

CHAPTER 1

The Challenge of Water Splitting in View of Photosynthetic Reality and of Research Trends

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1.1 Introduction

For half a century and two generations, physical chemistry and electrochemical science have been confronted with the challenge of artificial water splitting using solar light. The dream of a sustainable energy technology based on a cheap photocatalyst providing hydrogen from water splitting has stimulated a lot of research initiatives and has seen the rise of several new research disciplines: semiconductor photoelectrochemistry, interfacial science, photocatalysis, nano-material science, dye solar cell development and research on quantum size phenomena. It became clear that the real challenge is not liberating hydrogen from water. For this much-investigated process, cheap catalytic electrodes such as Ni–Mo alloys or NiMoN_x catalysts,

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on carbon supports, were identified, which can successfully replace the best performing Pt, since they keep the overpotential loss below 100 mV.¹⁻³

The big challenge turned out to be the evolution of oxygen, which involves the transfer of four electrons from water. A lot of progress in understanding basic mechanisms has been achieved over the years and many interesting new materials and catalysts were discovered. While scientists rightly feel that significant advances have been achieved and fully justified repeated funding initiatives towards solar energy utilisation, there are, however, some critical problems: few practically thinking analysts feel that an economically feasible photocatalytic water splitting technology is close to application. As outlined in Chapter 10, it is the much lower cost of hydrogen from fossil fuel, which is an important handicap, while the engineering aspects of solar water electrolysis are quite advanced.

Major technical obstacles towards cost reduction are the long-term instability of wet solar energy converting interfaces, the instability of catalysts, too high overpotentials for oxygen evolution, the formation of aggressive radical intermediates, theoretical problems in describing, understanding and tailoring multi-electron transfer, practical geometries for water splitting technology, the difficulty in handling high proton turnover rates and the cost of applied (noble) metal catalysts.

Facing a progressive deterioration of the environment our industrial civilisation requires convincing scientific and technical progress towards sustainability in energy technology. Here, the solar water splitting strategy remains an unequalled option, which, through photosynthesis, has also shaped and safeguarded the climate on earth.

To better understand the difficulties, and in order to learn what evolution has solved more elegantly and practically with photosynthesis and its fuel circuits than modern research, this analysis aims at a comparative evaluation. The challenges of energy conversion handled in nature should be compared with both past and present scientific and technical efforts aimed at solving the same problems. The aim is to identify key areas, into which extension of our knowledge is desirable or even unavoidable. An analysis of why such challenges have not yet been addressed before will be included. Figure 1.1 compares a simplified scheme for the solar water splitting strategy in nature (plants plus animals, left) with a scheme for a programmed technical solar hydrogen economy (centre). To the right a more general presentation of nature's energy-material strategy is given, which also emphasises its elegance in dealing with sustainable materials.

Nature has implemented a series of physical chemical technologies which cannot, at present, be reproduced technically: electronic processes are used for photon energy harvesting and fuel cell operation, because this is unavoidable, but proton gradients and proton currents are preferred for energy storage and production of mechanical and chemical energy (ATP). Nature is also, evidently, much more efficient in dealing with catalysis and, by fixing carbon dioxide, also provides materials for living activities. How the entire biological energy-material strategy could be approached bio-mimetically for

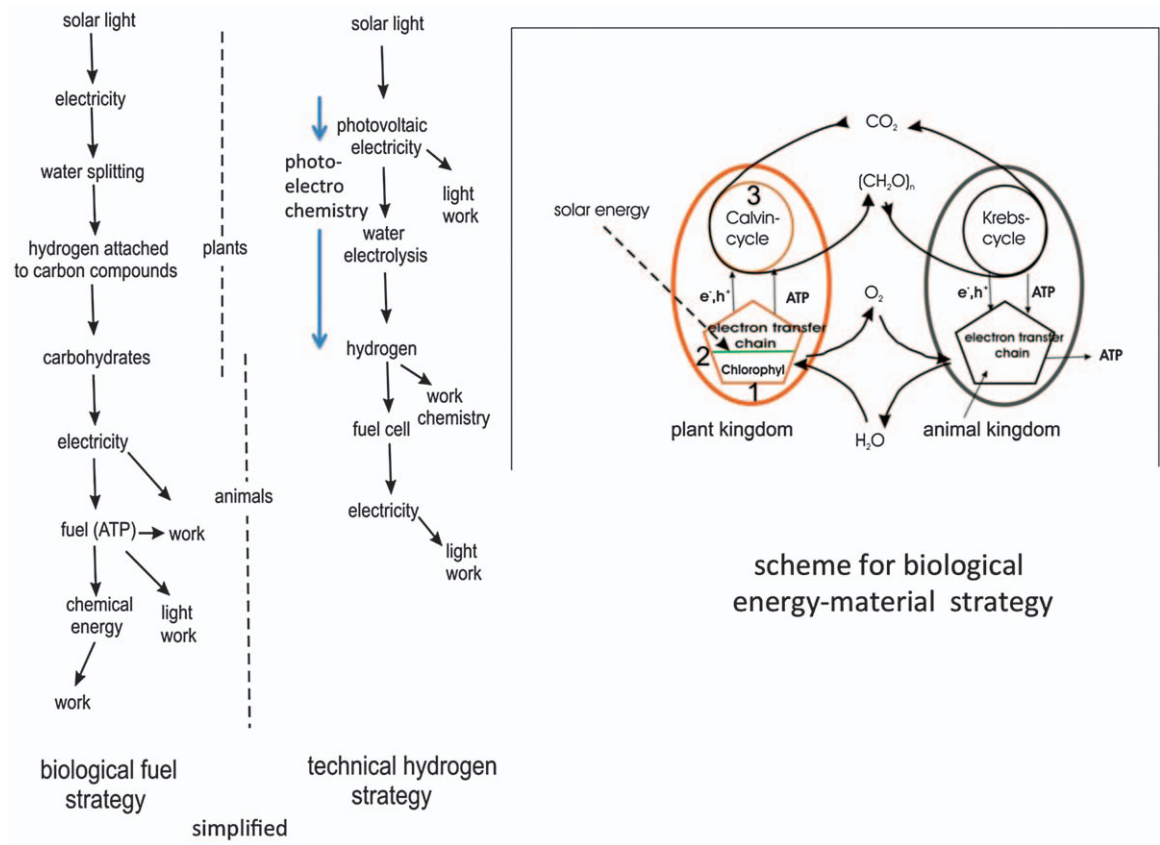


Figure 1.1 The scheme to the right explains the energy-material strategy applied in living nature. To the left two schemes are shown which compare essential energy steps in biology and in projected artificial hydrogen technology (centre).

human civilisation has been discussed elsewhere.⁴ For the simplified artificial solar hydrogen energy technology (Figure 1.1, centre) the key challenge is the cost of sustainable hydrogen from water splitting. It is at present approximately five times more expensive than hydrogen from natural gas. Making the process of photo-induced water splitting more efficient and cost-effective is here the key challenge.

1.2 The Evolution of Natural Photosynthetic Water Splitting: The Most Remarkable Facts

Oxygen-evolving photosynthetic-bacteria started to exist on earth around 3.2–3.5 billion years ago.⁵ Before their arrival, anoxygenic photosynthesis already existed. Here, molecules with greater negative oxidation potentials than water were used as electron donors. For major phyla of photosynthetic bacteria like Cyanobacteria it is accepted that at the very beginning of water splitting photosynthesis worked more or less as at present. The evolutionary discoveries for sustainable energy conversion were so well functioning that they were conserved and no simpler or more elegant water splitting mechanism has been discovered since. What were these pioneering inventions which evolution introduced? Let us first, for comparison, look at a modern artificial water splitting system:⁶ a photovoltaic cell supplying electricity *via* two wires for water electrolysis into oxygen and hydrogen. Photo-generated electrons and holes are separated by a thermodynamic potential gradient, permanently imprinted into a silicon or related junction, fabricated at high temperature. In photo-electrochemical cells the junction is present in the semiconductor interface bordering the liquid. From the generated electricity, electrons are extracted from water at a catalytically optimised electrode interface.

