

Electrode Reactions and Kinetics

From equilibrium to non-equilibrium: We have a cell, two individual electrode compartments, given composition, molar reaction Gibbs free energy as the driving force, $\Delta_r G$, determining EMF E_{cell} (open circuit potential) between anode and cathode!

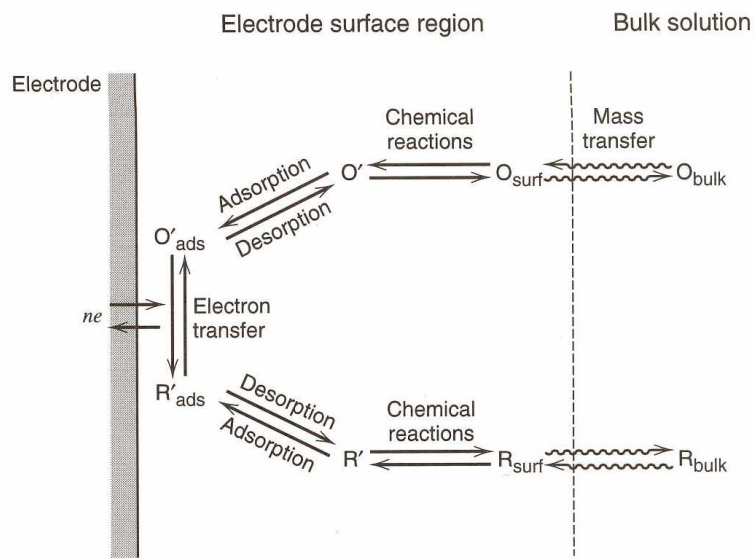
In other words: everything is ready to let the current flow! – Make the external connection through wires.

Current is **NOT** determined by equilibrium thermodynamics (i.e. by the composition of the reactant mixture, i.e. the reaction quotient Q), but it is controlled by resistances, activation barriers, etc

Equilibrium is a limiting case – any **kinetic model** must give the correct equilibrium expressions).

All the involved phenomena are generically termed

ELECTROCHEMICAL KINETICS!



This involves:

Bulk diffusion
Ion migration
(Ohmic resistance)
Adsorption
Charge transfer
Desorption

Let's focus on **charge transfer**! Also called: **Faradaic process**.

The only reaction directly affected by potential!

An electrode reaction differs from ordinary chemical reactions in that at least one partial reaction must be a **charge transfer reaction** – against potential-controlled activation energy, from one phase to another, across the electrical double layer. The reaction rate depends on the distributions of species (concentrations and pressures), temperature and electrode potential E .

Assumption used in the following: the electrode material itself (metal) is inert, i.e. a catalyst. It is not undergoing any chemical transformation. It is only a container of electrons.

The general question on which we will focus in the following is:

How does reaction rate depend on potential?

The electrode potential E of an electrode through which a current flows differs from the equilibrium potential E^{eq} established when no current flows.

The difference between these potentials is called overvoltage:

$$\eta = E - E^{\text{eq}} > 0 \text{ (anodic current)}$$

$$\eta = E - E^{\text{eq}} < 0 \text{ (cathodic current)}$$

Convention:

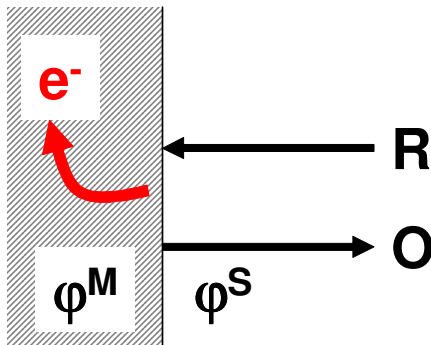
Current associated with reaction

Red \square **Ox** + **e^- (Me)** (anodic reaction)

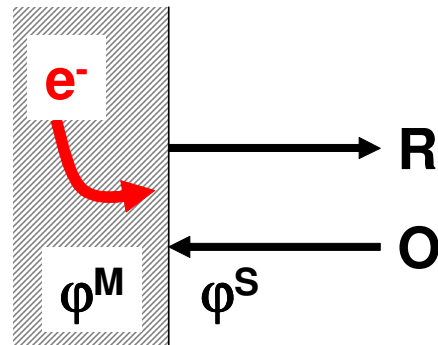
e.g. $\text{H}_{\text{ad}}, \text{Fe}^{2+}$ e.g. $\text{H}^+, \text{Fe}^{3+}$

