V.N. Karazin Kharkiv National University

Medical Chemistry

Module 2. Lecture 5

Electrochemistry. Physicochemical fundamentals of colloidal systems

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Lecture topics. Part I

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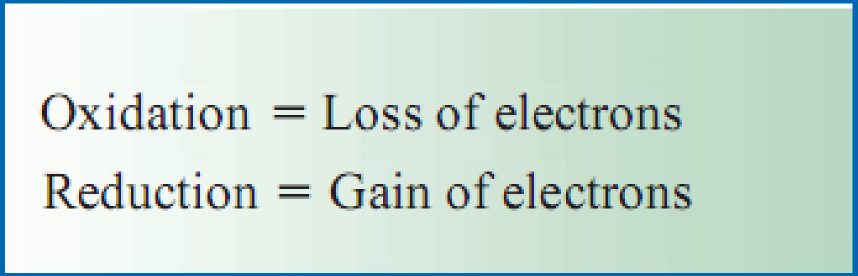
Electrochemistry: basic concepts

One form of energy that has tremendous practical significance is *electrical energy*. The area of chemistry that deals with ***the interconversion of electrical energy and chemical energy is electrochemistry***.



Oxidation = Loss of electrons

Reduction = Gain of electrons

Electrochemical processes are redox (oxidation-reduction) reactions in which the energy released by a spontaneous reaction **is converted to electricity** or **in which electricity is used to drive a nonspontaneous chemical reaction**. The latter type is called *electrolysis*.

A galvanic or voltaic cell*

A galvanic or voltaic cell *is a device that converts the energy released in a spontaneous chemical reaction into electrical energy.*

A battery *is a device consisting of one or more cells that can produce a direct current by converting chemical energy to electrical energy.*

A galvanic or voltaic cell consists essentially of two electrodes (half cells). *Each electrode* involves an electronic (metallic) and an electrolytic conductor in contact.

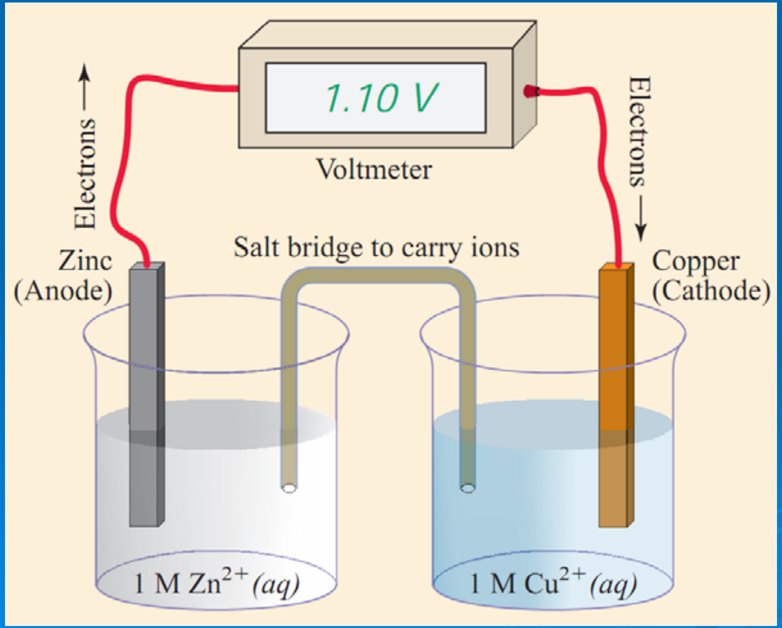


Figure. A laboratory galvanic cell.
As this galvanic cell operates, a reddish coating of impure copper metal begins to appear on the surface of the copper cathode. The overall equation for the reaction is given below

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$$

* is called a galvanic cell or voltaic cell, after the Italian scientists Luigi Galvani and Alessandro Volta, who constructed early versions of the device

A galvanic or voltaic cell

At the surface of separation between the metal and the solution there exists a difference of electrical potential, called ***the electrode potential***.

The algebraic difference of the two electrode potentials equals to the ***electromotive force (EMF) of the cell*** (is expressed in the unit called volt (V)).

A half-reaction is a type of chemical equation that shows the electrons either lost or gained.

The oxidation half-reaction shows the reactant that loses electrons, and the electrons appear on the product side of the equation.

The reduction half-reaction shows the reactant that gains electrons, and the electrons appear on the reactant side of the equation.

A galvanic cell always involves two half-reactions: one oxidation and the other reduction.

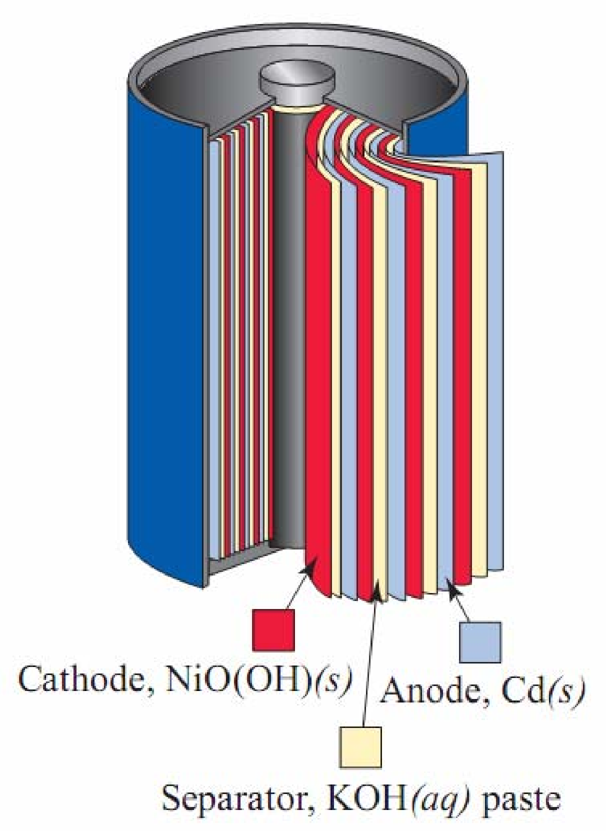
Nickel–Cadmium (NiCad) galvanic cell

A simplified version of the reaction that takes place in a nickel–cadmium (NiCad) battery

Oxidation half-reaction: $\mathrm{Cd} \longrightarrow \mathrm{Cd}^{2+} + 2\,e^-$

Reduction half-reaction: $2\,\mathrm{Ni}^{3+} + 2\,e^- \longrightarrow 2\,\mathrm{Ni}^{2+}$

Overall cell reaction: $2\,\mathrm{Ni}^{3+} + \mathrm{Cd} \longrightarrow 2\,\mathrm{Ni}^{2+} + \mathrm{Cd}^{2+}$



<ins>**The anode**</ins> is the electrode where oxidation takes place.

<ins>**The cathode**</ins> receives the electrons sent from the anode through the external circuit.

The NiCad battery is rechargeable, an important characteristic for consumer use.

$$\mathrm{Cd}(s) + 2\,\mathrm{NiO(OH)}(s) + 2\,\mathrm{H_2O}(l) \xrightleftharpoons[\text{recharging}]{\text{discharging}} 2\,\mathrm{Ni(OH)_2}(s) + \mathrm{Cd(OH)_2}(s)$$

Figure. A NiCad galvanic cell in which Cd is oxidized at the anode, and Ni^{3+} is reduced at the cathode

Some Common Batteries

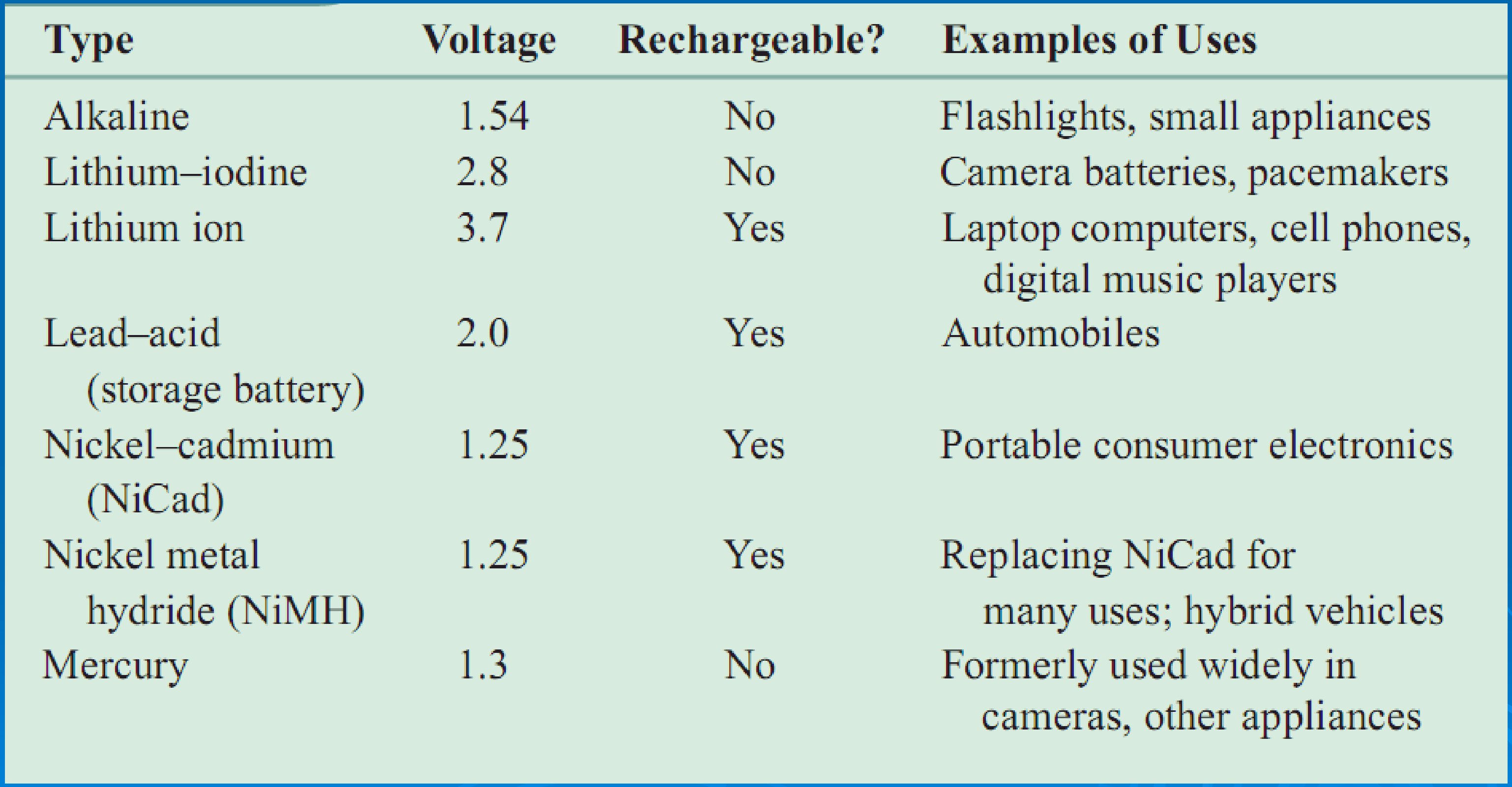
Almost everyone has used an alkaline battery such as one of those shown in Figure.

