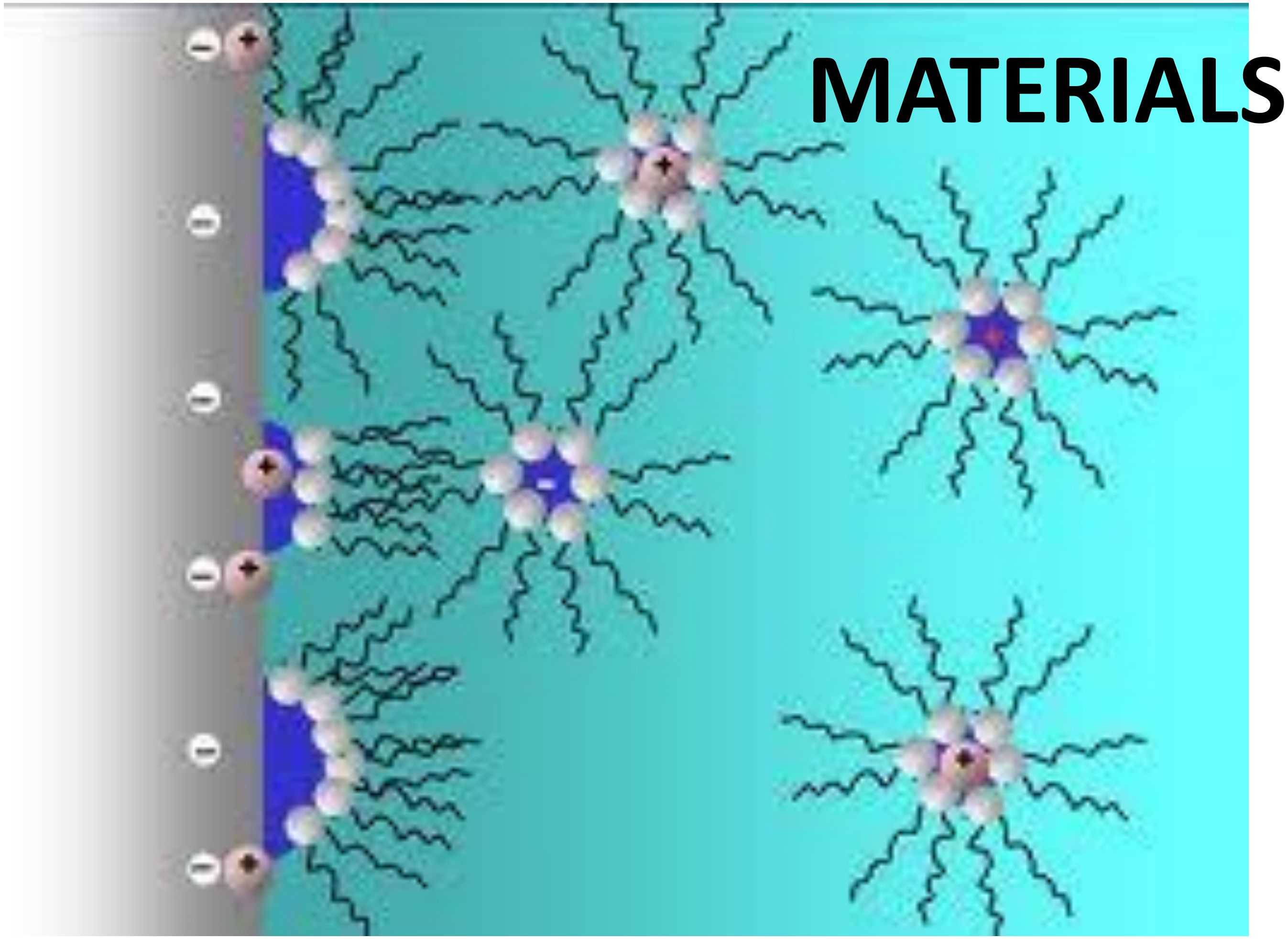
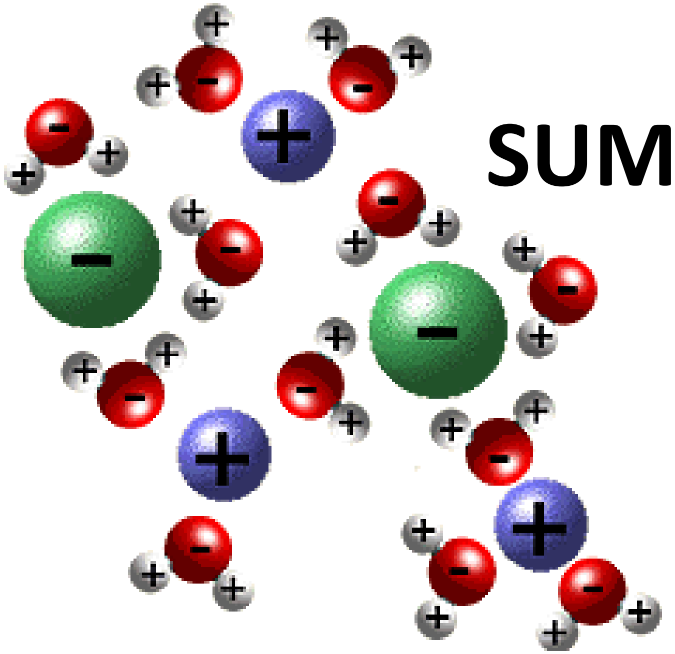
Institute of Metallurgy and Materials Science
Polish Academy of Sciences

ELECTROCHEMISTRY FOR MATERIALS SCIENCE



Ewa Bełtowska-Lehman

Electrochemistry for materials science



SUMMARY OF PART IIB

PROPERTIES OF AQUEOUS SOLUTION OF ELECTROLYTES

Ewa Bełtowska-Lehman

DISSOCIATION CONSTANT (weak electrolytes)

Free ions are formed by electrolytic dissociation when salts, acids or bases are dissolved in water.

Dissociation of the electrolyte into ions describes the general equation

$K_{\nu+}\ A_{\nu-}\ \leftrightarrows \nu_+K^{z+} + \nu_-A^{z-}$ (for reversible dissociations in a chemical equilibrium)

ν_+ and ν_+ – the stoichiometric numbers for cations *K* and anions *A* in electrolyte , respectively
z+ and z- – the charge numbers of cations *K* and anions *A*, respectively

In electrolytic dissociation an equilibrium is formed between the ions and undissociated molecules (for weak electrolytes).

$$K_d = \frac{[K^{z+}]^{\nu+} \cdot [A^{z-}]^{\nu-}}{[K_{\nu+}A_{\nu-}]}$$

where: $[K_{\nu+}A_{\nu-}]$ is the concentration of the undissociated moleclule, $[K^{z+}]$ that of the kation and $[A^{z-}]$ that of the anion. K_d is the **dissociation constant** (a constant that depends on the equilibrium between the dissociated and undissociated forms).

K_d depends (**for the weak electrolytes**) only on **the type of electrolyte and on temperature** of solution. ***K_d*** **is independent of the concentration**.

DISSOCIATION DEGREE

The type of electrolyte is quantitatively determines by the **degree of dissociation α**, which is defined as the ratio of the number of dissociated molecules to the total number of molecules prior to dissociation (introduced into the electrolyte solution)

$$\alpha = \frac{n}{N}$$

$$\alpha = \frac{no.\,of\ moles\ of\ the\ reactant\ dissociated\ (n)}{no.\,of\ moles\ of\ the\ reactant\ present\ initially\ (N)}$$

$0 < \alpha < 1$ or $0\% < \alpha < 100\%$

The **degree of dissociation α** depends on the following **factors**:

- type of electrolyte
- type of solvent
- **concentration of the solution** (generally increases with dilution)
- temperatures (generally slightly increases with increasing temperature)
- the presence of other compounds in a solution capable to dissociation

strong electrolytes – α is in the range 30% - 100%
medium electrolyte – α is in the range of 5% - 30%
weak electrolytes – α is between 0% - 5%

OSTWALD'S DILUTION LAW (weak electrolyte)

The degree of dissociation of a weak electrolyte depends on the electrolyte concentration and temperature, while the electrolytic dissociation constant depends only on the temperature.

Ostwald's dilution law is a relationship between the dissociation constant and the degree of dissociation of a **weak electrolyte**:

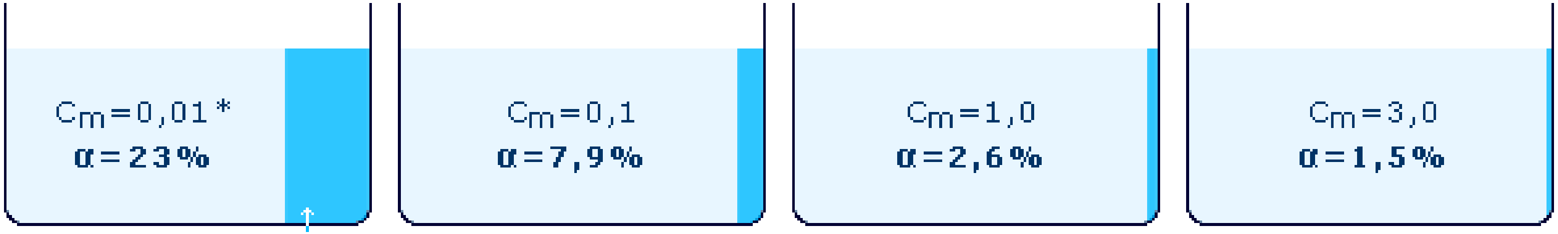
$$K_d = \frac{c\alpha^2}{1-\alpha}$$ (for binary electrolytes)

For weak electrolytes, under normal concentration, the degree of dissociation, α is very small as compared to unity and hence $(1 - \alpha)$ can be taken as 1 in the denominator of equation. So the equilibrium constant $K_d = c\,\alpha^2$

$K_d = c\,\alpha^2$

$\alpha^2 = K_d/c$

$$\alpha = \sqrt{\frac{K}{c}}$$



percent of the molecules dissociated

*mol/dm3
temp=25 °C

The degree of dissociation of hydrofluoric acid depending on the concentration

DIELECTRIC CONSTANT (DIELECTRIC PERMITTIVITY, RELATIVE ELECTRIC PERMITTIVITY) OF THE SOLVENT

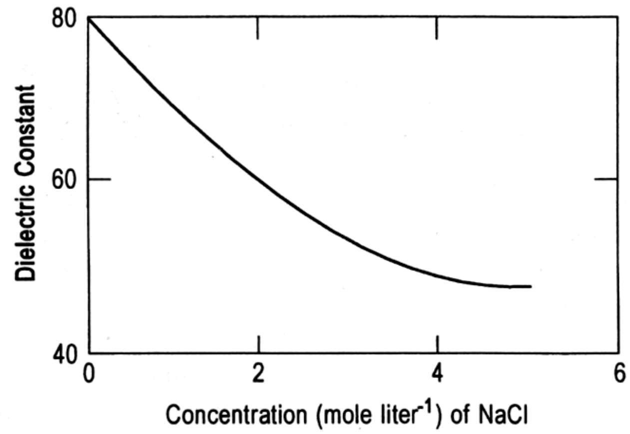
Dielectric constant (relative permittivity) ε is the ratio of the permittivity of a substance to that of free space or vacuum (ε_0).

The smaller the dielectric constant of a solvent, the greater is the mutual attraction between two oppositely charged ions present in it and thus the smaller the degree of dissociation α.

$$U = \pm\frac{q_1 q_2}{\varepsilon r^2}$$

If the medium is water the Coulombic interaction is reduced strongly, since ε of water is **78.5**. It is greater than that of other solvents, strong dissociation will take place.

(e.g. KCl – 4.7, acetone – 20, ethyl alcohol – 24)



The dielectric constant of NaCl solution vs. ionic concentration

CONCENTRATION AND ACTIVITY

The salt solutions employed in electroplating technology are in general representatives of the class of **strong electrolytes**. Despite their complete dissociation, they appear to have a low degree of dissociation, which is ascribed to **the effect of the electrostatic interionic forces**. For this reason, in the description of the properties of the electrolyte solutions the concentration (determined from total concentration and the degree of dissociation) is replaced by the **activity *a*.**

The difference between concentration and activity decreases with increasing dilution. For infinite dilution of a solution, concentration and activity are equal. These two magnitudes are related by:

$$a = fc$$

The activity coefficient ***f*** is less than 1 and attains unity only at infinite dilution

Activity coefficient ***f*** determines what **part** of the molar concentration is the **active concentration**

$f = 0.69$ **for 0.1 M HCl** $\longrightarrow$ $a = 0.1\ \mathrm{mol \cdot dm^{-3}} \times 0.69 = 0.069\ \mathrm{mol \cdot dm^{-3}}$

"Active concentration" is smaller than resulting from the concentration of the acid content of the solution.

