

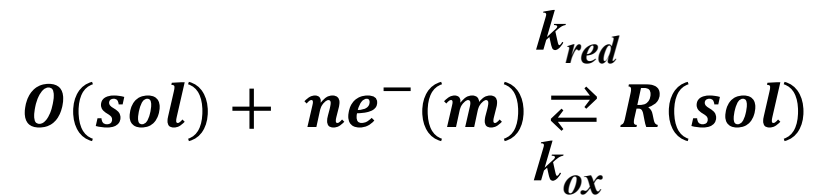
Energy Conversion by Semiconductor Devices

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- **Electrochemistry: electricity + chemical reactions.**
The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction.
- **Photoelectrochemistry: electricity + chemical reactions + light.**
Study within physical chemistry concerned with the interaction of light with electrochemical system (electron excitation in photoexcited material, charge transfer, electrochemical reaction)

- In redox reactions, electrons are transferred from one species to another.
- A species losing electrons is said to be oxidized; one gaining electrons is said to be reduced.
- The two processes together are called redox and one can never occur without the other.
- Both mass and charge must be balanced in any chemical reaction.

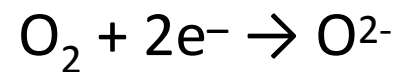


k_{red} : The rate constant for the reduction half-reaction

k_{ox} : The rate constant for the oxidation half-reaction

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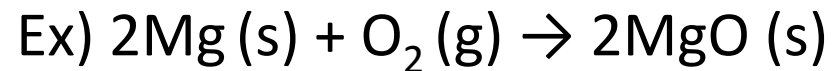
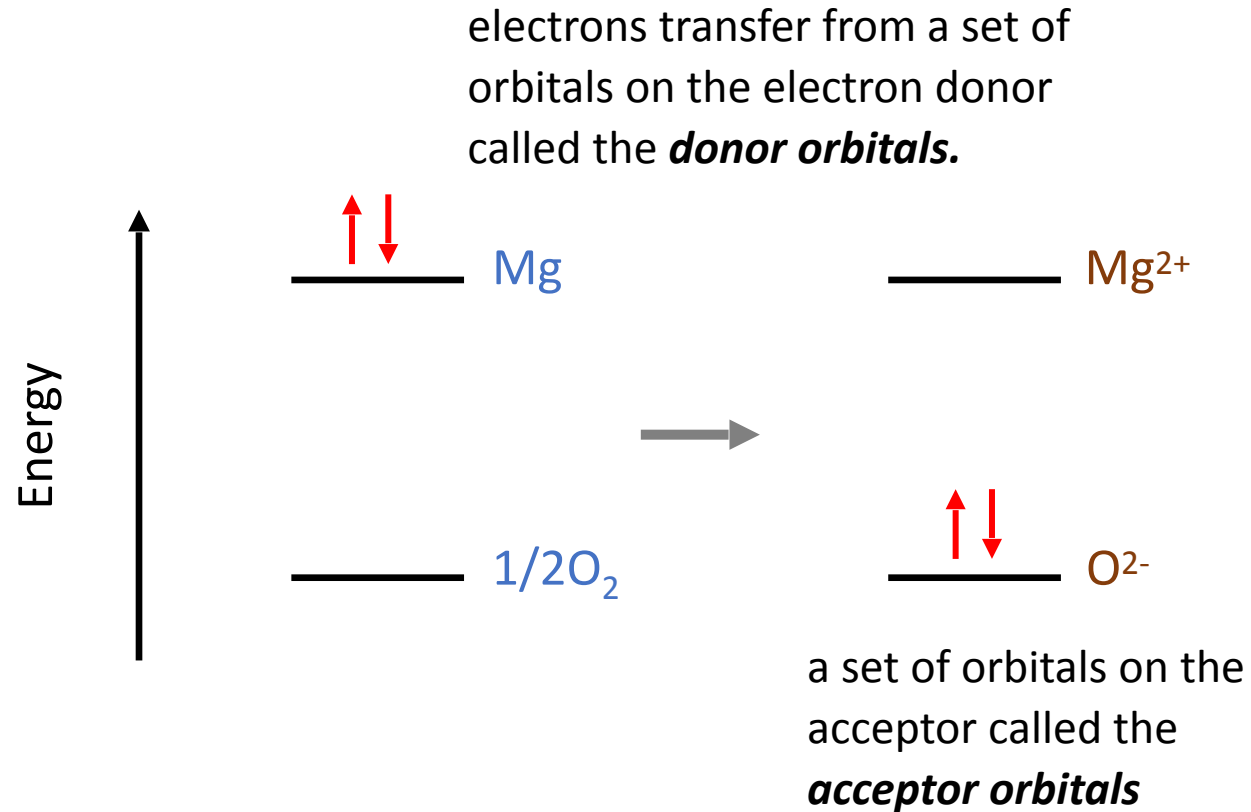
Ex) Balance the reaction: $2\text{Mg (s)} + \text{O}_2 \text{ (g)} \rightarrow \text{MgO (s)}$



Reduction half-reaction



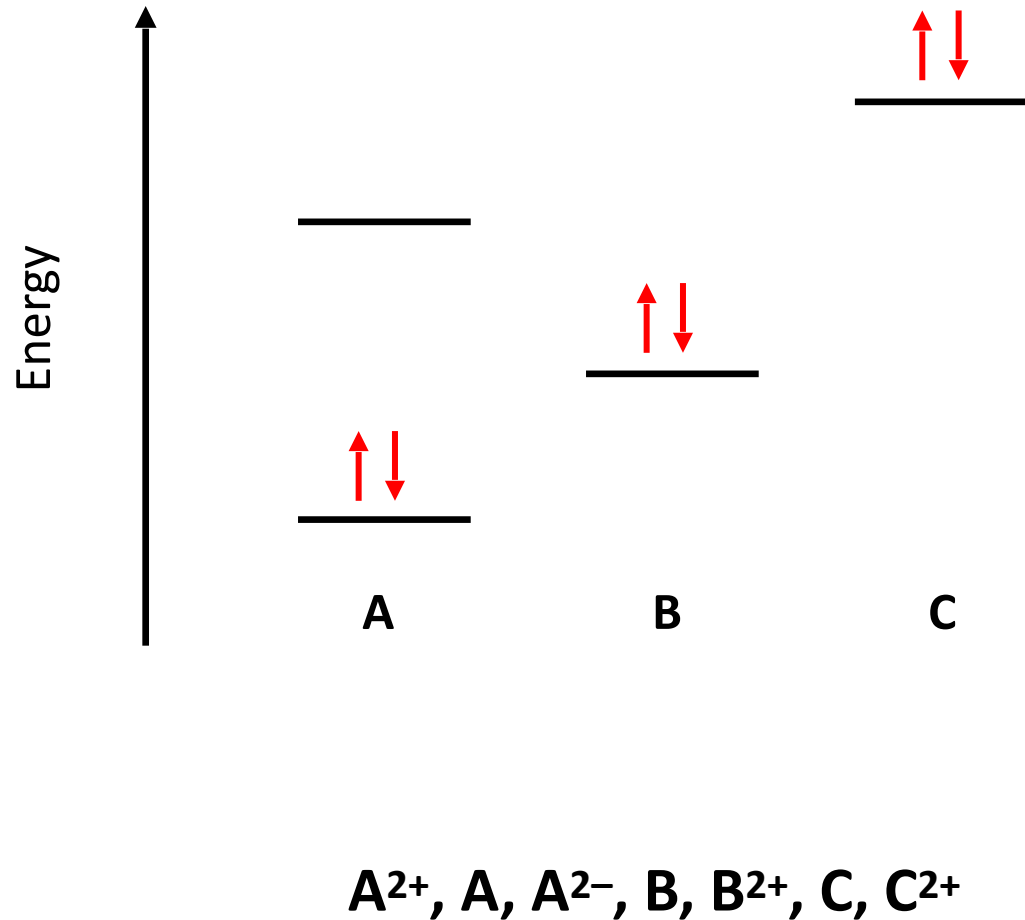
Oxidation half-reaction



The species that is oxidized by the reaction (= causes reduction in another substance) is referred to as the **reducing agent** or **reductant**.

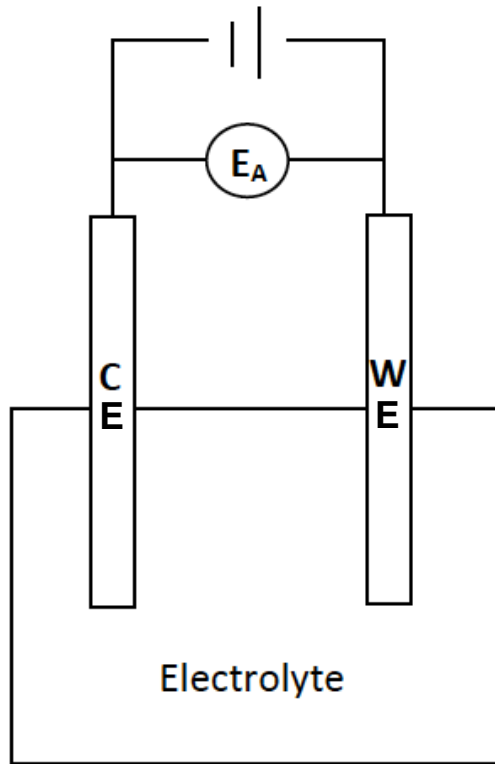
The species that is reduced by the reaction (= causes oxidation in another substance) is called the **oxidizing agent** or **oxidant**.

