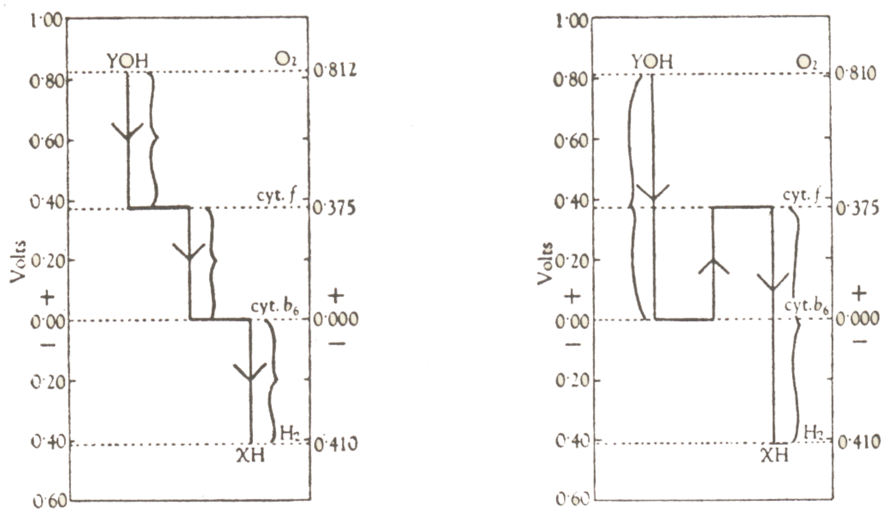
immediately appreciate its far-reaching importance. My work with Robin on photophosphorylation, newly discovered[13] by Arnon and Whatley had gone well enough. We had found that all manner of additives to chloroplast preparations would serve as co-factors of photophosphorylation. Had we ventured to add “spit, urine or floor-sweepings”, as Robin once suggested[2], there is little doubt that one of these would have worked, provided it contained something with an appropriate redox potential. This gave us much food for thought but this had evidently nourished many more far-reaching conclusions in Robins's mind than in mine. Of course I had learned at mother's knee, as we all have, that oxidation/reduction is central to all things biological. One of my childhood chores was to conjure flame out of a pile of old newspapers, sticks of wood and pieces of coal. The notion that oxidising reduced matter would yield some form of energy, which might then be put to use, was entirely familiar. So, of course, was the fact that the Sun's energy could be utilised by plants to reduce carbon dioxide to the oxidation status of coal. Thermochemical gradients seemed as familiar as the slopes that I free-wheeled down on my bicycle.

When one thing is oxidised another must be reduced. Contemporary knowledge said that metabolic oxidation of foods could lead to the reduction of NAD and that mitochondrial reoxidation of NADH proceeded in a stepwise fashion mediated by flavoproteins and cytochromes until hydrogens were finally transferred to oxygen. Energy made available by this process could be conserved as ATP. Although the actual mechanism of ATP formation from ADP and orthophosphate was still unknown and much argued about, this was a comfortable concept that must surely be equally applicable to photosynthesis. But then, in 1957, Arnon, Whatley and Allen turned everything upside down. At least that is how it seemed at the time when they reported ATP formation (in illuminated chloroplast preparations) which was associated with the *reduction* of NADP. In Arnon’s own words[13], this was “wholly unexpected”

