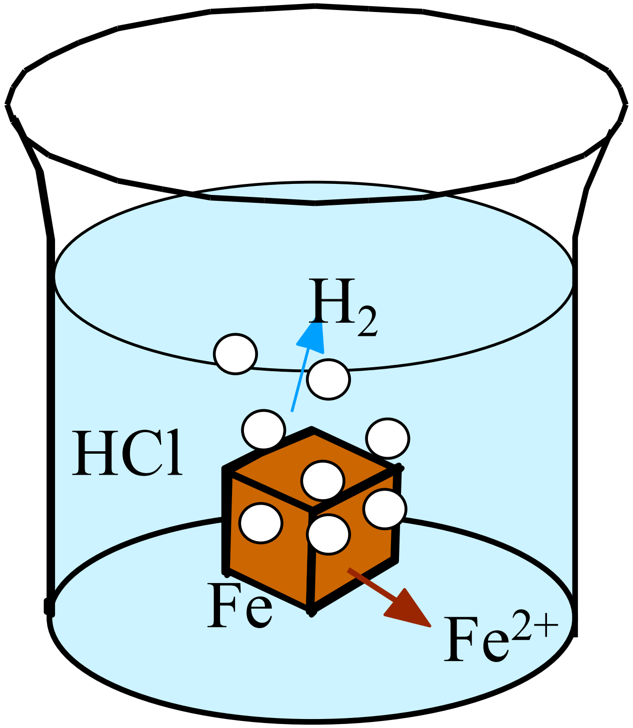
Electrochemistry for materials technology

Chapter 2

Electrode potential

ILLUSTRATIONS

Electrochemical reaction example: case of iron corrosion in acid

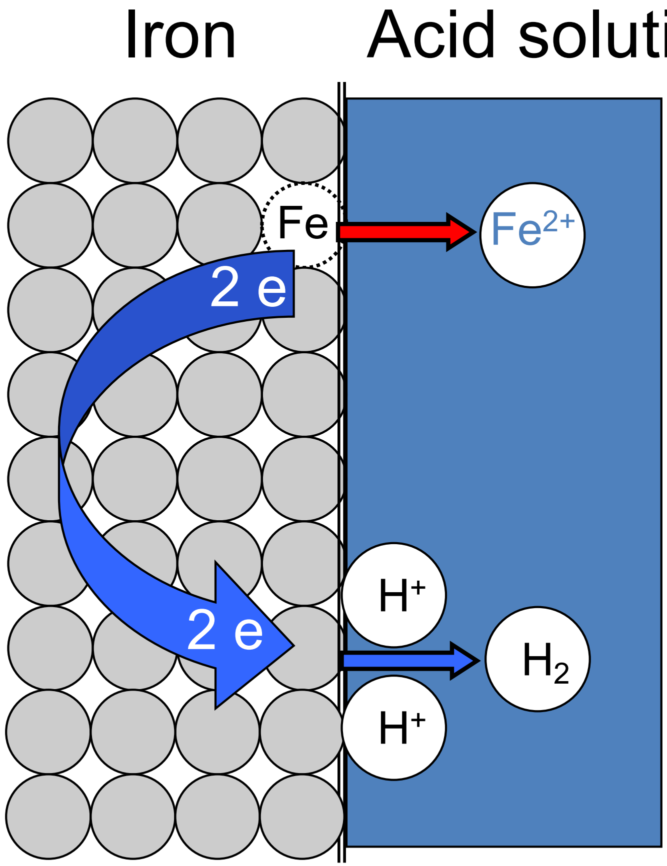


$$Fe \dashrightarrow Fe^{2+} + 2e$$

$$2H^{+} + 2e \dashrightarrow H_2$$

$$Fe + 2H^{+} \dashrightarrow Fe^{2+} + H_2$$

Corrosion of iron as an electrochemical reaction



Oxidation *half* reaction

$Fe \rightarrow Fe^{2+} + 2\ e-$

Reduction *half* reaction

$2H^+ + 2e- \rightarrow H_2$

Generalisation

- A corrosion reaction is a (special) case where (oxidation and reduction) electrochemical reactions take place on the ***same* electrode** (Fe in this case)
- More generally in electrochemistry, oxidation and reduction reactions take place on ***distinct* electrodes** (electrically connected externally)

Oxidation and reduction that occur on ***distinct*** but connected electrodes

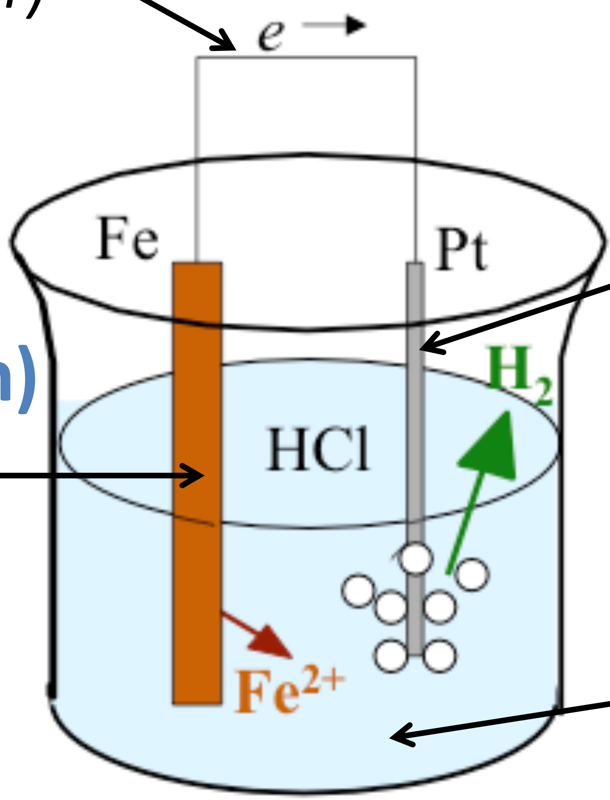
Electrical contact (electronic conductor)

Cathode (reduction)

$2H^+ + 2e \rightarrow H_2$

Anode (oxidation)

$Fe \rightarrow Fe^{2+} + 2e$



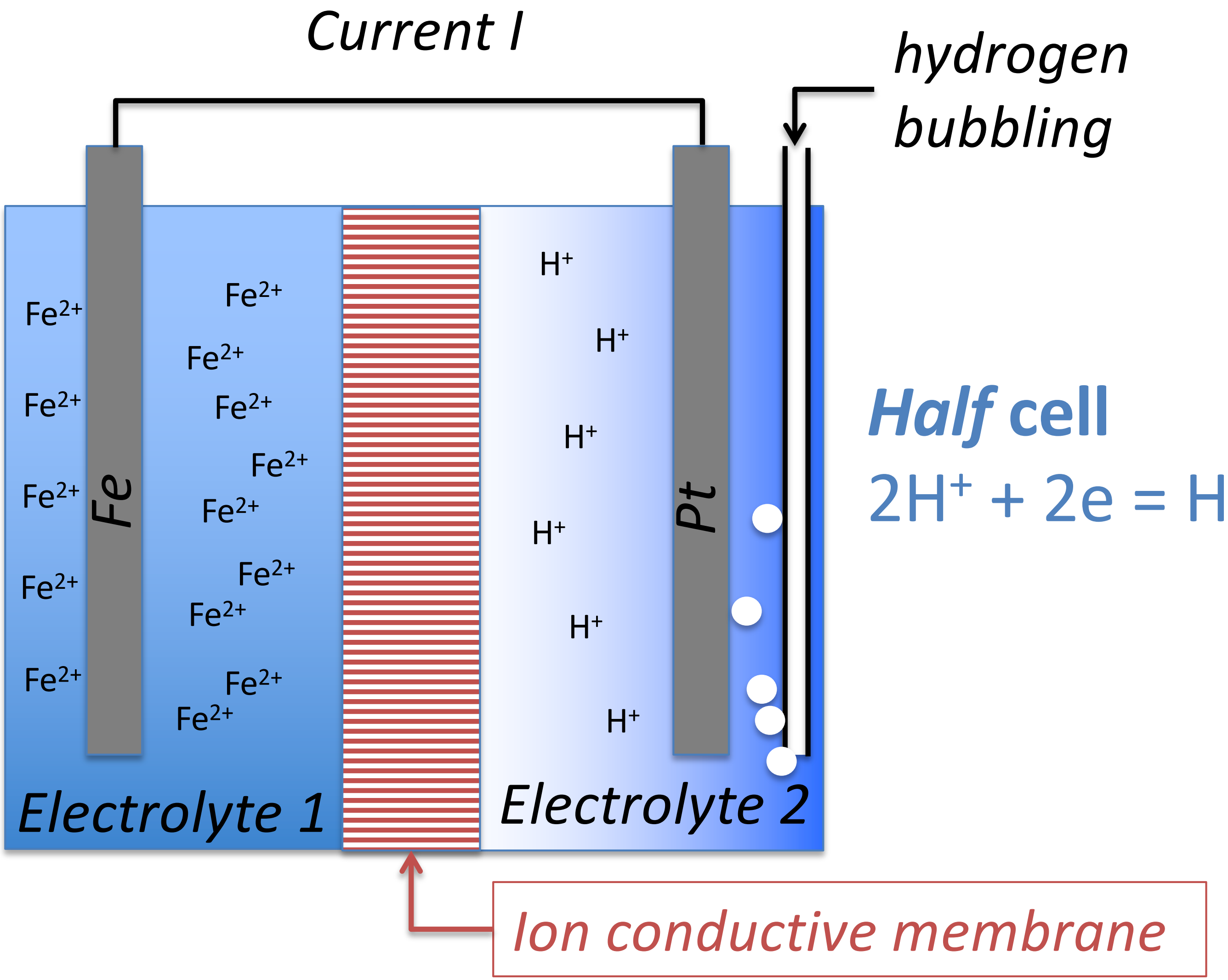
Electrolyte (ionic conduction)

Configurations

- The electrodes can furthermore be separated by membranes/diaphragms, and have their own electrolyte environment (catholyte, anolyte)
- => multitude of designs for batteries, fuel cells, electrolysers, sensors, …

=> Electrochemical cells and *half* cells

***Half* cell**
$Fe = Fe^{2+} + 2e$



***Half* cell**
$2H^{+} + 2e = H_2$

The reaction rate of electrochemical reactions is equivalent to **current**

Faraday's law

$$\frac{dm}{dt} = \frac{IM}{nF}$$

m: mass of reacted substance [g]
t : time [s]
I : current [A]
F: Faraday constant (96485 C mol^{-1})
M: the molar mass of the substance [g/mol]
n: **stoichiometric coefficient of the electrons** in the reaction

Ways of expressing electrode reaction rates

Current density i [A m^{-2}]

$$i = I / A_{electrode}$$

Number of moles n_m reacted per unit surface and per unit time [mol m^{-2} s^{-1}]

$$n_m = i / n F$$

Mass loss/gain m_r per unit surface and per unit time [g m^{-2} s^{-1}]

$$m_r = i M / n F$$

Reacted depth d_r per unit of time [µm/s]

$$d_r = i M / n F \rho$$

- *I : current [A]*
- *F: Faraday constant (96485 C mol^{-1})*
- *M: the molar mass of the substance [g mol^{-1}]*
- *n: stoichiometric coefficient of the electrons in the reaction*
- *$A_{electrode}$: surface area of the electrode [m^2]*
- *ρ: density [g cm^{-3}]*

ELECTRODE POTENTIAL (EQUILIBRIUM. THERMODYNAMICS)

Electrode potential

Reduction potential is a measure of a tendency of a chemical species to **acquire electrons**.

Other names: Reduction-oxidation potential
Redox potential
Midpoint potential

The **more positive** the reduction potential, the **more favorable** the reduction reaction

More thermodynamically favored

Based on values provided in Standard Reduction table

$$\boxed{Au^{3+}(aq) + 3e^- \rightarrow Au(s) \qquad E° = +1.50\ V}$$

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E° = +0.77\ V$$

Electrode potential

Reduction potential is a measure of a tendency of a chemical species to **acquire electrons**.

