Electrochemistry course
ACME Faculty, EHVE course
B.Sc. Studies, II year, IV semester
Leszek Niedzicki, PhD, DSc, Eng.

Half-cells and cells

Electrochemical potential

Energy of interparticle (between ions, electrons, molecules) interactions consists of the following shares:

– **coulombic** – outcome of the resultant particle charge – $z_i \cdot F \cdot \Phi$
where Φ is **inner potential** (Galvani potential)

– and **chemical** – resulting from the chemical structure of the particle (number and type of atoms, bond types, charge arrangement) - μ (chemical potential of particle in the given phase and temperature).
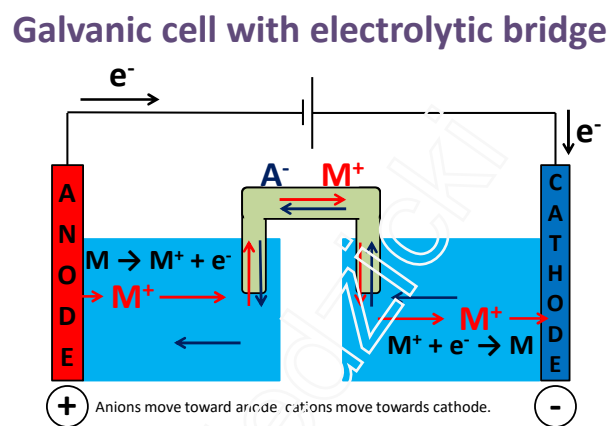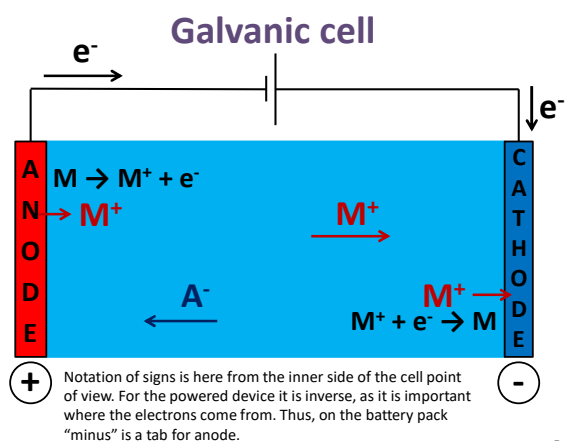
Electrochemical potential

- Electrochemical potential of "i" particles in the α phase: $\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i \cdot F \cdot \Phi^\alpha$

- Components of the potential are unfortunately non-measureable through the experiments. Absolute value of the electrochemical potential is also impossible to measure.

- However, the difference between two electrochemical potentials is possible to measure.

Why ions are moving towards electrodes?

The ion movement toward electrodes (and why do electrodes have charges at all) can have two reasons:
- Potential with the outer source applied to electrodes;
- Electrodes can be formed of different materials (of different electrochemical potential). If on every electrode immersed in the electrolyte spontaneous reactions happen, then at every electrode-electrolyte boundary potentials are formed (non-measureable parameter). Their difference is called the **electromotive force** (**EMF**) (it can be measured). EMF is determining current that is possible to obtain from the given electrode set (system).

Electromotive force

Electrons between electrodes move through the outer circuit (if they are connected through it). At one electrode oxidation can occur (thus electron can be sent to the outer circuit) and reduction can occur at the other electrode (and electron is received from the outer circuit). All those processes are components of the redox reaction, although its half-reactions are separated (without requirement of contact between reagents, as it was explained during the inorganic chemistry course).

Electrode, at which the oxidation occurs is called the **anode**.

Electrode, at which reduction occurs is called the **cathode**.

Galvanic cell

- Arrangement of anode, electrolyte and cathode is called the **galvanic cell**.

- Current (electrons) flowing through the circuit between electrodes can power the receiver (engine, bulb, *etc.*).

- Arrangement of one electrode and electrolyte surrounding it is called the **half-cell**.

