Electrochemistry–
A Question of Potential

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FOUNDATION

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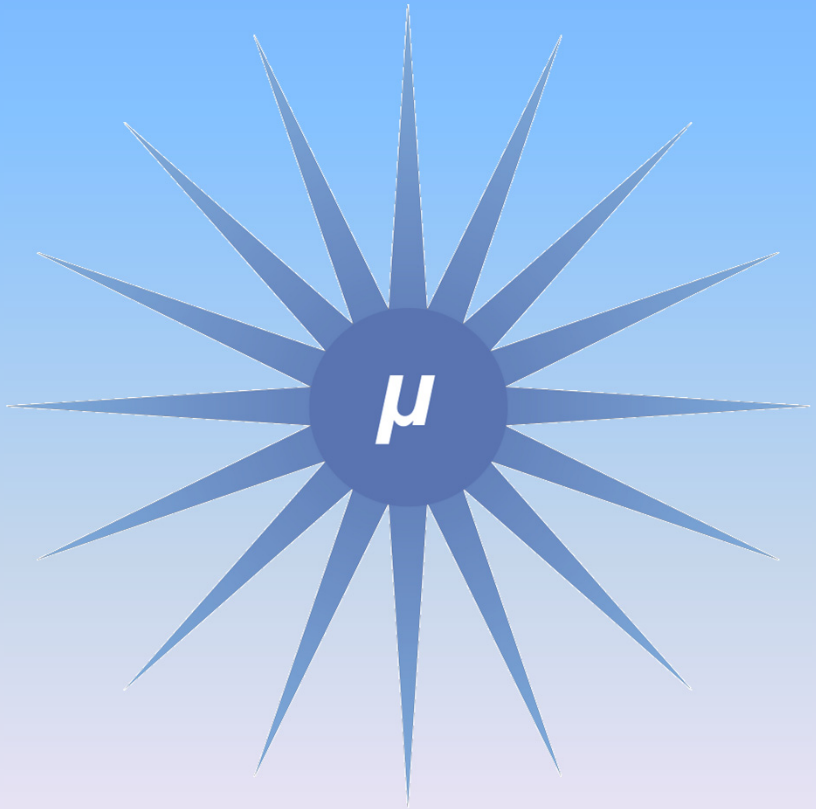
Outline

1. Introduction—Chemical Potential
2. Redox Reactions
3. Galvani Potential and Half-Cells
4. Redox Potentials and Galvanic Cells
5. Outlook

1. Introduction—Chemical Potential

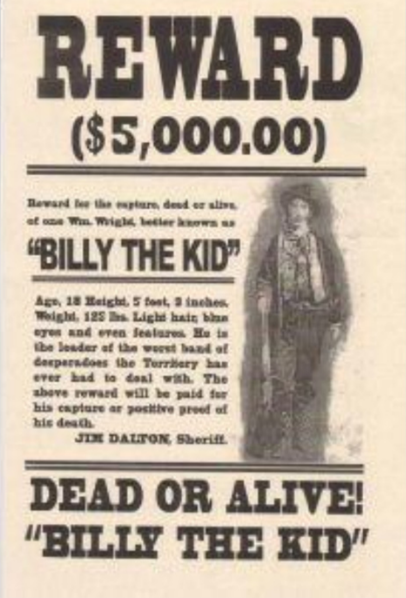


Fundamental Concept

We propose to introduce the chemical potential μ directly (i.e. without detour via other thermodynamic quantities) as "*tendency to transform*."

This "*tendency to transform*" is characterized by its most important and easily recognizable properties like a wanted person.

The phenomenological definition may be supplemented by a direct measuring procedure.



REWARD

($5,000.00)

Reward for the capture, dead or alive, of one Wm. Wright, better known as

"BILLY THE KID"

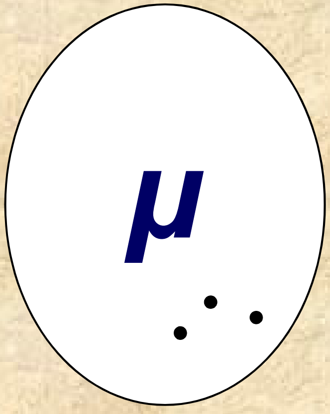
Age, 18 Height, 5 feet, 3 inches. Weight, 125 lbs. Light hair, blue eyes and even features. He is the leader of the worst band of desperadoes the Territory has ever had to deal with. The above reward will be paid for his capture or positive proof of his death.

JIM DALTON, Sheriff.

DEAD OR ALIVE!

"BILLY THE KID"

Wanted



- The tendency of a substance
  - to *react* with other substances,
  - to undergo a phase *transition*,
  - to *redistribute* in space,

  can be expressed by the same quantity —namely its chemical potential μ.

- The strength of this tendency, meaning the numerical value of μ
  - is determined by the *nature* of the substance, as well as
  - by its *milieu* (temperature, pressure, concentration, ...),
  - but <u>not</u> by the nature of reaction partners or the products.
- A *reaction*, *transition*, *redistribution* can only proceed spontaneously if the tendency for the process is more pronounced in the initial state than in the final state, i.e. it exists a

