

Overview of electrochemistry

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	Equilibrium electrochemistry (no current flows)	Dynamic electrochemistry (current does flow)
Homogeneous	Thermodynamics of electrolyte solutions: <ul style="list-style-type: none">• electrolytic dissociation• thermodynamics and activities of ions	Conductance of electrolytes: <ul style="list-style-type: none">• electrolytic conduction• mobilities of ions• Kohlrausch laws
Heterogeneous	Thermodynamics of electrodes and Galvanic cells: <ul style="list-style-type: none">• electrochemical cells• cell and electrode potential• types of electrodes	Kinetics of electrode reactions: <ul style="list-style-type: none">• exchange current• overpotential• Tafel equation• Butler-Volmer equation• electrolysis• batteries

HOMOGENEOUS EQUILIBRIUM ELECTROCHEMISTRY: THERMODYNAMICS OF ELECTROLYTES

- I. Thermodynamics of electrolytes.
 - A. Characterization of electrolytes
 - B. Thermodynamic formation functions of ions
 - C. Activities of ions in solution
 - D. The Debye–Hückel theory

I. Thermodynamics of electrolytes

A. Characterization of electrolytes

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- **Solutions** are homogeneous, multicomponent systems
- Ionic compounds dissociate into **anion**(s) and **cation**(s) in polar solvents (Svante Arrhenius, Nobel prize in 1903)
- Mostly the same general properties as for other (dilute) solutions:
 - ▣ colligative properties (freezing point depression, boiling point elevation, osmosis, distribution...)
 - ▣ may both be ideal and real
- Unique property:
 - ▣ conduction of electricity

I. Thermodynamics of electrolytes

A. Characterization of electrolytes

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- Electroneutrality – there are no solutions containing **cation** only, or **anion** only!
- Molten electrolytes (e.g. $\text{NaCl}(l)$) also conduct electricity.

I. Thermodynamics of electrolytes

A. Characterization of electrolytes

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- Acids, bases, salts are electrolytes:
 - ▣ Salts: practically complete dissociation
 - ▣ Acids and bases: weak or strong
- Dissociation is an equilibrium:
 - ▣ K_d dissociation constant or
 - ▣ α degree of dissociation
- Electrolytic dissociation:
 $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$
 - ▣ (acid-base equilibria, pH, buffers, indicators, pH-titration, pK_a
 - ▣ complexation)

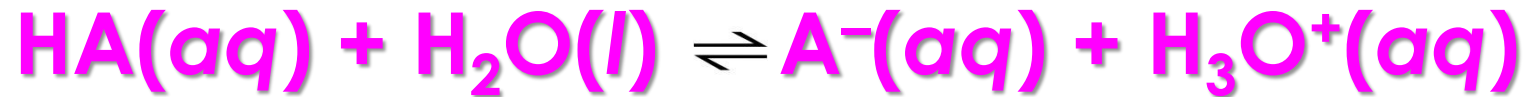
$$K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA}}$$

I. Thermodynamics of electrolytes

A. Characterization of electrolytes

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- Dissociation of **weak acids**:



- K_a dissociation constant ($K_a = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}}$) or

- α degree of dissociation.

- $0 < \alpha < 1$

- $\alpha = \frac{A_m}{A_m^0}$ (more later)

- $[\text{A}^-(aq)]_e = [\text{H}_3\text{O}^+(aq)]_e = c\alpha$

- $[\text{HA}(aq)]_e = c(1-\alpha)$

$$K_d = \frac{c\alpha^2}{1-\alpha}$$

- Ostwald's dilution law.

I. Thermodynamics of electrolytes

A. Characterization of electrolytes

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- Complete dissociation in the saturated solutions of **solid salts**.
- Ions are in equilibrium with a solid phase rather than individual molecules:



$$K_{\text{sol}} = \frac{a_{\text{K}^+} a_{\text{A}^-}}{a_{\text{KA}}} = a_{\text{K}^+} a_{\text{A}^-}$$

B. Thermodynamic formation functions of ions

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- Thermodynamic formalism:
 - ▣ behavior is close to *ideal* until ca. 10^{-3} mol/dm³,
 - ▣ above: *real* solutions.
 - ▣ Activity (*a*) instead of concentration (*c*).

