1, is not a spontaneous direction and requires the application of energy.

The change in free energy is independent of the reaction path. This is also illustrated in figure 2.2.1.1b. In this figure two possible reaction paths A and B are indicated. For either path, free energy change for the transition from state 2A or 2B is exactly the same. It is obvious, however, that the transformation along path B will require more time and will be slower than along path A. Chemical and electrochemical corrosion reactions behave in the same fashion. It is not possible to predict the velocity of a reaction from the change in free energy. This thermodynamic parameter reflects only the direction of a reaction by its sign, and any predictions of velocity may be erroneous.

Figure 2.2.1.1 a (left)
Mechanical analogy of free energy change.

Figure 2.2.1.1.b (right)
Affect of reaction path on reaction rate.

Fontana & Greene



The free energy change accompanying an electrochemical reaction can be calculated by the following equation:

$$\Delta G = -n.F.E$$

ΔG = free energy change.

n = number of electrons involved in the reaction.

F = Faraday constant ($9,65 \cdot 10^4$ Coulomb per (g)mol)

E = $E_C - E_A$

$$\Delta G = -n.F.(E_C - E_A)$$

F represents the total electric charge of N electrons.

N is the number of Avogadro (number of atoms per (g)mol of element) = 6.03×10^{23} (g)mol⁻¹. Since the charge of 1 electron $e = 1.6 \times 10^{-19}$ coulomb, $F = N \times e = 9.65 \times 10^4$ C (g)mol⁻¹.

The mass of 1 atom H is $1.008/N = 1.67 \times 10^{-24}$ gram = 1 dalton.

2.2.2 Cell potentials and EMF-series

For a good understanding of electrochemical corrosion one should have a correct comprehension of the electrochemical phenomena acting in a galvanic cell. If a solid piece of metal is placed in a solution containing its metal ions, a potential difference, $E [Me/Me^{n+}]$ exists between the metal atoms in the solid and the metal ions in solution, the half cell potential (Figure 2.2.2.1).

At the interface of metal / electrolyte following processes occur:

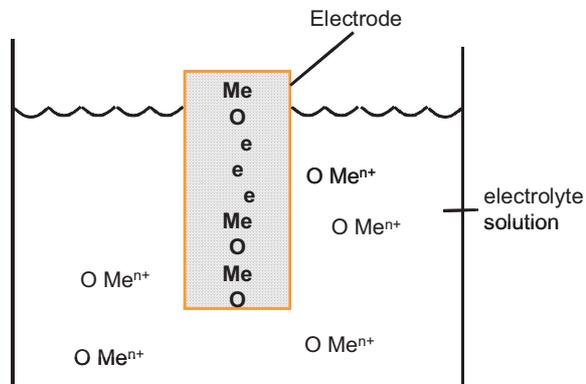
A: $Me \rightarrow Me^{n+} + ne$; at certain points on the metal surface, metal atoms are oxidized to metal ions leaving negatively charged electrons in the metal electrode.

B: $Me^{n+} + ne \rightarrow Me$; at other points on the metal surface metal ions are reduced to metal atom, picking up electrons out of the metal electrode and depositing on the metal surface.

In the first process the metal electrode will be charged negatively opposite the electrolyte; in the second process the metal electrode will be charged positively opposite the electrolyte. After some time an equilibrium situation will exist; this equilibrium condition dictates that the rate of both reactions

A and B be equal: $Me \rightleftharpoons Me^{n+} + ne$

Figure 2.2.2.1
Metal electrode Me in electrolyte solution containing Me^{n+} ions in dynamic equilibrium.



The potential of the metal electrode to the electrolyte (the real electrode potential) is called equilibrium potential.

The extent of this equilibrium potential is determined by two parameters:

- the type of the metal in contact with the electrolyte;
- the concentration of the metal ions (participating in the reaction) in the electrolyte.