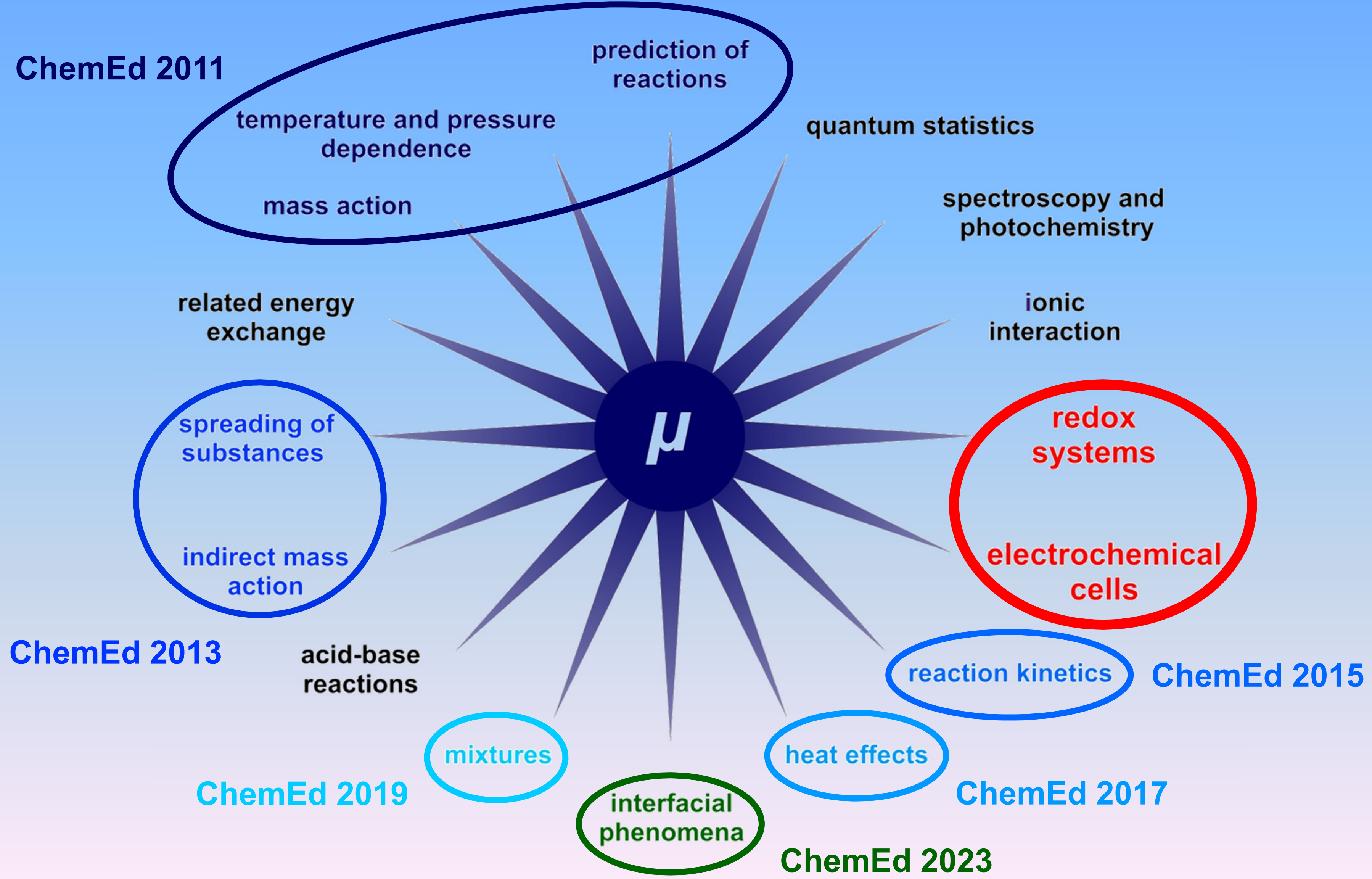
potential drop: $$\sum_{\text{initial}} \mu_i > \sum_{\text{final}} \mu_j$$

Application

The proposed approach is elementary, does not require any special previous knowledge and immediately leads to results that can be utilized practically. This allows to start teaching the subject even at introductory high school level.

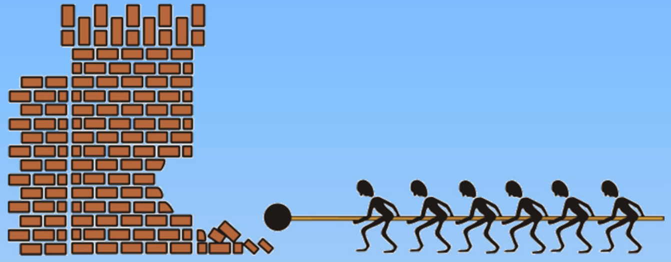
Numerous simple and safe demonstration experiments contribute essentially to deepen comprehension and forge links with everyday experiences.

Key Role of the Chemical Potential



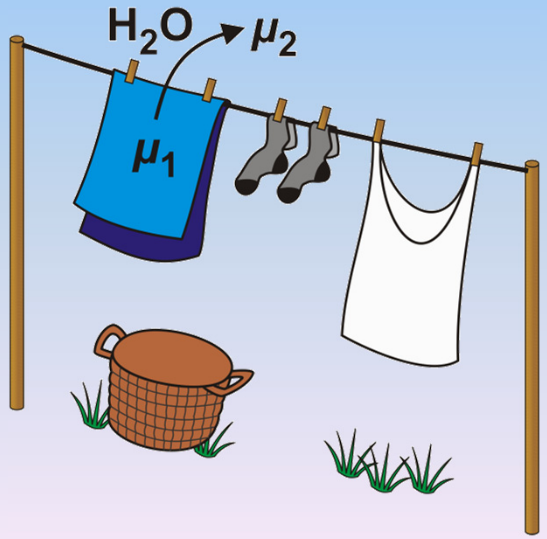
Mass Action

The tendency μ of substances to transform depends on their *amounts n* or more precisely, their *concentrations c* (= n/V).



The more concentrated the action the more intense the effect.

Not the *mass* of a substance is decisive for mass action, but its "*massing*," its "density" in space, i.e. not the *amount*, but the *concentration*.



Example: *Evaporation* of water

$$\begin{array}{ll} & \underline{H_2O|l \rightarrow H_2O|g} \\ \mu^{\ominus}/\text{kG} & -237 < -229 \end{array} \quad [\text{G(ibbs)} = \text{J mol}^{-1}]$$

However, if the water vapor is diluted by air, the value of its chemical potential decreases below that of liquid water.

Concentration Dependence

If the concentration change $\Delta c = c - c_0$ is small, a *linear* approach can be chosen:

$$\mu = \mu_0 + \gamma \cdot (c - c_0)$$

μ_0: initial value of the chemical potential at the concentration c_0

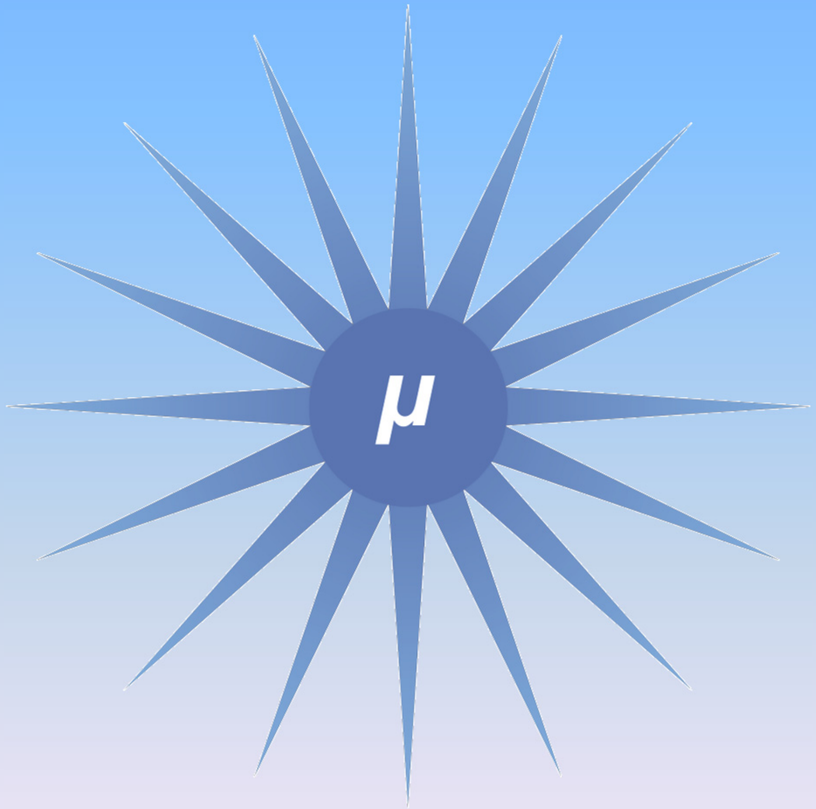
***concentration coefficient γ*: *universal quantity*, i.e. it is the same for all substances in every milieu:**

$$\gamma = \frac{RT}{c}$$ **for small *c* at constant *T***

combination of these two relations:

$$\mu = \mu_0 + RT\ln(c/c_0) = \mu_0 + RT\ln c_r$$ ***mass action equation***

2. Redox Reactions



Redox Reactions

It does not matter how we imagine the process in question working at the molecular level, whether it is by

