

2106NSC

Physical & Analytical Chemistry

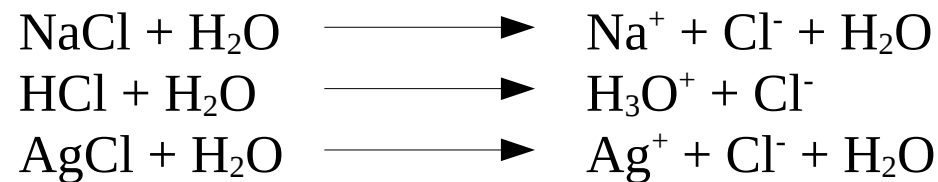
Thermodynamics 11

Fundamentals of electrochemistry

Ions in solution

So far, we have mostly assumed that we are working with non-electrolytes, i.e. non-dissociating solutes.

Strong electrolytes completely dissociate in solution:



Weak electrolytes do not fully dissociate in solution, due to inter-ionic interactions.



We will need to use **activities** and **ionic strength** to quantify the deviation from the complete dissociation behaviour.

$$\text{Activity } a: \quad \mu = \mu^* + R \cdot T \cdot \ln a, \text{ with } a = \gamma \cdot x$$

Ions in solution

Ions exist in solution at all times.

They are not produced by the electric current!

Ions have water molecules associated with them.

The degree of dissociation α describes the fraction of solute present as ions.

Ions in solution (moving charges) are responsible for conducting electricity.

The **specific conductance** measures the current-carrying capacity of all ions in a specific volume (\Rightarrow unit: 1 S m^{-3}). For strong electrolytes, the specific conductance decreases with dilution.

Charge

The charge Q describes the quantity of electricity; it can be positive or negative. Its unit is $[Q] = 1 \text{ C}$ (C: coulomb).

The **elementary charge** is the charge of the electron: $|Q(e^-)| = e = 1.602 \cdot 10^{-19} \text{ C}$.

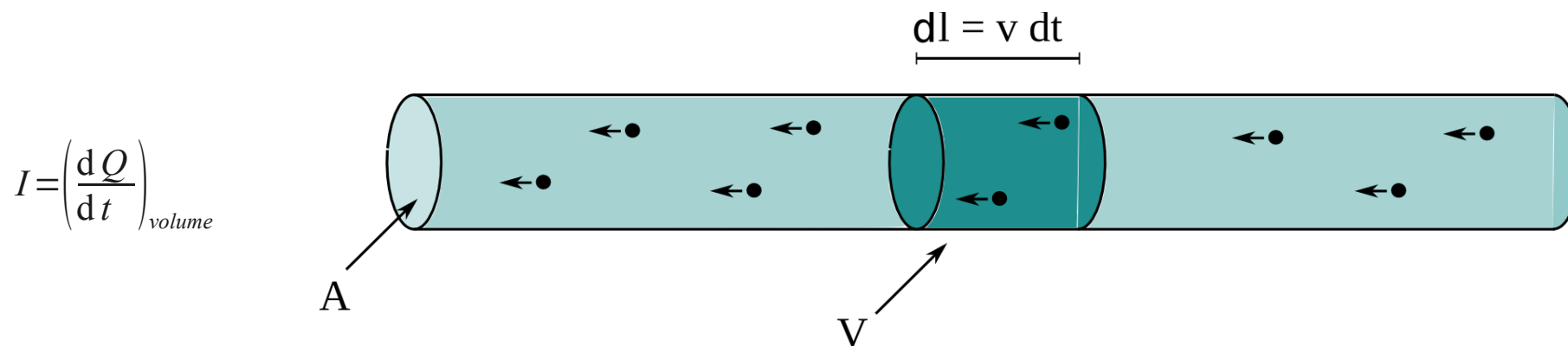
In 'normal' matter, there may be fixed charges (this is called an insulator) or mobile charges (this is called a conductor).