For dilute solutions: $c < 0.001\ \mathrm{mol\ dm^{-3}}, f \approx 1 \longrightarrow a \approx c$

MEAN MOLAR ACTIVITY

Since the cations and anions are always together, hence it is impossible the determination experimentally the activity of individual ions $a_i = f_i\ c_i$

For this reason the concept of **mean molar activity** is introduced, which is defined as the geometrical mean of the activites of the ions of given electrolyte.

For an electrolyte dissociating into ν_+ positive and ν_- negative ions:

$$a_{c,\pm} = \left[a_{c,+}^{\nu+} \cdot a_{c,-}^{\nu-}\right]^{1/\nu}$$

$$f_{\pm} = \left(f_{c,+}^{\nu+} \cdot f_{c,-}^{\nu-}\right)^{1/\nu}$$

$$\nu = \nu_+ + \nu_-$$

$$c_{\pm} = [c_+^{\nu+} \cdot c_-^{\nu-}]^{1/\nu}$$

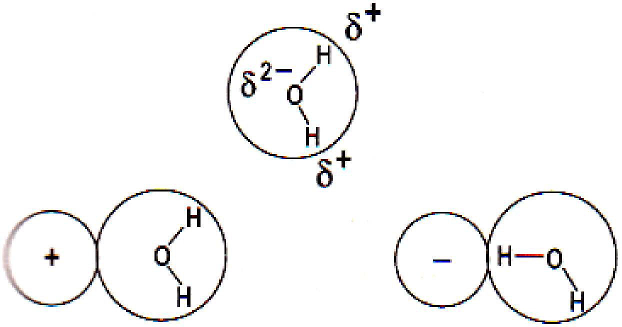
mean molar concentration of ions in solution with the molar concentration of the electrolyte (for strong electrolytes):

$$c_{\pm} = c\ (\nu_+^{\nu+} \cdot \nu_-^{\nu-})^{1/\nu}$$

$$a_{\pm} = [f_{c,+}^{\nu+} \cdot f_{c,-}^{\nu-}]^{1/\nu}\ [c_+^{\nu+} \cdot c_-^{\nu-}]^{1/\nu}$$

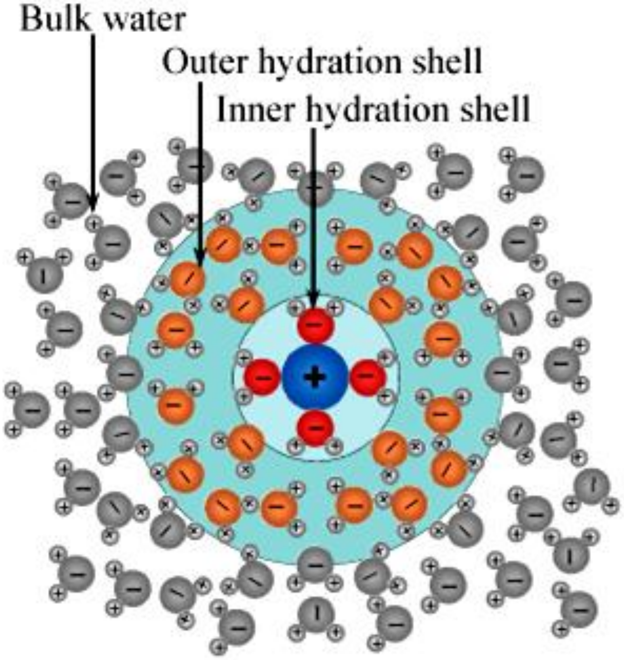
ION–WATER INTERACTION

THE ION-DIPOLE MODEL – the principal forces in the ion-water interaction are ion-dipole forces. The result of these forces is orientation of water molecules in the immediate vicinity of an ion. Formation of primary hydration shell of oriented water molecules, which do not move independently in the solution. Next to the primary water of hydration is the shell of secondary water hydration, where water molecules are partially oriented. Beyond the secondary water of hydratation is the bulk water.



Orientation of water molecules with respect to positive and negative ions

Ion-water interaction

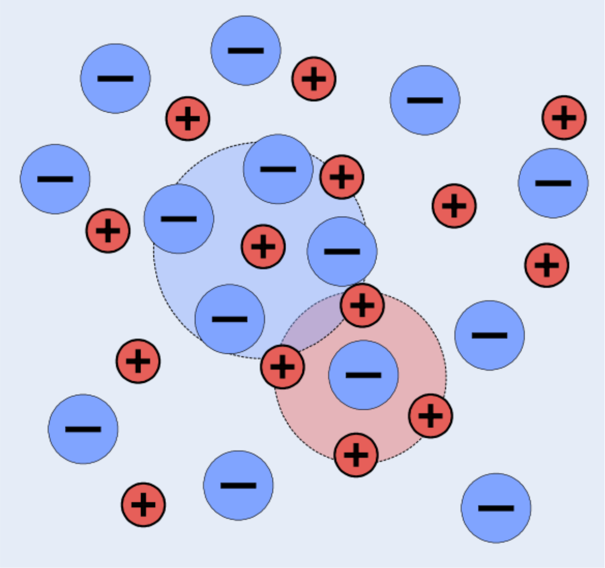


ION-ION INTERACTIONS, THE DEBYE - HÜCKEL THEORY OF STRONG ELECTROLYTES

Theory of strong electrolytes on the basis of a model according to which each ion (center) is surrounded by a spherical atmosphere of ions of opposite sign (the **ionic atmosphere)** of the resultant charge equal to the value of the central ioncharge.

This theory gives the expression for relationship between **activity coefficient** $f_{\pm}$ and **ionic strength** of the medium ***I.***

Debye-Hückel limiting law was derived with the approximation of negligible ion size (ions were treated as **point charges**).



For water at 25˚C and dielectric constant 78,54:

$$\log f_{\pm} = -0.509|z_{+}z_{-}|\sqrt{I}$$

$$I = \frac{1}{2}\sum_{i} c_i z_i^2$$

$$I = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + c_3 z_3^2 + \cdots)$$

c_1, c_2, c_3, c_i - molar concentrations of various ions

z_1, z_2, z_3, z_i - their respective charges

ELECTROLYTIC CONDUCTIVITY

The molar conductivity is the conductivity of the volume of solution containing one mole of the electrolyte. $\boldsymbol{\Lambda_m}$ is important for determining the degree of disociation $\boldsymbol{\alpha}$ and the disociation constant $\boldsymbol{K_d}$

The **molar conductivity** of a solution ($\boldsymbol{\Lambda_m}$):

The specific conductivity $\boldsymbol{\kappa}$ [$\Omega^{-1} \cdot m^{-1}$]
The molar concentration **c** [$mol \cdot m^{-3}$]

$$\Lambda_m = \frac{\kappa}{c_m} \; [S \cdot \; m^2 \cdot mol^{-1}]$$

Electrolytic conductivity (specific conductivity) $\boldsymbol{\kappa}$ is equal to the conductivity of the unitary volume of electrolyte solution:

$$\kappa = \frac{1}{R}\frac{l}{A}$$

by measuring the electrical resistance of the electrolyte solution *R* it is l easy to determine the electrolytic conductivity $\boldsymbol{\kappa}$, knowing the distance between the electrodes and the surface of electrodes A.

IONIC CONDUCTIVITY, IONIC MOBILITY

The rate of movement of ions (*v*) in the electric field (*E*); *u* - Ion Mobility, *E* - electric field intensity.

$$u_i = \frac{v_i}{E}$$

What determines the rate of movement of ions in the solution?

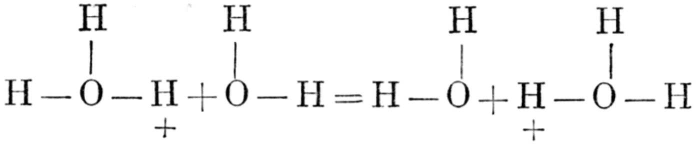
type of ions	$u \cdot 10^{-8}$ [$m^2 \cdot s^{-1} \cdot V^{-1}$]
H^+	36,30
OH^-	20,50
Li^+	4,01
Na^+	5,19
K^+	7,61
Cl^-	7,91

1. type of ions
2. concentration of ions
3. mass and diameter of ions
4. strength of the electrical interaction of ions
5. degree of solvation of ions (water solvent)
6. liquid viscosity
7. temperature;
8. potential gradient (electrical potential drop calculated per the unit of the distance between the electrodes)

ABNORMAL MOBILITY OF HYDROGEN AND HYDROXYL IONS

The movement of these ions in aqueous solution obeys a special mechanism of migration. The hydrogen ion is present in the form of the hydronium ion H_3O^+. The proton can migrate from one water molecule to the next. In the presence of an external electric field the probability of proton migration in the direction of the field increases (since the activation energy in this direction diminishes), and the process of proton movement will occur **by a chain mechanism**, i.e., the proton will be passed on from one water molecule to the next and so on:

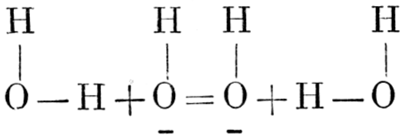
the direction of the field →



$$H-\overset{H}{\overset{|}{O}}-\underset{+}{H}+\overset{H}{\overset{|}{O}}-H=H-\overset{H}{\overset{|}{O}}+\underset{+}{H}-\overset{H}{\overset{|}{O}}-H$$

the direction of proton transfer →

the direction of the field →



$$\overset{H}{\overset{|}{O}}-H+\underset{-}{\overset{H}{\overset{|}{O}}}=\underset{-}{\overset{H}{\overset{|}{O}}}+H-\overset{H}{\overset{|}{O}}$$

the direction of movement of the hydroxyl ion ←

The orientation of the water molecule after the proton has left the hydronium ion is for the next proton jump unfavourable, a circumstance that lowers the rate of proton transfer.

The energy required to pull the proton away from the hydroxyl radical OH^- in a water molecule is higher than that needed to tear the hydrogen ion H^+ off the water molecule in a hydronium ion. So the probability of proton jumps and hence the velocity of movement of hydroxyl ions must be lower as compared to hydrogen ions.

