Electrochemistry

CHE 3053

Activation or Charge Transfer Controlled Reactions

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Activation overpotential, η_a

Reflects the energy ($nF\eta_a$) required to speed up the heterogeneous charge transfer (of η_{ct}) and the preceding and/or following chemical reactions.

Assumptions

$$\mathbf{Ox} + \mathbf{ne^-} \rightleftharpoons \mathbf{Red}$$

1) The concentrations at the surface and in the bulk solution for reactants and products are the same. To eliminate the concentration polarization, η_c.
2) Solution is so large around the electrode.
3) A large amount of a supporting electrolyte is added. To eliminate the migration polarization, η_m.
4) Solution and electrode are stagnant (no convection).
5) Only η_a is limiting.

Effect of η_a on the reaction Kinetics

$$\mathbf{Ox} + \mathbf{ne^-} \rightleftharpoons \mathbf{Red}$$

- For electrochemical Rxs at equilibrium, the potential difference across the double layer will have its equilibrium value, ΔE_r.

$$\frac{d\phi}{dx} \approx \frac{1\,V}{5\times10^{-8}\,cm} \approx 2\times10^{7}\,V cm^{-1}$$

- If the equilibrium is disturbed, net flow of current will occur and the potential difference changes to ΔE_i.

$$\eta_a = \Delta E_i - \Delta E_r$$

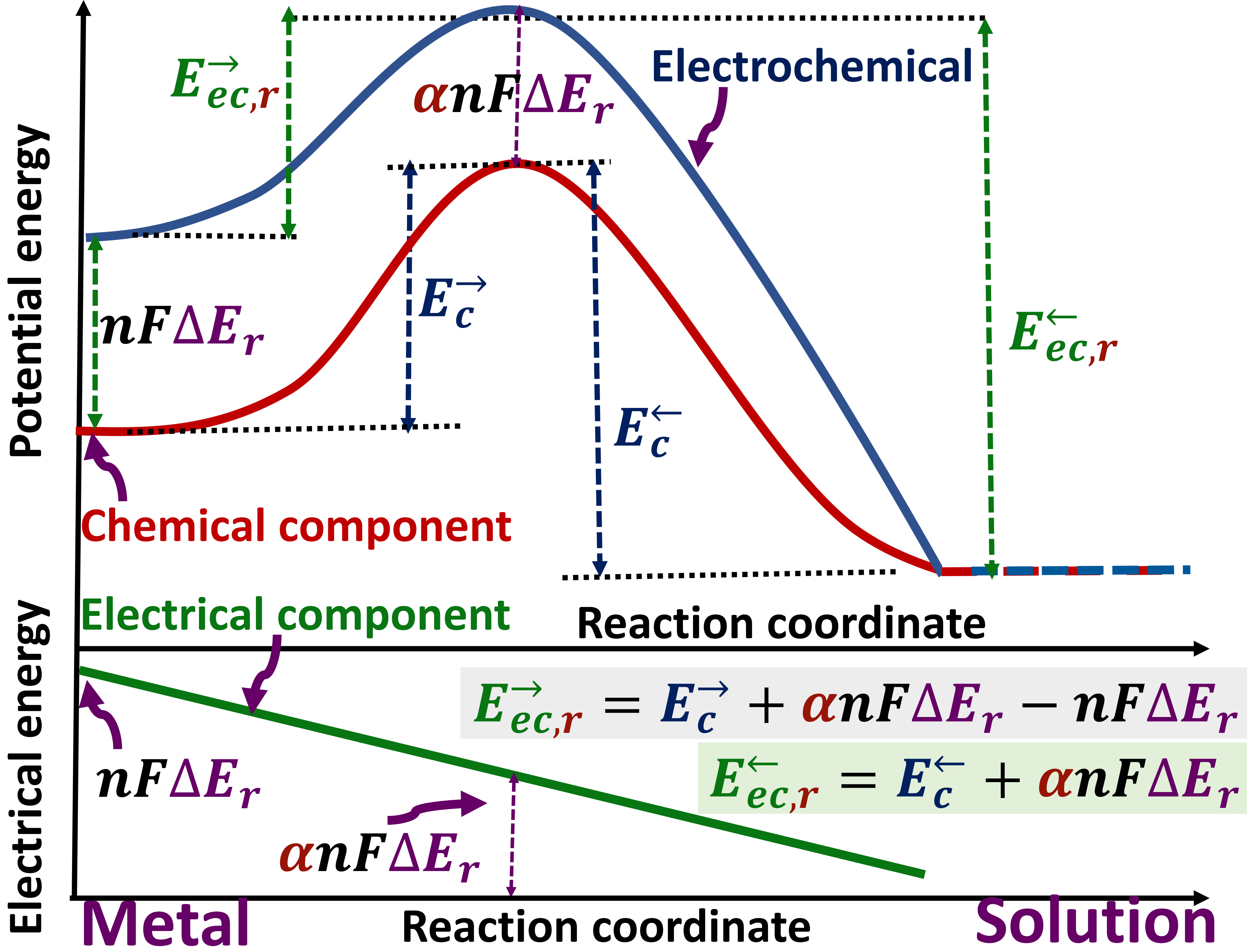
- If η_a was positive, the activation energy (E_a) of the anodic Rx will decrease while E_a of the cathodic Rx will simultaneously increase. This change may or may not be equal.

