Appendix 1 – Theory on Sustainable Energy from Water

BLUE ENERGY

Sustainable energy from water

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Contents

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1. Climate issues and renewable energy

The use of energy has a major impact on our footprint. Energy can be generated in different ways and each type of energy has a different impact on the size of our footprint.

1.1 The greenhouse effect

The temperature on earth fluctuates between -70° and 50°C, depending on the location on earth. Fortunately, these extremes only occur in a few places. The vast majority of the Earth's surface has temperatures that are comfortable for humans to live in.

The temperature on Earth is mainly determined by the sun. A very small part of the heat comes from the Earth itself as a result of processes in the Earth. The sun has periods with more and less radiation which influence the temperature on earth. Nevertheless, the temperature on Earth is fairly stable. Earth's geological history has warm and cold periods. These still fall between the extremes mentioned above, but determine whether a larger or smaller area is habitable.

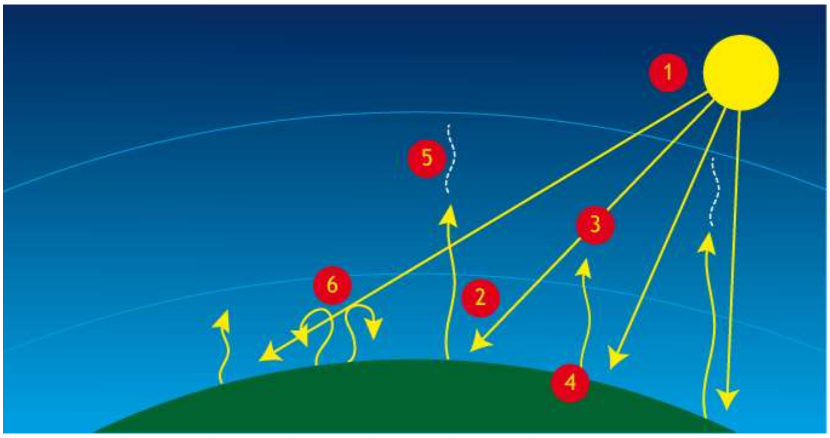

Figure 1: *The greenhouse effect: 1. solar radiation, 2: greenhouse gases in the atmosphere, 3: solar rays reach the earth's surface, 4: heat emitted after absorption, 5: part of the emitted heat escapes into space, 6: another part of the emitted heat is stopped by the greenhouse gases.*

We owe most of the fact that the Earth is livable to the atmosphere. Without oxygen, we're quickly running out of steam, but even without the greenhouse effect, life would become very tedious, if not impossible. Water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4) and other gases ensure that there is a balance between radiation from the sun, reflection of sunlight and radiation of heat. Therefore, rather than worrying about the greenhouse effect, we need to worry about the **amplified greenhouse effect**.

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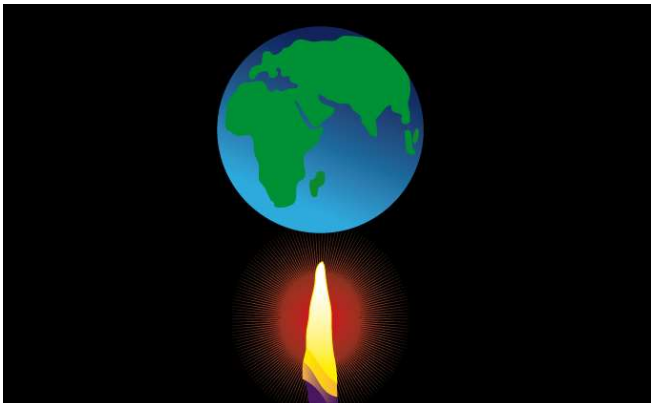

Figure 2: *Global warming*

The fact that the greenhouse effect is a complicated phenomenon is mainly due to the various **feedback effects**: processes in which the outcomes of an operation affect the causes of those same processes. For example, evaporation increases when temperatures rise. As a result, more clouds form and irradiation decreases. We call this a **negative feedback effect**. There are also **positive feedback effects**: the melting of the polar caps reduces the reflection of radiation, further increasing the temperature on Earth.

By now it is clear that many, not just Al Gore and Leonardo di Caprio, are concerned about the enhanced greenhouse effect. The increase in the concentration of greenhouse gases such as carbon dioxide and methane decreases the radiation of heat, thus increasing the temperature of the atmosphere.

The increase in carbon dioxide is due to the burning of fossil fuels such as coal, oil and gas. With some imagination, you can think of these as old stocks of stored solar energy.

Opponents of the theory of the enhanced greenhouse effect (the "skeptics") point to the usual variation in the amount of sunlight and average temperature. For example, in the late Middle Ages (between 1200 and 1400) the temperature was comparable to today's temperature, while afterwards (between 1500 and 1900) there was a period with a lower average temperature (the Little Ice Age is often referred to). The supporters of the greenhouse theory point, among other things, to the coincidence of the temperature increase with the increasing use of fossil fuels. Their conclusion is that carbon dioxide levels must be drastically reduced.

Make Assignment 2 in Appendix 3

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1.2 Forms of sustainable energy

Geothermal

Deep inside the globe, temperatures of thousands of degrees prevail. This could potentially mean a considerable supply of energy, but it is still too expensive to use on a large scale. Heat from the ground that has been put there by sunlight is already being used. A heat exchanger in the soil makes the heat from the soil available for heating.

Hydropower (or Hydroelectricity)

Flowing water (the term hydropower is, strictly speaking, a bit sloppy) has been contributing to the energy supply for a long time even in the very flat Netherlands. This varies from the centuries-old water mills in Limburg and Twente to the modern hydroelectric power stations in the Rhine and in the Meuse.

The power that can be generated from running water plants in our country is so far even 3.5 times greater than the power from direct solar energy.

It is not expected that hydropower will play a very large role in the Netherlands in the future. How the hydrological cycle can still be an important source of energy is described in more detail in section 3.3.

Wind Energy

Like flowing water, moving air is a sustainable source of energy. In 2006, there were over 1,700 wind turbines in the Netherlands capable of generating enough electricity to supply approximately 600,000 households. The government feels that the share of sustainable electricity, and of electricity generated by wind power in particular, must continue to increase in the coming years. Only then can the Netherlands meet the previously mentioned energy targets.

The direct use of space by wind turbines is limited; a base plate measures approximately 10 m by 10 m. However, the turbines must be positioned quite far apart, some 400 - 600 m, to prevent them from capturing wind from each other.

A rule of thumb is that a mill with a peak power of 1 MWp needs about 25 ha. Moreover, it should be taken into account that the average power is about 25% of the peak power. The wind is not always strong, sometimes not at all or sometimes even too strong.

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Biomass (biofuel/biogas)

Biomass is the dry weight of organic material derived directly from plants or animals. This can be gas from decaying material, but also alcohol from sugar cane or sugar beet and the oil pressed from, for example, rapeseed or animal fats. The biofuels obtained can literally be fuel, but they can also be used in electrochemical fuel cells. Fuel cells have been developed that are fed with wastewater. This method has two advantages: energy generation without additional CO_2 emissions and decomposition of waste, thus reducing environmental pollution.

Petrochemical companies in the Netherlands are required to blend 5.75% biofuel such as bioethanol or biodiesel into their fuel within 2 years and have now started blending in order to meet this target within the set time frame. By increasing this percentage further, a much higher share can be achieved in the Netherlands with sustainable energy, while maintaining the same fuel quality.

The biomass currently used in the Netherlands is a residual product. It only requires additional space for storage. If wood were to be grown especially for energy supply, that would require a great deal of space. From another possible biomass, rapeseed, about 4,500 kg per hectare per year can be harvested. This is good for 1,500 liters of oil.

Landfill sites produce biogas, known as landfill gas. This too is a form of biofuel. Landfill gas is collected and used in numerous places in the Netherlands.

Solar energy

In a photovoltaic solar cell (PV cell), solar energy is converted directly into electrical energy without any intermediate steps. This direct use of solar energy is also very attractive for the Netherlands in the long term. With the current technology, a lot of space is needed to harvest solar energy. If all buildings in the Netherlands were equipped with solar cells or solar collectors (which convert solar energy into heat), we would cover 10% of our current energy needs.

