COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
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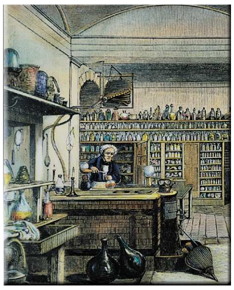
JF Chemistry 1101 2011

Introduction to Electrochemistry.



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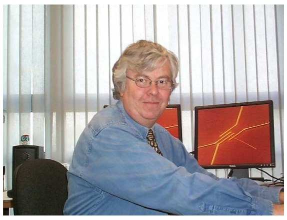

Recommended Reading

- Silberberg. Chemistry: the molecular nature of matter and change', Chapter 21. pp.892-949 (3rd Edition) ; pp.902-959 (4th edition).
- Atkins and Jones. Chemical Principles: the quest for insight. 3rd edition. Chapter 12.pp.444-482.
- Atkins & de Paula. Elements of Physical Chemistry.4th Edition. Chapter 9. pp.200-228.
- Kotz, Treichel & Weaver. Chemistry and Chemical Reactivity. 7th edition. Chapter 20. pp.896-961.
- Burrows et al. Chemistry^3, Chapter 17, pp.774-808.

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Lecture 16

Electrochemistry:
Simple ideas.

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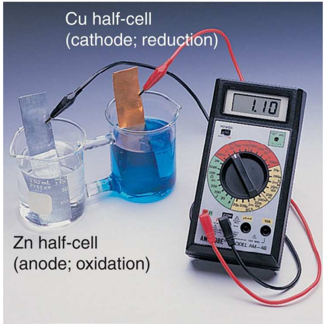


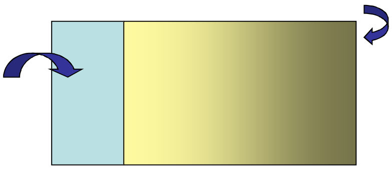
What is electrochemistry?

- Electrochemistry is the science which deals with the consequences of the transfer of electric charge from one phase to another.
- An electrochemical reaction is a heterogeneous process which involves electron transfer across a phase boundary or interface.
- Electrochemical reactions are labelled as redox (oxidation/reduction) processes.
- Electron transfer occurs at interfaces between a metallic conductor (an electrode) and an ionic conductor (an electrolyte).
- Oxidation is the loss of electrons.
- Reduction is the gain of electrons.

- Electrode : contains mobile electrons. Acts as source or sink of electrons.
  - Metals: Pt, Au, Ni, Cu, Hg
  - Non metals: glassy carbon, graphite.
  - Semiconductors.
  - Metal oxides.
  - Electroactive polymers : poly(pyrrole), poly(aniline).
- Electrolyte: contains mobile ions.
  - Solvents + salts.
  - Aqueous solutions.
  - Non aqueous solutions.
  - Solid elecrtrolytes.
  - Polymer electrolytes.

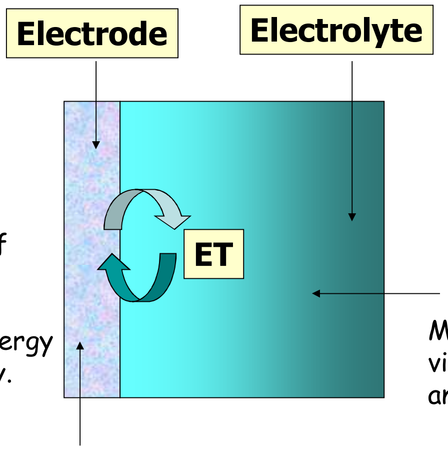
Chemistry^3, section 17.1,17.2.
Kotz, 20.1. Balancing redox reactions
pp.898-905.

Electrolyte:
Ionic conductor



Electrode:
Electronic conductor

The electrode/electrolyte interface.



Ionically conducting medium : electrolyte solution, molten salt, solid electrolyte, polymeric electrolyte, etc.

Conduction occurs via migration of electrons . Solid state Physics : energy band theory.

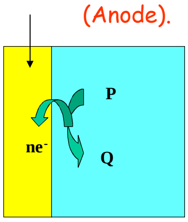
Material transport occurs via migration, diffusion and convection

Electronically conducting phase : metal, semiconductor, Conducting polymer material etc.

Anodes and cathodes.

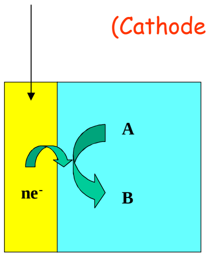
Electron sink electrode

(Anode).



Electron source electrode

(Cathode).



Oxidation or de-electronation

P = reductant (electron donor)

Q = Product

Reduction or electronation

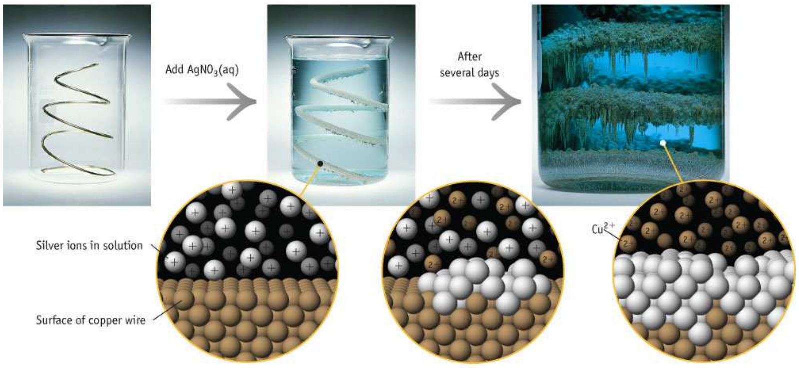
A = oxidant (electron acceptor)

B = Product

A clean piece of copper wire will be placed in a solution of silver nitrate, $AgNO_3$.

With time, the copper reduces Ag^+ ions to silver metal crystals, and the copper metal is oxidized to copper ions, Cu^{2+}.

The blue color of the solution is due to the presence of aqueous copper(II) ions.



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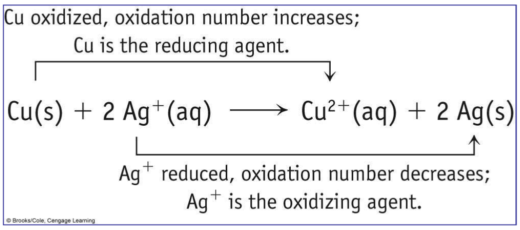

Cu oxidized, oxidation number increases;
Cu is the reducing agent.

$$Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$$

Ag^+ reduced, oxidation number decreases;
Ag^+ is the oxidizing agent.

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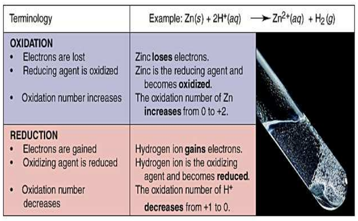
Redox reactions.

- Whether an electrochemical process releases or absorbs free energy it always involves the movement of electrons from one chemical species to another in an oxidation/reduction or redox reaction.
- In any redox process oxidation involves the loss of electrons and reduction involves the gain of electrons.
- An oxidising agent is the species that performs the oxidation, taking electrons from the species being oxidised.
- A reducing agent is the species that performs the reduction, giving electrons to the substance being reduced.
- After the reaction the oxidised substance has a higher (more positive, less negative) oxidation number, and the reduced substance has a lower (less positive, more negative) one.
- Oxidation (electron loss) always accompanies reduction (electron gain).
- The oxidizing agent is reduced and the reducing agent is oxidized.

- The number of electrons gained by the oxidizing agent always equals the number of electrons lost by the reducing agent.



Terminology	Example: $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$
OXIDATION • Electrons are lost • Reducing agent is oxidized • Oxidation number increases	Zinc **loses** electrons. Zinc is the reducing agent and becomes **oxidized.** The oxidation number of Zn **increases** from 0 to +2.
REDUCTION • Electrons are gained • Oxidizing agent is reduced • Oxidation number decreases	Hydrogen ion **gains** electrons. Hydrogen ion is the oxidizing agent and becomes **reduced.** The oxidation number of H^+ **decreases** from +1 to 0.

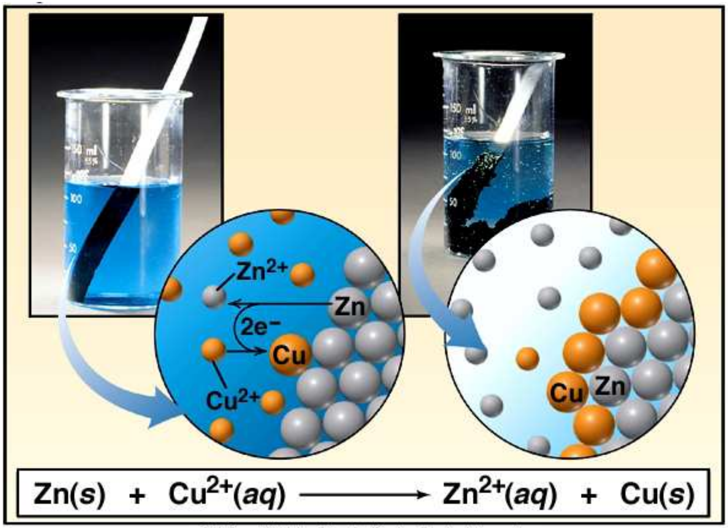
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

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

Oxidation and Reduction Movie I.

Oxidation-Reduction
Reactions - Part 1

Spontaneous redox chemistry involving copper and zinc.



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Oxidation and Reduction Movie II.

Oxidation-Reduction
Reactions - Part 2

Spontaneous coupled redox reactions:
Copper + Aluminium

Kotz, Example 20.1, pp.900-901.

$Cu(NO_2)_2$ + NaCl

(a) (b)

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Reduction

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
$$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$$

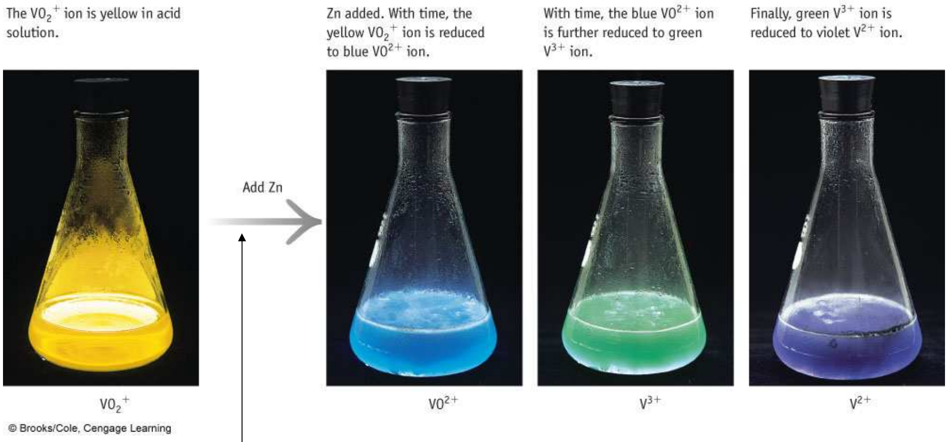
Oxidation

$$\boxed{3Cu^{2+}(aq) + 2Al(s) \rightarrow 3Cu(s) + 2Al^{3+}(aq) + heat}$$

Reduction of Vanadium(V) ion with zinc.

Kotz example 20.2. pp.901-903.

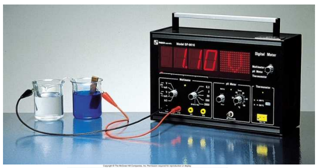
Mass balance, Charge balance required.



$$Zn(s)+4H^+(aq)+2VO_2^+(aq)\rightarrow Zn^{2+}(aq)+2VO^{2+}(aq)+2H_2O(\ell)$$

Read problem solving tips 20.1 & 20.2

Electrochemical cells.



- Electrochemistry is the study of the relationship between chemical change and electrical work.
- It is examined via the use of electrochemical cells which are systems that incorporate a redox reaction to produce or utilize electrical energy.
- Isolated oxidation and reduction processes are not much good. These reactions must be coupled together in some way to perform a technologically useful function.
- An electrochemical cell is formed by coupling together individual oxidation and reduction processes in a specific configuration.
- There are two types of electrochemical cells based upon the general thermodynamic nature of the reaction (expressed as whether the change in Gibbs energy is positive or negative.
- Oxidation and reduction reactions occurring at individual electrode/electrolyte interfaces can be coupled together either to produce an electrical voltage or to produce chemicals.

Electrochemical Cells.

- Galvanic cell.
  - This is an electrochemical power source.
  - The cell does work by releasing free energy from a spontanouus reaction to produce electricity.
    - Battery
    - Fuel cell

- Electrolytic cell.
  - This is an electrochemical substance producer.
  - The cell does work by absorbing free energy from a source of electricity to drive a non-spontaneous reaction.
    - Electrosynthesis.
    - Electroplating.

Electric power conversion in electrochemistry

Electrolysis / Power consumption

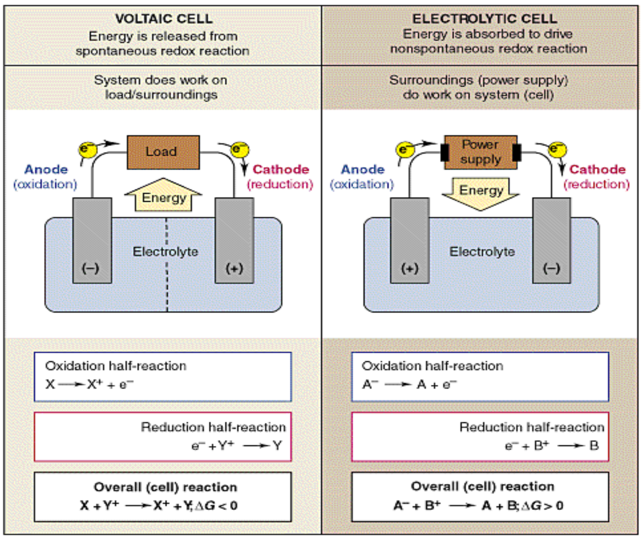
Electrochemical battery / Power generation

Galvanic and electrolysis cells.

- A voltaic cell (or a Galvanic cell) uses a spontaneous reaction (ΔG negative) to generate electrical energy. The reacting system does work on the surroundings. All batteries are made from voltaic cells.
- An electrolytic cell uses electrical energy to drive a non-spontaneous reaction (ΔG positive). Here the surroundings do work on the reacting system. Chemicals are prepared from electrical energy. This procedure is termed electrolysis or electrochemical synthesis.
- All electrochemical cells have several common features.
  - They have two electrodes.
  - Anode: the oxidation half reaction takes place at the anode.
  - Cathode: the reduction half reaction takes place at the cathode.
  - The two electrodes are dipped into an electrolyte, a medium that contains a mixture of ions which will conduct electricity.

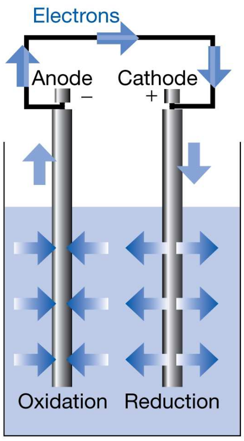
Kotz section 20.2, pp.905-915.

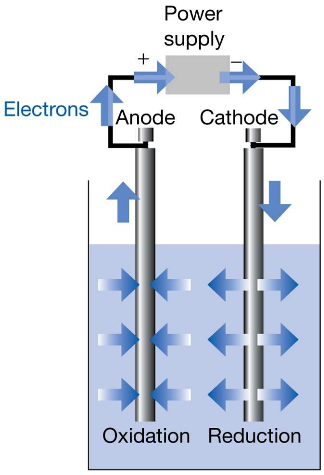
Electrochemical cells : Galvanic (self driving & energy producing) and electrolytic (driven & energy consuming).