- This, in turn, increases the rate of anodic RX and decreases the rate of cathodic Rx

$$k = Ae^{\left(\frac{-E_a}{RT}\right)}$$

Arrhenius Equation

- E_a is best described by potential energy profiles.
- These profiles should consider the chemical and electrical components of the electrochemical potential.
- The potential in solution is taking to be zero while the potential at the electrode surface is E_r where equilibrium is assumed.
- On the solution side, the contribution of the electrical component is zero while at the electrode surface is maximum ($nF\Delta E_r$).
- At the point where the activated complex occurs, the contribution of the electrical component is midway ($\alpha nF\Delta E_r$)


Potential energy
Electrical energy
Electrochemical
Chemical component
Electrical component
Reaction coordinate
Reaction coordinate
Metal
Solution
$E^{\rightarrow}_{ec,r}$
$\alpha nF\Delta E_r$
$E^{\rightarrow}_{c}$
$E^{\leftarrow}_{c}$
$E^{\leftarrow}_{ec,r}$
$nF\Delta E_r$
$nF\Delta E_r$
$\alpha nF\Delta E_r$
$E^{\rightarrow}_{ec,r} = E^{\rightarrow}_{c} + \alpha nF\Delta E_r - nF\Delta E_r$
$E^{\leftarrow}_{ec,r} = E^{\leftarrow}_{c} + \alpha nF\Delta E_r$

$$E_{ec,r}^{\rightarrow} = E_c^{\rightarrow} + \alpha nF\Delta E_r - nF\Delta E_r$$

$$E_{ec,r}^{\rightarrow} = E_c^{\rightarrow} - (1-\alpha)nF\Delta E_r$$

$$\beta = (1-\alpha)$$

$$E_{ec,r}^{\rightarrow} = E_c^{\rightarrow} - \beta\, nF\Delta E_r$$

$$E_{ec,r}^{\leftarrow} = E_c^{\leftarrow} + \alpha nF\Delta E_r$$

- The activation energy of the forward direction decreases by $(1-\alpha)nF\Delta E_r$ while that of the backward Rx increases by $\alpha nF\Delta E_r$, i.e., the potential difference across the double layer ΔE_r promotes the forward Rx and retards the backward Rx based on the fraction α which is known as the transfer coefficient or symmetry factor $(0 < \alpha < 1)$.

- α may be considered as the fraction of ΔE_r that retards the backward Rx while $\beta = (1-\alpha)$ is the fraction of ΔE_r that promotes the forward Rx .

- In simple one electron transfer RXs, α is often close to 0.5. $\boldsymbol{\beta = (1-\alpha) \approx 0.5}$
- Normally, α ranges from 0.3 to 0.7

Effect of η_a on activation energy

- Under conditions of electrochemical equilibrium, the rates of anodic and cathodic RXs are equal and no net flow of electrons occurs.

- Under conditions of polarization, this dynamic equilibrium is disturbed and electrons flow either to the electrode (in case of cathodic polarization, $\eta_a < 0$) or from the electrode (in case of anodic polarization, $\eta_a > 0$) .

Under non-equilibrium conditions, ΔE_r will be replaced by ΔE_i

$$\boldsymbol{E}_{ec,i}^{\rightarrow} = \boldsymbol{E}_{c}^{\rightarrow} - \boldsymbol{\beta}\, \boldsymbol{nF}\Delta \boldsymbol{E}_{i}$$

However, ➡

$$\Delta \boldsymbol{E}_{i} = \Delta \boldsymbol{E}_{r} + \eta$$

$$\boldsymbol{E}_{ec}^{\rightarrow} = \boldsymbol{E}_{c}^{\rightarrow} - \boldsymbol{\beta}\, \boldsymbol{nF}\Delta \boldsymbol{E}_{r} - \boldsymbol{\beta}\, \boldsymbol{nF}\eta$$

Since

$$\boldsymbol{E}_{ec,r}^{\rightarrow} = \boldsymbol{E}_{c}^{\rightarrow} - \boldsymbol{\beta}\, \boldsymbol{nF}\Delta \boldsymbol{E}_{r}$$

➡

$$\boldsymbol{E}_{ec,i}^{\rightarrow} = \boldsymbol{E}_{ec,r}^{\rightarrow} - \boldsymbol{\beta}\, \boldsymbol{nF}\eta$$