- **formation or cleavage of chemical bonds,**
- **rearranging crystal lattices,**
- **migration of particles or**
- ***transfer of electrons* as in the case of redox reactions.**

In general, the electron donation from a simple redox pair Rd/Ox, consisting of a reducing agent Rd and a corresponding oxidizing agent Ox, can be represented by

$$\mathrm{Rd} \rightarrow \mathrm{Ox} + \nu_e \mathrm{e}$$

ν_e: conversion number of the electrons

redox pair conceivable as electron reservoir

- **in state Rd completely filled,**
- **in state Ox completely empty.**

Electron Potential

The exchangeable electrons in the redox system can also be assigned a chemical potential, the electron potential μ_e:

$$\mathrm{Rd} \rightleftarrows \mathrm{Ox} + \nu_e \mathrm{e}$$

Equilibrium condition: $\mu_{\mathrm{Rd}} = \mu_{\mathrm{Ox}} + \nu_e \mu_e$

$$\boxed{\mu_e(\mathrm{Rd/Ox}) = {}^{1}\!/\!_{\nu_e}\,(\mu_{\mathrm{Rd}} - \mu_{\mathrm{Ox}})}$$

μ_e (Rd/Ox) describes the strength of the transfer tendency of electrons from the redox pair Rd/Ox to other substances:

$\mu_e < \mu_e$(Rd/Ox): electrons will be released to the environment
⇒ electron reservoir emptied, discharged

$\mu_e > \mu_e$(Rd/Ox): redox pair will accept electrons
⇒ electron reservoir filled, charged

Electron Potential

The electron potential measures the maximum "electron pressure" the redox pair is able to produce and thus its *reductive capacity*. It is characteristic for each pair.

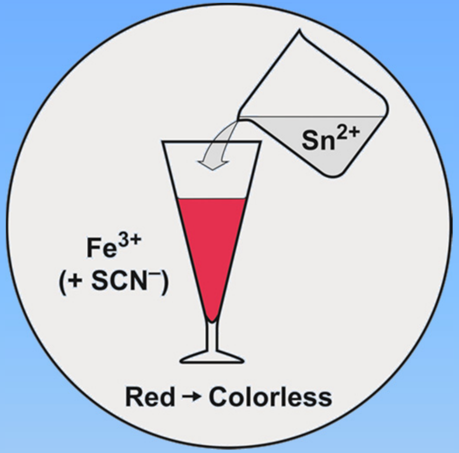
Reducing agent	/ Oxidizing agent	$\mu_e^\ominus$ / kG
$K\|s$	/ $K^+\|w$	+283
½ $H_2\|g + OH^-\|w$	/ $H_2O\|l$	0
$Sn^{2+}\|w$	/ $Sn^{4+}\|w$	–14
$Fe^{2+}\|w$	/ $Fe^{3+}\|w$	–74
$HF\|g + H_2O\|l$	/ ½ $F_2\|g + H_3O^+\|w$	–275

If an exchange of electrons between two redox pairs is allowed to take place, the "stronger" pair (μ_e higher) donates electrons to the "weaker" pair, which is reduced in the process.

Reduction of Fe^{3+} by Sn^{2+} ions

Procedure:

A deep red solution of iron(III) thiocyanate complexes is combined with a solution containing tin(II).



Observation:

The strong red color disappears completely in a few minutes.

Explanation:

If a tin (II) solution is added to an iron (III) solution, then according to

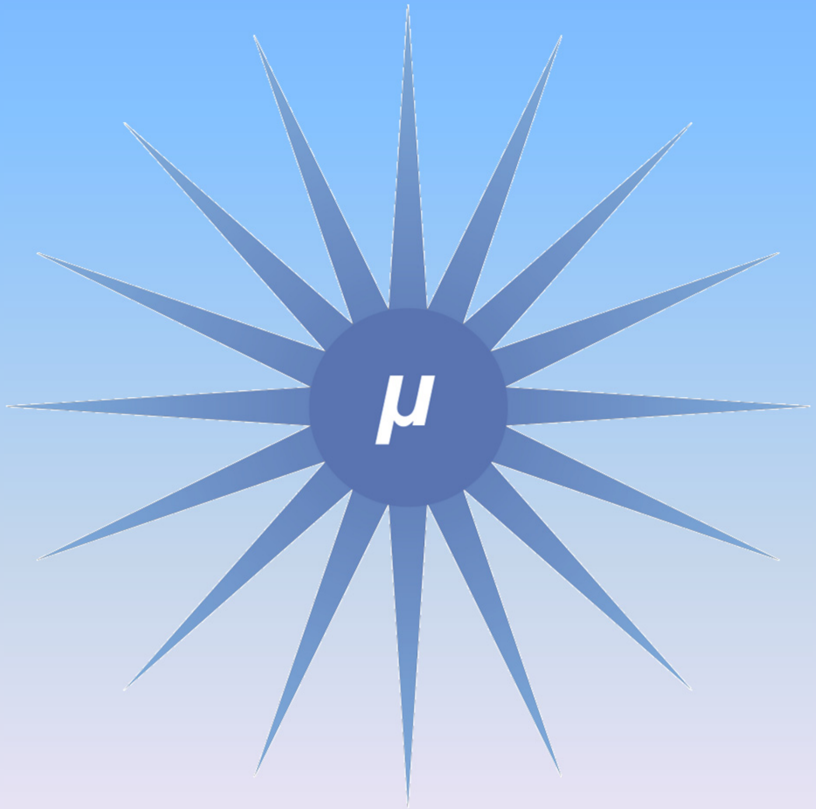
$$2\,Fe^{3+}|w + Sn^{2+}|w \rightarrow 2\,Fe^{2+}|w + Sn^{4+}|w$$

Fe^{3+} is reduced to Fe^{2+} and Sn^{2+} is oxidized to Sn^{4+} because due to

$$\mu^{\ominus}(Sn^{2+}/Sn^{4+}) = -14\ \mathrm{kG} > \mu^{\ominus}(Fe^{2+}/Fe^{3+}) = -74\ \mathrm{kG}$$

the redox pair Sn^{2+}/Sn^{4+} is more strongly reducing than the redox pair Fe^{2+}/Fe^{3+}.

