Overview of electrochemistry

	Equilibrium electrochemistry (no current flows)	Dynamic electrochemistry (current does flow)
Homogeneous	Thermodynamics of electrolyte solutions: • electrolytic dissociation • thermodynamics and activities of ions	Conductance of electrolytes: • electrolytic conduction • mobilities of ions • Kohlrausch laws
Heterogeneous	Thermodynamics of Galvanic cells and electrodes: • electrochemical cells • cell and electrode potential • types of electrodes	Kinetics of electrode reactions: • exchange current • overpotential • Tafel equation • Butler-Volmer equation • electrolysis • batteries

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HETEROGENEOUS EQUILIBRIUM ELECTROCHEMISTRY:

Thermodynamics of electrodes and Galvanic cells

I. **Galvanic *vs.* electrolytic cells**

II. Galvanic cells:
- A. chemistry and thermodynamics
- B. Parts and usual notations of Galvanic cells
- C. Potential of a Galvanic cell
- D. Electrolyte and electrode concentration cells
- E. Measuring cell potential
- F. Galvanic cells (chemical sources of electricity) in practice
- G. Fuel cells

HETEROGENEOUS EQUILIBRIUM ELECTROCHEMISTRY:

Thermodynamics of Galvanic cells and electrodes

I. **Galvanic *vs.* electrolytic cells**

III. Electrodes
- H. Dependence of the electrode potentials on the composition
- I. Measuring electrode potentials
- J. The scale of electrode potentials
- K. Types of electrodes

IV. **Summary**

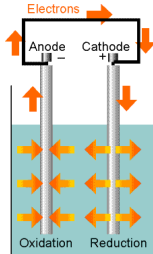## Thermodynamics of Galvanic cells and electrodes

- **Electrochemical cells**: Galvanic cells *vs.* electrolysis
- **Galvanic cells** :
  - connection between standard cell potential and standard reaction Gibbs free energy: $-\nu F E_{cell}^{\theta} = \Delta_r G^{\theta}$
  - connection between cell potential and composition (reaction quotient): $E_{cell} = E_{cell}^{\theta} - (RT/\nu F) \ln Q$ (Nernst equation)
  - Galvanic cell in equilibrium: $RT \ln K = \nu F E_{cell}^{\theta}$
  - types of Galvanic cells, practical applications
- **Electrodes**:
  - Nernst equation of the electrode:
    $E = E^{\theta} + (RT/\nu F) \ln a_i$
  - electrode reactions, types of electrodes

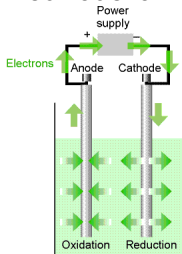## Thermodynamics of Galvanic cells and electrodes

- In electrochemical cells, redox reactions proceed in a spatially separated arrangement. [***Electrolytic dissociation*** *is also a chemical change, but does not involve changes in oxidation states, only charge separation in a single solution.* ***Acid-base reactions*** *cannot be separated in space.*]
  - 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 electrically, a **salt bride** or **diaphragm** is needed.
- Two different approaches:
  - spontaneous Galvanic cell *vs.*
  - forced electrolysis.

I. Galvanic *vs.* electrolytic cells

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

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

PhysChem10

I. Galvanic *vs.* electrolytic cells

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

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

I. Galvanic *vs.* electrolytic cells

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- Neither the **Galvanic cells** nor the **electrolytic cells** are in thermodynamic equilibrium, but if we allow the electron transition, the cell will go towards and finally reach the chemical equilibrium.
- There are chemical (redox) reactions in the cell:
  - this is always e^- transfer, sometimes also atom transfer,
  - reduction (e^- gain) and oxidation (e^- loss)
  - reduction and oxidation is separated in space
  - there is ionic conduction in the electrolyte solution
  - and metallic conduction in the outer circuit (wire).

- Note: The oxidizing agent oxidizes another substance while itself is reduced and *vice versa*.