B. Thermodynamic formation functions of ions

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- Problem: solutions never contain one type of ion (e.g. cation) only, there is always at least one other oppositely charged ion.
- Arbitrary conventions (but widely agreed on):
 - $\Delta_f H^\theta(\text{H}^+, \text{aq}) = 0 \text{ J/mol}$ and
 - $\Delta_f G^\theta(\text{H}^+, \text{aq}) = 0 \text{ J/mol}$.
- What' more:
 - $\Delta_f S^\theta(\text{H}^+, \text{aq}) = 0 \text{ J/(K mol)}$ at every temperature. This entropy is measured on a relative scale!

B. Thermodynamic formation functions of ions

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- Example: $\text{Ag(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 - $\Delta_r H^\theta = \Delta_f H^\theta(\text{Ag}^+, \text{aq}) + \Delta_f H^\theta(\text{Cl}^-, \text{aq}) = -61.5 \text{ kJ/mol}$,
 - but $\Delta_r H^\theta$ for the processes $\text{Ag(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{e}^-$ and $\frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{aq})$ are not measurable separately.
- Solution: start from $\text{H}^+(\text{aq})$ and proceed to other ions:
 - $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ $\Delta_r H^\theta = \Delta_f H^\theta(\text{H}^+, \text{aq}) + \Delta_f H^\theta(\text{Cl}^-, \text{aq}) = -167 \text{ kJ/mol}$, and thus $\Delta_f H^\theta(\text{Cl}^-, \text{aq}) = -167 \text{ kJ/mol}$.
 - Now $\Delta_f H^\theta(\text{Ag}^+, \text{aq})$ is available.

C. Activities of ions in solution

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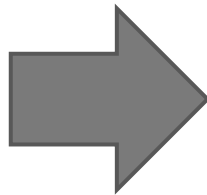
- Solutions containing ions (electrolytes) are not ideal because of electrostatic interactions. Therefore, **activities** are used instead of concentrations (e.g. equilibria or electrode potentials).

- So far:

- $\mu = \mu^\theta + RT \ln a$

- $a = \gamma \cdot m/m^\theta$

- where m is molality.



$$\begin{aligned}\mu &= \mu^\theta + RT \ln m/m^\theta + RT \ln \gamma \\ &= \mu^\theta + RT \ln \gamma\end{aligned}$$

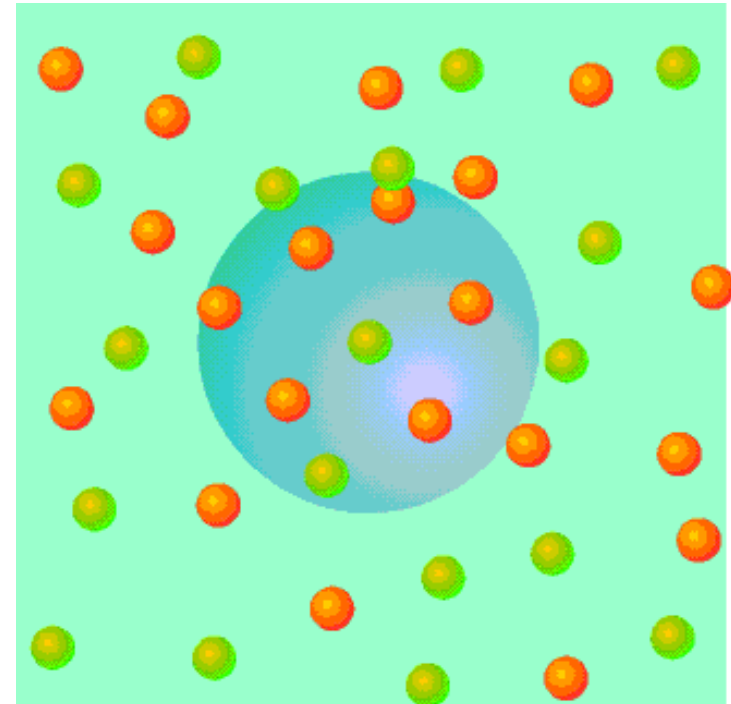
where μ^θ is the chemical potential of an ideal dilute solution with the same molality.

