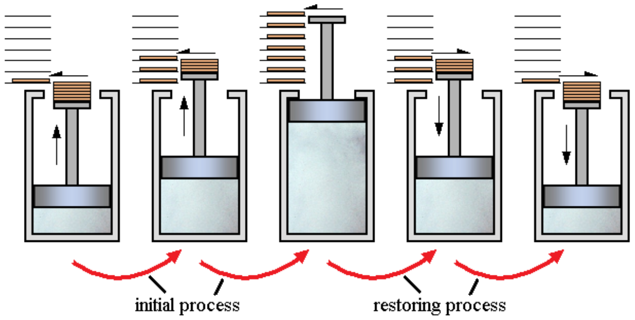
Physical Chemistry

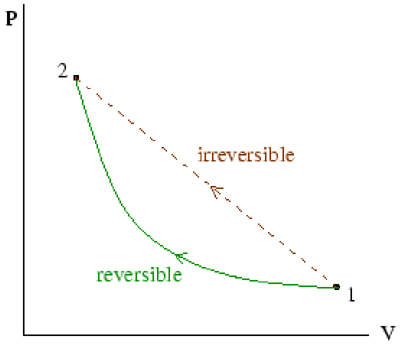
3rd Stage

Prof.Dr.Layla Jasim Abbas
2025-2026

Reversible process العملية العكوسة

A process or cycle is called reversible when it can be reversed by a slight change in one of the system's properties without loss of energy. Since the changes in the system are very slight, the system is in thermal equilibrium during this change. A reversible process takes a period of time to complete (a very slow process), so an ideally reversible process or cycle does not complete in a short time. A reversible cycle is characterized by the fact that the energy of the system and its surroundings does not change during the cycle, i.e. the energy of the system and its surroundings is the same at the beginning of the process and at its end.





Irreversible process العملية غير العكوسة

In chemistry, we know that a reaction that cannot be carried out in the opposite direction in isolation is “irreversible.” For example, when carbon combines with oxygen to form carbon dioxide, it cannot be broken down again into carbon and oxygen.

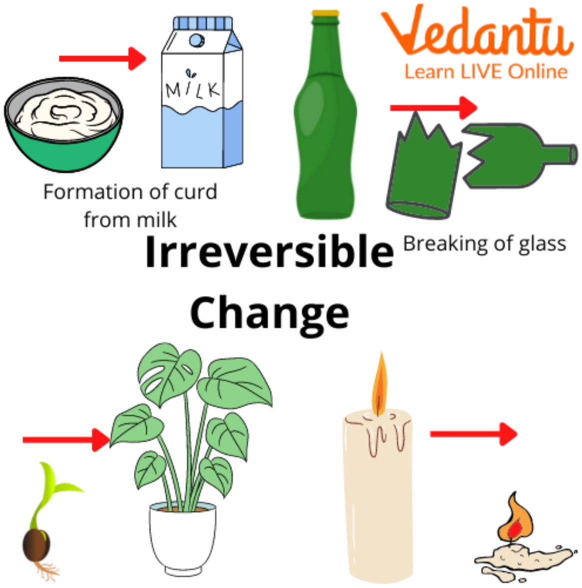
Irreversible reactions are reactions that occur in one direction, where the products of the reaction cannot combine with each other again to form the reactants under experimental or other laboratory conditions.

Reactions are irreversible when the free energy change is large (**greater than 30 kJ/mol**) and therefore the chemical equilibrium constant log K is large (**greater than 3**), so the reaction is practically one-way.

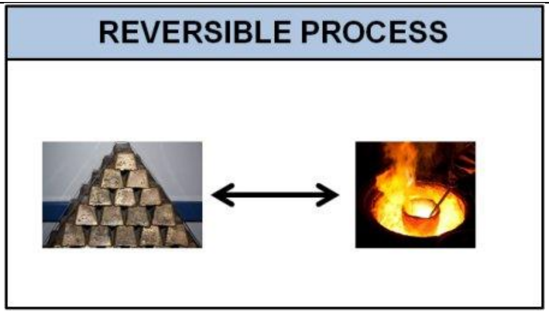
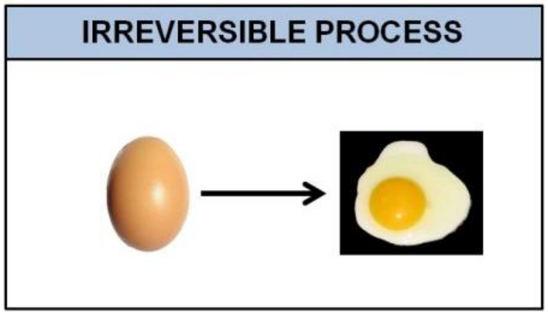
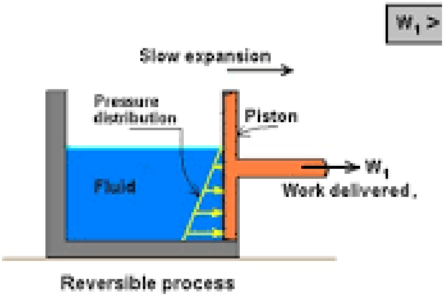
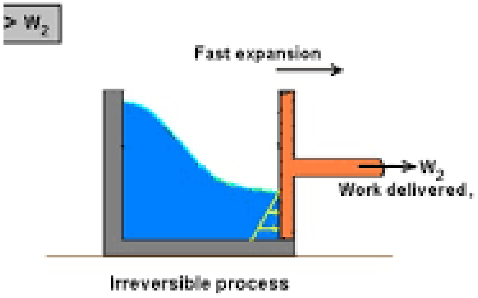
A process that is not reversible is called an "irreversible" process. When an irreversible process is performed, the system changes and is not in thermal equilibrium during the process. The system may be at the same point in a reversible cycle in the same state, but the surrounding atmosphere has changed after each cycle.

All matter is made up of atoms, and the forces between the atoms of a material are essentially electrical in nature because the atoms themselves are made up of charged particles (electrons and protons). In fact, it is the way in which the atoms themselves are arranged in a material and the groups of atoms are formed that determines the volumetric behavior of the material.

These volumetric properties of matter, commonly known as mechanical properties, are often of the greatest importance for most practical purposes.



	Reversible processes	Irreversible processes
1	Reversible processes occur when a system returns to its original state after being disturbed. A classic example of this is the water cycle. A classic example is melting ice and vice versa. Water is originally in liquid condition, then freezes to produce ice, which melts again to give water when heated.	Irreversible processes cannot be reversed or at least cannot be reversed without the great expense of time and money. Irreversible processes are controlled by economic considerations (costs), and these considerations usually eliminate one or more variables in the balanced equation. This is because if any of the variables were eliminated, it would destroy the balance of the reaction, and the system would be unable to sustain itself.
2	It is a slow process going through a series of smaller stages with each stage maintaining equilibrium between the system and surroundings.	In this process the system attains final state from the initial state with a measurable speed. During the transformation, there is no equilibrium maintained between the system and surroundings.
3	A reversible process is a process that can be obtained into the initial state of the system (made to proceed in forward or backward direction) without making an change in the adjacent surroundings.	Irreversible process is a thermodynamic process that cannot be reversed to obtain the initial state of a system without making a change in the surroundings(take place in one direction only).

		
4	In reversible process infinite change occurs in the system	In the irreversible process, finite changes occur in the system
5	There is an equilibrium between the initial state and the system's final state	In an irreversible process, there is no equilibrium in the system
6	The driving force for the reversible process is small since the process proceeds in smaller steps.	There is a definite driving force required for the progress of the irreversible process.
7	Work (W) done in a reversible process is greater than the corresponding work done in irreversible process. 	Work (W) done in a irreversible process is always lower than the same kind of work done in a reversible process. 

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Thermodynamics_and_Chemical_Equilibrium_(Ellgen)/06%3A_Equilibrium_States_and_Reversible_Processes/6.09%3A_Reversible_vs._Irreversible_Processes

Fluid mechanics is a sub-discipline of continuous materials mechanics and is primarily concerned with fluids, which are essentially liquids and gases. The efficient operation of various units in chemical industries such as reactors or separation units such as distillation or absorption towers or extraction devices depends in part on the velocity of the different phases relative to the solid walls of these units and also on the relative velocity between these phases. It studies the overall apparent physical behavior of these materials, and can be divided into:

- Fluid statics or its study in a state of motion.

- Fluid dynamics or its study in a state of motion.

Other specializations fall under it, such as aerodynamics and hydrodynamics. This specialization seeks to determine the physical quantities of fluids, such as speed, pressure, density, temperature, viscosity and flow rate. Modern computational applications have emerged to find solutions to problems related to fluid mechanics, and the specialization concerned with this is called computational fluid dynamics. The importance of fluid mechanics is also completely clear when we think about the role it plays in our daily lives. In the field of air conditioning and refrigeration, there is ice water that is pumped through pipes. Cold air is pushed by fans through air ducts to air condition homes, and the electricity we use and the methods of generating it from waterfalls that push water through turbines that generate electrical energy. Or from thermal energy from steam that is pushed through steam turbines to generate electrical energy, and the cars we drive, pneumatic tires give cars suspension, fuel is pumped through pipes.. In fact, our daily lives depend on fluids. The flow of blood in our veins and arteries is a fluid mechanics process.

Viscosity اللزوجة

Viscosity is the resistance of a fluid to flow, and the amount of its resistance to pressure that forces it to move and flow (a measure of the speed of flow of the fluid under the influence of certain forces). The higher the viscosity of a fluid, the less its ability to flow. For liquids, viscosity is equivalent to the common term thickness. Honey is thick and highly viscous, and water is smooth and low viscosity.

Viscosity arises from the frictional forces between the layers of the liquid during their movement against each other (caused by the presence of attractive forces (cohesion) between the liquid molecules causing internal friction), and this effect is weak in solutions with low viscosity such as ethyl alcohol and water with easy (fast) flow. Other solutions such as honey or engine oils with high viscosity, their flow is very slow.

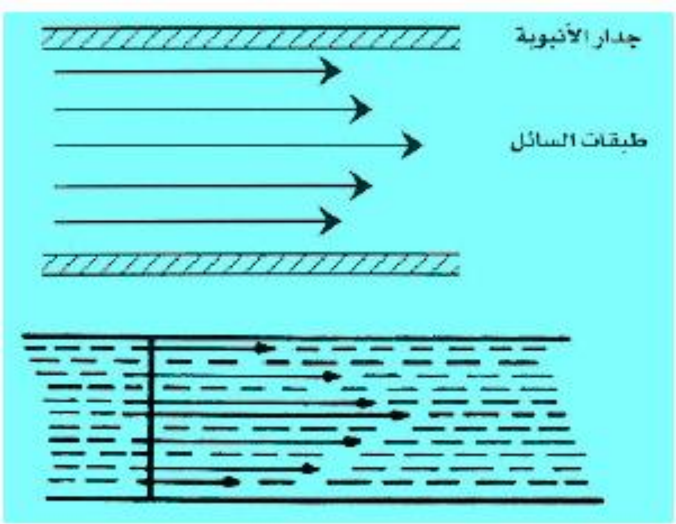
- It can also be said that the friction of adjacent layers in glycerin is greater than the friction of adjacent layers in water, and therefore the speed of glycerin flow is less than the speed of water flow and glycerin becomes more viscous than water.

The particles of a highly viscous fluid are tightly bound together, making them less able to move. Their friction with the solid body in contact increases, and viscosity can be described as internal friction between the particles of the fluid.

We experience viscosity in our daily lives, such as when a spoon falls into honey or a piece of iron falls into tar, as well as the flow of water inside water pipes. The resistance to movement that occurs during this is related to the viscosity of the fluid.

It is an important property of fluids, and through it the fluid resists the change in shape resulting from the effect of shear forces acting on it. If we assume the presence of a layer of fluid between two parallel flat plates, as in the figure, such that the lower plate is fixed and the upper plate moves quickly under the effect of the force.

If we assume that we put a liquid in a narrow tube and affect it with a force such as a difference in pressure between the two ends of the tube, then the liquid begins to flow in the tube, but the speed at which the layers of this liquid move differs from one layer to another. The thin layer in contact with the tube wall is almost stationary, and the speed of the movement of the layers increases the further we are from the tube wall, and this speed reaches its maximum in the middle layers of the liquid, then gradually decreases until it reaches the opposite tube wall (see the following figure).



Kinematic viscosity of a fluid

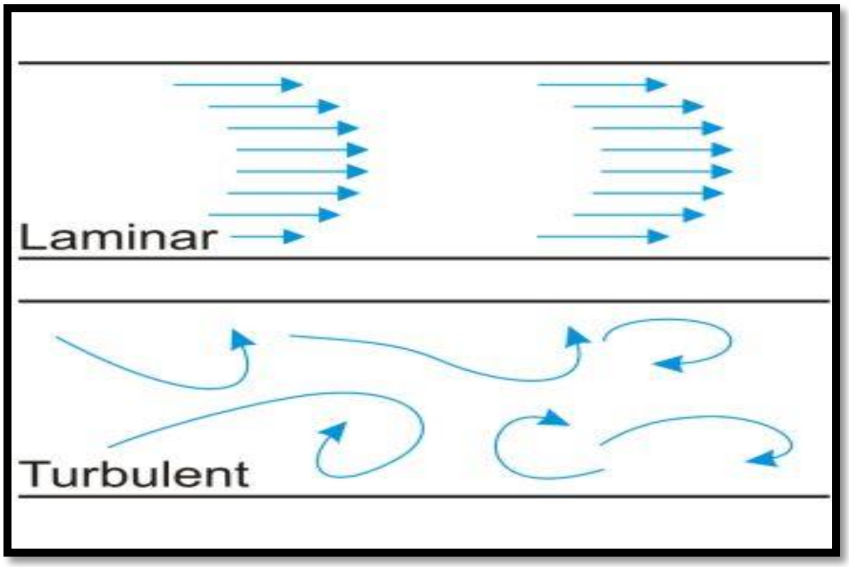
Kinematic viscosity is a measure of a fluid's internal resistance to flow under gravitational forces. It is determined by measuring the time in seconds, required for a fixed volume of fluid to flow a known distance by gravity through a capillary within a calibrated viscometer at a closely controlled temperature.

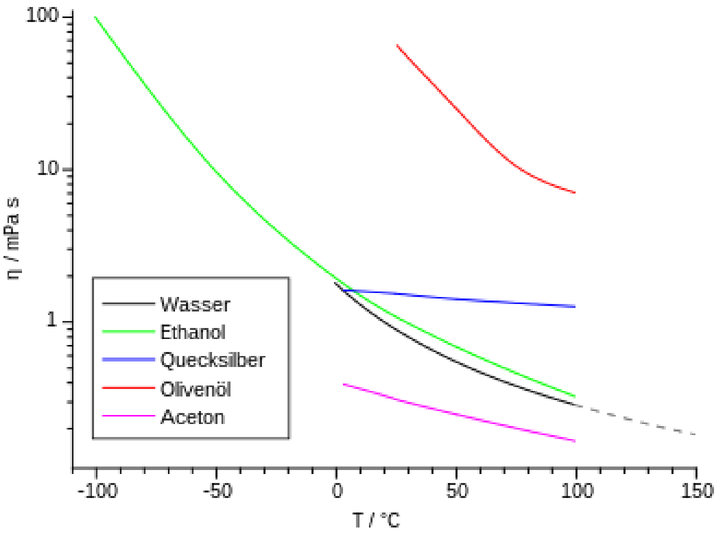
1- Laminar flow

The distinctive feature of this type of flow is that the fluid flows in parallel layers that do not mix with each other. Liquids are generally characterized when flowing at low speeds to the absence of mixing between the layers. What distinguishes laminar flow is the absence of vortices, unlike turbulent flow, which is a very regular flow so that the layers of the liquid flow parallel to the walls of the container that contains it.

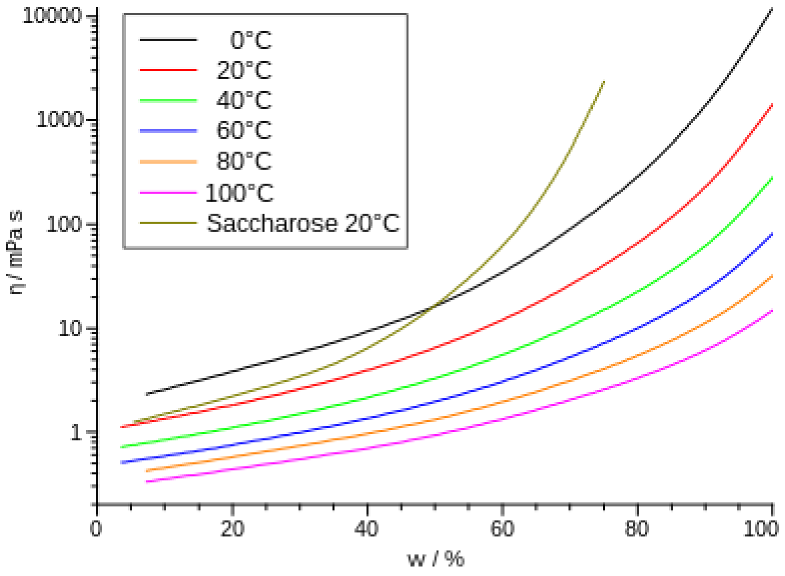
2- Turbulent flow

A fluid flow system characterized by chaos and random change in its properties. With increasing speed, there is no longer slippage, but the movement is disturbed and vortices occur. Here, the viscosity is completely different, so this viscosity is called vortex viscosity; that is, it is the resistance of the layers of the fluid that flows turbulently in the tube.





The viscosity of some liquids depends on temperature: black represents water, green represents ethanol, blue represents mercury, red represents olive oil, and purple represents acetone. The graph shows the change in viscosity between -100 and 150 degrees Celsius. The change in viscosity of a glycerol solution with a change in its concentration in the solution at different temperatures. The gray curve shows a mixture of glycerol and sucrose at 20 degrees Celsius.



The kinematic viscosity (dynamic viscosity) of a liquid shows the amount of resistance of the liquid to flow (flow) when moving and the relationship of this resistance to the temperature of the liquid. The higher the temperature, the lower the kinematic viscosity and the liquid becomes more fluid. This is due to the cohesive forces between the molecules which overwhelm the transfer of molecular momentum between these molecules, and this is also due to the close proximity of the molecules (this explains why the volume of liquids is smaller than gases). When the liquid is heated, the cohesive forces between the molecules decrease and thus the attractive forces between them decrease, ultimately leading to a decrease in the viscosity of the liquid. On the other hand, the higher the flow rate, the higher the viscosity, i.e. the resistance of the liquid to moving increases with increasing pressure. We assume that there are two parallel plates with a distance x between them and an area of each of them **A**, and we assume that there is a liquid filling the space between the two plates. If we start moving plate 2 at a constant speed **v**, the layer of liquid adjacent to plate 2 also moves at a speed **v**. Since plate 1 is fixed and does not move, the layer of liquid adjacent to it remains motionless. That is, the layers of fluid between the two plates will move at speeds directly proportional to the distance between the plates. The experiment can show that the force (frictional force) **F** that moves plate 2 is directly proportional to the area of plate **A**, directly proportional to the speed of the plate **v**, and inversely proportional to the distance **x** between the two plates, that is:

$$F \sim \frac{Av}{x}$$

The relationship can be transformed into an equation using the constant of proportionality η:

$$F = \eta \frac{Av}{x}$$

The constant of proportionality η is called the kinematic viscosity and is sometimes called the viscosity coefficient.

Unit of measurement of viscosity

It is Poise and it is equivalent to kg/s.m **or** written as g s^{-1} cm^{-1} **or** Newton. sec/m²

Since:

$$1N = 1\frac{kg.m}{s}$$

$$\frac{dynes}{cm^2} \text{ x } \frac{1}{(\frac{cm}{\sec})} \text{ x } \frac{1}{(1/cm)} = \text{ dynes cm}^{-2}\text{ sec}^{-1} = \text{poise}$$

A certain substance is said to have a viscosity of $N.s/m^2$ when the area of the plates is 1 square meter and the distance between them is 1 meter, then the force required is 1 Newton to move the plate relative to the other at a speed of 1 meter per second. When **η** does not depend on the speed **v**, the fluid is called a Newtonian fluid, referring to Newton. For this fluid, the speed of each layer of fluid between the plates is directly proportional. However, if **η** changes with the speed **v** (a function of speed), the fluid is called a non-Newtonian fluid.

