Quantum Efficiency in Photosynthesis

(A review and some new data)

By E. K. GABRIELSEN[1], Copenhagen

According to quantum theory, the number of molecules converted in a photochemical process is given by

$$n = k\frac{Q}{h\nu}, \qquad (1)$$

where Q is the absorbed radiation energy, $h\nu$ the size of the quantum (h is PLANCK'S constant and ν the radiation frequency) and k a proportionality factor indicating the number of molecules converted per absorbed quantum (quantum efficiency). For simple processes $k = 1$, the number of converted molecules corresponding to the number of absorbed quanta. For more complicated processes such as photosynthesis it appears that k becomes smaller than 1, since more than one quantum is necessary for the conversion of one molecule.

From the thermodynamical expression for photosynthesis

$$6\,CO_{2\,(0{\cdot}0003\ atm.)} + 6\,H_2O_{\,(liq.)} = 6\,O_{2\,(0{\cdot}2\ atm.)} + C_6H_{12}O_{6\,(sol.)} - 708 \cdot 10^3\ cal$$

it can be calculated that the quantum yield in the reduction of carbon dioxide during radiation with the least quanta within the photosynthetic spectrum from λ 300 to 700 mμ is at the most

$$k = \frac{6\,N\,h\,\nu}{Q} = \frac{6 \cdot 6{\cdot}06 \cdot 10^{23} \cdot 6{\cdot}7 \cdot 10^{-20}}{708 \cdot 10^3} = 0{\cdot}34,$$

on the assumption that all absorbed light energy is transformed into bound chemical energy in the photosynthates or, in other words, that no energy is lost during conversion (at λ 700 mμ, $h\nu = 6{\cdot}7 \cdot 10^{-20}$ cal, N is the number of molecules in a gram molecule). It results from the calculation that at least 3 quanta are needed for the reduction of one molecule of carbon dioxide.

The first experiment aiming at the determination of the quantum yield in photosynthesis was performed by WARBURG and NEGELEIN[2] in 1923. The experimental material consisted of monocellular green algæ (*Chlorella vulgaris*) suspended in a nutritive solution rich in carbon dioxide. The density of the cells in the experimental chamber was so high that all incident light was absorbed. The light sources were partly the spectral lines λ 436 and λ 578 mμ from a mercury vapour lamp, partly the red light from λ 610 to 690 mμ, obtained from an incandescent lamp by means of a monochromator. The intensity of the light reaching the algæ suspension was measured in energy units by means of a bolometer. The assimilation intensity was measured by connecting the experimental chamber with a Barcroft differential manometer and determining the differences between the oxygen exchange during short experiments alternately in light and in darkness. The determinations in light were made in weak intensities (on an average $3 \cdot 10^{-5}$ cal/cm^2/sec) in order to avoid the influence of factors which affect the non-photochemical partial processes of the photosynthesis at stronger illumination.

WARBURG and NEGELEIN found the following values for k:

	λ 436	λ 578	λ 660 mμ
mean value	0·196	0·234	0·226
maximum value .	0·213	0·267	0·244

and from the good agreement of the mean values at λ 578 and λ 660 mμ they concluded that the energy conversion in photosynthesis is in agreement with quantum theory (EINSTEIN'S photochemical law of equivalence). The lower quantum yield in blue light at λ 436 mμ was explained by the assumption that the light absorption at this wave-length, in contrast to the other wave-lengths, is not only located in the chlorophyll molecules, but also in xantophyll- and carotin molecules, and the light absorbed by the latter either has no photosynthetic effect at all or is working with a lower quantum efficiency than the light which is absorbed by the chlorophyll. Disregarding the results in blue light, the interpretation of which is made difficult in consequence of the light absorption of xantophyll and carotin, and taking into account the sources of error of the method, a consumption of four light quanta per carbon dioxide molecule converted or, in other words, a quantum efficiency of 0·25 has to be assumed (WARBURG[1]).