D. Debye–Hückel theory

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Debye–Hückel limiting law:

- Non-ideal behavior is caused by the electrostatic interaction between ions and it is sufficient to consider this one only in the theory.
 - ▣ Values of γ_{\pm} can be obtained.
- Model:
 - ▣ Around any given ion, counter ions form a spherical cloud and are in excess.
 - ▣ This ion cloud reduces the chemical potential of the ion in the center.



D. Debye–Hückel theory

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γ_{\pm} based on the Debye–Hückel theory:

- Result: $\lg \gamma_{\pm} = -A|z_+ z_-| \sqrt{I}$
 - A : a combination of constants (in water at 25 °C $0.509 \text{ (mol/kg)}^{1/2}$)
 - I : ionic strength of the solution: $I = \frac{\sum z_i^2 m_i}{2}$
 - I involves all ions!
- This formula is only valid at low concentrations, it is called the **Debye–Hückel limiting law**.
- **An extension**:

$$\lg \gamma_{\pm} = \frac{-A|z_+ z_-| \sqrt{I}}{1 + B\sqrt{I}}$$

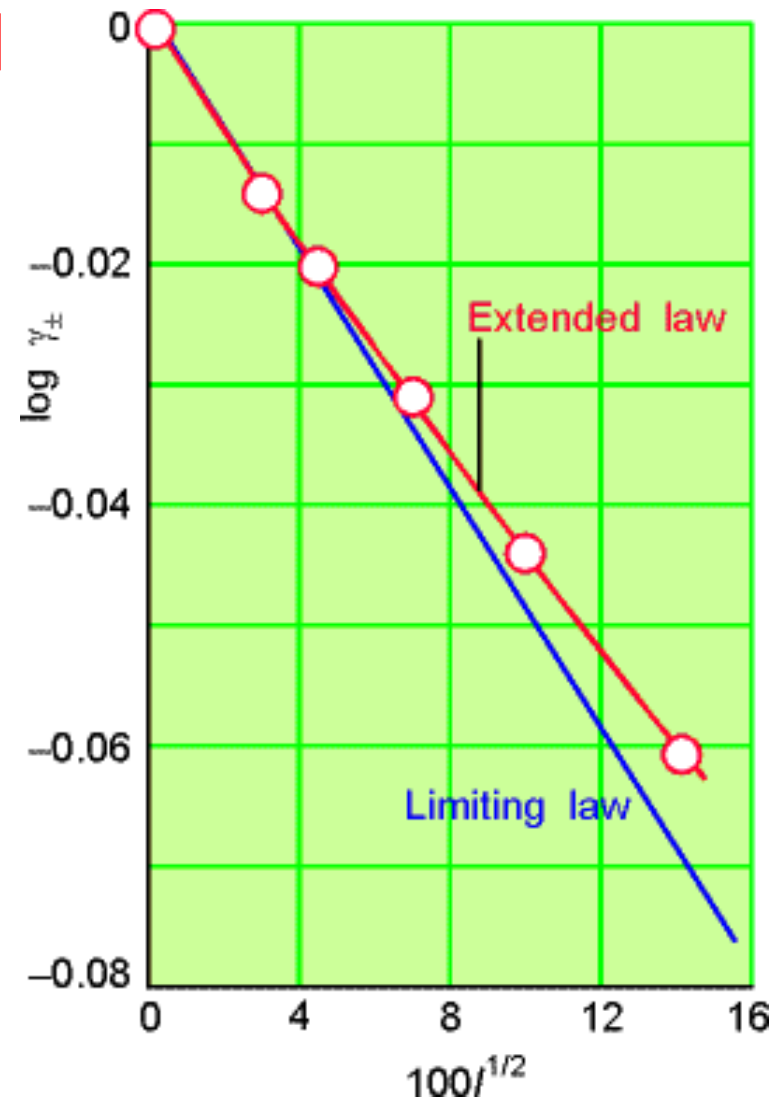
D. Debye–Hückel theory

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The **limiting** and the **extended** Debye–Hückel law:

$$\lg \gamma_{\pm} = -A|z_+ z_-| \sqrt{I}$$

$$\lg \gamma_{\pm} = \frac{-A|z_+ z_-| \sqrt{I}}{1 + B\sqrt{I}}$$



Overview of electrochemistry

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HETEROGENEOUS EQUILIBRIUM ELECTROCHEMISTRY:

- II. Thermodynamics of electrodes and Galvanic cells.
 - A. Galvanic vs. electrolytic cells
 - B. Galvanic cells: chemistry and thermodynamics
 - C. Parts and usual notations of Galvanic cells
 - D. Potential of a Galvanic cell
 - E. Measuring cell potential
 - F. Electrodes: Measuring electrode potentials
 - I. The scale of electrode potentials
 - J. Types of electrodes

II. Thermodynamics of Galvanic cells and electrodes

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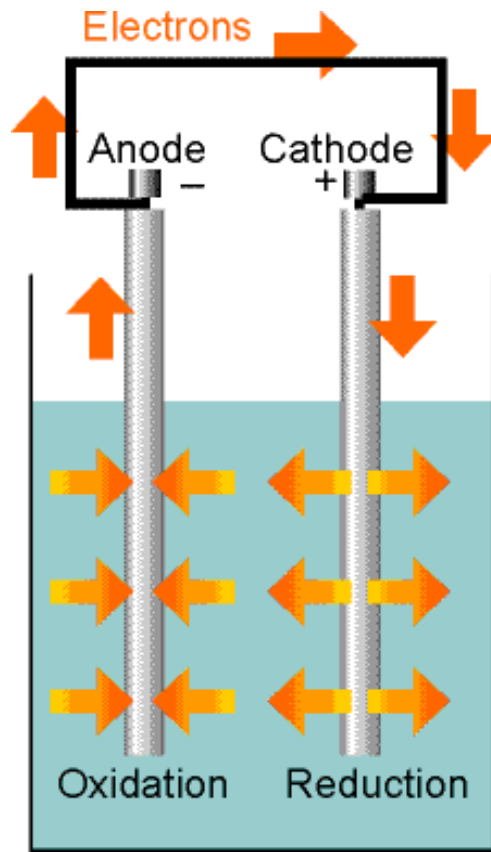
- In electrochemical cells, redox reactions proceed in a spatially separated arrangement.
 - ▣ Parts of the cell (heterogeneous system):
 - two (metal) electrodes (anode and cathode) immersed into
 - the solutions of their own ions (electrolytes)
 - ▣ Electrode and electrolyte together form the electrode compartment. To connect them electronically, a **salt bridge** or **diaphragm** is needed.

- Two different approaches:
 - ▣ spontaneous Galvanic cell vs.
 - ▣ forced electrolysis.

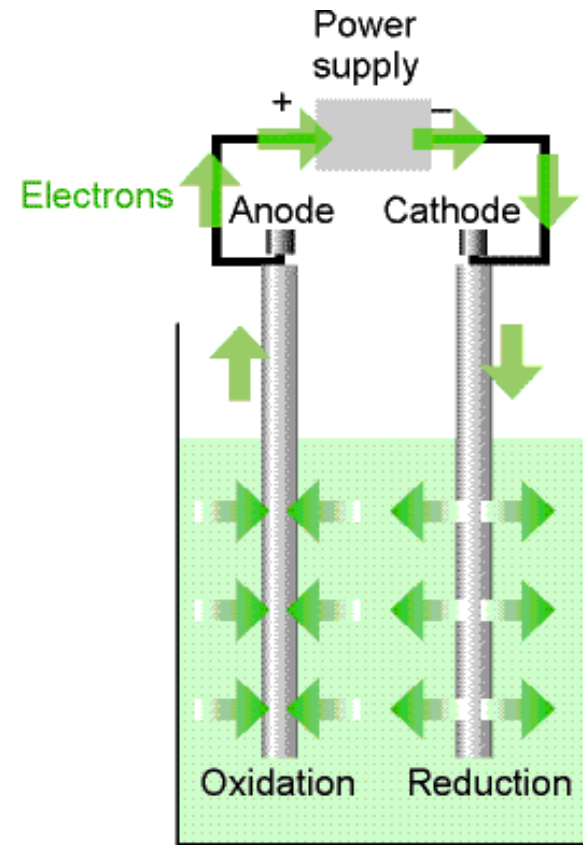
A. Galvanic *vs.* electrolytic cells

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- **Galvanic cell:**
spontaneous reaction produces electricity.



