6. Studying corrosion and corrosion inhibitors

According to NACE (National Association of Corrosion Engineers, USA), corrosion is "an object, usually a metal failure due to its interaction with the environment". According to the International Organization for Standardization (ISO), "Corrosion is a physical-chemical interaction between the metal object and its surroundings, by which the properties of a metal object change, and this interaction can lead to partial or complete destruction of the metal object." It can be seen that the definitions emphasize the negative effect of corrosion, which is not surprising given that some estimates indicate that around one fourth of the world's metal production is lost yearly. In addition to the direct damage (temporary or permanent unusable metal objects and the resulting material, energy and labor requirements), the magnitude of indirect damage is almost insurmountable.

Metal corrosion can be reduced in many ways. For example, by using a protective coating (e.g. paint), the metal and the corrosive media cannot come into contact and that makes the corrosion processes impossible. However, when the coating is somehow damaged very sudden corrosion may occur under the broken coating.

Electrochemical methods - anodic or cathodic protection - can inhibit or slow down the corrosion kinetically or thermodynamically. The disadvantage of these methods is the energy requirement.

If we do not try to eliminate corrosion completely, we can achieve excellent results with minimal effort when using appropriate methods. Such a method is the use of corrosion inhibitors. Corrosion inhibitors, when mixed with the corrosive medium, can also significantly reduce the rate of corrosion processes at very low concentrations without significantly altering the aggressiveness of the medium. Most of the corrosion inhibitors are organic compounds, but inorganic substances are among them (more commonly referred to as passivators). In this practical course you will study the effect of inhibitors on the rate of corrosion in a very corrosive medium.

1. Theoretical background

1.1. The thermodynamic basics of electrochemical corrosion

Oxidation of the metals is the corrosion process. Thermodynamically most metals are stable in the oxidized form under normal conditions. Oxidation always comes together with a reduction, and in normal (simplest) cases of corrosion (if other less readily reducible substances are not present) this process is the reduction of molecular oxygen or water.

$M \rightarrow M^{z+} + ze^-$	Ox1. oxidation if the product is well soluble; metal electrode
$M + X^{y-} \rightarrow MX^{(z-y)+} + ze^-$	Ox2. oxidation if the product is hardly soluble; metal insoluble salt electrode
$M^{z_1+} \rightarrow M^{(z_1+z)+} + ze^-$	Ox3. oxidation; redox electrode
$2H^+ + 2e^- \rightarrow H_2$	Red1. water reduction in acidic solution; hydrogen electrode
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	Red2. water reduction in neutral/basic solution; hydrogen electrode
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	Red3. oxygen reduction in acidic solution; oxygen electrode
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	Red4. oxygen reduction in neutral/basic solution; oxygen electrode

Electrochemical corrosion is thermodynamically possible if any combination of Ox1-Ox3 and Red1-Red4 processes can give a system in which:

$$\sum \nu_i \mu_i = \Delta G < 0$$

where ν_i is the stoichiometry coefficient of the i-th component, μ_i is the chemical potential of the i-th component, ΔG is the reaction free energy. Electrochemically this means that the cell reaction potential (E_{cell}),

$E_{cell} = -\dfrac{\Delta G}{zF} > 0$, that is, a Galvanic (Voltaic, a spontaneously working) cell can be formed from the oxidation and reduction processes. (F is the Faraday-constant, i.e. the molar elementary charge, 96485 C/mol)

The thermodynamic possibility of corrosion can be seen most obviously on the so-called Pourbaix diagrams. These diagrams show the stable components and phases as a function of the acidity, pH and of the electrode potential in aqueous medium. In Figure 1, the simplified Pourbaix diagram of iron can be seen where the lines correspond to standard conditions, i.e., when the activity of each component is one and the pressure of the gas components is the standard pressure of 1 atm (today it is rather 1 bar).

The diagram usually contains the stability limits of the solvent, as well, i.e. the hydrogen and oxygen line in aqueous media. Considering e.g., the oxygen line, oxidation of water can occur at potentials larger than the oxygen line: $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$. At lower potentials the reduction of molecular oxygen would happen: $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$.
At lower potential than the hydrogen line, reduction of water can occur: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
At larger potential, the oxidation of molecular hydrogen would happen: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
These processes limit the possible stable phases in a given system.

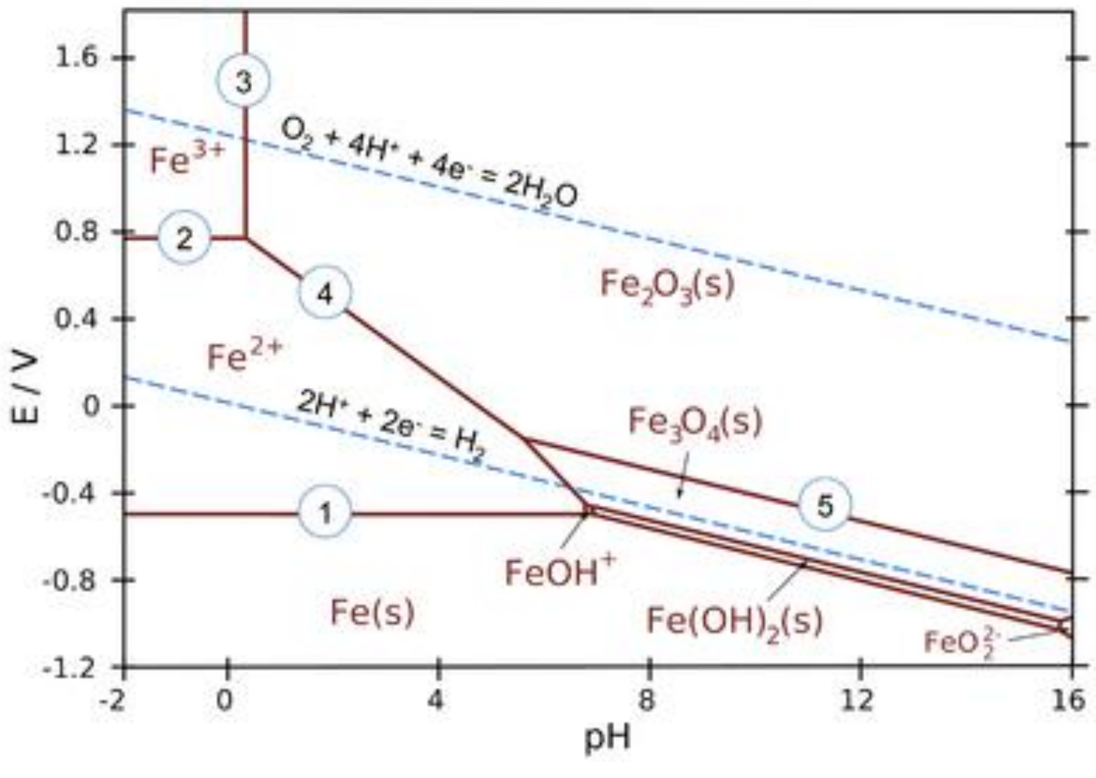

Figure 1 Pourbaix diagram of iron. The electrode potentials are given vs Standard Hydrogen Electrode (SHE).