What nature solved differently is well known: materials are not fabricated at high but at ambient temperature *via* dynamic self-organisation processes. No permanent thermodynamic potential gradient is used for the separation of photo-generated charges. Charge separation occurs kinetically, *via* specially tailored molecular mechanisms, and occurs at 3 ps in purple bacteria, strangely speeding up to a shorter time of 0.9 ps at 1 K. When the excited species is transferring an electron the singlet state is, among other temporary changes, converted into a triplet state *via* a simultaneous inversion of a nuclear spin (Figure 1.2, left). A back reaction of the electron transferred is strongly suppressed. When a far from equilibrium thermodynamic kinetic model for the electron transfer was calculated⁷ considering autocatalytic feedback, a negative effective activation energy, a very fast rate and a negligible reverse reaction resulted. The activated complex behaves as a transient ‘dissipative structure’ (term used by Prigogine’s group to describe self-organised order built up at the expense of energy dissipation and entropy generation). It obtains the energy not from entropy fluctuations, but from the reaction itself. The feedback is assumed to occur *via* the protein

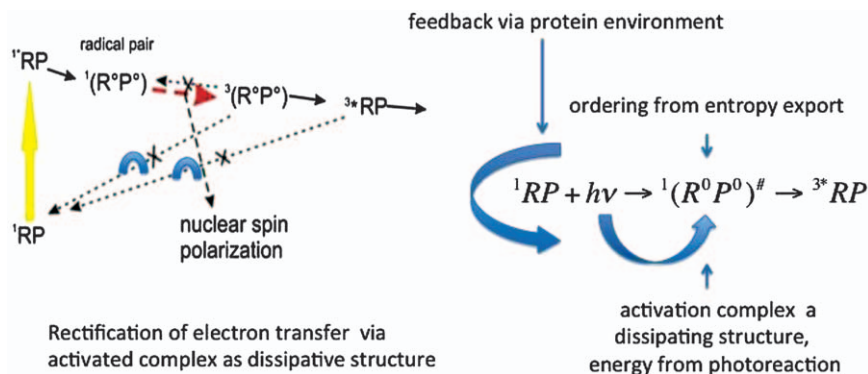


Figure 1.2 Nature in photosynthesis does not use an imprinted potential barrier for charge separation during water splitting but generates perfectly rectified electron transfer *via* a singlet–triplet transition in the excited radical pair facilitated by simultaneous nuclear spin polarisation (left). Electron transfers of this type, which considers polarisation and feedback of the environment leading to an activated, dissipative complex, is not accessible *via* Marcus theory (right).

environment (mechanism explained in Figure 1.2, right). Solar energy conversion here follows the principle of kinetic charge separation: not a thermodynamic potential gradient, but rectifying molecular-electronic mechanisms are responsible for charge separation.

Also dye solar cells, based on nano-material photo-electrochemistry, work due to kinetic charge separation. They only function well with a poorly reversible redox system such as I^-/I_3^- . The power output P of such kinetic solar cells, as well as the primary solar energy conversion process in photosynthesis, follow different laws, as compared with classical solar cells with inbuilt potential gradient. The mechanism has been derived from the principle of least action.⁸ It turns out that the power, P , of such kinetic solar cells is proportional to the rate constant w and the chemical affinity A of the system (eqn (1.1)). The latter (A) describes the distance from equilibrium and increases as the distance from equilibrium increases. Similarly, the rate constant (w) also increases as the back reaction is suppressed. This confirms that the kinetic solar cell only works well, when electron transfer is highly rectified and operation is pushed far from equilibrium.

$$P \approx wA \quad (1.1)$$

This will also be true for primary solar energy conversion in photosynthesis and is not the case for classical water splitting photoelectrochemical cells. There is a big advantage from such a biological strategy. By designing molecularly rectified electron transfer it is also possible to operate solar cells with soft materials produced at ambient temperature. They do not have to be stable against internal ion movement, which would gradually

degrade any imprinted thermodynamic potential gradient for charge separation.

Another remarkable difference between the biological and the technical approach is the nature of the electrochemical oxidation process of water. We are, in photosynthesis, definitively dealing with a multi-electron process of water oxidation. For the oxidation of water to molecular oxygen ideally a minimum of four times 1.23 eV of energy would have to be supplied. However, when a first electron is extracted approximately 2.8 eV would already be required for generating an OH radical. Only an efficient catalyst can avoid such an activation barrier by properly binding and handling intermediates. The best technical electrodes for water oxidation, such as RuO_2 , typically require, at 12 mA cm^{-2} of current density an overpotential of 250 to 350 mV. In contrast, an overpotential of only 60 mV is estimated for photosynthetic water splitting at a comparable current density for water oxidation⁹ (Figure 1.3) and should attract our special attention (see below). What could nature have accomplished to bypass limitations, which science and technology have experienced on the basis of electrochemical research and what is exactly the experimental evidence for

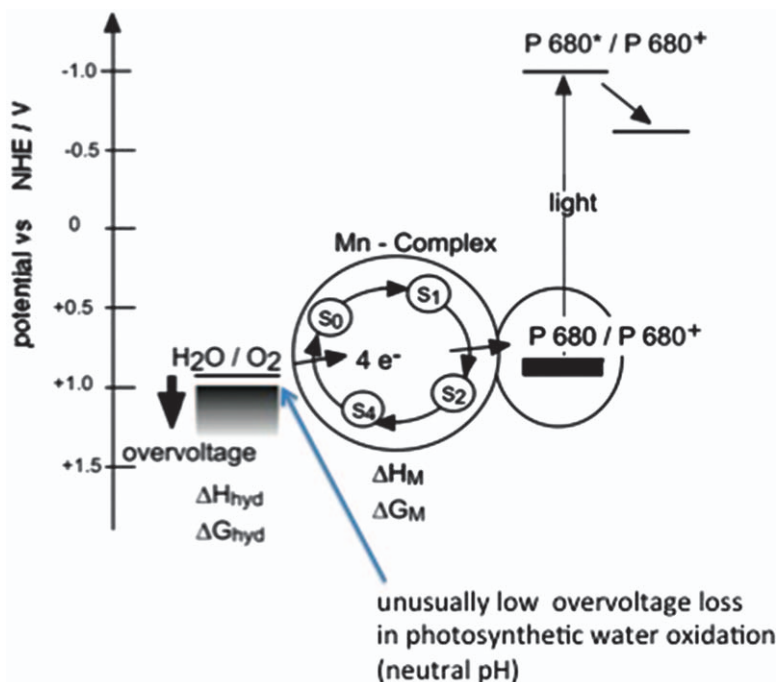


Figure 1.3 Potential scheme explaining the energetic conditions for oxygen evolution in photosynthesis (at neutral pH). Photoexcitation in the reaction centre leads to a stepwise oxidation of the $\text{Mn}_4\text{O}_5\text{Ca}$ -complex, which then induces oxygen evolution at an estimated current density of 12 mA cm^{-2} with only 60 mV overpotential losses.

such extraordinary electrochemical behaviour in photosynthesis? According to the author this is the most central question within the water splitting initiative. It should give an answer to both mysteries, that of high oxygen evolution efficiency and that of the use of the abundant transition metal manganese for catalysis.