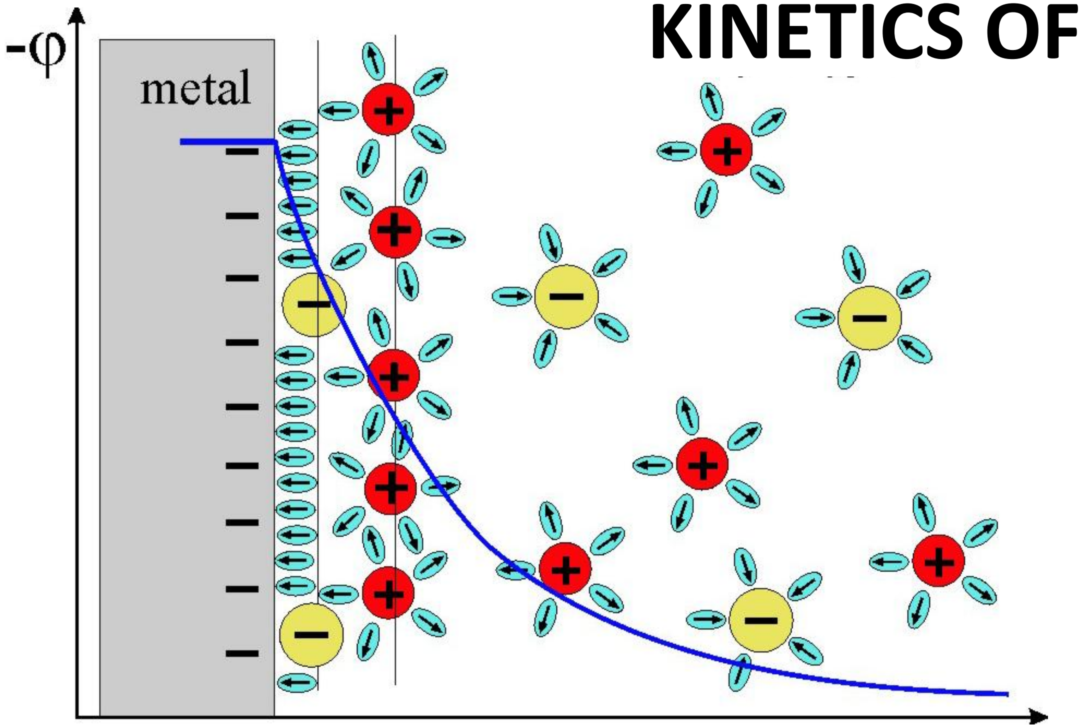
ELECTROCHEMISTRY FOR MATERIALS SCIENCE

PART III

METAL-SOLUTION INTERPHASE

EQUILIBRIUM ELECTRODE POTENTIAL

KINETICS OF ELECTRODEPOSITION

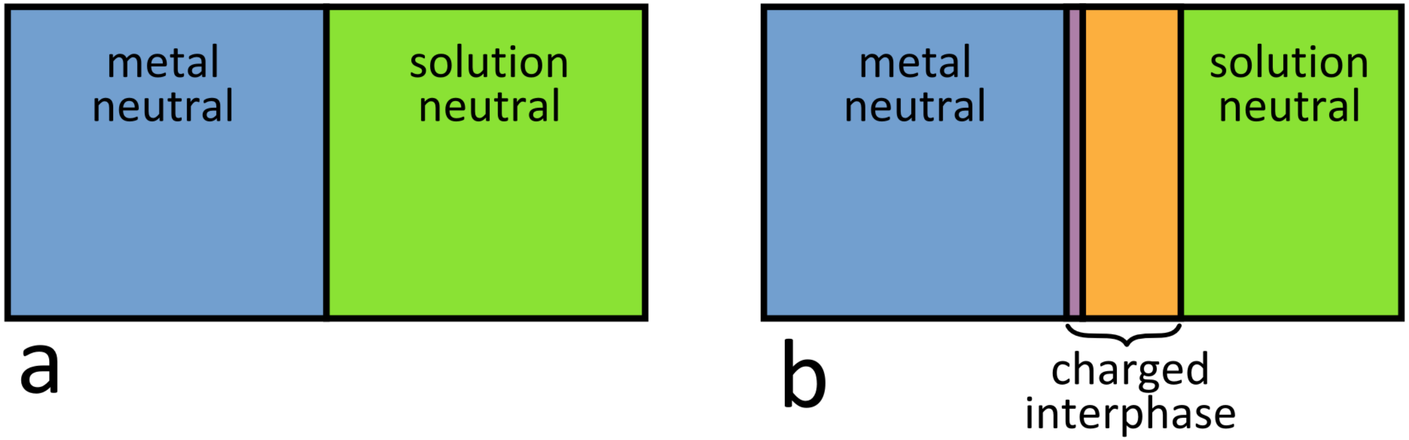


Ewa Bełtowska-Lehman

METAL-SOLUTION INTERPHASE

An interphase as a region between two phases that has different composition than bulk phases (here, bulk metal, and bulk solution).

Electrodeposition processes occur in a very thin region of the metal-solution interphase, where there is a very high electric field (10^6 or 10^7 V/cm). This field can be cotrolled by an external power source.

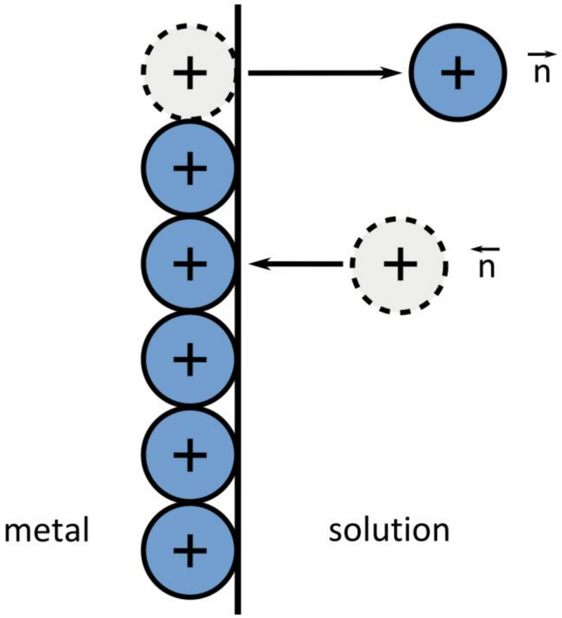


Two phases in contact: a) at t = 0, moment of contact; b) at equilibrium

METAL-SOLUTION INTERPHASE

Metal M is immersed in the aqueous solution of its salt MA. At the metal-solution interface there will be an exchange of metal ions M^+ between two phases. Some M^+ ions from the crystal lattice enter the solution, and some ions from the solution enter the crystal lattice. At equilibrium the interphase region is neutral:

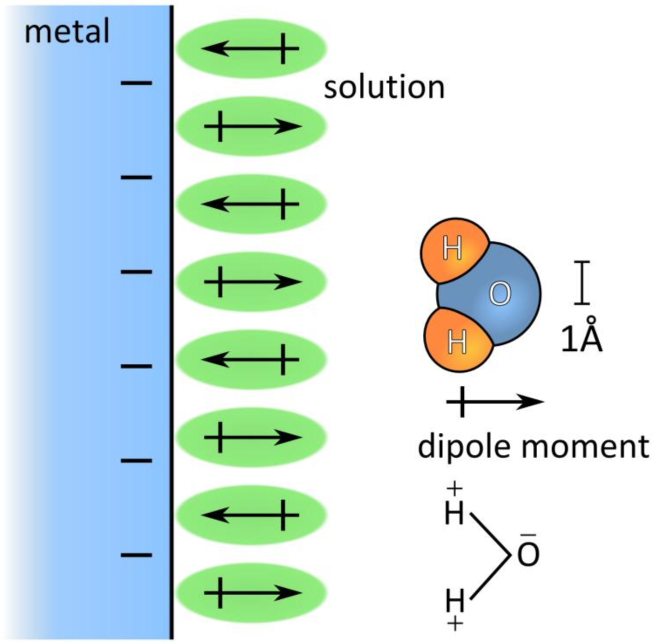
$q_M = -q_S$ (the charge per unit area on the solution and metal sides of interphase)



Formation of metal-solution interphase; equilibrium state: $\overrightarrow{n} = \overleftarrow{n}$ (n – the number per square centimeter of ionic species

WATER STRUCTURE AT THE INTERPHASE

The presence of the excess charge on the metal produces ion redistribution and reorientation of water dipoles in the solution. In the vicinity of the charged metal the structure of water is changed because of the presence of the electric field in the interphase.

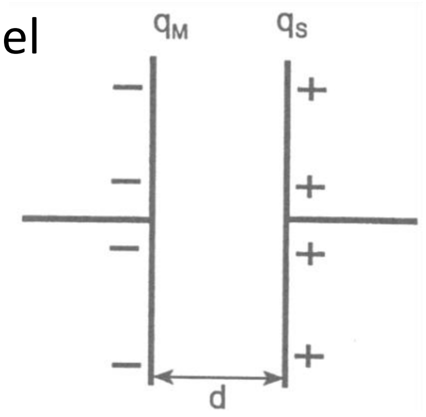


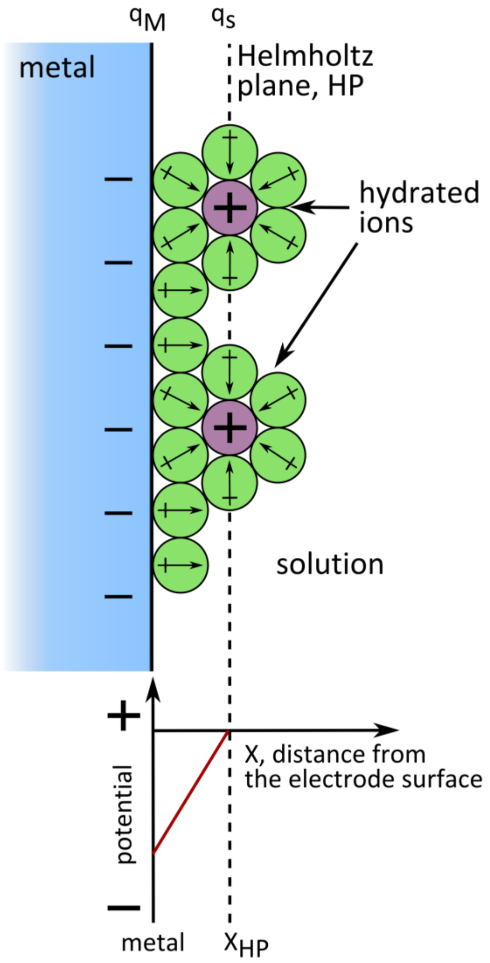
Structure of water in the interphase. At a negatively charged electrode, there is an excess of water dipoles with their positive hydrogen ends oriented towards the metal.

DOUBLE-LAYER MODELS (HELMHOLTZ COMPACT MODEL)

Helmholtz Double Layer (DL)

The earliest model of the electrical DL. Helmholtz treated the DL mathematically as a simple capacitor, based on a physical model in which a single layer of ions is adsorbed at the surface.





$$q_M = q_S$$

$$c = \frac{\varepsilon}{4\pi d}$$

This theory is a simplest approximation that the surface charge is neutralized by opposite sign counterions placed at an increment of *d* away from the surface.

The surface charge potential is linearly dissipated from the surface to the contertions satisfying the charge. The distance, *d*, will be that to the center of the countertions, i.e. their radius.

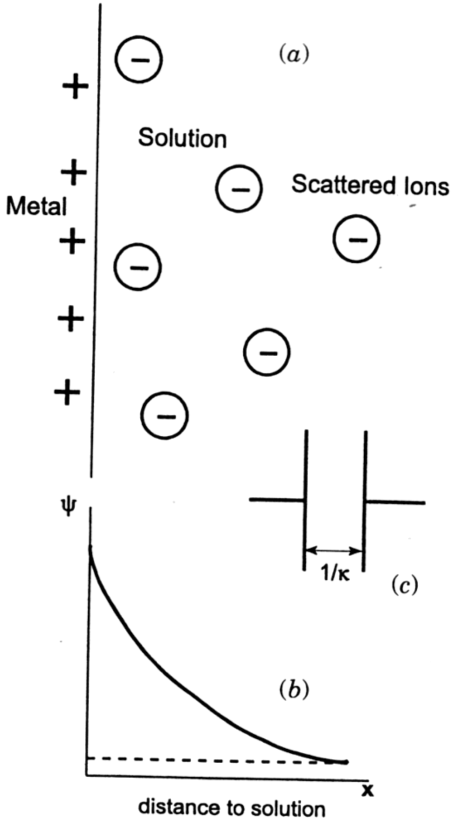
For constant values of ε and d, the model predicts a potential-independent capacitance. Experiments show that DL capacitance is a function of potential.

DOUBLE-LAYER MODELS (GOUY-CHAPMAN DIFFUSE MODEL)

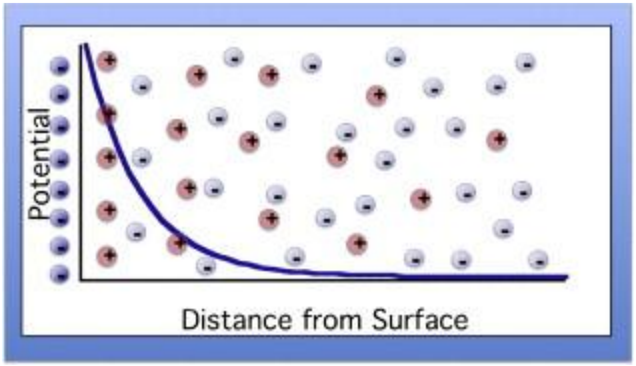
Louis Georgrs **Gouy** and David **Chapman** developed theories of this so called *diffuse double layer* in which the change in concentration of the counter ions near a charged surface follows the Boltzman distribution.

$$c_i = c_i^0 exp\left(-\frac{z_i e\psi(x)}{k_B T}\right)$$

c_i^0 – bulk concentration of *i* ion
z_i – ion charge
e – elementary charge
k_B – Boltzmann constant
T – absolute temperature
(x) – potential at a distance x



The counter ions are not rigidly held, but tend to diffuse into the liquid phase until the counter potential set up by their departure restricts this tendency. The kinetic energy of the counter ions will, in part, affect the thickness of the resulting diffuse double layer.



