Catalytic Reactions in Hydrogen Production

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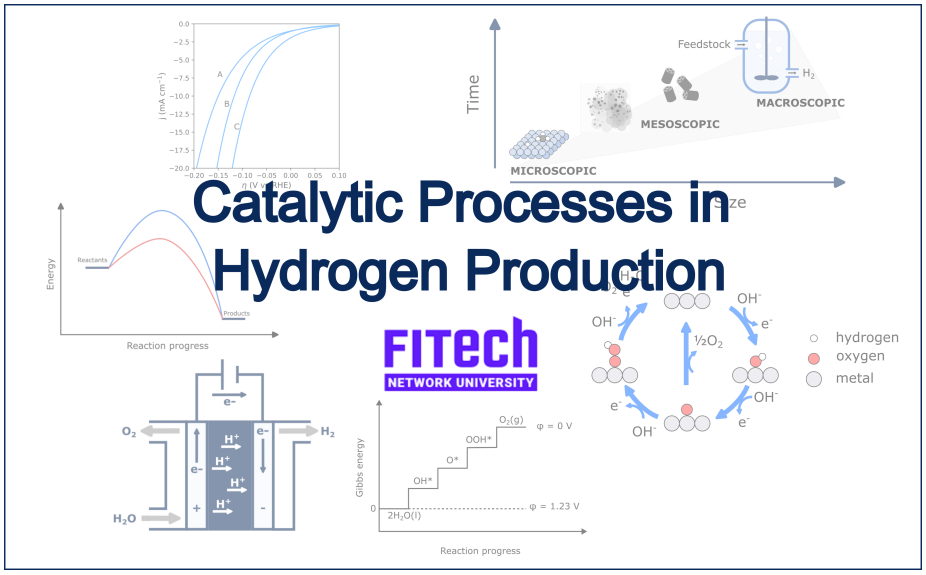


Introduction

Welcome to the "Catalytic Reactions in Hydrogen Production" course document! This document belongs to the two-part "Catalytic processes and materials in sustainable hydrogen production" course, and has been adapted from the material of the course Moodle to be shared publicly through JOTPA. Students from all over Finland from varying academic and professional backgrounds successfully completed the 3 ECT part of the course which was available through FITech studies in 2023-2025. The course was graded as pass-fail. Viewing all course content and a passing grade (85% of total points) from three online quizzes was required for course completion. The quizzes had an unlimited number of retries, and quiz grades had no effect on how many ECTS were awarded.

The first part of the course introduces conventional and novel hydrogen production methods at the atomic level and provides a primer for the fundamental physical and chemical concepts required for understanding the topics.

Learning Goals:

- student has an overview of conventional hydrogen production methods and how they relate to Finnish industry and economic/environmental goals
- student is introduced to fundamental physical and chemical phenomena that are key to understanding hydrogen production
- student is familiar with concepts that are central to electro- and photocatalysis
- student acquires an atomic level picture of hydrogen production methods

The contents are divided into chapters which contain text, images, and multiple choice questions (answers are given at the end). At the end of each chapter, there is a set of problems to test your understanding (these sets correspond to the Moodle quizzes).

Core Physical Concepts

H_2 production is a multiscale process

Hydrogen production spans many length and time scales. It starts at the atomic or microscopic level, where individual molecules react to form hydrogen at active sites, and ends up at the macroscopic scale where feedstock is fed into reactors to produce hydrogen in huge quantities. In fact, it goes even beyond: global hydrogen production, trade, transport, and industrial use. Atomic and global phenomena may be at the opposite ends of the scale, but they are fundamentally connected to each other.

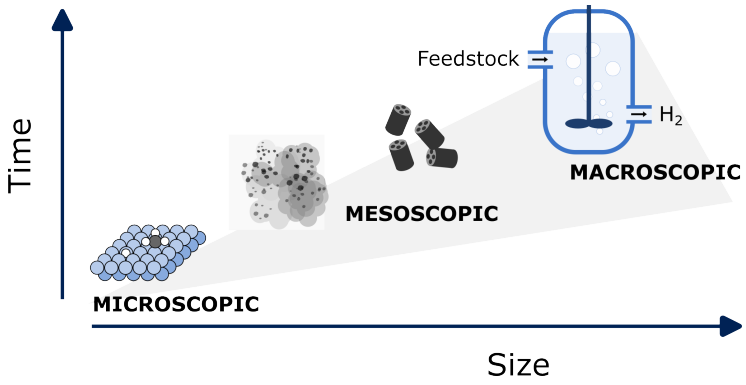


Figure 1: Scales in catalysis

The performance of a given hydrogen production process is ultimately determined by the reactions between atoms and molecules (i.e. atomic scale phenomena) in the vicinity of an active site on a catalyst. However, the active site or reaction mechanism are also affected by the external conditions such as temperature, pressure, mass transport (i.e. macroscale reactor design). Which particular production process is adopted also depends on global economics and politics, not just the intrinsic performance of a given process. This causes a feedback loop that spans all scales. To achieve increased efficiency and go beyond trial and error in the development of hydrogen production, research efforts

and planning must be dedicated at all scales.

This document will focus on the physical and chemical phenomena which govern the atomic scale. These phenomena are typically challenging to grasp, but it is not possible to simply ignore them. In order to form a genuine understanding, we will start with a refresher of fundamental concepts such as chemical reaction terminology, kinetics and thermodynamics, catalysis etc (Fig. 2).

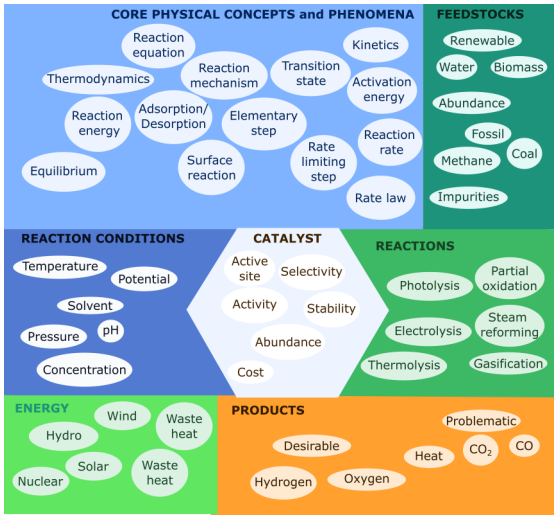


Figure 2: Map of core concepts related to H_2 production

The contents in this module are based on multiple chemistry textbooks. For a more detailed picture of the concepts, or to self-study (physical) chemistry in general, here are some textbooks that were also used as a basis for the document:

Atkins' physical chemistry (11th edition) by Peter Atkins, Julio de Paula, and James Keeler. ISBN: 978-0-19-876986-6 Physical chemistry: a molecular approach by Donald A. McQuarrie and John D. Simon. ISBN: 978-0-935702-99 Concepts of modern catalysis and kinetics by Ib Chorkendorff. ISBN: 9783527332687 Solar to chemical energy conversion, theory and application by Masakazu Sugiyama, Katsushi Fujii and Shinichiro Nakamura . ISBN: 978-3-319-79783-0

Chemical Reactions

Reactions conserve atoms and charge

Hydrogen is a chemical element that does not exist on Earth as a free resource which can be simply collected. Instead, hydrogen must be produced via chemical transformations of different hydrogen containing feedstocks.

This document features many different chemical reactions, all of which convert some feedstock (reactants) into hydrogen and other chemical substances (products).

Figure 3: Reaction between CO and H_2O

The cartoon in Figure 3 depicts a chemical reaction between a molecule of water and carbon monoxide that produces one molecule of hydrogen and carbon dioxide each. The atoms are depicted as coloured circles, red is oxygen, white is hydrogen, and dark grey is carbon. Notice how the atoms are redistributed among the molecules during the reaction, but the number and identity of the atoms does not change.

Chemical reactions transform the reactants into products by forming and breaking chemical bonds between the atoms and/or by transfer of electrons between species without changing the bonding. These processes do not alter the nuclei, only the electrons. Therefore the total number and type of atoms stays the same, and change in total charge is zero.

Q1. Which of the following statements is **not true** about what can occur during a chemical reaction?

1. Atom of one element changes into an atom of another element
2. Electrons move from one atom or molecule to another
3. Number of molecules changes
4. Chemical bonds are broken and/or formed

Reaction equations

Chemical reactions can be represented by reaction equations with reactants and products written as their chemical formulas connected by an arrow pointing from reactants to products.

The reaction equation describes the total atomic and charge balance of the reaction, i.e. a properly balanced reaction equation has the same number of atoms on both sides, and the change in total charge is zero.

Example reaction: Water-Gas Shift

The water-gas shift reaction (WGSR), one of the central reactions in contemporary hydrogen production where water (H_2O) and carbon monoxide (CO) react to form hydrogen (H_2) and carbon dioxide (CO_2):

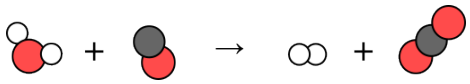


Figure 4: Pictorial representation of the water-gas shift reaction

The balanced reaction equation for the WGSR is:

$$1H_2O + 1CO \rightarrow 1H_2 + 1CO_2 \tag{1}$$

The stoichiometric coefficient is the number written in front of the chemical formula, which indicates how many molecules of each species takes part in the balanced reaction. All of the reactants and products of WGSR have a stoichiometric coefficient of one, meaning that one molecule of each of water and carbon monoxide react together to form one hydrogen and one carbon dioxide molecule.

By convention, when the stoichiometric coefficient is one, it is not explicitly shown, i.e.:

$$H_2O + CO \rightarrow H_2 + CO_2 \tag{2}$$

Q. Is it possible for water-gas shift reaction to yield more hydrogen than carbon dioxide?

1. Yes
2. No

Amount of substance

In the context of a real chemical reaction it is not convenient to refer to the number of individual molecules, as the number of molecules is always very large on the macro scale.

For example, a milliliter or gram of water contains over 3×10^{22} H_2O molecules, which is an inconveniently large number. On the other hand, it is not easy to directly translate the number molecules of a chemical species in a balanced chemical reaction to grams of that substance, as molecules have different masses.

It is more convenient to refer to the amount (n) of each reacting substance in moles (mol) instead.

The mole is an SI base unit, and has a value exactly equal to $6.022140762 \times 10^{23}$. The mole can be used to express the amount of any elementary entity such as atoms, molecules, electrons, ions etc.

Mole is simply a very large number, which means that the definite proportions of the molecules are preserved as they are written in the balanced reaction equation when switching from individual molecules to amounts of molecules in

moles. The stoichiometric coefficients in the balanced reaction equation indicate how many moles of each reactant/product is consumed/produced in a given reaction.

For chemical reactions, the important quantity to know is the number of moles of a chemical substance in a given volume. This is the concentration of a chemical species, c. The unit is mol L $^{-1}$, moles per liter.

Finish the sentence:

"A mole is ..."

> ... a base SI unit of amount of substance which contains exactly 6.022140762$\times$ 10^{23} elementary entities, which is a very large number.
>
> ... a small subterranean mammal.
>
> ... a base SI unit of amount of substance which contains exactly 6.022140762$\times$ 10^{23} elementary entities, which is a very small number.

Reaction quotient and extent of reaction

Below is the balanced reaction equation for a generic reaction where a moles of A and b moles of B are converted to c moles of C and d moles of D:

$$a\mathrm{A} + b\mathrm{B} \leftrightarrow c\mathrm{C} + d\mathrm{D} \tag{3}$$

The double arrow indicates that the reaction can proceed forward or backward. The reaction quotient (Q_r), is a quantity that measures the relative stoichiometric amounts of reactants and products for a reaction at a particular point in time. For the reaction above, the reaction quotient is written as:

$$Q_r = \frac{\{\mathrm{C}\}^c\{\mathrm{D}\}^d}{\{\mathrm{A}\}^a\{\mathrm{B}\}^b} \tag{4}$$

The symbols inside curly brackets indicate the thermodynamic activities of each species. For gas-phase reactions, the thermodynamic activity of a species is its partial pressure relative to standard pressure. For reactions in solutions, concentrations relative to standard concentration are used.

The extent of reaction, ξ, measures how far the reaction has proceeded since some initial point in time. The change in the extent of reaction for a given reaction, when an infinitesimal amount of reactant is converted to product can be defined as

$$d\xi = \frac{dn_i}{\nu_i} \tag{5}$$

where n_i is the number of moles of a reactant/product species i, ν_i is the stoichiometric number of species i. The symbol d indicates an infinitesimal (very tiny) change. The stoichiometric number has the same numerical value as the stoichiometric coefficient of the species in the balanced reaction equation, but

has a negative sign for reactants and positive sign for products. The unit of ξ is mole, and it is usually defined to be zero at the start of the reaction. For example, the above example reaction could start as a mixture of 0.5 mols of A and B each. The extent of reaction is zero at this point. After some time, there are only 0.25 mols of A and B each left, while 0.25 mols of C and D each have been produced. The extent of reaction is 0.25, regardless whether it is calculated with respect to the change in amount of A, B, C, or D.

Q Which of the expressions below is the correct reaction quotient for the water-gas shift reaction at 300 °C? The symbol P means pressure.

$$Q_r = \frac{P_{\mathrm{CO_2}} P_{\mathrm{H_2}}}{P_{\mathrm{CO}} P_{\mathrm{H_2O}}}$$

$$Q_r = \frac{P_{\mathrm{CO}} P_{\mathrm{H_2O}}}{P_{\mathrm{CO_2}} P_{\mathrm{H_2}}}$$

Reaction Thermodynamics

Thermodynamics of chemical reactions determine the equilibrium concentrations of the products and reactants, and place constraints on the reaction/operating conditions such as temperature, pressure, and electric potential. It is essential to consider these factors for industrial scale production of hydrogen.

Gibbs energy and chemical potential

Thermodynamic potentials describe the state of a given system. Different kinds of systems are described by different thermodynamic potentials. For closed systems at constant temperature and pressure, the relevant thermodynamic potential is Gibbs energy (G), which is related to the systems ability to do non-mechanical work. Another commonly used thermodynamic potential is Helmholtz energy (A), for systems under constant temperature and volume.

The word "system" refers here to the reactant and product molecules, while everything else (e.g. walls of the reaction vessel, the laboratory, outside world and so on) is referred to as the "environment". Chemical reactions often involve "closed" systems.

That the system is "closed" means that it doesn't exchange matter with the environment but does exchange energy with the environment. In other words, no reactant or product molecules escape the reaction vessel, but energy in the form of e.g. heat can be transferred through. Heat transfer enables controlling the reaction by heating (with a hotplate) or cooling (ice bath) the reaction vessel.

The Gibbs energy of a closed reacting system is a function of pressure (p), temperature (T), and number of species (N_i i.e. number of reactant and product molecules):

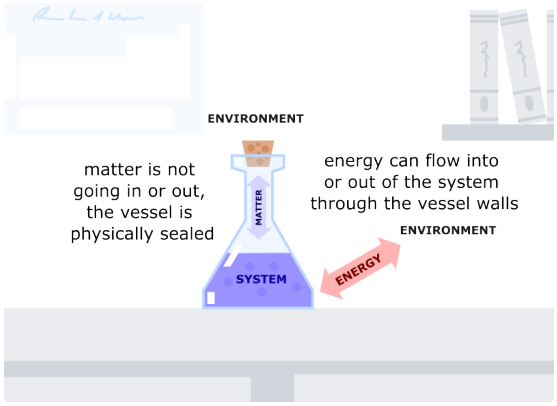


Figure 5: Illustration of a closed chemical system

$dG = -SdT + Vdp + \sum_i \mu_i dN_i$

where μ_i is the chemical potential of some species i, and S and V are entropy and volume, and d denotes a derivative i.e. infinitesimal change. The chemical potential is also referred to as partial molar Gibbs energy, and at constant pressure and temperature, the Gibbs energy of the system is a sum of the chemical potentials of all the species in the system:

$G = \sum_i \mu_i N_i$

Q For a closed flask containing an arbitrary amount of two substances A and B, which of the following is equal to the Gibbs energy of the system at constant pressure and temperature?

1. $\mu_A N_A + \mu_B N_B$
2. $\mu_A + \mu_B$
3. $\mu_A N_A \cdot \mu_B N_B$

Reaction energy

When a chemical reaction occurs in the system, the number of a given type of species (N_i) change, and so does the Gibbs energy. The standard Gibbs energy ($\Delta_r G^\circ$) of reaction is the energy change per mole of reaction for unmixed reactants and products in their standard states. $\Delta_r G^\circ$ is calculated as a sum of the formation Gibbs energies of the products minus the sum of formation Gibbs energies of the reactants :

$\Delta_r G^\circ = \sum G_f^\circ(products) - \sum G_f^\circ(reactants)$

The G_f° of reactant and product species can be obtained from thermodynamical tables, such as NIST-JANAF. Note that $\Delta_r G^\circ$ changes with temperature, but

it is usually given for 298 K and only has a single value for a reaction at a given temperature.

Another way to express $\Delta_r G^\circ$ is as:

$$\Delta_r G^\circ = \Delta H_r^\circ - \Delta S_r^\circ T \tag{6}$$

where ΔH_r° and ΔS_r° are the standard reaction enthalpy and entropy, respectively.

Reactions which have a negative ΔH_r° are called exothermic, whereas reactions with positive ΔH_r° are called endothermic. The entropy change can also be negative or positive. In general, when the number of molecules is larger on the product side the entropy increases, $\Delta S_r^\circ > 0$, and vice versa. Depending on the sign of both ΔH_r° and ΔS_r°, the sign of $\Delta_r G^\circ$ can change with temperature.

The sign of $\Delta_r G^\circ$ is important, as $\Delta_r G^\circ$ is equal to the portion of energy that either must be supplied to the reaction as non-expansion work ($\Delta_r G^\circ > 0$, i.e. non-spontaneous reaction), or equal to the amount of useful non-expansion work that can be extracted from the reaction ($\Delta_r G^\circ < 0$, i.e. spontaneous reaction).

Q At 298 K, the standard enthalpy of the WGS reaction is -41 kJ /mol, and the standard entropy is -42 J / K / mol. Assuming that the entropy and enthalpy do not change with respect to temperature (in reality, they do vary with temperature), which of the following statements about the reaction Gibbs energy is correct?

1. At temperatures below ca 1024 K, the Gibbs energy of reaction is negative.
2. The Gibbs reaction energy is always negative.
3. At temperatures above ca 1024 K, the Gibbs energy of reaction is negative.
4. The Gibbs reaction energy is always positive.

Chemical Equilibrium

All chemical systems tend towards chemical equilibrium, a state where the amounts of products and reactants no longer change with time. The reaction is still occurring at the molecular level, but in such a way that no changes in macroscopical concentrations are observed.

At constant temperature and pressure, a chemical reaction will spontaneously proceed in the direction which lowers the Gibbs energy of the system. Chemical equilibrium is reached when the Gibbs energy has reached a minimum. It is also possible that a reaction does not reach a true equilibrium due to e.g. kinetic limitations (more on those later), but will be stuck in a quasi- or metastable

equilibrium. Although it is not a true equilibrium, it is still possible to treat within equilibrium thermodynamics.

The Gibbs energy of a reaction ($\Delta_r G$) is the derivative of Gibbs energy of the system, with respect to the extent of reaction:

$\Delta_r G = \frac{dG}{d\xi}$

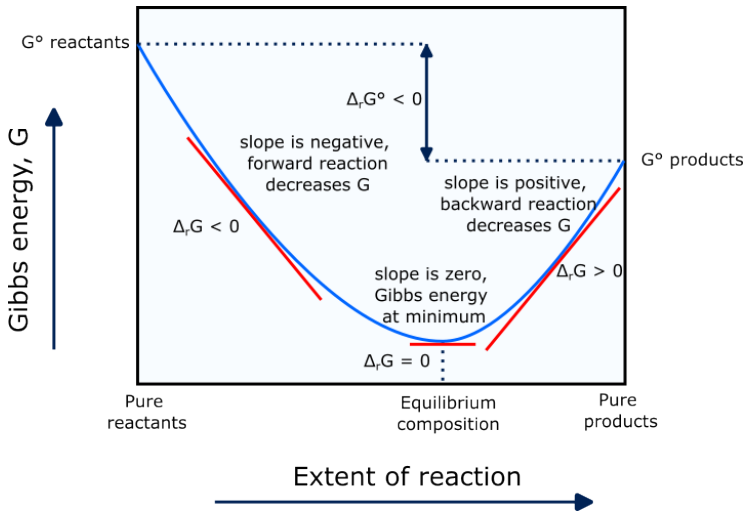
$\Delta_r G$ is related to $\Delta_r G^\circ$ by:

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q_r \tag{7}$$

At equilibrium, $\Delta_r G = 0$, and the reaction quotient Q_r is equal to the equilibrium constant, K_{eq}:

$$\Delta_r G^\circ = RT \ln K_{eq} \tag{8}$$

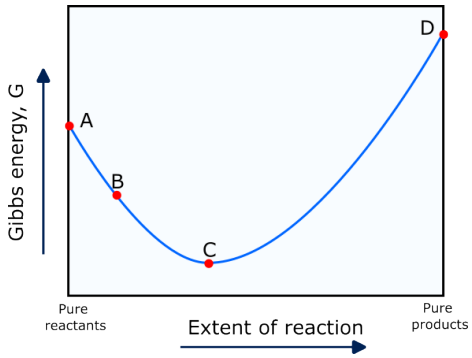
$\Delta_r G$ can be represented with the following diagram:



The sign of $\Delta_r G$ indicates wether the reaction is spontaneous. Notice how $\Delta_r G^\circ$ is negative in this example, however this does NOT imply the reaction is spontaneous over the entire interval of the reaction composition. This is clearly illustrated by the positive slope of the Gibbs energy curve to the left of the equilibrium composition in the figure above.

