Applied Chemistry

Electrochemistry — Redox Reactions, Electrolysis and Electrochemical Cells

1. Electronic Concept of Oxidation, Reduction and Redox Reactions

The modern, electronic concept of oxidation and reduction defines these processes in terms of the transfer of electrons between reacting species, providing a more general and unified explanation than the older definitions based solely on the gain or loss of oxygen or hydrogen.

Process	Electronic Definition	Example
Oxidation	Loss of one or more electrons by an atom, ion, or molecule	$Fe^{2+} \rightarrow Fe^{3+} + e^-$
Reduction	Gain of one or more electrons by an atom, ion, or molecule	$Cu^{2+} + 2e^- \rightarrow Cu$
Redox Reaction	A reaction in which oxidation and reduction occur simultaneously, with electrons transferred from the species being oxidised to the species being reduced	$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ (Zn is oxidised, Cu^{2+} is reduced)

Since oxidation (loss of electrons) and reduction (gain of electrons) must always occur together in any single chemical reaction, such reactions are collectively called redox (reduction-oxidation) reactions. In a redox reaction, the substance that loses electrons and gets oxidised is called the reducing agent (since it causes reduction of the other species), while the substance that gains electrons and gets reduced is called the oxidising agent (since it causes oxidation of the other species).

For example, in the reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, the zinc atom loses two electrons and is oxidised to Zn^{2+} (zinc acts as the reducing agent), while the copper ion gains those two electrons and is reduced to metallic copper (Cu^{2+} acts as the oxidising agent).

2. Electrolytes and Non-Electrolytes

Substances are classified as electrolytes or non-electrolytes, based on their ability to conduct an electric current when molten or dissolved in a suitable solvent, and to undergo chemical decomposition in the process:

Term	Definition	Examples

Electrolyte	A substance which, in its molten state or when dissolved in a suitable solvent (usually water), ionises (or dissociates into ions) and thereby conducts an electric current, undergoing chemical decomposition in the process	Sodium chloride (NaCl), dilute sulphuric acid (H_2SO_4), copper sulphate solution ($CuSO_4$)
Non-Electrolyte	A substance which, even when dissolved in a solvent or melted, does not ionise, and therefore does not conduct an electric current	Sugar (sucrose) solution, glucose solution, pure alcohol

Electrolytes are further classified as strong electrolytes (which ionise almost completely in solution, such as strong acids, strong bases, and most salts) and weak electrolytes (which ionise only partially in solution, such as acetic acid and ammonium hydroxide).

3. Faraday's Laws of Electrolysis

Faraday's laws of electrolysis describe the quantitative relationship between the quantity of electric charge passed through an electrolyte during electrolysis and the amount of chemical change (mass of substance liberated at an electrode) produced.

Law	Statement
Faraday's First Law of Electrolysis	The mass of a substance liberated (deposited or dissolved) at an electrode during electrolysis is directly proportional to the quantity of electric charge (current × time) passed through the electrolyte: $m \propto Q$, i.e., $m = Z I t$, where Z is the electrochemical equivalent of the substance.
Faraday's Second Law of Electrolysis	When the same quantity of electric charge is passed through different electrolytes connected in series, the masses of different substances liberated at the respective electrodes are directly proportional to their chemical equivalent weights: $m_1/E_1 = m_2/E_2$ (for the same quantity of charge passed).

Faraday's first law is expressed mathematically as $m = Z I t$, where m is the mass of the substance liberated (in grams), I is the current passed (in amperes), t is the time for which the current is passed (in seconds), and Z is the electrochemical equivalent of the substance (the mass of the substance liberated by the passage of one coulomb of charge).

The electrochemical equivalent Z of a substance is related to its chemical equivalent weight E by the relation $Z = E / F$, where F is the Faraday constant, equal to approximately 96,500 coulombs per mole of electrons (the quantity of charge required to liberate one gram-equivalent of any substance during electrolysis).

Worked Example 1:

A current of 2 A is passed through a solution of copper sulphate for 30 minutes. Calculate the mass of copper deposited at the cathode. (Electrochemical equivalent of copper, Z = 0.000329 g/C)

Solution: Time, $t = 30 \times 60 = 1800$ s. Using $m = Z I t$: $m = 0.000329 \times 2 \times 1800 = 1.1844$ g. Therefore, approximately 1.18 g of copper is deposited at the cathode.