- **Electrolysis:** external source of electricity drives chemical reaction



A. Galvanic *vs.* electrolytic cells

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Anode:

- Spontaneous **oxidation**
- **Increase in oxidation number**
- Substance loses electrons
- **Negative (-)**
- Forced **oxidation**
- **Increase in oxidation number**
- Substance loses electrons
- **Positive (+)**

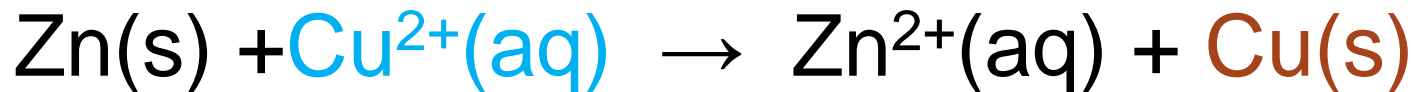
Cathode:

- Spontaneous **reduction**
- **Decrease in oxidation number**
- Substance gains electrons
- **Positive (+)**
- forced **reduction**
- **Decrease in oxidation number**
- Substance gains electrons
- **Negative (-)**

B. Galvanic cells: chemistry and thermodynamics

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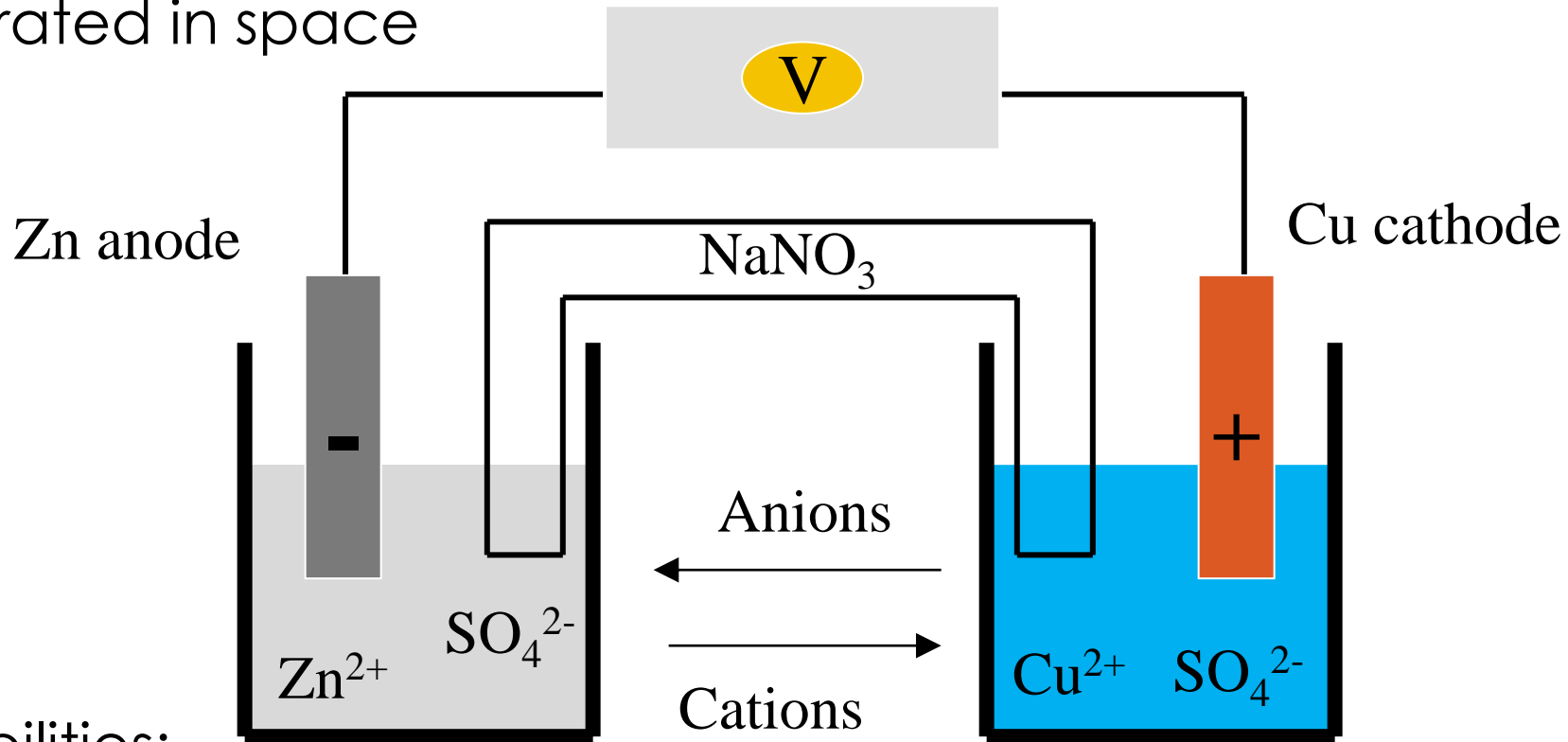
- **Simple experiment:** red elemental copper deposits on a zinc rod immersed into a solution of copper(II) sulfate, and – *although this is not directly visible* – zinc ions appear in the solution.
- The reduction of copper(II) and the oxidation of zinc proceeds in the same space:



B. Galvanic cells: chemistry and thermodynamics

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- Chemical Galvanic cells: reduction and oxidation separated in space

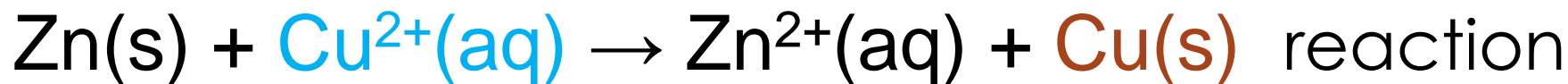


- Possibilities:
 - ▣ a single electrode compartment with diaphragm
 - ▣ two electrode compartments and a salt bridge.

B. Galvanic cells: chemistry and thermodynamics

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□ Separate the previous



□ into **oxidation** and **reduction**:

- $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
- $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$
- $\text{red1} \rightarrow \text{ox1} + \text{e}^-$
- $\text{ox2} + \text{e}^- \rightarrow \text{red2}$
- oxidation: e^- loss
- reduction: e^- gain
- **anode: (-) electrode**
- **cathode: (+) electrode**
- anodic oxidation
- cathodic reduction
- notation: (left) or (1)
- notation: (right) or (2)

B. Galvanic cells: chemistry and thermodynamics

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- In the convention of electrochemistry, both processes are written in the direction of reduction:
 - $-\{Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)\}$
 - $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
- The net reaction is now the difference of the two reduction processes: (right) – (left)
- This makes good common sense, as E_{cell} is always positive in agreement with the negative $\Delta_r G$ of the spontaneous process:
- $E_{cell} = E_{right\ electrode} - E_{left\ electrode}$

C. Parts and usual notations of Galvanic cells

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- Galvanic cell (or voltaic cell or electrochemical cell) =
 - ▣ 2 half cells or
 - ▣ 2 half reactions or
 - ▣ 2 electrodes
- Notation: $(-) \text{Zn(s)} \mid \text{ZnSO}_4(\text{aq}) \parallel \text{CuSO}_4(\text{aq}) \mid \text{Cu(s)} (+)$
- Particularly:
 - ▣ \mid phase boundary (solid/solution, solid/gas)
 - ▣ \parallel surface on the boundary – without liquid junction potential
- Liquid junction potential is minimized – salt bridge.

D. Potential of a Galvanic cell

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- Connection between the cell potential and reaction Gibbs energy: $-vFE_{cell} = \Delta_r G$
- In a reversible reaction, the actual value of $\Delta_r G$ depends on the reaction quotient Q :
$$\Delta_r G = \Delta_r G^\theta + RT \ln Q,$$
- For the cell reaction:
 - ▣ **Nernst equation for the cell**: $E_{cell} = E_{cell}^\theta - \frac{RT}{vF} \ln Q$

D. Potential of a Galvanic cell

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- In equilibrium, $E_{cell} = 0$ and $Q = K$. This gives the connection between the cell potential and the equilibrium constant:

$$E_{cell}^{\theta} = \frac{RT}{\nu F} \ln K$$

- In summary
 - ▣ **standard cell potentials** (E_{cell}^{θ}),
 - ▣ **equilibrium constants** (K) and
 - ▣ **standard reaction free energies** ($\Delta_r G^{\theta}$) are related:

$$\nu F E_{cell}^{\theta} = RT \ln K = -\Delta_r G^{\theta}$$

E. Measuring cell potentials

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- ▣ electromotive force (no current flows): **e.m.f.**
- ▣ with current (producing electric work): **actual cell potential of a working electrode**

