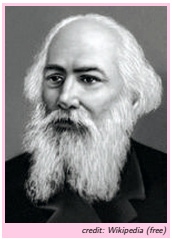
Electrochemistry: Elektrolytic and galvanic cell

Galvanic series (Beketov, cca 1860):

$$\ominus \text{ Li, Ca, Al, Mn, Cr} \approx \text{Zn, Cd} \approx \text{Fe, Pb, [H}_2\text{], Cu, Ag, Au} \oplus$$

Cell = system composed of two electrodes and an electrolyte.

- electrolytic cell: electric energy → chemical reaction
- galvanic cell: chemical reaction → electric energy
- reversible galvanic cell (zero current)



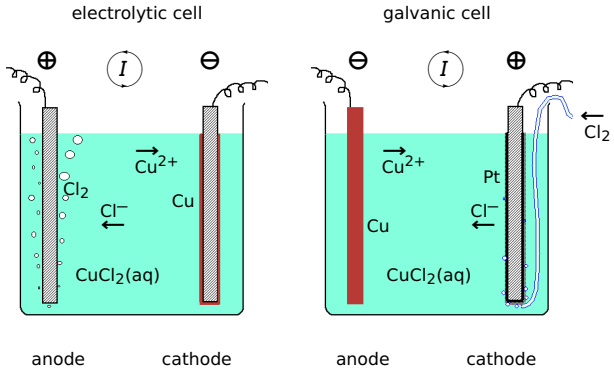
credit: Wikipedia (free)

Electrodes

- anode = electrode where oxidation occurs
  $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\,\text{e}^-$
  $2\,\text{Cl}^- \rightarrow \text{Cl}_2 + 2\,\text{e}^-$
- cathode = electrode where reduction occurs
  $\text{Cu}^{2+} + 2\,\text{e}^- \rightarrow \text{Cu}$
  $\text{Cl}_2 + 2\,\text{e}^- \rightarrow 2\,\text{Cl}^-$

Oxidation and reduction are separated in a cell. The charge flows through the circuit.

Anode and cathode



anode cathode anode cathode

"anions go to the anode"

Galvanic cells: electrodes, convention

Electrodes(= half-cells) may be separated by a porous separator, polymeric membrane, salt bridge.

- Cathode ⊕ is right (reduction)
- Anode ⊖ is left (oxidation)

⊖	negative electrode (anode)	⊕	positive electrode (cathode)
|	phase boundary	⁝	liquid junction (porous separator)
‖	salt bridge	⁝⁝	semipermeable membrane

Examples:

⊖ Cu(s) | $\text{CuCl}_2(c = 0.1\,\text{mol dm}^{-3})$ | $\text{Cl}_2(p = 95\,\text{kPa})$ | Pt ⊕

⊖ Ag(s) | AgCl(s) | $\text{NaCl}(\underline{m} = 4\,\text{mol kg}^{-1})$ | Na(Hg)
| $\text{NaCl}(\underline{m} = 0.1\,\text{mol kg}^{-1})$ | AgCl(s) | Ag(s) ⊕

⊖ Pt | $\text{Sn}^{2+}(0.1\,\text{mol dm}^{-3}) + \text{Sn}^{4+}(0.01\,\text{mol dm}^{-3})$ || $\text{Fe}^{3+}(0.2\,\text{mol dm}^{-3})$ | Fe ⊕

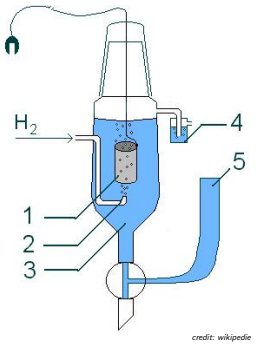
Equilibrium cell potential

- Also: electromotive potential/voltage, electromotive force (EMF).
- Should be measured at zero-current condition (balanced bridge, sensitive voltmeter)
- Cannot measure a potential of one electrode ⇒ zero defined by the standard hydrogen electrode:

$$2\,\text{H}^+(\text{aq}) + 2\,\text{e}^- \rightarrow \text{H}_2(\text{g})$$

where $a_{\text{H}^+} = 1$ (pH=0)
and $a_{\text{H}_2} = 1$ ($p_{\text{H}_2} = p^{\text{st}}$).