In the Netherlands, the sun shines an average of 600 hours per year. One square meter of land area in the Netherlands receives an average of 1,050 kWh of direct solar energy per year. This means that the average power falling on a solar cell is 1750 W m-2 (check this yourself, use block 1 if necessary) Of this, with the current state of technology, about 6% is used. The power of 1 m2 of PV solar cell is thus about 100 W.

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As we search for sustainable forms of energy, we must realize that we are allowing enormous amounts of solar energy to "escape. With the solar energy the earth receives per second (100 trillion kWh), we can cover almost three hours of the entire world's current energy consumption. Solar energy is a sustainable form of energy. No burning of fossil resources, but direct use of the sun's irradiation without production of greenhouse gases. So the question is: how do we capture this solar energy?

Not only direct solar energy, but all the forms of renewable energy described - except for "deep" geothermal energy - are in fact forms of solar energy. The hydrological cycle (and thus hydropower), is driven by the sun. Wind is created by the sun heating the earth unevenly, causing the air to rise in some places and fall in others. Biomass is actually a capture of solar energy through the process of photosynthesis.

This module deals with another, still relatively unknown, possibility of using solar energy: Blue Energy. Like hydropower, Blue Energy is based on the hydrological cycle.

1.3 The hydrological cycle and Blue Energy

Capturing solar energy can be done by using the hydrological cycle (see Figure 3). Solar heat causes water at the surface of seas and oceans to evaporate. The water vapor rises and part of it condenses into clouds that drift with the wind over continents. When the air above land cools (for example, by continuing to rise) part of the water will fall to Earth as precipitation (rain or snow). Water thus returns to the seas and oceans sooner or later, depending on where the precipitation has fallen.

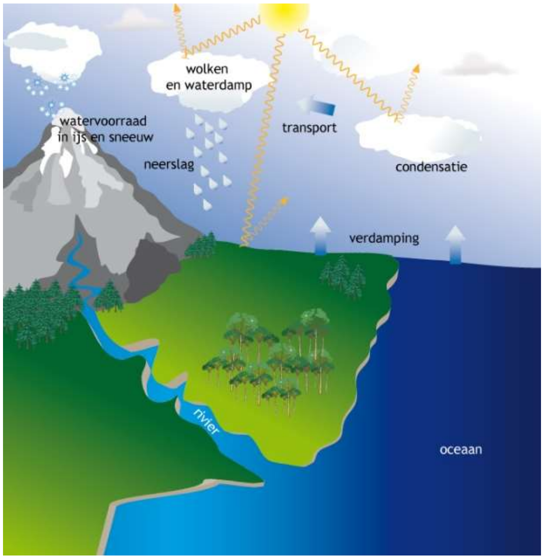

Figure 3: *the hydrological cycle*

Two forms of renewable energy generation are based on this hydrological cycle:

- **Hydroelectricity** relies on the difference in elevation between where precipitation falls and where the water flows back into the sea or ocean. Gravity plays a crucial role in extracting this energy. Large turbines are driven by falling ("white coal") or flowing water. The principle is the same as that of the bicycle dynamo, but the amount of energy is much greater. This amount of energy depends on the amount of water and the difference in height. We speak of high and low pressure power plants. The nice thing about high-pressure power stations (e.g. artificial reservoirs) is that you can let the water flow when the need for electricity is greatest. This relieves the burden on the peak power plants that only produce extra electricity when demand is highest (during the day when most companies are working). These peak load power plants are also the most expensive per kilowatt hour.

- The second, very surprising, way to recover solar energy using the hydrological cycle is **Blue Energy**. This uses the mixing of fresh and salt water at the point where the drained water flows back into the sea or ocean via rivers. How we can generate this energy, where it could be generated and what technical problems need to be solved are discussed in the remainder of this

1.4 Suitable location for Blue Energy

The generation of Blue Energy must be done at a place where fresh and salt water meet. There are plenty of such places in the world and certainly in the Netherlands (Figure 4): we find one at every river mouth. Yet the solution is not that simple either, because at open river mouths the fresh river water gradually becomes saltier. Without special measures, the amount of recoverable energy is very limited. The 'intake' of salt and fresh water must be kept separate from each other, and the discharge of brackish water must also be kept separate from the inflow.

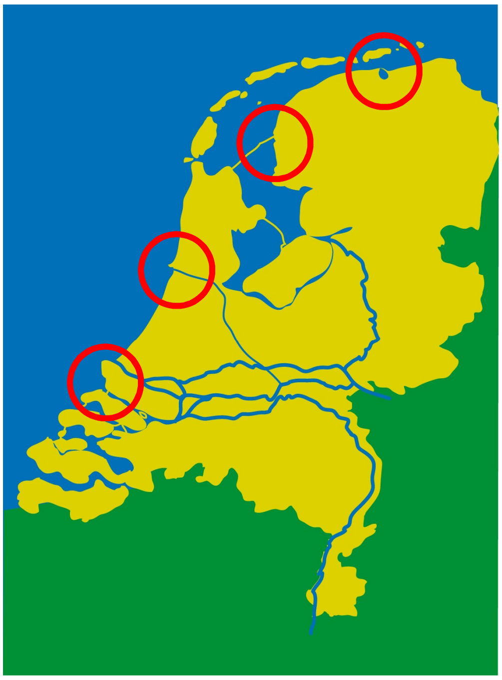

Figure 4: *possible locations for Blue Energy in the Netherlands*

There are several places in the Netherlands where fresh and salt water are kept sharply apart. We only need to make an outflow of brackish water there so that this brackish water does not mix with the fresh or salt water.

The first place we look is the sluices in the Afsluitdijk. Fresh water is regularly discharged into the Wadden Sea here at low tide. In addition to the sluices, there is also a pier to protect shipping from unwanted currents. This is very pleasant, because if the brackish water is discharged on the other side of the pier, it does not mix with the inflow of salt water. Conveniently, the tide also salts the brackish water twice a day.

Make Assignment 4 in Appendix 3

2. Blue Energy

It may seem too good to be true: gaining energy from mixing fresh and salt water. To understand how this is possible, it is necessary to dive into the theory of so-called thermodynamics. A central question here is why some processes occur and others do not. Here the concepts of enthalpy and entropy are indispensable. You will learn in this chapter
- the concepts of (reaction) enthalpy and entropy
- how these are related to Blue Energy
- and what the possibilities of energy generation by Blue Energy are.

2.1 Enthalpy

Suppose you are frying an egg and you look at what happens to the natural gas and what happens to the egg. One important difference is that while burning natural gas releases energy (mainly heat), frying an egg actually requires energy. If you stop the heat supply, then the frying also stops. This example shows that we can divide chemical reactions into **exothermic reactions** (reactions that release energy) and **endothermic reactions** (reactions that require energy to make the reaction proceed).
This division can also be applied to non-chemical processes, for example, phase transitions. Melting is endothermic, solidifying (in the case of water: freezing) is exothermic.

A reaction can take place at constant pressure or at constant volume. This makes a difference if gases are produced during the reaction. At constant pressure, in practice atmospheric pressure, the reaction product(s) have a larger volume than the starting substances. To occupy this larger volume, the reaction product(s) must perform work, namely pushing out an amount of air. For this labor ("volume labor") holds:

Formula (2) $$W = p\Delta V$$

where:

- W = labor in joules (J)
- p = pressure in pascals (Pa)
- ΔV = change in volume (m3).

The derivation of this formula follows from two definitions:

- the definition of pressure ($p = F / A$); in this, F = the force (N) and A the area (m2) and
- the definition of labor ($W = F \cdot s$)

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Combining the definition of pressure and the definition of work gives:

$$p = F / A \Rightarrow F = p \cdot A$$

$$W = F \cdot s \Rightarrow W = p \cdot A \cdot s$$

Recall that A.s (area x distance travelled) represents a change in volume, therefore:

$$\Delta V = A \cdot s \Rightarrow W = p\Delta V$$

The energy required to provide this labor comes from the chemical reaction. As a result, an exothermic reaction releases less heat than the energy supplied by the reaction. In fact, some of the energy goes into the labor, increasing the volume.
Conversely, an endothermic reaction requires more energy than you might expect. In fact, some of the energy required is used again for the volume increase.

In thermodynamics, we mean a system as a clearly defined object, such as a quantity of gas in a cylinder. That system has a certain internal energy. That internal energy includes the energy of motion of the molecules, but also the energy contained in all chemical bonds. During a reaction, either endothermic or exothermic, that internal energy changes: the molecules move faster or slower, bonds are broken or formed. For example, in the cylinder of an internal combustion engine, a gas is burned and the molecules start moving faster. Thus, an energy change (ΔE) of the system takes place. In addition, in the cylinder, a piston is pushed away: the volume of the gas increases. Thus, work is performed (pΔV). Energy change and work done are called enthalpy change (ΔH). The pressure is constant. H is derived from heat content. This enthalpy change corresponds to the heat of reaction.

Thus, the energy change of the system (ΔE) is not equal to the reaction heat or reaction enthalpy change at constant pressure (ΔH,). Some of the reaction heat goes into the volume work. In formula form:

Formula (4) $$\Delta H = \Delta E + p\Delta V$$

The unit of ΔH is joules. The pΔV term in formula (4) is small and usually negligible compared to the ΔE term. Then ΔH = ΔE and it is not a problem if reaction enthalpy and energy are used interchangeably. For clarity, we use (reaction) enthalpy in this chapter. In the following chapters, we mainly use energy, the term most commonly used in the situations at hand.

Make Assignment 5 in Appendix 3

2.2 Entropy

To determine whether or not processes can occur, we first look at the enthalpy change of the system. Exothermic reactions occur spontaneously, provided the temperature is high enough to start the reaction. This is because then the only obstacle has been overcome, the activation energy. This is the reason natural gas must be ignited.
A first rule for the progression of a reaction is therefore:

Rule 1 Every system strives to lower its enthalpy: $\Delta H < 0$.

Consider the following processes:

$H_2O(l) \rightarrow H_2O(g)$

$Na^+Cl^- (s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$

These spontaneous processes, the evaporation of water and the dissolution of table salt, are endothermic. In these processes heat is absorbed from the environment, the enthalpy of the system increases: $\Delta H > 0$! Nevertheless, these processes proceed. So the enthalpy is not the only determining factor.

Molecules are like freshmen: always moving. Even if they sit neatly in their chairs, they still move. If the teacher doesn't keep order, they get up from their chairs and even start running around the classroom. They then fill the whole room and no one is left in their seats. The students have a great deal of freedom. It's chaos. Actually, they behave like a gas.
From molecule theory we know that molecules move. If there are no strong forces between the molecules, this leads to maximum chaos. We see this most clearly with gases (the word "gas" is derived from chaos). A gas spreads out over the entire available volume. We say: the molecules then have a maximum number of **realization possibilities**. You can easily imagine the concept of realization possibilities when throwing dice. If you throw two dice, there is only one realization possibility to throw the total 2, but there are six realization possibilities to throw total seven.
For this module, diluting a salt solution is extremely important. In doing so, the number of realization possibilities for the dissolved particles (ions) increases because they can move in a larger volume.
We denote the number of realization possibilities by the term entropy (symbol S).

Thus, water vapor has a greater entropy than an equally large mass of liquid water. If we dissolve as much salt in 1 liter of water as in 10 liters, then the dilute salt solution has the greatest entropy.

It follows from the above that the entropy of 1 mole of a given solid is smaller than that of 1 mole of liquid, which in turn is smaller than that of 1 mole of gas. See also Figure 5, which shows the entropy of oxygen and that of copper as a function of temperature.

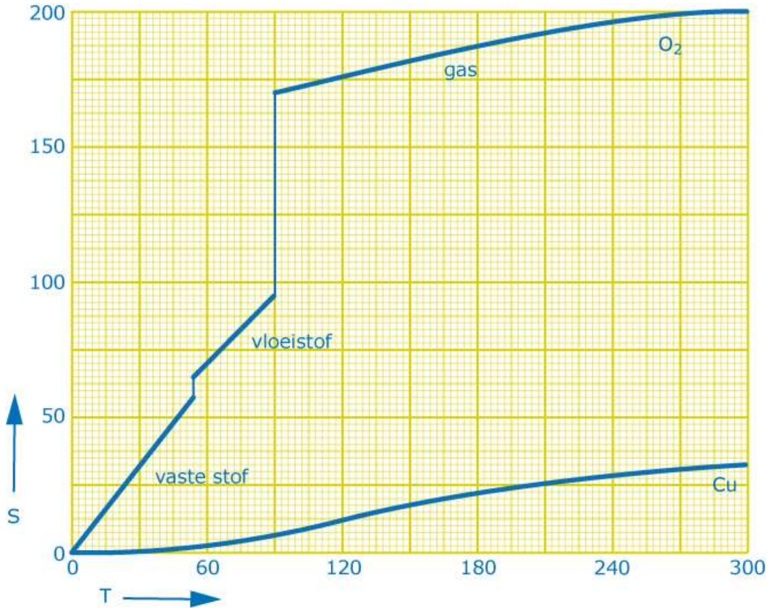

Figure 5: *The entropy (S, in J K-1) of one mole of oxygen and of one mole of copper as a function of temperature (T, in K) (p = p0).*

Three factors determine the potential for motion, thus also entropy:

The volume

- a mole of gas has a much greater entropy than a mole of liquid which has a greater entropy than a mole of solid
- if we dissolve an equal amount of solid in a solvent, the entropy is greater with a larger amount of solvent.

The amount of substance

- 2 moles of gas have twice the volume of 1 mole of gas at the same temperature and pressure and therefore twice the entropy
- the solution of 2 grams of salt dissolved in 1 liter of water has a greater entropy than that of 1 gram of salt in 1 liter of water.

The temperature

- At higher temperatures the entropy increases.

When comparing two systems, the number of moles of gas is usually the determining factor, since the entropy of solids and liquids is relatively small. In Binas, absolute entropies are listed in Table 63.
The second rule for running processes is:

Rule 2 Every system strives to increase its entropy: $\Delta S > 0$.

This rule explains the self-mixing of gases and of solutions, diffusion. In time, the concentrations become the same everywhere, a homogeneous gas mixture or solution has been created.

Make Assignments 7 and 8 in Appendix 3

2.3 Applying the two rules

In the previous sections we discussed the quantities enthalpy and entropy.
We saw two rules for how a process, such as a chemical reaction, proceeds.
I Each system strives to decrease enthalpy: $\Delta H < 0$.
II Every system strives to increase entropy: $\Delta S > 0$.

Thus, when we want to assess whether a process can proceed, there are three possibilities:

1. The occurrence of the process would mean that the enthalpy of the system is lowered and the entropy increased.
2. The occurrence of the process would mean that the enthalpy of the system is increased and the entropy is decreased.
3. The occurrence of the process would mean that the enthalpy of the system is lowered or the entropy increased.

The first category of processes will occur spontaneously. The second category will not be able to occur spontaneously. To assess whether the processes in the third category can proceed spontaneously, we need more information: we need to find a way to quantitatively assess the

influence of both factors. To do this, we look not only at the system, but also at the environment. Then it becomes apparent how fundamental entropy is, because there is derivation:
a process proceeds spontaneously when the **total entropy** increases:

$$\Delta S_{\text{systeem}} + \Delta S_{\text{omgeving}} > 0$$

With this a fundamental difference between energy and entropy becomes clear: when looking at the system and the environment of the system, the total amount of energy will remain constant (law of conservation of energy), but the total entropy will increase with every process (see also Figure 6).

