THERMODYNAMICS OF LIGHT EMISSION AND FREE-ENERGY STORAGE IN PHOTOSYNTHESIS

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ABSTRACT A Planck law relationship between absorption and emission spectra is used to compute the fluorescence spectra of some photosynthetic systems from their absorption spectra. Calculated luminescence spectra of purple bacteria agree well but not perfectly with published experimental spectra. Application of the Planck law relation to published activation spectra for Systems I and II of spinach chloroplasts permits independent calculation of the luminescence spectra of the two systems; if the luminescence yield of System I is taken to be one-third the yield of System II, then the combined luminescence spectrum closely fits published experimental measurement.

Consideration of the entropy associated with the excited state of the absorbing molecules is used to compute the oxidation–reduction potentials and maximum free-energy storage resulting from light absorption. Spinach chloroplasts under an illumination of 1 klux of white light can produce at most a potential difference of 1.32 ev for System I, and 1.36 ev for System II. In the absence of nonradiative losses, the maximum amount of free energy stored is 1.19 ev and 1.23 ev per photon absorbed for Systems I and II, respectively. The bacterium *Chromatium* under an illumination of 1 mw/cm^2 of Na D radiation can produce at most a potential difference of 0.90 ev; the maximum amount of free energy stored is 0.79 ev per photon absorbed.

The combined effect of partial thermodynamic reversibility and a finite trapping rate on the amount of luminescence is considered briefly.

I. INTRODUCTION

Photosynthesis in green plants converts radiant energy in the wavelength region from 400 to 700 nm into chemical free energy. A photon having a wavelength of 700 nm has an energy of 1.8 ev, but measurements of oxygen evolution from green plants indicate that only about 0.6 ev per quantum absorbed is stored as free energy in the form of stable chemical products. One of the major purposes of this paper is to understand the reasons for which much of the "missing" two-thirds of the photon's energy is "lost."

A significant amount of free energy is lost in the complex biochemical pathways between the absorption of light and the output of carbohydrate; it is possible that

these losses may be considered in a general thermodynamic manner, but in this paper we shall be concerned with two "losses" which are incurred immediately upon absorption of the light.

The first of these is simply a consideration of the entropy associated with the absorbed radiation; in other words, free energy is not the same as energy. The first worker to consider this limitation on the energy conversion process of photosynthesis was L. N. M. Duysens (1958), who did so by a general and somewhat intuitive thermodynamic approach which is strictly applicable only for systems which absorb only in a narrow frequency range. Since then, Mortimer and Mazo (1961) and Bell (1964) have considered the thermodynamics of monochromatic radiant energy conversion in a more general context; their work has expressed Duysens' insight in more formal terms, but it has not altered the basic argument. Application of the narrow-band theory to photosynthesis requires some extensions in order to make it applicable to photochemical systems absorbing over broad bands; this has been done recently (Ross, 1966 *b*; 1967), and we review this theory in the next section.

The second immediate loss is due to a degree of irreversibility which is necessary to cause a new flow of energy into any radiation absorber. If an absorber were in equilibrium with a radiation field, then it would reradiate at the same rate at which it received photons, meaning that the quantum yield for energy storage processes would be zero. In order to get a net retention of photons, the entropy of the absorber must be greater than the entropy of the radiation field. This and other losses have recently been considered for the general problem of narrow-band radiant energy conversion (Ross, 1966 *a*), and this loss has more recently been considered in the broad-band context (Ross, 1966 *b*; 1967). This theory will also be reviewed in the next section.

The evaluation of the thermodynamics of any broad-band-absorbing photochemical system rests largely on a universal Planck law relationship between the absorption and emission spectra of any photochemical system. This relationship has been derived by several authors (e.g., Stepanov, 1957; see Ross, 1967), and recently it has been used to confirm the existence of more than one photochemical system in algae (Szalay, Rabinowitch, Murty, and Govindjee, 1967).

In Section III we consider some of the available information on the absorption and fluorescence spectra of photosynthetic systems, and relate them to the theory developed. In Section IV we use these spectra and the theory, together with some estimates of the intensities of the light fields in which photosynthesis typically operates, in order to calculate the chemical potentials which may be developed in different photosynthetic systems. These are then related to observed biochemical oxidation–reduction potentials, and the agreement is found to be rather good.

II. THEORY

The thermodynamic theory which is used in this paper can be derived in a completely general manner (Ross, 1967). However, here we shall present a derivation which has

less generality, but which—hopefully—may assist the reader in getting a better physical picture.

In this particular derivation we assume that the thermodynamics and kinetics of any species considered is identical in behavior to an ideal gas; in other words, molecules are considered to be noninteracting and to obey Boltzmann statistics.

Consider a dilute solution of chlorophyll in complete thermal equilibrium in a black box which is at 295°K. The blackbody radiation and molecular vibrations present at room temperature are constantly causing transitions from the ground electronic state of the chlorophyll, Chl, up to the first excited singlet state, Chl*, and from the excited state down to the ground state. For equilibrium we know that the rate of upwards transitions must equal the rate of downwards transitions.