II.A. Galvanic cells: chemistry and thermodynamics

9

- **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:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

II.A. Galvanic cells: chemistry and thermodynamics

10
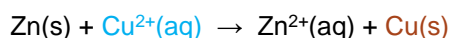
- Chemical Galvanic cells: reduction and oxidation separated in space

Zn anode | V | Cu cathode
NaNO$_3$
Anions
Zn^{2+} SO_4^{2-} | Cations | Cu^{2+} SO_4^{2-}
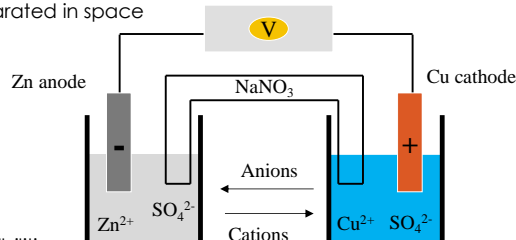
- Possibilities:
  - a single electrode compartment with a diaphragm
  - two electrode compartments and a salt bridge.

II.A. Galvanic cells: chemistry and thermodynamics

11

- Separate the previous
  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ reaction
- into **oxidation** and **reduction**:

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

- Both sides are redox pairs: ox + *v*e$^-$ → red

II.A. 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:
- $E_{cell} = E_{right\ electrode} - E_{left\ electrode}$

2

II.B. Parts and usual notations of Galvanic cells

`13`

- Galvanic cell (or voltaic/electrochemical cell) =
  - 2 half cells or
  - 2 half reactions or
  - 2 electrodes
- Notation:
- Particularly: $(-)$ $Zn(s)\,|\,ZnSO_4(aq)\,\|\,CuSO_4(aq)\,|\,Cu(s)$ $(+)$
  - $|$ phase boundary (solid/solution, solid/gas)
  - $\|$ surface on the boundary – no liquid junction potential (liquid junction potential is minimized with the use of an appropriate salt bridge.
  - $:$ electrolytes in contact with each other

II.C. Potential of a Galvanic cell

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- In a Galvanic cell, there is electric potential (potential difference): it is called cell potential.
- Connection between the cell potential and reaction Gibbs energy: $-\nu F E_{cell} = \Delta_r G$
- Derivation of the relationship:
  - the maximum useful work of the chemical reaction: $\Delta_r G$
  - electric work (in physics): $-\nu F E_{cell}$
  - In a Galvanic cell, the two must be the same.

II.C. Potential of a Galvanic cell

`15`

- 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:
  - $-\nu F E_{cell} = \Delta_r G^\theta + RT \ln Q$
  - $E_{cell} = -(\Delta_r G^\theta / \nu F) - (RT/\nu F)\ln Q$
  - Let $-(\Delta_r G^\theta / \nu F) = E_{cell}^\theta$, the **standard cell potential**
  - Finally, the **Nernst equation for the cell** :

$$E_{cell} = E_{cell}^\theta - (RT/\nu F)\ln Q$$
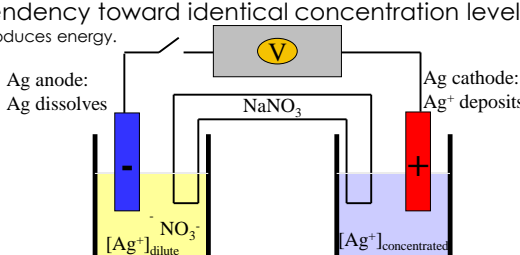
II.C. Potential of a Galvanic cell

`16`

- In equilibrium (*i.e.* when $E_{cell} = 0$), $Q = K$. From this, the connection between standard cell potential and equilibrium constant can be written:
  $E_{cell}^\theta = (RT/\nu F)\ln K$
- Relationship between
  - **standard cell potential** (E_{cell}^θ),
  - **equilibrium constant** (K) and
  - **standard reaction Gibbs free energy** $(\Delta_r G^\theta)$:

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

- So, *equilibrium electrochemistry* gives the connection between equilibrium chemistry and thermodynamics.

