Overview of electrochemistry

	Equilibrium electrochemistry (no current flows)	**Dynamic electrochemistry (current does flow)**
Homogeneous	Thermodynamics of electrolyte solutions: • electrolytic dissociation • thermodynamics and activities of ions	Conductance of electrolytes: • electrolytic conduction • mobilities of ions • Kohlrausch laws
Heterogeneous	Thermodynamics of electrodes and Galvanic cells: • electrochemical cells • cell and electrode potential • types of electrodes	Kinetics of electrode reactions: • exchange current • overpotential • Tafel equation • Butler-Volmer equation • electrolysis • batteries

HOMOGENOUS DYNAMIC ELECTROCHEMISTRY

Simultaneous or coupled t**ransport phenomena**

I. Conductivity of electrolytes (κ, Λ_m, Λ_m°)
   - law of the independent migration of ions: $\Lambda_m = \nu_+\lambda_+ + \nu_-\lambda_-$

II. Strong electrolytes:
   - Kohlrausch law: $\Lambda_m = \Lambda_m^\circ - Kc^{1/2}$

III. Weak electrolytes: ($a < 1$, $a = \Lambda_m/\Lambda_m^\circ$)
   - Ostwald's dilution law

IV. Mobilities of ions

I. Conductivity of electrolytes

- Ionic conductivity: Ohm's law is valid: $I = U / R_{res}$
- Conductance *G* is the reciprocal of R_{res}: $G = 1 / R_{res}$
- as *T* increases, do does κ (opposite to metals).
- Solution: κ conductivity: $\kappa = Gl / A = GC$
  (*l*: length of cell, *A*: surface, *C*: cell constant)
- Concentration is important, molar conductivity is used: $\Lambda_m = \kappa / c$
- The limiting value of Λ_m at infinite dilution is Λ_m^{o} (limiting molar conductivity).

