In equation (1), $\varkappa_2^2$ and $\varkappa_0^2$ are the values of the Debye-Hückel parameter of solutions I and II, sandwiching the membrane. k is the Boltzmann constant and T is the temperature in degrees Kelvin. ε is the dielectric constant of the solutions. J_σ and J_w are respectively the fluxes of ionic species and water, expressed in moles cm^{-2} sec^{-1}. r_σ is the resistance offered by the membrane to species σ, for transport. R_σ has a dimension of the order of moles/cm^4, and approximately equals (J_σ/D_σ), where D_σ is the diffusion coefficient of σ in the membrane phase. z_σ is the valence charge number of species σ, and e is the protonic charge. λ^2 is a parameter independent of x, approximately equal to -8.33×10^{-14} cm^2 $\{-(\varkappa_2^2+\varkappa_0^2)/\varkappa_2^2\varkappa_0^2=\lambda^2\}$. Thus, if one has knowledge of stationary state fluxes of permeant species, knowledge of the composition of boundary solutions and resistance properties of the membrane, one can relate the derivatives of electrical potential profile to known quantities. d is the region of aqueous solutions and the membrane in which microscopic electroneutrality does not hold. Assuming a Taylor expansion form for electrical potential profile, enables one to compute the first few Taylor expansion coefficients and thereby compute the stationary state electrical potential difference, as a function of fluxes and known parameters of the system. Values of membrane potentials calculated in this manner yield values for all axon systems listed by Hurlbut in the right order of magnitude of observed membrane potentials. Thus, the answer to basic question b) can be assumed to be at least partially known. Partial answer to other questions raised may be found in the references listed at the end of this review.

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Photosynthesis

by Helmut Metzner

Institut für Chemische Pflanzenphysiologie der Universität Tübingen, D-7400 Tübingen (Federal Republic of Germany)

The balance equation

$$6\,CO_2+6\,H_2O \xrightarrow{n \cdot h\nu} C_6H_{12}O_6+6\,O_2$$

characterizes photosynthesis as a reduction of CO_2 by water. It is difficult to understand how this strongly endergonic process might occur. The reaction obviously starts with a mixture of 2 molecular species, which undergo a catalytically enhanced interaction:

$$CO_2+3\,H_2O \rightleftharpoons HCO_3^- + H_3O^+ + H_2O \rightleftharpoons CO_3^{--} + 2\,H_3O^+$$

It remains to be decided, which species of the equilibrium system has to be regarded as the precursor of the released molecular oxygen. Mass spectrometric experiments have not yet given convincing results[1].

The production of 1 mole of $C_6H_{12}O_6$ requires a free energy supply of ~2870 kJ. To transfer a single C atom from the oxidation state of CO_2 to that of carbohydrate we therefore need $2870/6 \approx 480$ kJ. For a single molecule this corresponds to ~5 eV[2]. On the other hand, photosynthesis can be driven by the exclusive absorption of (red light) quanta with an energy content of 1.8 eV each. This simple comparison demonstrates that plant cells possess the capability of adding up the energies of several photons. Since the lifetime of the excited sensitizer (1-2 nsec) is orders of magnitude smaller than the average time interval between 2 photon absorption acts (~1 sec), there must be long-living 'intermediates' in the form of either chemical compounds, electric fields or energy-rich conformations.

If photosynthetically active cells are exposed to saturating light flashes, there is a remarkably small O_2 release: only 1 O_2 for 10^2-10^3 chlorophyll molecules[3]. This has been interpreted by the assumption of light-harvesting units, which today are described as pigment 'antennae'[4]. They consist not only of a 2-dimensional array of chlorophyll molecules, but contain additional, so-called 'accessory' pigments – in the case of higher plants carotenoids –, which transfer their excitation energy by an exciton migration mechanism to chlorophyll molecules[5]. By this means plant cells can utilize a broader spectrum than the responsible sensitizer.

Dispersed within these antennae we have to assume the existence of special 'reaction centers', at which the primary photochemical processes occur:

$$\mathrm{Don} + \mathrm{Acc} \xrightarrow{h\nu} \mathrm{Don}^+ + \mathrm{Acc}^- .$$

A comparison between the absorption spectrum of the antenna and the action spectrum of carbon dioxide reduction or oxygen release shows a surprising discrepancy. Whereas with wavelengths $\geqslant 690$ nm the antenna still absorbs quanta with rather high efficiency, the O_2 evolution rate drops to very low values[6]. The simultaneous irradiation with wavelengths $\geqslant 690$ and $\leqslant 670$ nm results in a strongly increased O_2 evolution rate, which is higher than that expected by a mere addition of the absorbed energies. This observation made EMERSON postulate *two* photosynthetic light reactions, driven by 2 different sensitizers[7].