II.C. Potential of a Galvanic cell

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- Connections between cell potential and other thermodynamic functions (H, S) :
  - Basis: temperature dependence of E_{cell} and E_{cell}^θ.
  - Well-known from thermodynamics: $-S = (\partial G/\partial T)_p$
  - from this: $-\Delta_r S = (\partial(-\nu F E_{cell})/\partial T)_p = -\nu F\left(\dfrac{\partial E_{cell}}{\partial T}\right)_p$
  - since $\Delta_r G = \Delta_r H - T\cdot\Delta_r S$, $\Delta_r H = \Delta_r G + T\cdot\Delta_r S =$
    $= -\nu F\left\{ E_{cell} - T\left(\dfrac{\partial E_{cell}}{\partial T}\right)_p \right\}$
- This is also valid for the standard values.
- So, $\Delta_r G^\theta$, $\Delta_r S^\theta$ and $\Delta_r H^\theta$ can be determined based on electrochemical measurements.

II.D. Concentration cells

`18`

- **Electrolyte concentration cells**
- Tendency toward identical concentration levels produces energy.

Ag anode: Ag dissolves — NaNO₃ — Ag cathode: Ag⁺ deposits

$[Ag^+]_{dilute}$ NO_3^- $[Ag^+]_{concentrated}$

- There are **electrode concentration cells** as well (Hg-Me).

3

II.D. Concentration cells

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- In an electrolyte concentration Galvanic cell:
  - a difference of 1 order of magnitude in concentration (or activity) yields 59 mV of cell potential (at 25 °C).
  - Across a biological membrane, typically there is a 20-30 times difference in [K$^+$] yielding *ca.* 77 mV of potential difference – also an electrolyte concentration cell.
  - This membrane potential has a role in nerve signal transmission.

II. Galvanic cells

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- **Galvanic cells with melted salts**:
  - Such Galvanic cells are seldom used.
  - <u>Melt electrolysis</u> is important in industry: *e.g.* electrolysis of Al_2O_3 (alumina).
- **Galvanic cells without solvents**:
  - The use of solvent should be avoided if possible: it may be sensitive to heat and/or environmentally pollutant.
  - Practical examples will be shown later (batteries).

II. Galvanic cells

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- With no current flowing ($I = 0$), the potential is called: **electromotive force (e.m.f.)**.
- The Galvanic cell is able to do work (maintain current), when it is far from chemical equilibrium. When it is in use the voltage is lower and it is called: **output voltage**.
- When (the redox reaction) reaches the chemical equilibrium, e.m.f. = 0, no more current flows (the battery is „dead").
- The process is (theoretically) always reversible and the battery can be „recharged" with electrolysis: this is called **rechargeable battery**.

II.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 (e.m.f.)**:
  - compensation method (fully current-free), classical: *DuBois–Reymond–Poggendorf*
  - voltmeter with large internal resistance ($R > 10^{10}$ Ω). Today this is a common piece of laboratory equipment (*e.g.* pH-meter).
  - In practice, voltages of $0 \leq 3$ V have to be measured with a precision of 0.1 mV (10^{-4} V).

II.F. Galvanic cells (chemical sources of electricity) in practice

23

- Galvanic cell (primary battery): non-rechargeable (when it reaches thermodynamic equilibrium)
- Accumulator (secondary or rechargeable battery): rechargeable many (hundreds of) times (cars, hearing aids, *etc.*)
- Fuel cell: production of electricity from combustion – with continuous input of reactants
- **Significance:**
  - (small) source of electricity anytime anywhere without access to the grid or a large generator,
  - operation is very easy (no training necessary),
  - portability (radio, watch, cell phone, pacemaker *etc.*).