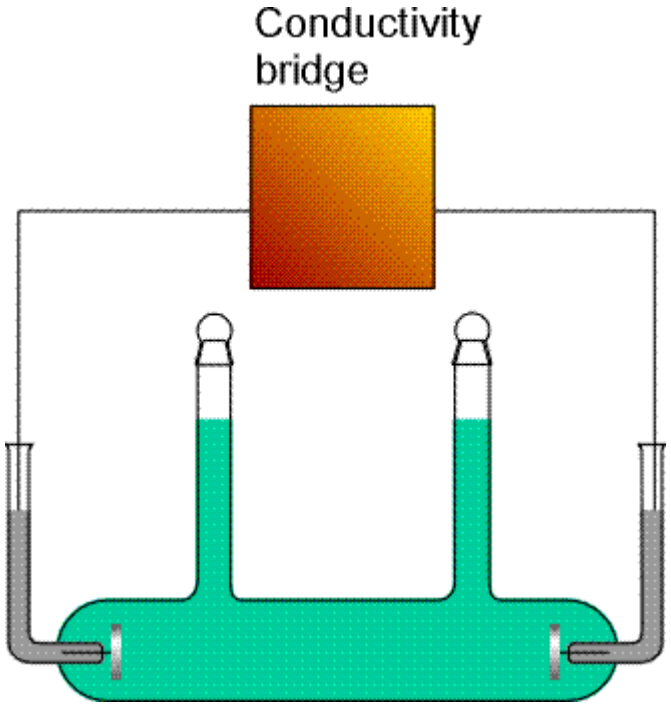
I. Conductivity of electrolytes

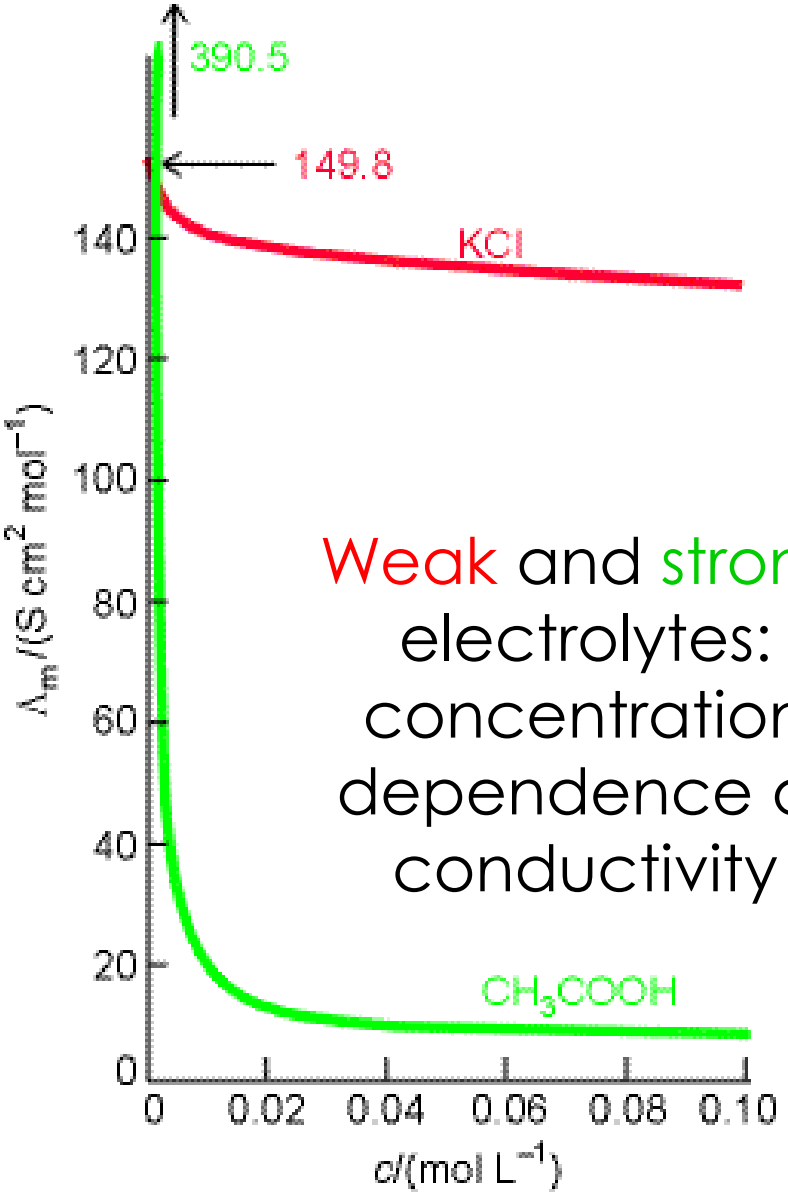
- The limiting value of Λ_m at infinite dilution is Λ_m^{o} (limiting molar conductivity).
- The conductivity of the electrolyte is obtained by adding the conductivities of ions: **law of the independent migration of ions**:

$$\Lambda_m^0 = \nu_+ \lambda_+ + \nu_- \lambda_-$$

  - λ_+ and λ_-: limiting molar conductivities of (individual) cations and anions
  - ν_+ and ν_-: stoichiometric number of the cation and anion

Cell: measuring the conductivity of electrolytes



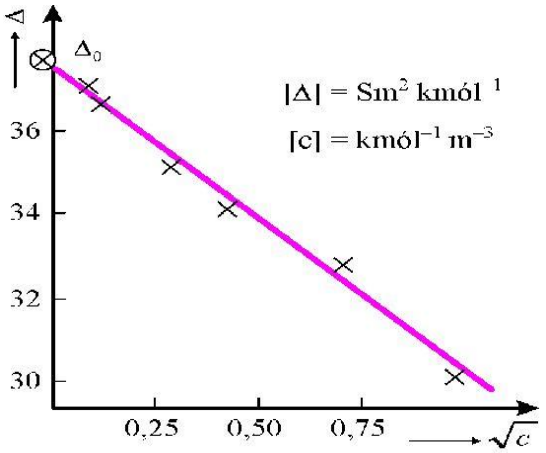


Weak and strong electrolytes: concentration dependence of conductivity

II. Strong electrolytes

- Concept (definition): in a solution of a strong electrolyte dissociation is practically complete independently of the concentration, so $a = 1$.
- Degree of dissociation (a): the ratio of dissociated molecules.
- Conductivity of electrolytes, **Kohlrausch law**:

$$\Lambda_m = \Lambda_m^0 - Kc^{1/2}$$



  - K: a constant to be determined experimentally; depends primarily on the type of the electrolyte and not on its identity