The **oxidation** potential is just the reverse reaction, which has the opposite sign → $(E_{oxidation})_{reactionA} = -(E_{reduction})_{reactionA}$

Based on values provided in Standard Reduction table

More thermodynamically favored

$Au^{3+}(aq) + 3e^{-} \leftarrow Au(s)$ $E° = -1.50\ V$

$\boxed{Fe^{3+}(aq) + e^{-} \leftarrow Fe^{2+}(aq) \quad E° = -0.77\ V}$

Electrode potential

Reduction potential is a measure of a tendency of a chemical species to **acquire electrons**.

The **oxidation** potential is just the reverse reaction, which has the opposite sign → $(E_{oxidation})_{reactionA} = -(E_{reduction})_{reactionA}$

$$A_{ox} + n\,e^- \underset{E_{oxidation}}{\overset{E_{reduction}}{\rightleftarrows}} A_{red}$$

$E_{reduction} >> 0$, reduction favored

$$\left.\begin{array}{l} E_{reduction} << 0 \\ E_{oxidation} >> 0 \end{array}\right\} \text{oxidation favored}$$

Electrode potential

Reduction potential is measured relative to a reference reaction (**reference electrode**).

vs. Standard Hydrogen Electrode (SHE)

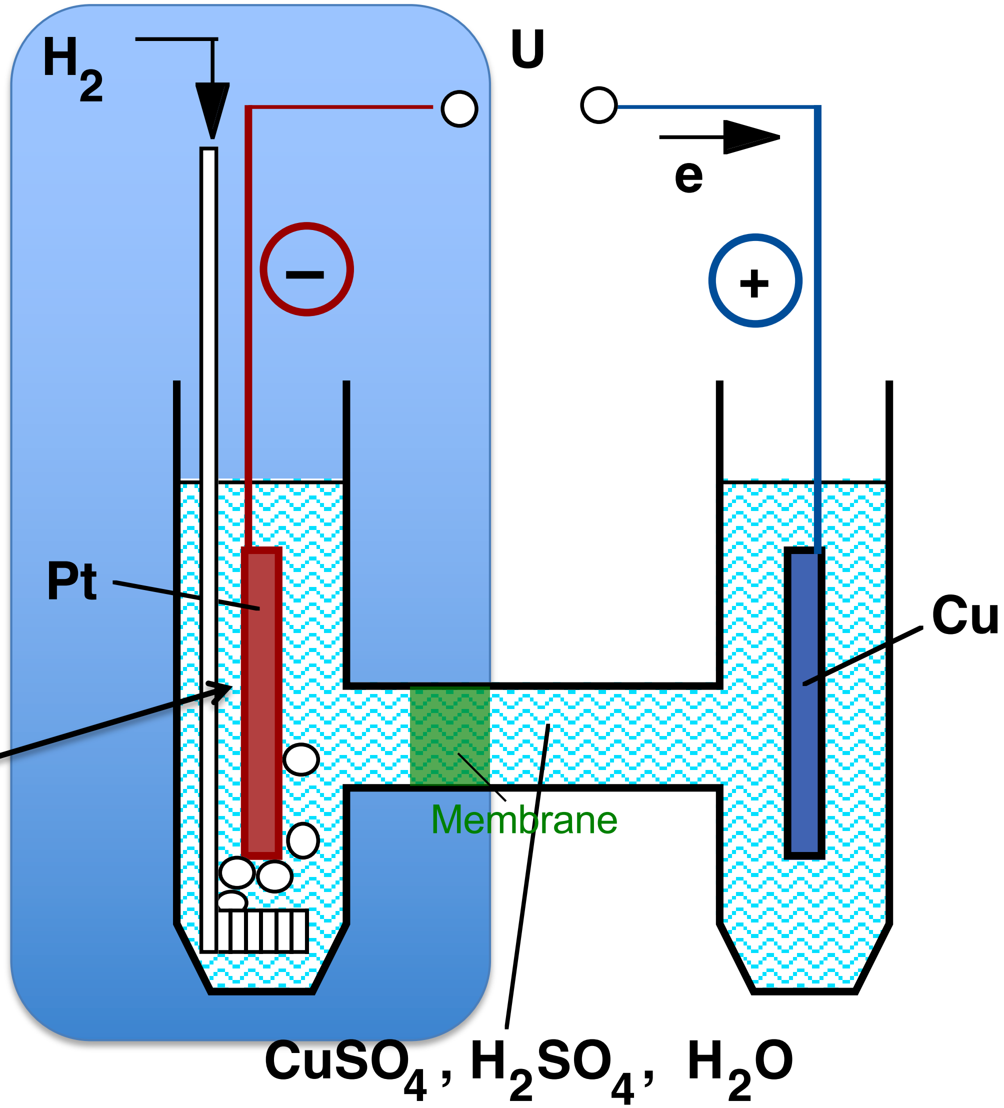
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	$E° = +1.50$ V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	$E° = 0.0$ V

vs. Ag/AgCl/saturated KCl reference electrode

$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	$E° = +1.278$ V
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	$E° = -0.222$ V
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	$E° = 0.0$ V

Reference electrodes: standard hydrogen electrode

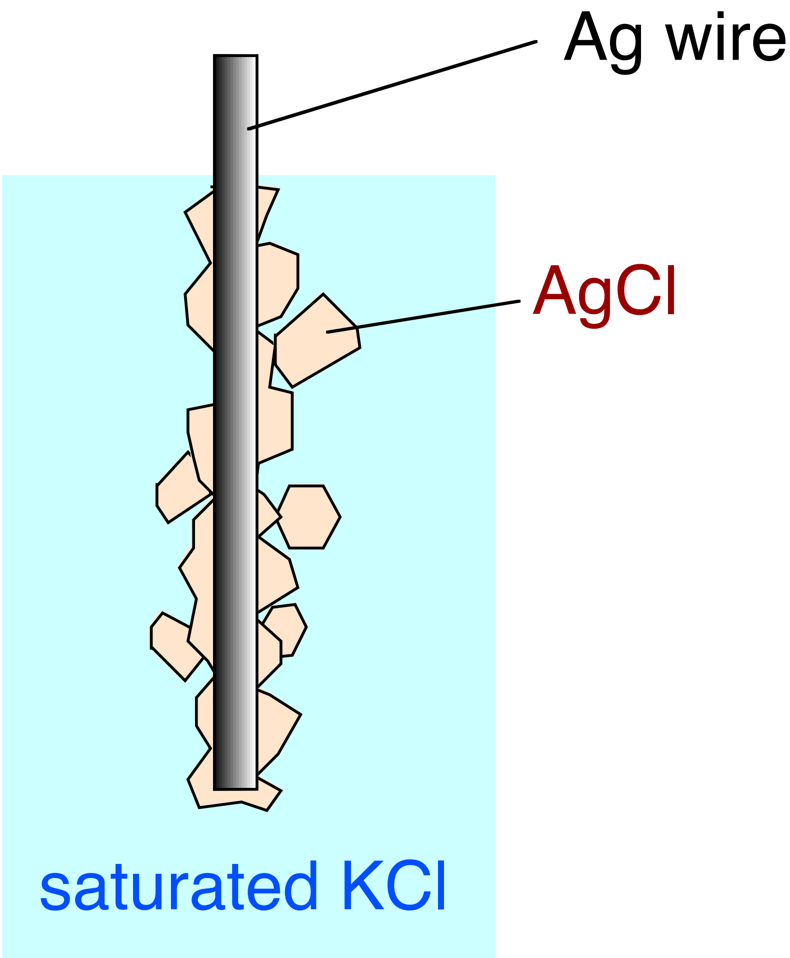
all activities = 1
p_{H_2} = 1 atm
a_{H^+} = 1 mol/kg