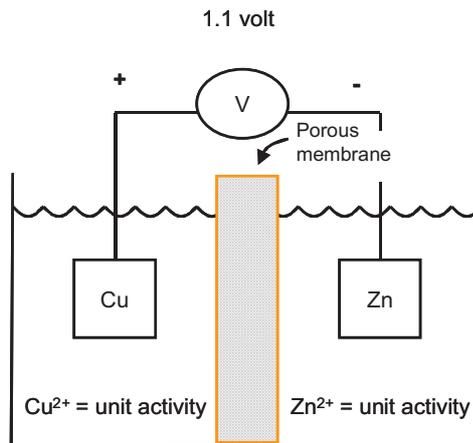
The different metals have a different tendency to send ions into the electrolyte. Noble metals like e.g. gold have a low tendency to go into solution while zinc has a high tendency to dissolve.

A metal electrode in a solution is called a half-cell. When the concentrations of the reactants are maintained at unit activity ($1N = 1\text{kmol/m}^3$), they are termed standard half-cells.

The potential difference between the solid piece of metal (a half-cell) and solution cannot be measured directly. It is possible to measure the potential difference between two half-cells as shown in Figure 2.2.2.2. In this figure an electrochemical cell is constructed containing copper and zinc electrodes in equilibrium with their ions separated by a porous membrane to retard mixing. For purposes of simplicity, the concentration of metal ions is maintained at unit activity. Both electrodes are at equilibrium. The reactions in each compartment are represented by the following equations:



Figure 2.2.2.2
Reversible cell containing copper and zinc in equilibrium with their ions.



The rates of metal dissolution and deposition are the same; there is no net change in the system. If a high resistance voltmeter is connected between the copper and the zinc electrodes, a potential difference of about 1.1 volt is observed. This is the cell potential (or EMF) which is used in determining the free energy of the overall electrochemical reaction. The positive terminal of the voltmeter must be connected to the copper electrode, and the negative terminal must be connected to the zinc electrode to have the voltmeter read on scale.

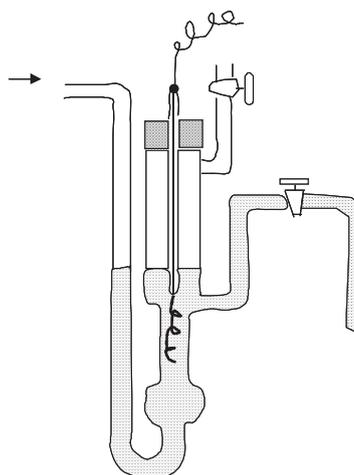
The cell potential is the difference between the electrode potentials of both electrodes: $E = E_{\text{Cu/Cu}^{2+}} - E_{\text{Zn/Zn}^{2+}}$

An electrode can be an electron conducting metal, which takes part in the electrode reactions. It can also be an inert metal at which the electrochemical reactions takes place while itself does not take part in the reaction as for instance the hydrogen electrode. A platinum electrode acts as an inert substrate for the electrochemical reaction. At different points on the platinum electrode, hydrogen ions are reduced to hydrogen gas and hydrogen gas is oxidized to hydrogen ions, with electron transfer occurring between these points: $2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$

It is important to note that the Pt electrode does not take part in this reaction but merely serves as a solid interface at which this reaction can occur. Many metals function as reversible hydrogen electrodes; Pt is usually preferred due to its inertness and the ease with which electron transfer occurs on its surface. If concentration of hydrogen ions is maintained at 1 gram atomic weight per liter (unit activity) and the solution is saturated with hydrogen gas at 1 atmosphere pressure we speak of the Normal Hydrogen Electrode. This half-cell reaction of NHE is arbitrary chosen as zero potential. The hydrogen half-cell is shown in figure 2.2.2.3.

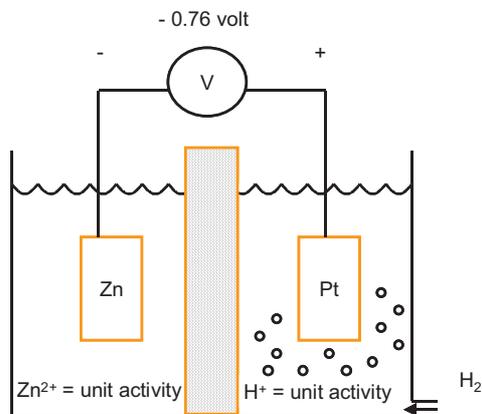
Combining a NHE with any metal electrode to an electrochemical cell, the measured potential is per definition the electrode potential of the metal electrode.

