

Detailed scientific explanations of the electrolysis of water, magnetic effects on water, electromagnetic effects on water and the water redox process

Detailed scientific explanations of the electrolysis of water is detailed below and the electric effects on water, magnetic effects on water, electromagnetic effects on water and the water redox process can all be accessed using the links immediately below: -

[Electric effects on water](#)

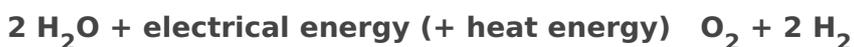
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Electrolysis of Water

Electrolysis of water is its decomposition to give hydrogen and oxygen gases due to an electric current.



'I propose to distinguish these bodies by calling those anions which go to the anodeand those passing to the cathode, cations '

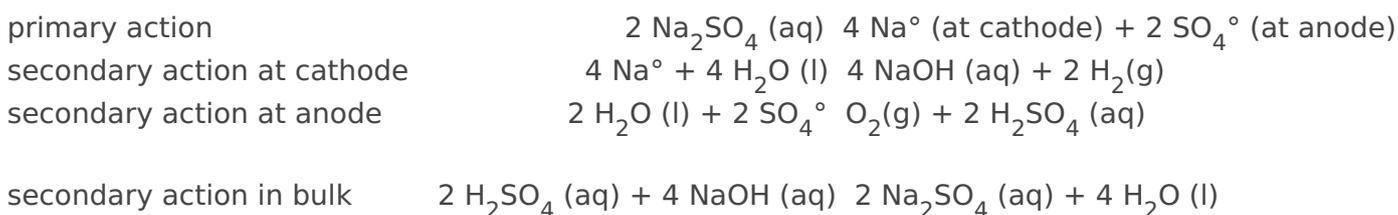
Introduction

Creating an electric potential through water causes positive ions, including the inherent hydrogen ions (H_3O^+), to move towards the negative electrode (cathode) and negative ions, including the inherent hydroxide ions (OH^-), to move towards the positive electrode (anode). With a sufficient potential difference, this may cause electrolysis with oxygen gas being produced at the anode and hydrogen gas produced at the cathode (see [1878] for current reviews).^f The electrolysis^g of water usually involves dilute, or moderately concentrated, salt solutions to reduce the power loss driving the current through the solution and catalyze the reaction (see below). However, the presence of salt is not a requirement for electrolysis.^h Although often taught as an uncomplicated topic, the electrolysis of water does not involve easy to understand concepts; particularly if including the necessary mass transport and kinetics [4168],

Thus,

Anode	+ve ⁱ	$6\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}_3\text{O}^+(\text{aq}) + 4\text{e}^-$ (to anode) ^b	$E^\circ = +1.229 \text{ V}$, pH 0 ^d	$E^{\circ'} = +0.815 \text{ V}$
Cathode	-ve	4e^- (from cathode) + $4\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq})$	$E^\circ = -0.828 \text{ V}$, pH 14	$E^{\circ'} = -0.414 \text{ V}$
Overall		$2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$	$\Delta G^{\circ'} = +474.3 \text{ kJ} \times \text{mol}^{-1}$	

where (l), (g), and (aq) show the states of the material as being a liquid, a gas, or an aqueous solution. The electrical circuit passes the electrons back from the anode to the cathode. The reactions are heterogeneous, taking place at the boundary between the electrode and the electrolyte with the aqueous boundary layer subject to concentration and electrical potential gradients, and with the presence of the generated gaseous nanobubbles and microbubbles. When salts are present, enabling greater electron flow, the primary reaction may differ; for example, on electrolysis of an aqueous solution of copper chloride, a deposit of metallic copper and chlorine gas are produced, with no production of oxygen or hydrogen gases. Even when oxygen and hydrogen gases are produced, their production may not be the primary reactions [4167],



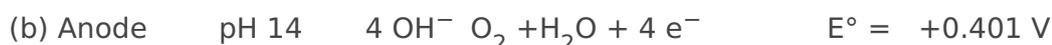
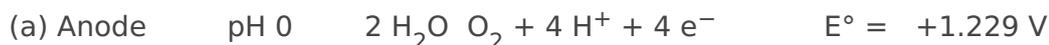
overall



with the (regenerated) Na_2SO_4 acting as a catalyst. Aqueous NaCl electrolysis, however, produces mainly oxygen and hydrogen gases with only traces of chlorine gas or sodium metal unless the NaCl is concentrated.