Q Which of the statements is true for the figure below?

1. At point C, the reaction has proceeded half way to completion, and will react further until point D.



2. For the reaction represented by this plot, the standard Gibbs energy change of reaction is negative, i.e.:

   $\Delta_r G^\circ < 0$.

3. At point B it is thermodynamically more favorable for the reaction to proceed in the forward direction to make more products.

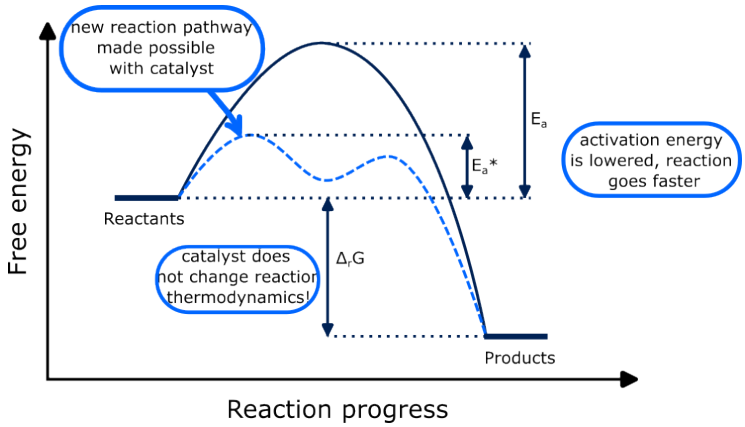
4. The standard Gibbs energy is positive,$\Delta_r G^\circ > 0$. Therefore the reaction is non-spontaneous.

Reaction Kinetics

Kinetics study how fast reactions are. The rate of reaction describes how much reactant is consumed and product is formed per unit time. The study of chemical reaction rates is called chemical kinetics. Reactions can occur fast, explosively fast, slow, or not at all, even if the reaction is thermodynamically favored and the reactants are mixed in proper amounts. It is clear that understanding kinetics is as crucial as thermodynamics for optimising the hydrogen production processes.

Perhaps the most famous example of the interplay of thermodynamics and kinetics is the main reaction of the Haber-Bosch process, which is spontaneous at room temperature, but is incredibly slow unless operated at very high temperatures. This is due to the minimum energy that the reactants must possess for the chemical reaction to occur. This energy cost is the activation energy (E_a) of the reaction.

The activation energy determines how fast a reaction can proceed: the greater the activation energy, the slower the reaction. Reaction rates typically increase with temperature, because at higher temperatures, a larger proportion of reactants will possess the required energy to overcome the activation energy.



Reaction rate - the macroscopic view

The average rate of a reaction can be determined by measuring the change in the concentration of a reactant/product over a time interval. Consider the reaction:

$$a\mathrm{A} + b\mathrm{B} \leftrightarrow c\mathrm{C} \tag{9}$$

The average rate between time t_i and t_f calculated from change in concentration of A is

$$r = -\frac{[\mathrm{A}]_f - [\mathrm{A}]_i}{t_f - t_i} \tag{10}$$

If the reaction is very fast, the concentration of species A goes from the initial value, e.g. 5 mol L^{-1}, to nearly zero (assuming the reaction goes to completion) in a very short time interval. After that, the concentration no longer changes. The measured average rate will depend on the chosen time interval, and in this case becomes slower when the time interval becomes longer. This clearly does not reflect the fact that the reaction is fast.

The instantaneous rate (r) is the differential change in concentration of any reactant or product (assuming no build up of intermediate species) at a given instant in time, expressed in mathematical form for the above example reaction as:

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{c}\frac{d[\mathrm{C}]}{dt} \tag{11}$$

where $[i]$ is the concentration of species i, and d indicates an infinitesimally small change. If the concentration of a species were plotted against time, the instantaneous rate at time t would be the slope of the curve at time t.

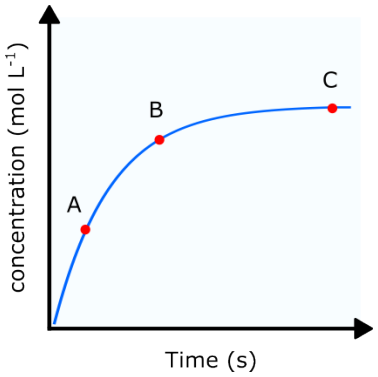
Using the WGSR as an example again, its rate (r_{WGS}) is:

$$r_{WGS} = -\frac{d[\mathrm{H_2O}]}{dt} = -\frac{d[\mathrm{CO}]}{dt} = \frac{d[\mathrm{H_2}]}{dt} = \frac{d[\mathrm{CO_2}]}{dt} \tag{12}$$

The reaction rate changes with time until the concentrations of the species are no longer changing.Note that this rate is only due to the chemical reaction. In situations where there is a flow of matter through the system (e.g. flow reactor), the mass balance has to also be taken into account.

If there is no flow of product/reactant through the system, the reaction rate changes until an equilibrium is reached, and the net rate is zero. If there is a flow out of the reactor, the rate no longer changes when a steady state is reached, i.e. the net rate of the chemical reaction is not zero, but it is balanced by the flow out of the reactor.

Q In the plot of product concentration versus time below, at which point is the rate of reaction the highest?



1. A
2. B
3. C

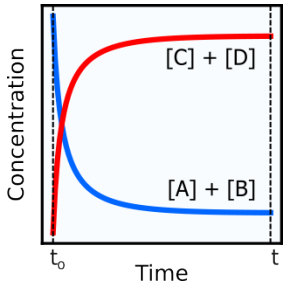
Rate equations, rate laws, and reaction orders

The rate at which products appear and reactants disappear is observed empirically, but it is more interesting to know why different reactions occur faster than others, and how the rate can be predicted or influenced. The reaction rate can be determined using a few parameters, provided that the rate equation, or rate law, for the reaction is known. The rate law is determined by conducting a series of experiments, for example by varying the concentrations of reactants (and product), and measuring the initial rate of the reaction (instantaneous rate at time $t = 0$).

Consider the hypothetical equilibrium reaction:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D} \tag{13}$$

Starting from a mixture containing only reactants, the plot of concentration versus time may look something like this:



After the beginning of the reaction, t_0, the concentrations of products and reactants change rapidly. At time t the concentrations of products and reactants are no longer changing with time, and the reaction has reached an equilibrium with rate $r = 0$. This is a dynamical equilibrium, where the forward and backward reactions have the same non-zero reaction rate, $r_f = r_b$.

In this example, the rate of the forward (backward) reaction is proportional to the product of the reactant (product) concentrations and a rate constant, k. The rate constant of a reaction is a function of temperature (increases with T), and is dependent on the activation energy of the reaction (decreases with increasing E_a). For now, you can think of it as a quantity that measures the intrinsic rate of a reaction between the reacting species. A fast reaction has a large rate constant, and a slow reaction has a very small rate constant.

The rate equation for the forward reaction is:

$$r_f = k_f[A][B] \tag{14}$$

where k_f is the rate constant of the forward reaction. Similarly, for the backward reaction the rate equation is:

$$r_r = k_r[C][D] \tag{15}$$

where k_r is the rate constant of the backward reaction.

The ratio of the forward and backward rate constants is equal to the equilibrium constant K_{eq}:

$$K_{eq} = \frac{k_f}{k_r} \tag{16}$$

The order of a reaction (typically written as 'n') is the sum of the exponents of the species concentrations in the rate equation. In the above example, all the exponents are one, which means that the forward reaction is first order with respect to A or B, and second order overall. The larger the reaction order of a given species is, the more its concentration affects the overall rate. For example, since the reaction order of species A is 1, doubling its concentration also doubles the (initial) reaction rate. If the reaction order with respect to a reactant is zero, it is not possible to increase the reaction rate by increasing its concentration.

Although in this case the exponents are the same as the stoichiometric coefficients of the species in the reaction equation, this does not hold for MOST reactions! It is not generally possible to derive the rate law from the stoichiometry of the total reaction. The rate equation can be derived from kinetic experiments of the influence of reaction conditions on the reaction rate, or derived from a reaction mechanism.

Q In an experiment, the initial rate of a reaction was found to increase when the starting concentration of one of the reactants was increased. Which of the below is the best explanation for the observed increase in rate?

1. The frequency of molecular collisions increased
2. The average kinetic energy of molecules increased
3. The activation energy decreased
4. The rate constant increased

Collision theory and Arrhenius law

As discussed in the previous sections, the rate of a reaction typically increases when the reactant concentration increases. But why? When reactants are mixed, the individual molecules will move around and occasionally collide into each other. Collision theory states that for a reaction to occur, the reactants have to collide with correct physical orientations and with enough energy to overcome the activation barrier. Therefore, not all collisions lead to a reaction. However, increasing the total number of collisions should also increase the number of successful collisions. Thus, when the concentration of a reactant is increased, the reaction rate also increases because having more molecules in a given volume leads to more collisions.

Another way to increase the number of successful collisions is to increase the temperature. Temperature is the average kinetic energy of the molecules in the system. As temperature is raised, molecules move faster, which leads to more collisions per unit time. More importantly, at higher temperatures a greater portion of the molecules will possess enough energy to overcome the activation energy of the reaction.

The temperature dependence of a reaction rate is contained in the rate constant. For many reactions, the rate constant varies with temperature according to the Arrhenius equation:

$k = Ae^{\frac{-E_a}{RT}}$

where A is a frequency or pre-exponential factor which relates to the frequency of successful collisions, E_a is the activation energy, and RT is gas-constant multiplied by temperature. The Arrhenius law/equation is based on empirical observations of how the rate of a reaction changes with temperature.

The linear form of the equation is:

$lnk = -E_a \frac{1}{RT} + lnA$

Therefore, when the natural logarithm of the rate constant is plotted against the inverse of temperature (Figure 6), the frequency factor and activation energy can be obtained from the y-intercept and slope, respectively.

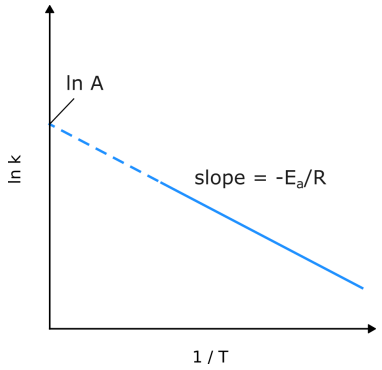


Figure 6: Linear Arrhenius plot.

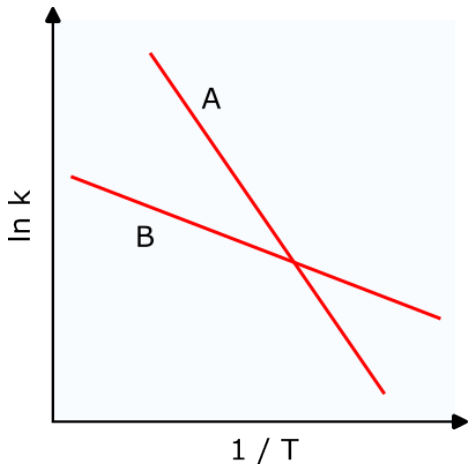
The Arrhenius slope of a reaction might change at a certain temperature. This could mean that there is a change in the rate limiting step, transport limitations, change in catalyst composition, or change in reaction mechanism etc.

Q Based on the Arhhenius plots for reactions A and B below which reaction has the larger activation energy?

1. A
2. B

Reaction mechanisms

Industrially relevant chemical reactions do not occur in a single step where reactants collide and at once form the product molecules, but via a sequence of elementary steps. The sequence of steps is known as the reaction mechanism.



The reaction mechanism is an atomic-level description of how the reaction proceeds from reactants to products in a step-wise fashion.

For a reaction mechanism to be correct, the elementary steps must sum to the overall balanced reaction equation. Another requirement for a proposed reaction mechanism is that any rate law derived from it must be consistent with experimental observations.

Each elementary step of a reaction has its own barrier and reaction energy. Stable reaction products of elementary reactions, which are not the final product of the overall reaction, are called intermediates. Sometimes certain intermediates can accumulate in large amounts before reacting further to give the final product.

At steady state, the rate of all elementary steps in a sequence must have the same rate. Therefore, the slowest step sets the limit on the total rate. This step is called the rate determining step (RDS), and typically has a high barrier compared to other steps. When a reaction has a single RDS, the overall rate can be written as the rate of that step.

A reaction may involve multiple competing reaction pathways and undesirable side reactions may also occur. The dominant reaction pathway may depend strongly on the reaction conditions. It is not always easy to determine what the underlying reaction mechanism is. Often both theoretical and experimental kinetic studies are needed to elucidate the reaction mechanism.

Q The rate law for the reaction:

$NO_2 + CO \rightarrow NO + CO_2$

was found to be

$r = k[NO_2]^2$

From the form of the rate law it was deduced that the reaction must occur in multiple steps. For the proposed mechanism below, which step would you expect to be the rate determining step (RDS)?

Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

1. Step 1
2. Step 2

Microscopic picture - Transition state theory

The Arrhenius plot is obtained from experimental measurements of the reaction rate at different temperatures. At the macroscopic scale, the reaction rate is an average/apparent value which results from a large number of collisions with differing energies and orientation, and cannot account for the fact that there may be more than one reaction step involved. In a strict sense, the Arrhenius activation energy cannot be interpreted as the energy barrier for any single atomic scale elementary step.

Transition state theory was developed to describe the rate constant in the microscopic picture. The Gibbs energies of reactant and product molecules are functions of the molecular geometries, they reside on a potential energy surface. When the reactants transform into products, the potential energy increases until a maximum is reached. This point (saddle point) on the potential energy surface is a maximum with respect to the reaction coordinate, and a minimum with respect to all other coordinates. The saddle point is called the transition state. The activation energy is the Gibbs energy difference between the reactant state and the transition state, ΔG_a.

The transition state theory rate constant (k_{TST}) can be calculated from the Eyring-Polanyi equation:

$k_{TST} = \frac{k_b T}{h} e^{\frac{-\Delta G_a}{RT}}$

where k_b is the Boltzmann constant. This form of the equation assumes that once the transition state has been reached, there is no re-crossing back to the reactants. The rigorous derivation of the transition state theory relies on statistical mechanics, and is out of the scope of this course.

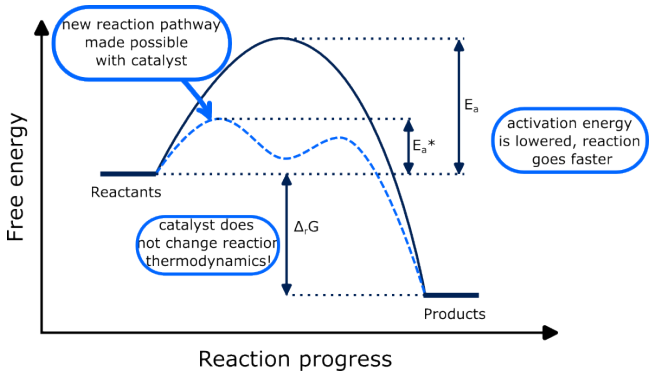
Q The activation energy ΔG_a does not change with temperature.

1. True
2. False

Catalysis

Catalysts speed up reactions

A catalyst is a substance or material that increases the rate of a chemical reaction without being consumed in the reaction itself. The catalyst increases the rate of reaction by facilitating an alternative reaction pathway which has lower activation barriers than the un-catalysed reaction: The catalyst does not change



the equilibrium composition of the reaction mixture, and does not "drive" a thermodynamically unfavorable reaction forward by changing the reaction energy.

Although the catalyst is not a reactant or product in the overall stoichiometric reaction, it does take part in the reaction, and has to come into contact with the reactants. In homogeneous catalysis the catalyst is in the same phase as the reactants and products (e.g. all are dissolved in a liquid), whereas in heterogeneous catalysis the catalyst is in a different phase than the rest of the reaction mixture (e.g. catalyst is a solid and reactants/products are gases). This course deals with heterogeneous catalysis.

Q A catalyst increases the rate of reaction by making the reaction energy smaller.

1. True
2. False

Adsorption and desorption

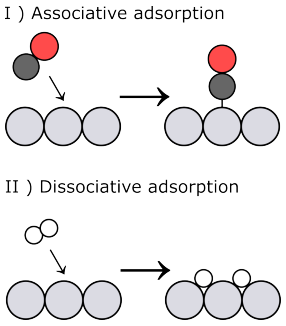
Adsorption of reactant(s) to the surface of the catalyst material is the first step of a heterogeneously catalysed reaction mechanism. Adsorption causes a change in energy, referred to as the adsorption energy, and it can be exothermic or endothermic.

Two main types of adsorption are

- Associative adsorption

- Dissociative adsorption

Associative adsorption means that the adsorbing molecule forms a bond with the surface without breaking any of its internal bonds. Carbon monoxide adsorption on metal surfaces is an example of associative adsorption. When a molecule adsorbs dissociatively, at least one internal bond breaks, and the molecule stays on the surface as separate fragments. A typical example of dissociative adsorption is the hydrogen molecule on transition metal surfaces.



In addition to wether a molecule adsorbs associatively or dissociatively, a distinction can also be made between

- Chemisorption
- Physisorption

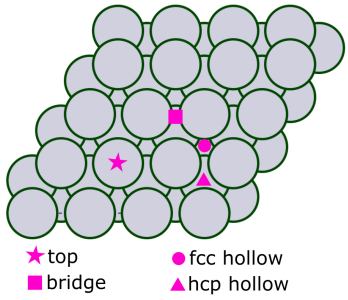
Chemisorption is typically stronger and there is a chemical bond formed between the adsorbate and the surface. CO typically forms strong chemical bonds with transition metal surfaces, and the adsorption energy can reach -150 kJ mol^{-1}.

Physisorption is weaker due to a smaller overlap between the adsorbate and surface electronic states. Adsorption energies are on the order of -30 kJ mol^{-1}, and the interaction is governed by van der Waals forces. Adsorption of methane on extended flat transition metal surfaces is an example of physisorption.

Molecules may have a strong preference towards binding to a certain adsorption site on a catalyst surface. When two or more adsorbates prefer the same type of site, this is referred to as competitive adsorption.

On extended metal surfaces adsorption sites are formed by metal atoms, and they mainly differ from each other by how many metal atoms the adsorbate binds or coordinates to. For example, on a Pt(111) surface there are top, bridge, and hollow sites:

On oxides, there are metal/cation and oxygen/anion sites which may also have different coordination, such as on the TiO_2 anatase (101) surface where half of the oxygens are coordinated to two Ti cations, and the other half to three.



The amount of adsorbates on the surface can be quantified in terms of coverage, commonly given the symbol θ, which is defined as the ratio between the number of adsorbed molecules and number of surface sites. The largest possible value is one, which means all sites are occupied, whereas a coverage of zero corresponds to a totally empty surface. In surface science, the coverage is often defined with respect to all surface atoms instead of specific adsorption sites.

Desorption is the reverse of adsorption, and is the last step that directly involves the catalyst surface in the reaction mechanism. During the desorption step, the bond between a stable product and the surface is broken, and the product molecule enters the gas or liquid phase leaving behind an empty surface site. The role of desorption is therefore two-fold:

- release of product molecules
- freeing of surface sites

The strength of adsorption of reactants and intermediates to the catalyst surface is very important for catalytic activity, and can be summarised with the Sabatier principle. It states that an ideal catalyst should bind the reactants and intermediates not too weakly nor too strongly. If a species is bound too weakly, it will leave the surface without reacting further. On the other hand, if a species is adsorbed too strongly, it will cover the whole surface and not desorb, leaving no free sites for reactions to occur. Both of these situations lead to low catalytic activity.

Active sites

A typical catalyst used in the industry is composed of an active catalyst, typically metal nanoparticles, which are deposited on a support, typically a metal oxide. The catalyzed reaction takes place on the surface of the catalyst, at special locations called active sites.

The active site is a collection of a few atoms (or even just a single atom!) which stabilize the reactants or intermediates, and the transition state in such a way that the activation barrier becomes lowered.

Four main properties that affect the nature of the active site are:

- Geometry
- Chemical composition
- Electronic structure
- Confinement

Geometry can be thought of as the spatial arrangement and coordination of the atom(s) that make up the active site. Sites such as terrace, edge, and corner atoms on metal nanoparticles have different geometries. Chemical composition is the identity of the atoms that form the active site, e.g. are both atoms that form a bridge site the same metal or not. Electronic structure of the active site is of course affected by the geometry and chemical composition, but even for the same particle shape the electronic structure can be quite different due to charge transfer to/from the support. Confinement can be the distance between active sites, distance between catalyst particles, or steric distance to e.g. ligands around the active site.

