Electrochemical cells

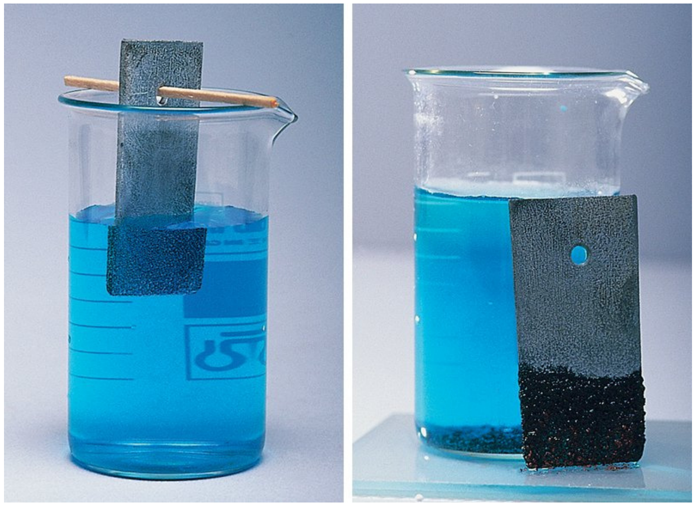
ver. 20191113

The redox reactions

An **oxidation-reduction** (**redox**) **reaction** is a type of chemical **reaction** that involves a transfer of electrons between two species.

iron in copper
sulphate solution

$Fe + Cu^{2+} = Fe^{2+} + Cu$



zinc in copper
sulphate solution

$Zn + Cu^{2+} = Zn^{2+} + Cu$

Can we separate the oxidation and reduction processes?

Electrodes, electrochemical cells

An **electrode** contains at least two conductive phases, one phase is electron conductor, another is ion conductor.

An **electrochemical cell** contains at least two electrodes which are connected to each other. Connection: through common liquid phases or a liquid-liquid junction.

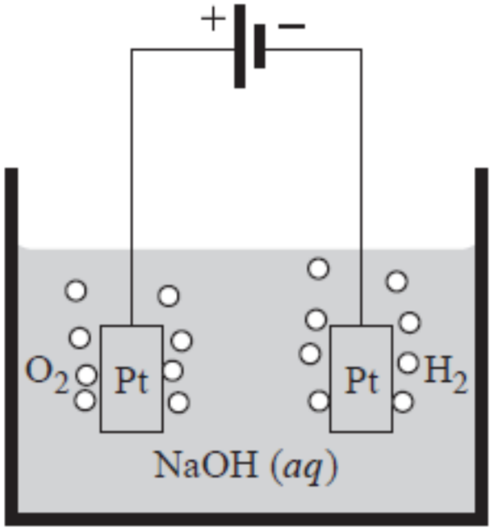


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Fig. 13.9

Electrolysis produces O_2 and H_2.

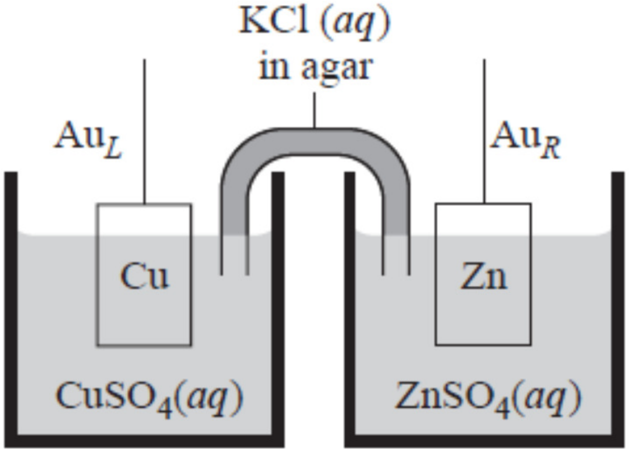

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Fig. 13.12

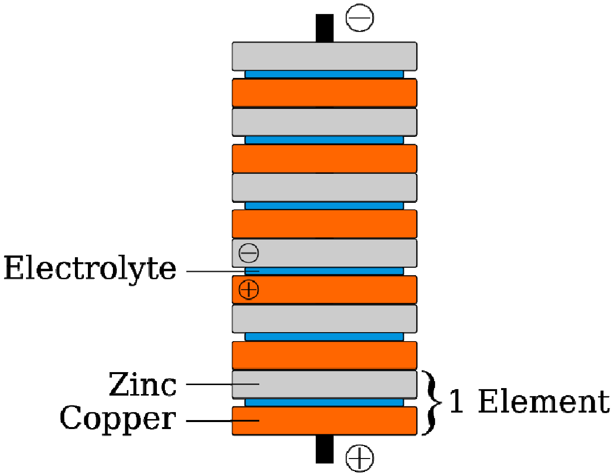
The Daniell cell.

Historical aspects

A. Volta invented the first device providing permanent electricity, the Valtaic pile (column).

It lead to the discovery of many new elements by electrolysis and the whole electrochemistry.

http://virtualtours.musei.unipd.it/itinerary/museo-di-storia-della-fisica/66/relic/volta-column-battery



By Borbrav, svg version by Luigi Chiesa - Image:Voltaic pile.png, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=5091724

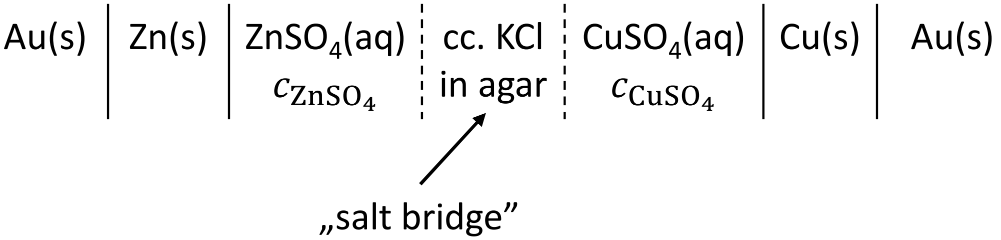
Alessandro Giuseppe Antonio Anastasio Volta
Born: 18 February 1745
Died: 5 March 1827
Italian physicist, chemist

The cell diagram

The most compact notation of an electrochemical cell (or electrode!) is the cell diagram.

The **cell diagram** must contain all the information which are needed to build essentially the same cell. It doesn't include physical dimensions, but describe the phases qualitatively and quantitatively, and gives their connections.

The cell diagram of the Daniell cell:



$$\mathrm{Au(s)} \;\Big|\; \mathrm{Zn(s)} \;\Big|\; \underset{c_{\mathrm{ZnSO_4}}}{\mathrm{ZnSO_4(aq)}} \;\vdots\; \underset{\text{in agar}}{\text{cc. KCl}} \;\vdots\; \underset{c_{\mathrm{CuSO_4}}}{\mathrm{CuSO_4(aq)}} \;\Big|\; \mathrm{Cu(s)} \;\Big|\; \mathrm{Au(s)}$$

„salt bridge”

Note: the terminals must be made from the same metal (e.g. gold metal (Au) here), but this choice is not unique, other metals can be used (e.g. Cu). Sometimes these phases are omitted from the cell diagram.

⋮	boundary of miscible phases
│	boundary of immiscible phases

The electrodes

Electrodes ara also called as half cells.