3. Galvani Potential and Half-Cells



Galvani Potential Difference

At the boundary between two chemically different electrically conductive phases 1 and 2, an electrical potential difference is formed, a so-called Galvani potential difference (or Galvani voltage):

$$U_{1\rightarrow 2} = -\Delta\varphi = \varphi_1 - \varphi_2$$

φ_1, φ_2 : inner electric potentials (*Galvani potentials*)

a small amount Δn_i of a substance *i* having a charge

$$\Delta Q = z_i \mathcal{F} \cdot \Delta n_i$$

where z_i : charge number, $\mathcal{F}$: Faraday constant = 96485 C mol^{-1}

- **is added to a phase with a Galvani potential of $\varphi = 0$, or**
- **alternatively to a second chemically identical phase with a potential of $\varphi \neq 0$**

⇒ expended energy differs by

$$W_{\rightarrow Q} = \varphi \cdot \Delta Q = \varphi \cdot z_i \mathcal{F} \cdot \Delta n_i$$

Electrochemical Potential

The chemical potential μ_i of a substance i in a phase with a Galvani potential of $\varphi = 0$ is defined as the energy $W_{\rightarrow n}$ necessary for a small change of amount of substance related to this amount:

$$\mu_i = W_{\rightarrow n}/\Delta n_i$$

The value $\tilde{\mu}_i$ in a phase having $\varphi \neq 0$ must be different by the energy change $\varphi \cdot \Delta Q$ per transferred amount of substance Δn_i, i.e. by $\varphi \cdot \Delta Q/\Delta n_i = \varphi \cdot z_i \mathcal{F}$:

$$\boxed{\tilde{\mu}_i = \underbrace{\mu_i}_{\text{chemical}} + \underbrace{\varphi \cdot z_i \mathcal{F}}_{\text{electric term}}}$$

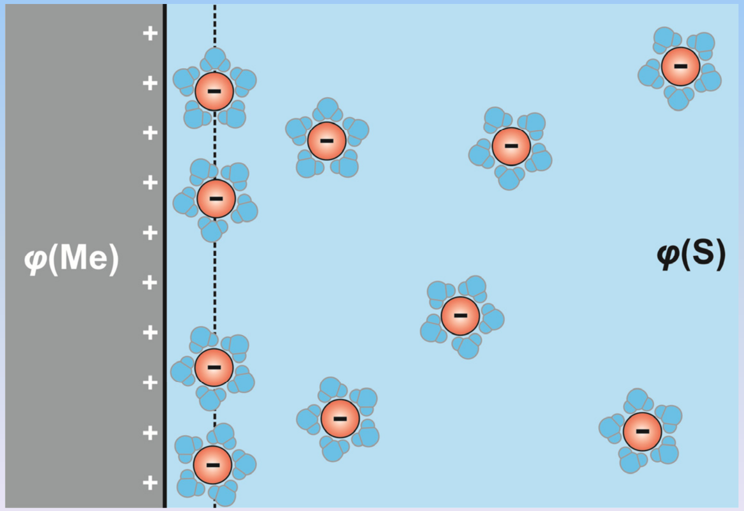
$\tilde{\mu}_i$: electrochemical potential

Half-Cell

combination of an electrode (metal rod, etc.) and the corresponding electrolyte (also often called an electrode in a wider sense)

Metal-Metal Ion Electrode

exchange of ions J (with the charge number z_J) as the charge carrying particles between a metal (Me) and a solution (S)



electrolytic double layer

Electrochemical equilibrium:

$$\mu_J(\mathrm{Me}) + z_J\mathcal{F}\varphi(\mathrm{Me}) = \mu_J(\mathrm{S}) + z_e\mathcal{F}\varphi(\mathrm{S})$$

$$\boxed{\Delta\varphi = \varphi(\mathrm{Me}) - \varphi(\mathrm{S}) = -\frac{\mu_J(\mathrm{Me}) - \mu_J(\mathrm{S})}{z_J\mathcal{F}}}$$

Metal-Metal Ion Electrode

Metal: **made up of freely moving negative electrons and positive metal ions arranged on lattice sites**

$$\mu(\mathrm{Me}) = \mu_\mathrm{J}(\mathrm{Me}) + z_\mathrm{J}\mu_\mathrm{e}(\mathrm{Me}) \quad \Rightarrow \quad \mu_\mathrm{J}(\mathrm{Me}) = \mu(\mathrm{Me}) - z_\mathrm{J}\mu_\mathrm{e}(\mathrm{Me})$$

Solution: **chemical potential of the metal ions in the solution dependent from the concentration (*mass action equation*)**

$$\mu_\mathrm{J}(\mathrm{S}) = \overset{\circ}{\mu}_\mathrm{J}(\mathrm{S}) + RT\ln(c_\mathrm{J}/c^\ominus) = \overset{\circ}{\mu}_\mathrm{J}(\mathrm{S}) + RT\ln c_{\mathrm{r,J}}$$

Inserting $\mu_\mathrm{J}(\mathrm{Me})$ and $\mu_\mathrm{J}(\mathrm{S})$ yields

$$\Delta\varphi = \varphi(\mathrm{Me}) - \varphi(\mathrm{S}) = -\frac{[\mu(\mathrm{Me}) - z_\mathrm{J}\mu_\mathrm{e}(\mathrm{Me})] - [\overset{\circ}{\mu}_\mathrm{J}(\mathrm{S}) + RT\ln c_{\mathrm{r,J}}]}{z_\mathrm{J}\mathcal{F}}$$

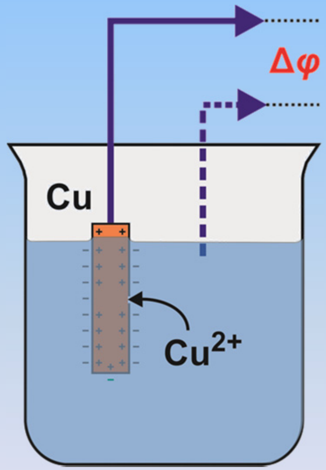
and finally

$$\Delta\varphi = \underbrace{\frac{\overset{\circ}{\mu}_\mathrm{J}(\mathrm{S}) - \mu(\mathrm{Me}) + z_\mathrm{J}\mu_\mathrm{e}(\mathrm{Me})}{z_\mathrm{J}\mathcal{F}}}_{\Delta\varphi^\circ} + \frac{RT}{z_\mathrm{J}\mathcal{F}}\ln c_{\mathrm{r,J}}$$

Metal-Metal Ion Electrode

$$\boxed{\Delta\varphi = \Delta\varphi^{\circ} + \frac{RT}{z_J\mathcal{F}}\ln c_{r,J}}$$

NERNST equation



Copper-copper ion electrode as an example of a metal-metal ion electrode

$$\Delta\varphi = \Delta\varphi^{\circ} + \frac{RT}{2\mathcal{F}}\ln\frac{c(\mathrm{Cu}^{2+})}{c^{\ominus}}$$

Ion-Ion Electrode

a chemically indifferent metal such as platinum (Pt) is immersed in a solution of a redox pair Rd/Ox

⇒ no exchange of metal ions possible, but that of electrons

$$\Delta\varphi = \varphi(\mathrm{Pt}) - \varphi(\mathrm{S}) = -\frac{\mu_\mathrm{e}(\mathrm{Pt}) - \mu_\mathrm{e}(\mathrm{S})}{z_\mathrm{e}\mathcal{F}} = \frac{\mu_\mathrm{e}(\mathrm{Pt}) - \mu_\mathrm{e}(\mathrm{S})}{\mathcal{F}}$$

