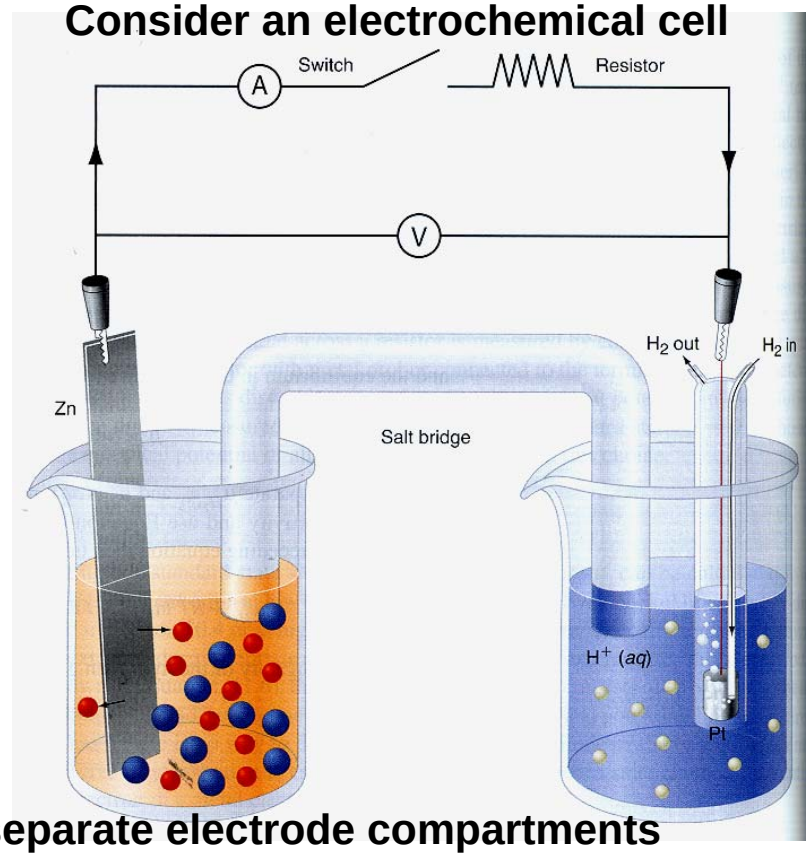
CHEM465/865, 2006-3, Lecture 13-15, Oct. 11, 2006

Electrode Reactions and Kinetics

From equilibrium to non-equilibrium:

Consider an electrochemical cell



- **two separate electrode compartments**
- **composition (concentrations, partial pressures, etc.)**
- **reaction Gibbs free energy as driving force**

$$E_{\text{cell}} = \varphi^{\text{C}} - \varphi^{\text{A}} = -\frac{\Delta_r G}{|\nu_e| F} = E^0 - \frac{RT}{|\nu_e| F} \ln Q$$

e.g. above cell: $E_{\text{cell}} = E^0 - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{\left(a_{H^+}\right)^2}$

Open circuit potential (OCV):

$\Delta_r G$ **determines EMF** E_{cell} **between anode and cathode!**

In other words:

everything is ready to let the electric current I **flow!**

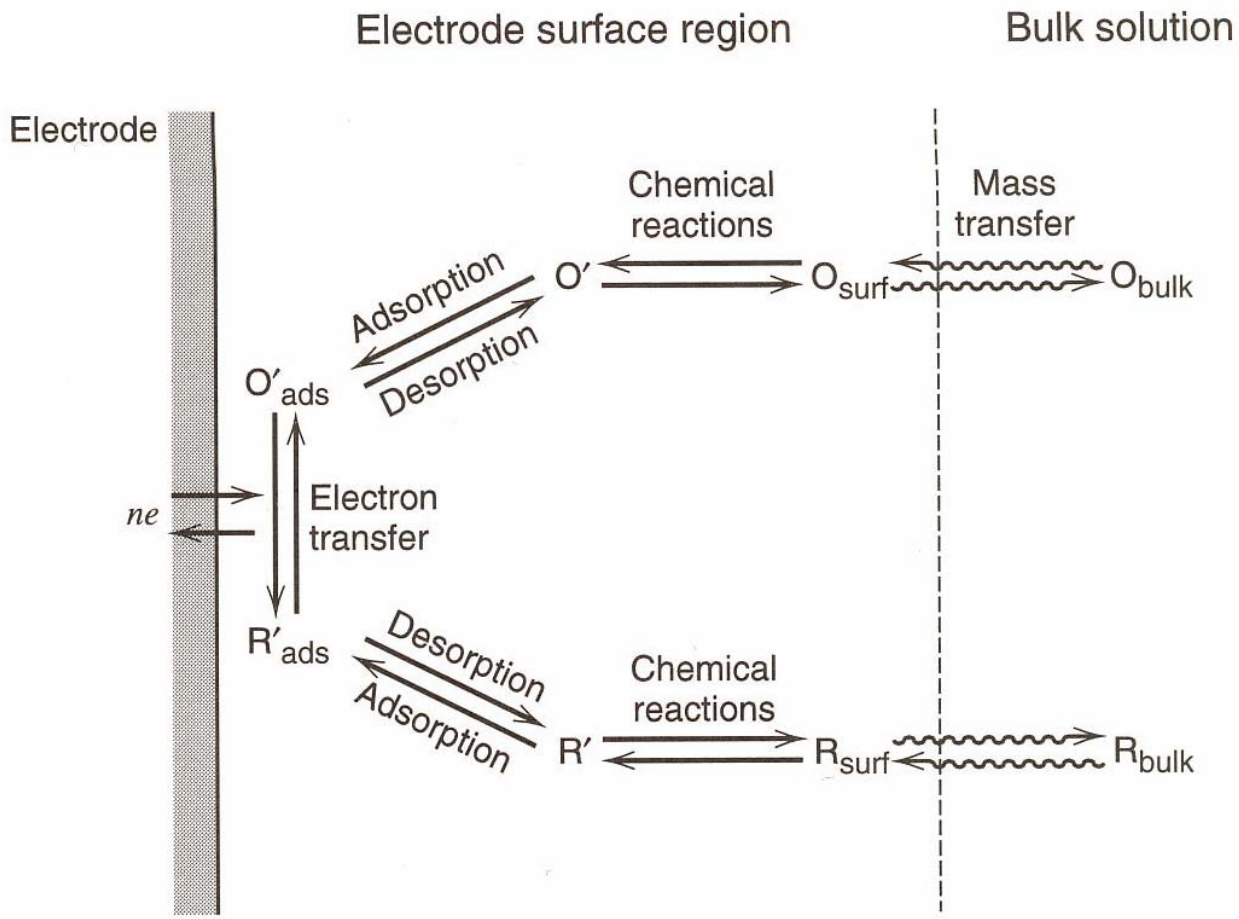
– i.e. make the external connection through wires.

Important observations:

- I **is NOT controlled by equilibrium TD, but 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!



Electrode processes, e.g. $Fe^{3+}(aq) + e^{-}(electrode) \leftrightarrow Fe^{2+}(aq)$**,**

involve:

- **bulk diffusion (mass transfer in solution)**
- **ion migration (Ohmic resistance in solution)**
- **rearrangement of ionic atmospheres**
- **reorientation of solvent molecules**
- **adsorption**
- **charge transfer**
- **desorption**

Let's focus next on charge transfer!

Also called: Faradaic process

The only process directly affected by potential!

Electrode reactions differ from ordinary chemical reactions:

at least one partial reaction is charge transfer reaction

- **against activation energy potential-controlled**
- **from one phase to another**
- **across the electrical double layer.**

Reaction rate depends on

- **distributions of species (conc., pressures, etc.)**
- **temperature**
- **electrode potential *E***

Assumption used in the following:

Electrode material itself (metal) inert – no chemical transformation. It is a catalyst, i.e. a source/sink of e^-.

General question: How does reaction rate depend on *E*?

Observation: Electrode potential *E* of an electrode through which a current flows differs from equilibrium potential E^{eq} established when no current flows.