Mobile charges may be electrons (electronic conductor) or ions (ionic conductor).

electronic conductors	ionic conductors	mixed
metals	seawater: $\text{Na}^+_{(\text{aq})}$, $\text{SO}_4^{2-}_{(\text{aq})}$	plasma
graphite	$\text{ZrO}_{2(\text{s})}$: O^{2-}	$e^-(\text{NH}_3) + \text{Na}^+(\text{NH}_3)$
semiconductors	RbAg_4I_5 : Ag^+	H_2 in Pd: H^+ , e^-
PbO_2	pure water: $\text{H}_3\text{O}^+_{(\text{aq})}$, $\text{OH}^-_{(\text{aq})}$	
polypyrrole		

Current

Current is the flow of charge in a particular time interval through a particular volume:



$$I = \left(\frac{dQ}{dt} \right)_{\text{volume}}$$

$$I = \left(\frac{dQ}{dt} \right)_{\text{volume}} = \frac{N_{\text{crossing}} \cdot (-e)}{dt} = \frac{N}{V} \cdot V \cdot (-e)$$

$$I = \frac{\frac{n \cdot N_A}{V} \cdot A \cdot dl \cdot (-e)}{dt} = \frac{c \cdot N_A \cdot A \cdot v \cdot dt \cdot (-e)}{dt}$$

$$I = c \cdot N_A \cdot A \cdot v \cdot (-e) = -c \cdot N_A \cdot A \cdot v \cdot e = -c \cdot A \cdot v \cdot F$$

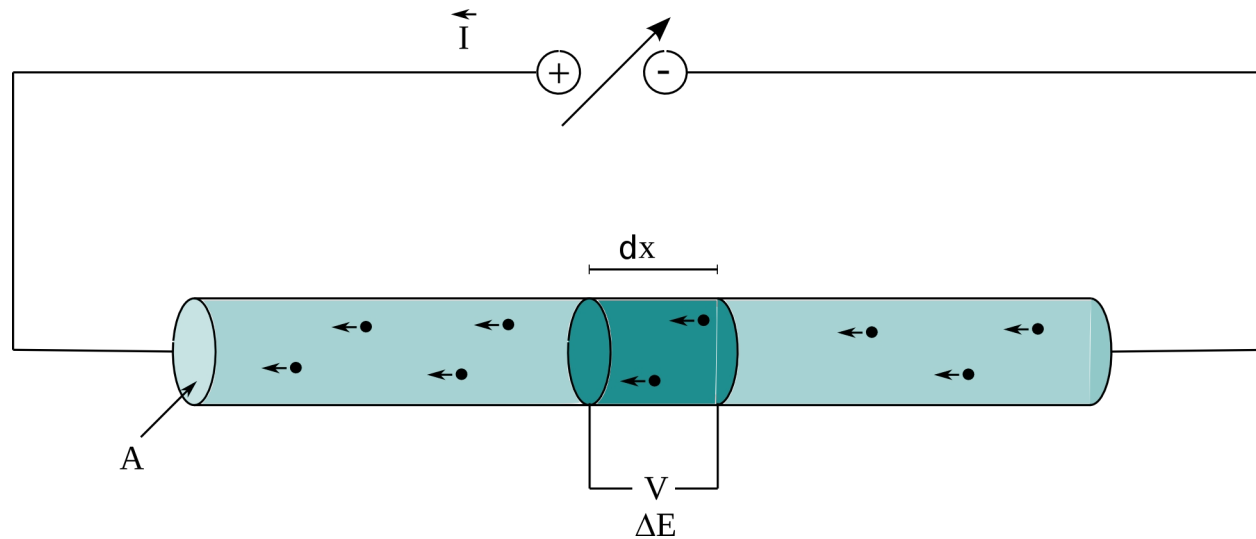
Faraday's constant: $F = N_A \cdot e = 6.022 \cdot 10^{23} \text{ mol}^{-1} \cdot 1.602 \cdot 10^{-19} \text{ C}$
 $F = 96485 \text{ C mol}^{-1}$

Electroneutrality

The principle of electroneutrality:

There can be no significant net charge in any macroscopic volume within a conductor.