Figure 2.2.2.3
Hydrogen half-cell.



In figure 2.2.2.4 an electrochemical cell containing reversible zinc and hydrogen electrodes is shown.

Figure 2.2.2.4
Cell containing reversible zinc and hydrogen electrodes.



The cell as shown in figure 2.2.2.4 has a potential of 0.76 and zinc is negative with respect to the hydrogen electrode. Using the above mentioned convention, the hydrogen electrode is defined as having the potential of zero, and it follows that the potential of the zinc half-cell is -0.76 volt. In this fashion, other half-cell potentials can be determined.

In Table 2.2.2.1 the half-cell potentials for some electrochemical reactions are listed. This table is frequently called the EMF series, half-cell, or reduction-oxidation potentials (abbreviated redox potentials).

In all cases these potentials refer to electrodes in which all reactants are at unit activity and at 25°C.

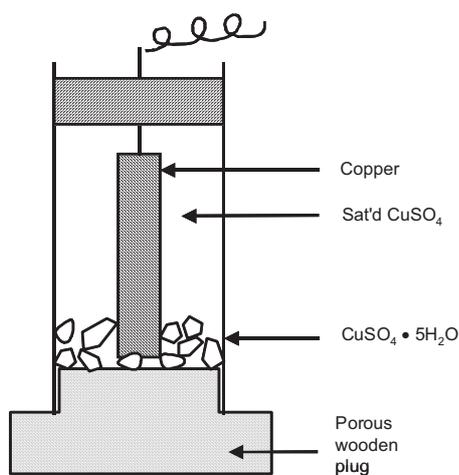
Table 2.2.2.1
Electrochemical series of metals.

<i>Electrode reaction</i>	<i>E₀ (Volts)</i>
$K^+ + e^- \rightleftharpoons K$	-2,92
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	-2,87
$Na^+ + e^- \rightleftharpoons Na$	-2,71
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2,34
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1,67
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0,76
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	-0,71
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0,44
$Cd^{2+} + 2e^- \rightleftharpoons Cd$	-0,40
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0,25
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	-0,14
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0,13
$2H^+ + 2e^- \rightleftharpoons H_2$	0,00
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0,34
$Ag^+ + e^- \rightleftharpoons Ag$	+0,80
$Hg^{2+} + 2e^- \rightleftharpoons Hg$	+0,85
$Pt^{2+} + 2e^- \rightleftharpoons Pt$	+1,20
$Au^+ + e^- \rightleftharpoons Au$	+1,68

For measurements as mentioned before it is not necessary to use the NHE. Each well defined, constant half-cell can be used as a reference electrode if the potential difference with the NHE is known. Generally more practical reference electrodes are used like:

- Saturated Calomel Electrode (SCE): +242 mV versus NHE
- Silver-Silverchloride Electrode: +288 mV versus NHE
- Copper-Coppersulphate Electrode: +335 mV versus NHE (Figure 2.2.2.5).

Figure 2.2.2.5
Saturated Copper-Coppersulphate Electrode



The EMF series as mentioned before is not very important in studying corrosion phenomena since this series is related to circumstances which are not likely to occur in practical situations. Next to the theoretical EMF series other "galvanic series" are determined. In some of these series the potentials of metals as well as alloys are measured in practical or standard solutions e.g. sea water or 2% NaCl.

Examples of these series are:

- Series of Von Zeerleder in 2% NaCl
- INCO series in seawater.

The galvanic series show quite some differences with the EMF series. They can give important information in comparing the differences in corrosion behaviour of metals and alloys in concerning environment. A practical galvanic series is given in table 2.2.2.2.

Table 2.2.2.2
Practical galvanic series for a number of alloys in air saturated, neutral seawater (INCO series).

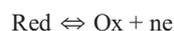
Metal	Potential (Volt)
magnesium	-1.32
zinc alloy zamak Z400	-0.94
zinc	-0.78
aluminium 99.5%	-0.67
mild steel	-0.40
cast iron GG-22	-0.35
13% Cr-steel (active)	appr. -0.30
18% Cr-8% Ni-steel (active)	appr. -0.30
lead 99.9%	-0.26
brass 60-40	-0.07
copper	+0.10
monel K	+0.12
70-30 cupronickel	+0.34
chromium and chromium- nickel steels (passive)	appr. +0.40

2.2.3 Electrode reactions

Of essential importance in the reaction at an electrode surface in an electrochemical cell is the transfer of charged particles through the interface electrode/solution. These reactions are called electrode reactions.