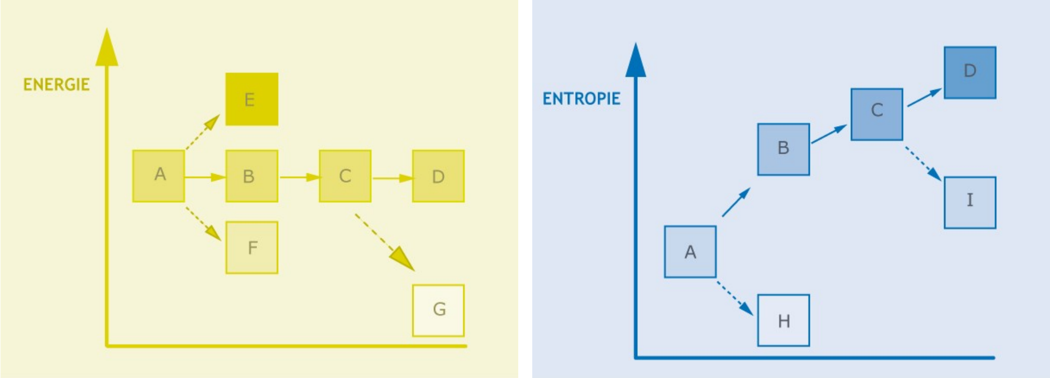

***Figure 6:** The fundamental difference between energy and entropy. In three consecutive processes (indicated by solid arrows) the total energy is constant, while the total entropy increases. Other processes (indicated by dotted arrows) cannot occur.*

If at constant temperature (T) a certain amount of heat (ΔH) is added, the entropy change is: $\Delta S = \Delta H / T$. This means that we can express the entropy change of the environment in terms of the amount of heat given up or absorbed by the process to the environment:

$$\Delta H_{\text{omgeving}} = -\Delta H_{\text{systeem}}$$

This gives filled:

$$\Delta \mathrm{S}_{\text{systeem}} + \Delta \mathrm{S}_{\text{omgeving}} > 0 \Leftrightarrow$$

$$\Delta \mathrm{S}_{\text{systeem}} - \frac{\Delta H_{\text{systeem}}}{T} > 0 \Rightarrow$$

$$\frac{\Delta H_{\text{(systeem)}}}{T} - \Delta \mathrm{S}_{\text{(systeem)}} < 0 \Rightarrow \Delta H \;\; - T\Delta \mathrm{S} \;\; < 0$$

Thus, to assess whether or not a process can proceed, we do not need to measure anything of the environment! It is sufficient to judge whether applies: . It is not always necessary to calculate this, in some cases looking at the signs suffices. We describe three situations, which correspond to the processes we described at the beginning of the section.

Situation 1: **$\Delta H < 0$ and $\Delta S > 0$** ⇒ $\Delta H - T\Delta S < 0$

If ΔH is negative and ΔS is positive, both rules for spontaneous processes are satisfied. Nothing, except the activation energy to be overcome, prevents the process from proceeding spontaneously. Examples of this are combustions, including explosions.

Situation 2: **$\Delta H > 0$ and $\Delta S < 0$** ⇒ $\Delta H - T\Delta S > 0$

We see the opposite when ΔH is positive and ΔS is negative: both unfavorable factors for the process to proceed. Examples of such reactions are reverse burns. Their occurrence is very unlikely: carbon dioxide and water will therefore not react to form gasoline and oxygen. Nevertheless, some reserve is necessary. In photosynthesis, carbohydrate (glucose) does form from carbon dioxide and water; 6 CO_2 + 6 H_2O → $C_6H_{12}O_6$ + 6 O

This endothermic process with entropy reduction (!), indispensable for our life, can therefore only take place under irradiation of light (supply of energy) and with a series of enzymes (biological catalysts) in the plant.

Situation 3: **$\Delta H > 0$ and $\Delta S > 0$** or **$\Delta H < 0$ and $\Delta S < 0$** ⇒ $\Delta H - T\Delta S < 0 \Leftrightarrow 0$

The third possibility is very interesting: ΔH and ΔS have the same sign. It is then possible that the following holds: $\Delta H - T\Delta S = 0$.

An example is the preparation of ammonia gas from the elements, an exothermic reaction. As an aside, the activation energy is high and therefore a catalyst is indispensable.

N_2(g) + 3 H_2(g) → 2 NH_3(g)

ΔH is negative, ΔS is negative (the number of moles of gas decreases). For the decomposition of ammonia into the elements, the reverse is true:

2 NH3(g) → N2(g) + 3 H2(g) (ΔH is positive, ΔS is positive).

As a result, both reactions occur simultaneously (the reactions are "reversible"):

N2(g) + 3 H2(g) → 2 NH3(g)

The driving force behind the reaction to the right is energy reduction. The driving force behind the reaction to the left is the entropy increase. This can create an equilibrium state (see Chemistry Block 5), a compromise between these two driving forces. After setting the 'dynamic' equilibrium, both reactions proceed at the same rate, so that the concentrations remain constant.

Because $\Delta H - T\Delta S = 0$, or $\Delta H = T\Delta S$, the equilibrium state allows entropy changes to be determined.

Make Assignments 9 and 11 in Appendix 3

2.4 Blue Energy models

As discussed in Chapter 3, there are two ways to generate energy from flowing water. The first way uses height differences, the second (Blue Energy) uses (salt) concentration differences. We compare both forms of energy generation.

In the Netherlands there is also a difference in height, although between Lobith and Hoek van Holland over a length of about 200 kilometers there is a drop of barely ten meters. This situation differs considerably from that in alpine countries, where there is large-scale use of running water. With flowing water, ten meters of drop corresponds to a water pressure of 1 bar (1 bar = 1×10^5 Pa = 1×10^5 N m^{-2}).

When mixing fresh and salt water, one also speaks of a pressure difference: the **osmotic pressure difference**, a concept that is also widely used in biology. If a salt solution is in contact with water via a semi-permeable membrane, water molecules move from the water through the membrane into the salt solution. Thus, if the salt solution is in a vertical tube, there will be a difference in height between the fluid levels: the osmotic pressure. This is the pressure delivered by the water column in the equilibrium situation. That equilibrium situation occurs when the pressure of added water column is as great as the force with which the water is driven to the side with the strongest concentration.

The formula of the osmotic pressure p of a table salt solution is:

Formula (5) $$p = 2cRT$$

where:

- c = concentration of salt in mol per liter (mol L^{-1})
- R = general gas constant (8.31 J mol^{-1} K^{-1})
- T= temperature in kelvin (K).

That factor of 2 is because table salt splits into two ions (Na^+ and Cl^-).

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It may be a little odd that the above formula contains the gas constant R. As you may have seen, the formula has similarities with the general gas law: $pV = nRT$. In this, p is the pressure and V is the volume, n represents the amount of gas. The Dutchman van 't Hoff proved that this formula can also be applied to solutions. For a concentration of a salt, c = n/V applies. Substitution in the gas formula then gives . You can see from this formula that the osmotic pressure is directly proportional to the concentration of dissolved particles. Van't Hoff was awarded the Nobel Prize for his work on osmosis. If you want to know more about osmosis look in a biology textbook.

We can also explain the energy generation from Blue Energy by using the rules for the course of reactions and the concept of entropy. For this we use two different models.

Model 1

We follow 1 liter of river water as it flows into the sea and assume in this model that it is mixed with infinitely many liters of sea water, so that the salt concentration of the mixed water is equal to that of the sea. We further assume that the river water contains no salt and that in the sea only table salt is dissolved. Finally, we neglect temperature differences and density differences between river water, sea water and the brackish water obtained.

The energy to be gained then comes exclusively from the entropy increase. With these assumptions, this energy is equal to TΔS. If the entropy increase ('mixing entropy') is known, the energy released is fairly easy to calculate.

This model is used in assignment 14.1.