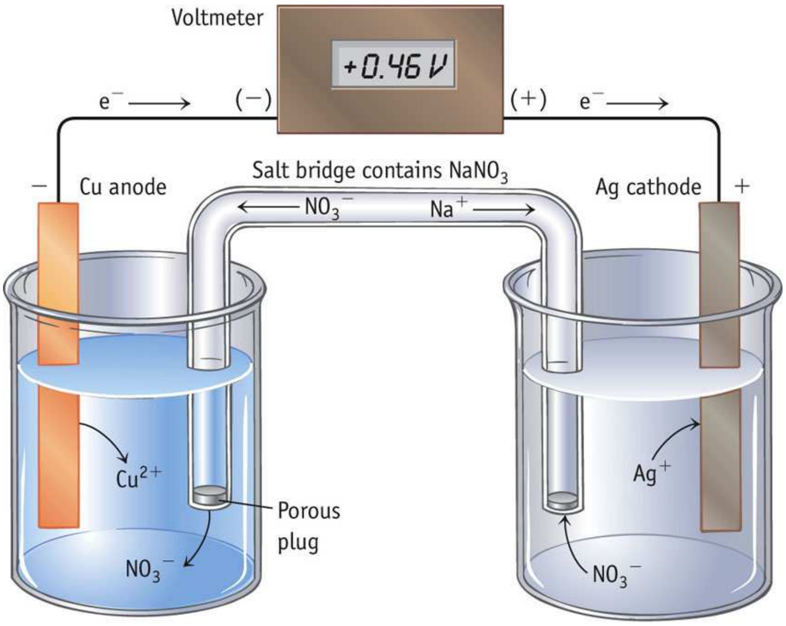


Self driving Galvanic cell :
Spontaneous redox reactions generate electrical energy.

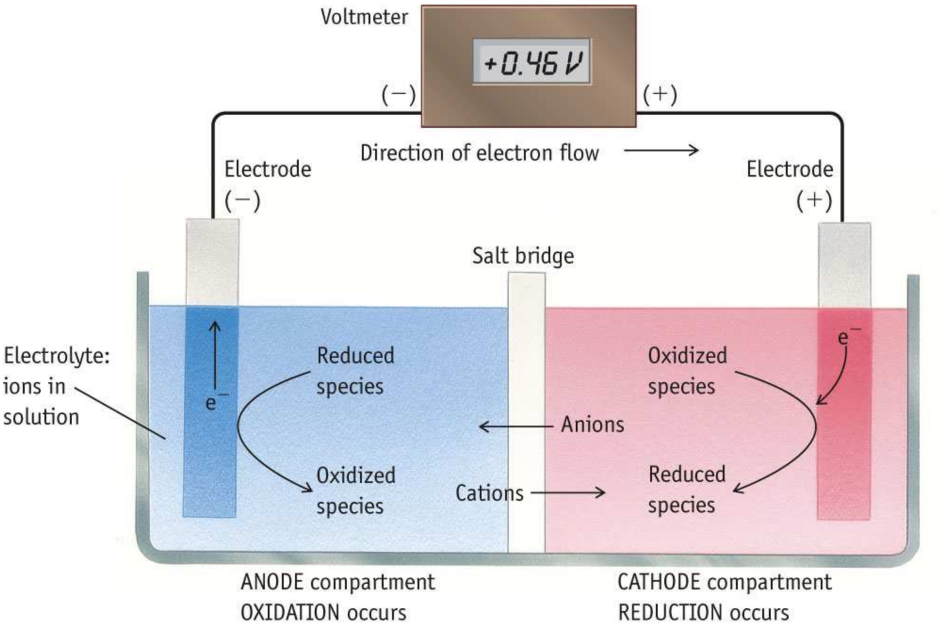
Driven Electrolysis cell :
Electrical energy drives Non spontaneous chemical Reactions : electrosynthesis.







Net reaction: $\mathrm{Cu(s)} + 2\,\mathrm{Ag^{+}(aq)} \longrightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{Ag(s)}$



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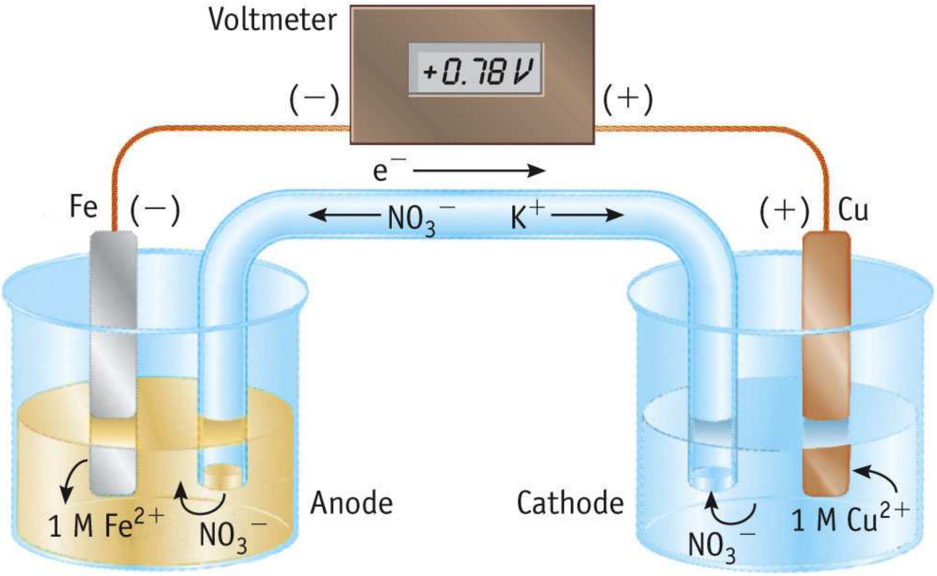

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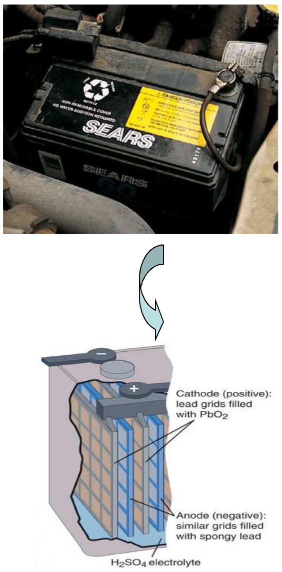
Electrochemical Power Sources.



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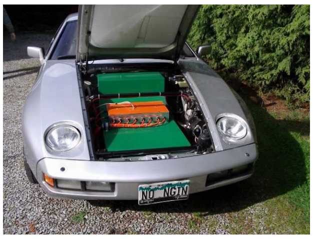
Fuel Cell Technology: Electric Cars.


Warren Gretz, NREL/PIX07070

Figure 9. Honda's newest fuel cell powered vehicle, the FCX-V4.



Fuel Cells: What are they?

- Fuel cells are devices which convert chemical energy directly to electrical energy. This is very different from conventional combustion based power plant which convert chemical energy to thermal energy, then thermal energy to kinetic energy, and only then kinetic energy to electrical energy.
- The thermal to kinetic and kinetic to electrical conversion stages have efficiency losses associated with them which engineers have spent the last 150 years or so trying to reduce. The key loss however is in the combustion process (chemical to thermal stage). Due to the inherent thermodynamics of combustion there is an ultimate efficiency which cannot be exceeded by any combustion engine - The Carnot Limit - a limit which does not apply to fuel cells.
- Using hydrogen as a fuel (which can be extacted from hydrocarbon fuels or renewable sources) a fuel cell electro-chemically oxidises the hydrogen using oxygen from the air generating electricity and some heat.
- The fuel cell makes more efficient use of the fuel and produces fewer pollutants e.g. reduced nitrgen oxides and carbon dioxide emissions, and no particulates.

Fuel Cells: some history

- The fuel cell concept arises directly from the operating principle of the galvanic cell; it is in effect a galvanic cell in which the electrodes are supplied with reactants, allowing continuous operation without depleting the electrodes.
- As early as 1880 Wilhelm Ostwald wrote: “I do not know whether all of us realise fully what an imperfect thing is the most essential source of power which we are using in our highly developed engineering – the steam engine” - indicating a growing awareness that chemical processes, such as those in galvanic cells, could approach 100% efficiency whereas the efficiencies of heat engines were limited by the Second Law to the Carnot efficiency of around 60%.
- The fuel cell was first demonstrated in 1839 by William Grove . Unfortunately development of viable technology for exploitation of the principle has been slow, primarily due to the incompatibility of the required material properties . Inevitably the first uses were space and military applications, in which cost is of secondary importance to performance.
- With increasing understanding of fuel cell and relevant materials science, driven by these specialist applications, there have been a number of false dawns when fuel cells have been proclaimed the solution to all of our energy needs, only to realise that there are inherent limitations on a particular technologies applications. This roller coaster road to development has however generated a wide range of fuel cell systems with one or more suitable for virtually every power application imaginable.

Fuel Cells power space vehicles.

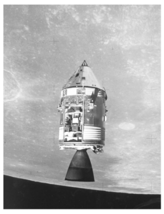
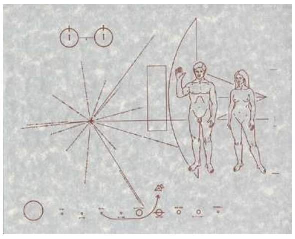


Figure 2. Apollo command and service modules.



Fuel cells: terrestial applications

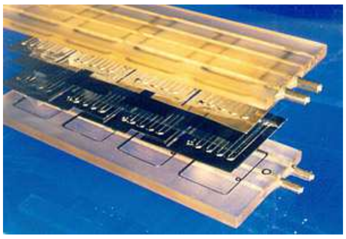
Avista Laboratory's 7.5KW PEM fuel cell power plant,
with 60-watt hot-swap submodules,
for residential applications

Plug Power's 7KW residential PEM fuel cell power plant

Fuel Cells can be small!

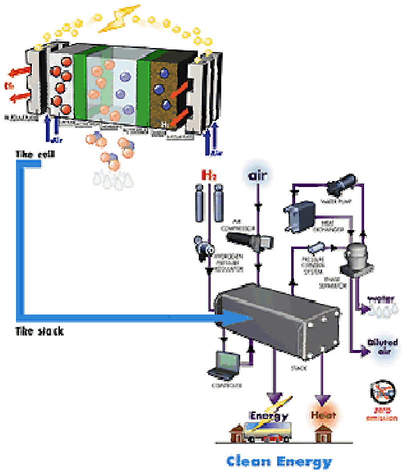
Warsitz Enterprises' portable fuel cell power unit

A Ballard fuel cell powers
a laptop computer.

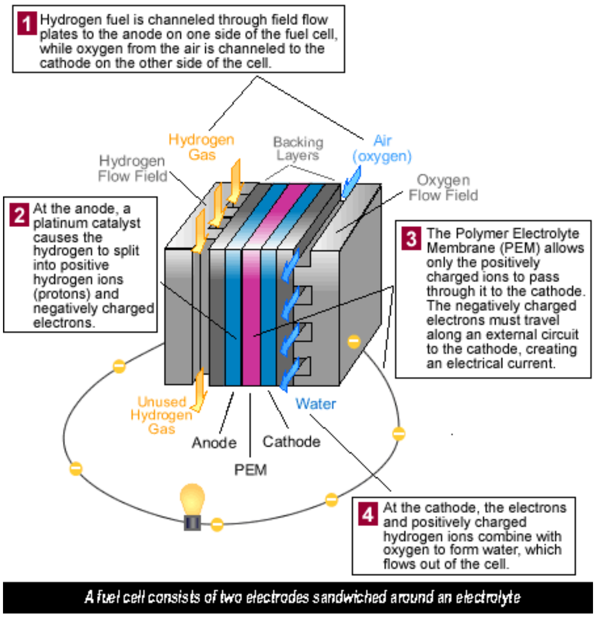


Micro-fuel cell developed by Fraunise ISE
for use in applications such as cellular phones

Fuel cells can be big!



Polymer electrolyte membrane (PEM) fuel cell.



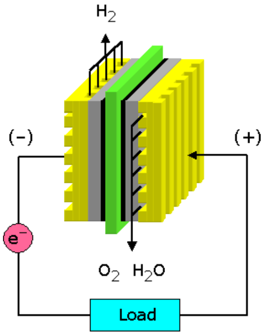
1 Hydrogen fuel is channeled through field flow plates to the anode on one side of the fuel cell, while oxygen from the air is channeled to the cathode on the other side of the cell.

2 At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.

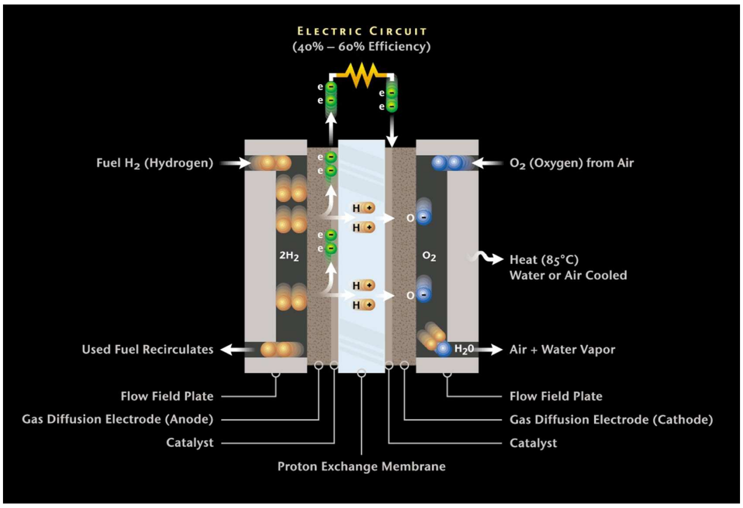
3 The Polymer Electrolyte Membrane (PEM) allows only the positively charged ions to pass through it to the cathode. The negatively charged electrons must travel along an external circuit to the cathode, creating an electrical current.

4 At the cathode, the electrons and positively charged hydrogen ions combine with oxygen to form water, which flows out of the cell.

A fuel cell consists of two electrodes sandwiched around an electrolyte



Ballard PEM Fuel Cell.



Engineering a PEM Fuel Cell

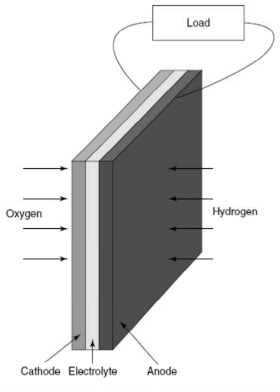


Figure 1.2 Basic cathode–electrolyte–anode construction of a fuel cell.

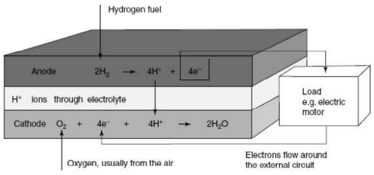


Figure 1.3 Electrode reactions and charge flow for an acid electrolyte fuel cell. Note that although the negative electrons flow from anode to cathode, the 'conventional current' flows from cathode to anode.

Figure 1.20 The 75-kW (approx.) fuel cell system for a prototype Mercedes Benz A-class car. (Photograph reproduced by kind permission of Ballard Power Systems.)

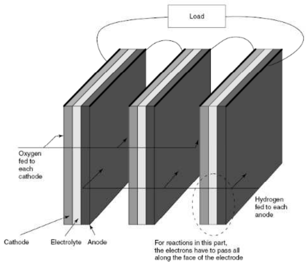


Figure 1.7 Simple edge connection of three cells in series.

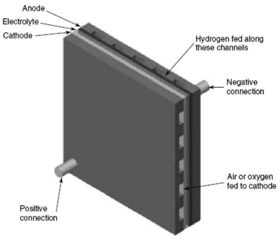


Figure 1.8 Single cell, with end plates for taking current from all over the face of the electrodes, and also supplying gas to the whole electrode.

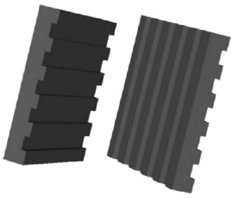


Figure 1.9 Two bipolar plates of very simple design. There are horizontal grooves on one side and vertical grooves on the other.

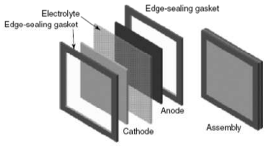


Figure 1.11 The construction of anode/electrolyte/cathode assemblies with edge seals. These prevent the gases leaking in or out through the edges of the porous electrodes.