Liquid	Viscosity [mPa s]
Water	1
Water (25º)	0.891
Combustion oil	0.65
Asphalt	10^5
Blood (37º)	4 to 25
Olive oil	10^2
Honey	10^4
Glass	10^2 to 10^4

Viscosity coefficient and its units of measurement

Definition of viscosity coefficient (or viscosity) η

- It is the force in dyne that affects two parallel layers of a liquid, each with a cross-sectional area of (1 cm^2) and a distance of (1 cm^2) from each other in order to maintain the flow velocity of one layer relative to the other at a speed of (1 cm/s).

- The relationship between the viscosity coefficient and the volume of the liquid (**v**) that passes through a thin tube (capillary) with a diameter (**r**) and a length (**L**) in time (**t**) per second under constant pushing pressure (**P**) is given by the Poisellieh relation

$$\boxed{\eta = \frac{\pi r^4 P t}{8 V L}}$$

- When measuring viscosity by the direct method using the Poiseuille relationship, where **Ostwald's device** is used, called the viscometer, a modification can be made to the Poiseuille equation for such a purpose, where the derived force (hydrostatic pressure) present in the Poiseuille equation is replaced by (ghd)

g = gravity

h = distance

d = density

$$\eta = \frac{\pi r^4 P t}{8 V L}$$

$$\eta = \frac{\pi r^4 g h d t}{8 V L}$$

Viscosity units:

$$\text{Viscosity} = \frac{\text{Force} \times \text{Distance}}{\text{Velocity} \times \text{Area}}$$

$$\eta = \frac{\text{Newton} \times \text{m}}{\text{ms}^{-1} \times \text{m}^2}$$

$$\eta = \frac{\text{Kg}\,\cancel{\text{m}}\,\text{s}^{-\cancel{2}}\ \text{x}\ \cancel{\text{m}}}{\text{m}\cancel{\text{s}}^{-\cancel{1}} \times \cancel{\text{m}}^{\cancel{2}}}$$

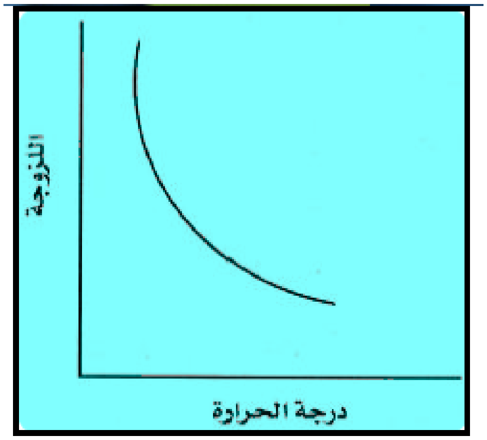
$$\eta = \text{Kg m}^{-1}\text{s}^{-1}$$

Factors affecting viscosity

(a) Temperature

- Viscosity decreases with increasing temperature, because increasing temperature increases the movement of molecules, so the forces of attraction between molecules decrease relatively, and if the attraction decreases, the viscosity decreases. Therefore, car drivers are advised to use high-viscosity oils in the summer. And low-viscosity oils in the winter.

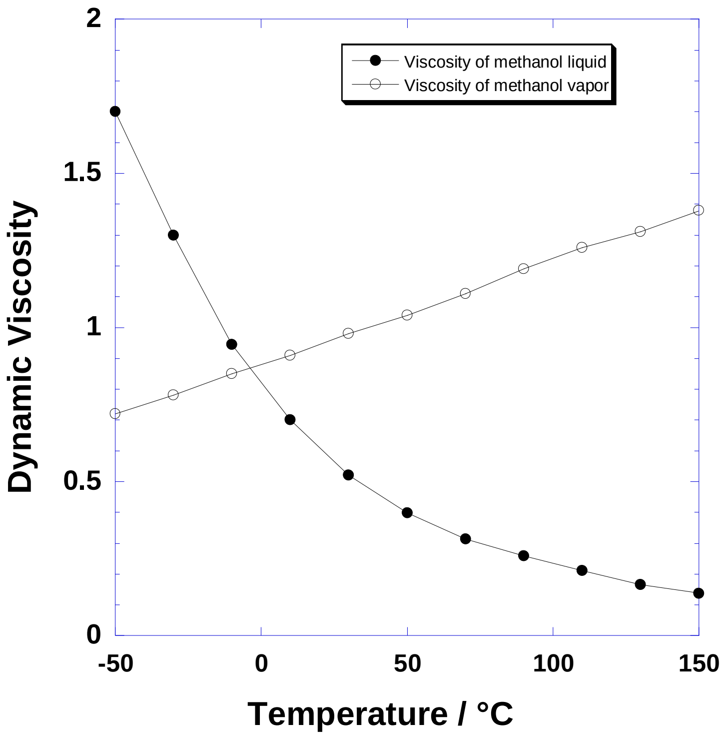
- It was found that the viscosity of the liquid decreases by (1-2%) for every increase in temperature of 1 degree Celsius (Celsius).

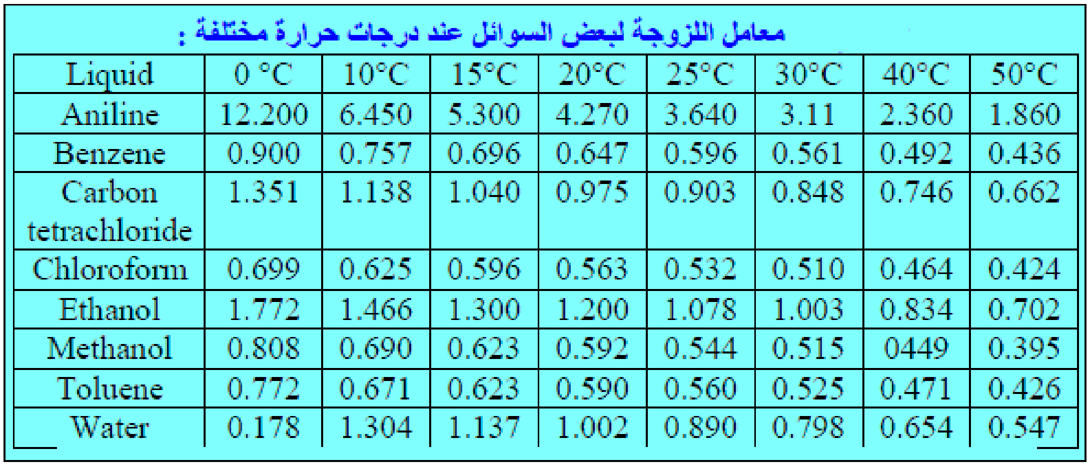


What is the effect of increasing temperature on the viscosity of liquids?

The viscosity of liquids decreases with increasing temperature because increasing temperature reduces the effect of attractive forces (increases the kinetic energy of the liquid molecules) and this behavior is different from the behavior of gases, whose viscosity coefficient increases with temperature.

From the figure below, we notice that the viscosity of the gas increases with increasing temperature, while the viscosity of the liquid decreases with increasing temperature.





معامل اللزوجة لبعض السوائل عند درجات حرارة مختلفة :

Liquid	0 °C	10°C	15°C	20°C	25°C	30°C	40°C	50°C
Aniline	12.200	6.450	5.300	4.270	3.640	3.11	2.360	1.860
Benzene	0.900	0.757	0.696	0.647	0.596	0.561	0.492	0.436
Carbon tetrachloride	1.351	1.138	1.040	0.975	0.903	0.848	0.746	0.662
Chloroform	0.699	0.625	0.596	0.563	0.532	0.510	0.464	0.424
Ethanol	1.772	1.466	1.300	1.200	1.078	1.003	0.834	0.702
Methanol	0.808	0.690	0.623	0.592	0.544	0.515	0449	0.395
Toluene	0.772	0.671	0.623	0.590	0.560	0.525	0.471	0.426
Water	0.178	1.304	1.137	1.002	0.890	0.798	0.654	0.547

Viscosity formula according to temperature: The dependence of a liquid on temperature can be found from the following relationship, which is known as the Andrade equation:

$$\eta = Ae^{\Delta E/RT}$$

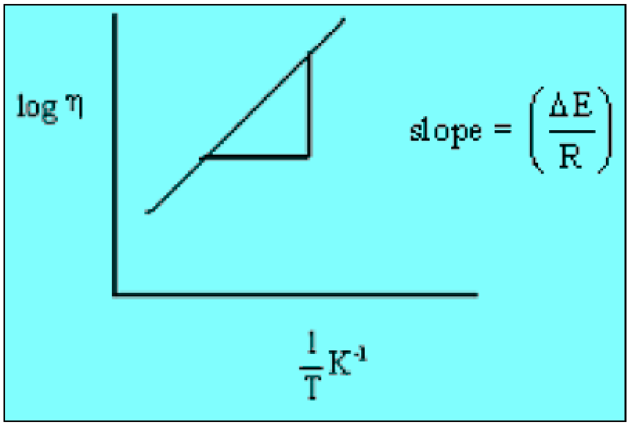
$$\log\eta = \frac{\Delta E}{RT} + \log A$$

$$\log\eta = \frac{\Delta E}{R}\left(\frac{1}{T}\right) + \log A$$

$$\boxed{\log\eta = \frac{\Delta E}{R}\left(\frac{1}{T}\right) + \log A}$$

where **A** is a constant independent of temperature and E_{visc} is the equation for the activation energy of viscous flow. It is the energy required and obtained in the vicinity of a fluid layer, creating a vacuum in which the molecules of the layer preceding it reside.

log η (on the y-axis) versus 1/T (on the x-axis) is a straight line, and varies from one fluid to another in terms of slope.



Where (ΔE): Activation energy for viscosity flow which can be determined from the figure by the slope of the straight line (ΔE/R) This is the transition energy that must be present before flow occurs.

This means that the molecules must take sufficient energy to push the surrounding molecules before taking any step in the process of fluid flow.

(b) Molecular weight:

Viscosity increases with increasing molecule size (molecular weight) in homogeneous compounds (of one type). For example, in hydrocarbons, the viscosity of the compound C_8H_{18} is greater than C_7H_{16}.

(c) Attractive forces:

The forces of attraction between molecules are considered a preliminary measure of the viscosity of liquids. The greater the attraction between molecules, the more difficult it is for the molecules to move and thus the viscosity of the liquid increases. For example, liquids with polar molecules have a higher viscosity.

Therefore, liquids whose molecules are characterized by high attractive forces have high viscosity.

(d) Presence of dissolved substances:

The dissolved substances in the liquid affect the viscosity, for example, the presence of sugar in water increases the viscosity of the water, while the presence of ionic salts in water reduces the viscosity of the water. The presence of suspended substances in the liquid increases its viscosity, for example, blood is more viscous than water due to the presence of proteins and platelets suspended in it.

(e) Pressure

With increasing pressure on the liquid, the attractive forces between the liquid molecules increase, and thus the viscosity increases slightly.

(f) The shape and composition of the molecule

The shape and composition of the liquid molecules play a major role in the amount of its viscosity. Liquids with large, irregularly shaped molecules (whose molecule shape hinders their movement) are more viscous than small, identically shaped molecules.

The value of viscosity varies greatly depending on the physical state of a liquid or a gas, as it decreases greatly in the gaseous state because the molecules are relatively far apart and the forces of attraction become weaker than in the liquid state.

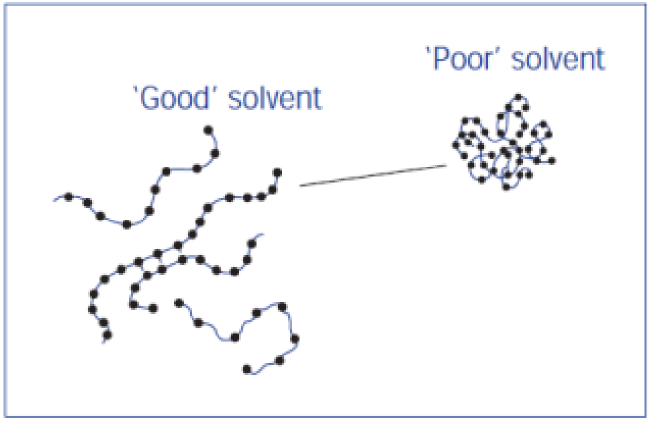
Viscosity of solutions of macromolecules (polymers)

The presence of macromolecules in solutions will greatly affect their viscosity, and viscosity depends on the concentration of the polymer used. The viscosity of polymer solutions is measured by the relative viscosity, which is given by the relationship:

$\eta_{rel} = \eta/\eta_0$

Where η represents the viscosity of the solution and η0 represents the viscosity of the pure solvent. The shape of polymeric materials affects their rheological properties and viscosity, and therefore any change in shape may be due to a change in the nature of the interaction between the polymer and the solvent (solvent-polymer interaction) or a change in the nature of the small-sized materials associated with the polymers, which will affect the viscosity of the solution.

The nature of the solvent also affects the properties of the resulting solution. In good solvents, polymers disperse linearly due to the dissolution of polar groups, while in poor solvents, the internal forces between the molecules are stronger than the affinity of these molecules for the solvent, which leads to the molecules wrapping around each other.



The viscosity of the solution resulting from the use of ionized polymers is more complex due to the changes in the electrical charges. The viscosity of the solution resulting from the use of ionized polymers is more complex due to the change in the concentration of the polymer used and the concentration and charge of other additives.

The shape of the flexible charged polymers changes with the change in the degree of ionization. At maximum ionization, the repulsive forces and viscosity of the medium increase, which leads to the expansion of the polymer molecules. When small amounts of charge-modifying ions are added to the medium, the charge of the molecules decreases, the molecules contract, and the viscosity of the medium decreases.

Gel formation

High concentration solutions of polymers show very high viscosity due to the arrangement of the polymer chains in a three-dimensional spatial structure to give a structure known as a gel. In order for gels to form, a critical concentration of gelation is required, as gels do not form when using polymers at concentrations lower than this concentration, which is determined by:

- The oil-water balance of the polymer

- The lipophile–hydrophile balance • The degree of regularity of the polymer structure

- The interaction between the polymer and the solvent

- The molecular weight of the polymer

- The flexibility of the chains forming the polymer, the more flexible these chains are, the higher the critical concentration of the gel.

Diffusion

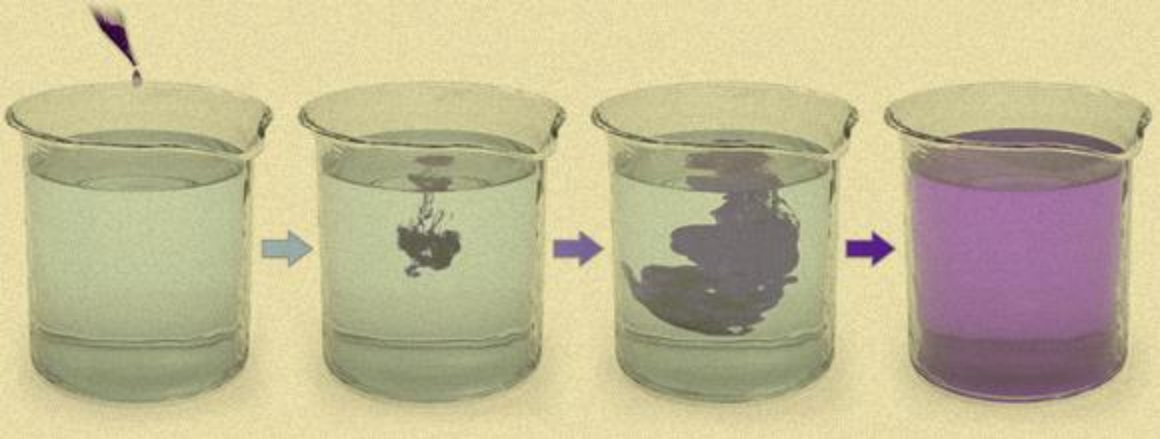
Diffusion: is the process of distributing molecules, atoms or particles evenly in a vacuum or in an available space or their penetration through a membrane barrier. Diffusion occurs by the transfer of molecules or atoms from an area of high concentration to an area of lower concentration until the concentration of molecules in both areas is equal.

The phenomenon of diffusion arises due to the random thermal movement of the molecules of the substance that collide with each other and move apart to occupy all the space available to them.

Explaining the diffusion process

The diffusion process takes place without any external intervention, i.e. without any movement of the liquid.

To explain the diffusion process, we can watch the process of coloring a transparent liquid with a dye and observe the process of color spreading in the transparent liquid as shown in the picture.



Note that the diffusion process takes place without any external intervention, i.e. without any movement of the liquid.

In this example, the dye is added to the liquid and left to diffuse in the liquid without any movement of the liquid or the table on which it stands. The distribution of color in the transparent liquid is done automatically due to the property of diffusion. In this case, there are also other factors affecting the distribution of color in the liquid, such as density and the temperature difference between the two liquids.

Diffusion Mechanism

Diffusion depends on the movement of Brownian molecules, which is the random movement of molecules in space, which causes molecules to collide with each other and move away from each other to fill any available space. This movement depends on the thermal energy stored in the substance. This movement is one of the properties of the substance and does not require external energy, and it is one of the characteristics of every substance whose temperature is above absolute zero.

The tendency of matter to fill all the space available to it causes matter to move from the area of high concentration to the area of low concentration and in the opposite direction from the area of low concentration to the area of high concentration, because the movement is random, but the large number of molecules in the area of high concentration causes a greater number of molecules to move towards the area of low concentration, meaning that the net movement of molecules is from the area of high concentration to the area of low concentration until the two concentrations are equal and equilibrium is achieved, which means equal movement in both directions. Therefore, diffusion can be viewed as the force that leads to the transfer of matter from A to B.

Factors affecting diffusion

There are several factors that affect the speed of diffusion, including:

- Temperature and its direct proportionality, as the temperature increases, the kinetic energy of the molecules of the substance increases, and the number of their collisions per second increases, and thus the diffusion pressure.

- The size of the molecules and its inverse proportionality.

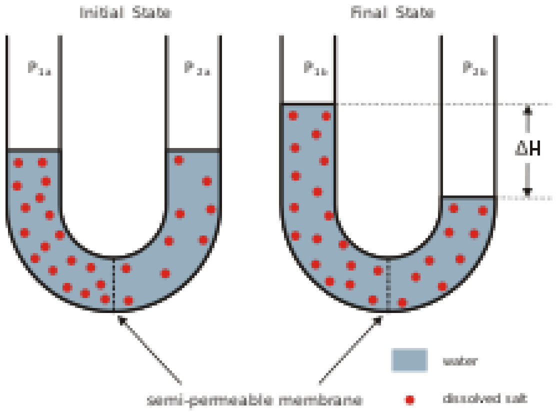
- The difference in concentration in the solution and the direct proportionality.

- The state of the substance, as diffusion in gases is faster than in liquids, and it is slowest in solids. This is due to the weak bonding of the molecules with each other in the gaseous state, and their random movement, which decreases in liquids and is almost non-existent in the solid state.