Reference electrodes: the silver chloride electrode

$AgCl + e \quad = \quad Ag \;+ Cl^- \qquad\qquad E^o = 0.222\ V$

$E_{rev} = E^0 - (RT/F)\ \ln a_{Cl^-}$

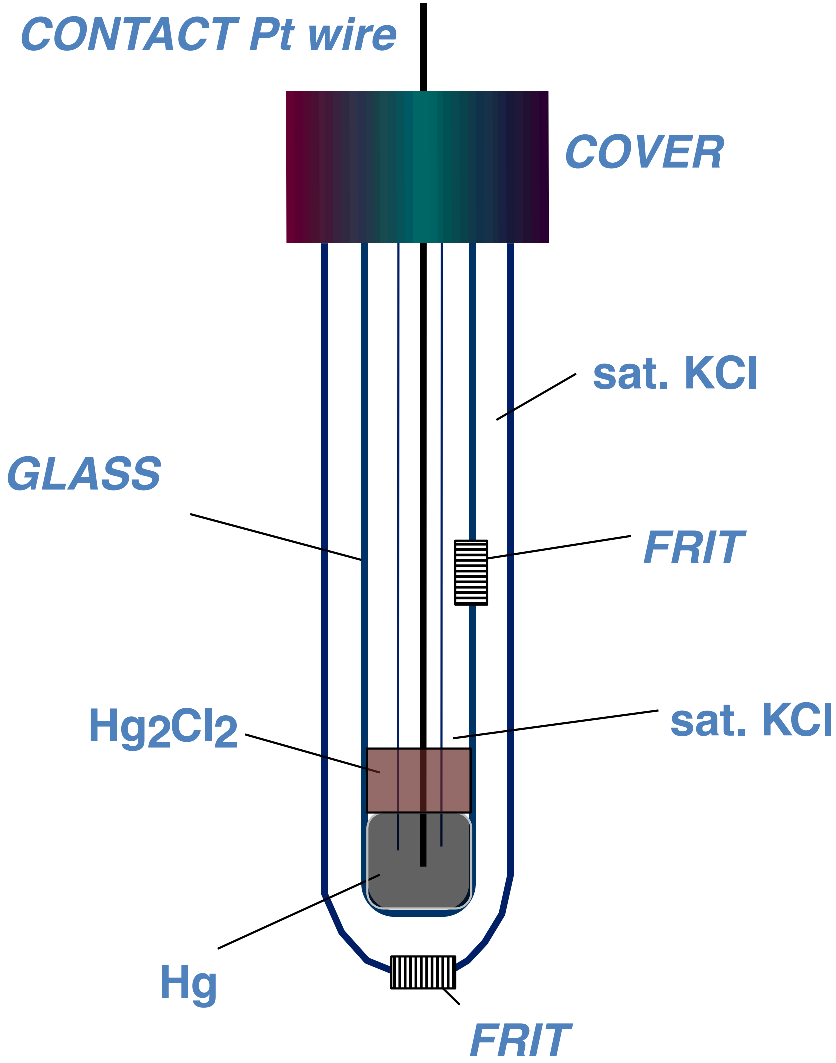


Reference electrodes: standard calomel electrode

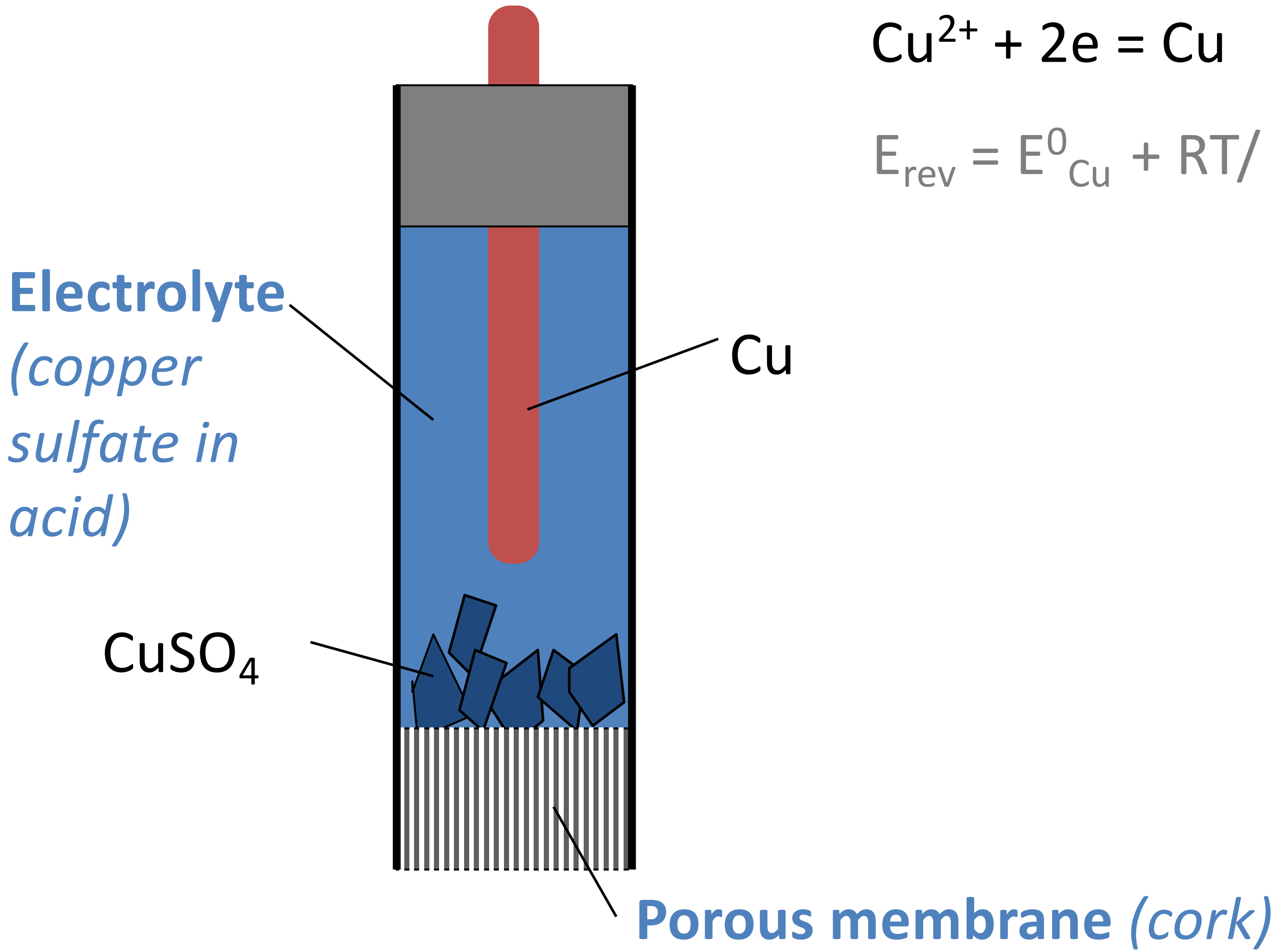
$Hg_2Cl_2 + 2e = 2\ Hg + 2\ Cl^-$

$E^0 = 0.268\ V$

$E_{rev}(25°) = 0.268\ V - 0.059 \log a_{Cl-}$



Reference electrodes: **copper sulphate** electrode



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

$E_{rev} = E^0_{Cu} + RT/\ 2\ F\ \ln\ (a_{\ Cu2+})$

Example : reference electrode used for measuring corrosion potential of concrete steel

= at what potential will the steel dissolve (release electrons) e.g. in contact with seawater or pH7 water (e.g. $O_2 + 4e + 4H^+ \Rightarrow H_2O$ as e- uptake (sink)).

Absolute potential / work function

Absolute potential is the electrode potential of a metal/substance measured with respect to a universal reference system that neglects the metal-solution interface. It is the difference in electronic energy between a point at the surface of an electrode of the metal/substance (=Fermi level) and a point outside the electrolyte in which the electrode is submerged (an electron at rest in vacuum).

Absolute potential is difficult to determine accurately, so the standard hydrogen electrode (SHE) is typically used as a reference potential. The SHE is one of the few systems for which the absolute potential has been accurately determined.

vs. vacuum (absolute potential)

$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$ $E° = +5.94$ V

$2H^+(aq) + 2e- \rightarrow H_2(g)$ $E° = +4.44$ V

$E° = 0.0$ V

Calculated from work function of the metal

Alternative definition

$$M^+_{solution} + e\text{-}(g) \rightarrow M_{metal}$$

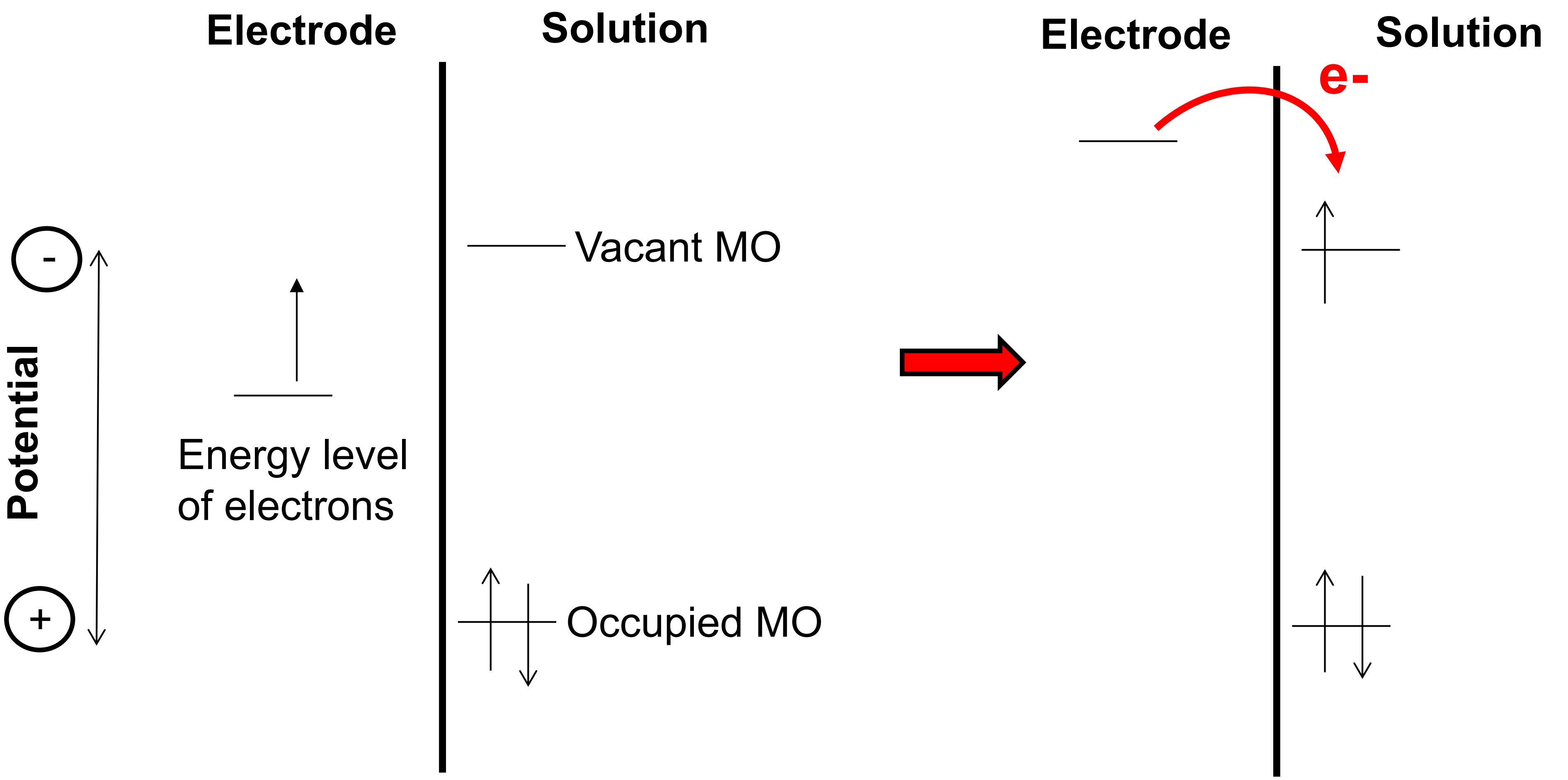
$$H^+_{solution} + e\text{-}(g) \rightarrow \tfrac{1}{2} H_2(g)$$

Calculated from Gibbs free energy change of this exact reaction at defined conditions