II.F. Galvanic cells (chemical sources of electricity) in practice

24

- **Qualification:**
  - voltage (can be increased by using several cells in a series)
  - capacity (scalable)
  - current output (can be increased by using several parallel cells)
  - power/mass ratio
  - efficiency
  - voltage stability (under current and in time)
  - fast/slow current output change
  - recharge cycles (for accumulators)
  - temperature range
  - environmental pollution (Hg, Cd free!)
  - price

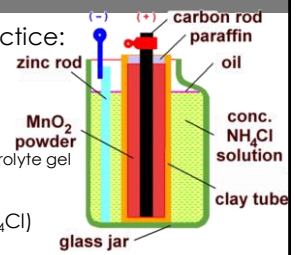## II.F. Galvanic cells (chemical sources of electricity) in practice

25

□ Galvanic cells in practice:
- Leclanché cell
- Alkaline manganese oxide
- Lithium battery
- Mercury oxide battery
- (Daniell cell)
- (Volta's battery / Voltaic pile)

II.F. Galvanic cells (chemical sources of electricity) in practice

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□ Galvanic cells in practice:
- Leclanché cell

- anode: Zn
- cathode: graphite + MnO_2
- medium: acidic NH_4Cl, $ZnCl_2$ electrolyte gel

⊖ $\frac{1}{2} Zn \rightarrow \frac{1}{2} Zn^{2+} + e^-$
(forms $[Zn(NH_3)_4]^{2+}$ with NH_4Cl)
⊕ $H^+ + e^- \rightarrow \frac{1}{2} H_2$
H_2 is „absorbed" by MnO_2 as $MnO(OH)$

G. Galvanic cells (chemical sources of electricity) in practice

27

□ Galvanic cells in practice:
- Alkaline manganese oxide (alkaline battery, 1.5 V)

- anode: Zn
- cathode: graphite + MnO_2
- medium: KOH, $ZnCl_2$ electrolyte gel

⊖ $\frac{1}{2} Zn + OH^- \rightarrow \frac{1}{2} Zn(OH)_2 + e^-$

⊕ $H^+ + e^- \rightarrow \frac{1}{2} H_2$
H_2 is „absorbed" by MnO_2 as $MnO(OH)$
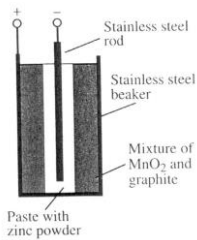
Most common battery today, 5-7 years of storage time.
AA size: 2000 mAh

G. Galvanic cells (chemical sources of electricity) in practice
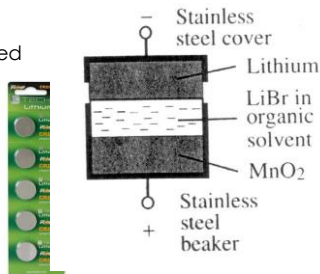
28

□ Galvanic cells in practice:
- 9 V battery

G. Galvanic cells (chemical sources of electricity) in practice

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□ Galvanic cells in practice:
- Lithium battery

⊖ $Li \rightarrow Li^+ + e^-$
Organic solvent needed because of Li.
⊕ $MnO_2 + e^- \rightarrow [MnO_2]^-$

3 V,
light,
temperature-tolerant,
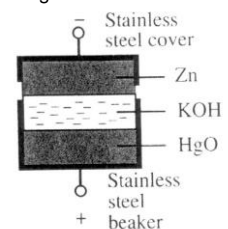can provide high current,
small size.

G. Galvanic cells (chemical sources of electricity) in practice

30

□ Galvanic cells in practice:
- Mercury oxide battery (*Ruben–Mallory*)

net reaction: $Zn + HgO \rightarrow ZnO + Hg$

1.25 V, constant!
Hearing aids, pacemakers
Hg – environmental concerns!

G. Galvanic cells (chemical sources of electricity) in practice

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- □ Galvanic cells in practice:
  - ◘ Daniell cell
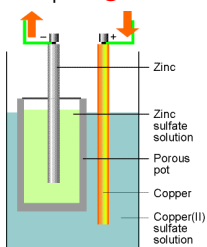- ⊖ Zn | ZnSO$_4$ solution | CuSO$_4$ solution | Cu ⊕

Cu deposition, Zn dissolution

Clay diaphragm needed!

