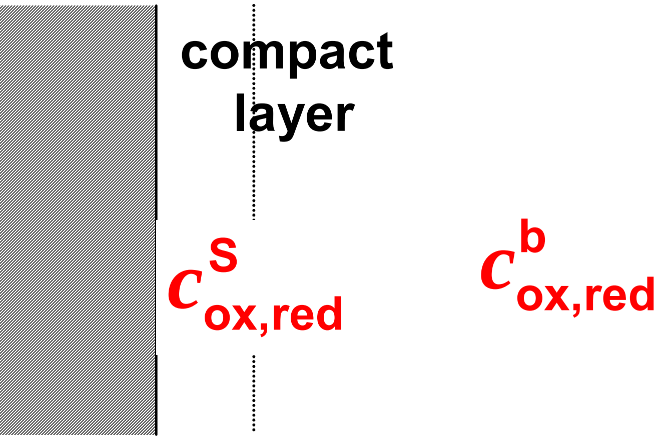


Note, that we explicitly distinguish concentrations at surface c^{s}_{red}, c^{s}_{ox} from those in bulk c^{b}_{red}, c^{b}_{ox}. Concentrations in bulk (far away from the interface) determine E^{eq}.

Under equilibrium conditions:

$$c^{s}_{red} = c^{b}_{red}, \qquad c^{s}_{ox} = c^{b}_{red}$$

No fluxes of species exist. We will see in the context of mas transport limitations why the distinction between surface and bulk concentrations is important!

At **finite current**, surface concentrations will generally be different from bulk concentrations, due to mass transport from bulk to surface:

$$c^{s}_{red} \neq c^{b}_{red}, \qquad c^{s}_{ox} \neq c^{b}_{red}$$

Particular case:

mass transport from bulk to surface is fast

rate of diffusion >> rate of reaction

(see section on mass transport)

$$\Rightarrow \qquad c_{\mathrm{red}}^{\mathrm{s}} = c_{\mathrm{red}}^{\mathrm{b}} \text{ and } c_{\mathrm{ox}}^{\mathrm{s}} = c_{\mathrm{ox}}^{\mathrm{b}}$$

(note: not in equilibrium!)

$\Rightarrow$ simplest variant 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: Three equations, each of them referred to as

“Butler-Volmer equation”

Which one should you use? – it depends!

General situation: complex, distributed electrode

(BV 3) is the least general form. It can only be used, when all sorts of mass transport limitations can be neglected (uniform distributions of reactants, simple electrodes, well-stirred solution) and 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 uniform (i.e. E^{eq} is well-defined).

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

Pre-exponential factor in (BV 2) and (BV 3)

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

is called exchange current density. It is an important parameter that characterizes a particular electrode reaction (Faradaic process). It is (like k^0) a measure of current density in anodic and cathodic directions at zero overpotential ($\eta = 0$), when the system is at equilibrium. It can be seen that it depends on the composition of the system (concentrations).

Physical meaning of j^0: how does system respond to deviation of E from E^{eq}, i.e. applied $\eta \neq 0$?

At given E, which information about a system do you need to determine, in which direction the reaction will proceed and which current density it will generate?

Definition of standard exchange current density:

$$j^{00} = Fk^0 \quad \text{(at standard concentration)}$$

$$\text{(hence } j^0 = j^{00}\left(c^{\mathrm{s}}_{\mathrm{red}}\right)^{(1-\alpha)}\left(c^{\mathrm{s}}_{\mathrm{ox}}\right)^{\alpha}\text{)}$$

- values of j^{00} are reported in literature
  (unless concentrations are explicitly specified)
- j^{00} is important property in electrode characterization

Values of j^{00} can widely differ for different reactions (Why?). In most cases, they are known only with low accuracy (within an order of magnitude). A few values:

$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O,$ $j^{00} \sim 10^{-10}$ A cm^{-2}