▣ Measuring **electromotive force**:

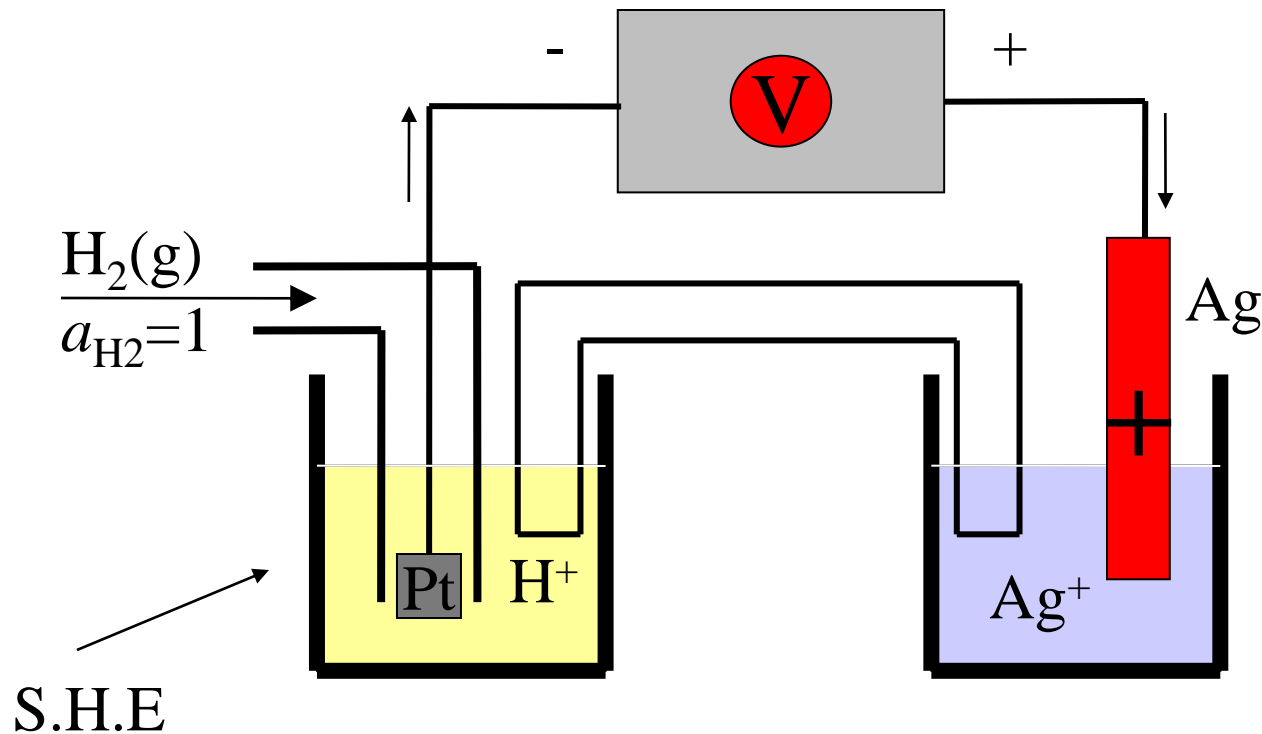
- ▣ compensation method (fully current-free), classical: *DuBois–Reymond–Poggendorf*
- ▣ voltmeter with large internal resistance ($R > 10^{10} \Omega$). Today this is a common piece of laboratory equipment (e.g. pH-meter).

In practice, voltages of $0 \leq 3 \text{ V}$ have to be measured with a precision of 0.1 mV (10^{-4} V).