Difference between these potentials: overvoltage

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

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

Convention:

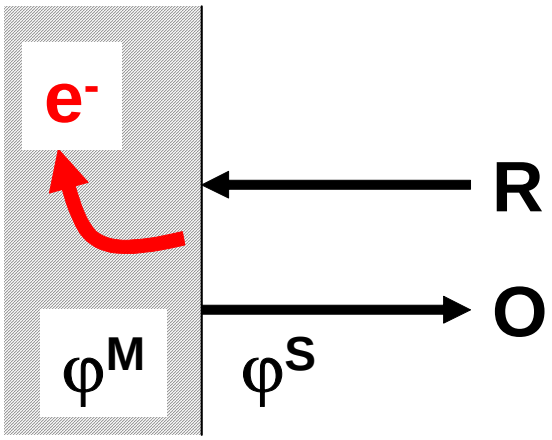
Current associated with reaction

Red → Ox + e^-(Me) (anodic reaction)

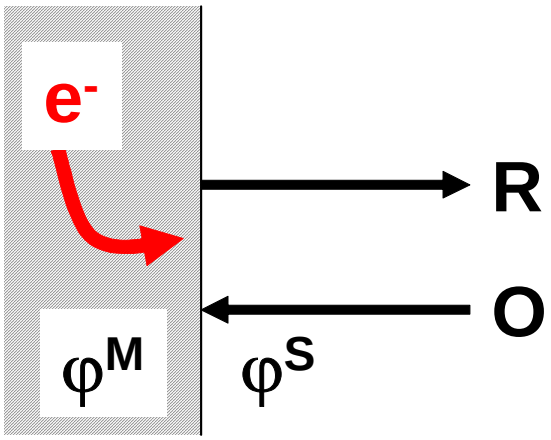
e.g. H_{ad},Fe^{2+} e.g. H^+,Fe^{3+}

⇒ anodic current, positive direction (positive rate)

anodic direction



cathodic direction



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

$$v_{net} = K_{ox} c^S_{red} - K_{red} c^S_{ox} \quad (*)$$

net rate = rate of oxidation – rate of reduction

c^S_{red}, c^S_{ox}: **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 (make a mental note)!

Anode:

anodic reaction dominates, positive net rate $v_{net} > 0$

Cathode:

cathodic reaction dominates, negative net rate $v_{net} < 0$

General observation

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

Charge transfer reactions are kinetically hindered!

Since species is charged:

activation energy depends on electrode potential

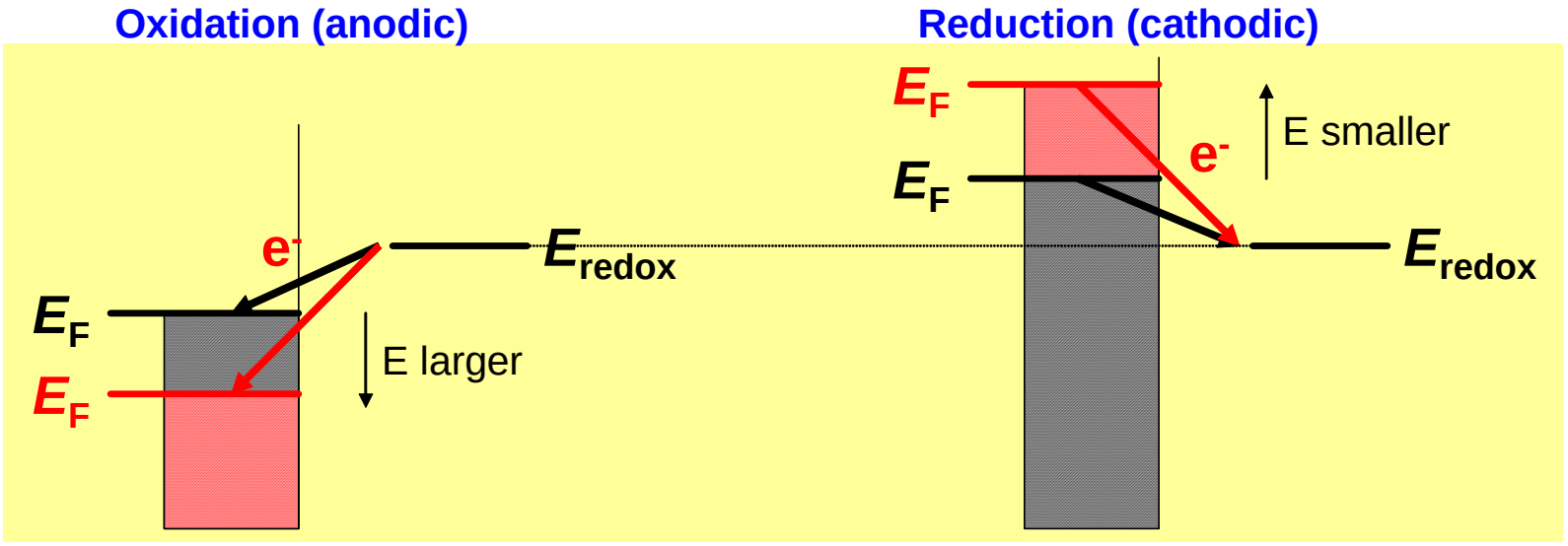
$$E = \varphi^{M} - \varphi^{S}$$

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 is actually controlled by applying *E* to electrode?

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



larger potential (E or φ^M larger)
favors oxidation

smaller potential (E or φ^M smaller)
favors reduction

Note: 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 (i.e. energy of electrons in metal).

In order to understand, how the reaction proceeds in detail, we need to determine the rate constants in Eq.(*):

Use absolute rate theory!

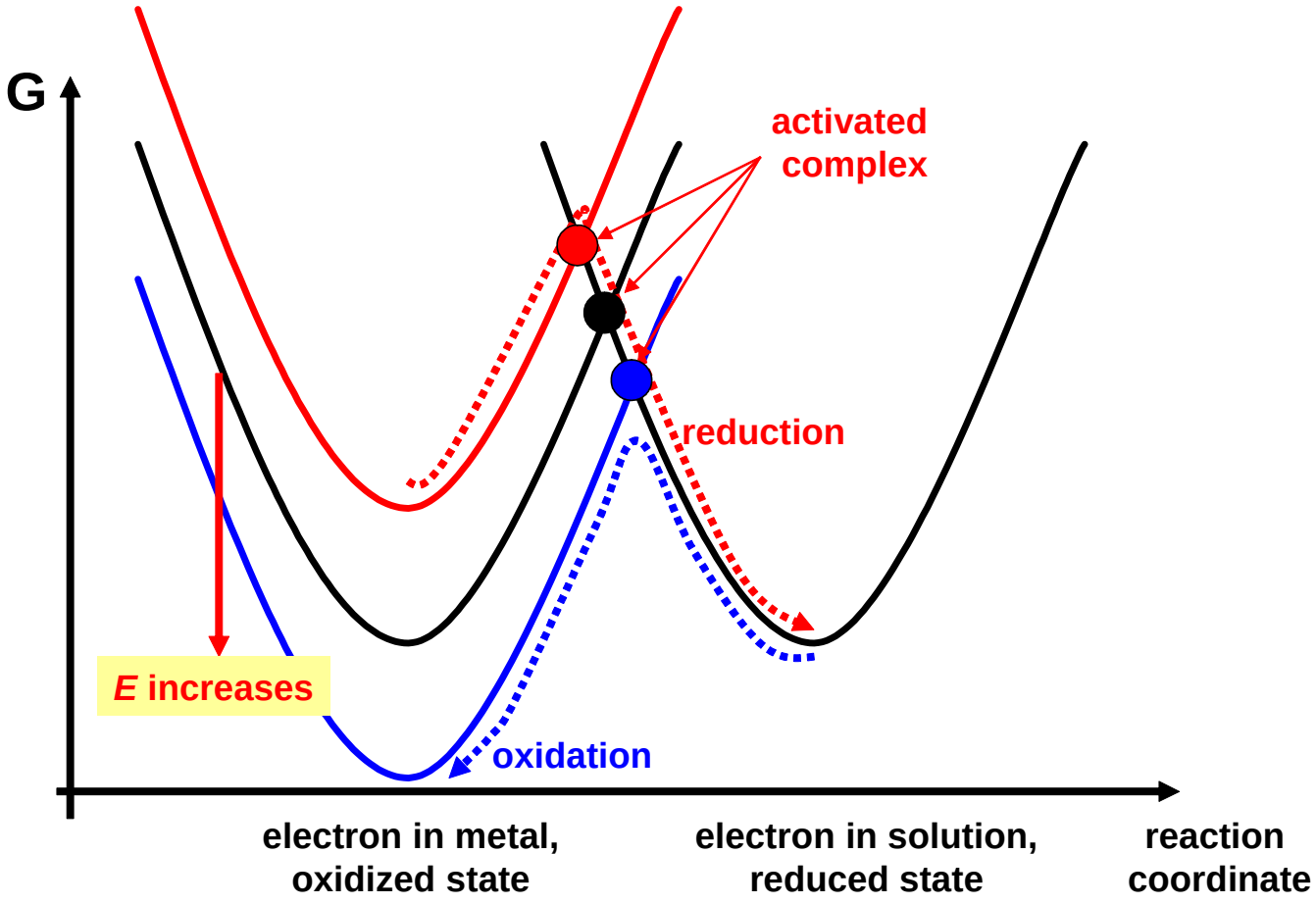
$$K_{ox} = A\exp\left(-\frac{\Delta G_{ox}^{\dagger}(E)}{RT}\right),\ K_{red} = A\exp\left(-\frac{\Delta G_{red}^{\dagger}(E)}{RT}\right)$$