$Fe(CN)_6^{3-} + e^- \leftrightarrow Fe(CN)_6^{4-},$ $j^{00} \sim 10$ A cm^{-2}

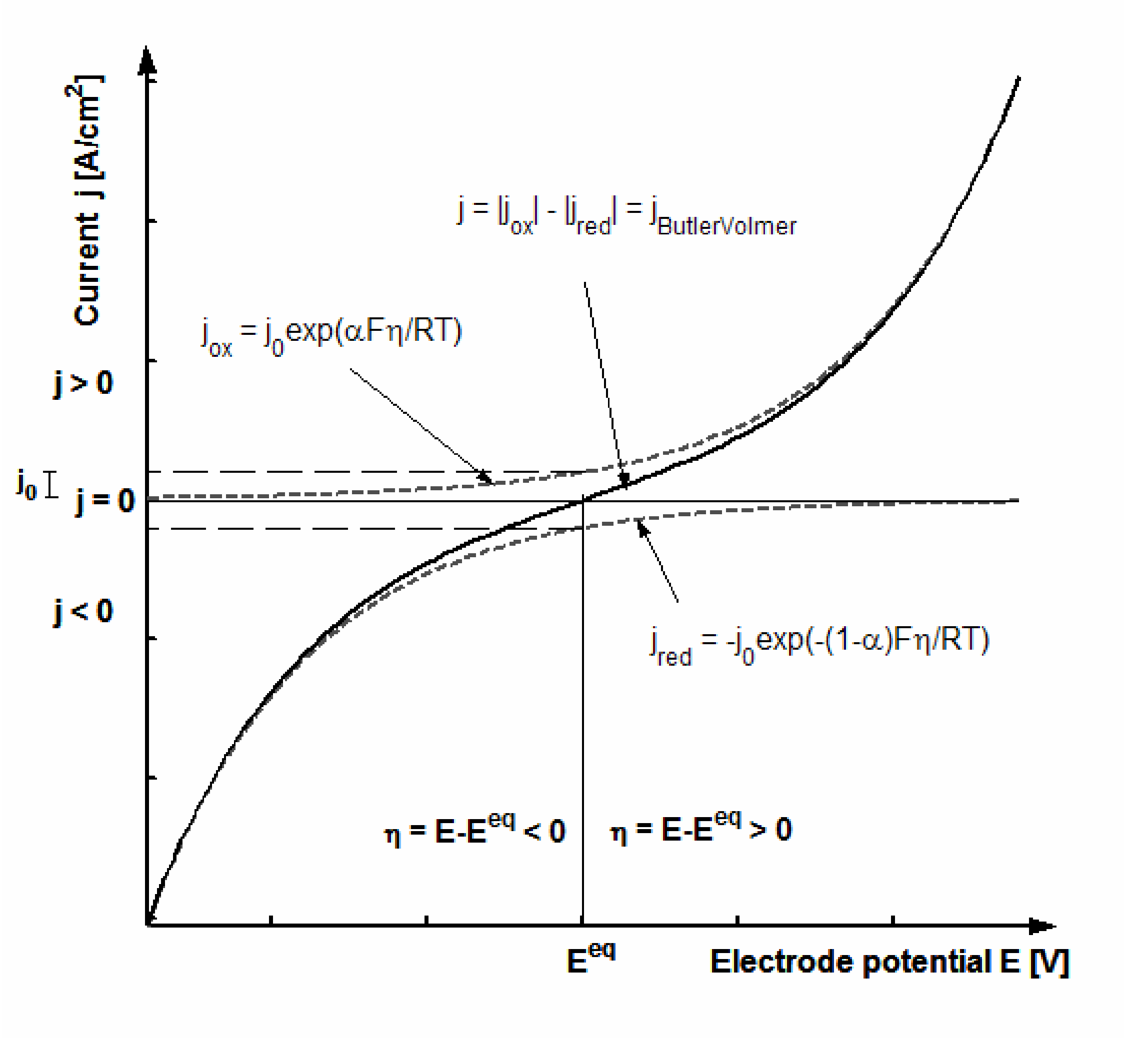
$Cl_2 + 2e^- \leftrightarrow 2Cl^-,$ $j^{00} \sim 10^{-1}$ A cm^{-2}

$2H^+ + 2e^- \leftrightarrow H_2,$ $j^{00} \sim 10^{-4}$ A cm^{-2}

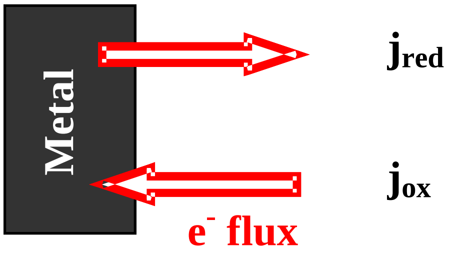
$j << j^0$: reversible electrode, Nernst-equation holds

ideally non-polarizable electrode: the potential will not change from equilibrium potential with the application of even a large current density