F. Measuring electrode potentials

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- Reference point SHE: $E^\theta(\text{H}^+/\text{H}_2) = 0.000 \text{ V}$
 - ▣ complicated, impractical, dangerous (H_2 gas!)
- Standard hydrogen electrode:



F. Measuring electrode potentials

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- Practical reference electrodes:
 - ▣ stable potential independent of many external conditions (metal/insoluble salt electrode)
 - ▣ $\text{Ag}(s) \mid \text{AgCl}(s) \mid \text{Cl}^-(\text{aq})$ (silver/silver chloride)
 $E^\theta = + 0.22 \text{ V}$
 - ▣ $\text{Pt} \mid \text{Hg}(\text{l}) \mid \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Cl}^-(\text{aq})$ (saturated calomel)
 $E^\theta = + 0.27 \text{ V}$

G. Scales of electrode potentials

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- As the potential of SHE is 0.000 V at each temperature by convention...
- the electromotive force of the Galvanic cell is the same as the potential of the electrode on the right.
- Result:
 - Positive and negative electrode potentials in the range from +3 V to -2 V
 - The electrode potential can be arranged as a series

G. Scales of electrode potentials

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□ Oxidizing agent

Standard Reduction Potentials at 25 °C

Reduction Half-Reaction	E° (V)
$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	2.87
$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51
$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33
$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	1.23
$Br_2(aq) + 2 e^- \longrightarrow 2 Br^-(aq)$	1.09
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	0.54
$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	0.15
$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	-0.13
$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-0.26
$Cd^{2+}(aq) + 2 e^- \longrightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76
$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04

Stronger oxidizing agent

Weaker oxidizing agent

Weaker reducing agent

Stronger reducing agent

H. Types of electrodes

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a) metal/metal ion electrode

- indicator electrodes

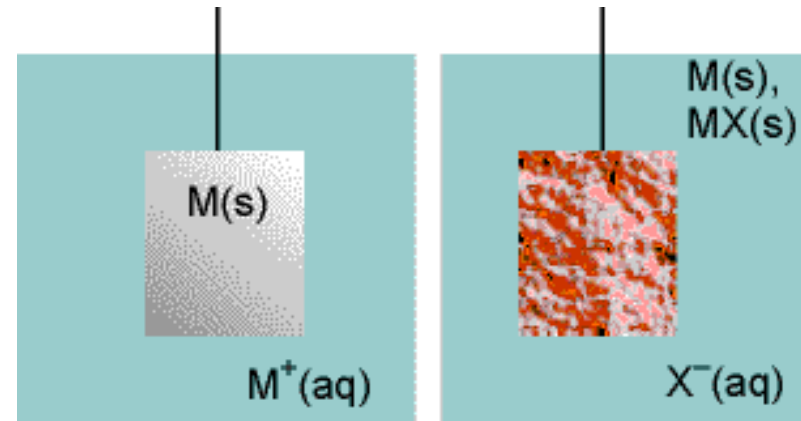
b) metal insoluble salt electrode

- reference electrodes
- (Ag/AgCl, Hg/Hg₂Cl₂)

c) gas electrodes (H₂, Cl₂, etc.)

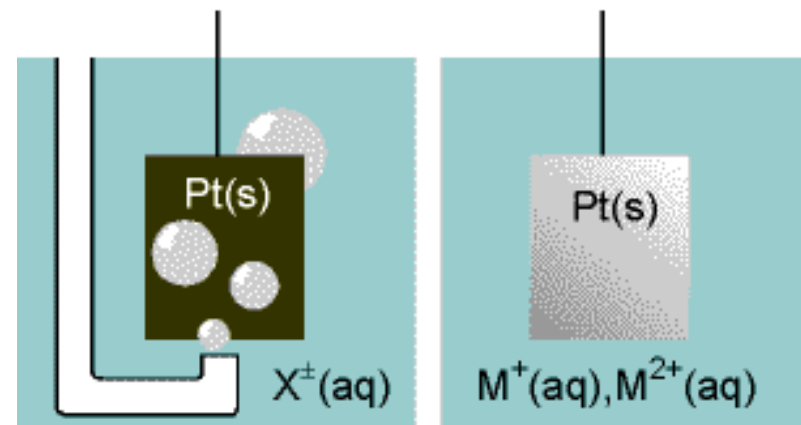
d) redox electrodes

- glass electrodes (single or combination)
- amalgam electrodes
- complex ion electrodes
- enzyme electrodes



(a)

(b)



(c)

(d)

H. Types of electrodes

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c) **Glass electrode** – hydrogen electrode

- ❑ Single or combination.
- ❑ Structure:
- ❑ Operation:

