

Electrochemical rate processes

Electrochemical processes are important in industry

E.g., production of aluminium, chlorine

Corrosion is also an electrochemical problem

Electrophoresis and polarography are based on electrochemical kinetics.

Fuel cells produce electrical energy from chemical fuels

Electrode kinetics, polarization

An electrochemical process on a metal electrode is a heterogeneous reaction. The electrode surface facilitates the transfer of electrons to reactants.

The electrode reaction is the succession of five steps:

1. Diffusion of reactants to electrode
2. Adsorption of reactants on electrode
3. Transfer of electrons
4. Desorption of products from electrode
5. Diffusion of products away from electrode.

Any of the five steps can be the rate determining (slowest) step.

On the surface of electrode, both anodic (oxidation) and cathodic (reduction) processes take place.

Anodic current: positive

Cathodic current: negative

Net current density: $j = j_A + j_C$

At equilibrium, the net current density is zero. That is, the anodic and cathodic current densities are equal (with opposite signs).

$$j_A = |j_C| = j_0$$

J_0 is called the **exchange current density**.

Since the electrode processes are heterogeneous reactions, the rate of reaction (v) expresses, how many moles react at unit surface in unit time.

$$[v] = \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-2}$$

The rate of reaction and the current density are connected by Faraday's law,

$$v \left[\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \right] = \frac{j \left[\text{A} \cdot \text{m}^{-2} \right]}{|z| \cdot F \left[\text{A} \cdot \text{s} \cdot \text{mol}^{-1} \right]}$$

where z is the charge number.

Electrodes that have high exchange current density for a given reaction are called nonpolarizable electrodes. Such electrode is the calomel electrode. In this case, charges move rapidly to and from the electrode. The electrode potential changes very little even if the current changes significantly. Thus, nonpolarizable electrodes are suitable for reference electrodes.

Electrodes that have low exchange current density for a given reaction are called polarizable electrodes. Even if the potential changes significantly, there is little change of current. An example is mercury electrode in solution of KCl.

Polarization. Under nonequilibrium conditions, the net current density is not zero, and the potential is not equal to the equilibrium electrode potential.

$$j_A \neq |j_C|, \quad \Delta\Phi \neq E$$

In a galvanic cell $\Delta\Phi < E$

In an electrolytic cell $\Delta\Phi > E$

The difference is called overpotential or polarization (η)

$$\eta = \Delta\Phi(j) - \Delta\Phi(0)$$

Part of η is due to the potential difference $I \cdot R$ in the electrolytes and leads. The remaining part of η is due to the rate-limiting processes at the electrodes. The corresponding electric energy is used to provide a part of the free energy of activation in one or more of the steps in the electrode reaction.

Activation overpotential

Consider the case when the rate limiting process is the transfer of electrons.

Since the current density is proportional to the rate of reaction (see before), we examine how the current density can be influenced by the potential.

At equilibrium (when $\Delta\Phi = E$), the net current density is zero. (That is the oxidation and reduction reaction take place at the same rate.)

If the potential of the electrode differs from the equilibrium value, it helps the transfer of electrons in one direction and inhibits it in the other direction.

Positive overpotential reduces the activation energy of oxidation (anodic) process, and increases the activation energy of reduction (cathodic) process.

Negative overpotential reduces the activation energy of reduction (cathodic) process, and increases the activation energy of oxidation (anodic) process.

The relationship between the current density (j) and overpotential (η) is given by the Butler-Volmer equation.

$$j = j_0 \cdot \left[e^{\frac{(1-\alpha) \cdot |z| \cdot F}{R \cdot T} \cdot \eta} - e^{-\frac{\alpha \cdot |z| \cdot F}{R \cdot T} \cdot \eta} \right]$$

where j is the current density, j_0 is the exchange current density, η is the overpotential.