Flash spectroscopic measurements together with the results of experiments with photosynthesis inhibitors and selected mutants strongly supported this view. This encouraged Hill and Bendall[8] to propose a scheme with 2 photoreactions working in series ('Z-scheme'), which – after some modifications and additions[9] – even today may be regarded as the best illustration of our present concept (figure 1).

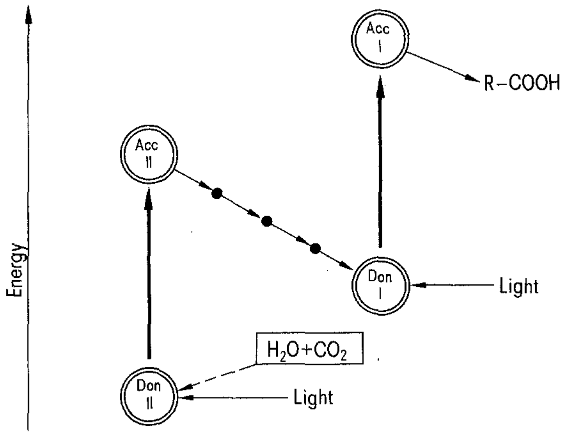

Fig. 1. Cooperation between the 2 photosystems of higher plants. Photoreactions are characterized by thick arrows, the interconnecting line (dark reactions) via different redox systems (given by dots) by thin arrows (from Metzner[31]).

In the phylogeny of plants, photosynthesis started with only *one* photosystem. A process of this kind is well known for bacteriochlorophyll-containing microorganisms[10]. In these species the oxidized donor regains its missing electron from reducing compounds of the medium, like SH^-[11]. During the evolution of higher plants a more complicated system for the replenishment of the electron gap has been 'invented'. Here the primary electron donor is a chlorophyll (chlor a_I), which due to a special 'environment' exhibits a rather long-wave absorption band near 700 nm[12]; it is therefore often called 'P 700'. The negative charges for the re-reduction of P 700^+ radicals are supplied by a reducing agent, which itself is continuously provided by a 2nd light reaction, the so-called photoreaction II. In this case a chlorophyll dimer (chlor a_{II}) with an absorption maximum near 670 nm acts as donor[13]. The corresponding acceptor, often called 'Q'[14], seems to be a quinone.

In biochemistry, oxidations and reductions are commonly described as an electron exchange between systems of different (standard) redox potential. This consideration may, however, be misleading. First of all we know the standard potentials only for the *free* molecules or ions, whereas in vivo most of them are adsorbed or incorporated into unknown complexes. Moreover we have no reliable data on the relative abundances of the oxidized and the reduced species. Besides, we have to realize that these ratios are changed during the processes, i.e. the distance between the redox potentials is no constant value. It would perhaps be more adequate to describe redox reactions by a comparison of electron affinities and ionization potentials[15]. For most biologically important compounds these figures are, however, still undetermined.

Nevertheless, if we, aware of these restrictions, apply the E_0' scale, the P 700 has to be characterized by a standard potential of $+0.43$ V[16]. The value for the (unidentified) primary acceptor is still unknown. Since this compound reduces not only the natural electron acceptor (ferredoxin), but also several artificial acceptors with strongly negative potentials, we may assume that its potential is near -0.6 V[17]. This means, that the photoreaction I spans a potential gap of ~ 1 eV. The redox potential of acceptor Q seems to lie near zero. If photosystem II worked with a similar efficiency to that of photosystem I, the potential of the primary donor should be near $+1$ V. The reduced acceptor of PS II transfers its surplus electron via a series of redox systems to the oxidized donor of PS I (P 700^+). Meanwhile it was possible to identify several of these intermediary compounds[18]. The first links of the connecting chain, which drain the electrons from Q^-, seem to be different quinones. They can neutralize their negative surplus charge by the uptake of protons from the surrounding space. The

2nd part of the chain contains several heavy-metal complexes (non-heme iron and copper compounds), which transport only electrons, not protons.

There remains the difficult - and still unsolved - question of how the oxidized donor of PS II, i.e. Chlor a_{II}^{+}, regains its electrons. This process is obviously connected with the partial reaction leading to the release of molecular oxygen. Experiments with short light flashes have shown that single flashes do not produce O_2. There seems to be a complex, which by successive photon absorptions can attain four different states (so-called 'S-states'), which are conceivably different oxidation states[19,20]. It is only the most positive state that accomplishes the release of molecular oxygen. There is good evidence that this complex contains bound manganese, which is known to be indispensable for O_2 evolution reactions[21].