Water electrolysis electrode potentials with pH

The structural and thermodynamic properties for water surfaces in the vicinity of the electric field exerted by the metal electrodes have been simulated [3829]. Generally, the water adjacent to the electrodes ^c will change pH due to the ions produced or consumed. If a suitable porous membrane separates the electrode compartments, then the concentration of H_3O^+ next to the anode (anolyte) and OH^- next to the cathode (catholyte) are both expected to increase more than if there is free mixing between the electrodes. There will also be an increase in their respective conductivities. Without such a membrane, most of these ions will neutralize each other. Small but expected differences in the anolyte and catholyte pHs cause only a slight change to the overall potential difference required (1.229 V). Increasing the anolyte acid content due to the H_3O^+ produced will increase its electrode potential (for example: at pH 4, $E = +0.992$ V), and increasing the catholyte alkaline content due to the OH^- produced will make its electrode potential more negative (for example: at pH 10, $E = -0.592$ V). If the anode reaction is forced to run at pH 14 and the cathode reaction is run at pH 0.0, then the electrode potentials are +0.401 V and 0 V, respectively (see above right). ^d



Although electrolysis can be achieved with a (minimum) voltage of +0.403 V (see equations b and c, above) [2515], it does not break the thermodynamic requirement of 1.229 V as further energy is required to keep the electrode compartments at the required solute concentrations and pHs.

The layer next to the surface of the electrode determines the rate of the reaction [3831]. If it is stagnant, molecules and ions have to diffuse to and from the electrode, restricting the rate of reaction (mass transfer limitation) that is reported for current densities below $1.3 \text{ kA} \times \text{m}^{-2}$ in chlor-alkali electrolysis. ^e The mobility of the hydration layer nearest to the electrode ($\sim 5 \text{ \AA}$) decreases upon positive potentials while increasing upon negative potentials [3863]. This is because, at positive potentials, the hydrogen bonding network gets ice-like structured parallel to the electrode, while at negative interfaces, it is disrupted due to the hydrogen atoms pointing at the surface. Additionally, there may be a high accumulation of hydroxide ions at positive electrodes that significantly lower the oxygen solubility. Above $3.9 \text{ kA} \times \text{m}^{-2}$, there is rapid convective transport and no mass transport limitations.

The current flowing indicates the rate of electrolysis. The amount of product formed can be calculated directly from the duration and current flowing, as 96,485 coulombs (*i.e.*, one faraday) delivers one mole of electrons, with one faraday ideally producing 0.5 moles of H₂ plus 0.25 moles of O₂. Thus, one amp flowing for one second (one coulomb) produces 5.18 μmol H₂ (10.455 μg, 0.1177 mL at STP) and 2.59 μmol O₂ (82.888 μg, 0.0588 mL at STD; 4.9 kW h/m³ H₂ at 60% efficiency), if there are no side reactions at the electrodes; that is

Number of moles = Coulombs/(unsigned numeric charge on the ion × faraday)

Number of moles = (Current in amperes × time in seconds)/(unsigned numeric charge on the ion × faraday)

The gases produced at the electrodes may dissolve, with their equilibrium solubility proportional to their partial pressure as gases in the atmosphere above the electrolytic surface. Oxygen gas is poorly soluble ($\approx 44 \text{ mg} \times \text{kg}^{-1}$, $\approx 1.4 \text{ mM}$ at 0.1 MPa and 20 °C, but only $\approx 0.29 \text{ mM}$ against its normal atmospheric partial pressure). Hydrogen gas is less soluble ($\approx 1.6 \text{ mg} \times \text{kg}^{-1}$, $\approx 0.80 \text{ mM}$ at 0.1 MPa and 20 °C but only $\approx 0.44 \text{ nM}$ against its very low normal atmospheric partial pressure). It may take a considerable time for the solubilities to drop from their initially-super-saturated state to their equilibrium values after the electrolysis.

Although theoretically, as described above, the current passing should determine the amounts of hydrogen and oxygen formed, several factors ensure that somewhat lower amounts of gas are actually found;

- (i) some electrons (and products) are used up in side-reactions,
- (ii) some of the products are catalytically reconverted to water at the electrodes, particularly if there is no membrane dividing the electrolysis compartments,
- (iii) some hydrogen may absorb into the cathode (particularly if palladium is used),
- (iv) some oxygen oxidizes the anode,
- (v) some gas remains held up in the nanobubbles for a considerable time, and
- (vi) some gas may escape measurement.

Current versus voltage in water electrolysis

The above description hides much important science and grossly over-simplifies the system. The potential required at any position within the electrolytic cell is determined by the localized concentration of the reactants and products, including the local pH of the solution, instantaneous gas partial pressure, and effective electrode surface area loss due to attached gas bubbles.