Although the active sites are traditionally thought to reside on the metal alone, an increasing number of studies show that the support, or the interface between the catalyst and the support, sometimes plays an active role in the catalytic process.

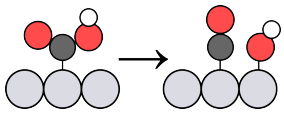
Further reading:

Vogt, C., Weckhuysen, B.M. The concept of active site in heterogeneous catalysis. Nat Rev Chem 6, 89–111 (2022). https://doi.org/10.1038/s41570-021-00340-y

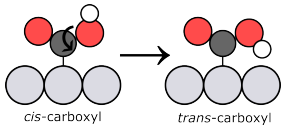
Surface reactions

Once the reactants have been adsorbed on the surface, they can take part in surface reactions. If the adsorption site is not the same as the active site, the adsorbate must travel to the active site by diffusion. Diffusion processes are often fast and not rate limiting, but sometimes there can be significant activation barriers associated with a molecule moving from site to site.

Adsorbates may react unimolecularly by isomerising or dissociating. Dissociation often requires there to be an empty site adjacent to the adsorbate so that all fragments can be accommodated:

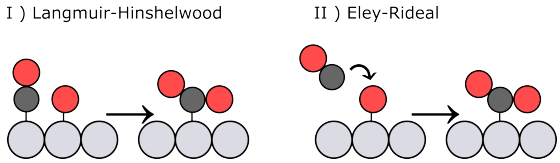


Isomerisation can occur on a single site by e.g. bond rotation:



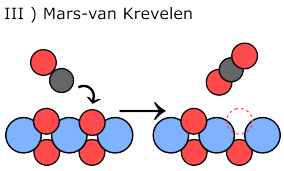
Bimolecular reactions can occur through two main types of mechanisms on metal surfaces:

- Langmuir-Hinshelwood
- Eley-Rideal



In a Langmuir-Hinshelwood mechanism two adsorbates on neighboring sites react together to form products, whereas in Eley-Rideal mechanism a molecule from the gas-phase reacts directly with an adsorbed species without being adsorbed first on the surface itself.

On oxide surface, the adsorbates can additionally react with the surface itself via the Mars-van-Krevelen mechanism. The adsorbate species abstracts a lattice oxygen from the oxide, creating an oxygen vacancy.



For the catalytic cycle to be complete, some other oxygen containing species must react with the vacancy to regenerate the surface.

What makes a good catalyst?

From a purely economical view point, an ideal catalyst should enhance a target reaction in such a way that it lowers the overall cost of operation while enabling a high production rate.

Along with low cost of the catalyst material, the three fundamental pillars for the ideal catalyst are:

- activity
- selectivity
- stability

Activity ('How fast are the products made') is a measure of the intrinsic catalytic performance towards the target reaction. In principle, the activity of at catalyst can be expressed in terms of the turnover frequency, which is the rate of reaction per catalytic site. However, determining the number of sites on the surface is rarely straightforward. In practice, the rate is often normalized in terms of mass of the active material, such as precious metal, in the catalyst, or the total surface area.

Selectivity ('How much desirable product vs total product is formed') is just as important as activity to the catalyst performance. Often, a catalyst can facilitate more than one reaction between the reactants, which can lead to undesired side products, lowering the yield and purity of the desired product. For example, in the synthesis of methanol from carbon dioxide and hydrogen, the desired main reaction that produces methanol competes with the reverse water-gas shift reaction which produces carbon monoxide. In the ideal case, a catalyst would only promote the main methanol synthesis reaction, i.e. it would be totally selective towards methanol.

Stability ('How long does the catalyst keep working') In order for a catalytic process to be commercially viable, it must be able to run for a long time without decreasing in performance. In principle, a catalyst does not get consumed in the reaction itself. However, in reality there are many chemical, thermal, and mechanical ways the catalyst can be degraded over time. Degradation of the catalyst leads to diminished activity (and selectivity), and eventually the whole catalyst might have to be replaced. An ideal catalyst is thermally, chemically, and mechanically stable, i.e. it can operate under the reaction conditions for a long time (even decades) without significant drops in performance.

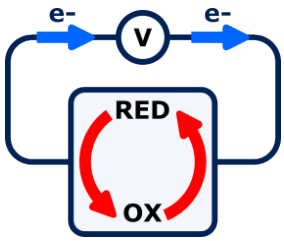
Electrochemistry

Chemistry + electric potential = electrochemistry

Electrochemistry is a field of chemistry that studies the interplay between electric potential and chemical transformations. In this branch of chemistry, spontaneous chemical reactions are used to produce electrical energy (release energy), or an applied electric potential is used to cause a chemical reaction (store energy).

A chemical reaction whose Gibbs free energy is positive must be driven forward by doing work on it. In electrochemistry this work is supplied via a potential difference (or voltage) across electrodes.

In an electrochemical system the movement of electrons and ions between the different components of the system is a central phenomenon. In the chemical part of the system, electrons are transferred between chemical species in reduction and oxidation (redox) reactions, and in the external circuit part, electrons move from one electrode to the other producing an electric current.



Q Electrostatic potential difference between two points in a system is the _____ required to move a test charge between the points, per unit charge.

1. work
2. force
3. electricity
4. current

Reduction and oxidation

The basis for electrochemical systems are redox reactions, where electrons are transferred from one chemical species to another. In a balanced redox reaction, the total number of electrons does not change. A redox reaction can be divided into the the reduction and oxidation half-reactions, which must always occur together. Loss of electrons is oxidation, gaining of electrons is reduction.

A generic reduction half-reaction is:

$$Ox + ze^{-1} \rightarrow Red \tag{17}$$

and the oxidation half-reaction is:

$$Red \rightarrow Ox + ze^{-1} \tag{18}$$

where z is the number of transferred electrons, Red is a reduced species and Ox is an oxidized species. Half-reactions have electrons as reactants (reduction) or products (oxidation). The half-reactions take place at electrodes, oxidation at the anode and reduction at the cathode.

The reaction quotient (Q_r) for the above half-reactions can be written as a ratio of the thermodynamic activities of products and reactants in a similar manner

as for a regular chemical reaction, for example for the reduction half-reaction :

$$Q_r = \frac{\{Red\}}{\{Ox\}} \tag{19}$$

Q In the reaction:

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2 \tag{20}$$

hydrogen is

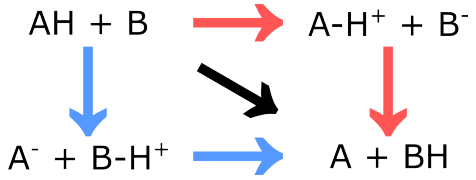
1. Oxidised
2. Reduced

Electron and proton transfer reactions

Many relevant electrochemical reactions not only involve movement of electrons from one species to another, i.e. electron transfer (ET), but also the movement of protons between species, i.e. proton transfer (PT). A redox process or elementary step in which both PT and ET occur are called proton coupled electron transfers (PCETs).

The transfer of the electron and proton may occur sequentially in two separate elementary steps (PT-ET or ET-PT mechanism). Alternatively, the proton and electron transfer may occur in a single concerted step (CEPT mechanism). The crucial difference between the stepwise and concerted mechanisms is that the stepwise mechanisms involve the creation of new charged intermediates.

The possible PCET mechanisms are often summarised using a square scheme:



In the scheme, the CEPT , PT-ET, and ET-PT mechanisms are indicated with black, blue, and red arrows, respectively.

Q The temperature behavior of the rate of a PCET reaction does not depend on whether it occurs through the concerted mechanism or step-wise electron-proton transfer mechanism.

1. True
2. False

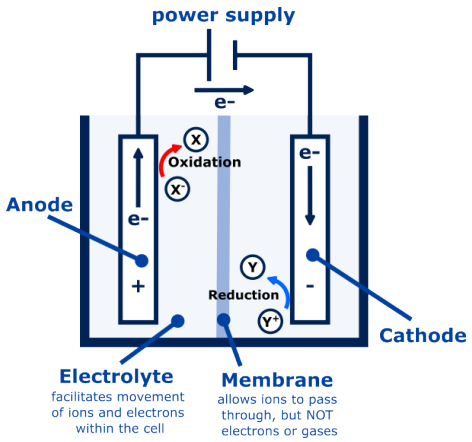
Electrochemical cells

Electrochemical cells are composed of (at least) two electrodes immersed in an electrolyte and an external circuit through which the electrons flow from one electrode to the other. Electrochemical cells can be broadly divided into two types:

- galvanic
- electrolytic

A galvanic cell converts chemical energy into electrical energy, while in an electrolytic cell electric energy is used to drive a non-spontaneous reaction.

There are many different kinds of cells with different electrode configurations, below is a schematic of a simple 'H-type' membrane electrolytic cell



Q Consider the reaction:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{21}$$

would it take place at the anode or cathode of an electrochemical cell?

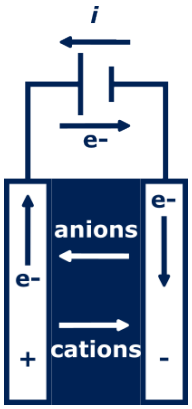
1. Anode
2. Cathode

Flow of charge in electrolytic cells

Electric current (I) is caused by the movement of charge carriers through a material due to a potential difference. It is the net rate of charge (q) moving across a surface, and the unit is Coulomb (C) per second (s), or ampere (A):

$$I = \frac{dq}{dt}$$

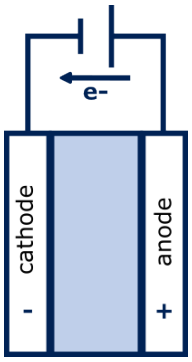
Negative charge carriers move in the opposite direction of the conventional current (arrow label 'i' in the diagram below), positive carriers move in the same direction as the current.



In the electrolytic cell, electrons are the charge carrier inside the electrodes and the external circuit. In the electrolyte, both negative and positive ions can carry charge.

For current to flow, a potential difference needs to be applied across the electrodes, and the redox reactions must occur at the electrodes. Both the external circuit and the electrochemical part are needed to complete the circuit.

Q In the diagram below, which direction would a positive ion move across the light blue region representing the electrolyte?



1. from right to left
2. from left to right

Electric work and cell potential

To drive a reaction whose standard Gibbs energy $\Delta_r G^\circ$ is positive, such as water splitting at room temperature, non-expansion work must be done on it. In electrochemistry this work is electric work. The minimum amount of work required is equal to the standard Gibbs energy of the reaction:

$$w_{min} = \Delta_r G^\circ$$

The work is supplied to the chemical reaction by applying a potential difference across the electrodes of the electrolysis cell. The standard cell potential ϕ°_{cell} is the difference between the standard single electrode potentials of the cathode and anode:

$$\phi^\circ_{cell} = \phi^\circ_{cathode} - \phi^\circ_{anode}$$

ϕ°_{cell} is related to the standard Gibbs energy of the reaction by

$$\Delta_r G^\circ = -nF\phi^\circ_{cell}$$

where n is the amount of electrons transferred per mole of product and F is the Faraday constant.

Combining the above expression with the relation $\Delta_r G = \Delta_r G^\circ + RT \ln Q_r$ leads to the Nernst equation, which can be used to obtain the cell potential for non-standard situations:

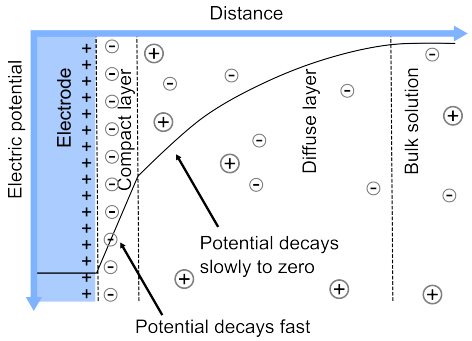
$$\phi_{cell} = \phi^\circ_{cell} - \frac{RT}{nF} \ln Q_r$$

Electrical double layer

Electrochemical reactions take place at the interface between the liquid electrolyte and solid electrode. The surface of the electrode is charged, and the electric field also affects the electrolyte structure, because the electrolyte contains charged ions.

The ions with charges opposite to the electrode surface are attracted to it, and re-arrange to form a layer together with some solvent molecules. This first layer closest to or in direct contact with the electrode is called the inner Helmholtz layer (IHL). Next to the IHL, ions with opposite charge to those in the IHL gather to form the outer Helmholtz layer (OHL). The ions in OHL are not in direct contact with the electrode, and are more solvated, or surrounded by solvent molecules, than the ions in the IHL. The OHL ions mainly interact with the electrode and adsorbate species through electrostatics.

The IHL and OHL from the "compact layer", which is around half a nanometer thick. After the compact layer, there is another "diffuse layer" before the bulk electrolyte, which is around 10 nm thick. The structure that emerges from the re-arrangement of the ions and solvent molecules near the electrode into layers is called the electrical double layer (EDL). The electrolyte in the EDL has a different concentration of ions than the bulk, but the net charge is electrically neutral.



Electrode potential controls the energy of electrons

In electrochemical applications, the contribution of the electrostatic potential is included in the free energy of a species, and this total chemical potential or electrochemical potential ($\tilde{\mu_i}$) is

$$\tilde{\mu_i} = \mu_i + z_i F \phi$$

where μ_i is the internal chemical potential of the species i, z_i is the charge of the species, F is the Faraday constant and ϕ is the local electrostatic potential. Note that the electrochemical potential of uncharged species, such as a water molecule, is not influenced by the change in electrostatic potential, i.e. they cannot be influenced/controlled by changing the voltage.

When the potential difference is introduced between the electrodes, the electrochemical potential of the electrons within the electrodes change according to the $z_i F \phi$ term to become oxidizing or reducing.

In an electrochemical experiment, the potential difference across the electrodes can be controlled, which changes the observed electric current measured in the circuit. The onset of the current depends on the thermodynamics of the redox reaction, but the kinetics of the reaction determine how high a current can be extracted from the system, ie how much product can be produced by the redox reaction.

Reference electrode potential

The half-cell reactions at the anode and cathode are independent of each other, so it is possible to study their properties one at a time. In fact, this is often much simpler to do experimentally rather than assembling and optimizing the entire cell.

However, potential difference has to be applied across a pair of electrodes, the cell potential being the difference in the electric potential of the two electrodes. The single electrode potential is the electrochemical potential of electrons inside the electrode, which is possible but difficult to obtain experimentally. Thus, single electrode potentials are reported with respect to reference electrodes, whose potentials are known and can be set to a certain value by convention.

In Figure 7, a typical three electrode setup is shown. The electrode under study is the working electrode (WE), and there is a current flowing between it and a counter electrode (CE). The reference electrode (RE) has very little or no current flowing through, and the cell potential is measured between it and the working electrode.

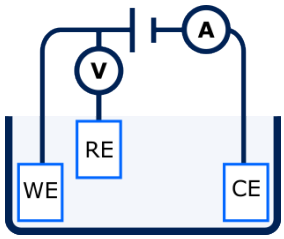


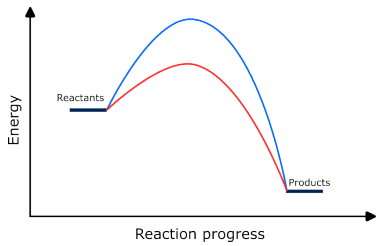
Figure 7: Shematic of a three electrode setup

The standard hydrogen electrode (SHE) is a common reference electrode, and its cell potential is defined as 0 V at all temperatures. The electrode is platinum, and the electrolyte is an ideal solution with 1 M H^+ concentration, connected to the WE side of the cell by a salt bridge.

As the SHE cell potential is 0 V by definition, the electrode potential of a WE measured against it changes with pH of the electrolyte that the WE is dipped in. In contrast, the reversible hydrogen electrode (RHE) is immersed in the same electrolyte as the WE, and its electrode potential changes with pH.

Core physical concepts Quiz

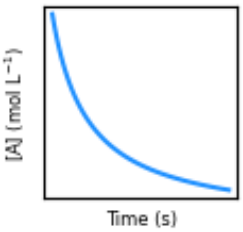
1. Which of the following cannot occur during a chemical reaction?
   (a) Electrons move from one atom or molecule to another
   (b) Atom of one element changes into an atom of another element
   (c) Chemical bonds are broken and/or formed.
   (d) Number of molecules changes.
2. Two reaction energy profiles are presented below. All other conditions being equal, which reaction would you expect to proceed faster?



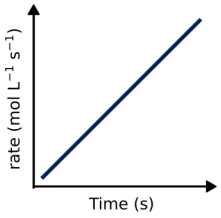
   (a) Reaction corresponding to the blue profile
   (b) Reaction corresponding to the red profile
3. Since an exothermic reaction gives out heat to the environment, its reaction rate is always decreased if the temperature is raised.
   (a) True
   (b) False
4. Consider the single step reaction

$$A \rightarrow B$$

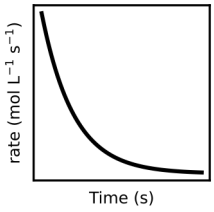
   The plot of concentration of A versus time is Which plot best describes



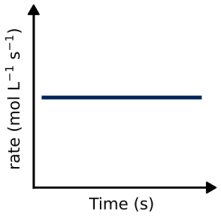
   the behavior of the reaction rate versus time?



(a)



(b)



(c)

5. A catalyst increases the rate of a reaction by changing the reaction mechanism.

   (a) True

   (b) False

6. Consider the reaction between Ni^{2+} and aluminium

$$2Al + 3Ni^{2+} \rightarrow 2Al^{3+} + 3Ni$$

   Which of the statements is true?

   (a) Ni^{2+} oxidation state increases

   (b) Al is reduced

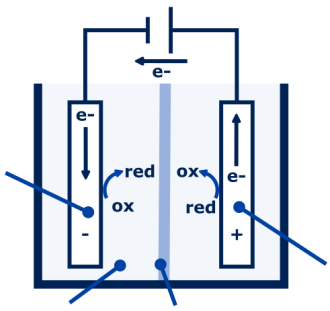
   (c) Al is the reducing agent

   (d) Ni loses electrons

7. Complete the following text by filling in appropriate missing words:

   _____ cells convert chemical energy into electrical energy, while in _____ cells electrical energy is used to drive _____ reactions. The water splitting reaction takes place in a/an _____ cell.

8. Label the electrolytic cell



Intro to Hydrogen Production

Towards Cleaner Energy

Hydrogen has the highest energy content per mass out of all known fuels, and can be used in a versatile manner as an energy carrier, raw material, and fuel. It is abundant on Earth, but only in a bound form such as water, methane and other organic compounds, i.e. it must be produced by chemically transforming those molecules.

If produced in a sustainable manner, hydrogen could be used as a green reactant in the chemical and steel industry, or an alternative to fossil fuels in applications where full electrification is not feasible. However, almost all hydrogen (95%) is produced from fossil feedstocks without carbon capture, producing enormous CO_2 emissions1. The challenge for the overall hydrogen economy is to reduce the carbon dioxide emissions of hydrogen production so that it can be considered a truly clean alternative, and contribute to the fight against climate change.

In Finland, 0.15 Mt/Yr of hydrogen (2020) is produced, also mainly from fossil feedstocks.2 Only a very small portion of hydrogen is produced cleanly at commercial scale by electrolysis. Electrolysis is an electricity intensive process, and the electricity must be produced with renewable energy for it to be considered clean or low-carbon. However, Finland sees the electrolysis based hydrogen economy as promising due to the existing, relatively low-carbon, electricity production, massive potential for wind power expansion, and robust electricity transmission network. Furthermore, Finland has no domestic fossil fuel resources, meaning that any application utilizing them is reliant on importation.

This module will cover the main conventional hydrogen production method currently used in Finland, steam reforming of methane. Other conventional processes are also briefly introduced. Finally, an overview of the current state of electrolysis and photo(electro)lysis are given.

1. Hydrogen society: From present to future. Guan, D. et al. Energy & Envi-

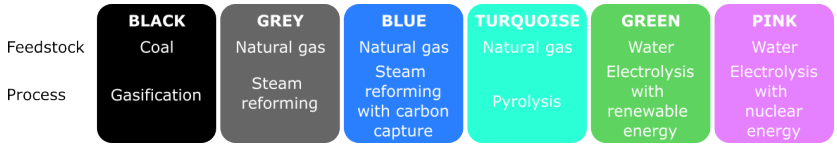
ronmental Science, 2023, 16(11), 4926–4943. DOI: 10.1039/d3ee02695g

2. Vetytalous – mahdollisuudet ja rajoitteet. Sivill, L. et al. Valtioneuvoston selvitys- ja tutkimustoiminnan julkaisusarja 2022:21 http://urn.fi/URN:ISBN:978-952-383-413-2

How is Hydrogen Made?

The Many Colours of Hydrogen

Hydrogen is a completely colourless gas, but you often hear it being referred to as green, grey or even pink. The colour codings correspond to the different feedstocks, energy sources, and processes that are used in hydrogen production. The most prominent (see referred article for more) colour codings are presented below1



From the perspective of the environment, the only type of hydrogen whose production should be promoted in the future is green (and possibly pink) hydrogen. All other types (out of the ones presented above) consume fossil fuel, produce large amounts of carbon dioxide, require massive centralized infrastructure, and/or are energy intensive.