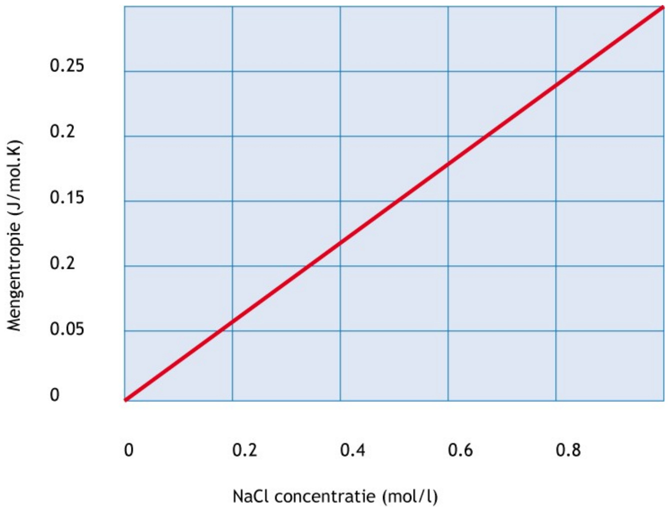

***Figure 7:** Entropy change of a NaCl solution when mixed with an infinite amount of concentrated NaCl solution.*

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Model 2

In Model 1, it was assumed that 1 liter of river water mixes with infinitely many liters of seawater. It is more realistic to develop a formula in which there are still unconfined volumes. The energy ΔE (in joules) released during mixing can then be calculated using:

Formula (6)

$$\Delta E = 2RT\left[c_z \cdot V_z \cdot 2{,}3 \cdot \log\left(\frac{c_z}{c_m}\right) + c_r \cdot V_r \cdot 2{,}3 \cdot \log\left(\frac{c_r}{c_m}\right)\right]$$

where:

- R = gas constant (8.31 J mol^{-1} K^{-1})
- T = temperature in kelvins (K)
- Vz, Vr = volumes in liters (L) of sea water and river water to be mixed
- cz, cr, cm = concentrations of salt in mol per liter (mol L^{-1}) in sea water, river water, and the mixed water, respectively.

The factor of 2 is again because table salt is split into two ion species in the solution. If necessary, review Math Block 6 for more information on the logarithm.
This model is used in assignment 14.3.

Make Assignments 13, 14.1 and 14.2 in Appendix 3

3. How do we convert Blue Energy into electricity?

In the previous chapters, you learned that the Blue Energy technique can be used to extract energy from salt concentration differences in river and sea water.

- This chapter will show you the techniques you can use to extract energy from salt gradients.
- In addition, you'll learn what that means for Blue Energy and how energy is generated from mixing fresh and salt water.
- You'll also learn about redox reactions, redox potentials, and membrane potentials here.

3.1 Four production techniques

The benefits of Blue Energy are great. This energy is renewable, because ultimately the sun is the energy source. No greenhouse gases such as carbon dioxide are released and no pollutant gases such as sulfur and nitrogen oxides. In addition, the required water types are available free of charge and in virtually unlimited quantities.

The principle of generating energy from running water is no different from that of the old-fashioned bicycle dynamo or the turbine in a power plant. The challenge with Blue Energy is to find a production technique with good efficiency so that little energy is lost.

We discuss four ways to use the salt gradient for energy extraction.

Katchalsky machine

A technique devised by the Israeli biophysicist Katchalsky (1914-1972). He observed that some fibers shrink in salt water and stretch again in fresh water. In principle, this is enough to power a machine, and working models have been made. A belt of collagen (a glue-forming protein, main component of connective tissue) rotates over two discs (pulleys). The disks are connected by a chain through gears of varying diameter. The collagen is alternately wetted by salt water, which causes the material to shrink, and by fresh water, which causes it to stretch.

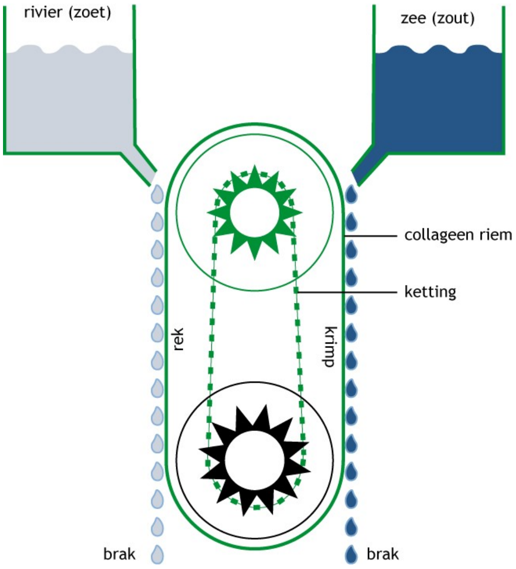

Figure 8: *Energy extraction from salt gradient. Katchalsky machine.*

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Vapor Pressure Difference Utilization (VPDU)

This method uses differences in vapor pressure above the salt water and fresh water. The setup includes a vessel with two compartments separated by a copper plate. Pressure differences between the vapor above the fresh water and that above the salt water create a water vapor stream in the direction of the salt water. In this vapor stream, a turbine converts the kinetic energy of the water molecules into electrical energy. The evaporating water cools down and is brought back to temperature by the heat of condensation on the seawater side through the heat exchanger.

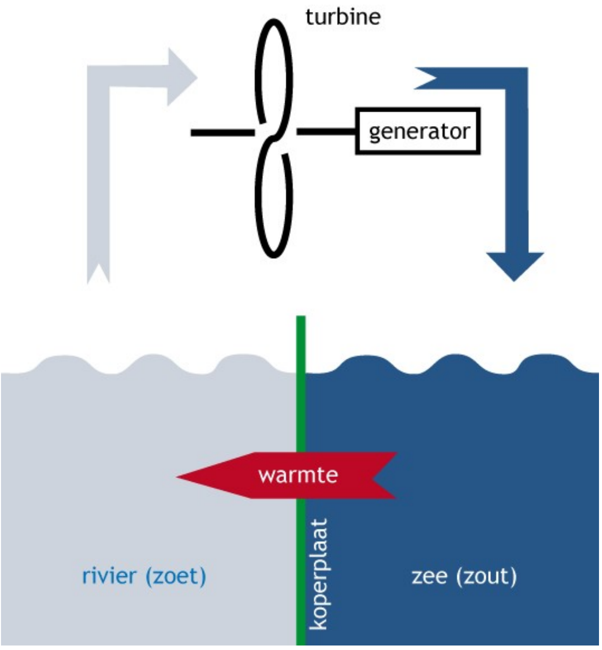

Figure 9: *Energy extraction from salt gradient. Vapor Pressure Difference Utilization.*

Pressure Retarded Osmosis (PRO)

This method relies on osmosis. Salt and fresh water are pumped into a pressure chamber, separated by a semi-permeable membrane. Due to the osmotic pressure difference, the fresh water will flow through the membrane into the salt water compartment. This causes the water pressure in the saltwater compartment to increase, causing the water to flow out of the compartment, driving a turbine.

This method is called pressure retarded osmosis, because the river water is transported through the membrane against the water pressure. Power is at its maximum at a water pressure equal to half the osmotic pressure difference between river and sea water.

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The power output is the product of the water pressure and the flow rate (the amount of water flowing through the pressure chamber per second). In Norway in particular, a small group from the energy company Statkraft is exploring this technique.

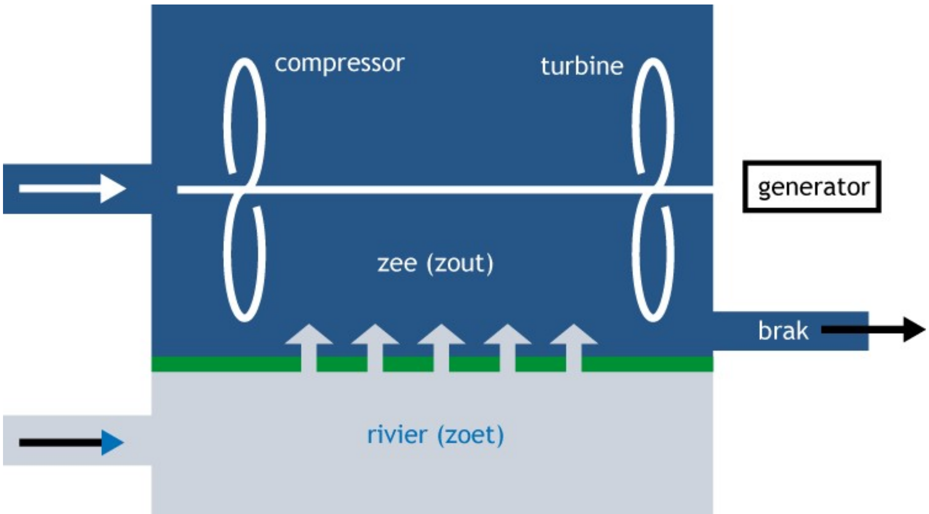

Figure 10: *Energy extraction from salt gradient. Pressure Retarded Osmosis.*

Reverse Electrodialysis (RED)

The aforementioned techniques use mechanical methods to generate electrical energy. The advantage of Reverse Electrodialysis (RED) is that the plant has no moving parts for direct production, although pumps are required for fresh and salt water supply and for electrode rinsing. We will discuss this technique in more detail.