1.2.1 The Missing Overpotential in Photosynthesis: What Is the Evidence?

The photooxidation process of water in photosynthesis is initiated by electron transfer from chlorophyll P680 to Plastquinone Q_A, *via* several intermediates, which generates the cationic radical P680⁺. This abstracts all together step-by-step, *via* a tyrosine Y_Z, four electrons from the manganese containing catalyst, whereby O₂ is evolved during the last step.^{10,11}

As pointed out in detail by Watanabe *et al.*⁹ there is a paradox linked with the oxygen evolution capacity of the oxygen evolution system: The redox potential of the Chla/Chla⁺ couple has been extensively measured. Six independent measurements, for example, confined a redox potential value in the following range (eqn (1.2)):⁹

$$E_0(\text{Chla}/\text{Chla}^+) = +0.807 \pm 0.045 \text{ V vs. NHE} \quad (1.2)$$

Dimerisation of chlorophyll is known to shift the potential even more negative so that complex formation cannot easily be used as an argument for a more positive shift of the redox potential. However, the reversible potential of the H₂O/O₂ couple and thus for oxygen evolution is (eqn (1.3)):

$$E_0 = +1.230 \text{ V} - 0.059 \text{ pH} \quad (1.3)$$

which, for a pH = 6 or pH = 5 solution in the thylakoid internal liquid, would yield a value of (eqn (1.4)):

$$E_0(\text{pH: 6}) = +0.876 \text{ V} \quad \text{and} \quad E_0(\text{pH: 5}) = +0.935 \text{ V} \quad (1.4)$$

respectively. The values obtained are surprisingly close to that of the Chla/Chla⁺ couple and do not account for electrochemical energy losses. Geometrical estimations within the photosynthetic system have shown that under typical conditions of photosynthetic solar energy conversion, the manganese centres carry effective oxidation current densities of 12 mA cm⁻².⁹ Under such conditions even the best artificial catalysts for oxygen evolution (*e.g.* RuO₂) require an overpotential of 250–350 mV.^{9,12} But the overpotential loss in photosynthetic oxygen evolution is estimated to only 60 mV.

Up to 300 mV of oxidation potential are missing, when photosynthetic oxygen evolution is compared to classical electrochemical experience, not speaking of the use of the abundant transition metal manganese for catalysis.

To understand how nature could accomplish electrochemical processes, which require a significantly smaller overpotential than typical technical electrochemical processes, some general considerations on energy limitations for water splitting are helpful. In laboratory experiments on water splitting with platinum black and RuO_2 electrodes it was shown that more than 90% of photovoltaic energy can be converted into chemical energy of hydrogen.¹³

These experiments demonstrate that by combining efficient photovoltaic devices with efficient water electrolysis using noble metal catalysts overall efficiencies for solar energy conversion in the range between 10 and 30% are technically possible. In this mentioned experiment¹³ (Figure 1.4), which combined a 20% efficient laboratory tandem solar cell with electrolysis *via* noble metal electrodes at 90% efficiency, an 18% total efficiency for hydrogen generation was confirmed in the laboratory. This appears to be a very high efficiency and it is a quite positive prospect for technical solar electrolysis of water, when comparing it to the 3% energy conversion efficiency into biomass for productive C4 plants during their growth period, and 0.5% biomass efficiency for a sugar cane field with three harvests over the year. But nature in photosynthesis follows not only the aim of energy conversion, it also turns over materials, provides energy for living activities themselves and deals with many issues of survival. Our technology has the advantage of being able to design water splitting mechanisms for energy conversion only, and could therefore become much more efficient than a living organism. However, we would have to

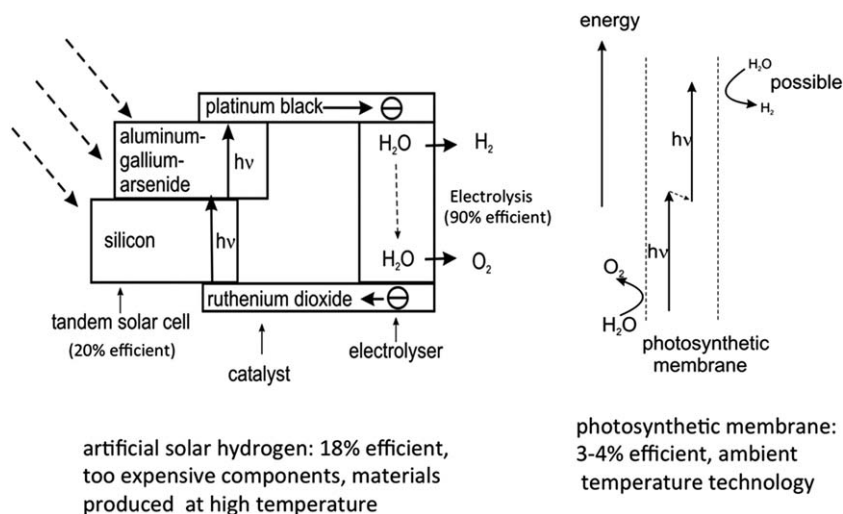


Figure 1.4 Schematic illustration of photovoltaically driven electrolysis cell (left), which yielded 18% efficiency for hydrogen evolution using a 20% efficient tandem photovoltaic cell.¹³ To the right the qualitatively equivalent process in a photosynthetic membrane is sketched.

learn to do that without expensive photovoltaic technology and without noble metal electrodes. We need therefore to explore principles, which allow implementation of cheap photocatalytic water splitting. Here biomimetic strategies could help us. For this reason, we should learn to understand the principles, involved in the natural energy conversion process. Water electrolysis itself can approach 100% efficiency, when the energy is adequately provided. This is possible because the energy conversion efficiency for water splitting is determined by the ratio of enthalpy turnover (enthalpy change) for water splitting ΔH_{hyd} and for catalyst (manganese complex) function ΔH_{M} (see Section 1.3.1 below). The question now arises, how such a ratio of enthalpies could be manipulated to yield an electrochemical efficiency higher than empirically known from technical electrochemistry and the properties of the best technical catalyst for water splitting, RuO_2 electrodes.

1.3 How Can Photosynthetic Water Oxidation Be More Efficient Than Technical?

The oxygen evolution reaction in photosynthesis (photosystem II + water oxidation system) is, because of its relevance for life and as a model for regenerative energy conversion, one of the most intensely studied processes in science.^{14–20} But it is also one of the most intriguing ones, to which numerous theoretical studies have been dedicated.^{21,22} After the approximate nature of the manganese complex became known, many artificial manganese complexes have been synthesised to mimic oxygen evolution.²¹ However, the efforts were essentially in vain. Theoretical calculations even suggested so high energy barriers for oxygen evolution that equilibrium structures of manganese clusters were considered not to be able to oxidise water.²² Distorted non-equilibrium clusters were consequently invoked.²² In spite of these apparent complications the oxygen evolution reaction from water is, in photosynthetic literature, typically considered to be preceded by a stepwise oxidation of the manganese complex. This essentially occurs *via* manganese states. The three to four residues within the surrounding amino acids are expected to essentially stabilise the cluster and to adjust charges. Various concepts on the function of $\text{Mn}_4\text{O}_5\text{Ca}$ clusters and their interaction with water have been developed.²³ Basically, the interaction of the nanostructured $\text{Mn}_4\text{O}_5\text{Ca}$ cluster with water should be understood as an ordinary electrochemical oxidation reaction of water. It should, however, not be overlooked that manganese compounds have never shown catalytic activity in any relevant scientific-technological process. It was for this reason, and because classical (Marcus) electron transfer theory is not allowing to consider multi-electron transfer without intermediates, that self-organised multi-electron transfer catalysis has been suggested as a possible mechanism of oxidative water splitting.^{24,25} Why is it necessary and why must irreversible thermodynamics be invoked?

1.3.1 Thermodynamics of Photo-induced Water Splitting

The thermodynamic limit of efficiency η_{hyd} for driving the hydrolysis reaction has been investigated in some detail in the past with respect to technical electrolysis.²⁶ The efficiency was found to be determined by eqn (1.5):

$$\eta_{\text{hyd}} = \frac{\Delta H_{\text{hyd}}}{\Delta G_{\text{hyd}} + \text{losses}} = \frac{\Delta G_{\text{hyd}} + T\Delta S_{\text{hyd}}}{\Delta G_{\text{hyd}} + \text{losses}} \quad (1.5)$$

with ΔH_{hyd} and ΔG_{hyd} being the enthalpy and free energy change, respectively, for the reaction $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$ (the losses could arise from resistance losses or overpotentials). Eqn (1.5) means that the temperature dependent entropy change occurring during water splitting has to be accounted for in the overall reaction.