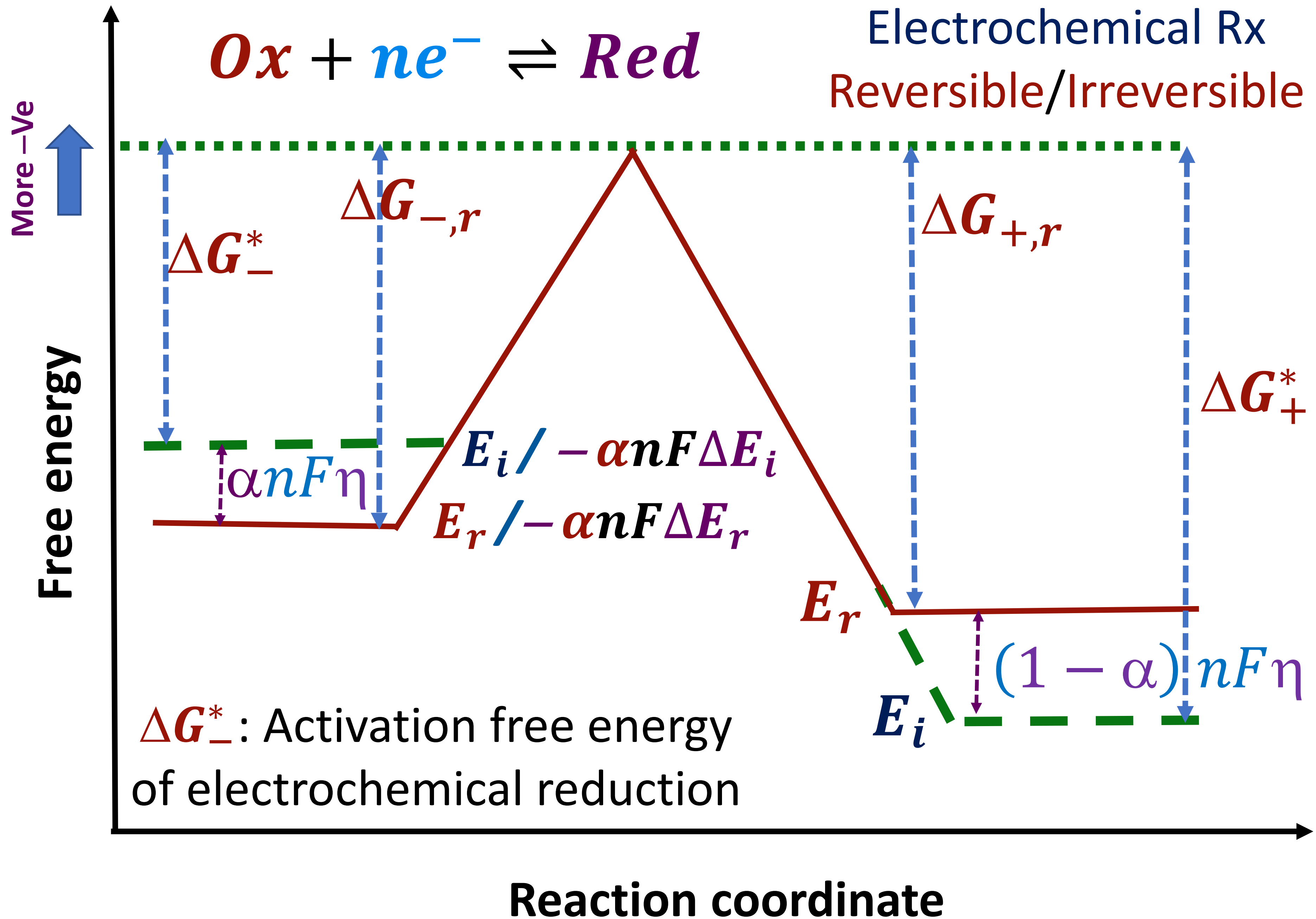
Similarly,

$$\boldsymbol{E}_{ec,i}^{\leftarrow} = \boldsymbol{E}_{c}^{\leftarrow} + \boldsymbol{\alpha} \boldsymbol{nF}\Delta \boldsymbol{E}_{i}$$

$$\boldsymbol{E}_{ec,i}^{\leftarrow} = \boldsymbol{E}_{c}^{\leftarrow} + \boldsymbol{\alpha} \boldsymbol{nF}\Delta \boldsymbol{E}_{r} + \boldsymbol{\alpha} \boldsymbol{nF}\eta$$

➡

$$\boldsymbol{E}_{ec,i}^{\leftarrow} = \boldsymbol{E}_{ec,r}^{\leftarrow} + \boldsymbol{\alpha} \boldsymbol{nF}\eta$$



$Ox + ne^- \rightleftharpoons Red$
Electrochemical Rx
Reversible/Irreversible
More −Ve
Free energy
ΔG^*_-
$\Delta G_{-,r}$
$\Delta G_{+,r}$
ΔG^*_+
$E_i / -\alpha nF\Delta E_i$
$\alpha nF\eta$
$E_r / -\alpha nF\Delta E_r$
E_r
$(1-\alpha)nF\eta$
E_i
ΔG^*_-: Activation free energy of electrochemical reduction
Reaction coordinate

For the forward cathodic direction, at E_{rev}

$$\Delta G_{-}^{*} = \Delta G_{-} + \alpha n F E_{i}$$

$$\Delta G_{-}^{*} = \Delta G_{-} + \alpha n F E_{r} + \alpha n F \eta$$

ΔG_{-} : free energy change of activation for the chemical component of cathodic Rx

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$$\Delta G_{+}^{*} = \Delta G_{+} - (1-\alpha) n F E_{r} - (1-\alpha)\, n F \eta$$

$$Ox + ne^{-} \rightleftharpoons Red$$

- ❑ α may be considered as the fraction of electrical energy promoting the reduction process and $(1-\alpha)$ is the fraction slowing down the oxidation process.
- ❑ η is supposed to be –Ve in the cathodic polarization.

Rate of electrochemical Rxs

- The rate of electrochemical reaction at an electrode of a surface area (A) is related to the current via Faraday's law of electrolysis.

$$I = nF \times \text{rate of chemical change} \times A$$

$$\text{rate of chemical change} = \frac{I}{nF \times A}$$

Current density $$i = \frac{I}{A}$$

$$\text{rate of chemical change} = \frac{-dn_{Ox}}{dt} = \frac{i_{-}}{nF}$$

However ➡

$$\frac{-dn_{Ox}}{dt} = k_{-} C_{0(Ox)} e^{-\Delta G^{*}_{-}/RT}$$

Therefore ➡

$$\frac{i_{-}}{nF} = k_{-} C_{0(Ox)} e^{-\Delta G^{*}_{-}/RT}$$

➡

$$i_{-} = nF\, k_{-} C_{0(Ox)} e^{-\Delta G^{*}_{-}/RT}$$

k_{-} is called the heterogeneous rate constant of the reduction

Substitute with the value of ΔG^{*}_{-} ,

$$i_{-} = nF\, k_{-} C_{0(Ox)} e^{-(\Delta G_{-} + \alpha nFE_{r} + \alpha nF\eta)/RT}$$

Similarly,

$$i_+ = nF\,k_+ C_{0(Red)} e^{-(\Delta G_+ - (1-\alpha) nFE_r - (1-\alpha)\, nF\eta)/RT}$$

$$i_{net} = i_+ - i_- =$$

$$\left(nF\,k_+ C_{0(Red)} e^{-(\Delta G_+ - (1-\alpha) nFE_r - (1-\alpha)\, nF\eta)/RT}\right) -$$

$$\left(nF\,k_- C_{0(Ox)} e^{-(\Delta G_- + \alpha nFE_r + \alpha nF\eta)/RT}\right)$$

At equilibrium, $\eta = i_{net} = 0$ and $i_+ = i_- = i_0$

Exchange current density

$$i_0 =$$

$$\left(nF\,k_+ C_{0(Red)} e^{-(\Delta G_+ - nFE_r + \alpha nFE_r)/RT}\right) =$$

$$\left(nF\,k_- C_{0(Ox)} e^{-(\Delta G_- + \alpha nFE_r)/RT}\right)$$

Assume and substitute

$$k'_+ = k_+ e^{-(\Delta G_+)/RT}$$

$$k'_- = k_- e^{-(\Delta G_-)/RT}$$

$$\left(k'_+ C_{0(Red)} e^{nFE_r/RT}\right) = \left(k'_- C_{0(Ox)}\right)$$

$$e^{nFE_r/RT} = \frac{k'_- C_{0(Ox)}}{k'_+ C_{0(Red)}}$$

Let $E^0 = \frac{k'_-}{k'_+}$

$$e^{nFE_r/RT} = E^0 \frac{C_{0(Ox)}}{C_{0(Red)}}$$

$$\ln\left(e^{nFE_r/RT}\right) = ln\ E^0 + \ln\left(\frac{C_{0(Ox)}}{C_{0(Red)}}\right)$$

$$nFE_r/_{RT} = ln\ E^0 + \ln\left(\frac{C_{0(Ox)}}{C_{0(Red)}}\right)$$

$$E_r = \frac{RT}{nF} ln\ E^0 + \frac{RT}{nF}\ln\left(\frac{C_{0(Ox)}}{C_{0(Red)}}\right)$$

Nernst equation (equilibrium conditions)

Under Non equilibrium conditions $\mathbf{E_i \neq E_r}$

$$i_{net} = i_0\left(e^{(1-\alpha)\ nF\eta/_{RT}} - e^{-\alpha nF\eta/_{RT}}\right)$$

Butler-Volmer equation (Non-equilibrium conditions)

Limiting cases of Butler-Volmer equation

1) Linear (near reversible) polarization

In case of small η

$$\eta \ll \frac{RT}{nF}$$

$$\eta \ll 10\ mV$$

Taylor expansion, ➡ $e^{x} = 1 + x, \quad e^{-x} = 1 - x$

$$i_{net} = i_0\left(e^{(1-\alpha)\,nF\eta/RT} - e^{-\alpha nF\eta/RT}\right)$$

$$i_{net} = i_0\left[\left(1 + \frac{(1-\alpha)\,nF\eta}{RT}\right) - \left(1 - \frac{\alpha nF\eta}{RT}\right)\right]$$

$$i_{net} = i_0\left(\frac{nF\eta}{RT}\right)$$

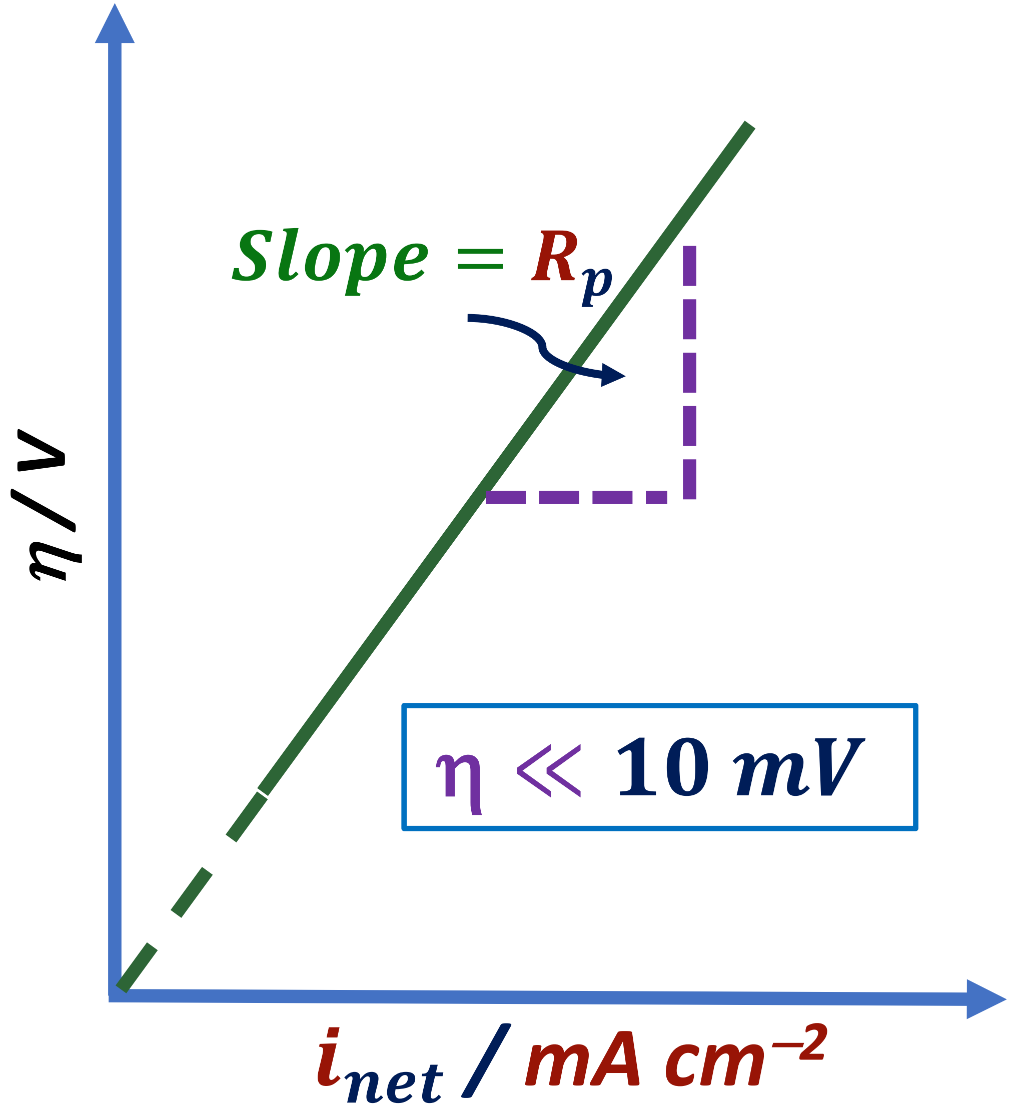
$$\eta = \frac{RT\,i_{net}}{nF\ i_0} = R_p\ i_{net}$$

Polarization resistance, $\Omega\ cm^2$

$R = 8.314\ JK^{-1}\ mol^{-1}$

$$\eta = \frac{RT\, i_{net}}{nF\ i_0} = R_p\ i_{net}$$

- R_p is the slope of the polarization curve near equilibrium.
- R_p is an important characteristic of any electrode system.
- R_p is inversely proportional to i_0 ,i.e., an interface with a large i_0 has a lower R_p .



2) High polarization (Tafel equation)

In case of high η

$$|\eta| >> \frac{RT}{nF}$$

$$\eta > -100\ mV$$

$$i_{net} = i_0\left(e^{(1-\alpha)\,nF\eta/RT} - e^{-\alpha nF\eta/RT}\right)$$

$$i_{net} = i_+ - i_-$$

high cathodic polarization

Current is mainly cathodic

$$i_{net} \approx -i_- = i_0\left(e^{-\alpha nF\eta/RT}\right)$$

$$\ln(i_{net}) = \ln\ i_0 - \frac{\alpha nF\eta}{RT}$$

Tafel equation

$$\eta = \frac{2.303\ RT \log\ i_0}{\alpha n F} - \frac{2.303\ RT}{\alpha n F} \log(i_{net})$$