On the diagram it is clear that metallic iron phase is below the hydrogen line at any pH value, i.e. even without the presence of oxygen (air), it can spontaneously be oxidized. In acidic-neutral medium to Fe^{2+} ion, $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$, in alkaline medium to iron(II)-hydroxide,
$Fe + 2H_2O \rightarrow Fe\ (OH)_2 + H_2$

In reality, the situation is less dangerous by the formation of iron(III)-oxide (Fe_2O_3, normally called rust) from iron(II)-hydroxide in the presence of oxygen, since Fe_2O_3 can form a more or less closed protective layer onto the surface of the iron and thus inhibits further contact with water which significantly slows down further dissolution. Unfortunately, the other side is true, as well. In acidic, neutral media Fe^{2+} ion is oxidized by oxygen to Fe^{3+}, which in turn is a catalyst for the oxidation of Fe.

1.2. The kinetic basics of electrochemical corrosion

1.2.1. Basic concepts of electrochemistry

At an electron conductor-ion conductor interface (at an electrode), even in the simplest case, charge separation can occur, electron, ion accumulation may occur at the boundaries of the two phases (Figure 2). The interface behaves like a capacitor and it can be characterized by its capacitance (C). If there is a substance in the ion conducting phase that is capable of giving or picking up electrons at a given interfacial potential difference, it is also possible that charge passes through the interface, charge transfer process, so called Faradaic process can take place (Figure 3). The charge transfer process can be divided into several stages (steps), kinetically (generally) complex. It is necessary to reach the surface by the reactant (mass transport, i.e., convection, migration or diffusion), possible intermediate chemical reaction can occur (e.g., protonation, deprotonation, ligand exchange, any other chemical reaction), adhesion to the electrode surface (adsorption) and after the charge transfer reaction everything can happen vice versa.

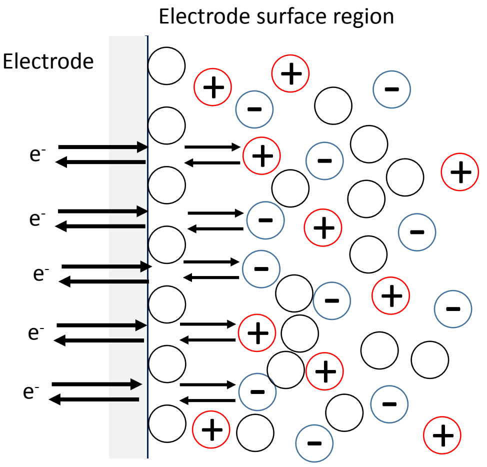

Figure 2 Ideally polarizable electrode. The empty circles represent the solvent molecules.

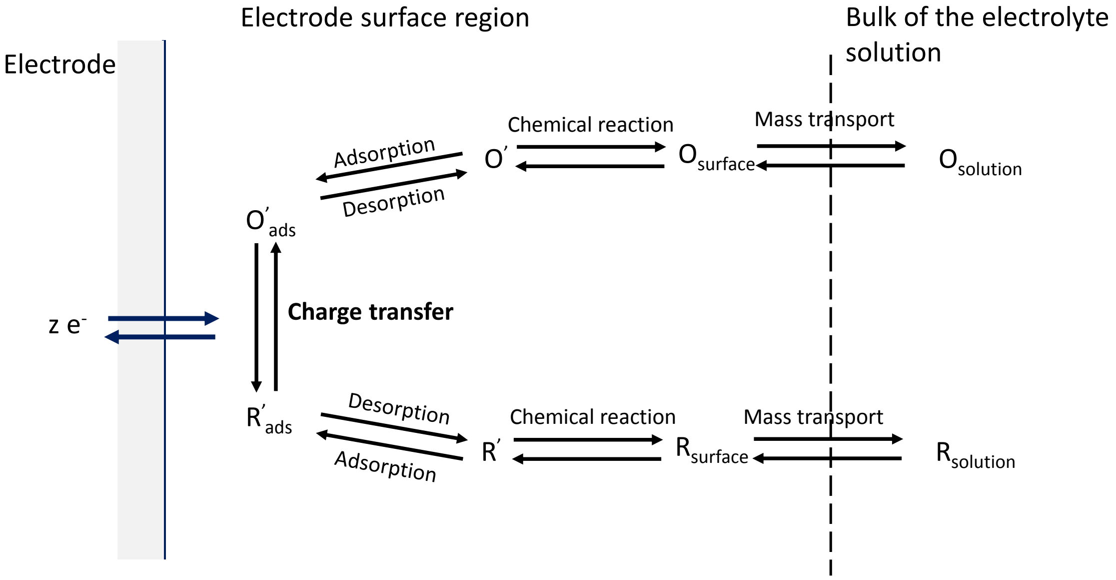

Figure 3 Possible stages (steps) of the charge transfer processes.

As with the complex heterogeneous kinetic processes, the rate of the Faradaic process will be determined by the slowest step. In the simplest case, the competition of charge transfer and mass transport may occur. Charge transport means the flux of electrical charges, i.e. current, but this can not be greater than the flux provided by the mass transport, the two being connected to each other. In a simple (elementary) redox process, e.g.

$$\mathrm{Ox} + \mathrm{ze} \underset{k_{ox}}{\overset{k_{red}}{\rightleftharpoons}} \mathrm{Red}$$

(hypothetically this could be an $Fe^{2+} + 2e \rightarrow Fe$ reaction) where no prior or subsequent chemical processes have to be considered, the rate of reaction (r) can be given as

$$r = \frac{1}{A}\frac{dn}{dt} = \frac{1}{A}\frac{\frac{1}{zF}dQ}{dt} = \frac{I}{AzF} \qquad 1.1.$$

where A is the surface area, dn/dt is the time derivative of the amount of substance transformed, z is the charge number change, F is the Faraday constant (molar elementary charge), Q is the amount of charge transmitted during the charge transfer process, I is the measurable current.

Since r and I are in direct proportion with each other and the proportionality factor is constant for a given system, therefore, in electrochemistry it is usual to express the reaction rate simply by the measured current (or with the I/A, current density). As it is common in heterogeneous kinetics, this is proportional to the concentration of substances reacting, and in a simpler case, e.g.

$$I = AzF \cdot r = (AzF) \cdot k \cdot \prod_{i=1}^{n} c_i^{\beta_i} \qquad 1.2.$$

where c_i is the concentration of the i-th substance on the surface, β_i is the reaction order of the i-th component, k is the rate coefficient. If the redox process is a first order reaction in both directions, then

$$r_{ox} = k_{ox} \cdot c_{\mathrm{Red}}(0,t) = \frac{I_{ox}}{AzF} \qquad 1.3.$$

$$r_{red} = k_{red} \cdot c_{Ox}(0,t) = \frac{I_{red}}{AzF} \qquad 1.4.$$

where r_{ox} and r_{red} are the rate of oxidation and reduction, k_{ox} and k_{red} are the rate coefficients of the two processes, $c_{Ox}(0,t)$ and $c_{Red}(0,t)$ are the surface (x=0) concentration of Ox and Red at the time t, I_{ox} and I_{red} is the absolute value of the oxidation (anodic) and reduction (cathodic) current.