The variation in potential across the cell is not uniform, and there is evidence of the formation of somewhat kinetically stable large-scale charge zones [3557]. In addition, a greater potential difference (called overpotential [3141]) is required at both electrodes to overcome the activation energy barriers and insulating bubble coverage, and then to deliver a significant reaction rate. Typically at suitable electrodes, such as those made of platinum, the overpotential adds about half a volt to the potential difference between the electrodes. The use of different catalysts to reduce the overpotential has been discussed [4213]. In addition, a further potential difference is required to drive the current through the electrical resistance of the electrolytic cell and circuit. For a (typical) one-ohm cell circuit resistance, ^a each amp current flow would require a further one volt and waste one watt of power. This power (and consequent energy) loss ($\approx 20\%$, [1978]) causes the electrolyte to warm up during electrolysis.

To clarify:

The minimum necessary cell voltage to start water electrolysis is the potential 1.229 V.

The potential necessary to start water electrolysis without withdrawing heat from the surroundings is

$$-\Delta H^\circ/nF = 1.481 \text{ V}$$

This results in at least a 21% unavoidable loss of efficiency. Usually, further heat is generated, and efficiency lost, from the overpotentials applied. Additionally, energy is wasted due to the evaporation of water from within the wet gases evolved.

The efficiency of electrolysis [1876] increases with the temperature as the hydrogen-bonding reduces. However, due to the endergonic process, the heat demand increases as the electrical demand decreases, mostly balancing overall energy demand. If the pressure over the electrolysis is increased, then more current passes for the same applied voltage. However, the output of gas per coulomb and the heating effect are both decreased. This is due to the increased solubility of the gases and smaller bubbles, reducing cell resistance and increasing recombination reactions. Although reducing the distance between electrodes reduces the resistance of the electrolysis medium, the process may suffer if the closeness allows a build-up of gas between these electrodes [1876]. Low to higher pulsed potential increases the reaction (current) and accelerates both the movement of bubbles from the electrode surface and the mass transfer rate in the electrolyte, which lowers the electrochemical polarization in the diffusion layer and further increases hydrogen production efficiency [2075]. The rate of change of the current density (and hence efficiency) can be increased using a magnetic field [2075, 3041] with or without optical enhancement. [2941]. The investment costs of electrolysis have been reviewed [3255].

Pure water conducts an electric current very poorly and, for this reason, is difficult (slow) to electrolyze, except if using deep-sub-Debye-length nanogap electrochemical cells [4304]. Usually,

however, some salts will be added or present in tap and ground waters which will be sufficient to allow electrolysis to proceed significantly. The gases produced may be due to secondary reactions (see above) [4167]. Such salts, and particularly chloride ions, may then undergo redox reactions at an electrode. These side reactions both reduce the efficiency of the electrolysis reactions (above) and produce new solutes. Other electrolytic reactions may occur at the electrodes so producing further solutes and gases. In addition, these solutes may react together to produce other materials. Together the side reactions are complex, and this complexity increases somewhat when the voltage applied to the cell is greater than that required by the above reactions and processes. The likely reactions within the electrode compartments are described below. Some of these may only occur to a minimal extent, and other reactions may also be occurring that are not included.

Standard electrode potentials are shown below.

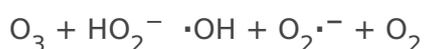
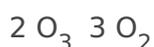
Electrode compartment contents in water (NaCl) electrolysis

Electrolysis compartments.

The effects of current, salt concentration, and time on the pH and alkalinity of the electrolytic solutions has been investigated [4039]. A representation of the compartments in the electrolytic cell is shown right, with some of their constituent molecules, ions, and radicals. Other materials may be present, and some of the materials given may be at very low concentrations or have short half-lives.

Ozone, O₃

Noteworthy amongst the side products is ozone (O₃, see left). The relative amount of O₃ produced (relative to molecular oxygen) depends on the overpotential, pH, radicals present, and anode material. O₃ evolution is much lower than that for O₂ due to the higher potential required. Very little O₃ may be produced at low overpotentials, but at high current densities and overpotential, up to a sixth (or more) of the oxidized molecules may be O₃. As O₃ is more soluble than O₂, there may be twice the dissolved O₃ than O₂, but the bubble gas will contain about 20 times the O₂ than O₃ [2358]. Tin oxide anodes have proved helpful for the production of O₃, particularly if doped with Sb and Ni, as they bind both oxygen molecules and hydroxyl radicals to facilitate the O₃ production [2359]. Ozone decomposes in water in a few minutes. Decomposition of ozone (particularly in alkaline solution) gives rise to several strong oxidants, including hydroxyl radicals (·OH), that form a powerful oxidizing agent capable of killing viruses, amoebae, algae, and dangerous bacteria, such as MRSA and Legionella.