Similar to

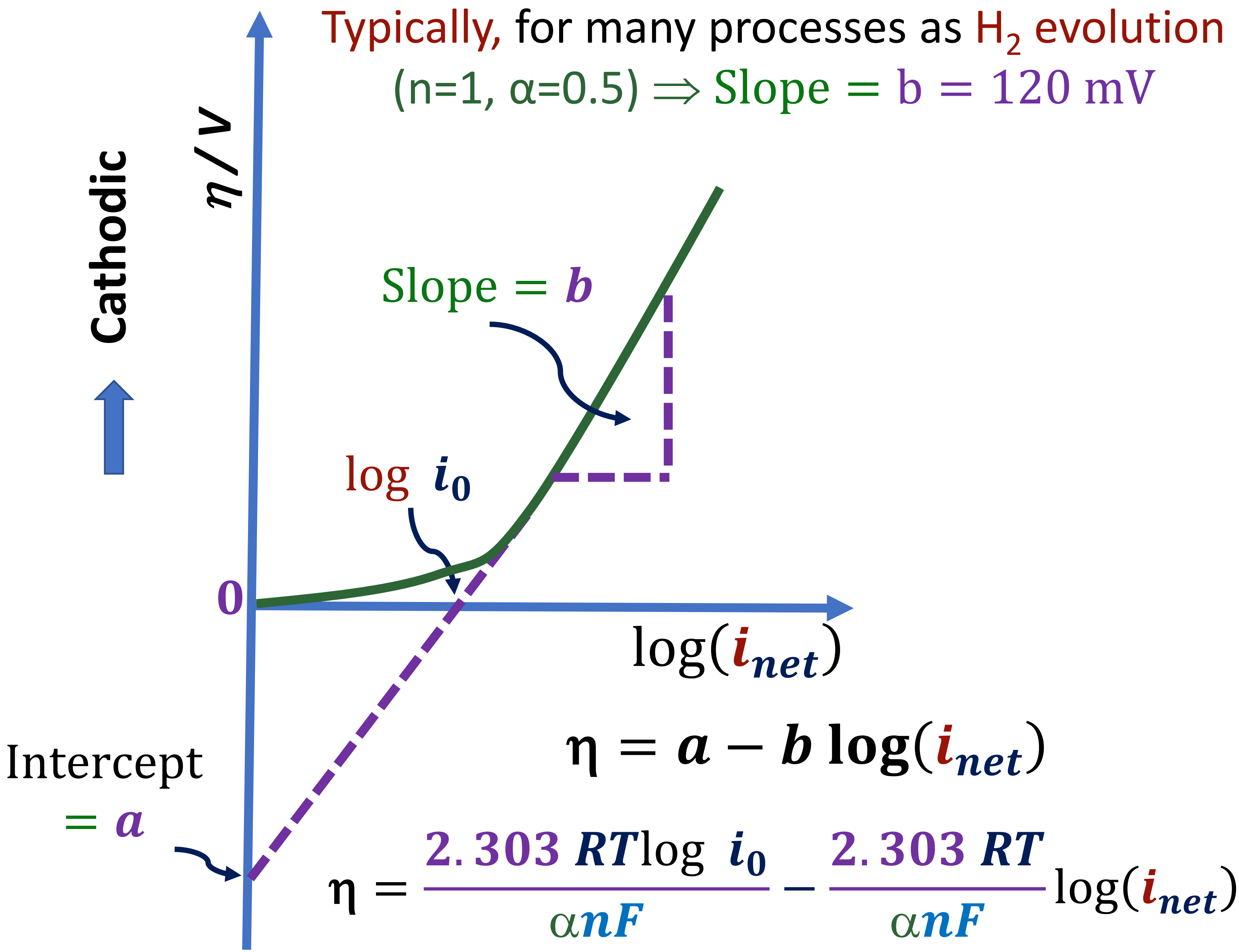
$$\eta = a - b \log(i_{net})$$

$$a = \text{intercept} = \frac{2.303\ RT\, log\ i_0}{\alpha n F}$$

$$b = \text{slope} = \frac{2.303\ RT}{\alpha n F}$$

b is reported in decade of current density

$$\log\ i_0 = \frac{-a}{b}$$


Typically, for many processes as H_2 evolution
(n=1, α=0.5) ⇒ Slope = b = 120 mV
Cathodic
η / V
Slope = b
log i_0
0
$\log(i_{net})$
Intercept
= a
$\eta = a - b\log(i_{net})$
$\eta = \frac{2.303\,RT \log i_0}{\alpha nF} - \frac{2.303\,RT}{\alpha nF}\log(i_{net})$

2) High (irreversible) polarization (Tafel equation)

In case of high η

$$|\eta| >> \frac{RT}{nF}$$

$$\eta > +100\ mV$$

$$i_{net} = i_0\left(e^{(1-\alpha)\, nF\eta/RT} - e^{-\alpha nF\eta/RT}\right)$$

$$i_{net} = i_+ - i_-$$

high anodic polarization

Current is mainly anodic

$$i_{net} \approx i_+ = i_0\left(e^{(1-\alpha)nF\eta/RT}\right)$$

$$\ln(i_{net}) = \ln\ i_0 + \frac{(1-\alpha)nF\eta}{RT}$$

Tafel equation

$$\eta = \frac{-2.303\, RT \log\, i_0}{(1-\alpha)nF} + \frac{2.303\, RT}{(1-\alpha)nF}\log(i_{net})$$