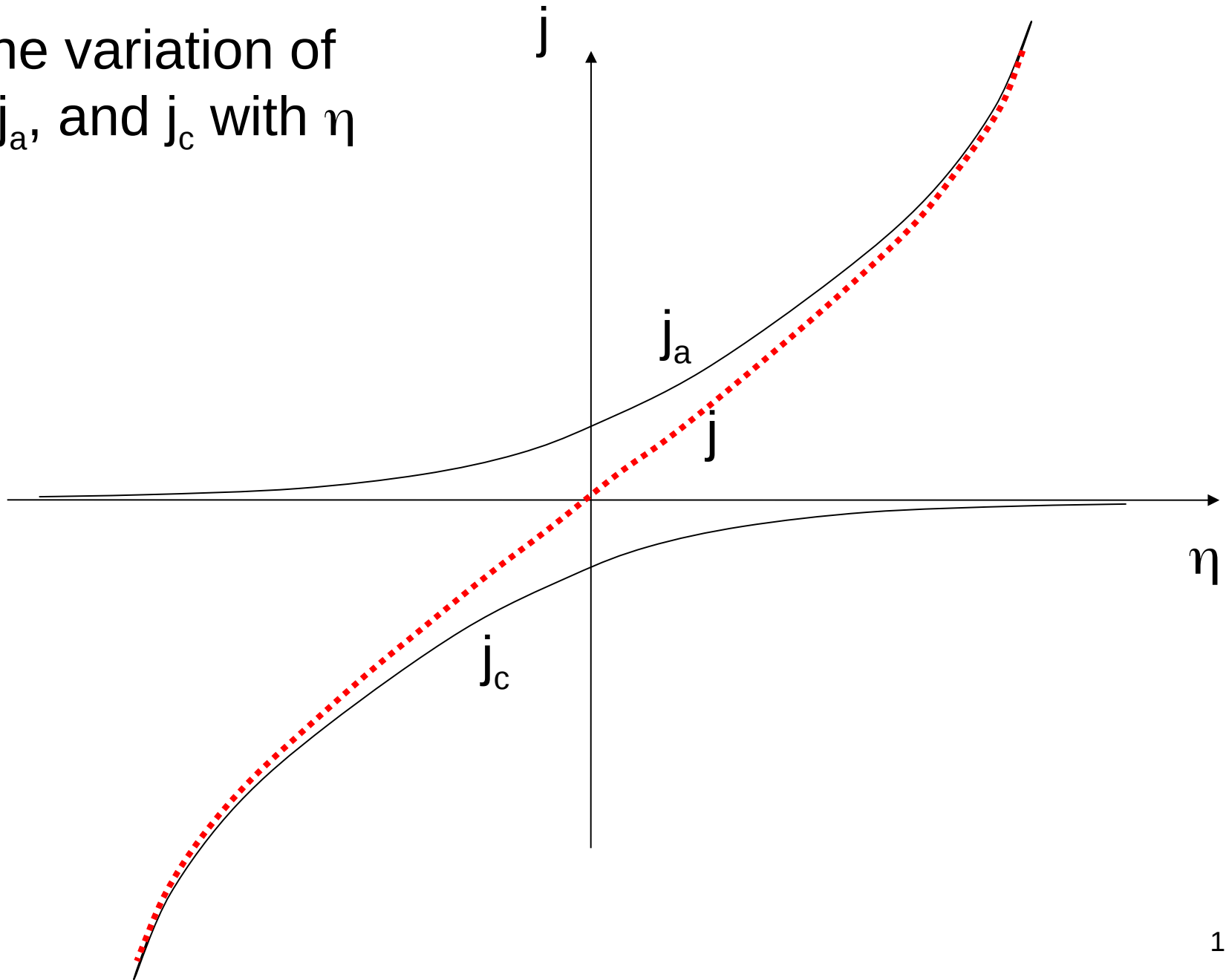
α is called the transfer coefficient. It expresses that part of $|z| \cdot F \cdot \eta$ changes the activation energy of the cathodic process ($\alpha \cdot |z| \cdot F \cdot \eta$), and another part changes the activation energy of the anodic process ($(1-\alpha) \cdot |z| \cdot F \cdot \eta$).