The overall cell reaction is the sum of the two half-reactions:

$$Zn(s) + 2\ MnO_2(s) + H_2O(l) \longrightarrow Zn(OH)_2(s) + Mn_2O_3(s)$$

Figure. These AAA to D alkaline cells all produce 1.54 V, but the larger cells can sustain the transfer of electrons through the external circuit for a longer time

Some Common Galvanic Cells



Type	Voltage	Rechargeable?	Examples of Uses
Alkaline	1.54	No	Flashlights, small appliances
Lithium–iodine	2.8	No	Camera batteries, pacemakers
Lithium ion	3.7	Yes	Laptop computers, cell phones, digital music players
Lead–acid (storage battery)	2.0	Yes	Automobiles
Nickel–cadmium (NiCad)	1.25	Yes	Portable consumer electronics
Nickel metal hydride (NiMH)	1.25	Yes	Replacing NiCad for many uses; hybrid vehicles
Mercury	1.3	No	Formerly used widely in cameras, other appliances

A galvanic or voltaic cell

During the operation of a galvanic cell **a chemical reaction** takes place at each electrode, and it is the energy of these reactions that provides the electrical energy of the cell.

In some cells, however, there is no resultant chemical reaction, but there is a change of energy due to the transfer of solute from the solution with one concentration to another; such cells are called ***concentration cells***:

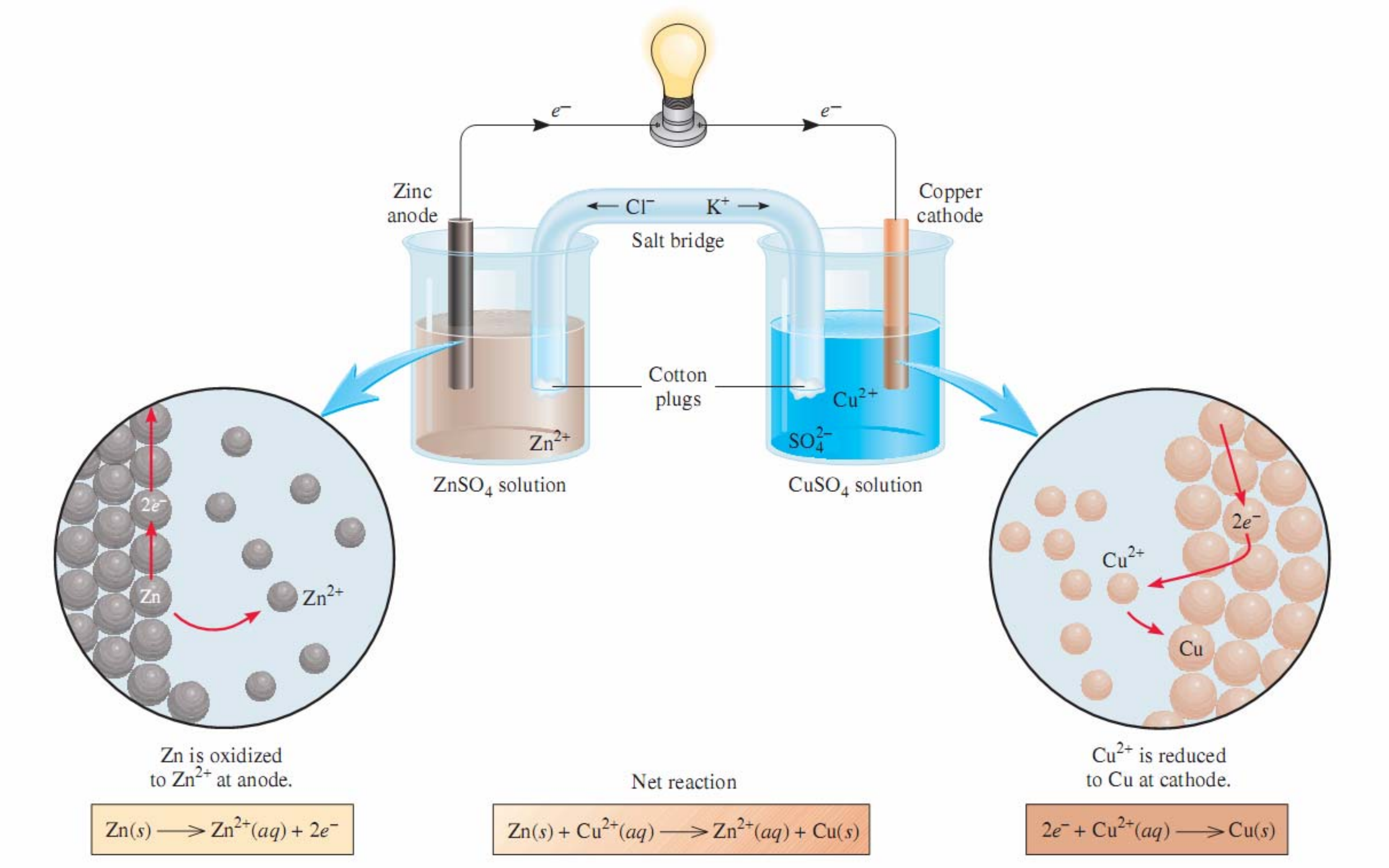
$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(0.10\,M)\,\|\,\mathrm{Zn}^{2+}(1.0\,M)\,|\,\mathrm{Zn}(s)$$

$$\text{Overall:}\qquad Zn^{2+}(1.0\,M) \longrightarrow \mathrm{Zn}^{2+}(0.10\,M)$$

The Daniell cell

An instance of a reversible cell is *the Daniell cell*, consisting of a zinc electrode immersed in an aqueous solution of zinc sulfate, and a copper electrode in copper sulfate solution, i.e.,

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \mid\mid \mathrm{CuSO_4} \mid \mathrm{Cu}$$



Zn is oxidized to Zn^{2+} at anode.

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

Net reaction

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Cu^{2+} is reduced to Cu at cathode.

$2e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$

A galvanic or voltaic cell

To complete the electrical circuit, the solutions must be connected by a conducting medium through which the cations and anions can move from one electrode compartment to the other.

This requirement is satisfied by **a salt bridge**, which, in its simplest form, is an inverted U tube containing an inert electrolyte solution, such as KCl or NH_4NO_3, whose ions will not react with other ions in solution or with the electrodes (see Figure above).

During the course of the overall redox reaction, electrons flow externally from the anode (Zn electrode) through the wire to the cathode (Cu electrode). In the solution, the cations (Zn^{2+}, Cu^{2+}, and K^+) move toward the cathode, while the anions (SO_4^{2-} and Cl^-) move toward the anode.

A galvanic or voltaic cell

The conventional notation for representing galvanic cells is *the cell diagram*. For the Daniell cell shown in Figure above, if we assume that the concentrations of Zn^{2+} and Cu^{2+} ions are 1 M, the cell diagram is

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(1\ M)\,\|\,\mathrm{Cu}^{2+}(1\ M)\,|\,\mathrm{Cu}(s)$$

The single vertical line represents **a phase boundary**. For example, the zinc electrode is a solid and the Zn^{2+} ions (from $ZnSO_4$) are in solution. Thus, we draw a line between Zn and Zn^{2+} to show the phase boundary. **The double vertical lines** denote **the salt bridge**.

*By convention, **the anode is written first**, to the left of the double lines and the other components appear in the order in which we would encounter them in moving from the anode to the cathode.*

The Nernst equation

All types of reversible electrode are made up from the reduced and oxidized states of a given system, and in every case the electrode reaction may be written in the general form: Oxidized State + $z\bar{e}$ $\Leftrightarrow$ Reduced State

or in a brief form: Ox^{z+} + $z\bar{e}$ $\Leftrightarrow$ Red,

where *z* is the number of electrons by which the oxidized and reduced states differ. In general the potential of reversible electrode is given by the *Nernst equation*:

$$\varphi = \varphi^o + \frac{RT}{zF}\ln\frac{a_{\mathrm{Ox}^{z+}}}{a_{\mathrm{Red}}}$$

where $a_{\mathrm{Ox}^{z+}}$, a_{Red} – activities or concentrations of oxidized and reduced states, respectively, that must be raised to the power of the number of its molecules taking part in the electrode reaction; φ^o – standard electrode potential, that is, the potential of the electrode when all the substances concerned are in their standard states of unit activity.