Special cases

Osmosis:

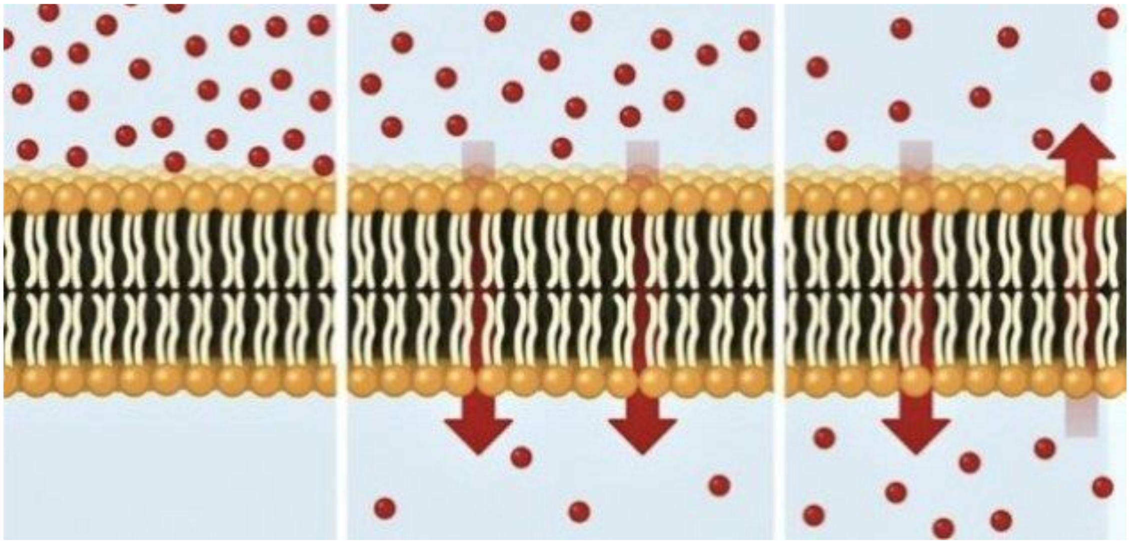
One of the special cases of diffusion is diffusion through a permeable membrane, in this case there is a membrane separating two spaces, but it is permeable to the liquid and the substance dissolved in it. In this case, the resultant transfer of the molecules of the dissolved substance is towards the side with the lower concentration, as shown in the picture. One of the conditions for diffusion is that the separating "barrier" be permeable to the dissolved substance. If the separating membrane is semipermeable, the molecules of the dissolved substance are unable to move to the other side, and here a pressure called osmotic pressure arises.



Diffusion applications

In liquids, the diffusion of substances is slower. If a cube of sugar is dissolved in a cup of water, the time needed for the sugar to dissolve and distribute in the cup is relatively long, so methods are used to speed up the process by moving or shaking the cup. As for cooking food, the time is sufficient, which makes the diffusion process useful in cases where stirring and mixing is difficult. Also, the salt that is sprinkled on the surface of the meat is transferred over time to reach the inner layers of the piece of meat, and the salt is transferred here by diffusion through the meat juice.

Diffusion over short distances is effective. If we look at the distances that substances must travel in cells, we will find that they bridge distances in micrometers. At the level of single-celled organisms, these organisms obtain food and secretion processes by simple diffusion across the cell membrane. In multicellular organisms such as humans, for example, the circulatory system bridges long distances by the movement of blood in the blood vessels. At the level of living tissues, vital exchange, food transport and secretion processes depend on properties such as diffusion, osmosis and biotransport.



Ion channels in cell walls allow selective diffusion of materials. When these channels open, ions cross the channel based on the concentration difference on both sides of the cell wall.

The importance of this situation is in living cells, where the cell wall is permeable to materials, and impermeable or semi-permeable to others, depending on the type of cell and the type of material. Cells can also open special channels such as ion channels for limited periods, to allow some materials to enter or exit. The transfer of materials here is automatic by diffusion without expending any energy or active transport that consumes energy.

There are also other methods for the transfer of molecules and fluids between cells and the interstitial fluid. In addition to diffusion, there is osmosis and active transport, both of which consume energy to achieve transport.

Electrochemistry

Electrochemistry includes chemical transformations resulting from the passage of electricity as well as the production of electricity by chemical transformations. The fact that electricity can be obtained by chemical reactions allows us to say that electrical energy can be stored in the form of chemicals that can be used to produce electrical energy at another time or place.

Electrochemistry gives us information about a large number of phenomena such as corrosion and purification of metals as well as the interactions of ions with each other and with the solvent in the solution. Another phenomenon is electrolysis.

Anode: is the electrode towards which negatively charged ions move.

Cathode: is the electrode towards which positively charged ions move.

Electrolyte

Is any substance that contains free ions (when dissociated) that form a medium that conducts electricity, and electrolytes are either in the form of solutions (Aqueous Solutions), an example of which is the aqueous solution of sulfuric acid, which consists of positive hydrogen ions and negative sulfate ions.

$$H_2SO_4 \leftrightharpoons 2H^+ + SO^=_4$$

Electrochemical cells الخلايا الالكتروكيميائية

Electrochemical cells are devices that can produce electrical energy from chemical energy and chemical energy from electrical energy. No heat is evolved from the electrochemical cells.

Half cell نصف الخلية

The two halves of the cells in which electrolytic solutions are present are the half cells. Each half-cell contains an electrode. The electrodes can be the same or different.

Electrolytes الالكتروليتات

Electrolytes are the substances that give an electrically conducting solution when dissolved in polar solvents, such as water. This is because when the electrolyte is dissolved in the polar solvents, it breaks into cation and anions and gets distributed uniformly throughout the solution. These cations and anions under an electrical potential in the solution move to the electrode with an abundance of electrons and a deficit of electrons, respectively. This movement of cation and anions in the direction opposite to each other generates current and forms the electrolytic cells.

While salts, acids and bases form an electrolyte, few gases under certain conditions can also behave like an electrolyte, such as hydrogen chloride at high temperature and low pressure.

So, a substance or an element that dissociates into ions (when put in a solution), has the ability to conduct electricity. Salts are most commonly used to make electrolytes. Molten salts such as molten sodium chloride also form electrolytes and conduct electricity. In fact, ionic liquids are molten salts that have a melting point below 100° C and are highly conductive non-aqueous electrolytes. These have many applications in fuel cells and batteries. Hydroxides made from alkaline metals are also strong electrolytes but do not dissolve in water after a limit. Due to which their application is restricted to certain situations only.

The two types of electrochemical cells are: نوعا الخلايا الالكتروكيميائية هي

1. **Voltaic cells:** The electrochemical cells that produce electrical energy with the use of chemical energy are called voltaic cells. These are **also known as galvanic cells**.
2. **Electrolytic cells**: The type of electrochemical cells that produce a chemical reaction are electrolytic cells (converts electrical energy to chemical energy).

Salt bridge الجسر الملحي

It is a device that connects two halves of the electrochemical cells and is formed of a strong electrolyte. **It maintains the electrical neutrality in the circuit. It also completes the electrical circuit.**

The solution in the salt bridge must be inert and nonreactive with other solutions. This prevents a reaction between the solution and the salt bridge and allows movement of ions between the two half cells.

The two types of the salt bridge are glass tube bridge and filter paper bridge.

Glass tube bridge is a tube that has a U-shape. It is filled with electrolytes like sodium chloride and potassium nitrate.

The filter paper bridge is formed by a porous material such as filter paper that has electrolytes soaked.

The solution in the salt bridge must be inert and nonreactive with other solutions. This prevents a reaction between the solution and the salt bridge and allows movement of ions between the two half cells.

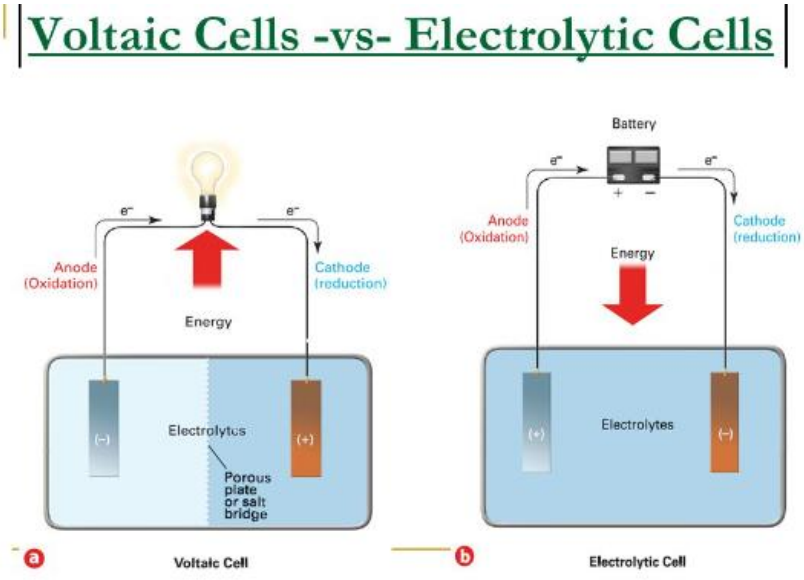
Components of Electrochemical Cells مكونات الخلايا الالكتروكيميائية

An electrochemical cell splits the oxidant and reductant in a manner that allows electrons to flow through an external circuit from the reductant (which gets oxidized) to the oxidant (which causes reduction) while preventing them from physically touching each other. The two compartments of an electrochemical cell where the half reactions occur are called the anode and the cathode, and they must have an electrode that you can connect the external circuit to.

- **Anode:** Oxidation occurs at the anode. This is always the case, but the sign of the anode switches between galvanic and electrolytic modes .
  - In a galvanic cell this is the negative electrode. This can be understood from two perspectives. From the reaction perspective, as the reductant (Zinc in the images on this page) lose electrons and enter the solution the electrode gains these electrons and thus acquires a negative charge, which can be transferred to something positive. The second is from the perspective of the external circuit, where the negative electrons flow to the positive terminal, which is the other electrode, making the anode the negative electrode
  - In an electrolytic cell this is the positive electrode. Here the electrode sign is not being determined by the cell reaction, but by the external power supply that is driving the reaction in the nonspontaneous direction. The right side of the figure shows the Daniel Cell being driven by an external power supply which has its [+] electrode connected to the cell with the copper. This causes the nonspontaneous reaction of electrons leaving the copper and moving towards the positive electrode. Since the wire connecting this to the power source has negligible resistance, this electrode is at roughly the same potential, and is thus the positive electrode. It must be emphasized that the reaction is being driven by the coupling of an external power supply that produces a negative free energy in the nonspontaneous direction, and this must be greater in magnitude than the spontaneous free energy that occurs in the galvanic cell, resulting in a net negative free energy that causes the intrinsically nonspontaneous reaction to occur. Because of this, the electrode sign is dictated by the external power supply. But the anode is still where oxidation occurs.

- **Cathode:** Reduction occurs at the cathode.
    - The cathode has the opposite signs of the anode, so it is [+] in a galvanic/voltaic cell, and [-] in an electrolytic cell.
- **Electrodes**: In order to hook up an external circuit you need have something to physically connect the wire to. There are two types of electrodes, active and inert.
    - **Active electrode**: This is an electrode that takes part of the half reaction, and thus must be a solid. In the Daniels (Zn^{+2}/Cu) cell both electrodes are active, and as the reaction proceeds the anode loses mass (as Zn converts to Zn^{+2} and enters the solution), while the cathode gains mass (as Cu^{+2} gains electrons from the external circuit and becomes Cu(s).
    - **Inert electrode**: This is an electrode that is made of a substance that does not undergo oxidation or reduction. Often times oxidants or reductants are not solids but gases or solutes, like in the hydrogen half reaction $2H^{+}(aq)+2e^{-}\leftrightharpoons H2(g)$, which has no solid material that can function as an electrode, and would thus require an additional substance like platinum or graphite, that would function as an inert electrode.
- **Electrolyte:** An electrolyte is a charged mobile ion that functions as a conducting medium and in the case of "wet cells" is typically an aqueous solution of ionic compounds. In the case of active electrodes this will often by a soluble salt that has a common ion that also makes a soluble salt with the metal of that half-cells electrode. For example, copper(II) sulfate is a soluble salt, so sodium sulfate would be a good electrolyte for that half-cell. Sodium phosphate would not work because copper(II)phosphate would precipitate out.
- **External Circuit:** The external circuit allows electrons to flow from the anode to the cathode. In the case of a galvanic cell, this is a spontaneous flow and can be used to provide energy that can produce heat or do work. In the case of an electrolytic cell this requires an energy source to make it work.
- **Salt Bridge:** The salt bridge has two basic functions. First it completes the circuit and prevents charge buildup, which would stop the flow of electrons. That is, electrons flow towards a positive object and as they accumulate they reduce its "positiveness", and thus its ability to attract more electrons. The salt bridge prevents the buildup of negative charge by enabling an internal circuit that allows ions to complete the circuit and prevent charge buildup at the electrode.

    The second function of the salt bridge is to prevent the oxidant (Cu^{+2} in the Daniel cell) from migrating to the anode and being directly reduced by directly accepting electrons from the anode, and thus preventing the electrons from entering the external circuit. Thus it functions as a sort of "semipermeable membrane" allowing the electrolyte ions to freely migrate between half cells, but preventing the ions involved in the actual redox reaction from migrating. In reality some of the ions involved in the redox reaction do migrate through the salt bridge.

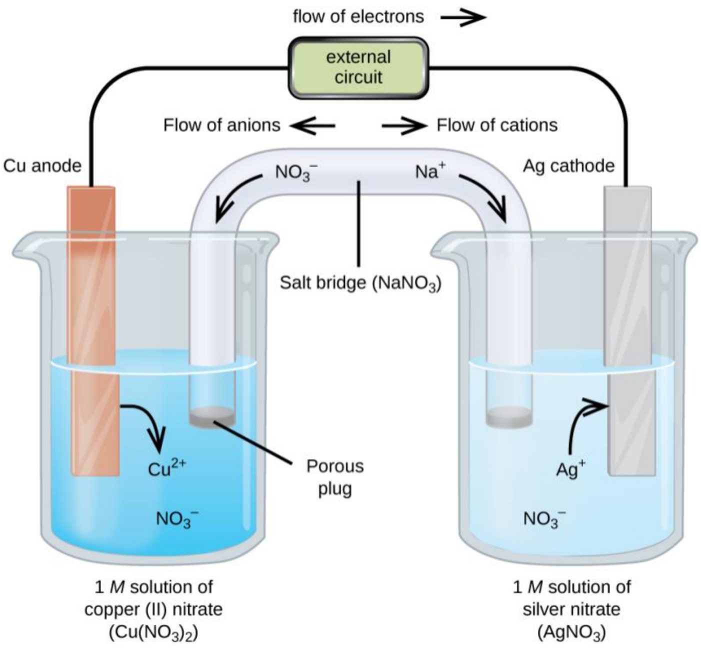


The electrochemical cells have a cathode and an anode. The cathode is the electrode at which electrons are accepted or consumed. The anode is an electrode at which the electrons are released or liberated. These electrodes are made from various conducting metals that are conducting or semiconducting. Other than metals, graphite and some conductive polymers are used too.

The tendency of an electrode to lose or accept an electron is described by its electrode potential. The differences between the electrode potentials of both the electrodes help to calculate the cell potential. The cell potential gives the measure of the voltage of the cell. A standard hydrogen electrode is used as a reference electrode to measure the electrode potential. The hydrogen electrode is the primary reference electrode. Another electrode known as a secondary reference electrode is calomel electrode.

Galvanic or voltaic cells الخلايا الكلفانية او الفولتية

These are named after Luigi Galvani or Alessandro Volta. He created the first electrochemical cell that generated a direct current. When electrons shift from species to species through a **spontaneous redox reaction**, energy is released. This energy can be used to perform tasks when the reaction is divided into 2 half-reactions which are oxidation and reduction. **These 2 reactions are carried out in 2 separate containers**, and a wire is used as a bridge between the 2 containers to take electrons from one container to another. By this, a galvanic or voltaic cell is formed.



Galvanic cell

The galvanic cell mostly has 2 types of metals in each of the electrolyte solutions which are connected by using a salt bridge. It may also have half-cells with a porous membrane between them.

Galvanic cells are electrochemical cells that can be used to do work. The below Figure shows a typical galvanic cell that uses the spontaneous (Zn^{+2}/Cu) reaction (eq. above). If the Zn^{+2} and Cu^{+2} ion concentrations in the two half cells is 1M a volt meter will read 1.10 volts. This is actually the open circuit potential that the voltmeter is reading, which correlates to no current flowing. The moment current flows [Zn^{+2}] increases while the [Cu^{+2}] decreases and this can be seen by the images in part (b) the below figure as the Zinc anode dissolves and copper ions attach themselves to the electrode and become reduced to neutral copper.

Daniel cell خلية دانيل

These are the type of electrochemical cells that have copper sulphate solution filled in the container which is made from copper. This also contains unglazed earthenware containers that contain sulphuric acid and electrodes of zinc. The aim of the Daniel cell was to eliminate the problem of hydrogen bubbles. This cell was invented by a British chemist and meteorologist, John Frederic Daniel, in 1836. It is an example of a Galvanic cell.

In this cell, the oxidation of zinc takes place at the anode, and the following half-reaction takes place:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

While copper undergoes reduction at the cathode and the following reaction takes place:

$$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu$$

So, the entire reaction can be written as:

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

This reaction leads to the formation of copper in solid-state at the cathode electrode, and the zinc electrode undergoes corrosion into the solution to form cation of zinc.

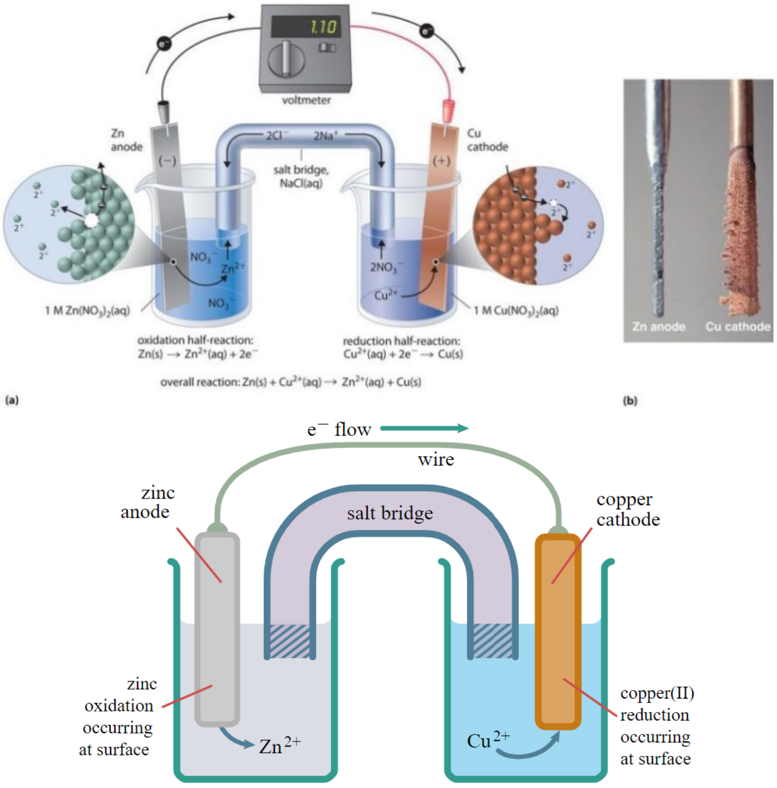


Figure: Daniell Cell using the spontaneous (Zn^{+2}/Cu) reaction.

Let's see an example.

We can make Galvanic / voltaic cells with solid copper (Cu(s)) in a silver nitrate solution ($AgNO_3$(s)).

During this reaction, $AgNO_3$ breaks into Ag^+ and NO^{3-} ions. Then, when the copper electrode is introduced in this solution having silver ions $Ag^+(aq)$, it will instantly oxidize Cu(s) to $Cu^{2+}(aq)$ and reduce itself to Ag(s). This reaction will generate energy, and the reaction has to be split into 2 separate containers, as discussed above. Otherwise, the energy released will be lost and cannot be used. Then after connecting a wire (between the two containers) to allow the floor of electrons between them, the Galvanic/ voltaic cell is ready.
These reactions take place on metal strips, known as electrodes. The electrode on which reduction takes place, i.e. the metal electrode which gains an electron(s) is called a cathode and the electrode at which the oxidation takes place, i.e. the metal electrode that loses an electron(s) is called an anode.