Some of these transitions occur with the absorption or emission of a photon. From

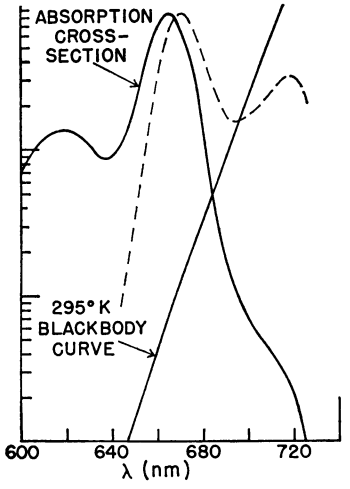

FIGURE 1 Multiplication of the absorption spectrum of chlorophyll by the room temperature blackbody curve to compute the wavelength distribution of spontaneous radiative transitions (dotted curve). Arbitrary logarithmic vertical scale: absorption cross-section from the extinction coefficient of monomeric chlorophyll *a* in CCl_4 (Sauer, K. 1966, private communication); blackbody curve for 295°K in units of quanta/cm² sec per unit wavelength interval; curve for the distribution of radiative transitions in units of quanta/sec per unit wavelength interval.

the principle of detailed balance, we know that the number of radiative transitions from Chl* down to Chl equals the number of radiative transitions from Chl up to Chl*. We know further that the number of downward transitions accompanied by the emission of radiation within a certain frequency interval must be equal to the number of upward transitions which are accompanied by the absorption of radiation in the same band.

It is possible to calculate the wavelength distribution of these thermal radiative transitions by simply taking the product of the electronic absorption spectrum of chlorophyll with the blackbody radiation curve for 295°K. This is shown in Fig. 1.

In general, this rate is

$$8\pi\, \sigma(\nu)(n\nu/c)^2 \exp(-h\nu/kT), \tag{1}$$

in units of quanta/cm² sec Hz, where $\sigma(\nu)$ is the absorption cross-section of the

chlorophyll and n is the refractive index of the medium. This expression has been simplified by omission of a term corresponding to induced emission.

Now let us shine light from an external source into the solution. This additional light will increase the rate of excitations, and thus increase the number of Chl* molecules.

If, in the presence of the external light, thermal equilibrium is maintained among all of the vibrational levels of the Chl*, then the proportion of Chl*-to-Chl transitions which occurs by any particular mechanism will remain the same as it was without the light. One consequence of this is that the proportion of radiation emitted at any frequency will be the same as that computed for the rate of Chl*-to-Chl transitions in a thermal enclosure, regardless of the frequency distribution of the impinging radiation. This means that the wavelength or frequency distribution of radiative transitions shown in Fig. 1 and given by equation (1) is always the emission spectrum of chlorophyll at 295°K. This Planck law relation between absorption and emission spectra enables one to calculate emission spectra from absorption spectra. We consider its application to photosynthetic systems in Section III.

Let us specify that the intensity of the external light is such that the population of Chl* becomes Q times what it was in the absence of the external lamp.

We can express Q as

$$Q = R'/R_0, \tag{2}$$

where R_0 is the rate of Chl–Chl* thermal transitions, and R' is the rate of Chl-Chl* transitions in the presence of the external light.

The rate of thermal transitions is

$$R_0 = \int I_{BB}(\nu)\, \sigma(\nu)\, d\nu + R_{nr}, \tag{3}$$

where I_{BB} is the blackbody intensity at the ambient temperature and R_{nr} is the rate of nonradiative transitions.

The rate in the presence of the external light is

$$R' = \int I_e(\nu)\, \sigma(\nu)\, d\nu + R_0, \tag{4}$$

where I_e is the intensity of the external light. We shall assume that R_0 is negligible compared to the rate of transitions stimulated by the external light, so that

$$Q = \int I_e(\nu)\, \sigma(\nu)\, d\nu/\alpha \int I_{BB}(\nu)\, \sigma(\nu)\, d\nu, \tag{5}$$

where we have expressed the rate of nonradiative thermal transitions (R_{nr}) as being ($\alpha - 1$) times the rate of radiative thermal transitions. The proportion of Chl*-to-Chl transitions which occurs radiatively is $1/\alpha$, so that α is simply the inverse of the quantum yield of luminescence.

We now have the situation that the population of the excited state is Q times the

thermal population. This means that the partial molecular free energy of the Chl* is increased by $kT \ln Q$ over its thermal value. We are considering light levels at which the population of the ground state is not seriously depleted by excitations into the Chl* state, so that the partial molar free energy of the Chl remains at its thermal value. This means that the difference in the partial molecular free energies of the Chl and Chl* is $kT \ln Q$, or

$$\mu = kT \ln[\phi_{\text{lum}} \int I_s(\lambda)\, \sigma(\lambda)\, d\lambda / \int I_{\text{BB}}(\lambda)\, \sigma(\lambda)\, d\lambda]. \tag{6}$$

Note that for the evaluation of this potential difference one needs only to know a temperature and index of refraction (which will give I_{BB}), the wavelength distribution of the incident radiation, and an absorption spectrum (which does not need to be normalized). Using this formula with a knowledge of the absorption spectrum and typical illumination intensities, it is possible to evaluate a typical μ for various photosynthetic organisms. It should be noted that equation (6) can be derived in a completely general fashion, and is dependent only on the assumption of thermal equilibrium within the electronic states (Ross, 1967).