The resulting net reaction rate (and the net current, I):

$$r_{net} = k_{ox} \cdot c_{\mathrm{Red}}(0,t) - k_{red} \cdot c_{Ox}(0,t) = \frac{I}{AzF} \qquad 1.5.$$

(By definition, oxidation is the positive current and reduction is the negative current, except in the USA!) That is,

$$I = I_{ox} - I_{red} = AzF\left(k_{ox} \cdot c_{\mathrm{Red}}(0,t) - k_{red} \cdot c_{Ox}(0,t)\right) \quad 1.6.$$

The specificity of the electrochemical charge transfer processes is that the rate coefficient depends not only on the temperature, but also on the potential difference at the interface between the electrode and electrolyte (Δφ, absolute electrode potential), i.e., on the electrode potential (a potential difference compared to another electrode being in equilibrium). This potential difference (or its change) oppositely acts on the activation energy of the oxidation and reduction processes and thus on the rate coefficients (Figure 4).

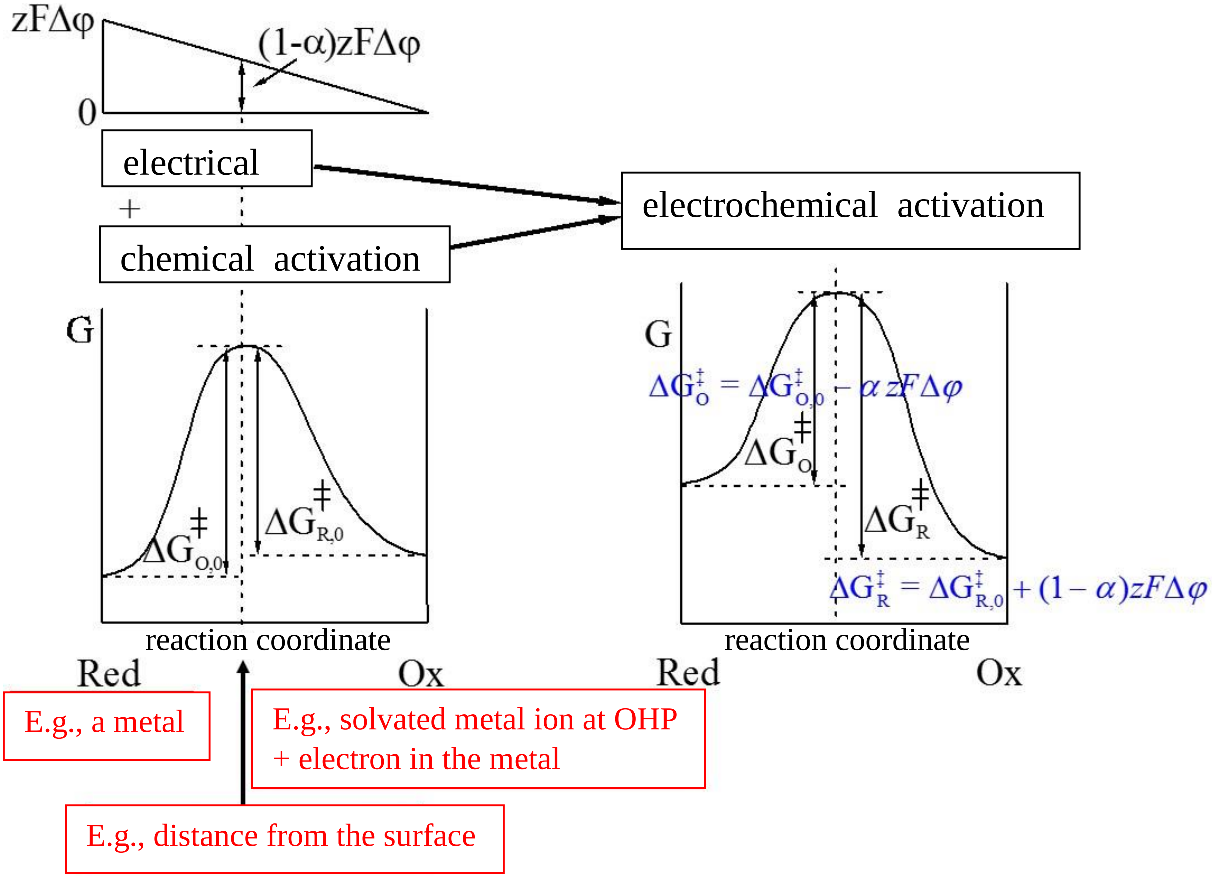

Figure 4 The combined effect of chemical and electrical activation on the activation free energy (and thus on the rate coefficient). zFΔφ is the electrical energy difference for zF charge between the surface of the electrode and the Outer Helmholtz Plane (OHP), $\Delta G^{\ddagger}_{0}$ is the hypothetical chemical part of the activation energy, $\Delta G^{\ddagger}$ is the activation energy of the electrochemical process (oxidation and reduction), α is the so called transfer coefficient or symmetry factor.

The rate coefficients can be expressed as parameters showing only the dependence on the interfacial potential difference:

$$k_{ox} = k_{ox,chemical} \cdot \exp\left[\alpha \frac{zF}{RT} \Delta\varphi\right] \quad 1.7.$$

$$k_{red} = k_{red,chemical} \cdot \exp\left[-(1-\alpha) \frac{zF}{RT} \Delta\varphi\right] \quad 1.8.$$

where α is the so-called transfer coefficient (or symmetry factor), showing the energetic symmetry of the transition state between the initial and the final states (activated complex) along the reaction coordinate. In a fully symmetric case $\alpha = 1/2$, but its normal value could be $0.3 < \alpha < 0.7$. R is the molar gas constant, T is the thermodynamic temperature.

Δφ can not be determined (measured), but its difference from the state where the rate of oxidation and reduction is the same, i.e. the electrode is in equilibrium, yes.

$$\eta = \Delta\varphi - \Delta\varphi_{eq} = E - E_{eq} \qquad 1.9.$$

η is the so-called (activation) overvoltage, E is the actual electrode potential (measured against a reference electrode being in equilibrium), E_{eq} is the equilibrium electrode potential for the given composition, $c_{Ox}(0, t)$ and $c_{Red}(0, t)$.