\square anodic current, **positive direction**

anodic direction



cathodic direction



Overall rate of electrochemical reaction (per unit electrode surface area, units of $[\text{mol}/(\text{cm}^2\text{s})]$):

net rate = rate of oxidation – rate of reduction

$$v_{\text{net}} = K_{\text{ox}} c_{\text{red}}^{\text{s}} - K_{\text{red}} c_{\text{ox}}^{\text{s}} (*)$$

$c_{\text{red}}^{\text{S}}, c_{\text{ox}}^{\text{S}}$: surface concentrations of reduced and oxidized species

This definition of the net reaction rate is the same in anode and cathode. Both partial reactions take place at both electrodes. However, in the anode the anodic reaction dominates and in the cathode the cathodic reaction dominates.

Remember: Boths processes occur at both electrodes!

anode: $\nu_{\text{net}} > 0$, positive net rate

cathode: $\nu_{\text{net}} < 0$, negative net rate

General observation, e.g. Arrhenius (T-dependence of reation rate):

Charge transfer reactions are kinetically hindered!

Since species is charged: strong dependence of activation energy on electrode potential

$$E = \varphi^{\text{M}} - \varphi^{\text{S}}$$

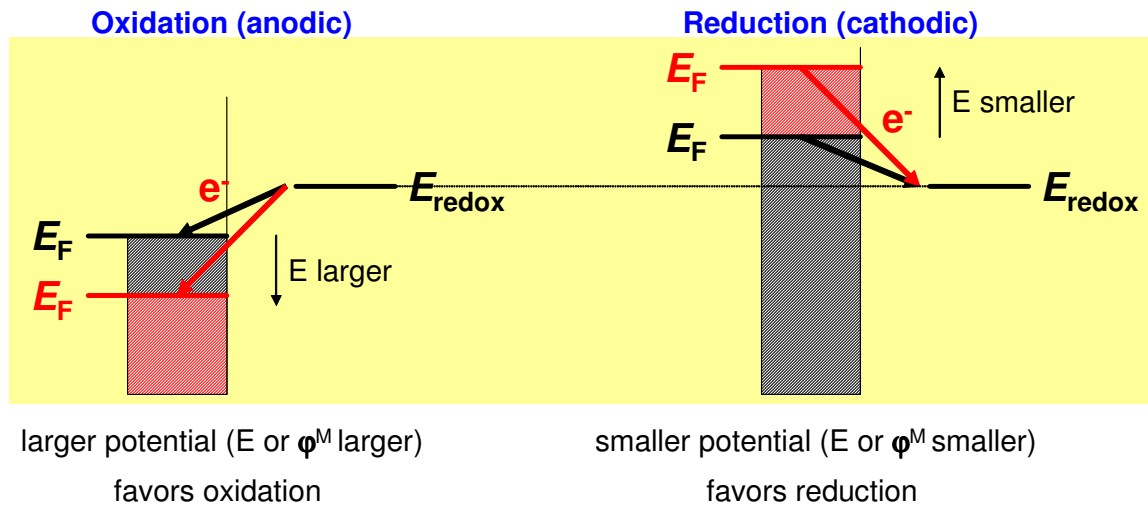
Discuss: where to take the value of the solution potential φ^{S} ????

close to metal surface, at position of compact layer

role of supporting electrolyte (problem sets!)

What do you actually control by applying a potential to an electrode?

The highest occupied electron level in the electrode is the Fermi-level. Electrons are always transferred to or from this level.



The energy of the redox couple in solution is not affected by the potential variation (no double layer corrections). Under ideal conditions, a shift in electrode potential only affects the position of the Fermi-level.

In order to understand, how the reaction proceeds in detail, we need to determine the rate constants in Eq.(^{*}): Use absolute rate theory!

$$K_{\text{ox}} = A \exp\left(-\frac{\Delta G_{\text{ox}}^{\dagger}(E)}{RT}\right)$$