Although charged ions are attracted into the compartments under the applied potential, oppositely charged ions are created in both compartments due to the electrolytic reactions. Thus, for

example, Na^+ ions enter the catholyte from the anode compartment, but excess OH^- is produced simultaneously at the cathode. The concentration of the OH^- ions will be generally expected to be greater than the increase in cations in the catholyte, and the concentration of the H_3O^+ ions will be generally expected to be greater than any increase in anions in the anolyte. Often a conductive but semi-permeable membrane (for example, Nafion, a highly hydrated sulfonated tetrafluoroethylene based copolymer [1880]) is used to separate the two compartments and reduce the movement of the products between the electrode compartments; a process that improves the yield by reducing back and side reactions [1978]. Due to the easier electrolysis of water containing ^1H rather than ^2H (D) or ^3H (T), electrolysis can produce water with reduced or enriched isotopic composition.

Local inhomogeneities of surface tension in the produced gas bubbles may be caused by temperature or altered material concentration gradients at the interface. The resulting solute currents enhance the mass transfer and bubble growth [3264].

When electrolysis uses short voltage pulses of alternating polarity at above 100 kHz, the nanobubbles produced contain both H_2 and O_2 gases that can spontaneously react (combust) to form water while producing pressure jumps [2900].

Proposed mechanism for electrolysis on platinum

What is less well understood?

Although much time has been spent on investigating and modeling the electrolytic system [1877], it is still not entirely clear how water is arranged on the surface of the electrodes. Alignment of the water dipoles with the field is expected, together with the consequential breakage of a proportion of the water molecules' hydrogen bonds. Whether the water at the electrode surface is "free" or coordinated to strong electrolytes (such as Li^+ and Na^+) affects the ease of electrolysis, with coordinating water more reactive than "free" water [3516].

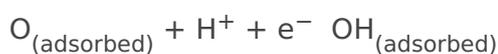
When the electrode processes occur, singly-linked hydrogen atoms and singly-linked oxygen atoms are bound to the platinum atoms at the cathode and anode. The binding energies of these hydrophilic intermediates are strongly influenced by hydrogen-bonding (HB) to surface water molecules and the electrode composition [3082]. These bound atoms can diffuse around in two dimensions on the surface of their respective electrodes until they take part in their further reaction. Peroxide ($\cdots\text{O}-\text{O}-\text{H}$) may also be bound to the electrode as part of the O_2 dissociation process [3913]. Other atoms and polyatomic groups may also bind similarly to the electrode surfaces and subsequently undergo reactions [2899]. Molecules such as O_2 and H_2 produced at the surfaces may enter nanoscopic cavities in the liquid water (nanobubbles) as gases, or become solvated by the water.

Gas-containing cavities in liquid solution (often called bubbles) grow or shrink by diffusion according to whether the solution is over-saturated or under-saturated with the dissolved gas. Given suitable electrodes, the size of the cathodic hydrogen bubbles depends on the overvoltage,

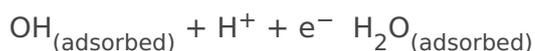
with nanobubbles being formed at low overvoltages and larger bubbles being formed at higher overvoltages [2068]. Larger micron-plus sized bubbles have sufficient buoyancy to rise through the solution and release contained gas at the surface before all the gas dissolves. With smaller bubbles a pressure is exerted by the surface tension in inverse proportion to their diameter, and bubbles may be expected to collapse. However, as the nanobubble gas/liquid interface is charged, an opposing force to the surface tension is introduced, slowing or preventing their dissipation. Electrolytic solutions have been proven to contain vast numbers of gaseous nanobubbles [974]. The 'natural' state of such interfaces appears to be negative [1266]. Other ions with low surface charge density (such as Cl^- , ClO^- , HO_2^- and $\text{O}_2^{\cdot-}$) will also favor the gas/liquid interfaces [928a] as probably do hydrated electrons [1841, 1874]. Aqueous radicals also prefer to reside at such interfaces [939]. From this known information, it seems clear that the nanobubbles present in the catholyte will be negatively charged. However, those in the anolyte [1881] will probably possess little charge (with the produced excess positive H_3O^+ ions canceling out the natural negative charge). Therefore, catholyte nanobubbles are not likely to lose their charge on mixing with the anolyte stream and are otherwise known to be stable for many minutes [974]. Additionally, gas molecules may become charged within the nanobubbles (such as the superoxide radical ion, $\text{O}_2^{\cdot-}$), due to the decay of ozone present. Also, the excess potential on the cathode increases the overall charge of the nanobubbles and the stability of that charge. The raised temperature at the electrode surface, due to the excess power loss over that required for the electrolysis, may also increase nanobubble formation by reducing local gas solubility. Raising the pressure on solutions containing nanobubbles will also slow down their dissipation if this pressure increases the dissolved gas content.