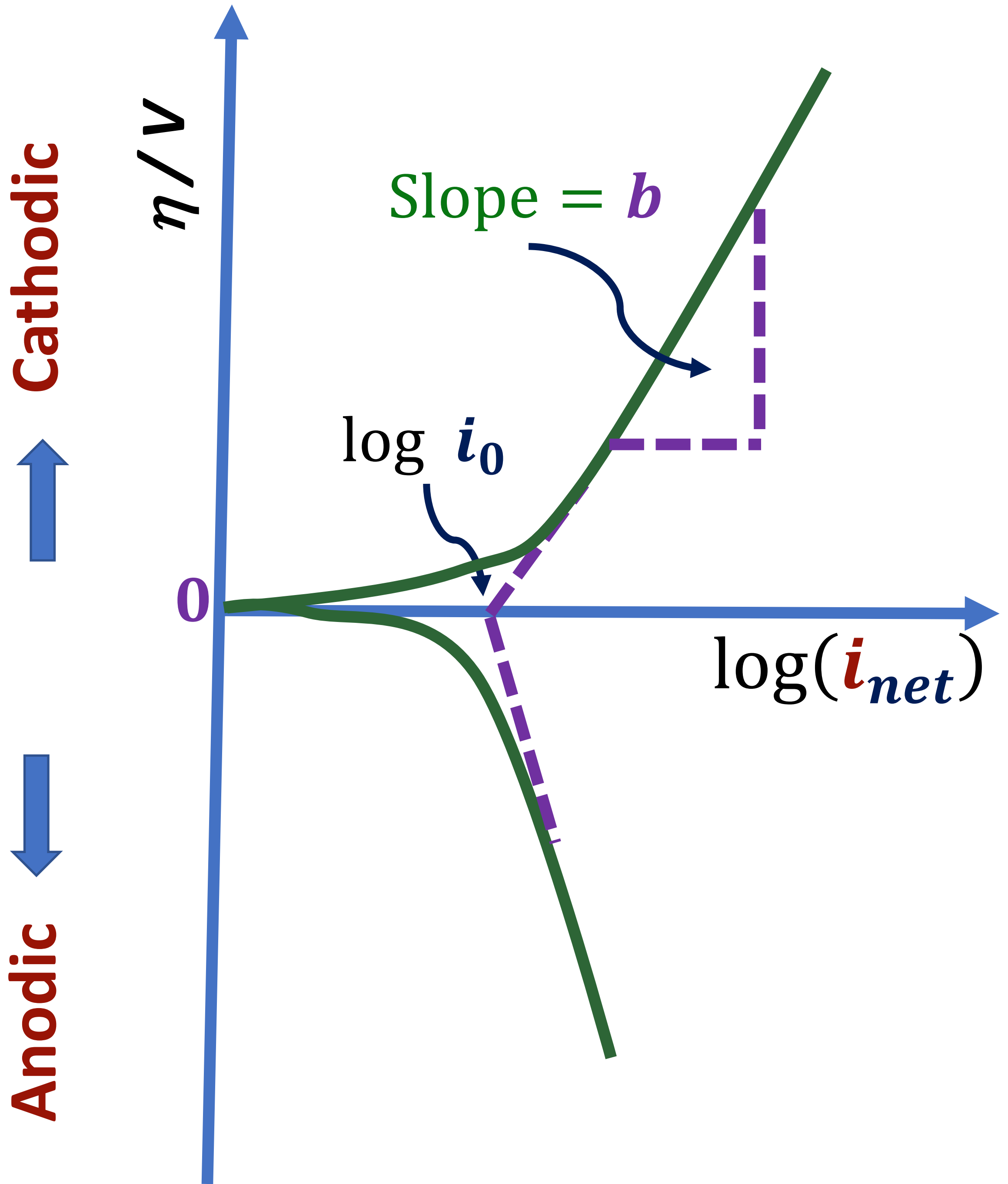
Similar to

$$\eta = a + b\,\log(i_{net})$$

$$a = \text{intercept} = \frac{-2.303\, RT \log\, i_0}{(1-\alpha)nF}$$

$$b = \text{slope} = \frac{2.303\, RT}{(1-\alpha)nF}$$

$$\log\, i_0 = \frac{-a}{b}$$


η / V
Cathodic
Anodic
Slope = b
log i0
0
log(inet)

3) Butler-Volmer Eqn with no approximation

For some processes the region of high η is ill-defined and analysis of Butler-Volmer Eqn. is preferred without approximation.

(Quasi- reversible) η

$$10\ \text{mV} \ll \eta \ll 100\ \text{mV}$$

$$i_{net} = i_0\, e^{\frac{-\alpha n F \eta}{RT}} \left(e^{\frac{nF\eta}{RT}} - 1\right)$$