If 4 photons transfer 4 electrons to the PS II acceptor, 4 additional absorption acts are necessary to lift these electrons to the potential level of the PS I acceptor. We therefore need 8 photons, corresponding to 14.4 eV, to drive the photosynthetic process, which itself stores ~5 eV of free energy. This means that the quantum efficiency is ~35%.

If we assume, that the S-state with the most positive potential directly oxidizes H_2O molecules, the resulting H_2O^+ radicals would probably exchange protons with neighbouring water molecules:

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH\cdot$$

Suppose the resulting $OH^\cdot$ radicals then combined to give water and oxygen, this reaction sequence might seem similar to that of water electrolysis. This again encouraged many authors to claim, that the necessary redox potential for photosynthetic water decomposition must only slightly exceed that of the oxygen electrode ($E_0' = 0.8$ V). In fact the ionization of H_2O molecules requires ~3 eV[22]. There remain 3 possible explanations:

1. 'Bound' water needs less energy to become oxidized than free water[23];
2. the oxidation process is a 'concerted action' of 4 positive charges, so that we actually have 2 - energetically less 'expensive' - *two*-electron steps:

$$S^{4+} + 2\,O^{2-} \rightarrow S + O_2;$$

3. the oxidized S-states do not accept electrons from water, but from an as yet unidentified 'photolyte'[15].

Actually the release of O_2 requires the presence of CO_2[24,25]. This does not mean that the photosynthetic oxygen results from a decomposition of CO_2, but it seems conceivable that both H_2O and CO_2 participate in the synthesis of the real oxygen precursor[15].

The primary electron acceptors and donors of both photosystems are localized on opposite sides of an asymmetric membrane, which forms closed vesicles, so-called thylakoids[26]. There is good evidence that the electron acceptors are nearer the outer surface, whereas the donors (together with the O_2 releasing system) are nearer the inner thylakoid space[27]. This makes the electron exchange reactions vectorial processes (figure 2), creating a strong electric field across the ~10 nm thick membrane[28]. This again represents a form of energy in addition to that stored by the redox couples Don^+/Acc^-.

There are 'wanted' and 'unwanted' back reactions. The 'wanted' reaction is a charge recombination, which is somehow connected to the formation of oxygen-phosphorus bonds ('photophosphorylation', see Arnon et al.[29]). The chemical energy of the produced ATP molecules is part of the conversion of electromagnetic (photon) energy into the energy of chemical bonds. In addition to this there is a small energy loss by uncontrolled back reactions, which leads to the emission of red light quanta (so-called 'delayed light emission')[30]. Fortunately enough the yield of this 'unwanted' process is very low.

Studying oxidations and reductions biochemists were mainly interested in electron transfer reactions. Our knowledge of the 'path of protons' is rather limited. There are actually 2 reactions, which create a proton gradient across the thylakoid membrane: first the reduced acceptors - at least of PS II - can attract protons from the adjacent outer space (chloroplast stroma); besides the photosynthetic oxidation by the S-states could release additional protons within the inner thylakoid space. We must not ignore, however, the fact that thylakoids represent extremely small compartments. They have a volume of only $5 \cdot 10^{-4}$ μm^3. With a neutral reaction the probability of finding a proton - and a hydrogen ion - inside this space is <0.05. Even if we concede a proton enrichment - corresponding to a 'macroscopic' H_3O^+ concentration of 10^{-5} M - there would be only 3 protons within

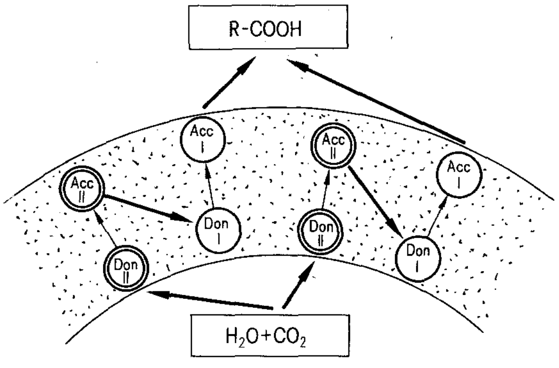

Fig. 2. Arrangement of electron donors and acceptors of the 2 photosystems within the thylakoid membrane of higher plant chloroplasts. Light-induced transfer characterized by thick, dark transfer by thin arrows. Final electron acceptor given as CO_2 fixation product R–COOH (from Metzner[31]).

a thylakoid. The term 'gradient' should therefore be used with the utmost reserve.

Many misunderstandings and misinterpretations result from a noncritical blend of macroscopic and microscopic concepts. In the future we should discriminate more carefully between the 'thermodynamic' considerations, using terms like gradient, field strength, redox potential, and the quantum mechanical interpretation, which regards the probabilities for excitation transfer and electron or proton tunneling.

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