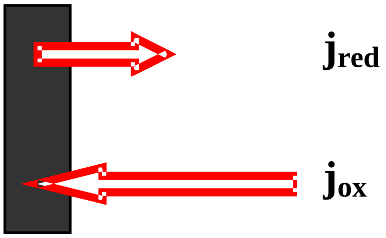
Meaning of the different parameters in BV equation:



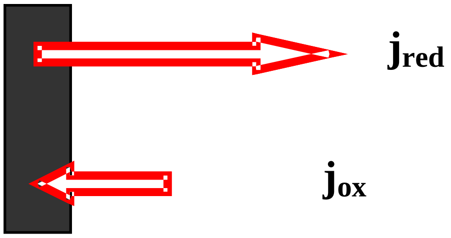
Three potential regions



$E = E^{eq}$; $\eta = 0$, $j = 0$



$E > E^{eq}$; $\eta > 0$; $j > 0$



$E < E^{eq}$; $\eta < 0$; $j < 0$

1) Exchange current density: 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 .

As a pre-exponential factor, j^0 largely determines the overall kinetics:

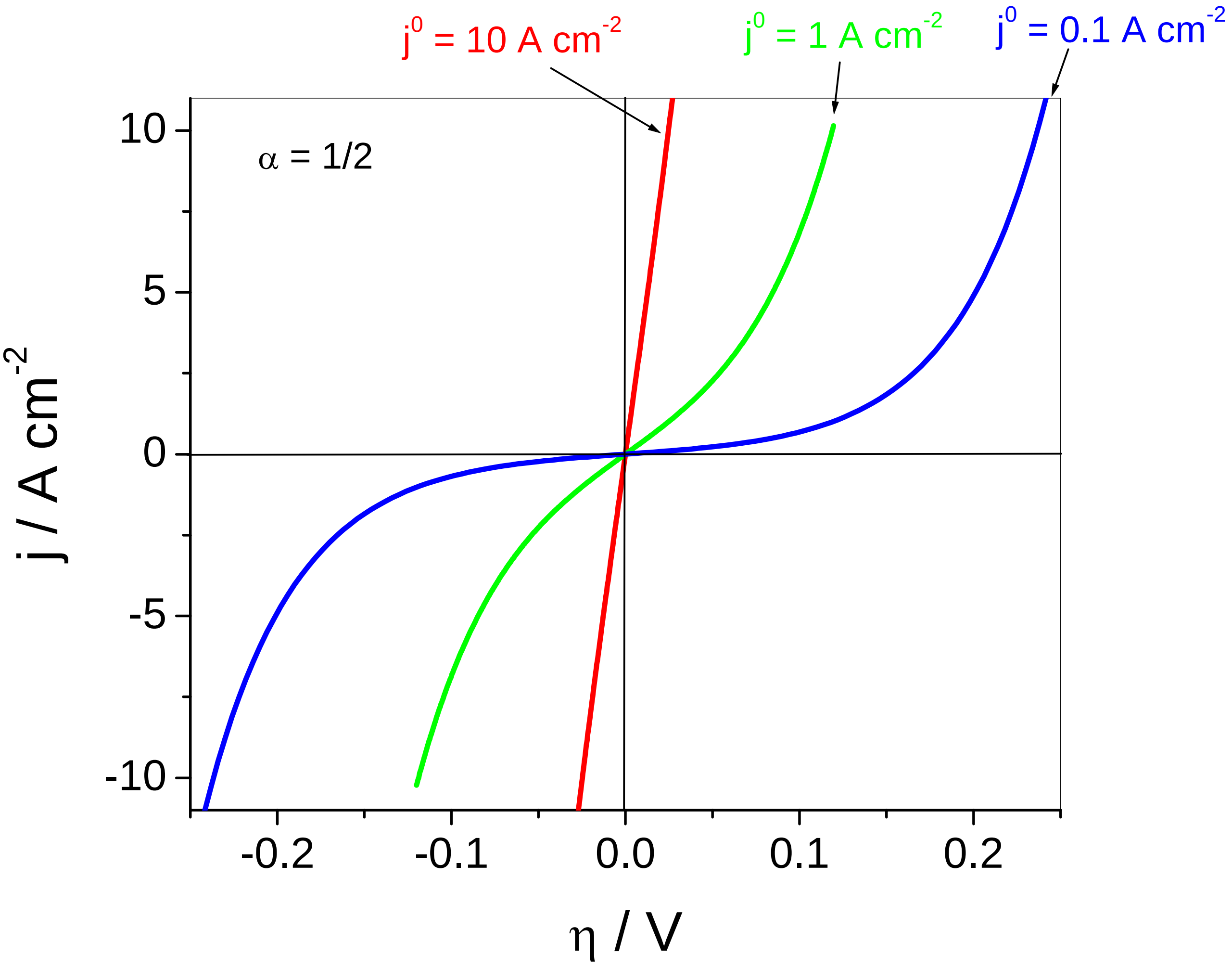
a) j^0 large (fast electrode kinetics):