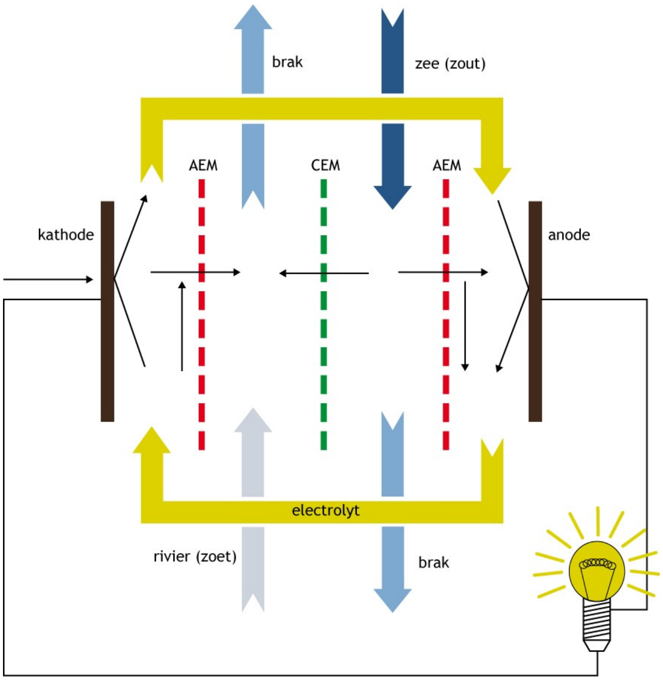

Figure 11: *Energy extraction from salt gradient. Reverse Electrodialyses.*

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3.2 Direct electricity generation with RED

Figure 20 shows a schematic drawing of the setup for electricity generation with RED. The setup consists of two parts: the compartments separated by membranes, through which the water flows (blue in Figure12) and the electrodes where the electricity is generated (yellow).

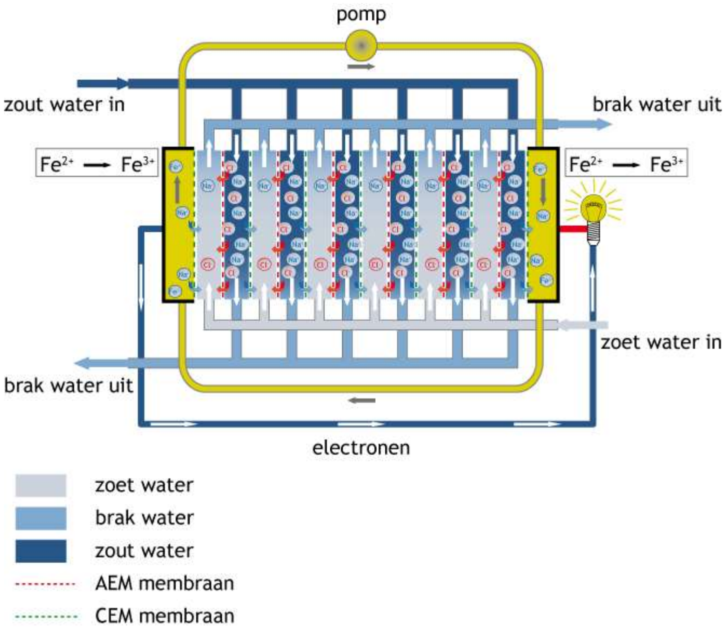

Figure 12: *Reverse Electro Dialysis (RED) or reverse electrodialysis.*

Through the compartments flows seawater and river water, separated by membranes. The seawater and river water cannot now mix, because the membranes do not allow water to pass through. However, the ions dissolved in the seawater can diffuse through the membranes. The membranes have special properties that allow the sodium ions and the chloride ions in the seawater to both diffuse in different directions.

In the drawing, the negative chloride ions go to the left and the sodium ions go to the right. So both ionic currents cause a (positive) current to flow to the right. This ionic current still has to be converted into an electron flow, or electricity. This happens at the electrodes, through redox reactions, where at one electrode (the anode, in the figure on the left) an electron is released (Fe^{2+} $Fe^{3+} + e^-$), which then flows through a live wire the other electrode (the cathode, in the figure on the right), where it is used again (Fe^{2+} $Fe^{3+} + e^-$)

We now look at the two components of the RED (the membrane-separated compartments and the electrodes) in more detail.

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Compartments and membranes

The heart of the RED consists of freshwater and saltwater compartments, which are separated by **ion-exchange membranes**. The RED plant has two types of membranes, neither of which allows water to pass through: an **anion exchange membrane** (AEM) and a **cation exchange membrane** (CEM). The anion-exchange membranes can only transport anions - negative ions, for example chloride from seawater. The cation exchange membranes can only transport cations - positive ions, for example sodium from seawater. The plant contains alternating CEMs and AEMs, see Figure 12.

Looking in more detail at how those membranes are constructed, all the ion-exchange membranes used here appear to consist of two parts: a **skeleton** and an ion-exchange group. The skeleton consists of organic polymers (macromolecules) such as polyethene, polystyrene or PVC. Polythene is the cheapest plastic; it is also used to make garbage bags. The difference between **CEM** and AEM membranes has to do with the **ion exchange group**. In CEM, the ion-exchange group is usually the sodium salt $\sim SO_3^-Na^+$. The sign ~ indicates the binding of the sulfonic acid residue to the solid skeleton. Thus, the membrane contains large (negative) sulfanic ions and small (positive) sodium ions. As a result, this membrane is exclusively permeable to positive particles: a sodium ion inserted at one end takes the place of another sodium ion. That other ion goes to the next place, etc. etc. etc. At the very opposite end, a Na^+ ion leaves the membrane. The membrane allows only Na+ ions to pass through and no Cl^- ions. The latter cannot enter the membrane due to the repulsion between two minus charges.

In **AEM**, the active group is also a salt, bound to the skeleton. A simple salt is $\sim NH_3^+Cl^-$. The AEM membrane allows only Cl^- ions to pass through. Na^+ ions cannot enter the membrane due to the repulsion between two positive charges. There are also AEM membranes in which the hydrogen atoms have been replaced by methyl groups. The formula of this ion-exchange group is $\sim N(CH_3)_3^+Cl^-$.

The spaces between the membranes, the compartments, are alternately flushed with seawater and with river water, which remain separated by the membranes that do not allow water to pass through. However, the dissolved salt ions of the seawater can mix with the salt ions of the river water. Sodium ions in the seawater can only diffuse through the CEM and move to the right in the drawing, causing a positive ion flow to the right. The chloride ions pass through the AEM, forming a negative ionic current to the left, which can be construed as a positive current to the right.

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Redox reactions

The ionic current must now be converted into an electron flow, or electricity. This is done at the electrodes, through redox reactions, which are chemical reactions that involve the transfer of electrons. The Background document, chapter 6 explains a little more about redox reactions.

Make Assignments 15, 16, 17 and 18 in Appendix 3

The RED works like an electrochemical cell. An example of such a cell is the Daniell cell, which is the subject of the following demonstration experiment.

Demonstration test: the electrochemical cell

As an example of an electrochemical cell (a battery), the Daniell cell is taken. This is one of the oldest known cells, named after the English physicist J.F. Daniëll (1790-1845). This cell is constructed as follows (Figure 13):

- Half-cell I consists of a beaker slide containing a 1.0 M CuSO4 solution. In it is a copper rod.
- Half-cell II is constructed in the same way as half-cell I, but now with a zinc rod in a 1.0 M ZnSO4 solution.
- The copper rod and the zinc rod are connected, via wires and a light bulb. A voltmeter is also connected.
- Both half cells are connected with a salt bridge.