When there is only one reaction at an electrode then it is called a single electrode. In case more reactions take place at one electrode then it is called a mixed electrode. When in electrode reactions a transfer of metal ions takes place we speak of a metal ions electrode. The electrode itself does take part in the reaction; e.g. Fe and Zn.

If the electrode does not take part in the reaction but merely serves as a solid interface at which a transfer of electrons takes place, we speak of a redox-electrode; e.g. Pt and C. The general formula for redox-reactions is:



The electrode potentials of redox reactions can be fixed in the same way as metal ions-reactions. These electrode potentials are called redox-potentials.

In Table 2.2.3.1 some redox reactions with the standard potentials are listed.

Table 2.2.3.1
Redox reactions with standard potentials.

<i>Electrode reaction</i>	<i>E₀ (Volt)</i>
$\text{Cr}^{3+} + \text{e}^- \rightleftharpoons \text{Cr}^{2+}$	-0,41
$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	0,15
$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	0,36
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$	0,40
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	0,53
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2$	0,69
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	0,77
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{NO} + 2\text{H}_2\text{O}$	0,94
$\text{Br}_2 + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	1,06
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	1,23
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1,24
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	1,36
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1,52
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	1,77
$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	2,85

In case of corrosion there is more than one electrode-reaction at the corroding metal surface. One of the reactions is the transfer of metal to metal ions which is the anodic or oxidation reaction. The other reactions are redox-reactions or other metal ions reactions or both beside each other; these are the cathodic or the reduction reactions.

Anodic reaction (oxidation):

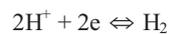


In case an alloy corrodes, several anodic reactions will take place simultaneously.

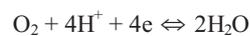
Cathodic reactions (reduction):

Various types of reduction can occur; common reduction reactions in corrosion processes are:

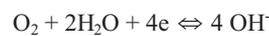
- Hydrogen evolution in acid solution:



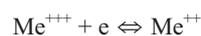
- Oxygen reduction in acid solutions:



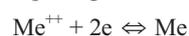
- Oxygen reduction in neutral or alkaline solutions:



- Metal-ion reduction:



- Metal plating:



2.2.4 Nernst equation

The electrode potential is influenced by the concentration of the species involved in the electrode reaction. If the concentration of all components is 1 gram atomic weight per litre or kmol per m³ (unit activity) the electrode-potential is mentioned standard half-cell potential. To determine the potential of a system in which the reactants are not at unit activity, the Nernst equation can be employed.

$$E = E_0 + 2.3 \frac{RT}{nF} \log \frac{a_{\text{oxid}}}{a_{\text{red}}}$$

E = half-cell potential

E₀ = standard half-cell potential

R = gas constant of Joule

T = absolute temperature in degree Kelvin

n = number of electrodes transferred

F = Faraday constant

a_{oxid} and a_{red} are the activities (concentrations) of the oxidized and reduced species.

If the temperature is 25°C the Nernst equation is as follows:

$$E = E_0 + \frac{0.059}{n} \log \frac{a_{\text{oxid}}}{a_{\text{red}}}$$

For the anodic reaction $\text{Me} \Leftrightarrow \text{Me}^{n+} + n\text{e}$, the Nernst equation is as follows:

$$E_{\text{Me}/\text{Me}^{n+}} = E_{0_{\text{Me}/\text{Me}^{n+}}} + \frac{0.059}{n} \log [\text{Me}^{n+}]$$

For the cathodic reaction $2\text{H}^+ + 2\text{e} \Leftrightarrow \text{H}_2$ the equation is:

$$E_{\text{H}^+/\text{H}_2} = E_{0_{\text{H}^+/\text{H}_2}} + \frac{0.059}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}} = 0.059 \log [\text{H}^+] = -0.059 \cdot \text{pH}$$

(P_{H₂} = 1 atm.)