Electrode potential

Reduction process of a species at an electrode

MO = Molecular Orbital

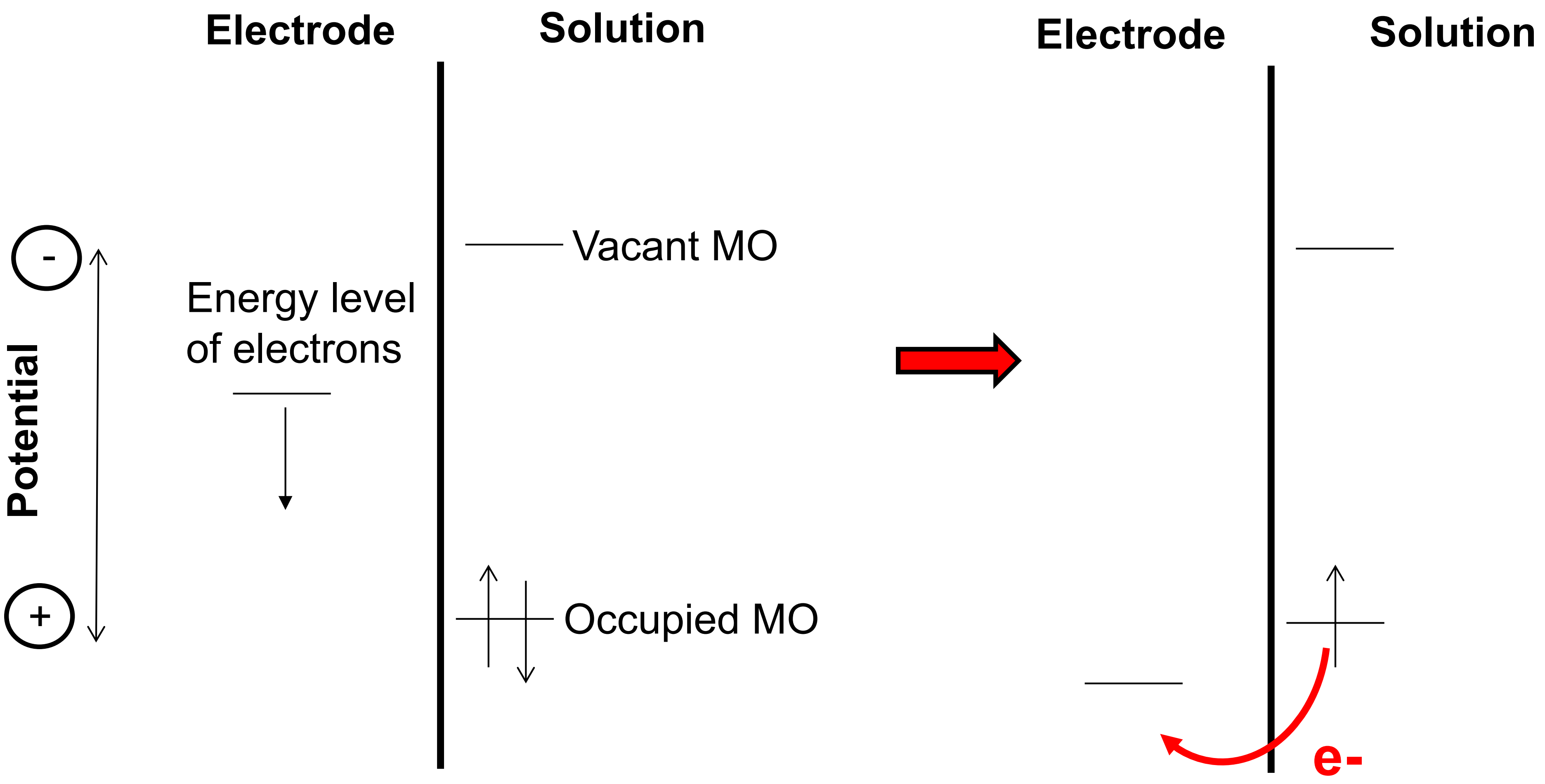


$A + e^- \rightarrow A^-$

Electrode potential

Oxidation process of a species at an electrode

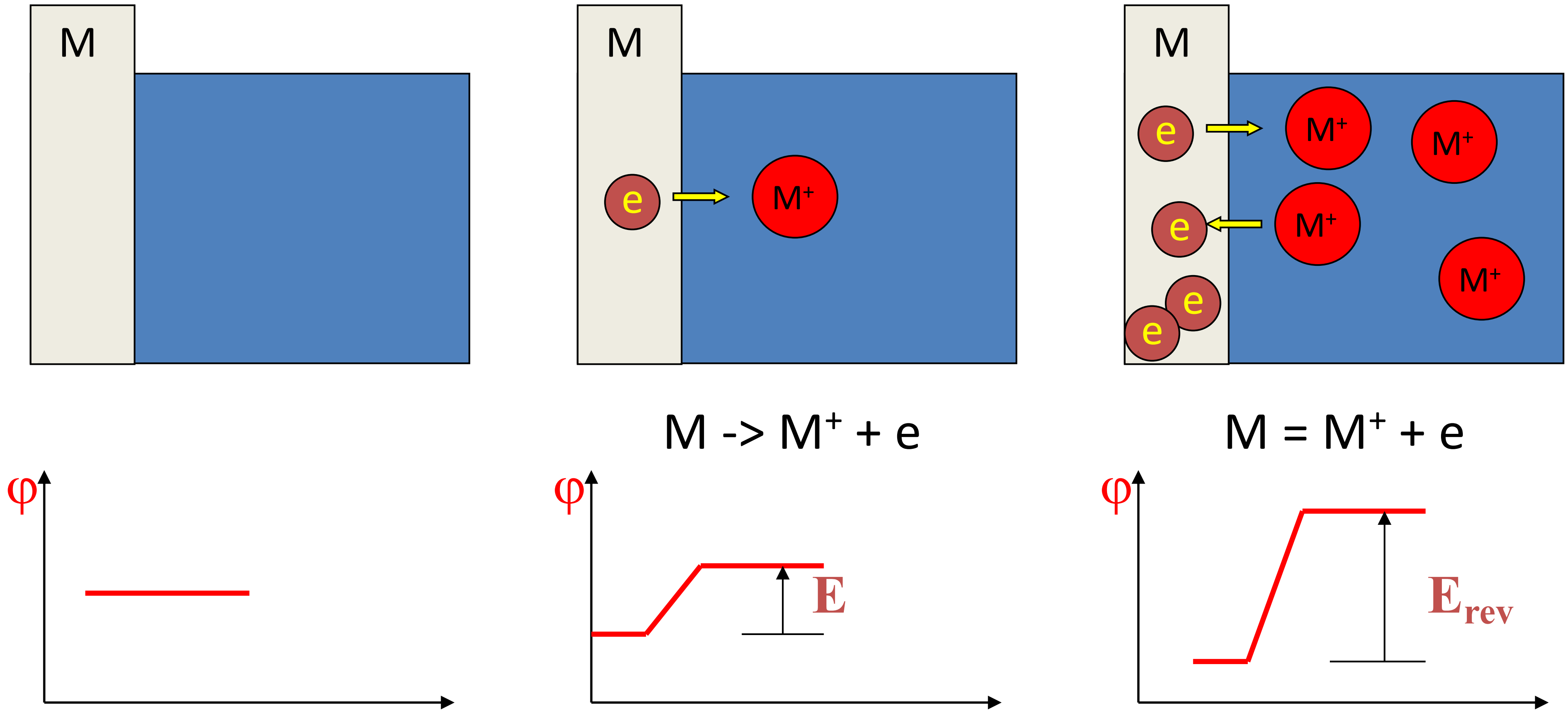
MO = Molecular Orbital



$A^- \rightarrow A + e^-$

Electrode in contact with electrolyte

(difference in electric potential φ between electrode and electrolyte)



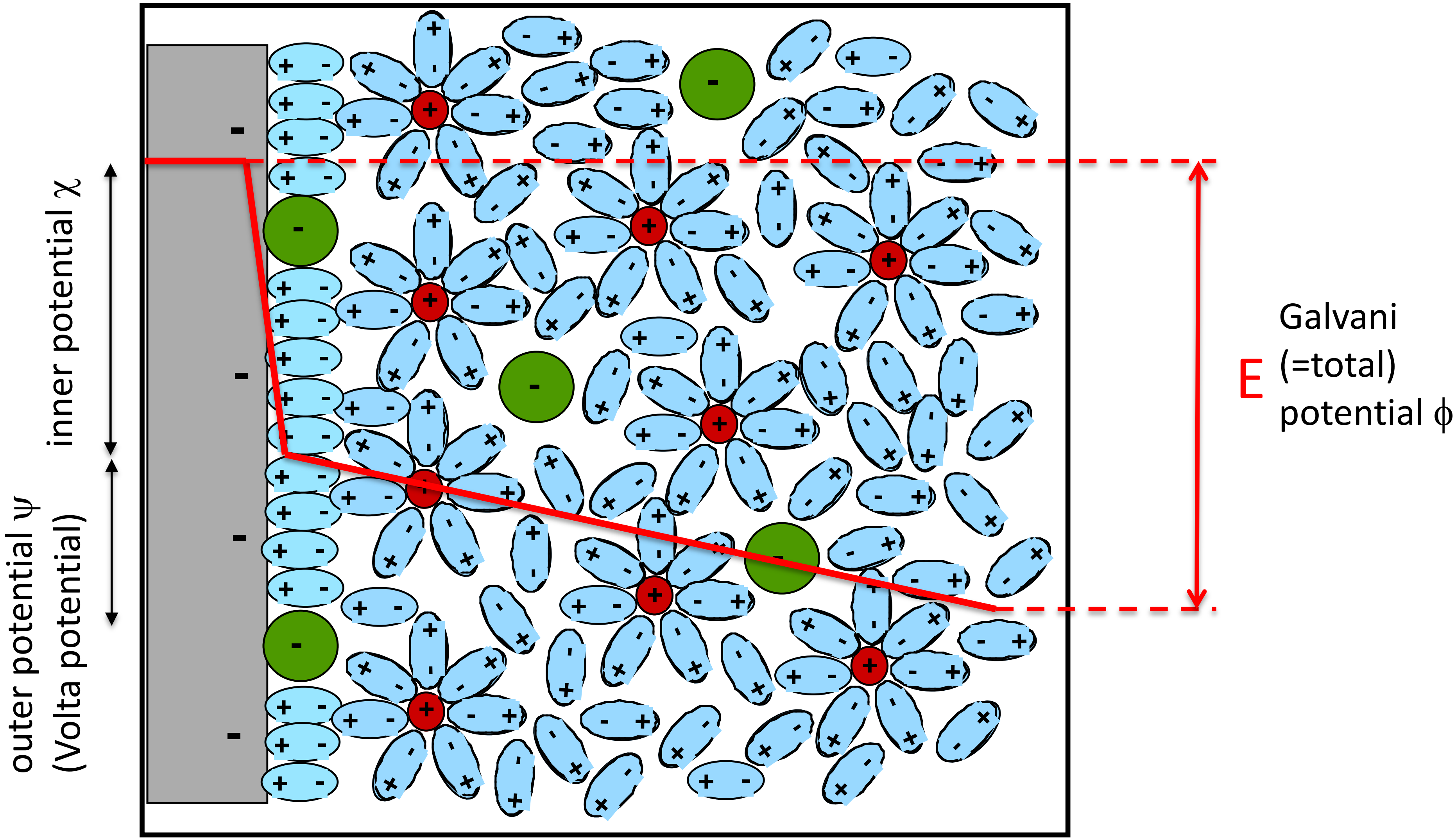
Initial situation

Dissolution

Equilibrium

($E_{rev} = - \Delta G \ / \ n \ \ F$)

Electrical double layer (capacitance) at electrode-electrolyte **interface**



Total = Galvani potential (ϕ) : potential difference between the bulks of 2 (different) phases, which can be 2 solids or a solid and liquid.
Cannot be measured with a voltmeter since always a second reaction is needed !
Inner potential = χ   Outer potential (or Volta potential) = ψ
The double layer represents an electrical capacitance.

Principle of hydrogen/oxygen electrochemical (fuel) cell

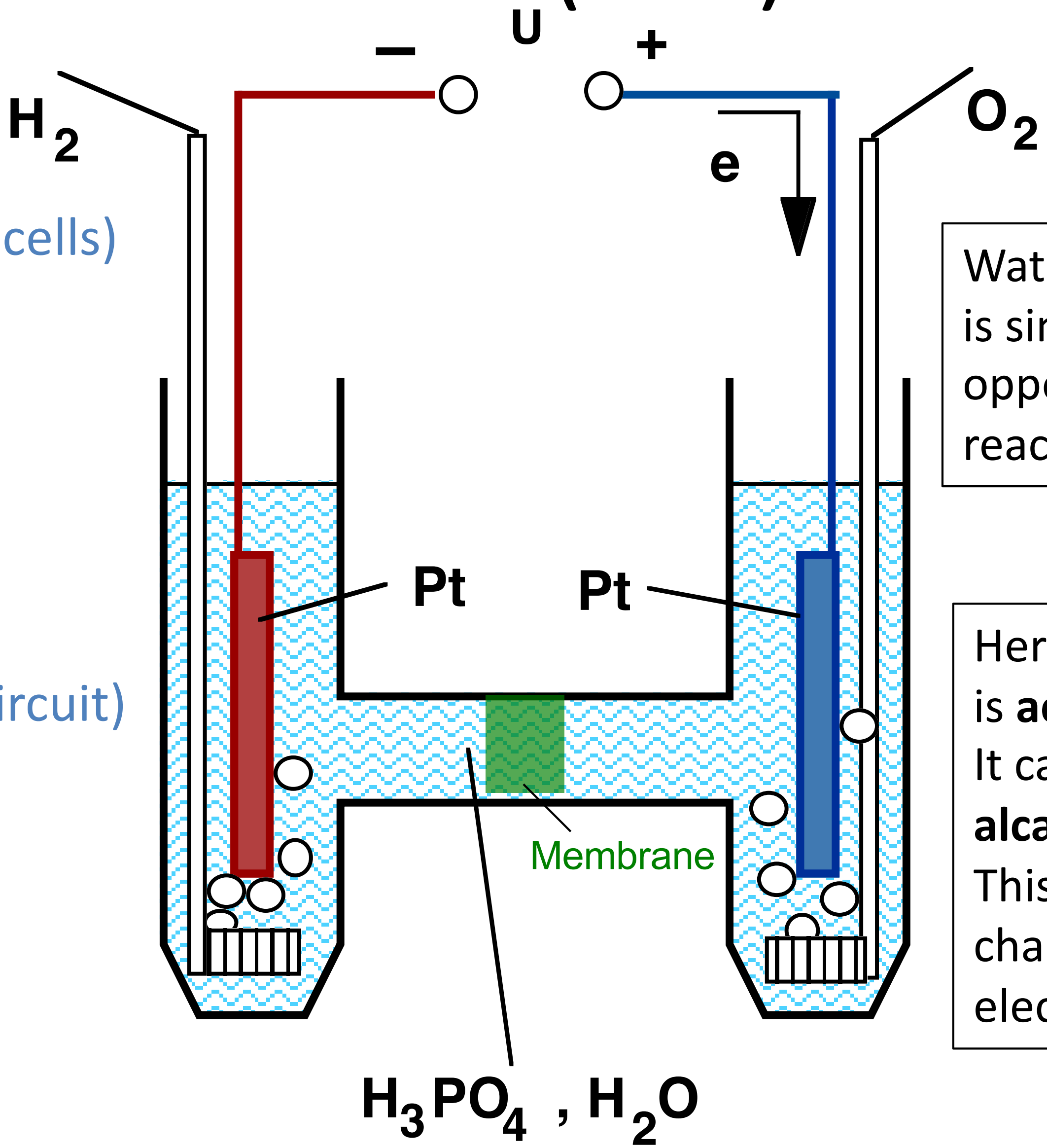
Electrode reactions (half cells)

