Electrolysis: Chemical Change from Electric Energy

An electric current can be produced by a chemical change. Equally important, however, is the opposite process, **electrolysis**, the use of an electric current to bring about chemical change. **Electrolysis** involves the decomposition of a molten or aqueous compound by electricity. The process takes place in an **electrolytic cell**. The compound decomposed during electrolysis is called an **electrolyte.** The energy which causes the chemical change during electrolysis is provided by an **electric current**. An electric current is simply a flow of electrons.

What happens if a pair of inert electrodes, which are connected to a battery, are inserted into a bath of molten NaCl? (Because the NaCl is molten, the Na^{+1} and Cl^{-1} ions are free to move in the melt) The external battery, or other source of electric potential, acts as an "**electron pump**" and electrons flow from this source into one of the electrodes, thereby giving it a negative charge. Sodium ions are attracted to this **negative electrode** and are reduced when electrons from the electrode are accepted, making the electrode the **cathode**.

The battery simultaneously draws electrons from the other electrode, giving it a **positive electric charge**. Chloride ions are attracted to this electrode and surrender electrons. Because oxidation has occurred, this is the **anode**.

Thus, the following reactions have occurred in molten NaCl:

$$Na^{+1} + e^{-1} \longrightarrow Na$$

$$Cl^{-1} \longrightarrow Cl + e^{-1}$$

The chlorine atoms immediately pair up to form molecules of chlorine gas, Cl_2.
We obtain a value of about - 4 V for the electrode potential. The reaction is clearly not product-favoured in the direction written:

Anode, oxidation: $2\,Cl^{-1} \longrightarrow Cl_{2\,(g)} + 2\,e^{-}$
Cathode, reduction: $2\,Na^{+1} + 2\,e^{-} \longrightarrow 2\,Na_{(s)}$
Net reaction: $2\,Cl^{-1} + 2\,Na^{+1} \longrightarrow 2\,Na_{(s)} + Cl_{2\,(g)}$ $\quad E^0 = -4\ V$

and this is the reason that an external battery has been attached. The battery, with a potential greater than 4 V, forces the reactant-favoured reaction to occur by "pumping" electrons in the proper direction.

A Summary of Electrochemical Terminology

Whether you are describing a voltaic cell or an electrolysis cell, the terms *anode* and *cathode* always refer to the electrodes at which oxidation and reduction occur, respectively.
The polarity of the electrodes is reversed, however, in a battery or electrolysis cell.

Type of Cell	Electrode	Function	Polarity
Battery	Anode	Oxidation	-
	Cathode	Reduction	+
Electrolysis	Anode	Oxidation	+
	Cathode	Reduction	-

In a voltaic cell, the negative electrode is the one at which electrons are produced.
In an electrolysis cell, the negative electrode is the one onto which the external source is "pumping" the electrons.

Sample

What if an aqueous solution of a salt, say sodium iodide, is used instead of a molten salt (without water)? With water now present, are Na^{+1} and I^{-1} ions reduced and oxidized, respectively, or is water involved?

What happens if an aqueous solution of NaI is electrolysed? The Part Played By Water
Possible **reduction reactions** are

$$Na^{+1}_{(aq)} + e^- \longrightarrow Na_{(s)} \qquad E^0 = -2.71\ V$$
$$2\,H_2O_{(l)} + 2\,e^- \longrightarrow H_{2(g)} + 2OH^{-1}_{(aq)} \qquad E^0 = -0.83\ V$$

When several reactions at an electrode are possible, the cathode in this case, we must consider not only which is the most easily reduced (best oxidizing agent) but also which is reduced most *rapidly*. (Complications usually occur when currents are large – as in a commercial electrolysis cell – and when reactant concentrations are small.)

In this case, H_2 and OH^{-1} are clearly observed as products.
This is reasonable because water is certainly reduced more readily than sodium. Furthermore, because the hydronium ion concentration is only about 10^{-7} M in a NaI solution, the second reaction is the best description of the net change occurring at the cathode.