Worked Example 2:

In an electrolysis experiment, the same quantity of electric charge is passed through solutions of silver nitrate and copper sulphate connected in series. If 1.08 g of silver (equivalent weight 108) is deposited, calculate the mass of copper (equivalent weight 31.75) deposited in the other cell.

Solution: By Faraday's second law, $m(Ag)/E(Ag) = m(Cu)/E(Cu)$. So, $1.08/108 = m(Cu)/31.75$. Therefore, $m(Cu) = (1.08/108) \times 31.75 = 0.01 \times 31.75 = 0.3175$ g. The mass of copper deposited is approximately 0.318 g.

4. Elementary Concept of pH and Buffer

4.1 pH

The pH of a solution is a numerical scale used to express the concentration of hydrogen ions (H^+) present in the solution, and hence to indicate the degree of acidity or basicity (alkalinity) of the solution. The pH scale conventionally ranges from 0 to 14, with lower values indicating greater acidity and higher values indicating greater basicity, as summarised below:

Type of Solution	pH Range	Nature
Strongly acidic solution	0 – 3	Highly acidic
Weakly acidic solution	3 – 6.9	Mildly acidic
Neutral solution	7 (approximately, at 25°C)	Neither acidic nor basic (e.g. pure water)
Weakly basic (alkaline) solution	7.1 – 11	Mildly basic
Strongly basic (alkaline) solution	11 – 14	Highly basic

A pH value of exactly 7 (at 25°C) represents a neutral solution, such as pure water, in which the concentration of hydrogen ions and hydroxide ions are exactly equal.

4.2 Buffer Solution

A buffer solution is a solution that resists a significant change in its pH when a small amount of acid or base is added to it, or when it is diluted. Buffer solutions are typically prepared from a mixture of a weak acid and its conjugate salt (formed with a strong base), or a weak base and its conjugate salt (formed with a strong acid), which together allow the solution to neutralise small additions of either acid or base, keeping the pH of the solution relatively stable.

Buffer solutions are of considerable practical importance, for example, in maintaining the nearly constant pH of blood and other biological fluids within the human body, and in numerous industrial and laboratory processes where a stable pH must be maintained for the process or reaction to proceed correctly.

5. Industrial Applications of Electrolysis

5.1 Electrometallurgy

Electrometallurgy refers to the extraction of highly reactive metals, such as sodium, aluminium, magnesium, and calcium, from their molten ores or compounds by the process of electrolysis. Since such reactive metals cannot be extracted by ordinary chemical reduction methods (such as reduction with carbon), electrolysis of the molten compound is used instead, in which the metal ions are reduced (gain electrons) and deposited at the cathode, while the corresponding non-metal ions are oxidised (lose electrons) at the anode. The extraction of aluminium from molten alumina (dissolved in cryolite) by the Hall-Héroult process, discussed earlier under metallurgy, is a well-known example of electrometallurgy.

5.2 Electroplating

Electroplating is the process of depositing a thin, uniform, and adherent layer of one metal (such as chromium, nickel, silver, gold, or zinc) onto the surface of another metal object, using electrolysis, in order to improve the appearance, corrosion resistance, or wear resistance of the underlying object.

In electroplating, the object to be plated is made the cathode, and a piece (or plate) of the metal to be deposited is made the anode, both being immersed in an electrolyte solution containing ions of the metal to be deposited. On passing an electric current, metal ions from the solution are reduced and deposited as a thin metallic layer on the surface of the cathode (the object being plated), while, in many arrangements, the anode dissolves to continuously replenish the metal ions in the electrolyte solution.

5.3 Electrolytic Refining

Electrolytic refining is an industrial process used to purify an impure (crude) metal, obtained from earlier stages of metallurgical extraction, by electrolysis, in order to obtain the metal in a very high state of purity. In this process, a slab of the impure metal is made the anode, while a thin sheet of pure metal is made the cathode, both being immersed in a suitable electrolyte solution containing ions of the metal being refined.

On passing an electric current, the impure metal at the anode dissolves into the electrolyte solution as metal ions, while an equivalent amount of pure metal ions from the solution are simultaneously reduced and deposited onto the cathode, building up a layer of high-purity metal. Less reactive impurities present in the original impure metal do not dissolve and instead settle beneath the anode as a residue called anode mud (or anode slime), which is collected separately and, in the case of metals such as copper, is itself often a valuable source of precious metal by-products. This method is widely used for the refining of copper, silver, gold, and several other metals.