Now it has to be considered that the manganese complex will mediate the photogenerated energy (the photogenerated holes). Some of the introduced energy (from the reaction center) will also be dissipated during the build-up and termination of the water splitting process which requires the free energy $\Delta G_{\text{hyd}} + \text{losses} = \Delta G_{\text{M}} + \text{losses}$ (ΔG_{M} determines the free energy which has to be provided by the manganese complex for water splitting to which energy losses have to be added that occur during hydrolysis and which also have to be supplied by the manganese complex) (Figure 1.3). For comparison: if water would be photo-oxidised by a semiconductor, ΔH would correspond to the forbidden energy gap and ΔG to the (much smaller) light intensity dependent photo-induced splitting of the Fermi-level. The energy lost due to relaxation of charge carriers from the energy bands will contribute to $T\Delta S$. A catalytic semiconductor photoelectrode, the energy band gap of which is well matched to the energetic requirements of electrolysis will involve a much smaller $T\Delta S$ loss than a photoelectrode with excess band gap.

The efficiency for providing the necessary energy for hydrolysis *via* the manganese complex will thus be (eqn (1.6)):

$$\eta_{\text{M}} = \frac{\Delta G_{\text{M}} + \text{losses}}{\Delta H_{\text{M}}} \quad (1.6)$$

with ΔH_{M} being the enthalpy with $\Delta H_{\text{M}} = \Delta G_{\text{M}} + T\Delta S_{\text{M}}$, and $\Delta G_{\text{M}} + \text{losses}$ the sum of free energy provided plus additional losses during hydrolysis, which will eventually occur. The total efficiency (η_{tot}) will thus become (eqn (1.7)):

$$\eta_{\text{tot}} = \eta_0 \eta_{\text{M}} \eta_{\text{hyd}} \sim \eta_{\text{M}} \eta_{\text{hyd}} \sim \frac{\Delta G_{\text{M}} + \text{losses}}{\Delta H_{\text{M}}} - \frac{\Delta H_{\text{hyd}}}{\Delta G_{\text{hyd}} + \text{losses}} \quad (1.7)$$

where η_0 considers the remaining losses in the complex photosynthetic water splitting system, and η_{hyd} only considers the anodic part of the hydrolysis reaction, which occurs in the manganese complex (eqn (1.8)):



Since water splitting will occur when the free energy generated in the manganese complex matches the free energy requirement for hydrolysis, that is when, in eqn (1.7), $\Delta G_{\text{hyd}} + \text{losses} = \Delta G_{\text{M}} + \text{losses}$ the total thermodynamic efficiency for photosynthetic oxygen evolution will be (eqn (1.9)):

$$\eta \sim \frac{\Delta H_{\text{hyd}}}{\Delta H_{\text{M}}} \quad (1.9)$$

or, since ΔH_{hyd} and ΔH_{M} are given thermodynamic quantities, and since the necessary free energy has to be provided by the manganese complex ($\Delta G_{\text{M}} \approx \Delta G_{\text{hyd}}$):

$$\eta \sim \frac{\Delta H_{\text{hyd}}}{\Delta G_{\text{hyd}} + T\Delta S_{\text{M}}} \quad (1.10)$$

Eqn (1.10) is an interesting result, since it clearly shows that the entropy loss or turnover ($T\Delta S_{\text{M}}$) in the manganese complex is a most critical factor for the efficiency of water splitting. This seems trivial at the first glimpse, because the dynamics of the manganese complex will define its catalytic activity. The situation will become more interesting when the following question is asked: how would evolution of the chemistry and dynamics of the manganese complex have responded to such a boundary condition?

1.3.2 How Did Evolution Optimise Photosynthetic Water Oxidation?

It should now be investigated how nature, during evolution, could have improved oxygen liberation from water. At first, of course, a decrease of the entropy loss ($T\Delta S_{\text{M}}$) in eqn (1.10) would have improved the efficiency (Figure 1.5). The contribution of entropy production to the overpotential in electrochemical processes has been discussed in the literature.²⁷ A stepwise improvement of the manganese complex to reduce the entropy losses would have been necessary. A better matching of electronic states for positive charges in the manganese complex with respect to states in the Chla/Chla⁺ redox system would be an example. But would the minimisation of this quantity have finally stopped the energetic improvement of the manganese complex? It is proposed that this was not the case. The manganese complex could have ‘learned’ to invert the sign of entropy, that is to generate negative entropy (negentropy), chemical electronic order (within the manganese complex) (Figure 1.5), which is possible through self-organisation. In this way, the process would have shifted from reversible to irreversible thermodynamics. Practically this could have worked in the following way: the mineral hollandite ($\text{Mn}_4\text{CaO}_9 \cdot 3\text{H}_2\text{O}$), believed to have been adapted for early biological water splitting activity, would have been incorporated into a dynamically self-organised molecular energy conversion process with

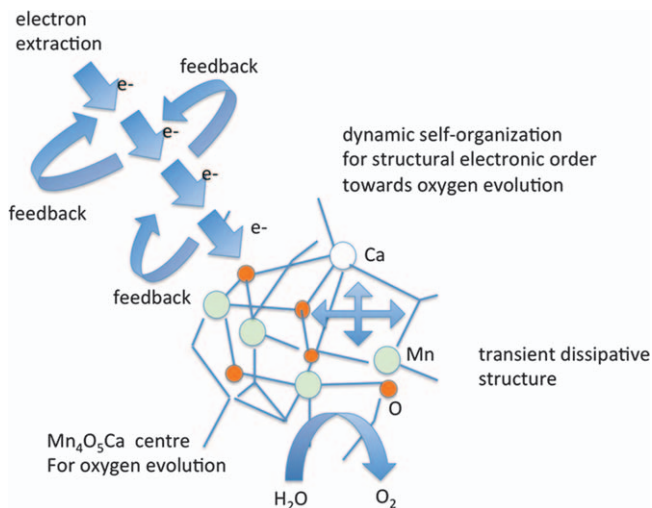


Figure 1.5 To reduce the overpotential loss for water splitting in photosynthesis the manganese Mn₄O₅Ca complex was allowed to develop, *via* feedback processes, an activation complex in the form of a dissipative (dynamically ordered) structure. With this complex a multi-electron transfer, without intermediates, is possible.

feedback processes allowing local entropy reduction at the expense of increased entropy production elsewhere.

The positive sign of the entropy term in eqn (1.10) would have gradually changed to a negative one (eqn (1.11)):

$$\eta \sim \frac{\Delta H_{\text{hyd}}}{\Delta G_{\text{hyd}} - T\Delta S_{\text{Neg}}} \quad (1.11)$$

thus, permitting a further increase of efficiency η (in eqn (1.11) the sign of ΔS has been inverted to show the possibility of further decreasing the denominator. ΔS_{Neg} has therefore to be introduced as a positive quantity). This may have happened by allowing feedback processes *via* the protein environment of the manganese complex. A negative activation energy facilitated by an activation complex functioning as a dissipative structure allowed to build-up favourable temporary dynamic order within the manganese complex for efficient oxygen evolution. Mathematically this can be shown in a similar way as demonstrated for the activated complex in primary photosynthetic charge separation.⁷ However multi-electron transfer would be the preceding reaction.^{24,25} Nature would, after systematically decreasing entropy losses in the manganese complex, have simply discovered that increasing dynamic order and generating negentropy within an activation complex, functioning as a dissipative structure, would have allowed to continue optimisation. It would have been optimisation towards maximum entropy turnover, within the given restraints, for the entire photosynthesis system.

What were the preconditions for such further improvements? First the process had to shift to a situation sufficiently far from thermodynamic equilibrium, a condition which was not difficult to fulfil in the combination with the second condition: autocatalytic feedback loops *via* the protein environment would have been needed to allow dynamic build-up of order during the last step of the manganese complex cycle, during which oxygen is evolved. To accomplish this some energy would have to be channelled through this feedback loop to maintain the structural order during catalysis.

The option for evolution of water oxidation efficiency, evident from eqn (1.10), to follow up the decrease of entropy losses by changing the sign of the entropy term (eqn (1.11)) implies a very 'elegant' strategy: some energy is converted into structural order (or information, negative entropy) which may significantly improve catalytic activity (such property of information handling is also known from other catalytic centres in biology²⁸). In this way, a catalytically non-suspicious manganese catalyst may have been upgraded to become highly catalytic. However, a shift from a reversible thermodynamic situation (eqn (1.10)) to irreversible thermodynamics would also be a transition to new efficiency relations, so that eqn (1.11) with entropy inverted to negentropy can only be understood as a formula indicating a trend of development.