Replacing into 1.6. -1.8. and assuming that the surface concentrations are constant:

$$I = I^0\left(\exp\left[\alpha\frac{zF}{RT}\left(E - E_{eq}\right)\right] - \exp\left[-(1-\alpha)\frac{zF}{RT}\left(E - E_{eq}\right)\right]\right) \qquad 1.10.$$

(time-independent Butler-Volmer equation) where I^0 is the so-called exchange current (the absolute value of the oxidation and reduction current equal at the equilibrium electrode potential). I^0:

$$I^0 = k_{ox,chemical}\; c_{\mathrm{Red}} \exp\left(\alpha\frac{zF}{RT}\Delta\varphi_{eq}\right) = k_{red,chemical}\; c_{\mathrm{Ox}} \exp\left(-(1-\alpha)\frac{zF}{RT}\Delta\varphi_{eq}\right) \qquad 1.11.$$

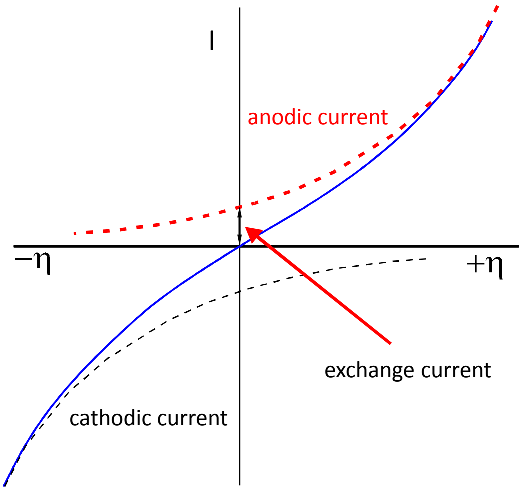

Figure 5 Linear representation of the current-overvoltage function

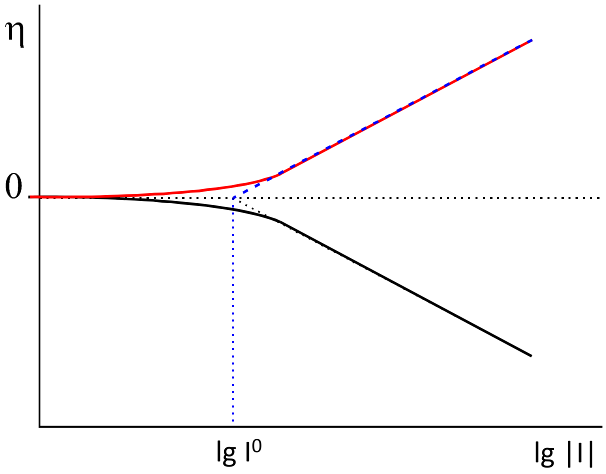

Figure 6 Half logarithmic representation of the overvoltage - current function (Tafel representation)

If $\eta = E - E_{eq}$ is small, i.e. the exponential functions can be replaced by the first two components of their power series ($e^x \approx 1 + x$):

$$I = I^0\left(\left[1 + \alpha\frac{zF}{RT}\left(E - E_{eq}\right)\right] - \left[1 - (1-\alpha)\frac{zF}{RT}\left(E - E_{eq}\right)\right]\right) = I^0\frac{zF}{RT}\eta \qquad 1.12.$$

That is, the current is the linear function of the overvoltage close to the equilibrium electrode potential (η ≈ 0). In this range, it is usual to define, in corrosion studies, the so-called polarization resistance. (Just to remind you: Ohm's law $R = \frac{U}{I}$, where U is the voltage between the two ends of a conductor, I is the current flowing through the conductor, R is the resistance of the conductor.)

$$R_{polarization} = \frac{\eta}{I} = \frac{RT}{zFI^0} \qquad 1.13.$$

If η >> 0 the cathodic part can be neglected (becomes so small), i.e.

$$I = I^0 \exp\left(\alpha \frac{zF}{RT}\eta\right) \qquad 1.14.$$

That is, the logarithm of the current is a linear function of the overvoltage. Traditionally, we do not use this relationship, but the reverse function, and not the "natural" logarithm, but the ten-based logarithm (Tafel representation)

$$\lg I = \lg I^0 + \alpha \frac{zF}{\ln 10 \cdot RT}\eta \qquad 1.15.$$

$$\eta = -\frac{\ln 10 \cdot RT}{\alpha zF}\lg I^0 + \frac{\ln 10 \cdot RT}{\alpha zF}\lg I \qquad 1.16.$$

where $\frac{\ln 10 \cdot RT}{\alpha zF} = \beta_a$ is the so-called anodic Tafel slope.

η - lgI therefore gives a straight line (see Figure 6) whose slope is βa, its value (extrapolation) at η = 0 is $\lg I^0$.

If η << 0 the anodic part is negligible, i.e.

$$I = -I^0 \exp\left(-(1-\alpha)\frac{zF}{RT}\eta\right) \qquad 1.17.$$

That is, the logarithm of the absolute value of the current is a linear function of the overvoltage.

$$\lg |I| = \lg I^0 - (1-\alpha)\frac{zF}{\ln 10 \cdot RT}\eta \qquad 1.18.$$

$$\eta = \frac{\ln 10 \cdot RT}{(1-\alpha)zF}\lg I^0 - \frac{\ln 10 \cdot RT}{(1-\alpha)zF}\lg |I| \qquad 1.19.$$

where $\frac{\ln 10 \cdot RT}{(1-\alpha)zF} = \beta_k$ is the so-called cathodic Tafel slope.

η – lg|I| therefore gives a straight line (see Figure 6) whose slope is -βk, its value (extrapolation) at η = 0 is $\lg I^0$.

1.2.2. The kinetic basics of electrochemical corrosion

Electrochemical corrosion is due to (at least) two electrochemical processes.

Dissolution of one (or more) metal (oxidation, anodic process), M → M^{z+} + ze^-; or M + X → MX + ze^- if the product is slightly soluble (e.g., an oxide), and the reduction of a substance (cathodic process) occurs together, though **not necessarily at the same place**. When other less readily reducible substance is not present, the cathodic process is mainly oxygen reduction in oxygen-containing neutral or alkaline media, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, or the reduction of water / hydrogen ion in oxygen-free aqueous media or in acidic solutions, $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$; $2H^+ + 2e^- \rightarrow H_2$

The potential of the metal object (the electrode) is controlled by the processes together. Since one component of the reactions, the electron, is common, therefore the reactions can not be independent, but result in a so-called mixed-electrode. When the external current is zero, a stationary state may develop in which the rate (the current) of the anodic (oxidation) and cathodic (reduction) processes is equal, but this is not an equilibrium state.