$2\ H_2 = 4\ H^+ + 4\ e^-$

$O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$

Global reaction (closed circuit)

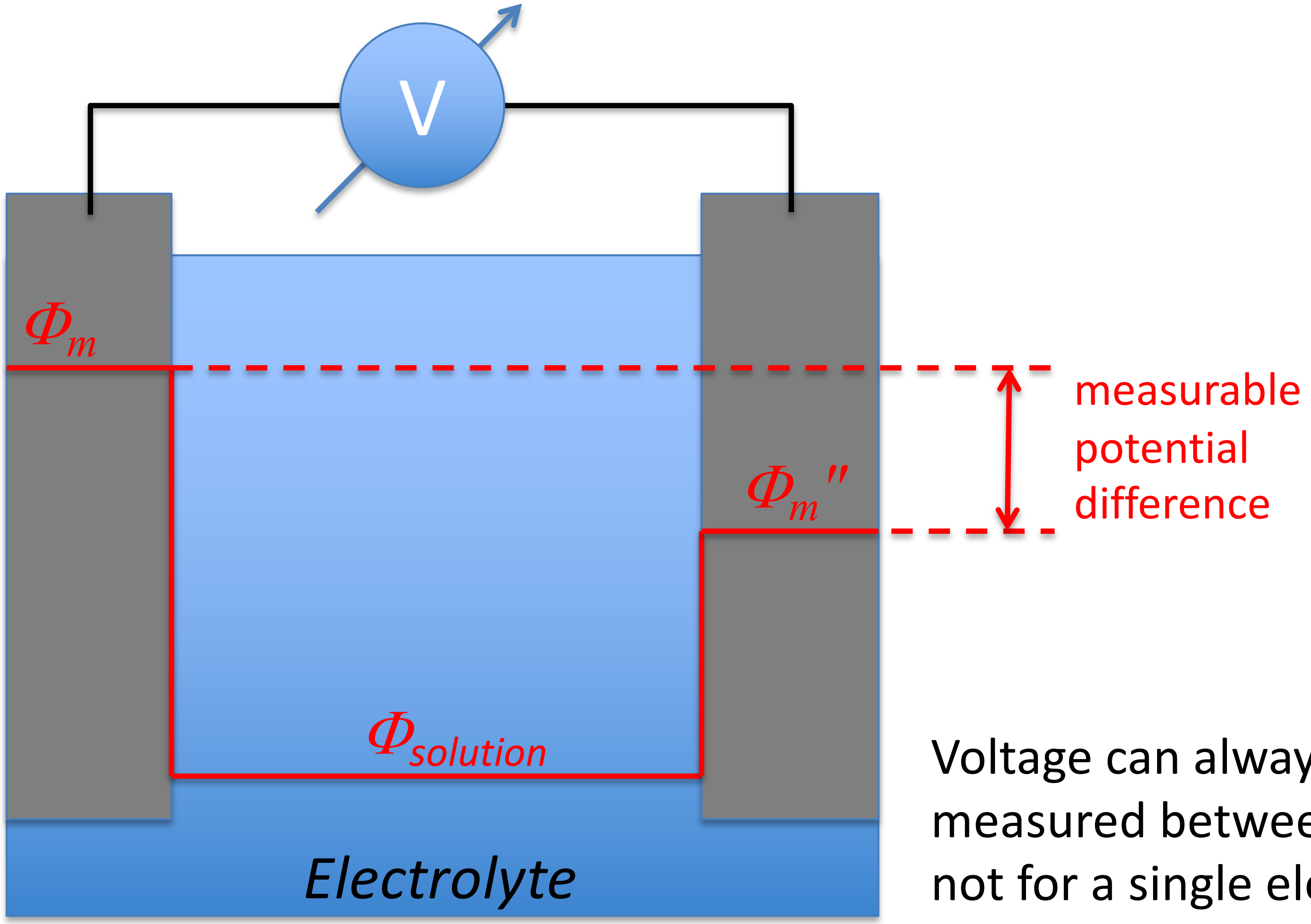
$2\ H_2 + O_2 = 2\ H_2O$



Water **electrolysis** is simply the exact opposite, with the reactions reversed.

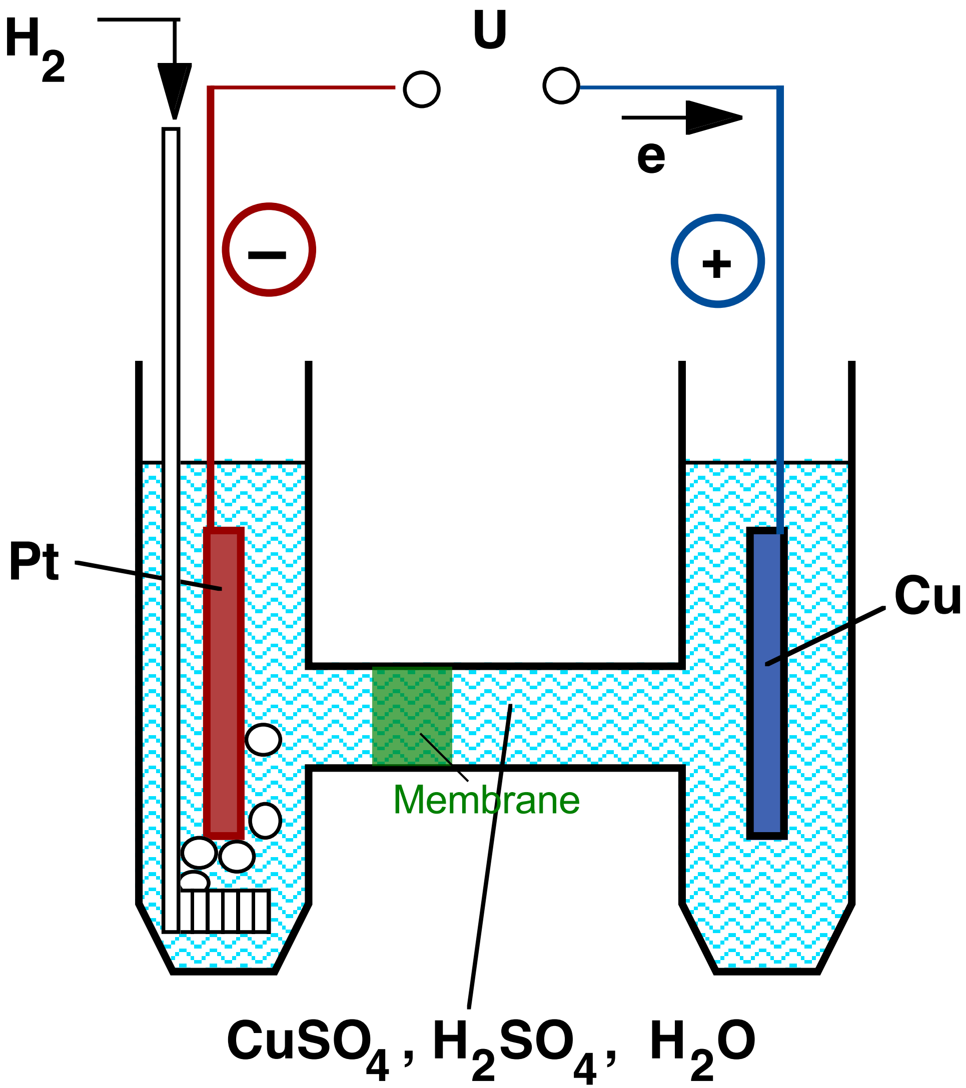
Here the medium is **acidic** (low pH). It can also be **alcaline** (high pH). This radically changes the electrochemistry!

Potential levels in electrochemical cells



Voltage can always only be measured between 2 electrodes, not for a single electrode.

Copper/hydrogen cell



Electrode reactions

$2\ H^+ + 2\ e^- = H_2$

$Cu^{2+} + 2\ e^- = Cu$

Standard electrode potentials $\mathbf{E^0}$ of electrode reactions

Standard conditions:
activities = 1
1 atm pressure

Electrode	E°/V
$Li^{+} + e = Li$	–3.045
$Mg^{2+} + 2e = Mg$	–2.34
$Al^{3+} + 3e = Al$	–1.67
$Ti^{2+} + 2e = Ti$	–1.63
$Cr^{2+} + 2e = Cr$	–0.90
$Zn^{2+} + 2e = Zn$	–0.76
$Fe^{2+} + 2e = Fe$	–0.44
$Ni^{2+} + 2e = Ni$	–0.257
$\boxed{2H^{+} + 2e = H_2}$	$\boxed{0.0}$
$Cu^{2+} + 2e = Cu$	0.340
$Ag^{+} + e = Ag$	0.799
$O_2 + 4H^{+} + 4e = 2H_2O$	1.229
$Au^{3+} + 3e = Au$	1.52

Values for 25°C (298K)

determines the relative scale

water electrolysis
1.23 V (**25°C, 1 atm**)

NERNST EQUATION

OF ELECTRODE POTENTIAL

Nernst equation for the **reversible** potential E_{rev} of electrode reactions

$$\sum \nu_{ox,i}\, B_{ox,i} + n\, e^- = \sum \nu_{red,i}\, B_{red,i}$$

B_{ox} : species at « oxidized » state (left side of reduction reaction)
B_{red} : species at « reduced » state (right side of reduction reaction)
ν : stoichiometry coefficient a: activity f(concentration)

$$E_{rev} = E^0 + (RT/\, n\, F) \ln \prod \frac{a_{ox,\, i}^{\ \nu\ ox,i}}{a_{red,\, i}^{\ \nu\ red,i}}$$

Reversible potential, 1 atm, a = 1

Follows directly from $\Delta G = \Delta G^0 + RTlnK$ and $\Delta G = -nFE$

E° of a full cell

ΔG° is not directly measureable. It relates to the measureable voltage difference in an electrochemical cell:

$$\Delta G° = -n\,F\,E°$$

n e^- transferred per mole product

Faraday's constant: 9.6×10^4 C/mol e^-

Oxidation half-reaction (anode)

$H_2(g) \rightarrow 2H^+ + 2e^-$

Reduction half-reaction (cathode)

$1/2O_2\,(g) + 2e^- + 2H^+ \rightarrow H_2O(l)$

$$E° = (E°_{oxidation}) + (E°_{reduction})$$

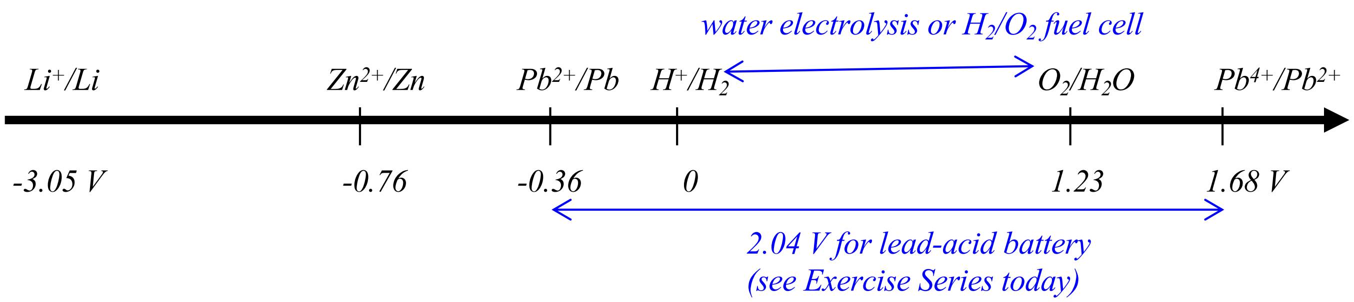
anode cathode

Link between equilibrium cell voltage E^0 and thermodynamics (Gibbs free enthalpy)