(If the activation energy decreases in one direction, it increases in the opposite direction.)

The first term in the bracket multiplied by j_0 gives the anodic current density, j_a . It increases exponentially with increasing positive overpotential. The intercept (when $\eta = 0$) is j_0 .

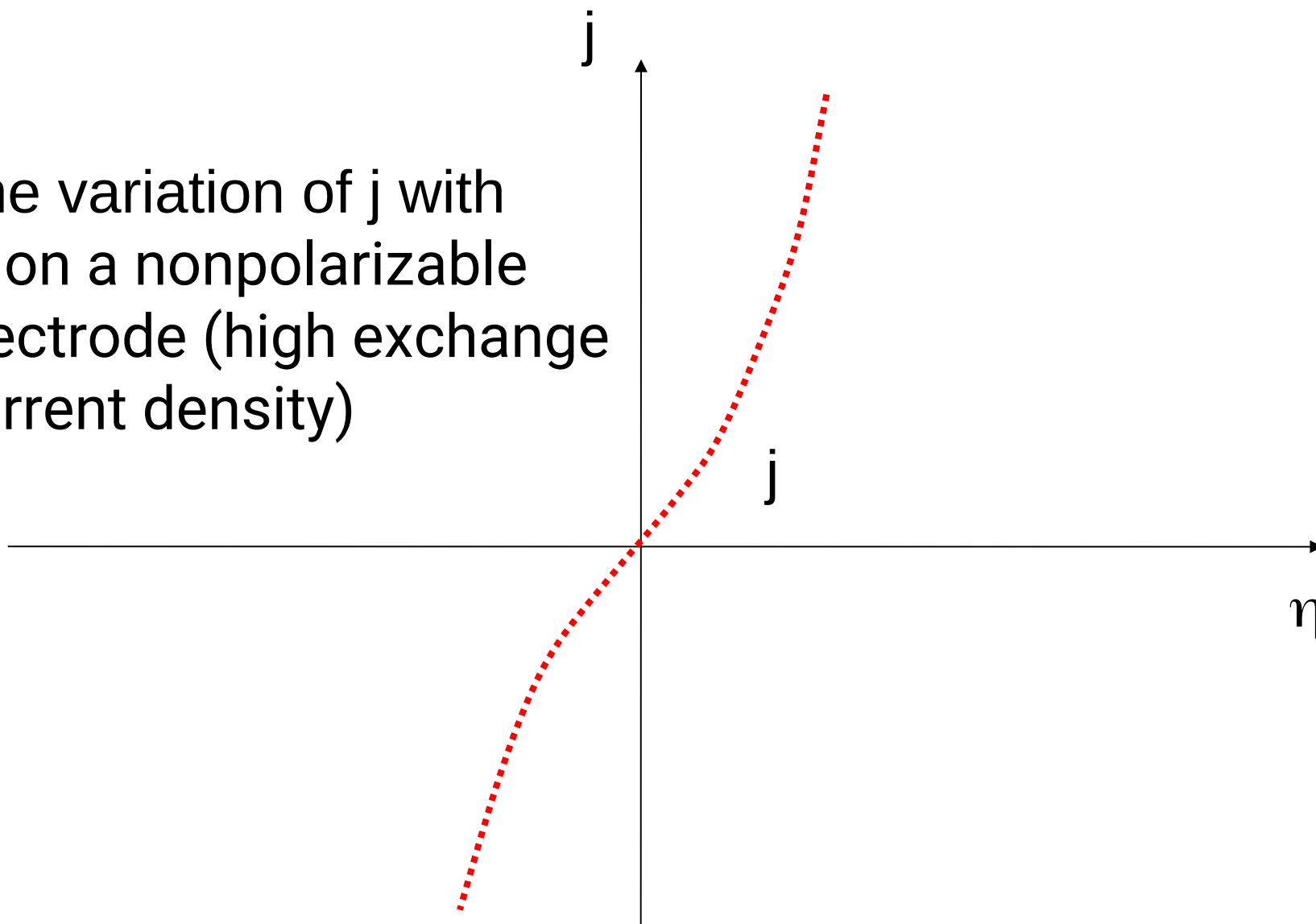
The second term in the bracket multiplied by j_0 gives the cathodic current density, j_c . Its absolute value increases exponentially with increasing negative overpotential. The intercept (when $\eta = 0$) is $-j_0$.