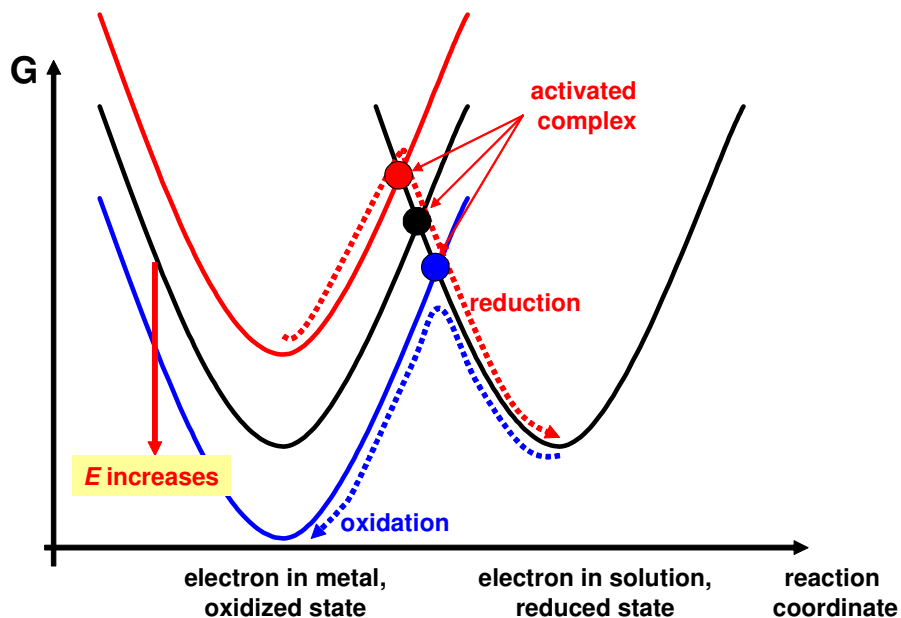
$$K_{\text{red}} = A \exp\left(-\frac{\Delta G_{\text{red}}^{\dagger}(E)}{RT}\right)$$

where $\Delta G_{\text{ox}}^{\dagger}(E)$ and $\Delta G_{\text{red}}^{\dagger}(E)$ are molar Gibbs free energies of activation

□ depend on potential!

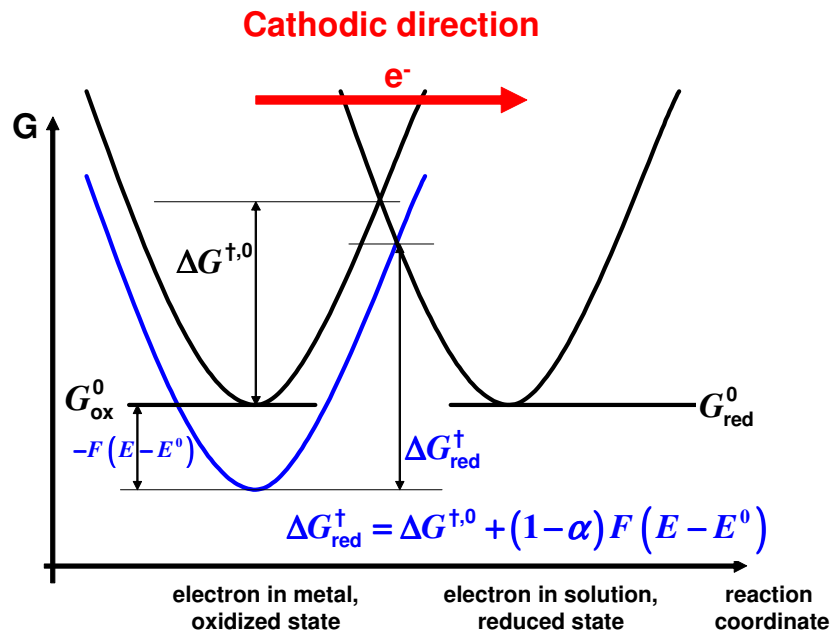
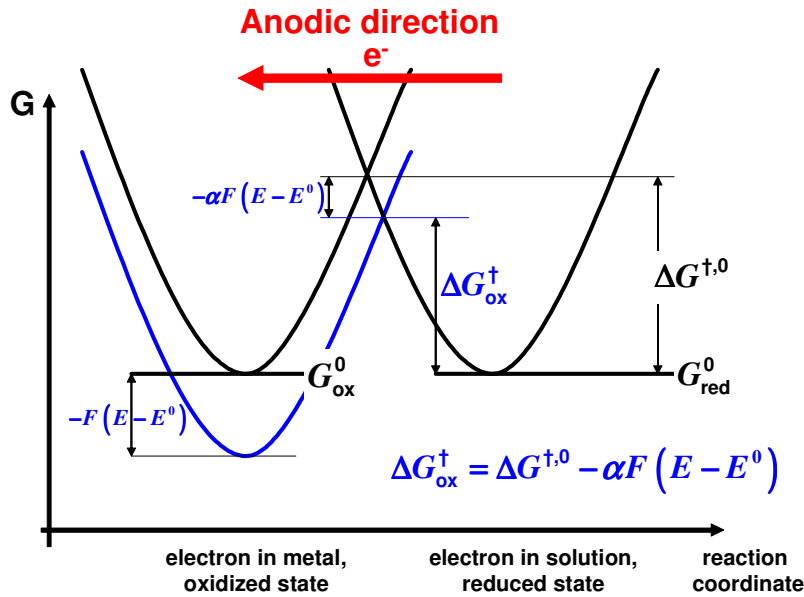
Which tendency do you expect upon variation of potential? Let's say the value of potential E is increased. Does the rate of the anodic reaction increase or decrease? What about the cathodic reaction?