- in a fuel cell or battery at equilibrium (start-up, no net current), e.g. fed with H_2/O_2 (or air), one observes the **creation of a voltage**, characteristic for the reaction H_2/O_2 : **1.229 V** (at 298K and 1 atm)
- likewise, in an electrolyser, no reaction occurs before exceeding this voltage
- the theoretical **work** (here: **electricity**) *retrieved* from (fuel cell or battery discharge) or *invested* in (electrolysis or battery charging) the reaction is given by the **Gibbs free enthalpy** of the corresponding chemical reaction $\Delta G_r = \Delta H_r - T\,\Delta S_r$:
  for $H_2 + 0.5\ O_2 \ \text{->} \ H_2O$
  ΔG^0_r(298K, 1 atm) = **-237'150 J/mole**

- the link between ΔG_r (J/mole) and the created (applied) voltage, E (or V, or U) is given by the amount of charge (C) that can be exchanged across this voltage :
  $\Delta G_r = -\ nF.E_{rev}$
  (with n = 2 exchanged electrons for H_2, F = Faraday const. = 96484 C / mole e^-)
  whence the value E^0= **1.229 V** (for H_2/O_2 at **1 atm, 298 K**)

=> Electrochemical potential ‘series’



- Only a voltage ***<u>difference</u>*** between any 2 electrodes can be experimentally <u>measured</u>, not a single potential
- The scale value of ‘0’ is attributed to one electrode (H_2/H^+) which then defines all the others
- A value *negative* to H^+/H_2 means the material is oxidized by H^+ (=corroded (dissolved) by acid); a value *positive* to H^+/H_2 means the material oxidizes (‘combusts’) H_2
- Historically, this attribution of H^+/H_2 as ‘0’ value comes from the observation that it separates noble metals (positive) from non-noble metals (negative, and thus corroded by acid)

Thermodynamic Cell Potential

The **Nernst Equation** is an equation that relates the **reduction** potential E_{rev} of an electrochemical reaction to the standard electrode potential E^0, temperature, and activities (approximated by concentrations) of the chemical species undergoing reduction and oxidation.

Reaction quotient

$$\frac{\Delta G}{-nF} = \frac{\Delta G° + RT \ln Q}{-nF}$$

$$Q = \frac{[\text{products}]^a}{[\text{reactants}]^b}$$

a, b = corresponding stoichiometric coefficients

$$\boxed{E_{cell} = E°_{cell,T} - \frac{RT}{nF} \ln Q}$$

$E°_{cell,T}$ based on ΔG at temperature of reaction

Thermodynamic Cell Potential

Standard conditions:
Activities (~concentrations) of solutes: 1 M
Pressure of gases: 1 atm
Temperature: 25 °C

Standard concentrations/pressures and standard temperature

$$E_{cell} = E°_{cell}$$

Non-standard concentrations/pressures and standard temperature

$$E_{cell} = E°_{cell} - \frac{RT}{nF} \ln Q$$

Non-standard concentrations/pressures and non-standard temperature

$$E_{cell} = E°_{cell,T} - \frac{RT}{nF} \ln Q$$

accounts for change in standard potential with temperature (= heat capacity calculations…)

How to compute the Gibbs free reaction enthalpy for any reaction (or thus potential 'battery')

$$\Delta H_r(T) = \Delta G_r(T) + T.\Delta S_r(T)$$

ΔG_r = fraction of ΔH_r (total heat) that can theoretically be converted to work.
Entropy S : unavoidable heat loss (T. ΔS_r)

ν = stoechiometric factors of the reaction

$$\Delta H_r(T) = \sum_{prod} \nu_{prod} \Delta H_f(T) - \sum_{reac} \nu_{reac} \Delta H_f(T) \qquad \Delta S_r(T) = \sum_{prod} \nu_{prod} S_f(T) - \sum_{reac} \nu_{reac} S_f(T)$$

Products of the reaction (H_2O, CO_2,…) of formation Educts of the reaction (H_2, CO, CH_4, O_2,…)

$$\Delta H_f(T) = \Delta H_f^0(298K) + \int_{298}^{T} C_p(T)\,dT \qquad S_f(T) = S_f^0(298K) + \int_{298}^{T} \frac{C_p(T)}{T}\,dT$$

thdynam. tables

thdynam. tables

$$C_p(T) = a + b.T + c/T^2$$

→ *Message: the Nernst voltage $E^0(T)$ can be computed for any reaction, from the thermodynamic data tables of the reactants and product species of the reaction*

→ *See exercise series today for H_2 and CH_4 oxidation at 25° C and 1000° C*

Thermodynamic Cell Potential

$$Q = \frac{[\text{products}]^a}{[\text{reactants}]^b}$$

a, b = corresponding stoichiometric coefficients

For the reversible reaction

$$aA + bB \rightleftarrows cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a\,[B]^b}$$

Q is dimensionless

Activity (a_i) is non-dimensional quantity

$$Q = \frac{a_C^{\,c} a_D^{\,d}}{a_A^{\,a}\, a_B^{\,b}} \quad \text{where} \quad a = \gamma_i \frac{c_i}{c_0} \overset{\gamma_i = 1}{\sim} \frac{c_i}{c_0}$$

γ_i = activity coefficient of species i

c_i = concentration of species i

c_0 = reference concentration (1 M)

For ideal or dilute solutions, activity can be approximated as concentration.

For ideal gases or gases at low pressure, activity can be approximated as pressure.

Note: solids and pure liquids are not included in the calculation of Q, since their activities are 1.

Thermodynamic Cell Potential

Reaction quotient (Q) does not include contributions from solids in the reaction

$$Q = \frac{[\text{products}]^a}{[\text{reactants}]^b}$$

a, b = corresponding stoichiometric coefficients

Under standard concentrations/pressures, the Nernst equation simplifies to the standard cell potential

$$E_{cell} = E°_{cell,T} - \underbrace{\cancel{\frac{RT}{nF} \ln Q}}_{0} \qquad Q = 1$$

$$E_{cell} = E°_{cell,T}$$

Thermodynamic Cell Potentials at Non-Standard Conditions

$$E_{cell} = E^\circ_{cell,T} - \frac{RT}{zF} \ln Q$$

- accounts for any change in standard potential with temperature (= heat capacity calculations…).
- Calculated from ΔG, so **only reactants and products** taken into consideration.
- Inert gases do not contribute.

Account for **partial pressure and concentration**/dilution effects, including inert gases and water vapor, even when water is not a reactant/product.

EXAMPLES

Nernst equation for electrode reactions

Example 1: reaction $Cu^{2+} + 2e^- = Cu$

$E_{rev,Cu} = E^0_{Cu} + RT/2F \ln (a_{Cu2+} / a_{Cu})$

In case of pure metal, and at T=25°C, the expression becomes:

$E_{rev,Cu} = 0.34\ V + (0.059 / 2)\ \log_{10} (a_{Cu2+})$

Example 2: reaction $2H^+ + 2e^- = H_2$

$E_{rev,H2} = E^0_{H2} + (RT/2F) \ln (a_{H+}^2 / a_{H2})$

$= (RT/F) \ln a_{H+} - (RT/2F) \ln p_{H2}\ (a_{H2} = p_{H2})$

At T=25°C, the expression becomes:

$= 0.059 \log a_{H+} - 0.0295 \log p_{H2}$

$= -0.059\ pH - 0.0295 \log p_{H2}\quad (pH = -\log_{10} a_{H+})$

Nernst equation for the oxygen half cell (oxygen as dissolved species in water)

$$O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$$

$$E_{rev,O2} \;=\; E^0_{O2} + (RT/\ 4F)\ \ln\left(a_{H+}^4\ a_{O2}\ /\ a_{H2O}^2\right)$$

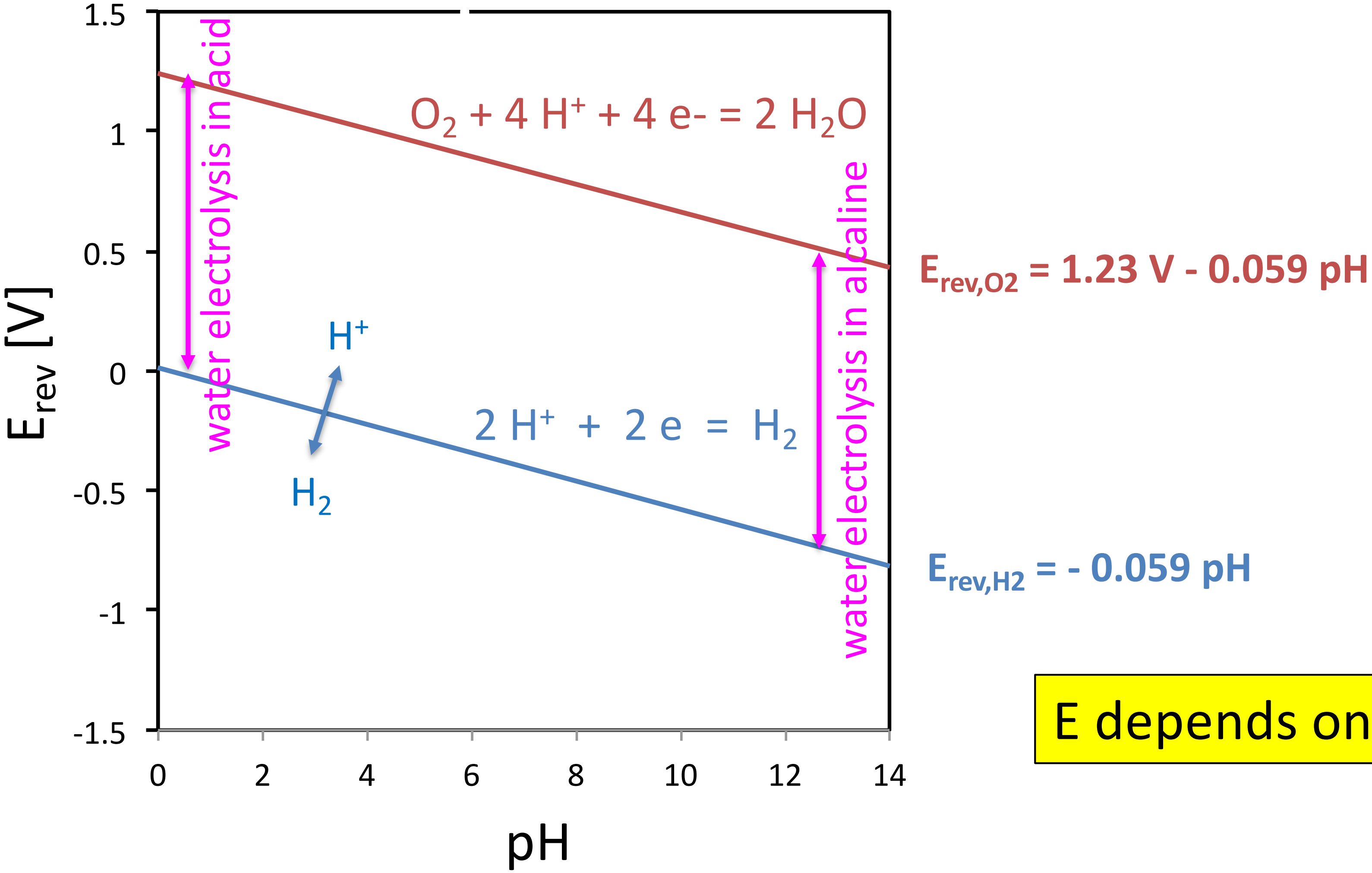
$$E^0_{O2} = 1.23\ V \qquad a_{O2} = p_{O2} \qquad a_{H2O} = 1$$

$$E_{rev,O2} = 1.23\ V + (RT/F)\ \ln a_{H+} + (RT/\ 4F)\ \ln p_{O2}$$

$$E_{rev,O2} \;=\; 1.23\ V + 0.059\ \log_{10} a_{\ H+} + 0.01475\ \log_{10} p_{O2} \qquad (T = 25°C)$$

$$\mathbf{E_{rev,O2} \;=\; 1.23\ V - 0.059\ pH + 0.01475\ \log_{10} p_{O2}} \qquad (pH = -\log_{10} a_{H+})$$