Strong reducing agents have high-energy electrons, and strong oxidizing agents have unfilled orbitals at low energy: driving force for electron transfer

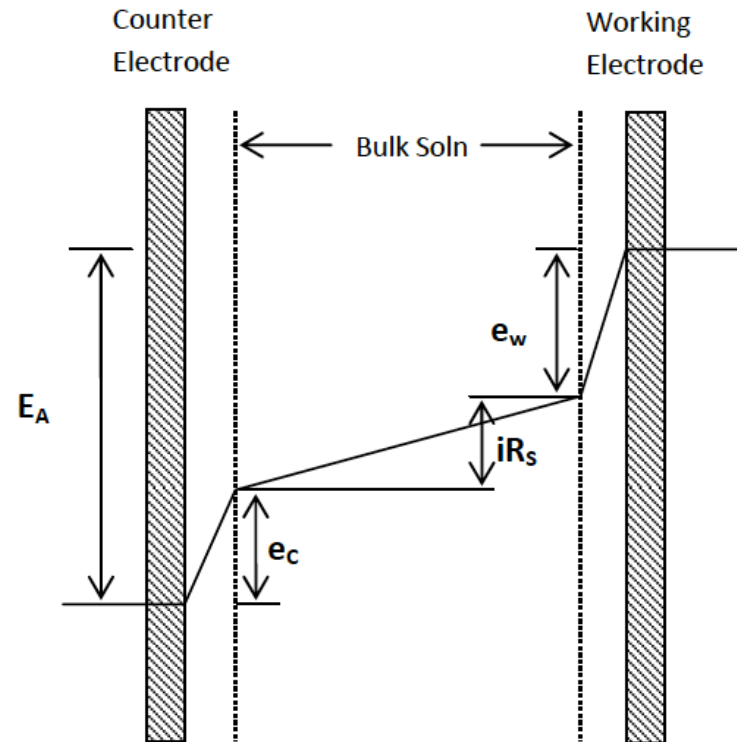


1. Which is the best oxidizing agent?
2. Which is the best reducing agent?
3. Which oxidizes A^{2-} but not A?
4. Which reduces B^{2+} but not C^{2+} ?

- **Anode (oxidation):** the electrode that releases electrons to the external circuit and oxidizes during the electrochemical reaction.
- **Cathode (reduction):** the electrode that acquires electrons from the external circuit and is reduced during the electrochemical reaction.
- When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an **electrolyte**: the medium that provides the ion transport mechanism between the cathode and anode of a cell, thereby maintaining the system's electrical neutrality.
- Electrolytes are often thought of as liquids, such as water or other solvents, with dissolved salts, acids, or alkalis that are required for ionic conduction. It should however be noted that many batteries including the conventional batteries contain solid electrolytes that act as ionic conductors at RT.

Two electrode cell: iR_s problem due to high current flow (**IR drop**)

WE: Working Electrode
CE: Counter Electrode

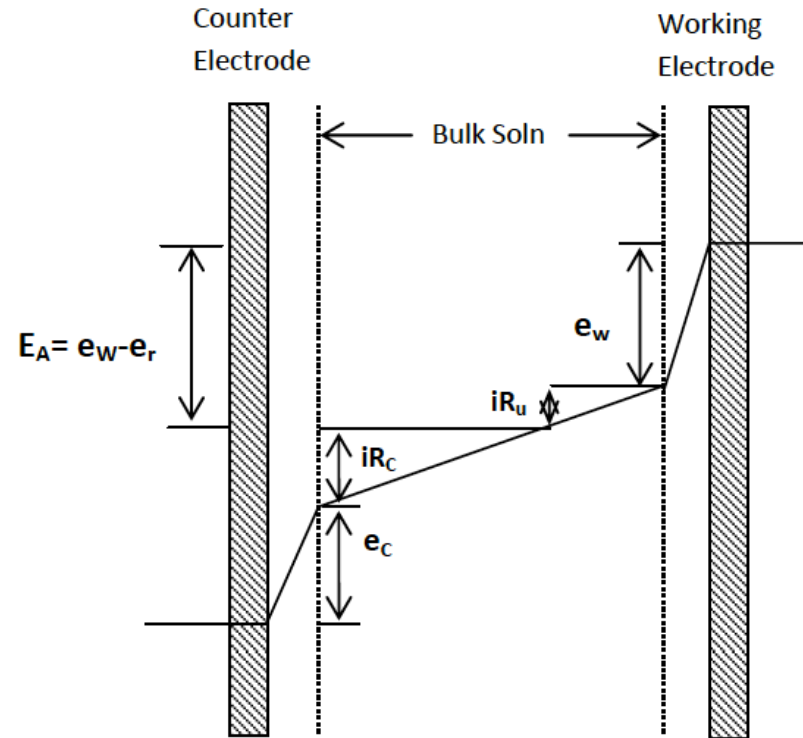
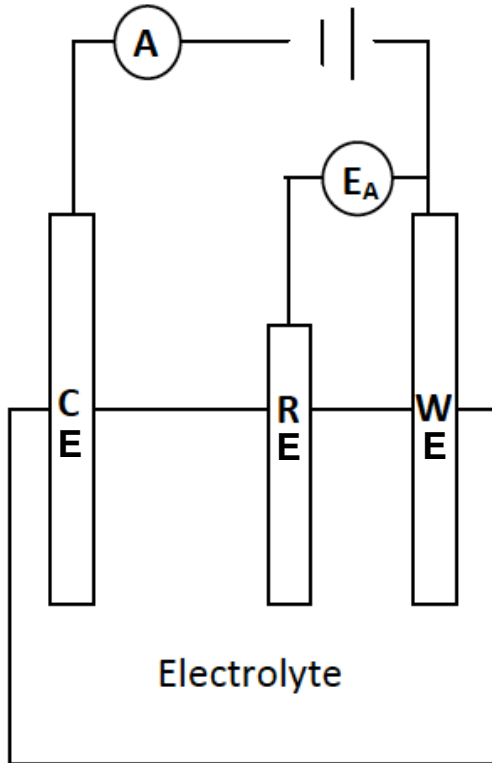


E_A : Applied potential

- The CE in the two electrode set-up serves two functions: It completes the circuit allowing charge to flow through the cell, and it also maintains a constant interfacial potential, regardless of current.
- The applied potential (E_A) is measured between WE and CE.
- In a two electrode system, it's very difficult to maintain a constant CE potential (e_c) while current is flowing.
- Along with a lack of compensation for the voltage drop across the solution (iR_s), it leads to poor control of the WE potential (e_w) with a two electrode system.

Three electrode cell: Current between WE and CE

Potential measurement between WE and RE

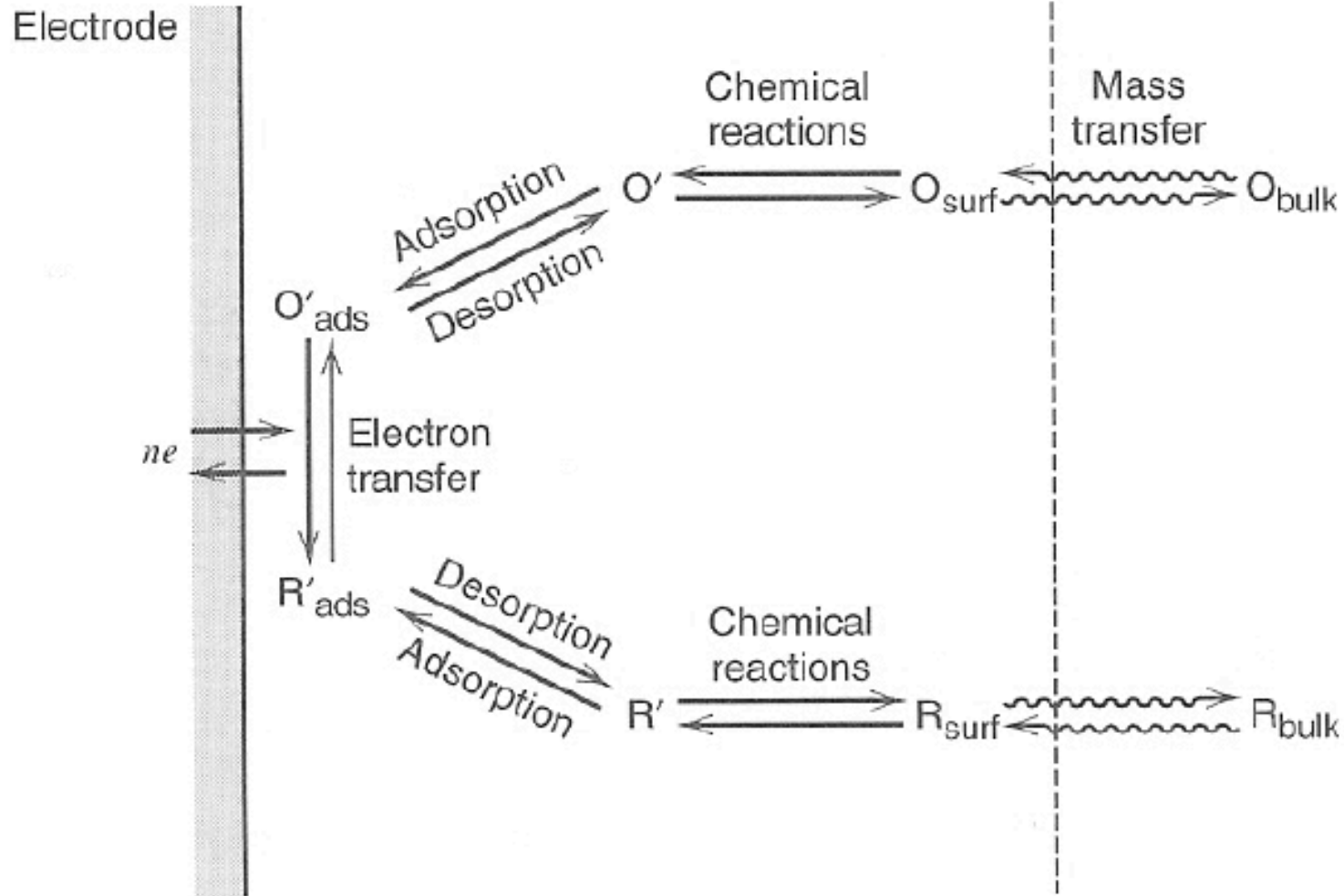


- The RE's role is to act as a reference in measuring and controlling the WE potential, without passing any current: a constant electrochemical potential at low current density.
- As the RE passes negligible current, the iR drop between the RE and WE (iR_u) is very small.
- In the three electrode configuration, the only role of the CE is to pass all the current needed to balance the current observed at the WE.
- The RE potential is much more stable.