For the cathodic reduction reaction of oxygen in acid solution

$\text{O}_2 + 4\text{H}^+ + 4\text{e} \Leftrightarrow 2\text{H}_2\text{O}$, the Nernst equation is:

$$E_{\text{O}_2/\text{H}_2\text{O}} = E_{0_{\text{O}_2/\text{H}_2\text{O}}} + \frac{0.059}{4} \log p_{\text{O}_2} [\text{H}^+]^4$$

Note: The coefficients in the reaction equation are exponents in the Nernst equation.

2.2.5 Pourbaix diagrams.

As discussed before, there is a definite relation between the free-energy change and the cell potential of an electrochemical reaction. In most instances, the actual magnitude of the free-energy change is relatively unimportant in corrosion applications. The most important factor is the sign of the free-energy change for a given reaction, since this indicates whether or not the reaction is spontaneous. Hence, although the equation $\Delta G = -nFE$ forms the basis for the thermodynamic calculations, it is rarely used in studying corrosion phenomena. However a simple rule derived from the equation $\Delta G = -nFE$ is used to predict the spontaneous direction of any electrochemical reaction. This rule can be simply stated as: In any electrochemical reaction, the most negative or active half-cell tends to be oxidized, and the most positive or noble half-cell tends to be reduced.

From the above rule it follows that all metals with reversible potentials more active (negative) than hydrogen will tend to be corroded by acid solutions. Copper and silver, which have more noble potentials, are not corroded in acid solutions. However, if dissolved oxygen is present there is a possibility of oxygen reduction, indicating that in presence of oxygen, copper and silver tend to corrode spontaneously.

As the reversible potential of a metal becomes more noble its tendency to corrode in the presence of oxidizing agents decreases. Metals such as platinum and gold are very inert since there will be no tendency to corrode except in the presence of extremely powerful oxidizing agents.

Thermodynamics, or more specifically, half-cell potentials, can be used to state a criterion for corrosion: corrosion will not occur unless the spontaneous direction of the reaction indicates metal oxidation.

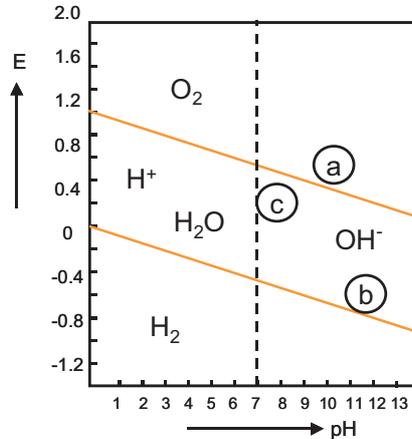
It is important to note that although the spontaneous direction of a reaction may be in the direction of metal corrosion, this does not necessarily indicate that serious corrosion will occur. If the reaction proceeds at a negligible rate, then the metal will be essentially inert. Hence, the major use of thermodynamic calculations is a negative one. That is, thermodynamics can indicate unambiguously that corrosion will not occur.

The applications of thermodynamics to corrosion phenomena have been further generalized by means of potential - pH plots. These are frequently called Pourbaix diagrams after Dr. M. Pourbaix who first suggested their use.

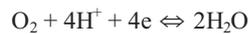
Such diagrams are constructed from calculations based on the Nernst equation and solubility data for various metal compounds.

A simplified form of the E - pH diagram of water is shown in figure 2.2.5.1.

Figure 2.2.5.1
Simplified Pourbaix diagram for water at 25°C.



Line a in the diagram represents the equilibrium of the reaction:

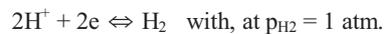


with the Nernst equation:

$$E_{\text{O}_2/\text{H}_2\text{O}} = E_{\text{O}_2/\text{H}_2\text{O}}^0 + \frac{0.059}{4} \log P_{\text{O}_2} \cdot [\text{H}^+]^4$$

or at $p_{\text{O}_2} = 1 \text{ atm.}$: $E_{\text{O}_2/\text{H}_2\text{O}} = 1.228 - 0.059 \text{ pH}$

Similarly line b represents the equilibrium of the reaction:



$$E_{\text{H}^+/\text{H}_2} = 0.000 - 0.059 \text{ pH} = -0.059 \text{ pH.}$$

In the region marked H₂O between the lines a and b water is stable with respect to hydrogen and oxygen at 1 atm. In other words: in that region the reaction: $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$ has a $\Delta G < 0$ and tends to proceed spontaneously to the right.