Pourbaix diagram (=E_{rev} *vs pH* plot) for hydrogen and oxygen half cells



T = 25°C

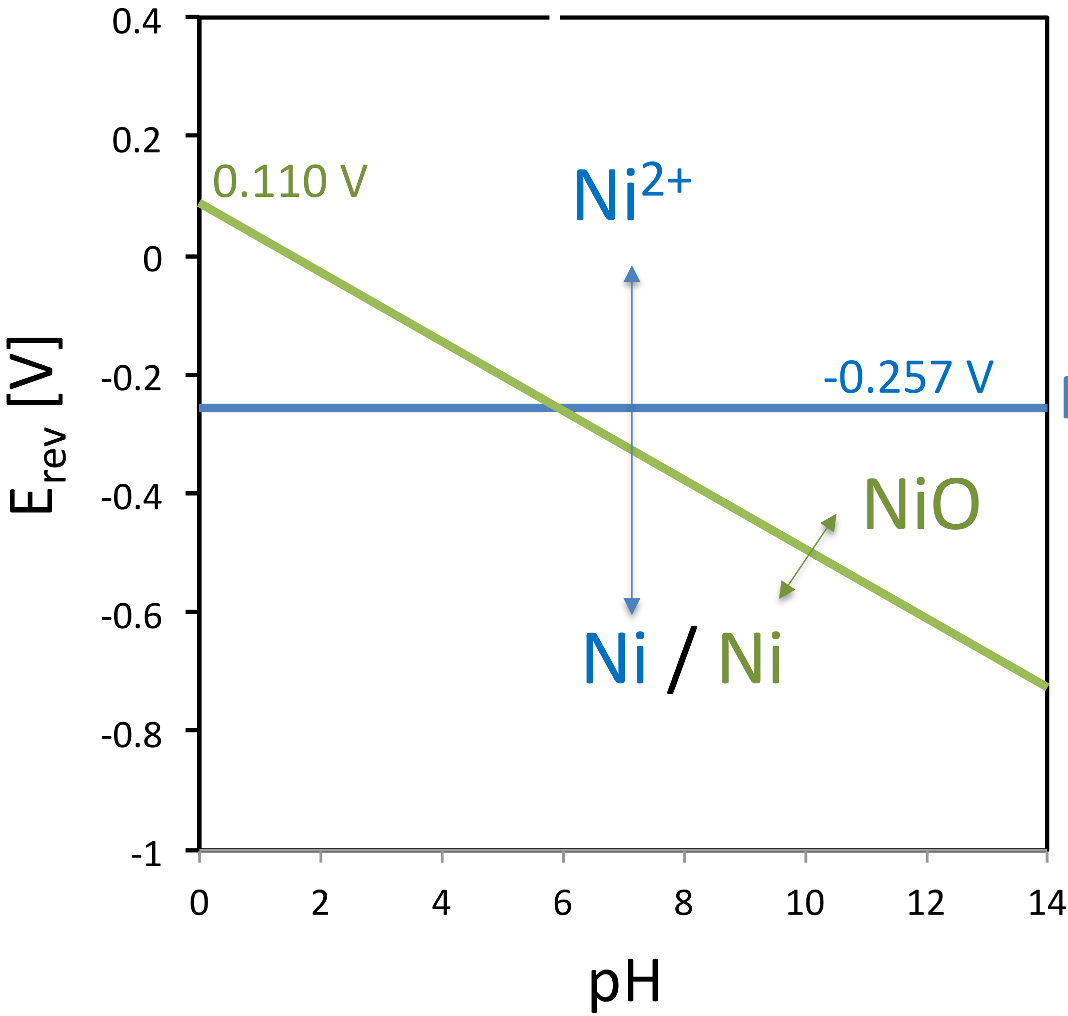
$a_{O2} = 1$

$a_{H2} = 1$

E depends on the pH

Going from left to right to higher pH means less and less H^+, and hence the H^+ reduction reaction is more and more shifted from right to left (=oxidation) and not from left to right (=reduction), and in other words, it becomes more and more difficult to reduce H^+ and O_2 (we have to push the electrode potential to more and more negative, injecting electrons), since so little H^+ is present.

Pourbaix diagram for Nickel



T = 25°C

$a_{Ni^{2+}} = 1$

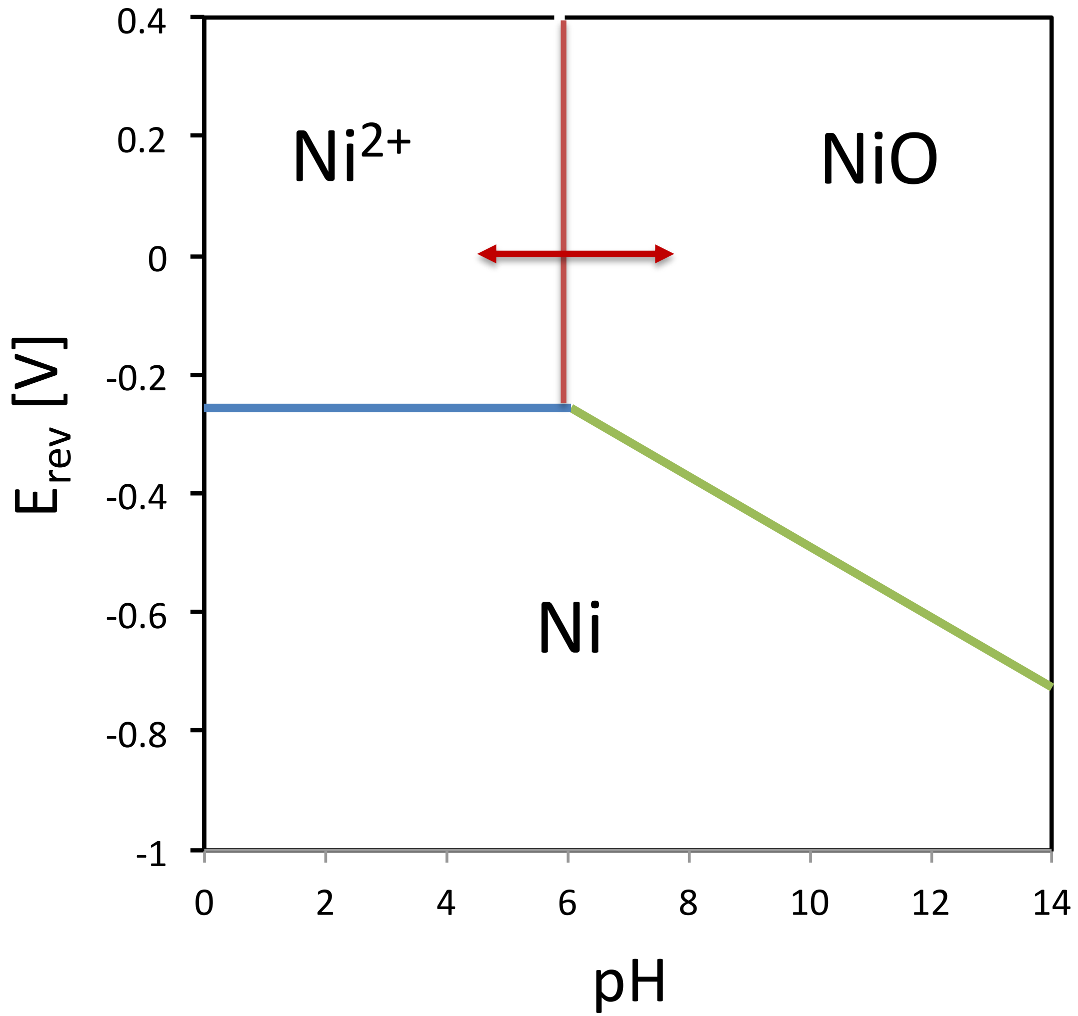
$Ni^{2+} + 2\ e^- = Ni$

(no pH dependence, since no H^+ in the reaction)

$NiO + 2\ H^+ + 2\ e^- = Ni + H_2O$

$E_{rev} = 0.110\ V – 0.059\ pH$

Pourbaix diagram for Nickel



T = 25°C

$a_{Ni^{2+}} = 1$

pH = 6

$NiO + 2\,H^+ = Ni^{2+} + H_2O$

$K = a_{Ni^{2+}} / (a_{H^+})^2 = 10^{12}$

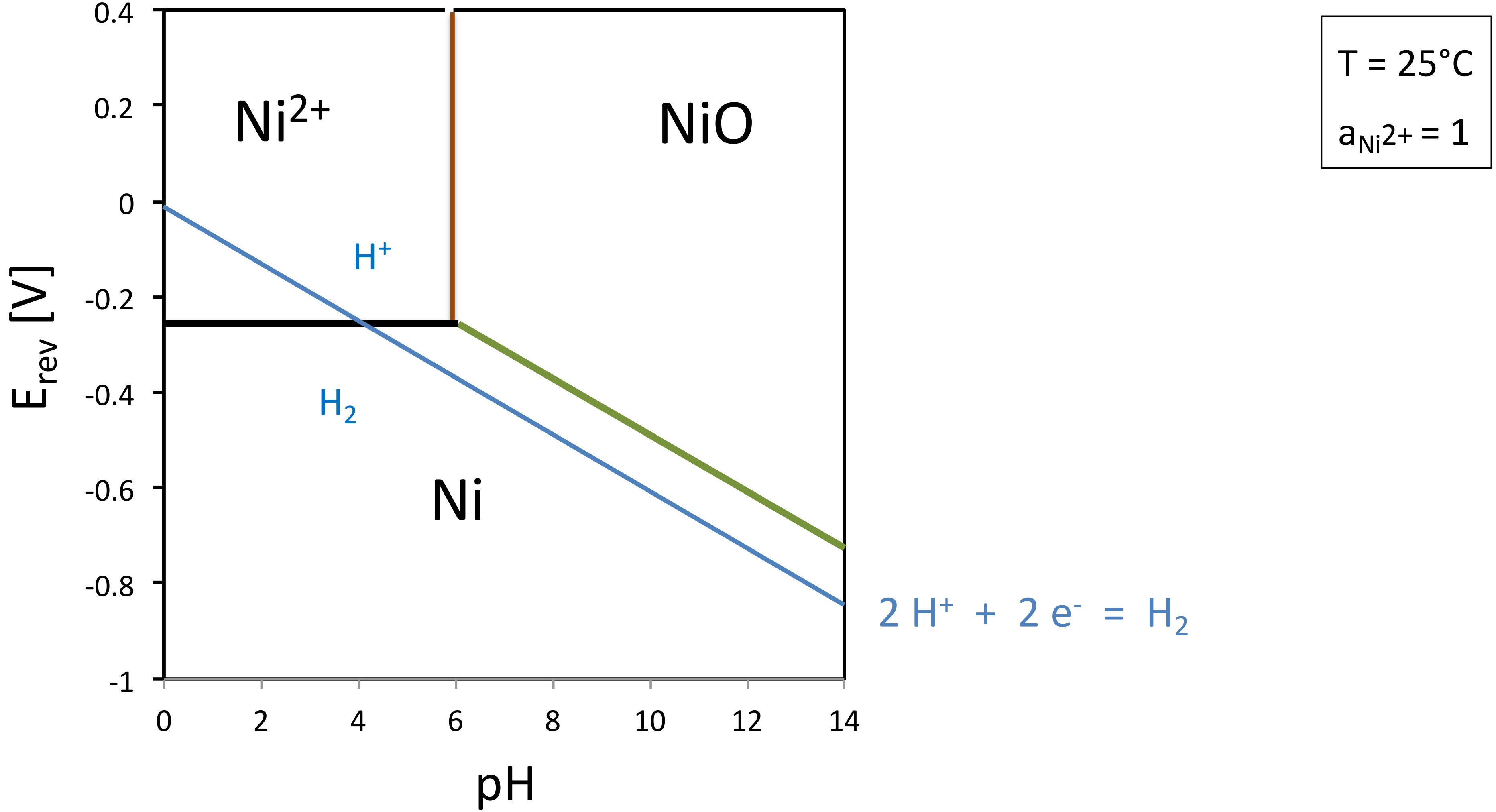
$pH_{eq} = -\log_{10} (a_{Ni^{2+}} / K)^{0.5}$