The EMF of the cell

The electromotive force (*EMF*) *of the cell* is equal to the difference between the potentials of electrodes:

$$E = \varphi_+ - \varphi_-$$

where φ_+ and φ_- – potentials of positive and negative electrodes, respectively. According to the convention widely adopted, the EMF of the cell is positive when in its normal operation oxidation takes place at the left-hand electrode (negative electrode) of the cell as written, reduction occurring at the right-hand electrode (positive electrode).

The EMF of a cell depends not only ***on the nature of the electrodes*** and the ions, but also ***on the concentrations of the ions and the temperature*** at which the cell is operated.

The types of electrodes

The first type of electrode involves a metal in contact with a solution of its own ions, e.g., zinc in zinc sulfate solution, or copper in copper sulfate solution, as in the Daniell cell:

$Zn \mid Zn^{2+}$(solution), $Cu \mid Cu^{2+}$(solution).

Electrodes of the first type are reversible with respect to the ions of the electrode material. If the electrode material is a metal, represented by Me, with valence that equals to *z*, the reaction which takes place at such an electrode, when the cell of which it is part operates, is then: $\boxed{Me^{z+} + z\bar{e} \rightarrow Me,}$

where $\bar{e}$ denotes an electron, and Me^{z+} implies a solvated ion in solution. The direction of the reaction depends on the direction of the flow of current through the cell.

The types of electrodes

The potential of electrodes of this kind depends on the concentration (or activity) of the reversible ions in the solution:

$$\varphi = \varphi^{o} + \frac{RT}{zF}\ln\frac{a_{\mathrm{Me}^{z+}}}{a_{\mathrm{Me}}} = \boxed{\varphi^{o} + \frac{RT}{zF}\ln a_{\mathrm{Me}^{z+}}}$$

where φ^{o} – standard electrode potential; $a_{\mathrm{Me}^{z+}}$ – activity of Me^{z+} ions in solution; a_{Me} – activity of solid metal, this value is taken as unity.

Electrodes of ***the second type*** involve a metal and a sparingly soluble salt of this metal in contact with a solution of a soluble salt of the same anion.

The types of electrodes

An example is silver-silver chloride electrode consisting of silver, solid silver chloride and a solution of a soluble chloride, such as hydrochloric acid:

Ag | AgCl (solid) | HCl (solution)

The electrode reaction in this case may be written as

$$AgCl + \bar{e} \rightarrow Ag + Cl^-,$$

it's potential is given by the Nernst equation:

$$\varphi = \varphi^o + \frac{RT}{F}\ln\frac{a_{AgCl}}{a_{Ag}\cdot a_{Cl^-}} = \boxed{\varphi^o - \frac{RT}{F}\ln a_{Cl^-}}$$

where φ^o – standard electrode potential; a_{Cl^-} – activity of chloride ions in solution; a_{Ag} and a_{AgCl} – activity of solid substances, these values are conventionally taken as unity.

The types of electrodes

Electrodes of a special type are electrodes that are called ***gas electrodes***. They may be reversible with respect to cations (hydrogen electrode) or anions (oxygen and the chlorine electrodes). The most important of these electrodes is ***the hydrogen gas electrode***.

The hydrogen electrode, shown in Figure below, serves as the reference for this purpose. Hydrogen gas (H_2) is bubbled into a hydrochloric acid (HCl) solution at 25°C. The platinum electrode has two functions. First, it provides a surface on which the dissociation of hydrogen molecules can take place:

$$\mathrm{H_2} \longrightarrow 2\mathrm{H}^+ + 2e^-$$

Second, it serves as an electrical conductor to the external circuit.

The hydrogen electrode

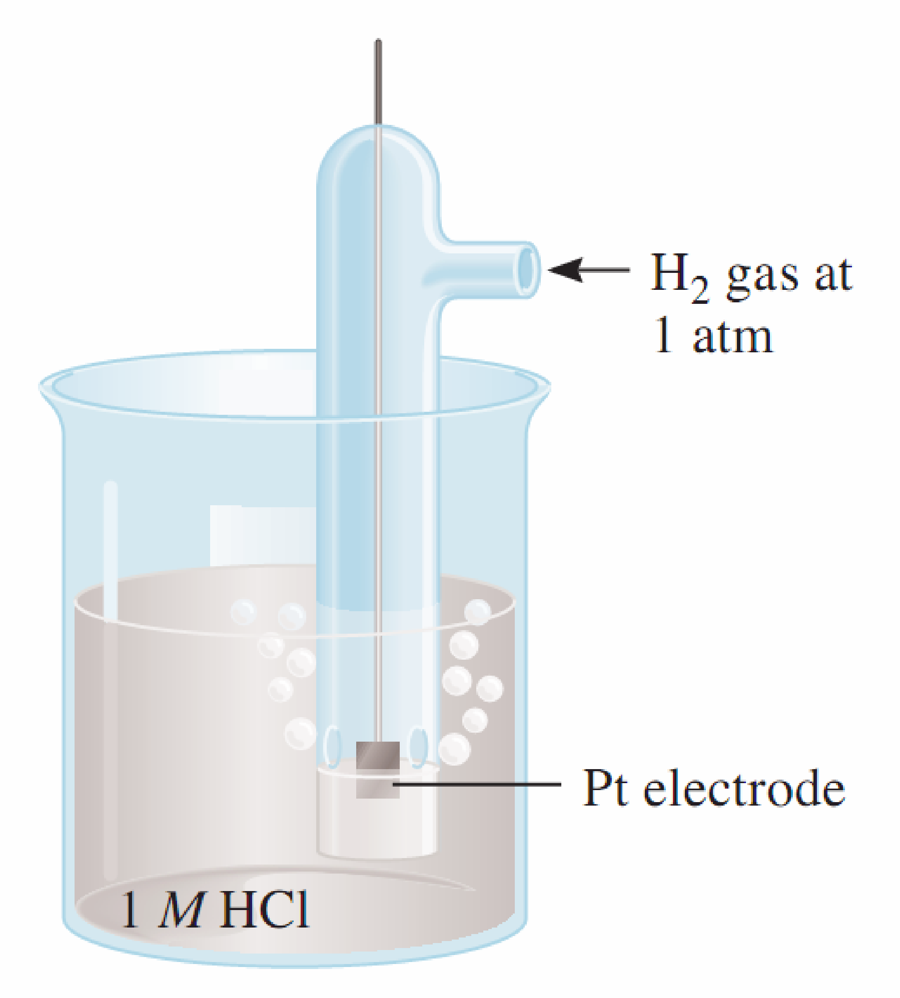


Figure. A hydrogen electrode operating under standard-state conditions. Hydrogen gas at 1 atm is bubbled through a 1 M HCl solution. The platinum electrode is part of the hydrogen electrode.

It may be schematically written as:
Pt | H_2 (gas) | H^+ (solution)

The hydrogen electrode

The potential of hydrogen electrode is given by the equation:

$$\varphi = \varphi^{o} + \frac{RT}{2F}\ln\frac{a_{\mathrm{H}^+}^{2}}{p_{\mathrm{H}_2}} = \boxed{\frac{RT}{F}\ln\frac{a_{\mathrm{H}^+}}{p_{\mathrm{H}_2}^{1/2}}}$$

where φ^{o} – *standard electrode potential, this value of hydrogen electrode is equal to zero by the convention*; value a_{H^+} – activity hydrogen ions in solution; p_{H_2} – pressure of gaseous hydrogen.

The superscript “°” denotes standard-state conditions, and value φ^{o} is the standard reduction potential, or the voltage associated with a reduction reaction at an electrode when all solutes are 1 M and all gases are at 1 atm.

Standard reduction potential

It is impossible to measure the potential of just a single electrode, but *if we arbitrarily set the potential value of a particular electrode at zero*, we can use it to determine the relative potentials of other electrodes.

Thus, the ***standard reduction potential of the hydrogen electrode is defined as zero***. The hydrogen electrode is called the standard hydrogen electrode (SHE).

Under standard-state conditions (when the pressure of H_2 is 1 atm and the concentration of the HCl solution is 1 M), the potential for the reduction of H^+ at 25°C is taken to be exactly zero $\varphi^o = 0$:

$$2H^+(1\ M) + 2e^- \longrightarrow H_2(1\ \text{atm})$$

The types of electrodes

Next of important type of electrode (*oxidation-reduction electrodes*) consists of on unattackable metal, e.g., gold or platinum, immersed in a solution containing both oxidized and reduced states of an oxidation-reduction system, e.g., Sn^{4+} and Sn^{2+}, Fe^{3+} and Fe^{2+}, or $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$.

The purpose of the unattackable metal is to act as a conductor for making electrical contact, just as in the case of a gas electrode.

The oxidized and reduced states are not necessarily ionic; for example, an important type of electrode is the *quinhydrone electrode*.

It involves the organic compound quinone, together with hydrogen ions, as the oxidized state, while the neutral molecule hydroquinone is the reduced state.

The types of electrodes

Electrodes of the kind under consideration, consisting of conventional oxidized and reduced forms, are sometimes called *oxidation-reduction electrodes.*

The chemical reactions taking place at these electrodes are either oxidation of the reduced state or reduction of the oxidized state, e.g.

$$Sn^{4+} + 2e \Leftrightarrow Sn^{2+},$$

$$C_6H_4O_2 + 2H^+ + 2e \Leftrightarrow C_6H_4(OH)_2,$$

Corresponding electrode potential are given by the equations:

$$\varphi = \boxed{\varphi^o + \frac{RT}{F}\ln\frac{a_{Sn^{4+}}}{a_{Sn^{2+}}}}$$

$$\varphi = \varphi^o + \frac{RT}{2F}\ln\frac{a^2_{H^+}a_{Hq}}{a_Q} = \boxed{\varphi^o + \frac{RT}{F}\ln a_{H^+}}$$

where a_{Hq} , a_Q – activities of hydroquinone and quinone in solution, correspondingly, these two values are equal so their ratio is unity.

