

# ELECTROLYSIS:

-the process of supplying electrical energy to a molten ionic compound or a solution containing ions so as to produce a chemical change (causing a non-spontaneous chemical reaction to occur).

Electrochemical cells use spontaneous redox reactions to convert chemical energy to electrical energy.

An ELECTROLYTIC CELL or ELECTROLYSIS CELL is an apparatus in which electrolysis can occur.

**VERY IMPORTANT DIAGRAM IN TEXT OF  
ELECTROCHEMICAL CELL vs. ELECTROLYTIC CELL p. 537**

## **ELECTROCHEMICAL    versus    ELECTROLYTIC**

energy is generated by cell

energy is supplied to cell

anode is negative

anode is positive

cathode is positive

cathode is negative

cations flow to cathode

anions flow to anode

electrons flow from anode to cathode

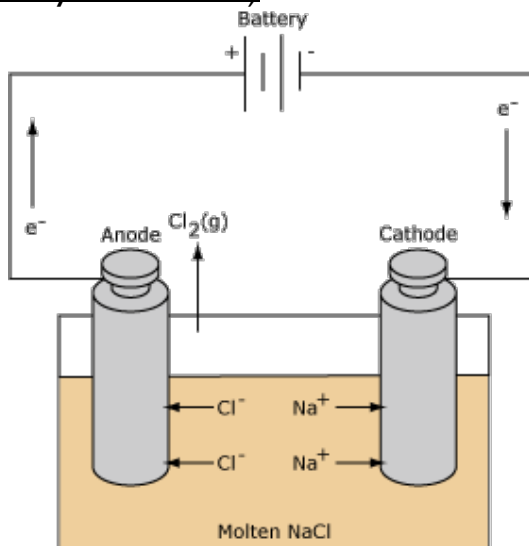
oxidation occurs at the anode

reduction occurs at the cathode

For an electric current to flow through these solutions, electrons must be transported through the solution by ions or molecules.

# ELECTROLYSIS OF A MOLTEN BINARY SALT

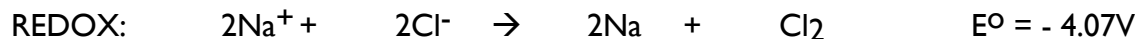
(binary salt is made up of only 2 elements)



Electrolytic Cell

BOTH ANODE & CATHODE ARE MADE OF INERT MATERIALS such as PLATINUM or CARBON

The only reactants present are  $\text{Na}^+$  and  $\text{Cl}^-$



Notice that the reaction is NON-spontaneous and requires electrical energy for the reaction to occur. ( $E^\circ =$  negative value).

To make this reaction occur, AT LEAST **+4.07 V** must be added.

There are no products at the start of the reaction, so we do not say that the products are at standard state conditions. Therefore in actual practice, more than 4.07 V may be required, even up to 10 V.

READ p. 538-552 - UNDERSTAND HOW TO CHOOSE WHICH IS THE OXIDIZING AND REDUCING AGENT - this is especially important to practice the next page of notes (YOU SHOULD HAVE BEEN READING ABOUT ELECTROCHEMICAL CELLS AS WELL AS WE WENT ALONG AND YOU SHOULD BE KEEPING UP WITH THE SECTION END QUESTIONS!!!!)

**APPLICATION:** read p. 541 Consumer Beware: Electrolysis and Electrochemistry application!

## ELECTROLYSIS OF A MOLTEN BINARY SALT

(binary salt is made up of only 2 elements)

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The only reactants present are

ANODE:

CATHODE:

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REDOX:

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**example #1:** Write the half reactions occurring at the anode and cathode when KBr (l) is electrolyzed.

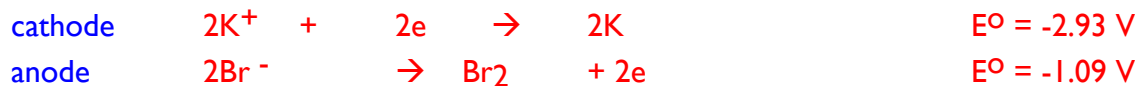
**PROCEDURE:**

- this should look familiar! It is the same set of steps we used for Electrochemical.