So long as Chl-to-Chl* excitations are caused with a quantum yield of one or less, this free-energy difference represents an upper limit on the amount of free energy which can result from the absorption of a photon. By our approach of perturbing a perfect thermal equilibrium, it should be clear that μ is not determined by the energy of the quanta involved, and can be much less than $h\nu$.

Losses from the Irreversibility of Net Flow

At this point, let us note that the free-energy difference which we have been calculating has taken no note whatsoever of the quantum yield for the energy storing process. As we turn on an energy-utilizing pathway which had not been considered in our previous discussion, the population of the excited state will be decreased to some population P^* which will be less than the population in the absence of the energy storage process P^*_{max} . The quantum yield for the processes which lead to energy storage is then

$$\phi_{\text{st}} = 1 - (P^*/P^*_{\text{max}}), \tag{7}$$

assuming first-order rate constants for the energy storage process and for the loss processes.

As the population of the excited state is decreased, so is the free-energy difference between the excited and ground states. One can write this potential as being

$$\mu = \mu_{\text{max}} - kT \ln (P^*/P^*_{\text{max}}). \tag{8}$$

We are interested in maximizing the product of this potential, and the quantum yield for energy storage. It is easy to solve for the condition for this maximum power

storage, and it is approximately that

$$P^*/P^*_{\max} \approx kT/\mu_{\max}. \tag{9}$$

This means that the optimum free-energy difference between the ground and excited states is roughly

$$\mu \approx \mu_{\max} - kT \ln (\mu_{\max}/kT). \tag{10}$$

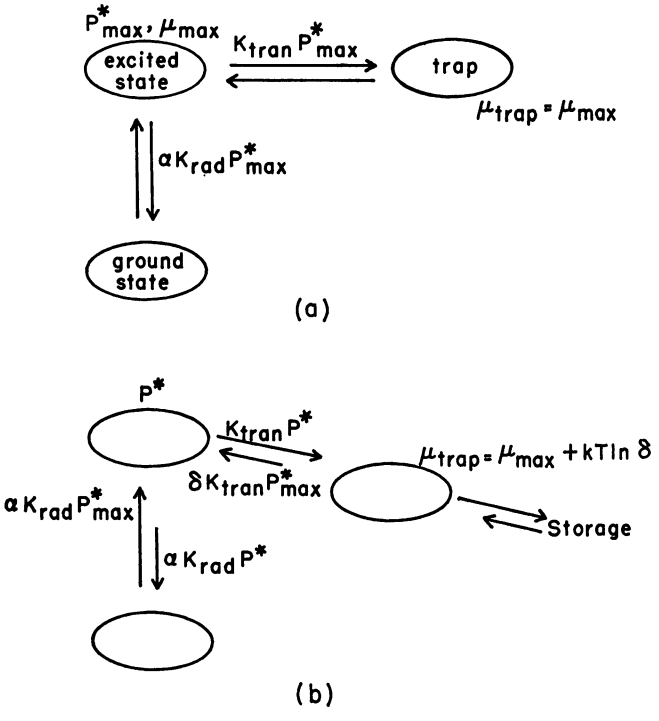

FIGURE 2 Kinetics and thermodynamics of a photochemical system (a) in the absence of energy storage, and (b) in the presence of energy storage when the thermodynamic activity of the trap is a fraction δ of that in (a).

As with the calculation of $\mu_{\max}$, this optimal potential and its associated quantum yield may be derived without reference to any specific mechanistic assumptions about the system (Ross, 1967). We compare the results of thermodynamic calculation with the current state of experimental knowledge about photosynthesis in Section IV.

Losses from Slow Excitation Transfer

There is a kinetic limitation on the amount of free energy stored due to the finite

rate of transfer of excitations from the absorbing pigment molecules into species in which excitations do not decay rapidly.

Consider the situation diagrammed in Fig. 2 a. Here the energy storage process is assumed to be blocked, so that the trap is in thermal equilibrium with the excited state Chl*. The diagram suggests that the trap is some state of the pigment molecule, but the arguments which follow apply equally where the trap is a distinct chemical species.

Excitations are transferred from the excited state to the trap with what we assume to be a first-order rate constant, K_{tran}. Since Fig. 2 a describes a quasi-equilibrium situation, the return rate must be the same, and the chemical potential of the trap is equal to the potential of the excited state, μ_{max}. The population of the excited state is P^*_{max}, and the rate of excitations is equal to the rate of radiative and nonradiative decay, $\alpha K_{rad} P^*_{max}$.