High current densities reached at small $|\eta|$

b) j^0 small (sluggish electrode kinetics):

Large $|\eta|$ needed to obtain significant current density.

Effect of exchange current density



2) **Transfer coefficient** α: determines how strongly current density depends on the dependence of the on $|\eta|$ (often termed **symmetry factor**). Consider change $\Delta E = \Delta\eta$

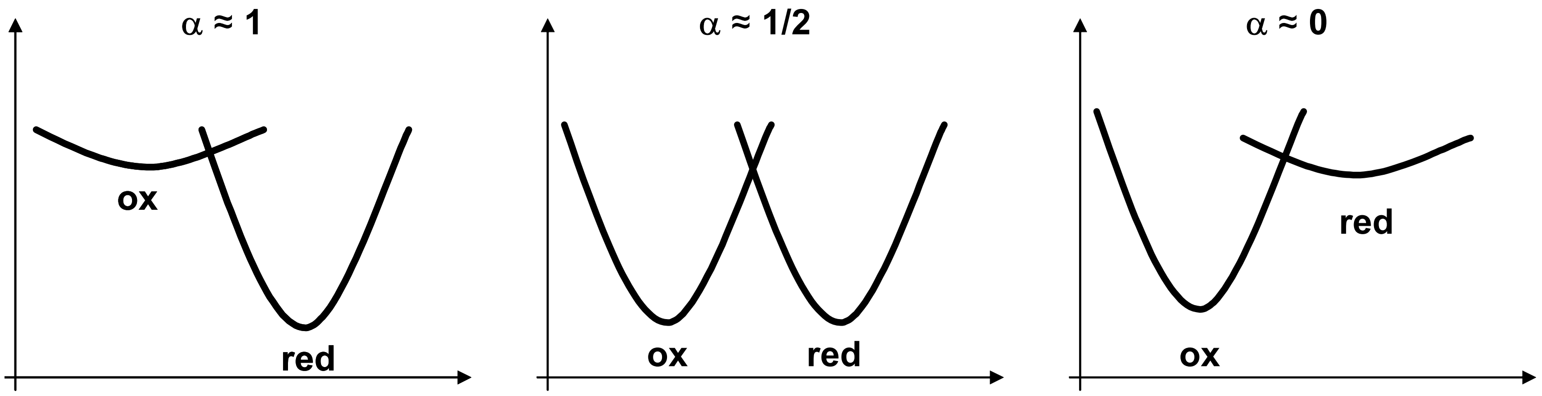
   a) **If α = 0.5**: jox increases by the same factor by which jred decreases. The current density-overpotential graph is point-symmetric about ($E = E^{eq}$, $j = 0$).

   b) **If α > 0.5**: $|j|$ increases faster for oxidation than for reduction with the same $|\eta|$.

   c) **If α < 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

(anodic process: "ox" corresponds e^- in metal)