The variation of j , j_a , and j_c with η

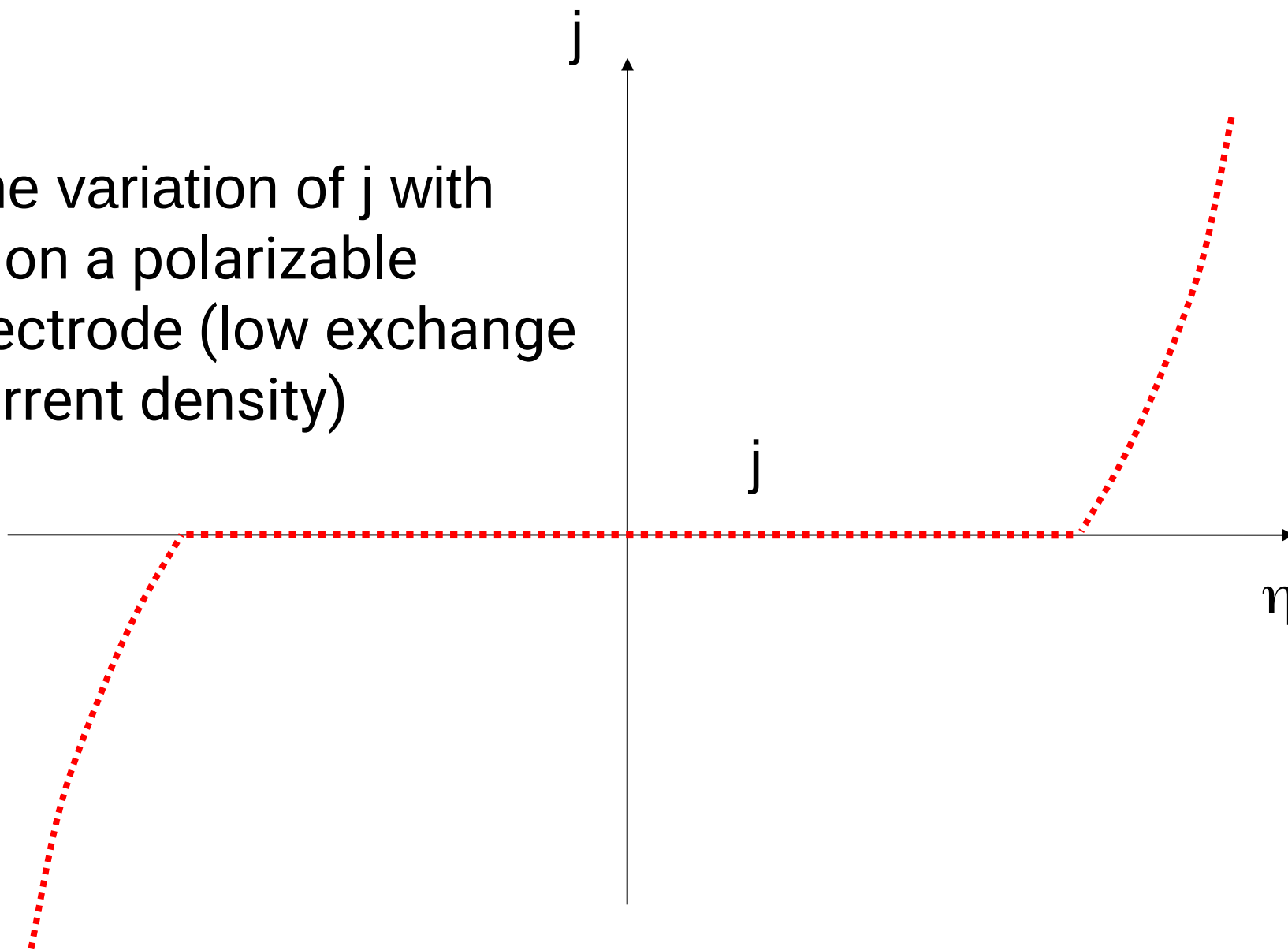


The exchange current density depends on the type of the electrode. It can vary by more than seventy orders of magnitude.