Sunlight, as an external electric field in water electrolysis, has proven to increase hydrogen production. This increase has been associated with an effect on the surface tension [3291].

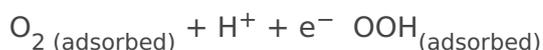
Oxygen may be reduced (hydrogenated) in acid solution at the cathode. On platinum, Pt(111), there are two possibilities for the reduction route, that shift with the electrode potential [4092],



possibly followed by,



or,



possibly followed by,



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Commercial systems

Commercial systems are more complex relative to the above descriptions. They must be safe, efficient, and cheap to run. The electrodes must reduce the overpotentials required while keeping their capital costs low. The electrolytes must be clear of impurities that may poison the electrode surfaces and usually consist of concentrated alkali or acid. As the efficiency of an electrolyzer improves with the increased temperature, industrial electrolyzers run warm to hot. The best electrolyzers operate at 70-80% electricity-to-hydrogen efficiency and produce high-purity (about 99.9%) hydrogen at about one MPa pressure while providing intrinsically safe operation at all times [3367]. A close collaboration between chemists and engineers is required to develop industrially relevant catalysts for the hydrogen and oxygen evolution reactions [4314]. There are 2021 reviews of hydrogen production from solar powered water electrolysis [4350] and from seawater [4360]. Although electrolysis of seawater to make hydrogen gas might seem attractive, it has many drawbacks. Impurities, such as ions, bacteria, plastics and small particulates, limit the membrane lifetime, and pH changes cause precipitation and electrode degradation [4437]. Because of these drawbacks, seawater must be somewhat purified by reverse osmosis before electrolysis, with the extra cost of this stage being marginal compared with the cost of electrolysis [4438].

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Footnotes

^a The approximate resistivities of pure water, tap water, and seawater are 18 MΩ × cm, 5 kΩ × cm, and 20 Ω × cm, respectively. Thus the electrolysis rate is speeded up by factors of about 1000 × or 1,000,000 × using tap water or seawater respectively, rather than pure water. The overpotential is increased in deuterated water (up to about twice) and is affected by the ion species present and electrolyte concentrations [3840]. [Back]

^b Traditionally, such equations are written with the electrons on the left-hand side and (however written) the redox potential refers to so directed equations. Here it is written reversed to show how the cell reaction is balanced, as this is how the reaction occurs.



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^c The electrodes should preferably be made from a material with high conductivity, resistance to corrosion and erosion during the electrolysis, and catalyzing the electrode reactions. Also, for industrial use, they should be relatively inexpensive. Platinum is an excellent but expensive electrode material. Industrial cathodes may be made from steel or nickel, and those used as anodes are metals such as titanium coated with the oxides and mixed oxides of metals such as nickel and cobalt. Water next to the surface will organize dependent on the surface material [2521] and considerably reduce their refractive index; the Pockels electro-optical effect [2874]. [Back]

^d At the anode, $E^\circ = +1.229 - 0.059 \text{ pH V}$. At the cathode $E^\circ = -0.059 \text{ pH V}$. The value '0.059' is derived from the Nernst constant = $\text{Log}_e(10) \times \text{RT/F} = 0.059 \text{ V (25 }^\circ\text{C)}$. [Back]

^e Chlor-alkali electrolyzers convert oxygen to hydroxide ions.



The industrial operating conditions have NaOH concentrations exceeding 10 M, temperatures in the range of 80°C to 90°C, and current densities of 4 - 6 kA × m⁻². [Back]

^f Electrolysis was first discovered by Alessandro Volta (1745-1827) with his invention of the battery in 1799 (The Voltaic pile). A. Volta, On the electricity excited by the mere contact of conducting substances of different kinds, *Philosophical Transactions of the Royal Society*, **90** (1800) 403-431.[Back]

^g 'Electrolysis' is the process of being decomposed by the direct action of electricity. [Back]

^h Many high-school textbooks give the reactions,



to simplify the progressive learning of this complex subject [4167]. [Back]

ⁱ The anode is negatively charged for galvanic cells (part of batteries generating voltages) but positive for electrolytic cells (where the potential is applied to the electrodes). [Back]

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