6. Application of Redox Reactions in Electrochemical Cells

An electrochemical cell is a device that converts the chemical energy released by a spontaneous redox reaction directly into electrical energy (in the case of a galvanic or voltaic cell), or, conversely, uses electrical energy to drive a non-spontaneous redox reaction (in the case of an electrolytic cell). Electrochemical cells used to generate electrical energy for practical use are broadly classified as primary cells, secondary cells, and other specialised devices such as fuel cells and solar cells, described below.

Cell	Type	Basic Reaction / Composition	Application
Dry Cell (Leclanché Cell)	Primary Cell (non-rechargeable)	Zinc container as anode, a central carbon rod as cathode, surrounded by a moist paste of ammonium chloride and manganese dioxide as the electrolyte and depolariser	Torches, remote controls, clocks, toys, and other small, low-drain portable electronic devices
Lead Storage Battery (Lead-Acid Battery)	Secondary Cell (rechargeable)	Lead (Pb) as anode, lead dioxide (PbO2) as cathode, with dilute sulphuric acid as the electrolyte; can be recharged by passing current in the reverse direction	Automobile batteries (starting, lighting, ignition), backup power supplies (UPS/inverters)
Fuel Cell	Continuous-supply electrochemical cell	Combines a fuel (commonly hydrogen) with an oxidant (oxygen), continuously supplied, to directly generate electricity	Spacecraft power generation, and increasingly in fuel-cell electric vehicles

		through a redox reaction, producing water as a by-product (in the case of a hydrogen fuel cell)	and stationary/backup power generation
Solar Cell (Photovoltaic Cell)	Photovoltaic energy conversion device	A semiconductor device (typically silicon-based) that directly converts light energy from the Sun into electrical energy through the photovoltaic effect, without an intervening chemical redox reaction as in batteries	Solar power generation for homes, streetlights, satellites, and remote/off-grid electrical power applications

Primary cells, such as the common dry cell, are designed for one-time use, since the redox reaction that generates electricity within them is not easily reversible, and the cell must be discarded once its chemical reactants are exhausted. Secondary cells, such as the lead storage battery, in contrast, can be recharged repeatedly by passing an electric current through them in the reverse direction, which drives the redox reaction backwards and restores the original chemical reactants, allowing the cell to be reused many times over its working life.

Fuel cells differ from conventional batteries in that the reactants (fuel and oxidant) are continuously supplied from an external source, rather than being stored within the cell itself, allowing a fuel cell to generate electricity continuously for as long as fuel and oxidant continue to be supplied. Solar cells, meanwhile, operate on an entirely different principle from the other cells discussed here, converting light energy directly into electrical energy through the photovoltaic effect in a semiconductor material, without relying on a chemical redox reaction at all.

7. Multiple Choice Questions (MCQs)

Answer the following questions by selecting the most appropriate option.

1. According to the electronic concept, oxidation is defined as:

A) Gain of electrons
B) Loss of electrons
C) Gain of protons
D) Loss of protons

2. According to the electronic concept, reduction is defined as:

A) Loss of electrons
B) Gain of electrons
C) Loss of protons

D) Gain of protons

3. In a redox reaction, the species that loses electrons is called the:

A) Oxidising agent
B) Reducing agent
C) Catalyst
D) Electrolyte

4. In a redox reaction, the species that gains electrons is called the:

A) Reducing agent
B) Oxidising agent
C) Catalyst
D) Non-electrolyte

5. An electrolyte is a substance that, in molten or dissolved form:

A) Does not conduct electricity
B) Ionises and conducts an electric current, undergoing chemical decomposition
C) Remains completely un-ionised
D) Only conducts heat, not electricity

6. Sugar solution is an example of a:

A) Strong electrolyte
B) Weak electrolyte
C) Non-electrolyte
D) Molten electrolyte

7. According to Faraday's first law of electrolysis, the mass of substance liberated at an electrode is directly proportional to:

A) The resistance of the circuit
B) The quantity of electric charge passed
C) The temperature of the electrolyte alone
D) The colour of the electrolyte