- Construction of a hydrogen electrode:
  Pt sheet covered by platinum black, saturated by hydrogen
- symbols: E, $\mathcal{E}$, $\Delta\phi$; in physics: U



credit: wikipedia

Cell potential II

Electrode potential of electrode X = voltage of cell

$$\ominus \text{ H}_2\,(a = 1) \mid \text{H}^+\,(a = 1) \mid \text{X} \oplus$$

NB: always the reduction potential

Standard (reduction) potential of an electrode: all reacting compounds have unit activities

Examples: $E^{\ominus}_{\text{Cu}^{+2+}|\text{Cu}} = 0.337\,\text{V}$, $E^{\ominus}_{\text{Cl}_2|_2\text{Cl}^-} = 1.360\,\text{V}$ (at 25 °C)

If the reaction are written in the way the cell produces energy:
reaction = (reduction at cathode) + (oxidation at anode)

$$E = E^{\text{red}}_{\text{cathode}} + E^{\text{ox}}_{\text{anode}}$$

If all reactions are written as a reduction:
reaction = (reduction at cathode) − (reduction at anode)

$$E = E^{\text{red}}_{\text{cathode}} - E^{\text{red}}_{\text{anode}}$$

Termodynamics of a reversible cell

Reversibility = reactions can be reversed by a small voltage change. No irreversible processes (metal dissolution, diffusion, liquid junction. . .)

$$\Delta_{\text{r}}G_{\text{m}} = W_{\text{el}} = -qE = -zFE \qquad [p, T]$$

⇒ **Nernst equation**:

$$E = E^{\ominus} - \frac{RT}{zF} \ln \prod_i a_i^{\nu_i}$$

where $\Delta_{\text{r}}G^{\ominus}_{\text{m}} = -zFE^{\ominus}$, $K = \exp[-\Delta_{\text{r}}G^{\ominus}_{\text{m}}/RT] = \exp[zFE^{\ominus}/RT]$

$$E^{\ominus} = E^{\ominus,\text{red}}_{\text{cathode}} + E^{\ominus,\text{ox}}_{\text{anode}} = E^{\ominus,\text{red}}_{\text{cathode}} - E^{\ominus,\text{red}}_{\text{anode}}$$

- $\Delta_{\text{r}}G < 0$ i.e. $E > 0$ ⇒ the cell produces current
  $E = 0$ i.e. $\Delta_{\text{r}}G = 0$ = uncharged cell (equilibrium)
  distiguish from: equilibrium potential (at zero current)
- $E^{\ominus}_{\text{Cu}^{2+}|\text{Cu}} = -E^{\ominus}_{\text{Cu}|\text{Cu}^{2+}}$ (oxidation) but $E^{\ominus}_{\text{Cl}_2|2\text{Cl}^-} = E^{\ominus}_{\frac{1}{2}\text{Cl}_2|\text{Cl}^-}$
- hydrogen electrode right at 25 °C: $E = E_0 - \text{pH} \cdot 0.05916\,\text{V}$

Termodynamics of a reversible cell II

- only electric work W_{el}
- reversible $[p, T]$

$$\Delta_{\text{r}}S_{\text{m}} = -\left(\frac{\partial \Delta_{\text{r}}G_{\text{m}}}{\partial T}\right)_p = zF\left(\frac{\partial E}{\partial T}\right)_p$$

$$\Delta_{\text{r}}H_{\text{m}} = -T^2\left(\frac{\partial(\Delta_{\text{r}}G_{\text{m}}/T)}{\partial T}\right)_p = zFT^2\left(\frac{\partial(E/T)}{\partial T}\right)_p$$

$$Q_{\text{m}} = T\Delta_{\text{r}}S_{\text{m}} \quad \text{(II. Law for reversible processes)}$$