For many years, WARBURG'S value of the quantum efficiency was undiscussed and it served as the basis for numerous hypotheses concerning the photochemical partial processes in photosynthesis. Not before about ten years ago, when the quantum efficiency was studied by applying methods for the determination of the assimilation intensity other than the manometer method, the correctness of this value

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[1] O. WARBURG, Biochem. Z. *166*, 386 (1925).

became dubious. MANNING *et al.*[1] determined the assimilation intensity by aerating a Chlorella suspension and measuring the CO_2 consumption and the oxygen liberation by means of a Burrel-Haldane air analysis apparatus; they considered $k = 0{\cdot}05$ to be the most probable value. The measurements of the oxygen liberation by means of Winkler titration were in good agreement herewith. PETERING *et al.*[2] and DUTTON and MANNING[3], using *Chlorella pyrenoidosa* and the diatom *Nitzschia closterium*, respectively, determined the oxygen balance by means of the dropping mercury electrode[4] and found values of k varying between 0·04 and 0·10. Similarly low values for the quantum efficiency were found by MAGEE *et al.*[5], using a method based upon a principle not applied before. These authors placed Chlorella cells in a specially constructed photocalorimeter and measured the energy conversion during photosynthesis as the difference between the light energy absorbed by the algæ suspension and the heat developed in the calorimeter. From the results k was calculated to have a value between 0·05 and 0·11, with a mean value of 0·08. TONNELAT[6] who also worked with a calorimetric method found a somewhat higher value, viz. $k = 0{\cdot}14$.

EMERSON and LEWIS[7] gave an explanation for the remarkable discrepancy between the efficiency values primarily observed and those found later. In experiments with WARBURG and NEGELEIN's original method they showed that the measured quantum efficiency was largely dependent on the conditions under which the Chlorella cells were cultivated. After addition of micro-nutritients to the culture medium or when cultivating in weak light, the efficiency could be raised above 0·25 molecules per quantum and even close to the theoretical maximum value $k = 0{\cdot}34$. Furthermore, the temperature at which the experiments were performed had a marked influence on the result. None of these facts is in favour of the reliability of the method.

In a subsequent work[8], EMERSON and LEWIS succeeded in detecting a systematical error in WARBURG and NEGELEIN's method. The source of error turned out to be a process independent of photosynthesis and resulting in the fact that, in the dark, the plant cells accumulate carbon dioxide which is suddenly liberated on illumination. Thus, the manometer deflections were influenced during the short experimental periods applied by WARBURG and NEGELEIN[1], and the assimilation intensity appeared higher than it actually was. If the source of error was eliminated—for example by placing the algæ (*Chlorella pyrenoidosa*) in a carbonate-bicarbonate buffer so that the CO_2-balance did not affect the manometer—a quantum efficiency higher than 0·11 was never observed. When applying this procedure, the results were independent both of the experimental temperature and of the cultivation conditions, except for the fact that the efficiency decreased with increasing age of the cultures if these were grown in strong light. The least quantum efficiency measured was 0·06. Measurements of the quantum efficiency on plant species other than *Chlorella pyrenoidosa* were in agreement with those given above. On 7 among 8 green algæ (*Chlorella vulgaris*, *Eudorina*, *Stichococcus*, *Scenedesmus*, etc.) the highest values observed were between 0·09 and 0·11; on one species only k was 0·07. Experiments with the blue-green algæ *Chroococcus* led to $k = 0{,}09$. Experiments with the small water flowering plant *Wolffiella lingulata* (Lemnaceae) resulted in a quantum efficiency of 0·06. However, it should be mentioned that for the latter plant the light absorption was not so complete as in the case of the different algæ.

The k values found by EMERSON and LEWIS in their latest investigations are for *Chlorella pyrenoidosa* between 0·08 and 0·09[2] and for *Chroococcus* between 0·07 and 0·08[3].

EMERSON and LEWIS' observations made with the manometer method were confirmed to a certain degree by RIEKE[4]. Using WARBURG and NEGELEIN'S method, RIEKE found a quantum efficiency between 0·17 and 0·21, while when using a carbonate buffer a few experiments led to values of 0·12–0·13. On the other hand, EICHHOFF[5], when applying the same buffer solution, obtained values very close to those reported by WARBURG, viz. $k = 0{\cdot}25$. The reliability of EICHHOFF's method, however, is doubtful due to the fact that he measured efficiency values in the ultrared spectrum (up to λ 833 mμ) whereas no other investigators ever succeeded in detecting assimilation in this part of the spectrum (cf., for example, EMERSON and LEWIS[6] and GABRIELSEN[7]). Apart from EICHHOFF, also WASSINK *et al.*[8] and DORRESTEIN *et al.*[9], using the buffer method, registered values higher than those given by EMERSON and LEWIS (0·11–0·20).

[1] W. M. MANNING, J. F. STAUFFER, B. M. DUGGAR, and F. DANIELS, J. Am. Chem. Soc. *60*, 266 (1938). – W. M. MANNING, C. JUDAY, and M. WOLF, ib. *60*, 274 (1938).