8. According to Faraday's second law of electrolysis, for the same quantity of charge passed through different electrolytes in series, the masses of substances liberated are proportional to their:

A) Densities
B) Chemical equivalent weights
C) Boiling points
D) Colours

9. The pH scale ranges from:

A) 0 to 7
B) 0 to 14
C) 1 to 10

D) −10 to 10

10. A solution with a pH value less than 7 is:

A) Basic
B) Acidic
C) Neutral
D) A buffer only

11. A buffer solution is best described as a solution that:

A) Has a pH that changes drastically with small additions of acid or base
B) Resists significant changes in pH on the addition of small amounts of acid or base
C) Is always strongly acidic
D) Contains no dissolved ions

12. Electrometallurgy refers to the industrial application of electrolysis for:

A) Coating one metal with another
B) Extraction of reactive metals from their molten ores or compounds
C) Measuring the pH of a solution
D) Manufacturing plastics

13. Electroplating is an industrial application of electrolysis used mainly to:

A) Extract a metal from its ore
B) Deposit a thin, protective, or decorative layer of one metal onto another
C) Measure the pH of a solution
D) Generate electricity

14. In electrolytic refining of a metal, the impure metal is generally made the:

A) Cathode
B) Anode
C) Electrolyte
D) Salt bridge

15. The lead storage battery, commonly used in automobiles, is an example of a:

A) Primary cell
B) Secondary (rechargeable) cell
C) Fuel cell
D) Solar cell

16. A dry cell (Leclanché cell) is an example of a:

A) Secondary cell
B) Primary (non-rechargeable) cell
C) Fuel cell
D) Solar cell

17. A fuel cell generates electricity by:

A) Converting sunlight directly into electricity

B) A continuous redox reaction between a fuel (such as hydrogen) and an oxidant (such as oxygen)
C) Discharging a pre-charged solid electrode
D) Simple mechanical rotation

18. A solar (photovoltaic) cell converts:
A) Chemical energy into electrical energy
B) Light energy directly into electrical energy
C) Heat energy into electrical energy only
D) Electrical energy into light energy

Answer Key

1. B) Loss of electrons | 2. B) Gain of electrons | 3. B) Reducing agent | 4. B) Oxidising agent | 5. B) Ionises and conducts an electric current, undergoing chemical decomposition | 6. C) Non-electrolyte | 7. B) The quantity of electric charge passed | 8. B) Chemical equivalent weights | 9. B) 0 to 14 | 10. B) Acidic | 11. B) Resists significant changes in pH on the addition of small amounts of acid or base | 12. B) Extraction of reactive metals from their molten ores or compounds | 13. B) Deposit a thin, protective, or decorative layer of one metal onto another | 14. B) Anode | 15. B) Secondary (rechargeable) cell | 16. B) Primary (non-rechargeable) cell | 17. B) A continuous redox reaction between a fuel (such as hydrogen) and an oxidant (such as oxygen) | 18. B) Light energy directly into electrical energy

8. Broad / Long Answer and Numerical Questions

1. Explain the electronic concept of oxidation and reduction, giving a suitable example of each.

2. Define a redox reaction, and explain, with a suitable example, how oxidation and reduction occur simultaneously in such a reaction.

3. Define electrolyte and non-electrolyte, giving two examples of each.

4. State Faraday's first and second laws of electrolysis.

5. A current of 2 A is passed through a solution of copper sulphate for 30 minutes. Calculate the mass of copper deposited at the cathode. (Electrochemical equivalent of copper, Z = 0.000329 g/C)

6. In an electrolysis experiment, the same quantity of electric charge is passed through solutions of silver nitrate and copper sulphate connected in series. If 1.08 g of silver

(equivalent weight 108) is deposited, calculate the mass of copper (equivalent weight 31.75) deposited in the other cell.

7. Explain the concept of pH, and describe how the pH scale indicates whether a solution is acidic, neutral, or basic.

8. Explain the concept of a buffer solution, and state its general significance in maintaining a stable pH.

9. Describe the industrial applications of electrolysis in electrometallurgy, electroplating, and electrolytic refining, giving a brief explanation of each process.

10. Explain the working principle and applications of a dry cell (primary cell) and a lead storage battery (secondary cell), and briefly describe fuel cells and solar cells as further examples of electrochemical energy conversion devices.