For the **oxidation processes** possible in aqueous sodium iodide, we need to compare the two reactions:

$$2\,I^{-1}_{(aq)} \longrightarrow I_{2(aq)} + 2\,e^- \qquad E^0 = -\ 0.535\ V$$
$$6\,H_2O_{(l)} \longrightarrow O_{2(g)} + 4\,H_3O^{+1}_{(aq)} + 4\,e^- \qquad E^0 = -\ 1.23\ V$$

The iodide is the more readily reduced species.

The best description of the chemistry that occurs on electrolysis of aqueous NaI is therefore the reactions:

Anode, oxidation: $2\,I^{-1}_{(aq)} \longrightarrow I_{2(aq)} + 2\,e^{-1} \qquad E^0 = -\ 0.535\ V$
Cathode, reduction: $2\,H_2O_{(l)} + 2\,e^{-1} \longrightarrow H_{2(g)} + 2OH^{-1}_{(aq)} \qquad E^0 = -\ 0.83\ V$
Net reaction: $2\,I^{-1}_{(aq)} + 2H_2O_{(l)} \longrightarrow H_{2(g)} + 2OH^{-1} + I_{2(aq)} \qquad E^0 = -\ 1.37\ V$
The products are hydrogen, hydroxide ion, and iodine, all of which are easily identified in an experiment.

What happens if an aqueous solution of some other metal halide such as $CuCl_2$ is electrolyzed?

As before, consult Electrode Potential Table, and considering all possible reactions, find the oxidation and reduction reactions that require the smallest potential.
In this case, aqueous **Cu^{2+} ion is *much*** more easily reduced ($E^0 = +\ 0.34$ V) than water ($E^0 = -\ 0.83$ V) **at the cathode**, so copper metal is produced.

At the anode, two oxidations are possible: $Cl^{-1}_{(aq)}$ to $Cl_{2(g)}$ and H_2O to $O_{2(g)}$.
Experiments show that chloride ion is generally oxidized more rapidly than water, so the reactions occurring on electrolysis of aqueous copper(II) chloride are...
Anode, oxidation: $2\,Cl^{-1}_{(aq)} \longrightarrow Cl_{2(g)} + 2\,e^{-1} \qquad E^0 = -\ 1.36\ V$
Cathode, reduction: $Cu^{2+}_{(aq)} + 2\,e^{-1} \longrightarrow Cu_{(s)} \qquad E^0 = +\ 0.34\ V$

Net reaction: $Cu^{2+}_{(aq)} + 2\,Cl^{-1}_{(aq)} \longrightarrow Cu_{(s)} + Cl_{2(g)} \qquad E^0 = -\ 1.02\ V$
Again, this process is of obvious commercial importance. The copper used in wiring, in coins, and for other purposes is purified by electrolysis.

A **useful general principle** can be derived from the preceding examples.

If an electric current is passed through a solution the electrode reactions are most likely those requiring the least potential (and those that occur most rapidly). In water, this means that a substance will be reduced if it has a reduction potential **less negative** than about - 0.83 V, the potential for the reduction of pure water.

If a substance has a reduction potential **more negative** than about -0.83 V, then only water is reduced. Substances falling into this category include Na, K, Mg, and Al. To produce these metals requires methods other than the reduction of their ions in aqueous solution.
The electrochemical series lists the cations in order of ease of discharge at a cathode; thus the ions of metals lower down in the electrochemical series are discharged in preference to those higher up.

The order of discharge for anions is:

$$SO_4^{-2},\ NO_3^{-1},\ Cl^{-1},\ OH^{-1},\ Br^{-1},\ I^{-1}$$

$$\longrightarrow$$

Ions discharge more easily

(Note: the discharge of the ions is affected by the concentration of ions.)

<u>Predict what happens when an electric current is passed through aqueous NaOH.</u>

First, list all the species in solution. In this case they are Na^{+1}, OH^{-1}, and H_2O.
Next, use Table of E^0 to decide which of the species can be oxidized and which can be reduced, and note the potential of each possible reaction.