Conductivity



$$\Delta E \sim \frac{-I \cdot dx}{A}$$

$$j = \frac{I}{A} \sim \frac{-\Delta E}{dx} \quad \text{with } j \text{ being the **current density**.$$

$$j = \frac{I}{A} = -\kappa \cdot \frac{\Delta E}{dx} = -\kappa \cdot \frac{d\phi}{dx}$$

Conductivity:

$$[\kappa] = 1 \frac{\text{A}}{\text{V} \cdot \text{m}} = 1 \frac{\text{S}}{\text{m}}$$

Conductivity and Conductance

Conductivity:

- The gradient $d\phi/dx$ is called the electric field.
- The electric field is the first derivative of the electric potential.
- The current density j is proportional to the electric field; the constant relating the electric field with the current density is the conductivity κ .

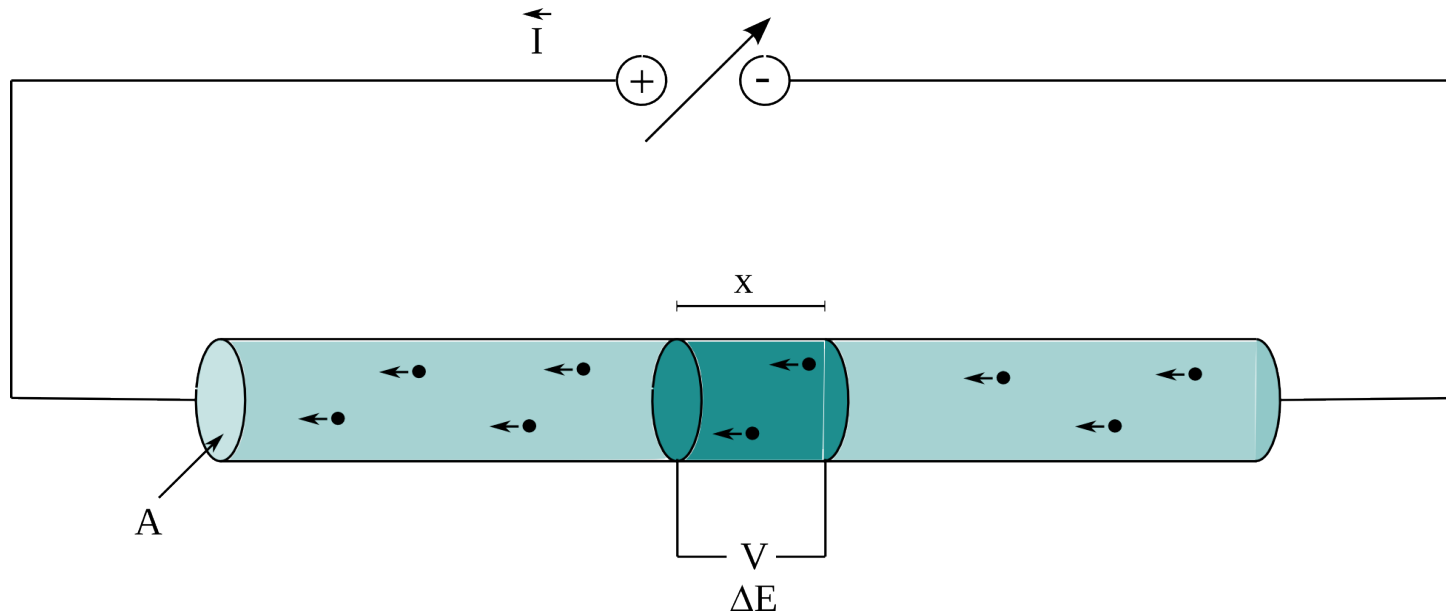
Conductance :

- The conductance G measures the current-carrying capacity of solutions with the same number of ions.

$$G = \frac{\kappa \cdot A}{l}$$

- It increases with dilution for a strong or weak electrolyte because there is less hindrance from neighbours.

Resistance



$$j = \frac{I}{A} = -\kappa \cdot \frac{\Delta E}{x} = -\kappa \cdot \frac{d\phi}{dx}$$

$$I = -\kappa \cdot \frac{\Delta E \cdot A}{x}$$

$$\Delta E = -I \cdot \frac{x}{\kappa \cdot A} = -I \cdot R \quad \text{with } R \text{ being the } \mathbf{resistance}, [R] = 1 \Omega$$

Resistance and conductivity

Two forms of Ohm's Law:

$$j = \frac{I}{A} = -\kappa \cdot \frac{\Delta E}{x} = -\kappa \cdot \frac{d\phi}{dx}$$

$$\Delta E = -I \cdot \frac{x}{\kappa \cdot A} = -I \cdot R$$

Molar conductivity:

$$\Lambda_m = \frac{\kappa}{c} \quad [\Lambda_m] = 1 \text{ S m}^2 \text{ mol}^{-1}$$

Conductivity of different systems

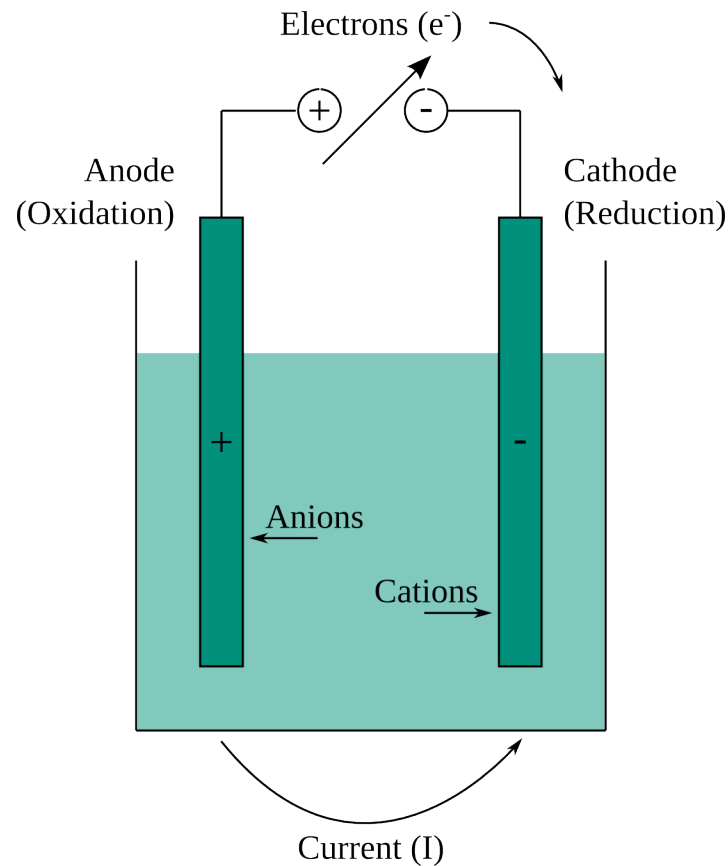
Material	κ in S m^{-1}	Charge carrier	
superconductors	∞ (at low temperature)	electron pair	↑ conducting
Cu	$6 \cdot 10^7$	e^-	
Hg	$1 \cdot 10^6$	e^-	
Graphite	$4 \cdot 10^4$	π -electrons	
molten KCl	220 (at $T=1043 \text{ K}$)	K^+ , Cl^-	continuum
battery acid	80	$\text{H}_3\text{O}^+_{(\text{aq})}$, $\text{HSO}_4^-_{(\text{aq})}$	
seawater	5.2	cations, anions	
Ge	2.2	e^- , holes	insulating ↓
0.1 M $\text{KCl}_{(\text{aq})}$	1.3	$\text{K}^+_{(\text{aq})}$, $\text{Cl}^-_{(\text{aq})}$	
H_2O	$6 \cdot 10^{-6}$	$\text{H}_3\text{O}^+_{(\text{aq})}$, $\text{OH}^-_{(\text{aq})}$	
typical glass	$3 \cdot 10^{-10}$	univalent cations	
teflon	10^{-15}	impurities	
vacuum, most gases	0	none	

Electrochemical reactions

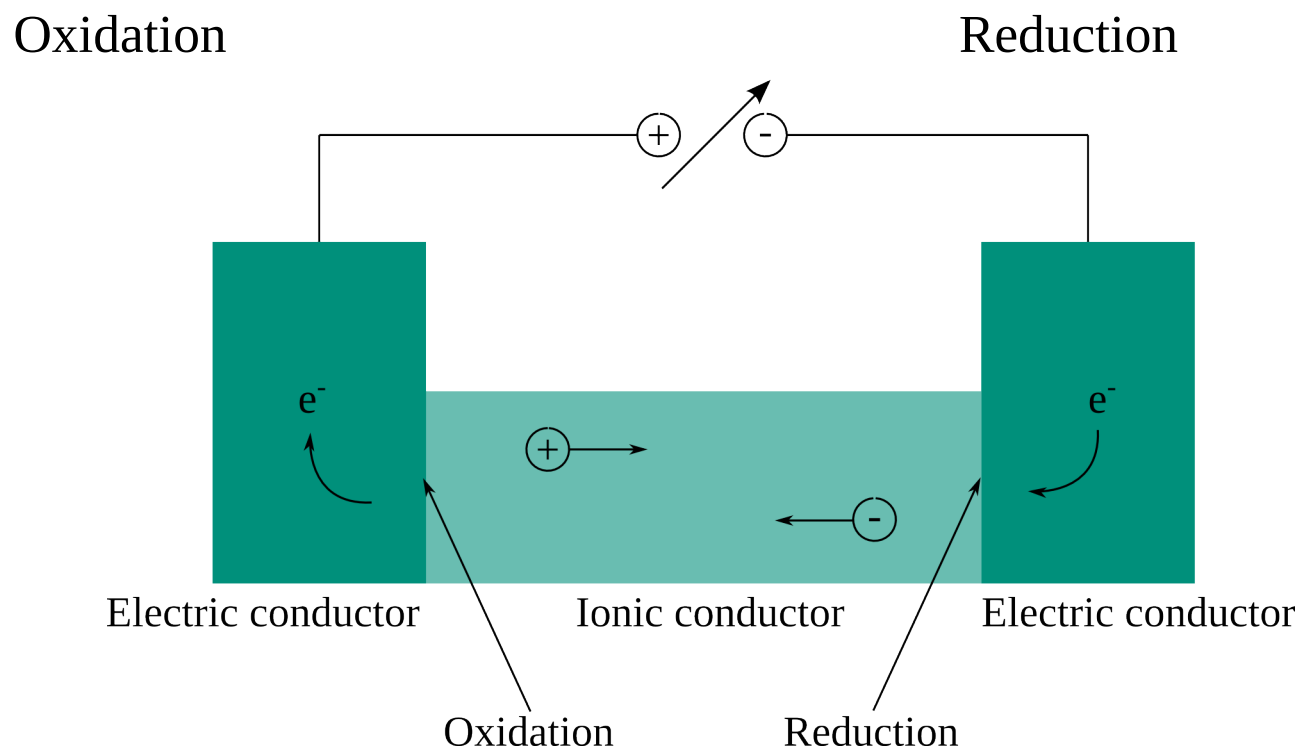
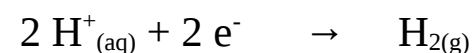
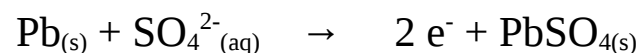
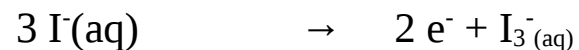
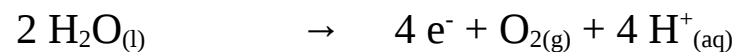
Electrochemical reactions are induced by an electric potential.

The electric potential can be applied externally or generated internally.

Electrolysis: a chemical reaction is forced to occur due to current flowing through a cell.

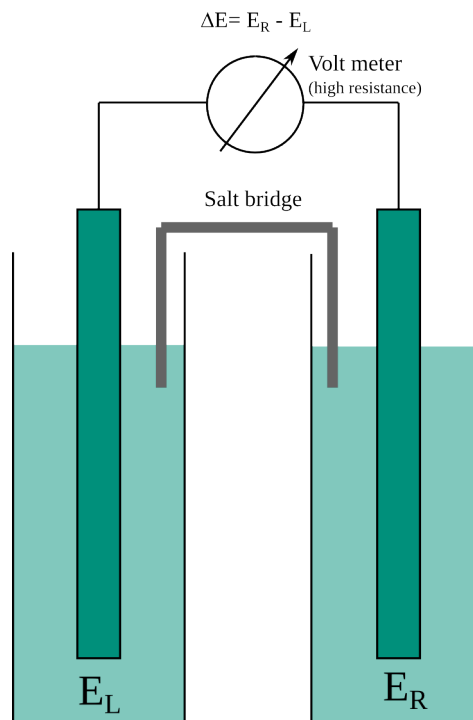


Electrochemical half reactions: RedOx



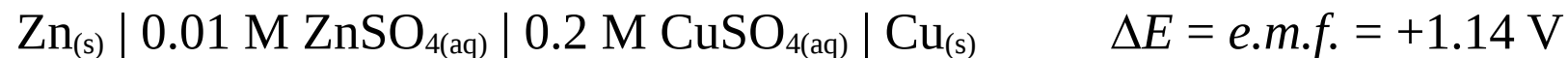
*Bromo-naphthalene: an insulating liquid in graphite paste electrodes

The electromotive force



The potential difference measured between two electrodes when negligible current is drawn is called the **electromotive force** (*e.m.f.*) of the cell.

Example:



Electromotive force and equilibrium

When two half-cells are combined, the standard *e.m.f.* (ΔE^\ominus) is the difference between two standard electrode potentials (Redox potentials):

$$\Delta E^\ominus = E^\ominus_{\text{right}} - E^\ominus_{\text{left}} \quad \text{a.k.a.} \quad \Delta E^\ominus = E^\ominus_{\text{reduction cell}} - E^\ominus_{\text{oxidation cell}}$$

The concentration dependence of the *e.m.f.* is given by the Nernst equation:

$$E = E^\ominus + \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{\prod c_{\text{oxidised species}}}{\prod c_{\text{reduced species}}}$$

Therefore, the *e.m.f.* (ΔE) at any concentration of components in the two half-cells is:

$$\Delta E = \Delta E^\ominus - \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{\prod c_{\text{products}}}{\prod c_{\text{reactants}}}$$

Electromotive force and equilibrium

$$\Delta E = \Delta E^\ominus - \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{\prod c_{\text{products}}}{\prod c_{\text{reactants}}} \quad \Rightarrow \quad \Delta E = \Delta E^\ominus - \frac{R \cdot T}{z \cdot F} \cdot \ln K$$

When the reactants of the cell have reached their equilibrium concentrations, there is no electric current flowing between the two half cells (flat battery).

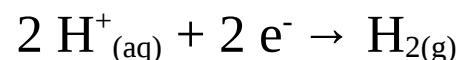
$$\Rightarrow \quad \Delta E^\ominus = \frac{R \cdot T}{z \cdot F} \cdot \ln K$$

The reference electrode potential

In order to determine standard electrode potentials, we need to measure the *e.m.f.* of a cell in which the concentration of solutions are all 1 M.

The problem is that measurements are only possible using two half cells and determine the difference in the potentials.

Therefore, the standard hydrogen electrode



is chosen to have $E^\ominus = 0$.

When determining the standard electrode potentials of any electrode, the standard hydrogen electrode is chosen as the left electrode.

$$\Delta E^\ominus = E^\ominus_{\text{right}} - E^\ominus_{\text{left}}$$

Standard electrode potentials

By looking at the table of standard electrode potentials, we can predict the value for the equilibrium constant for a reaction that combines two half cells.

Half cell	E° (V)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.76
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2(\text{g})$	0.00
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{O}_3(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	2.07
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	2.87

1. Measured against standard hydrogen electrode
2. Concentration of electrolytes: 1 M
3. Pressure of gases: 1 bar
4. Temperature: 25°C

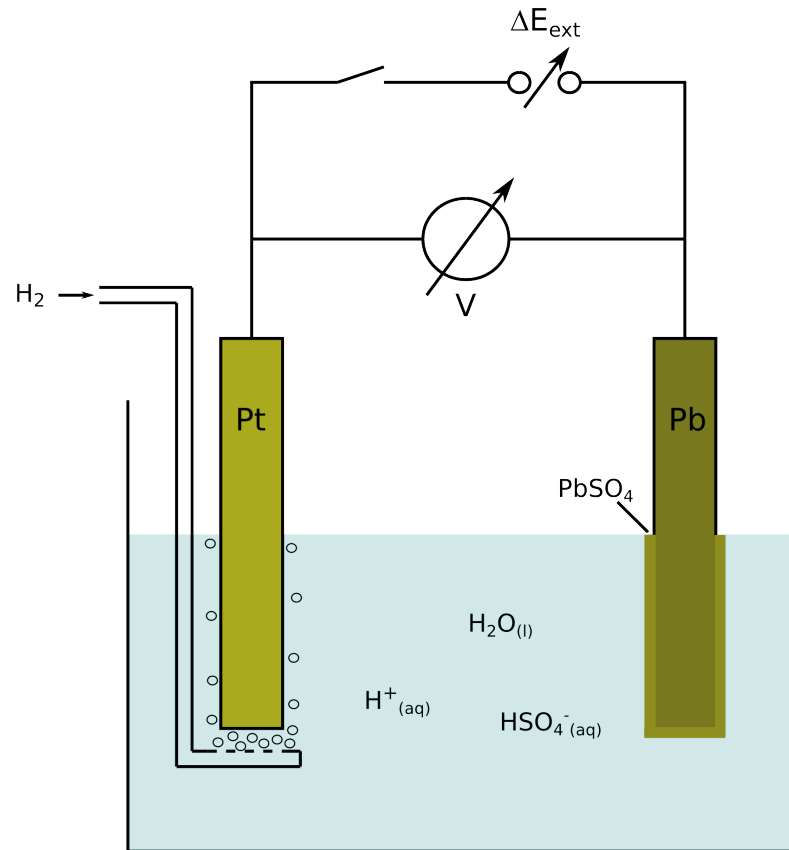
The electrode with the higher potential is where the reduction occurs.

The electrode with lower potential is where the oxidation occurs.

The electron flow is from lower to higher electric potential.

[Standard electrode potentials etc at Georgia State University](#)

Electrode potentials



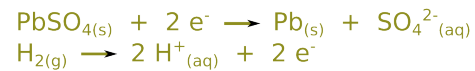
Equilibrium cell

$$\Delta E_{\text{ext}} = -360 \text{ mV} \quad I = 0$$

No reaction

Electrolytic cell

$$\Delta E_{\text{ext}} = -370 \text{ mV}$$

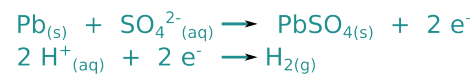


Cathode (reduction)

Anode (oxidation)

Galvanic cell

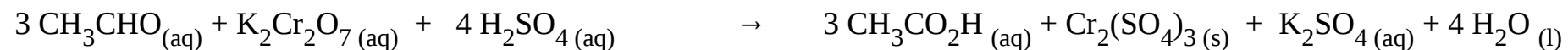
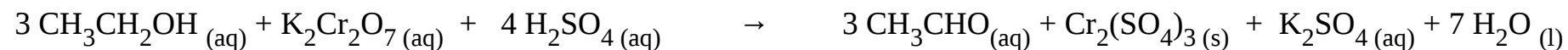
$$\Delta E_{\text{ext}} = -350 \text{ mV}$$



Anode (oxidation)

Cathode (reduction)

Applied redox chemistry: BreathalyzerTM



[Redox chemistry inside the Breathalyzer \(Duke University\)](#)

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University.
Sections IV.1.1-IV.2.9

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press.
Sections 6.5 – 6.9, I6.3 (pp. 227-240)