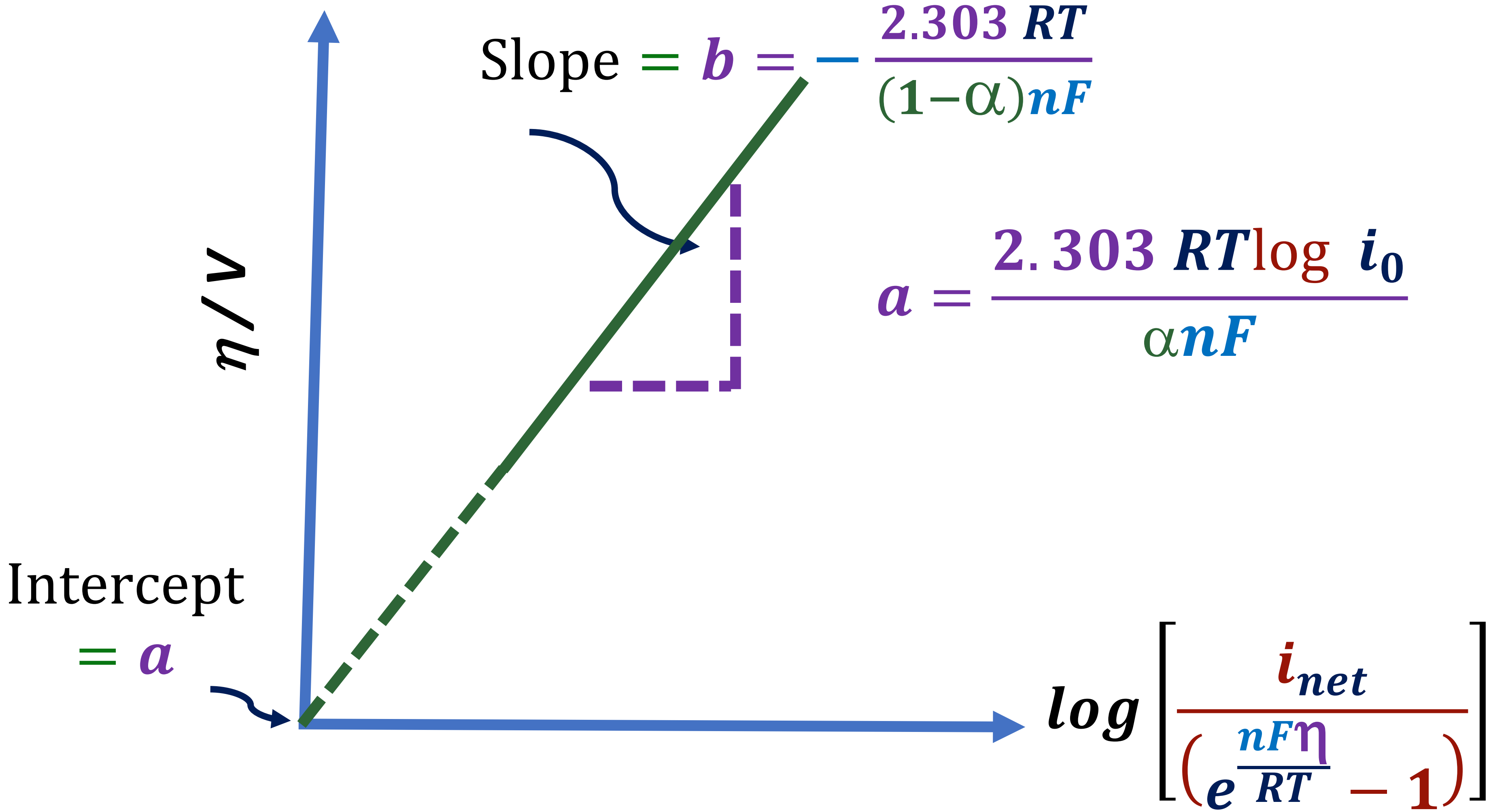
$$\left[\frac{i_{net}}{\left(e^{\frac{nF\eta}{RT}} - 1\right)}\right] = i_0\, e^{\frac{-\alpha n F \eta}{RT}}$$

$$\ln\left(\frac{i_{net}}{\left(e^{\frac{nF\eta}{RT}} - 1\right)}\right) = \ln i_0 - \frac{\alpha n F \eta}{RT}$$

$$\eta = \frac{2.303\ RT \log\ i_0}{\alpha n F} - \frac{2.303\ RT}{(1-\alpha) n F} \log\left[\frac{i_{net}}{\left(e^{\frac{nF\eta}{RT}} - 1\right)}\right]$$

$$\eta = \frac{2.303\,RT \log\, i_0}{\alpha n F} - \frac{2.303\,RT}{(1-\alpha)nF}\log\left[\frac{i_{net}}{\left(e^{\frac{nF\eta}{RT}} - 1\right)}\right]$$

$$\eta = a + b\,\log(i_{net})$$



Fundamental Kinetic parameters

1) Exchange current density, i_0

is a measure of the speed of naturally occurring redox processes (in absence of external electrical activation).

Importance of i_0

- ❑ is used to assign better electrocatalysts in fuel cells.
- ❑ is used to determine the rate of metal dissolution (corrosion rate).
- ❑ is used to predict the value of mixed potentials in systems containing more than one redox processes. The highest i_o value will most likely decide the value of mixed potential.

Fundamental Kinetic parameters

2) Standard heterogeneous rate constant, k_0

Since i_0 depends on the concentration of redox species, k_0 is developed to probe only the nature of the redox species.

$$k_0 = \frac{i_0}{nF\left(C_{0(Ox)}\right)^{1-\alpha}\left(C_{0(Red)}\right)^{\alpha}}$$

unit of $k_0 = cm\ s^{-1}$

Velocity

$k_0 / cm\ s^{-1}$	Nature of Process
$> 2 \times 10^{-2}$	Reversible
$> 5 \times 10^{-3} < 2 \times 10^{-2}$	Quasi-reversible
$< 5 \times 10^{-3}$	Irreversible

Fundamental Kinetic parameters

3) Transfer coefficient/ symmetry factor, α

- For simple redox processes involving one or two electron transfer and for many processes equals 0.5.
- It indicates how the electrical energy $nF\eta$ will change the energy barrier of the process via activating one direction (reduction by decreasing the barrier by $\alpha nF\eta$) and deactivating the other (oxidation by increasing the barrier by $-(1-\alpha)\, nF\eta$).
- For complex redox processes, it is helpful in the elucidation of the probable mechanism(s). It is mathematically related to the numbers of electrons, all steps in the process, steps before and after rds, and the repetition of rds.