III. Weak electrolytes

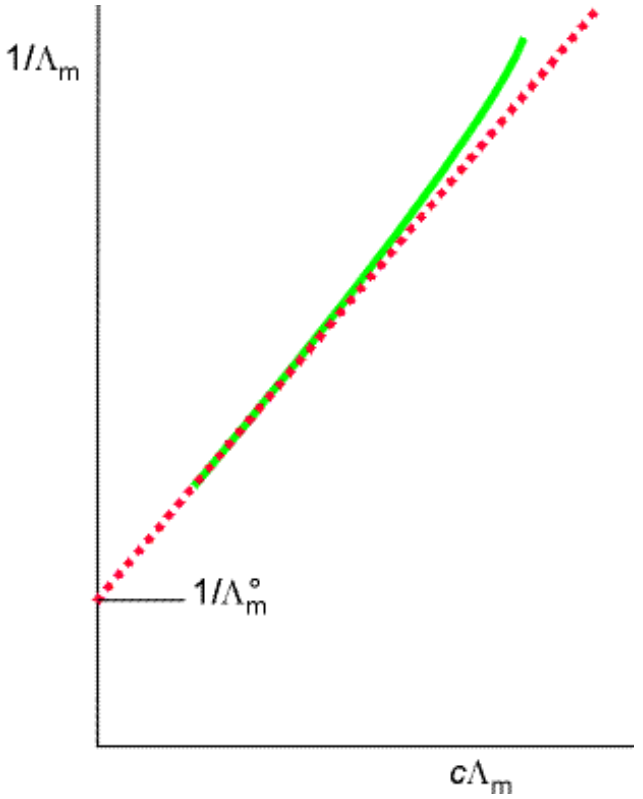
- The degree of dissociation is reflected by the ratio of Λ_m and limiting Λ_m° : $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$

- Acid dissociation constant:

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

- **Ostwald's dilution law**:

$$\frac{1}{\Lambda_m} = \frac{1}{K_a\left(\Lambda_m^0\right)^2} \cdot c\Lambda_m + \frac{1}{\Lambda_m^0}$$



IV. Mobilities of ions

Molar conductivities of a few ions at 298 K

Cation	Λ^{∞}/(S cm^2 mol^{-1})	Anion	Λ^{∞}/(S cm^2 mol^{-1})
H^+	349.8	OH^-	198.3
Li^+	38.7	F^-	55.4
Na^+	50.1	Cl^-	76.3
K^+	73.5	Br^-	78.1
Be^{+2}	90.0	I^-	76.8
Mg^{2+}	106.2	NO_3^-	71.5
Ca^{2+}	119.0	SO_4^{2-}	160.0
Ba^{2+}	127.2	CH_3COO^-	40.9
Al^{3+}	183.0	$C_6H_5CO^-$	32.4
Cu^{2+}	107.2	HCO_3^-	44.5
Ag^+	61.9	CO_3^{2-}	138.6
Zn^{2+}	105.6	$Fe(CN)_6^{3-}$	302.7
Ce^{3+}	209.4	$Fe(CN)_6^{4-}$	442.0

- mobility (u)
- frictional coefficient (f)
- viscosity (η)
- radius (a_{hydr})

$$u = \frac{ze}{f} = \frac{ze}{6\pi\eta a_{hydr}}$$

Overview of electrochemistry

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HETEROGENEOUS DYNAMIC ELECTROCHEMISTRY

1. Observations
2. Interpretation of the observations
3. Practical electrochemistry

Kinetics of electrode processes (heterogeneous dynamic electrochemistry)

- In **equilibrium electrochemistry** (thermodynamics of electrolytes, Galvanic cells and electrodes), states of equilibrium are described and the possibility of changes. No current flows in such systems, the Galvanic cell does no useful work, no change occurs on the electrodes.
- In **non-equilibrium electrochemistry [dynamic electrochemistry],** dynamic processes are described: the system is not in equilibrium: current flows in the solutions, substances deposit or dissolve on electrodes. In addition to equilibrium electrode potential, overpotential occurs.

1. Observations

Quantities in dynamic electrochemistry:

Potential / voltage related: The original equilibrium electrode potentials (E) are not valid in a working Galvanic or electrolytic cell. The differences are formally described as:

- On electrodes: η overpotential (polarization potential)
- Galvanic cells: actual cell potential ($< E$) [not necessarily constant, depends on the current]
- Electrolytic cells: η overpotantial ($> E$) [set by the experimenter based on the objectives]
- All of these quantities are measurable – similarly to E.

1. Observations

Quantities in dynamic electrochemistry:

Current density, exchange current(s):

- Observations show that current density *j* changes when the overpotential η is changed: increase and decrease, even a sign change are possible.
- On all electrodes , cathodic $j_c = Fk_c[\mathrm{Ox}]$ And anodic $j_a = Fk_a[\mathrm{Red}]$ current densities are. The actual (and measurable) current density *j* is the difference of these two:
  - if $j_a > j_c$, then $j > 0$, the net current is anodic,
  - if $j_a < j_c$, then $j < 0$, the net current is cathodic,
  - if $j_a = j_c$, then $j = 0$, the net current is zero.