Let's consider the free energy profile:



Charge transfer between reduced and oxidized state always proceeds via an activated intermediate complex. The height of the potential barrier depends on the electrode potential E . In the following pictures, the potential is shifted from the equilibrium value (black curves) to a more

positive potential (blue curve). Note: only the state corresponding to the electrons in the metal is affected by the potential shift, as discussed earlier. An increase in E favors the anodic direction (oxidation) and disfavors the cathodic direction (reduction).



Now, let's expand $\Delta G_{\text{ox}}^{\dagger}(E)$ about the standard equilibrium potential E^0 .

Recall: E^0 is a characteristic value of the redox pair that we are considering (at one particular electrode). At this potential, no net current would flow in this electrode under standard conditions. The equilibrium potential E^{eq} and the standard equilibrium potential E^0 are related by

$$E^{\text{eq}} = E^0 - \frac{RT}{|v_e|F} \ln Q \text{ (Nernst-equation)}.$$

Anodic reaction (in one electrode compartment):

$$\Delta G_{\text{ox}}^{\dagger}(E) = \Delta G_{\text{ox}}^{\dagger}(E^0) - \alpha F (E - E^0) \quad (\#)$$

anodic transfer coefficient:

$$\alpha = - \frac{1}{F} \left. \frac{\partial \Delta G_{\text{ox}}^{\dagger}}{\partial E} \right|_{E^0} > 0 \text{ (dimensionless)}$$

Cathodic reaction (in the same electrode compartment):

$$\Delta G_{\text{red}}^{\dagger}(E) = \Delta G_{\text{red}}^{\dagger}(E^0) + \beta F (E - E^0) \quad (\#\#)$$

cathodic transfer coefficient:

$$\beta = \frac{1}{F} \left. \frac{\partial \Delta G_{\text{red}}^{\dagger}}{\partial E} \right|_{E^0} > 0 \text{ (dimensionless)}$$

Now, the trends of changing the potential E are obvious:

Larger $E \Rightarrow \Delta G_{\text{ox}}^{\dagger}$ smaller \Rightarrow anodic reaction faster, in other words:
at larger electrode potential, electrons are more easily transferred
from the solution to the metal

Smaller $E \Rightarrow \Delta G_{\text{red}}^{\dagger}$ smaller \Rightarrow cathodic reaction faster, in other words:
at larger electrode potential, electrons are more easily transferred
from the metal to the solution

In going from E^0 to $E > E^0$ the Gibbs free energy of electrons in the metal is lowered which makes electron transfer to the metal more likely.

Note: Deviations from the linear approximations in Eqs.(#) and (##) arise at

large values of $|E - E^0| \approx \frac{RT}{F}$

Particular relation:

$$\Delta G_{\text{ox}}^{\dagger}(E^0) = \Delta G_{\text{red}}^{\dagger}(E^0) = \Delta G^{\dagger,0}$$

Consider a case with a high concentration of an inert electrolyte (recall your calculation involving a supporting electrolyte! – what was the effect that you found!?):

this inert (i.e. non-reacting) electrolyte screens the electrode potential

□ there will be practically no potential drop in the diffuse layer on the solution side

□ the electrostatic potential of reactants in solution is unchanged, when the electrode potential is varied, a variation in electrode potential is equal to a variation in the metal potential, $\Delta E = \Delta \phi^{\text{M}}$

□ in this case, the solution potential serves as a constant reference

$$\Delta G_{\text{ox}}^{\dagger}(E) - \Delta G_{\text{red}}^{\dagger}(E) = G_{\text{ox}} - G_{\text{red}} = -F(E - E^0) \text{ and } \alpha + \beta = 1$$

This simple relation between the Gibbs free energy of the charge transfer and potential E is fulfilled, if the entire potential drop occurs in the compact layer and reactants are not specifically adsorbed. The reaction is a so-called “outer-sphere reaction”.