Considering the reaction in the above example, Cu is the anode and Ag is the cathode.

Note: Electrons always flow from anode to cathode. ملاحظة

Cell notation كيفية تمثيل تفاعل الخلية

It is the symbolic representation of the two halves of the galvanic cells by using abbreviations and symbols of the elements. Guidelines of cell notation are as follow:

1. The two halves are represented by using symbols of the elements and chemical formulas of the compounds.
2. The anode half is written first and the cathode half is written later. First, the reactants are mentioned within each half and then the products are mentioned.
3. Reactions of both the halves are separated by using two vertical parallel lines in between. This double vertical line indicates the salt bridge of the galvanic cell.
4. The phased of each of the element and compound is mentioned in parentheses as **s, g and aq** for solid, gas and aqueous respectively.

The cell notation of the above mentioned galvanic cell is:

$$\mathbf{Cu(s)\,|\,1M\ Cu(NO_3)_2(aq)\,\|\,1M\ AgNO_3(aq)\,|\,Ag(s)}$$

Cell Notation

Cell Notation is a shorthand way for describing an electrochemical cell. In cell notation you start with the **anode on the left**, and write down the reactants and products separated by a vertical line, which indicates a phase boundary (the salt bridge involves two phase boundaries). It should be noted that there needs to be a solid electrode at the very left of the anode and very right of the cathode. Finally, it is also important to note that these do not represent balanced equations, but identify what is being oxidized and what is being reduced.

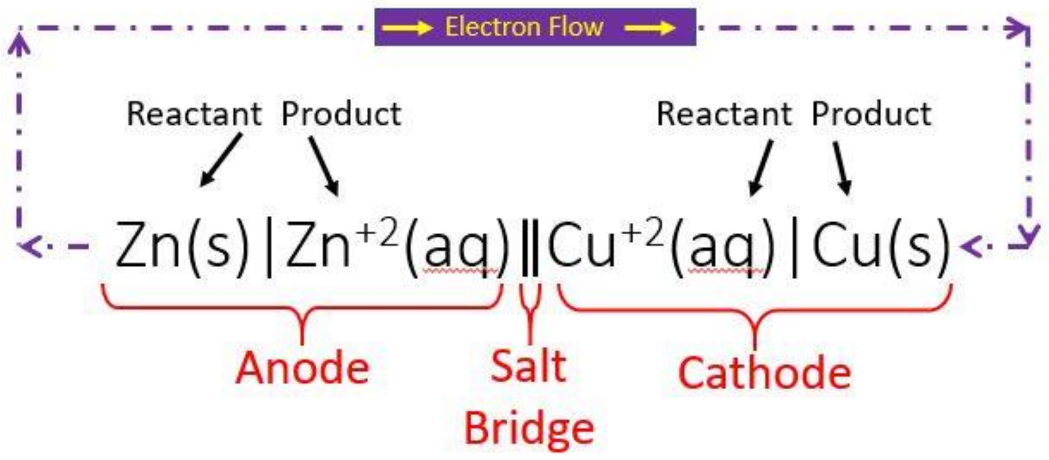


Figure: Cell notation for zinc copper cell operating in galvanic mode. Note, the purple dotted line is not part of the cell notation, but shown here. That is, the above would be written as Zn(s)|Zn^{+2}(aq)||Cu^{+2}(aq)|Cu(s).

If the ion concentrations were known the (aq) would be changed with the molarity. So at standard one molar conditions the zinc copper cell would be written as

Zn(s)|Zn^{+2}(1M)||Cu^{+2}(1M)|Cu(s)

If the above cell was operating in electrolytic mode it would be written as

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

The half-cell notation does not represent a balanced equation, and the ends must be solid, as they function as the electrode.

Example : Cell Notation

What is the cell notation for the redox reaction:

$Cu(s)+2Fe^{3+}(aq)\rightarrow Cu^{2+}(aq)+2Fe^{2+}(aq)$

$Cu(s)+2Fe^{3+}(aq)\rightarrow Cu^{2+}(aq)+2Fe^{2+}(aq)$

Solution

This can be broken into the following oxidation reactions

- Oxidation: $Cu(s)\rightarrow Cu^{2+}(aq)+2e^{-}$
- Reduction: $Fe^{3+}+e–\rightarrow Fe^{2+}$

Which gives the cell of

$$Cu|Cu^{2+}||Fe^{3+},Fe^{2+}|Pt$$

There are three things to note in the above equation .

1. First, the reduction half reaction involves two ions and so there is no solid, and an inert electrode had to be added (Pt) to the end of the cathode half reaction.
2. Second, the Fe^{+2} and Fe^{+3} are in the same phase and so you use a comma to separate them and not a vertical line (the vertical line represents a phase boundary).
3. And third, you are only identifying what is being oxidized (in the anode) and reduced (in the cathode), and so the cell notation does not represent a balanced chemical equation.

Dry cell الخلية الجافة

The Ever Ready cells are dry cells. It is a type of voltaic cell. These are known as dry cells because the electrolyte used is not a liquid. It is a paste. The dry cells use a paste of manganese dioxide and ammonium chloride in order to generate acidic ions and to complex the zinc ions received from the chemical reaction around the positive electrode made by carbon rods. These cells are also known as Leclanché cells. The dry cells are used in the remote controls or flashlights.

Uses of voltaic cells استخدامات الخلية الكلفانية

1. The voltaic cells are used to get electrical power. These are used to make the chargeable batteries present in the laptops and cell phones.
2. The solar cells are made from the galvanic cells, and so are rechargeable.
3. The chargeable electric vehicles, like bikes and cars, have galvanic cell batteries.

Advantages of voltaic cells محاسن الخلايا الكلفانية

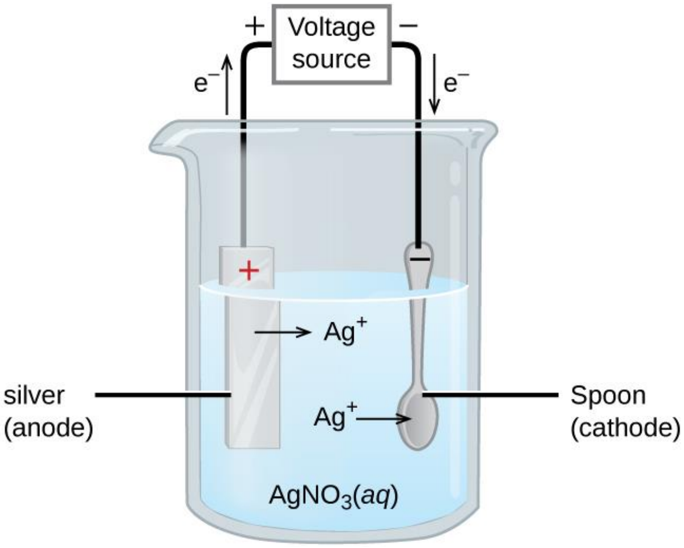
1. These are easy to make and are easily available.
2. They last for a long period of time as most of them can be charged.

Disadvantages of voltaic cells مساوئ الخلايا الكلفانية

1. Some of the galvanic cell batteries are very heavy.
2. They are expensive than the electrolytic cells.
3. Some of them show rusting or spoilage very easily.

Electrolytic cells الخلايا الالكتروليتية

These are the type of electrochemical cells that drive a nonspontaneous reaction using electrical energy. These can decompose chemical compounds, like water into hydrogen and oxygen. This decomposition takes place by the process called *electrolysis*. So, electrolytic cells need a DC power supply, two electrodes and an electrolyte to perform electrolysis.



An electrolytic cell

The three components of electrolytic cells are an electrolyte and two electrodes.

Uses of electrolytic cells: استخدامات الخلايا الالكتروليتية

1. Electroplating: This is the process of coating an electrically conductive object with a thin layer of metal using an electrical current. The electroplating with a particular element adds many properties to metal, such as protection against corrosion, abrasion resistance and wear resistance. This is also used in jewellery and other for several aesthetic reasons.

2. Batteries: Batteries are used in various appliances and machines. These can be formed by electrochemical cells.

3. Electrowinning or electro-refining: It helps to produce various pure metals such as sodium, calcium, aluminium and magnesium. Both electrowinning and electro-refining are electroplating on a large scale. Both processes are used to purify metals by removing impurities. These are an economical and straightforward process for purification of non-ferrous metals.

In electrowinning, a metal is kept in a liquid leach solution, and then a current is passed from an inert anode to the leach solution. This extracts the metal, and then the metal gets deposited on the cathode. While in the electro-refining process, the unrefined impure metals are present on the anodes and when the current is made to pass through the acidic electrolyte the anodes get corroded, and because of electroplating, the pure refined metal gets deposited on the cathode.

4. Oxygen production: The oxygen used in the spacecraft and submarines is prepared with the help of electrolytic cells.
5. Hydrogen fuel is also produced by using electrolytic cells.

electrowinning of copper:
In the electrowinning process of copper, a bar made from impure copper will behave like the anode, and a piece of pure copper (with little impurities) will act as a cathode. The solution of aqueous $CuSO_4$ and H_2SO_4 will make electrolyte.

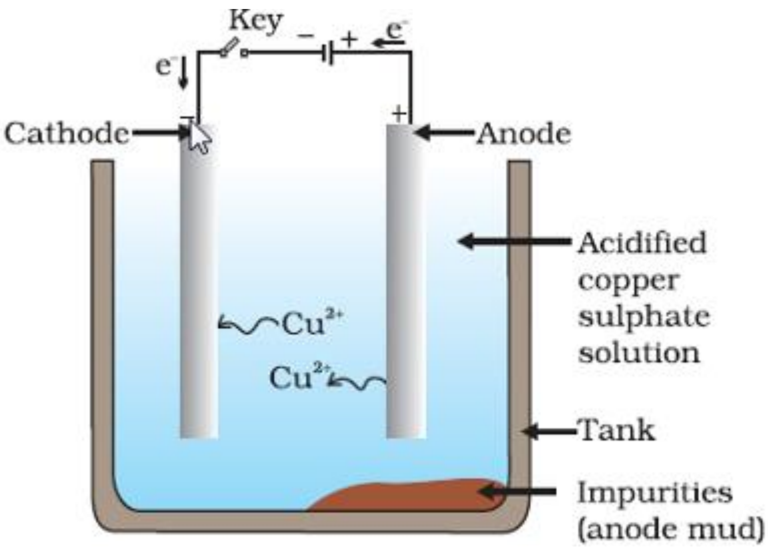


Diagram of electrowinning of copper

Now, when the current is passed in the cell, it results in electrolysis. Due to electrolysis, the impure copper anode is oxidised and forms Cu^{2+} ions, and at the cathode electrode, positive copper ions undergo reduction that produces pure copper metal. The impurities of metals other than these do not get dissolved and instead form a solid sludge at the bottom of the container.

Types of Electrochemical cells انواع الخلايا الالكتروكيميائية

The **electrochemical cells** can also be divided as rechargeable, non-rechargeable and fuel cells.
As we have seen that in fuel cells the fuel is the source of chemical energy required to generate electricity and it has to be supplied externally, in rechargeable and non-rechargeable batteries the fuel is already stored internally, i.e. inside the battery.

Non-Rechargeable batteries البطاريات غير القابلة للشحن

The non-rechargeable batteries are capable of producing electricity only till the time the fuel inside them is available to generate the chemical reaction. Once these batteries run out of charge, they cannot be reused and have to be disposed of. These are also known as *Primary cells.* These types of cells are considered as harmful for the environment as they need a lot of energy in manufacturing and cannot be reused.

Rechargeable batteries البطاريات القابلة للشحن

Rechargeable batteries are used in cars, and these can be recharged and reused. These types of batteries can be used several times by recharging whenever they get out of charge as they have reversible cell reactions that allow them to recharge again. These are **also known as *secondary cells***. These batteries can run both as a galvanic cell and an electrolytic cell.

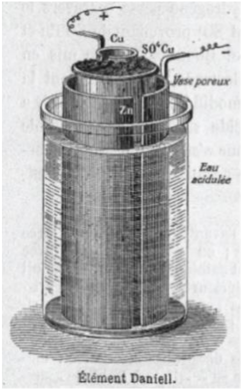
Examples of rechargeable or secondary batteries are Lead-Acid battery, nickel-cadmium (NiCd) battery and Silver-zinc batteries.

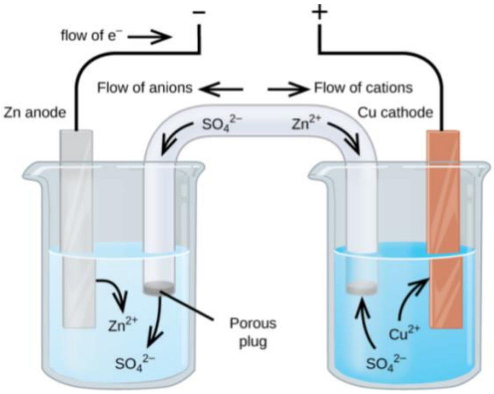
Lead-acid/Lead storage battery بطاريات الرصاص الحامضية

These batteries are formed by joining many electrochemical cells. These are used as a power source in the vehicles. These are known as secondary cells as these can be used for a period of time without an electric supply and can be charged by an electric supply too. Thus, it acts both as an electrolytic and galvanic cell.

Fuel cells خلايا الوقود

Fuel cells are the type of electrochemical cells that convert the chemical energy of fuel into electricity. This is done when an electrochemical reaction takes place between hydrogen fuel and oxygen or any other oxidizing agent. While in batteries chemical energy is generated from the chemicals that are already filled in it, fuel cells need a continuous flow of oxygen and supply of fuel. So, the electricity from fuel cells is dependent on the flow of oxygen and fuel.





The first fuel cell was used commercially by NASA to generate power for space capsules and satellites.

Uses of fuel cells: استخدامات خلاليا الوقود

1. These are used as a primary source of power in industries and residential buildings. Fuel cells are very useful in remote areas.
2. These are also used in vehicles, boats and submarines powered by fuel cells.
3. With the low-quality gas coming from landfills or wastewater treatment plants, fuel-cells can be used to decrease the release of methane in the atmosphere.

A fuel-cell system that runs on hydrogen is generally very light in weight and small in size. They also have no part in moving condition in any situation and also involve no combustion in any of its parts, that's why their reliability of up to 99.9999% is achievable.

Summary: الخلاصة

1. Electrochemical cells are capable of producing electrical energy by using the chemical energy generated through chemical reactions and chemical energy by using electrical energy.
2. The types of electrochemical cells are Galvanic or Voltaic cells, electrolytic cells, Fuel cells, chargeable and non-rechargeable cells.
3. Galvanic cells use the energy generated by the chemical-filled in the cells to generate electrical energy. These cells can be recharged.
4. Electrolytic cells are used to decompose elements, i.e. to break them into different elements. These cells cannot be recharged.
5. Electroplating and electrowinning are the two very useful applications of electrolytic cells that are widely used in industries.
6. Fuel cells use chemical energy from the fuel to generate electricity. Fuel cells are widely used in remote places and areas which are hard to reach. Fuel cells work only until they receive the supply of fuel and oxygen.
7. Rechargeable cells can be used for dozens of times by recharging them whenever they get discharged.
8. Non-rechargeable cells cannot be reused like the rechargeable cells and need to be disposed of once they stop working.
9. Lead storage batteries and dry cells are advance types of electrochemical cells used in daily life.

If a redox reaction can be split into half reactions it becomes possible to build a device, called an electrochemical cell, that has separate compartments (cells) for the oxidant and reductant. This physically prevents them from contacting each other and reacting, but allows for charge transfer in the form of electrons through an external circuit and in the form of counter ions in a salt bridge that connects the cells.

A type of reaction called a **single displacement reaction**, where in a metal displacement reaction a pure metal could displace a the cation of an ionic compound. Let's look at the net ionic equations for the two possible single displacement reactions involved with zinc and copper.

$$\mathbf{Zn(s)+Cu^{+2}\rightarrow Cu(s)+Zn^{+2}}$$

or

$$\mathbf{Cu(s)+Zn^{+2}\rightarrow Zn(s)+Cu^{+2}}$$

To identify which is spontaneous we used the activity series , we see that zinc is more active than copper, meaning metallic zinc will spontaneously dissolve in a solution with copper (II) ions. This means the top reaction above has a negative free energy (it is spontaneous) and could be used to do work, and the bottom reaction above has a positive free energy, which means nothing would happen, unless we added an external source of energy to drive it. In this section we will describe electrochemical cells, and focus on the above reaction to explain how they work. We will show that the spontaneous reactions above

$$\mathbf{Zn(s)+Cu^{+2}\rightarrow Cu(s)+Zn^{+2}}$$

can be used to build a battery, which is commonly known as the Daniell cell, that was originally build by the British chemist John Frederic Daniell.

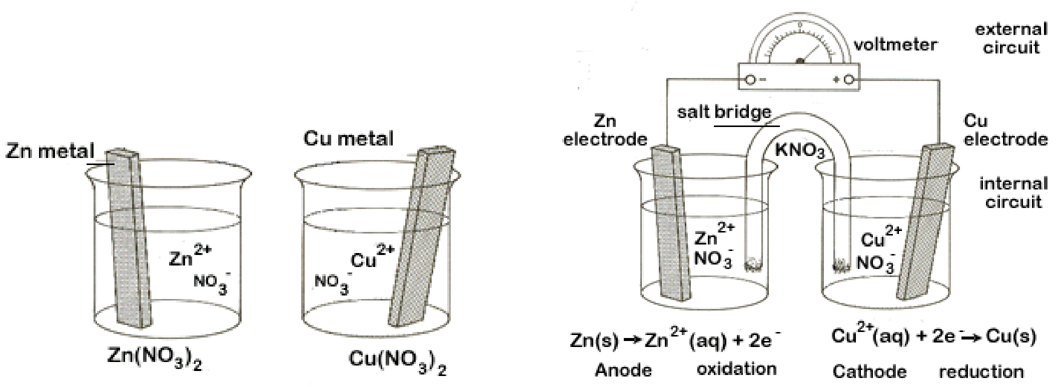
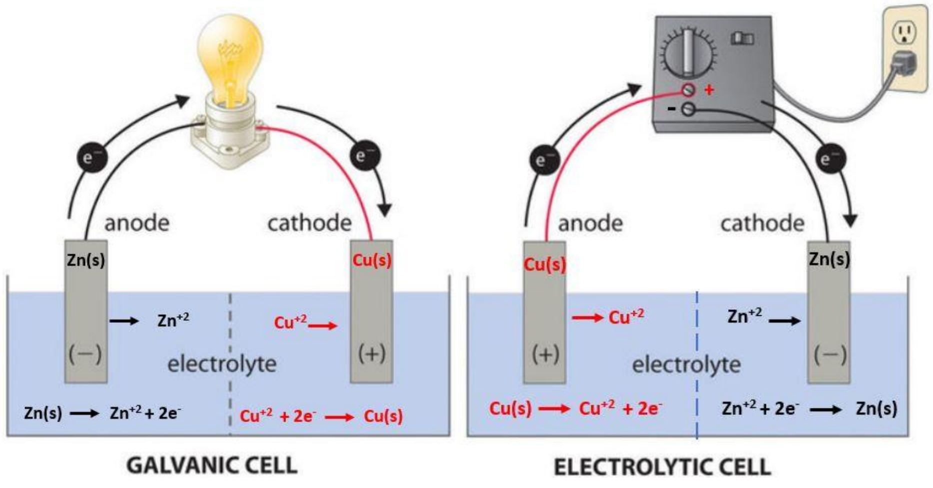


Figure : On the left are two isolated beakers with $Zn(s)/Zn^{+2}(aq)$ and $Cu(s)/Cu^{+2}(aq)$ and nothing happens. On the right is an electrochemical cell which allows electrons to flow from the reductant to the oxidant through an external circuit. In a spontaneous reaction electrons leave the zinc, go through the wire and are then taken up by the copper ions. The salt bridge prevents the copper ions from migrating to the zinc compartment.