- 1) List all the species present.  $K^+, Br^-$
- 2) Determine whether the conditions are acidic or neutral.  
 Since there is no acid present, the conditions are neutral.  
 ALWAYS assume neutral conditions unless one of the chemicals used is an acid.
- 3) Start at the UPPER LEFT (reduction side) of the table and look down the table until you find the first ion that that is in your list in #1  
 THIS IS THE SPECIES THAT WILL HAVE THE GREATEST TENDENCY TO REDUCE since it is highest on the list of reduction potentials.



- 4) Start at the LOWER RIGHT (oxidation side) of the table and look UP the table until you find a match from #1.  
 THIS IS THE SPECIES THAT WILL HAVE THE GREATEST TENDENCY TO OXIDIZE since it is stronger on the list of reducing agents.



MUST APPLY A MINIMUM OF 4.02 V, maybe up to 10 V to overcome internal resistance of the cell.

*The preferred reaction will be the one requiring the least voltage input.*

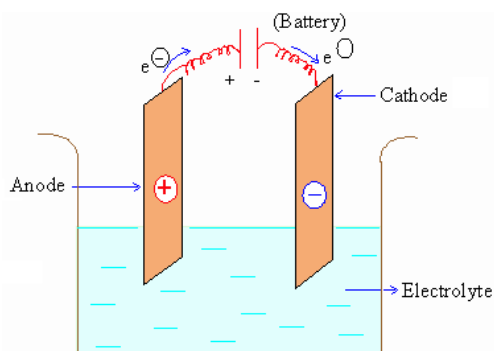


Figure 20 An electrolytic cell

*Cell is more elaborate than this, in reality*

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cathode

anode

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REDOX

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## THE OVERPOTENTIAL EFFECT:

IN PRACTICE, it is found that a higher potential than calculated must be applied in order for electrolysis to occur. The causes of this are things such as the nature of the electrodes, temperature, current density, and time.

The difference between the actual potential required and the calculated potential that is termed HALF CELL OVERPOTENTIAL.

Two adjustments that must be made to electrolysis theory:

1) Because of the high hydrogen overpotential, it is possible to plate out metals that have half cell potentials lower than the one for the reduction of water, down to and including zinc.

(see table p. 8 - the overpotential effect is labeled here, bottom left).

2) Because of the high oxygen overpotential, it is possible to oxidize  $\text{Br}^-$  and  $\text{Cl}^-$  to  $\text{Br}_2$  (g) and  $\text{Cl}_2$  (g) before water will oxidize to produce  $\text{O}_2$ .

That is, the overpotential for oxygen is higher than that for chlorine.

(see table p. 8 - the overpotential effect is labeled here, top right).

**Overpotential:** The difference in the electrode potential of an electrode between its equilibrium potential and its operating potential when a current is flowing. The overpotential represents the extra energy needed (an energy loss that appears as heat) to force the electrode reaction to proceed at a required rate (or its equivalent current density). Consequently, the operating potential of an anode is always more positive than its equilibrium potential, while the operating potential of a cathode is always more negative than its equilibrium potential. The overpotential increases with increasing current density, see Tafel equation. The value of the overpotential also depends on the "inherent speed" of the electrode reaction: a slow reaction (with small exchange current density) will require a larger overpotential for a given current density than a fast reaction (with large exchange current density). Also referred to as "polarization" of the electrode. See also overvoltage. An electrode reaction always occurs in more than one elementary step, and there is an overpotential associated with each step. Even for the simplest case, the overpotential is the sum of the concentration overpotential and the activation overpotential.

**Activation overpotential (overvoltage):** Contribution to the total overpotential due to the charge transfer step at the electrode interface.

**Concentration overpotential (polarization):** The overpotential (alternatively called polarization) associated with the diffusional transport of the reactants to the electrode surface from the bulk of the electrolyte and the reverse transport of the products. The diffusion is an elementary step in the overall electrode reaction. Also called "diffusion overpotential" or "mass-transport overpotential."