$\Delta G_{ox}^{\dagger}(E)$, $\Delta G_{ox}^{\dagger}(E)$: **molar Gibbs free energy 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?

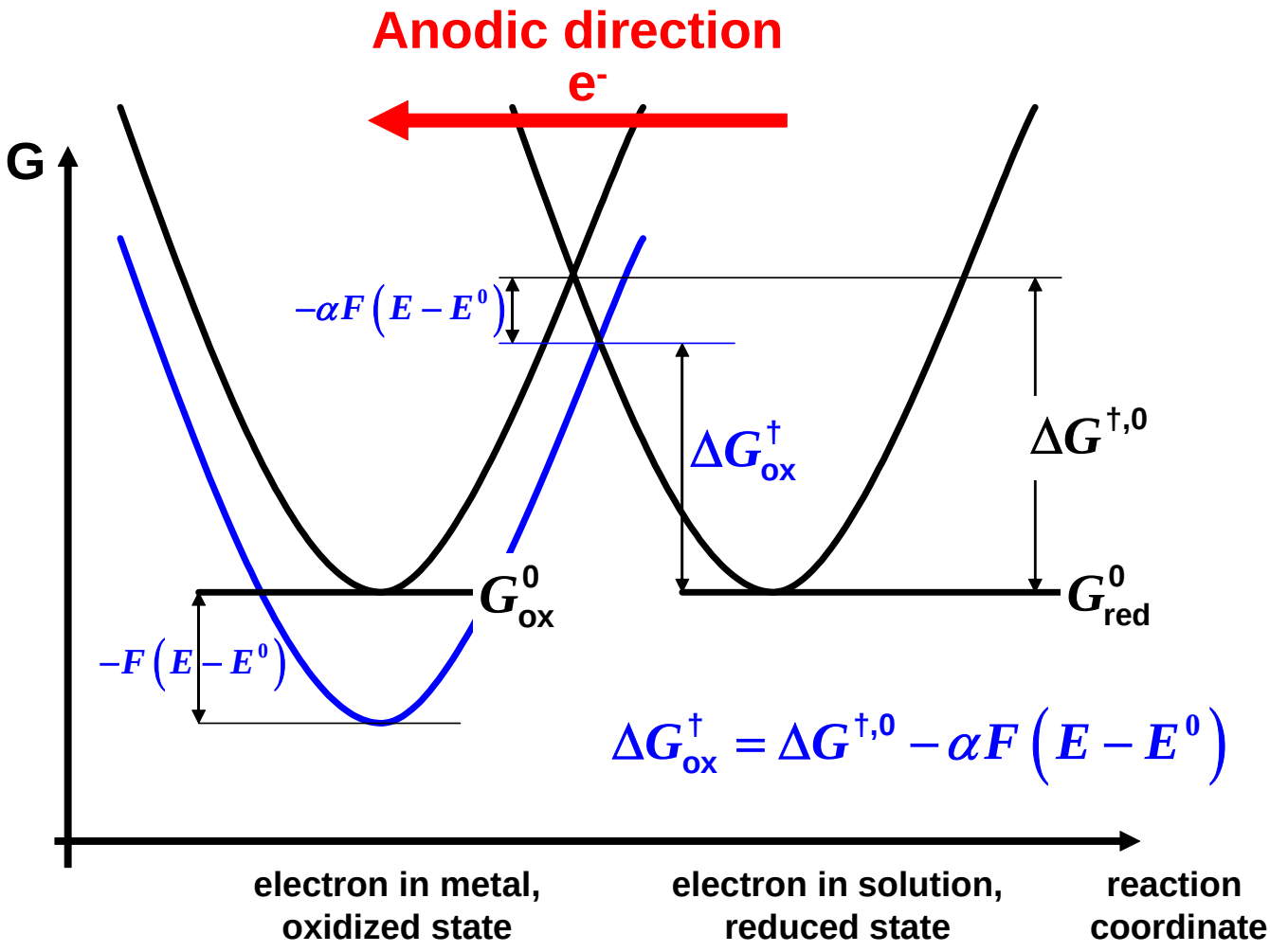
Let's consider the free energy profile for electron transfer reaction:

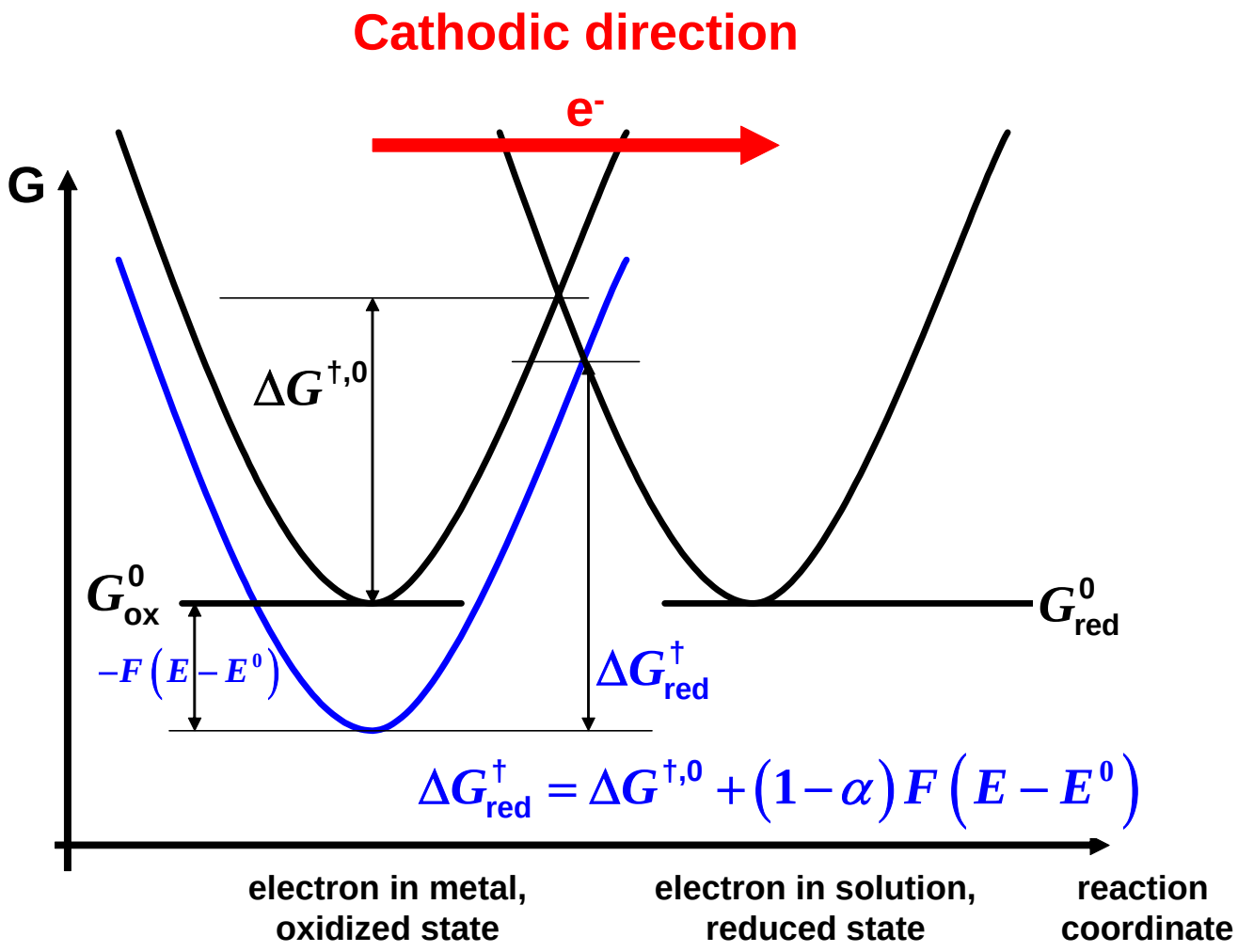


- Electron transfer between reduced and oxidized state proceeds via an activated intermediate complex
- Height of the potential barrier depends on the electrode potential *E*.