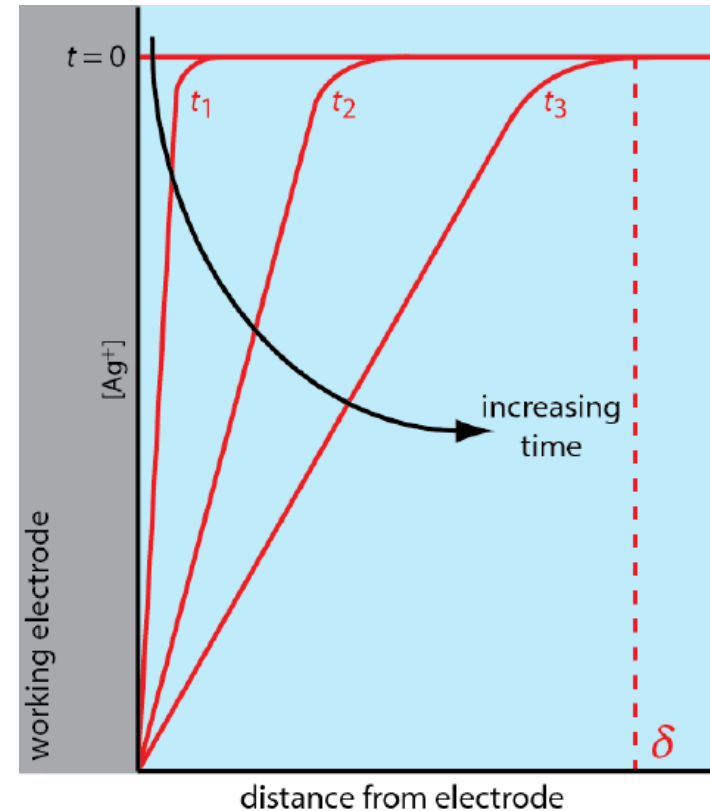
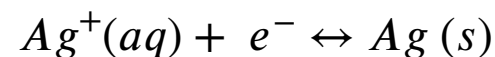
WE: Working Electrode
RE: Reference Electrode
CE: Counter Electrode

Electrode surface region

Bulk solution

**1. Mass transfer****2. Electron transfer at the electrode surface****3. Chemical reactions****4. Other surface reactions: adsorption, desorption, growth (electrodeposition)**

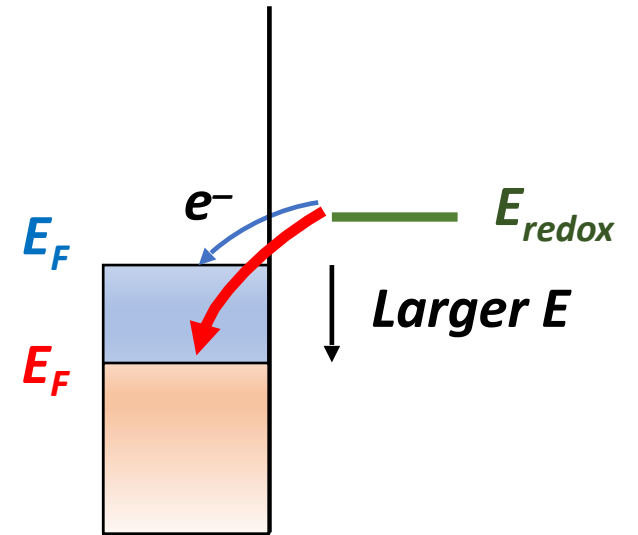
- 1. Migration:** movement of a charged species under the influence of an electric field (a gradient of electric potential). An anion will move toward the electrode and a cation will move toward the bulk solution if the electrode is positively charged.
- 2. Diffusion:** movement of species under the influence of gradient of chemical potential (a concentration gradient)
- 3. Convection:** stirring or hydrodynamic transport. The most common form of convection is stirring the solution with a stir bar and other methods include rotating the electrode and incorporating the electrode into a flow-cell.



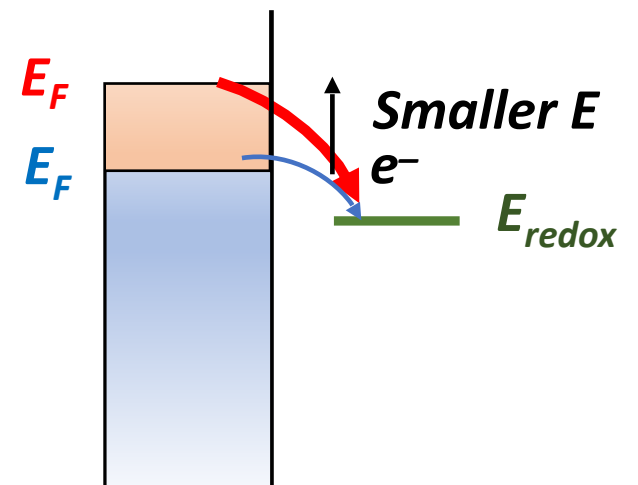
EPFL Electron Transfer (Faradaic Process)

- Assumption: the electrode material itself is inert (catalyst), not undergoing any chemical transformation.
- The electrode reaction (different from ordinary chemical reactions) in that at least one partial reaction must be a **charge transfer reaction**.
- The reaction depends on the distributions of species (concentrations and pressures), temperature, and electrode potential.
- The highest occupied electron level in the electrode = E_F . Electrons are always transferred to or from this level.
- The electrode potential E of an electrode through which a current flows differs from the equilibrium potential E_{eq} established when no current flows.

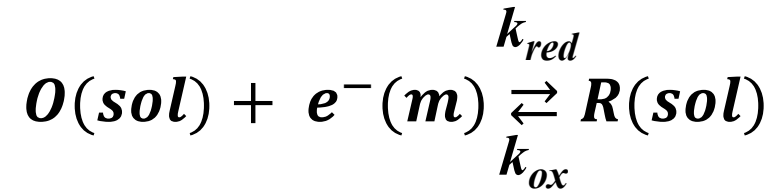
Oxidation (anodic)



Reduction (cathodic)



- For simplicity, let's consider a single electron transfer reaction between two species (O) and (R).



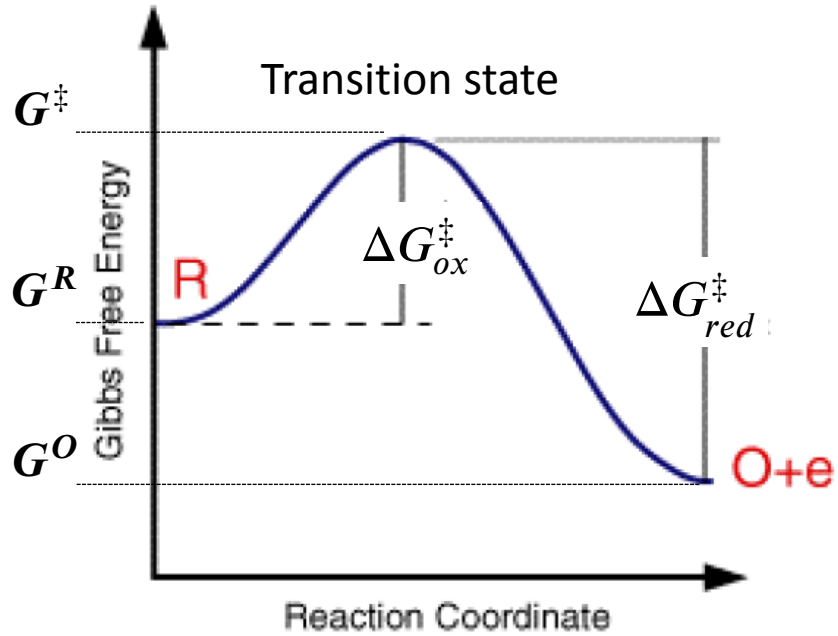
- The current flowing in either the reductive or oxidative steps can be predicted using the following expressions:

$$i_{red} = i_c = F A k_{red} [O]_0$$

$$i_{ox} = i_a = F A k_{ox} [R]_0$$

- The cathodic or anodic current (i_c or i_a) is related to the electrode area (A), the surface concentration of the reactant $[O]_0$ or $[R]_0$, the rate constant for the electron transfer (k_{red} or k_{ox}). F is the Faraday constant, 96485 C/mol.

Electron Transfer (Faradaic Process)



The activation free energy for the reduction and oxidation reactions are:

$$\Delta G_{red}^{\ddagger} = G^{\ddagger} - G^O$$

$$\Delta G_{ox}^{\ddagger} = G^{\ddagger} - G^R$$

The reaction rates are:

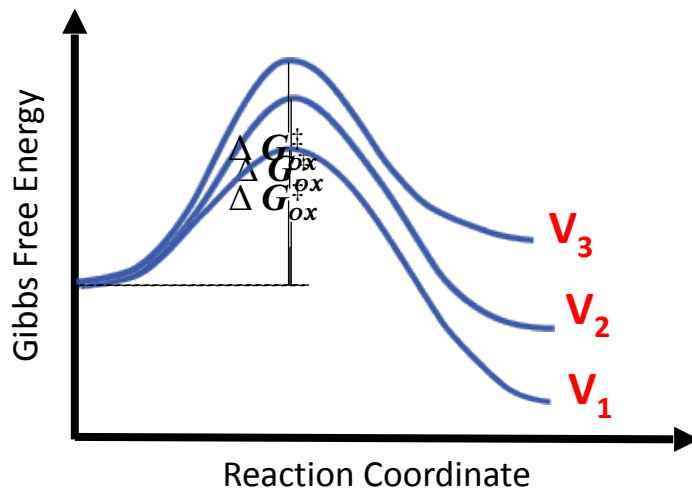
$$k_{red} = A_{red} \exp\left(\frac{-\Delta G_{red}^{\ddagger}}{RT}\right)$$

$$k_{ox} = A_{ox} \exp\left(\frac{-\Delta G_{ox}^{\ddagger}}{RT}\right)$$

As a function of voltage, the plots alter:

$$\Delta G_{red}^{\ddagger} = \Delta G_{red, no V}^{\ddagger} + \alpha FV$$

$$\Delta G_{ox}^{\ddagger} = \Delta G_{ox, no V}^{\ddagger} - (1 - \alpha)FV \quad (\alpha = \text{transfer coefficient})$$



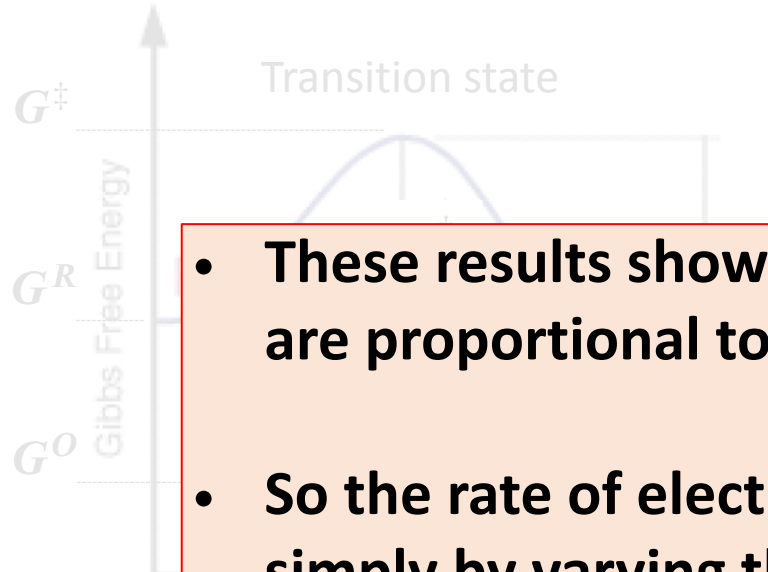
The reaction rates are: $k_{red} = A_{red} \exp\left\{\left(\frac{-\Delta G_{red, no V}^{\ddagger}}{RT}\right)\left(\frac{-\alpha FV}{RT}\right)\right\}$

$$k_{ox} = A_{ox} \exp\left\{\left(\frac{-\Delta G_{ox, no V}^{\ddagger}}{RT}\right)\left(\frac{(1 - \alpha)FV}{RT}\right)\right\}$$

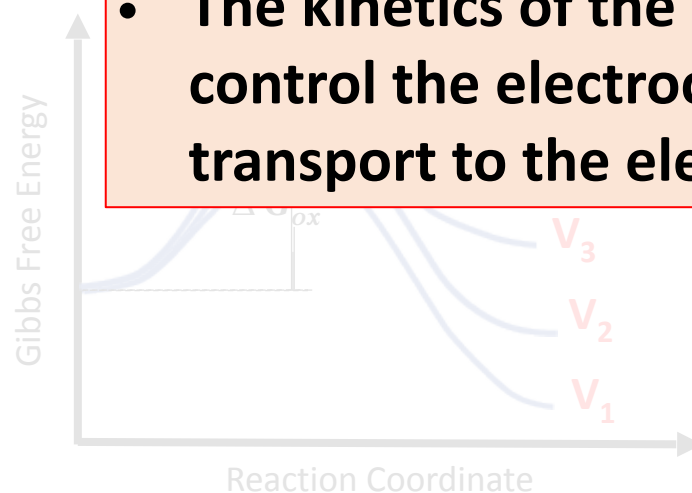
The activation free energy for the reduction and oxidation reactions are:

$$\Delta G_{red}^{\ddagger} = G^{\ddagger} - G^0$$

$$\Delta G_{ox}^{\ddagger} = G^{\ddagger} - G^R$$

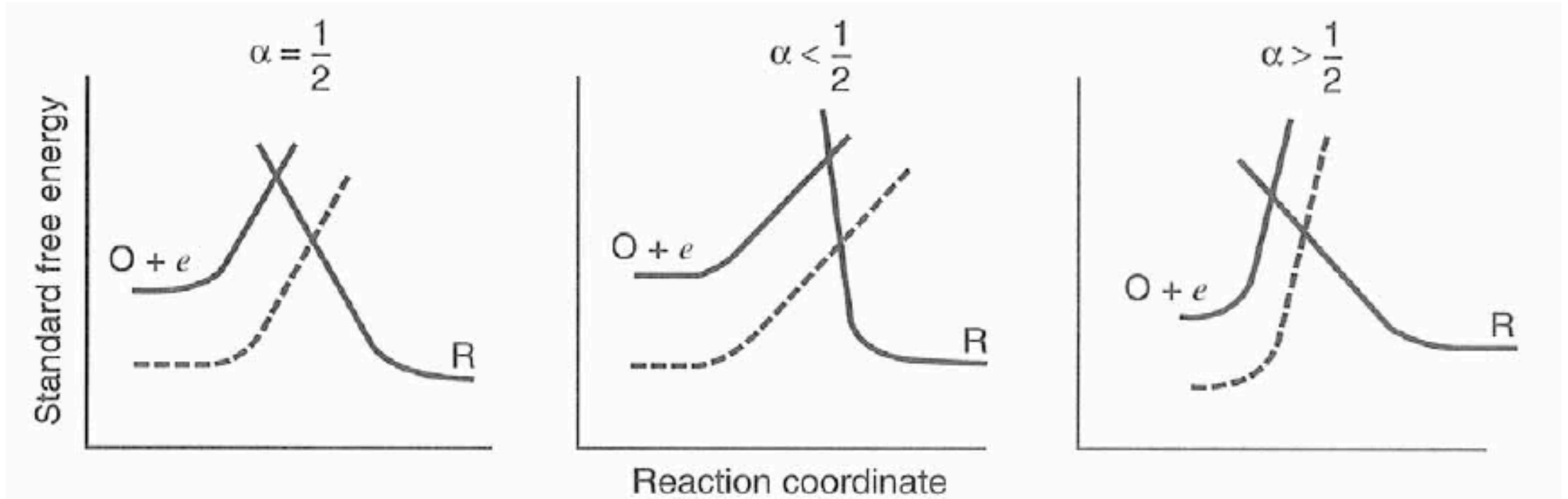


- These results show us that the rate constants for the electron transfer steps are proportional to the exponential of the applied voltage.
- So the rate of electrochemical reaction e.g. electrolysis can be changed simply by varying the applied voltage.
- The kinetics of the electron transfer is not the only process which can control the electrochemical reaction. In many circumstances it is the rate of transport to the electrode which controls the overall reaction.



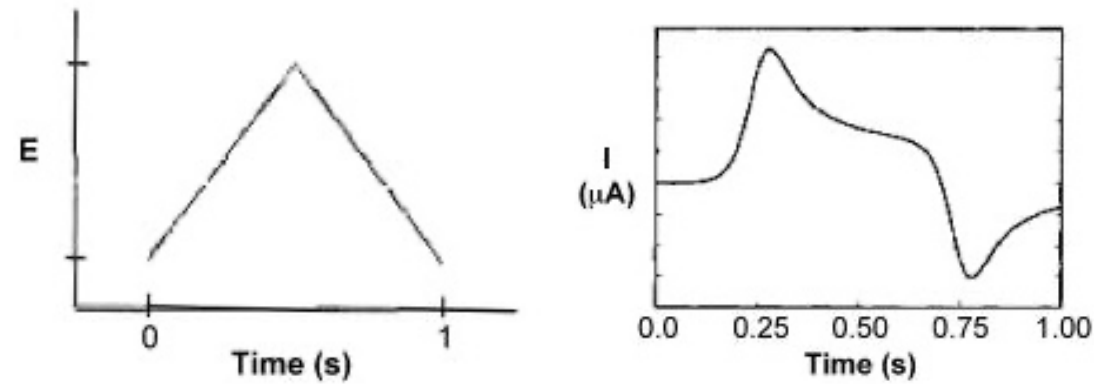
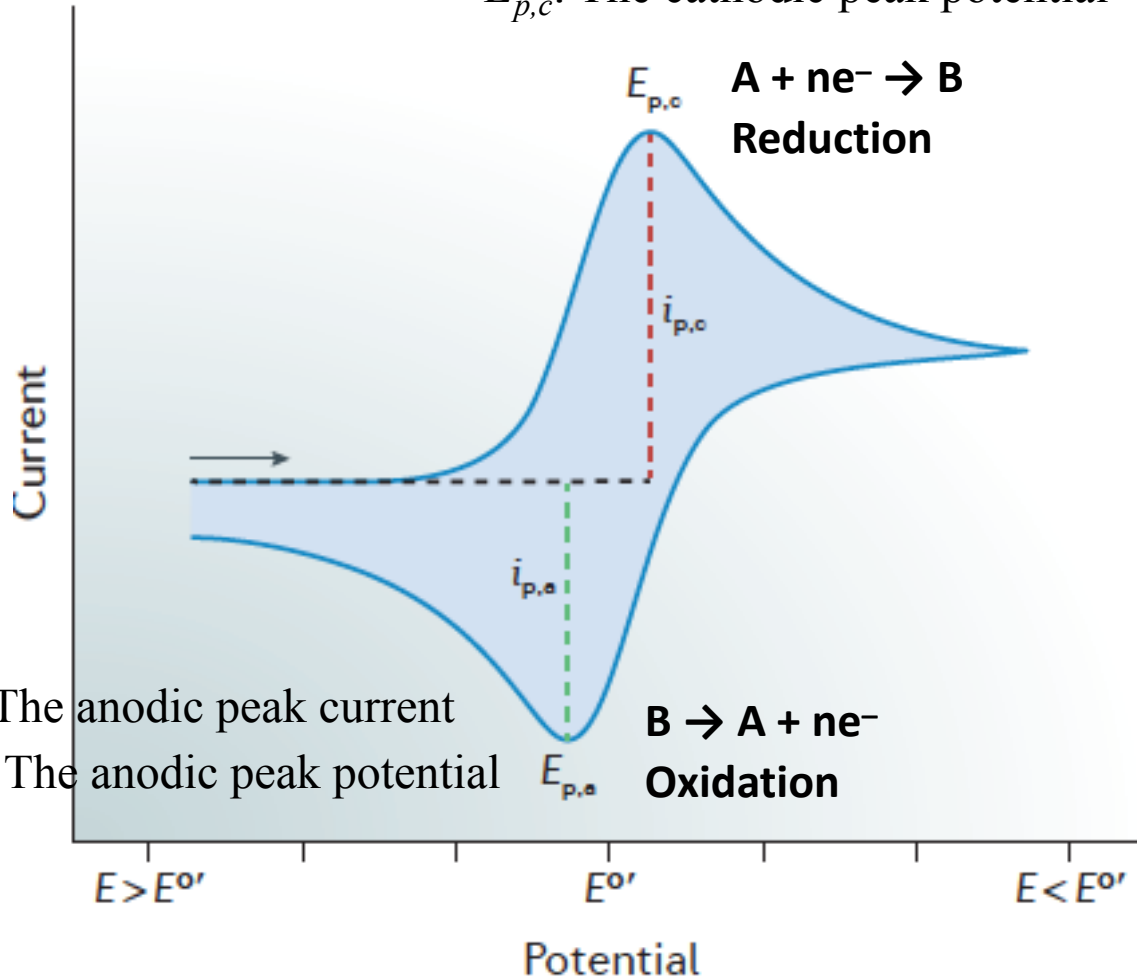
The reaction rates are: $k_{red} = A_{red} \exp \left\{ \left(\frac{-\Delta G_{red, no V}^{\ddagger}}{RT} \right) \left(\frac{-\alpha FV}{RT} \right) \right\}$

$$k_{ox} = A_{ox} \exp \left\{ \left(\frac{-\Delta G_{ox, no V}^{\ddagger}}{RT} \right) \left(\frac{(1 - \alpha) FV}{RT} \right) \right\}$$



In most systems, $0.3 < \alpha < 0.7$

$i_{p,c}$: The cathodic peak current
 $E_{p,c}$: The cathodic peak potential



- The potential is swept negative: Cathodic current flows to effect reduction reaction.
- More negative potential = greater driving force for reduction.
- But the concentration of A is depleted near the electrode surface due to the limited diffusion rate of A to the electrode surface → A is depleted and B is accumulated.
- After the direction of the potential is reversed, a second current peak appears, corresponding to oxidation reaction.

Image taken from K. J. Lee et al., *Nat. Rev. Chem.*, **1**, 0039 (2017)

EPFL Cell Potential & Gibbs Energy

- The total amount of energy produced by an electrochemical cell (the amount of energy available to do electrical work) depends on both **the cell potential** and **the total number of electrons** that are transferred from the reactant to the product during the course of a reaction.
- The maximum amount of work that can be produced by an electrochemical cell (W_{max}) = product of the cell potential (E_{cell}) and the total charge transferred during the reaction (nF)

$$\begin{aligned}W_{max} \text{ or } \Delta G \text{ (J)} &= -E_{cell} \text{ (V or J/C)} \times \text{charge (C)} \\ &= -E_{cell} \times \text{number of electrons} \times \text{electric charge per electron} \\ &= -E_{cell} \times \text{number of moles of electrons} \times \text{electric charge per mole} \\ &= -E_{cell} \times n \times F\end{aligned}$$

F (Faraday constant) = the charge on 1 mol of electrons = $(6.02214 \times 10^{23} \text{ J/mol}) \times (1.60218 \times 10^{-19} \text{ C})$
= 96,485 C/mol (J/(V · mol))

$$W_{max} \text{ or } \Delta G = -nFE_{cell} \quad \text{If the reaction is spontaneous, } \Delta G < 0$$
$$E_{cell} > 0$$

- When both reactants and products are in their standard states, $\Delta G^\circ = -nFE_{cell}^\circ$
- The standard cell potential (V) is the potential difference between the cathode and anode: $E_{cell}^\circ = E_{cathode (red)}^\circ - E_{anode (red)}^\circ$
- The cell potential is called the cell electromotive force (emf) of the cell when no current is drawn through the cell.
- Standard Reduction Potential: $A^{z+} + ze^- \rightarrow A$
- Standard oxidation potential = $-(\text{standard reduction potential})$: $A \rightarrow A^{z+} + ze^-$
- The standard cell potential (V): $E_{cell}^\circ = E_{cathode (red)}^\circ + E_{anode (ox)}^\circ$

Reduction potential measures the tendency of a chemical species to acquire electrons and thereby be reduced.

The standard reduction potential (E^0) is measured under standard conditions:

- 25 °C (298 K)
- 1 M concentration for each ion participating in the reaction
- Partial pressure of 1 atm for each gas that is part of the reaction
- Metals in their pure states

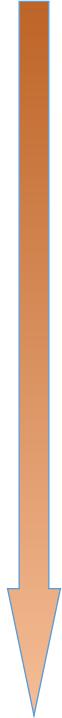
Universally, hydrogen has been recognized as having reduction and oxidation potentials of zero.

Reaction	E^0 (V) (SHE)	Reaction	E^0 (V) (SHE)
$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	-3.045	$\text{HgO} + \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{Hg} + 2\text{OH}^-$	0.098
$\text{K}^+ + e^- \rightleftharpoons \text{K}$	-2.935	$\text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+}$	0.154
$\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}$	-2.866	$\text{Cu}^{2+} + e^- \rightleftharpoons \text{Cu}^+$	0.153
$\text{Na}^+ + e^- \rightleftharpoons \text{Na}$	-2.714	$\text{AgCl} + e^- \rightleftharpoons \text{Ag} + \text{Cl}^-$	0.2224
$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	-2.363	$\text{HgCl}_2 + 2e^- \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$	0.2676
$\text{Al}^{3+} + 3e^- \rightleftharpoons \text{Al}$	-1.662	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	0.337
$\text{Ti}^{2+} + e^- \rightleftharpoons 2e^- \rightleftharpoons \text{Ti}$	-1.628	$\text{Fe}(\text{CN})_6^{3-} + e^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	0.36
$\text{Zn}(\text{OH})_2 + 2e^- \rightleftharpoons \text{Zn} + 2\text{OH}^-$	-1.245	$\text{Cu}^{2-} + e^- \rightleftharpoons \text{Cu}$	0.521
$\text{Mn}^{2+} + 2e^- \rightleftharpoons \text{Mn}$	-1.180	$\text{I}_2 + 2e^- \rightleftharpoons 2\text{I}^-$	0.536
$2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{OH}^{2-}$	-0.822	$\text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}_2$	0.682
$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0.764	$\text{Fe}^{3+} + e^- \rightleftharpoons e^- \rightleftharpoons \text{Fe}^{2+}$	0.771
$\text{S} + 2e^- \rightleftharpoons \text{S}^{2-}$	-0.48	$\text{Br}_2 + 2e^- \rightleftharpoons 2\text{Br}^-$	1.065
$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	-0.441	$\text{O}_2 + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O}$	1.229
$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}$	-0.403	$\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Cl}^-$	1.358
$\text{Ni}^{2-} + 2e^- \rightleftharpoons \text{Ni}$	-0.250	$\text{PbO}_2 + 4\text{H}^+ + e^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.455
$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	-0.136	$\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+}$	1.61
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	0.0000	$\text{F}_2 + 2e^- \rightleftharpoons 2\text{F}^-$	1.87

High tendency to oxidise



High tendency to reduce



Ex) Standard cell potential in the galvanic cell reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

Half-cell reactions:

Cathode (reduction): $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

Anode (oxidation): $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$

The cell can be represented as:

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

$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.337 \text{ V}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.764 \text{ V}$$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = 0.337 \text{ V} - (-0.764 \text{ V}) = 1.101 \text{ V}$$

The Nernst equation allows us to calculate the reduction potential of a redox reaction under “non-standard” conditions, at any temperature and concentration of reactants and products.

$$E = E^0 - \left(\frac{RT}{nF}\right) \ln Q = E^0 - \frac{0.0592}{n} \log Q \quad (\text{at } 298 \text{ K})$$

- E is the reduction potential for the specified non-standard state (not 1 M).
- E^0 is the standard reduction potential.
- R and F are the gas and Faraday constants, respectively.
- n is the number of electrons transferred in the reaction.
- Q is the reaction quotient. The brackets are concentrations and the lowercase letters are stoichiometric coefficients for the each species: $aA + bB \rightarrow cC + dD$

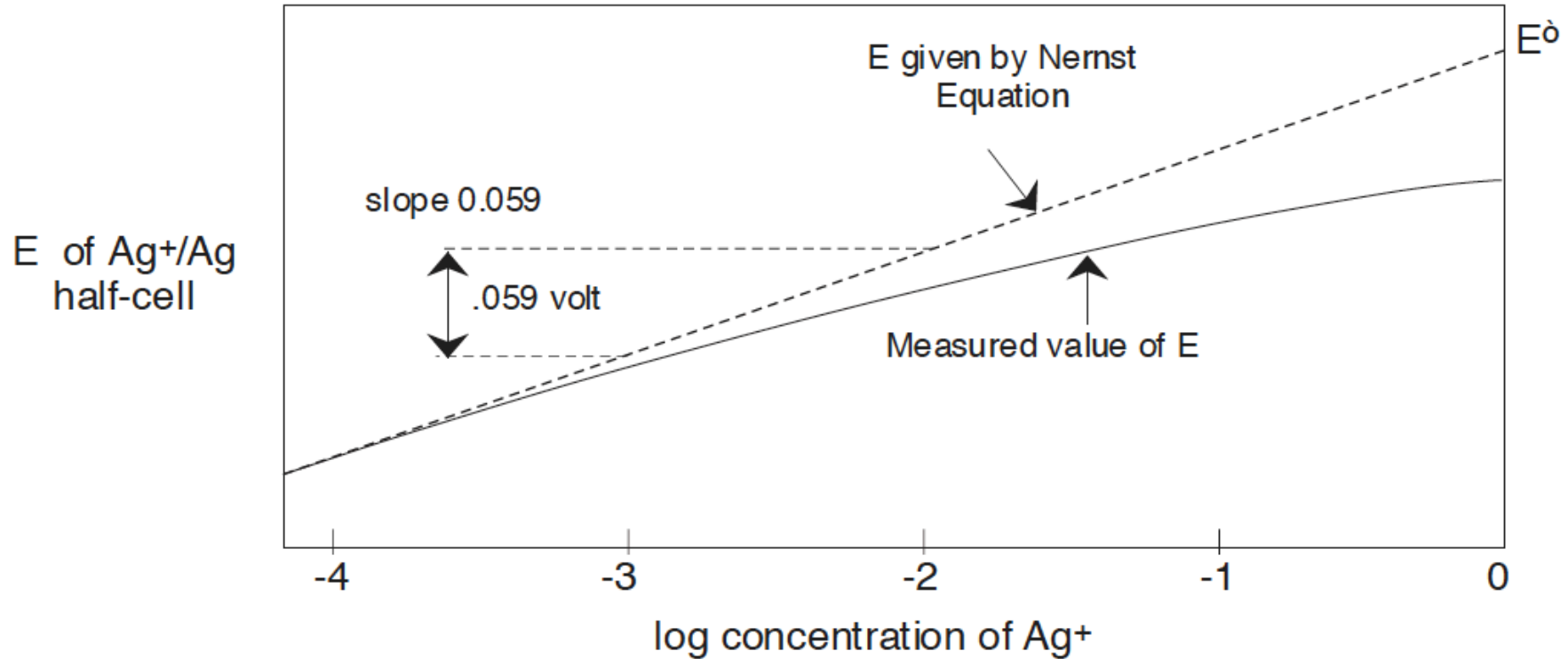
A and B are the reactants
C and D are the products
The lowercase letters: stoichiometric coefficients

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad \rightarrow \quad Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

a: chemical activity

at low concentration

$$E = E^0 - \left(\frac{RT}{nF}\right) \ln Q = E^0 - \frac{0.0592}{n} \log Q \text{ (at 298 K)}$$



$$a_{Red} = \gamma_{Red}[Red] = [Red] \text{ (at low concentration)}$$

$$a_{Ox} = \gamma_{Ox}[Ox] = [Ox] \text{ (at low concentration)}$$

a : chemical activity, γ = activity coefficient

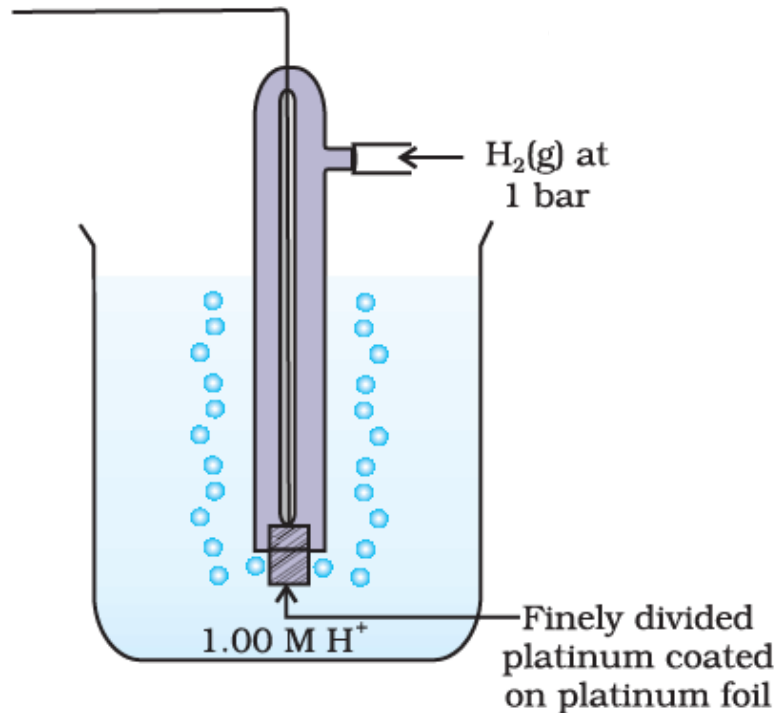
Ex) What is the cell potential of the following reaction at 298 K?



$$[\text{Al}^{3+}] = 0.1\text{M} \text{ and } [\text{Cu}^{2+}] = 3\text{M}$$

Reaction	E^0 (V) (SHE)	Reaction	E^0 (V) (SHE)
$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	-3.045	$\text{HgO} + \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{Hg} + 2\text{OH}^-$	0.098
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$\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni}$	-0.250	$\text{PbO}_2 + 4\text{H}^+ + e^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.455
$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	-0.136	$\text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+}$	1.61
$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	0.0000	$\text{F}_2 + 2e^- \rightleftharpoons 2\text{F}^-$	1.87

The potential of individual half-cell cannot be measured.



- One half-reaction, the reduction of 1 M hydrogen ion on a (catalytic) platinum electrode to hydrogen gas at 1 atm is arbitrarily assigned a standard reduction potential of **zero** volts.
- All other half-cell potentials are calculated relative to the hydrogen half-cell voltage.



$E^0 = 0.00 \text{ V}$ by definition

NHE (Normal Hydrogen Electrode): potential of a platinum electrode in 1 N acid solution. NHE is constructed by immersing a platinum electrode into a solution of 1 N (normal concentration, for protons, 1 N = 1 M) protons (strong acid) and bubbling pure hydrogen gas through the solution at 1 atm pressure.

SHE (Standard Hydrogen Electrode): potential of a platinum electrode in a theoretical ideal solution (the current standard for zero potential for all temperatures). SHE is composed of a platinum electrode dipped in an ideal acidic solution containing 1 M (effective concentration) protons and bubbling pure hydrogen gas at 1 bar. The absolute potential of SHE is 4.44 ± 0.02 V at 25 °C but its potential is set to be zero.

RHE (Reversible Hydrogen Electrode): a practical hydrogen electrode whose potential depends on the pH of the solution.

$$E_{RHE} = -0.0592pH$$

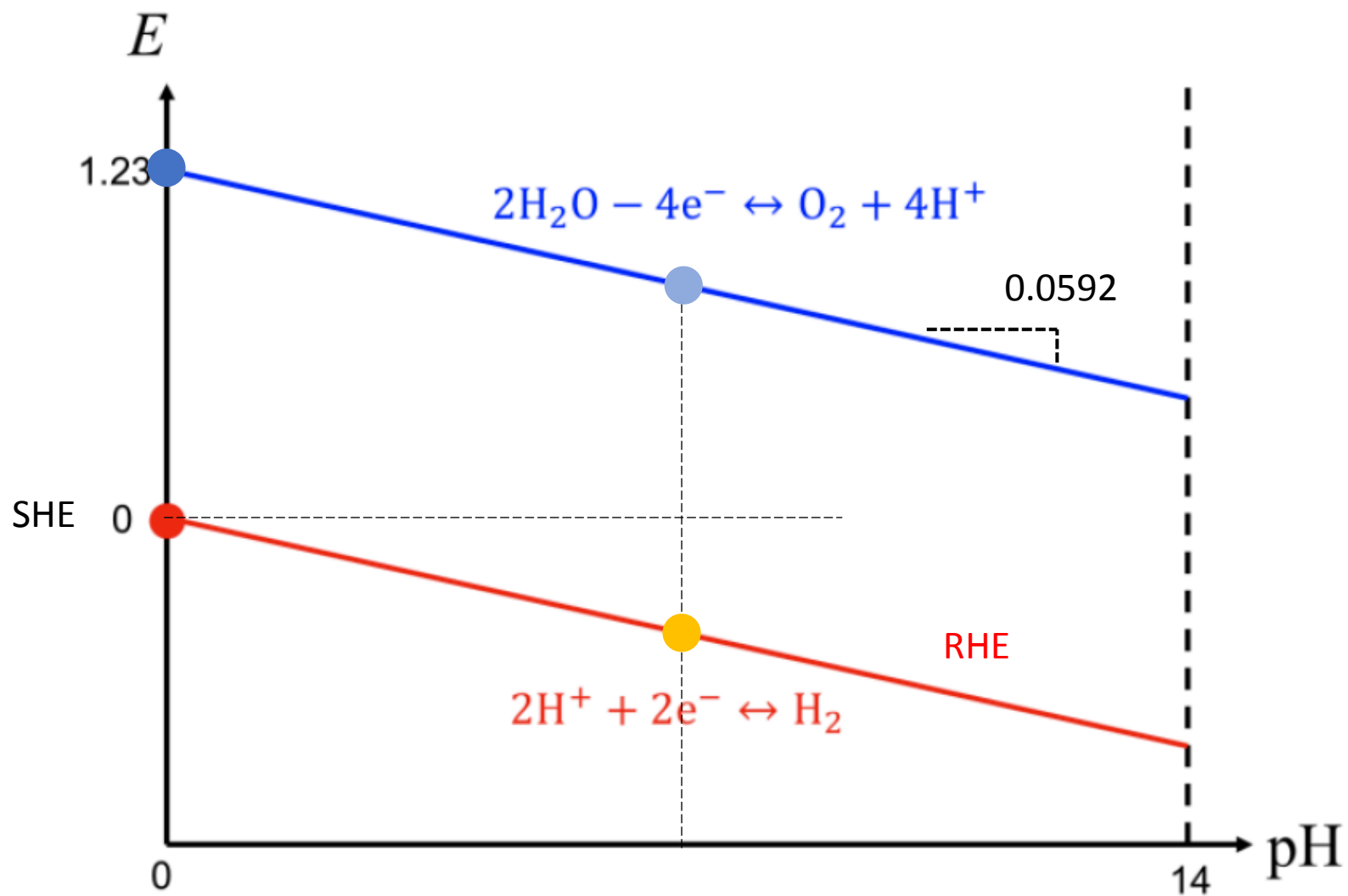
$$E_{RHE} = -0.0592pH$$



$$E_{H^+/H_2} = E_{H^+/H_2}^0 - \frac{RT}{nF} \ln\left(\frac{p_{H_2}}{[H^+]^2}\right)$$

at 25°C and unit H₂ partial pressure

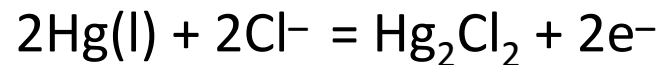
$$E_{H^+/H_2} = E_{H^+/H_2}^0 - \frac{0.0592}{2} \times 2pH = -0.0592pH$$



- In most electrochemical experiments, our interest is concentrated on only one of the electrode reactions.
- It is common practice to employ a reference electrode as the other half of the cell.
- The major requirements of a reference electrode is that it be **easy to prepare** and **maintain**, and that its potential be **stable**.
- The last requirement essentially means that the concentration of any ionic species involved in the electrode reaction must be held at a fixed value.

EPFL Saturated Calomel Reference Electrodes

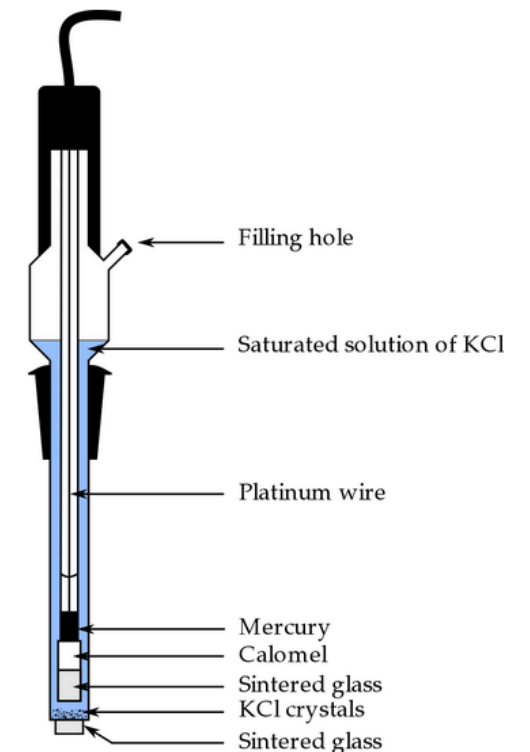
Saturated Calomel Electrode (SCE): A reference electrode based on the reaction between elemental mercury and mercury(I) chloride (calomel). Mercury provides a stable and conductive medium for the electrode to operate. Calomel paste serves as a salt bridge that allows ion exchange while maintaining a constant chloride ion concentration. Saturated KCl solution ensures that the chloride ion concentration remains constant and prevents deviations in potential over time. A platinum wire immersed in the mercury layer allows contact with an external circuit such as a potentiometer.



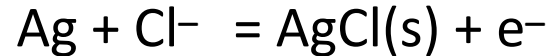
$$\begin{aligned} E_{SCE} &= E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^0 - 0.0592 \log(a_{\text{Cl}^-})^2 \\ &= 0.268 \text{ V} - 0.0592 \log(a_{\text{Cl}^-})^2 \end{aligned}$$

@ a 1.00 M of KCl, the potential is +0.280 V vs SHE at RT

@ a saturated solution of KCl, the potential is +0.241 V vs SHE at RT



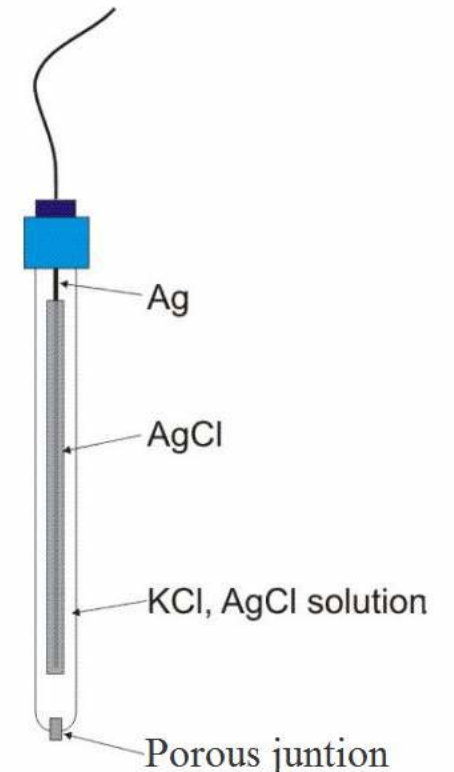
Silver-silver chloride electrode: the silver/silver chloride electrode, which is based on the reduction of AgCl to Ag. This electrode usually consists of a silver wire, coated with a thin of AgCl. The silver-silver chloride reference electrode develops a potential proportional to the chloride concentration, whether it is sodium chloride, potassium chloride, ammonium chloride or some other chloride salt and remains constant as long as the chloride concentration remains constant. A porous plug serves as the salt bridge.



$$\begin{aligned} E_{\text{AgCl}/\text{Ag}} &= E_{\text{AgCl}/\text{Ag}}^0 - 0.0592 \log a_{\text{Cl}^-} \\ &= 0.222 \text{ V} - 0.0592 \log a_{\text{Cl}^-} \end{aligned}$$

@ a solution of 3.5 M KCl, the potential is +0.205 V vs SHE at RT

@ a saturated solution of KCl, the potential is +0.197 V vs SHE at RT



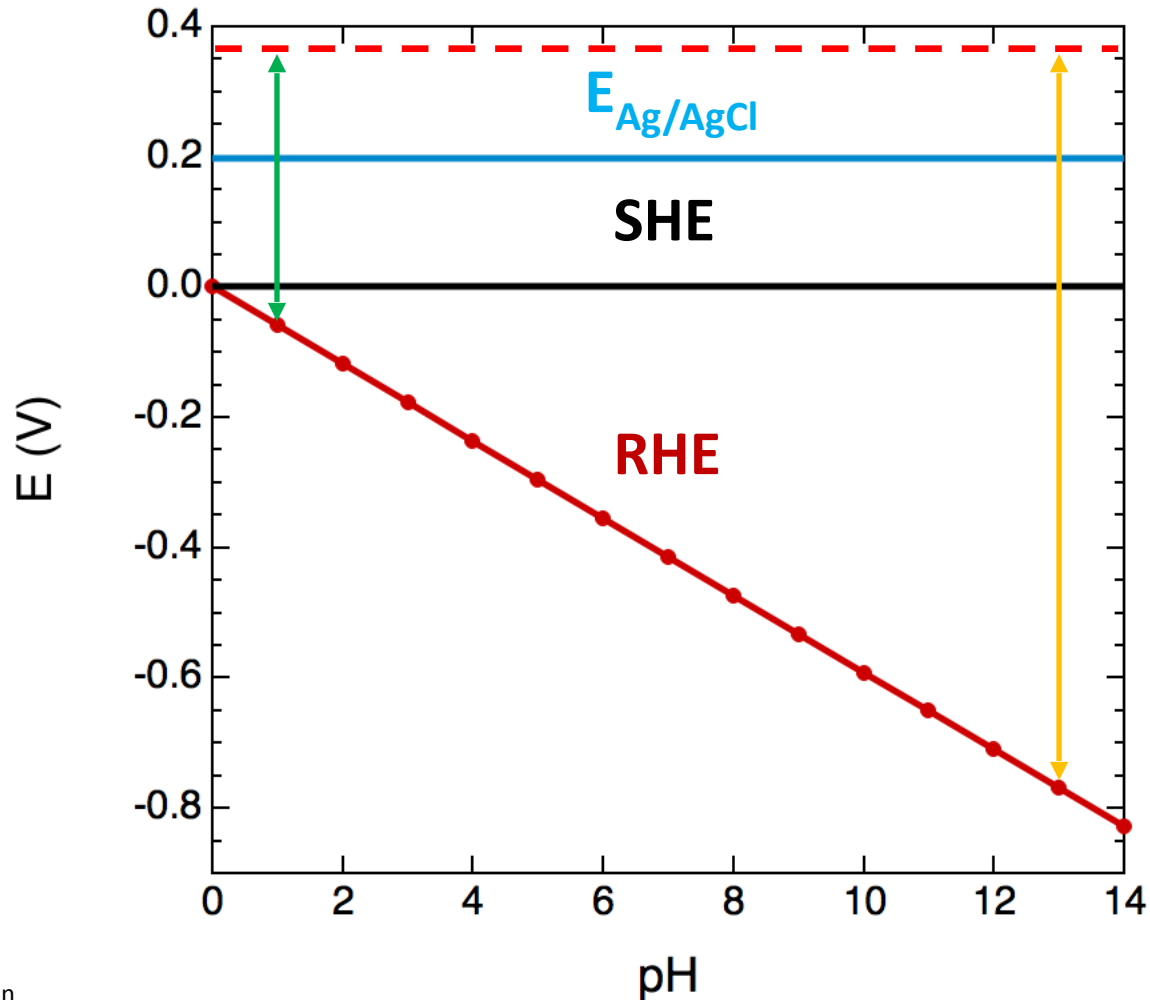
Ex) If an electrode has a potential of -0.435 V with respect to a SCE (sat), what is the potential with respect to a silver-silver chloride electrode (saturated KCl)? What would be the potential with respect to the SHE?

SCE: a saturated solution of KCl, the potential is $+0.241$ V vs SHE at RT

Ag/AgCl: a saturated solution of KCl, the potential is $+0.197$ V vs SHE at RT

$$E \text{ vs SHE} = \text{Recorded } E + E_{\text{Ag/AgCl}} (\text{sat})$$

$$E \text{ vs RHE} = \text{Recorded } E + E_{\text{Ag/AgCl}} (\text{sat}) + 0.0592 \text{ pH}$$

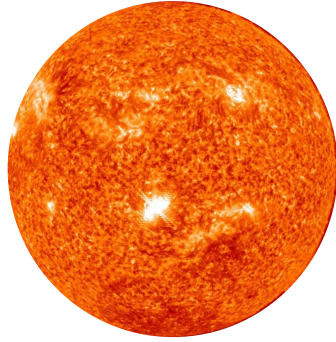


Ex) If an electrode has a potential of 0.153 V with respect to a Ag/AgCl RE at pH 1, what is the potential with respect to a RHE? What would be the potential with respect to the RHE at pH 13?

At pH = 1, $E \text{ vs RHE} = 0.153 + 0.197 + 0.0592 \times 1 =$
0.409 V

At pH = 13, $E \text{ vs RHE} = 0.153 + 0.197 + 0.0592 \times 13 =$
1.120 V

0.350 V vs SHE (pH independent)



Storable

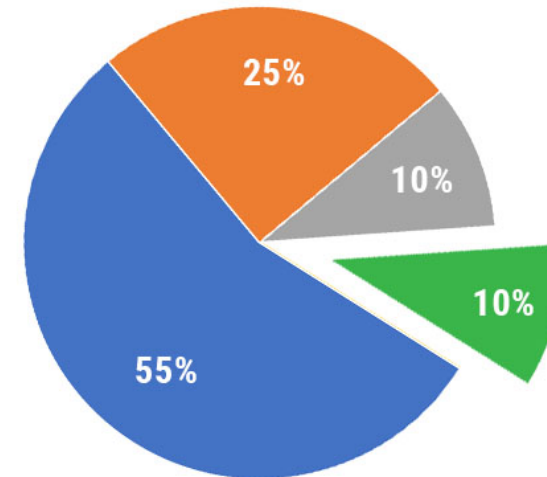


Intermittency



Petroleum Refining
25%

GLOBAL HYDROGEN CONSUMPTION BY INDUSTRY



Methanol Production
10%



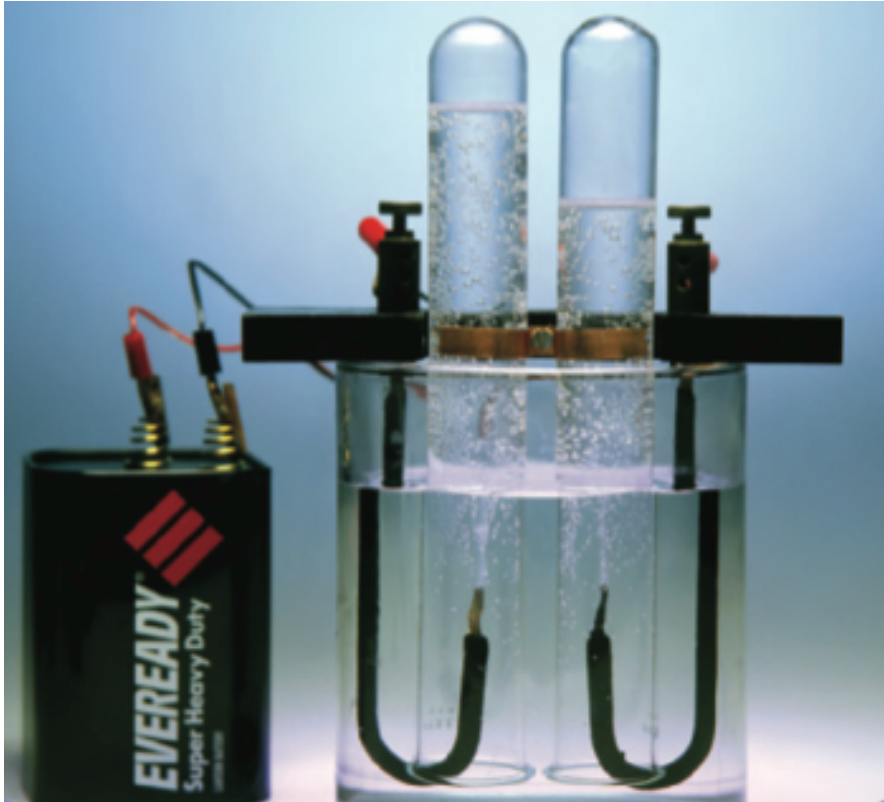
Ammonia Production
55%



Other
10%

Data from Hydrogen Europe (hydrogeneurope.eu/hydrogen-applications)
Illustration © WHA International, Inc. (wha-international.com)

- The most abundant element in the universe, hydrogen, does not exist in the form of H_2 on Earth (0.00005% in the atmosphere), but rather in molecular forms such as water and other organic compounds.
- Hydrogen's highly combustible characteristics enable it to be pursued as a promising energy vector (as a comparison, 3kg of H_2 corresponds to about 100 kWh of chemical energy, whereas a 450 kg lithium ion battery is needed to produce the same quantity of electrical energy).
- Hydrogen is primarily utilized in oil refining and ammonia production for the petroleum and chemical industries, more precisely in the Haber process to synthesize ammonia from atmospheric nitrogen for the production of fertilizer.
- Unfortunately the manufacture of hydrogen from fossil fuels is nonrenewable and furthermore leads to CO_2 as a byproduct, consequently contributing to greenhouse gas production (Steam Methane Reforming).



Ferrero et al., *Energy Procedia*, **101**, 50-57 (2016)
Hinkley et al., CSIRO Energy (2016)

- **Electrolyzer**
 - This technological concept uses electricity to split water molecules in order to form oxygen and hydrogen gases in a device.
 - First demonstrated in 1789 by Jan Rudolph Deiman and Adriaan Paet van Trootswijk using an electrostatic generator to produce an electrostatic discharge between two Au electrodes.
 - Abundant starting material (H_2O)
 - **Clean process** to split water into H_2 and O_2

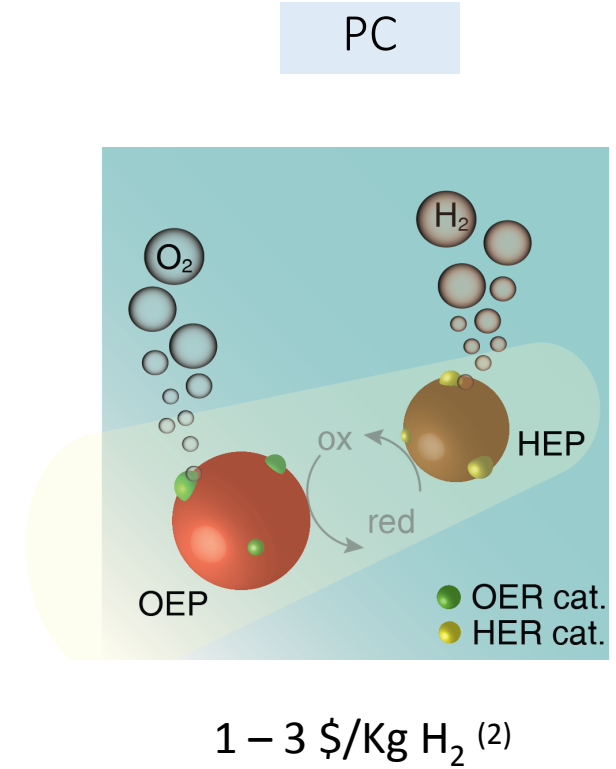
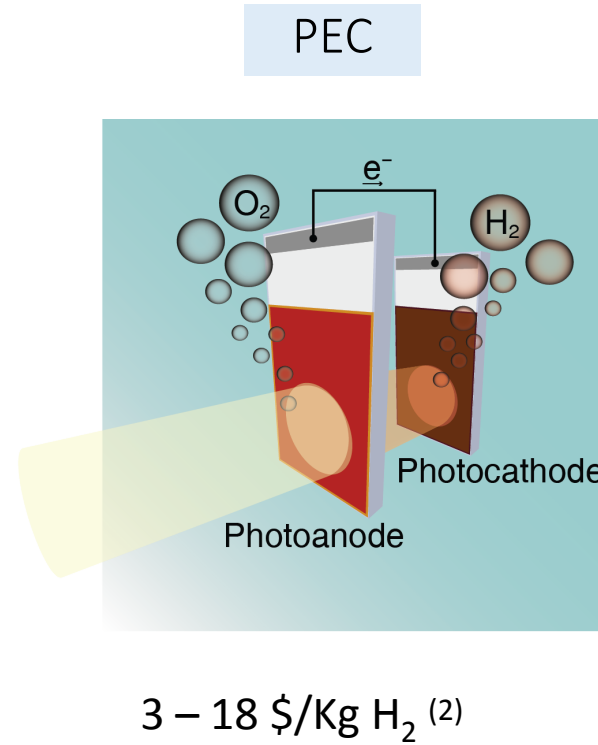
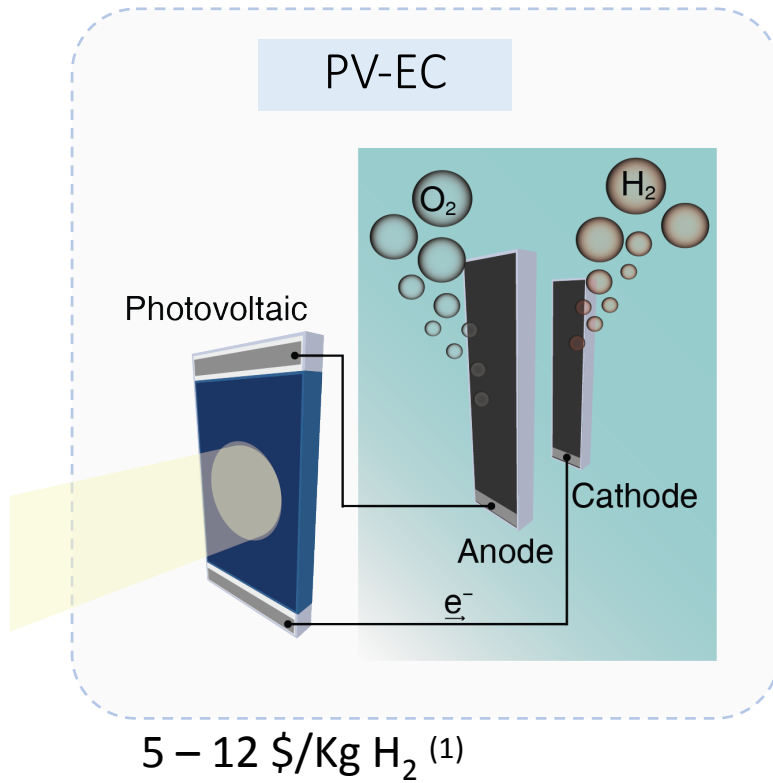
Cost 5.20 \$ Kg H_2

Mostly due to cost of electricity

Today's >100 Mt (10^9 kg) of Hydrogen (> 95%) is produced at large scale by ***steam reforming of natural gas vs 4% from electrolysis.***

Cost approx. 1.50-2.50\$ Kg H_2

- Amongst the current potential clean hydrogen production methods, the most developed solution is water electrolysis: alkaline electrolyzers (which have been used since the early 20th century), proton exchange membrane electrolyzers (otherwise known as polymer electrolyte membrane electrolyzers which are recently commercially available), and solid oxide electrolyzers (which can work at higher temperatures).
- However, the energy required by the process is roughly four times larger than the energy required for the production of hydrogen from natural gas reforming/gasification processes.
- Electrolysis-based solutions are only beneficial for the environment if the electricity used for the electrolysis is produced from carbon-free fuels.
- Therefore, combining this known water splitting technology with solar energy, a renewable source of electricity, has been adopted within the last few decades.



- Higher efficiency
- Complexity of the system and higher cost

(1) "DOE Technical Targets for Hydrogen Production from Electrolysis" <http://www.energy.gov>

(2) B.A. Pinaud, et al. *Energy Environ. Sci.*, **6**, 1983 (2013)