**Overvoltage:** The difference between the cell voltage (with a current flowing) and the open-circuit voltage (ocv). The overvoltage represents the extra energy needed (an energy loss that appears as heat) to force the cell reaction to proceed at a required rate. Consequently, the cell voltage of a galvanic cell (e.g., a rechargeable battery during discharging) is always less than its ocv, while the cell voltage of an electrolytic cell (e.g., a rechargeable battery during charging) is always more than its ocv. Occasionally also referred to as "polarization" of the cell. The overvoltage is the sum of the overpotentials of the two electrodes of the cell and the ohmic loss of the cell. Unfortunately, the terms "overvoltage" and "overpotential" are sometimes used interchangeably

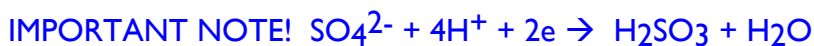
**example #2:** Write the half reactions occurring at the anode and cathode when  $K_2SO_4$  (aq) is electrolyzed.

**PROCEDURE:**

- 1) List all the species present.  $K^+$ ,  $SO_4^{2-}$ ,  $H_2O$
- 2) Determine whether the conditions are acidic or neutral.  
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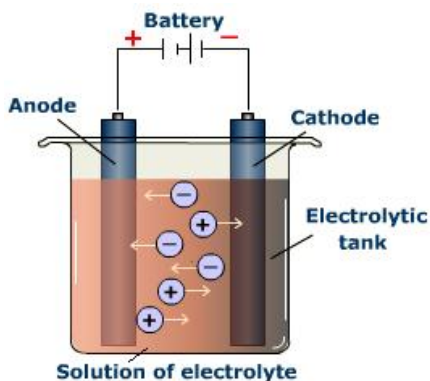
**\*\* The preferred reaction will be the one requiring the least voltage input. \*\***

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does not work because there is no  $H^+$  present - our problem is under neutral conditions, not acidic conditions. The presence of  $H^+$  would require acidic conditions.

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## **ELECTROPLATING:**

An electrolytic process in which a thin uniform layer of metal is deposited on a conducting surface.

The CATHODE is the material that is to receive the metal plating.

The ELECTROPLATING SOLUTION contains ions of the metal which is to be plated onto the cathode.

The ANODE may be made out of the same metal which is to be plated out onto the cathode.

See the silver plating example on p. 542.

Note the cyanide ions used to keep the silver (and gold) ions in alkaline solution.

example: Design a cell which can be used to electroplate copper onto a strip of Ag. Include in your design: the ions in solution, the direction of ion flow, the substances used for the anode and cathode, and the direction of electron flow when the cell is connected to a DC power source. (you will need a detailed diagram for this)

### **SOLUTION:**

In order of oxidizing agents, we find the equations:

Electroplating Copper onto Silver:

PRACTICE QUESTION IN TEXT P. 544 # 17a)

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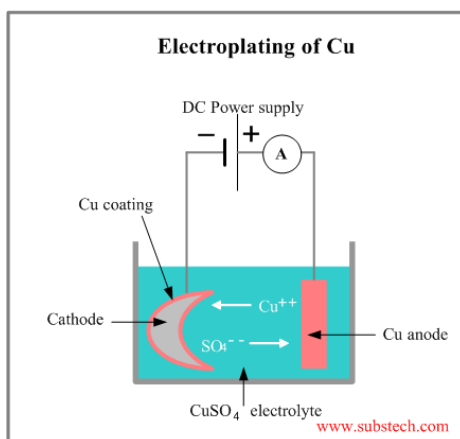
In order of oxidizing agents (= reduction strength), we find the equations:

$\text{Cu}^{2+} + 2e \rightarrow \text{Cu (s)}$        $E^\circ = +0.34 \text{ V}$     Cathode = reduction = electroplating = Ag (s) strip

$\text{Cu(s)} \rightarrow \text{Cu}^{2+} + 2e$        $E^\circ = -0.34 \text{ V}$     Anode = oxidation = corrosion = Cu (s) strip

What is actually happening ON TOP of the Ag (s) is the  $\text{Cu}^{2+}$  ions move to the Ag (s) electrode and reduce there, forming Cu(s) electroplate.