Now consider that excitations are tapped from the trap for storage, so that the thermodynamic activity (e.g., the concentration) of the trap species drops to some fraction, δ, of the activity which would be in equilibrium with an excited state population of P^*_{max}. The resulting situation is diagrammed in Fig. 2 b.

The rate of the reverse reaction Trap $\rightarrow$ Chl* is dropped to $\delta K_{tran} P^*_{max}$, causing the population of the excited state to drop to P^*. The quantum yield for storage is, as before,

$$\phi_{st} = 1 - (P^*/P^*_{max}), \tag{7}$$

but our object in the current situation is to maximize the free energy stored as measured at the trap: in other words, to maximize the product $\phi_{st}\mu_{trap}$.

By equating the fluxes into and out of the excited state, we find the relationship

$$\alpha K_{rad}(P^*_{max} - P^*) + K_{tran}(\delta P^*_{max} - P^*) = 0, \tag{11}$$

which can be rearranged to give

$$P^*/P^*_{max} = (\alpha K_{rad} + \delta K_{tran})/(\alpha K_{rad} + K_{tran}). \tag{12}$$

Substituting equation (12) into equation (7), we find that the quantum yield for energy storage is

$$\phi_{st} = [K_{tran}/(\alpha K_{rad} + K_{tran})](1 - \delta). \tag{13}$$

The expression within the brackets is the usual kinetically determined quantum yield in the absence of any reversibility in the Chl*, Trap reaction (i.e., $\delta = 0$), and the expression $(1 - \delta)$ is thermodynamically equivalent to the $(1 - P^*/P^*_{max})$ of equation (7). This means that the quantum yield for energy storage factors into two independent components, one of which is determined kinetically and the other

of which is determined thermodynamically. Derivation of the optimal μ_{trap} and maximal free-energy storage is equivalent to the earlier treatment where the excited state itself was considered. The only difference is that the quantum yield is lowered by the kinetic factor shown in equation (13).

When the kinetic factor of equation (13) is close to 1, then the quantum yield for processes not leading to energy storage is approximately

$$\phi_{loss} \approx \alpha K_{rad}/(\alpha K_{rad} + K_{tran}) + \delta. \tag{14}$$

The luminescence yield is $1/\alpha$ of this, or

$$\phi_{lum} \approx K_{rad}/(\alpha K_{rad} + K_{tran}) + \exp[(\mu-\mu_{max})/kT], \tag{15}$$

where μ_{max} is the potential computed from equation (6) when $\phi_{lum} = 1$.

The first term in equation (15) is due to the finite rate of transfer out of the excited state, and the second is due to the reversibility of the system. The kinetic term is simple fluorescence which is independent of any chemistry, and this portion of the luminescence should decay rapidly and exponentially when illumination is terminated. On the other hand, the thermodynamic term *is* dependent on chemistry, so that the decay of this light emission may be expected to be considerably slower and have complex kinetics.

Chemiluminescence was first observed in plants by Strehler and Arnold (1951) and is currently being studied in several laboratories (see Clayton, 1966). Although some other source is possible, we feel that this chemiluminescence is due to the partial reversibility of the energy storage process. The production of chemiluminescence on the addition of exogenous chemicals (Mayne and Clayton, 1966) supports this contention.

III. LUMINESCENCE SPECTRA

Bacteria

Olson and Stanton (1966) have recently published absorption and fluorescence spectra for several species of photosynthetic bacteria. By multiplying their absorption spectra with the Planck curve for 295°K, we have calculated the luminescence spectra for these species. The results of this calculation are compared with experiment in Fig. 3.

The calculated and observed spectra have been normalized so that their peak heights match. Agreement between prediction and experiment is reasonably good, and is probably within the accuracy of the experimental data. This agreement adds confidence to our assumption of reasonably good thermal equilibrium in the excited states of photosynthetic pigment systems,[1] and provides one more evidence that there is only one photosynthetic system in bacteria.

[1] However, the variation which Clayton (1965 *a*) has obtained between the prompt fluorescence and chemiluminescence spectra of green bacteria indicates that thermal equilibration is not complete.

Spinach

For the purpose of making quantum yield measurements, Sauer and Biggins (1965) made careful measurements of the absorption spectrum of the photosynthetic apparatus of spinach. Using a tabulation of their absorption data, we applied the Planck curve to calculate the luminescence spectrum which is displayed in Fig. 4. This is the luminescence spectrum which one would expect if the excited states of all of the pigment molecules in plant photosynthesis were in thermal equilibrium.