Oops! ($W_{p\text{-}V}$)

$$\Delta_{\text{r}}U = Q + W = Q - p\Delta_{\text{r}}V + W_{\text{el}}$$
$$\Delta_{\text{r}}H = \Delta_{\text{r}}U + \Delta_{\text{r}}(pV) \overset{[p]}{=} \Delta_{\text{r}}U + p\Delta_{\text{r}}V = Q + W_{\text{el}}$$

Eq. $Q = \Delta_{\text{r}}H$ holds true only if the only work is pressure-volume

And similarly for standard state ($p = p^{\text{st}}$, $a = 1$), e.g.:

$$\Delta_{\text{r}}S^{\ominus}_{\text{m}} = -\left(\frac{\partial \Delta_{\text{r}}G^{\ominus}_{\text{m}}}{\partial T}\right)_p = zF\left(\frac{\partial E^{\ominus}}{\partial T}\right)_p$$

Reduction potentials and different valences

Example.
$E^{\ominus}(\text{Cr}^{2+}|\text{Cr}) = -0.913\,\text{V}$, $E^{\ominus}(\text{Cr}^{3+}|\text{Cr}) = -0.744\,\text{V}$.
Calculate $E^{\ominus}(\text{Cr}^{3+}|\text{Cr}^{2+})$.

Gibbs energies are additive (not potentials)

$\text{Cr}^{2+} + 2\,\text{e}^-$	→	Cr	$\Delta_{\text{r}}G^{\ominus}_{\text{m}} = -2F \cdot (-0.913\,\text{V})$
$\text{Cr}^{3+} + 3\,\text{e}^-$	→	Cr	$\Delta_{\text{r}}G^{\ominus}_{\text{m}} = -3F \cdot (-0.744\,\text{V})$
$\text{Cr}^{3+} + 1\,\text{e}^-$	→	Cr^{2+}	$\Delta_{\text{r}}G^{\ominus}_{\text{m}} = -1F \cdot E^{\ominus}(\text{Cr}^{3+}|\text{Cr}^{2+})$

$$-1F \cdot E^{\ominus}(\text{Cr}^{3+}|\text{Cr}^{2+}) = -3F \cdot (-0.744\,\text{V}) + 2F \cdot (-0.913\,\text{V})$$

$$E^{\ominus}(\text{Cr}^{3+}|\text{Cr}^{2+}) = 3 \cdot (-0.744\,\text{V}) - 2 \cdot (-0.913\,\text{V}) = -0.406\,\text{V}$$

Electrodes

- of the first kind (one reaction electrode—ion)
  - cationic, anionic
  - metal, amalgam (metal in Hg), nonmetallic, gas
- of the second kind (nonsoluble salt—two reactions)
- of the third kind
- redox (two oxidation states)
- ion selective (membrane)

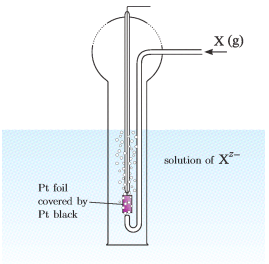
Electrodes of the first kind

- cationic, metal
  ox: ⊖ Zn|Zn^{2+}, red: Zn^{2+}|Zn ⊕
  not for Fe, Al + ions, which are covered by oxides
- amalgam
  ox: ⊖ Na(Hg)|Na^+, red: Na^+|Na(Hg) ⊕

$$E_{Na^+|Na} = E^{\ominus}_{Na^+|Na} - \frac{RT}{F}\ln\frac{a_{Na(Hg)}}{a_{Na^+}}$$

  saturated amalgam: $a_{M(Hg)=1}$
- cationic gas: hydrogen
- anionic gas: chlorine, oxygen ⟶

$$Cl^-|Cl_2|Pt\ \oplus\ :\ Cl_2 + 2\,e^- \to 2\,Cl^-$$
$$OH^-|O_2|Pt\ \oplus\ :\ \tfrac{1}{2}O_2 + 2\,e^- + H_2O \to 2\,OH^-$$
$$:\ \tfrac{1}{2}O_2 + 2\,e^- + 2H^+ \to H_2O$$