placing zinc metal into the copper(II) solution results in a spontaneous redox reaction ($\Delta G<0$), and if we placed the copper metal into the zinc solution no reaction would occur ($\Delta G>0$)

In an electrochemical cell, we allow electrons to be transferred, which will spontaneously occur in the direction of $\Delta G < 0$, and a cell operating in this fashion is called a galvanic or voltaic cell, which can be used to provide energy to do work, like the common "battery" we use in flashlights and electrical devices. Just as we could drive a nonspontaneous reaction by coupling it to a spontaneous reaction, we could hook up an external supply of power with the opposite polarity and drive the reaction in the intrinsically nonspontaneous direction. In this case the electrochemical cell is operating in the electrolytic mode and being driven by an external source of energy.



$$\underbrace{Zn(s) + Cu^{+2} \to Cu(s) + Zn^{+2}}_{\substack{\text{operating in spontaneous galvanic mode} \\ \text{releases energy that can do work}}} \qquad \underbrace{Cu(s) + Zn^{+2} \to Zn(s) + Cu^{+2}}_{\substack{\text{operating in nonspontaneous electrolytic mode} \\ \text{requires external energy to make it work}}}$$

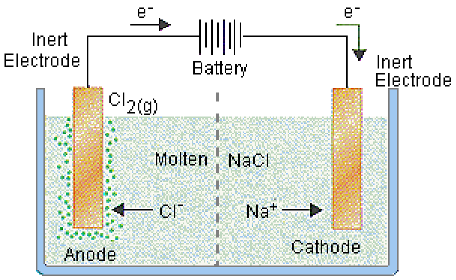
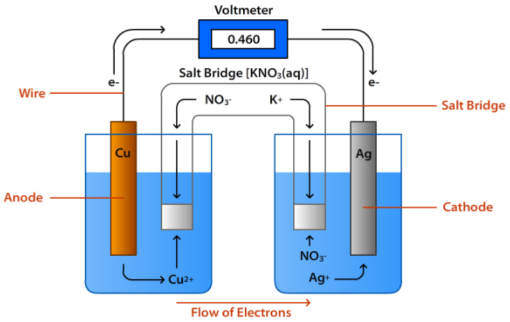
Figure: The two modes an electrochemical cell operates in. The left mode is the spontaneous redox reaction and can be used to provide energy to do work. The right mode is the electrolytic mode, which will not occur unless an external energy source is added to drive it. That is, the reaction on the electrolytic cell is not spontaneous unless it is driven by an external source

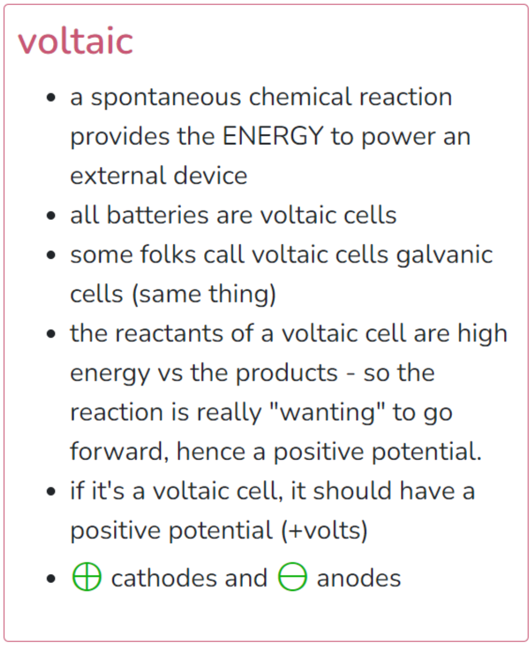
Sign Convention of Galvanic and Electrolytic Cells. Students are often confused that the sign convention of the anode and cathode switch for galvanic and electrolytic cells. What you need to realize is oxidation occurs at the anode and electrons leave the anode, and reduction occurs at the cathode, this is always true. In the Galvanic cell is is easy to see, and electrons flow from the Anodes through a load (light bulb) and to the cathode [+]. Now in an electrolytic cell the electrochemical cell sort of becomes like the load on the galvanic cell, and the sign of the electrodes are defined by the power supply. The copper electrode is hooked to the [+] electrode and there is no load between it and the electrode, so it is the [+] electrode, but it is the anode as electrons flow from it to the [+] electrode of the power supply, and then to the [-] anode. Simply speaking, the electrolytic cell must have an external power supply that drives the reaction, and the sign is based on the electrodes of the power supply

The summary الخلاصة

Electrochemical Cells الخلايا الالكتروكيميائية

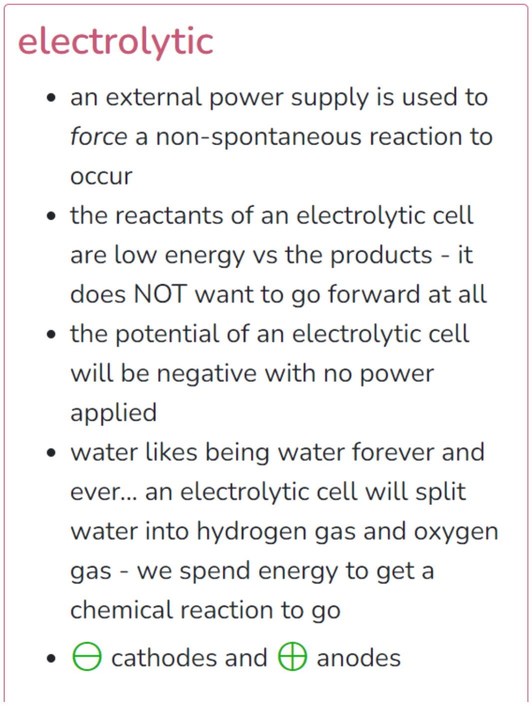
Differences between electrolytic cell and voltaic cell الاختلافات بين نوعي الخلايا الالكتروليتية والجلفانية

1.	It is a designed apparatus where **electrolysis** is carried out.	It is an experimental set up or advice where **chemical energy** is converted into electrical energy.
2.	This cell consists of a glass vessel or made up of any suitable plastic material, in which **two electrodes** are dipped into an electrolyte solution.	Two electrodes are dipped into the same or two **different electrolyte** solution in this type of cell.
3.	Electric current is passed through the solution by connecting the two electrodes to a battery.	Electric current is established only when the two electrodes are joined by a conducting wire.
4.	In this cell, a **chemical reaction** occurs as a result of electric current.	In this cell, **electrical energy** is produced as a result of chemical change or chemical reactions.
5.	**Anode** is positive electrode and cathode is negative electrode.	**Anode** is negative electrode here and cathode is positive electrode.
6.	The **redox- reaction** is nonspontaneous and electrical energy is supplied to make reaction to occur.	The **redox-reaction** is spontaneous and is responsible for the production of electrical energy.
7.	The electrons are supplied by the external battery and enter through cathode and come out through anode.  الخلية الالكتروليتية	The electrons move from anode to cathode in external circuit.  Graphic by Shamsher Singh الخلية الكلفانية



voltaic

- a spontaneous chemical reaction provides the ENERGY to power an external device
- all batteries are voltaic cells
- some folks call voltaic cells galvanic cells (same thing)
- the reactants of a voltaic cell are high energy vs the products - so the reaction is really "wanting" to go forward, hence a positive potential.
- if it's a voltaic cell, it should have a positive potential (+volts)
- ⊕ cathodes and ⊖ anodes

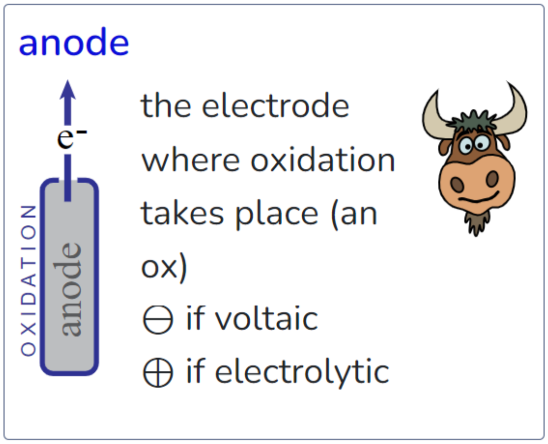


electrolytic

- an external power supply is used to *force* a non-spontaneous reaction to occur
- the reactants of an electrolytic cell are low energy vs the products - it does NOT want to go forward at all
- the potential of an electrolytic cell will be negative with no power applied
- water likes being water forever and ever... an electrolytic cell will split water into hydrogen gas and oxygen gas - we spend energy to get a chemical reaction to go
- ⊖ cathodes and ⊕ anodes

The current flows directly unimpeded from the anode to the cathode here. A bit of a waste of energy but it DOES allow you to see how we "intercept" the electron transfer between copper(II) ions and zinc metal to get electric current.

I am also following a convention in that I'm putting the anode on the left side and the cathode on the right. Make sure you know the definitions of the two electrode here:

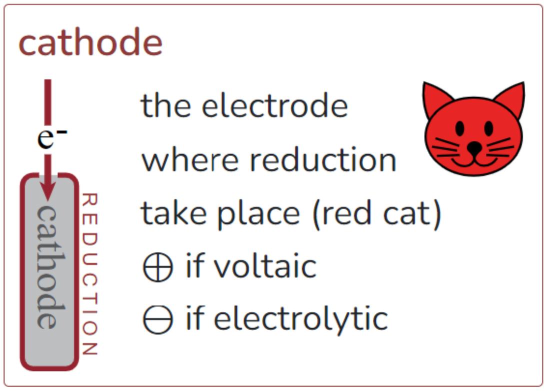


anode

the electrode where oxidation takes place (an ox)

⊖ if voltaic

⊕ if electrolytic



cathode

the electrode where reduction take place (red cat)

⊕ if voltaic

⊖ if electrolytic

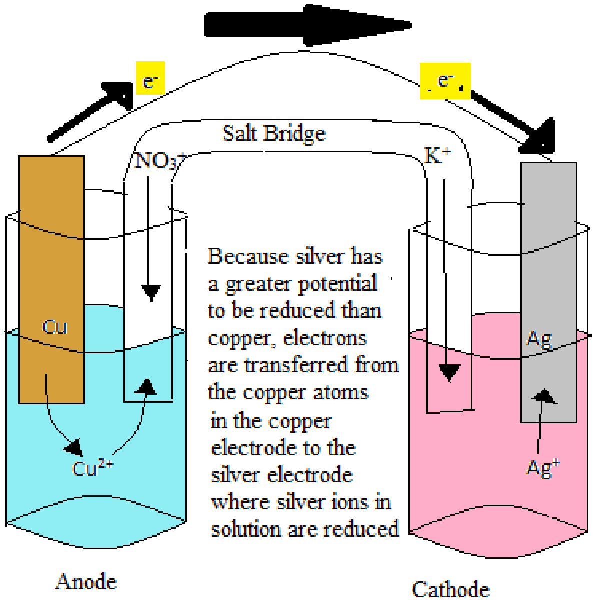
Because oxidation is *always* at the anode, electrons will always leave the anode through the external circuit (wire). And in a likewise manner... because the cathode is *always* where reduction occurs, electrons will always enter the cathode from the external circuit (wire).

The cell potential [Electromotive Force (EMF)] جهد الخلية

The cell potential, Ecell, is the measure of the potential difference between two half cells in an electrochemical cell. The potential difference is caused by the ability of electrons to flow from one half cell to the other. Electrons are able to move between electrodes because the chemical reaction is a redox reaction. A redox reaction occurs when a certain substance is oxidized, while another is reduced. During oxidation, the substance loses one or more electrons, and thus becomes positively charged. Conversely, during reduction, the substance gains electrons and becomes negatively charged. This relates to the measurement of the cell potential because the difference between the potential for the reducing agent to become oxidized and the oxidizing agent to become reduced will determine the cell potential. The cell potential (E_{cell}) is measured in voltage (V), which allows us to give a certain value to the cell potential.

Electrochemical Cell الخلايا الالكتروكيميائية

An electrochemical cell is comprised of two half cells. In one half cell, the oxidation of a metal electrode occurs, and in the other half cell, the reduction of metal ions in solution occurs. The half-cell essentially consists of a metal electrode of a certain metal submerged in an aqueous solution of the same metal ions. The electrode is connected to the other half cell, which contains an electrode of some metal submerged in an aqueous solution of subsequent metal ions. The first half cell, in this case, will be marked as the anode. In this half-cell, the metal in atoms in the electrode become oxidized and join the other metal ions in the aqueous solution. An example of this would be a copper electrode, in which the Cu atoms in the electrode loses two electrons and becomes Cu^{2+} .



Because silver has a greater potential to be reduced than copper, electrons are transferred from the copper atoms in the copper electrode to the silver electrode where silver ions in solution are reduced

The Cu^{2+} ions would then join the aqueous solution that already has a certain molarity of Cu^{2+} ions. The electrons lost by the Cu atoms in the electrode are then transferred to the second half cell, which will be the cathode. In this example, we will assume that the second half cell consists of a silver electrode in an aqueous solution of silver ions. As the electrons are passed to the Ag electrode, the Ag^+ ions in solution will become reduced and become an Ag atom on the Ag electrode. In order to balance the charge on both sides of the cell, the half cells are connected by a salt bridge. As the anode half-cell becomes overwhelmed with Cu^{2+} ions, the negative anion of the salt will enter the solution and stabilized the charge. Similarly, in the cathode half-cell, as the solution becomes more negatively charged, cations from the salt bridge will stabilize the charge.

How does this relate to the cell potential?

For electrons to be transferred from the anode to the cathode, there must be some sort of energy potential that makes this phenomenon favorable. The potential energy that drives the redox reactions involved in electrochemical cells is the potential for the anode to become oxidized and the potential for the cathode to become reduced. The electrons involved in these cells will *fall* from the anode, which has a higher potential to become oxidized to the cathode, which has a lower potential to become oxidized. This is analogous to a rock falling from a cliff in which the rock will fall from a higher potential energy to a lower potential energy.

Note 1:

The difference between the anode's potential to become reduced and the cathode's potential to become reduced is the cell potential.

$$E^{o}_{Cell} = E^{o}_{Red,Cathode} - E^{o}_{Red,Anode}$$

or

$$E^{o}_{Cell} = E^{o}_{Red,Cathode} + E^{o}_{Oxd,Anode}$$

Note 2:

- Both potentials used in this equation are standard reduction potentials, which are typically what you find in tables. However, the reaction at the anode is actually an oxidation reaction - the reverse of a reduction reaction. This explains the minus sign. We would have used a plus sign had we been given an oxidation potential
- $E^{o}_{Ox\,,\,Anode}$ instead, since $E^{o}_{Red} = E^{o}_{Ox}$.
- The superscript "^{o}" in E^{o} indicates that these potentials are correct only when concentrations are 1 M and pressures are 1 bar and 298 k. A correction called the "Nernst Equation" must be applied if conditions are different.

Standard Cell Potential

The standard cell potential (E^o_{cell}) is the difference of the two electrodes, which forms the voltage of that cell. To find the difference of the two half cells, the following equation is used:

$$E^o_{Cell}=E^o_{Red,Cathode} - E^o_{Red,Anode}$$

with

- E^o_{Cell} is the standard cell potential (under 1M, 1 Barr and 298 K).
- $E^o_{Red,Cathode}$ is the standard reduction potential for the reduction half reaction occurring at the cathode
- $E^o_{Red,Anode}$ is the standard reduction potential for the oxidation half reaction occurring at the anode

The units of the potentials are typically measured in volts (V). Note that this equation can also be written as a sum rather than a difference

$$E^o_{Cell} = E^o_{Red,Cathode} + E^o_{Ox,Anode}$$

where we have switched our strategy from taking the difference between two reduction potentials (which are traditionally what one finds in reference tables) to taking the sum of the oxidation potential and the reduction potential (which are the reactions that actually occur). Since $E^o_{\{Red\}} = -E^o_{\{Ox\}}$, the two approaches are equivalent.

Standard Cell Potential Example

The example will be using the picture of the Copper and Silver cell diagram. The oxidation half-cell of the redox equation is:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \quad E^o_{Ox} = -0.340\ V$$

where we have negated the reduction potential $E^o_{Red} = 0.340$ V, which is the quantity we found from a list of standard reduction potentials, to find the oxidation potential E^o_{Ox}. The reduction half-cell is:

$$(\ Ag^+ + e^- \rightarrow Ag(s)\ ) \times 2 \quad E^o_{Red} = 0.800\ V$$

where we have multiplied the reduction chemical equation by two in order to balance the electron count **but we have not doubled E^o_{Red} since E^o values are given in units of voltage**. Voltage is energy per charge, not energy per reaction, so it does not need to account for the number of reactions required to produce or consume the quantity of charge you are using to balance the equation. The chemical equations can be summed to find:

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

and simplified to find the overall reaction:

$$Cu(s) + 2Ag^{+} \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

where the potentials of the half-cell reactions can be summed

$$E^{o}_{Cell} = E^{o}_{Red,\ Cathode} + E^{o}_{Ox,\ Anode}$$

$$E^{o}_{Cell} = 0.800\ V + (-0.340\ V)$$

$$E^{o}_{Cell} = 0.460\ V$$

to find that the standard cell potential of this cell is 0.460 V. **We are done.**

Note that since $E^{o}_{\{Red\}} = -E^{o}_{\{Ox\}}$ we could have accomplished the same thing by taking the difference of the reduction potentials, where the absent or doubled negation accounts for the fact that the **reverse** of the reduction reaction is what actually occurs.

$$E^{o}_{Cell} = E^{o}_{Red,\ Cathode} - E^{o}_{Red,\ Anode}$$

$$E^{o}_{Cell} = 0.800\ V - 0.340\ V$$

$$E^{o}_{Cell} = 0.460\ V$$

Note

The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

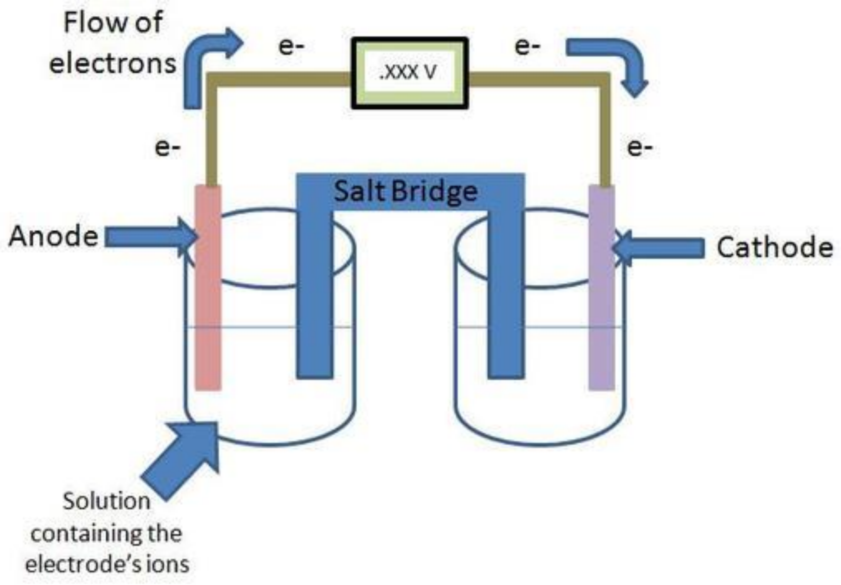
Electrochemical cell

Here is the list of the all the components:

1. Two half cells
2. Two metal electrodes
3. One voltmeter
4. One salt bridge
5. Two aqueous solutions for each half cell

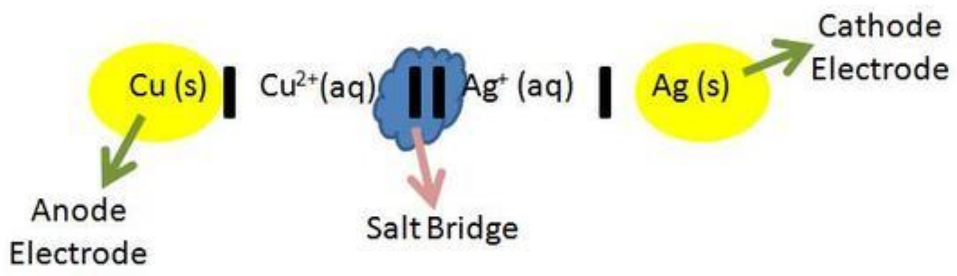
All of these components create the Electrochemical Cell.