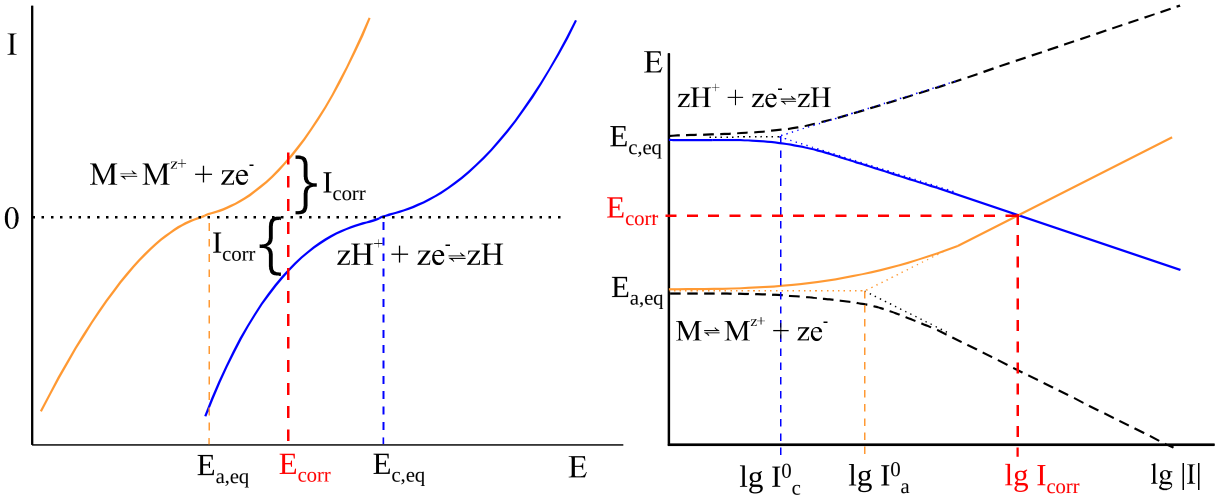

Figure 7: Simplified „Evans" diagram of electrochemical corrosion only considering M and H^+. Left - linear, right - half logarithmic (Tafel) representation. $E_{a,eq}$ is the equilibrium electrode potential of the anodic, oxidation process, I^0_a is the exchange current of the oxidation process. $E_{c,eq}$ is the equilibrium electrode potential of the cathodic, reduction process, I^0_c is the exchange current of the reduction process. E_{corr} is the mixed-potential when the sum of the current of the oxidation and reduction process is zero (corrosion potential), I_{corr} is the corrosion current.

For example, the rate of hydrogen evolution equals the rate of metal dissolution, I_{corr}, and the electrode potential is set to a common (non-equilibrium, only stationary) value, to the mixed-potential, i.e. to the corrosion potential E_{corr}.

At electrode potentials other than the corrosion potential (polarization of the electrode from the stationary state), a net current will flow, and its value can be given by the combination of the two sub-processes, and thus quantitatively (in the simplest case) can be given with the combination of Butler-Volmer equations.

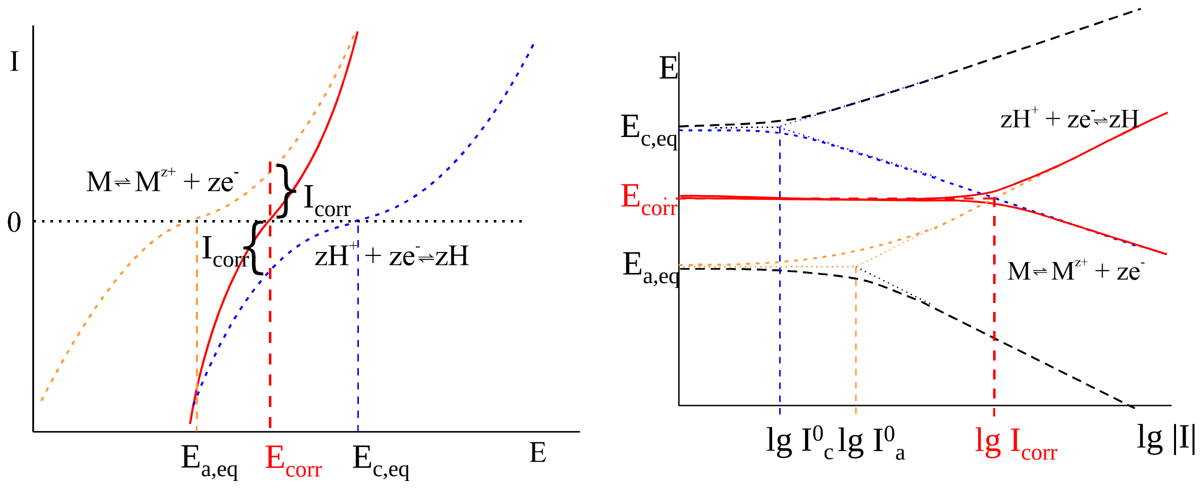

Figure 8 Linear and half logarithmic (Tafel) representation of the polarization, Evans diagram

If the metal dissolution is a simple charge transfer process:

$$I_M = I_M^0\left[\exp\left(\frac{\alpha_M zF(E-E_{M,e})}{RT}\right)-\exp\left(-\frac{(1-\alpha_M)zF(E-E_{M,e})}{RT}\right)\right] \tag{1.20.}$$

where I^0_M is the exchange current for the metal dissolution, α_M is the transfer coefficient for this process, $E_{M,e}$ is the equilibrium electrode potential of the metal dissolution.

If the hydrogen evolution is a simple charge transfer process:

$$I_H = I_H^0\left[\exp\left(\frac{\alpha_H zF(E-E_{H,e})}{RT}\right)-\exp\left(-\frac{(1-\alpha_H)zF(E-E_{H,e})}{RT}\right)\right] \tag{1.21.}$$

where I^0_H is the exchange current for hydrogen evolution, α_H is the transfer coefficient for this process, $E_{H,e}$ is the equilibrium electrode potential of the hydrogen evolution.

Without polarization (i.e., zero current, stationary potential), and if the corrosion potential is far enough both from $E_{H,e}$ and $E_{M,e}$, that is, the oxidation part for hydrogen and the reduction part for the metal is negligible:

$$I_M + I_H = 0 \approx I_M^0 \exp\left(\frac{\alpha_M zF(E-E_{M,e})}{RT}\right) - I_H^0 \exp\left(-\frac{(1-\alpha_H)zF(E-E_{H,e})}{RT}\right) \tag{1.22.}$$

That is

$$I_{corr} = I_M^0 \exp\left(\frac{\alpha_M zF(E_{corr}-E_{M,e})}{RT}\right) = I_H^0 \exp\left(-\frac{(1-\alpha_H)zF(E_{corr}-E_{H,e})}{RT}\right) \tag{1.23.}$$

Polarizing the system from E_{corr} to some E electrode potential:

$$I = I_{corr}\left[\exp\left(\frac{\alpha_M zF}{RT}(E-E_{corr)})\right)-\exp\left(-\frac{(1-\alpha_H)zF}{RT}(E-E_{corr)})\right)\right] \tag{1.24.}$$

Changing to the ten-base power,

$$I = I_{corr}\left[10^{\left(\frac{\alpha_M zF}{\ln 10\cdot RT}(E-E_{corr)})\right)} - 10^{\left(-\frac{(1-\alpha_H)zF}{\ln 10\cdot RT}(E-E_{corr)})\right)}\right] \qquad 1.25.$$

$$I = I_{corr}\left(10^{\left(\frac{E-E_{corr}}{\beta_a}\right)} - 10^{-\left(\frac{E-E_{corr}}{\beta_k}\right)}\right) \quad \text{where } \beta_a = \frac{\ln 10\cdot RT}{\alpha_M zF} \quad \beta_k = \frac{\ln 10\cdot RT}{(1-\alpha_H)zF} \qquad 1.26.$$

where I is the net current, I_{corr} is the corrosion current, E is the electrode potential, E_{corr} is the corrosion potential (the steady state, the stationary electrode potential), βa is the so-called anodic Tafel slope, βk is the so-called cathodic Tafel slope on the Evans diagram.

For large polarization, if E >> E_{corr},

$$I = I_{corr}\cdot 10^{\left(\frac{E-E_{corr}}{\beta_a}\right)} \text{ or } \left(\mathrm{E}-\mathrm{E}_{corr}\right) = \beta_a \lg I - \beta_a \lg I_{corr} \qquad 1.27.$$

That is, a linear E-lgI relationship can be measured and the intersection at E = E_{corr} is $\lg I_{corr}$. (See the Tafel representation of the Evans Diagram, Figure 8.)

If E << E_{corr},

$$I = -I_{corr}\cdot 10^{-\left(\frac{E-E_{corr}}{\beta_k}\right)} \text{ or } \left(\mathrm{E}-\mathrm{E}_{corr}\right) = -\beta_k \lg|I| + \beta_k \lg I_{corr} \qquad 1.28.$$

That is, a linear E-lg|I| relationship can be measured and the intersection at E = E_{corr} is $\lg I_{corr}$. (See the Tafel representations of the Evans Diagram, Figure 8.)

For small polarization, E≈E_{corr}, the current - electrode potential function is linear:

$$I = I_{corr}\left(\frac{1}{\beta_a} + \frac{1}{\beta_k}\right)\ln 10\left(E - E_{corr}\right) \qquad 1.29.$$

whose slope gives the polarization resistance,

$$R_{polarization} = \frac{E - E_{corr}}{I} = \frac{\beta_a \beta_k}{I_{corr}(\beta_a + \beta_k)\ln 10} \qquad 1.30.$$

The situation is much more complicated if oxygen is present in the solutions. Although E^0_{Oxygen} is much larger than $E^0_{Hydrogen}$, but oxygen reduction is usually slow on metals (I^0_{Oxigen} is much smaller than $I^0_{Hydrogen}$) and the amount of oxygen is often limited at the surface by mass transport, i.e., diffusion. Even so, the corrosion current can be much larger!

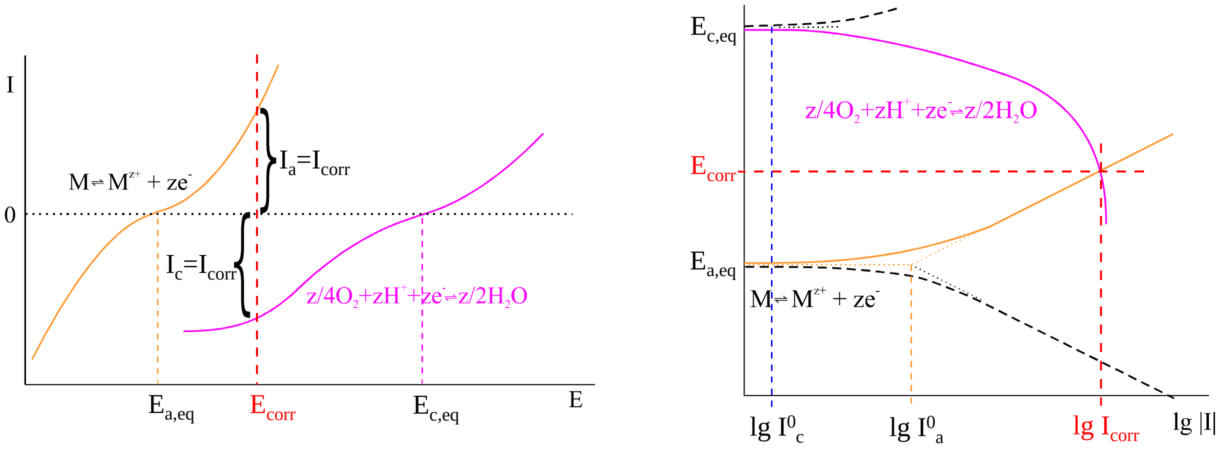

Figure 9 Metal dissolution with oxygen reduction. The rate of the reduction of oxygen is diffusion limited in the corrosion process (it does not change exponentially with the electrode potential, but it is almost constant).

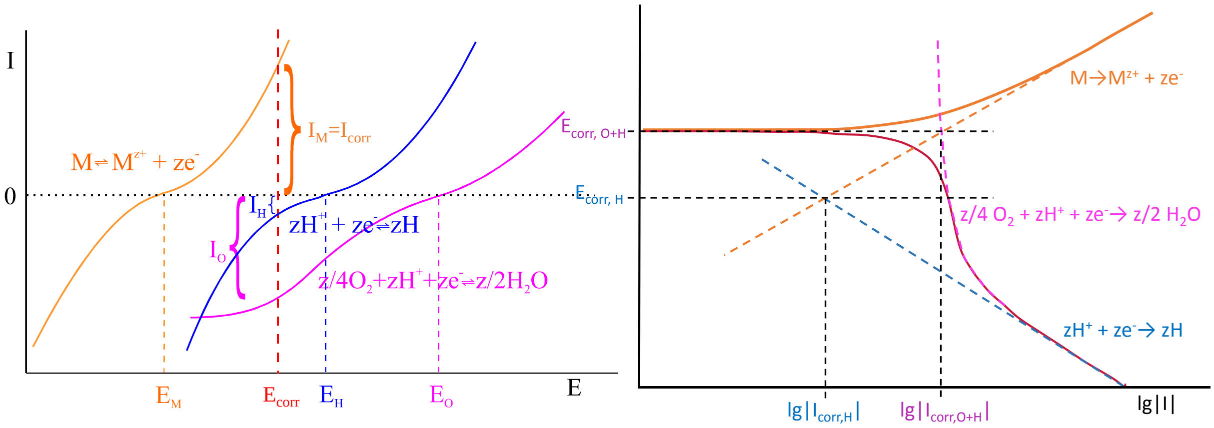

Figure 10 Metal dissolution with hydrogen and oxygen reduction. The logarithmic diagram shows only the sum of the currents. $E_{corr,H}$ and $I_{corr,H}$ would be oxygen-free corrosion potential and current, $E_{corr,O+H}$ and $I_{corr,O+H}$ is the result of the combined effect.

1.2.3. Adsorption inhibitors

They adsorb on the metal-electrolyte interface without affecting substantially the potential of the metal, i.e., it remains in the active dissolution range, but some process of corrosion becomes kinetically inhibited. By their binding to the surface (usually chemisorption, but it can also be film formation) they can be affect primarily the rate of the anodic process (metal dissolution, anodic inhibitors) or primarily the cathodic process (water or oxygen reduction, cathodic inhibitors). Or they can affect both (mixed inhibitors).

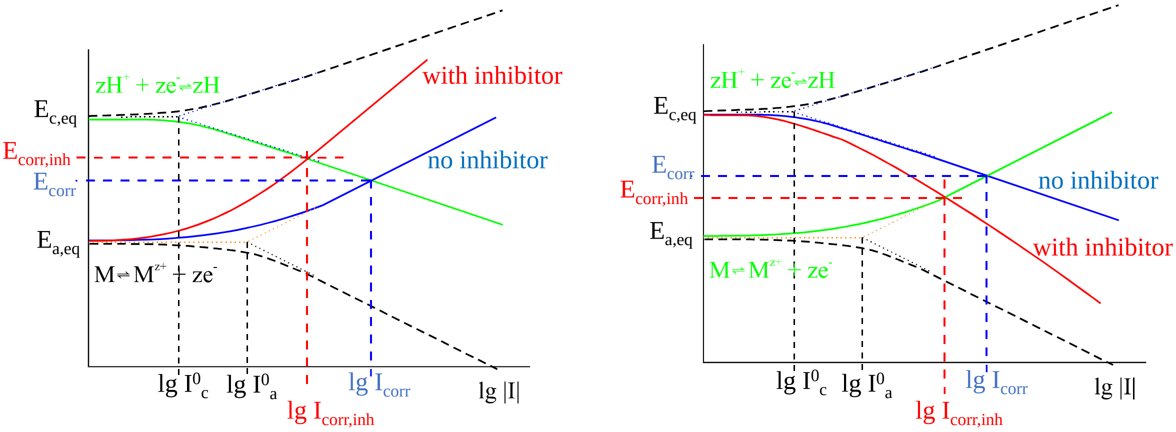

Figure 11 Effect of adsorption inhibitors on corrosion. Figure on the left: anodic inhibition (slowing down the metal dissolution), the corrosion potential will be more positive. Figure on the right: cathodic inhibition (slowing down the hydrogen evolution), the corrosion potential will be more negative.

The efficiency of the inhibitors can be characterized by their percentage of protection, which is

$$protection\% = \frac{I_{corr} - I_{corr,inh}}{I_{corr}} \cdot 100 \qquad 1.31.$$

2. Measurements

2.1. Preparation of the solutions

If the instructor does not specify anything else, prepare 100 cm^3, 1 mol/dm^3 HCl solution by diluting concentrated hydrochloric acid. Using this solution, prepare 50 cm^3, 30 mmol/dm^3 inhibitor solution containing 1 mol/dm^3 HCl solution, as well. That is, calculating the mass of the inhibitor based on the composition and molar mass of the inhibitor, measure the necessary amount into a 50 cm^3 flask, e.g., using a pipette and fill the flask with the 1 mol/dm^3 HCl solution.

If the instructor does not specify anything else, prepare 50 cm^3 of 1 mol/dm^3 KCl solution, as well!

2.2. Preparation of the metal object to be tested, electrode preparation

The carbon steel electrode used for the measurements must be grinded on an abrasive paper wetted with distilled water. Hold the electrode vertically, move it circularly and in a rosette form to avoid deformation and distortion on the flat surface (see Figure 12). After grinding (about 5 minutes), the electrode should be thoroughly cleaned with distilled water and placed immediately in the prepared cell with the solution to be examined.

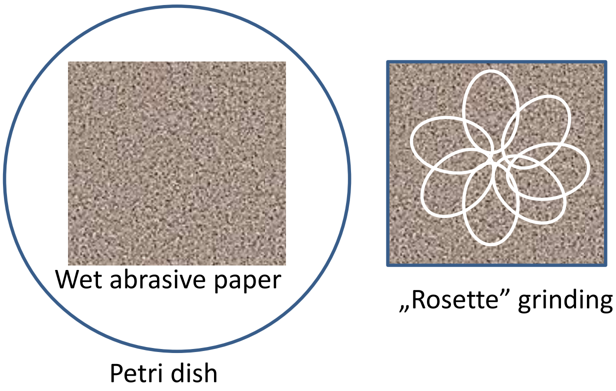

Figure 12 Preparing (grinding) the electrode

2.3. Assembling the cell

Use a low 50 ml beaker! Place the working electrode in the center of the beaker, next (or below) the counter electrode (Pt), and the Luggin capillary or the reference electrode itself on the other side. If using capillary, fit the reference electrode into the capillary and use a syringe to suck the electrolyte solution through the side stem to the reference electrode. Make sure that the rubber seal of the reference electrode is properly positioned and the solution does not leak during the measurement, because the system may be damaged if the electric contact to the cell is missing. Connect the three electrodes to the appropriate terminals of the potentiostat.

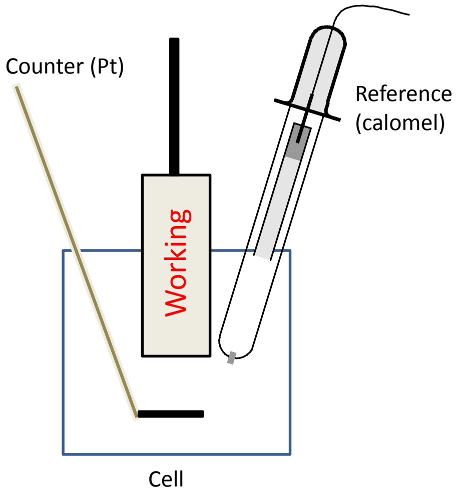

Figure 13 Arrangement of electrodes

As a reference electrode, use a saturated calomel electrode with 1 M KCl solution. (Normal Calomel Electrode, NCE, i.e. Hg|Hg_2Cl_2 (s)|cc. Hg_2Cl_2 (aq) + 1 M KCl)
The instruction for the potentiostat can be found within the equipments of the exercise.

2.4. Corrosion measurement in inhibitor containing hydrochloric acid solution

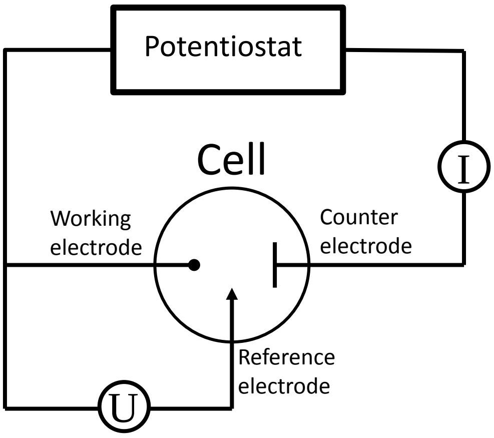

Figure 14 Schematic of 3 electrode measurement

Fill the appropriate amount of the inhibitor containing solution into the cell, insert the three electrodes, and connect them to the potentiostat. During the measurement, the potential difference between the working (electrode to be tested) and the reference (comparison, NCE) electrode is linearly varied in time while measuring the current that flows between the working and the counter electrode (auxiliary electrode, Pt). That is, we usually use a three-electrode system. The "job" of the potentiostat is to pass so much current through the working electrode (the electrode tested) that its potential compared to the reference electrode (an electrode being in equilibrium) would be the specified value. The current does not flow through the reference electrode (in that case it could not be in equilibrium), but between the working and the counter (auxiliary) electrode. It means that the potential and the current measurement takes place in two separate circuits.
Start the cathodic (reduction) polarization measurement according to the measurement description of the actual potentiostat, i.e. when the potential dependence of the reduction of hydrogen ions (or water or oxygen) is measured on the given electrode surface. The first part of this measurement is the determination of the Open Circuit Potential (OCP, when the counter electrode is cut off, the electric circuit is open, i.e. the current is zero). Wait until it stabilizes (ca. 10 min), i.e. the stationary state is formed, the system sets to the corrosion potential! Then, the actual polarization measurement (i.e., a slow **decrease** of the electrode potential with 1 mV/s scan rate from the OCP to 250 to 300 mV lower value) is initiated automatically. (Evans diagram cathodic polarization stage.)