For demonstration and education purposes: simple, spectacular.

Impractical for actual use.

<u>Voltaic pile</u>: a lot of pairs of Cu/Zn sheets with electrolyte-soaked cloths

Zinc
Zinc sulfate solution
Porous pot
Copper
Copper(II) sulfate solution

II.G. Fuel cells

32

- □ Chemical energy → electricity: indirect in a **power plant** (two steps with heat as the intermediate): maximum efficiency about 40%
- □ **Fuel cell**: special Galvanic cell that produces electricity directly based on combustion (75-90%).
- □ The hydrogen + oxygen reaction (in KOH) is separated in space.
- □ Catalyst needed, T = 70–140 °C
  - ◘ anode reaction: $2H_2(g) + 4OH^- \rightarrow 4H_2O + 4e^-$
  - ◘ cathode reaction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-$
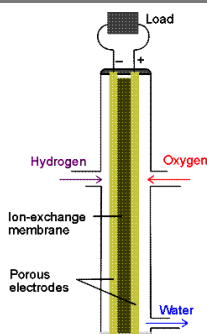- □ Other fuels (methane, ethane, methanol) can also be used in a similar fashion.

II.G. Fuel cells

33

- □ Fuel cells in practice:
  - ◘ Bacon battery

E_{cell} = 1.2 V

Load
Hydrogen
Oxygen
Ion-exchange membrane
Porous electrodes
Water

III. Electrodes

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- □ Connection between **cell potentials** and **electrode potentials**, a formal interpretation of electrode potentials:
  - ◘ the cell potential is the difference of two electrode potentials: $E_{cell} = E_{right} - E_{left}$
  - ◘ The (absolute) potential of a single electrode can never be measured, neither it can be calculated.
  - ◘ A successful solution: preparation of a Galvanic cell in which the left hand electrode is the **standard hydrogen electrode (SHE)**.

## III.H. Dependence of the electrode potential on the composition: the Nernst equation

35

- □ The principle of the definition is SHE-reference:
  Pt | H$_2$(g) | H$^+$(aq) ‖ Ag$^+$(aq) | Ag(s)
- □ Cell reaction: ½ H$_2$(g) + Ag$^+$(aq) → H$^+$(aq) + Ag(s)
- □ The Nernst equation of the cell expressed with Q (as v = 1 and E_{SHE} = 0):

  $E_{cell} = E_{cell}^{\ominus} - RT/F \ln Q = E^{\ominus}(Ag^+/Ag) - RT/F \ln Q$
- □ as $Q = 1/a(Ag^+)$ is valid:

  $E(Ag^+/Ag) = E^{\ominus}(Ag^+/Ag) + RT/F \ln a(Ag^+)$
- □ Nernst equation for the (Ag$^+$/Ag) electrode.
- □ Generally (metal/metal ion electrodes):
  $E_i = E_i^{\ominus} + (RT/vF) \ln a_i$

III.I. Measuring electrode potentials

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- □ Measurement using a standard hydrogen electrode

V
H$_2$(g)
a_{H2}=1
Ag
Pt H$^+$
Ag$^+$
S.H.E
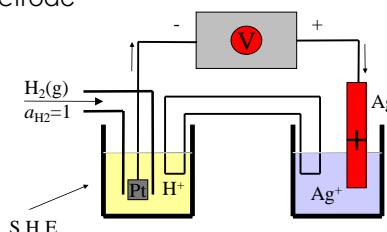
III.I. Measuring electrode potentials

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- Reference point SHE: $E^\theta(H^+/H_2) = 0.000$ V
  - complicated, impractical, dangerous (H_2 gas!)
- Practical reference electrodes:
  - stable potential independent of many external conditions (metal/insoluble salt electrode)

  - Ag(s) | AgCl(s) | Cl$^-$(aq)
    $E^\theta = + 0.22$ V   (silver/silver chloride electrode)

