Chemistry electrolysis Cheat Sheet

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What is electrolysis

Electrolysis is the process of using electricity to break down or decompose a compound (usually an ionic compound in the molten state or aqueous solution). It takes place in an electrolytic cell.

How does electrolysis work?

In the external circuit: Electrons flow from the positive terminal to the negative terminal

within the electrolyte: The flow of Ions flow towards the electrodes constitutes the flow of electric current through the electrolyte

Anode: During electrolysis, Anions move to the Anode and are discharged at the anode by losing electrons; oxidation occurs

cathode: During electrolysis, cations move to the cathode and are discharged at the cathode by gaining electrons; reduction occurs

Aqueous solutions of ionic compounds

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Electrolysis of concentrated solutions

Example: Concentrated NaCl solution

At the anode, (1) OH– and Cl– ions are attracted to the anode. (2) Being concentrated, Cl– ions are preferentially discharged as chlorine gas. (3) OH– ions remain in solution.

At the cathode, (1) H+ and Na+ ions are attracted to the cathode. (2) H+ ions are preferentially discharged as hydrogen gas. (3) Na+ ions remain in solution.

Observations: Effervescence of chlorine gas is seen at the anode. Chlorine gas can be collected. Effervescence of hydrogen gas is seen at the cathode. Hydrogen gas can be collected. The ratio of volumes of chlorine to hydrogen is 1:1. The electrolyte becomes alkaline as NaOH is left behind, pH increases.

Equal volumes of hydrogen gas and chlorine gas are produced. The resulting solution becomes alkaline because the remaining Na+ and OH– ions recombine to form sodium hydroxide.

Types of simple cells

Galvanic or voltaic cells

A galvanic cell, or voltaic cell, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.

Types of simple cells (cont)

It is made up of two separate half-cells. A half-cell is composed of an electrode (a strip of metal, M) within a solution containing Mn+ ions in which M is any arbitrary metal. The two half cells are linked together by a wire running from one electrode to the other. A salt bridge also connects to the half cells.

Salt bridge

The role of the salt bridge which contains a salt solution (e.g. NaCl / KCl) is to maintain electrical neutrality in the cell and allow the free flow of ions from one cell to another. The solution at the anode side will turn more positively charged when more Zn dissolves to form Zn2+ ions and the solution at the cathode side will turn more negatively charged when more Cu2+ ions form Cu atoms. The ions from the salt bridge will move to the respective solutions at the anode and cathode to balance the charges. Without the salt bridge, positive and negative charges will build up around the electrodes causing the reaction to stop.

Parts of a electrolytic cell

(1) Battery Acts as an electron pump and draws electrons away from the anode. Anode becomes positively charged. Electrons enter the positive terminal of the battery and are ‘pumped out’ at the negative terminal thus the cathode becomes negatively charged.

Parts of a electrolytic cell (cont)

(2) Electrodes Conduct electricity. They are usually carbon (i.e. graphite) rods or metal plates. Anode - Electrode connected to positive terminal and is positively charged. Cathode - Electrode connected to negative terminal and is negatively charged.

(3) Electrolyte Conducts electricity. It contains free-moving ions which allow electricity to flow through. It is a molten ionic compound or an aqueous solution. The electrolyte will be decomposed to form cations and anions. Examples: dilute H_2SO_4, molten NaCl, $CuSO_4$ solution.

Electrolysis using inert electrodes

Inert electrodes such as carbon (graphite) or platinum electrodes are used to prevent reactions from occurring between the products of electrolysis and the electrode.

Example of electrolysis of aqueous solution

Example: NaCl

At the anode, (1) OH^- and Cl^- ions are attracted to the anode. (2) OH^- ions are preferentially discharged as water and oxygen gas. (3) Cl^- ions remain in solution.

At the cathode, (1) H^+ and Na^+ ions are attracted to the cathode. (2) H^+ ions are preferentially discharged as hydrogen gas. (3) Na^+ ions remain in solution.

Observations: Effervescence of oxygen gas is seen at the anode. Oxygen gas can be collected. Effervescence of hydrogen gas is seen at the cathode. Hydrogen gas can be collected. The ratio of volumes of oxygen to hydrogen is 1:2. The electrolyte becomes more concentrated sodium chloride solution.

Simple cells

A simple cell is a device that converts chemical energy into electrical energy. It is also known as an electric cell. It is made by placing two different metals in contact with an electrolyte. The metals act as electrodes for the simple cell.

The more reactive metal (higher in electrochemical series) will become the negative terminal. The atom of the reactive metal will lose electron(s) to form positive ions and dissolves into the solution. Oxidation takes place.

The electrons lost by the more reactive metal are then moved to the other metal plate through the wire. As a result, current is produced (there is a potential difference) and the ammeter /voltmeter deflects.

The less reactive metal (lower in electrochemical series) will become the positive terminal. At the positive terminal, the positive ions in the solution (electrolyte) will gain electrons (from the negative terminal) and be discharged.

If the positive ions are less reactive than hydrogen, a metal coating will be formed at the positive terminal.

If the positive ions are more reactive than hydrogen, effervescence (hydrogen gas) is formed at the positive terminal.

In a voltaic cell, the negative terminal is the anode while the positive terminal is the cathode.

Simple cell- voltage

The further apart the two metals are in the reactivity series, the greater the voltage produced.

Electrolyte- molten or aqueous solution?

In the solid state, ions are held in the lattice structure. Thus, they cannot conduct electricity. In the molten state, or in aqueous solution, ions are free to move and can conduct electricity.

Electrolysis of molten compounds

Example: NaCl

At the anode: Negatively charged Cl^- ions are attracted to the anode. Cl^- ions lose electrons to form chlorine gas. Cl^- ions are said to be discharged. They are oxidized.

At the cathode: Positively charged Na^+ ions are attracted to the cathode. Each Na^+ ion gains one electron to form a sodium atom. Na^+ ions are said to be discharged. It is reduced. Observation: Silvery beads of liquid sodium found on the cathode or found at the bottom of the container.

Electrolysis using reactive electrodes

Electrodes which react with the electrolyte or products of electrolysis are called reactive electrodes. E.g. Copper

example: Copper (II) sulfate using reactive copper electrodes

At the anode, (1) OH^- and SO_4^{2-} ions are attracted to the anode. (2) Since copper is a reactive electrode, OH^- and SO_4^{2-} ions, copper electrode dissolves to form Cu^{2+} ions in the solution. (3) The anode decreases in mass.

Electrolysis using reactive electrodes (cont)

At the cathode, (1) H^+ and Cu^{2+} ions are attracted to the cathode. (2) Cu^{2+} ions are preferentially discharged as copper metal (atoms). (3) The cathode increases in mass.
Observations: The anode decreases in mass. The cathode increases in mass. The colour and concentration of copper(II) sulfate remain unchanged. This is because the Cu^{2+} ions that are discharged at the cathode come mainly from the anode.There is no net loss of Cu^{2+} ions from the solution.

Simple cell example

Example: Zinc- copper cell
Zinc electrode: zinc atoms being more reactive give up electrons and go into the solution as zinc ions
The electrode from which electrons flow out is the negative electrode, thus zinc is the negative electrode
Zinc electrode becomes smaller
Copper electrode: Cu^{2+} ions from the electrolyte ($CuSo_4$) take up electrons to form copper metal
Copper is the positive electrode
Reddish brown copper is formed
In a simple cell, the flow of electrons is always from the more reactive metal to the less reactive metal. The more reactive metal becomes the negative electrode and the less reactive metal the positive electrode.