After the measurement is completed, move out the electrode from the solution several times to remove the hydrogen bubbles attached to the surface and start the anodic (oxidation) polarization measurement, i.e. when measuring the potential dependence of the metal oxidation with the given electrode. The first part of this measurement is also the determination of the Open Circuit Potential (OCP). Wait until it stabilizes, i.e. the stationary state is formed, the system sets to the corrosion potential! Then, the actual polarization measurement (i.e., the slow **increase** of the electrode potential with 1 mV/s scan rate from the OCP to 200 to 250 mV to more positive values) is initiated automatically. (Evans diagram anodic polarization stage.)

2.5. Corrosion measurement in hydrogen chloride solution without inhibitor

The electrode must be grinded again, the cell and electrodes washed and the solution replaced with the inhibitor-free hydrochloric acid solution. Insert the three electrodes, connect them to the potentiostat. Repeat step 2.4. measurements!

2.6. Corrosion measurement in KCl solution

The electrode should be grinded again, washing the cell and electrodes, replacing the solution with the KCl solution. Do not foget to change the reference electrode to a new one, which is not contaminated by the acid! Insert the three electrodes, connect them to the potentiostat. Repeat step 2.4. measurements!

3. Evaluation of the results

3.1. Products of corrosion processes

Determine what corrosion processes can occur in each system based on the measured corrosion potentials and the estimated pH values in each solution (and taking into account the shape of polarization curves)! Use the Pourbaix diagram, Figure 1. For this, calculate the corrosion potentials against Standard Hydrogen Electrode. Take the potential of NCE (vs SHE) at room temperature as 0.285 V!

$E_{corr,meas}$ (vs NCE) = E_{corr} (vs SHE) - E_{NCE} (vs SHE)

Make the following summary.

System	**HCl**		**KCl**	
	chatodic	anodic	chatodic	anodic
$E_{corr, meas}$(vs NCE)/V				
E_{corr}(vs SHE)/V				
Estimated pH				
possible main corrosion process				
possible other processes				

3.2. Determination of corrosion potential

Collect the values of open circuit potentials (corrosion potentials) for different systems and polarization directions in a table. E.g.

System	**Inh** **cathodic**	**Inh** **anodic**	**HCl** **cathodic**	**HCl** **anodic**	**KCl** **cathodic**	**KCl** **anodic**
E_{corr}/V						

3.3. Determination of polarization resistances

Plot the electrode potentials of the beginning of 2.4.-2.6. measurements (cathodic and anodic polarization from the first to the 20th point) as the function of the current. The slope of the straight line fitted is the polarization resistance (R_p) for the given system and for the given direction of the polarization.

Summarize your results in a table. E.g . continue the previous table!

System	**Inh** **cathodic**	**Inh** **anodic**	**HCl** **cathodic**	**HCl** **anodic**	**KCl** **cathodic**	**KCl** **anodic**
…						
R_p/Ω						

3.4. Determination of Tafel slopes

For the 2.4.-2.6. measurements, plot the electrode potential - lg |I/A| curves and determine the Tafel slopes fitting straight lines onto the linear sections.

Summarize your results in a table. E.g.

System	**Inh** **cathodic**	**Inh** **anodic**	**HCl** **cathodic**	**HCl** **anodic**	**KCl** **cathodic**	**KCl** **anodic**
…						
β/(V/decade)						

Attention! Tafel slopes were defined as positive values!

3.5. Determination of corrosion currents from Tafel lines

From the intersection of the straight lines (plotted in 3.4.) at the actual corrosion potential (E_{corr}), determine the logarithm of the corrosion currents and calculate the corrosion current ($I_{corr)}$

System	**Inh** **cathodic**	**Inh** **anodic**	**HCl** **cathodic**	**HCl** **anodic**	**KCl** **cathodic**	**KCl** **anodic**
…						
I_{corr}/A						

3.6. Determination of corrosion currents from polarization resistances

From the polarization resistances determined in 3.3. and the Tafel slopes determined in 3.4., calculate the corrosion currents (see Eq. 1.30.).

System	**Inh cathodic**	**Inh anodic**	**HCl cathodic**	**HCl anodic**	**KCl cathodic**	**KCl anodic**
…						
I_{corr}/A (from R_p)						

3.7. Calculation of corrosion rate

Knowing corrosion currents determined in 3.5 and 3.6., also knowing the change in charge number, and the surface area of the electrode, calculate the rate of corrosion in the usual mm/year units. (Iron density is 7.87 g/cm^3, the relative atomic mass is 55.85.)

System	**Inh cathodic**	**Inh anodic**	**HCl cathodic**	**HCl anodic**	**KCl cathodic**	**KCl anodic**
…						
corrosion rate/(mm/year) (from I_{corr})						
corrosion rate/(mm/year) (from R_p)						

3.8. The protection of the inhibitor

Calculate the protection percentage of the inhibitor (Eq. 1.31.) by both the Tafel lines and the I_{corr} values calculated from polarization resistances. (For the system where it makes sense!)

System	**Inh cathodic**	**Inh anodic**	**HCl cathodic**	**HCl anodic**	**KCl cathodic**	**KCl anodic**
…						
protection% (from Tafel)			▨	▨	▨	▨

protection % **(from R_p)**						

Estimate the type of inhibition, anodic, cathodic or mixed, based on the shift in corrosion potential, change in polarization resistance, and the change in Tafel curves.

3.9. Determination of symmetry factors

Estimate the symmetry factor for (the most likely) oxidation and reduction processes on the basis of the change in charge (z) and Tafel slopes (see Eq. 1.26.). E.g.

System	**HCl (without inhibitor)**		**KCl**	
	cathodic	**anodic**	**cathodic**	**anodic**
β (Tafel slope)				
z				
$1-\alpha_{cathodic}$				
α_{anodic}				

3.10. Conclusion

Discuss the results! Did the inhibitor have any effect? Did the rate of corrosion change with the change of the medium, and if so, why? Did the presence of oxygen have an effect on the corrosion? How would you protect metallic objects from corrosion in such media? Any other comments!

Control questions

1. What is the electrode potential and what is the standard electrode potential?
2. The electrode potential of the Standard Electrode Hydrogen Electrode (SHE) at 25 °C is defined as zero. How much will be its electrode potential at 0 °C and 50 °C?
3. What electrode can be a reference electrode? What reference electrodes do you know?
4. In what thermodynamic conditions can the corrosion of metals occur in simple aqueous electrolyte solutions?
5. Write the Nernst equation for the cell reaction potential for a $Fe|Fe^{2+}$ (a_{Fe}) ⁞⁞ H^+ (a_H)|H_2 (p_H)|Pt Galvanic (Voltaic) cell.
6. What sub-processes should be considered in the kinetic treatment of a charge transfer process?
7. Write the Butler-Volmer equation for a simple charge transfer process. How does the current depend on the electrode potential?

8. What does diffusion-limited current mean?

9. What is polarization resistance? How can it be determined?

10. What is the Tafel slope and how can it be determined?

11. What is the symmetry factor and how can it be determined?

12. What are adsorption inhibitors and how do they work?

13. How to determine the corrosion current with Tafel curves?

14. Calculate the rate of corrosion (mm/year) when 10 µA corrosion current occurs on an iron of 1 cm^2 surface area while Fe^{2+} ions are formed during corrosion. The iron has a density of 7.87 g/cm^3, its relative atomic mass is 55.85, the Faraday constant is 96485 C/mol.