[2] H. G. PETERING, B. M. DUGGAR, and F. DANIELS, ib. *61*, 3525 (1939).

[3] H. J. DUTTON and W. M. MANNING, Am. J. Botany *28*, 516 (1941).

[4] H. G. PETERING and F. DANIELS, J. Am. Chem. Soc. *60*, 2796 (1938).

[5] J. L. MAGEE, T. W. DE WITT, E. C. SMITH, and F. DANIELS, ib. *61*, 3529 (1939).

[6] J. TONNELAT, C. R. *218*, 430 (1944).

[7] R. EMERSON and C. M. LEWIS, Am. J. Botany *26*, 808 (1939).

[8] R. EMERSON and C. M. LEWIS, ib. *28*, 789 (1941).

[1] J. TONNELAT, C. R. *218*, 430 (1944).

[2] R. EMERSON and C. M. LEWIS, Am. J. Botany *30*, 165 (1943).

[3] R. EMERSON and C. M. LEWIS, J. gen. Physiol. *25*, 578 (1941).

[4] F. F. RIEKE, J. Chem. Phys. *7*, 238 (1939).

[5] H. J. EICHHOFF, Biochem. Z. *303*, 112 (1939).

[6] R. EMERSON and C. M. LEWIS, J. gen. Physiol. *25*, 578–95 (1941).

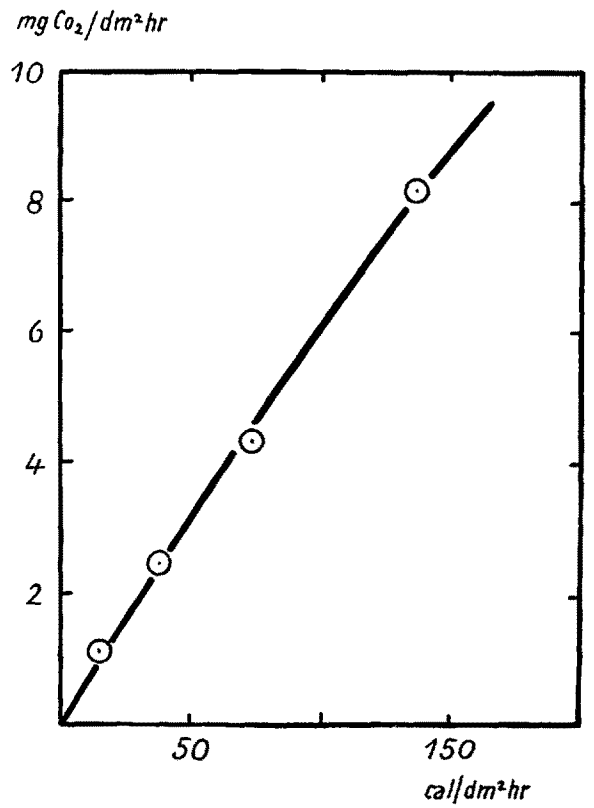
[7] E. K. GABRIELSEN, Einfluß der Lichtfaktoren auf die Kohlensäureassimilation der Laubblätter. Diss. Copenhagen, 1940. Dansk bot. Ark. *10*, 1 (1940).

[8] E. C. WASSINK, D. VERMEULEN, G. H. REMAN, and E. KATZ, Enzymologia *5*, 100 (1938).

[9] R. DORRESTEIN, E. C. WASSINK, and E. KATZ, ib. *10*, 355 (1942).

It is the aim of the present paper to report the fact that also in experiments on foliage leaves of land plants results have been obtained which are in agreement with the recently observed low efficiency values of water plants.

The figure shows the carbon dioxide assimilation as a function of the light intensity as determined on the leaves of *Sinapis alba* according to GABRIELSEN[1]. The determinations were performed in red light from an incandescent lamp, using a filter permeable to wave-lengths from 580 to 740 mμ (maximum permeability at λ 640 mμ). The intensity of the light effective in



Photosynthesis in leaves of *Sinapis alba*. Red light (λ 580–700 mμ).