Currently, there is little incentive for the industry to switch to using only green hydrogen, as it is much more expensive: grey hydrogen costs around 1.50 € / kg, while green hydrogen costs 3.50–6 € / kg. The demand for hydrogen also exceeds the current capacity for green hydrogen production.

White hydrogen

In recent years, there have been reports of natural deposits of hydrogen around the world, including Finland. This type of natural hydrogen is also referred to as 'white' hydrogen.

1. "colors" of hydrogen: Definitions and carbon intensity. Incer-Valverde, J. et al. Energy Conversion and Management, 2023, 291, 117294. DOI: 10.1016/j.enconman.2023.117294

2. The occurrence and geoscience of natural hydrogen: A comprehensive review. Zgonnik, V. Earth-Science Reviews, 2020, 203, 103140, DOI: 10.1016/j.earscirev.2020.103140

Q All hydrogen produced via electrolysis is green hydrogen

1. True
2. False

Gasification

Gasification is a mature and cost effective process for hydrogen production where a solid carbon containing raw-material is partially combusted to produce a gaseous mixture of hydrogen and other products such as carbon monoxide, methane, and water. Steam, air or oxygen is used as an oxidant in the process.1

Possible gasification feedstocks are

- coal
- biomass, e.g. wood, saw dust, crop husks
- waste , e.g. sewage sludge, plastic, car tyres

with coal being the typical industrial feed.

Depending on the process and carbon raw-material, the product gas may also contain ash, tar, H_2S, NH_3, HCl and HCN. To obtain hydrogen and the other useful gas products, CO and CH_4, the gas must be carefully purified, which lowers the energy efficiency of the total process.

1. Midilli, A., Kucuk, H., Topal, M. E., Akbulut, U., & Dincer, I. (2021). A comprehensive review on hydrogen production from coal gasification: Challenges and opportunities. International Journal of Hydrogen Energy, 46(50), 25385–25412. DOI: 10.1016/j.ijhydene.2021.05.088

Coal Gasification

The coal gasification process is endothermic, and requires high temperatures of 460-1700 °C, depending on the gasifier technology and specific type of coal.[1] Catalysts have been utilized in coal gasification for around 100 years, the most active catalysts are alkali catalysts such as sodium and potassium.

Among all hydrogen production methods, coal gasification produces the most carbon dioxide per kg of hydrogen. In principle, the carbon dioxide emissions could be mitigated by using carbon capture technologies.

Finland does not have domestic coal resources, and coal gasification is not a significant method of hydrogen production here.[2] Globally (in 2015) about 17% of hydrogen is still produced via coal gasification.

1. Midilli, A., Kucuk, H., Topal, M. E., Akbulut, U., & Dincer, I. (2021). A comprehensive review on hydrogen production from coal gasification: Challenges and opportunities. International Journal of Hydrogen Energy, 46(50), 25385–25412. DOI: 10.1016/j.ijhydene.2021.05.088

2. Vetytalous – mahdollisuudet ja rajoitteet. Sivill, L. et al. Valtioneuvoston selvitys- ja tutkimustoiminnan julkaisusarja 2022:21 http://urn.fi/URN:ISBN:978-952-383-413-2

Biomass Gasification

A promising development is the increasing interest in gasification of biomass or carbon-based waste instead of coal.1

Biomass (and carboneous waste) gasification is much more complex than e.g. coal gasification due to the inherently heterogeneous nature of the feedstock. The concentration of obtained hydrogen depends on the nature of the biomass itself, operating conditions such as temperature, pressure, and gasification agent. The process is not mature, and requires a lot of further studies to be applied on the industrial scale. Utilization of novel catalysts is one of the ways to improve the performance of biomass gasification.2

While Finland has plenty of biomass resources that could be used for hydrogen production by biomass gasification, those resources are already being utilized for other processes. For example, around half of all of the wood output from Finnish forests is used for energy production and the other half is used for various wood-based products such as timber, pulp, or paper.3

1. Midilli, A., Kucuk, H., Topal, M. E., Akbulut, U., & Dincer, I. (2021). A comprehensive review on hydrogen production from coal gasification: Challenges and opportunities. International Journal of Hydrogen Energy, 46(50), 25385–25412. DOI: 10.1016/j.ijhydene.2021.05.088

2. Song, H., Yang, G., Xue, P., Li, Y., Zou, J., Wang, S., Yang, H., & Chen, H. (2022). Recent development of biomass gasification for H_2 rich gas production. Applications in Energy and Combustion Science, 10, 100059. DOI: 10.1016/j.jaecs.2022.100059

3. IRENA (2018), Bioenergy from Finnish forests: Sustainable, efficient and modern use of wood, International Renewable Energy Agency, Abu Dhabi. Link to report

Partial Oxidation

Partial oxidation (POX) is an alternative way to produce hydrogen from methane. In POX, methane is reacted with a sub-stoichiometric amount of oxygen to yield carbon monoxide and hydrogen. The amount of oxygen is limited so that it is not able to oxidize, i.e. combust, the methane all the way to carbon dioxide and water.

The reaction equation for POX is:

$$CH_4 + \frac{1}{2}O_2 \rightarrow 2H_2 + CO$$

Compared to steam methane reforming (SMR), POX is less energy intensive as it is exothermic and also has faster reaction kinetics.[1] However, the hydrogen to CO ratio after reaction is 2:1, whereas for SMR it is 3:1. In Finland, only a small percentage of dedicated hydrogen production utilizes POX.[2]

1. Makaryan, I. A., Salgansky, E. A., Arutyunov, V. S., & Sedov, I. V. (2023). Non-catalytic partial oxidation of hydrocarbon gases to syngas and hydrogen: A systematic review. Energies, 16(6), 2916. https://doi.org/10.3390/en16062916

2.Vetytalous – mahdollisuudet ja rajoitteet. Sivill, L. et al. Valtioneuvoston selvitys- ja tutkimustoiminnan julkaisusarja 2022:21 http://urn.fi/URN:ISBN:978-952-383-413-2

Summary

The European Union has set ambitious goals for a green transition, including no net emissions of greenhouse gases by 2050 and economic growth decoupled from resource use. The proposal for how to achieve these goals is presented in the European Green Deal.[1] Massive investments in renewable wind and solar energy and decarbonisation of industry are central to the plans.

The role of hydrogen in the green transition could be vital in three ways

lowering the environmental impact of applications that already use fossil based hydrogen such as the chemical and steel production industries as a buffer for the intermittent nature of wind and solar energy as a fuel in applications where decarbonisation/electrification is otherwise difficult to achieve

The first point is fairly straightforward. Hydrogen is already being used for various industrial processes on a massive scale, and virtually none of it is sustainably produced.[2] Switching to using green hydrogen only could help decarbonise these sectors and lower their sizeable contribution to global green house gas emissions.

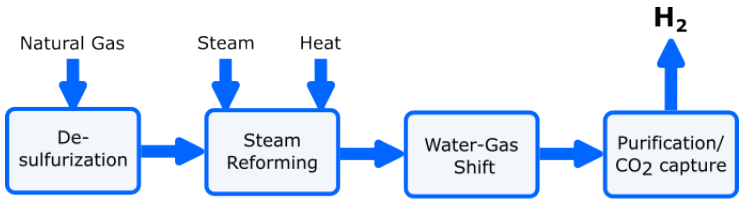
If hydrogen is used as a carbon free alternative to traditional fuels and feedstocks, the production of that hydrogen must be as carbon neutral as possible too. Meanwhile, almost all contemporary methods of hydrogen production rely on fossil feedstocks such as coal and natural gas. Therefore, hydrogen cannot currently be called a carbon free or green based on the net emissions.

To fulfill its role as an energy buffer, firstly hydrogen must be produced using renewable energy. This requires increasing renewable energy capacity and integration of hydrogen production facilities to the grid. In the next section, the main method for hydrogen production in Finland, steam methane reforming, is introduced in more detail.

Sources:

2. European Green Deal

1. Rambhujun, N., Salman, M.S., Wang, T. et al. Renewable hydrogen for the chemical industry. MRS Energy & Sustainability 7, 33 (2020). https://doi.org/10.1557/mre.2020.33



Schematic SMR process flow

Steam Methane Reforming

What is Steam Reforming?

Steam reforming (SR) is a mature process which has been used for producing hydrogen for nearly 100 years. Globally (and in Finland) steam methane reforming (SMR), is the most popular method for dedicated hydrogen production.1 The source of methane is natural gas.

In SMR, methane is reacted with steam typically at high (700°C - 1250°C) temperature, in the presence of a nickel catalyst. The steam partial pressure can reach up to 30 bar. The main steam methane reforming reaction is coupled with the water-gas shift reaction which removes CO and produces additional hydrogen. The final products are H_2 and CO_2.

The CO_2 product is inherent to the stoichiometry of the reforming and water-gas shift reactions, and the process does produce massive amounts of CO_2. The emissions can be mitigated by CO_2 capture. The overall SMR process is very energy intensive due to the high operating temperature, and also requires massive infrastructure.

1. Ighalo, J. O., & Amama, P. B. (2024). Recent advances in the catalysis of steam reforming of Methane (SRM). International Journal of Hydrogen Energy, 51, 688–700. https://doi.org/10.1016/j.ijhydene.2023.10.177

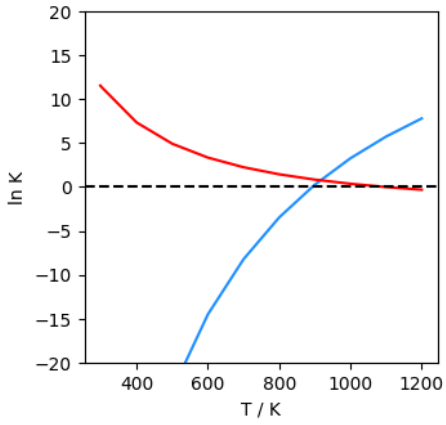
Q Given the typical operating temperature of steam methane reforming, which curve of the equilibrium constant K versus temperature T (in Kelvin) belongs to the methane reforming reaction? The curves are calculated at standard conditions.

1. The blue curve
2. The red curve

SMR Reactions

The main reaction in SMR is the titular reaction, steam methane reforming:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{22}$$



Methane and water react to produce a mixture of hydrogen and carbon monoxide, commonly referred to as syngas.

The second most important reaction is the exothermic water-gas shift (WGS) reaction, which is commonly coupled with SMR to increase the hydrogen yield and remove CO from the syngas:

$$\mathrm{CO} + \mathrm{H_2O} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2} \tag{23}$$

The CO_2 product must be separated by e.g. pressure swing adsorption or a selective membrane to obtain pure hydrogen.

Q Based on the stoichiometry of the SMR and WGS reactions, how much CO_2 is emitted per each kilogram of H_2 produced?

1. 5.5 kg
2. 2 kg
3. 1 kg
4. 0.5 kg

SMR Mechanism

The SMR is a catalyzed reaction, and takes place on the catalyst surface. The first steps of the reaction mechanism must be the adsorption of methane and water. It is clear from just the reaction equation that all C-H bonds and both H-O bonds in the reactants must be broken, and H-H and C-O bonds must be formed. Theoretically, there are many different pathways that could result in these bond breakages/formations.

Two general types of routes have been established:

- total decomposition of methane followed by oxidation of atomic carbon
- partial decomposition of methane followed by oxidation of CH_x intermediates

In principle, both pathways are always occurring to some extent. Either reaction pathway could be the dominant one depending on the catalyst and reaction conditions.

The rate-limiting step of the SMR reaction over nickel based catalysts is likely the activation of the CH_4 molecule, although other steps such as oxidation of carbon ad-atoms and CO desorption may also be kinetically important.

Carbon Formation

Unwanted production of carbon becomes thermodynamically favorable at high reaction temperatures during SMR. Atomic carbon is mainly formed on the catalyst surface, although gas-phase reactions followed by carbon deposition can also occur.

Two typical carbon producing surface reactions are

1. Methane decomposition
2. Boudouard reaction

$$CH_4 \rightleftharpoons C + 2H_2 \quad (1) 2CO \rightleftharpoons C + CO_2 \quad (2) \tag{24}$$

The formed carbon ad-atoms can further polymerize or form films on the catalyst surface, which leads to the deactivation of the catalyst and is a major issue for SMR. In order to prevent the formation of carbon structures that can block active sites or disintegrate the catalyst, the reaction of atomic carbon with some other species such as oxygen must be faster.

The gasification of carbon is a reaction which can remove atomic carbon before it can grow to form larger deposits:

$$C + H_2O \rightleftharpoons CO + H_2 \tag{25}$$

Increasing the partial pressure of steam favors the forward reaction, which leads to the enhanced removal of carbon. Therefore even though a 1:1 ratio of water and methane react stoichiometrically in SMR, higher steam to carbon (S/C) ratios are used in practice.

SMR catalysts and active sites

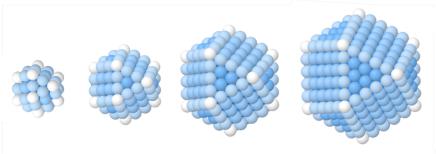
The most popular industrial catalysts for SMR are supported nickel materials due to their high activity and low cost. The support is typically an oxide such as Al_2O_3, MgO, or SiO_2.

Noble metals have been reported to be more active and coke resistant than the Ni based catalysts, however they are too expensive and scarce to be suitable for industrial use. The main issue for the conventional Ni catalyst is deactivation by sintering and coking. Effects of different supports and promotors have been investigated in recent years to improve the performance, especially stability, of the Ni catalyst.

SMR is known to be a structure sensitive reaction, i.e. different surface sites on the catalyst have differing intrinsic activities towards the reaction. On Ni-based catalysts the active site for C-H activation has been proposed to be highly uncoordinated Ni atoms, such as edges and corners. The relative number of differently coordinated sites on the catalyst surface depends on the shape and size of the metal nanoparticles. The particle shape and size can therefore influence the rate and the dominant reaction mechanism.

Q The number of under-coordinated edge and corner sites relative to terrace sites decreases when particle size increases.

Hint:



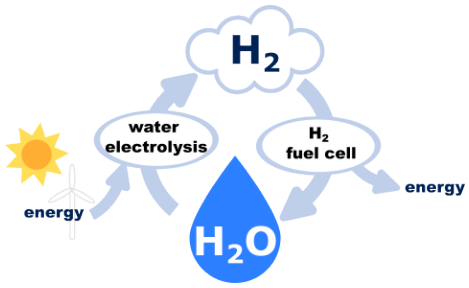
1. True
2. False

Electrolysis and photo(electro)lysis

Hydrogen from water

There is a lot of water on Earth, and water contains hydrogen which can be separated from it by chemical means. When hydrogen combusts, or combines with oxygen in a fuel cell, only water is formed. Based on atom balance, these processes do not have a direct source of carbon emissions, as opposed to fossil fuel or biomass based solutions. Water as a feedstock is the basis of an ideal circular hydrogen economy.

Converting water to hydrogen and oxygen is thermodynamically uphill, i.e. work is required to drive the reaction. In electrocatalytic methods this work comes from electrical energy, whereas solar methods utilize photon energy to drive the reaction. Ideally, the electrical energy used in electrocatalysis should be produced from renewables, such as wind or solar.



How much water do we need?

The water splitting reaction takes one mole of water to make one mole of hydrogen. But what is this in more day-to-day units? From the molecular weights of water (M_w) and hydrogen (M_{H_2}), and density of water (ρ_w), the minimum amount of feed water required in liters (V_w) to produce one kilogram of H_2 can be calculated as:

$$V_w = \frac{M_w}{\rho_w \cdot M_{H_2}} = \frac{0.018 \text{ kg mol}^{-1}}{1 \text{ kg L}^{-1} \cdot 0.002 \text{ kg mol}^{-1}} = 9 \text{ L kg}^{-1} \tag{26}$$

The process requires at least 9 liters of water per kilogram of hydrogen.

In order to operate optimally (or even at all), current commercial electrolyzers require the feed water to contain as few ions, molecules, or bacteria as possible. This is referred to as ultrapure water. However, naturally occurring water on Earth is not ultrapure, and must be purified by filtration. Furthermore, over 96 % of naturally occurring water is sea water, which has an even more complex composition (i.e. dirty and salty) than fresh water. As seawater is a practically infinite resource, utilizing it is very attractive despite the complex challenges. Currently, it remains unclear whether direct seawater electrolysis or electrolysis coupled to mature desalination technologies will provide a better alternative.1

In addition to the chemical products, water electrolysis also produces heat. To keep the operating temperature constant, the system has to be continuously cooled. In small electrolyzers this can be achieved via dry cooling (i.e. with air circulation), but for more centralized electrolysis plants coolant water is needed. This further increases the water demand of electrolysis.

In reality, commercial electrolyzers use more than twice the amount of water that is required stoichiometrically, about 18 L per kg of hydrogen. This may sound like a lot, however, other hydrogen production methods also consume water, even if it is not the direct hydrogen source. Green hydrogen has the smallest estimated water footprint out of all currently available hydrogen production technologies! 2

According to some recent estimates, transitioning to a water electrolysis based hydrogen economy would actually lower water consumption compared to the current state.3 The strain on water resources must still be considered on the local scale, as it may have a greater effect in areas where water is already more scarce.

1. Farràs, P., Strasser, P., & Cowan, A. J. (2021). Water electrolysis: Direct from the sea or not to be? Joule, 5(8), 1921–1923.
https://doi.org/10.1016/j.joule.2021.07.014

2. Olaitan, D., Bertagni, M., & Porporato, A. (2024). The water footprint of hydrogen production. Science of The Total Environment, 927, 172384.
https://doi.org/10.1016/j.scitotenv.2024.172384

3. Beswick, R. R., Oliveira, A. M., & Yan, Y. (2021). Does the green hydrogen economy have a water problem? ACS Energy Letters, 6(9), 3167–3169.
https://doi.org/10.1021/acsenergylett.1c01375

Further reading on seawater electrolysis and desalination:

Jin, H., Xu, J., Liu, H., Shen, H., Yu, H., Jaroniec, M., Zheng, Y., & Qiao, S.-Z. (2023). Emerging materials and technologies for electrocatalytic seawater splitting. Science Advances, 9(42).
https://doi.org/10.1126/sciadv.adi7755

Electrolysers

Electrolysers are technologies that convert water into hydrogen and oxygen using electrical energy as the driving force. Often the term 'electrolyser' is used when referring to the electrolysis stack, the component where the water splitting reaction takes place in an electrolysis cell. The electrolysis stack technologies are also the focus of this course. However, an equally important part of the system is the balance of plant (BoP), which provides the power and water supply, water purification, hydrogen processing etc. Without an optimal BoP, the lifetime and performance of the stack can be severely compromised.

The four main types of cell technologies existing today are

- liquid alkaline (AEL)
- proton exchange membrane (PEM)
- anion exchange membrane (AEM)
- solid oxide (SOEC) cells

Some advantages and disadvantages of the stack technologies are tabulated below AEL and PEM technologies are already commercialized, although great improvements in the efficiency and material costs must be made in order to compete with the price of hydrogen produced from fossil feedstocks. No single electrolyser technology is superior to others across all performance parameters,

Cell technology	Advantages	Disadvantages
AEL	• Mature technology • Commercial/industrial stage • Non-noble metal electrocatalysts • Relatively low cost • Long life-time	• Limited current density • Gas crossover • High concentrated (5M KOH) electrolyte
AEM	• Non-noble metal electrocatalysts • Low concentrated (1M KOH) electrolyte	• Limited stability • Early development stage
PEM	• Commercial stage • Higher current densities • High gas purity • Thin cell	• High cost cell components • Noble metal electrocatalysts • Acidic electrolyte
SOEC	• High operating temperature • High efficiency	• Limited stability • Early development stage

and it is likely that a diversity of solutions will be needed so that ideal electrolysers can be provided for a broad range of applications.

Solar-driven H_2 production

With approximately 170 000 TW of sunlight hitting Earths surface, solar energy is the largest energy reserve available on Earth. The amount of potentially recoverable energy overshadows all other finite and renewable sources.

Solar energy comes from the fusion process taking place in the Suns core. In the large scale of things, even the Sun will stop providing us energy as it eventually runs out of hydrogen, but by that time we will have some bigger problems. From our perspective, solar energy is considered a renewable energy source, as it is not depleted by harvesting it.

Solar energy can be used in different ways for hydrogen production. One strategy is to provide heat for thermocatalytic processes, which lowers the carbon dioxide emissions from e.g. combustion of natural gas during steam methane reforming. Solar power can also be converted to electricity which can then be used to drive conventional electrolysis processes. Another attractive alternative is to use the photon energy directly in photo(electro)catalytic water splitting applications. Hydrogen produced via solar-driven methods is sometimes called 'yellow hydrogen' to distinguish it from other types of renewable hydrogen.1

Solar to hydrogen conversion via photocatalytic splitting of water is at a much earlier stage of development than electrolysis. Significant advances in photocatalyst efficiency and stability, process optimization etc. are needed to scale up hydrogen production using solar power.