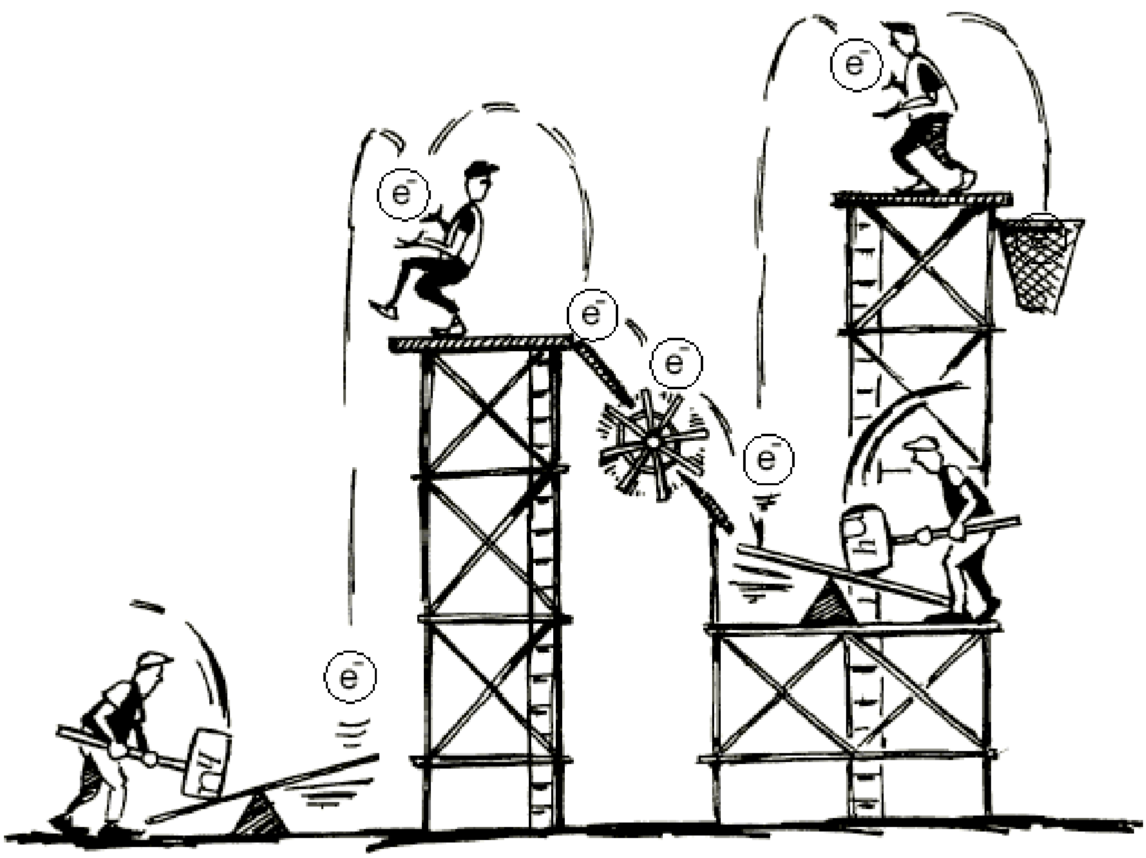
Genius, it is said, is the ability to recognise the obvious before anyone else. That is how I have come to regard the formulation of the Z-scheme even if the manner of its first appearance in ‘Nature’[12] was true to Hill's well known reluctance to labour the obvious. Water running downhill can be used to drive a turbine. Electrons running down a thermochemical gradient can be used to operate an ATP generator. If NADPH, formed by light driven transfer of electrons from water, were to be reoxidised by the chloroplast cytochromes so dear to Hill's heart[14], a concomitant formation of ATP would be understandable. Conversely ATP formation associated with NADP reduction was difficult to accommodate within this same framework. Moreover, as Hill and Bendall[12] pointed out, if the process of photophosphorylation proceeded by NADPH oxidation this would imply less NADPH formation, or at the very least, the same amount of NADPH formation, whereas in the Berkley experiments[13] more NADP was reduced when ATP was formed simultaneously. [Here it should also be remembered that our present understanding is that much easier after Mitchell's chemiosmotic hypothesis[15] and its application[16,17] to photosynthetic events. Both coupling (by ADP + Pi) and uncoupling by a variety of agents (e.g. NH_3 and nigericin) of photosynthetic electron transport[18] can now be seen as different ways of discharging the back pressure exerted by a proton gradient.]

For these reasons[12] Davenport and Hill's 1951 proposal of cytochrome mediated electron transport needed modification. On paper, this could be done by postulating three light reactions



Three light reactions (left) abandoned in favour of two (right)-from Hill & Bendall