1. Observations

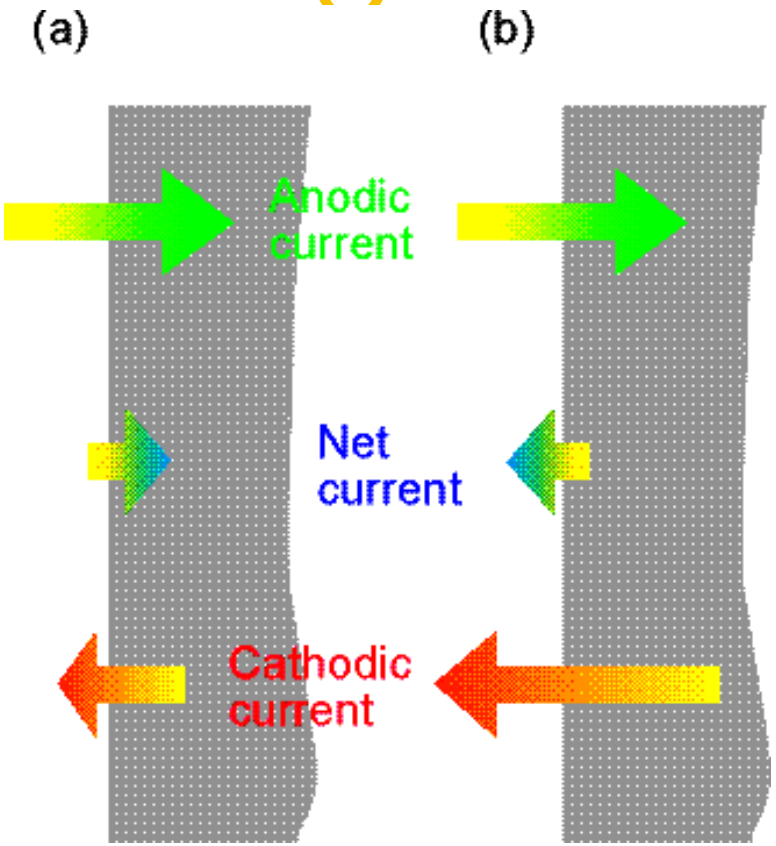
Quantities in dynamic electrochemistry:

Current density, exchange current(s):

- (a) anodic and
- (b) cathodic
  net current density:

$$j_a = Fk_a[\mathrm{Red}]$$

$$j_c = Fk_c[\mathrm{Ox}]$$



1. Observations

Quantities in dynamic electrochemistry:

Relationship between the overpotential and current density, the Tafel equation:

- At small overpotential, current density increases linearly with the overpotential: $j = j_0 f \eta \qquad (f = F/RT)$
- At intermediate overpotential, the relationship is exponential (logarithmic). This is the **observed Tafel equation**: $j = j_0 e^{(1-\alpha) f\eta}, \quad \ln j = \ln j_0 + (1-\alpha) f\eta$
- At large overpotential, current density reaches an upper limit, this is the **limiting current**.

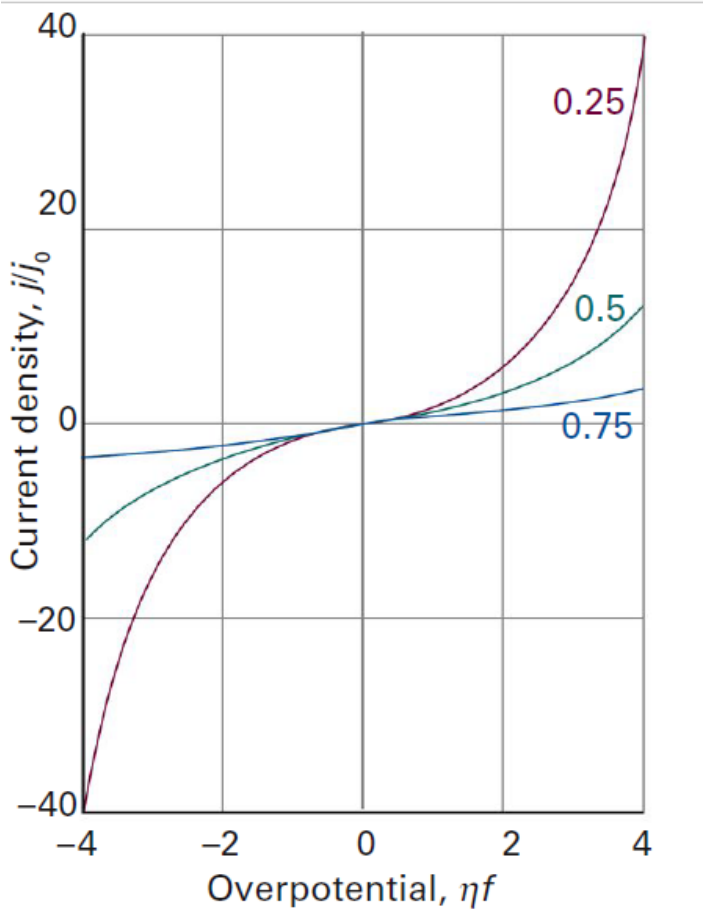
- If $\eta < 0$, then $j < 0$: $\ln(-j) = \ln j_0 - \alpha f \eta$

