Electrochemical cell

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Introduction to Electrochemical cell

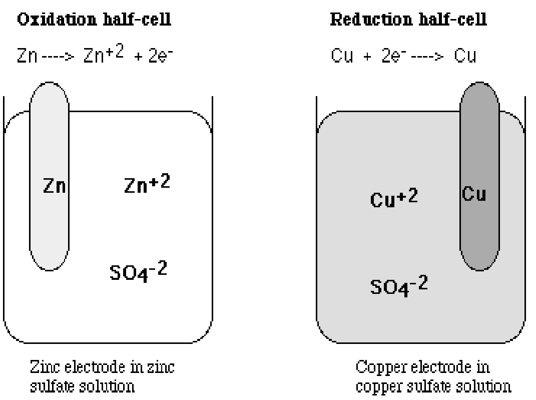
Batteries are electrochemical cells that convert chemical energy to electrical energy. The reactants in batteries are at non-equilibrium concentrations. As you use them, the reactants form products to approach equilibrium and the voltage drops until the battery is no longer usable. The half-cells are connected by two paths: one that allows for flow of electrons (like a wire) and another that allows for flow of ions (like a porous material). This arrangement of half-cells is called an electrochemical cell, which is also known as a galvanic cell or sometimes a voltaic cell.

Composition of Electrochemical cell

An electrochemical cell consists of two electrodes, or metallic conductors, in contact with an electrolyte, an ionic conductor (which may be a solution, a liquid, or solid). A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous reaction occurring inside it. An electrolytic cell is an electrochemical cell in which a non-spontaneous reaction is driven by an external source of current. An electrochemical cell is composed to two compartments or half-cells, each composed of anelectrode dipped in a solution ofelectrolyte. These half-cells are designed to contain the oxidation half-reaction and reduction half-reaction separately as shown below.

Half-reactions

Oxidation is the removal of electrons from a species and reduction is the addition of electrons to a species. A redox reaction is a reaction in which there is a transfer of electrons from one species to another. The electron transfer may be accompanied by other events, such as atom or ion transfer, but the net effect is electron transfer and hence a change in oxidation number of an element. The reducing agent (or 'reductant') is the electron donor; the oxidizing agent (or 'oxidant') is the electron acceptor. Any redox reaction may be expressed as the difference of two reduction half reactions,
which are conceptual reactions showing the gain of electrons. For example, the reduction of Cu2+ ions by zinc (a process which occurs spontaneously in the Daniell galvanic cell) can be expressed as the difference of the following two half-reactions:



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

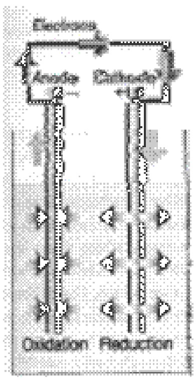
The difference of the two (copper - zinc) is

Cu^{2+}(aq) + Zn(s) . . Cu(s) + Zn^{2+}(aq)

The half-cell, called the anode, is the site at which the oxidation of zinc occurs as shown below.

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

During the oxidation of zinc, the zinc electrode will slowly dissolve to produce zinc ions (Zn^{+2}), which enter into the solution containing Zn^{+2} (aq) and SO_4^{-2} (aq) ions.



Reactions at electrodes

The electrode at which oxidation occurs is called the anode; the electrode at which reduction occurs is called the cathode.

In a galvanic cell, the positive electrode is the cathode. This is because the species undergoing reduction withdraws electrons from its electrode (the cathode), so leaving a net positive charge on it.

Fig 2 A galvanic cell depicting the transport of electrons around the circuit.The cathode is the positive electrode.

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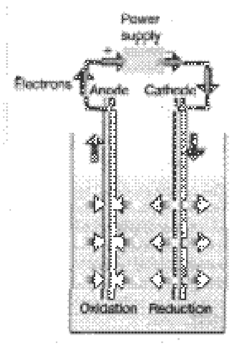

Fig 3 An electrolytic cell showing the transport of electrons. The cathode is the negative electrode

In an electrolytic cell the situation is reversed.

Reduction still occurs at the cathode (by definition), however reduction does not occur spontaneously, so electrons must be supplied to the cathode to drive the reduction. Consequently the cathode must be the negative electrode.

Cell notation

In the notation for cells, phase boundaries are denoted by vertical lines, a liquid junction by : and a salt bridge by ||. Thus the Daniell cell is denoted by

Zn(s) | ZnSO4(aq) : CuSO4(aq) | Cu(s)
anode | electrolyte || electrolyte | cathode

To write the cell reaction corresponding to a cell diagram, we first write both half reactions as reductions. Then we subtract the left-hand half-reaction from the right hand half-reaction to yield the overall cell reaction. So for instance for the Daniell cell,

Zn(s) | ZnSO4(aq) : CuSO4(aq) | Cu(s)

Right-hand electrode: Cu^{2+}(aq) + 2^{e-} . . Cu(s)

Left-hand electrode: Zn^{2+}(aq) + 2^{e-} . . Zn(s)

Hence, overall cell reaction is

Cu^{2+}(aq) + Zn(s) . .   Cu(s) + Zn^{2+}(aq)

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