However, plant photosynthesis does not appear to be comprised of one photochemical system, but rather two. One of these, called System II, can be driven only

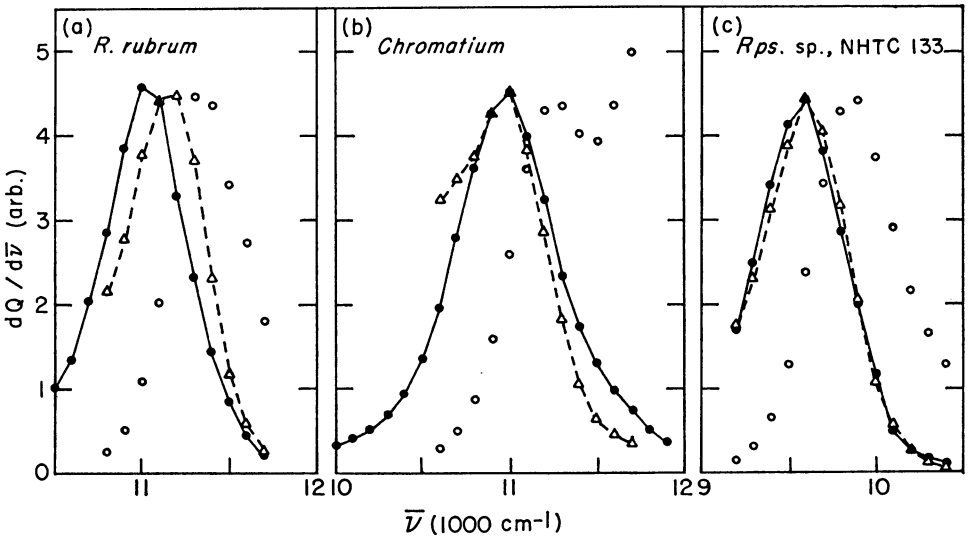

FIGURE 3 Comparison of calculated and experimental luminescence spectra of purple bacteria. Experimental absorption, ○, and luminescence, ●, data were taken at 100 cm^{-1} intervals from the curves of Olson and Stanton (1966) [luminescence data in (c) by Clayton] Solid line: experimental luminescence spectrum; dashed line: luminescence spectrum calculated from the absorption spectrum with the Planck factor for 295°K.

with light having a wavelength less than about 680 nm; the other, called System I, can utilize radiation of longer wavelengths. The manner and degree of any interaction between these two systems at the level of electronic excitations is not known; the most popular current hypothesis is that there is no significant interaction, and that each system may be considered as an independent entity with its own independent absorption spectrum. For simplicity in the following discussion, we shall assume that this "separate package" hypothesis is correct (see Weiss, 1966).

One way of separating the two photochemical systems is to take a preparation of the photosynthetic apparatus of a plant, chloroplasts, and add to it metabolic poisons and spectroscopically observable redox agents with appropriate potentials.

By use of the appropriate chemicals, one may observe the light-driven progress of only one of the two photochemical systems.

By using this technique, Sauer and Park (1965) and Kelly and Sauer (1965) have determined quantum yields for each of the two systems in spinach over a wide range of wavelengths. Their original data were distorted slightly because of the band pass of their instrument, but correction for this indicates that the quantum yield

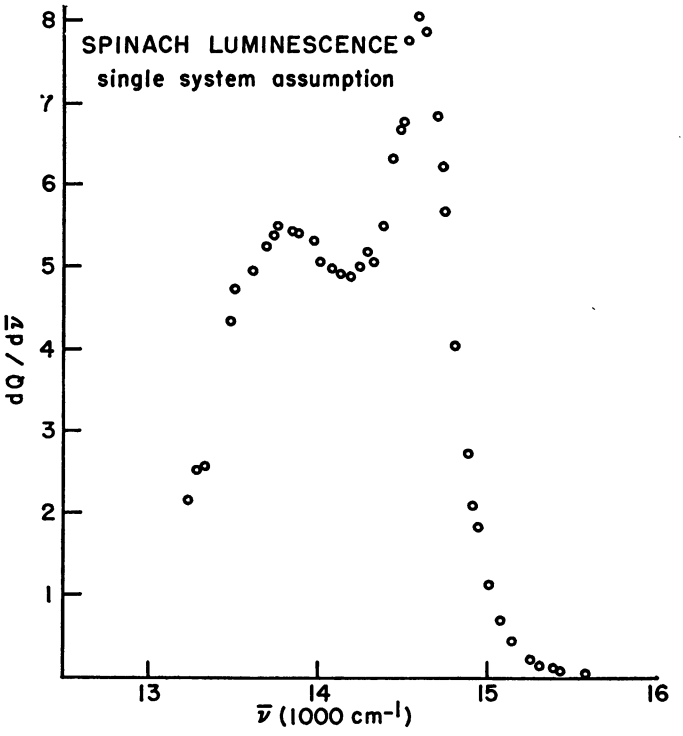

FIGURE 4 The luminescence spectrum of spinach calculated with the assumption that plants contain a single photochemical system. The plotted points were obtained by multiplying the tabulated absorption spectrum of Sauer and Biggins (1965; Sauer, K., 1966, private communication) by the Planck law factor for 295°K.

for System I plus the quantum yield for System II is within experimental error of 1.0 at all wavelengths (Kelly and Sauer, 1965).