For a_Ni^{2+} = 1, pH = 6

For a_Ni^{2+} = 0.01, pH = 7

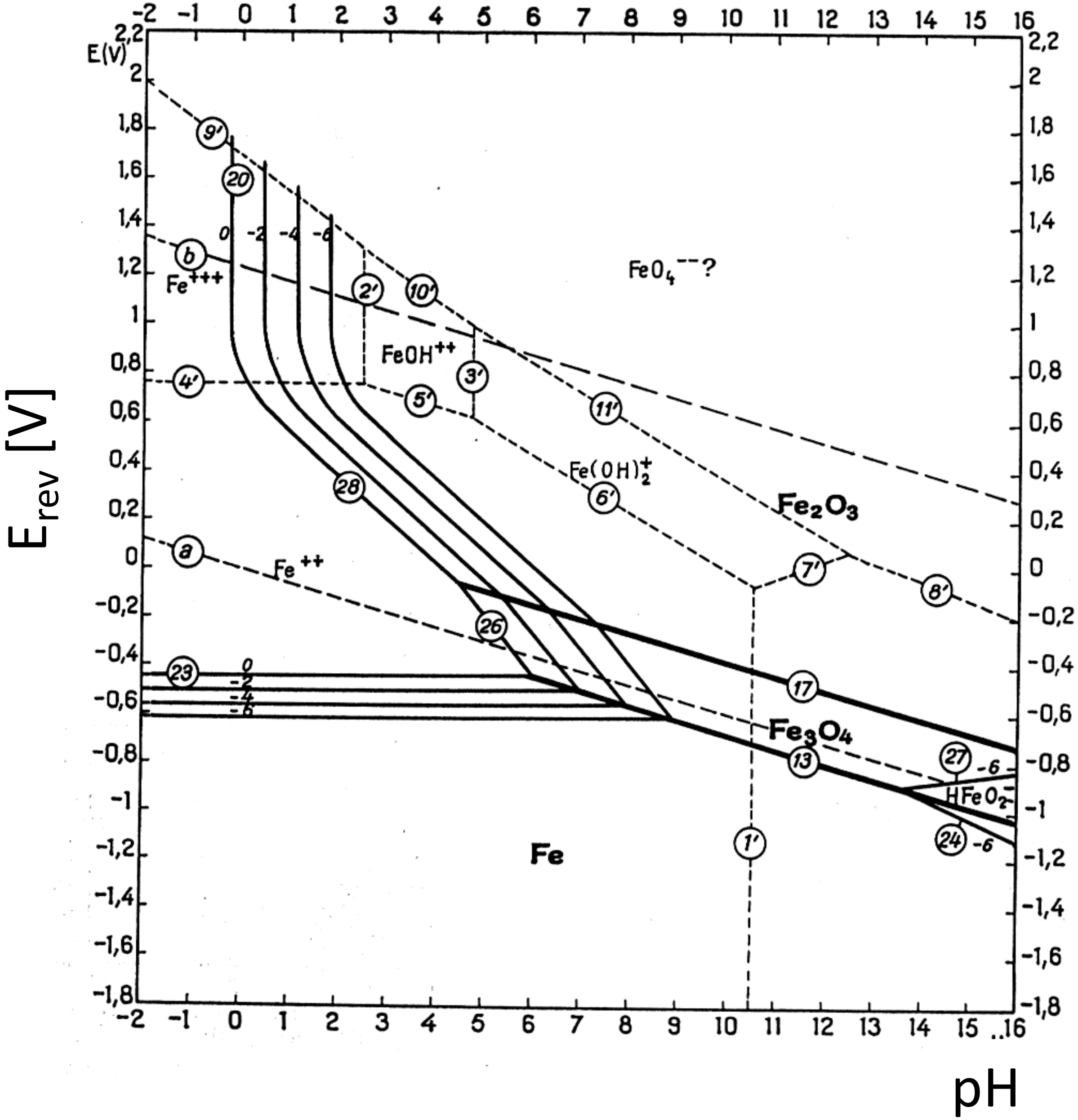
For lower Ni^{2+} , eq. is shifted from left to right, hence H$^+$ is consumed, therefore to less H$^+$ and thus higher pH.

Pourbaix diagram for Nickel



Adding the H_2 reaction from slide 44.
Acidic solution below pH4 will dissolve (corrode) the Ni electrode into Ni^{2+}, generating H_2 from H^+
However, Ni is stable in alkaline solution down to -0.8 V NHE, allowing its use as electrode catalyst in alkaline electrolysis !

Pourbaix diagram of Iron

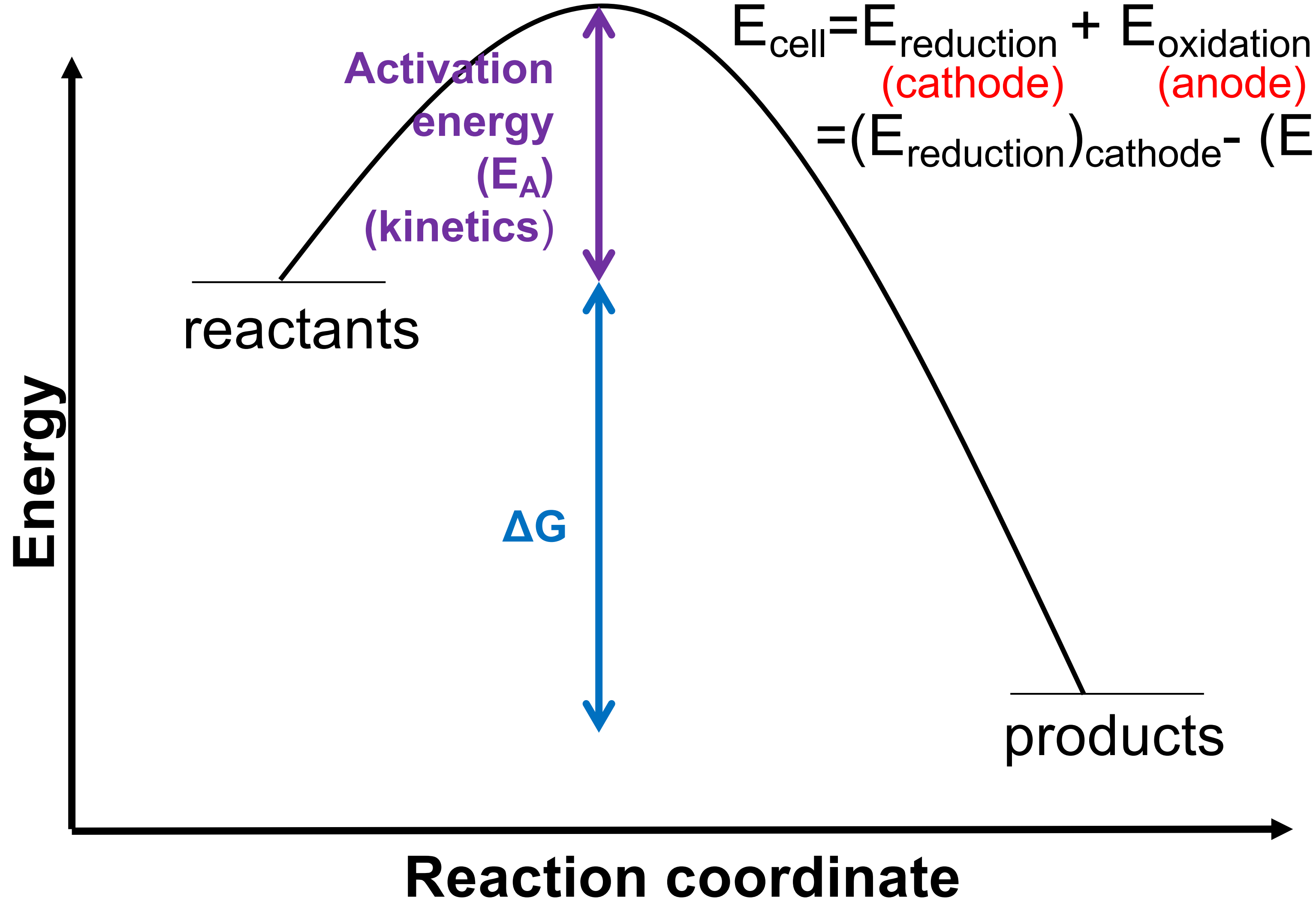


Analogy between Chemical Reactivity and Electrochemistry

$$\Delta_r G = \Sigma\, \Delta_f G_{products} - \Sigma\, \Delta_f G_{reactants}$$

$$E_{cell} = \underbrace{E_{reduction}}_{(cathode)} + \underbrace{E_{oxidation}}_{(anode)}$$

$$= (E_{reduction})_{cathode} - (E_{reduction})_{anode}$$



Relationship between Equilibrium Constant (K), $\Delta G°$, and $E°_{cell}$

From Nernst Equation

$$\Delta G = \Delta G° + RT\ln Q$$

At equilibrium,

$\Delta G = 0$ and $Q = K$

$$\Delta G° = -RT \ln K$$

$\Delta G°$

$$\Delta G° = -nFE°_{cell}$$

K

$E°_{cell}$

$$E°_{cell} = \frac{RT}{nF} \ln K$$

$$K = \frac{[\text{products}]^a}{[\text{reactants}]^b} = \frac{k_{forward}}{k_{reverse}}$$

concentrations @ equilibrium

$E°_{reduction} + E°_{oxidation}$

(cathode) (anode)

Relationship between Equilibrium constant (K), $\Delta G°$, and $E°_{cell}$

As the system approaches equilibrium
$Q \rightarrow K$

$\Delta G°$	K	$E°_{cell}$	Reaction @ standard conditions
<0	>1	>0	forward reaction spontaneous
0	1	0	@ equilibrium
>0	<1	<0	Reverse reaction non-spontaneous

Thermodynamic vs. Kinetic Parameters

	Thermodynamic Parameters	Kinetic Parameters
General Chemistry	Equilibrium Constant (K)	Rate Constants ($k_{forward}$, $k_{reverse}$)
Electrochemistry	Cell Potential (E_{cell})	Current ($i_{cathode}$, i_{anode}) or Current density ($j_{cathode}$, j_{anode})

- In chemistry, the relationship between K and the rate constants, $k_{forward}$ (k_f) and $k_{reverse}$ (k_r), is simple.

$$K = \frac{k_{forward}}{k_{reverse}}$$

- In electrochemistry, the relationship between potential and current is more complex => Chapter 3