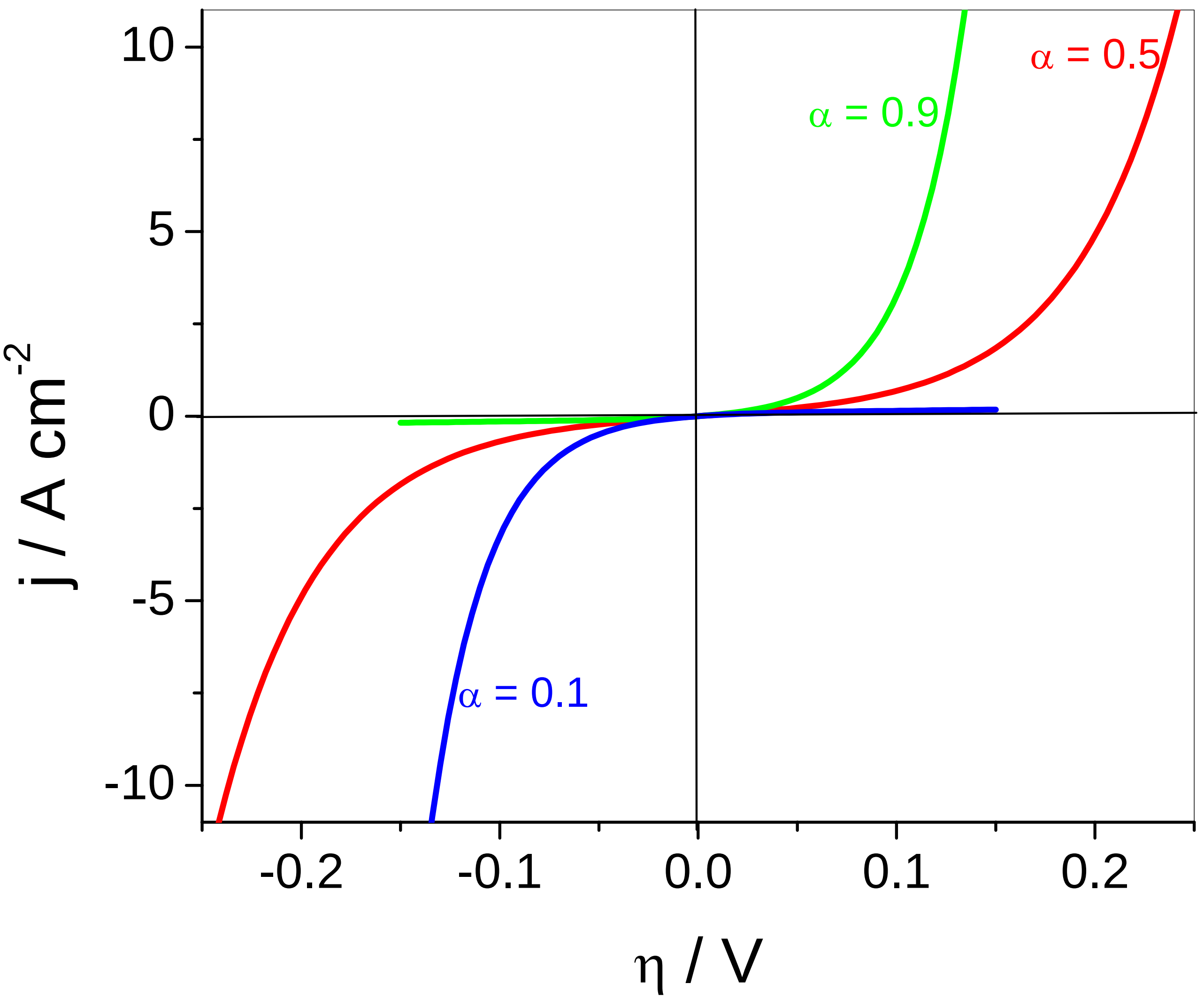
- **usually (for metals) α ≈ 1/2**

  ⇒ symmetric e^--transfer!
- **activated complex has predominantly structure of oxidized state: α ≈ 1**

  ⇒ anodic reaction strongly dependent on *E*
- **activated complex has predominantly structure of reduced state: α ≈ 0**

  ⇒ anodic reaction weakly dependent on *E*

Effect of transfer coefficient



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

- negligible mass transport limitations - use (BV 3)
- both exponential terms important
- Taylor expansion in (BV 3) gives

$$j \approx j^0 \frac{F\eta}{RT} = \frac{\eta}{R_{\text{ct}}} \qquad \text{where} \qquad R_{\text{ct}} = \frac{RT}{j^0 F}$$

- linear relation between j and η
- form of Ohm's law with charge transfer resistance R_{ct} .

We can use the low overpotential regime to determine the exchange current density!