### Electroplating Copper onto Silver:



### PRACTICE QUESTION IN TEXT P. 544 # 17a)

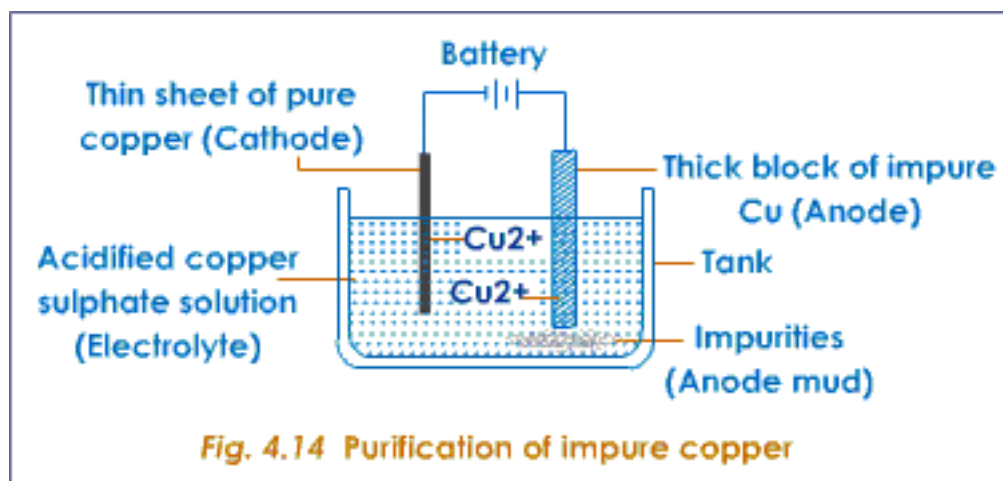
## ELECTROREFINING:

An electrolytic process of purifying a metal.

The electrolytic cells used for this purpose consist of many closely packed anodes and cathodes.

The anodes consist of the impure metal.

The cathodes consist of thin sheets of very pure metal.



The “pig” copper at the anode contains impurities: Zn, Pb, Ag, Au, Pt

When the current is passed through the cell, the anodes dissolve slowly as the pure metal is deposited on the cathodes.

Cu has the greatest tendency to oxidize because it is present in the greatest quantity (after the lead and zinc have oxidized).

Au, Ag fall to the bottom of the electrolytic cell as “sludge” and are sold for a \$\$\$ profit!!

See the electrolytic purification of lead example on p. 543-544.

PRACTICE QUESTION IN TEXT P. 544 # 17b)

## PRACTICAL LOCAL APPLICATIONS:

1) Canadian Occidental Petroleum Ltd has chlorine-caustic operations in North Van and Nanaimo. These plants rely on a specially designed electrolytic cell to convert NaCl into Cl<sub>2</sub> and NaOH.

2) Cominco Ltd. in Trail applies an electrolytic process as the last chemical step in the production of lead and zinc metals from their ores.

Leads are used in storage batteries, solders, paints, leaded gasoline (not in Canada), crystalware, as shields against Xray radiation...

Zinc is used in protecting steel against corrosion by galvanizing (electrochemistry) or by the use of zinc anodes (cathodic protection). Metals used in homes and auto parts also contain zinc.

Cominco uses electrorefining to purify lead and zinc. (in Zinc refining, it is called electrowinning).

3) Alcan in Kitimat produces Aluminum. Al is rust proof, corrosion resistant, 3 times lighter than steel, high strength when alloyed, and a good conductor of electricity and heat. It is used as a structural metal, and for aluminum foil, electrical wire, and kitchen utensils.

4) CXY Chemical in North Van (by the second narrows Bridge and the Transfer Station) produce Cl<sub>2</sub> (g) that is used to make HCl, bleach, pool chemicals (bleach), but mostly products for the pulp and paper industry (bleaching paper).