The observed current density, in units of $[A/cm^2]$, of the electrode reaction can be expressed as:

$$j = F v_{\text{net}} = F [K_{\text{ox}} c_{\text{red}}^s - K_{\text{red}} c_{\text{ox}}^s]$$

Hence, the observed net current can be split up in an oxidation current j_{ox} and a reduction current j_{red} :

$$j_{\text{ox}} = F K_{\text{ox}} c_{\text{red}}^s \quad \text{and} \quad j_{\text{red}} = F K_{\text{red}} c_{\text{ox}}^s$$

Using the linear approximations for $\Delta G_{\text{ox}}^\ddagger(E)$ and $\Delta G_{\text{red}}^\ddagger(E)$ in the expressions for the rate constants we can write:

$$K_{\text{ox}} = A \exp \left\{ -\frac{\Delta G_{\text{ox}}^\ddagger(E)}{RT} \right\} = k_0 \exp \left\{ \frac{\alpha F (E - E^0)}{RT} \right\}$$

$$K_{\text{red}} = A \exp \left\{ -\frac{\Delta G_{\text{red}}^\ddagger(E)}{RT} \right\} = k_0 \exp \left\{ -\frac{(1-\alpha) F (E - E^0)}{RT} \right\}$$

where $k_0 = A \exp \left\{ -\frac{\Delta G^{\ddagger,0}}{RT} \right\}$ is the rate constant (in units of $[cm/s]$). It is a measure of the reaction rate at E^0 and where we used $\beta = 1 - \alpha$

Accordingly, we can now write an equation relating the electrode potential E to the observed current density for the electrode reaction as:

$$(BV \ 1) \quad j = F k^0 \left\{ c_{\text{red}}^s \exp \left(\frac{\alpha F (E - E^0)}{RT} \right) - c_{\text{ox}}^s \exp \left(-\frac{(1-\alpha) F (E - E^0)}{RT} \right) \right\}$$

This equation is widely known as the **BUTLER-VOLMER** equation.

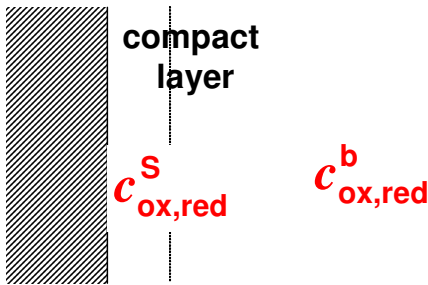
However, in general, the deviation of the electrode potential E from the situation of zero net current, i.e. at E^{eq} , under any experimental conditions is considered. Hence, we have to use the Nernst equation to determine the

equilibrium potential E^{eq} for a given composition in the bulk to establish the link between composition in the bulk and equilibrium

$$E^{\text{eq}} = E^0 + \frac{RT}{F} \ln \frac{c_{\text{ox}}^{\text{b}}}{c_{\text{red}}^{\text{b}}}$$

Using this relation in (BV 1) and recalling the definition of overpotential, $\eta = E - E^{\text{eq}}$, we can rewrite after some rearrangement (exercise!!) the Butler-Volmer equation in a different form, as a relation between current density and overpotential:

$$(BV\ 2) \quad j = Fk^0 c_{\text{red}}^{\text{b} \cdot (1-\alpha)} c_{\text{ox}}^{\text{b} \cdot \alpha} \left\{ \frac{c_{\text{red}}^{\text{s}}}{c_{\text{red}}^{\text{b}}} \exp\left(\frac{\alpha F \eta}{RT}\right) - \frac{c_{\text{ox}}^{\text{s}}}{c_{\text{ox}}^{\text{b}}} \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \right\}$$



Note, that we explicitly distinguish surface concentrations from bulk concentrations. Bulk concentrations (far away from the interface) determine the equilibrium potential. Under equilibrium conditions, surface concentrations, $c_{\text{red/ox}}^{\text{s}}$ (at the position of the

compact layer), are equal to bulk concentrations, $c_{\text{red/ox}}^{\text{b}}$, and no fluxes of species exist. At finite current, surface concentrations will generally be different from bulk concentrations, due to mass transport from bulk to surface.