Using the assumption of separate packages, we have smoothed their data somewhat to obtain the quantum yield partitioning diagrammed in Fig. 5. These quantum yields may be used to calculate an activation spectrum for each of the two systems; this has been done by Kelly and Sauer, and Fig. 6 shows this on a logarithmic plot.

Separate activation spectra for the two systems permit a decomposition of the

luminescence spectrum shown in Fig. 4 into a component due to System I and a component due to System II. The result is displayed in Fig. 7. The curve for System II has been magnified by a factor of 5 in order to make the area under the two curves approximately equal. If the luminescence yields for Systems I and II were about the same, then the emission spectrum of spinach would look something like the sum indicated in the figure.

Comparison of the experimental fluorescence spectrum of spinach chloroplasts (Murata, Nishimura, and Takamiya, 1966) with Fig. 7 suggests that the fluorescence yield for System I is less than the fluorescence yield for System II. By adjusting the relative magnitudes of System I luminescence and System II luminescence to

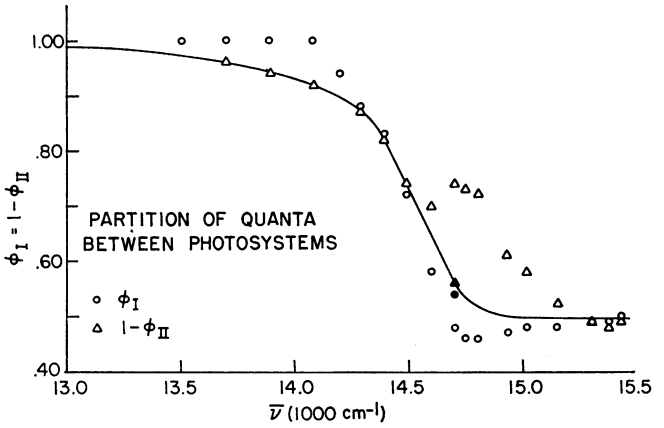

FIGURE 5 Partition of quanta between photosystems I and II in spinach as a function of photon energy. Quantum yield of System I as measured by Kelly and Sauer (1965), ○; difference from 1 of the quantum yield for System II as measured by Sauer and Park (1965), △. Filled symbols indicate corrected quantum yield obtained by extrapolating instrument band width to zero. The solid line indicates the partition assumed in subsequent calculations.

obtain the best fit with the experimental curve of Murata et al., it appears that the fluorescence yield for System I is about ⅓ that of System II. The resulting fit between the theoretically calculated luminescence spectrum and the experimental spectrum is shown in Fig. 8. Considering all the sources of error, we feel that the agreement between the two is quite good.

These calculations reinforce the notion that the fluorescence yield for System I is less than that for System II, and that the luminescence at 740 nm has a relatively greater contribution from System I than does the luminescence around 685 nm (see Butler, 1966).

Similar calculations on other plants would be very interesting, and would require an accurate absorption spectrum out to the longest wavelengths possible, and the partitioning of light between photosystems as a function of wavelength.

IV. POTENTIAL DIFFERENCES AND FREE-ENERGY STORAGE

We saw in Section II that the first step in evaluating the energetics of a photochemical system is to determine the light-driven potential which is developed when the rate of luminescent emission is equal to the rate of absorption.

Recalling the equation we derived,

$$\mu = kT \ln[\phi_{\text{lum}} \int I_s(\nu)\, \sigma(\nu)\, d\nu / \int 8\pi\, \sigma(\nu)\, (n\nu/c)^2 \exp(-h\nu/kT)\, d\nu], \qquad (6')$$

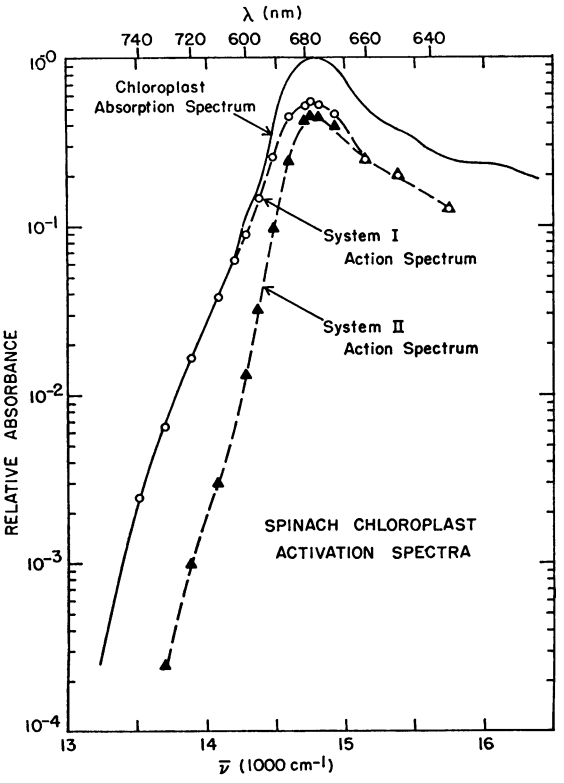

FIGURE 6 Activation spectra for the two photosystems of spinach.

we remember that only four quantities are necessary to evaluate the maximum potential: an incident light flux, $I_s(\nu)$, an absorption spectrum, $\sigma(\nu)$, the ambient temperature, and the refractive index.