Electrode or half cell reactions:

The zinc electrode: $\left|\begin{array}{c|c} \mathrm{Zn(s)} & \mathrm{ZnSO_4(aq)} \\ & c_{\mathrm{ZnSO_4}} \end{array}\right.\vdots$

$$\mathrm{Zn} \leftrightarrows \mathrm{Zn^{2+}} + 2\mathrm{e^-}$$

The copper electrode: $\vdots\left.\begin{array}{c|c} \mathrm{CuSO_4(aq)} & \mathrm{Cu(s)} \\ c_{\mathrm{CuSO_4}} & \end{array}\right|$

$$\mathrm{Cu^{2+}} + 2\mathrm{e^-} \leftrightarrows \mathrm{Cu}$$

The cell reaction is the sum of the electrode reactions: $\mathrm{Zn} + \mathrm{Cu^{2+}} \leftrightarrows \mathrm{Zn^{2+}} + \mathrm{Cu}$

Electron number or **charge number of the cell reaction (*z*)** is the number of electrons moved in the redox reactions.

For the Daniell cell: $z = 2$

Classification of the electrodes

Based on the chemical systems involved:

- **First kind electrodes**: an element and its reduced/oxidized form is involved
  - **Metal electrodes**: metal / metal ions, e.g. Cu/Cu^{2+} electrode (or copper electrode)
  - **Gas electrodes**: the element is gas, e.g. H_2/H^+ electrode (or hydrogen electrode)
- **Second kind electrodes**: a metal contacts to its weakly soluble salt and it is immersed in the solution of the anion of the salt
  - e.g. $Ag/AgCl$ electrode
  - e.g. Hg/Hg_2Cl_2 electrode(or calomel electrode)
- **Redox electrodes**: both the oxidized and reduced forms are in the same phase
  - e.g. Fe^{2+}/Fe^{3+} electrode

Note: redox electrodes are NOT third kind electrodes (they exist, but it means something else).

Examples of electrode cell diagrams

Silver electrode (Ag/Ag$^+$ electrode):

⁞ AgNO$_3$(aq) | Ag(s) |
$c_{\mathrm{AgNO_3}}$

$$\mathrm{Ag^+_{(aq)}} + 2\mathrm{e^-} = \mathrm{Ag_{(s)}}$$

Hidrogen electrode (H$_2$/H$^+$ electrode):

⁞ H$^+$(aq) | H$_2$(g) |
$c_{\mathrm{H^+}}$

$$\mathrm{H^+_{(aq)}} + \mathrm{e^-} = {}^1\!/_2\, \mathrm{H_{2(g)}}$$

Silver/silver chloride electrode (Ag/AgCl electrode):

⁞ Cl$^-$ (aq) | AgCl(s) | Ag(s) |
$c_{\mathrm{Cl^-}}$

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

Calomel electrode (Hg/Hg$_2$Cl$_2$ electrode):

⁞ Cl$^-$ (aq) | Hg$_2$Cl$_2$(s) | Ag(s) |
$c_{\mathrm{Cl^-}}$

$$\mathrm{Hg_2Cl_{2\,(s)}} + 2\mathrm{e^-} = 2\mathrm{Hg_{(s)}} + 2\mathrm{Cl^-_{(aq)}}$$

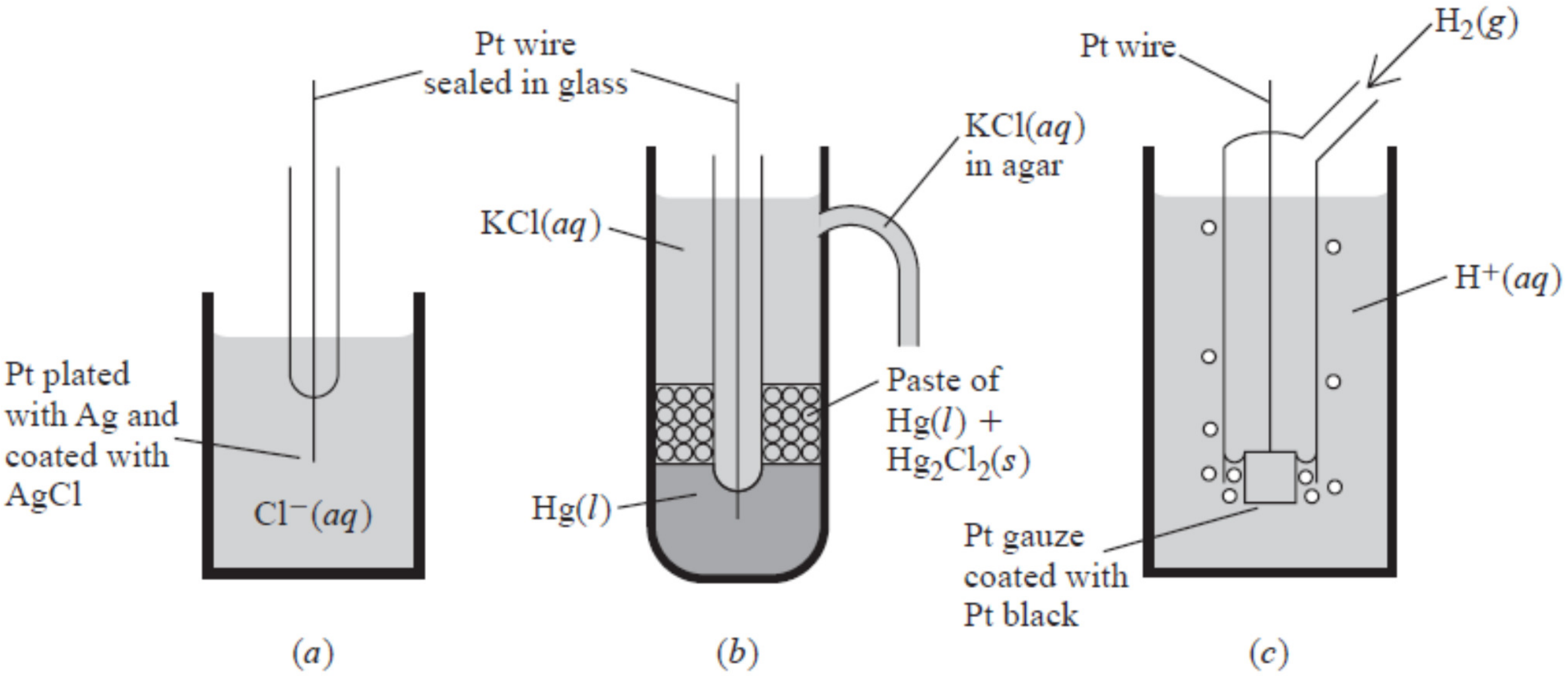
Iron redox electrode (Fe^{2+}/Fe^{3+} electrode):

⁞ Fe^{2+}(aq), Fe^{3+}(aq) | Pt(s) |
$c_{\mathrm{Fe^{2+}}}$, $c_{\mathrm{Fe^{3+}}}$

$$\mathrm{Fe^{3+}_{(aq)}} + \mathrm{e^-} = \mathrm{Fe^{2+}_{(aq)}}$$

Platinum metal is only for electric conductivity,
this material is not compulsory, others can be used.

Some electrodes of high practical importance



Ag/AgCl electrode calomel electrode hydrogen electrode

Levine: Physical Chemistry 6th Edition
Fig. 13.10

Basic notions

Galvanic cell: one kind of an electrochemical cell in which chemical reactions produce electric work.

Electrolytic cell: another kind of an electrochemical cell in which electric work cause chemical changes

Electrolysis: electric work cause chemical changes

Anode: the electrode on which mostly oxidation occures

Cathode: the electrode on which mostly reduction occures

Note: anode and cathode are not permanent attributes of the electrodes.

E.g. in this Daniell cell no electrolysis happens, neither electric work is produced (open circuit), therefore there are no anode and cathode!