1. Observations

Quantities in dynamic electrochemistry:

Cases in the overpotential–current density landscape,
the Tafel equation:

- Current density j as a function of overpotential η:



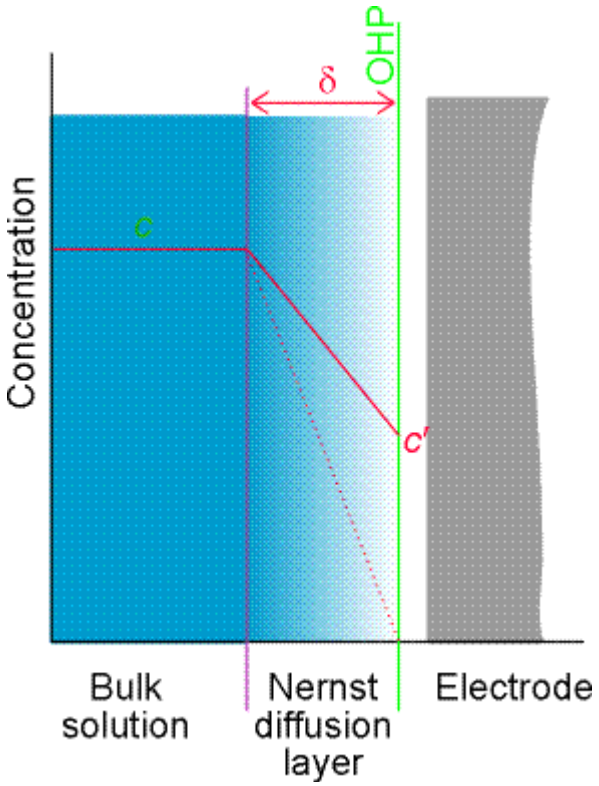
2. Interpretation of observations

To interpret the observations, we need:

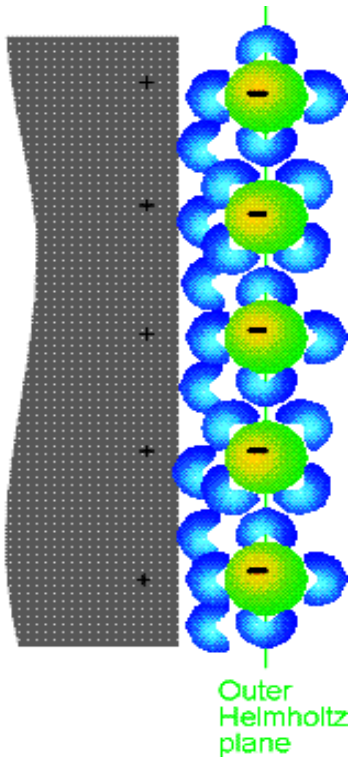
- an understanding of the structure of the surface boundary between the electrode and the electrolyte: a description of the electric double layer and the Nernst adsorption layer.
- the mechanisms of the rate limiting step: the activation free energy $\Delta^{\#}G$ of the charge transfer step and its possible dependence on the overpotential η.
- to clarify the role of diffusion and activation. Recognizing the relationship between η and $\Delta^{\#}G$ is the core issue in the kinetic description of electrode processes.