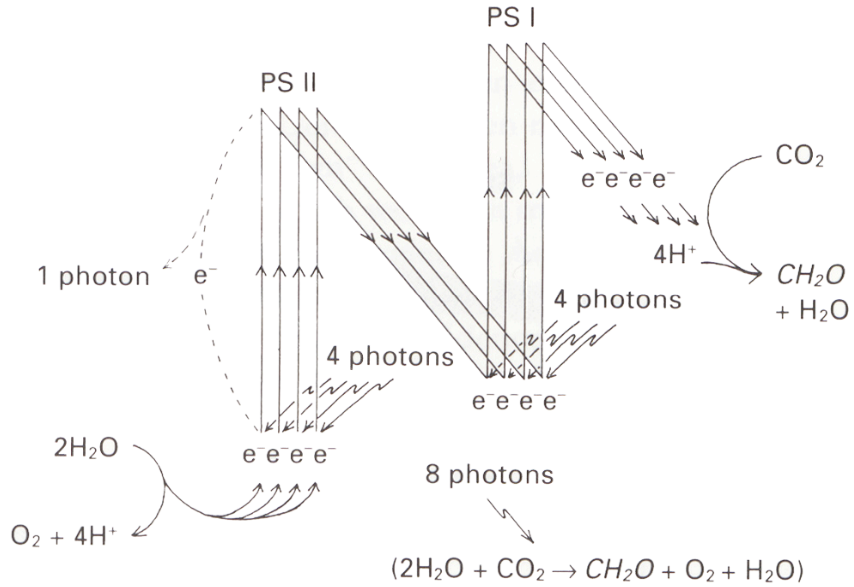
but photophosphorylation would then be reductive in nature as electrons were pushed up all parts of the electron transport chain. Hill and Bendall therefore concluded that "*two light driven steps, rather than three, would be better in accord with present* *experimental results*". This retained the oxidative nature of photophosphorylation. Water running down a hill can drive a turbine. Electrons running down a thermochemical gradient can be made to operate an ATP generator. Removed from the esoteric world of research into the simplistic world of scientific illustration this facilitates understanding. If we need water to run down a hill to operate a turbine, it must first be taken to the top of the hill, then allowed to run down a gradient and finally taken to new heights. My son Richard, as he moved from being a tenor saxophone player with the 'Potato Five' into the equally esoteric realms of higher education, preferred to illuminate this in terms of the once



Cartoon representation of Z-scheme courtesy of Richard Walker[7]

familiar device in travelling fairs. Here a young man was invited to demonstrate his strength by striking a device with a hammer in order to propel a projectile as far as possible up a vertical scale. In Richard Walker's cartoon[7] the hammer blows became photons which raised electrons to the tops of the two successive photosystems. Running down the thermochemical gradient between the two, the electrons turned an ATP generating turbine, Frequently reproduced, though rarely acknowledged, since it was first published in 1979, it seems to have struck a chord with those charged with teaching or learning about this subject. It is now available in animated form[19]. Of course neither father nor son ever imagined that the actual turbine would really have revolving parts but it seems that art has anticipated science once again and this is the sort of things that Nobel prizes are made of[2o].

Purely in terms of slightly more formal visual representation (below), the Z-scheme can make it immediately apparent why, if it truly summarises reality, the minimum quantum requirement for photosynthesis must be eight photons rather than four or less.



Z-scheme to show requirement for eight photons[21]

Moreover, since the conception of the Z-scheme it has proved possible to study both photosystens separately by using different qualities of light, fractionation procedures and a variety of potential hydrogen donors[18]. For example a quantum requirement of unity has been recorded for the photoxidation of ferrocytochrome c by

PSI chloroplast preparations in 710 nm light. In many other similar experiments the quantum requirement predicted by the Z-scheme has been substantiated.

Somewhere, Crick (of double helix fame) once said of his own epoch-making work "it might be nonsense or it might go to the heart of the matter". Similarly, Robin Hill regarded the Z-scheme as a suggestion, "a working hypothesis"[12]. As such it has stimulated massive and continuing experimentation that has done much to further our understanding of photosynthesis.

In this brief account I have attempted to focus, without the detail but otherwise in the same way as the Hill and Bendall paper[12] does, on the underlying thermodynamic concept of the Z-scheme and the fact that the role of leaf cytochromes seemingly puts phosphorylation in chloroplasts and mitochondria in the same oxidative category. That I believe was its essence and, given Hill's earlier work on "The haematin compounds of Plants"[14] why the emphasis was placed on this aspect and two light reactions were mentioned only as a means of establishing the thermochemical gradient which was a requirement for photophophorylation of an *oxidative* nature. Clearly the concept of two light reactions *per se* was not new. This, as Hill himself was at pains to point out in 1965[12] derives[18] from the earlier work of Emerson such as the 'Enhancement Effect'. Put the two together and as George Porter[22] put it on the occasion of Hill's eightieth birthday in 1979 "it still provides today, the chart by which nearly all explorers of photosynthesis navigate".

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