1. Incer-Valverde, J., Korayem, A., Tsatsaronis, G., & Morosuk, T. (2023). "colors" of hydrogen: Definitions and carbon intensity. Energy Conversion and Management, 291, 117294.
https://doi.org/10.1016/j.enconman.2023.117294

Hydrogen production intro Quiz

1. Match the typical feedstock for the different hydrogen production methods

(a) Partial Oxidation	A Coal
(b) Solar-to-hydrogen	B Biomass
(c) Steam reforming	C Water
(d) Electrolysis	D Wood
(e) Gasification	E Ammonia
	F Natural Gas

2. Complete the following text by filling in appropriate missing words:

   The electrolyser is a technology that produces _____ through a chemical process called _____ capable of separating the hydrogen and _____ molecules of which water is composed of using _____ to drive the thermodynamically _____ reaction forward.

3. Choose the option which best represents the stoichiometry and heat of reaction of the main reforming reaction in steam methane reforming:

   (a) $CH_4 + H_2O \rightleftharpoons 3H_2 + CO \qquad \Delta H = +206\text{kJ/mol}$

   (b) $CH_4 + H_2O \rightleftharpoons 3H_2 + CO \qquad \Delta H = -206\text{kJ/mol}$

   (c) $CH_4 + H_2O \rightleftharpoons 3H_2 + CO_2 \qquad \Delta H = +206\text{kJ/mol}$

   (d) $CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad \Delta H = -41\text{kJ/mol}$

4. What property of hydrogen makes it attractive as an energy carrier?

   (a) It is easy to transport

   (b) It has a high energy content by weight

   (c) It has a high volumetric energy density

   (d) It is abundant on Earth

5. What is the main method used for hydrogen production in Finland?

   (a) Steam methane reforming

   (b) Thermolysis

   (c) Partial oxidation of methane

   (d) Biogas reforming

   (e) Water electrolysis

6. Excess water is usually used in industrial steam methane reforming. Why?

(a) It lowers the operation temperature.

(b) It helps the nickel catalyst to stay oxidized.

(c) It reduces coke formation.

(d) It reduces the energy demand.

7. Why is nickel a popular metal used in stem methane reforming?

   (a) It has a low cost and high activity

   (b) It can resist deactivation caused by coke formation

   (c) It increases the hydrogen yield

   (d) It has the highest activity out of all metals

8. Almost all hydrogen is produced from fossil fuels

   (a) True

   (b) False

9. Hydrogen is currently produced in a clean and sustainable way.

   (a) True

   (b) False

10. What is the main advantage of producing hydrogen by water electrolysis compared to steam methane reforming, partial oxidation of methane, or coal gasification?

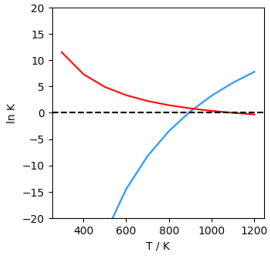
    (a) It costs less per kg of hydrogen produced

    (b) There is no inherent source of carbon

    (c) The catalyst material is cheaper

    (d) It consumes less electricity

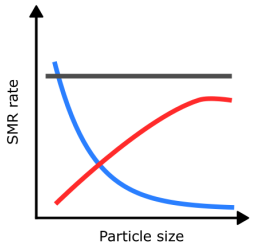
11. Given the typical operating temperature of steam methane reforming, which curve of the equilibrium constant K versus temperature T (in Kelvin) belongs to the methane reforming reaction? The curves are calculated at standard conditions.



(a) Blue

(b) Red

12. Consider a hypothetical supported metal catalyst that has been found to catalyze the steam methane reforming reaction. The sole rate determining step has been found to be C-H bond activation. If the active site for C-H activation are the undercoordinated edges or corners of metal nanoparticles, which of the rate vs particle size curves would best describe the behavior of SMR over this catalyst? Rate is defined here as moles per second per surface metal atom.



(a) Blue

(b) Red

(c) Grey

13. Select one advantage and disadvantage for each electrolysis technology from the available options.

Cell technology	Advantages	Disadvantages
(a) Liquid alkaline	A Can operate at high current densities	E Membrane stability
(b) Proton exchange membrane	B High efficiency (laboratory test)	F Electrode stability
(c) Anion exchange membrane	C Low concentration of alkaline electrolyte	G Corrosive electrolyte
(d) Solid oxide	D Relatively low cost	I Noble metal electrocatalyst

14. What is one major challenge in producing hydrogen from solar energy?

(a) Sunlight is not a large enough energy source

(b) Efficiency of solar-to-hydrogen energy conversion

(c) Low availability of water feedstock

(d) Environmental impact due to materials used

Electrocatalytic Hydrogen Production

A Promising Alternative

Finland has sizable potential for increased wind power and plenty of fresh water, however less than 1 % of hydrogen in Finland is produced by water electrolysis. In order for water electrolysis to overtake traditional fossil fuel based methods, the productivity and cost-effectiveness of the processes must be significantly improved.

The most significant cost factor for water electrolysis is the price of renewable electricity. The price of renewables continues to decline which makes electrolysis more competitive even in its current technological stage, however reducing the amount of electricity required by the process is desirable as even renewables aren't infinite energy sources.

At the atomic scale, increased efficiency can be achieved by using more active and stable catalytic materials. To find the optimal catalyst for a process is not an easy task, and it requires fundamental understanding of the electrochemical reactions.

This module will go into more detail on the reaction mechanism, thermodynamics and kinetics of electrocatalytic water splitting, and introduce the main electrolyser technologies existing today.

Water Splitting

Overall reaction and some thermodynamics

One water molecule contains two hydrogen atoms and one oxygen atom. Therefore the balanced water splitting reaction is

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H_2} + \frac{1}{2}\mathrm{O_2} \tag{27}$$

The reaction is endothermic at room temperature, and the standard Gibbs energy change is +237 kJ /mol. This means that at least 237 kJ /mol of energy must be provided to the system as work. Using the formula

$$\Delta_r G^\circ = -nF\phi^\circ_{cell} \tag{28}$$

and the fact that each mole of products in this case requires the transfer of 2 moles of electrons, the theoretical minimum cell potential required is

$$phi^\circ_{cell} = \frac{\Delta_r G^\circ}{-nF} = \frac{237000\text{J/mol}}{-2\text{mol} \cdot 96485\text{C}} = -1.23\text{V}$$

The Gibbs energy change of the reaction is less positive at higher temperatures due to the positive entropy change of the reaction, which means the portion of energy that must be supplied to the reaction as work is smaller at high temperatures. As heat is (usually) cheaper than electricity, it can be more economical to operate at higher temperatures to lower the electricity demand of electrolysis. High-temperature electrolysis (HTE) takes advantage of this. Temperature of over a few thousand Celsius is required for pure thermochemical splitting (thermolysis) of water.

Half reactions

The water electrolysis redox reaction can be divided into two half-reactions: the hydrogen evolution (HER) and oxygen evolution (OER) reaction. Hydrogen evolution is a reduction reaction, and therefore takes place at the cathode, whereas oxygen evolution is an oxidation reaction and takes place at the anode.

The form of the water splitting half-reactions depend on the pH.

In alkaline media (high pH) the half-reactions are

$2\text{H}_2\text{O}(l) + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(aq) + \text{H}_2(g)$ (HER)
$4\text{OH}^-(aq) \rightleftharpoons \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4\text{e}^-$ (OER)

and in acidic media (low pH) the half-reactions are

$\text{H}^+(aq) + 2\text{e}^- \rightleftharpoons \text{H}_2(g)$ (HER)
$2\text{H}_2\text{O}(l) \rightleftharpoons 4\text{H}^+(aq) + \text{O}_2(g) + 4\text{e}^-$ (OER)

The labels $(aq), (l)$ and (g) indicate the physical state of the species and stand for aqueous, liquid, and gaseous, respectively. Note that $\text{H}^+(aq)$ is a solvated proton, which in water exists in the form of a hydronium ion, H_3O^+.

In general, HER is much faster than OER, making OER the bottle neck of the overall redox process. No matter how much faster you make HER, if OER remains unchanged, then the overall reaction will not be faster either. HER is simpler, and can be sometimes thought of as the "main" reaction since it

gives the desired product. However, as HER and OER are a package deal, both reactions must work equally well for efficient water splitting.

Q Under acidic conditions, which of the options below is the correct equilibrium constant for the water electrolysis half-reaction occurring on the cathode side?

Note: a_i and p_i are the activity and partial pressure of species i, and p^0 is the standard pressure (1 bar).

1. $\frac{p_{\mathrm{H_2}}/p^0}{a^2_{\mathrm{H^+}}}$
2. $\frac{p_{\mathrm{H_2}}}{a_{\mathrm{H^+}}}$
3. $\frac{p_{\mathrm{H_2}}}{a_{\mathrm{H^+}}}$

HER Mechanism

HER is the cathodic reaction, and has been studied more widely than OER. The balanced half-reaction for HER changes depending on the acidity or basicity of the surrounding solution, and so does the form of the reaction mechanism.

In both basic and acidic media, the generally accepted HER mechanism comprises 2-3 steps:

- adsorption on the electrode (Volmer)
- chemical desorption (Tafel)
- and/or electrochemical desorption (Heyrovsky)

HER under acidic conditions

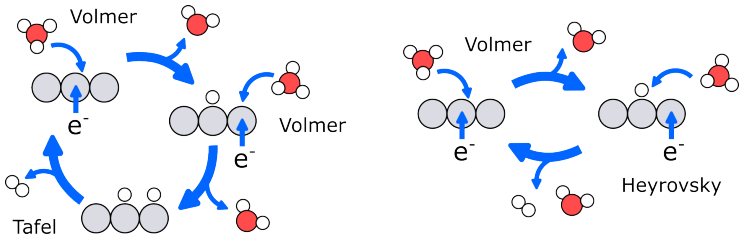
$$
\begin{aligned}
&(1) \quad \mathrm{H^+}(aq) + * + \mathrm{e^-} \rightleftharpoons \mathrm{H_{ads}} \\
&(2) \quad \mathrm{H_{ads}} + \mathrm{H_{ads}} \rightleftharpoons 2* + \mathrm{H_2}(g) \\
&(3) \quad \mathrm{H_{ads}} + \mathrm{H^+}(aq) + \mathrm{e^-} \rightleftharpoons * + \mathrm{H_2}(g)
\end{aligned}
$$

HER under basic conditions

$$
\begin{aligned}
&(1) \quad \mathrm{H_2O}(l) + * + \mathrm{e^-} \rightleftharpoons \mathrm{H_{ads}} + \mathrm{OH^-}(aq) \\
&(2) \quad \mathrm{H_{ads}} + \mathrm{H_{ads}} \rightleftharpoons 2* + \mathrm{H_2}(g) \\
&(3) \quad \mathrm{H_{ads}} + \mathrm{H_2O}(l) + \mathrm{e^-} \rightleftharpoons * + \mathrm{H_2}(g) + \mathrm{OH^-}(aq)
\end{aligned}
$$

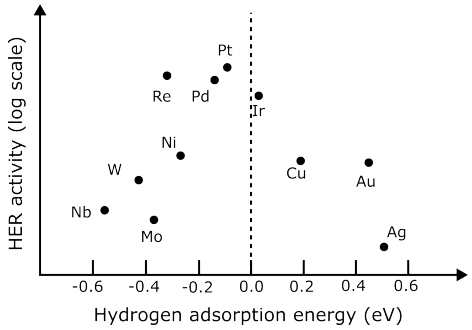
The Volmer-Tafel mechanism (left scheme below) involves two Volmer steps followed by a Tafel step where two adsorbed hydrogen atoms react together and desorb. The Volmer-Heyrovsky (right scheme below) mechanism has only

one Volmer step, followed by Heyrovsky reaction were the adsorbed hydrogen reacts with the proton donor and the formed hydrogen molecule desorbs. Note that the schemes below depict the reaction mechanism under acidic conditions.



Regardless of the basicity/acidity, the HER is a two electron process. Note how the from of purely chemical Tafel reaction is the same under both conditions. The alkaline HER is much slower (over 100 times) than the acidic HER. In acidic media the proton donor is a hydronium ion (H_3O^+), whereas in alkaline media the proton comes from a water molecule. The hydronium ion is a much better proton donor than water, which is suggested to be the main reason for the faster reaction under acidic conditions.

The first step in the reaction mechanism is the Volmer adsorption step, which is commonly proposed to be the rate-determining step (RDS). Hydrogen is the most important surface intermediate, hence the hydrogen adsorption energy is commonly used as an activity descriptor for acidic HER catalysts. This means that it would be possible to predict the activity of a new material towards HER by only calculating the hydrogen adsorption energy for that material. When measured HER activities of known materials are plotted against hydrogen adsorption energy calculated using computational methods, one obtains a volcano-like relationship (below). The top of the volcano represents the highest



activity. The optimal adsorption energy corresponding to the top of the volcano is predicted to be nearly thermoneutral for HER. Platinum is considered the most active (acid) HER catalyst, as it appears at the top of the volcano i.e.

has a nearly optimal hydrogen adsorption energy. However, these types of simple volcano-like relationships between a calculated hydrogen adsorption energies and experimentally measured HER activity/exchange current do not represent the whole picture. The are issues with the accuracy of activity measurements, influence of hydrogen coverage on the adsorption energies, and the nature of the catalyst under reaction conditions which the plots do not account for.

Note: Data for HER volcano plot obtained from:

Nørskov, J. K., Bligaard, T., Logadottir, A., Kitchin, J. R., Chen, J. G., Pandelov, S., Stimming, U. (2005). Trends in the exchange current for Hydrogen Evolution. Journal of The Electrochemical Society, 152(3). https://doi.org/10.1149/1.1856988

OER Mechanism

OER is the anodic reaction, and is more complex and kinetically demanding than the HER. This is partly due to OER being a four electron process compared to the two electron HER. A process cannot occur faster than its slowest step, therefore the slower OER half-reaction determines the overall efficiency of water splitting.

There are numerous proposed reaction mechanisms for OER. Below are examples of mechanisms for the reaction in acidic and basic media which include steps that are generally thought to occur.

OER under acidic conditions

$$
\begin{aligned}
&(1) \quad \mathrm{H_2O}(l) + * \rightleftharpoons \mathrm{OH_{ads}} + \mathrm{e^-} + \mathrm{H^+}(aq) \\
&(2) \quad \mathrm{OH_{ads}} \rightleftharpoons \mathrm{O_{ads}} + \mathrm{e^-} + \mathrm{H^+}(aq) \\
&(3) \quad \mathrm{O_{ads}} + \mathrm{O_{ads}} \rightleftharpoons 2* + \mathrm{O_2}(g) \\
&(4) \quad \mathrm{O_{ads}} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OOH_{ads}} + \mathrm{H^+}(aq) + \mathrm{e^-} \\
&(5) \quad \mathrm{OOH_{ads}} + \mathrm{H_2O}(l) \rightleftharpoons * + \mathrm{O_2}(g) + \mathrm{H^+}(aq) + \mathrm{e^-}
\end{aligned}
$$

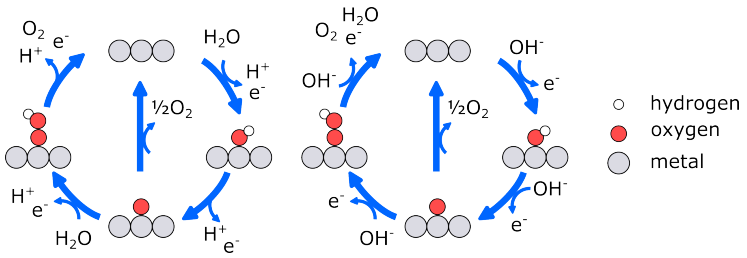
OER under basic conditions

$$
\begin{aligned}
&(1) \quad \mathrm{OH^-}(aq) + * \rightleftharpoons \mathrm{OH_{ads}} + \mathrm{e^-} \\
&(2) \quad \mathrm{OH_{ads}} + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{O_{ads}} + \mathrm{H_2O}(l) + \mathrm{e^-} \\
&(3) \quad \mathrm{O_{ads}} + \mathrm{O_{ads}} \rightleftharpoons 2* + \mathrm{O_2}(g) \\
&(4) \quad \mathrm{O_{ads}} + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{OOH_{ads}} + \mathrm{e^-} \\
&(5) \quad \mathrm{OOH_{ads}} + \mathrm{OH^-}(aq) \rightleftharpoons * + \mathrm{O_2}(g) + \mathrm{H_2O}(l) + \mathrm{e^-}
\end{aligned}
$$

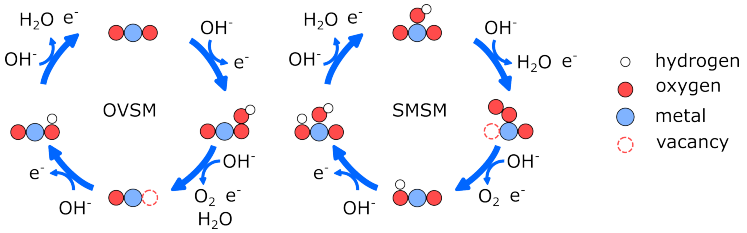
The reaction mechanism generally involves multiple proton-coupled electron transfers (PCET) to the electrode, the generation of $\mathrm{OH_{ads}}$ and $\mathrm{O_{ads}}$ inter-

mediates, and $O_2(g)$ production via chemical desorption or alternatively electrochemical desorption through OOH_{ads} intermediate.

The generic adsorption site ('*') can be a metal center on the metal surface, with the reaction mechanisms classified as adsorbate evolution mechanisms (AEM). These are analogous to the Langmuir-Hinshelwood or Eley-Rideal type mechanisms found in thermocatalysis. Proposed AEM mechanism under acidic (left) and alkaline (right) conditions are presented below:



However, some of the best OER electrode materials are metal oxides and perovskites. There the active site can be an oxygen vacancy (i.e. missing lattice oxygen), and the reaction is thought to occur through the lattice oxygen mediated (LOM) mechanism, which is Mars-van-Krevelen-like. Two proposed alkaline LOM mechanisms are shown schematically below:



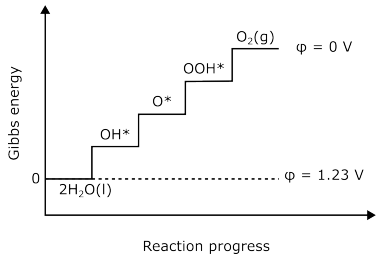
In the oxygen vacancy-site mechanism (OVSM) the oxygen vacancy acts as an active site. It is created by the release of an O_2 molecule, and filled by an OH^- species. In the single metal-site mechanism (SMSM), the active site is a metal cation, and the oxygen vacancy is formed by surface reconstruction.

An ideal OER catalyst would be able to facilitate the reaction near the equilibrium potential (1.23 V), however no such catalyst was been discovered. The thermodynamic criterion is that all elementary steps in the reaction mechanism should have a reaction free energy of zero at the equilibrium potential (dashed line in the Gibbs energy diagram). An ideal catalyst would stabilise all surface species in such a way that the reaction free energies of all steps are of equal magnitude at zero potential (solid line in the Gibbs energy diagram). However, because the adsorption energies of surface species are not usually independent of each other, this kind of reaction energy landscape is extremely difficult to achieve.

What do we do with the oxygen?

Using the water splitting reaction for hydrogen production is a great improvement compared to fossil fuel based reactions already based on the stoichiometry of the reaction. Since water is a completely carbon free reactant, there is no inherent source of CO_2.

However, if atom economy is considered, water splitting may or may not be regarded as an optimal reaction. Atom economy is a measure of how efficient



the reaction is in terms of how many atoms of the reactant are present in the desired product as opposed to being lost as part of unwanted side products. It is calculated as:

$$\text{atom economy} = \frac{\text{molecular weight of desired product}}{\text{sum of molecular weights of all products}} \times 100\%$$

For every 2 moles of hydrogen, 1 mole of oxygen is always formed, meaning that large scale production of hydrogen from water electrolysis leads to large scale production of oxygen too. Currently the oxygen gas produced by electrolysis is not considered a desired product, and is usually vented into the atmosphere. This corresponds to an atom economy of only 11%, which is severely sub-optimal!

In principle, oxygen is a valuable substance especially if it is very pure. Currently, highly pure oxygen is made by separating it from air by cryogenic distillation or vacuum swing adsorption. Oxygen is used in medical care, glass making, waste water treatment, and in various combustion and gasification processes, to name a few. Electrolysis side stream oxygen could potentially be used in these applications, which would improve the overall atom economy of the process. Synergistic systems that couple water electrolysis to other reactions, such as partial oxidation methane, could simultaneously utilize the byproduct oxygen and provide heat to electrolysis. Another strategy would be to operate a different oxidation reaction at the anode, producing a more valuable fuel/platfrom chemical such as methanol. This would require a carbon containing molecule, such as CO_2, in addition to water as a feedstock.

Further reading:

Kato, T., Kubota, M., Kobayashi, N., & Suzuoki, Y. (2005). Effective utilization of by-product oxygen from electrolysis hydrogen production. Energy, 30(14), 2580–2595.
DOI: 10.1016/j.energy.2004.07.004

Mohammadpour, H., Cord-Ruwisch, R., Pivrikas, A., & Ho, G. (2021). Utilisation of oxygen from water electrolysis – assessment for wastewater treatment and Aquaculture. Chemical Engineering Science, 246, 117008.
DOI: 10.1016/j.ces.2021.117008

Kinetics of Water Electrolysis

Electrolyser Performance

In order to replace fossil fuel based hydrogen production methods with water electrolysis, the overall performance of electrolysers must be improved.