How to measure the cell potential?



The image above is an electrochemical cell. The voltmeter at the very top in the gold color is what measures the cell voltage, or the amount of energy being produced by the electrodes. This reading from the voltmeter is called the voltage of the electrochemical cell. This can also be called the potential difference between the half cells, E_{cell}. Volts are the amount of energy for each electrical charge; 1V=1J/C: V= voltage, J=joules, C=coulomb. The voltage is basically what propels the electrons to move. If there is a high voltage, that means there is high movement of electrons. The voltmeter reads the transfer of electrons from the anode to the cathode in Joules per Coulomb.

Cell Diagram



The image above is called the cell diagram. The cell diagram is a representation of the overall reaction in the electrochemical cell. The chemicals involved are what are actually reacting during the reduction and oxidation reactions. (The spectator ions are left out). In the cell diagram, the anode half-cell is always written on the left side of the diagram, and in the cathode half-cell is always written on the right side of the diagram. Both the anode and cathode are separated by two vertical lines (ll) as seen in the blue cloud above. The electrodes (yellow circles) of both the anode and cathode solutions are separated by a single vertical line (l). When there are more chemicals involved in the aqueous solution, they are added to the diagram by adding a comma and then the chemical. For example, in the image above, if copper wasn't being oxidized alone, and another chemical like K was involved, you would denote it as (Cu, K) in the diagram. The cell diagram makes it easier to see what is being oxidized and what is being reduced. These are the reactions that create the cell potential.

Electrodes الاقطاب

Gas Electrodes:

A gas electrode consists of a gas (e.g. H_2, Cl_2, O_2) in contact with a solution containing the ions derivable from the gas e.g. H+, Cl-, OH-. The potential of the gas electrode depends upon the concentration of its ions in the solution and the pressure of a gas.

A gas electrode consists of gas, bubbled about inert metal wire (platinized platinum electrode) immersed in a solution containing ions with which gas is irreversible. Platinum is used as conductor and to adsorb the gas. e.g. Standard hydrogen electrode.

Examples of gas Electrodes:

Standard Hydrogen Electrode (SHE): SHE is represented as,

$$\text{Pt}|\ H_{2(g)}\ (1\ \text{atm.})|\ H^+_{(aq)}\ (1\ \text{M})$$

The half-cell reactions are

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-\ \text{(oxidation) (L.H.S.)}$$
$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}\ \text{(reduction) (R.H.S.)}$$

The electrode potential is arbitrarily assigned zero. This electrode is cation electrode.

Chlorine gas electrode: قطب غاز الكلورين

This electrode is anion electrode. Chlorine gas electrode is represented as,

$$\text{Pt}|\ Cl_{2(g)}\ (1\ \text{atm.})|\ Cl^-_{(aq)}\ (1\ \text{M})$$

The half-cell reactions are

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \quad \text{(oxidation) (L.H.S.)}$$
$$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)} \quad \text{(reduction) (R.H.S.)}$$

Oxygen gas electrode: قطب غاز الاوكسجين

Oxygen gas electrode is represented as,

$$Pt \mid O_{2(g)}\ (1\ atm) \mid OH^-_{(aq)}\ (1M)$$

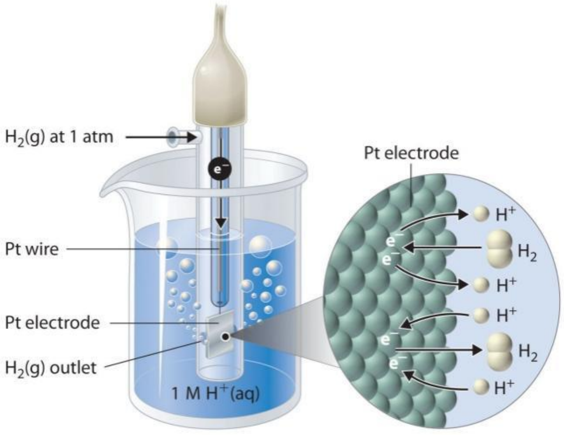
The half-cell reaction is

$$4OH^- \rightarrow 2H_2O + O_{2(g)} + 4e^- \quad \text{(oxidation) (L.H.S.)}$$
$$2H_2O + O_{2(g)} + 4e^- \rightarrow 4OH^- \quad \text{(reduction) (R.H.S.)}$$

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure below) **.**Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$\mathbf{2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.



Figure

The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Figure below shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$\mathbf{Zn_{(s)}|Zn^{2+}{}_{(aq)}\|H^{+}{}_{(aq,1M)}|H_{2(g,1atm)}|Pt_{(s)}}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$\mathbf{2H^{+}{}_{(aq)}+2e^{-}\rightarrow H_{2(g)} \quad E^{\circ}{}_{cathode} = 0V}$$

- anode:

$$\mathbf{Zn_{(s)}\rightarrow Zn^{2+}{}_{(aq)}+2e^{-} \quad E^{\circ}{}_{anode} = -0.76V}$$

- overall:

$$\mathbf{Zn_{(s)}+2H+_{(aq)}\rightarrow Zn^{2+}{}_{(aq)}+H_{2(g)}}$$

$$\mathbf{E^{\circ}{}_{cell}=E^{\circ}{}_{cathode}-E^{\circ}{}_{anode} = 0.76V}$$

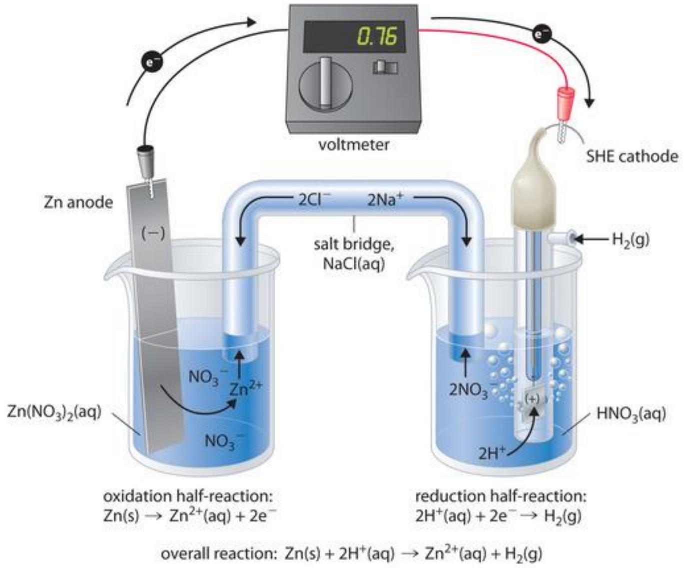


Figure : Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E^{\circ}{}_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^+(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction.In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain $E°_{cell}$: 0 − (−0.76 V) = 0.76 V.

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

Note

E° values do **NOT** depend on the stoichiometric coefficients for a half-reaction, because it is an *intensive* property.

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in above Figure but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$\mathbf{Pt_{(s)}|H2_{(g,1atm)}|H^{+}_{(aq,1M)}\|Cu^{2+}_{(aq,1M)}|Cu_{(s)}}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$\mathbf{Cu^{2+}(aq)+2e^{-}\rightarrow Cu_{(g)}E°_{cathode} = 0.34\ V}$$

- Anode:

$$\mathbf{H2_{(g)}\rightarrow 2H_{+(aq)}+2e–E°_{anode} = 0\ V}$$

- Overall:

$$\mathbf{H2_{(g)}+Cu^{2+}{}_{(aq)}\rightarrow 2H^{+}{}_{(aq)}+Cu_{(s)}}$$

$$\mathbf{E°_{cell}=E°_{cathode}-E°_{anode} = 0.34\ V}$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

In potentiometry we measure the difference between the potential of two electrodes. The potential of one electrode—the working or indicator electrode—responds to the analyte's activity and the other electrode—the counter or reference electrode—has a known, fixed potential. By convention, the reference electrode is the anode; thus, the short hand notation for a potentiometric electrochemical cell is

reference electrode || indicator electrode

and the cell potential is

$$E_{cell} = E_{ind} - E_{ref}$$

The ideal reference electrode provides a stable, known potential so that we can attribute any change in E_{cell} to the analyte's effect on the indicator electrode's potential. In addition, the reference electrode should be easy to make and easy to use. Although the standard hydrogen electrode is the reference electrode used to define electrode potentials, it use is not common. Instead, the two reference electrodes discussed in this section find the most applications.

Calomel Electrodes اقطاب الكالوميل

A calomel reference electrode is based on the following redox couple between Hg_2Cl_2 and Hg (calomel is the common name for Hg_2Cl_2)

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$$

for which the potential is

$$E = E^{o}_{Hg_2Cl_2/Hg} - \frac{0.05916}{2}\log(a_{Cl^-})^2 = +0.2682V - \frac{0.05916}{2}\log(a_{Cl^-})^2$$

The potential of a calomel electrode, therefore, depends on the activity of Cl^- in equilibrium with Hg and Hg_2Cl_2.

As shown in Figure , in a saturated calomel electrode (SCE) the concentration of Cl^- is determined by the solubility of KCl. The electrode consists of an inner tube packed with a paste of Hg, Hg_2Cl_2, and KCl, situated within a second tube that contains a saturated solution of KCl. A small hole connects the two tubes and a porous wick serves as a salt bridge to the solution in which the SCE is immersed. A stopper in the outer tube provides an opening for adding addition saturated KCl. The short hand notation for this cell is

$$Hg(l)|Hg_2Cl_2(s), KCl(aq, sat'd)||$$

Because the concentration of Cl^- is fixed by the solubility of KCl, the potential of an SCE remains constant even if we lose some of the inner solution to evaporation. A significant disadvantage of the SCE is that the solubility of KCl is sensitive to a change in temperature. At higher temperatures the solubility of KCl increases and the electrode's potential decreases. For example, the potential of the SCE is +0.2444 V at 25°C and +0.2376 V at 35°C. The potential of a calomel electrode that contains an unsaturated solution of KCl is less dependent on the temperature, but its potential changes if the concentration, and thus the activity of Cl^-, increases due to evaporation.

For example, the potential of a calomel electrode is +0.280 V when the concentration of KCl is 1.00 M and +0.336 V when the concentration of KCl is 0.100 M. If the activity of Cl^- is 1.00, the potential is +0.2682 V.

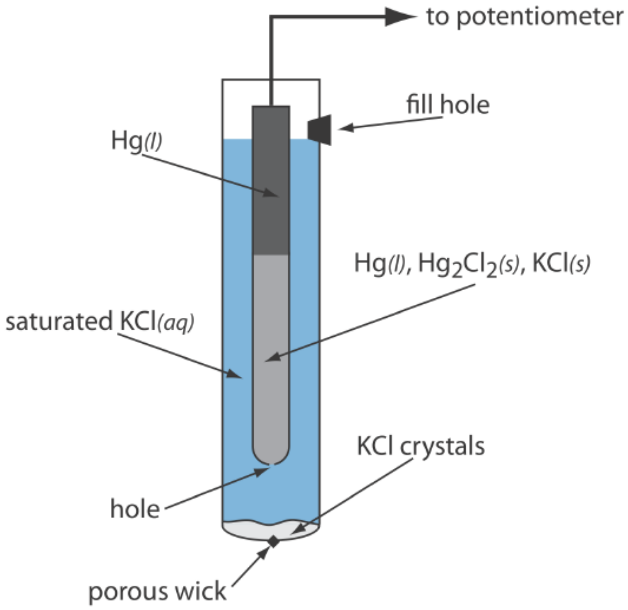


Figure . Schematic diagram showing the saturated calomel electrode.

Advantages of using calomel electrodes include:

- Easy set-up and reproduction.
- Convenient transportation.
- Less auxiliary assets required. Calomel electrodes come with a side tube containing a KCl solution, so no separate salt bridge is required.
- Stable potential. Calomel electrodes' potential does not change appreciably with time nor with slight temperature changes.

Test Yourself اختبر نفسك

Questions اسئلة

What is an electrochemical cell? **ما الخلية الكهروكيميائية**
An electrochemical cell is a device which either uses chemical reactions occurring in it to generate electricity or electricity is used to run different chemical reactions in it.

What are the types of electrochemical cells? **ما انواع الخلايا الكهروكيميائية**
Electrochemical cells are divided into two basic types; voltaic cells and electrolytic cells. Voltaic cells generate an electric current from chemical reactions, while electrolytic cells use electric current to drive chemical reactions.

What is a half-cell? **ما نصف الخلية**
The half-cell is a component of the full cell in which half of the electrochemical process occurs. It contains an electrode suspended in the solution of a specific electrolyte.

What is a salt bridge? **ما الجسر الملحي**
A salt bridge is a part of a cell containing a strong electrolyte that connects the two halves of the cell. It maintains the electrical neutrality in the two halves of an electrochemical cell.

Exercise تمرين

Write the following reactions in standard electrochemical cell notation at standard state conditions.

a. $Cu(s)+Cd^{2+}(aq)\rightarrow Cu^{2+}(aq)+Cd(s)$
b. $2Na(s)+Fe^{2+}(aq)\rightarrow 2Na_{+}(aq)+Fe(s)$
c. $3Zn(s)+2Fe^{3+}(aq)\rightarrow 3Zn^{2+}(aq)+2Fe(s)$
d. $2Al(s)+3Mn^{2+}(aq)\rightarrow 2Al^{3+}(aq)+3Mn(s)$
e. $2H^{+}(aq)+Zn(s)\rightarrow H_2(g)+Zn^{2+}(aq)$
f. $Hg(l)+Sn^{4+}(aq)\rightarrow Hg^{2+}Sn(s)$

Answer a.
Answer b.
Answer c.
Answer d.
Answer e.
Answer f.

Voltaic Cell

Exercise

What is the half-reaction at the anode and what is the reaction occurring at the cathode in the voltaic reaction?

$2Cu^{+}(aq)+I_2(l)\rightarrow 2Cu^{2+}(aq)+2I^{-}(aq)$

Answer الاجابة

Exercise

Which one can occur at the cathode of an electrochemical cell?

a. $NO\rightarrow NO^{-}_{2}$
b. $Cr_2O^{2-}7\rightarrow Cr^{7+}$
c. $I_2\rightarrow I-$
d. none of the above

Answer?

Exercise

Which one can occur at the anode of an electrochemical cell?

a. $Cr_2O^{2-}7\rightarrow Cr^{7+}$
b. $Fe^{2+}\rightarrow Fe$
c. $I_2\rightarrow I^{-}$
d. none of the above

Answer?

Using the information given, determine which reaction occurs at the anode.

i. $Al(s)\rightarrow Al^{3+}(aq)+3e^{-}$
ii. $ClO^{-}_{3}(aq)+6H^{+}(aq)+6e^{-}\rightarrow$
iii. $Cl^{-}(aq)+3H_2O(l)$

a. i.
b. ii.
c. neither
d. both

Answer…………….?

Exercise

Determine the standard potential (V) for the cell reaction.

$2I^-(aq)+2Fe^{3+}(aq)\rightarrow 2Fe^{2+}(aq)+I_2(s)$

Answer………………..?

Exercise

Determine the standard potential (V) for the cell reaction.

$Cr(s)+3Fe^{3+}(aq)\rightarrow 3Fe^{2+}(aq)+Cr^{3+}(aq)$

Exercise

Determine the standard potential (V) for the cell reaction.

$Fe(s)+2Fe^{3+}(aq)\rightarrow 3Fe^{2+}(aq)$

Answer………………..?

Exercise

Determine the standard potential (V) for the cell reaction.

$2Cr(s)+3Fe^{2+}(aq)\rightarrow 3Fe(s)+2Cr^{3+}(aq)$

Answer………………..?

Exercise

Determine the standard potential (V) for the cell reaction.

$3I_2(s)+2Cr(s)\rightarrow 2Cr^{3+}(aq)+6I^-(aq)$

Answer………………..?

Standard Electrochemical Potentials

Exercise

What is the $E°_{cell}$?

$Cu(s)+Cd^{2+}(aq)\rightarrow Cu^{2+}(aq)+Cd(s)$

Answer………………..?

Exercise

What is the expression for Q, in the equation:

$3Zn(s)+2Fe^{3+}(aq)\rightarrow 3Zn^{2+}(aq)+2Fe(s)$

Answer………………..?

Exercise

What is the E_{cell}?

$3Zn(s)+2Au^{3+}(0.004M)\rightarrow 3Zn^{2+}(0.0051M)+2Au(s)$

Answer……………….?

……………………………………………………………………………………………

بعض الاسئلة مع الحلول

1. For this redox reaction

$$Sn(s)+Pb^{2+}(aq)\rightarrow Sn^{2+}(aq)+Pb(s)$$

write out the oxidation and reduction half reactions. Create a cell diagram to match your equations.

2. From the image above, of the cell diagram, write the overall equation for the reaction.
3. If Cu^{2+} ions in solution around a Cu metal electrode is the cathode of a cell, and K^{+} ions in solution around a K metal electrode is the anode of a cell, which half-cell has a higher potential to be reduced?
4. What type of reaction provides the basis for a cell potential?
5. How is the cell potential measured and with what device is it measured?
6. The E^{o}cell for the equation

$$4Al(s)+3O_2(g)+6H_2O(l)+4OH^{-}(aq) \rightarrow 4[Al(OH)_4]^{-}(aq)$$

is +2.71 V. If the reduction of O_2 in OH^{-} is +0.401 V. What is the reduction half-reaction for this reduction half reaction?

$$[Al(OH)_4]^{-}(aq)+3e^{-}\rightarrow Al(s)+4OH$$

Answers الاجابات

1. **oxidation**: $Sn_{(s)} \rightarrow Sn^{2+}_{(aq)} + 2e^{-}_{(aq)}$
   reduction: $Pb^{2+}_{(aq)} + 2e^{-}_{(aq)} \rightarrow Pb_{(s)}$
   cell diagram: $Sn_{(s)} \mid Sn^{2+}_{(aq)} \parallel Pb^{2+}_{(aq)} \mid Pb_{(s)}$

2. $Cu_{(s)} + 2Ag^{+}_{(aq)} \rightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$
3. Because the half-cell containing the Cu electrode in Cu^{2+} solution is the cathode, this is the half-cell where reduction is taking place. Therefore, this half-cell has a higher potential to be reduced.
4. The redox reaction.
5. Cell potential is measured in Volts (=J/C). This can be measured with the use of a voltmeter.
6. We can divide the net cell equation into two half-equations.

- Oxidation: $\{Al(s) + 4OH^-(aq) \rightarrow [Al(OH_4)]^-(aq) + 3e^-\}$ x4; $-E^o$= ? This is what we are solving for.
- Reduction: $\{O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)\}$ x3 E^o= +0.401V
- Net: $4Al(s) + 3O_2(g) + 6H_2O(l) + 4OH^-(aq) \rightarrow 4[Al(OH)_4]^-(aq)$ E^o_{cell} = 2.71V

E^o_{cell}= 2.71V= +0.401V - $E^o\{Al(OH)_4]^-(aq)/Al(s)\}$

$E^o\{[Al(OH)_4]^-(aq)/Al(s)\}$ = 0.401V - 2.71V = -2.31V

Confirm this on the table of standard reduction potentials

……………………………………………………………………………………………..