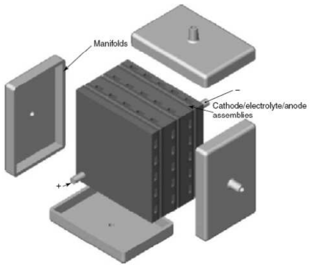


Figure 1.12 Three-cell stack, with external manifolds. Unlike Figure 1.10, the electrodes now have edge seals.

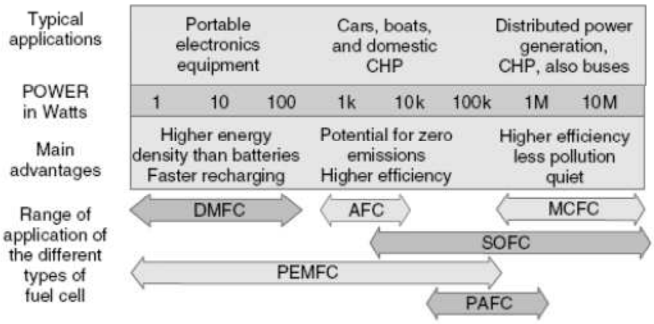
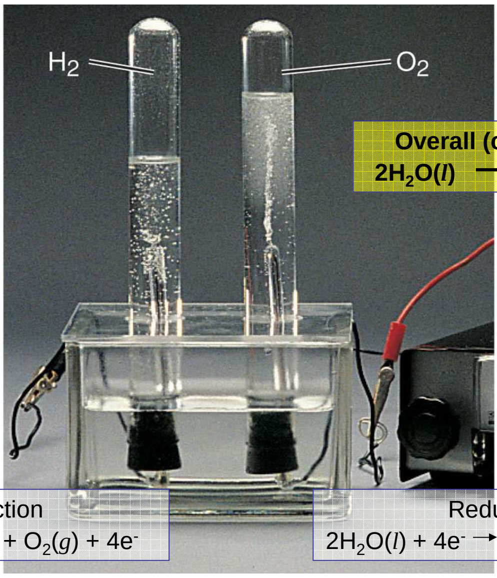


Figure 1.21 Chart to summarize the applications and main advantages of fuel cells of different types, and in different applications.

Electrolysis.

- Redox reactions in which the change in Gibbs energy ΔG is positive do not occur spontaneously.
- However they can be driven via application of either a known voltage or a known current.
- Electrolysis is the process of driving a reaction in a non spontaneous direction by using an electric current.
- Hence an electrolytic or driven cell is an electrochemical device in which an electric current from an external source is used to drive a non spontaneous chemical reaction.
- Electrolysis provides the basis of electrosynthesis and industrial electrochemistry.

The electrolysis of water



Overall (cell) reaction
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

Oxidation half-reaction
$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

Reduction half-reaction
$2H_2O(l) + 4e^- \rightarrow 2H_2(g) + 2OH^-(aq)$

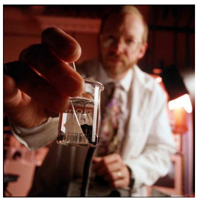
Electrolysis: Hydrogen energy

Today, almost all hydrogen is produced via steam reforming of natural gas at oil refineries.

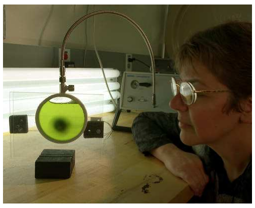
Today, hydrogen is transported to where it will be used by cryogenic liquid tankers.

Hydrogen Technologies for Our *Future*
In the future, hydrogen will be produced from water, using high-tech photoelectrochemical devices and specially designed microorganisms, and in electrolyzers that run on electricity generated by the sun and wind.

Solar-powered electrolysis system at SunLine Transit Agency



Photoelectrochemical hydrogen production

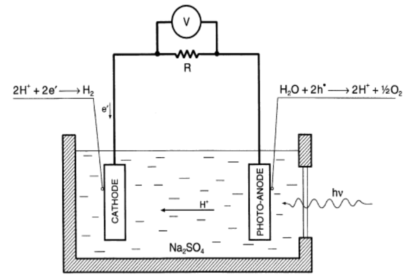


Algal hydrogen production

Photoelectrochemical cells

PECs are solar cells which generate electrical energy from light, including visible light. Each cell consists of a semiconducting photoanode and a metal cathode immersed in an electrolyte.

Some photoelectrochemical cells simply produce electrical energy, while others produce hydrogen in a process similar to the electrolysis of water.



PEC Cell :
Fujishima & Honda 1973

The PEC cell consists of a semiconductor photo anode which is irradiated with electromagnetic radiation. The counter electrode is a metal. The following processes take place in the cell when light is incident on the semiconductor electrode:

1. Photo generation of charge carriers (electron and hole pairs)

2. Charge separation and migration of the holes to the interface between the semiconductor and the electrolyte and of electrons to the counter electrode through the external circuit. Now, holes are simply vacancies created in the valence band due to promotion of electrons from the valence band to the conduction band. However, in the study of electronic behavior of materials, "holes" are considered to be independent entities, with their own mass.

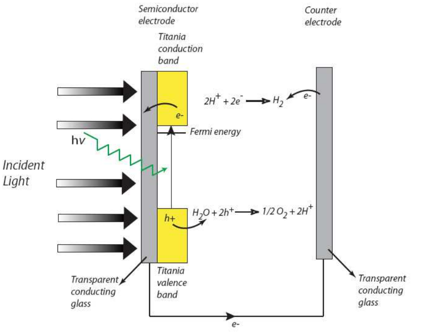
3. Electrode processes: oxidation of water to H^+ and H_2O by the holes at the photo anode and reduction of H^+ ions to H_2 by electrons at the cathode.

The lower yellow band is the valence band of the n-type semiconductor, while the upper yellow band is the conduction band. The energy difference between the top of valence band and the bottom of conduction band is termed as the band gap of semiconductor, E_g. Photons having energy greater than E_g are absorbed by the semiconductor and free electrons are generated in the conduction band and free holes in the valence band.

$2hv = 2e^- + 2h^+$

The electrons and holes are separated due to the potential generated at the interface of the semiconductor-electrolyte due to band bending. The holes move to the interface and react with water producing oxygen:

$2h^+ + H_2O = 1/2\ O_{2(gas)} + 2H^+_{(aq)}$



The electrons travel in the external circuit and arrive at the interface between the counter electrode and electrolyte. There, they reduce the H^+ ions to H_2:

$2e^- + 2H^+_{(aq)} = H_{2(gas)}$

The complete reaction is absorption of photon and splitting of water into hydrogen and oxygen.

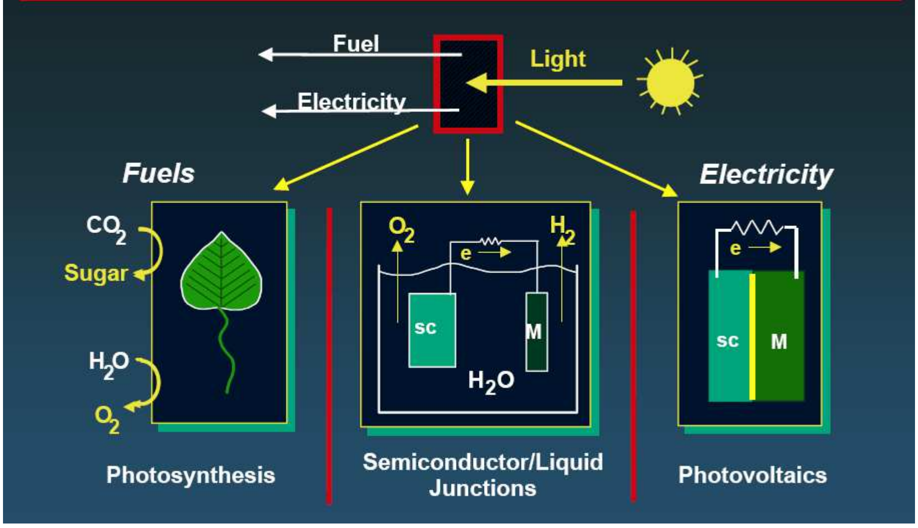
Some other configurations of the PEC cell are also possible:

1. The semiconducting material may be a p-type material. In this case, it will act as photo cathode, and reduction of H^+ ions to H_2 will take place at this electrode. The counter electrode may me a metal in this case.

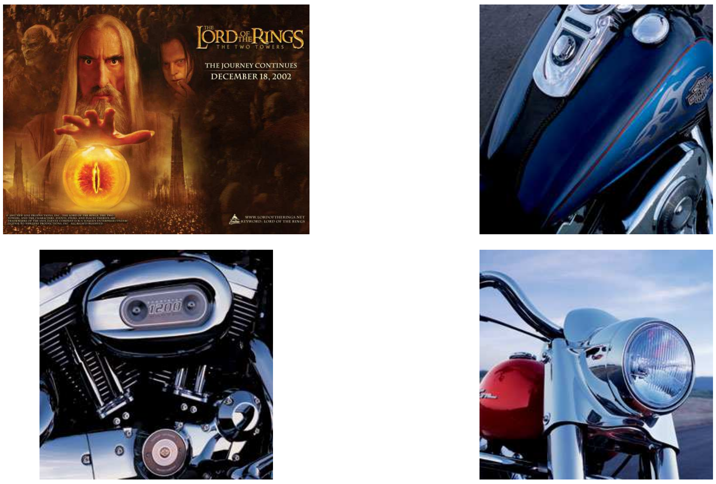
2. Both electrodes, the cathode and anode, are photo active semiconducting materials. In this case, the n-type electrode will act as anode and oxidation of water to oxygen and H^+ will take place at this electrode. The p-type electrode will act as cathode, where H^+ ions will be reduced to H_2.

http://www.nature.com/nature/journal/v414/n6861/pdf/414338a0.pdf

Energy Conversion Strategies

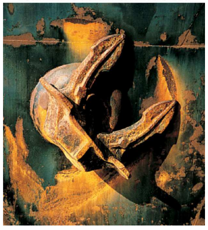


Electrolysis:
Metal Plating

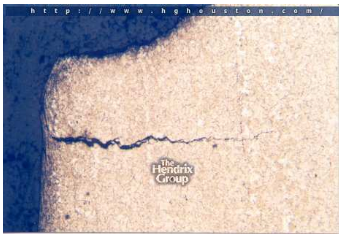


Electrochemical Corrosion

The Hendrix Group, Inc.
15823 N. Barkers Landing
Houston, Texas 77079



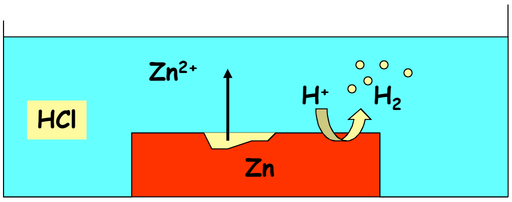
17-4 pH Stainless Steel H_2S SSC Cracks



Chloride Stress Corrosion Cracking Photograph

Hydrogen Embrittlement of Valve Capscrew Fasteners

Uniform corrosion of metals.



$$Zn + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

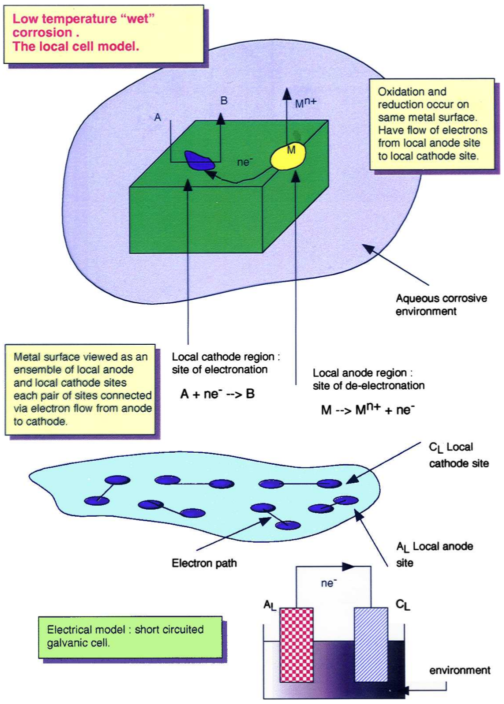
- 2 e^-

Oxidation, electron loss

+ 2 e^-

Reduction, electron gain

Uniform corrosion consists of two coupled redox reactions:
Oxidation : metal dissolution
Reduction : either hydrogen evolution or oxygen reduction.
Electrons flow through the metal from a local anode site where metal dissolution occurs, to a local cathode site where reduction of a species present in the environment occurs.
Both oxidation and reduction occur with equal rates.
The mechanism can be quite complex involving other chemical reactions resulting in oxide layer formation on the metal surface (rust).



**Low temperature "wet" corrosion .
The local cell model.**

Oxidation and reduction occur on same metal surface. Have flow of electrons from local anode site to local cathode site.

Metal surface viewed as an ensemble of local anode and local cathode sites each pair of sites connected via electron flow from anode to cathode.

Local cathode region : site of electronation

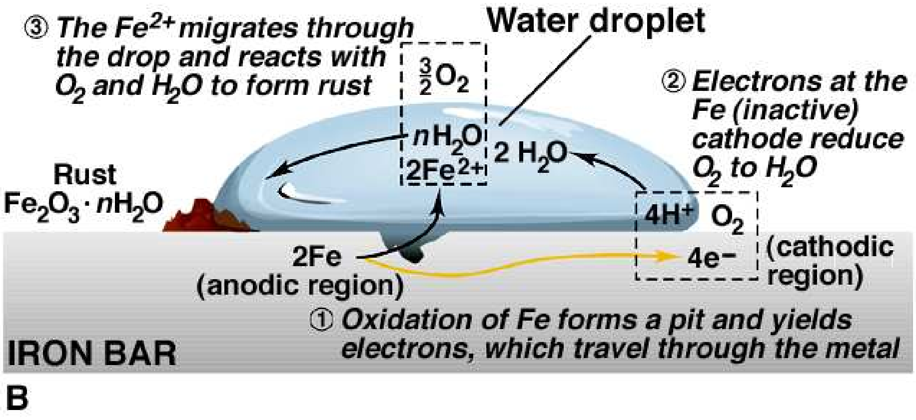
$A + ne^- \rightarrow B$

Local anode region : site of de-electronation

$M \rightarrow M^{n+} + ne^-$

Electrical model : short circuited galvanic cell.

The Corrosion of Iron



③ The Fe^{2+} migrates through the drop and reacts with O_2 and H_2O to form rust

② Electrons at the Fe (inactive) cathode reduce O_2 to H_2O

① Oxidation of Fe forms a pit and yields electrons, which travel through the metal

The Corrosion of Iron

About 25% of the steel produced in the United States is made just to replace steel already in use that has corroded. Rust arises through a complex electrochemical process.

1) Iron does not rust in dry air: moisture must be present.
2) Iron does not rust in air-free water: oxygen must be present.
3) The loss of iron and the deposition of rust often occur at *different* places on the *same* object.
4) Iron rusts more quickly at low pH (high [H^+]).
5) Iron rusts more quickly in contact with ionic solutions.
6) Iron rusts more quickly in contact with a less active metal (such as Cu) and more slowly in contact with a more active metal (such as Zn).