- similarly: $Br^-|Br_2|Pt\ \oplus$

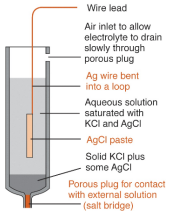
Electrodes of the second kind

- silver chloride

$$Cl^- \mid AgCl \mid Ag\ \oplus$$

$$\begin{array}{rcl} AgCl(s) & \to & Ag^+ + Cl^- \\ Ag^+ + e^- & \to & Ag(s) \\ \hline AgCl(s) + e^- & \to & Ag + Cl^- \end{array}$$

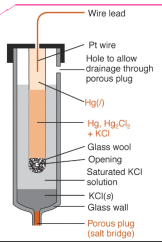
$$E_{AgCl\,|\,Ag\,|\,Cl^-} = E^{\ominus}_{AgCl\,|\,Ag\,|\,Cl^-} - \frac{RT}{F}\ln\frac{a_{Ag}\cdot a_{Cl^-}}{a_{AgCl}} = E^{\ominus}_{AgCl\,|\,Ag\,|\,Cl^-} - \frac{RT}{F}\ln a_{Cl^-}$$



- mercury chloride (calomel)

$$Cl^- \mid Hg_2Cl_2 \mid Hg\ \oplus$$

$$Hg_2Cl_2(s) + 2\,e^- \to 2\,Hg + 2\,Cl^-$$



Usage: reference electrodes

Pictures by: Analytical chemistry an introduction, 7th edition, Harcourt College, 2000

Curiosity: Electrodes of the third kind +

$$Ca^{2+}(aq) \mid Ca(COO)_2(s) \mid Zn(COO)_2(s) \mid Zn(s)\ \oplus$$

Three reactions:

$$\begin{array}{rcl} Ca^{2+} + (COO)_2{}^{2-} & \to & Ca(COO)_2 \\ Zn(COO)_2 & \to & (COO)_2{}^{2-} + Zn^{2+} \\ Zn^{2+} + 2\,e^- & \to & Zn \\ \hline Ca^{2+} + Zn(COO)_2 + 2\,e^- & \to & Ca(COO)_2 + Zn \end{array}$$

$$E = E^{\ominus} - \frac{RT}{2F}\ln\frac{1}{a_{Ca^{2+}}}$$

Can measure $c_{Ca^{2+}}$—there is no Ca | Ca^{2+}(aq) electrode, because Ca reacts with water

(Ion-selective electrodes are more advantageous)

Redox electrodes

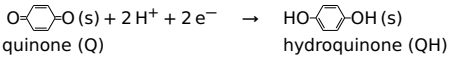
- metal:

$$Sn^{4+} \mid Sn^{2+} \mid Pt\ \oplus$$

$$Sn^{4+} + 2\,e^- \to Sn^{2+}$$

- quinhydrone electrode (pH 1–8):

quinone (p-benzoquinone) + hydroquinone 1:1, sat. ⊙ in a buffer



Nernst equation:

$$E_{Q|QH} = E^{\ominus}_{Q|QH} - \frac{RT}{2F}\ln\frac{a_{QH}^{\,1}}{a_Q\cdot a_{H^+}^2} = E^{\ominus}_{Q|QH} + \frac{RT}{F}\ln a_{H^+}$$
$$\doteq (0.699 - 0.059\cdot \mathrm{pH})\,\mathrm{V}$$

Usage: measuring pH

Ion-selective electrodes

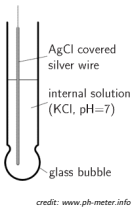
Semipermeable membrane (for some ions only)

Glass electrode

Membrane of special thin glass permeable for H^+ (and other ions).
Difference of chem. pot. of both solutions

$$\mu(H^+, \odot) - \mu(H^+, \text{electrode})$$
$$= \frac{1}{RT}\ln\frac{a(H^+, \odot)}{a(H^+, \text{electrode})}$$

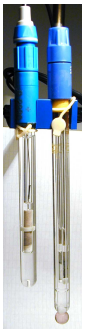
is compensated by the electric work $-FE$. ⇒ Nernst equation



credit: www.ph-meter.info

ref. silver chloride ↗

glass →



credit: wikipedie

$$E = \text{const} - \frac{RT}{F}\ln a(H^+, \odot) = \text{const} - \frac{RT}{F}\cdot\ln 10\cdot \mathrm{pH}$$