Electron potential of the redox pair in the solution:

$$\mu_\mathrm{e}(\mathrm{S}) = \mu_\mathrm{e}(\mathrm{Rd/Ox}) = {}^{1}\!/_{\nu_\mathrm{e}}\,(\mu_\mathrm{Rd} - \mu_\mathrm{Ox})$$

Considering the effect of mass action, the following results

$$\mu_\mathrm{e}(\mathrm{S}) = {}^{1}\!/_{\nu_\mathrm{e}}\,[(\overset{\circ}{\mu}_\mathrm{Rd} + RT\ln(c_\mathrm{Rd}/c^\ominus) - (\overset{\circ}{\mu}_\mathrm{Ox} + RT\ln(c_\mathrm{Ox}/c^\ominus))]$$

or also

$$\mu_\mathrm{e}(\mathrm{S}) = {}^{1}\!/_{\nu_\mathrm{e}}\,[(\overset{\circ}{\mu}_\mathrm{Rd} - \overset{\circ}{\mu}_\mathrm{Ox}) + RT\ln(c_\mathrm{Rd}/c_\mathrm{Ox})]$$

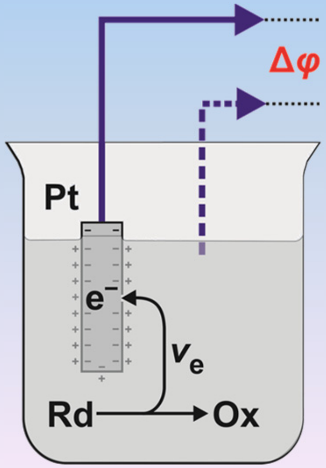
Ion-Ion Electrode

Inserting these results yields:

$$\Delta\varphi = \varphi(\mathrm{Pt}) - \varphi(\mathrm{S}) = \underbrace{\frac{\nu_e\mu_e(\mathrm{Pt}) + \overset{\circ}{\mu}_{\mathrm{Ox}} - \overset{\circ}{\mu}_{\mathrm{Rd}}}{\nu_e\mathcal{F}}}_{\Delta\varphi^\circ} + \frac{RT}{\nu_e\mathcal{F}}\ln\frac{c_{\mathrm{Ox}}}{c_{\mathrm{Rd}}}$$

$$\boxed{\Delta\varphi = \Delta\varphi^\circ + \frac{RT}{\nu_e\mathcal{F}}\ln\frac{c_{\mathrm{Ox}}}{c_{\mathrm{Rd}}}}$$

NERNST equation

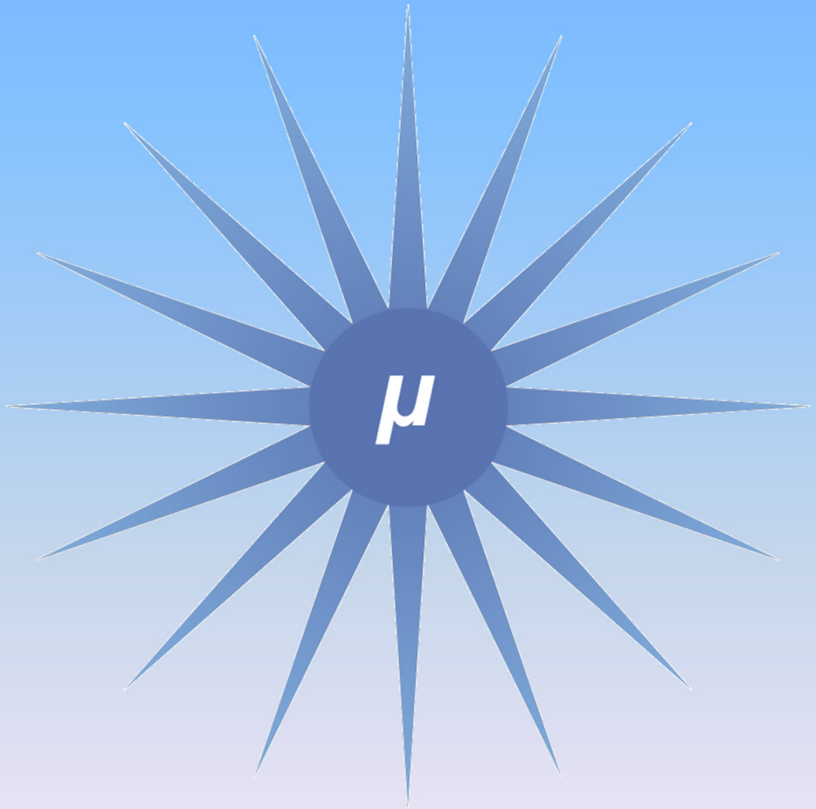


$c_{\mathrm{Ox}} \ll c_{\mathrm{Rd}}$: electron reservoir Rd/Ox almost completely filled ⇒ strong tendency to donate electrons to the noble metal

Example: Redox pair of bivalent and trivalent iron ions

$$\Delta\varphi = \Delta\varphi^\circ(\mathrm{Fe}^{2+}/\mathrm{Fe}^{3+}) = \frac{RT}{\mathcal{F}}\ln\frac{c(\mathrm{Fe}^{3+})}{c(\mathrm{Fe}^{2+})}$$

4. Redox Potentials and Galvanic Cells



Redox Potentials

Problem: Galvani potential difference across a single interface not directly measurable, because connection of the electrolyte solution to an electrical measuring device by a second electrode produces a new interface with an additional Galvani potential difference

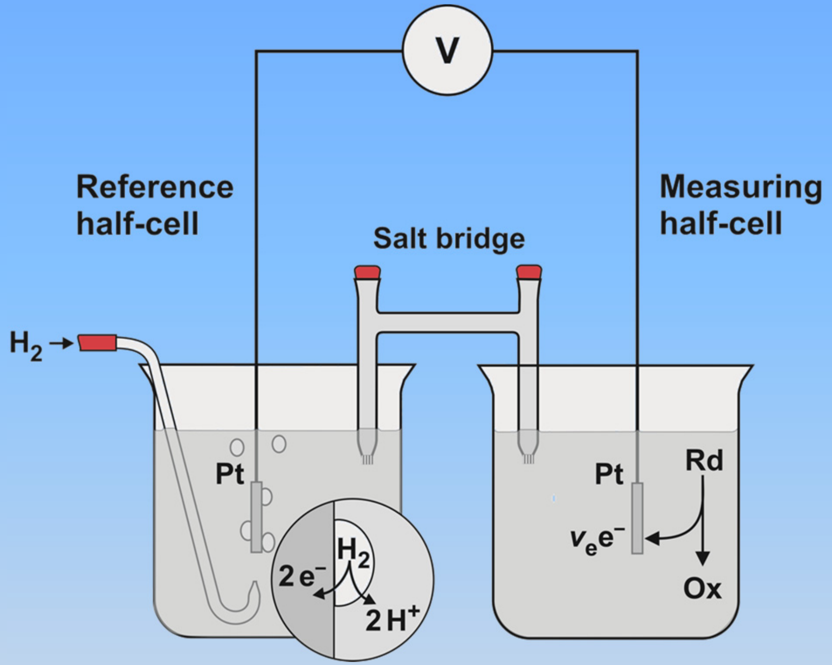
Way out: Use of a reference half-cell which is always the same, so that the measured total voltage is only determined by the measuring half-cell

usual reference half-cell: standard hydrogen electrode (SHE)

heterogeneous redox pair: H_2/H^+ (hydrogen gas at standard pressure of 100 kPa / solution of hydrogen ions with pH value of 0)

$$\Rightarrow \quad \mu_e(H_2/H^+) = \overset{\circ}{\mu}_e(H_2/H^+) \qquad \text{resp. for } T = 298\ \text{K: } \mu_e^{\ominus}(H_2/H^+) = 0$$