In the particular case, when mass transport from bulk to surface is fast enough (rate of diffusion much larger than rate of reaction, see section on mass transport), we have $c_{\text{red}}^{\text{s}} = c_{\text{red}}^{\text{b}}$ and $c_{\text{ox}}^{\text{s}} = c_{\text{ox}}^{\text{b}}$. In this case, we can write the simplest form of the Butler-Volmer equation (historically the first version),

(BV 3)
$$j = j^0 \left\{ \exp\left(\frac{\alpha F \eta}{RT}\right) - \exp\left(-\frac{(1-\alpha) F \eta}{RT}\right) \right\}$$

Now, we have three different ways to write the Butler-Volmer equation. You will find all the different forms used throughout electrochemical literature. Which one is most appropriate? (BV 3) is the least general form. It can only be used, when all sorts of mass transport limitations can be neglected and the current-potential relation is only determined by the kinetics of charge transfer. Whenever you see people using (BV 3) in a situation with significant mass transport limitations, something is screwed.

(BV 2) can be used for simple electrode structures, when the bulk concentrations are controlled.

(BV 1) is the most general form. It explicitly displays all dependencies on concentrations and electrode potential. All other quantities in it are constants.

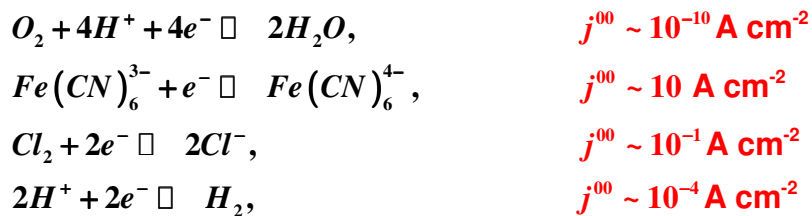
The factor in front of the brackets (pre-exponential factor) on the right hand side of (BV 2) and (BV 3)

$$j^0 = F k^0 c_{\text{red}}^{\text{b} (1-\alpha)} c_{\text{ox}}^{\text{b} \alpha}$$

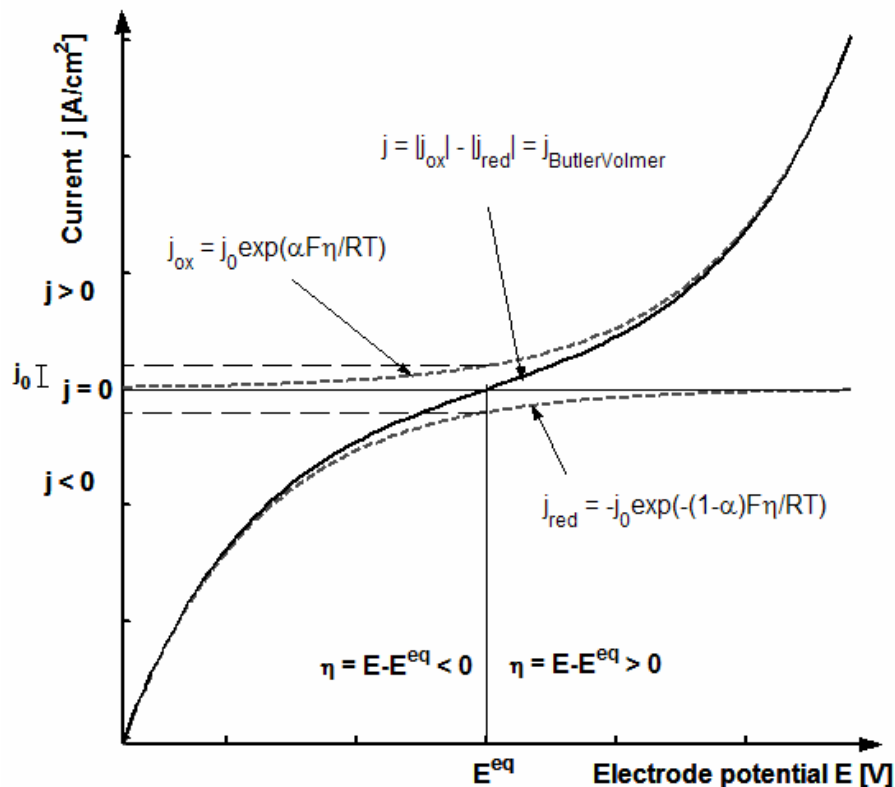
is called exchange current density and from the last equation, it can be seen that it is concentration dependent. It is a measure of the current at zero overpotential, when no net current is flowing.