Resources: المصادر

1. https://alevelchemistry.co.uk/notes/electrochemical-cells/
2. Hyperphysics: http://hyperphysics.phy-astr.gsu.edu/hbase/Chemical/electrochem.html
3. Openstax chemistry 2e
4. Wikipedia
5. Science direct https://www.sciencedirect.com/topics/chemistry/electrochemical-cell
6. http://chembook.org/page.php?chnum=7&sect=4
7. https://chem.libretexts.org/Courses/University_of_Arkansas_Little_Rock/Chem_1403%3A_General_Chemistry_2/Text/19%3A_Electron_Transfer_Reactions/19.03%3A_Electrochemical_Cells
8. https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Voltaic_Cells/The_Cell_Potential
9. Petrucci, Harwood, Herring, and Madura. General Chemistry: Principles and Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson Education, 2007
10. https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Instrumental_Analysis_(LibreTexts)/23%3A_Potentiometry/23.01%3A_Reference_Electrodes

Theories of electrical conductivity

The relationship between molar conductivity (Λ_m^c) and concentration is inverse

$$\Lambda_m^c = \frac{1000 \times K}{C}$$

Λ_m = malar conductivity , C = concentration.

Therefore, as the concentration increases, the molar conductivity decreases because the movement of ions decreases.

The scientist Arrhenius explained the relationship between conductivity and concentration depending on the degree of disintegration (∝). As the degree of disintegration decreases, the conductivity decreases, and with an increase in the degree of disintegration (∝), the conductivity increases. This opinion is wrong for the following reasons:

$$NaCl \rightarrow Na^+ \quad + Cl^-$$

It is an electrical conductor and the degree of dissociation for (NaCl) is equal to one (∝=1)

Therefore, the conductivity does not depend on the degree of disintegration (∝) .

Because the degree of dissociation (∝) in the solution is equal to one, (as well as ∝=1) for (NaCl) in the solid state, (meaning that ∝=1) in the crystal lattice.

That is, (NaCl) in both cases is completely ionized.

If Arrhenius' interpretation is correct, the conductivity of NaCl in the solution must be equal to its conductivity in the solid state.

But it was found that (NaCl) in the solid state is not an electrical conductor, but in the solution it is a conductor. Because conductivity depends on the movement of ions within the solution, NaCl is therefore non-conductive. Because its ions are free to move in the solution, while in the crystal lattice their movement is restricted, so it is non-conductive in the solid state.

This proves that Arrhenius' interpretation is wrong. It was later corrected by **Debye, Höckel, and Onsacker:**

لذا فان عند زيادة التركيز تقل التوصيلية المولارية وذلك لأن حركة الأيونات تقل.

العالم ارينيوس فسر العلاقة بين التوصيلية والتركيز بالاعتماد على درجة التفكك (∝) حيت تقل درجة التفكك تقل التوصيلية وبزيادة درجة التفكك (∝) تزداد التوصيلية وهذا الرأي خاطئ للسب الاتي :

$$NaCl \rightarrow Na^{+} \quad + Cl^{-}$$

يكون موصل للكهربائية ودرجة التفكك لـ (NaCl)تساوي واحد ($\propto = 1$)
لذا فأن التوصيلية لا تعتمد على درجة التفكك (∝) .
لأن درجة التفكك (∝) في المحلول تساوي واحد وكذلك ($\propto = 1$) لـ ($NaCl$) في الحالة الصلبة أي ان ($\propto = 1$) في الشبكة البلورية .
اي ان ($NaCl$) في الحالتين يتأين تأين تام .
فأذا كان تفسير ارينيوس صحيح يجب ان تكون توصيلية ($NaCl$) في المحلول مساوية الى توصيليته في الحالة الصلبة .
لكن وجد ان ($NaCl$) في الحالة الصلبة غير موصل للكهربائية اما في المحلول فهو موصل . لأن التوصيلية تعتمد على حركة الأيونات داخل المحلول لذا فيكون ($NaCl$) غير موصل .لأن أيوناته تكون حرة الحركة في المحلول أما في الشبكة البلورية مقيدة الحركة لذا فهو غير موصل في الحالة الصلبة .
وهذا يثبت ان تفسير ارينيوس خاطئ . وقد صحح فيما بعد من قبل كل من (ديباي و هوكل وأونساكر) :

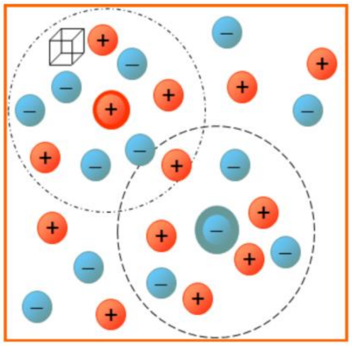
Debye, Hückel and Onsaker theory: : نظرية ديباي وهوكل وأونساكر

It is the most general theory, as they believe that the increase in conductivity in dilute solutions is due to the movement of ions within the electrolyte solution.

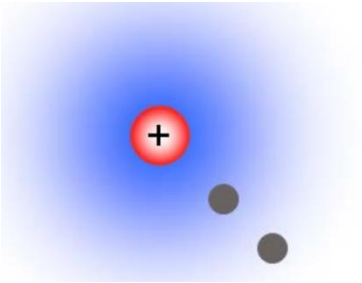
In dilute solutions (∝=1) because $\Lambda_{m}^{c} = \Lambda_{m}^{o}$

Q/ How did they visualize the solution before passing the electric current or before starting to measure the conductivity?

A/ 1- A solution consists of ionic clusters as a result of the attraction between positive (+) and negative (-) ions.



2- Each ion appears as if it is located in the center of a sphere surrounded by negative and positive ions and polarized solvent molecules.



3- The ion located at the center of the ball is called the central ion and the surrounding negative and positive ions and polarized solvent molecules (ionic atmosphere).

4- The resultant charge in the ionic atmosphere (surrounding) is equal in magnitude to the charge of the central ion and opposite to it in sign.

س/ كيف تصور هؤلاء المحلول قبل امرار التيار الكهربائي او قبل البدء بقياس التوصيلية؟
ج/ 1- يتكون المحلول من تجمعات ايونية نتيجة التجاذب بين الأيونات الموجبة (+) والسالبة (-).

2- يظهر كل ايون وكأنه موجود في مركز كرة تحيط به ايونات سالبة وموجبة وجزيئات المذيب المستقطب

3- يسمى الأيون الموجود في مركز الكره بالأيون المركزي وما يحيط به من الأيونات سالبة وموجبة وجزيئات المذيب المستقطب (بالجو او المحيط الأيوني).

4- تكون محصلة الشحنات الموجودة في الجو الأيوني مساوية في المقدار لشحنة الأيون المركزي ومخالفة له في الإشارة .

Q: What happens when electric current passes through?

C/ The following effects occur

1- It moves a certain distance, which leads to distortion of the ionic atmosphere around it

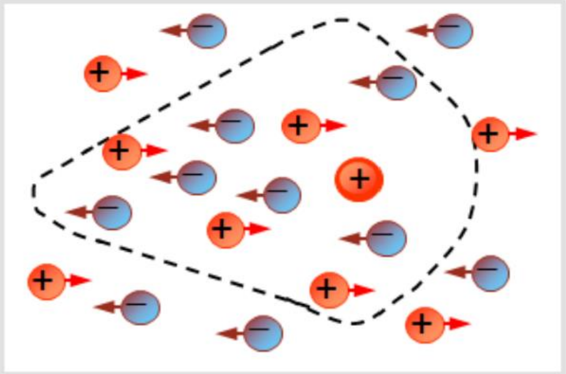
•The ionic atmosphere can return to its symmetry around the reference ion if

•Its contents were such that it could change their position immediately

•Or if the reference ion does not continue to move, then it takes time for the ionic atmosphere to return to its symmetry around the reference ion.

This time is called the relaxation time.

The effect of asymmetry (relaxation effect) when an electric current is passed, the central ion moves toward the negative electrode and the ionic atmosphere toward the positive electrode. The time required for the central ion to get rid of the ionic atmosphere and for the ionic atmosphere to return to its previous form is called relaxation, and the resulting decrease in conductivity is due to obstructing the movement of the central ion. It is called the asymmetry effect or (relaxation effect) and its symbol is (A) and its value is equal to:



س/ ماذا يحدث عند امرار التيار الكهربائي ؟

ج/ تحدث التأثيرات التالية

1- فإنه يتحرك مسافة معينة مما يؤدى الى تشوه الجو الايونى حوله •يستطيع الجو الايونى العودة الى تماثله حول الايون المرجعى إذا •كانت محتوياته أن تستطيع أن تغير وضعها فى الحال •أو إذا لم يستمر الايون المرجعى فى الحركة لذلك يلزم وقت حتى يستطيع الجو الايونى العودة الى تماثله حول الايون المرجعى هذا الوقت يسمى زمن الاسترخاء.

تأثير عدم التناسق (تأثير الاسترخاء) عند امرار التيار الكهربائي يتجه الأيون المركزي باتجاه القطب السالب والجو الأيوني باتجاه القطب الوجب وان الزمن اللازم لتخلص الأيون المركزي من الجو الأيوني وأعاده الجو الأيوني الى شكلة السابق يسمى الاسترخاء والنقصان الناتج بالتوصيلية هو بسبب اعاقة حركة الأيون المركزي يسمى بتأثير عدم التناسق او (تأثير الاسترخاء) ويرمز له (A) وقيمته تساوي :

$$\mathrm{A} = \frac{82.4}{(\varepsilon.T)^{1/2}.\,\text{ɧ}} \quad (\mathrm{S}.Cm^2.\mu^2)$$

حيث ان (A) يمثل تأثير عدم التناسق
و(ε)يمثل ثابت العزل الكهربائي
و(T) درجة الحرارة المطلقة
و(ɧ) تمثل اللزوجة

-2 التأثير الكهرو فورتي :

بما أن الجو الأيوني ممحل بجزيئات المذيب المستقطب وتتحرك بالاتجاه المعاكس لحركة الجو(المحيط) الأيوني والتي هي عكس حركة الأيون المركزي ونتيجة ذلك سيكون هناك قوى احتكاك بين الأيون المركزي وجزيئات المذيب وتسمى هذه الإعاقة بالتأثير الكهرو فوريتي ويرمز له بالرمز (B).

$$\mathbf{B} = \frac{\mathbf{8.2 \times 10^5}}{(\boldsymbol{\varepsilon}.\boldsymbol{T})^{3/2}}$$

ووحدته ($\mu^{1/2}$)

Therefore, these scientists proposed a modification to the equation:

لذلك اقترح هؤلاء العلماء تعديل على المعادلة

$$\Lambda_{\boldsymbol{m}}^{\boldsymbol{c}} = \Lambda_{\boldsymbol{m}}^{\boldsymbol{o}}$$

- The Debye, Hückel and Onsager equation is valid for monovalent electrolytes in the range of concentrations M 0.001, while at higher concentrations the deviation from it is large.
- In polyvalent electrolytes, deviation from this equation occurs at concentrations lower than those for monovalent electrolytes.

فى حين عند تركيزات 0.001 M معادلة ديباى و هوكل واونساجر صالحة للالكتروليتات احادية التكافؤ فى مدى تركيزات• أعلى فإن الحيود عنها يكون كبيرا.

فى الالكتروليتات متعددة التكافؤ فإن الحيود عن هذه المعادلة يكون عند تركيزات اقل من تلك للالكتروليتات أحادية التكافؤ.•

But due to the electrophoretic effect and lack of relaxation,(Λ_m^c) does not equal(Λ_m^o), but rather:

لكن بسبب التأثير الكترو فورتي وعدم الاسترخاء فأن (Λ_m^c) لا تساوي (Λ_m^o) وإنما :

$$\Lambda_{m}^{c} = \Lambda_{m}^{o} - \{ A + B\Lambda_{m}^{o} \}\sqrt{C}$$

This equation is called the Onsaker equation for strong and very dilute electrolytes, and from the Kohlorousch equation:

وتسمى هذه المعادلة بمعادلة اونساكر للإلكتروليتات القوية والمخففة جدا ومن معادلة كرلاوش :

$$\Lambda_{m}^{c} = \Lambda_{m}^{o} - R\sqrt{c}$$

وبمقارنتها مع معادلة اونساكر نحصل على

Comparing it with the Onsaker equation we get:

$$R = A + B\Lambda_{m}^{o}$$

The Kohlorousch constant combines the two effects discussed by Debye, Höckel, and Onsaker

There is a table showing the values of (A, B) for some solvents at (25ºC).

حيث ان ثابت كرلاوش يجمع بين التأثيرين الذي ناقشها **دیباي وهوكل وأونساكر**

هناك جدول يوضح قيم (A,B) لبعض المذيبات عند (25ºc) .

المذيب	**A**	**B**
H_2O	60.2	0.229
CH_3OH	151.1	0.923
CH_3CN	22.7	0.716
CH_3CH2OH	89.7	0.719

Example: The molar conductivity of KCl solution changes with concentration as follows:

مثال / تتغير قيمة التوصيلية المولارية لمحلول (KCl) مع التركيز كما يلي :

C	0.001	0.005	0.01	0.02
Λ_m^c	146.6	143.5	141.2	138.2

جد قيمة (Λ_m^o) وثابت كرلاوش باستخدام او بدلالة (A,B) حيث المذيب هو الماء وبدرجة حرارة (25ºc) باستخدام الجدول السابق ؟

R = A+B Λ_m^o ∴ R = 60.2 +0.229Λ_m^o

المحلول غير المائي

A non-aqueous solution is a solution obtained by dissolving a solute in any solvent other than water. The solvent can be an organic compound such as acetone, toluene, ether, alcohol, benzene, etc. Electrical conductors are materials through which charges can pass without resistance. Non-aqueous solutions are organic liquids, and most organic liquids or solvents are covalent and therefore non-conductive.

Electrolytes are classified based on their ability to ionize into two types:

1- Strong electrolytes

2- Weak electrolytes

Strong electrolytes: are electrolytes that ionize largely or completely in solution, such as strong acids, strong bases, and inorganic salts. An example of this is sodium chloride salt (NaCl), which consists of Na and Cl ions, where the different charges are linked together by an electrical attraction force. When the salt is dissolved in water, its crystal structure is destroyed by the solvent molecules, and the ions are released into the solution and head towards the electric field applied to them, carrying the electric current within the solution.

The conductivity of strong electrolytes is high, and their conductivity increases slightly upon dilution.

Weak electrolytes are those electrolytes that undergo little ionization, and their conductivity ratio is a measure of the degree of dissociation. Examples include acetic acid, all organic acids, amine solutions, and ammonia. Note: The conductivity coefficient increases with increasing dilution of the electrolyte solution to reach its final value at infinite dilution. To measure the conductivity of strong electrolytes, we use Kohlrausch's law, as strong electrolyte solutions obey this law. Kohlorousch's law, where the scientist Kohlorousch was able in 1864 to obtain the values of the molar conductivity at infinite dilution Λ_0 for a number of strong electrolytes and noticed for pairs of salts between which there is a common ion that the difference between the conductivity of these salts was very close to the constant value) for strong electrolytes (and he concluded that the molar conductivity at a concentration equal to zero for weak electrolytes can be expressed as a set of independent contributions from the ions that make up the molecule in the electrolyte (these conclusions reached by the scientist Kohlorousch were called Kohlorousch's law for independent ion migration. Studying the conductivity coefficient for many solutions, where he was able to confirm the following:

Electrolytes at infinite dilution, each ion contributes a specific amount (called ionic conductivity) to the molar conductivity of the electrolyte that includes the ion in its composition and regardless of the other ion) meaning that the dissociation of each electrolyte is complete and thus the internal effect of the ions is not apparent on each ion moves or migrates through the solution independently of its co-ion (and the equivalent conductivity of the electrolyte depends on its nature and not on all the ions combined within the solution). This law is known or called Kohlrausch's law of independent ionic migration.

$$\Lambda_0 =(\lambda^{+\,0}) +(\lambda^{-\,0})$$

Conductivity at infinite dilution $\Lambda_0{}^{+}$ We denote the ionic conductivity of the positive ion at infinite dilution λ − We denote the ionic conductivity of the negative ion at infinite dilution λ According to Kohlrausch's law, we write the infinite conductivity of the electrolyte with the formulas $+ M\upsilon -, x\upsilon$, in the following form:

$$\Lambda_0 =(v^{+}\lambda^{+})+ (v^{-}\lambda^{-})$$

The numbers of positive and negative ions that make up electrolytes. For example, NaCl salt

For NaCl : $v- = 1, v+ = 1$

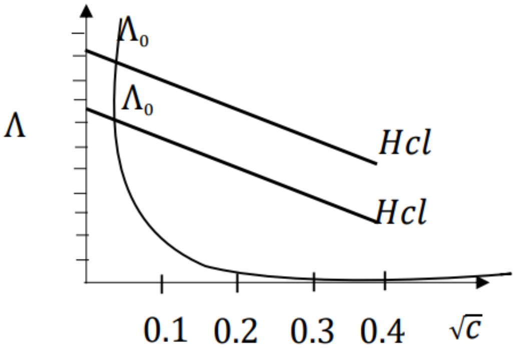
For $CuSO_4$: $v- = 1, v+ = 1$

For $MgCl_2$: $v- =2, v+= 1$

There are special tables for positive and negative ions that indicate the conductivity of these ions. Through the tables, the molar conductivity can be calculated at infinite dilution Λ_0 of the electrolyte. By plotting Λ for the strong electrolyte solution against the square root of the concentration √c, the curve approaches linearity in dilute solutions and the molar conductivity is calculated according to the following equation

$$\Lambda_0 = \Lambda - b\sqrt{c}$$

When plotting the molar conductivity values Λ_m versus the reciprocal of the concentration (diluted) √c, we notice that the molar conductivity approaches a specific value in the case of KCl whenever the concentration of KCl decreases significantly. The same is the case for HCl, and the difference between the conductivities of the two electrolytes is almost a constant value. While acetic acid behaves completely differently, as the molar conductivity increases steadily as the solution becomes more diluted, i.e. the molar conductivity when the concentration is equal to zero will give accurate Λ_0 valuesfor strong electrolyte solutions, while the result is not accurate. Completely. With weak electrolyte solutions, due to the sudden speed of change in molar conductivity versus concentration when the concentration approaches zero.



Example

Find the molar conductivity of aqueous solutions LiCl, MgCl2 at infinite dilution, given that the molar ionic conductivity is Cl^{-} = 76.3

$\Omega^{-1} cm^2 mol^{-1}$ Mg^{+2} = 116 Li^{+} = 38.2

الحل: 1- المحلول $Licl$

$$\lambda^{+} = 38.7\ \Omega^{-1}\ cm^2 mol^{-1} \qquad \lambda^{-} = 76.3\ \Omega^{-1} cm^2 mol^{-1}$$

$$\Lambda^0 = \lambda_+^0 + \lambda_-^0 = 38.7 + 76.3 = 115$$

$$or\ 1.15\ x10^2 \Omega^{-1} cm^2 mol^{-1}$$

2- المحلول $MgCl_2$

$$\Lambda^0 = \lambda_0^+ + 2\lambda_0^-$$

$$\Lambda^0 = {}_{v+}\lambda_+^0 + \lambda_-^0 v_-$$

$$= 1 \times 116 + 2 \times 76.3 = 116 + 152.6$$

$$= 268.6\ \Omega^{-1} cm^2 mol^{-1}$$

Applicaticonductivity measurements ons of

One of the most important applications of conductivity measurements to solve chemical problems can be explained as following:

1- Finding the solubility of sparingly soluble salts:

It is very difficult to determine the solubility of sparingly soluble salts in solutions by chemical methods, but the conductivity coefficient of saturated solutions of such salts and the appropriate means to calculate their solubility are can be measured:

A saturated solution of silver chloride and barium sulfate (sparingly soluble salt) is taken in water with a known specific conductivity(LH) and then we measure the conductivity coefficient of the saturated solution(Lt). This value includes the specific conductivity of the water with a known vity and the salt together, so the specific conductivity conducti value of the salt is:

$$L_s\,(\text{salt}) = (L_t - L_{H_2O})$$

The conductivity coefficient of Ls (salt) can be measured by following equation:

$$\Lambda_0 = \frac{10^3}{S} L_{s\,(\text{salt})}$$

Where (**S**) is the solubility (equivalents/liter) of the salt, while the saturated solution is very dilute and does not differ much from Λ_0, if we take the substitution to be:

$$S = \frac{10^3}{\Lambda_0} L_{s\,(\text{salt})}$$

$$\Lambda_0 = \upsilon_+ \lambda^+ + \upsilon_- \lambda^-$$

Knowing the ionic conductivity of the components of the ions given in the table and knowing the known value of Λ_0, we can practically find the $L_{s(\text{salt})}$.