DOUBLE-LAYER MODELS (GOUY-CHAPMAN DIFFUSE MODEL)

Gouy and Chapman made significant improvements by introducing a diffuse model of the electrical DL, in which the electric potential decreases exponentially away from the surface to the fluid bulk.

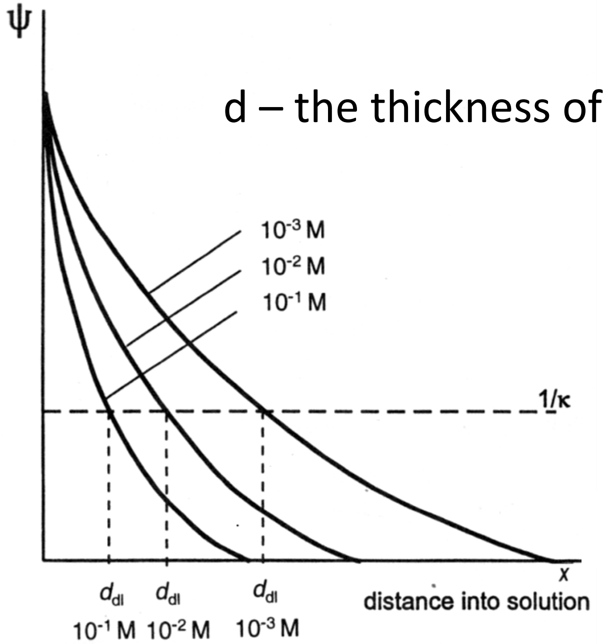
They derived the equation, which describes the variation of potential in the double layer in the direction (x) perpendicular to the electrode:

$$\psi(x) = \psi(0)\exp\left(-\kappa x\right)$$

$$\kappa = \left[\left(\frac{4\pi e^2}{\varepsilon k_B T}\right) c_b\right]^{1/2}$$

c_b – the bulk concentration mol/L

$$d = \frac{1}{\kappa}$$



d – the thickness of diffuse double layer for T= 298 K, ε = 78

$$d = \frac{1}{3 \cdot 10^7 |z| (c_b)^{1/2}}\ cm$$

For 1 M solution (1:1 electrolyte) *d* is aproximately 3 Å (the distance of closest approach of hydrated ios at the electrode)

For 0.01 M – *d* is aproximately 30 Å

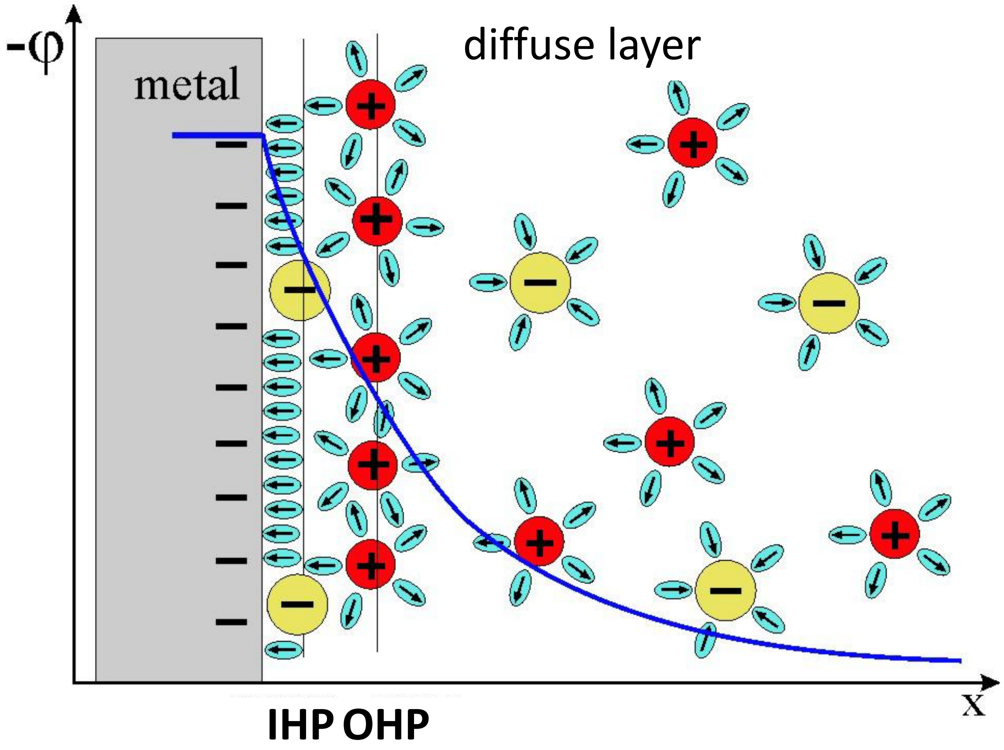
GOUY-CHAPMAN DIFFUSE MODEL - LIMITATIONS

The combined Gouy-Chapman model has some limitations, such as:

- ions are effectively modeled as point charges
- the only significant interactions in the diffuse layer are Coulombic
- dielectric permittivity is assumed constant throughout the double layer
- the viscosity of fluid is constant above slipping plane.

DOUBLE-LAYER MODELS (STERN and GRAHAME MODELS)

Stern suggested the combination of the Helmholtz and Gouy-Chapman models, giving an internal **Stern layer** (i.e. Helmholtz layer), and an outer diffuse layer (i.e. Gouy-Chapman layer). Grahame modified Stern’s model by introducing the inner plane of closest approach (IHP).



IHP (inner Helmholtz plane)

OHP (outer Helmholtz plane)

IHP is the plane of centres of partially or fully dehydrared, specifically adsorbed ions.

OHP – is the plane of centers of hydrated ions; at the distance *x* of the closest approach of the fully hydrated ions

M. Bełtowska-Brzezinska, Wprowadzenie do elektrochemii, UAM, Poznań 2009 (www.wbc.poznan.pl)

DOUBLE-LAYER CAPACITANCE

The separation of the interphase into two regions is equivalent to the separation of the total double-layer capacitance as due to two contributions: C_H, the Helmholtz capacity, and the C_{GC}, the Gouy-Chapman capacity. Thus, the interphase according to the Stern model is equivalent to two capacitors in series.

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_{GC}}$$

For **low solution concentration** the double-layer capacitance behaves as the Gouy-Chapman capacitance $\mathbf{C_{GC}}$.

At **high solution concentration** C_{GC} is large, and $1/C_{GC} \ll 1/C_H$ resulting in $1/C \approx 1/C_H$, or $\mathbf{C \approx C_H}$

Capacitance of DL: metal (eg. Pt, Au) / electrolyte is in the range of 16-50 μF/cm^2.

EQUILIBRIUM ELECTRODE POTENTIAL, NERNST EQUATION

Each metal immersed in an electrolyte solution has some potential. This potential is associated with the oxidation or reduction reaction of the metal, or the orientation of the molecules in solution, and is equal to the potential difference at the interface metal / solution. The potential is a result of the equilibrium of the chemical and electrical forces. This potential is defined as the electrochemical potential.

$$Me^{+z} + ze^{-} \leftrightarrow Me$$

The **Nernst equation** is a fundamental equation of electrochemistry. It establishes the relationship between the electrode potential and the concentration (activity) of the ionic species involved in the electrode reaction.

$$E_{Me/Me^{z+}} = E^0 + 2.303\frac{RT}{zF}\log a_{Me^{z+}}$$

RT/F = 0.0257 V at 298 K (25°C)
2.303 RT/F = 0.0592 V

R = 8,314 J/mol K

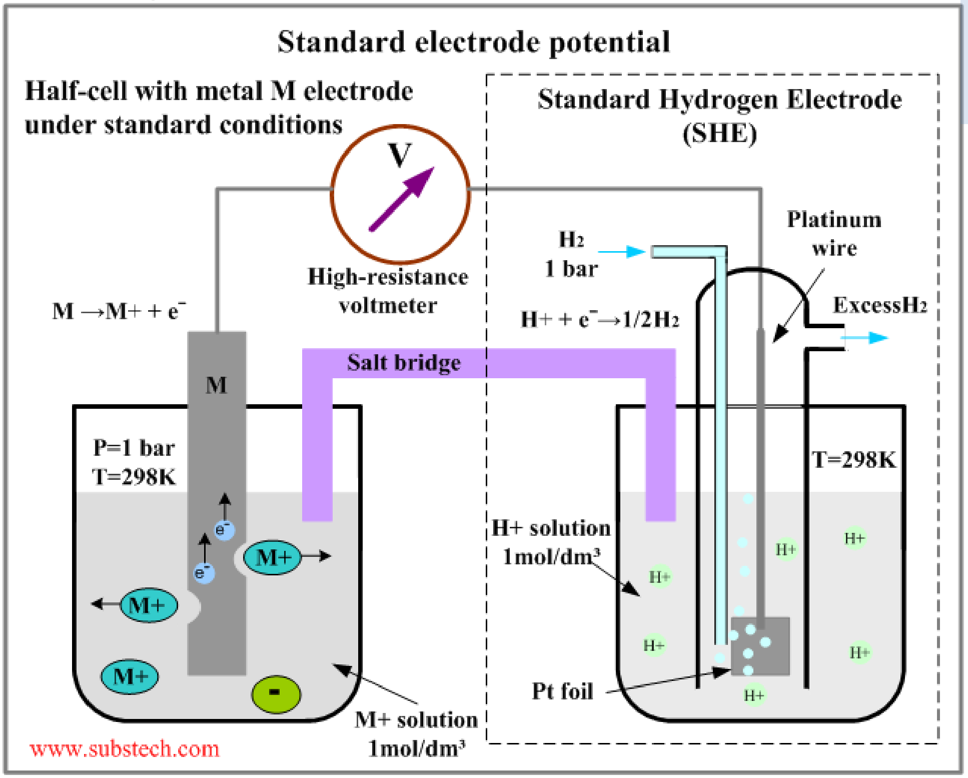
$E_{Me/Me^{z+}}$ - electrode potential

$$E_{Me/Me^{z+}} = E^0 + \frac{0.0592}{z}\log[Me^{z+}]$$

E^0 - standard electrode potential (the characteristic value for a given metal)

MEASUREMENT OF EQUILIBRIUM ELECTRODE POTENTIAL
THE HYDROGEN ELECTRODE

In order to measure the equilibrium electrode potential: 1) the selection of a reference electrode; 2) the coupling of the reference electrode with the electrode whose potential is being measured.