The quinhydrone electrode

The quinhydrone electrode potential is evidently *dependent on the hydrogen ion activity* (concentration) of the solution, and hence it offers possibilities for the determination of the latter.

For this purpose a small quantity of the compound quinhydrone, which consists of equimolar amounts of quinone and hydroquinone, is dissolved in the solution. The ratio of the concentrations of these two substances is thus equal to unity, and if the ratio of the activities is taken as equal to the ratio of the concentrations, equal to unity. The electrode gives accurate results in solutions of pH less than 8; in more alkaline solutions errors arise, first, because of oxidation of the hydroquinone by oxygen of the air, and second, on account of the ionization of the hydroquinone as an acid.

The ion-selective electrodes

As an example of this kind of electrodes *the glass electrode* may be considered. *Glass electrode* is often used as an indicator electrode, because its potential depends on activity of hydrogen ions in solution.

Glass electrode represents a glass tube with thin-walled glass ball (glass membrane) on the end (Figure).

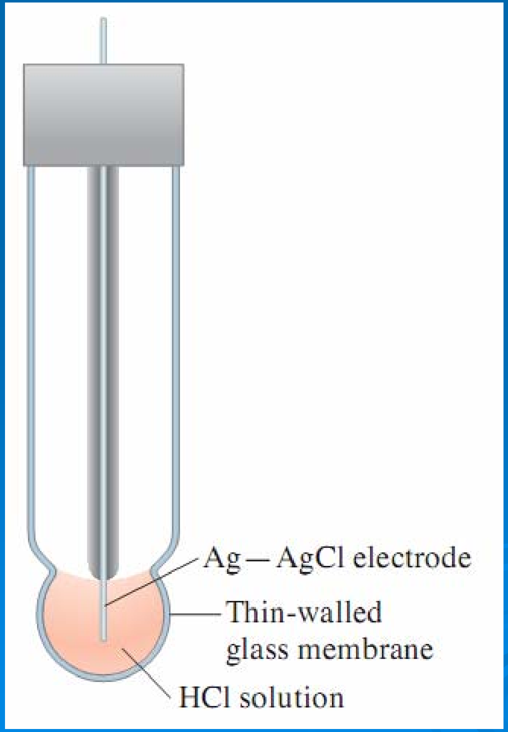


Figure. Glass electrode

The glass electrode

The inner part of glass electrode is an auxiliary electrode. It is immersed in solution with constant pH value, containing ion to which the auxiliary electrode is reversible. As an internal electrode silver-silver chloride or calomel electrodes are usually used, so hydrochloric acid or potassium chloride solution is used as internal solution. Auxiliary electrode is supplied by shunt.

The principle of glass electrode work is based on an exchange of alkaline metals ions (M^+), contained in structure of a glass, with hydrogen ions (H^+) in solution. This process may be represented by equilibrium equation:

$$H^{+(solution)} + M^{+(glass)} \rightleftarrows H^{+(glass)} + M^{+(solution)}$$

The glass electrode

Schematically glass electrode may be written as follows:

Ag | AgCl, HCl | glass membrane | H^+ (solution)

The potential of a glass electrode in the field of reversibility to H^+ is given by the Nernst equation:

$$\varphi = \varphi^0 \pm \frac{2.303RT}{F} \log a_{\mathrm{H}^+}^{solution} = \boxed{\varphi^0 \pm \theta \mathrm{pH}}$$

where φ^0 – standard potential of glass electrode; $\theta = \frac{2.303RT}{F}$, *R* – universal gas constant, 8.31 J/(mol·K); *T* – absolute temperature, K; *F* – Faraday number, 96485 coulombs/mol; the sign "+" or "–" depends on the glass type.

The standard potential of a glass electrode and its temperature change are defined by the type of internal electrode, internal solution, and a grade of glass.

Applications of electrode potentials

There are numerous applications of electrode potentials in various branches of chemistry.

The determination of any properties by measuring the EMF of a galvanic cell is known as a *potentiometric determination*. The most widely used potentiometric determinations are pH measurements and potentiometric titration.

Potentiometric measurements can also be used to determine various thermodynamic parameters of oxidation-reduction reactions. The most important of these is determination of the equilibrium constants for a reactions proceeding in the cell.

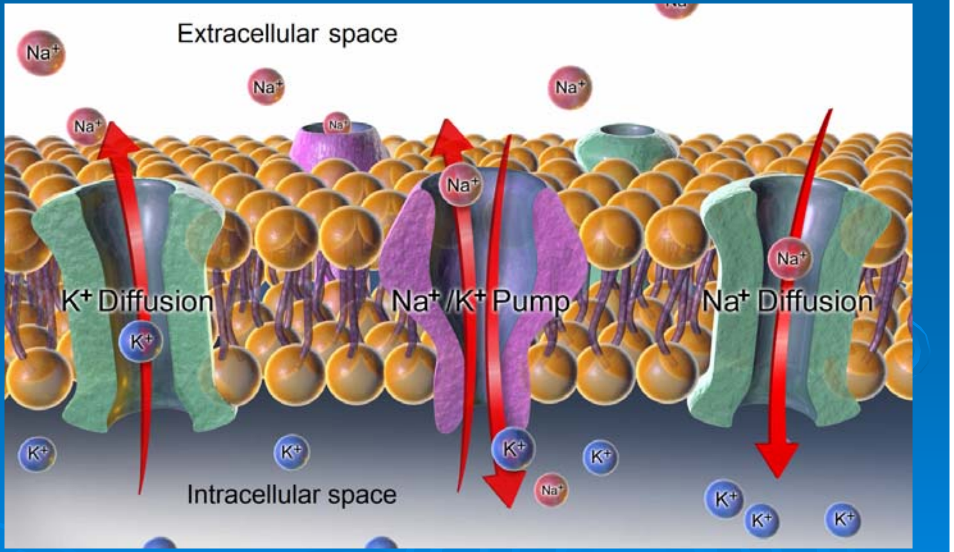
Biological concentration cells

A biological cell can be compared to a concentration cell for the purpose of calculating its membrane potential.

Membrane potential is the electric potential that exists across the membrane of various kinds of cells, including muscle cells and nerve cells.

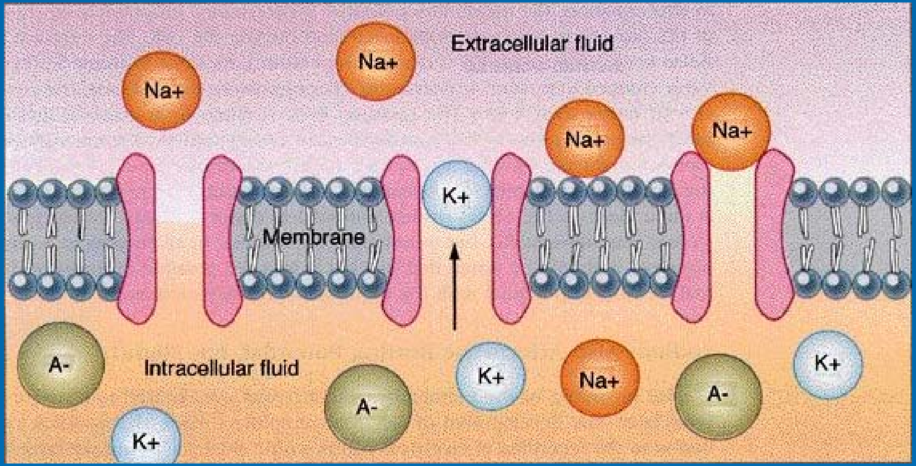
This potential is responsible for the propagation of nerve impulses and heartbeat.

A membrane potential is established whenever there are unequal concentrations of the same type of ion in the interior and exterior of a cell – and the membrane is permeable to the ion.



Biological concentration cells

For example, the concentrations of Na^+ ions in the interior and exterior of a nerve cell are $1.5 \cdot 10^{-2}$ M and $1.5 \cdot 10^{-1}$ M, respectively. Treating the situation as a concentration cell and applying the Nernst equation for a single ion, we can write:



$$E_{\mathrm{Na}^+} = E^{\circ}_{\mathrm{Na}^+} - \frac{0.0592\ \mathrm{V}}{1} \log \frac{[\mathrm{Na}^+]_{\mathrm{ex}}}{[\mathrm{Na}^+]_{\mathrm{in}}}$$

$$= -(0.0592\ \mathrm{V}) \log \frac{1.5 \times 10^{-1}}{1.5 \times 10^{-2}}$$

$$= 0.059\ \mathrm{V} \quad \text{or} \quad 59\ \mathrm{mV}$$

where the subscripts “ex” and “in” denote “exterior” and “interior,” respectively. We have set $E^{\circ}(Na^+) = 0$ because the same type of ion is involved. Thus, an electric potential of 59 mV exists across the membrane due to the unequal concentrations of Na^+ ions.