Usage: measuring pH (2–12), other ions

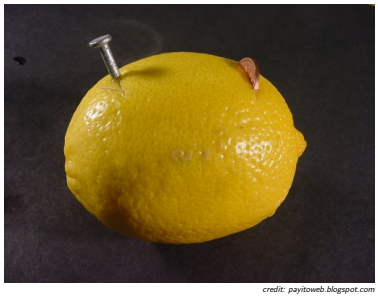
Galvanic cells

By the source of ΔG:

- chemical
- concentration
  - electrolyte
  - electrode

By ion transfer:

- one electrolyte
- with salt bridge
- with membrane



credit: payitoweb.blogspot.com

anode: $Fe(s) \to Fe^{3+}(aq) + 3\,e^-$ (−0.04 V)
$Fe(s) \to Fe^{2+}(aq) + 2\,e^-$ (−0.44 V)
cathode: $\frac{1}{2}O_2 + 2\,e^- + 2H^+ \to H_2O$ (1.23 V)
or reduction of organic compounds (vitamin C)

Simple chemical cell

- Single electrolyte + electrodes

Example. Consider a Pt electrode saturated by hydrogen and Ag wire covered by AgCl submerged in a solution of HCl ($c = 0.01\,\mathrm{mol\,dm^{-3}}$) on the top of the highest Czech mountain, Sněžka (1602 m above sea level). The standard reduction potential of the Ag/AgCl/Cl^- electrode is 0.222 V (p^{st} = 101 325 Pa). Calculate the cell voltage. A sea-level-reduced pressure is 999 mbar, temperature 25 °C.

$p = 83128$ Pa
0.4561 V (γ = 1)
0.4621 V (lim. DH)
0.4616 V (DH)

Chemical cell—separated electrolytes

Porous barrier (liquid junction) (⁝).
Irreversible ⇒ liquid junction (diffusion) potential.
Reduced by the **salt bridge** (||).

Example:

$$\ominus\ \mathrm{Zn(s)} \mid \mathrm{ZnSO_4} \parallel \mathrm{CuSO_4} \mid \mathrm{Cu(s)}\ \oplus$$

Electrode concentration cell

Examples:

$$\ominus\ \mathrm{Pt{—}H_2}(p_1) \mid \mathrm{HCl(aq.)} \mid \mathrm{H_2}(p_2)\mathrm{{—}Pt}\ \oplus$$

(Given polarity for $p_1 > p_2$)

$$\ominus\ \mathrm{Li(Hg)}(x_1) \mid \mathrm{LiCl(aq)} \mid \mathrm{Li(Hg)}(x_2)\ \oplus$$

(Given polarity for $x_1 > x_2$)

Battery

(One or) more connected cells.

Common disposable batteries:

- Alkaline battery (Zn, MnO_2 + C)

$$\ominus\ \mathrm{Zn} \mid \mathrm{KOH\,(gel)} \mid \mathrm{MnO_2}\ \oplus$$

$$\begin{aligned} \mathrm{Zn} + 2\,\mathrm{OH^-} &\rightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\,\mathrm{e^-} \\ 2\,\mathrm{MnO_2} + \mathrm{H_2O} + 2\mathrm{e^-} &\rightarrow \mathrm{Mn_2O_3} + 2\,\mathrm{OH^-} \end{aligned}$$

- Lithium (Li metal is light, has high potential)
  Electrolyte = salt (e.g., $LiBF_4$) in organic polar solvent
  Several possibilities, e.g.:

$$\begin{aligned} \mathrm{Li} &\rightarrow \mathrm{Li^+} + \mathrm{e^-} \\ \mathrm{Mn^{IV}O_2} + \mathrm{Li^+} + \mathrm{e^-} &\rightarrow \mathrm{Mn^{III}LiO_2} \end{aligned}$$

Rechargeable batteries

- Li-ion, Li-polymer: Li is in C (max. 1 Li in 6 C)

$$\ominus\ \mathrm{Li\ (in\ C)} \mid \mathrm{LiBF_4\ or\ polymer} \mid \mathrm{LiCoO_2.CoO_2}\ \oplus$$