The variation of j with η on a nonpolarizable electrode (high exchange current density)



The variation of j with η on a polarizable electrode (low exchange current density)



If the overpotential has large positive or negative values, one of the partial currents becomes much greater than the other, which is then negligible.

If η has large positive value,

$$j = j_0 \cdot e^{\frac{(1 - \alpha) \cdot |z| \cdot F}{R \cdot T} \cdot \eta}$$

$$\ln j = \ln j_0 + \frac{(1 - \alpha) \cdot |z| \cdot F}{R \cdot T} \cdot \eta$$

If η has large negative value,

$$j = -j_0 \cdot e^{-\frac{\alpha \cdot |z| \cdot F}{R \cdot T} \cdot \eta}$$

Here, j is negative.

$$-j = j_0 \cdot e^{-\frac{\alpha \cdot |z| \cdot F}{R \cdot T} \cdot \eta}$$

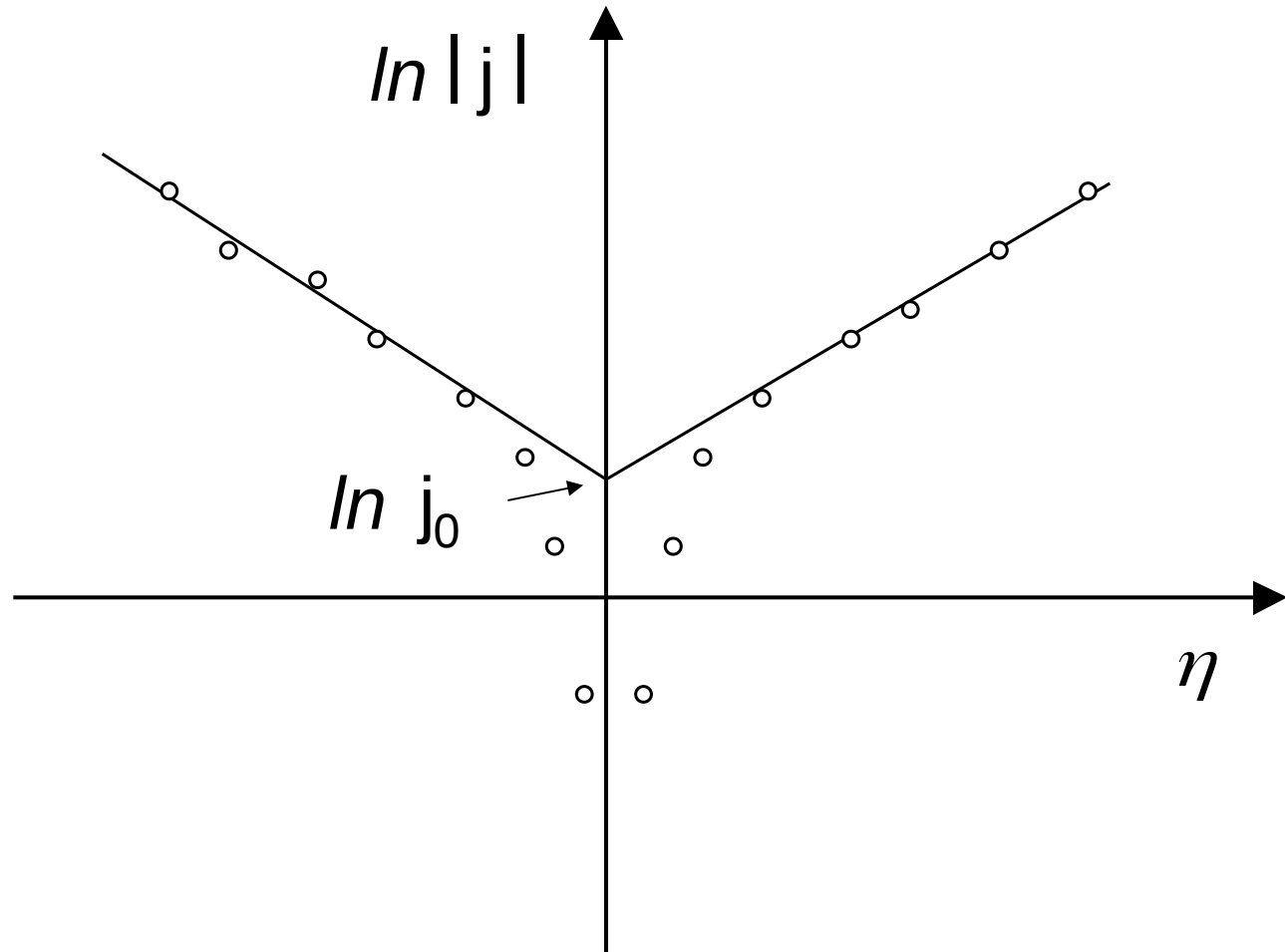
(Only positive values have logarithms.)