Reductions:

$$Na^{+1}_{(aq)} + e^{-1} \longrightarrow Na_{(s)} \qquad E^0 = -2.71\ V$$

$$2\ H_2O_{(l)} + 2\ e^{-1} \longrightarrow H_{2(g)} + 2\ OH^{-1}_{(aq)} \qquad E^0 = -0.83\ V$$

Oxidation:

$$4\ OH^{-1}_{(aq)} \longrightarrow O_{2(g)} + 2\ H_2O_{(l)} + 4\ e^{-1} \qquad E^0 = -0.40\ V$$

It is evident that water is reduced to H_2 at the cathode and OH^{-1} is oxidized O_2 at the anode.
The cell reaction is:

$$2\ H_2O_{(l)} \longrightarrow H_{2(g)} + O_{2(g)}$$

and the potential under standard conditions is - 1.23 V.

Predict the results of passing an electric current through each of the following solutions:

1. Molten NaBr

2. Aqueous NaBr

3. Aqueous $SnCl_2$

4. $Pb(NO_3)_{2(aq)}$

5. Concentrated $NaCl_{(aq)}$

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A FAIRY STORY FOR CHEMISTS

Once upon a time there was a happy little particle family, which lived down in the shade of a lithium atom. There was Papa Proton, Mama Neutron, the little 1s twins and the youngest member of the family, 2s. Little 2s was a merry little fellow whose favorite pastime was spreading out and behaving like a wave, which caused his Mother no end of worry. She had always had trouble finding him since the day he was delivered by Dr. Heisenberg.

One day Mama Neutron struck her head out through the dotted swiss orbitals covering the window of their happy little nucleus and shouted, “Junior”; she always called Little 2s ‘Junior’ because she couldn’t remember his name. “Junior”, she said, “You may play anywhere you please (as long as you fulfill the Schrödinger wave equation), but don’t go near the fluorine atom. He is a horrible, mean electronegative, old ogre who loves to take little 2s electrons and chain them up to 2p bonds.

“All right, Mama,” said little 2s, and he went skipping merrily up the energy levels in the garden behind the nucleus. It was a wonderful day and 2s was so full of energy (hf) that he gamboled about, emitting childish ultra violet waves of joy.

Suddenly little 2s felt a tug at his probability function. There leering over the garden wall, was the fluorine atom. "Come into my 2p level," said the fluorine atom to the trembling little electron meanwhile kicking another unfortunate electron back into its orbital. “You’ll have lots of playmates there." And before he knew it, little 2s found himself snatched away screaming as the fluorine atom (now ion) went racing down the road chortling to himself.

Suddenly the fluorine ion stopped short. On the path ahead was a beautiful, irresistibly obvious, member of the opposite sex. “Hi, Big Boy,” she said, “Come up and see me sometime. Just try the third electrolytic vat on the left, and ask for Anne”

Little did the fluorine ion know, but this was the little electron’s Fairy Godmother, Anne Ode, who just happened to be speeding down the path in her cadmium hot- rod.

Fluorine ion felt irresistibly drawn by her magnetic personality. “you and I could emit beautiful spectra together, Baby,” he said, pushing eyes back in and straightening his 2p orbitals.

“To coin a phrase, I’ll bet you tell that to all the cute little electrodes,” rejoined Anne.

All at once, Anne noticed something strange about the fluorine ion. “my what big orbitals you have. Have you been indulging in stray electrons again, in spite of my warnings?”

The fluorine ion was caught red (7500 Å) handed. Suddenly he made a break for it, but too late.

The Fairy Godmother was too quick for him. With a wave of her magic wand (a reconverted Mohr buret) she freed the electron, and the fluorine ion was whisked away into a platinum cell at the top of an extremely high mountain of a very hard vacuum. There he was left all by himself to meditate on his crimes for the next mega-century.

And, so, dear children if someday you are slaving away in your laboratory over a hot test tube and you find a lithium atom, which won’t react, look very closely at it. You will see Papa Proton, Mama Neutron, and three little electrons sitting on the front porch of their happy little nucleus and you will notice that little 2s always stays near at hand because he promised never to stray away from home again.

Moral: Never kidnap an electron, it may be a shocking experience.

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