  Positive electrode (e.g., in discharged state) $LiCoO_2$ = layers of CoO_2 intercalated by layers Li^+. Charging: Li^+ to the solution, $Co^{III} \rightarrow Co^{IV}$

- Ni-MH: hydrogen in metal hydride (M = $LaNi_5$, $CeAl_5$, $TiNi_2$ . . .)

$$\ominus\ \mathrm{H} \mid \mathrm{MH} \mid \mathrm{KOH(aq.)} \mid \mathrm{Ni(OH)_2} \mid \beta\text{-NiOOH} \mid \mathrm{Ni}\ \oplus$$

- lead–acid battery (high current)

$$\ominus\ \mathrm{Pb} \mid \mathrm{PbSO_4(s)} \mid \mathrm{H_2SO_4\,(20{–}30\,wt.\,\%)} \mid \mathrm{PbO_2(s)} \mid \mathrm{PbSO_4(s)} \mid \mathrm{Pb}\ \oplus$$

  Summary reaction:

$$\mathrm{Pb} + \mathrm{PbO_2} + 2\,\mathrm{H_2SO_4} \underset{\text{recharge}}{\overset{\text{discharge}}{\rightleftarrows}} 2\,\mathrm{PbSO_4} + 2\,\mathrm{H_2O}$$

  or for anode and cathode:

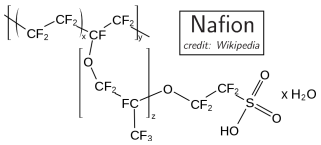
$$\begin{aligned} \mathrm{Pb} + \mathrm{SO_4^{2-}} &\rightarrow \mathrm{PbSO_4(s)} + 2\,\mathrm{e^-} \\ \mathrm{PbO_2} + \mathrm{SO_4^{2-}} + 4\,\mathrm{H^+} + 2\mathrm{e^-} &\rightarrow \mathrm{PbSO_4(s)} + 2\,\mathrm{H_2O} \end{aligned}$$

Fuel cells

e.g., oxygen and hydrogen

$\ominus$: $\mathrm{H_2} \rightarrow 2\,\mathrm{H^+} + 2\,\mathrm{e^-}$

protons permeate through a membrane



$\oplus$: $\frac{1}{2}\mathrm{O_2} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \rightarrow \mathrm{H_2O}$

expensive catalysts (Pt)
purity of gases (CO)

isopropanol fuel cell ⟶

Solubility product

Example. Determine the solubility product of AgCl using the standard potentials at 25 °C.
Data: $E^{\circ}(\mathrm{Ag|Ag^+}) = 0.799\,\mathrm{V}$, $E^{\circ}(\mathrm{Ag|AgCl|Cl^-}) = 0.222\,\mathrm{V}$.

$$\ominus\ \mathrm{Ag} \mid \mathrm{AgCl(aq.)} \mid \mathrm{AgCl(s)} \mid \mathrm{Ag}\ \oplus$$

$$\begin{aligned} \ominus, \mathrm{red}: \quad \mathrm{Ag^+} + \mathrm{e^-} &\rightarrow \mathrm{Ag} & \Delta_r G_m^{\circ} &= -F E^{\circ}_{\mathrm{Ag^+|Ag}} & \times(-1) \\ \oplus, \mathrm{red}: \quad \mathrm{AgCl} + \mathrm{e^-} &\rightarrow \mathrm{Ag} + \mathrm{Cl^-} & \Delta_r G_m^{\circ} &= -F E^{\circ}_{\mathrm{Ag|AgCl|Cl^-}} & \times(+1) \\ \hline \mathrm{AgCl} &\rightarrow \mathrm{Ag^+} + \mathrm{Cl^-} & \Delta_r G_m^{\circ} &= -F(E^{\circ}_{\mathrm{Ag|AgCl|Cl^-}} - E^{\circ}_{\mathrm{Ag^+|Ag}}) \end{aligned}$$

$$K_s = \exp\left(-\frac{\Delta_r G^{\circ}}{RT}\right) = \exp\left[\frac{F}{RT}(E^{\circ}_{\mathrm{Ag|AgCl|Cl^-}} - E^{\circ}_{\mathrm{Ag^+|Ag}})\right] = 1.76\times10^{-10}$$