Biological concentration cells

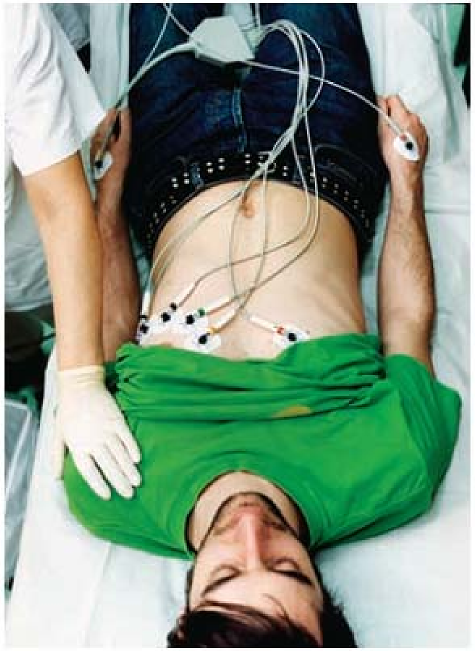
When a nerve cell is stimulated, there is a large change in the membrane permeability, decreasing the membrane potential temporarily to about 34 mV.

This sudden change in the potential is called *the action potential*. Once created, the action potential propagates along the nerve fiber until it reaches either a synaptic junction (the connection between nerve cells) or a neuromuscular junction (the connection between a nerve cell and a muscle cell).

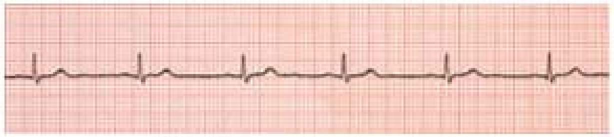
In the muscle cell of the heart, *an action potential is generated during the heartbeat*.

Biological concentration cells

This potential produces enough current to be detected by electrodes placed on the chest. The amplified signals can be recorded either on a moving chart or displayed on an oscilloscope. The record, called an electrocardiogram (ECG, also known as an EKG, where K is from the German word kardio for heart), is a valuable tool in the diagnosis of heart disease.



Patient with ECG electrodes



ECG strip

How electrochemistry can cause dental pain

Anyone who accidentally bites on a piece of aluminum foil in such a way that the foil touches an amalgam dental filling will experience a momentary sharp pain.

Historically, the material most commonly used to fill cavities is known as dental amalgam. (An amalgam is a substance made by combining mercury with one or more other metals.) Dental amalgam consists of liquid mercury mixed in roughly equal parts with an alloy powder containing silver, tin, copper, and sometimes smaller amounts of other metals such as zinc.

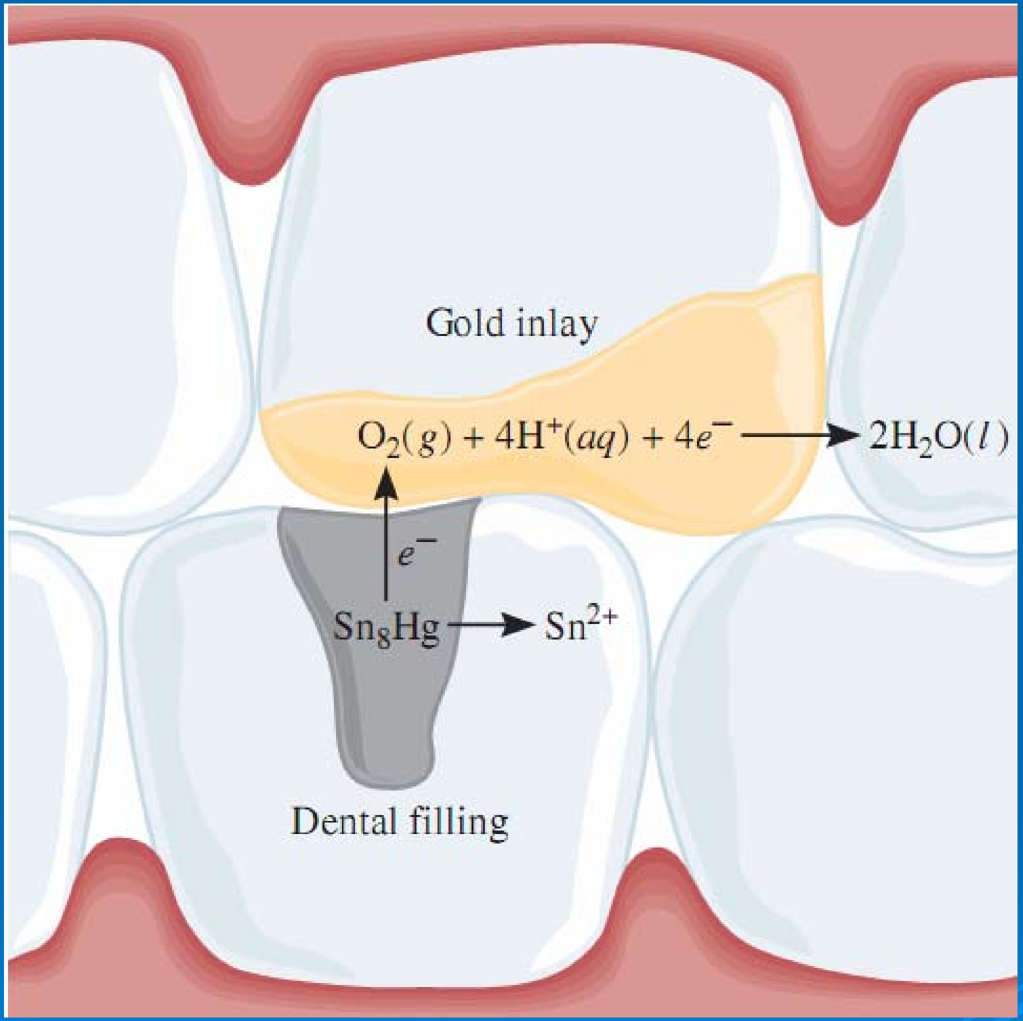
What happens is this: the aluminum and the dental filling act as electrodes in a galvanic cell. Aluminum acts as the anode, and the amalgam acts as the cathode. In effect, when the aluminum comes into contact with the amalgam, an electrochemical cell is established in the mouth, causing a current to flow. This current stimulates the nerve of the tooth, causing a very unpleasant sensation.

How electrochemistry can cause dental pain

The pain caused by having aluminum foil contact an amalgam dental filling results from the filling being made the cathode in an electrochemical cell. Another type of discomfort can result from the filling being made the anode in an electrochemical cell. This occurs when the filling touches a metal with a greater reduction potential than the components of the amalgam, such as gold. When an amalgam filling comes into contact with a gold inlay, the tin in the filling (the most easily oxidized of the major amalgam components) is oxidized – creating an unpleasant metallic taste in the mouth. A simplified, unbalanced equation for the redox reaction that takes place is:

$$\mathrm{Sn}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{Sn}^{2+}(aq) + \mathrm{H_2O}(l)$$

How electrochemistry can cause dental pain



Gold inlay touching amalgam dental filling

Lecture topics. Part II

√ The colloidal state
√ Classification of colloidal systems
√ Preparation of colloidal systems
√ Tyndall effect
√ The structure of colloidal particles
√ Purification of colloidal systems
√ Hemodialysis or kidney dialysis
√ The colloid stability
√ Coagulation of lyophobic colloidal systems
√ Coagulation threshold
√ Schultze-Hardy rule
√ Kinetic and aggregate stabilities of colloidal systems
√ Protective action
√ Flocculation
√ Introduction to blood coagulation

The colloidal state

Colloidal systems or colloids (from Greek word ‘κωλλα’, meaning ‘glue’) are a specific state of matter endowed with certain characteristic properties.

It is not a given class of substances, for instance, salt (potassium chloride, KCl) forms a colloidal solution in benzene (C_6H_6), but forms a true solution in water.

Examples of colloidal systems from daily life

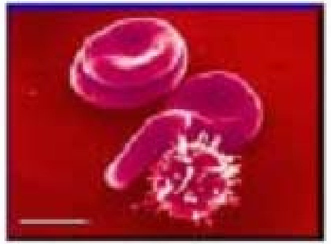

Foams


Milk

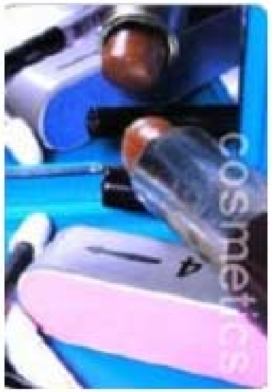

Fog, smoke

Detergents


Aerogel


Blood


Paints



Cosmetics

The colloidal state

The first important characteristic **of the colloidal state** is **the presence of particles** which are larger than molecules, but not large enough to be seen in microscope. The size of particles in the colloidal state is from 10−9 to 10−7 meter, although those limits are far from rigid.

***The second essential property*:** *the colloidal solutions consist of two or more phases*. The two phases may be distinguished by the terms:

dispersed phase (for the phase forming the particles) and

dispersion medium or *continuous phase* for the medium in which the particles are distributed (or dispersed).

Classification of colloidal systems

All colloidal systems may be classified in the following manner.

1. Classification in accordance with *aggregative state of dispersed phase* and *dispersion medium* (see Table below). The medium may be solid, liquid or gaseous; similarly the dispersed phase may be solid, liquid or gaseous, thus leading to a number of possible types of colloidal systems.

If the dispersed phase and medium are nonmixable liquids the result is an ***emulsion*.**

Table. Examples of commonly encountered colloidal systems

System	Type	Dispersed phase	Continuous phase or dispersion medium
Fog, mist	Liquid aerosol	Liquid	Gas
Smoke	Solid aerosol	Solid	Gas
Shave cream	Foam	Gas	Liquid
Styrofoam	Solid foam	Gas	Solid
Milk	Direct emulsion	Liquid (fat)	Liquid (water)
Butter	Reverse emulsion	Liquid (water)	Liquid (fat)
Paint	Dispersion	Solid	Liquid
Suspension	Dispersion	Solid	Liquid
Sol	Dispersion	Solid	Liquid
Opal	Dispersion	Solid	Solid
Jello	Gel	Macromolecules	Liquid
Liquid soaps and detergents	Micellar solution	Micelles (aggregates) of detergent molecules	Liquid

Classification of colloidal systems

2. Classification in accordance with *interaction between dispersed phase and dispersion medium.* This classification is used only for colloidal solution with *a liquid dispersion medium*. Sols may be divided into ***lyophobic*** and ***lyophilic*** or *hydrophobic* and *hydrophilic*, if dispersion medium **is aqueous**.