The explanation proposed here for this paradox of missing overpotential would be, that evolution indeed succeeded in developing dynamic self-organisation by supplying the manganese complex with dynamic steric order or information (negentropy) and thus significantly increasing efficiency as evident from transition from eqn (1.10) to eqn (1.11). The entire process will consequently not be subject to reversible thermodynamics any more, but to non-linear irreversible thermodynamics. Local transient entropy reduction, or entropy export, of course, occurs at the expense of overall entropy production within the photosynthetic system.

1.3.3 How Could Such a Self-organisation Mechanism Be Experimentally Dealt With?

The key claim from the presented analysis is that during photosynthetic oxygen evolution the manganese complex is not generating entropy but negentropy. It is manifesting itself in molecular electronic order within an activation complex, which is generated as a self-organised, 'dissipative structure'. Approximately 0.2–0.3 V of potential difference, which correspond to 0.2–0.3 eV per electron, which are not available as oxidation potential, should therefore be made available as negentropy for the oxygen evolution process. This would amount to up to $-105 \text{ J mol}^{-1} \text{ K}^{-1}$, that is 105 entropy units of negentropy. To give a point of reference, approximately 300 entropy units of decreased entropy have been detected through thermodynamic studies to occur during the light induced Bacteriorhodopsin cycle.^{15,29} Such a significant entropy decrease involves a quite substantial increase of order,

and may be compared to an entropy increase, that accompanies the unfolding of a protein like lysozyme (though in the opposite direction). This means that a search should be undertaken for a transient entropy decrease occurring during photosynthetic oxygen evolution or with model systems using calorimetric techniques. The magnitude of negentropy change required would be reasonable and significantly smaller than that observed during the bacteriorhodopsin photoreaction. Also in this case the negentropy gain has been associated with a synergetic mechanism of energy transduction.³⁰

The arguments developed in this contribution directly support the proposal that the kinetic efficiency of photosynthetic oxygen evolution is based on transient, dynamic self-organisation. In order to show that the activation complex becomes a 'dissipative structure' (a local decrease of entropy) it is sufficient to assume that a small portion of the available energy is used *via* a feedback loop involving the protein environment of the manganese complex. The mathematical procedure will be more or less the same as for the calculation of the self-organised activation complex in primary photosynthesis (Figure 1.2).⁷

As indicated in Figure 1.5, the proposed mechanism for photosynthetic oxygen evolution which achieves a transient build-up of negentropy (structural order or information) will involve autocatalysis. After accumulation of the required charges in the manganese complex, the transfer of the first electron from water will stimulate the transfer of the second and so on. Some energy will of course be needed for the feedback loops *via* the protein environment. It will be ultimately derived from photon energy. Calculations show that sufficient non-linear feedback will lead to self-organisation of electrons during electron transfer and catalysis.^{24,25} The first electron slaves the other electrons which means that one mathematical equation will describe the interdependent behaviour of all transferred electrons. No radical intermediates will be formed that way and a real multi-electron transfer, as described by eqn (1.8) will be possible. Such a multi-electron process is excluded by classical (Marcus) theory, which only allows subsequent individual electron transfer steps and does not consider polarisation and feedback coupling *via* the environment. Order is built up during such a self-organisation process, equivalent to negentropy. This negentropy, corresponding to a negative activation complex in form of a dissipative structure,⁷ will increase the efficiency of oxygen evolution as indicated in eqn (1.11) and may be the ultimate reason why manganese clusters are catalytic in photosynthesis but not behaving exceptionally well in traditional electrochemical experiments (where autocatalysis and self-organisation does not occur). Manganese has apparently been selected by nature to provide optimal coordination chemistry, whereby four manganese centres within a protein matrix are better for building up and releasing order (negentropy) than two manganese centres. The manganese complex may, in fact, have also evolved for the purpose of withholding oxygen evolution during the charging process, until, when the autocatalytic process (*via* the protein environment)

provides negentropy and order, the four-electron transfer from water occurs. The proposed autocatalytic nature of the oxygen evolution process would also have the consequence that this mechanism would be highly non-linear. In fact, clear oscillative oxygen evolution transients have been reported for photosynthetic systems.³¹

An important consequence from these considerations would also be that understanding the presently evidenced structure of the manganese complex would not yet reveal its full function. Its dynamics and its non-linear reaction behaviour has to be evaluated and quantified before the reactivity of this unparalleled catalyst can be understood. This situation also explains why the large number of artificial manganese cluster compounds did not give evidence for high catalytic activity (see also below).

Mathematically the expected strategy in nature has been calculated and it was found that extraction of the first electron from water indeed leads to a 'slaving' of the following ones. An energy efficient multi-electron transfer becomes possible. One can talk about self-organised electron transfer (Figure 1.5).^{24,25}

Such a notion of self-organised electron transfer for multi-electron catalysis appears to open a new frontier, but faces a quite fundamental theoretical problem, when considering quantum mechanical calculation. When electrons move in a molecular system, there will be an immediate effect on electron density around. There will be a polarisation of the environment. However, with the now well-established Marcus theory for electron transfer^{32,33} consideration of such a polarisation is not possible. It consequently does not allow consideration of feedback mechanisms either. This would in addition require a distinction between 'before' and 'after', which is not evident for a quantum process (into the time dependent Schrödinger equation classical time was introduced *via* perturbation theory).

1.4 Progress with Artificial Photo-electrochemical Water Splitting

Here is an evaluation of the trends and state of artificial water splitting. The first realistic interest in light induced water splitting arose with the advent of photoelectrochemistry and the study of oxides with large energy gaps such as ZnO, TiO₂ and SrTiO₃. TiO₂ turned out to be reasonably stable and became the prototype of a photocatalyst releasing oxygen from water.³⁴ Many material studies followed, including nitrides and oxynitrides and oxides doped for band gap tailoring, in the hope to learn about the art of catalytic water splitting.³⁵ However TiO₂ and related oxide materials simply extracted a first electron from water at a potential of +2.8 V forming a radical, instead of extracting all four electrons near the thermodynamic potential of 1.23 V. Such a mechanism of radical formation automatically eliminates the ability of a system for high energetic efficiency, since 1.5 eV of energy are already dissipated during the first electron transfer step. TiO₂ nevertheless received

a tremendous amount of attention, which finally led to its successful secondary application in self-cleaning interfaces.^{36,37} Because of the need to use visible light for solar energy conversion many water splitting studies were focussed on semiconductors with lower energy gaps such as Si, GaAs, GaP, CdS, CdTe, InP, CuInSe₂. Much experience has been accumulated.^{38–40} But many open questions remain, for example as to a practical geometry of water splitting systems. A coiled up, light transparent tube with an internal photovoltaic/catalytic membrane was proposed, which is separating hydrogen generation from oxygen generation. With water in the tube the gases could be transported to a fuel cell and heat to a heat exchanger.⁴⁰

While hydrogen evolution and oxygen evolution was observed and optimised with numerous materials, a persistent problem turned out to be electrode degradation in contact with aqueous solutions. The reasons were quite understandable. The holes generated in the valence bands of these semiconductors were simultaneously eliminating chemical bonds from the electrode material. Whenever holes were allowed to accumulate in the interface the integrity of the crystalline electrode structure was consequently bound to collapse. An additional problem turned out to be reaction products such as elemental hydrogen that reacted, for example, with surface bound P, in InP, to yield toxic PH₃ gas. Only selected materials were proposed to be practical for hydrogen evolution. Quite a lot of research on water splitting catalysis still focuses on photo-induced hydrogen evolution, considering the oxidation of chemicals as sacrificial processes. As a more recent review with 267 references shows,⁴¹ a main emphasis is focussed on TiO₂ and other oxides such as ZrO₂, KTaO₃, SrTiO₃ or BiVO₄, which show conduction bands suitable for hydrogen evolution, when supported by added catalysts or dopants. An example is TiO₂ covered by gold particles.^{42,43} The involvement of TiO₂ excitons with Au plasmons is invoked for explaining efficient hydrogen evolution. This may be scientifically interesting, but also shows some exaggeration in the orientation of modern water splitting research as compared to photosynthetic reality. When nature aims at hydrogen evolution, which occurs under special conditions, hydrogenases are used as catalysts, which apply abundant transition metals. An impressive example of a useful hydrogen evolution catalyst is an ‘iron only’ catalyst operating in certain bacteria (*Clostridium pasteurianum*, *Desulfovibrio* spp., *Scenedesmus obliquus*). Turnover frequencies for hydrogen evolution of 10 000 s⁻¹ have been measured.⁴⁴ The overpotential is very low, comparable to and even lower than for platinum. How is nature able to apply abundant transition metals for efficient energy catalysis? The apparent trick is that the bonding around the catalytic centre, a few Fe–S clusters embedded within a protein, is stabilised through coordination *via* strong CO and CN bonds. Catalytic activity is facilitated while the catalytic centre is chemically preserved and stabilised. We need to understand more.