If water is brought into the region marked O₂ the reaction

$\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightleftharpoons 2\text{H}_2\text{O}$ will proceed spontaneously to the left with oxygen evolution. In a closed system this means that the pH will decrease and the oxygen pressure will increase.

Similarly in the region marked H₂ reaction $2\text{H}^+ + 2\text{e} \rightleftharpoons \text{H}_2$ proceeds spontaneously to the right with hydrogen evolution and increasing pH.

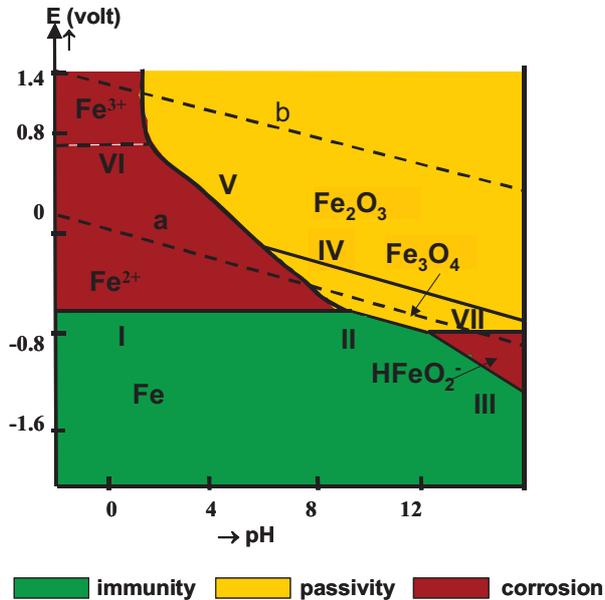
The line c represents the equilibrium: $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

In this reaction electrons do not play a part. This means that it is not influenced by the potential and thus runs vertically.

The simplified potential - pH diagram for the Fe-H₂O system is shown in figure 2.2.5.2.

Figure 2.2.5.2
Simplified potential - pH diagram for the Fe - H₂O system.

- I $\text{Fe}^{2+} + 2\text{e} \rightleftharpoons \text{Fe}$
- II $\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8\text{e} \rightleftharpoons 3\text{Fe} + 4\text{H}_2\text{O}$
- III $\text{HFeO}_2^- + 3\text{H}^+ + 2\text{e} \rightleftharpoons \text{Fe} + 2\text{H}_2\text{O}$
- IV $3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2\text{e} \rightleftharpoons 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$
- V $\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e} \rightleftharpoons 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$
- VI $\text{Fe}^{3+} + \text{e} \rightleftharpoons \text{Fe}^{2+}$
- VII $\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{e} \rightleftharpoons 3\text{HFeO}_2^- + \text{H}^+$



All lines for the iron equilibria are drawn for $(\text{Fe}^{2+}) = 10^{-6}$ mole/l. This concentration is often chosen in corrosion work as being so low that this corresponds to "natural" conditions.

We will now discuss the application of this type of diagram to the corrosion of iron. We see that in acid solutions the line I is below line a of the hydrogen evolution reaction. This means that reaction I cannot be in equilibrium in acidic water because the total reaction: $\text{Fe} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2$

will proceed spontaneously to the right and iron corrodes. Only when, with the help of an external voltage source, iron is brought to a potential below line I the dissolution of iron will stop. In this region iron is said to be immune. The hydrogen evolution will of course continue.

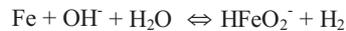
If the pH of the solution is raised we come to line II.

Again this is below the hydrogen evolution line and the total reaction



will tend to proceed spontaneously to the right. However, it now depends on the form in which the solid iron oxide (magnetite) is produced whether this reaction continues or not. If the oxide forms a closed, adherent layer the reaction, although remaining spontaneous, will nevertheless (almost) stop because the direct contact between metal and solution is broken. When this occurs we say that iron has become passive. If the oxide is porous or non-adherent no passivity occurs and the dissolution reaction continues. The E - pH diagram shows the regions in which passivity may be expected to occur, but not if it will indeed so, because that depends upon the form in which the oxide is produced.