$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2\ e^-$ [anodic region; oxidation]

$O_{2\ (g)} + 4\ H^+_{(aq)} + 4\ e^- \longrightarrow 2\ H_2O_{(l)}$ [cathodic region; reduction]

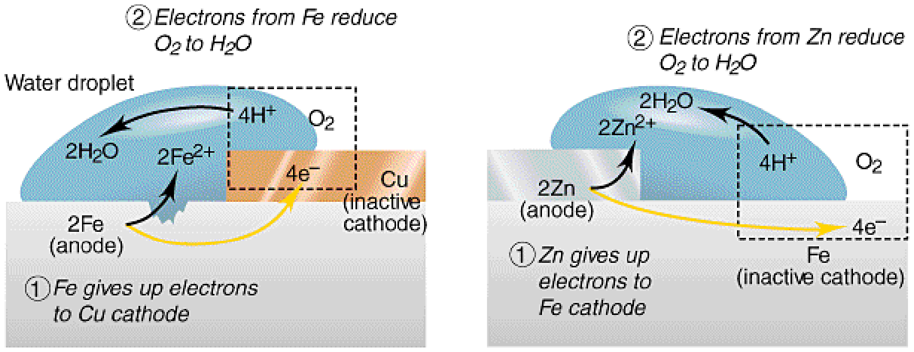
$$2\ Fe_{(s)} + O_{2\ (g)} + 4\ H^+_{(aq)} \longrightarrow 2\ Fe^{2+}_{(aq)} + 2\ H_2O_{(l)}$$

$$4Fe^{2+}(aq)+O_2(g)+(4+2x)H_2O \rightarrow 2Fe_2O_3.xH_2O+8H^+(aq)$$

The Effect of Metal-Metal Contact on the Corrosion of Iron

$E^0(Cu^{2+},Cu) = 0.34V$
$E^0(Fe^{2+},Fe) = - 0.44V$

$E^0(Zn^{2+},Zn) = - 0.76V$
$E^0(Fe^{2+},Fe) = - 0.44V$

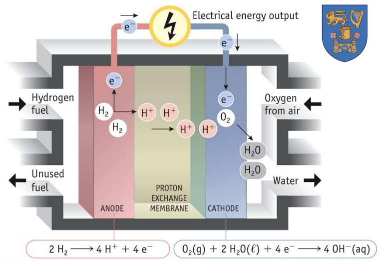


A Enhanced corrosion

B Cathodic protection

Corrosion protection schemes :
- coat metal surface with paint.
- passivate metal surface with thin protective oxide layer.

- Galvanize iron surface with electroplated Zinc film.
- Cathodic protection : metal to be protected made cathode in electrochemical cell by combining it with a more active metal.
- Alloy formation (stainless steel: Fe/Cr alloy).



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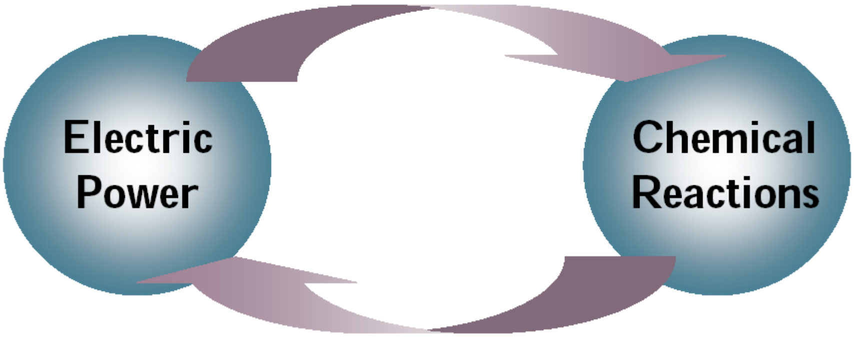
Ollscoil Átha Cliath | The University of Dublin

Lecture 17

Thermodynamics of Galvanic (Voltaic) Cells.

Electric power conversion in electrochemistry



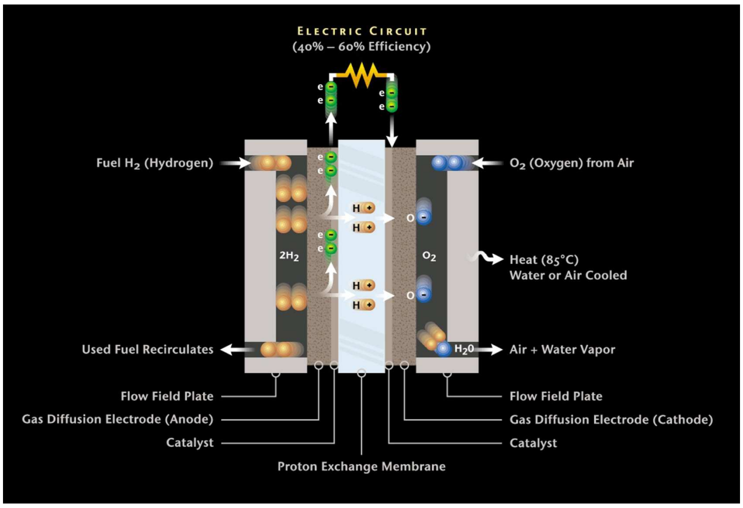
Electrolysis / Power consumption

Electric Power

Chemical Reactions

Electrochemical battery / Power generation

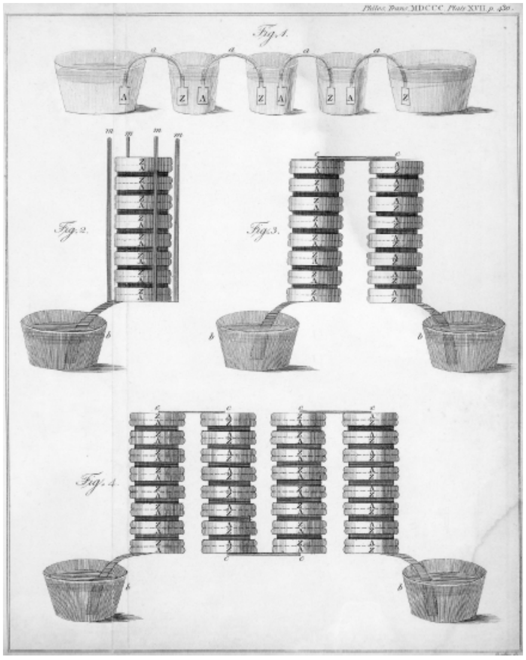
Ballard PEM Fuel Cell.



Electrochemistry

Alessandro Volta, 1745-1827, Italian scientist and inventor.

Luigi Galvani, 1737-1798, Italian scientist and inventor.



The Voltaic Pile

Drawing done by Volta to show the arrangement of silver and zinc disks to generate an electric current.

What voltage does a cell generate?

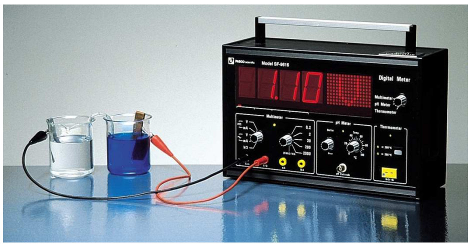
Operation of a Galvanic cell.

- In a Galvanic cell a spontaneous cell reaction produces electricity.
- Galvanic cells form the basis of energy storage and energy conversion devices (battery systems and fuel cells).
- Electrons leave a Galvanic cell at the anode (negative electrode), travel through the external circuit, and re-enter the cell at the cathode (positive electrode). The circuit is completed inside the cell by the electro-migration of ions through the salt bridge.
- We need to answer the following questions regarding Galvanic cells.
  - Can we devise a quantitative measure for the tendency of a specific redox couple to undergo oxidation or reduction?
  - Is the net cell reaction energetically feasible?
  - Can we compute useful thermodynamic quantities such as the change in Gibbs energy ΔG or the equilibrium constant for the cell reaction ?
  - The answer is yes to all of these questions.
  - We now discuss the thermodynamics of Galvanic cells.

Electrochemical Cells

The difference in electrical potential between the anode and cathode is called:

- **cell voltage**
- **electromotive force (emf)**
- **cell potential**



Cell Diagram

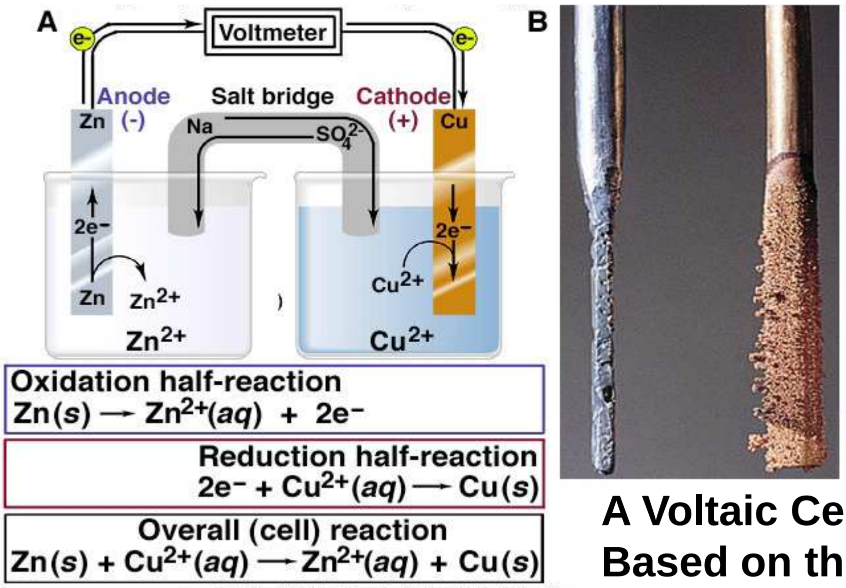
$$Zn\ (s) + Cu^{2+}\ (aq) \longrightarrow Cu\ (s) + Zn^{2+}\ (aq)$$

$$[Cu^{2+}] = 1\ M\ \&\ [Zn^{2+}] = 1\ M$$

$$Zn\ (s)\ |\ Zn^{2+}\ (1\ M)\ ||\ Cu^{2+}\ (1\ M)\ |\ Cu\ (s)$$

anode cathode

Galvanic cell movie.



Oxidation half-reaction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

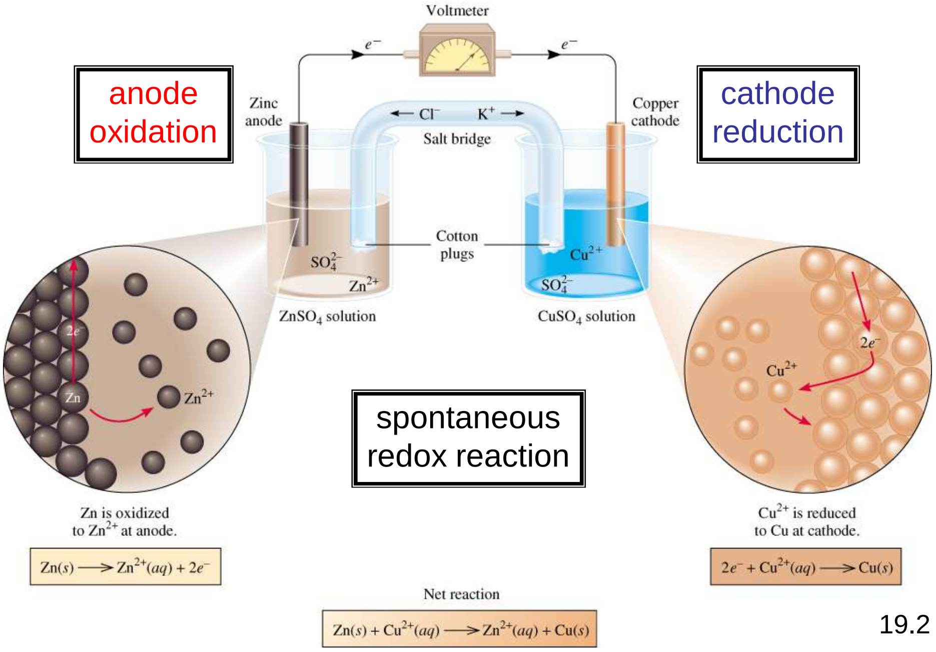
Reduction half-reaction
$2e^- + Cu^{2+}(aq) \rightarrow Cu(s)$

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

© McGraw-Hill Higher Education/Stephen Frisch, photographer

A Voltaic Cell Based on the Zinc-Copper Reaction

Electrochemical Cells



anode
oxidation

cathode
reduction

spontaneous
redox reaction

Zn is oxidized to Zn^{2+} at anode.

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cu^{2+} is reduced to Cu at cathode.

$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$

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

19.2

Electron flow in a Galvanic Cell.

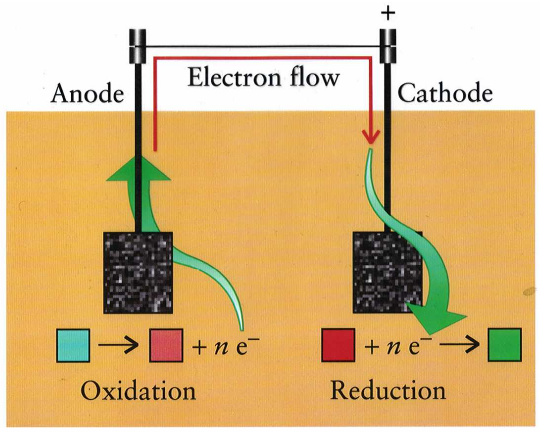


Figure 18.9
Loretta Jones and Peter Atkins, CHEMISTRY: MOLECULES, MATTER, AND CHANGE, Fourth Edition

T173

Notation for a Voltaic Cell

components of anode compartment (oxidation half-cell)		components of cathode compartment (reduction half-cell)	
phase of lower oxidation state	phase of higher oxidation state	phase of higher oxidation state	phase of lower oxidation state

phase boundary between half-cells

Examples: $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

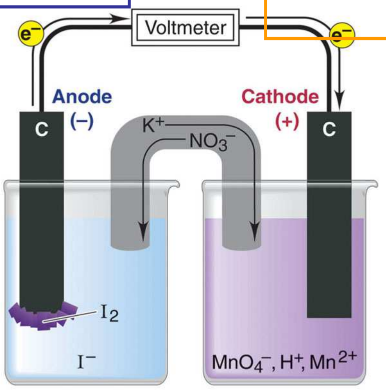
$\underset{\uparrow}{graphite} \mid I^-(aq) \mid I_2(s) \parallel H^+(aq), MnO_4^-(aq) \mid Mn^{2+}(aq) \mid graphite$

inert electrode

Figure 21.6 **A voltaic cell using inactive electrodes**

Oxidation half-reaction
$2I^-(aq) \longrightarrow I_2(s) + 2e^-$

Reduction half-reaction
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$



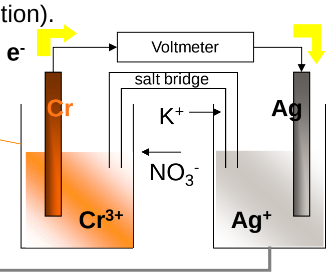
Overall (cell) reaction
$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$

Sample Problem 21.2: **Diagramming Voltaic Cells**

PROBLEM: Diagram, show balanced equations, and write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $Cr(NO_3)_3$ solution, another half-cell with an Ag bar in an $AgNO_3$ solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.

PLAN: Identify the oxidation and reduction reactions and write each half-reaction. Associate the (-)(Cr) pole with the anode (oxidation) and the (+) pole with the cathode (reduction).

SOLUTION:



Oxidation half-reaction
$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$

Reduction half-reaction
$Ag^+(aq) + e^- \longrightarrow Ag(s)$

Overall (cell) reaction
$Cr(s) + Ag^+(aq) \longrightarrow Cr^{3+}(aq) + Ag(s)$

$Cr(s) \mid Cr^{3+}(aq) \parallel Ag^+(aq) \mid Ag(s)$

Why Does a Voltaic Cell Work?

The spontaneous reaction occurs as a result of the different abilities of materials (such as metals) to give up their electrons and the ability of the electrons to flow through the circuit.

E_{cell} > 0 for a spontaneous reaction

1 Volt (V) = 1 Joule (J)/ Coulomb (C)

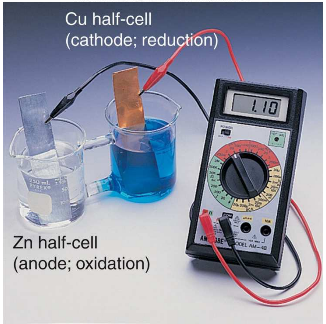


Table 21.1 Voltages of Some Voltaic Cells

Voltaic Cell	Voltage (V)
Common alkaline battery	1.5
Lead-acid car battery (6 cells = 12V)	2.0
Calculator battery (mercury)	1.3
Electric eel (~5000 cells in 6-ft eel = 750V)	0.15
Nerve of giant squid (across cell membrane)	0.070

Standard redox potentials.