Catalysis of light induced oxygen evolution, however, remained a significant challenge. One research strategy was inspired by bio-mimetic considerations: electron transfer catalysis in photosynthetic structures is always

handled *via* centres of abundant transition metals. Their involvement makes sense because they can engage in coordination chemical mechanisms. Water does not necessarily react with a photo-generated hole in an interface. But if interfacial transition metals are oxidised by holes water species from the electrolyte will engage in coordination reactions. Hole reactions *via* d-states involve the attachment of water species. This requires transition metal compounds with valence bands derived from d-states of transition metals. Identified materials with energy bands suitable for harvesting visible solar light included RuS_2 , FeS_2 , PtS_2 , ZrS_2 , MoS_2 , MoSe_2 , WS_2 , and WSe_2 .^{45,46}

The photoelectrode RuS_2 actually turned out to oxidise water to molecular oxygen with a quantum efficiency of up to 60% while remaining stable.⁴⁷ Also, illuminated FeS_2 reacted with water. However, the OH^- species attached to the generated interfacial Fe^{3+} ion is passed on to the $(\text{S}_2)^{2-}$ sulfur pairs yielding $\text{S}_2\text{O}_3^{2-}$ species, which are soluble. As Figure 1.6 explains, this is the consequence of the energy state density distribution in the valence band. While the transition metal d-states of ruthenium and iron in RuS_2 and FeS_2 are forming the upper edge of the semiconductor valence band, the sulfur 3p states below are quite prominent in FeS_2 . This provides the possibility to shift attached water oxidation species to sulphur. A soluble product, sulfate is thus finally formed instead of molecular oxygen. Also, the freshly split Van der Waal surface of MoS_2 liberates molecular oxygen. But when increasingly step sites are formed, SO_4^{2-} is generated instead of O_2 . Such experience demonstrates that light induced coordination chemical reactions may lead to efficient oxygen liberation from water. No radical intermediates are formed and electrons are successively extracted from water *via* the coordination chemical complex formed. However, the

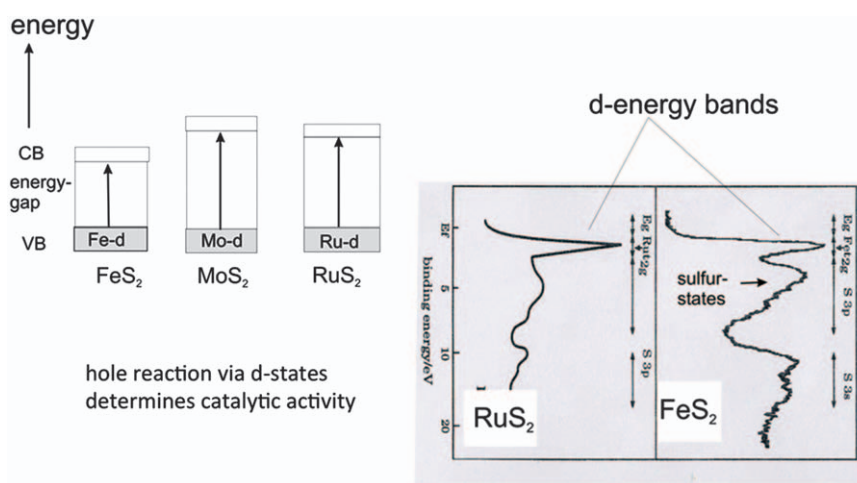


Figure 1.6 The valence band edges in the energy scheme of RuS_2 , MoS_2 and FeS_2 show strong transition metal d-character and facilitate coordination-type interaction with water species. When there is an overlap with S-p states, as in FeS_2 , corrosive side reactions leading to SO_4^{2-} are observed.

intermediate water species attached to the metal may switch to the sulfur or other catalyst components, when the corresponding states are energetically or spatially available for reaction. The conclusion to be drawn is that a quite high degree of electronic and steric order is required for a successful and efficient water oxidation. Ruthenium is, of course, a too expensive noble metal for water oxidation catalysis. But both, as photoelectrode in RuS_2 and as dark catalyst as RuO_2 , it provides the presently most efficient catalyst for oxygen evolution. RuO_2 undergoes under high pressure a phase transition from rutile, the most common phase, to marcasite, pyrite and fluorite structure. They yield metallic properties, with the exception of the fluorite structure, which shows semiconducting behaviour with a band gap of 0.47 eV.⁴⁸ Theoretical calculations show that in the metallic rutile conductor a sharp Ru-d peak is placed just below the Fermi level and clearly above a weak O-p distribution.⁴⁹ This corresponds to the specific density of state distribution measured for the valence band of RuS_2 (Figure 1.6).

Positive electronic charges generated by photoexcitation have consequently to be handled *via* pure transition metal d-states when electrons are to be extracted from water without side products. In addition, ruthenium offers oxidation states III, IV, and V, which are needed for accommodating four electrons for the liberation of one molecule of oxygen from water. A similar range of accessible oxidation states is only offered by Mn, which nature selected for the oxygen evolution cluster in photosynthesis, since it is the 12th most abundant element in the earth crust. Also, Mn in the photosynthetic water oxidation complex is mostly active *via* its oxidation states III and IV in the storage of positive charge, with a probable participation of Mn V during the final oxygen evolution step. Even though many details are known about manganese redox chemistry, and major efforts were developed towards understanding multi-electron transfer, a consistent concept of catalytic oxygen evolution is not yet available.^{50,51}

Recently, more and more attention is attributed to crystallised models for the Mn complex in photosynthesis such as CaMnO_3 , CaMn_2O_5 , $\text{Ca}_{1-x}\text{Pr}_x\text{MnO}_3$ and $\text{Ca}_{2-x}\text{Pr}_x\text{MnO}_4$.⁵²⁻⁵⁴ This is not surprising, since it had been suggested that systems preceding cyanobacteria originally assimilated the manganese complex as crystalline hollandite ($\text{Mn}_4\text{CaO}_9 \cdot 3\text{H}_2\text{O}$).⁵⁵ While catalytic properties significantly vary for different stoichiometries of calcium manganate crystals it can generally be said that oxygen evolution activity of these perovskites is modest compared to RuO_2 , and photoactive RuS_2 . Of course, it is even much more modest compared to the CaMn_4O_9 centre of photosynthesis. Deposited manganese oxide could be electrochemically activated for reasonable activity (1 mA cm^{-2} at an overpotential of 450 mV).⁵⁶ For $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, $\text{Ca}_{0.75}\text{Pr}_{0.25}\text{MnO}_3$ or $\text{Ca}_{1.75}\text{Pr}_{0.25}\text{MnO}_4$ the current density for oxygen evolution from water observed at an overpotential of approximately 460 mV was $50 \mu\text{A cm}^{-2}$.⁵³ This should be compared to a current density of 12 mA cm^{-2} observed with RuO_2 at an overpotential of 250–300 mV, or in photosynthetic oxygen evolution estimated to occur at an overpotential of only 60 mV. The manganese oxide model catalysts also

always show a significant degree of corrosive deterioration. Theoretical calculations indicate that in the energetic region, where electrons are accepted from water, calcium manganite O 2p states show significant overlapping with Mn 3d t_{2g} states.⁵⁷ This would explain the involvement of oxygen states from the manganese oxide in electron transfer reactions with the consequence of lower rates and electrochemical corrosion activities.