One can also define a **standard exchange current density** as:

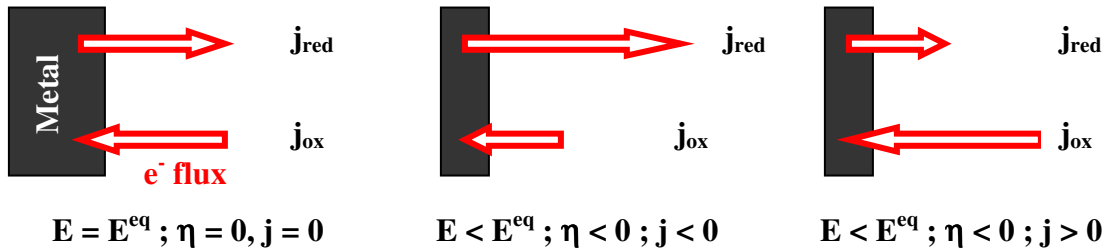
$j^0 = Fk^0$ and hence $j^0 = j^{00} (c_{\text{red}}^s)^{(1-\alpha)} (c_{\text{ox}}^s)^\alpha$. Usually, these values are reported in the literature (unless specific concentrations are explicitly specified). Values of exchange current densities can widely differ for different reactions. In most cases, they are known only with low accuracy (within an order of magnitude). A few values are listed in the following:



Now, let us explore the meaning of the different parameters of the Butler-Volmer equation:



- 1) The exchange current density represents the current density, which flows in each direction, anodic and cathodic, when the overall current is zero, i.e. in the electrochemical equilibrium. Hence, at E^{eq} we have a dynamic equilibrium where both oxidation and reduction take place at the same rate, given by j^0 .



At positive overpotentials, the oxidation current prevails whereas at negative overpotentials, the reduction rate is higher. As a pre-exponential factor, the exchange current density largely determines the overall kinetics:

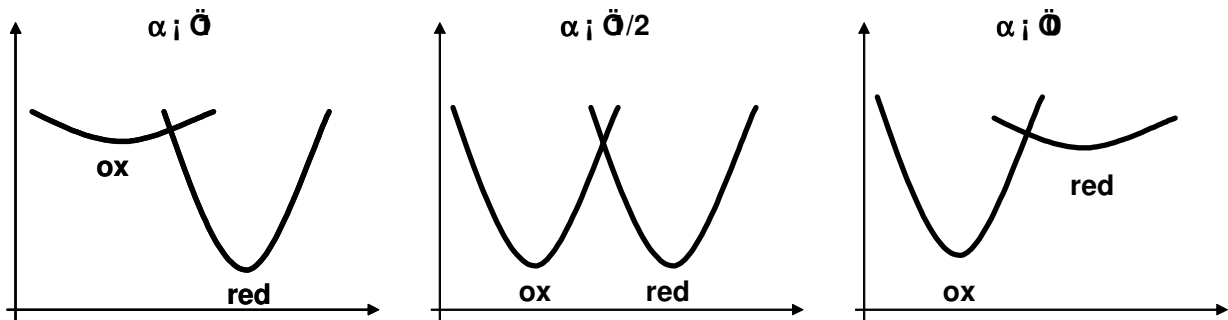
- a) j^0 large: Fast electrode kinetics. High current densities are already reached at small overpotentials.
- b) j^0 small: Sluggish electrode kinetics. A large overpotential is needed to obtain a significant current density.

- 2) The transfer coefficient α is often termed **symmetry factor** because it determines the dependence of the current density on overpotential.

- a) If $\alpha = 0.5$: The increase in the absolute value of j , $|j|$, is equal for the oxidation as well as for the reduction current density. The current density-overpotential graph is point-symmetric about ($E = E^{eq}$, $j = 0$).

- b) If $\alpha > 0.5$: $|j|$ increases faster for oxidation than for reduction with the same $|\eta|$.
- c) If $\alpha < 0.5$: $|j|$ increases slower for oxidation than for reduction with the same $|\eta|$.

The following picture shows free energy profiles for different values of α .



usually (for metals) $\alpha \approx 1/2 \rightarrow$ symmetric electron transfer!

activated complex has predominantly structure of oxidized state:

$\alpha \approx 1$ \square anodic reaction strongly dependent on E

activated complex has predominantly structure of reduced state:

$\alpha \approx 0$ \square anodic reaction weakly dependent on E

3) Small overpotentials $|\eta| \ll \frac{RT}{F}$:

Under these conditions mass transport limitations are negligible. We can use (BV 3). Both exponential terms are important. We can linearize the exponential terms in (BV 3) to get

$$j \approx j_0 \frac{F\eta}{RT} = R_{ct}\eta \quad \text{where} \quad R_{ct} = \frac{j_0 F}{RT}$$

A linear current-voltage dependence in the form of Ohm's law is found. R_{ct} is the charge transfer resistance. We can use the low overpotential regime to determine the exchange current density!