  - Pt | Hg(l) | Hg$_2$Cl$_2$(s) | Cl$^-$(aq)
    $E^\theta = + 0.27$ V   (saturated calomel electrode)

III.J. 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

III.J. Scales of electrode potentials

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- Oxidizing agent

Standard Reduction Potentials at 25 °C

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

Stronger oxidizing agent / Weaker reducing agent (top) → Weaker oxidizing agent / Stronger reducing agent (bottom)

- Reducing agent

Electrochemical series of metals

40

- Highly reducing
- Reacts readily with cold water
- Reacts slowly with cold water

- Reacts slowly with water vapor
- Reacts readily with acids

- Reacts slowly with acids

- No reaction with acids

- Almost non-reducing
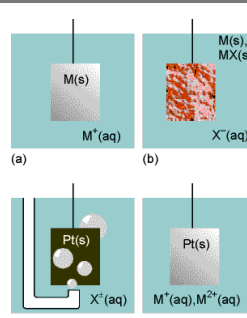
Metal	Oxidation Reaction
Lithium	$Li \rightarrow Li^+ + e-$
Potassium	$K \rightarrow K^+ + e-$
Barium	$Ba \rightarrow Ba^{2+} + 2e-$
Calcium	$Ca \rightarrow Ca^{2+} + 2e-$
Sodium	$Na \rightarrow Na^+ + e-$
Magnesium	$Mg \rightarrow Mg^{2+} + 2e-$
Aluminum	$Al \rightarrow Al^{3+} + 3e-$
Zinc	$Zn \rightarrow Zn^{2+} + 2e-$
Chromium	$Cr \rightarrow Cr^{3+} + 3e-$
Iron	$Fe \rightarrow Fe^{2+} + 2e-$
Cobalt	$Co \rightarrow Co^{2+} + 2e-$
Nickel	$Ni \rightarrow Ni^{2+} + 2e-$
Tin	$Sn \rightarrow Sn^{2+} + 2e-$
Lead	$Pb \rightarrow Pb^{2+} + 2e-$
Hydrogen	$H_2 \rightarrow 2H^+ + 2e-$
Copper	$Cu \rightarrow Cu^{2+} + 2e-$
Silver	$Ag \rightarrow Ag^+ + e-$
Mercury	$Hg \rightarrow Hg^{2+} + 2e-$
Platinum	$Pt \rightarrow Pt^{2+} + 2e-$
Gold	$Au \rightarrow Au^{3+} + 3e-$

Increase in Ease of Oxidation

III.K. Types of electrodes

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- **a)** **metal/metal ion electrode (electrode of the first kind)**
  - indicator electrodes
- **b)** **metal insoluble salt electrode (electrode of the second kind)**
  - reference electrodes
  - (Ag/AgCl, Hg/Hg$_2$Cl$_2$)
- **c)** **gas electrodes (H_2, Cl_2, etc.)**
- **d)** **redox electrodes**
  - glass electrodes (single or combination)
  - amalgam electrodes
  - complex ion electrodes
  - enzyme electrodes

(a) M(s), M$^+$(aq)   (b) M(s), MX(s), X$^-$(aq)
(c) Pt(s), X$^-$(aq)   (d) Pt(s), M$^+$(aq),M^{2+}(aq)
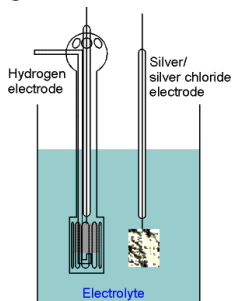
III.K. Types of electrodes

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- **a)** **Electrodes of the first kind**
  - Electrode potential is determined primarily by the metal ion activity (so these electrodes are often used to determine activity values):
    $E_i = E_i^\theta + (RT/\nu F)\ln a_i$
- **b)** **Electrodes of the second kind**
  - Electrode potential is determined by the counter ion concentration of the weakly soluble salt:
    $MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$ $K_{sol} = a(M^+)\, a(X^-)$
  - Using a high and constant [X$^-$], the electrode potential can be kept constant, so, these electrodes are used as reference electrodes.
  - K_{sol} solubility product can be determined by measuring the potential value.