A reference electrode should not change its potential during the measurement procedure

The hydrogen electrode is made of a platinum wire in contact with hydrogen gas and solution containing hydrogen ions: Pt I H^+ I H_2

$$2H^+ + 2e \leftrightarrow H_2$$

The hydrogen electrode potential:

$$E = E^0 + \frac{RT}{2F} ln \frac{[H^+]^2}{p(H_2)}$$

For $[H^+] = 1$ (1.18 M HCl at 25°C) and $p(H_2) = 1$ atmosphere,

$E = E^0$ = the standard hydrogen electrode potential

$pH = -lg[H^+] \rightarrow$ **$E = 0.059\ pH$**

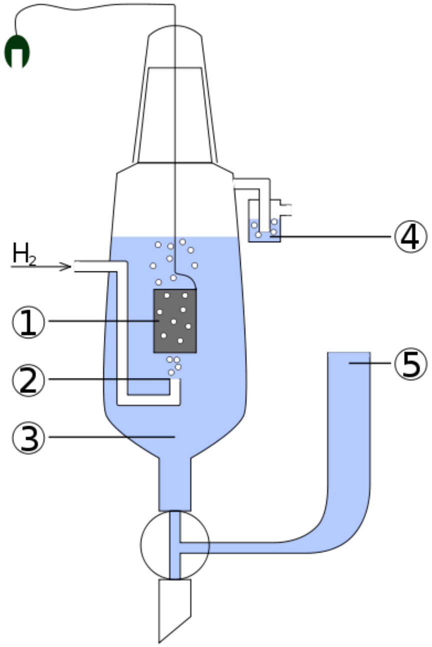
The potential of the hydrogen electrode is a linear function of the pH of the solution (slope coefficient equal to 0.059)

MEASUREMENT OF EQUILIBRIUM ELECTRODE POTENTIAL
THE HYDROGEN ELECTRODE

standard conditions ⟶ **Standard Hydrogen Electrode (SHE)**

298 K for temperature (**25ºC**),
1000 hPa (0,986 atm) of hydrogen gas ($H_{2(g)}$ for hydrogen electrode),
1 mol dm^{-3} concentration of $H^{+}_{(aq)}$ (hydrogen ions for hydrogen electrode), e.g. 1M $HCl_{(aq)}$ or 0.5M $H_2SO_{4(aq)}$

(1013,25 hPa – 1 atm)



normal conditions ⟶ **Normal Hydrogen Electrode (NHE)**

273 K for temperature (**0ºC**),
1013 hPa (1 atm) of hydrogen gas ($H_{2(g)}$ for hydrogen electrode),
1 mol dm^{-3} concentration of $H^{+}_{(aq)}$ (hydrogen ions for hydrogen electrode), e.g. 1M $HCl_{(aq)}$ or 0.5M $H_2SO_{4(aq)}$

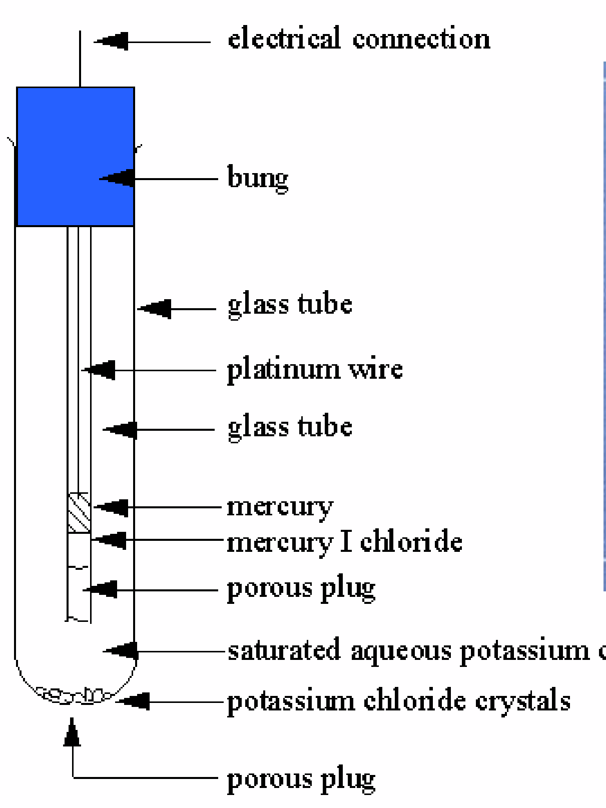
Standard hydrogen electrode scheme

1. platinized platinum electrode
2. hydrogen gas
3. acid solution with an activity of H^{+}=1 mol/l
4. hydroseal for prevention of oxygen inteference
5. reservoir via which the second half-element of the galvanic cell should be attached

MEASUREMENT OF EQUILIBRIUM ELECTRODE POTENTIAL CALOMEL ELECTRODE

The calomel electrode consists of mercury covered with mercurous chloride (calomel) in contact with a solution of KCl: Hg I Hg_2Cl_2 I Cl^-

The overall electrode reaction in the calomel electrode: **$Hg_2Cl_2 + 2e \leftrightarrow 2Hg + 2Cl^-$**



Calomelel ectrode potential:

$$E = E^0 - \frac{RT}{2F} ln[Cl^-]$$

The most frequency used calomel electrode is the saturated calomel electrode (SCE), in which the concentration of KCl is at saturation (about 3.5 M). The potential of the SCE, at 25°C, is 0.242 V versus NHE.

SCE has a large temperature coefficient: $E = 0.242 - 7.6 \cdot 10^{-4} (t - 25)$
t – temperature in centigrade.

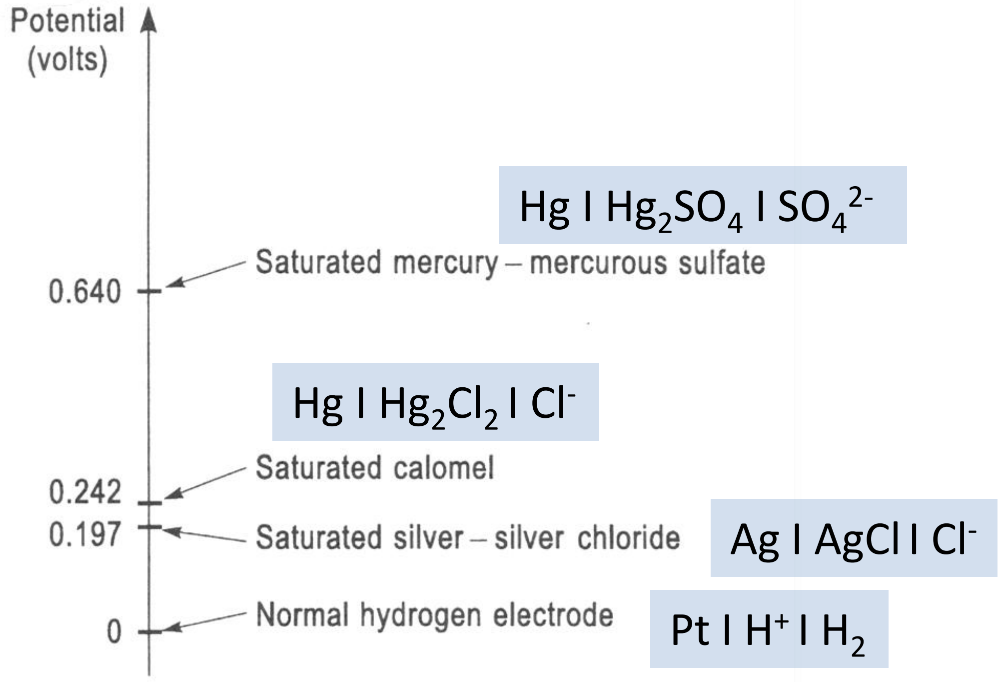
0.257 V (0 °C),
0.242 V (25 °C),
0.223 V (50 °C)

MEASUREMENT OF EQUILIBRIUM ELECTRODE POTENTIAL
REFERENCE ELECTRODES

The Saturated Calomel Reference Electrode (SCE) is the world's most commonly used reference electrode.

The Silver-Silver Chloride Reference Electrode (Ag/AgCl) is simpler in construction than the SCE and has a similar potential. It contains no mercury.

The Mercury/Mercurous Sulfate Reference Electrode is recommended when chloride ion cannot be tolerated in the electrolyte. The Hg/Hg_2SO_4 Reference Electrode uses a filling solution of potassium sulfate.



$Hg\ I\ Hg_2SO_4\ I\ SO_4^{2-}$

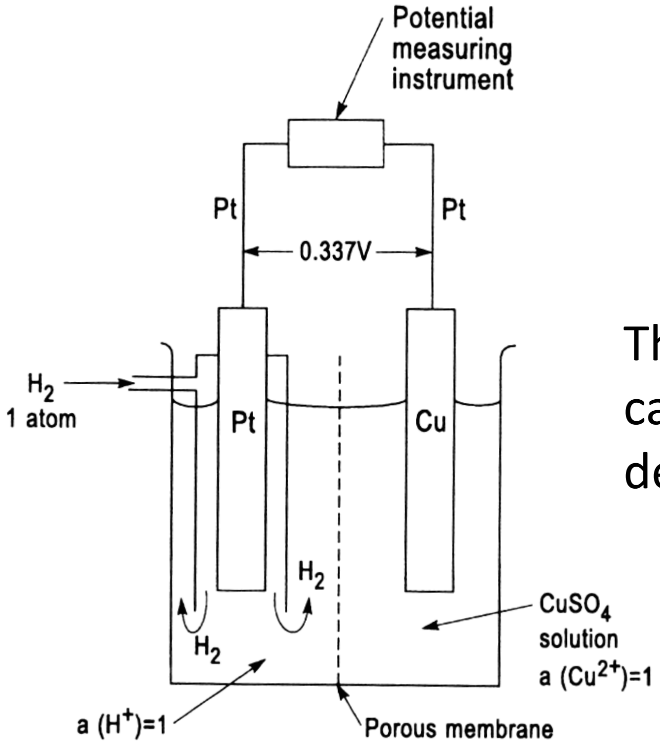
$Hg\ I\ Hg_2Cl_2\ I\ Cl^-$

$Ag\ I\ AgCl\ I\ Cl^-$

$Pt\ I\ H^+\ I\ H_2$

STANDARD ELECTRODE POTENTIALS

The standard hydrogen electrode (SHE) is chosen as the reference electrode when a series of relative electrode potentials is presented. The standard potential of this electrode is set to zero, by convention. Connecting this reference electrode with other metal electrodes into a cell, one can determine a series of relative values of electrode potentials (potential differences across interphase.



$\text{Pt, } H_2(p=1) \text{ I } H^+(a=1) \text{ II } Cu^{2+}(a=1) \text{ I Cu I Pt}$

p – the pressure of H_2, a – the activity, at 25°C

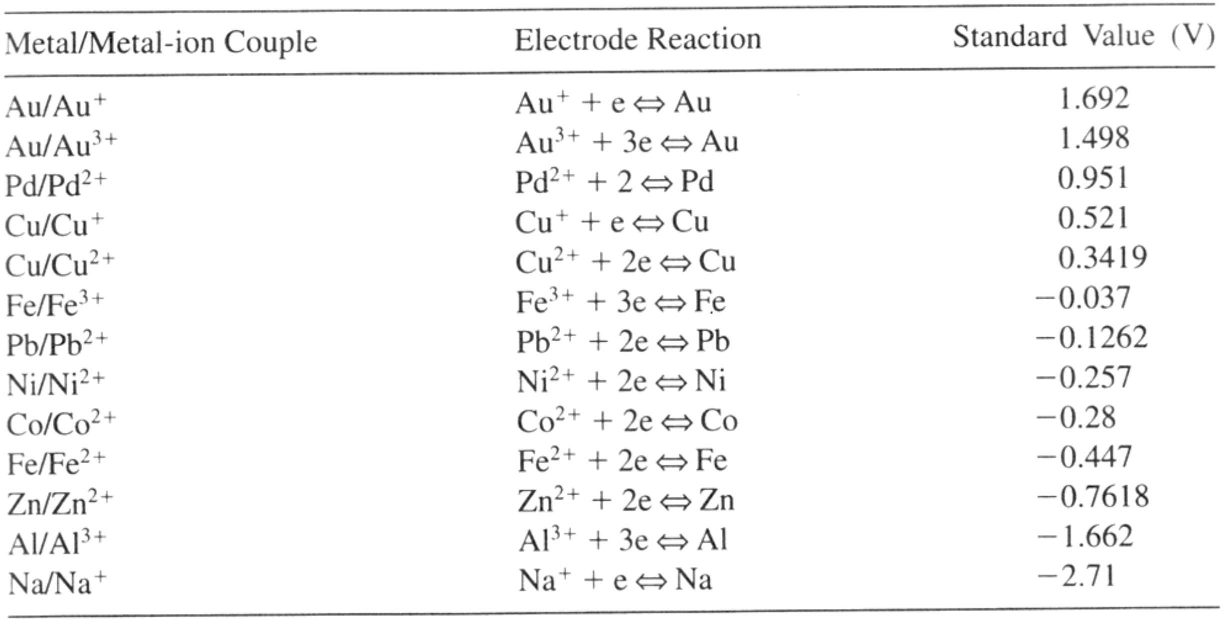
The measured cell of potential difference +0.337 V is called the standard electrode potential of Cu and is denoted $\boldsymbol{E^0}$