Redox Potentials



Measuring set-up:

- **reference half-cell: standard hydrogen electrode**
- **salt bridge to avoid the diffusion voltage**
- **currentless measurement**

$$-U = \Delta\varphi(\text{left}) + \Delta\varphi(\text{right})$$

disturbing potentials negligible

$$-U = \underbrace{[\varphi(\mathrm{S})_\mathrm{l} - \varphi(\mathrm{Pt})_\mathrm{l}]}_{-\Delta\varphi(\text{ref})} + \underbrace{[\varphi(\mathrm{Pt})_\mathrm{r} - \varphi(\mathrm{S})_\mathrm{r}]}_{\Delta\varphi(\text{meas})}$$

Redox potential *E*: $E = \Delta\varphi(\text{meas}) - \underbrace{\Delta\varphi^\ominus(\mathrm{H_2/H^+})}_{0}$

Redox Potentials

The redox potentials under standard conditions (i.e. $T^\ominus = 298$ K, $p^\ominus = 100$ kPa, $c^\ominus = 1$ kmol m^{-3} in aqueous solutions) are often compiled according to their values in a table, the so-called electrochemical series.

Half-cell	Electrode reaction	$E^\ominus$ / V
$Zn\|Zn^{2+}$	$Zn^{2+} + 2\,e^- \leftrightarrow Zn$	–0.762
$Pb\|Pb^{2+}$	$Pb^{2+} + 2\,e^- \leftrightarrow Pb$	–0.126
$Cu\|Cu^{2+}$	$Cu^{2+} + 2\,e^- \leftrightarrow Cu$	+0.342
$Ag\|Ag^{+}$	$Ag^{+} + e^- \leftrightarrow Ag$	+0.800
$Pt\|H_2\|H^{+}$	$2\,H^{+} + 2\,e^- \leftrightarrow H_2$	0.000
$Pt\|Sn^{2+},Sn^{4+}$	$Sn^{4+} + 2\,e^- \leftrightarrow Sn^{2+}$	+0.151
$Pt\|Fe^{2+},Fe^{3+}$	$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+0.771

Galvanic Cells

Initially, the reaction of zinc shavings with copper sulfate solution is considered:

total reaction: $\mathrm{Zn|s + Cu^{2+}|w \rightarrow Zn^{2+}|w + Cu|s}$

half-reactions: $\mathrm{Zn|s \rightarrow Zn^{2+}|w + 2\,e^{-}}$

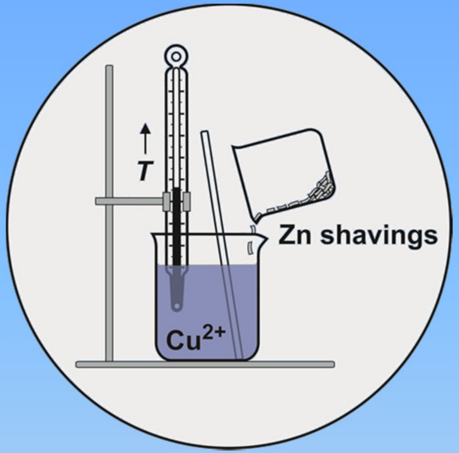
$\mathrm{Cu^{2+}|w + 2\,e^{-} \rightarrow Cu|s}$

potential difference: $\Delta\mu = [\mu(\mathrm{Zn^{2+}}) + \mu(\mathrm{Cu})] - [\mu(\mathrm{Zn}) + \mu(\mathrm{Cu^{2+}})]$

Reduction of Cu^{2+} ions by Zinc

Procedure:

Zinc shavings are poured into a saturated copper sulfate solution.



Observation:

They precipitate densely and immediately turn black. The precipitate then slowly turns coppery brown. The temperature rises considerably. The solution eventually becomes colorless.

Explanation:

If zinc shavings are added to a cupper (II) solution, then according to

$$\mathrm{Zn|s} + \mathrm{Cu^{2+}|w} \rightarrow \mathrm{Zn^{2+}|w} + \mathrm{Cu|s}$$

Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu because due to

$$\mu^{\ominus}(\mathrm{Zn/Zn^{2+}}) = +66\ \mathrm{kG} > \mu^{\ominus}(\mathrm{Cu/Cu^{2+}}) = -147\ \mathrm{kG}$$

the pair Zn/Zn^{2+} is more strongly reducing than the pair Cu/Cu^{2+}.

Reduction of Cu^{2+} ions by Zinc

(https://www.youtube.com/watch?v=kxQOLDPbAGc

Galvanic Cells

Initially, the reaction of zinc shavings with copper sulfate solution is considered:

total reaction: $\mathrm{Zn|s + Cu^{2+}|w \rightarrow Zn^{2+}|w + Cu|s}$

half-reactions: $\mathrm{Zn|s \rightarrow Zn^{2+}|w + 2\,e^{-}}$

$\mathrm{Cu^{2+}|w + 2\,e^{-} \rightarrow Cu|s}$

potential difference: $\Delta\mu = [\mu(\mathrm{Zn^{2+}}) + \mu(\mathrm{Cu})] - [\mu(\mathrm{Zn}) + \mu(\mathrm{Cu^{2+}})]$

chemical energy W_ξ occurring at a conversion $\Delta\xi$ of the total reaction given by

$$W_\xi = \underbrace{\left[[\mu(\mathrm{Zn^{2+}}) + \mu(\mathrm{Cu})] - [\mu(\mathrm{Zn}) + \mu(\mathrm{Cu^{2+}})]\right]}_{<\,0} \cdot \Delta\xi$$