For the most accurate determination of μ_{max}, both the absorption spectrum and the light intensity should refer to naturally occurring conditions of growth. From equation (6') we see that the potential increases by 0.06 v for each tenfold increase in the light intensity. Photosynthetic organisms vary their absorption spectra depending on the light intensity under which they are grown (Cohen-Bazire, Sistrom, and Stanier, 1957; Ghosh and Govindjee, 1966), and it appears that this change

in absorption properties is in a direction which would tend to keep the potential developed independent of light intensity. In the following discussion we will not be too careful about this point, partly because the data are not available, but chiefly because an error of a few millivolts in the computed potential is insignificant when compared to other sources of error.

Once the maximum potential has been calculated, then the potential for maximum power storage can be obtained in the manner outlined in Section II.

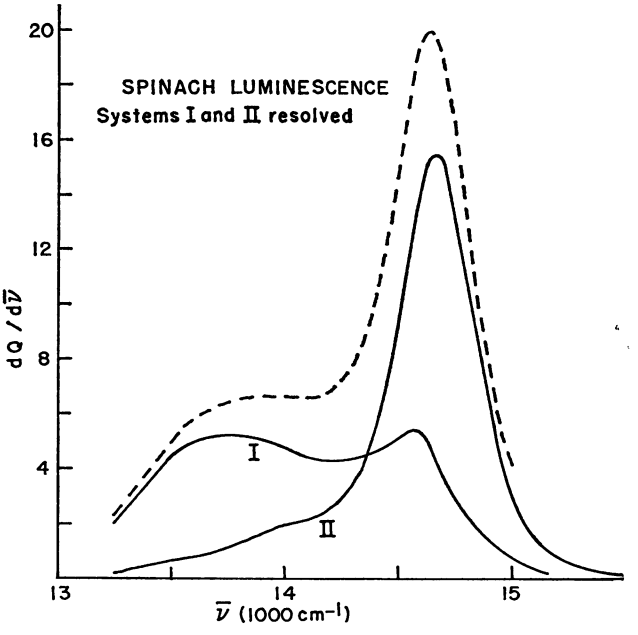

FIGURE 7 Calculated luminescence spectra of Systems I and II of spinach. Vertical scale is the same as in Fig. 3, but the curve for System II has been magnified by 5 × in order to make the area under the two curves approximately equal.

Spinach

The range of light intensities for effective plant growth is limited at the lower end by the compensation point, at which the rate of photosynthesis is just adequate to balance respiration. The upper limit is set by the saturation of the various chemical reactions which make up the energy-storing process. The compensation point generally occurs at a light intensity of between 20 and 500 lux of white light.[2] Photosynthesis becomes half-saturated somewhere between 1 and 10 klux (Rabinowitch, 1951).

The spinach whose absorption spectrum we used in Section III was grown at a light intensity of about 15 klux.[3] However, because of the high optical density of

[2] 100 lux = 9.3 foot-candles.

[3] Park, R. B. 1966. Private communication.

spinach leaves, a typical photosynthetic unit might see a light intensity of closer to 1 klux. We shall use this figure in our calculations.

By taking the product of the spectral distribution of the light from a tungsten bulb with the absorption spectrum of spinach, we find that 1 klux of white light produces pigment excitation at the same rate as would 0.9 nanoeinsteins/cm² sec incident at the red absorption maximum at about 680 nm. This gives us the numerator for equation (6), and we assume that this is split equally between Systems I and II.

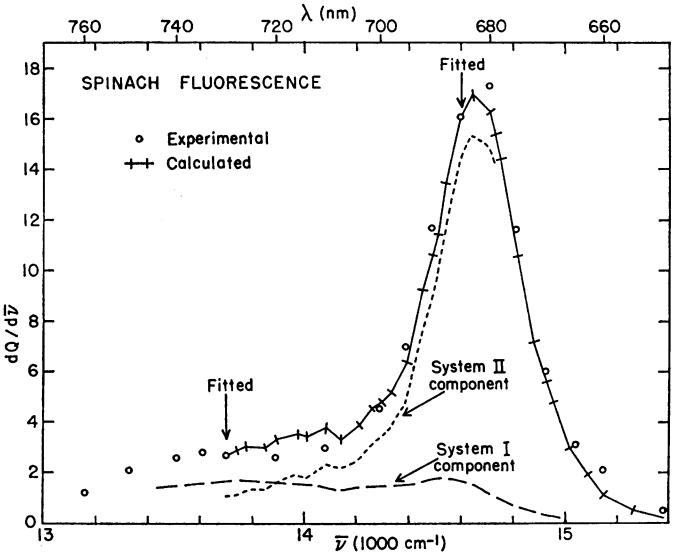

FIGURE 8 Comparison of the calculated and experimental luminescence spectra of spinach chloroplasts. Experimental points from Murata, Nishimura, and Takamiya (1966). Calculated curve obtained by adjusting the amounts of System I and System II luminescence so as to match the experimental luminescence intensities at 685 and at 730 nm. Hatch marks indicate points at which the spectrum was calculated.