Short-circuit cell(virtual Ag in ⊙ AgCl): the Nernst equation is

$$E = 0 = (E^{\circ}_{\mathrm{Ag|AgCl|Cl^-}} - E^{\circ}_{\mathrm{Ag^+|Ag}}) - \frac{RT}{F}\ln(a_{\mathrm{Cl^-}} \cdot a_{\mathrm{Ag^+}})$$

= equilibrium condition

$$a_{\mathrm{Cl^-}} \cdot a_{\mathrm{Ag^+}} = K_s$$

Kinetics of electrode phenomena

Electrode reaction:

1. diffusion of reactants to the electrode,
2. reaction in the adjacent layer),
3. adsorption of reactants to the electrode,
4. electron transfer of adsorbed molecules/ions and the electrode,
5. desorption of the products,
6. reaction in the adjacent layer),
7. diffusion of products out of the electrode.

In case of slowdown: polarization of electrodes:

- concentration polarization (1., 7.)
- chemical polarization

Overpotential

is the voltage needed above the equilibrium potential (at one electrode) for the reaction to be actually observed—a sort of the activation energy.

- Depeds on the electrode material
  (hydrogen on Pt: small, on Cu: 0.5 V, on Zn: 0.7 V),
- decreases slightly with increasing temperature,
- depends on the current density ($\eta \approx a + b \ln j$),
- ⊖ increases power consumption during electrolysis
- ⊕ high hydrogen overpotential on metals allows electrochemical deposition of metals with (slightly) negative potentials (Cr, Co), lead-acid battery
  some compounds catalyze H_2 production, can be used in analysis

Corrosion

- anodic phase: ⊖ metal is dissolved
- cathodic phase: ⊕ metal is deposited

Cathodic protection:

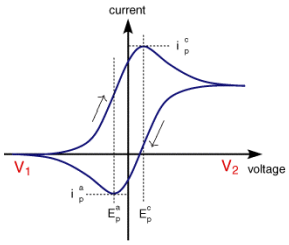
- passive – by anode of a more reactive metal (Zn, Al), which dissolves and produces a negative protective voltage on an object (ship hull) – "sacrificial anode"

credit: RSmi Kaupp (Wikimedia Commons)

- active – additional ⊖ voltage on the object, anode is ⊕ (large pipes upto 50 V, 50 A)

Electroanalytical methods

- coulometry – charge or current needed for a chemical reaction (Faraday's laws of electrolysis; Cu, Ag, O_2+H_2)
  - calibration of ammeters (ampere meters)
  - coulometric titration (const. current, time to equivalence)
- potentiometry – voltage of a cell, (almost) zero current activity (concentration) of a substance is determined, then:
  - pH (glass electrode, quinhydrone, . . .)
  - other ions
  - acidity constants
  - solubility products
  - activity coefficients
  - potentiometric titrations (pH etc.)
- voltammetry – current vs. applied voltage:
  - cyclic voltammetry (right)
  - polarography

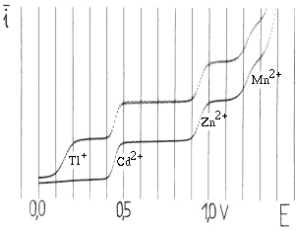


credit: http://www.ceb.cam.ac.uk/research/groups/rg-eme/teaching-notes/linear-sweep-and-cyclic-voltametry-the-principles

Polarography

Voltammetric technique with a dropping mercury electrode

- Linear E: sensitivity up to 1×10^{-5} mol dm^{-3}
  Problem: capacitive current
- Differential pulse polarography (DPP):
  sensitivity to 1×10^{-7} mol dm^{-3}



Jaroslav Heyrovský

credits: http://canov.jergym.cz/objevite/objev2/hey.htm, picture of polarograph by Luká Mioch, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=4079721