At still higher pH the iron starts to corrode again according to the reaction:



All iron-dissolution reactions also lie under the oxygen reduction line b. In oxygen containing solution we will thus simultaneously have reactions such as: $2\text{Fe} + \text{O}_2 + 4\text{H}^+ \Leftrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$, proceeding spontaneously to the right.

As shown, it is possible to delineate areas in which iron, iron hydroxide, ferrous ions etc. are thermodynamically stable. That is, these forms represent states of lowest free energy.

The main uses of these diagrams are:

- predicting the spontaneous direction of reaction;
- estimating the composition of corrosion products;
- predicting environmental changes, which will prevent or reduce corrosive attack.

For example the large region in labeled Fe indicates that iron is inert under these conditions of potential and pH.

Potential - pH diagrams are subject to the same limitations as any thermodynamic calculation. They represent equilibrium conditions and should never be used to predict the velocity of a reaction.

Thermodynamic arguments only lead to conclusions about the direction of possible reactions and not about the rates with which they take place.

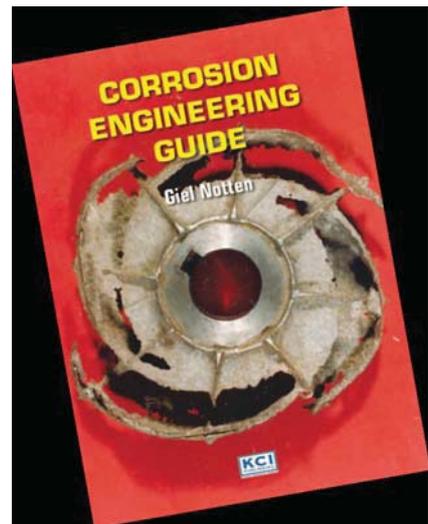
Summarizing we can say that a metal tends to corrosion when it is in contact with a solution where a cathodic reaction is possible with an equilibrium potential higher than that of the metal dissolution reaction in that solution.

Giel has written the Corrosion Engineering Guide, a valuable asset for any engineer working in a urea plant.

This guide is available via:

<http://www.stainless-steel-world.com/>

Please find the Table of Content of this Corrosion Engineering Guide herebelow.



About Giel Notten

Giel is a true materials and corrosion expert who, before his retirement in 2004, spent thirtyeight years working with DSM in The Netherlands. After gaining his Engineering degree at the Higher Technical School of Heerlen, The Netherlands, he joined DSM's central laboratory.

He was to remain with the company for the rest of his career and held several positions as a materials and corrosion expert there. For the last twenty years before he retired, Giel worked in the Corrosion Department as Managing Senior Corrosion Engineer. He has further participated in numerous conferences spreading the word about his broad experiences as a corrosion and materials specialist in chemical process plants.

For Stamicarbon, a subsidiary company of DSM, and licensing DSM's know-how, he set up programmes for lifetime extension studies in urea and ammonia plants and supervised them.

He was also involved in the development of Safurex[®], the super-duplex stainless steel grade (developed by Sandvik in cooperation with Stamicarbon) for application in Stamicarbon urea plants.

Giel has always enjoyed teaching so, after only five years working in the field at DSM, he already began to develop a Corrosion Engineering course. Since then he has taught many young engineers from both inside and outside DSM about the ins and outs of corrosion control in chemical plants. He was also a board member of NACE Benelux and a member of the Contact Group Corrosion of the Dutch Chemical Process Industry and the Studiekern Corrosion of the Dutch Corrosion Society (NCC).

Since his retirement from DSM, Giel Notten has remained active as a corrosion engineering consultant. He has devoted much of his time to passing on his extensive knowledge and experience on the complicated topic of corrosion engineering to a new generation of engineers.

He has done this in the form of numerous corrosion courses and workshops.

Alongside his professional career, Giel has been very active in local societies and has been a Rabobank board member for about thirty-five years, twenty-five years of which as Chairman of the Board. Furthermore, he is an active cyclist. Together with his wife, Lianne, he has made trips up to 2500 km by bicycle to Santiago de Compostela, Spain and Rome, Italy.



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