4) For large values of |η|, $|\eta| > 3\frac{RT}{F}$ (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 neglibible.

a) $|\eta| > 3\frac{RT}{F}$ and $\eta > 0 \Rightarrow j \approx j_{\text{ox}}$ and $j_{\text{red}} \approx 0$:

$$\boxed{\log_{10}(j) = \log_{10}(j^0) + \frac{\alpha F}{2.3RT}\eta}$$

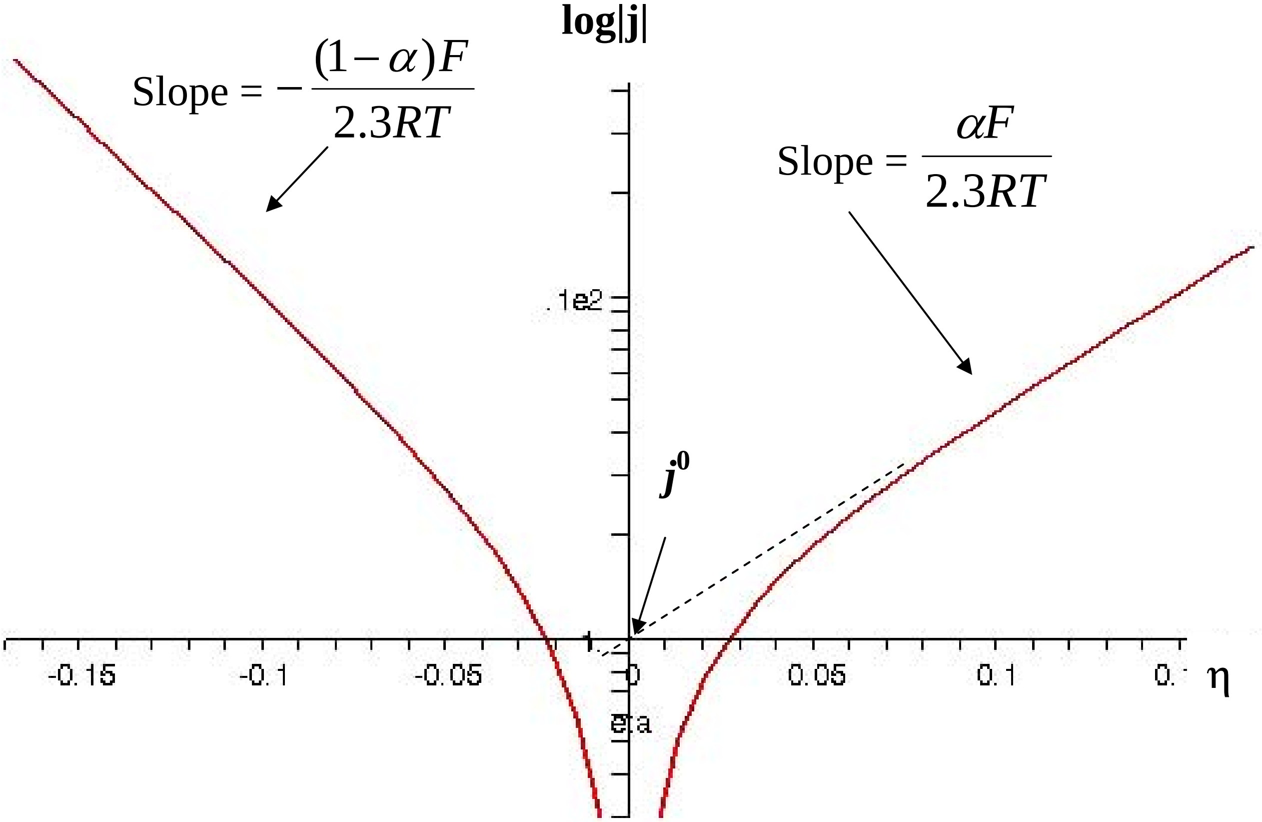
b) $|\eta| > 3\frac{RT}{F}$ and $\eta < 0 \Rightarrow j \approx j_{\text{red}}$ and $j_{\text{ox}} \approx 0$:

$$\boxed{\log_{10}(|j|) = \log_{10}(|j^0|) - \frac{(1-\alpha)F}{2.3RT}\eta}$$

We can draw so-called Tafel-plots: *log|j|* vs. η

From such a plot, we can extract

- transfer coefficient α from the slope of a fit of the experimental data to a straight line at |η| >> 0
- exchange current density j^0 from the crossing point with the ordinate of this linear fit.



5) The inverse of the oxidation current slope in a Tafel plot is called the **Tafel-constant**:

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

Typical value?

6) At very large $|\eta|$, $|j|$ reaches a **limiting value** because the reaction rates is **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. However, j still depends on η. It is convenient to retain the form of the Butler-Volmer equation with empirical transfer coefficients α and β:

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

In general: α and β depend on η and T and $\alpha + \beta \neq 1$