$Cu^{2+} + 2\,e- \rightarrow Cu$ $\qquad$ $H_2 \rightarrow 2\,H^+ + 2\,e^-$

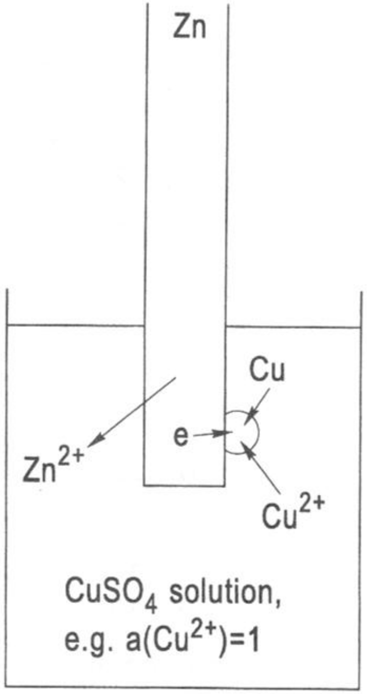
$Cu^{2+} + H_2 \rightarrow Cu + 2\,H^+$

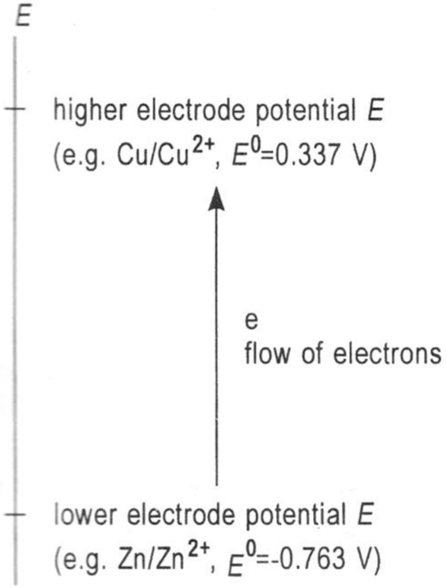
STANDARD ELECTRODE POTENTIALS

Standard Electrode Potentials



Metal/Metal-ion Couple	Electrode Reaction	Standard Value (V)
Au/Au^{+}	$Au^{+} + e \Leftrightarrow Au$	1.692
Au/Au^{3+}	$Au^{3+} + 3e \Leftrightarrow Au$	1.498
Pd/Pd^{2+}	$Pd^{2+} + 2 \Leftrightarrow Pd$	0.951
Cu/Cu^{+}	$Cu^{+} + e \Leftrightarrow Cu$	0.521
Cu/Cu^{2+}	$Cu^{2+} + 2e \Leftrightarrow Cu$	0.3419
Fe/Fe^{3+}	$Fe^{3+} + 3e \Leftrightarrow Fe$	−0.037
Pb/Pb^{2+}	$Pb^{2+} + 2e \Leftrightarrow Pb$	−0.1262
Ni/Ni^{2+}	$Ni^{2+} + 2e \Leftrightarrow Ni$	−0.257
Co/Co^{2+}	$Co^{2+} + 2e \Leftrightarrow Co$	−0.28
Fe/Fe^{2+}	$Fe^{2+} + 2e \Leftrightarrow Fe$	−0.447
Zn/Zn^{2+}	$Zn^{2+} + 2e \Leftrightarrow Zn$	−0.7618
Al/Al^{3+}	$Al^{3+} + 3e \Leftrightarrow Al$	−1.662
Na/Na^{+}	$Na^{+} + e \Leftrightarrow Na$	−2.71





In general, an electrode with lower potential will reduce ions of an electrode with higher potential. High positive standard electrode potential indicates a strong tendency toward reduction. A low negative standard electrode potentials indicates a strong tendency toward the oxidized state.

$Zn \rightarrow Zn^{2+} + 2e$ and $Cu^{2+} + 2e \rightarrow Cu$

The overall reaction:
$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

A layer of metallic Cu is deposited on the zinc while Zn dissolves into solution. **This reaction is called a displacement deposition** of Cu on Zn.

KINETICS AND MECHANISM OF ELECTRODEPOSITION

When current is flowing through the electrochemical cell, electrode potential will differ from the equilibrium potential.

***E* – the equilibrium potential of the electrode (potential in the absence of external current)**
***E(I)* – the potential of the same electrode as a result of external current flowing**

The different *η* between these two potentials is called *overpotential*

$$\eta = E(I) - E$$

η is required to overcome hindrance of the overall electrode reaction, which is usually composed of the sequence of partial reactions.

The slowest partial reaction is rate-determining for the total overall reaction.

There are four main possible partial reactions and thus four types of rate control:

1. **charge transfer**
2. **diffusion**
3. **chemical reaction**
4. **crystallization**

OVERPOTENTIAL, CHARGE TRANSFER REACTION

Four different kinds of overpotential η are distinguished and the total overpotential can be considered to be composed of four components:

$$\eta = \eta_{ct} + \eta_d + \eta_r + \eta_c$$

η_{ct} charge-transfer overpotential

η_d diffusion overpotential

η_r reaction overpotential

η_c crystallization overpotential

CHARGE-TRANSFER REACTION involves transfer of charge carriers (ions or electrons) across the double layer. This transfer occurs between the electrode and an ion or molecule.

The charge-transfer reaction is the only partial reaction directly affected by the electrode potential.

The rate of charge-transfer reaction is determined by the electrode potential

Pure charge-transfer overpotential $\boldsymbol{\eta_{ct}}$ exists only if the charge-transfer reaction is hindered and none of the other partial reactions is hindered. In this case the charge-transfer reaction is the rate-determining step.

OVERPOTENTIAL cd

MASS TRANSPORT PROCESSES are involved in the overall reaction.
The substances consumed or formed during the electrode reaction are transported from the bulk solution to the interphase (electrode surface) and from the interphase to the bulk solution.

This mass transport takes place by diffusion. Pure diffusion overpotential η_d occurs if the mass transport is the slowest process among the partial processes involved in the overall electrode reaction. In this case diffusion is the rate-determining step.

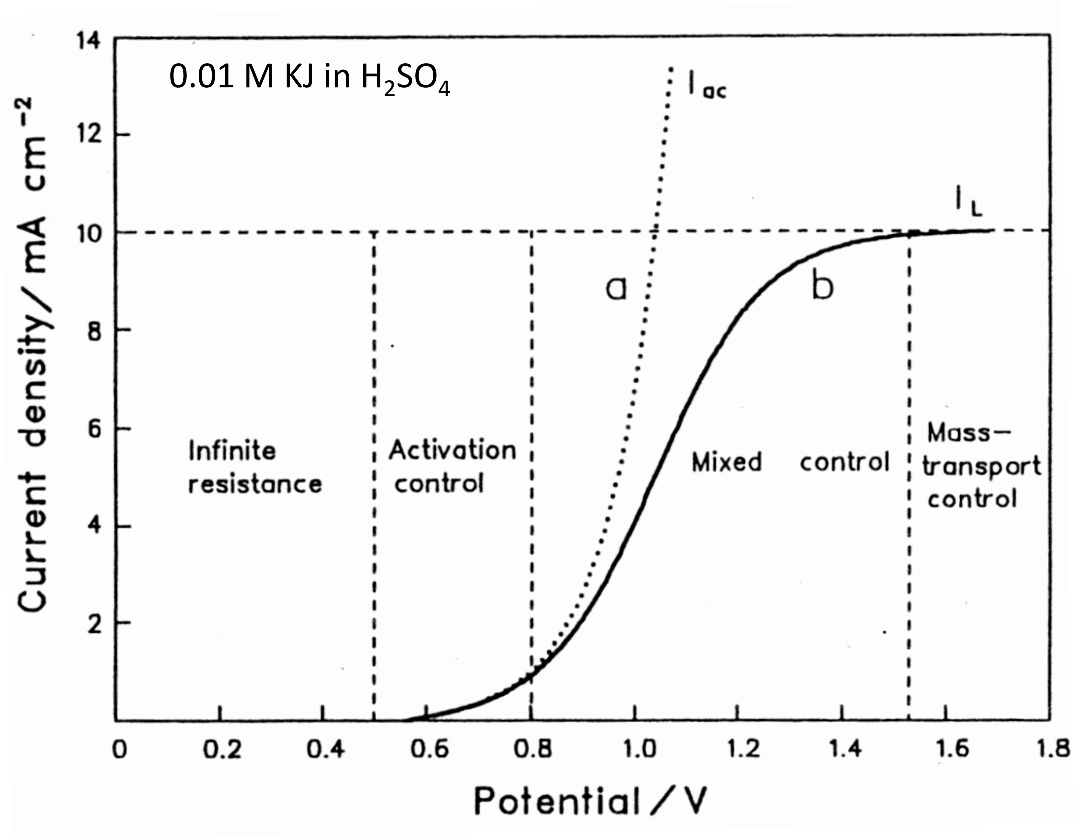
CHEMICAL REACTIONS can be involved in the overall electrode process. They can be homogeneous reactions in the solution and heteregeneous reaction at the surface. The rate constant of chemical reactions are independent of potential.

Chemical reactions can be hindered, and thus the reaction overpotential η_r can hinder the current flow.

Processes at metal/metal-ion electrodes include **CRYSTALLIZATION PARTIAL REACTION.**
These are processes by which atoms are either incorporated into or removed from the crystal lattice. Hindrance of these processes results in crystallization overpotential η_c

THE CURRENT-POTENTIAL RELATIONSHIP

The study of electrode kinetics involves the determination of the dependence of current on potential *E* = f(*i*) or on overpotential η = f(*i*).



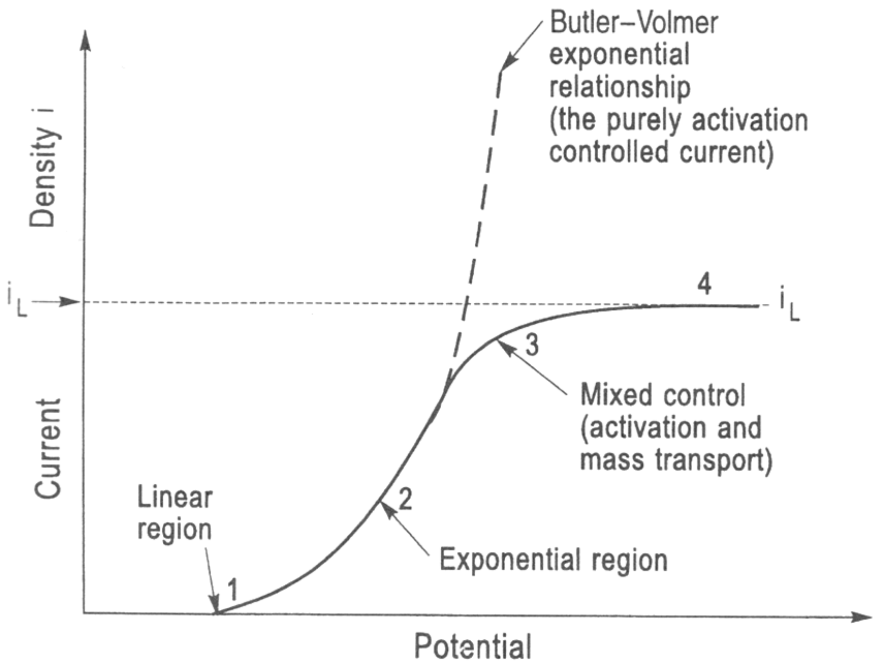
The potential E is measured versus a fixed reference electrode and current is reffered to the current density.

Curve ***a*** represents the dependence when the process is controlled by the kinetics of the reaction alone.

Curve ***b*** takes into account the effect of mass transport.

In the initial rising part of the curve the reaction is „**charge-transfer controlled**” or „**activation controlled**”.

THE CURRENT-POTENTIAL RELATIONSHIP



Four regions in the general current-overpotential relationship: 1 – linear, 2 – exponential, 3 – mixed control, 4 – limiting current density region

The **Butler–Volmer equation** is one of the most fundamental relationships in electrochemical kinetics. It describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and an anodic reaction occur on the same electrode:

$$I = A \cdot i_0 \cdot \left\{ \exp\left[\frac{\alpha_a n F}{RT}(E - E_{eq})\right] - \exp\left[-\frac{\alpha_c n F}{RT}(E - E_{eq})\right] \right\}$$

or in a more compact form:

$$i = i_0 \cdot \left\{ \exp\left[\frac{\alpha_a n F \eta}{RT}\right] - \exp\left[-\frac{\alpha_c n F \eta}{RT}\right] \right\}$$

M. Paunovic, M. Schlesiger, Fundamentals of Electrochemical Deposition, Wiley Interscience, USA, 1998

BUTLER–VOLMER EQUATION

An equation for the rate of an electrochemical reaction; it describes the current density at an electrode in terms of the overpotential.