- Half-cells can share one electrolyte or can be connected through the electrolytic bridge (ionic conductor with ion selective membranes that prevent electrolytes of half-cells to mix with each other).

Galvanic cell

Notation of signs is here from the inner side of the cell point of view. For the powered device it is inverse, as it is important where the electrons come from. Thus, on the battery pack "minus" is a tab for anode.

Galvanic cell with electrolytic bridge

Anions move toward anode, cations move towards cathode.

Interphase

- The boundary between phases is very important – it is the contact of electrolyte and electrode where all processes connected to electron transfer occur. Only at the boundary ions can give away or receive electron. Electrode can conduct electrons and electrons only. Electrolyte can conduct ions exclusively.

Electrochemical series

- Electrodes (and specific reactions going at them) individually do not possess any potential. It is only after connecting them to any other electrode (redox reaction) one can measure their relative potentials.
- Electrode potentials relative to each other are measured at the standard conditions (25°C, 1013hPa).
- Measured redox reactions are positioned in so-called **electrochemical series**.
- **Standard hydrogen electrode** (SHE) works as a reference point in the electrochemical series ($H_3O^+ + e^- \rightarrow \frac{1}{2}H_2 + H_2O$; half-cell notation: $Pt,H_2|H^+$).
- Above standard potential (of the given half-cell) oxidation occurs (and below it reduction takes place).

Electrochemical series

Li^+/Li	-3.045 V	$AgCl/Ag$	+0.222 V
Ca^{2+}/Ca	-2.864 V	$Hg_2Cl_2/2Hg$	+0.268 V
Na^+/Na	-2.711 V	Cu^{2+}/Cu	+0.338 V
Mg^{2+}/Mg	-2.370 V	$I_2/2I^-$	+0.536 V
Al^{3+}/Al	-1.700 V	MnO_4^-/MnO_4^{2-}	+0.558 V
SO_4^{2-}/SO_3^{2-}	-0.932 V	Fe^{3+}/Fe^{2+}	+0.771 V
Zn^{2+}/Zn	-0.763 V	Ag^+/Ag	+0.799 V
Cr^{3+}/Cr	-0.744 V	Pt^{2+}/Pt	+0.963 V
Fe^{2+}/Fe	-0.441 V	Cl_2/Cl^-	+1.358 V
Ni^{2+}/Ni	-0.234 V	Au^{3+}/Au	+1.498 V
Pb^{2+}/Pb	-0.126 V	MnO_4^-/Mn^{2+}	+1.531 V
H_3O^+/H_2	0.000 V	F_2/F^-	+2.866 V

($SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$)   ($2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$)
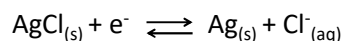
Half-cell types

Half-cells are divided according to their construction:

- I type – metal immersed into solution of its highly soluble/dissociated salt, *e.g.* $Pb_{(s)}|Pb^{2+}_{(aq)}$. Metal is acting here as both reagent and electrical conductor for electrons. Reaction:

$$Pb^{2+}_{(aq)} + 2e^- \rightleftarrows Pb_{(s)}$$
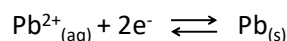
Half-cell types

- II type – metal covered with its poorly soluble salt I, whole immersed in the solution of highly soluble salt II that shares the common anion with salt I, *e.g.* $Ag_{(s)}|AgCl_{(s)}|Cl^-_{(aq)}$. Metal here is acting as an electrical conductor and reacts with the anion forming/decomposing poorly soluble salt I, but whole electrode is reversible against chlorine. Reaction:

$$AgCl_{(s)} + e^- \rightleftarrows Ag_{(s)} + Cl^-_{(aq)}$$

Half-cell types

- III type – metal covered with its poorly soluble salt I, whole is covered with poorly soluble salt II that share the common anion with salt I, whole electrode is immersed in the solution of highly soluble salt III that shares the common cation with salt II, *e.g.* $Pb_{(s)}|PbC_2O_{4(s)}|CaC_2O_{4(s)}|Ca^{2+}_{(aq)}$. Metal and anion of salt II react forming (decomposing) poorly soluble salt I. Reaction:

$$Pb_{(s)} + CaC_2O_{4(s)} \rightleftarrows PbC_2O_{4(s)}\downarrow + Ca^{2+}_{(aq)} + 2e^-$$

Half-cell types

- Redox half-cells – noble metal not taking part in the reaction, its presence required for electron conductivity only, immersed in reagent solution, that can change its oxidation state, *e.g.* $Pt_{(s)}|MnO_4^-_{(aq)},Mn^{2+}_{(aq)}$
- Gas half-cell is a subtype of redox half-cells. Instead of solution, electrode is rinsed with gas taking part in electrode reaction, *e.g.* $Pt_{(s)}|H_{2(g)}|H^+_{(aq)}$. Reaction:

$$H_{2(g)} \rightleftarrows 2H^+_{(aq)}+2e^-$$
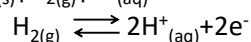
Electromotive force of the cell

- It is calculated as a difference between half-cells potentials. From the higher potential the lower one is subtracted:
  EMF = E_2-E_1 (thus EMF value is always above 0)
- Apart from the **standard half-cell potentials** (E^0) the final half-cell potential is influenced also by: temperature, reagent concentration, number of electrons exchanged in the single reaction and pressure (if any reagent is gaseous).

Half-cell potential

$E = E^0 + R·T/(z·F) · \ln(c_{ox}^n/c_{red}^m)$ [Nernst equation]
T – absolute temperature in kelvins;
z – number of electrons exchanged in a single reaction;
F – Faraday constant; R – gas constant;
n and m – stoichiometric coefficients of a given reagent in a half-reaction;
$C_{ox/red}$ – concentration of the oxidized/reduced form if the form is solid (metal) than $c = 1$, if form is gaseous, than the pressure/p_{atm} is used instead.
ln – natural logarithm, to use decimal one, one has to multiply whole term by 2.303 ($\ln(x) = 2.303·\log(x)$)
E_0 – standard half-reaction potential.

Half-cell potential

- $E = E^0 + R·T/(z·F) · \ln(c_{ox}/c_{red})$ simplifies at the standard conditions ($T = 25°C$, $p = 1atm$) to
  $E = E^0 + 0.0592/z · \log(c_{ox})$
- Thus, for 1M Li^+ solution in the lithium cell ($z = 1$, $c = 1$, $E^0 = -3.04$ V) it is
  $E = -3.04 + 0.0592 · \log(1) = -3.04$ [V]
- Although for 0.01M Li^+ solution it will be:
  $E = -3.04 + 0.0592 · \log(0.01) =$
  $= -3.04 + 0.0592 · (-2) = -3.1582$ [V]

Half-cell potential

Concentration change can cause change of the reaction direction in the cell. It is the surrounding – the relative potential of the other half-cell – that decides is it oxidation or reduction taking place spontaneously in the given half-cell. In the half-cell with the lower potential oxidation occurs, in the half-cell with the higher potential reduction occurs.

u=+1,10V

Zn^{2+}/Zn Cu^{2+}/Cu
$E_\ominus$ =-0,76V $E_\oplus$ =+0,34V
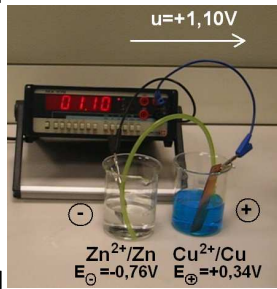
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Half-cell potential

Example: the cell consisting of silver and iron half-cells:

$E^0_{Fe3+/Fe2+}$ = 0.771 V

$E^0_{Ag+/Ag}$ = 0.799 V

For both solutions (both Fe^{3+} and Ag^+) at 1M conc.:

EMF = 0.799 – 0.771 = 0.028 [V] (28mV)

silver reduces and iron oxidizes

ALTOUGH for 0.01M Ag^+ and 1M Fe^{3+} solutions

EMF = 0.771 - (0.799 + (-2)·0.0592) ≈ 0.090[V] (90mV)

This time iron reduces and it is silver that oxidizes!

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