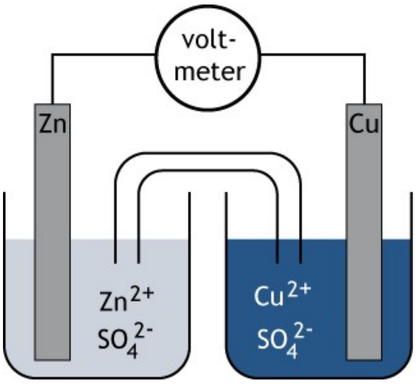

Figure 13: *Daniell cell.*

a. Using the voltmeter, determine the (+) and (-) pole.

b. What is now the direction of electron flow through the leads?

c. Devise the reaction equation for the process that occurs at the copper electrode.

d. Also devise the reaction equation for the process occurring at the zinc electrode.

e. After a few days, the supply of current through the Daniell cell will cease. Think of two possible causes for this.

We measure a voltage, a current flows. How is this possible? Both half-cells contain particles, namely metal atoms and ions of that metal that can interact:

$Cu^{2+} + 2\,e^- \leftrightarrows Cu$

$Zn^{2+} + 2\,e^- \leftrightarrows Zn$

Zinc is more base than copper, so zinc donates electrons more easily than copper. In this case, zinc will go into solution, thus releasing electrons. In half-cell II, the following half-reaction occurs:

$$Zn \rightarrow Zn^{2+} + 2\,e^-$$

These electrons pass through the wire to half-cell I where they are absorbed by copper ions. The following semi-reaction occurs in half-cell I:

$$Cu^{2+} + 2\,e^- \rightarrow Cu$$

This causes the copper rod to get thicker and thicker and the zinc rod to go into solution. The reaction stops when the copper ions run out or, more unlikely, the zinc rod runs out.

The voltmeter result shows that the copper rod has a higher potential than the zinc rod. The copper rod is therefore the + pole and the zinc rod the - pole. This also follows from the reactions that occur:

- Electrons are released from Zn and react with Cu^{2+} The zinc bar becomes negatively charged (by the released electrons) and is therefore the negative electrode.
- Because Cu^{2+} ions take up electrons, the copper rod is continuously short of electrons. This is therefore the positive electrode. This electron deficit is replenished by the electrons released at the zinc electrode. Electrons flow from - to +, thus from the zinc rod through the wire to the copper rod.

The salt bridge creates a closed circuit. Without the salt bridge, the voltmeter will not read. The salt bridge consists of a gel made with a saturated salt solution. Thus, the salt bridge contains many mobile ions that make up for the charge deficiencies in the half-cells:

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- In half-cell I, Cu^{2+} is converted to Cu. The solution in half-cell I becomes increasingly negative. The salt bridge compensates for this by sending positive ions into the solution of half-cell I.
- The same reasoning applies to half-cell II. In this half-cell, more and more Zn^{2+} ions enter (the zinc rod reacts to Zn^{2+}), so the solution becomes more and more positive. This too is counteracted by the salt bridge bringing negative ions into half-cell II.

Figure 14 shows what the charge transport in the Daniell cell and the similar electrolysis cell looks like schematically.

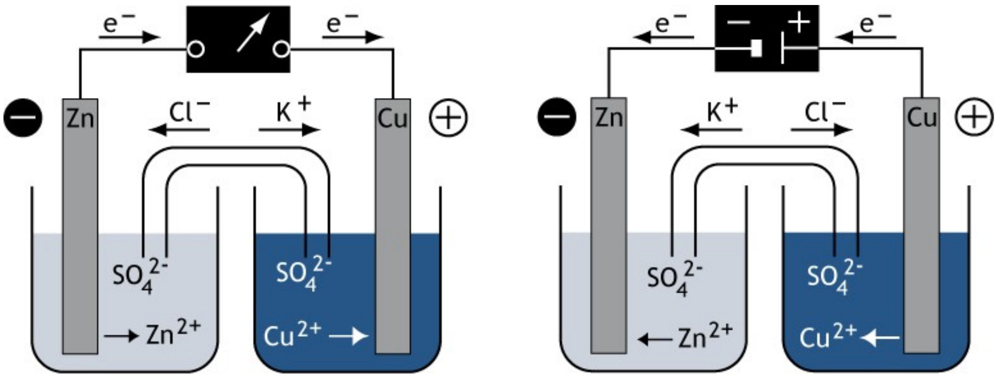

Figure 14: *Electron and ion flow in a Daniell cell (left) and an electrolysis cell (right).*

This process is an example of a redox process:

Ox: $Cu^{2+} + 2\,e^{-} \rightarrow Cu$ | 1x

Red: $Zn \rightarrow Zn^{2+} + 2\,e^{-}$ | 1x

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

How much voltage can such a cell (battery) supply? The formula for determining this is as follows:

Formula (7) $$V_{\text{bron}} = V_{\text{ox}} - V_{\text{red}}$$

The potentials for the half-reactions is given in Binas table 48. These apply to standard conditions (all concentrations 1.00 M and 298 K and p = p0).

This is the case with the Daniell cell described here. Thus, this battery can supply 1.10 V:

$$V_{\text{bron}} = V_{\text{Cu}^{2+}} - V_{\text{Zn}} = 0{,}34\ \text{V} - \left(-0.76\ \text{V}\right) = 1{,}10\ \text{V}$$

Make Assignment 19 and 20 in Appendix 3

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If the concentrations deviate from 1.00 M, the corresponding potentials also deviate from the Binas values. The potentials can then be calculated using Nernst's equation (see Binas Table 37D):

Formula (8) $$V = V_0 + \frac{RT}{nF}\ln\frac{[\text{ox}]}{[\text{red}]} = V_0 + \frac{0,059}{n}\log\frac{[\text{ox}]}{[\text{red}]}$$

Where:

- V = voltage in volts (V)
- V0 = electrode potential at standard conditions (Binas table 48) in volts (V)
- R = gas constant (8.314 J mol^{-1} K^{-1}, see Binas table 7)
- T = temperature in kelvin (K)
- n = number of mol electrons transferred per mol oxidizer
- F = Faraday's constant (9.6485·10^{4} Cmol^{-1}, see Binas table 7)
- [ox], [red] = concentrations of the particles in the half-reaction under consideration. Note: the concentration of a solid is set to 1 M, as in the equilibrium constant.

This gives for a Daniell cell, where the concentration of the $CuSO_4$ solution is 0.10 M and that of the $ZnSO_4$ solution is 0.50 M:

Half-cell I:

$$V = 0,34 + \frac{0,059}{2}\log\frac{0,10}{1} = 0,31\text{ V}$$

Half-cell II:

$$V = -0,76 + \frac{0,059}{2}\log\frac{0,50}{1} = -0,77\text{ V}$$

$$V_{\text{bron}} = V_{\text{ox}} - V_{\text{red}} = 0,31 - \left(-0,77\right) = 1,08\text{ V}$$

Nernst's equation uses logarithms. If necessary, see Background Chapter 5 for a recap of logarithms

Make Assignment 21 and 22 in Appendix 3

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In the RED (see Figure 12), an iron couple is used, where at the anode (in the figure on the left) Fe^{2+} is oxidized to Fe^{3+} and at the cathode (on the right) Fe^{3+} is reduced to Fe^{2+}. Thus, an electron is released at the anode and flows to the cathode via a live wire: an electric current is generated.

Although the operation of the electrodes in a RED are similar to the operation of a Daniell cell, there is also an important difference: the RED electrodes both use the same redox couple Fe^{2+}/Fe^{3+}. Therefore, the voltage difference that occurs is not due to the redox reactions, but to the ion transport through the membranes. This is depicted in Figure 15 for a CEM. A slightly modified version of the Nernst equation applies to the potential across a membrane:

Formula (9)

$$V_{\mathrm{bron}} = \frac{RT}{nF}\ln\frac{[\mathrm{Na}^+]_z}{[\mathrm{Na}^+]_r} = 0{,}059\log\frac{[\mathrm{Na}^+]_z}{[\mathrm{Na}^+]_r}$$

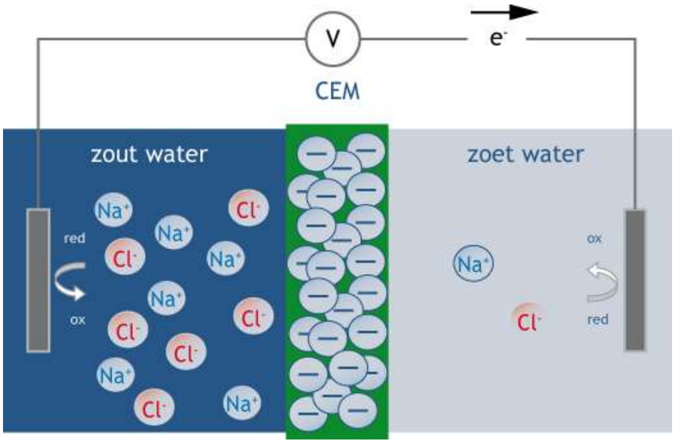

Figure 15: *Ion transport through a cation exchange membrane (CEM).*

Stacking ion-exchange membranes in a RED creates an accumulation of voltage sources with the same source voltage. You can therefore add these together. At the electrode of a RED we then measure the sum of all source voltages, the so-called stack voltage.