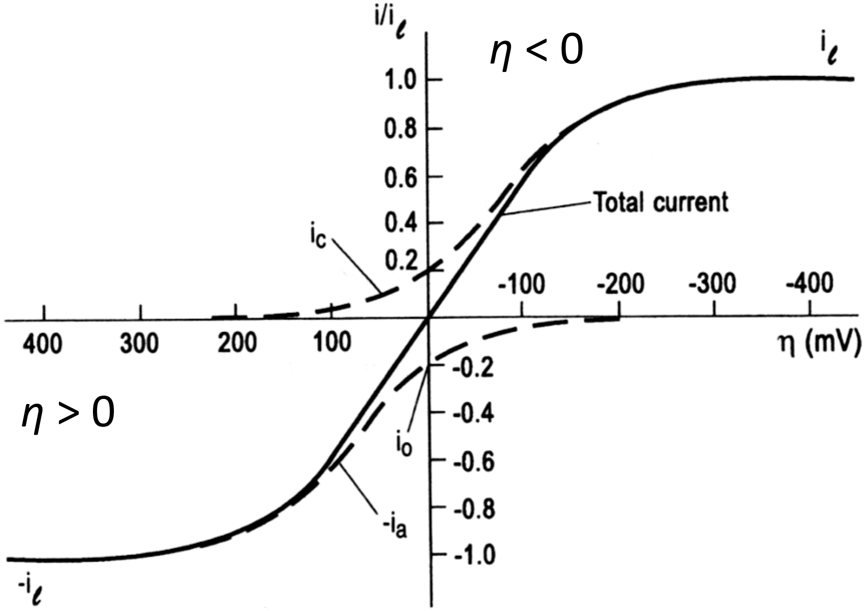
$$I = A \cdot i_0 \cdot \left\{ \exp\left[\frac{\alpha_a n F}{RT}(E - E_{eq})\right] - \exp\left[-\frac{\alpha_c n F}{RT}(E - E_{eq})\right]\right\}$$

$$i = i_0 \cdot \left\{ \exp\left[\frac{\alpha_a n F \eta}{RT}\right] - \exp\left[-\frac{\alpha_c n F \eta}{RT}\right]\right\}$$

I - electrode current, A; ***A*** - electrode active surface area, m^2 ; ***i*** - electrode current density, A/m^2 (defined as $i = I/A$); $\boldsymbol{i_0}$ – exchange current density, A/m^2; ***E*** – electrode potential, V; $\boldsymbol{E_{eq}}$ - equilibrium potential, V; ***T*** – absolute temperature, K; ***n*** - number of electrons involved in the electrode reaction; ***F*** – Faraday constant; ***R*** – universal gas constant; $\boldsymbol{\alpha_c}$ **-** so-called cathodic charge transfer coefficiet, dimensionless; $\boldsymbol{\alpha_a}$ **-** so-called anodic charge transfer coefficient, dimensionless; $\boldsymbol{\eta}$ **-** activation overpotential defined as $\eta = (E - E_{eq})$

$\alpha_a + \alpha_c = 1$

$\alpha_a \approx \alpha_c \approx \alpha \approx 0.5$



The variation of the partial current densities and total current density with overpotential.

HIGH-OVERPOTENTIAL APPROXIMATION

$$i = -i_0\, exp\left(\frac{-\alpha z F \eta}{RT}\right)$$ Large Cathodic Current

$$i = i_0\, exp\left(\frac{(1-\alpha) z F \eta}{RT}\right)$$ Large Anodic Current

TAFEL EQUATION

Tafel equation is a special case of a general Butler-Volmer equation. The linear relationship between *η* and *log i* was experimentally established by Tafel.

For large cathodic curret densites (omitting the minus sign): $|i| = i_0\, exp\left(\frac{-\alpha z F \eta}{RT}\right)$

Taking the logarithm of both sides of the equation:

$$ln|i| = ln\, i_0 - \left(\frac{\alpha z F \eta}{RT}\right) \longrightarrow \left(\frac{\alpha z F \eta}{RT}\right) = ln\, i_0 - ln|i|$$

$$\eta = f(i) \qquad \eta = \frac{RT}{\alpha z F} ln i_0 - \frac{RT}{\alpha z F} ln|i|$$

With transformation of the natural logarithm (ln) into decimal log:

$$\frac{2.303RT}{\alpha z F} log i_0 = a \qquad \frac{2.303RT}{\alpha z F} = b \qquad \eta > 0.06\ V$$

$\eta = a - b\ log|i|$ For the anodic process: $\eta = a + b \log i$

$$\eta = a \pm b\ log|i|$$

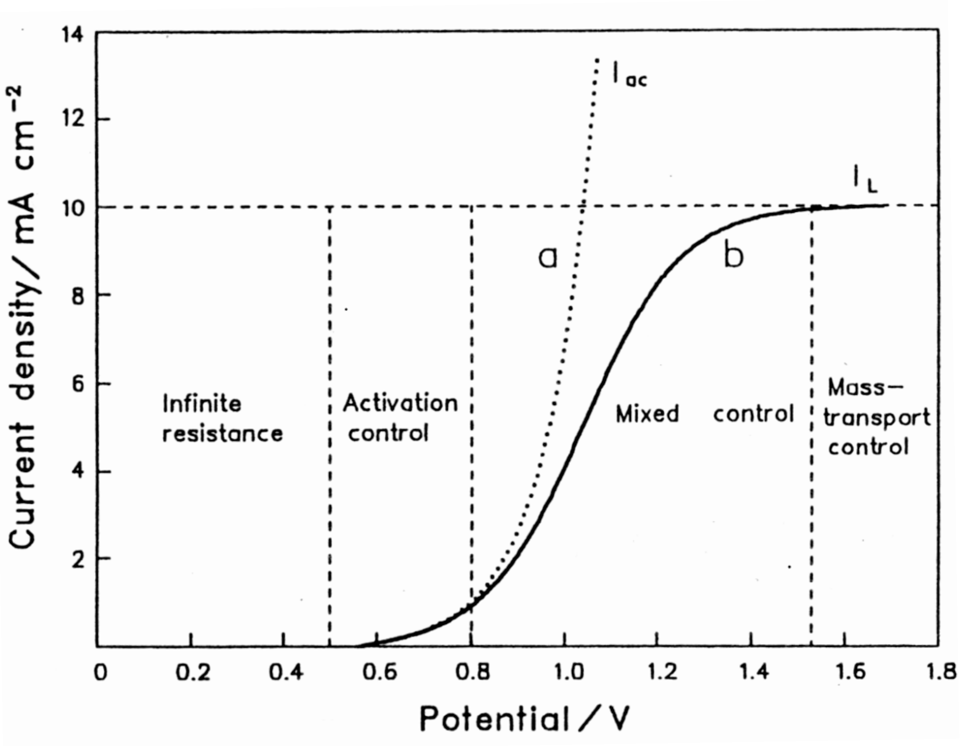
The theoretical values of the constant *a* and *b* are different for anodic and cathodic processes

TAFEL EQUATION

- The Tafel slope is an intensive parameter and does not depend on the electrode surface area.
- i_0 is and extensive parameter and is influenced by the electrode surface area and the kinetics or speed of the reaction.
- the Tafel slope is restricted to the number of electrons, z, involved in the charge transfer controlled reaction and the so called symmetry factor, α.
- for z = 1 although the symmetry factor can vary between 0 and 1 it is normally close to 0.5.
- the Tafel slope should be close to 120 mV if z = 1 and 60 mV if z = 2.

MASS TRANSPORT LIMITATION

Mass transport to the interphase can occur through three independent mechanisms: **migration, covection and diffusion**



MIGRATION – the driving force for migration is **the electric field in solution**. This effect is eleminated by adding a high concentration of supporting electrolyte (compared to the concentration of the electroactive ions). Most of the electricity is carried by the inert ions.

CONVECTIVE MASS TRANSPORT is caused by **the movement of the solution**. The driving force is external energy, usually in the form of mechanical energy of stirring the solution, rotating the electrode etc.

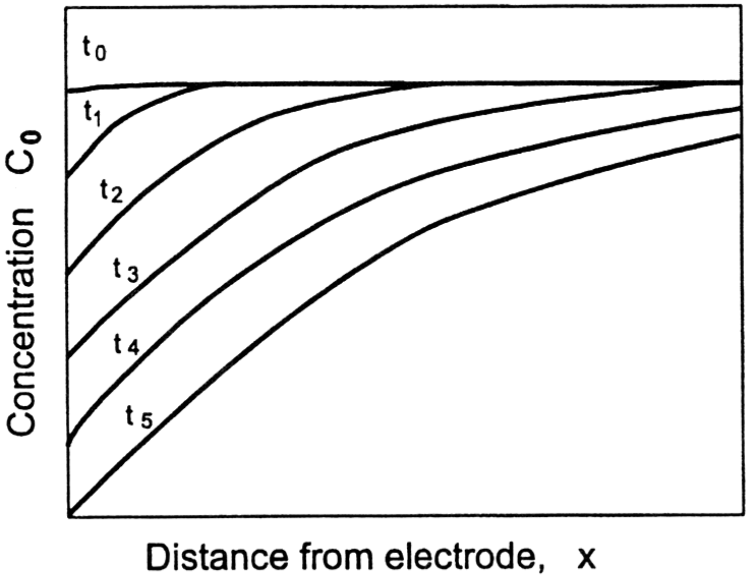
MASS TRANSPORT BY DIFFUSION – the driving force is **the gradient in concetration**. It is relatively slow process, with diffusion coefficient ranging from about $5 \cdot 10^{-6}$ to $8 \cdot 10^{-6}$ cm^2/s for ions and small molecules (in dilute aqueous solutions at room temperature).

E. Gileadi, Electrode Kinetics for Chemist, Chemical Engineers, and Materials Scientists, VCH Publishers (printed in USA), 1993.

MASS TRANSPORT LIMITATION

The reaction Ox + ze → Red occurs at the electrode, the reactant is consumed at the electrode and its concentration at the interface decreases.

The concentration of the reactant Ox is a function of the distance *x* from the cathode and the time *t* [Ox] = f(x, t). (Ox would be replaced by M^{z+})



Variation of concentration of reactant during non steady-state electrolysis

The concentraton gradient dc_{ox}/dx changes with time and assumes a maximum value when the reactant is completely depleted at the electrode, c_{ox} $(x = 0) = 0$.

The maximum concentration gradient $\left(\frac{dc}{dx}\right)_{x=0}$

The rate of the reaction at the surface (the current flowing across the interphase) is given by:

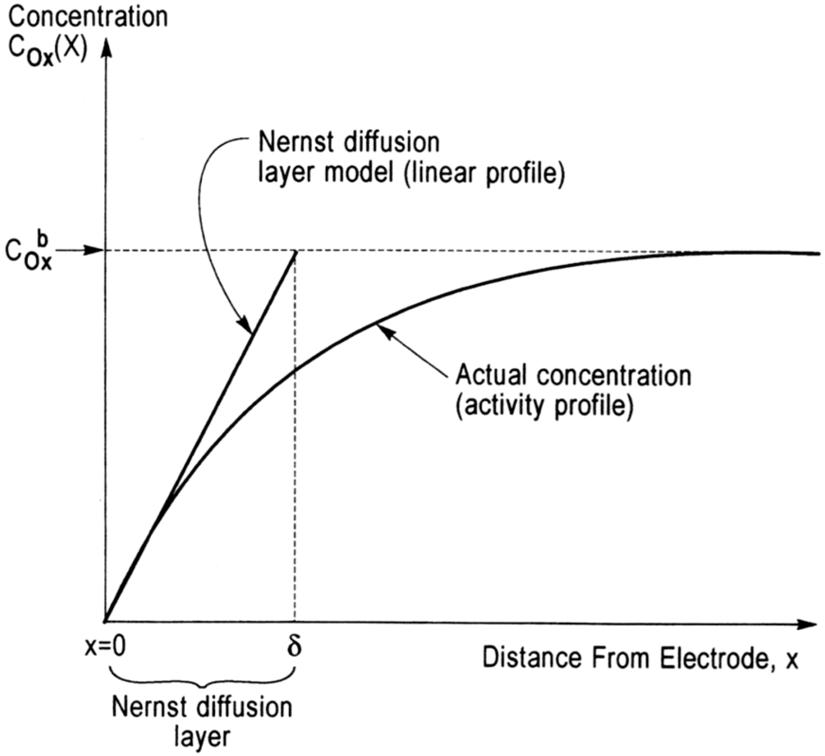
$$i = zFD_{Ox}\left(\frac{\partial c_{Ox}}{\partial x}\right)_{x=0}$$

D_{ox} the diffusion coefficient of species *Ox*

M. Paunovic, M. Schlesiger, Fundamentals of Electrochemical Deposition, Wiley Interscience, USA, 1998

NERNST DIFFUSION-LAYER MODEL

The model assumes that the concentration of Ox has a bulk concentration c_{Ox}^{b} up to a distance δ from the electrode surface and then falls off linearly to c_{Ox} (x=0) at the electrode (eglecting the double-layer effect).