Lyophobic sols are relatively unstable (particles aggregate and sediment); have low affinity for the solvent; addition of electrolytes causes coagulation and precipitation. *Typical examples of lyophobic sols* are sols of metals, sulfur, sulfides, silver halides, and also inks, paints.

Lyophilic sols have strong affinity between dispersed phase and dispersion medium and are stable (particles stay separate). *Typical examples of lyophilic sols* are surfactant solutions at defined concentration and sols of proteins.

Classification of colloidal systems

3. Classification in accordance with the *size of particles of dispersed phase.* If diameter of particles is more than 10–4 meter, it is ***heterogeneous systems***; if diameter of particles lies in the range from 10–5 to 10–7 meter, it is ***microheterogeneous systems***; if diameter of particles less than 10–7 meter, but more than 10–9 meter it is ***'true' colloidal systems or ultramicroheterogeneous systems.***

4. Classification in accordance with the *shape of particles of dispersed phase.* For example, shape can be spherical, cylindrical, cubic, needle-like, etc.

Preparation of colloidal systems

Lyophilic systems may be prepared when substances with high molecular weight are warmed with a suitable dispersion medium. For example, gelatin and starch in water, rubber in benzene.

Lyophobic systems *may be prepared* by special methods:

(1) *condensation methods*

or

(2) *dispersion methods*.

Preparation of colloidal systems

<u>Condensation methods</u> **<u>are:</u>**

(1) ***<u>physical condensation</u>*** *<u>is based on physical processes</u>*, such as solvent replacement or vapor condensation (for example, the fog formation);

(2) ***<u>chemical condensation</u>*** is based *<u>on different chemical reactions</u>*, hydrolysis, ion-exchange reactions, oxidation-reduction, etc. For example, hydrolysis of ferric chloride FeCl3:

$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3HCl$,

by adding boiling water dropwise to a solution of ferric chloride one obtains the dark brown sol of ferric hydroxide.

A common feature of both classes of condensation method is that formation of <u>the colloidal particles in the new phase occurs at strong supersaturation</u>.

Preparation of colloidal systems

Dispersion methods. In these methods the starting material consists of the substance in the massive form; by means of suitable devices **it is disintegrated into particles of colloidal dimensions**. Colloidal mill or electrical disintegration (a direct current electrical arc) are used. For example, when a coffee is milled in a grinder, ultrasonic destruction of kidney stones, and etc.

Peptization is the direct disintegration or dispersion of the coagulation products of a sol into particles of colloidal size by an added *peptizing agent*.

For example, a deposit of ferric hydroxide can be peptized by treatment with very small quantities of ferric chloride solution after preliminarily removing of the coagulating substances. In this case peptization is due to adsorption of Fe^{3+} ions which again stabilize the particles.

Tyndal effect

Presence of colloidal particles can be made evident by optical means.

If a strong beam of light is passed through a colloidal solution, ***colloidal particles will scatter the light***.

True solutions are optically clear, *but colloidal solutions scatter light, producing so-called the **Tyndall effect***.

The path of the light through the sol, which is rendered visible as a result of the scattering, is called the ***Tyndal beam***.

The structure of colloidal particles

Necessary conditions for the stability of lyophobic sols are:

√ the particles must be very small (offsets sedimentation);

√ must carry electrical charges (hinder coagulation);

√ must form solvate shells (hinder coagulation).

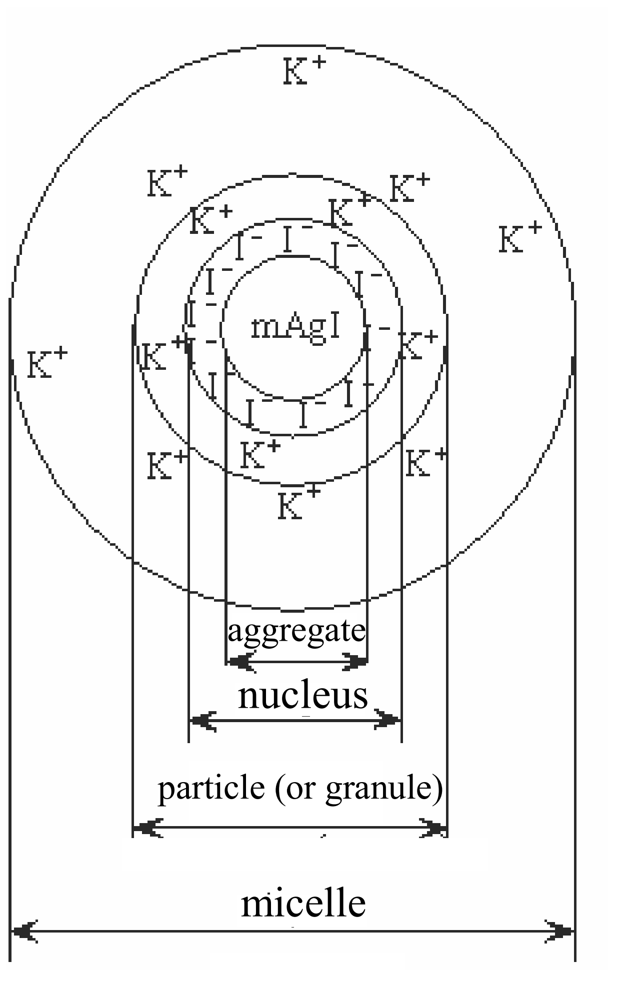
Electrical charges appear on the colloidal particles as a result of adsorption processes, when the particles preferentially adsorb ions of a given species from the solution, depending on the nature of the colloidal and experimental conditions.

The structure of colloidal particles

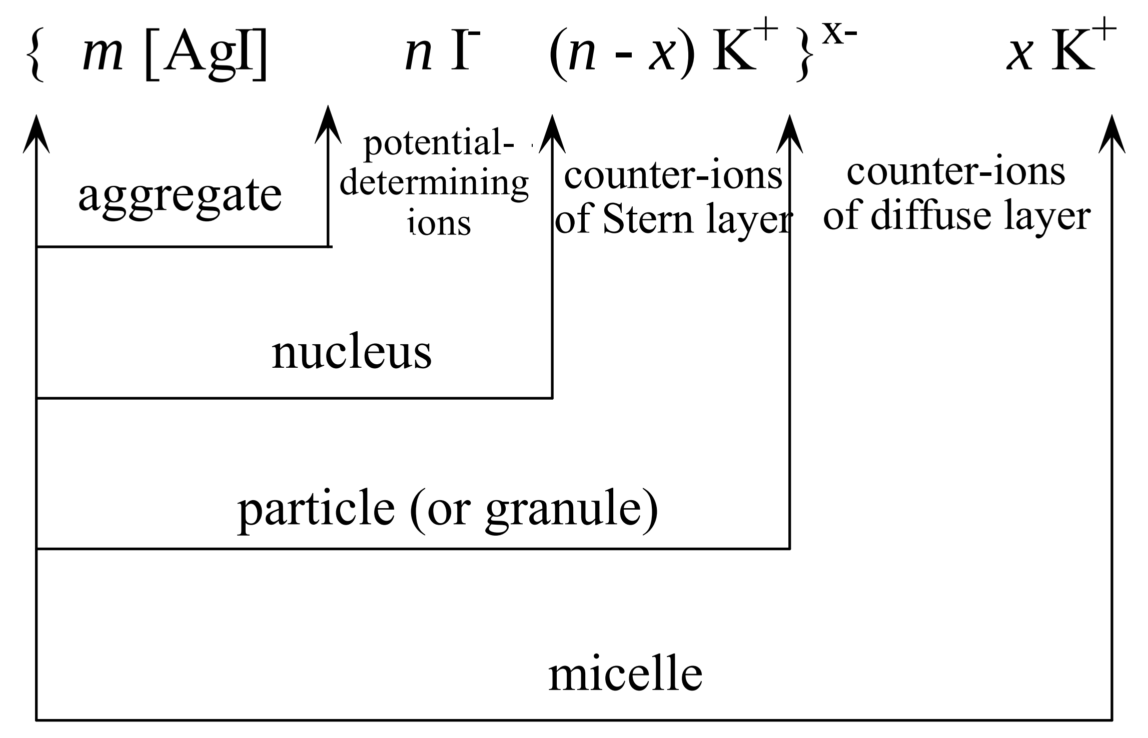
The particles of a colloid preferentially adsorb ions of a certain species from the electrolyte solution.

The entire part, consisting of ***the particles*** of the dispersed phase with the ***adsorbed ions (potential-determining ions)*** and ***counter-ions of Stern layer (ions of opposite charge)*** partially bound to them, migrates through the solution as a single unit so-called ***particle or granule***.

The counter-ions in the surrounding solution experience an attraction to the charged particles. Those nearest to it are more strongly attracted and become bound to the particle. The entire unit with the ***counter-ions of diffuse layer*** is called ***a micelle***.



The structure of colloidal particles



$$\{\ m\,[\mathrm{AgI}]\quad n\,\mathrm{I}^-\quad (n - x)\,\mathrm{K}^+\ \}^{x-}\quad x\,\mathrm{K}^+$$

aggregate

potential-determining ions

counter-ions of Stern layer

counter-ions of diffuse layer

nucleus

particle (or granule)

micelle

Figure. Structure of silver iodide micelle with negatively charged particles

Purification of colloidal systems

Dialysis

The use of membranes for separating particles of colloidal dimensions is termed ***dialysis***.