Another important research initiative concerns, of course, molecular studies of metal–organic manganese clusters in relation to the function of the oxygen evolution complex in photosynthesis. A review from 2004 already discusses 171 manganese clusters including 54 Mn_4 clusters, on the basis of 410 references.⁵⁸ Achieving a working analogue for the active manganese cluster in photosynthesis is considered one of the greatest challenges in bioinorganic chemistry. Until today this aim could not yet be approached in spite of sophisticated experimental tools and much progress in theoretical understanding of Mn–oxo complexes. The positions of Mn-3d states are apparently not optimised for reaction and they simply do not show the expected favourable water oxidation properties. The poor catalytic activity of artificial Mn–cluster complexes has already longer time ago been theoretically addressed.²² As explained *via* eqn (1.11) positive charges accumulating in them have low interest in reacting with water until they become involved in self-organisation for a build-up of temporary order (information) within an activation complex functioning as dissipative structure for energy efficient water oxidation. Such a (low entropy) activation complex may expose the required Mn-d states (not overlapping with oxygen states) for electron extraction from water. A theoretical model for self-organisation,⁷ when applied to Mn complexes, even suggests a negative activation energy, explaining the ‘missing’ overpotential for photosynthetic oxygen evolution.

1.5 Bio-mimetic Approaches Require Progress in Non-equilibrium, Irreversible Thermodynamics

This review has sketched the path of energy in photosynthetic water splitting and compared it to the rise in knowledge and practical experience in artificial photoelectrochemical water splitting. Half a century in this field has seen the development of understanding semiconductor junctions, of photo-induced interfacial reactions, of catalyst function, of nanomaterial properties and of mechanisms of bioinorganic chemistry. During the same period, many new materials became available and were studied with increasingly sophisticated experimental techniques. Significant progress in artificial water splitting has been achieved and an on-going progress is seen, as this book is documenting. But is it always a progress in the required direction?

It is presently not at all sure, whether technological water splitting, as we are investigating and handling it today, will ever reach the qualitative level

we see in nature. This is disturbing, considering the much higher overall efficiency which could be reached *via* an artificial technology, which could be better focussed on energy output. Photosynthetic oxygen evolution has reached a level, which has facilitated evolution of higher life and shaped our climate. If nature would not have been able to implement photosynthetic water splitting of that quality, humans would simply not exist. The challenge for industrial society to imitate that process has therefore to be taken seriously. It cannot be excluded, that efforts in artificial water splitting based on mechanisms shaped by reversible thermodynamics will reach a technological standard, which enables a breakthrough in harvesting solar fuel. This is, in fact, the projected aim of on-going projects. But the author is sceptical because nature and present research are based on different limiting conditions and are operating in different ranges of thermodynamics (Figure 1.7). When relying on present research trends, a breakthrough in artificial water splitting would have to occur with a less sophisticated and different kind of technology. Nature has efficiently exploited the possibilities of non-linear irreversible thermodynamics for water splitting and has been relying on such technology for more than 3 billion years. During that period, no simpler technology close to reversible thermodynamics has been discovered by nature. There are obvious reasons: dynamic self-organisation gives access to abundant materials, to temporary stability and to dissipative

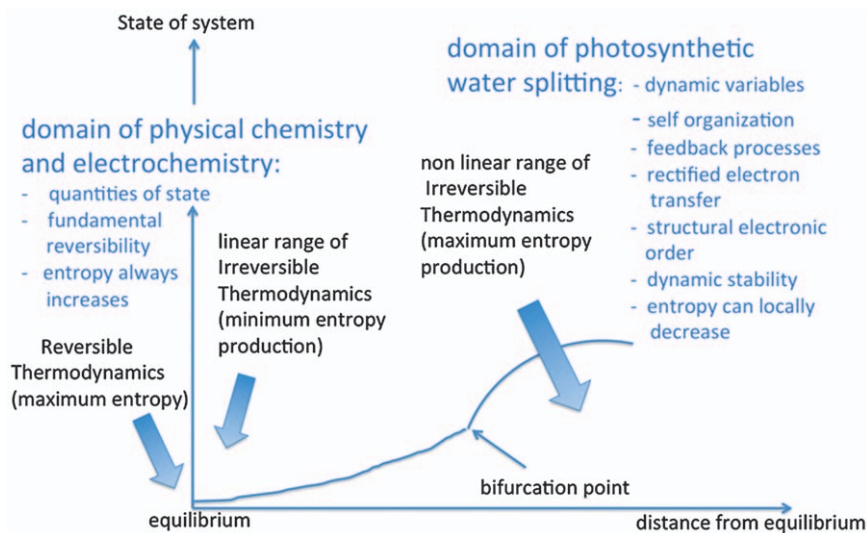


Figure 1.7 A scheme for the state of the system, with an axis showing the distance from equilibrium is used to show where present electrochemistry and physical chemistry is addressing problems of water splitting (equilibrium thermodynamics and linear range of irreversible thermodynamics), and where biological evolution has found appropriate solutions (non-linear range of irreversible thermodynamics).

structures (negentropy, information) for much improved catalysis. The problem is: present research is still struggling to even understand the foundations of irreversible thermodynamics. In spite of significant progress in science generally it has not even been possible to derive basic entropy laws for non-linear irreversible thermodynamics. It should not be forgotten that even the empirical second law of thermodynamics could not yet be derived from fundamental principles, based on time-invertible fundamental mechanism and time-neutral elementary particles.

At the beginning of this chapter it was explained that essential energy strategies, which nature has successfully applied for energy harvesting (rectified electron transfer, kinetic solar energy conversion, self-organised catalysis *via* activation complexes functioning as dissipating structures, self-organised materials) are presently not attractive or accessible for dynamic research and development activities. In spite of some early efforts dating back 25 years^{7,8,23,25} there are not sufficient research activities in direction of self-organised catalysis. Why are, for example, so many manganese cluster compounds studied⁵⁸ to find out that they are catalytically not really attractive, but practically no efforts developed to get them to form functioning dissipative structures, as proposed for photosynthesis?⁷ What is the reason for such a situation and how can one overcome it?

1.5.1 A Paradigm Change Towards a Fundamental Time Arrow Is Needed

According to the author the answer is relatively simple, but radical: all fundamental laws that have been identified to govern physics and chemistry are time invertible. They are designed to work both in positive and negative time direction. The properties of elementary particles are time neutral. Time is explained statistically as an entropy arrow by mathematically deriving an entropy increase for particles subject to time-invertible laws. However, this was only achieved by drastic simplification of the originally very complex mathematical situation. With the introduction of this simplification, information was thrown out of the system. Today one knows that information involves energy turnover, which means that energy was thrown out of the system *via* the simplifications introduced. The calculated statistical entropic time arrow is the result of mathematical manipulation. Anyway, the same mathematical formalism should also allow a system to develop into the past. This has never been observed (Loschmidt paradox). The applied considerations are consequently not consistent.