Make Assignment 23, 24.1 and 24.2 in Appendix 3

4. How much power can we make?

Chapter 2 showed that mixing of river water and seawater releases energy. Chapter 3 explained how this mixing energy is converted into an electric potential in a RED plant.

- In this chapter you will learn how to calculate how much power you can get out of a RED.

4.1 Electric circuit

In the RED of Figure 12, a light bulb is connected to the RED. When this lamp is replaced by a voltmeter, no current can flow, as the resistance of such a voltmeter is very large. A stack to which no device is connected is called an unloaded stack. By switching many membranes in a row in a stack, the desired voltages can be made (task 24.2). With a stack of, say, 13 membranes, the stack voltage is about 1 volt, as long as the stack is unloaded. With N membranes, the voltage of the unloaded stack (**the open circuit voltage, OCV**) is:

Formula (10) $$OCV = (N-1) \cdot V_{bron}$$

Where:
- OCV = open circuit voltage in volts (V)
- N = number of membranes
- V source = source voltage in volts (V).

When we connect a device, for example a light bulb, to the RED stack a current starts flowing. As a result, the stack voltage is no longer equal to the OCV. In fact, two currents flow simultaneously:

- **An internal ion transport** from salt to fresh water: negatively charged chloride ions flow towards the anode and positively charged sodium ions flow towards the cathode. Thus, a positive charge flows from anode to cathode. This charge current is as large as ('equivalent to') the electric current. During the charge transport the ions lose part of their energy due to friction. We can think of this friction as internal resistance.
- **An external electric current** of electrons from -pole to +pole. The electrons flow through the connected device that has a certain external resistance, and in doing so, they donate electrical energy to the device. A light bulb, for example, lights up, converting electrical energy into light and heat.

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We can represent the above in the circuit shown in Figure 16. In this, the left side is the stack containing a voltage source and an internal stack resistor Ri (i of internal). The device is connected to the poles of the stack and has a resistor Ru (u from external). The voltmeter (V) measures the stack voltage, the ammeter (A) measures the current.

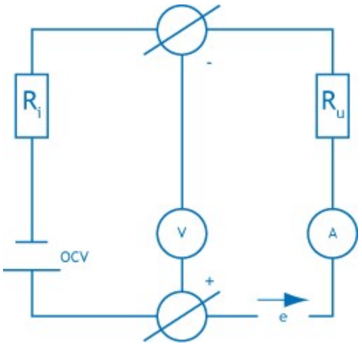

Figure 16: *schematization of stack and connected device.*

The resistors R_i and R_u are in series. It follows from the well-known relationship between voltage, current and resistance ( ) that the stack voltage U is not equal to the OCV:

$$U = I \cdot R_u = OCV - (I \cdot R_i)$$

For the current I (in amps), the following holds true:

$$I = \frac{OCV}{R_i + R_u}$$

Thus, the power delivered by the stack P (in watts) is:

$$P = U \cdot I = I^2 \cdot R_u = \left(\frac{OCV}{R_i + R_u} \right)^2 \cdot R_u$$

To compare small and large RED installations, the specific power p is important. This is the power generated per m^2 of membrane area A. The unit of p is therefore W m^{-2}:

Formula (11) $$p = \frac{P}{N \cdot A}$$

Make Assignments 25, 26 and 27 in Appendix 3

Thus, the power output depends on three variables:

- the open circuit voltage *OCV*,
- the external resistance R_u,
- the internal resistance R_i.

If we want to get the electrical power as large as possible, we will have to consider these three terms. You already examined the first term in Chapter 3. The second term you looked at in questions 25 through 27. All that remains is the internal resistance.

4.2 Internal resistance of RED

Before we can discuss the influence of internal resistance on the RED's power output, let's look at what is meant by **electrical resistance**. Electrical resistance is the property of materials that makes the passage of electric current difficult; it requires energy. The simplest "device" to study this resistance is a metal wire. The electrical resistance of a metal wire is given by:

Formula (12) $R = \rho \cdot \frac{\ell}{A}$

Wherein:
- R = resistance in ohms (Ω)
- ρ = specific resistance in ohm-meter ($\Omega m^2\ m^{-1} = \Omega m$)
- l = length in metres (m)
- A = area in square meters (m^2).

You may already know this law (**Pouillet's law**) from physics class. In Background Chapter 7, its derivation is briefly repeated. The inverse of specific resistance is the **(specific) conductivity** (σ) or **conductivity**:

Formula (13) $\sigma = \frac{1}{\rho}$

Specific conductivity is expressed in siemens per meter ($S\ m^{-1}$). The unit siemens (S) is the inverse of the unit of resistance ohm. Siemens is therefore also called mho by electrical engineers.

Make Assignment 28 in Appendix 3

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As with the transport of electrons through a wire or device, charge transport in the stack also requires energy: the ion flow also experiences resistance, it requires energy. This internal resistance (R_i), like 'ordinary' electrical resistance, depends on the length, cross-sectional area (the surface area) and the specific resistance or conductivity of the substances.

The internal resistance of a RED stack follows from the following formula ($N = 1,3,5\ldots$):

$$R_i = \frac{(N-1)}{2}\cdot\left(R_{\text{CEM}} + R_r + R_{\text{AEM}} + R_r\right) + R_{\text{CEM}} + R_{\text{elektr}}$$

For a stack with many membranes (e.g. $N>11$), this can be simplified to:

$$R_i \approx \frac{(N-1)}{2}\cdot\left(R_{\text{CEM}} + R_r + R_{\text{AEM}} + R_r\right)$$

The internal resistance then consists of the following partial resistances:
- of the cation-exchange membranes R_{CEM}
- of the layer of river water between the membranes R_r
- Of the cation exchange membranes R_{AEM}
- of the layer of sea water between the membranes R_z.

$$R_i = \frac{(N-1)}{2}\cdot\left(R_{\text{CEM}} + R_r + R_{\text{AEM}} + R_z\right) + R_{\text{CEM}} + R_{\text{elektr}} \approx \frac{(N-1)}{2}\cdot\left(R_{\text{CEM}} + R_r + R_{\text{AEM}} + R_z\right)$$

The resistance of the membranes is known to the manufacturer, who speaks of the so-called surface resistance. A typical value is 3 Ωcm^2 or $3\cdot10^{-4}$ Ωm^2. It follows from Pouillet's law that this is the specific resistance times the length, i.e. $\rho\cdot l$. The length in this case is the thickness of the membrane, because the ions pass through the membrane from one side of the membrane to the other. Thus, the resistance of a membrane with a surface area of 1 m^2 is $3\cdot10^{-4}$ Ω.

The resistance of river water and seawater also follows from Pouillet's law. The conductivity of salt solutions such as river water and seawater is measured with a conductivity meter or salinometer. The more salt dissolved in the water, the better the conductivity. For seawater of 30 g NaCl L^{-1} at a temperature T = 298 K the conductivity is about 50 mS cm^{-1} = 5 S m^{-1}, for river water of 1 g NaCl L^{-1} it is 2 mS cm^{-1} = 0.2 S m^{-1}. If the distance between the membranes is known, the resistance of each layer of sea water and river water can be calculated.

Make Assignments 29.1 and 29.2 in Appendix 3