- Given a specific redox couple we would like to establish a way by which the reducibility or the oxidizibility of the couple can be determined.
- This can be accomplished by devising a number scale, expressed in units of volts of standard electrode potentials E^0.
- Redox couples exhibiting highly negative E^0 values are readily oxidised.
- Redox couples exhibiting highly positive E^0 values are readily reduced.
- Hence the more positive the E^0 value of a redox couple, the greater the tendency for it to be reduced.
- The electrode potential of a single redox couple A/B is defined with respect to a standard zero of potential. This reference is called the standard hydrogen reference electrode (SHE).
- $E^0(A,B)$ is called the standard reduction potential for the reduction process $A + ne^- \rightarrow B$, and it is defined as the measured cell potential obtained for the Galvanic cell formed by coupling the A/B electrode system with a hydrogen reference electrode.
- The cell configuration is

$$\boxed{Pt, H_2 \middle| H^+(aq) \middle\| A(aq), B(aq) \middle| M}$$

$$\boxed{E^0{}_{Cell} = E^0_{Cathode} - E^0_{anode}}$$

Standard Reduction Potential E^0

- E^0 (measured in volts V) is for the reaction as written.
- The more positive E^0 the greater the tendency for the substance to be reduced.
- The half-cell reactions are reversible.
- The sign of E^0 changes when the reaction is reversed.
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of E^0.

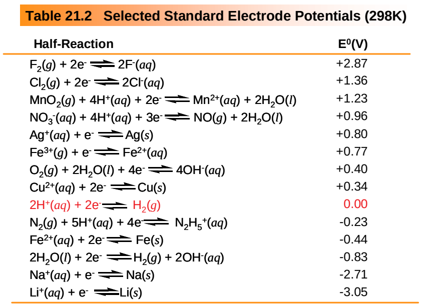


Table 21.2 Selected Standard Electrode Potentials (298K)

Half-Reaction	E^0(V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(g) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(g) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	-0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.05

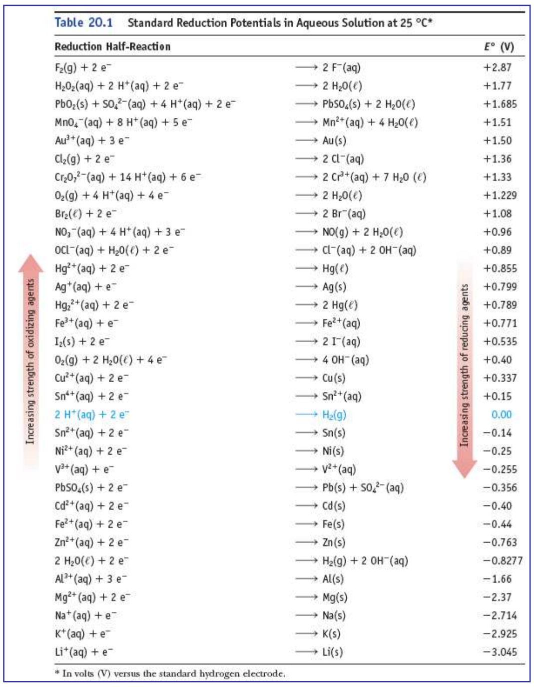
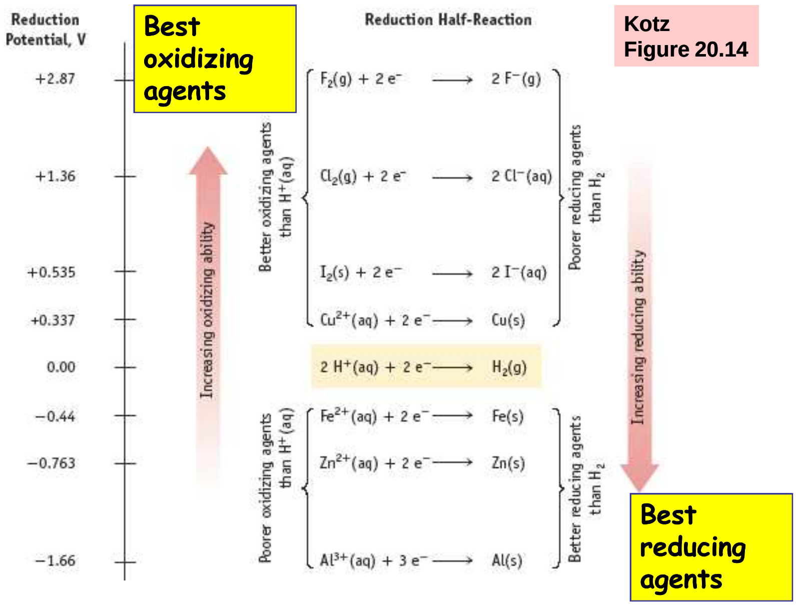


Table 20.1 Standard Reduction Potentials in Aqueous Solution at 25 °C*

Reduction Half-Reaction		E° (V)
$F_2(g) + 2 e^-$	$\longrightarrow 2 F^-(aq)$	+2.87
$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\longrightarrow 2 H_2O(\ell)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^-$	$\longrightarrow PbSO_4(s) + 2 H_2O(\ell)$	+1.685
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^-$	$\longrightarrow Mn^{2+}(aq) + 4 H_2O(\ell)$	+1.51
$Au^{3+}(aq) + 3 e^-$	$\longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2 e^-$	$\longrightarrow 2 Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^-$	$\longrightarrow 2 Cr^{3+}(aq) + 7 H_2O (\ell)$	+1.33
$O_2(g) + 4 H^+(aq) + 4 e^-$	$\longrightarrow 2 H_2O(\ell)$	+1.229
$Br_2(\ell) + 2 e^-$	$\longrightarrow 2 Br^-(aq)$	+1.08
$NO_3^-(aq) + 4 H^+(aq) + 3 e^-$	$\longrightarrow NO(g) + 2 H_2O(\ell)$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2 e^-$	$\longrightarrow Cl^-(aq) + 2 OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2 e^-$	$\longrightarrow Hg(\ell)$	+0.855
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	+0.799
$Hg_2^{2+}(aq) + 2 e^-$	$\longrightarrow 2 Hg(\ell)$	+0.789
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2 e^-$	$\longrightarrow 2 I^-(aq)$	+0.535
$O_2(g) + 2 H_2O(\ell) + 4 e^-$	$\longrightarrow 4 OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2 e^-$	$\longrightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2 e^-$	$\longrightarrow Sn^{2+}(aq)$	+0.15
$2 H^+(aq) + 2 e^-$	$\longrightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2 e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2 e^-$	$\longrightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\longrightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2 e^-$	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2 e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2 e^-$	$\longrightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2 e^-$	$\longrightarrow Zn(s)$	−0.763
$2 H_2O(\ell) + 2 e^-$	$\longrightarrow H_2(g) + 2 OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3 e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2 e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.045

* In volts (V) versus the standard hydrogen electrode.



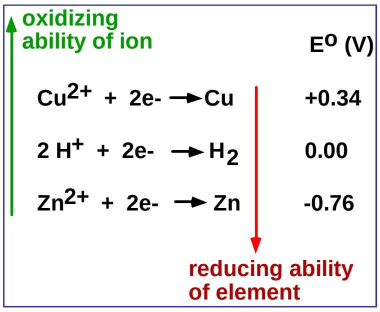
Best oxidizing agents

Kotz Figure 20.14

Best reducing agents

Potential Ladder for Reduction Half-Reactions

Standard Redox Potentials, E^o



oxidizing ability of ion

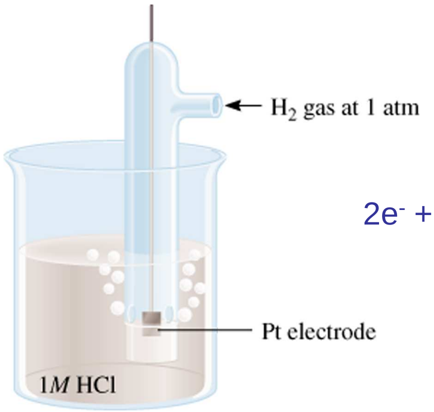
	E^o (V)
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76

reducing ability of element

- Any substance on the right will reduce any substance higher than it on the left.
- Zn can reduce H^+ and Cu^{2+}.
- H_2 can reduce Cu^{2+} but not Zn^{2+}
- Cu cannot reduce H^+ or Zn^{2+}.

Standard Electrode Potentials

Standard reduction potential (E^0) is the voltage associated with a **reduction reaction** at an electrode when all solutes are 1 *M* and all gases are at 1 atm.



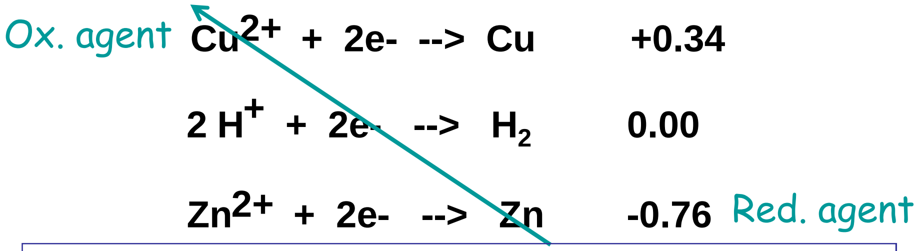
Standard hydrogen electrode (SHE)

Reduction Reaction

$$2e^- + 2H^+ (1\ M) \longrightarrow 2H_2 (1\ atm)$$

$$E^0 = 0\ V$$

Standard Redox Potentials, E°



Ox. agent $Cu^{2+} + 2e^- \rightarrow Cu$ +0.34

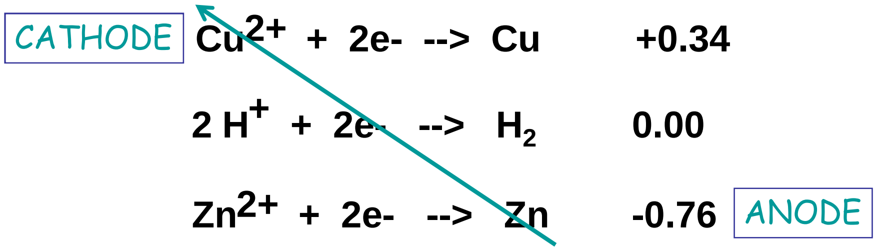
$2\,H^+ + 2e^- \rightarrow H_2$ 0.00

$Zn^{2+} + 2e^- \rightarrow Zn$ -0.76 Red. agent

Any substance on the right will reduce any substance higher than it on the left.

Northwest-southeast rule: product-favored reactions occur between
- reducing agent at southeast corner
- oxidizing agent at northwest corner

Standard Redox Potentials, E°



CATHODE $Cu^{2+} + 2e^- \rightarrow Cu$ +0.34

$2\,H^+ + 2e^- \rightarrow H_2$ 0.00

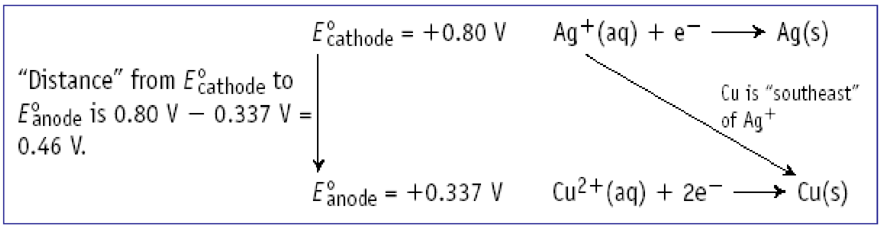
$Zn^{2+} + 2e^- \rightarrow Zn$ -0.76 ANODE

Northwest-southeast rule:
- reducing agent at southeast corner
  = ANODE
- oxidizing agent at northwest corner
  = CATHODE

Standard Redox Potentials, E°

E°_{net} = "distance" from "top" half-reaction (cathode) to "bottom" half-reaction (anode)

$$E^\circ_{net} = E^\circ_{cathode} - E^\circ_{anode}$$



"Distance" from $E^\circ_{cathode}$ to E°_{anode} is 0.80 V − 0.337 V = 0.46 V.

$E^\circ_{cathode}$ = +0.80 V $Ag^+(aq) + e^- \longrightarrow Ag(s)$

Cu is "southeast" of Ag^+

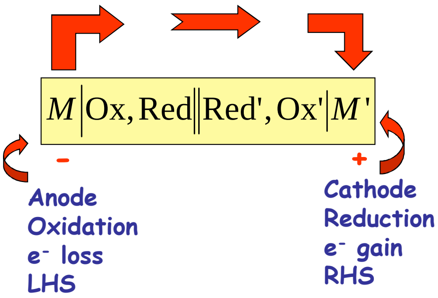
E°_{anode} = +0.337 V $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

E°_{net} for Cu/Ag^+ reaction = +0.46 V

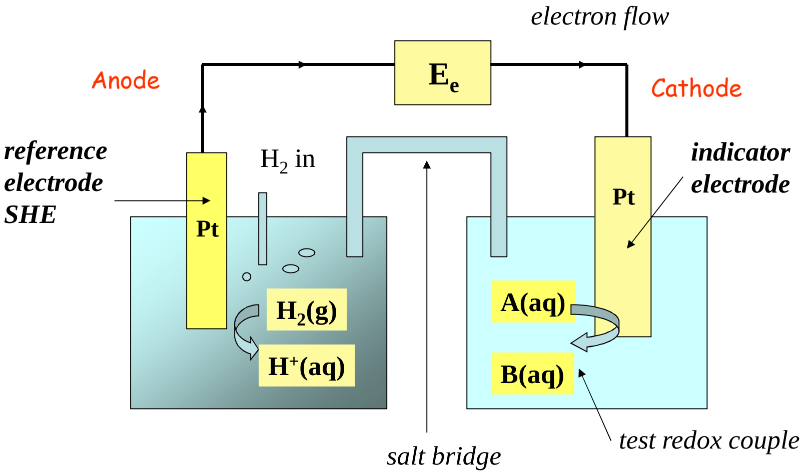
Standard cell potentials.

- The standard potential E^0_{cell} developed by a Galvanic cell reflects the values of the standard potentials associated with the two component half reactions.
- This can be computed using the following simple procedure.
- The two half reactions are written as reduction processes.
- For any combination of two redox couples to form a Galvanic cell, the half reaction exhibiting the more positive E^0 value occurs as a reduction process and is written on the RHS of the cell diagram, as the positive pole of the cell.
- In contrast, the half reaction which has the more negative E^0 value is written on the LHS of the cell diagram as the negative pole of the cell, and will occur as an oxidation process.
- The overall cell reaction is given as the sum of the two component redox processes and the net cell potential is given by the expression presented across.

$$\boxed{E^0_{cell} = E^0_{RHS} - E^0_{LHS} = E^0_{cathode} - E^0_{anode}}$$

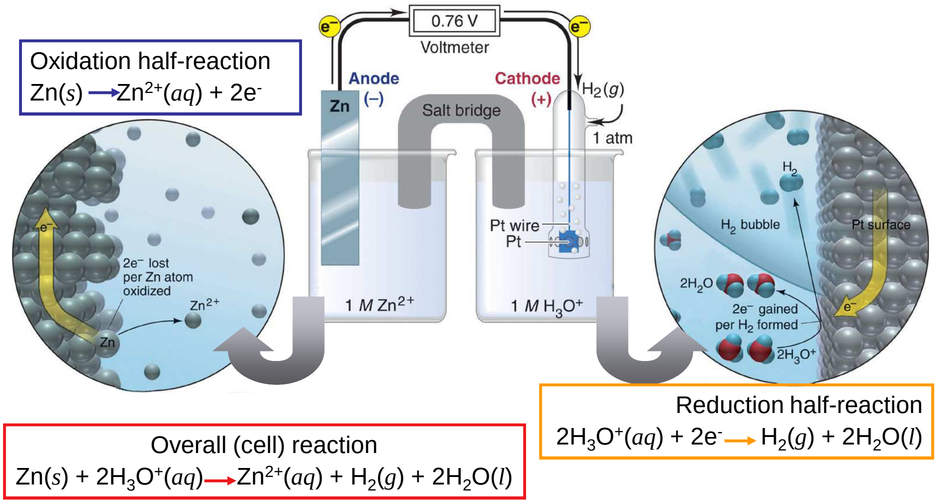


$$M\,|\,\mathrm{Ox},\mathrm{Red}\,||\,\mathrm{Red}',\mathrm{Ox}'\,|\,M'$$



$$Pt, H_2\left|H^+(aq)\right\|A(aq), B(aq)\left|M\right.$$

Figure 21.7 **Determining an unknown $E^0_{\text{half-cell}}$ with the standard reference (hydrogen) electrode**



Oxidation half-reaction
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction
$2H_3O^+(aq) + 2e^- \rightarrow H_2(g) + 2H_2O(l)$

Overall (cell) reaction
$Zn(s) + 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) + 2H_2O(l)$

Sample Problem 21.3: Calculating an Unknown $E^0_{half\text{-}cell}$ from E^0_{cell}

PROBLEM: A voltaic cell houses the reaction between aqueous bromine and zinc metal:

$$Br_2(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + 2Br^-(aq) \qquad E^0_{cell} = 1.83V$$

Calculate $E^0_{bromine}$ given $E^0_{zinc} = -0.76V$

PLAN: The reaction is spontaneous as written since the E^0_{cell} is (+). Zinc is being oxidized and is the anode. Therefore the $E^0_{bromine}$ can be found using $E^0_{cell} = E^0_{cathode} - E^0_{anode}$.