$$\ln(-j) = \ln j_0 - \frac{\alpha \cdot |z| \cdot F}{R \cdot T} \cdot \eta$$

If we plot $\ln |j|$ against η , the interpolation of the linear part to $\eta = 0$, the intercept produces $\ln j_0$. From the slopes, the transfer coefficient α can be determined.

The equations expressing the linear function of $\ln |j|$ and η are called the **Tafel equations**.

Tafel plot



Diffusion overpotential

If the transfer of electrons is fast enough, the rate limiting process may be the diffusion of ions to the surface or from the surface of electrode.

Consider a metal electrode where the following electrode process takes place.



(E.g., copper ions are neutralized on the surface of a copper electrode.)

The equilibrium electrode potential (when the current is zero) can be expressed by the Nernst equation.

$$\varepsilon = \varepsilon^0 + \frac{RT}{zF} \ln \frac{\gamma \cdot c}{c^0}$$

When current flows across the electrode and the rate determining step is the diffusion of the ions to the surface of the electrode, the concentration on the surface (c') is different from the bulk concentration. Therefore, the electrode potential changes to ε' .

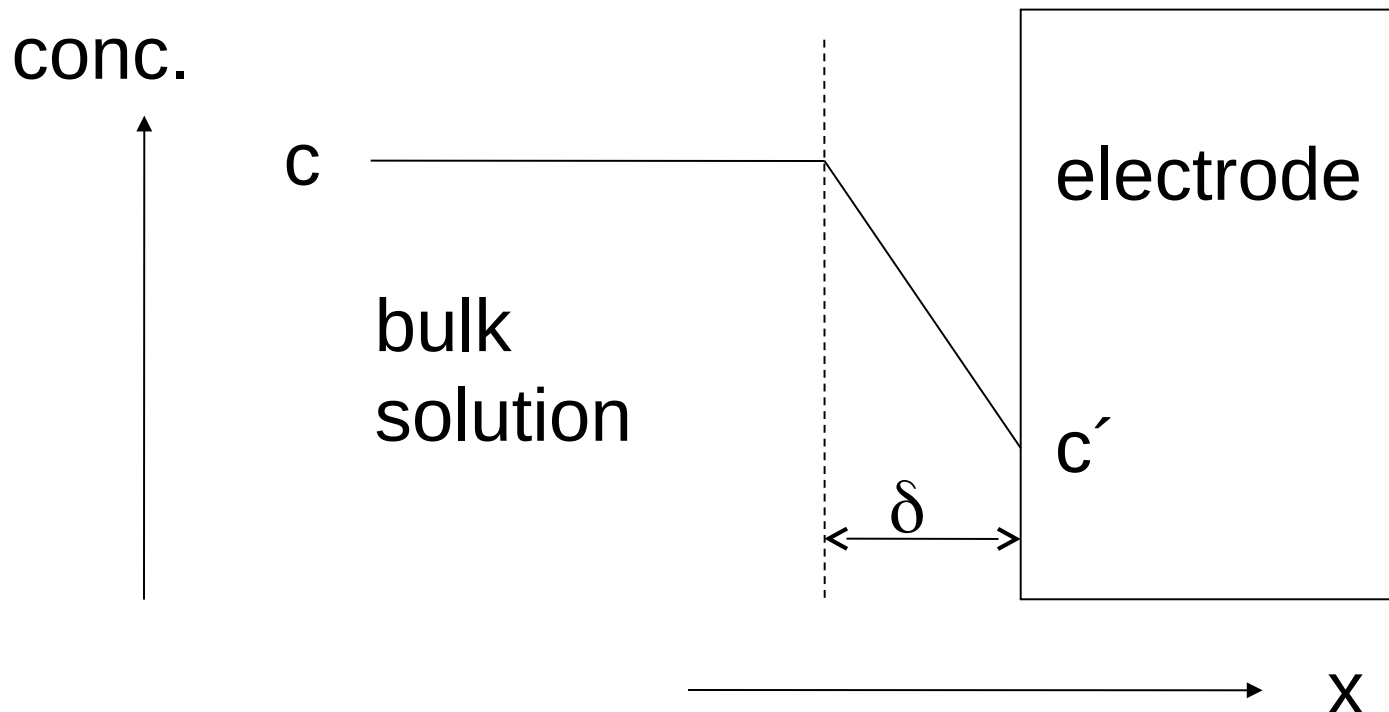
$$\varepsilon' = \varepsilon^0 + \frac{RT}{zF} \ln \frac{\gamma' \cdot c'}{c^0}.$$

The difference of the two electrode potentials is the diffusion overpotential.

$$\eta = \varepsilon' - \varepsilon = \frac{RT}{zF} \ln \frac{c'}{c}$$

(The activity coefficients γ and γ' are supposed to be equal.)