III.K. Types of electrodes

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c) **Gas electrodes** – Hydrogen electrode

- $H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$
  $Q = (f(H_2)/p^\theta) / a(H^+)$
- $E(H^+/H_2) = RT/F \ln a(H^+) =$
  $= -(RT/F)\ln 10 \cdot pH$
- accurate measurement of pH
- The SHE is the 0 point of the potential scale.
- Accurate but difficult to handle.

Hydrogen electrode
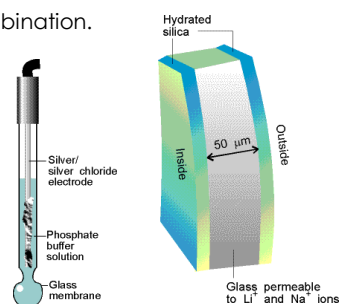
Silver/ silver chloride electrode

Electrolyte

III.K. Types of electrodes

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c) **Glass electrode** – Hydrogen electrode

- Single or combination.
- Structure:
- Operation:

Hydrated silica

Silver/ silver chloride electrode

Phosphate buffer solution

Glass membrane

50 μm

Inside

Outside

Glass permeable to Li$^+$ and Na$^+$ ions

III.K. Types of electrodes

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c) **Ion selective electrodes**

- Structure:
- Operation:
  - the complexed ions migrate through the lipophilic membrane to increase the membrane potential which is measured against a Ag/AgCl reference electrode.

Silver/ silver chloride electrode

Reservoir of hydrophobic liquid + chelating agent

Porous lipophilic membrane
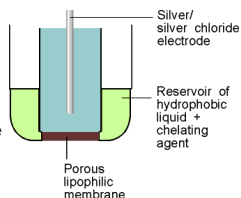
III.K. Types of electrodes

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d) **Redox electrodes**

- „Old" nomenclature
- $E_i = E_i^\theta + (RT/\nu F) \ln(a_{ox}/a_{red})$
- There are two different oxidation states of the same (metal) ion in a solution (*e.g.* Fe^{3+}/Fe^{2+}) and an inert Pt electrode.

e) **Amalgam electrodes**

- Metal mercury amalgams can also be electrodes: their potential depends on the metal concentration of the amalgam. (Example: electrolysis of NaCl.)

IV. Summary

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Practical use of electrochemistry:

- to find the spontaneous direction of a chemical reaction using standard electrode potentials,
- (from these) determining the value of K equilibrium constant,
- determining solubility products (K_{sol}),
- measuring pH and determining pK_a's,
- determining complex stability constant values,
- measuring ion activities and mean activity coefficients experimentally,
- determining thermodynamic functions (G, S, H).

IV. Summary

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In galvanic cells:

- A non-equilibrium, redox-type chemical process can perform electrical work when the two half-reactions are separated in space.
- The two electrodes thus formed – individually – has potential, and the potential difference is called cell potential. As a result, and external current flow (work) is generated.
- To calculate e.m.f.: $E_{cell} = E_{cathode, right} - E_{anode, left}$
- E depends of the chemical identities and the activities of the substance. E also depends on the temperature and solvent. (see: Nernst equations)

IV. Summary

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- **In galvanic cells:**
  - The reaction proceeds until the equilibrium is reached.
  - In equilibrium (when $E_{cell} = 0$) Q equals K. In this stage, there is no more work, no more chemical reaction.
  - E^0 describes the equilibrium state when every reactants and products are in standard state ($a_i = 1$).

IV. Summary

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- **Methods of utilizing chemical energy:**
  - Chemical reactions (*e.g.* combustion, neutralization, *etc.*) often produce heat (these are called exothermic reactions). In **heat engines**, chemical energy is transformed to mechanical energy (work) through heat.
  - In **power plants**, they generate electrical work from chemical energy through mechanical work.
  - In a **Galvanic cell**, chemical energy is directly transferred to electrical work.