SOLUTION: anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $E = +0.76$

E^0_{Zn} as $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ is $-0.76V$

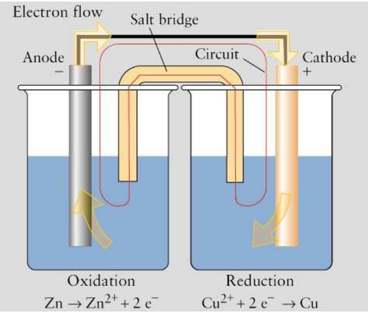
$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 1.83 = E^0_{bromine} - (-0.76)$$

$$E^0_{bromine} = 1.86 - 0.76 = 1.07V$$

- By convention, electrode potentials are written as reductions.
- When pairing two half-cells, you must reverse one reduction half-cell to produce an oxidation half-cell. Reverse the sign of the potential.
- The reduction half-cell potential and the oxidation half-cell potential are added to obtain the E^0_{cell}.
- When writing a spontaneous redox reaction, the left side (reactants) must contain the stronger oxidizing and reducing agents.

Example:	$Zn(s)$	+	$Cu^{2+}(aq)$	$\longrightarrow$ $Zn^{2+}(aq)$	+	$Cu(s)$
	stronger reducing agent		*stronger oxidizing agent*	*weaker oxidizing agent*		*weaker reducing agent*

Relationship between the change in Gibbs energy for the cell reaction and the cell potential.



- When a spontaneous reaction takes place in a Galvanic cell, electrons are deposited in one electrode (the site of oxidation or anode) and collected from another (the site of reduction or cathode), and so there is a net flow of current which can be used to perform electrical work W_e.
- From thermodynamics we note that the maximum electrical work W_e done at constant temperature and pressure is equal to the change in Gibbs energy ΔG for the net cell reaction.
- We apply basic physics to evaluate the electrical work W_e done in moving n mole electrons through a potential difference given by E_{cell}.

Transferring 1 electron :

$$W_e = qE_{cell} = -eE_{cell}$$

Transferring 1 mole electrons :

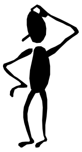
$$W_e = -N_A eE_{cell}$$

Transferring n mole electrons :

$$W_e = -nN_A eE_{cell}$$

Relationship between thermodynamics of cell reaction and observed cell potential.

$$\Delta G = W_e = -neN_A E_{cell}$$
$$= -nFE_{cell}$$



What is the standard emf of an electrochemical cell made of a Cd electrode in a 1.0 *M* $Cd(NO_3)_2$ solution and a Cr electrode in a 1.0 *M* $Cr(NO_3)_3$ solution?

$Cd^{2+}\ (aq) + 2e^- \longrightarrow Cd\ (s)$ $\quad E^0 = -0.40$ V Cd is the stronger oxidizer

$Cr^{3+}\ (aq) + 3e^- \longrightarrow Cr\ (s)$ $\quad E^0 = -0.74$ V Cd will oxidize Cr

Anode (oxidation): $Cr\ (s) \longrightarrow Cr^{3+}\ (1\ M) + \boxed{3e^-}$ x 2

Cathode (reduction): $\boxed{2e^-} + Cd^{2+}\ (1\ M) \longrightarrow Cd\ (s)$ x 3

$$2Cr\ (s) + 3Cd^{2+}\ (1\ M) \longrightarrow 3Cd\ (s) + 2Cr^{3+}\ (1\ M)$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.40 - (-0.74)$$

$$E^0_{cell} = 0.34\ \text{V}$$

19.3

Thermodynamics of cell reactions.

- The change in Gibbs energy for the overall cell reaction is related to the observed net cell potential generated.
- When the standard cell potential E^0_{cell} is positive, the Gibbs energy ΔG^0 is negative and vice versa.
- Once ΔG^0 for a cell reaction is known, then the equilibrium constant K for the cell reaction can be readily evaluated.
- These expressions are valid for standard conditions : T = 298 K, p = 1 atm (or 1 bar); c = 1 mol L^{-1}.

Faraday constant : 96,500 C mol^{-1}

$$\Delta G^0 = -nFE^0_{cell}$$

electrons transferred in cell reaction

$$\Delta G^0 = -RT\ln K$$

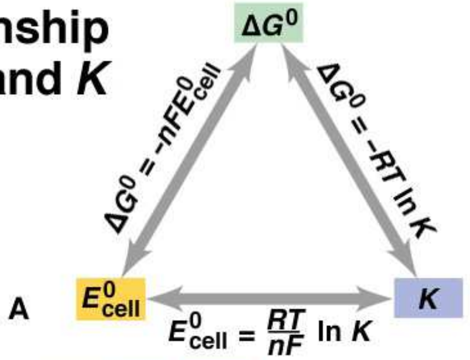
$$K = \exp\left[-\frac{\Delta G^0}{RT}\right] = \exp\left[\frac{nFE^0_{cell}}{RT}\right]$$

Gas Constant : 8.314 J mol^{-1} K^{-1}

Temperature (K)

Interrelationship of ΔG^0, E^0, and K

A. Any one of these thermodynamic parameters can be used to find the other two.



B. The signs of ΔG^o and E^o_{cell} determine the reaction direction at standard-state conditions.

B

ΔG^0	K	E^0_{cell}	Reaction at standard-state conditions
< 0	> 1	> 0	Spontaneous
0	1	0	At equilibrium
> 0	< 1	< 0	Nonspontaneous

Sample Problem 21.5: Calculating K and ΔG^0 from E^0_{cell}

PROBLEM: Lead can displace silver from solution:

$$Pb(s) + 2Ag^+(aq) \longrightarrow Pb^{2+}(aq) + 2Ag(s)$$

As a consequence, silver is a valuable by-product in the industrial extraction of lead from its ore. Calculate K and ΔG^0 at 25^0C for this reaction.

PLAN: Break the reaction into half-reactions, find the E^0 for each half-reaction and then the E^0_{cell}.

SOLUTION:

$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$ $E^0 = -0.13V$

$Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E^0 = 0.80V$

$$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$$

$$2X\left[Ag^+(aq) + e^- \longrightarrow Ag(s) \right]$$

$E^0 = 0.13V$

$E^0 = 0.80V$

$E^0_{cell} = 0.93V$

$$E^0_{cell} = \frac{0.592V}{n} \log K$$

$$\log K = \frac{n \times E^0_{cell}}{0.592V} = \frac{(2)(0.93V)}{0.592V}$$

$$\boxed{K = 2.6\times10^{31}}$$

$$\Delta G^0 = -nFE^0_{cell} = -(2)(96.5kJ/mol{*}V)(0.93V)$$

$$\boxed{\Delta G^0 = -1.8\times10^2 kJ}$$

The Nernst equation.

The potential developed by a Galvanic cell depends on the composition of the cell.
From thermodynamics the Gibbs energy change for a chemical reaction ΔG varies with composition of the reaction mixture in a well defined manner.
We use the relationship between ΔG and E to obtain the Nernst equation.

Nernst eqn.holds for single redox couples and net cell reactions.

$$\boxed{\Delta G = \Delta G^0 + RT\ln Q}$$

Reaction quotient

$$Q \cong \frac{[\text{products}]}{[\text{reactants}]}$$

$$\boxed{\begin{array}{l} \Delta G - -nFE \quad \Delta G^0 = -nFE^0 \\ -nFE = -nFE^0 + RT\ln Q \end{array}}$$

$$\boxed{E = E^0 - \frac{RT}{nF}\ln Q}$$

T = 298K

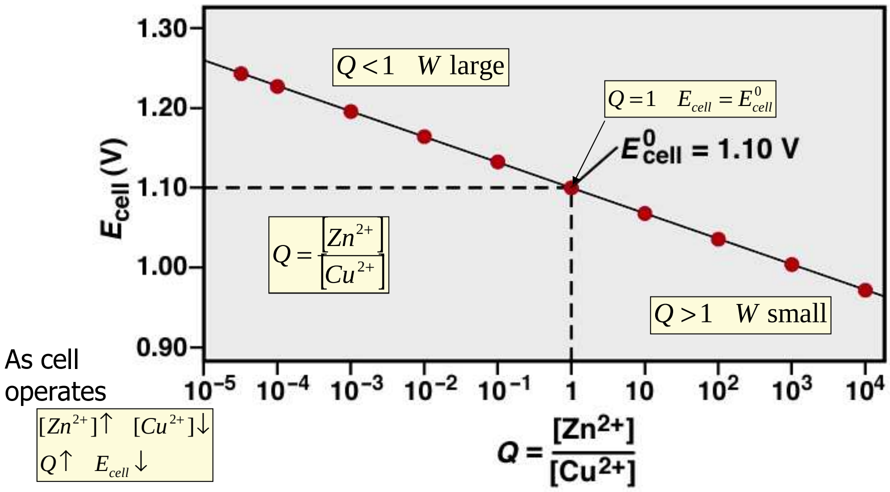
$$\boxed{E = E^0 - \frac{0.0592}{n}\log Q}$$

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

$$E_{cell} = E^0_{cell} - \frac{0.059}{2}\log\left\{\frac{[Zn^{2+}]}{[Cu^{2+}]}\right\}$$

Equilibrium $\Delta G = 0$
$E_{cell} = 0 \quad Q = K$
$W = 0$

Dead cell



As cell operates

$[Zn^{2+}]\uparrow \quad [Cu^{2+}]\downarrow$
$Q\uparrow \quad E_{cell}\downarrow$

Sample Problem 21.6: Using the Nernst Equation to Calculate E_{cell}

PROBLEM: In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn^{2+} half-cell and an H_2/H^+ half-cell under the following conditions:

$[Zn^{2+}]$ = 0.010M $\quad$ $[H^+]$ = 2.5M $\quad$ P_{H_2} = 0.30atm

Calculate E_{cell} at 25⁰C.

PLAN: Find E^0_{cell} and Q in order to use the Nernst equation.

SOLUTION: Determining E^0_{cell} :

$2H^+(aq) + 2e^- \longrightarrow H_2(g)$ $\quad E^0 = 0.00V$

$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ $\quad E^0 = -0.76V$

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $\quad E^0 = +0.76V$

$$Q = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2}$$

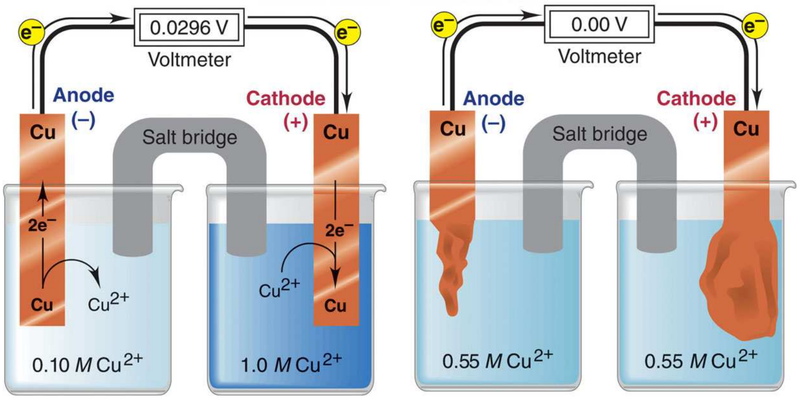
$$Q = \frac{(0.30)(0.010)}{(2.5)^2}$$

$Q = 4.8\times10^{-4}$

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{n}\log Q$$

$E_{cell} = 0.76 - (0.0592/2)\log(4.8\times10^{-4}) = \boxed{0.86V}$

Figure 21.11 **A concentration cell based on the Cu/Cu^{2+} half-reaction**



Oxidation half-reaction
$Cu(s) \rightarrow Cu^{2+}(aq, 0.1M) + 2e^-$

Reduction half-reaction
$Cu^{2+}(aq, 1.0M) + 2e^- \rightarrow Cu(s)$

Overall (cell) reaction
$Cu^{2+}(aq, 1.0M) \rightarrow Cu^{2+}(aq, 0.1M)$

Sample Problem 21.7: Calculating the Potential of a Concentration Cell

PROBLEM: A concentration cell consists of two Ag/Ag$^+$ half-cells. In half-cell A, electrode A dips into 0.0100M AgNO$_3$; in half-cell B, electrode B dips into 4.0x10^{-4}M AgNO$_3$. What is the cell potential at 298K? Which electrode has a positive charge?

PLAN: E^0_{cell} will be zero since the half-cell potentials are equal. E_{cell} is calculated from the Nernst equation with half-cell A (higher [Ag$^+$]) having Ag$^+$ being reduced and plating out, and in half-cell B Ag(*s*) will be oxidized to Ag$^+$.

SOLUTION: $Ag^+(aq, 0.010M)$ half-cell A $\longrightarrow$ $Ag^+(aq, 4.0 \times 10^{-4}M)$ half-cell B

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{1} \log \frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}}$$

$$E_{cell} = 0\ V - 0.0592 \log 4.0 \times 10^{-2} = 0.0828V$$

Half-cell A is the cathode and has the positive electrode.

Determination of thermodynamic parameters from E_{cell} vs temperature data.

Measurement of the zero current cell potential E as a function of temperature T enables thermodynamic quantities such as the reaction enthalpy ΔH and reaction entropy ΔS to be evaluated for a cell reaction.

$$E = a + b(T - T_0) + c(T - T_0)^2 + \cdots$$

a, b and c etc are constants, which can be positive or negative.
T_0 is a reference temperature (298K)

$$\left(\frac{\partial E}{\partial T}\right)_P \leftarrow$$

Temperature coefficient of zero current cell potential obtained from experimental E=E(T) data. Typical values lie in range 10^{-4} – 10^{-5} VK^{-1}

Gibbs-Helmholtz eqn.

$$\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\downarrow$$

$$\Delta G = -nFE$$

$$\Delta H = -nFE - T\left\{\frac{\partial}{\partial T}(-nFE)\right\}$$

$$= -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta H = -nF\left\{E - T\left(\frac{\partial E}{\partial T}\right)_P\right\}$$

- Once ΔH and ΔG are known then ΔS may be evaluated.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$$\Delta S = \frac{1}{T}\left\{-nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P + nFE\right\}$$

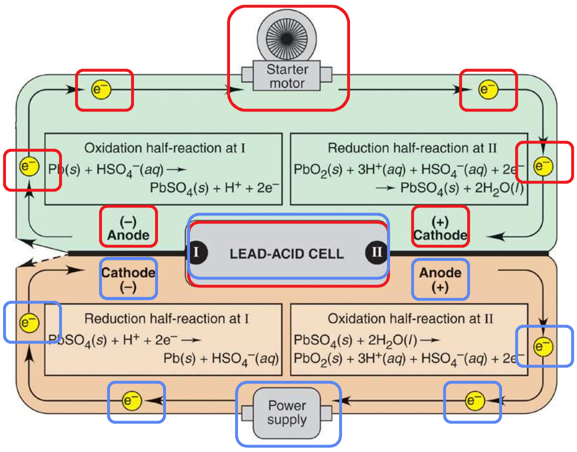
$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

- Electrochemical measurements of cell potential conducted under conditions of zero current flow as a function of temperature provide a sophisticated method of determining useful thermodynamic quantities.