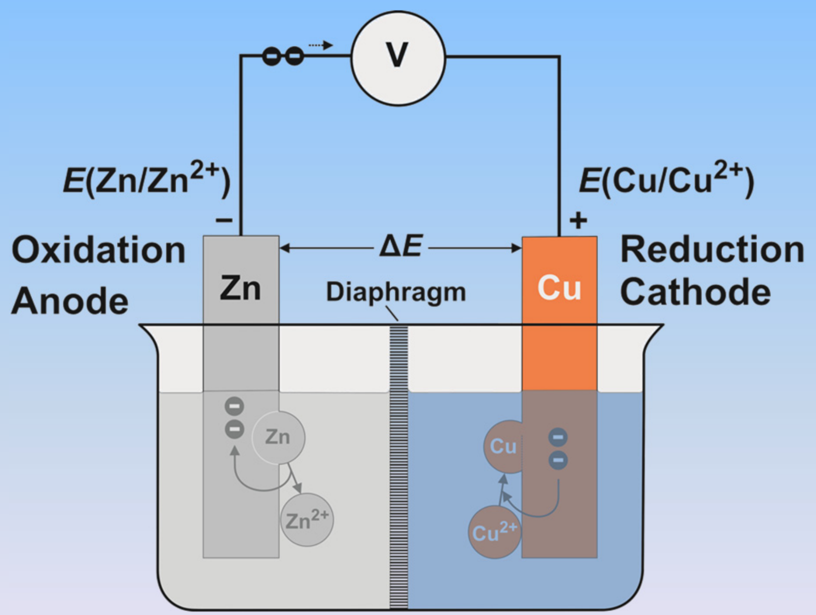
with $\xi = \dfrac{n_i - n_{i,0}}{v_i}$ **(extent of reaction)**

is released ($W_\xi < 0$) and "burnt up" under entropy generation

Galvanic Cells

half-reactions can alternatively be spatially separated from each other by dividing them into two half-cells of a galvanic cell where they are connected to each other by an external circuit

⇒ ***DANIELL cell***



currentless measured voltage of the cell:

$$-U = \Delta E = E(\mathrm{Cu/Cu^{2+}}) - E(\mathrm{Zn/Zn^{2+}})$$

with Δ*E*: "*reversible cell voltage*"

under standard conditions:

$$\Delta E^{\ominus} = +0{,}340\ \mathrm{V} - (-0{,}763\ \mathrm{V})$$

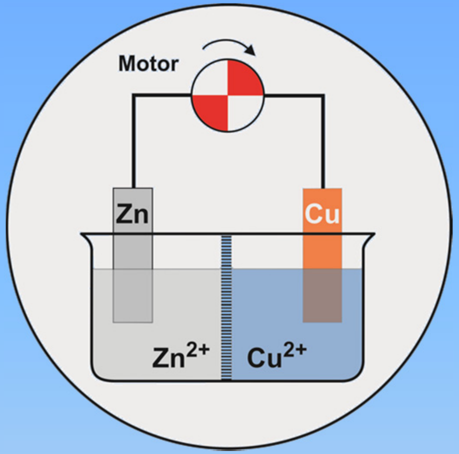
$$= +1{,}103\ \mathrm{V}$$

The chemical reaction (divided into two partial reactions) can also be used to drive an electron current.

DANIELL Cell

Procedure:

Zinc sulfate solution is filled into the crystallizing dish and copper sulfate solution into the flower pot. Then the zinc and copper electrodes are immersed and connected to the voltmeter or the electric motor.



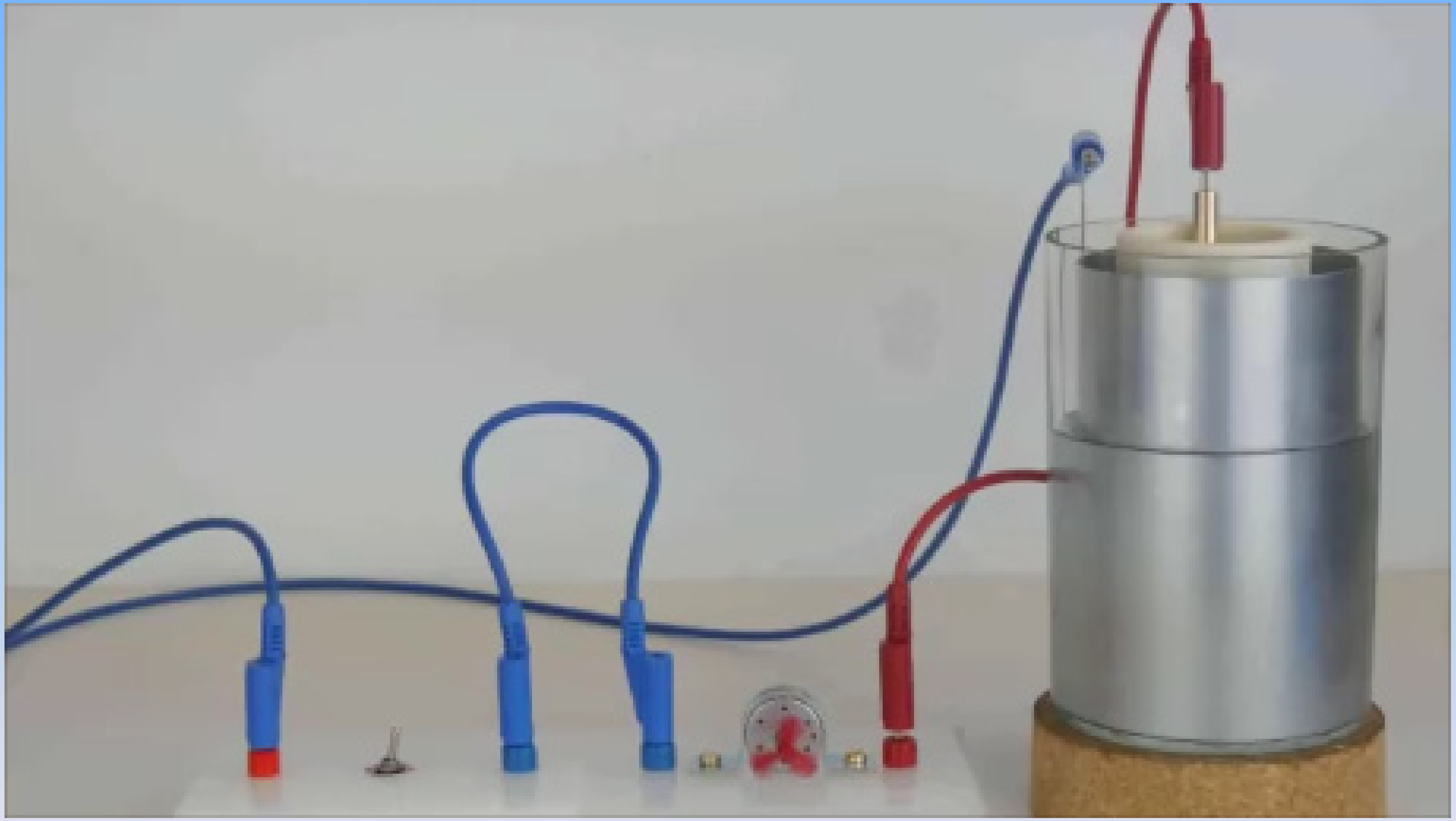
Observation:

A voltage of about 1 V can be measured; the motor is running.

Explanation:

The DANIELL cell enables the direct conversion of chemical energy into electrical energy. The necessary electrical contact between the electrolyte solutions is achieved via the clay wall of the pot (diaphragm).