An ideal electrolyser

- produces large quantities of high purity H_2
- consumes little electricity
- uses cheap and abundant materials
- uses environmentally friendly and conflict free materials
- has a long lifetime
- has unproblematic end of life management

All of these qualities are affected by atomic level properties and phenomena.

The performance of an electrolysis cell can be quantified using several parameters, for example:

- Faradaic efficiency: how efficiently electrons from external circuit are used in the electrochemical reactions. Ratio of the experimentally detected quantity of H_2 or O_2 to the theoretically calculated quantity of H_2 or O_2
- Turnover frequency (TOF): how many reactants are converted to the desired product per catalytic site per unit time
- Chronoamperometry (I–t curve) or chronopotentiometry (E–t curve): how the current varies with time under a fixed potential / potential change with time at a fixed current. Measures stability, the longer the current/potential stays unchanged, the better the stability
- Cyclic voltammetry (CV): applied potential is cycled (typically ca 5000 cycles) and current is measured. The smaller the change, the better the stability.
- Voltage efficiency: ratio between thermodynamic potential difference and potential difference required to drive the reaction in practice. Expressed as a percentage

These are macroscopic properties, however they are resultant of microscopic processes such as electron/proton transfer, movements of charge carriers, surface reactions, diffusions, tunneling etc.

Q In a cyclic voltammetry (CV) experiment, the applied potential is cycled and current is measured. The change in the current between different cycles is a measure of the _____ of the electrolysis cell.

1. stabilility

2. efficiency

Current and reaction rate

One of the main observables in electrolysis is the current, which can be measured using an ammeter. The measured current is the basis for many of the methods that evaluate the performance of electrochemical systems, because it is directly related to the reaction rate.

Half-reactions at electrode surfaces occur both forwards and backwards, leading to current flowing in two directions. Consider the generic half-reaction at an electrode:

$$Ox + ze^{-1} \rightleftharpoons Red \tag{29}$$

In the backwards reaction, electrons are transferred from the electrolyte to the electrode (oxidative current, i_{OX}) and in the forward reaction from the electrode to the electrolyte (reductive current, i_{RED}). The total current through the electrode surface is the difference of the oxidative and reductive currents:

$$i = i_{OX} - i_{RED} \tag{30}$$

As the current is the amount of electrons transferred through a surface per unit time, the current is written in terms of the rates of the reactions as

$$\frac{i}{nF} = r_{OX} - r_{RED} \tag{31}$$

The reaction rates of electrochemical reactions can be directly observed by measuring the current in the external circuit.

The rates of the reduction and oxidation reactions occurring at the same electrode can be expressed as functions of the surface coverages (c_i^s) and rate constants (k_i):

Reduction:

$$r_{RED} = k_{RED}(\phi)c_{OX}^s \tag{32}$$

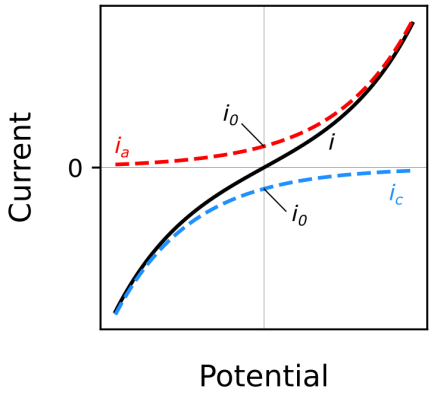
Oxidation:

$$r_{OX} = k_{OX}(\phi)c_{RED}^s \tag{33}$$

Note that the rate constants do not depend only on the free energy of activation and temperature, but also on the potential ϕ.

Exchange current

At equilibrium, the rate in the forward direction (r_{RED}) is equal to the rate in the backward direction (r_{OX}), and the net rate is zero. This means that the net current i through the working electrode is also zero. However, this is a dynamic equilibrium i.e. at microscopic level the reaction is still taking place in both directions. The oxidation/anodic (i_a) and reduction/cathodic (i_c) currents balance each other but are not zero. The current in either direction when the net current is zero is the exchange current (i_o).



Of course, only the net current can be experimentally measured. This means that the exchange current cannot be directly measured, as there is no net current to measure by definition. In practice, the exchange current is obtained from Tafel analysis, which will be introduced later.

The current is the flow of charge carriers through the entire material, i.e. it depends on the size of the electrode. However, for electrolysis applications it is important to compare the flow in more absolute terms. Dividing the current by the area of the electrode (or area of electrocatalyst) yields the current density (j), which has units of A/m^2. The exchange current density (j_0) is essentially the intrinsic rate of a redox reaction at an electrode at equilibrium, and is a measure of the electrocatalyst performance.

Overpotential

The equilibrium potential for the water splitting reaction at atmospheric pressure and room temperature is 1.23 V. However, in reality a much higher applied potential is required to experimentally observe a current, i.e. the onset of the water splitting reaction. The overpotential, (η), is the difference between the applied potential (ϕ) required to achieve a given current density, and the equilibrium potential (ϕ_{eq}).

$$\eta = \phi - \phi_{eq} \tag{34}$$

The bigger the overpotential, the more extra electric work is supplied to the system. The overpotential is a sum of different effects such electrolyte resistance, activation barriers of the redox reactions, electronic resistance of electrodes, and concentration loss or mass transfer limitations.

The role of the catalyst in electrocatalysis is to lower the contribution of the activation barriers to the overpotential, although how exactly the catalyst modifies the barriers is not always well understood. Nevertheless, overpotential is a useful parameter for comparing the activity of different electrocatalysts. To make a direct comparison possible, the current density for which the overpotential is reported must be specified, often it is chosen as 10 mA cm^{-1}.

The overpotential of the water splitting reaction can be reduced by lowering the activation barriers of the HER and OER reactions, particularly OER which tends to have larger barriers. An ideal electrocatalyst for HER/OER would minimize the cathodic/anodic overpotential so that a smaller applied potential can be used to achieve high reaction rates.

Q For efficient electrolysis, the overpotential of HER/OER should be made as low as possible.

1. True
2. False

Butler-Volmer model

The Butler-Volmer model is the most widely used model for electrochemical reaction rates. It describes how the measured current density depends on the applied potential for simple electrochemical reactions. Different formulations of the Butler-Volmer equation exist, and it can be derived by empirical methods or based on quantum mechanics.

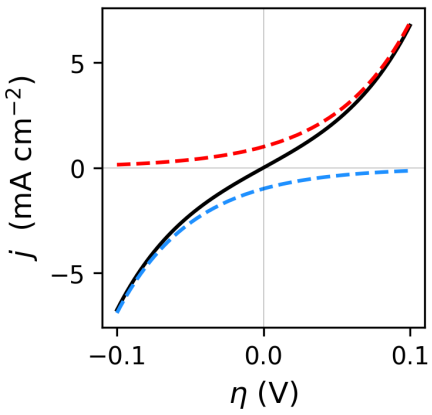
In the case that the reaction is not limited by mass transfer, i.e. the concentrations at the electrode are practically equal to the concentrations in the bulk electrolyte, the Butler-Volmer equation has the form:

$$j = j_0[e^{\frac{(1-\alpha)\eta z F}{RT}} - e^{\frac{-\alpha\eta z F}{RT}}] \tag{35}$$

where j and j_0 are the current density and the exchange current density, α is the dimensionless charge transfer coefficient, and z is the number of electrons transferred during the reaction. F, R, and T are the Faraday constant, gas constant, and absolute temperature, respectively.

The first exponential term in the brackets belongs to the anodic reaction, and the second term to the cathodic reaction. Using the given B-V expression, and

$j_0 = 1$ mA cm^{-2}, $\alpha = 0.5$, $T = 300$, the current density vs overpotential curve looks like



The red curve corresponds to the anodic reaction and the blue curve to the cathodic reaction. The black curve is the total current density.

Note how the total current density is zero at zero overpotential, but the anodic and cathodic currents have the absolute value equal to the exchange current density. At more negative (positive) values of the overpotential, the cathodic (anodic) reaction starts to dominate the overall current density.

Increasing the applied overpotential increases the total rate of the reaction, however it also leads to a larger energy consumption. It is desirable to obtain a faster increase in the reaction rate with a small change in overpotential.

Tafel equation and analysis

The Tafel equation relates the rate of an electrochemical reaction, expressed as a current density, to the applied overpotential at highly anodic (oxidative) or cathodic (reductive) overpotentials. Originally, the Tafel relation was found empirically, but it can also be derived from the Butler-Volmer equation.

At highly negative (positive) overpotentials the current density is dominated by the cathodic (anodic) reaction, and the Butler-Volmer equation reduces to the Tafel equation.

For one half-reaction on a single electrode the Tafel equation has the linear form:

$\eta = a + b \log j$

where η is the overpotential and j is the current density, and a and b are empirical constants. The constant b is the slope of a plot of η vs $\log j$, also known as the Tafel slope, and a is the intercept. The Tafel slope is usually

reported in the units of millivolts per decade (mV dec^{-1}). A "decade" is a ten fold increase or decrease in the current density, e.g. from 0.1 to 1 mA cm^{-2}.

In the ideal case, the Tafel slope can provide information on the reaction mechanism, while the intercept can be used to obtain the exchange current density, which is a measure of the activity. A low Tafel slope indicates that a small increase in overpotential leads to a large increase in current density. A high exchange current density indicates fast intrinsic charge transfer rate.

Experimentally obtained Tafel plots can be compared to those obtained from theoretical kinetic models. Used in this way, Tafel analysis is a valuable tool for assessing the activity of electrocatalysts and evaluating possible reaction mechanisms. Experimentally, a better electrocatalyst can, in principle, be identified by a low Tafel slope and large exchange current density. In turn, simulated Tafel plots could be used to predict catalytic performance of new materials.

Electrolysis cells

Existing Technologies

Four main types of electrolysis cells exist today:

- alkaline
- proton exchange membrane (PEM)
- anion exchange membrane (AEM)
- solid oxide (SOEC)

The technologies differ greatly in maturity and cost, as well as operating conditions and materials used. Alkaline electrolysis and PEM cells are considered mature and are commercially available, while AEM and SOEC are in early research and development stages. Typical features of the four technologies are summarized in the table below. The key differing feature is the electrolyte, as

	PEM	Alkaline	AEM	SOEC
operating temperature	50-80 °C	70-90 °C	40-60 °C	700-850 °C
operating pressure	<70 bar	1-30 bar	<35 bar	1 bar
electrolyte	PFSA-membrane	KOH, NaOH (5-7 M)	polymeric membrane, KOH, $NaHCO_3$	YSZ
separator	solid electrolyte	diaphragm (Zirfon)	solid electrolyte	solid electrolyte
anode material	IrO_2	Ni plated steel	Ni or NiFeCo	Perovskite
cathode material	Carbon supported Pt	Ni plated steel	Ni	YSZ supported Ni

it determines the pH, the need for a separator, and which electrode materials

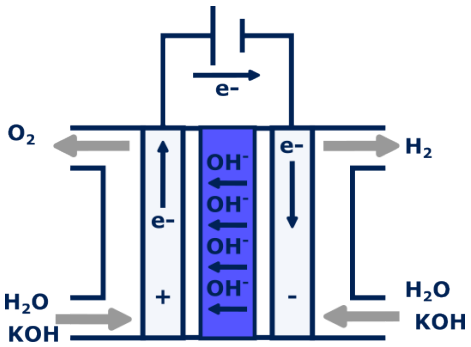
can be used. The function of the electrolyte is to conduct ions between the electrodes while simultaneously keeping the product gases separate and allowing no electron flow in order to prevent short circuiting.

Q Based on only the typical operating temperatures and the thermodynamics of the water electrolysis reaction, which of the technologies requires the least electricity for operation?

1. Solid oxide electrolysis
2. Proton exchange electrolysis
3. Alkaline electrolysis
4. Anion exchange membrane electrolysis

Liquid alkaline cells

Alkaline (AEL) cells are the most mature water electrolysis technology available. In an AEL cell (see schematic below), the electrodes are suspended in the liquid electrolyte (white areas in schematic) and are separated by a thin diaphragm (blue area in schematic). In modern 'zero gap' configurations the electrodes are in direct contact with the diaphragm in order to minimize Ohmic resistance. The diaphragm is an open mesh polyphenylene sulfide fabric that is coated



with a mixture of a polymer and zirconium oxide. The state-of-the-art material is marketed under the name Zirfon, which was originally developed as a replacement for Asbestos. The role of the diaphragm is to allow water and OH- ions to diffuse through its pores, while keeping the product gases separated.

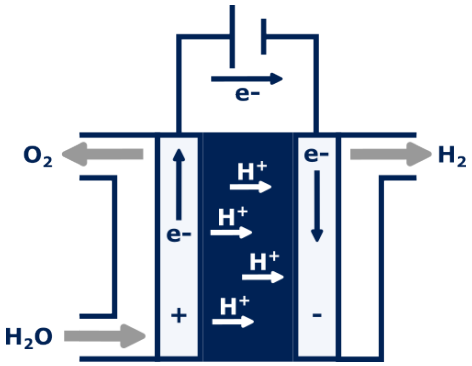
One drawback of using a liquid electrolyte with a diaphragm is the possibility of gas cross-over. Gas crossover is a phenomenon where some product gas, especially hydrogen, can be dissolved and carried through the diaphragm by the electrolyte. Crossover mainly occurs due to differential pressure by convective transport in the pores of the diaphragm. This not only may reduced the Faradaic efficiency and product purity, but is a serious safety concern as mixtures of oxygen and hydrogen can be explosive. This leads to the requirement of low operational pressures for AEL cells.

The most-used electrode material is nickel on both anode and cathode side, however other electrocatalytic materials such as iron and molybdenum are added to lower the high overpotentials of the OER and HER, respectively. As there is no need to use precious metals, the cost of AEL cells is much lower than PEM cells, which use noble metal electrocatalysts.

A strongly alkaline solution of 5 M KOH (or NaOH) is used as the liquid electrolyte, which is continuously supplied to the cell. The product gases and electrolyte must be separated after they exit the cell. The operational temperature is between 70 and 90 °C which increases ionic conductivity. High KOH concentration results in better ionic conductivity and lower product gas solvation, however one disadvantage is that it is highly corrosive.

PEM cells

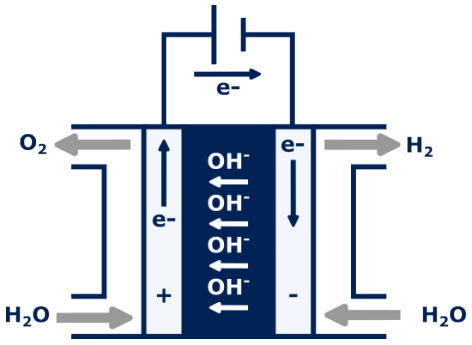
In a proton exchange membrane (PEM) cell, there is no liquid electrolyte, and electrodes are instead separated by a membrane material which permits protons to move from the anode to the cathode, but prevents mixing of the product gases. Compared to the AEL cell, a PEM cell can operate at higher current



densities and pressures. This is due to using a membrane instead of a liquid electrolyte and diaphragm. Overall, the performance of the PEM cell is superior to the AEL cell and the operational costs are lower. However, due to the acidic conditions, it is not possible to use cheap Earth abundant electrode materials, which drives up the capital cost of PEM cells.

Platinum is used on the cathode side to catalyse the HER reaction, as it is the most active and stable HER catalyst under acidic conditions. Replacing platinum with a cheaper material, or lowering the amount of platinum required is crucial for lowering the cost of PEM cells. Novel strategies include use of monolayer thin Pt coatings on other metals, miniaturization of the Pt particles all the way into single-atoms, or mimicking Pt electronic structure using binary metal alloys.

Most OER catalysts perform much better in alkaline solutions than in acids.



In addition, the existing catalysts are susceptible to degradation in acidic conditions. Currently, the only suitable OER catalyst for PEM cells are iridium based materials, such as IrO_2. The drawback is that iridium is very rare and even more expensive than platinum, therefore the search for cheaper acidic OER catalyst alternatives continues.

AEM cells

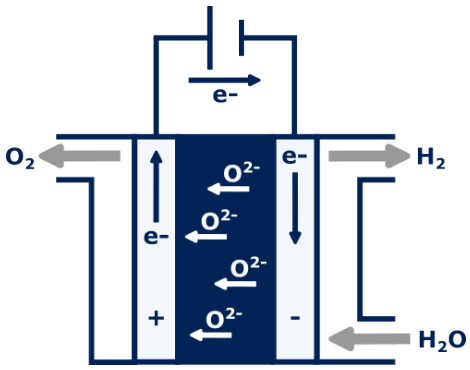
Anion exchange membrane (AEM) cells aim to combine the benefits of AEL and PEM electrolysers by utilizing a solid membrane (dark blue area in schematic below) instead of liquid electrolyte, while avoiding the use of rare metals. In principle, the membrane should be ionically conductive, allowing for OH- to move from cathode to anode within the solid material, which removes the need for a liquid electrolyte. However, dilute KOH is still used, because existing non-precious electrocatalysts pefrom poorly under neutral conditions . While still an improvement compared to the high concentration KOH used by AEL cells, the aim is to only use pure water. More research is needed to identify efficient neutral condition OER/HER electrocatalysts .

The biggest challenge in the development of commercially viable AEM cells is the stability and ionic conductivity of the anion exchange membrane itself. For commercial usage, the membrane should exhibit high ionic conductivity (¿ 0.1 S/cm according to an estimate), and be stable enough to operate for thousands of hours in oxidizing and alkaline conditions with high current density and temperatures over 60 °C. The currently used membranes are anion-exchange polymers, which have polymeric backbones with cationic head groups. The OH ions can attack cations in the membrane, which leads to chemical degradation of the cationic head-groups.

SOEC

The solid oxide electrolysis cell consists of a solid electrolyte, typically yttria-stabilized zirconia (YSZ), and porous cathode (typically YSZ supported Nickel) and anode (typically perovskite). The water is fed to the cathode as steam, which reacts to form hydrogen gas and oxygen anions. The oxygen anions are

transported through the electrolyte to the anode to form oxygen gas. The electrodes are porous so that the gases formed at the electrode-electrolyte interface can be transported to the electrode surface. The electrolyte material



must:

- be chemically and thermally stable
- have high ionic conductivity but low electronic conductivity
- must be non-permeable to gaseous H_2 and O_2 even in thin layers, in order to minimize the recombination and ohmic losses
- be low cost

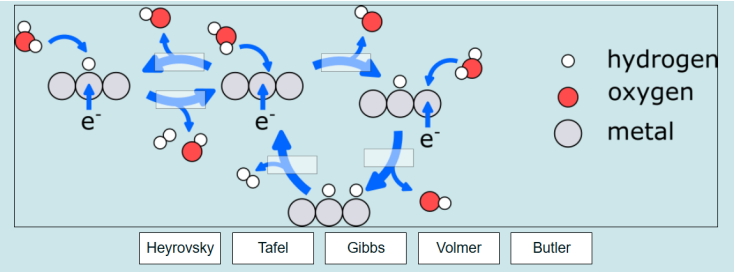
Zirconium oxide is a material with high thermal and chemical stability, however it exists in several different polymorphs ad can undergo phase change from one structure to another when temperature is varied. This can be prevented by doping the zirconia with alkaline or rare earth metals, where the dopant atom (such as yttrium) takes the place of a zirconium atom in the tetragonal or cubic crystal lattice. This stabilizes the doped zirconia against phase transformation, and also increases oxygen ion conductivity by increasing the number of oxygen vacancies in the lattice.

Compared to the other electrolysis cell technologies, the SOEC operating temperature is much higher, which enables high water splitting reaction rate and reduces the electrical energy consumption. The reduction in electrical energy consumption at higher temperatures is a consequence of the thermodynamics of the water splitting reaction.

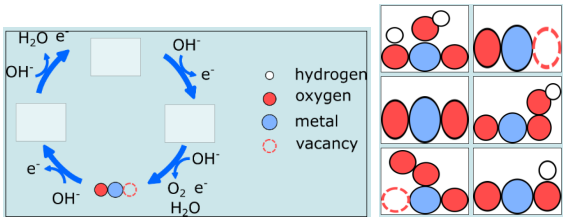
One caveat of higher operation temperature is that cell components must be thermally stable, which limits the selection of materials. Operating SOEC at more moderate temperatures would improve long-term stability of the cell and increase the range of suitable materials. However, lower temperatures also lead to lower ion conductivity in the solid oxide electrolyte. One strategy to improve ion conductivity is by co-doping the electrolyte material with other oxides.