photosynthesis ($\lambda < 700$ mμ) was measured with a selenium photocell calibrated in absolute units. The assimilation intensity was determined in streaming atmospheric air in experiments of 10 minutes duration. The linear course of the curve near the zero point indicates that the carbon dioxide factor, despite the low carbon dioxide tension in the streaming air, was optimal at the lowest illumination intensities. At an illumination of 40 cal/dm^2/hr, where the curve does not yet bend towards the abscissæ, the assimilation intensity is 2·55 mg CO_2/dm^2/hr, corresponding to $5{\cdot}8 \cdot 10^{-5}$ mol CO_2/dm^2/hr. The number of reduced carbon dioxide molecules (n) are $5{\cdot}8 \cdot N \cdot 10^{-5} = 3{\cdot}51 \cdot 10^{19}$ per dm^2/hr. The quantity of light absorbed within the photosynthetic spectrum can be calculated from the illumination intensity (40 cal/dm^2/hr) if we know the light absorption of the leaves, expressed in fractions of the illumination (A), the energy emission (L) of the lamp, and the transmission of the light filter (T) as functions of the wave-length:

$$Q = 40 \frac{\int_{580\ m\mu}^{700\ m\mu} A\,L\,T\,d\lambda}{\int_{580\ m\mu}^{700\ m\mu} L\,T\,d\lambda} \text{ cal/dm}^2\text{/hr} \qquad (2)$$

The values of L and T used in the calculations are taken from GABRIELSEN[1] (Fig. 18, curve 2, and Table XVII, filter OR_2). The values of A are unknown for the leaves of *Sinapis*. On the basis of numerous investigations on the light absorption of green leaves (cf., for example, SEYBOLD and WEISSWEILER[2,3]) it may, however, be assumed that the absorption does not vary considerably from one plant to another; this holds true especially if the chlorophyll concentration per surface unit and the thickness of the leaf are of similar dimensions. Taking SEYBOLD and WEISSWEILER's figures for the light absorption in leaves of *Fagus silvatica*[2] whose leaf thickness and chlorophyll content are similar to those of *Sinapis* leaves (6·5 mg chlorophyll/dm^2 and 7·0 mg/dm^2, respectively) we obtain from equation (2) $Q = 33{\cdot}5$ cal/dm^2/hr. Inserting the values for n, Q, and the mean quantum size $h\nu = 7{\cdot}26 \cdot 10^{-20}$ in (1), we find $k = 0{\cdot}076$.

Using the same procedure and data from the same source, the efficiency values for the leaves of *Corylus maxima* and *Fraxinus excelsior* are $k = 0{\cdot}072$ and $k = 0{\cdot}076$, respectively.

In these calculations it is assumed that all light absorbed in the leaves is absorbed by chlorophyll molecules and has a possibility of being utilized during photosynthesis. However, this assumption does not hold true. Light is also absorbed by cell walls, cytoplasm and other non-green parts of the leaves, and this absorption is not of a negligible magnitude. From SEYBOLD and WEISSWEILER's measurements of the light absorption in chlorophyll-free leaves of *Pelargonium zonale*[2] it appears that the absorption in the red part of the spectrum varies gradually from 20 per cent of the illumination (at λ 600 mμ) to 18 per cent (at λ 700 mμ). Naturally, we cannot expect that the absorption in green leaves by substances other than chlorophyll (the unproductive absorption) will be of the same dimensions as in white leaves, since a large part of the light is absorbed in the uppermost cell-layers rich in chlorophyll and, thus, has no opportunity of being unproductively absorbed farther inside the

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[2] A. SEYBOLD and A. WEISSWEILER, Bot. Arch. (Leipzig) *43*, 252 (1942).

[3] A. SEYBOLD and A. WEISSWEILER, ib. *44*, 102 (1942).

leaves. On the basis of his measurements on the light absorption in green algæ with only one single layer of plastids (Ulvaceae), SEYBOLD[1] estimated that the unproductive absorption in green leaves at the most amounts to 10 per cent of the illumination. This value appears to be rather reasonable if it is taken into account that the light, before entering the cells of the palisade tissue rich in chlorophyll, passes an epidermis which, apart from the guard cells around the stomata, does not contain any chlorophyll. Correcting the value of Q for an unproductive absorption amounting to 10 per cent of the illumination leads to $Q = 29{\cdot}5$, and the k values of the *Sinapis*, *Corylus* and *Fraxinus* leaves are then placed between 0·082 and 0·087.