It is assumed that the liquid layer of thickness δ is practically stationary and at distances greater than δ from the surface, the concentration of the reactant is equal to the bulk concentration. At x > δ stirring is efficient.

The reacting species must diffuse through the diffusion layer to reach the electrode surface.

According to the Nernst model, the concentration gradient at the electrode is given by:

$$\left(\frac{dc}{dx}\right)_{x=0} \approx \frac{c_b - c_{x=0}}{\delta}$$

The rate of reaction:

$$i = zFD_{Ox}\left(\frac{c_b - c_{x=0}}{\delta}\right)$$

M. Paunovic, M. Schlesiger, Fundamentals of Electrochemical Deposition, Wiley Interscience, USA, 1998

LIMITING CURRENT DENSITY

The current density i is a function of the concentration gradient $\dfrac{c_b - c_{x=0}}{\delta}$

The maximal concentration gradient value is $\dfrac{c_b}{\delta}$ for $c_{x=0} = 0$

This is the steady-state value for constant gradient and steady-state diffusion.

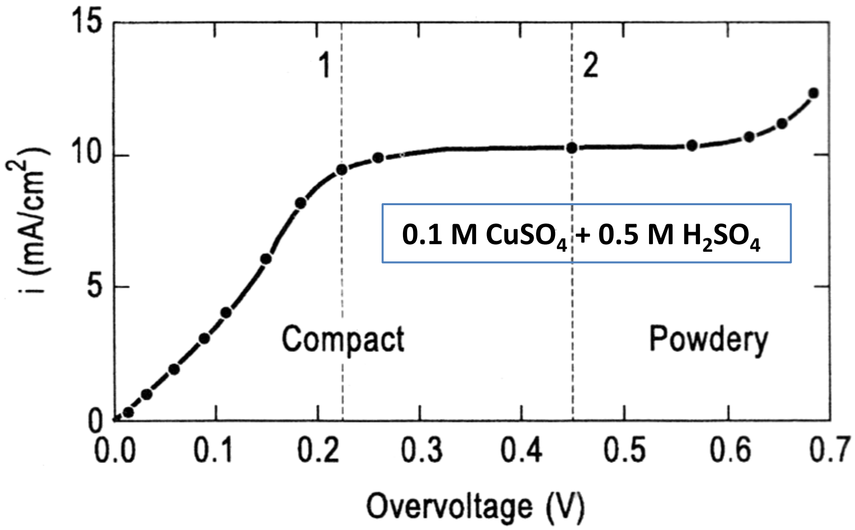
The maximum current density (corresponding to the maximum concentration gradient) is called the limimting diffusion current density i_L

Ox + ze → Red

$$i_L = \frac{zFD_{Ox}c_b}{\delta}$$

At the value of the limiting current density the species Ox are reduced as soon as they reach the electrode. At these conditions the concentration of Ox at the electrode is zero and the rate of reaction Ox + ze → Red is controlled by the rate of transport of the reactant Ox to the cathode.

Limiting current density is of great importance in metal deposition since the type and quality of coatings depend on the relative values of the deposition current and the limiting current.



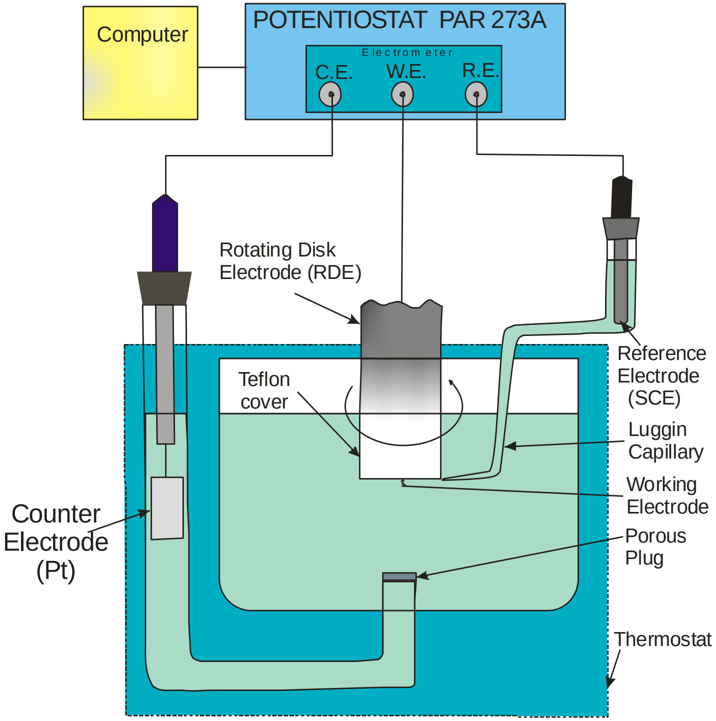
M. Paunovic, M. Schlesiger, Fundamentals of Electrochemical Deposition, Wiley Interscience, USA, 1998

ROTATING DISC ELECTRODE (RDE)

Limitation by diffusion is one of the main obstacles in an electrochemical process.
Two possibilites for increasing i_L: an increase of concentration and a decrease of the thickness of the diffusion layer

$$i_L = \frac{zF D_{Ox} c_b}{\delta}$$

The most effective and reproducible way of controlling the diffusion layer thickness is the rotating disc electrode (RDE).



The thickness of the diffusion layer on RDE is given by:

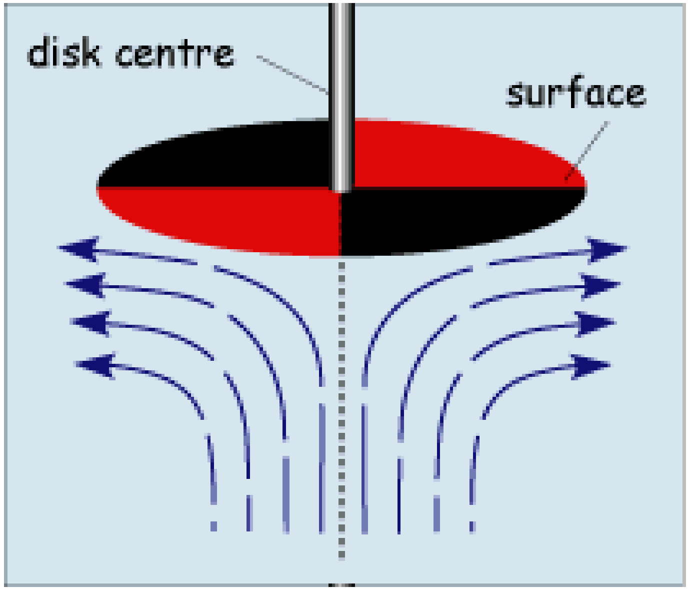
$$\delta = 1.61 \frac{D^{1/3} \nu^{1/6}}{\omega^{1/2}}$$

$\delta \approx 10^{-3}$ cm

D – diffusion coefficient, $cm^2\ s^{-1}$; ν - the kinematic viscosity (the ratio between viscosity and density), $cm^2 \cdot s^{-1}$
ω – (2πm) angular rotation velocity, $rad \cdot s^{-1}$.

ROTATING DISC ELECTRODE (RDE), LEVICH EQUATION

The forces acting on the RDE



The centrifugal forces of the rotation leas to a constant increase of the electrolyte velocity towards the edge of the disc. The diffusion layer thickness tends to decrease.

The most important feature of RDE:

- uniformly accessible surface (the rate of mass transport to the surface is uniform)
- flow of the solution is laminar (up to high rotation rates)

The transition from laminar to turbulent flow is characterized by a dimensionless number called the Reynolds number, *Re*. If the surface is rought, turbulence may set in at a lower Reynolds umber.

Since flow is laminar, it is possible to calculate precisely the rate of mass transport.

$$Re = \frac{\omega r^2}{\nu} < 1 \cdot 10^5$$

The corresponding equation for the limiting current density, developed by Levich:

$$i_L = 0.62 zFD^{2/3} \nu^{-1/6} \omega^{1/2} c_b$$

c_b analyte concentration

The limiting current is proportional to the square root of RDE rotation rate

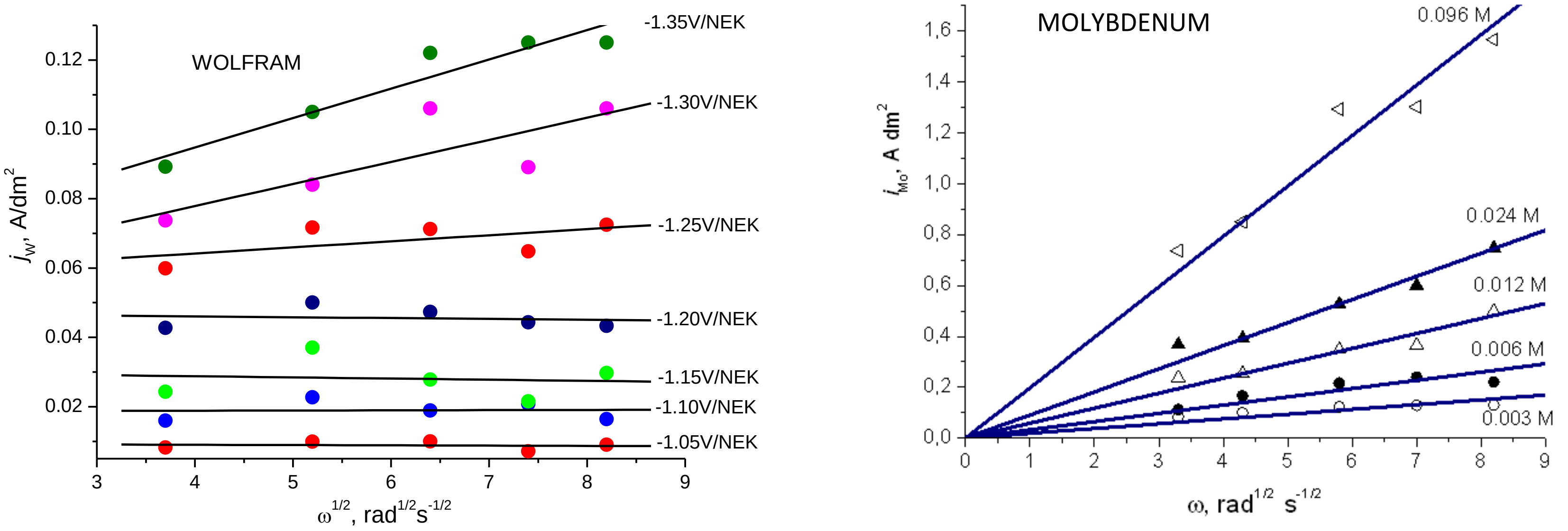
ROTATING DISC ELECTRODE (RDE), LEVICH EQUATION

For a purely activation-controlled process, the current should be independent of rotation rate.
For mixed control, the activation and mass transport-controlled current densities combine to yield the total current density as the sum of reciprocals:

$$\frac{1}{i} = \frac{1}{i_{ac}} + \frac{1}{i_L}$$

$$\frac{1}{i} = \frac{1}{i_{ac}} + \frac{1}{B\omega^{1/2}}$$

The constant B is practically independent of potential.



Current density of electroreduction of molybdenum and tungsten ions in function of square root of the angular velocity of rotation of the disk electrode (examples IMIM PAN)

THANK YOU

FOR YOUR ATTENTION