Electrocatalytic Hydrogen Quiz

1. Write the names of the elementary steps to the correct arrows in the hydrogen evolution reaction mechanism diagram.

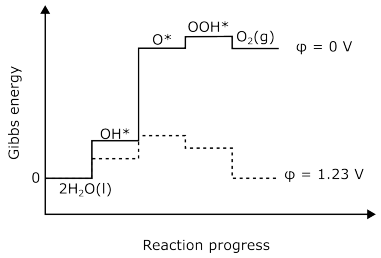


2. Is the mechanism presented in the previous question for HER under basic or acidic conditions?
   (a) Acidic
   (b) Basic
3. The Volmer step is commonly thought to be the rate determining step of the alkaline HER reaction
   (a) True
   (b) False
4. Oxygen evolution reaction is a four electron process.
   (a) True
   (b) False
5. Complete the schematic reaction mechanism for OER by placing the appropriate icons on to the schematic.



6. The reaction mechanism is question 5 is an example of
   (a) lattice oxygen mediated mechanism
   (b) adsorbate evolution mechanism

7. In the Gibbs energy diagram below, the reaction profile for OER in the presence of some catalyst is shown as a solid line with no applied potential, and with a dashed line at OER equilibrium potential. Is the catalyst optimal from the thermodynamic perspective?



   (a) No, because some of the steps are still thermodynamically uphill at the equilibrium potential.

   (b) Yes, because the overall Gibbs energy change is 0 at the equilibrium potential.

   (c) No, because the Gibbs energy change of the reaction is thermodynamically uphill at zero potential.

   (d) Yes, because all of the Gibbs energies of the individual reaction steps are much lower at the equilibrium potential.

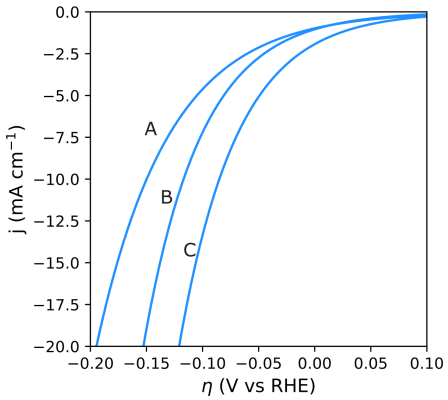
8. Match the electrolyte material with the appropriate electrolysis cell technology.

(a) Anion exchange membrane cell	A perfluorosulfonic acid
(b) Liquid alkaline cell	B Yttrium stabilised zirconia
(c) Proton exchange membrane cell	C 5 M potassium hydroxide
(d) Solid oxide electrolysis cell	D dilute potassium hydroxide

9. Complete the following text by filling in appropriate missing words:

   Electrolytic water _____ is a redox reaction that can be divided into _____ reactions: the _____ (HER) reaction and the _____ (OER) reaction. HER takes place at the _____ , whereas the OER takes place at the _____. HER is typically much _____ than OER, making _____ the kinetic bottle neck of the overall reaction.

10. The steady state current densities versus applied overpotentials were measured for electrodes with catalyst samples A, B, and C. Based on the polarization curves below, which of the electrodes requires the smallest overpotential to reach a current density of -10 mA cm^{-1}?



A

B

C

11. The polarization curves in question 10 correspond to:

    (a) an anodic (reduction) process

    (b) an anodic (oxidation) process

    (c) a cathodic (reduction) process

    (d) a cathodic (oxidation) process

12. Based on the polarisation curves in question 10, what can be said about the intrinsic activities of the catalysts?

    (a) Catalyst A is the most active

    (b) Catalyst B is the most active

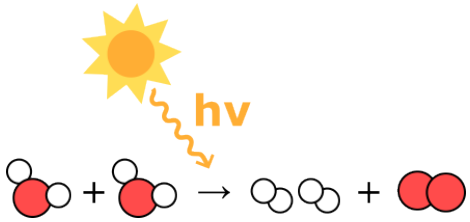
    (c) Catalyst C is the most active

    (d) More information is required

Solar Hydrogen Production

Solar energy for hydrogen production

Solar-to-hydrogen systems utilize sunlight to produce hydrogen. There are different ways to couple sunlight to a hydrogen production technology. In photo(electro)chemical systems light is used to directly produce charge carriers that take part in the desired water splitting reaction. Alternatively, solar energy can be used to produce heat, which can then be used to drive conventional thermocatalytic processes as usual. These types of methods will not be discussed further in this course.



Currently, none of the solar-driven hydrogen production technologies can operate on the industrial scale due to low efficiencies. It is clear that more research and development in this area is needed. Photo(electro)chemistry is a complicated subject, and atomic-level understanding is vital to achieve the required improvements.

Of course, one might ask if producing hydrogen with solar power is feasible in dark and northern Finland. Indeed, solar accounts for only 0.3 % of the electricity produced in Finland as of 2020.[1] However, the potential capacity is much more than that, and the low production during dark winters is partially compensated for by the longer days during Finnish summertime. Another reason to investigate solar to hydrogen technologies in Finland could be to facilitate the development of new products directed to international customers.

This module covers the atomic-level principles behind photochemical water split-

ting, such as electron and hole pair creation, semi conductors, and electron-hole migration. The main photochemical water-splitting technologies are also introduced. Finally, the challenges and outlook of the techniques are reviewed.

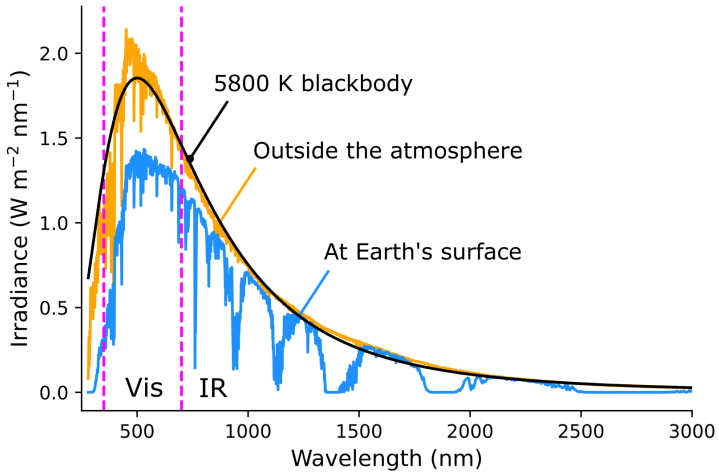
1. Suomen virallinen tilasto (SVT): Sähkön ja lämmön tuotanto [verkkojulkaisu]. ISSN=1798-5072. 2020. Helsinki: Tilastokeskus [viitattu: 5.4.2024]. Saantitapa: https://www.stat.fi/til/salatuo/2020/salatuo_2020_2021-11-02_tie_001_fi.html

Harvesting photons

Photons from the Sun

Sunlight is electromagnetic radiation from the sun, and it consists of photons of differing energies. The range of the electromagnetic radiation produced by the Sun is called the solar spectrum, which consists of ultraviolet (UV), visible, and infrared (IR).

The spectrum is quite well approximated by blackbody radiation corresponding to a temperature of ca 5800 K (black curve in the figure). However, the spectrum of sunlight at Earth's surface is somewhat different, due to absorption and scattering by atoms/molecules in the atmosphere:



At Earth's surface, the majority of incoming sunlight is IR (¿700 nm) and visible light (380 to 700 nm). The visible range corresponds to photon energies between 1.77 to 3.26 eV. As will be seen in the following sections, this sets some constraints on what kind of materials can be used in photocatalytic applications.

Link to original data used to plot irradiance(accessed: 12.6.2023)

Q The contribution to the energy of sunlight from UV light is very small because ...

1. ... UV light photons have less energy than IR or visible light photons
2. ... fewer UV light photons hit Earth than IR or visible light photons

Typical Photocatalytic Process

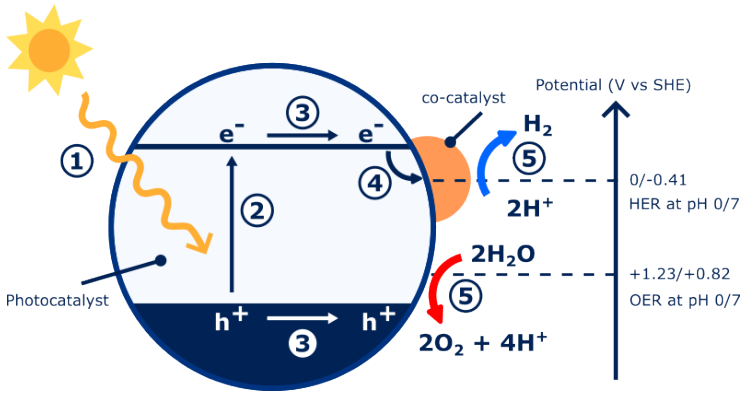
Photocatalysis is a phenomenon where light is used to facilitate a chemical reaction. Materials which facilitate this process are photocatalysts. Water splitting is a thermodynamically unfavorable reaction that can be driven by irradiation. The most simple photocatalyst for water splitting consists of particles of one semiconductor (SC) material, however the performance can be vastly improved by introducing a co-catalyst as nanoparticles on the SC surface.

The role of a co-catalyst can be to

- provide active sites for reduction/oxidation
- improve light absorption properties of SC
- promote charge separation and transport

Titanium dioxide (TiO_2) is one of the most extensively studied SC photocatalytic materials, while noble metals such as Pt and Au have gathered interest as co-catalysts.

A typical scheme for photocatalytic water splitting by a one-step photoexcitation system consists of 5 steps:



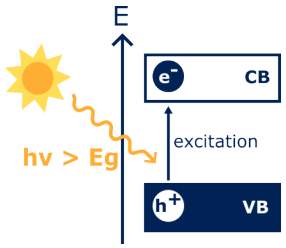
- Absorption of photon with appropriate energy by semiconductor (SC) particle
- Photoexcitation of electron, creation of electron-hole pair
- Charge separation and transport from SC bulk to surface
- Charge transfer from SC to co-catalyst
- Redox reaction with surface species

Q A photocatalyst is typically a

- conductor
- semiconductor
- insulator

Electron-hole pair formation

Regardless of the specific type of solar-to-hydrogen technology, the first and most critical step is the absorption of light and formation of charge carriers by a light absorber material. In this process, an incoming photon is absorbed, which causes an electron to be promoted from the valence band (VB) to the conduction band (CB). An electron vacancy, or hole, is left behind in the valence band. The hole is a positively charged quasiparticle which acts as a charge carrier in the valence band.



For the photon absorption process to take place successfully, the energy difference (E_g) between the valence band and conduction band (band gap), must be smaller than the energy of the incoming photon ($h\nu$).

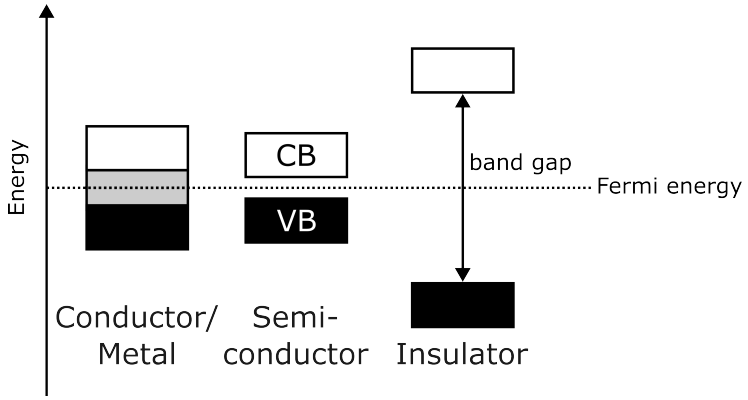
The electron and hole can migrate to the surface of the material to react with some molecule (photochemical reaction). Alternatively, in photovoltaic cells the creation and separation of the charge carriers leads to a potential difference, which can be used to do electric work (photovoltaic effect).

Semiconductors as light absorbers

The light absorbing materials used in solar hydrogen production are semiconductors. In a solid material, the atomic orbitals of adjacent atoms overlap forming bonding and anti-bonding energy levels, and because the number of atoms is very large (ie bulk material) the discrete electron energy levels combine into (nearly) continuous bands of allowed energies.

An energy band may be filled or partially filled by electrons, or empty. In many materials there is an energy gap (band gap), between the highest energy filled band (valence band) and the lowest energy unfilled band (conduction band). Empty and filled bands do not contribute to electrical current, so these materials are either electrical insulators or semiconductors. Semiconductors differ from

insulators in that the band gap is small enough (¡4 eV) for there to be thermal excitation of electrons from the VB to the CB, which enables current to flow. In



order for light absorption and charge carrier creation to occur under sunlight, the band gap of a semiconductor must be smaller than energy of the incoming light. To drive the water splitting reaction, the energy must also greater than the standard potential of the reaction, meaning that the theoretical minimum band gap is 1.23 eV. In practice, the required energy is even higher (ca 2 eV) due to e.g. the overpotentials of HER and OER. In addition to the size of the band gap, the CB (VB) edge potential must be positioned above (below) the standard potential of the HER (OER) half-reaction.

Charge carrier separation and recombination

Once the electron-hole pair is formed, the charges can separate and move in the material, take part in reactions, or recombine. Recombination can occur both in the bulk and on the surface, and it is not desirable as it produces heat/light and doesn't contribute to the desired photochemical reaction. Reducing the recombination of the charge carriers is vital for improving the water splitting performance of photocatalytic systems.

Spatial separation of the charge carriers reduces the possibility of a recombination event, however on a photocatalyst the oxidation and reduction sites may be separated by only nanometer scale distances. Charge separation can also be promoted by selective transport of electrons and holes towards the reductive and oxidative surface sites, respectively. In a semiconductor particle this process may be driven by asymmetric energetics, e.g. the presence of an internal electric field in the material which causes the drift of charge carriers. The charge carriers may also be transported by diffusion, which is driven by a concentration gradient of charge carriers.

Certain sites, such as defects, in the semiconductor material can 'trap' electrons or holes, and become recombination centers. During the trapping process the charge carrier relaxes to a localized state and becomes immobile. If the energy

difference between the electron/hole trap state and conduction/valence band edge is small enough in comparison to available thermal energy, the charge carrier can be detrapped and become mobile again. However, for so-called deep traps, the energy difference is so large that detrapping cannot occur. An electron/hole in a deep trap is most likely going to eventually recombine with an incident opposite charge. It is crucial to know what kind of sites in the material could act as traps, whether they're deep or shallow, where they are located, and how to avoid their formation. Some have proposed that one of the roles of a metallic co-catalyst is to trap electrons on the nanoparticle where they can initiate reduction reactions, while physically separating them from the oxidation half-reaction that takes place on the semiconductor surface.

What makes a good photocatalyst?

The optimal photocatalytic system must be efficient, stable, and cheap. To be suitable for use in photocatalytic hydrogen production, the light absorber material must fulfill several criteria:

- The band gap must be compatible with the energy of the incoming light, i.e. it should match the visible part of the solar spectrum (1.7-3.3 eV)
- Effective charge-carrier separation to minimize loss through recombination
- Fast diffusion/drift of electrons and holes
- Alignment of the band edges with the HER and OER potentials
- Non-precious materials and easy synthesis
- Stable under reaction conditions

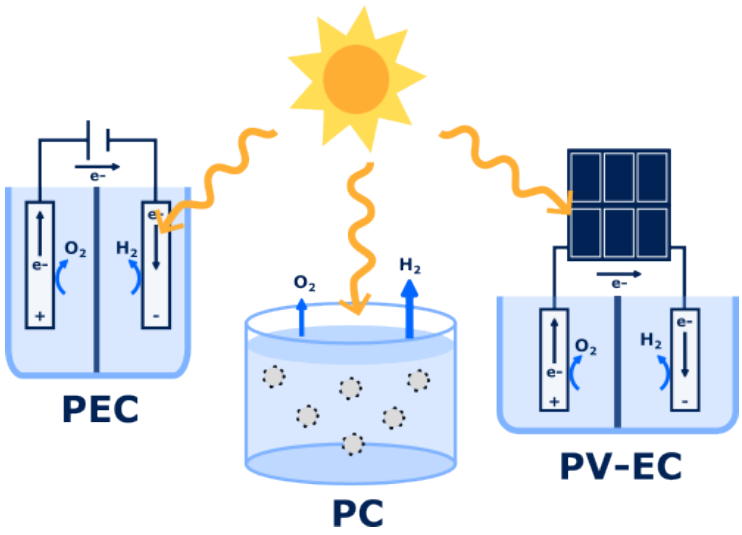
The second part "Materials in Hydrogen Production" of the course goes into more detail on the fundamentals of material science, and properties and design of materials that are suitable for solar to hydrogen conversion technologies, including semiconductors.

Solar-to-hydrogen systems

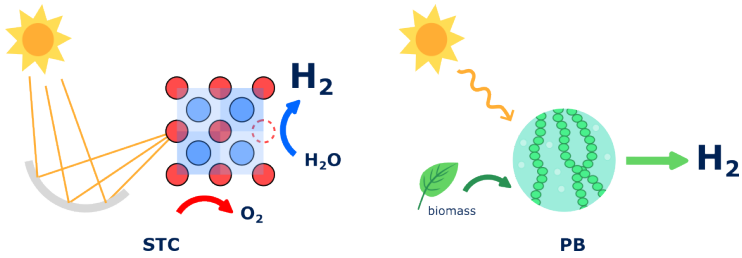
Different approaches

Different solar-to-hydrogen technologies all utilise sunlight, but there are different approaches to introducing the photon energy with the chemical system. All systems need some sort of light absorber material, the technical requirements depend on the application.

Pure photocatalytic (PC) water splitting systems use light and semiconductor particles to split water, with no external potential difference to drive the reaction. In contrast, photo electrochemical (PEC) systems combine the use of irradiation and electricity as driving forces. Photovoltaic-electrochemical (PV-EC) systems first convert the incoming light into electricity and then use it to



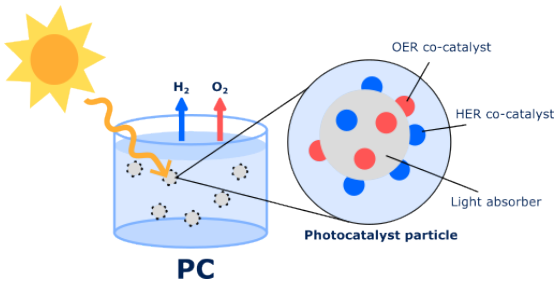
drive the water splitting reaction electrocatalytically. Other types of methods that will not be discussed further in this course include solar thermochemical (STC) water splitting and photobiological (PB) hydrogen production. Solar thermochemical water splitting converts concentrated solar radiation to heat in order to drive the thermolysis of water. Photobiological technologies take advantage of micro organisms such as algae and bacteria that are capable of converting biomass to hydrogen using light as an energy source.



Photocatalytic Cells

Photocatalytic (PC) systems are in principle the simplest type of solar-to-hydrogen technology, and can utilise cheap materials under mild conditions.

The simplest PC systems use only pure water as the electrolyte, with photocatalyst particles suspended in it. The same particles are responsible for both hydrogen and oxygen evolution, which means that downstream product separation is needed. In addition to the semiconductor material, co-catalysts are often used to provide oxidation and reduction sites on the particle surface, and to aid in charge separation. A good photocatalyst is able to reduce the over-

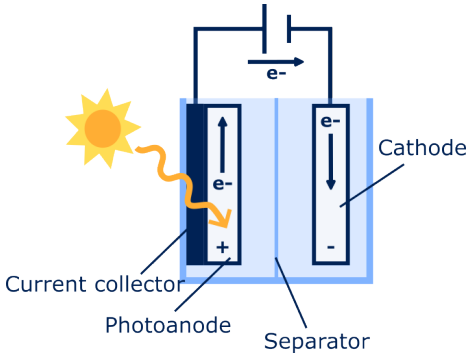


potentials associated with the HER/OER reactions, which lowers the required energy.

The requirement for the semiconducting material to have a suitable band gap for light absorption, and for the band edges to straddle the HER/OER potentials severely lowers the number of suitable light absorber materials for PC systems. The main strategy to side-step this issue is to use more than one semiconductor with different band gaps.

Photoelectrocatalytic cells

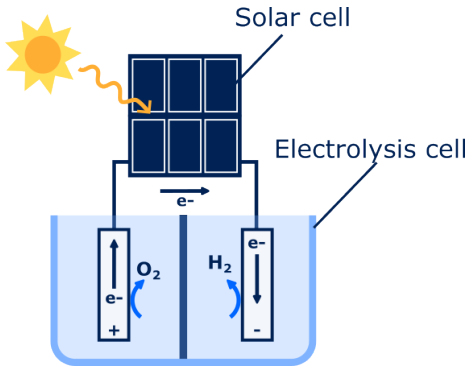
Photoelectrocatalytic (PEC) cells combine electrochemistry with photochemistry, by introducing a potential difference while also utilising a light absorber material on one or both of the electrodes. An electrode that also absorbs light is called a photoelectrode (also photoanode or photocathode). The photoelectrode consists of a light absorber material connected to a charge collector which is electrically connected to the other half-cell but not in direct contact with the electrolyte. It is possible for the cell to be configured in such a way that the photoanode and photocathode do not need an additional applied bias.