Example:

It was found that the specific conductivity of a saturated solution of silver chloride at 25 °C is 3.88×10^{-4} Ohm^{-1}.m^{-1} while the water used to dissolve it was 1.6×10^{-4} and the ionic conductivity for λ_+^0 Ag = 0.00619 ohm.m, the ionic conductivity of chlorine is 0.007638 ohm.m^{-1}. Calculate the solubility of silver chloride in water in grams/liter at this temperature, knowing that the gram equivalent weight for AgCl is 143.42.

$$L_{s_{(AgCl)}} = L_l - L_{H_{(H_2o)}}$$
$$= 3.88 \times 10^{-4} - 1.6 \times 10^{-4} ohm^{-1} m^{-1}$$
$$= 2.28 \times 10^{-4} ohm^{-1} m^{-1}$$
$$\Lambda_{0_{(Agcl)}} = u_+ \lambda^0_{Ag^+} + U_- \lambda^0_{cl^-}$$
$$= 1 \times 0.006192 + 1 \times 0.007638$$
$$= 0.01383 ohm^{-1} m^2 mol^{-1}$$
$$S = \frac{1000}{\Lambda_0} L_{s_{(Agcl)}}$$
$$S = \frac{1000 \times 2.28 \times 10^4 ohm^{-1} m^{-1}}{0.013830 hm^{-1} m^2 mol}$$
$$S = 1.63 \times 10^{-5} m^{-3} mol^{-1}$$

الوزن المكافئ الغرامي لـ $Agcl$ هو 143.42

$$\therefore 1.65 \times 10^{-5} \times 143.74 = 2.36 \times 10^{-4} g/liter$$

Solubility of $A_g cl$ at 25C°

2- sociation of weak electrolyteDegree of dis

The scientist Arens suggested that the degree of dissociation of weak electrolyte solution such as CH_3COOH can be calculated from the equivalent conductivity of the electrolyte and from the equivalent conductivity at infinite dilutionΛ_0 according to the following equation

$$\Lambda_0 = \lambda_0^+ + \lambda_0^- \quad \text{............eq. 1}$$

esent in the solution and their Electrolytic conductivity depends on the number of ions pr mobility. Accordingly, the dilution process increases the dissociation of the weak electrolyte into ions and does not change its mobility.

This is the Arrens principle. Let us assume that one gram equivalent of the electrolyte dissociates to give

(**α g**) an equivalent of each ion in the solution when diluted by(v).

So the conductivity is given by the following relation:

$$\Lambda\upsilon = \alpha\lambda^0_+ + \alpha\lambda^0_-$$
$$\Lambda\upsilon = \alpha(\lambda^0_+ + \lambda^0_-) \quad \text{-----------} \quad \text{eq 2}$$

Where **Λv** is the equivalent conductivity measured upon dilution, meaning that one gram equivalent is dissolved in 1 m^3 of the solution.

α it symbolizes the degree of dissociation of the electrolyte. By dividing equation (2) by equation (1), we get:

$$\frac{\Lambda_\upsilon = \alpha\,(\lambda^0_+ + \lambda^0_-)}{\Lambda_0 = (\lambda_+^0 + \lambda^0_-)} \quad \text{---------------} \quad \text{eq. 3}$$

$$\alpha = \frac{\Lambda_\upsilon}{\Lambda_0}$$

strong Equation 3 can be applied to weak electrolytes but not to strong electrolytes, because electrolytes dissociate completely at all practical dilutions. That is, the conductivity rate of a strong electrolyte depends on the rate of migration of ions and not on the degree of dissociation.

Now let us assume that the weak electrolyte, let it be acetic acid, dissociates in water according to the following equation:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

initial conc =	c	0	0
conc. after dessosiation(αc)	c-αc	xαc	yαc

لو كان تركيز الالكتروليت c (مول/ لتر) . ودرجة التفكك هي درجة التفكك هي α إذا تركيز الالكتروليت A^- هي αx و M^+ هي αc أما كمية المادة المارة المتفككة هي $c(1-x)$ مول ومن تطبيق قانون فعل الكتلة فإن ثابت التفكك يمكن إيجاده بهذه العلاقة:

(27)

$$K_\alpha = \frac{C_{M^+}C_{A^-}}{C_{MA}} = \frac{\alpha^2 c}{1-\alpha} \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

وعند ثبوت درجة الحرارة فإن قيمة K_α هي ثابتة وعند تغير التركيز C فإن درجة التفكك α يجب ان تتغير حتى تجعل قيمة K_α ثابتة

إن المعادلة رقم (4) تبين تغير درجة التفكك مع التركيز التي يعبر عنها بقانون اوستفالد له للتخفيف **Ostwald dilution low** هذا القانون يطبق على الالكتروليتات الضعيفة مثل الأحماض العضوية والقواعد الضعيفة.

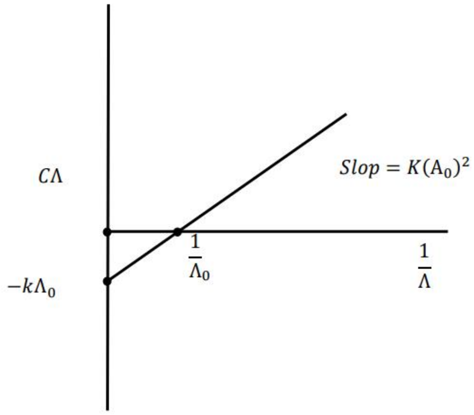
$$k = \frac{c\left(\frac{\Lambda}{\Lambda_0}\right)^2}{1-\frac{\Lambda}{\Lambda_0}}$$

بإعادة ترتيب المعادلة نحصل

$$K = \frac{C\Lambda^2}{\Lambda_0(\Lambda_0-\Lambda)}$$

وإعادة ترتيب أخرى نحصل

$$C\Lambda = K\,(\Lambda^0)^2\left(\frac{1}{\Lambda}\right) - k\Lambda_0$$



Example:

The equivalent conductivity of a solution of acetic acid with a concentration of 1.288 x 10^{-3} was found to be 0.0004815 ohm $^{-1}$.m^{2} at 25°C and the equivalent conductivity of the solution at infinite dilution was 0.03906 ohm $^{-1}$. m^{2}. Calculate the dissociation constant of the acid at this concentration.

Solution: Acetic acid decomposes according to the equation:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

The dissociation constant is given by the relation:

$$K\alpha = \frac{C_{H^+}\, C_{CH_3COO^-}}{C_{CH_3COOH}}$$

By applying Ostwald's law of dilution:

$$K\alpha = \frac{\alpha^2 c}{1-\alpha}$$

$$\alpha = \frac{\Lambda_\upsilon}{\Lambda_0} = \frac{0.004815}{0.03906} = 0.1230$$

$$\therefore \quad K\alpha = \frac{\alpha^2 c}{1-\alpha} \Longrightarrow K\alpha = \frac{(0.1230)^2\,(0.00178)}{1-0.1232}$$

$$= 1.78 \times 10^{-5}$$

Faraday's Laws of Electrolysis

Michael Faraday in the year 1834 AD studied the electrolysis and reached process of electrolysis two laws that govern the.

Faraday was the first to discover quantitatively the relationship between the amount of current used and the extent of the chemical change that occurs at the electrodes during electrolysis.

The first Law:

It states:

substance The amount of m (g) that undergoes a chemical change) (oxidation or reduction ,dissolution, precipitation, or gas evolution) at the electrodes is directly proportional to the amount of electricity (Q) that passes in the electrolytic solution or molten metal.

The amount of electricity (Q) is measured in coulombs, which is the number of amperes (current intensity) passing in time unit.

Formulate the first law mathematically

Assuming that the amount of matter which undergoes a change at the poles (dissolution, sedimentation, ascent),

m= its mass and the intensity of the applied current is **I, and the time of the current** passage is (s**) = t**

Then the first law in its mathematical form:

$$m \propto Q \Rightarrow m \propto I \cdot t$$

$$m = K \cdot I \cdot t$$

Where K proportionality constant, called the electrochemical equivalent. Its value depends on the type of substance that underwent a change and is measured in g/coulomb.

The electrochemical equivalent K can be defined mathematically:

$$K = \frac{m}{I.\,t}$$

$$K = \frac{m}{Q} = g/C$$

p (m/Q) = (K), the electrochemical equivalent can be defined asFrom the mathematical relationshi

The amount of a substance (in grams or kilogram)that undergoes a change (oxidation or reduction) as a result of the passage of an amount of electricity equal to one coulomb.

the electrochemical equivalent Calculation of

It is calculated from the following relationship

$$K = \frac{Mw}{Z\,F} = \frac{Ew}{F}$$

or

$$K = \frac{Aw}{Z\,F} = \frac{Ew}{F}$$

Where (Mw) expresses the molecular weight when the product is a molecule such as (H_2, Cl_2)

While (Aw) expresses the atomic weight when the product is a metal such as Cu, Ag…..

and (Ew) expresses the equivalent weight which is the division of the molecular weight or atomic weight by (z) the number of electrons transferred in the balanced reaction.

Example

Calculate the electrochemical equivalent weight of hydrogen (H_2) and silver(Ag) if you know that the atomic masses : (Ag = 108, H =1)

$$2H^+ + 2\bar{e} \longrightarrow H_2(g)$$

$$K_{H_2} = \frac{2 \times 1}{2 \times 96500} = 1.036 \times 10^{-5} g/C = 1.04 \times 10^{-8}\ Kg/C$$

$$Ag^+(aq) + \bar{e} \longrightarrow Ag$$

$$K_{Ag} = \frac{108}{1 \times 96500} = 1.119 \times 10^{-3}\ g/C = 1.12 \times 10^{-6}\ Kg/C$$

وبالتعويض بقيمة $K = \frac{Aw}{ZF}$ في القانون الأول : $m = K . I . t$ نحصل على:

$$m = K . I . t$$

$$m = \frac{Aw}{ZF} . I . t$$

$$m = \frac{Aw . I . t}{Z \times 96500}$$ (where **Aw** for deposited atoms : Na, K, Cr, Cu, Ag)

or

$$m = \frac{Mw . I . t}{Z \times 96500}$$ (where **Mw** for released molecules as : H_2,Cl_2)

Explanation of Faraday's first law

Let us take as an example the precipitation of sodium ions (atomic weight of one mole = 23 g)

$$Na^+(aq) + \bar{e} \longrightarrow Na(s)$$

ium atom. If we have a mole of sodiumWhen a sodium ion gains one electron, it forms one sod

Ions (Avogadro's number of sodium ions). It gains one mole of eletrons (Avogadro's number of electrons) to deposit a mole of sodium atoms (Avogadro's number of sodium atoms). And the weight of a mole of sodium is 23 g.

$$1 \text{ mol of } \bar{e} = 6.023 \times 10^{23} \text{ electrons} \longrightarrow 23 \text{ g (Na)}$$

$$2 \text{ mol of } \bar{e} = 2 \times 6.023 \times 10^{23} \text{ electrons} \longrightarrow 2 \times 23 \text{ g (Na)}$$

That is, the amount of matter formed depends on the number of moles of electrons, i.e. the amount of electricity passing through the electrolytic cell.

Definition of Faraday

one mole of electrons It is the amount of electricity whose charge is equivalent to the charge of and has the ability to deposit one gram equivalent of any element.

Or Faraday is the amount of eleactricity that must be supplied to a cell in order to produce one mole of electrons.

1 Faraday = charge of one mole of electrons

Since the charge of one electron is equal to = 1.60198×10^{-19} Coulomb

Therefore, the charge of one Faraday is equal to:

$$\boxed{1\text{Faraday} = 1.60198 \times 10^{-19} \times 6.023 \times 10^{23} = 96487 \text{ Coulomb}}$$

For approximation, we will use Faraday's value of 96500 C to facilitate calculation, and the number for the Faraday (96487 C) was found experimentally before being proven by calculation.

Definition of coulomb

It is the amount of change that moves past any given point in the circuit when a current of one amper (A) passes through it for one second (1 S).

$$1 \text{ coulomb} = 1 \text{ ampere} \times 1 \text{ second}$$

$$1 \text{ C} = 1 \text{ A.S}$$

Calculating the amount of electricity Q

1-The amount of electricity is calculated from the relationship:

$$Q = I \cdot t$$

I: Current intensity in amperes (A)

t: Time in seconds (S)

The unit of electricity (Q) is (A.S) or coulomb (C)

2-To convert the amount of electricity to Faraday, we follow the relationship:

$$F = \frac{Q}{96500}$$

1) The value I.t/F expresses the faraday number (F) where

$$m = \frac{Aw \,.\, I.\, t}{Z \,.\, F}$$

$$F = \frac{I \,.\, t}{96500}$$

And by substituting **F** in the above equation we get:

$$m = \frac{Aw \,.\, F}{Z}$$

The number of moles n

$$n = \frac{m}{Aw}$$

$$m = n \,.\, Aw$$

And by substituting the value of m = n. Aw in the equation

$$n \cdot Aw = \frac{Aw \cdot F}{Z}$$

Dividing both sides by Aw, we get:

$$n = \frac{F}{Z}$$

Where F: the amount of electricity in faradays.

When converting the amount of electricity in coulombs, the relationship is

: $n = \frac{F}{Z}$

$$n = \frac{F}{Z}$$

$$n = \frac{Q}{Z \times 96500}$$

$$n = \frac{I \times t}{Z \times 96500}$$

Faraday's Second Law

Its text:

hen the same amount of electricity passes through two electrolytic ce" (respectively) the , amounts of substances that undergo a change at the electrodes (oxidation, reduction, precipitation) are directly proportional to their equivalent weights. That is, the amount of arge through the chemical precipitation at the electrodes resulting from passing an electric ch .electrolytic solution is directly proportional to its chemical equivalent or equivalent weight

Since the passage of one Faraday (96500 Coulombs) in a cell Electrolysis leads to the stance that undergoes a change deposition or elevation of one gram equivalent of the sub .oxidation or reduction) at the electrode)

If (m2, m1) are the masses of the two substances that undergo a change (in grams), and their equivalent weights are (Ew2, Ew1), in g/mol, then the second law can be formulated :aticallymathem

$$m_1 \ \alpha \ Ew_1 \Rightarrow m_1 = K \,.\, Ew_1$$

$$m_2 \ \alpha \ Ew_2 \Rightarrow m_2 = K \,.\, Ew_2$$

$$\frac{m_1}{m_2} = \frac{\cancel{K} \,.\, Ew_1}{\cancel{K} \,.\, Ew_2}$$

$$\frac{m_1}{m_2} = \frac{Ew_1}{Ew_2}$$

The last formula:

$$\boxed{\frac{m_1}{m_2} = \frac{Ew_1}{Ew_2}}$$

.Expression of Faraday's second law

To calculate the equivalent weight of any metal deposited on the electrode, we divide its atomic .weight by the number of electrons transferred in the reaction

Ex.

$$Cr^{3+}(aq) + 3\bar{e} \longrightarrow Cr(s)$$

$$Ew_{Cr} = \frac{Aw_{Cr}}{3}$$

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

$$Ew_{Cu} = \frac{Aw_{Cu}}{2}$$

:Example

is passed through a solution of copper(II) chloride for an hour. If the A current of 1.5 amperes ?weight of the copper deposited is 1.778 g, what is the equivalent weight of copper

Solution

$$m = \frac{Aw \,.\, I.\, t}{Z \,.\, F}$$

$$m = \frac{Ew_{Cu}. I \,.\, t}{F}$$

$$Ew_{Cu} = \frac{m \,.\, F}{I \,.\, t}$$

$$Ew_{Cu} = \frac{1.778 \times 96500}{1.5 \times 60 \times 60}$$

$$Ew_{Cu} = 31.77 \text{ g/Eq}$$

:Example

for up to an hour. A 1.5 amp electric current was passed through a solution of copper(II) chloride If the weight of the copper that was deposited was 1.778 grams, calculate the equivalent weight of copper

Solution

First, we convert the hour to seconds = 3600 seconds

current intensity X time of Amount of the precipitated material = (equivalent weight of copper X current passage) / Faraday's constant

3600) / equivalent weight of copper X 1.5 X) = 1.778 96500

:Example

,If an electric current of 10.4 A is passed for 23 min in a solution of potassium iodide KI

.bstances that collect at the electrodesCalculate the mass of the su

Knowing that the atomic masses are: 39.1 = I = 127, K

Solution

The equations for the precipitation reactions of iodine and potassium

$$K^+ + \bar{e} \xrightleftharpoons{reduction} K$$

$$2I^- \xrightarrow{oxidation} I_2 + 2e^-$$

$$\longleftarrow$$

By applying Faraday's first law, the masses of potassium and iodine deposited can be calculated:

$$m_{I_2} = \frac{Mw \, . \, I \, . \, t}{Z \, . \, F}$$

$$m_{I_2} = \frac{(2 \times 127) \times (10.4) \times (23 \times 60)}{2 \times 96500}$$

$$m_{I_2} = 18.89 \text{ g}$$

$$m_K = \frac{Aw \, . \, I \, . \, t}{Z \, . \, F}$$

$$m_K = \frac{39.1 \times 10.4 \times 23 \times 60}{1 \times 96500}$$

$$m_K = 5.8 \text{ g}$$

Example

Cl2) during the) Calculate the mass of aluminum precipitated (Al) and chlorine evolved electrolysis of molten aluminum chloride AlCl3, if the current strength is 5 amperes for two hours between platinum electrodes. Atomic masses Cl = 35.5 , Al =27

We write the reactions of the anode and cathode as follows:

$$2Cl^{-}(aq) \rightleftarrows Cl_2(g) + 2\bar{e} \qquad \text{oxidation at anode}$$

$$Al^{3+}(aq) + 3\bar{e} \rightleftarrows Al(s) \qquad \text{reduction at cathode}$$

To calculate the mass of aluminum deposited and chlorine evolved, we apply Faraday's law:

$$m_{Cl_2} = \frac{Mw_{Cl_2} \, . \, I \, . \, t}{Z \, F}$$

$$m_{Cl_2} = \frac{(2 \times 35.5) \times (5) \times (2 \times 3600)}{2 \times 96500}$$

$$m_{Cl_2} = 13.24 \text{ g}$$

$$m_{Al} = \frac{(Aw_{Al}) \times I \times t}{Z \times F}$$

$$m_{Al} = \frac{27 \times 5 \times 2 \times 3600}{3 \times 96500} = 3.36 \text{ g}$$

:Example

an electric current of 32 amperes Calculate the time required to deposit (2.16 g) of silver when is passed through a silver nitrate solution, knowing that the atomic mass of silver is=108

Solution:

$$Ag^{+}(aq) + \bar{e} \longrightarrow Ag(s)$$

$$m_{Ag} = \frac{Aw. \, I. \, t}{Z. \, F}$$

$$t = \frac{m_{Ag} . Z. \, F}{Aw \, . \, I}$$

$$t = \frac{2.16 \times 1 \times 96500}{108 \times 32}$$

$$t = 60.31 \text{ S}$$

Example:

How many minutes are needed to precipitate g7 of chromium by passing a constant current of solution where 3A) through a CrCl3) AwCr = 52

$$Cr^{3+}(aq) + 3\bar{e} \longrightarrow Cr(s)$$

$$m_{Cr} = \frac{Aw.\, I.\, t}{Z.\, F}$$

$$t = \frac{m_{Cr}\ .\, Z\, .\, F}{Aw_{Cr}\, .\, I}$$

$$t = \frac{7\ \times 3\ \times 96500}{52\ \times 3}$$

$$t = 12990.38\ S$$

$$t = \frac{12990.38\ \cancel{S}}{60\ \cancel{S}\ \text{min}^{-1}}$$

$$t = 216.51\ \text{min}$$