2. Interpretation of observations

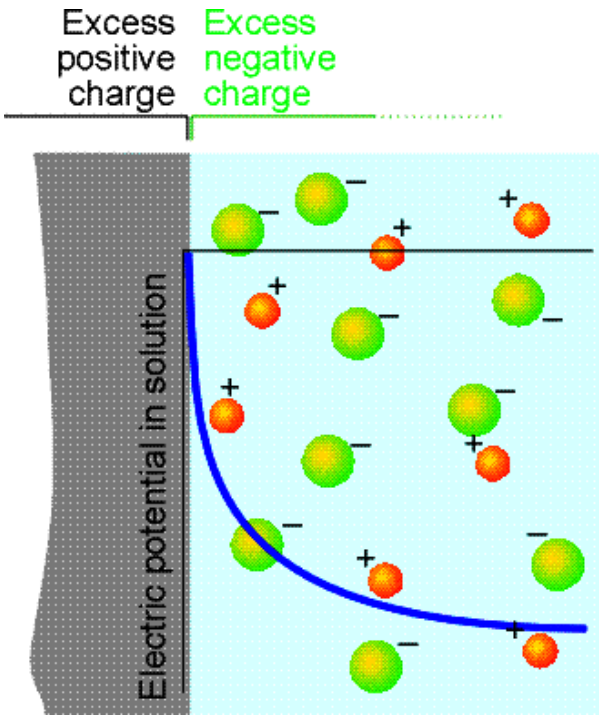
The structure of the electrode /electrolyte boundary:



Gouy–Chapman diffusion model



Helmholtz planar capacitor model

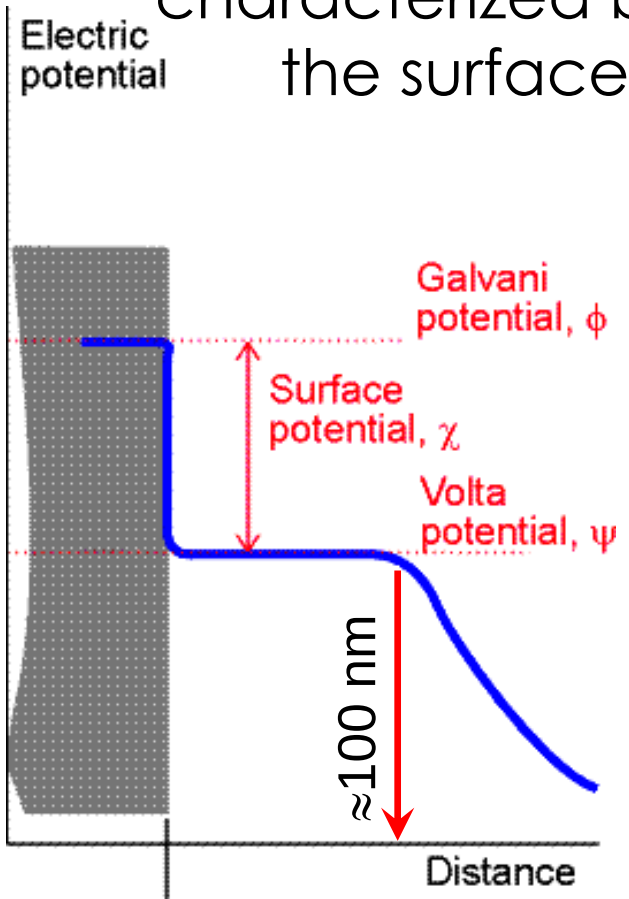


Stern model

2. Interpretation of observations

The structure of the electrode /electrolyte boundary:

- Within the double layer, the electric field is characterized by the potential of a unit charge (e^-) vs. the surface.



  - On approaching from a large distance, the potential increases exponentially, then remains constant close to the (quasiplanar) surface (ψ Volta potential).
  - A sudden jump on the surface (χ surface potential potential).
  - Together: φ Galvani potential.
  - Only the Galvani potential is available experimentally, it is the same as the electrode potential.

2. Interpretation of observations

Kinetics of electrode processes, the Butler–Volmer equation:

1. If in the electrode reaction $\mathrm{Ox} + \mathrm{e}^- = \mathrm{Red}$ (cathodic reduction), the electrode becomes more positive (is polarized), the activation free energy of the electrode process increases: $\Delta^{\neq}G_c = \Delta^{\neq}G_c(0) + \alpha \mathrm{F}\eta$
2. In a $\mathrm{Red} - \mathrm{e}^- = \mathrm{Ox}$ oxidation (anodic) process, the effect of polarization: $\Delta^{\neq}G_a = \Delta^{\neq}G_a(0) - (1-\alpha)F\eta$

- With these two modified values of activation free energy, the net current density is obtained, which connects j and η. This is called the **Butler–Volmer equation**:

$$j = j_a - j_c = FB_a[\mathrm{Red}]\mathrm{e}^{[-\Delta^{\neq}G_a + (1-\alpha)\mathrm{F}\eta]/\mathrm{R}T} - FB_c[Ox]\mathrm{e}^{[-\Delta^{\neq}G_c - \alpha\mathrm{F}\eta]/\mathrm{R}T}$$

2. Interpretation of observations

Kinetics of electrode processes, the Butler–Volmer equation:

- Without any overpotential ($\eta = 0$), the formula gives the exchange current density j_0 arising from the equilibrium cell potential E_{cell} without current: $j_0 = j_a = -j_c$

$$j_a = FB_a[\mathrm{Red}]\mathrm{e}^{\left[-\Delta^{\neq}G_a + (1-\alpha)FE\right]/RT}$$

$$j_c = FB_c[\mathrm{Ox}]\mathrm{e}^{\left[-\Delta^{\neq}G_c - \alpha FE\right]/RT}$$

- Exchange current density j_0 is not measurable directly, but can be extrapolated based on the Tafel equation ($\eta \to 0$). The introduction of j_0 gives a simpler from for the Butler–Volmer equation:

$$j = j_0\left[e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}\right]$$

2. Interpretation of observations

c) Limits of the overpotential:

- The lower limit of overpotential:
  - At low overpotentials of η << 0.01 V, i.e. $f\eta$ << 1, series expansion ($e^x = 1 + x + \ldots$) gives:

$$j = j_0 [1 + (1 - \alpha) f\eta + \ldots - 1 - (-\alpha f\eta) - \ldots] \approx j_0 f\eta$$

  - Ohm' law is valid in this regime, and – in agreement with the observations – a linear relationship is valid between j and η.

$$j = j_0 [e^{(1-\alpha) f\eta} - e^{-\alpha f\eta}]$$

2. Interpretation of observations

c) **Limits of the overpotential:**

- Upper limit of the overpotential:
  - At $\eta > 0.12$ V (intermediate overpotential), the second term in the Butler–Volmer equation becomes negligible, so $j = j_0 e^{(1-\alpha)f\eta}$, i.e.: $\ln j = \ln j_0 + (1-\alpha)f\eta$.
  - At $\eta < -0.12$ V (intermediate cathodic overpotential), the first term becomes negligible, so $j = -j_0 e^{-\alpha f\eta}$, i.e.: $\ln(-j) = \ln j_0 - \alpha f\eta$.

These are the same as the **Tafel equation**. The transfer coefficient α and exchange current density j_0 can be determined in this way.

$$j = j_0 [e^{(1-\alpha) f\eta} - e^{-\alpha f\eta}]$$

3. Practical electrochemistry

The practical significance of overpotential:

- Ion reactions do not really start at the reversible potentials. For cations, more negative, for anions, more positive potentials are needed. E.g.
  - H_2 production on Pt: 0 V, on Pb 0.6 V, on Hg: 0.8 V.
  - O_2 production on Pt: 0.4 V, on Pb: 0.3 V.
- The overpotential adds to the energy needs of electrolysis, so minimizing it is an important objective.

3. Practical electrochemistry

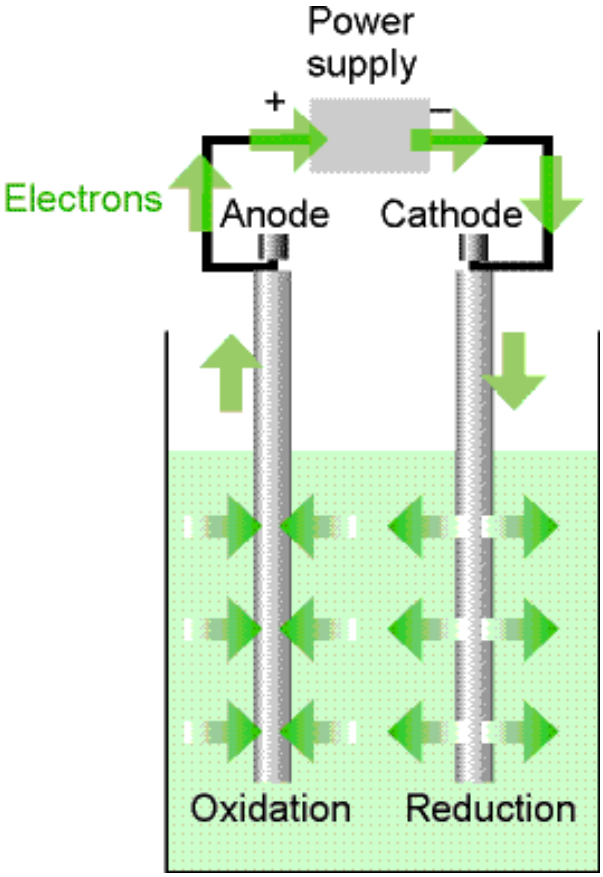
Working Galvanic cells:

- In working Galvanic cells ($I > 0$), the cell potential E' is always smaller than the equilibrium potential E_{cell} without current ($I = 0$) (electromotive force):
  $E' = \Delta\Phi_J - \Delta\Phi_B = E_{cell} + \eta_J - \eta_B - IR_s$.
  - The term IR_s (Ohmic term) gives the heat production within the solution as a result of the current. This causes energy loss in the Galvanic cell.