In the following pictures, the electrode potential ***E*** is shifted from the equilibrium value (black curve) to a more positive value (blue curve).

An increase in ***E*** favors the anodic direction (oxidation) and disfavors the cathodic direction (reduction).




Cathodic direction
e-
G
$\Delta G^{\dagger,0}$
G^0_{ox}
G^0_{red}
$-F\left(E-E^0\right)$
$\Delta G^{\dagger}_{red}$
$\Delta G^{\dagger}_{red} = \Delta G^{\dagger,0} + \left(1-\alpha\right) F\left(E-E^0\right)$
electron in metal, oxidized state
electron in solution, reduced state
reaction coordinate

Expand $\Delta G_{ox}^{\dagger}(E)$ about standard equilibrium potential E^0.

Recall: E^0 is characteristic value of the considered redox pair (at a 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

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

- Anodic reaction (at one electrode):

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

anodic transfer coefficient:

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

- Cathodic reaction (at the same electrode):

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

cathodic transfer coefficient:

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

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

- **Larger *E* ⇒ $\Delta G_{ox}^{\dagger}$ smaller ⇒ anionic reaction faster**

  in other words: at larger *E* electrons are more easily transferred from the solution to the metal

- **Smaller *E* ⇒ $\Delta G_{red}^{\dagger}$ smaller ⇒ cathodic reaction faster**

  in other words: at smaller *E*, 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.

<u>Note</u>: Deviations from the linear approximations in Eqs.(#) and (##) arise at large values of $\left|E - E^0\right| >> \frac{RT}{F}$

Particular relation

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

(reference concentrations: standard concentrations!)

Consider: high concentration of inert electrolyte

⇒ screens the electrode potential

⇒ no potential drop in diffuse layer (solution)

⇒ φ^{S} unchanged upon variation of E

⇒ variation in electrode potential is equal

to a variation in the metal potential,

$$\Delta E=\Delta\varphi^{M}$$

⇒ i.a.w.: solution potential serves as constant reference

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

Note: 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".

Now we can easily determine the current density of the electrode reaction, in units of [A/cm^2]:

$$j = F\nu_{\text{net}} = F\left[K_{ox}c^{s}_{\text{red}} - K_{red}c^{s}_{\text{ox}}\right]$$

Net current can be split up in an oxidation current j_{ox} and a reduction current j_{red}:

$$j_{\text{ox}} = FK_{\text{ox}}c^{s}_{\text{red}} \qquad \text{and} \qquad j_{\text{red}} = FK_{\text{red}}c^{s}_{\text{ox}}$$

Using the linear approximations for $\Delta G^{\dagger}_{\text{ox}}(E)$ and $\Delta G^{\dagger}_{\text{red}}(E)$ in the expressions for the rate constants:

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

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

where we used $\beta = 1-\alpha$.

The rate constant $k_0 = A\exp\left\{-\frac{\Delta G^{\dagger,0}}{RT}\right\}$ (units [cm/s]) is a measure of the reaction rate at E^0.

We can now write an equation relating *E* to current density *j* for the electrode reaction:

(BV 1)

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

This is the famous BUTLER-VOLMER equation.

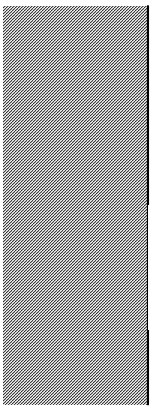
General: the deviation of *E* from the situation of zero net current, i.e. at E^{eq}, is considered. Hence, we have to involve the Nernst equation to establish the link between composition (in the bulk) and E^{eq} for a given

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

Use this relation in (BV 1) and recall the definition of overpotential, $\eta = E - E^{eq}$. After some rearrangement (exercise!!) the Butler-Volmer equation can be written as a relation between *j* and η:

(BV 2)

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



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.