The most commonly used membranes are prepared from regenerated cellulose products such as collodion (a partially evaporated solution of cellulose nitrate in alcohol plus ether), cellophane and visking (a type of seamless cellulose tubing used as a membrane in dialysis and as an edible casing for sausages).

Dialysis is particularly useful for removing small dissolved molecules from colloidal solutions or dispersions. The process is hastened by stirring so as to maintain a high concentration gradient of diffusible molecules across the membrane and by renewing the outer liquid from time to time (see Figure below).

Purification of colloidal systems

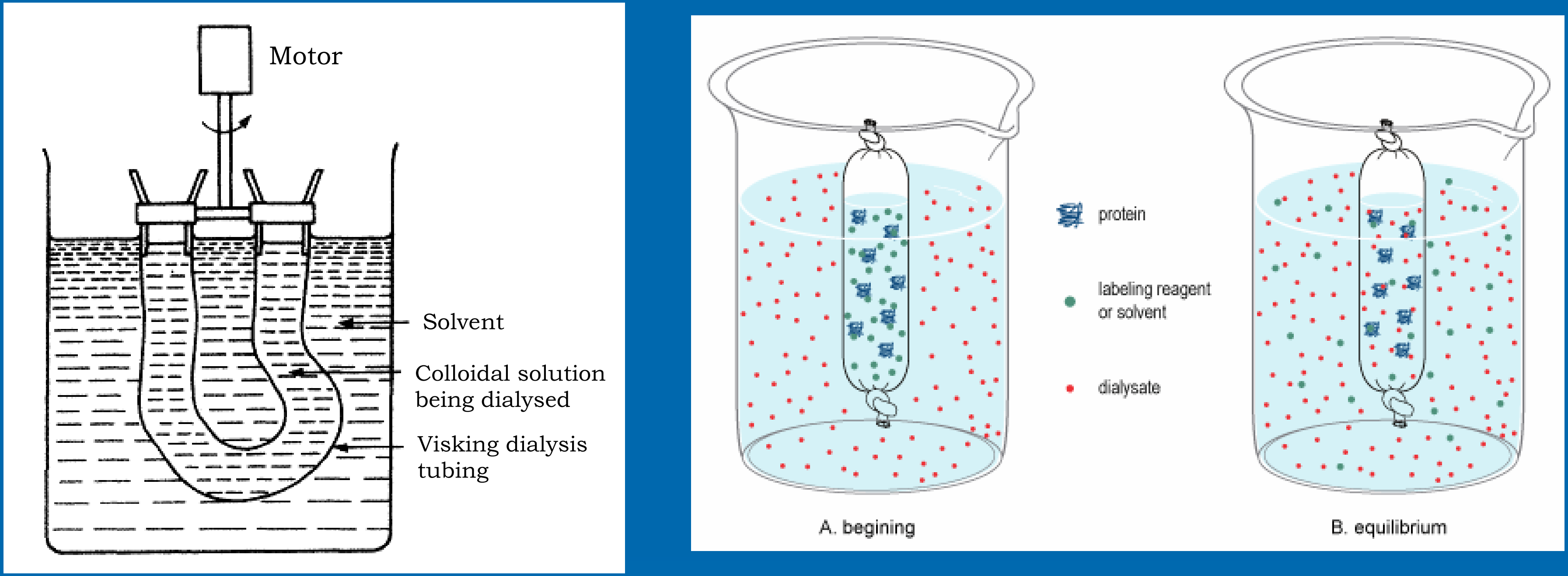


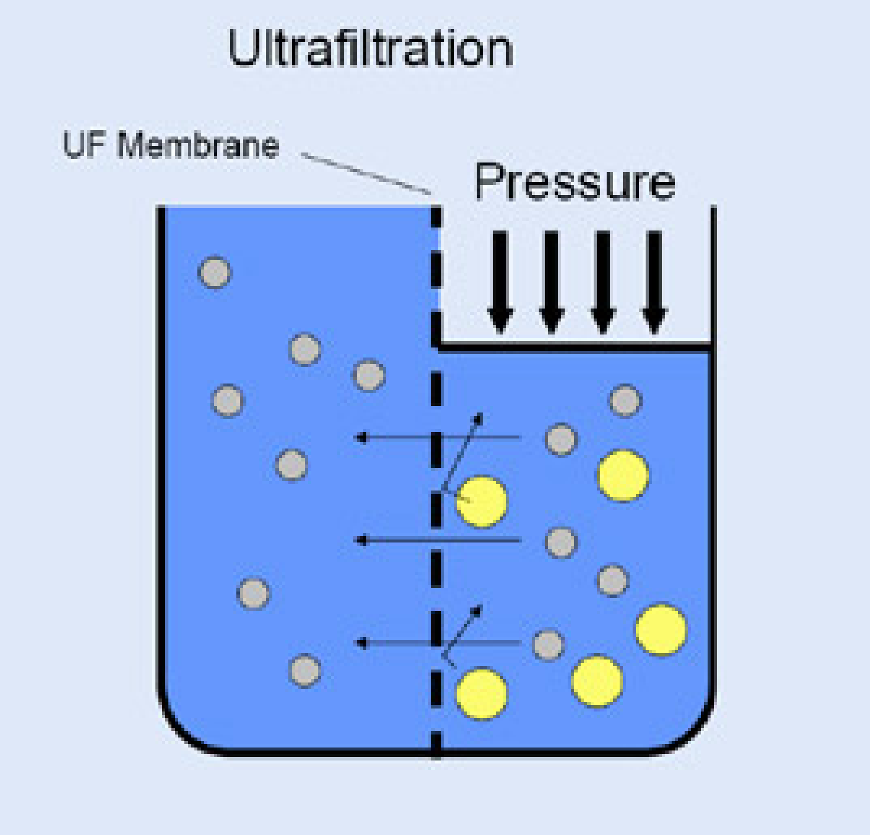
Figure. A simple dialysis set-up

Purification of colloidal systems

Ultrafiltration is the application of pressure or suction to force the solvent and small particles across a membrane while the larger particles are retained.

The membrane is normally supported between fine wire screens or deposited in a highly porous support such as a sintered glass disc.

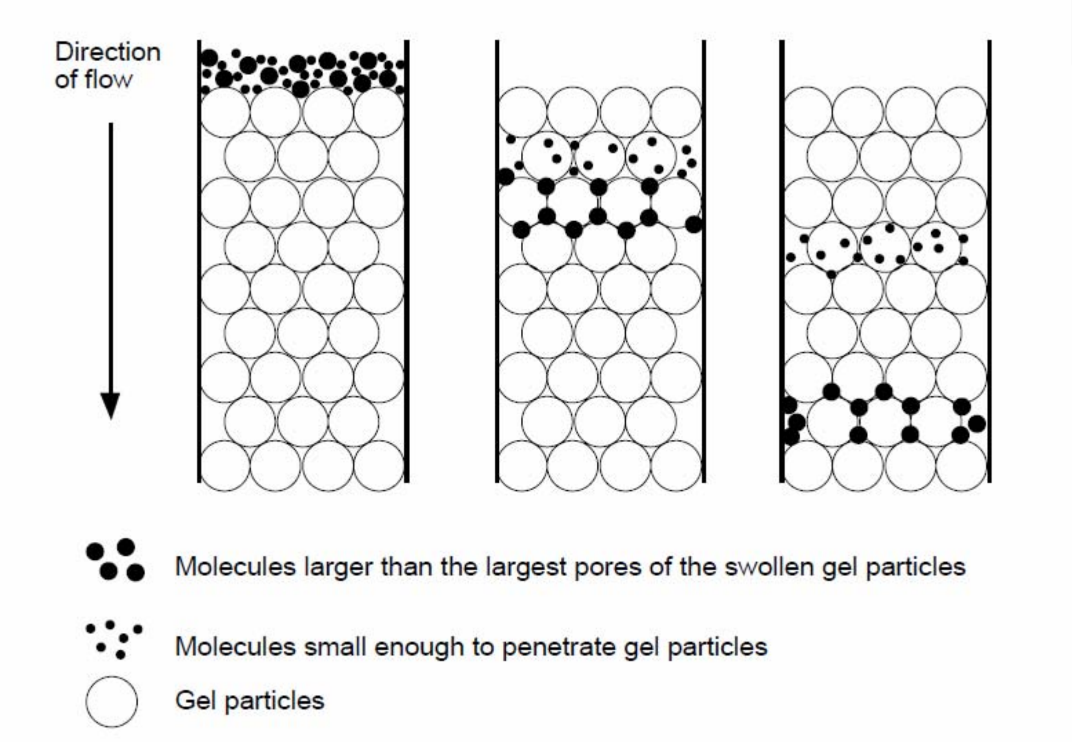
An important application of ultrafiltration is the so-called *reverse osmosis method of water desalination*.



Purification of colloidal systems

Another most valuable development of the ultrafiltration principle is the technique of *gel permeation chromatography* for the separation of the components of a polymeric sample and determination of the relative molecular mass distribution.

The usual experimental arrangement involves the application of a pressure to force polymer solution through a chromatographic column filled with porous beads.