Figure 21.18

The processes occurring during the discharge and recharge of a lead-acid battery

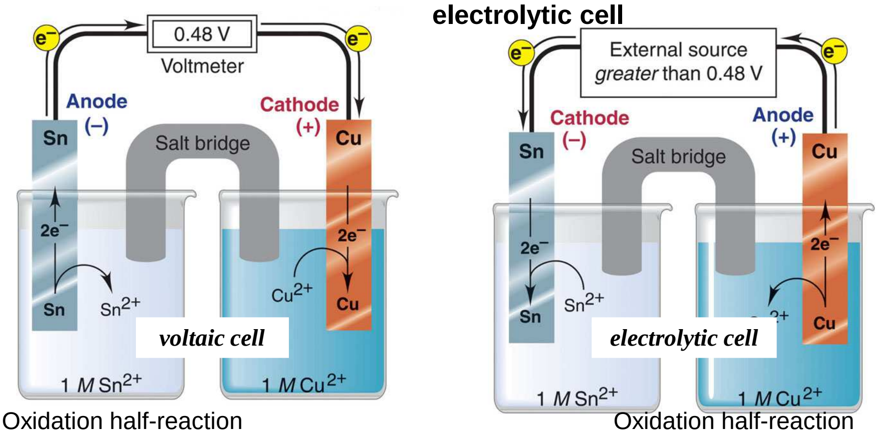
VOLTAIC(discharge)



ELECTROLYTIC(recharge)

Figure 21.17

The tin-copper reaction as the basis of a voltaic and an electrolytic cell



Oxidation half-reaction

$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

Reduction half-reaction

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

Overall (cell) reaction

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

Oxidation half-reaction

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

Reduction half-reaction

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

Overall (cell) reaction

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

Lecture 18

Electrolysis: Electrosynthesis and Electroplating.

Electrolysis.

- Redox reactions in which the change in Gibbs energy ΔG is positive do not occur spontaneously.
- However they can be driven via application of either a known voltage or a known current.
- Electrolysis is the process of driving a reaction in a non spontaneous direction by using an electric current.
- Hence an electrolytic or driven cell is an electrochemical device in which an electric current from an external source is used to drive a non spontaneous chemical reaction.
- Electrolysis provides the basis of electrosynthesis and industrial electrochemistry.

Michael Faraday
1791-1867

Originated the terms anode, cathode, anion, cation, electrode.

Discoverer of

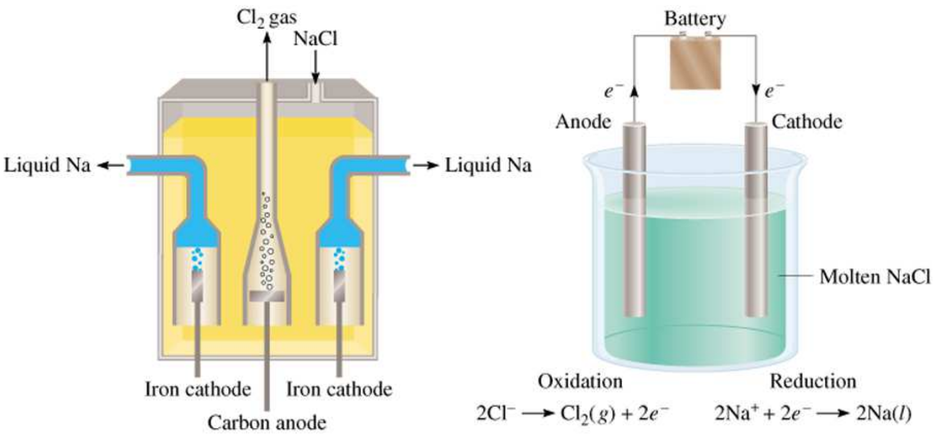
- electrolysis
- magnetic props. of matter
- electromagnetic induction
- benzene and other organic chemicals

Was a popular lecturer.

Table 21.4 Comparison of Voltaic and Electrolytic Cells

			Electrode		
Cell Type	**ΔG**	**E_{cell}**	**Name**	**Process**	**Sign**
Voltaic	< 0	> 0	Anode	Oxidation	-
Voltaic	< 0	> 0	Cathode	Reduction	+
Electrolytic	> 0	< 0	Anode	Oxidation	+
Electrolytic	> 0	< 0	Cathode	Reduction	-

Electrolysis is the process in which electrical energy is used to cause a **nonspontaneous** chemical reaction to occur.



19.8

Sample Problem 21.8: **Predicting the Electrolysis Products of a Molten Salt Mixture**

PROBLEM: A chemical engineer melts a naturally occurring mixture of NaBr and $MgCl_2$ and decomposes it in an electrolytic cell. Predict the substance formed at each electrode, and write balanced half-reactions and the overall cell reaction.

PLAN: Consider the metal and nonmetal components of each compound and then determine which will recover electrons(be reduced; strength as an oxidizing agent) better. This is the converse to which of the elements will lose electrons more easily (lower ionization energy).

SOLUTION: Possible oxidizing agents: Na^+, Mg^{2+}

Possible reducing agents: Br^-, Cl^-

Na, the element, is to the left of Mg in the periodic table, therefore the IE of Mg is higher than that of Na. So Mg^{2+} will more easily gain electrons and is the stronger oxidizing agent.

Br, as an element, has a lower IE than does Cl, and therefore will give up electrons as Br^- more easily than will Cl^-.

$$Mg^{2+}(l) + 2Br^-(l) \longrightarrow Mg(s) + Br_2(g)$$

cathode anode

Sample Problem 21.9: Predicting the Electrolysis Products of Aqueous Ionic Solutions

PROBLEM: What products form during electrolysis of aqueous solution of the following salts: **(a)** KBr; **(b)** $AgNO_3$; **(c)** $MgSO_4$?

PLAN: Compare the potentials of the reacting ions with those of water, remembering to consider the 0.4 to 0.6V overvoltage.

The reduction half-reaction with the less negative potential, and the oxidation half-reaction with the less positive potential will occur at their respective electrodes.

SOLUTION: **(a)** $K^+(aq) + e^- \longrightarrow K(s)$ $E^0 = -2.93V$

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$ $E^0 = -0.42V$

The overvoltage would make the water reduction -0.82 to -1.02 but the reduction of K^+ is still a higher potential so $H_2(g)$ is produced at the cathode.

$2Br^-(aq) \longrightarrow Br_2(g) + 2e^-$ $E^0 = 1.07V$

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^0 = 0.82V$

The overvoltage would give the water half-cell more potential than the Br^-, so the Br^- will be oxidized. $Br_2(g)$ forms at the anode.

Sample Problem 21.9: Predicting the Electrolysis Products of Aqueous Ionic Solutions

continued

(b) $Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E^0 = -0.80V$

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$ $E^0 = -0.42V$

Ag^+ is the cation of an inactive metal and therefore will be reduced to Ag at the cathode. $Ag^+(aq) + e^- \longrightarrow Ag(s)$

The N in NO_3^- is already in its most oxidized form so water will have to be oxidized to produce O_2 at the anode. $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$

(c) $Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$ $E^0 = -2.37V$

Mg is an active metal and its cation cannot be reduced in the presence of water. So as in (a) water is reduced and $H_2(g)$ is produced at the cathode.

The S in SO_4^{2-} is in its highest oxidation state; therefore water must be oxidized and $O_2(g)$ will be produced at the anode.

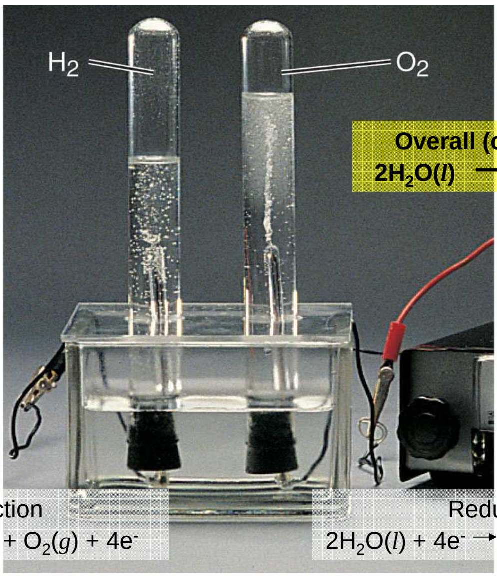
Faraday's laws of electrolysis.

- The quantity (moles) of product formed by the passage of an electric current is stoichiometrically equivalent to the amount (moles) of electrons supplied.
- The amount of product formed during an electrolysis process is calculated from the stoichiometry of the reaction, the magnitude of the current flowing, and the time during which the current flows.

Michael Faraday : 1791-1867.

Figure 21.19

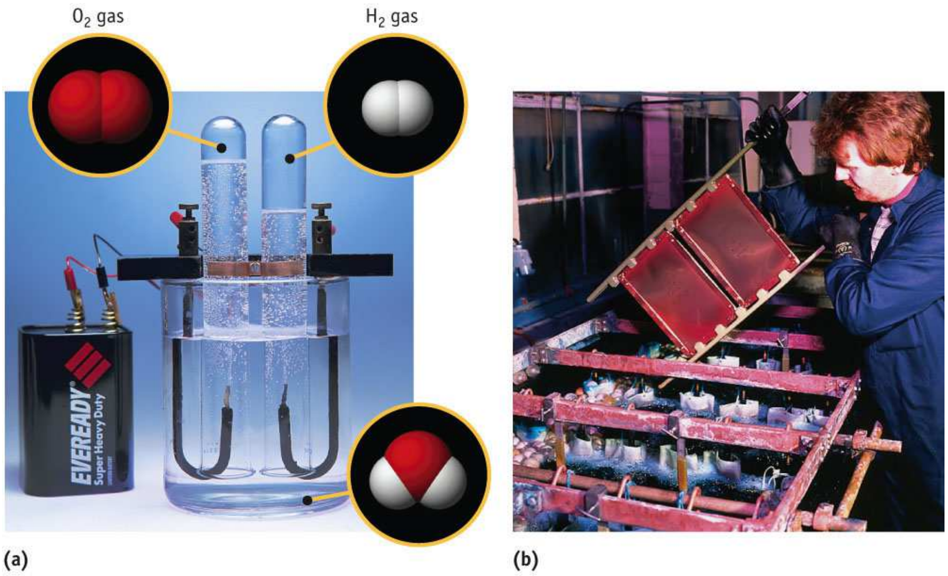
The electrolysis of water



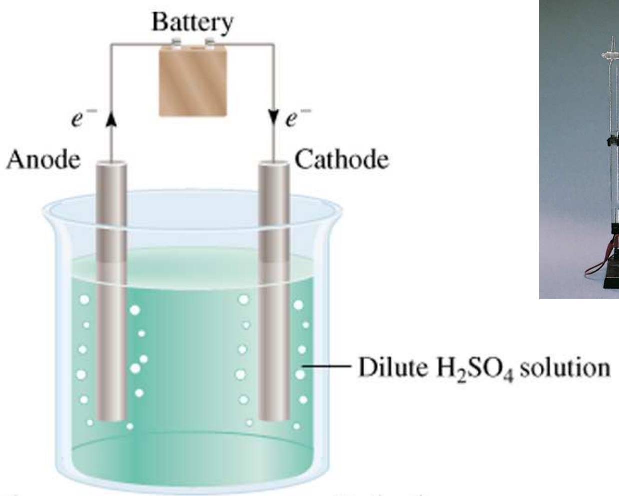
Overall (cell) reaction
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

Oxidation half-reaction
$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

Reduction half-reaction
$2H_2O(l) + 4e^- \rightarrow 2H_2(g) + 2OH^-(aq)$



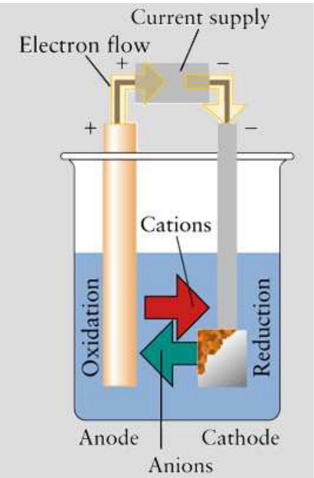
Electrolysis of Water

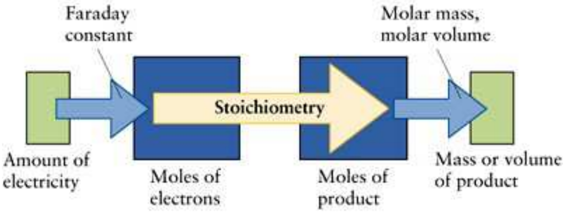


Oxidation	Reduction
$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$	$4H^+(aq) + 4e^- \longrightarrow 2H_2(g)$

Quantitative electrolysis.

1





We will focus a lot on metal plating or metal electrodeposition reactions.

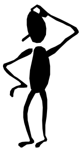
$M^{n+} + ne^- \rightarrow M$

Required equations. **n mol e^- = 1 mol M**

Charge = current flowing x time taken

Coulombs C Amperes A Seconds s

Charge passed by 1 mole electrons = 1F = 96, 500 C.



How much Ca will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

Anode: $2Cl^- (l) \longrightarrow Cl_2 (g) + 2e^-$

Cathode: $Ca^{2+} (l) + \boxed{2e^-} \longrightarrow Ca (s)$

$$Ca^{2+} (l) + 2Cl^- (l) \longrightarrow Ca (s) + Cl_2 (g)$$

2 mole e^- = 1 mole Ca

$$\text{mol Ca} = 0.452 \frac{\cancel{C}}{\cancel{s}} \times 1.5 \cancel{hr} \times 3600 \frac{\cancel{s}}{\cancel{hr}} \times \frac{1 \cancel{mol\ e^-}}{96{,}500 \cancel{C}} \times \frac{1 \text{ mol Ca}}{2 \cancel{mol\ e^-}}$$

= 0.0126 mol Ca

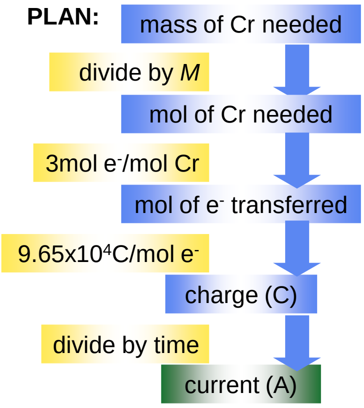
= 0.50 g Ca

19.8

Sample Problem 21.10: Applying the Relationship Among Current, Time, and Amount of Substance

PROBLEM: A technician is plating a faucet with 0.86g of Cr from an electrolytic bath containing aqueous $Cr_2(SO_4)_3$. If 12.5 min is allowed for the plating, what current is needed?

PLAN:



mass of Cr needed

divide by *M*

mol of Cr needed

3mol e^-/mol Cr

mol of e^- transferred

9.65×10^4C/mol e^-

charge (C)

divide by time

current (A)

SOLUTION: $Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$

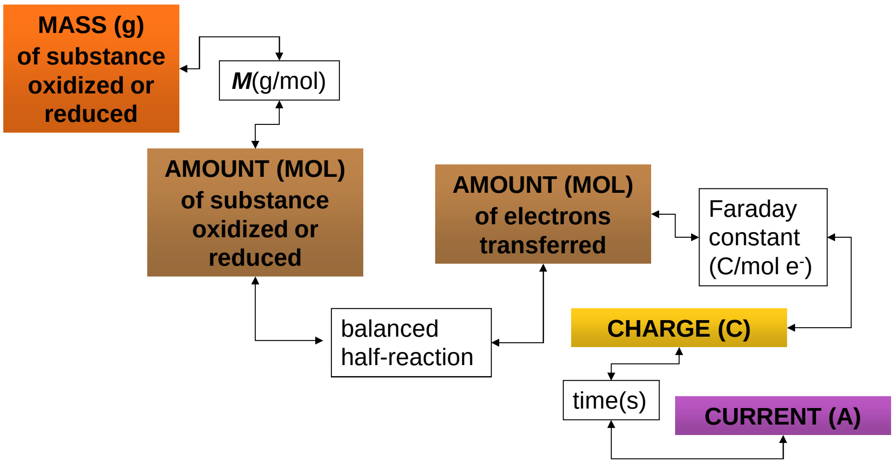
$$\frac{0.86\text{g (mol Cr)}\ (3\text{mol } e^-)}{(52.00\text{gCr})\ (\text{mol Cr})} = 0.050\text{mol } e^-$$

$$0.050\text{mol } e^-\ (9.65\times10^4\text{C/mol } e^-) = 4.8\times10^3\text{C}$$

$$\frac{4.8\times10^3\text{C}\quad(\text{min})}{12.5\text{min}\quad(60\text{s})} = 6.4\text{C/s} = 6.4\text{ A}$$

Figure 21.20

A summary diagram for the stoichiometry of electrolysis



MASS (g) of substance oxidized or reduced

M(g/mol)

AMOUNT (MOL) of substance oxidized or reduced

balanced half-reaction

AMOUNT (MOL) of electrons transferred

Faraday constant (C/mol e^-)

CHARGE (C)

time(s)

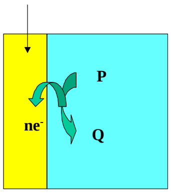
CURRENT (A)

Kinetics of interfacial ET.