We assume that the concentration changes linearly within a diffusion layer δ , which is about 0.1 mm thick.



In this layer, the concentration gradient is the following.

$$\frac{dc}{dx} = \frac{c' - c}{\delta}.$$

The j_n flux of ions (in $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) can be expressed by Fick's first law.

$$j_n = -D \left(\frac{\partial c}{\partial x} \right).$$

The current density towards the electrode is the product of the particle flux and the charge each particle carries: $j = z \cdot F \cdot j_n$

$$j = z \cdot F \cdot j_n = z \cdot F \cdot D \cdot \frac{(c - c')}{\delta}.$$

Rearranging this equation:

$$c' = c - \frac{j\delta}{zFD}.$$

The maximum rate of diffusion occurs when the gradient is steepest, i. e., $c' = 0$. The corresponding current density is called **limiting current density**, j_L .

$$j_L = \frac{z \cdot F \cdot D}{\delta} \cdot c$$

Substituting c' for the expression of overpotential:

$$\eta = \frac{RT}{zF} \ln \left(1 - \frac{j\delta}{z \cdot c \cdot F \cdot D} \right)$$

Since $\delta/(z \cdot c \cdot F \cdot D)$ is the reciprocal of the limiting current density, this expression can be written as

$$\eta = \frac{RT}{zF} \ln \left(1 - \frac{j}{j_L} \right)$$

As $j \rightarrow j_L, \eta \rightarrow -\infty$, but before this happens, some other ion will begin to be discharged.

The current density as a function of overpotential:

$$j = j_L \cdot \left(1 - e^{\frac{z \cdot F}{R \cdot T} \cdot \eta} \right)$$