In addition to the data presented above, some observations on photosynthesis in leaves made by BRIGGS in 1929[2] may serve as a basis for analogous calculations. BRIGGS' experiments were performed in light of wave-lengths 570 to 640 mμ. The assimilation was determined by air analysis, applying BLACKMAN'S palladium-black method in a hydrogen atmosphere with 5 vol. % carbon dioxide. Using the leaves of *Phaseolus vulgaris* (the only species on which several experiments were performed) and an average illumination of 33·5 cal/dm^2/hr, he observed a mean value for the oxygen evolution of 1·03 ml/dm^2/hr. Applying SEYBOLD and WEISSWEILER'S figure for the light absorption in *Phaseolus* leaves[3], we can calculate $k = 0{\cdot}077$ if no correction is made for unproductive absorption, and $k = 0{\cdot}088$ if a correction is performed in the manner described above. These values are in reasonable agreement with those calculated for the leaves of *Sinapis*, *Corylus* and *Fraxinus*.

The present calculations of the quantum efficiency in foliage leaves seem to indicate that the correct value is between 0·08 and 0·09. Thus, the results are in good agreement with numerous investigations on the quantum efficiency in monocellular algæ performed in recent years, especially those carried out with great thoroughness in methodical respect by EMERSON and LEWIS. There is much reason to assume that within the whole plant kingdom the conversion of one carbon dioxide molecule by photosynthesis requires about 12 quanta (12 quanta per molecule $\sim k = 0{\cdot}083$). Presumably, the true figure will never be determined quite accurately. With regard to the algæ, it will scarcely be feasible to measure the gas exchange during photosynthesis with sufficient accuracy; with respect to leaves, where this difficulty does not exist, the unproductive absorption, which eludes measurement, makes an accurate determination of the quantum yield impossible. Finally, the possibility cannot be excluded that an unproductive absorption exists also in algæ, and here it might also build a barrier, which would make impossible an exact determination of the quantum efficiency.

[1] A. SEYBOLD, Planta (Berlin) *21*, 251 (1933).
[2] G. E. BRIGGS, Proc. Roy. Soc. London (B) *105*, 1 (1930).
[3] A. SEYBOLD and A. WEISSWEILER, Bot. Arch. (Leipzig) *43*, 252 (1942).

Zusammenfassung

Nach der thermodynamischen Gleichung für die Photosynthese kann die Quantenausbeute bei dem Prozeß (k = Anzahl von umgesetzten CO_2-Molekülen pro absorbiertes Lichtquant) höchstens einen Wert $k = 0{,}34$ haben. Für den Umsatz von 1 CO_2-Molekül müssen mindestens 3 Quanten verwendet werden. WARBURG und NEGELEIN fanden 1923 bei Versuchen mit einzelligen Grünalgen $k = 0{,}23$ und haben hieraus geschlossen, daß der Umsatz von einem CO_2-Molekül 4 Lichtquanten erfordere. Später wurde die Richtigkeit dieser Angabe bezweifelt, da zahlreiche Untersuchungen mit anderen Methoden einen k-Wert zwischen 0,04 und 0,14 ergaben. Die Diskrepanzen wurden durch EMERSON und LEWIS (1939–41) erklärt: sie fanden in den Versuchen von WARBURG und NEGELEIN einen methodischen Fehler. EMERSON und LEWIS beobachteten bei einzelligen Grünalgen k-Werte zwischen 0,07 und 0,11.

In der vorliegenden Arbeit wird darauf hingewiesen, daß man auch bei Laubblättern k-Werte von weniger als 0,23 erhält. Nach den Beobachtungen von BRIGGS und von GABRIELSEN sind bei *Sinapis-*, *Corylus-*, *Fraxinus-* und *Phaseolus*-Blättern k-Werte zwischen 0,08 und 0,09 zu berechnen. Diese Werte deuten ebenso wie die bei Algen erhaltenen darauf hin, daß der Umsatz von einem CO_2-Molekül bei allen grünen Pflanzen 12 Quanten erfordert; das entspricht einem k von 0,083.

The Trephocytes and their Functions

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Though white blood cells had been seen before, T. WHARTON JONES[2] is usually credited with their discovery and their first brief description as cellular elements. WILLIAMS[3], in a careful study of numerous invertebrates, gives a detailed account of "non-locomotive", more or less spherical leucocytes, filled "with oil molecules and granules" and stresses their large size, which in some species makes them discernible with the naked eye.

WILLIAMS, like his predecessor, also saw ameboid elements but considered them as "jagged and broken

[1] N. Y. Zool. Society.
[2] T. WHARTON JONES, Philos. Trans. *136*, 63 (1846).
[3] TH. WILLIAMS, Philos. Trans. *142*, 595 (1852).