- Estimation of equilibrium redox potentials provides a quantitative measure for the tendency for a specific redox reaction to occur. Kinetic information is not derived.
- In short thermodynamics provides the tools by which the possibility of an oxidation or reduction event can be established. To determine the speed at which the oxidation or reduction process occurs a kinetic approach is required.
- We seek an answer to the following questions:
  - How can we quantitatively model the rate of an ET process which occurs at the interface between a metallic electrode and an aqueous solution containing a redox active couple?
  - How can kinetic information about ET processes be derived?
- This information will enable us to obtain a modern quantitative picture of electrolysis at electrodes, and to recast Faraday's ideas in a compact modern form.

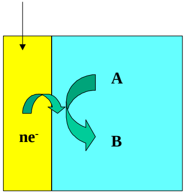
Interfacial electron transfer at electrode/solution interfaces: oxidation and reduction processes.

Electron sink electrode (Anode).



Oxidation or de-electronation.
P = reductant (electron donor)
Q = Product

Electron source electrode (Cathode).



Reduction or electronation.
A = oxidant (electron acceptor)
B = Product

- The greater the applied voltage, the larger the resulting current flow, and the greater the rate of the chemical reaction.
- The rate at which charge is moved across the M/S interface = the rate at which chemistry is accomplished at the M/S interface.

Current (A)

\# electrons transferred

Electrode area (cm^2)

$$\boxed{i = \frac{dq}{dt} = nFA\frac{dN}{dt} = nFAf_{\Sigma}}$$

Charge (C)

Time (s)

Faraday Constant ($Cmol^{-1}$)

Amount of Material (mol)

Reaction flux (rate) mol $cm^{-2}s^{-1}$

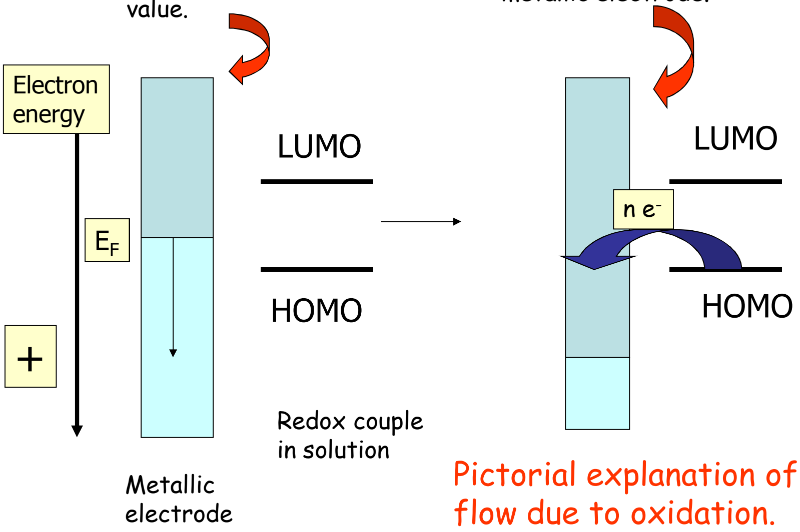
- In electrolysis we use an applied voltage to perform chemistry at a M/S interface.
- The applied voltage drives the chemical reaction which does not occur spontaneously.
- The current flowing across the M/S interface is a measure of the rate of the chemical transformation at the interface.

Basic concepts of electrode kinetics.

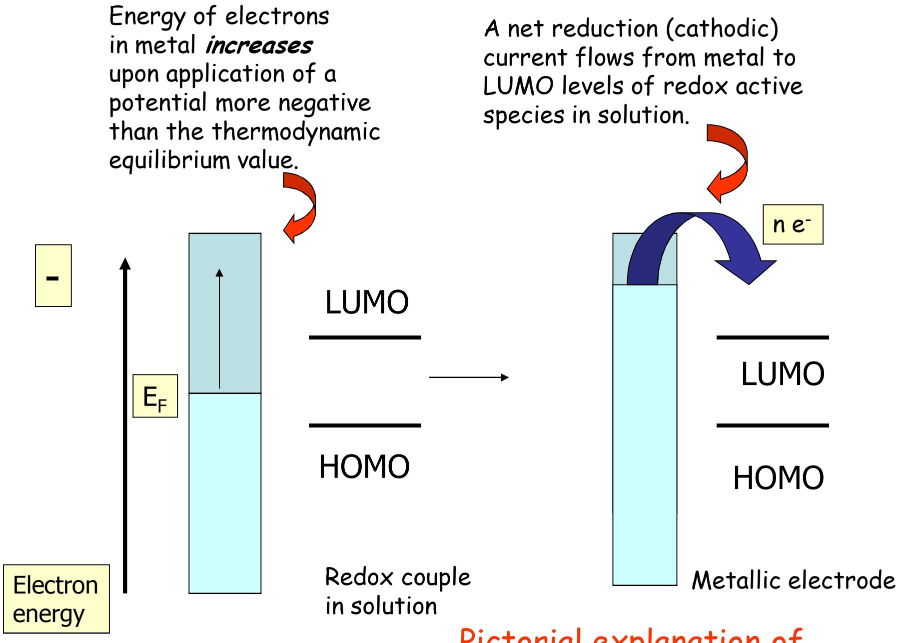
- For an interfacial ET process:
  - current flow is proportional to reaction flux (rate).
- Reaction rate is proportional to reactant concentration at interface.
- As in chemical kinetics:
  - the constant of proportionality between reaction rate f_Σ (molcm^{-2}s^{-1}) and reactant concentration c (molcm^{-3}) is termed the *rate constant* k (cms^{-1}).
- All chemical and electrochemical reactions are activated processes.
  - An activation energy barrier exists which must be overcome in order that the chemical reaction may proceed.
  - Energy must be supplied to surmount the activation energy barrier.
  - This energy may be supplied thermally or also (for ET processes at electrodes) via the application of a potential to the metallic electrode.
  - Application of a potential to an electrode generates a large electric field at the electrode/solution interface which reduces the height of the activation energy barrier and thereby increases the rate of the ET reaction.
  - Hence the applied potential acts as a driving force for the ET reaction.
  - We intuitively expect that the current should increase with increasing driving force. This can be understood using a simple pictorial approach.

Energy of electrons in metal ***decreases*** upon application of a potential more positive than the thermodynamic equilibrium value.

A net anodic (oxidation) current flows from the HOMO level of the redox species in solution to the metallic electrode.



Pictorial explanation of current flow due to oxidation.



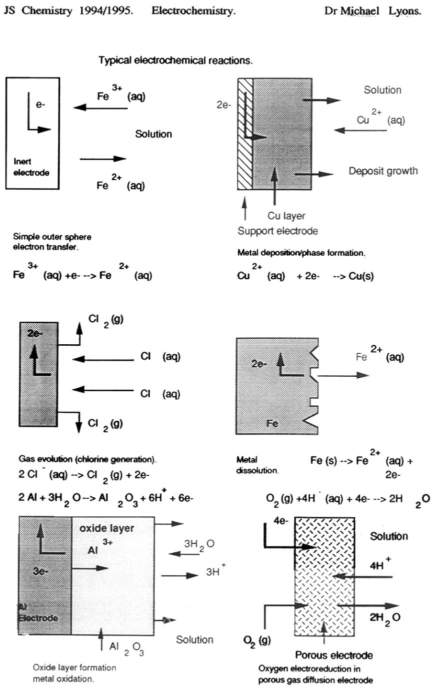
Energy of electrons in metal ***increases*** upon application of a potential more negative than the thermodynamic equilibrium value.

A net reduction (cathodic) current flows from metal to LUMO levels of redox active species in solution.

Pictorial explanation of current flow due to reduction.

A survey of electrochemical reaction types.

- Electrochemical reactions are usually complex multistep processes involving the transfer of more than one electron.
- In this course we focus on simple single step ET processes involving the transfer of a single electron.
- The kinetics of simple ET processes can be understood using the activated complex theory of chemical kinetics (see SF Kinetics notes).



JS Chemistry 1994/1995. Electrochemistry. Dr Michael Lyons.

Typical electrochemical reactions.

Simple outer sphere electron transfer.

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$

Metal deposition/phase formation.

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

Gas evolution (chlorine generation).

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Metal dissolution.

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$

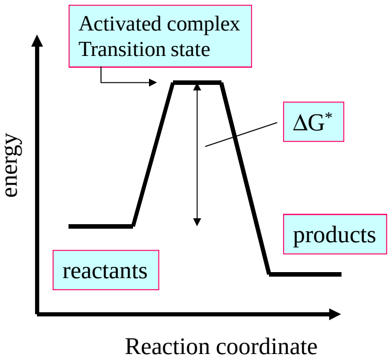
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$

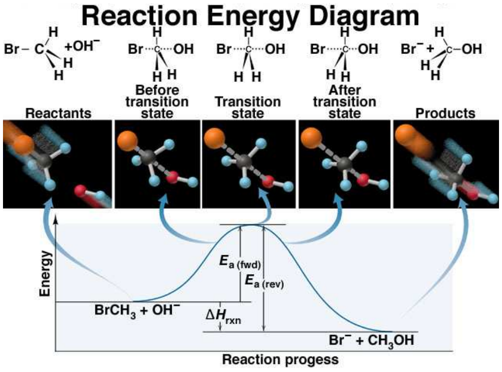
Oxide layer formation metal oxidation.

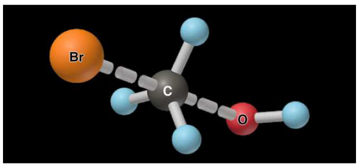
Oxygen electroreduction in porous gas diffusion electrode

Activated Complex Theory (ACT) of chemical reaction kinetics.

Progress of a chemical reaction can be expressed in terms of a plot of energy versus reaction co-ordinate.
The reaction coordinate may be described in terms of changes in particular bond lengths since these will vary as the reaction progresses.







Activated Complex or Transition State

- In electrochemistry the rate constant k varies with applied potential E because the Gibbs energy of activation ΔG^* varies with applied potential.

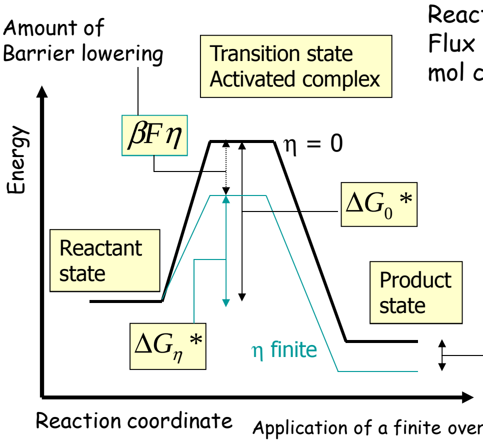
$$i = \frac{dq}{dt} = nFA\frac{dN}{dt} = nFAf_{\Sigma}$$

$$f_{\Sigma} = k'_{ET}\, c_0$$

Reaction Flux mol cm^{-2} s^{-1}

Heterogeneous ET rate constant cm s^{-1}

Interfacial reactant concentration mol cm^{-3}



Application of a finite overpotential η lowers the activation energy barrier by a fixed fraction β .

$$\Delta G_\eta * = \Delta G_0 * - \beta F\eta$$

Total added Electrical energy

$F\eta$

Symmetry factor

overpotential

$$\eta = E - E_N$$

Applied potential

Thermodynamic Nernst potential

We use the result of TST to obtain a value for the ET rate constant.

overpotential

$$\boxed{f_\Sigma = k'_{ET}\, c_0}$$

$$\boxed{\Delta G_\eta{}^* = \Delta G_0{}^* - \beta F\eta}$$

Electrochemical Gibbs energy of activation

$$\boxed{k'_{ET} = Z\exp\left[-\frac{\Delta G_\eta{}^*}{RT}\right]}$$

Symmetry factor

$$\boxed{Z = \kappa\left(\frac{k_B T}{h}\right)\sigma}$$

Characteristic ET distance (molecular diameter).

Transmission coefficient

$$\boxed{\begin{aligned} k'_{ET} &= Z\exp\left[-\frac{\Delta G_0{}^*}{RT}\right]\exp\left[\frac{\beta F\eta}{RT}\right] \\ &= k_{ET}^0\exp\left[\frac{\beta F\eta}{RT}\right] \end{aligned}}$$

The important result is that the rate constant for heterogeneous ET at the interface depends in a marked manner with applied electrode potential. As the potential is increased the larger will be the rate constant for ET.

Butler-Volmer Equation.

For the moment we neglect the fact that mass transport may be rate limiting and focus attention on the act of electron transfer at the electrode/ solution interface.
We examine the kinetics of a simple ET process in which bonds are not broken or made, involving the transfer of a single electron in a single step.

$$\boxed{\begin{aligned} A(aq) &\xrightarrow{-e^-} B(aq) \\ B(aq) &\xrightarrow{+e^-} A(aq) \end{aligned}}$$

- Oxidation and Reduction processes are microscopically reversible.
- Net current i at interface reflects a balance between i_{ox} and i_{red} .
- Symmetry factor β determines how much of the input electrical energy fed into the system will affect the activation energy barrier for the redox process. Note 0< β < 1 and typically β = 0.5.

$$\boxed{i = i_{ox} - i_{red}}$$

Net rate

Symmetry factor

Normalised potential

$$\boxed{i = i_0\{\exp[\beta\theta] - \exp[-(1-\beta)\theta]\}}$$

BV equation

Exchange current

Oxidation component

Reduction component

- Exchange current provides a measure of kinetic facility of ET process.

overpotential

Thermodynamic Nernst potential

$$\boxed{\theta = \frac{F\eta}{RT} = \frac{F(E - E_N)}{RT}}$$

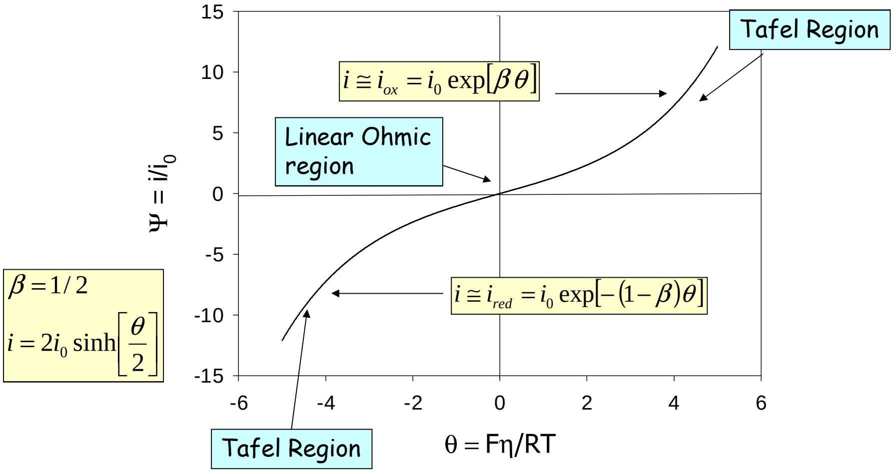
Applied potential

Exchange current →

$$\boxed{i_0 = FAk^0 a^{\infty^{1-\beta}} b^{\infty^{\beta}}}$$

Standard rate constant

$$i = i_0\left\{\exp[\beta\theta] - \exp[-(1-\beta)\theta]\right\}$$



Tafel Region

$i \cong i_{ox} = i_0 \exp[\beta\theta]$

Linear Ohmic region

$i \cong i_{red} = i_0 \exp[-(1-\beta)\theta]$

Tafel Region

$\beta = 1/2$

$i = 2i_0 \sinh\left[\dfrac{\theta}{2}\right]$