3. Practical electrochemistry

Electrolysis: In an electrolytic cell, the potential necessary to force the reaction is larger than the equilibrium potential (**overpotential**).

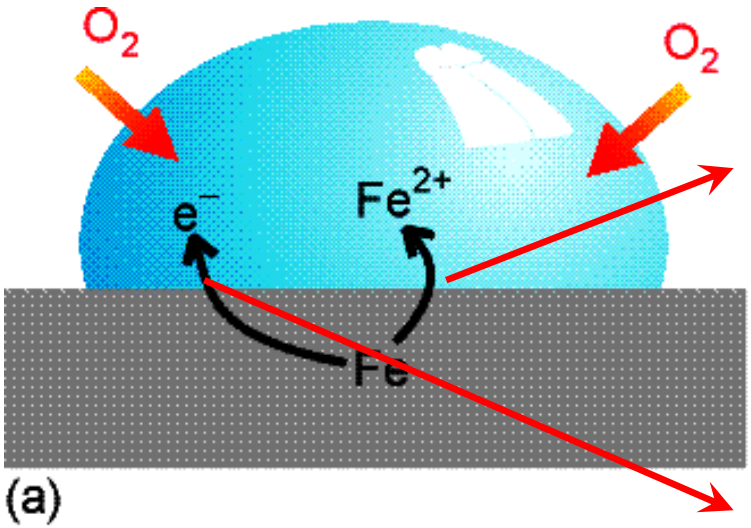
- Faraday's laws of electrolysis:
  I. The electric charge necessary to force 1 mol of electron is F = 96485 C (Faraday constant.
  II. The mass of the substance produced by electrolysis is directly proportional to the current and the electrolysis time: $m = F \cdot I \cdot t$ (coulombmetry).



3. Practical electrochemistry

Electrochemical corrosion:

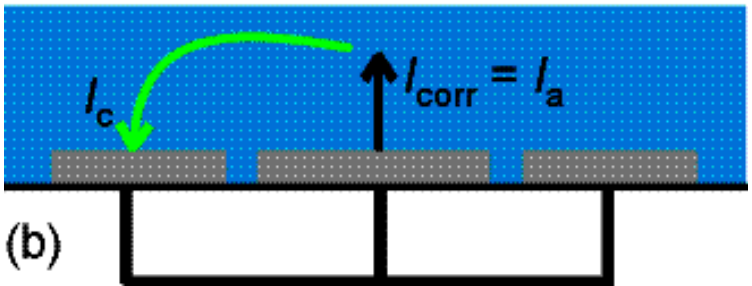
- O_2 is reduced, gains electrons from the metal



(a)

local cell

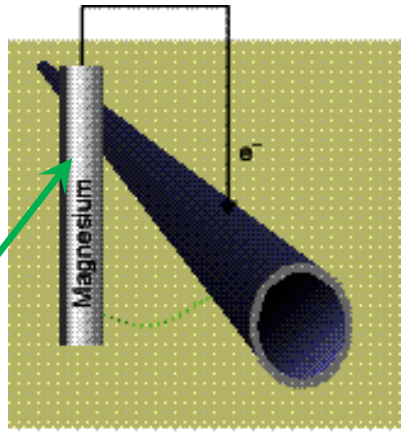
anode: iron dissolves (internal part, little O_2)
cathode: H^+ is reduced.



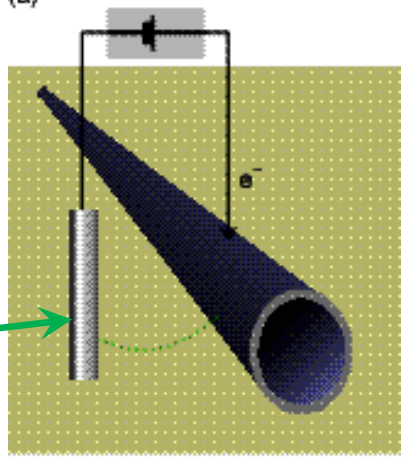
(b)

O_2 depolarizes

„sacrificial" anode



(a)



(b)