4) For large values of $|\eta|$, $|\eta| \gg \frac{RT}{F}$ (the so-called Tafel-regime), one of the partial currents dominates so that the other one can be neglected in (BV 3). We still assume, that mass transport limitations are negligible.

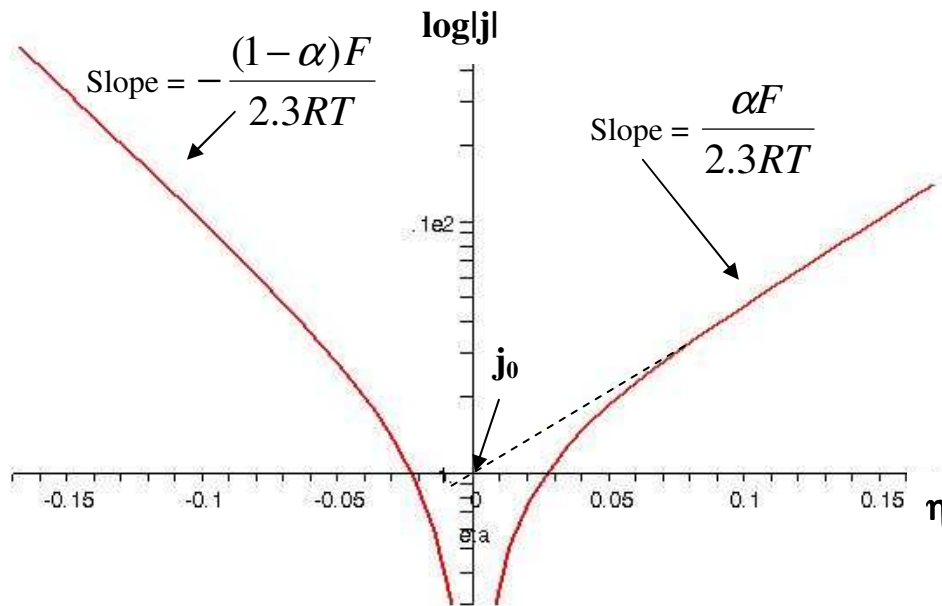
a) $|\eta| \gg \frac{RT}{F}$ and $\eta > 0 \Rightarrow j \approx j_{\text{ox}}$ and $j_{\text{red}} \approx 0$:

$$\log_{10}(j) = \log_{10}(j_0) + \frac{\alpha F}{2.3RT} \eta$$

b) $|\eta| \gg \frac{RT}{F}$ and $\eta < 0 \Rightarrow j \approx j_{\text{red}}$ and $j_{\text{ox}} \approx 0$:

$$\log_{10}(|j|) = \log_{10}(|j_0|) - \frac{(1-\alpha)F}{2.3RT} \eta$$

We can draw so called **Tafel-plots** by plotting $\log|j|$ vs η . From such a plot, we can extract the transfer coefficient α from the slope of a fit of the experimental data to a straight line at $|\eta| \gg 0$ as well as the exchange current density from the crossing point with the ordinate of this linear fit.



- 5) The inverse of the oxidation current slope in a Tafel plot is usually called the **Tafel-constant** and is commonly denoted as b .

$$b = \frac{2.3RT}{\alpha F}$$

- 6) At very large absolute overpotentials, the net current density reaches a limiting value because the reaction rates become limited by diffusion of reactant to the reaction zone – see later lectures.

- 7) Most charge transfer reactions are in fact inner-sphere reactions and the Butler-Volmer equation does in general not apply anymore. However, it could be observed that the current density still depends on overpotential within certain ranges of η . It is convenient to retain the form of the Butler-Volmer equation and **define empirical transfer coefficients α and β** :

$$K_{\text{ox}} = k^0 \exp\left\{\frac{\alpha F \eta}{RT}\right\} \text{ and } K_{\text{red}} = k^0 \exp\left\{-\frac{\beta F \eta}{RT}\right\}$$

However, now, α and β generally depend on electrode potential and temperature. Also, $\alpha + \beta \neq 1$.