Photovoltaic-electrocatalytic cells

Photovoltaic-electrocatalytic (PV-EC) systems are the most mature solar-to-hydrogen system available. PV-EC systems combine the technologies of solar

cells with electrolysis cells. The PV cell harvests photons and converts solar energy to power the water splitting reaction taking place in the electrolysis cell. For the coupled system to work optimally, it is critical that the current-voltage characteristics of the PV match the electrolysis cell. If the PV cell outputs a higher voltage than what is required to drive the reaction in the electrolysis cell, the extra energy is wasted as heat. This can be circumvented by connecting multiple PV and/or electrolysis cells in series. The best choice of electrolyser



technology to be used in tandem with PVs is the proton exchange membrane (PEM) cell. Although they are more expensive and less mature technology than liquid alkane electrolysis (AEL) cells, PEM cells benefit from having a wider range of operating current densities and a shorter cold start times. This makes them better suited for direct coupling to intermittent power sources, i.e. solar cells.

Solar-to-hydrogen efficiency

Solar-to-hydrogen efficiency (STH) is the most commonly used metric for comparing the performance of various photocatalytic water splitting systems. In order to become commercially viable, it is estimated that a STH of 10 % and a lifetime of 10 years must be achieved, but the goal set by the US Department of Energy is even higher, 25 %.[1] This is currently not the case for PC and PEC systems.

The theoretical maximum STH efficiency is different for PC, PEC, and PV-EC systems. For PC systems, the theoretical maximum is determined by the required optimal band gap of the photocatalyst (in the case of a single semiconductor), which is around 2 eV. This leads to ca 18% theoretical STH efficiency. However, most reported PC systems achieve an STH efficiency on the order of 1% or less. Efficiencies of 9% have been reported for PC systems.[1]

For PEC systems the maximum STH efficiency ranges from ca 11% to 30% depending on the light absorber and photoelectrode configuration. The record STH efficiency as of 2018 is 19% for a PEC system that utilized a dual-junction photocathode.[2] The photocathode consisted of GaInP and GaInAs subcells on

a GaAs substrate, a TiO_2 protective layer on top, and a rhodium nanoparticle catalyst.

Total STH efficiencies well over 10% have been achieved for PV-EC systems, as the PV and EC technologies are already mature and capable of achieving high efficiencies individually. The theoretical efficiency of PV-EC systems depend on the configuration of the PV cell and electrolyser technology, the total STH efficiency being a product of the efficiencies of the individual components. Roughly a 37% theoretical STH efficiency can be achieved when PV cells with three-junction III–V materials are used in tandem with a PEM electrolyser. At laboratory scale, a record STH efficiency of ca 30% was achieved with InGaP/GaAs/GaInNAsSb triple-junction PV cell coupled to two in series PEM electrolysers in 2016.[3] PV-EC systems are currently the best performing and closest to commercial application, but there is still room for improvement.

1. The route for commercial photoelectrochemical water splitting: A review of large-area devices and key upscaling challenges. Vilanova, A. et al. Chemical Society Reviews, 2024, 53 (5), 2388–2434 DOI: 10.1039/d1cs01069g

2. Monolithic Photoelectrochemical Device for Direct Water Splitting with 19% Efficiency. Cheng, W-H et al. ACS Energy Letters, 2018, 3 (8), 1795-1800 DOI: 10.1021/acsenergylett.8b00920

3. Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%.Jia, J. et al. Nature Communications, 2016, 7, 13237 DOI: 10.1038/ncomms13237

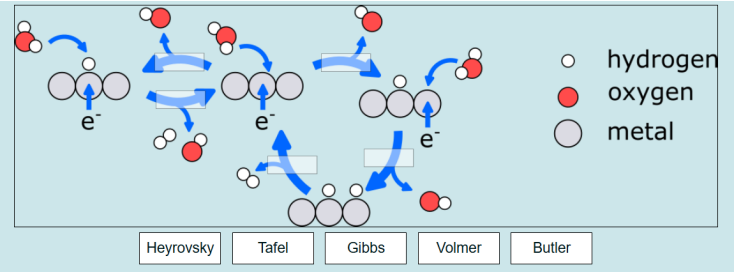
Solar Hydrogen Quiz

1. Which of the technologies below does not involve a potential difference between anode and cathode to drive water splitting?

   (a) Photovoltaic-electrocatalytic

   (b) Photoelectrocatalytic

   (c) Photocatalytic



2. Why shouldn't a photo(electro)catalytic system utilise only ultraviolet radiation?

   (a) UV is not energetic enough for water splitting

   (b) Majority of irradiation from the Sun is not in the UV range

   (c) UV radiation leads to a lower quantum efficiency

3. PV-EC systems have the greatest theoretical solar-to-hydrogen efficiency out of the photocatalytic water splitting technologies.

   (a) True

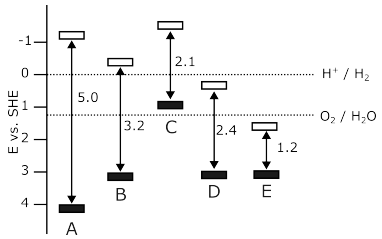
   (b) False

4. Complete the following text by filling in appropriate missing words:

   When light of a frequency that matches the energy of the _____ of a cting as the light absorber, _____ is excited from the _____ to the _____. The process leaves behind _____ in the _____, where it acts as a charge carrier. The charge carriers migrate to the surface where the _____ takes part in the oxidation reaction, while the _____ takes part in the reduction reaction. Alternatively, the charge carriers can _____, which leads to a loss of efficiency of the photolysis of water.

5. The figure below shows band gap energies and band position (in relation with the redox potentials of water splitting) of some candidate materials. Based on this figure, which material has the most potential to be suitable for use as a light absorber?

   A



B

C

D

E

6. What region of solar radiation does the best candidate material from the previous question absorb in?

   (a) Ultraviolet

   (b) Visible

   (c) Infrared

7. In order to increase the water splitting efficiency of the best candidate material in the previous questions, the material should be modified in such a way that the band gap ...

   (a) becomes as small as possible

   (b) becomes as large as possible

   (c) becomes smaller, but above 1.23 eV

   (d) stays the same

8. Match the material with the most suitable role for it in photocatalytic water splitting

(a) Platinum nanoparticle	A Hole trap
	B Co-catalyst
(b) TiO_2 nanoparticle	C Light absorber

9. Which of the options below is NOT a typical role of a co-catalyst in a solar-to-hydrogen photocatalytic system?

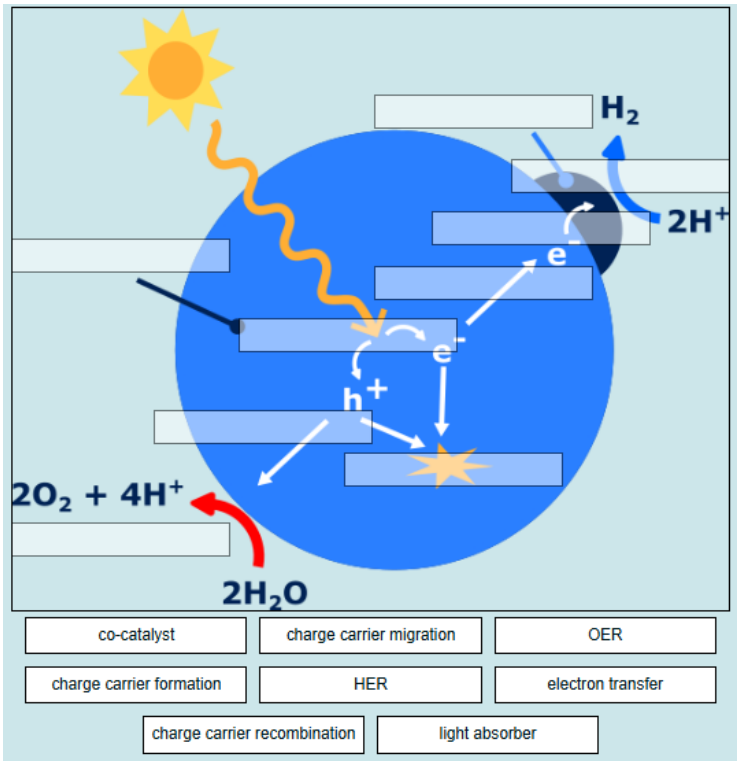
   (a) Facilitating electron-hole separation

   (b) Mediating charge transfer from semiconductor to reactant molecules

(c) Lowering of HER overpotential

(d) Charge carrier generation

10. Write the names of the photocatalysis steps to the correct spots in the diagram.



Answers

Which of the following statements is **not true** about what can occur during a chemical reaction?

1. Correct. The identity of atoms does not change as a result of a chemical reaction. Hydrogen stays hydrogen, and carbon stays carbon. This ultimately means that if a feedstock molecule contains a lot of carbon atoms per hydrogen atom, more CO_2 is produced as a side product.
2. Electrons moving from one species to another, i.e. electron transfer may take place during a chemical reaction. This is a central phenomenon in electrochemical reactions, which will be encountered later in the course.
3. While some chemical reactions do not result in a change of the total number of molecules, it is possible that there will be fewer or more reactant than product molecules. For example, in a simple dissociation reaction, a big molecule splits to form smaller molecules, which increases the total number of molecules.
4. Transformation of reactants to products via a chemical reaction always involve bond breaking and/or formation.

Q. Is it possible for water-gas shift reaction to yield more hydrogen than carbon dioxide?

1. Incorrect. The stoichiometric coefficient of hydrogen and carbon dioxide are both one, so the same amount of each is always produced in WGSR. However, it is possible to remove the carbon dioxide after the reaction has occurred.
2. Correct! WGSR produces one carbon dioxide per one hydrogen, i.e. they are formed in equal amounts. It is not possible to obtain more hydrogen than CO_2 through the reaction, however, it is possible to remove the CO_2 after the reaction has occurred to purify the hydrogen gas.

Q Finish the sentence:

"A mole is ..."

1. Correct! This official definition of the mole was introduced in 2019.

2. Well yes, but actually no.

3. Incorrect. The scientific notation "$\times 10^{23}$" means that the number 6.02214076 is multiplied by ten to the power of 23, i.e. approximately 602 billion trillion.

Q Which of the expressions below is the correct reaction quotient for the water-gas shift reaction at 300 °C? The symbol P means pressure.

1. Correct! The products should appear in the numerator. The reactants and products are gaseous at 300°C, so their activities can be represented as their partial pressure with respect to the standard pressure. The standard pressure terms cancel out.

2. Incorrect.

Q For a closed flask containing an arbitrary amount of two substances A and B, which of the following is equal to the Gibbs energy of the system at constant pressure and temperature?

1. Correct! The Gibbs energy of a closed system at constant temperature and pressure is:

   $G = \sum_i \mu_i N_i$

   and for the two component system of A and B the summation is:

   $\mu_A N_A + \mu_B N_B$

2. Incorrect.

3. Incorrect.

Q At 298 K, the standard enthalpy of the WGS reaction is -41 kJ /mol, and the standard entropy is -42 J / K / mol. Assuming that the entropy and enthalpy do not change with respect to temperature (in reality, they do vary with temperature), which of the following statements about the reaction Gibbs energy is correct?

1. Correct! Assuming the enthalpy and entropy of reaction stay constant for all temperatures, the Gibbs reaction energy can be estimated with

   $\Delta_r G = \Delta_r H^\circ - T\Delta_r S^\circ$

   setting Gibbs reaction energy to zero and solving the equation for temperature with the given values for entropy and enthalpy:

   $$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{-41000\text{J/mol}}{-42\text{J/K/mol}} = 1024\text{K}$$

   In other words, at 1024 K the Gibbs energy is zero, and changes sign above and below this temperature. Due to the negative signs of both the entropy and enthalpy, temperatures above this value will yield a positive Gibbs energy, and values below will yield a negative Gibbs energy.

(Note: The enthalpy is commonly expressed in units of kJ / mol, whereas entropy is in J / K / mol. Remember to convert them to the same unit, i.e. kJ or J with the conversion formula 1 kJ = 1000 J.)

2. Incorrect.

3. Incorrect.

4. Incorrect.

Q Which of the statements is true for the figure below?

1. False. Point C is positioned at the minimum of the curve, where the slope of G versus the extent of reaction, $\Delta_r G = 0$, is zero. This is the equilibrium position, there is no thermodynamic driving force towards point D.

2. False. Although no numerical values are given, the arrow indicates that G increases when moving higher along the y-axis. The point where the curve for G touches the y-axis is higher up on the product side (point D) than reactant side (point A) which means that $G°reactants$ at point D must be greater than $G°products$ at point A. $\Delta_r G°$ is the difference between the value of $G°$ for pure products and pure reactants, therefore if $G°products$ ¿$G°reactants$, $\Delta_r G°$ must be greater than zero.

3. True. The reaction is spontaneous in the direction which minimizes the value of G. The negative value of $\Delta_r G$ at point B means that increasing the extent of reaction, i.e. proceeding in the forward direction, is thermodynamically favoured. This will give more products.

4. False. Although $\Delta_r G°$ is positive in this case, it does not mean the reaction is always spontaneous. A reaction is spontaneous at points where the derivative of Gibbs energy with respect to the extent of reaction is negative. There are clearly points on this graph where the slope is negative (all points to the left of point C), i.e. the reaction is spontaneous, even though the standard Gibbs energy is positive.

Q In the plot of product concentration versus time below, at which point is the rate of reaction the highest?

1. Correct! The slope of the concentration vs time curve is the largest at this point, i.e. the instantaneous rate is the highest.

2. Incorrect.

3. Incorrect.

Q In an experiment, the initial rate of a reaction was found to increase when the starting concentration of one of the reactants was increased. Which of the below is the best explanation for the observed increase in rate?

1. Correct! Increasing the reactant concentration increases the number of collisions that occur between reactants per unit time, which in turn increases the number of collisions leading to a successful chemical reaction

per unit time, i.e. increased reaction rate. Why does increasing concentration lead to more collisions? Think of people on a busy street: the more people there are, the more likely it is that they bump into each other.

2. Incorrect.

3. Incorrect.

4. Incorrect.

Q Based on the Arhhenius plots for reactions A and B below which reaction has the larger activation energy?

1. Correct! The slope of A is steeper (more negative), and because slope $= -\frac{E_a}{R}$, its activation energy E_a must be greater than that of B.

2. Incorrect.

Q The rate law for the reaction:

$NO_2 + CO \rightarrow NO + CO_2$

was found to be

$r = k[NO_2]^2$

From the form of the rate law it was deduced that the reaction must occur in multiple steps. For the proposed mechanism below, which step would you expect to be the rate determining step (RDS)?

Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

1. Correct! The rate of Step 1 is $r_1 = k_1[NO_2][NO_2] = k_1[NO_2]^2$, which matches the observed rate law. The rate of Step 2 is $k_2[NO_3][CO$, which is not consistent with the observed rate law. As the rate of the RDS determines the overall rate, Step 1 being the RDS is more consistent with the experimental data.

2. Incorrect.

Q The activation energy does not change with temperature.

1. Incorrect.

2. Correct! The activation energy is the difference between the reactant and transition state Gibbs energies. Gibbs energy is a function of temperature, and it is possible for the transition state and reactant Gibbs energies to change by a different amount with temperature, which leads to a change in the Gibbs energy difference as well.

Q A catalyst increases the rate of reaction by making the reaction energy smaller.

1. Incorrect. A catalyst does increase the rate of reaction but not by altering the reaction energy.
2. Correct! A catalyst increases the rate of a reaction by lowering the activation energy of the reaction, not the reaction energy, which is determined by the thermodynamic potentials of the products and reactants that cannot be changed by a catalyst.

Q Electrostatic potential difference between two points in a system is the _____ required to move a test charge between the points, per unit charge.

1. Correct!
2. Incorrect.
3. Incorrect.
4. Incorrect.

Q In the reaction:

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2 \tag{36}$$

hydrogen is

1. Incorrect.
2. Correct! Hydrogen gains electrons, which is reduction.

Q The temperature behavior of the rate of a PCET reaction does not depend on whether it occurs through the concerted mechanism or step-wise electron-proton transfer mechanism.

1. Incorrect.
2. Correct! The concerted reaction goes through a single transition state, while the step-wise reaction mechanism occurs in two steps with their own associated transition states. The activation energies for these steps can be very different, i.e. they would also exhibit different behavior with respect to temperature.

Q Consider the reaction:

$$\mathrm{O}_2 + 4e^- + 4\mathrm{H}^+ \rightarrow 2\mathrm{H}_2\mathrm{O} \tag{37}$$

would it take place at the anode or cathode of an electrochemical cell?

1. Incorrect.
2. Correct! This reaction is the oxygen reduction reaction, reduction always takes place at the cathode.

Q In the diagram below, which direction would a positive ion move across the light blue region representing the electrolyte?

1. Correct! The direction of electron flow is indicated from anode to cathode in the external circuit, so in the electrolyte a positive ion must move from anode to cathode, i.e. right to left in this case.
2. Incorrect.

Q All hydrogen produced via electrolysis is green hydrogen

1. Incorrect.
2. Correct! Even though electrolysis is in principle a clean process, the electricity that is used to drive the reaction must be produced from renewable sources (wind, solar, hydro, and possibly biomass). The hydrogen is pink if the electricity is produced with nuclear power.

Q Given the typical operating temperature of steam methane reforming, which curve of the equilibrium constant K versus temperature T (in Kelvin) belongs to the methane reforming reaction? The curves are calculated at standard conditions.

1. Correct! The SMR reaction is strongly endothermic, and its standard Gibbs energy change is positive until around 900 K (627°C). At low temperatures the equilibrium constant is much less than one (ln K ¡ 0), i.e. reactants are favored over products. Products are favored over reactants at temperatures over 900 K, when the equilibrium constant is more than one (ln K ¿ 0).
2. Incorrect. The red curve corresponds to the water-gas shift reaction. WGSR is exothermic, and has a negative standard Gibbs energy change until very high temperature. The equilibrium constant of WGS is greater than one at low and moderate temperatures (ln K ¿ 0, marked by horizontal dashed line), i.e. the products are favored over reactants, and only becomes less than one (ln K ¡ 0) at around 1100 K.

Q Based on the stoichiometry of the SMR and WGS reactions, how much CO_2 is emitted per each kilogram of H_2 produced?

1. Correct! In fact, the SMR process actually produces even more CO_2 per kg of H_2. One of the main reasons is that methane combustion, which produces CO_2, is used to provide the heat to the reaction.
2. Incorrect.
3. Incorrect.
4. Incorrect.

Q The number of under-coordinated edge and corner sites relative to terrace sites decreases when particle size increases.

1. Correct! Differently shaped (cubic, spherical, cuboctahedron) particles have a different number of undercoordinated atoms, such as edge and corner atoms, however in general their relative number becomes smaller as particle size increases.

2. Incorrect. Compare the ratio of the number of white atoms to the number of darker blue atoms in the picture. Does it become smaller or larger from left (small particle) to right (big particle)?

Q Under acidic conditions, which of the options below is the correct equilibrium constant for the water electrolysis half-reaction occurring on the cathode side?

Note: a_i and p_i are the activity and partial pressure of species i, and p^0 is the standard pressure (1 bar).

1. Correct! The water electrolysis half-reaction that occurs on the cathode is the HER, which under acidic conditions has the form

$$2\mathrm{H}^+(aq) + 2\mathrm{e}^- \rightleftharpoons \mathrm{H}_2(g)$$

   An equilibrium constant for a reaction is written as a ratio of the product and reactant activities. The activity of the hydrogen molecule is its partial pressure divided by the standard pressure, while the activity of an electron is unity, i.e. it does not have to be explicitly written in the equilibrium constant.

2. Incorrect.

3. Incorrect.

Q In a cyclic voltammetry (CV) experiment, the applied potential is cycled and current is measured. The change in the current between different cycles is a measure of the _____ of the electrolysis cell.

1. Correct!

2. Incorrect.

Q For efficient electrolysis, the overpotential of HER/OER should be made as low as possible.

1. Correct!

2. Incorrect.

Q Based on only the typical operating temperatures and the thermodynamics of the water electrolysis reaction, which of the technologies requires the least electricity for operation?

1. Correct! As the $T\Delta S$ term for water splitting increases with temperature, more heat (as opposed to electric energy) can be used to drive the reaction.

2. Incorrect.

3. Incorrect.

4. Incorrect.

Q The contribution to the energy of sunlight from UV light is very small because ...

1. Incorrect. The wavelength of UV light is shorter than IR or visible light, its photons have more energy than IR or visible light photons.

2. Correct! Although UV light has a shorter wavelength than IR or visible light, i.e. its photons have more energy per photon, the amount of those photons is much smaller. Therefore UV light accounts for only ca. 3 % of the energy content of sunlight at Earth's surface.

Q A photocatalyst is typically a

- Incorrect. Conductors (metals) are not suitable as photocatalysts, as the excited carrier life-times are too short for them to be able to take part in the chemical reaction. However, they are often used as co-catalysts or deposited as plasmonic metals to boost charge carrier separation in other materials.

- Correct! Photocatalysts are typically semiconductor materials.

- Incorrect. The bandgap of an insulator is usually too large for excitation by visible or UV light, and are therefore more rare in photocatalytic applications than semi-conductors. Insulators are more rare in photocatalytic applications than semiconductors, although they can be modified by e.g. doping, defect engineering, and plasmonic effects. Insulators can also be utilised as co-catalysts, catalyst supports, or insulating barrier layers between two semiconductors.