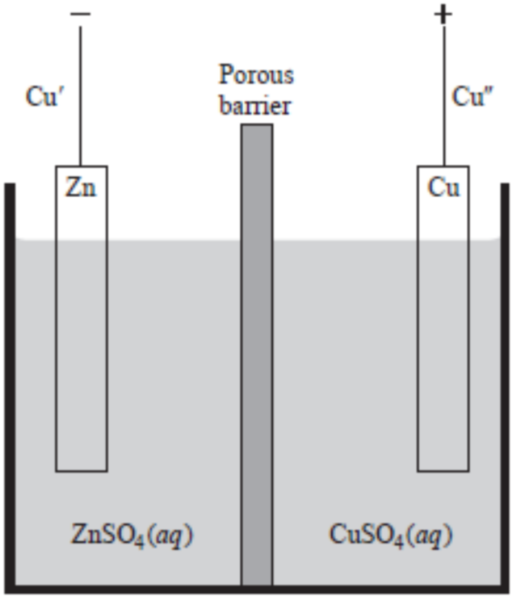


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Fig. 13.7 left

Open circuit Daniell cell.

Measurable quantities

Terminal voltage (*E*): the terminal potential difference measured according the cell diagram

$$E = \phi_{\mathrm{right}} - \phi_{\mathrm{left}}$$

We compare the potential of the electrode in the right in the cell diagram to that of in the left in the cell diagram.

Note: there are no other restrictions, current can flow, no statement about equilibrium.

Electromotive force (E_{MF}): the terminal voltage of an open circuit electrochemical cell which is equilibrium (except the liquid-liquid junctions).

In other words: the electromotive force is a limit of the terminal voltage where no current flows through the cell and equilibrium is everywhere (except the liquid-liquid junctions).

Note: electromotive force is not a real force, but a voltage.

Sign of E and E_{MF}

Terminal voltage: $E = \phi_{\mathrm{right}} - \phi_{\mathrm{left}}$

When the cell produce electric work E is positive, therefore the potential of the right electrode is higher than the left one. This due to the oxidation occured on the left electrode (oxidation: electrons are left on the terminal, can be called: anode), and the reduction on the right electrode (electrons are removed by the reduction process, can be called: cathode).

The spontaneous chemical process can be read from the cell diagram reading left to right:

Au(s) | Zn(s) | $ZnSO_4$(aq) $c_{\mathrm{ZnSO_4}}$ ¦ cc. KCl in agar ¦ $CuSO_4$(aq) $c_{\mathrm{CuSO_4}}$ | Cu(s) | Au(s)

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \leftrightarrows \mathrm{Zn}^{2+} + \mathrm{Cu}$$

When we measure negative voltage the spontaneous process is the reverse!

The same applies to the electromotive force.

Note: the sign of E changes if we reverse the cell diagram, but the cell reaction also reversed!

How to measure the electromotive force?

Measure the terminal voltage under specific circumstances:

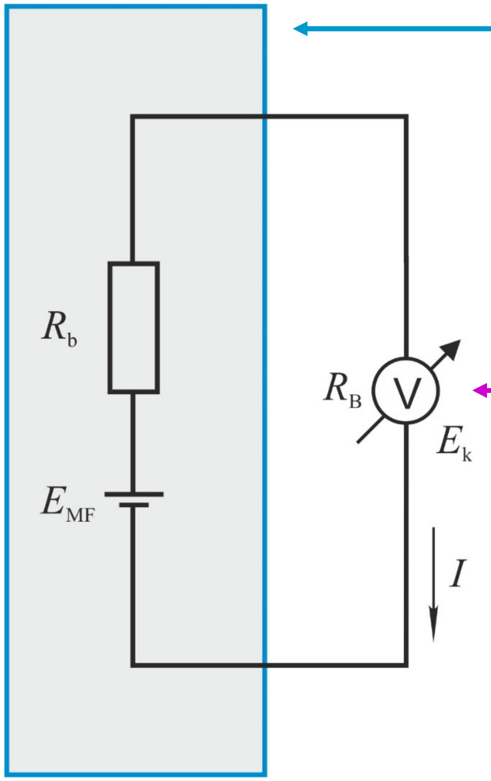
- No electric current flows between the terminals of the cell (I = 0).
- Equilibrium exist in each phases and interphases except the liquid-liquid junctions.

How to establish equilibrium? Compose your system and wait, wait, wait…

How to fulfill I = 0 AND measure the terminal voltage?

- ➢ Use a voltmeter of high internal resistance
- ➢ Use the compensation technique
- ➢ Use the extrapolation technique

E_{MF} measurement using a voltmeter of high internal resistance



We connect a voltmeter to the terminals of the electrochemical cell.

The internal resistance of the voltmeter must be very high.

If the conditions for the equilibrium are fulfilled the measured terminal voltage is a good approximation of the electromotive force.

E_{MF} measurement using a voltmeter of high internal resistance

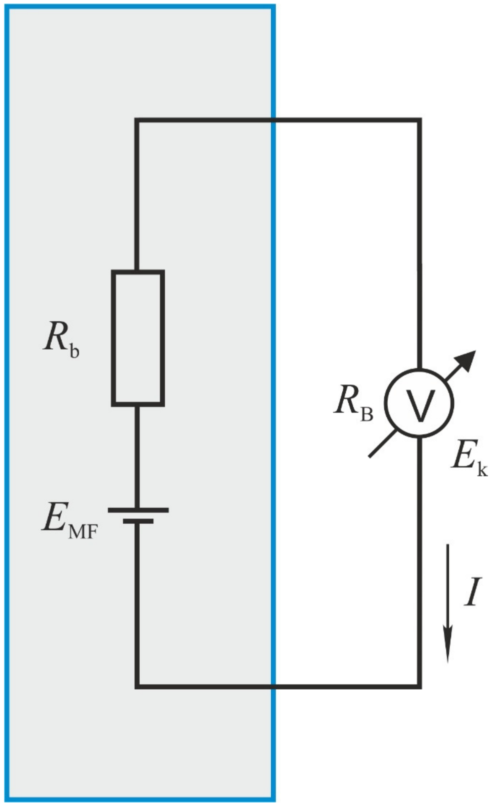
Let us write the Ohm's law for the whole circuit and the measuring resistance:

$$I = \frac{E_{\mathrm{MF}}}{R_{\mathrm{b}} + R_{\mathrm{B}}} \qquad I = \frac{E_{\mathrm{K}}}{R_{\mathrm{B}}}$$

The current written in two forms are the same:

$$\frac{E_{\mathrm{MF}}}{R_{\mathrm{b}} + R_{\mathrm{B}}} = \frac{E_{\mathrm{K}}}{R_{\mathrm{B}}}$$

$$E_{\mathrm{K}} = E_{\mathrm{MF}} \frac{R_{\mathrm{B}}}{R_{\mathrm{b}} + R_{\mathrm{B}}}$$



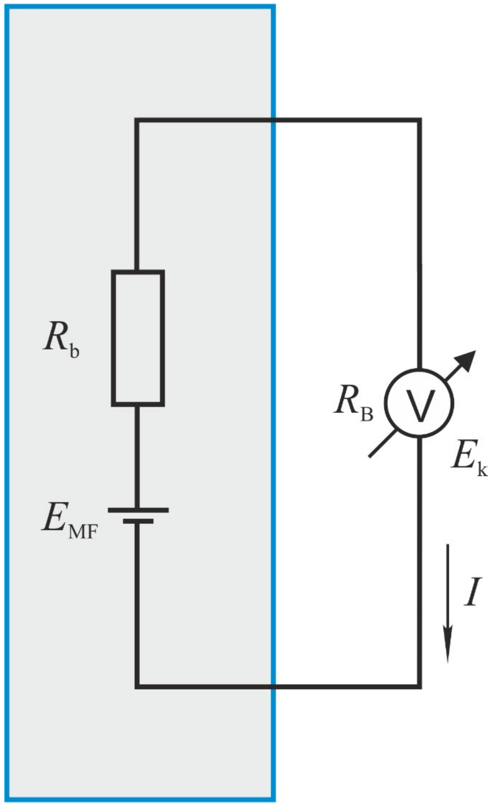
E_{MF} measurement using a voltmeter of high internal resistance

If $R_B >> R_b$, than R_b is negligible:

$$E_K = E_{MF}\frac{R_B}{\cancel{R_b} + R_B}$$

After simplification:

$$E_K \approx E_{MF}$$



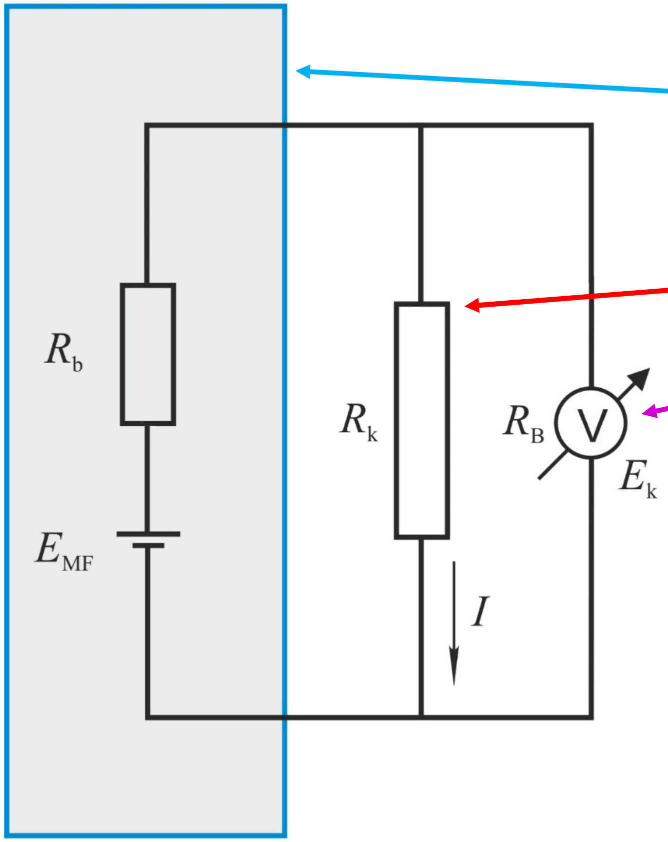
E_{MF} measurement using a voltmeter of high internal resistance

„If the conditions for the equilibrium are fulfilled the measured terminal voltage is a good approximation of the electromotive force.”

- We have to **wait enough time** for the equilibrium (it could be formed slowly at the interphases).
- The **measuring current ($I = \frac{E_K}{R_B}$) is negligible to the exchange current** of the electrodes. This case we are slightly out of equilibrium, but the shift is negligible.

Note: exchange current is explained in electrochemical kinetics.

E_{MF} measurement using the extrapolation technique



The electrochemical cell is loaded with different external resistances (R_k) and the voltage (potential drop) is measured on them.

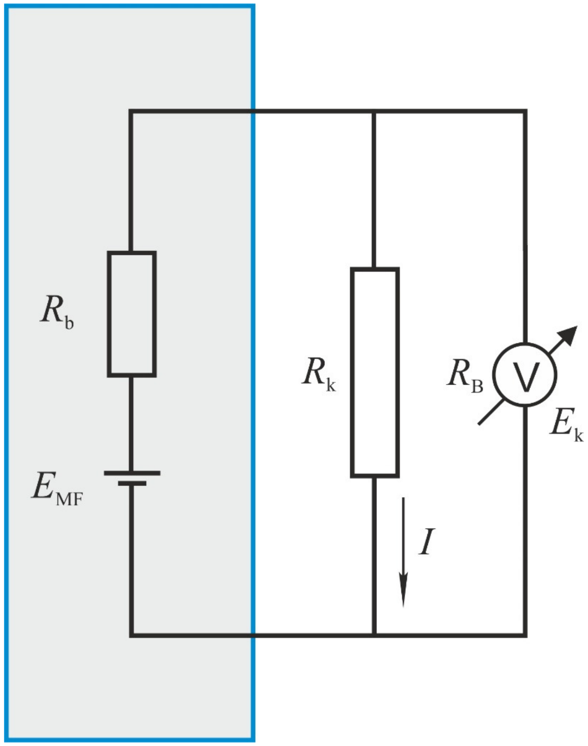
E_{MF} measurement using the extrapolation technique

The electromotive force drops on both the internal and external resistances:

$$E_{\mathrm{MF}} = E_{\mathrm{b}} + E_{\mathrm{k}}$$

Reordering it:

$$E_{\mathrm{k}} = E_{\mathrm{MF}} - E_{\mathrm{b}}$$



Let us write Ohm's law for the internal and the external resistances:

$$E_{\mathrm{b}} = IR_{\mathrm{b}} \qquad I = \frac{E_{\mathrm{K}}}{R_{\mathrm{k}}}$$

Using these:

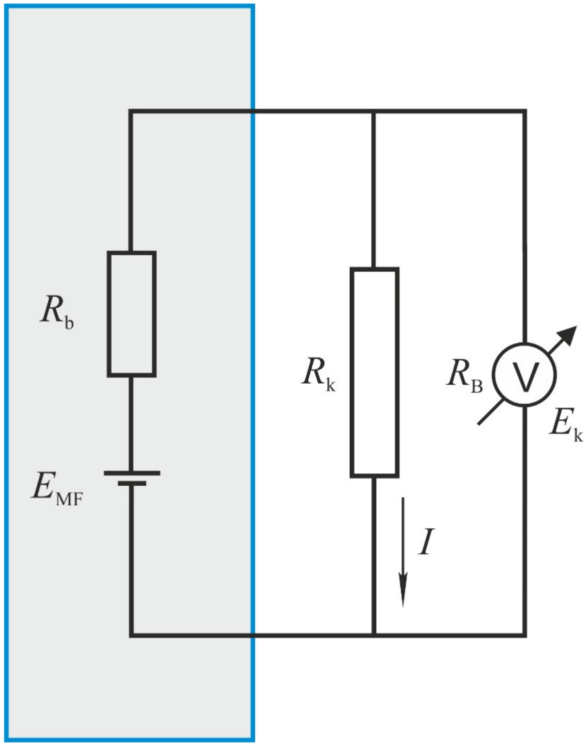
$$E_{\mathrm{k}} = E_{\mathrm{MF}} - R_{\mathrm{b}}\frac{E_{\mathrm{k}}}{R_{\mathrm{k}}}$$

E_{MF} measurement using the extrapolation technique

$$E_{\mathrm{k}} = E_{\mathrm{MF}} - R_{\mathrm{b}} \frac{E_{\mathrm{k}}}{R_{\mathrm{k}}}$$

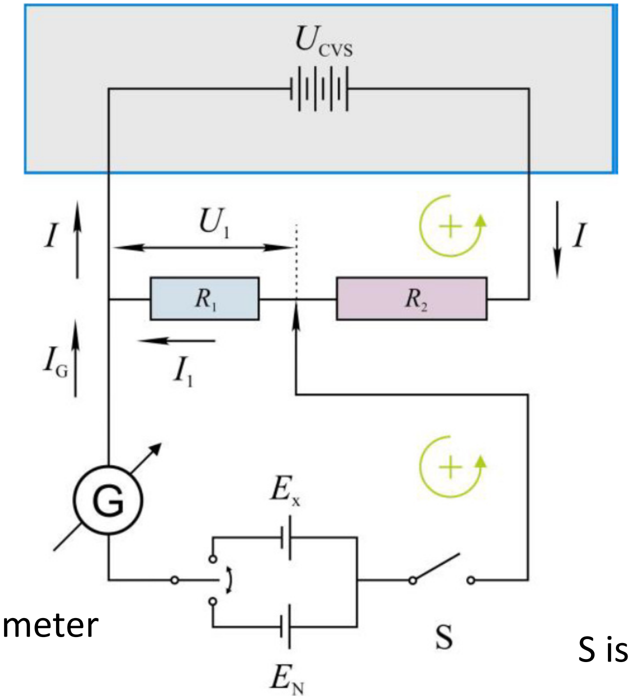
According to this the measurable voltage – current resistance function is linear. Note: $I = \frac{E_{\mathrm{K}}}{R_{\mathrm{k}}}$

The slope of it is $-R_{\mathrm{b}}$ (negative signed value of the internal resistance), the intercept is E_{MF} (the electromotive force).



E_{MF} measurement
using the compensation technique

The zero current condition can be directly fulfilled if we put **the same voltage, but with opposite sign to the electromotive force** (we compensate it).



U_{CVS} is the compensing voltage source

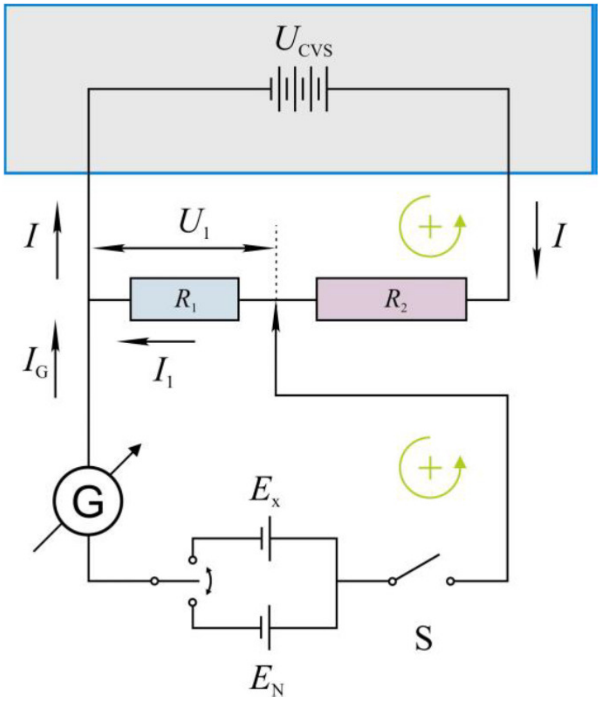
R_1 and R_2 are adjustable resistances

G is the ammeter

S is a switch

E_X is electrochemical cell with the unknown electromotive force
E_N is a voltage source having a well-known voltage value (standard cell)

E_{MF} measurement using the compensation technique



If the S switch is open, the current in the upper circuit containing the voltage source equals $I = U_{\mathrm{CVS}}/(R_1 + R_2)$. If U_{CVS} and $R_1 + R_2$ are constant *I* remains constant during the measurement.

If we switch S on to E_{X}: $E_{\mathrm{X}} = I_{\mathrm{X}} \cdot R_{\mathrm{X}}$
If we switch S on to E_{N}: $E_{\mathrm{N}} = I_{\mathrm{N}} \cdot R_{\mathrm{N}}$

Therefore $\frac{E_{\mathrm{X}}}{R_{\mathrm{X}}} = \frac{E_{\mathrm{N}}}{R_{\mathrm{N}}}$ and $E_{\mathrm{X}} = E_{\mathrm{N}} \frac{R_{\mathrm{X}}}{R_{\mathrm{N}}}$

Knowing the resistance ratios and the voltage of the standard cell the electromotive force can be determined.

The electrode potential

Terminal voltage and electromotive force are for the whole cell, but it is worth to introduce an electrode related quantity, the **electrode potential (ε)**: the terminal voltage of the electrochemical cell which left electrode is in equilibrium.
The electrode potential of the right electrode is referenced to the left electrode.

If the right electrode is also in equilibrium we have the **equilibrium electrode potential (ε_e)**. This is an electrode centric name of the electromitive force.

The junction potential

At liquid-liquid junctions there is no equilibrium, therefore a small potential drop occurs. We can emphasize it putting another member into the addition:

$$E = \phi_{\text{right}} - \phi_{\text{left}} + \phi_{\text{junction}}$$

Our aim is all the time to make experimentally this junction potential low
when we want to measure electromotive force.

Potential of the cell reaction

During the chemical reaction according to the equation of the cell reaction *zF* charge is transferred and the maximum work can be given as the Gibbs free energy change of the cell reaction : $W_{\mathrm{max}} = \Delta_{\mathrm{r}}G$

The **potential of the cell reaction** $(\boldsymbol{E}_{\mathbf{cell}})$ is defined as: $E_{\mathrm{cell}} = -\frac{\Delta_{\mathrm{r}}G}{zF}$

Note that $\boldsymbol{\Delta_r G}$ **and *z* are extensive quantities** (depend on the stoichiometric coefficients of the cell reaction), but $\boldsymbol{E}_{\mathbf{cell}}$ **is intensive**!

If we determine the potential of the cell reaction $\Delta_{\mathrm{r}}G$ can be calculated:

$$\Delta_{\mathrm{r}}G = -zFE_{\mathrm{cell}}$$

The electromotive force without the liquid-liquid junction potential is a good approximation of the potential of the cell reaction: $E_{\mathrm{cell}} \approx E_{\mathrm{MF}}$

Practical considerations

When the cell is in equilibrium it is unable to do any work ($\Delta_\mathrm{r}G = 0$) and $E_\mathrm{cell} = 0$.

If we know E_cell we can calculate the theorethical maximum work of the cell.

Problem: E_cell of a Daniell cell is 1324 mV. Estimate the maximum work can be done by the cell if the salt concentration of both electrolytes are 0.15 mol/dm^3 and we have 70 ml solutions, respectively!

For the Daniell cell z=2.

$$\Delta_\mathrm{r}G = -zFE_\mathrm{cell} = -2 \cdot 96485 \frac{\mathrm{C}}{\mathrm{mol}} \cdot 1.324\ \mathrm{V} = 255492.28\ \mathrm{J/mol}$$

The maximum work of the cell is appr. 255.5 kJ/mol.

We have 0.0105 mol Cu^{2+} ions (calculated from c and V) and they will be consumed while the spontaneous reaction occurs, therefore the maximum work can be done by this reaction is W_max = 0.0105 mol· 255.5 kJ/mol = 2.68275 kJ ≈ 2.7 kJ

The standard potential of the cell reaction

E_{cell} can be expressed using standard values and activities:

$$E_{\mathrm{cell}} = -\frac{\Delta_{\mathrm{r}} G}{zF} = -\frac{\Delta_{\mathrm{r}} G^{\circ} + RT\sum_{\mathrm{i}} \nu_{\mathrm{i}} \ln a_{\mathrm{i}}}{zF} = E^{\circ}_{\mathrm{cell}} - \frac{RT}{zF}\sum_{\mathrm{i}} \nu_{\mathrm{i}} \ln a_{\mathrm{i}} = E^{\circ}_{\mathrm{cell}} - \frac{RT}{zF}\ln K_{\mathrm{a}}$$

where a_{i} is the relative activity of component i, $E°$ is the standard potential of the cell reaction.

In equilibrium $\Delta_{\mathrm{r}} G = 0$, therefore $zFE_{\mathrm{cell}} = 0$, so $E_{\mathrm{cell}} = 0$.

This case $E^{\circ}_{\mathrm{cell}} - \frac{RT}{zF}\ln K_{\mathrm{a}} = 0$, reordered to the equilibrium constant: $\ln K_{\mathrm{a}} = \frac{zFE^{\circ}_{\mathrm{cell}}}{RT}$

Problem: The standard potential of the Daniell cell is 1.101 V at 25 °C.
Calculate the equilibrium constant!

$$\ln K_{\mathrm{a}} = \frac{zFE^{\circ}_{\mathrm{cell}}}{RT} = \frac{2 \cdot 96485\ \frac{\mathrm{C}}{\mathrm{mol}} \cdot 1.101\ \mathrm{V}}{8.314\ \frac{\mathrm{J}}{\mathrm{mol \cdot K}} \cdot 298.15\ \mathrm{K}} = 85.71$$

$$K_{\mathrm{a}} = 1.67 \cdot 10^{37}$$

The potential of the electrode reaction

It is useful to define a quantity, the **potential of the electrode reaction (E_{r})** which is similar to E_{cell}, but correspond to one electrode only.

Potential of the electrode reaction is the E_{cell} of the electrochemical cell where the electrode in interest is at right hand side of the cell diagram and the electrode at left hand side is a standard hydrogen electrode.

Note 1: **the potential of the electrode reaction of the standard hydrogen electrode is 0** by definition.

Note 2: similar to the electrode potential, but not a measurable quantity and the reference electrod can not be any equilibrium electrode, but the standard hydrogen electrode.

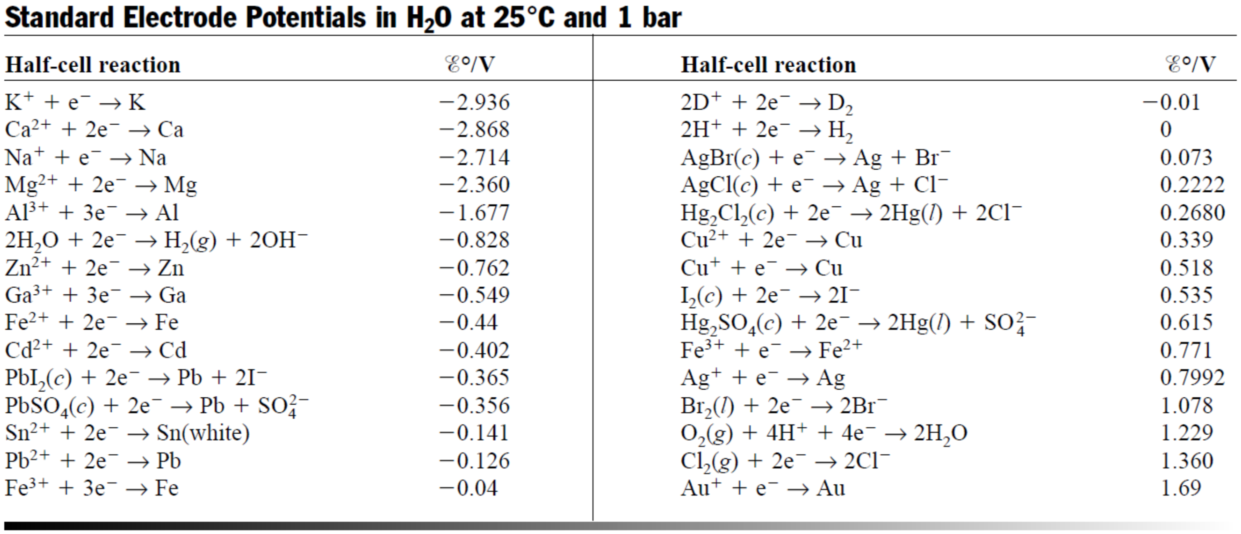
As a consequence: $E_{\mathrm{cell}} = E_{\mathrm{r,right}} - E_{\mathrm{r,left}}$

The Nernst equation

The potential of the electrode reaction depends on the activity of species, temperature and pressure according to the **Nernst equation**.

$$E_\mathrm{r} = E_\mathrm{r}^\circ - \frac{RT}{zF}\sum_\mathrm{i} \nu_\mathrm{i} \ln a_\mathrm{i}$$

where E_r° is the standard potential of the electrode reaction (also called standard electrode potential).



Standard Electrode Potentials in H_2O at 25°C and 1 bar

Half-cell reaction	$\mathscr{E}^\circ$/V	Half-cell reaction	$\mathscr{E}^\circ$/V
$K^+ + e^- \rightarrow K$	−2.936	$2D^+ + 2e^- \rightarrow D_2$	−0.01
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.868	$2H^+ + 2e^- \rightarrow H_2$	0
$Na^+ + e^- \rightarrow Na$	−2.714	$AgBr(c) + e^- \rightarrow Ag + Br^-$	0.073
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.360	$AgCl(c) + e^- \rightarrow Ag + Cl^-$	0.2222
$Al^{3+} + 3e^- \rightarrow Al$	−1.677	$Hg_2Cl_2(c) + 2e^- \rightarrow 2Hg(l) + 2Cl^-$	0.2680
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$	−0.828	$Cu^{2+} + 2e^- \rightarrow Cu$	0.339
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.762	$Cu^+ + e^- \rightarrow Cu$	0.518
$Ga^{3+} + 3e^- \rightarrow Ga$	−0.549	$I_2(c) + 2e^- \rightarrow 2I^-$	0.535
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44	$Hg_2SO_4(c) + 2e^- \rightarrow 2Hg(l) + SO_4^{2-}$	0.615
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.402	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$PbI_2(c) + 2e^- \rightarrow Pb + 2I^-$	−0.365	$Ag^+ + e^- \rightarrow Ag$	0.7992
$PbSO_4(c) + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.356	$Br_2(l) + 2e^- \rightarrow 2Br^-$	1.078
$Sn^{2+} + 2e^- \rightarrow Sn(white)$	−0.141	$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.360
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04	$Au^+ + e^- \rightarrow Au$	1.69

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Table 13.1

Look at the direction of all reactions! **The electrode reactions are written as reduction reactions by convention.**

Nernst equation in practice

Individual activities are not measurable, therefore the Nernst equation is used with **molar concentrations** in the practice. The structure of this equation remains the same, but the standard value includes the activity -> concentration conversion, the activity coefficients. It is not a real standard, therefore called **formal standard potential.**

$$E_\mathrm{r} = E_\mathrm{c}^{\circ\prime} - \frac{RT}{zF}\sum_\mathrm{i} \nu_\mathrm{i} \ln\left({}^{c_\mathrm{i}}/_{c^\circ}\right)$$

where c° is the standard concentration (1 mol/dm^3).

If we have a simple metal electrode the electrode reaction can be written as:

$$\mathrm{M}^{z+} + z\mathrm{e}^- = \mathrm{M}$$

And the potential of the electrode reaction:

Be aware of the sign!

$$E_\mathrm{r} = E_{\mathrm{c,M/M}^{z+}}^{\circ\prime} + \frac{RT}{zF}\ln\left({}^{c_{\mathrm{M}^{z+}}}/_{c^\circ}\right)$$

Nernst equation in practice

Problem: Calculate the potential of the copper/copper ion electrode if the electrolyte solution contains 0.087 mol/litre $\mathrm{CuSO_4}$and *T* =22.4 °C!

The electrode reaction: $\mathrm{Cu^{2+} + 2e^- = Cu}$

$E^{\circ\prime}_{\mathrm{c,M/M}^{z+}}$ = 0.339 V

The potential of the electrode reaction:

$$E_\mathrm{r} = E^{\circ\prime}_{\mathrm{c,Cu/Cu^{2+}}} + \frac{RT}{2F}\ln\left({}^{c_{\mathrm{Cu^{2+}}}}\!\big/_{c^\circ}\right)$$

$$= 0.339\ \mathrm{V} + \frac{8.314\,\frac{\mathrm{Pa\cdot m^3}}{\mathrm{mol\cdot K}} \cdot 295.55\ \mathrm{K}}{2 \cdot 96485\,\frac{\mathrm{C}}{\mathrm{mol}}}\ln\left(\left.0.087\,\frac{\mathrm{mol}}{\mathrm{dm^3}}\right/ 1\,\frac{\mathrm{mol}}{\mathrm{dm^3}}\right) = 0.308\ \mathrm{V}$$

Potentiometry

Potentiometry is an electroanalytical method which utilizes the Nernst equation for concentration determination.

Problem: The electrode potential of the silver electrode is 484 mV versus saturated calomel electrode (SCE) at 27 °C. $\varepsilon_{\mathrm{SCE}} = 240\ \mathrm{mV};\ \varepsilon^{\circ\prime}_{\mathrm{Ag/Ag^+}} = 0.799\ \mathrm{V}$
Calculate the silver ion concentration!

$\varepsilon_{\mathrm{r,Ag/Ag^+}} = 484\ \mathrm{mV} + 240\ \mathrm{mV} = 724\ \mathrm{mV} = 0.724\ \mathrm{V}$

Let us write the Nernst equation for this electrode! $E_{\mathrm{r}} = E^{\circ\prime}_{\mathrm{c,Ag/Ag^+}} + \frac{RT}{F}\ln\left({}^{c_{\mathrm{Ag^+}}}/_{c^\circ}\right)$

After substitution: 0.724 V = 0.799 V + 8.314 J/(molK) · $300.15\ \mathrm{K}/96485\ \frac{\mathrm{C}}{\mathrm{mol}} \cdot \ln\left({}^{c_{\mathrm{Ag^+}}}/_{c^\circ}\right)$

$\ln\left({}^{c_{\mathrm{Ag^+}}}/_{c^\circ}\right) = -2.8998$

$c_{\mathrm{Ag^+}} = 0.055\,\frac{\mathrm{mol}}{\mathrm{dm^3}}$

Connection of the potential of the Ag and the Ag/AgCl electrodes

For the silver electrode: $E_\mathrm{r} = E^\circ_{\mathrm{Ag/Ag^+}} + \frac{RT}{F}\ln\left({}^{a_{\mathrm{Ag^+}}}/_{a_{\mathrm{Ag}}}\right)$

In the Ag/AgCl electrode the potential depends on the activity of silver ions, therefore the same equation is valid! $E_\mathrm{r} = E^\circ_{\mathrm{Ag/Ag^+}} + \frac{RT}{F}\ln\left({}^{a_{\mathrm{Ag^+}}}/_{a_{\mathrm{Ag}}}\right)$
However, if the solution is in equlibrium with silver chloride salt the silver ion concentration depends on the chloride ion concentration through the solubility product constant.
$L = a_{\mathrm{Ag^+}} \cdot a_{\mathrm{Cl^-}}$

$$E_\mathrm{r} = E^\circ_{\mathrm{Ag/Ag^+}} + \frac{RT}{F}\ln\left({}^{L}/_{a_{\mathrm{Ag}}a_{\mathrm{Cl^-}}}\right) = E^\circ_{\mathrm{Ag/AgCl}} - \frac{RT}{F}\ln(a_{\mathrm{Cl^-}})$$

The chloride ion concentration typically large in the Ag/AgCl electrodes (0.1 M – saturated KCl or NaCl salt solution), therefore its potential is very stable.

Potential of the hydrogen electrode

The electrode reaction: $H^+_{(aq)} + e^- = {}^1/_2\, H_{2(g)}$

$\vdots$ $H^+(aq)$ $\big|$ $H_2(g)$ $\big|$
c_{H^+}

The **potential of the hydrogen electrode** depends on the activity of the hydrogen ions and the partial pressure of hydrogen gas:

$$E_r = \frac{RT}{F} \ln \left({}^{a_{H^+}}\Big/_{\frac{p_{H_2}}{p^\circ}} \right) \qquad p^\circ = 1 \text{ bar}$$

Note: $E^\circ_{H_2/H^+} = 0$

Standard hydrogen electrode means that both the temperature, pressure and hydrogen ion activity are standards in the electrode. This is simple from the theoretical point of view, but very hard to establish and maintain from the experimental point of view.

Measurement of pH

Sørensen defined pH in a simple form in 1909: $\mathrm{pH} = -\lg\left({c_{\mathrm{H}^+}}/_{(1\ \mathrm{mol/dm^3})}\right)$

But we know that **for not very diluted solutions activities have to be used** instad of concentrations: $\mathrm{pH} = -\lg(a_{\mathrm{H}^+})$

Problem: induvidual activities can not be measured.

Solution: **Let us define the pH scale by measument of electromotive force!**

Measure the E_{MF} of two similar cell under the same circumstances avoiding the liquid-liquid junction potential: one electrode is the same reference electrode, the other is a hydrogen ion selective electrode with either the unknown pH solution or a standard pH solution (S).

Note: not only the hydrogen electrode is sensitive to the hydrogen ion activity!

E.g. quinhydrone electrode, glass electrode

Measurement of pH

Having the same reference electrode and circumstances the E_{MF} difference is related to the hydrogen ion activity:

$$\Delta E_{\mathrm{MF}} = E_{\mathrm{MF,X}} - E_{\mathrm{MF,S}} = \frac{RT}{F} \ln\left({}^{a_{\mathrm{H^+,X}}}/_{a_{\mathrm{H^+,S}}} \right)$$

Reordering and introducing pH we have this equation:

$$\mathrm{pH(X)} = \mathrm{pH(S)} + \frac{E_{\mathrm{MF(S)}} - E_{\mathrm{MF(X)}}}{\frac{RT}{F}\ln(10)}$$

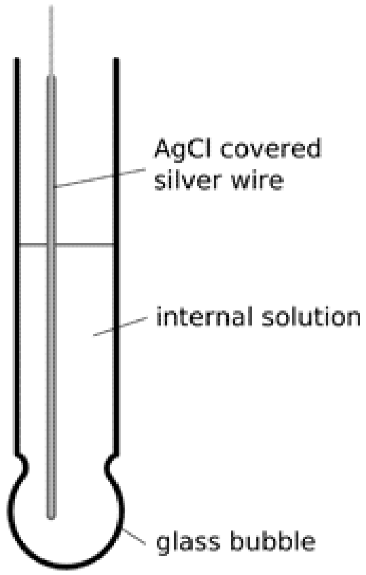
Where the standard pH value solutions are coming from?

They can be bought from the market or created in the lab using literature prescriptions.

Measurement of pH using glass electrode

Glass electrode is a special hydrogen ion selective electrode. The potential of the glass electrode mostly depends on the hydrogen ion activity.

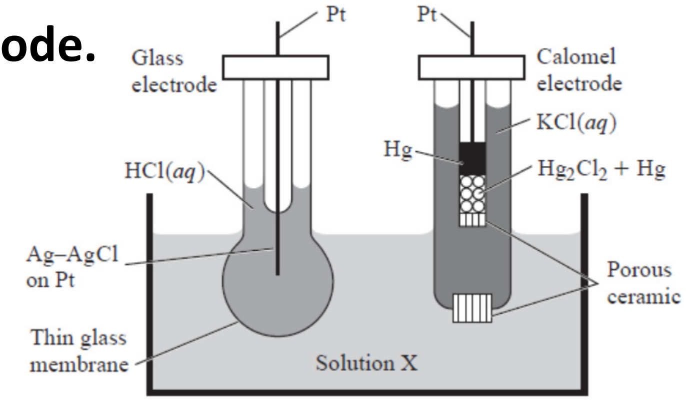
The sensitive part of his electrode is a very thin layer of glass. The potential drop through this layer shows the same logarithmic relationship to the hydrogen ion activity as for the hydrogen electrode.



The glass electrode does not work well in strongly acid or high alkaline ion solutions.

To measure pH one has to **compose an electrochemical cell with a reference electrode.**

Due to this incenvenience,
we typically use combined glass electrode.



Levine: Physical Chemistry 6th Edition
Fig. 13.17 (a)

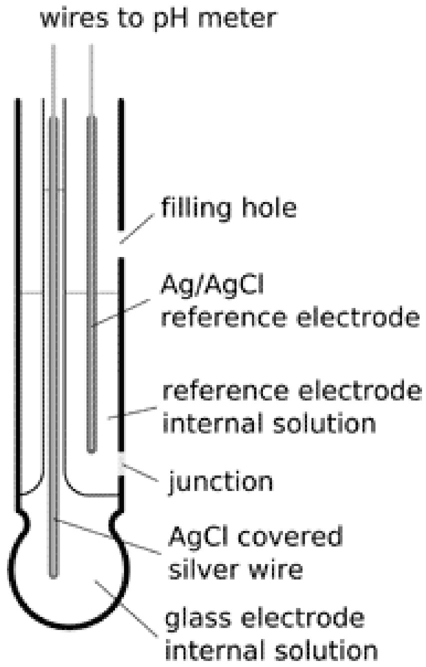
Measurement of pH using glass electrode

The combined glass electrode is not one electrode, but a whole electrochemical cell!

There are special devices (called **pH meters**) which
can be calibrated and provide the pH of a solution directly.

HI 2020 edge© pH meter
with combined glass electrode

Methrohm
Combined pH glass electrode



The concentration cells

When we form an electrochemical cell from two electrodes which electrode reactions differ we have a real chemical cell reaction and the cell is called chemical cell.

However, we can use two electrodes having the same electrode reaction, but different concentration of electrolyte. In this case a **concentration cell** is formed.

E.g.

Cu(s)	$CuSO_4$(aq)	cc. KCl	$CuSO_4$(aq)	Cu(s)
	$c_{\mathrm{CuSO_4,left}}$	in agar	$c_{\mathrm{CuSO_4,right}}$	

The concentration cells can work until the concentrations of the two sides become the same.

$$E_{\mathrm{cell}} = E_{\mathrm{r,right}} - E_{\mathrm{r,left}} = -\frac{RT}{zF}\sum_{\mathrm{i}} \ln a_{\mathrm{i}}$$

Note: the standard electode reaction potential is the same for both electrodes, therefore does not count in the potential of the cell reaction.

Electrolysis

Electrolysis: electric work cause chemical changes.

chemical changes + physical changes

electrode reactions polarization, heat effect of the current

In general, electrode reactions resulting the lowest possible potential difference will take place.

E.g. in sodium sulphate solution in water we can produce hydrogen and oxygen by electrolysis on platinum metals, and neither sodium is formed, nor the sulphate ions are decomposed. But if we use mercury metal sodium ions are reduced forming sodium amalgam.

In a more sophisticated way: more than one chemical reaction can run parallel in the same electrode with different speed. For details see the Electrochemical kinetics.

Faraday’s laws of electrolysis

Quantitative relationships stating that the amount of material produced at an electrode (or liberated from it) during an electrochemical reaction is directly proportional to the total conducted charge.

Do not memorize the Faraday’s laws! These are simple application of basic electric laws and a stoichiometric calculation.

Basic equations:

$$q = I \cdot t$$

$$q = F \cdot n_{\mathrm{e}}$$

Simple calculation

Problem:

Let us electrolyze a copper sulphate solution with 2.0 A current for 1.2 hours. How many gramms of copper is deposited on the anode and the cathode?

The electrode reaction: $\mathrm{Cu}^{2+} + 2\mathrm{e}^- = \mathrm{Cu}$
It goes on the cathode (reduction), therefore 0 g Cu is deposited on the anode.

$$q = I \cdot t = 2\ \mathrm{A} \cdot 1.2 \cdot 3600\ \mathrm{s} = 8640\ \mathrm{C}$$

$$n_\mathrm{e} = \frac{q}{F} = \frac{8640\ \mathrm{C}}{96485\ \frac{\mathrm{C}}{\mathrm{mol}}} = 0.0895476\ \mathrm{mol}$$

$$n_\mathrm{Cu} = \frac{n_\mathrm{e}}{2} = 0.0447738\ \mathrm{mol}$$

$$m_\mathrm{Cu} = n_\mathrm{Cu} \cdot M_\mathrm{Cu} = 0.0447738\ \mathrm{mol} \cdot 63.5\,\frac{\mathrm{g}}{\mathrm{mol}} = 2.8431\ \mathrm{g} \approx 2.8\ \mathrm{g}$$

2.8 g copper is deposited on the cathode.

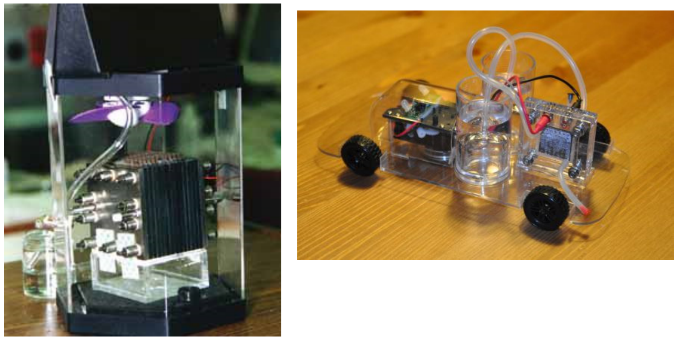
Batteries

Battery: a single galvanic cell or several galvanic cells connected in series intended to produce electrocity.

Classified into several categories, but the most important one is the working principle.

- **Primary batteries**: **reactants are built in** and **cannot be recharged** once depleted
  e.g. alkaline batteries, zinc–carbon batteries

- **Secondary batteries**: **reactants are built in**, but **can be recharged**
  e.g. lead-acid batteries, lithium batteries



- **Fuel cells**: the **reactants are continously fed** to the electrodes
  e.g. Solid Oxide, Proton Exchange Membrane

Important features of batteries

1. Energy Density: The energy density is the total amount of energy that can be stored per unit mass or volume. This determines how long your device stays on before it needs a recharge.

2. Power Density: Maximum rate of energy discharge per unit mass or volume. Low power: laptop, i-pod. High power: power tools.

3. Safety: It is important to consider the temperature at which the device you are building will work. At high temperatures, certain battery components will breakdown and can undergo exothermic reactions. High temperatures generally reduces the performance of most batteries.

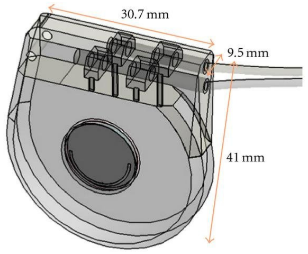
4. Life cycle durability: The stability of energy density and power density of a battery with repeated cycling (charging and discharging) is needed for the long battery life required by most applications.

5. Cost: Cost is an important part of any engineering decisions you will be making. It is important that the cost of your battery choice is commensurate with its performance and will not increase the overall cost of the project abnormally.

6. Stability of the output voltage: when the batteries are exhausted its terminal voltage drops. The less voltage decrease the longer time is the best.

7. Enviromental friendness: Heavy metals are especially dangerous, but all kind of batteries could cause potential environmental problems. Production and full recollection are impontant.

8. Size: There are critical applications, like pacemakers.



Typical dimensions of cardiac pacemaker battery pack, must last for 7-10 years.