DANIELL Cell

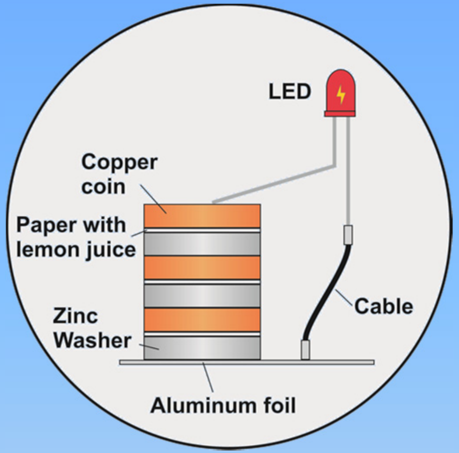


((https://www.youtube.com/watch?v=91lh23dEplc)

Homemade VOLTAic Pile

Procedure:

Zinc washers, pieces of paper soaked with lemon juice and copper coins are alternately piled to form a stack on a aluminum strip. Then, a LED is connected with the copper coin on top and the aluminum strip.



Observation:

The LED lights up.

Explanation:

The half-reaction that occurs at the anode, where oxidation takes place, is the same as in the DANIELL cell, meaning

$$Zn|s \rightarrow Zn^{2+}|w + 2\ e^-.$$

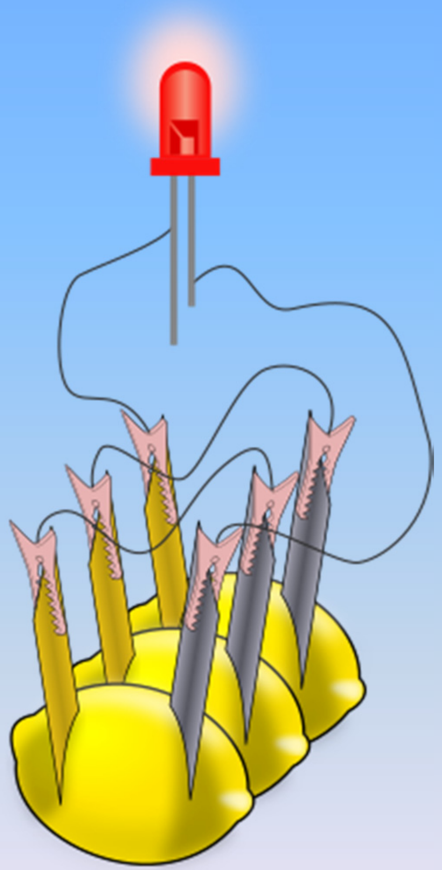
At the copper electrode, however, H^+ ions are reduced to H_2 gas,

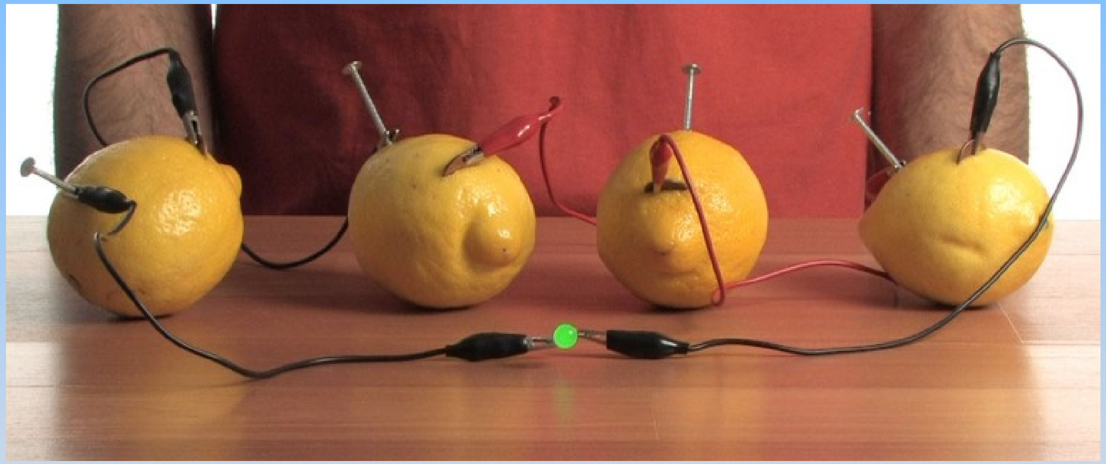
$$2\ H^+|w + 2\ e^- \rightarrow H_2|g.$$

Homemade VOLTAic Pile

((https://www.job-stiftung.de/videos/Voltaic_Pile.mp4

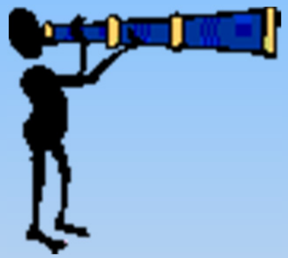
Lemon Battery





https://stevespangler.com/experiments/fruit-power-battery/

5. Outlook



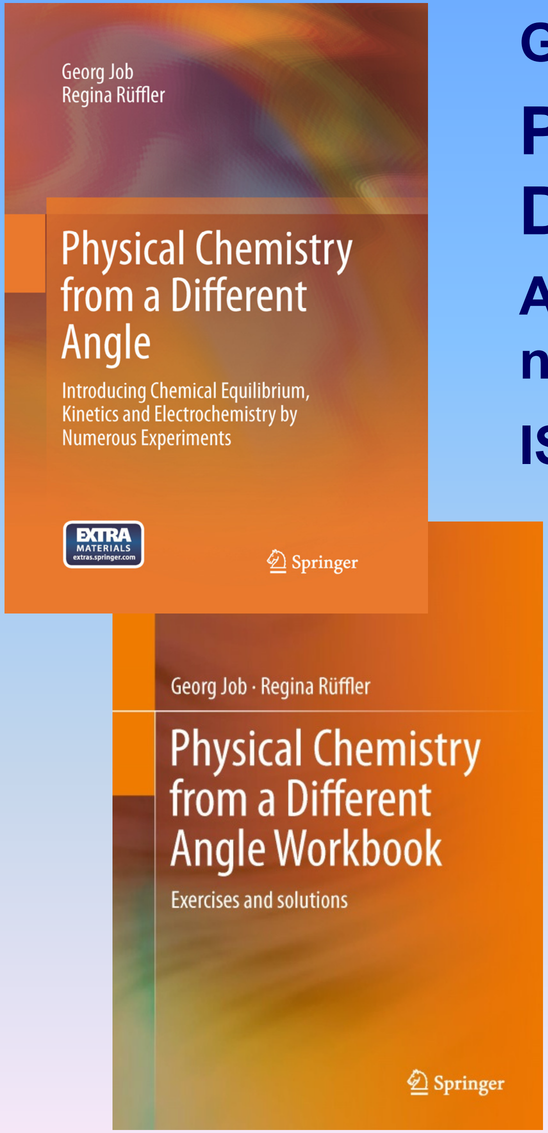
Application

The DANIELL cell and the VOLTAic pile represent historical designs of galvanic cells. However, with the fundamental understanding of these cells, the gateway to

technically important galvanic cells such as batteries, accumulators or fuel cells is open to us.

In the last decades, electrochemistry has witnessed a renaissance, especially because of the strongly increasing importance of electromobility.

5. Outlook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Thank you very much for your friendly attention.

Further information

(PowerPoint Presentation, instructions for the experiments, videos, etc.):

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