Self-organisation and the build-up of order for activation complexes as dissipative structures (ordered structures build-up *via* energy dissipation) requires feedback processes to occur. Feedback processes need a 'before' and an 'after'. They can in a transient catalytic complex, which is building up order, not rely on a statistical time mechanism. How should such a probabilistic, statistical time be read by a self-organised feedback

reaction anyway? Feedback processes require a fundamental time orientation *via* an energy driven flow of action. In addition, quantities of state have to become dynamic variables and this should also be reflected in quantum processes during electron transfer. The fact that everything is moving into one direction is not considered as convincing evidence for a time arrow for actual science, which believes time to be ‘an illusion’ (comment by A. Einstein), and should not enter into crucial formulas. The author of this chapter, in two recent publications^{59,60} addressed the problem and showed that a fundamental time arrow can already be derived from the important principle of least action. When the time integral over energy, action, is split up in infinitesimal sections, energy and time in it still have to minimise. A scalar energy (an energy, which has the ability to perform work, but no interest) and a time which is just an ordering parameter, cannot do that. They are just numbers. They have to be oriented in order to minimise, which also means that the principle of least action expresses nature’s profound property of being fundamentally oriented. Free energy has, within the limitation of the system concerned, the ‘property to decrease its presence per state’. It thus drives time, which is the flow of action generated by energy conversion. The process, which is believed to bring a snowflake to form, free energy approaching a minimum, should just be accepted as a fundamental law. It was shown that, on the basis of such a dynamic energy, which implements a time arrow, rational explanations can be derived for relevant quantum and cosmic phenomena.^{59,60} On the basis of such a paradigm change leading to a fundamentally time-oriented universe, counter intuitive and bizarre natural phenomena can be understood rationally and differently.⁶¹ A fundamentally irreversible nature can simply not easily be described by time reversible laws.

Those phenomena attributed to the statistical time arrow however actually exist. A compressed gas indeed becomes an expanded, statistically distributed, chaotic one. The distribution of gas particles becomes a more probable one with less information content. The entropy S of this gas, thereby, following the statistical time arrow towards increasing entropy, grows from S_1 to S_2 by ΔS . When multiplying the entropy with the temperature T of the system, however, one realises that this means, that the non-useful (entropic) energy of the system is simply increasing by the non-useful (entropic) energy $T\Delta S$. Since energy cannot be created from nothing and cannot be lost (1st law of thermodynamics) this means that the statistical time arrow is simply explaining that original free (available) energy, contained in the more ordered system, is being converted into non-available (entropic) energy. Instead of saying that a system assumes a more probable state of disorder (compared to a time-neutral initial state) it is therefore entirely equivalent saying that (original) free energy has the tendency or drive to decrease its presence per state while generating entropic, non-available energy ($T\Delta S$). Such a phenomenon is actually observed and can accordingly be interpreted without claiming

time-neutral gas particles. This however is exactly the proposed definition of the 'fundamental' energy driven time arrow.⁵⁹ These simple considerations are, besides of the conclusions derived from the principle of least action, another support for an energy concept, in which energy is not dormant, but dynamic (within the restraints of a system). It can also generate statistical disorder (simulate a statistical time arrow) while converting energy and producing action and entropy.

Such a paradigm change from a statistical to a fundamental time arrow is justified and reasonable, especially since it makes research accessible for the domain of irreversible thermodynamics.

Important consequences for physical chemistry would be that quantities of state become dynamic, entropy generation becomes rate controlling, and non-linear irreversible phenomena consequently develop towards maximum entropy production within the restraints of the system concerned.⁶⁰ This would not only allow to adequately deal with self-organised energy phenomena, but would also explain why evolution conducted the manganese based oxygen evolution catalyst towards maximum performance *via* phenomena of irreversible thermodynamics. Photosynthetic oxygen evolution from water reflects a situation of maximum entropy turnover within the restraints of the system. It is achieved by allowing a static manganese catalyst with sluggish response for oxygen evolution to develop an activation complex in form of a dissipative structure for efficient multi-electron extraction from water. Here the protein environment must provide support *via* feedback activities⁷ and some energy for the well-ordered, dissipative transient activation complex must be deduced from the energy providing primary photoreaction.

What would, in terms of research strategy, be the advantage of adopting the idea of a fundamentally oriented, irreversible world? The advantage would be both practical and psychological. First, all presently tried and tested concepts for physical chemistry and electrochemistry could remain valid, can be considered to be limiting cases for situations where time orientation can be neglected. However, the possibility to access the driving forces, the dynamic variables for irreversible processes, and to handle them as nature did in photosynthetic processes, will open productive new theoretical and experimental routes towards self-organised energy conversion mechanisms. A growing research community, which is now restricted by the dogma of time neutral elementary particles and a probabilistic time concept, would attempt to access opportunities from irreversible thermodynamics. At the long term this may help to reduce costs for hydrogen from photo-electrochemical water splitting *via* more elegant and more efficient mechanisms (compare Chapter 11).

A simple example may underline this necessity to introduce a fundamental time arrow into physical chemical considerations. The self-similar structure of a cauliflower is considered to be the product of dynamic self-organisation with energy flowing through the system while feedback processes function. The mechanism for its generation cannot be derived from

basic time-invertible principles and a statistical time arrow. The formation of an ice crystal is considered to occur *via* passive self-organisation. The explanation and the experience is that it occurs because the free energy of the system is minimising within its restraints. However, such behaviour cannot be derived from basic principles either, since, according to present scientific standard, only the generation of statistical disorder is creating the time orientation. If, however, the decrease of free energy per state (which makes the ice crystal grow) is assumed to drive time (as also derivable from the principle of least action),^{59,61} both phenomena are immediately accessible. In other words: the well-known mechanism, by which an ice crystal forms *via* a minimisation of free energy should be recognised as a fundamental law that opens irreversible thermodynamics for research and understanding. As a consequence, free energy, up to now handled as a quantity of state, which has no interest in performing work, would be accepted as a dynamic variable implementing the flow of time. It is the reduction of free energy, which accompanies the growth of the ice crystals and, through the action generated, determines the visible time flow. A fundamental time arrow results, which is driven by a minimisation of free energy per state, as well as a time, in form of a flow of action, which allows feedback processes for dynamic self-organisation. The second law of thermodynamics can, of course, also immediately be derived from such a paradigm change. Its derivation was not possible up to now, which should encourage steps towards such a fundamental time arrow.

Our present understanding and handling of physical chemical and electrochemical mechanisms, using concepts of reversible thermodynamics and quantities of state would still be valid, but as a limiting case. However, relevant paradoxes in quantum physics and cosmology would simply disappear, because they result from the assumption of a fundamentally time invertible world.^{60,61}

Without such a courageous step in favour of irreversible thermodynamics there would be, within the research community, neither the tolerance nor the interest in addressing the complex challenges for water splitting as handled in nature. To give an example: only when quantum phenomena can be understood as dynamic processes in a fundamentally oriented world⁵⁸ it will be possible to consider, *via* quantum mechanical mechanisms, polarisation and feedback processes for electron transfer, kinetic rectification, and self-organisation.

If such a door towards new insight and exploration is not opened, water splitting efforts, based on concepts of thermodynamic equilibrium, may finally turn out to lead into a dead-end. It would be a road which nature herself, during three billion years of evolution, has not found passable. We therefore need a paradigm change in understanding and dealing with energy and time for successfully joining and addressing nature's far from equilibrium water splitting strategy. Bio-mimetic considerations request that.

Is there also an experimental frontier for research to get started with the handling of negentropy for catalysis? Let us look at the well-known Belousov–Zhabotinsky reaction, which, when certain parameters are adjusted, develops beautiful waves and rings until its chemical energy (malonic acid) is exhausted.⁶² This self-organised reaction is used as a simple model system explaining build-up of order in early life. Three billion years ago life learned to harvest solar energy. Also, the Belousov–Zhabotinsky reaction can do that following the identified principle of maximum entropy production (within the restraints of the system).⁶⁰ It is sufficient to add the dye tris(bipyridine)ruthenium(II)chloride for replacement of dark induced by light induced electron transfer. Now light energy flows into the oscillating system and illumination patterns determine the spatial and temporal course of oscillating self-organisation. Early chlorophyll driven life forms may have indeed started like that. Now the light induced self-organised reaction should be coupled to nano-structured interfaces. This could best be achieved *via* the dye tris(bipyridine)ruthenium(II)chloride within the geometry of nano-structured dye solar cells. When the parameters are found within which photo-induced oscillating self-organisation continues in such an environment, attention should be focussed on the fate of photo-generated holes. They should be channelled into potential catalysts for water oxidation. In trying to maximise entropy turnover, and in presence of suitable chemical agents the system may attempt to self-organise the water oxidation reaction. The first steps in experimental learning may proceed.

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