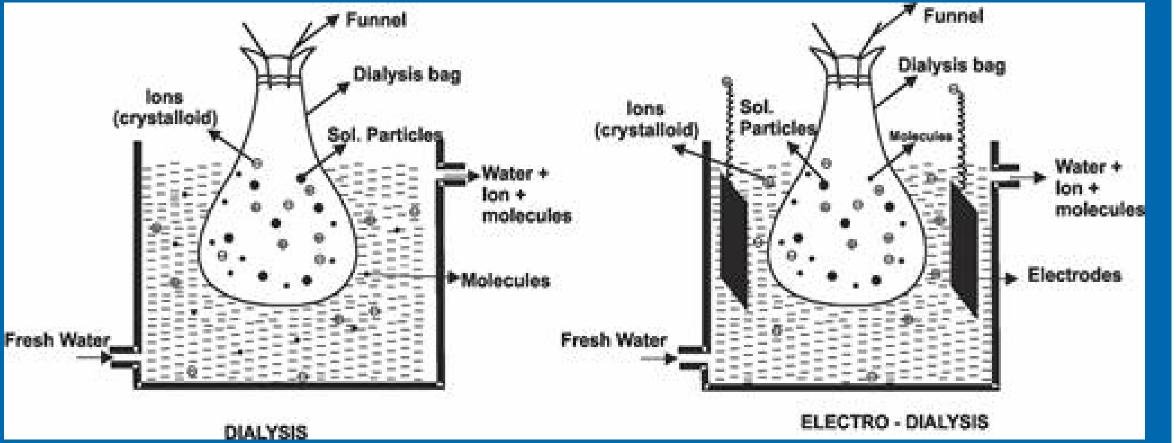
The larger polymer molecules tend not to enter the pores of the beads and so pass through the column relatively quickly, whereas **the smaller polymer molecules tend to diffuse** through the pore structure of the beads and so take longer to pass through the column.

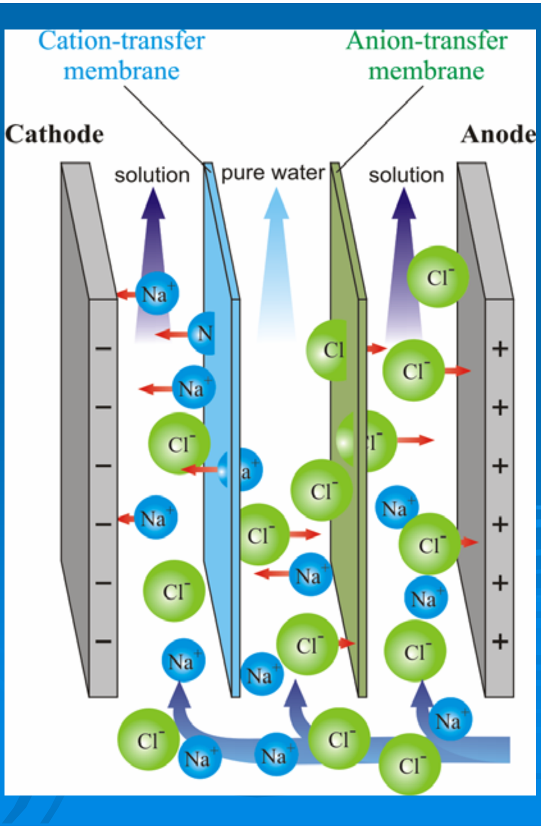
Purification of colloidal systems

A further modification of dialysis is the technique of *electrodialysis*, as illustrated in Figure.

The applied potential between the metal screens supporting the membranes speeds up the migration of small ions to the membrane surface prior to their diffusion to the outer liquid.

The accompanying concentration of charged colloidal particles at one side and, if they sediment significantly, at the bottom of the middle compartment is termed ***electrodecantation***.





Hemodialysis or kidney dialysis

Hemodialysis or **kidney dialysis** is a process of purifying the blood of a person whose kidneys are not working normally.

This type of dialysis achieves the extracorporeal removal of waste products such as creatinine and urea and free water from the blood when the kidneys are in a state of renal failure.

The principle of hemodialysis is the same as other methods of dialysis; it involves diffusion of solutes across a semipermeable membrane (see Figure).

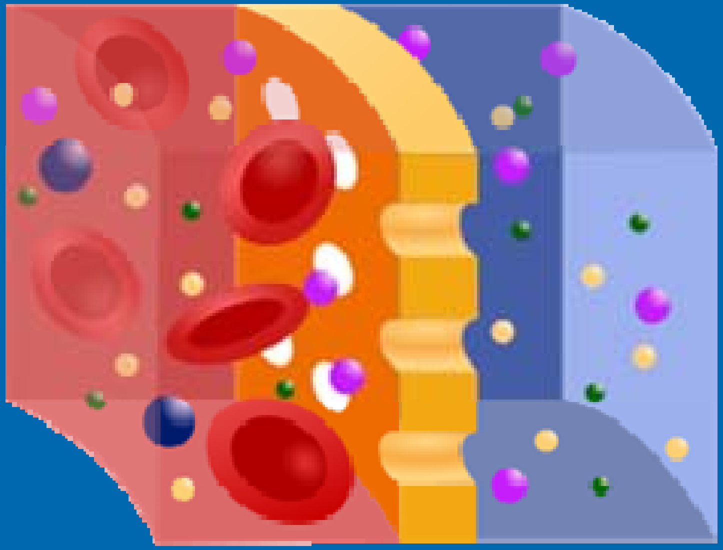


Figure. Semipermeable membrane

Hemodialysis or kidney dialysis

Hemodialysis utilizes counter current flow, where the dialysate is flowing in the opposite direction to blood flow in the extracorporeal circuit. Counter-current flow maintains the concentration gradient across the membrane at a maximum and increases the efficiency of the dialysis.

Fluid removal (ultrafiltration) is achieved by altering the hydrostatic pressure of the dialysate compartment, causing free water and some dissolved solutes to move across the membrane along a created pressure gradient.

The dialysis solution that is used may be a sterilized solution of mineral ions. Urea and other waste products, potassium, and phosphate diffuse into the dialysis solution. However, concentrations of sodium and chloride are similar to those of normal plasma to prevent loss. Sodium bicarbonate is added in a higher concentration than plasma to correct blood acidity. A small amount of glucose is also commonly used.

Hemodialysis or kidney dialysis

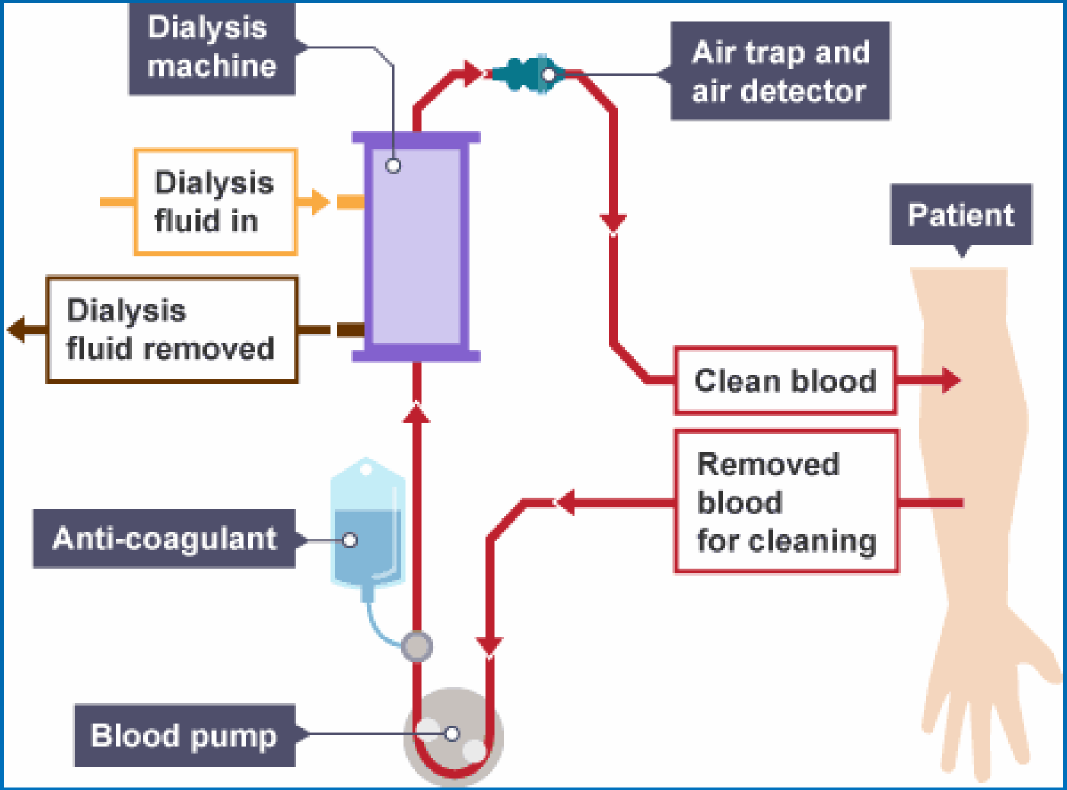


Figure. Principle of hemodialysis

Figure. Hemodialysis machine

References

1. Chang, Raymond; Overby, Jason. Chemistry. – 13-th ed. New York: McGraw-Hill, 2019.
2. Burdge, Julia R. Chemistry. – 5-th ed. New York: McGraw-Hill, 2019.
3. Atkins, Peter; de Paola, Julio; Keeler, James. Atkins' Physical Chemistry. – 11-th ed. Oxford University Press, 2018.
4. Eltsov, Sergey V.; Vodolazkaya, Natalya A. Practical Medical Chemistry: Manual. – 2-nd ed. Kharkiv: V. N. Karazin Kharkiv National University, 2018.
5. Brown, Theodore L. *et al*. Chemistry: the Central Science. – 14-th ed. Glenview: Pearson, 2018.
6. Silberberg, Martin S. Chemistry: the Molecular Nature of Matter and Change. – 6-th ed. New York: McGraw-Hill, 2012.
7. Laird, Brian B. University Chemistry. New York: McGraw-Hill, 2009.

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