The integral in the denominator of equation (6) is evaluated by finding the area under the curves in Fig. 7, with appropriate consideration of how the vertical scale is defined. Performing the necessary arithmetic, we find that μ_{max} for System I is 1.32 ev and that μ_{max} for System II is 1.36 ev.

These maximum potentials have been evaluated with the assumption that nonuseful nonradiative decay is negligible. This is probably not true, and the potential must be corrected downwards by $kT \ln \alpha$, where α is the reciprocal of the quantum yield of fluorescence in the absence of the energy storage process.

The fluorescing species in plants is chlorophyll *a*, dilute solutions of which have an α of 3 (see Clayton, 1966). If the pigments of System II have an equivalent or

greater amount of nonradiative losses, then the maximum potential for this system is 1.33 ev or less.

Evidence is accumulating that the species responsible for the longest wavelength absorption in plants are one or more aggregated forms of chlorophyll (Butler, 1966; Dratz, Schultz, and Sauer, 1967). Presumably these aggregated forms belong largely to System I, so that if nonradiative losses from aggregated chlorophyll should be greater than from monomers, System I would be most affected.

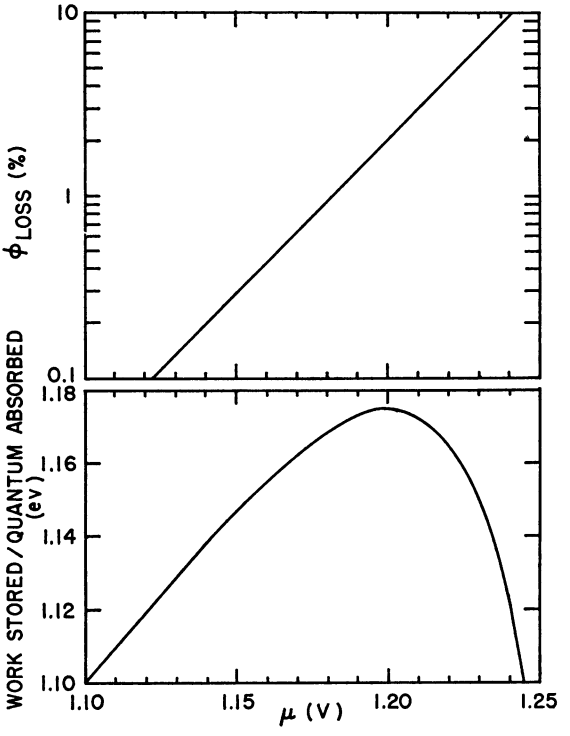

FIGURE 9 Work stored and quantum yield for loss processes as a function of excited state potential when μ_{max} = 1.30 ev. Losses due to a finite transfer rate are not considered.

Recall from Section III that the observed fluorescence yield of System I of spinach appears to be only ⅓ that of System II. One cause for this could be a greater rate of nonradiative decay in System I. If this were the sole reason, then α for System I would be 9, giving a maximum potential of 1.26 ev for this system. If α is 3 for System I, then the maximum potential is 1.29 ev.

Applying the theory outlined in Section II to the assumed maximum potentials of 1.26–1.29 and 1.33 ev for Systems I and II under 1 klux of illumination, we find that the optimal fraction of quanta lost for thermodynamic reasons is slightly more

than 2% for each system. The optimum potentials at the trap are 1.16–1.19 ev for System I and 1.23 ev for System II.

At this point we should ask how critically dependent the amount of free energy stored is on the potential at the trap. The dependence of power stored on the potential is shown in Fig. 9 for a μ_{max} of 1.30 ev. The potential for maximum work storage is 1.20 ev, but the potential can range between 1.12 ev and 1.24 ev with the amount of power stored remaining greater than 95% of this maximum.

Over this range of potential for nearly maximum free-energy storage, the quantum yield for loss processes caused by thermodynamic reversibility ranges from 0.1% to 10%. Because work storage is so insensitive to the fraction of quanta lost (in the current theory at least), and because the kinetically determined losses may differ between Systems I and II, we have no assurance that ϕ_{loss} should be the same for Systems I and II. For this reason, although it seems quite plausible, the assignment of a larger proportion of nonradiative decay to System I remains speculative with the information accumulated so far.

Recent work by Bertsch, Azzi, and Davidson (1967) indicates that the delayed light emission from System I of plants is several hundred times weaker than the delayed light from System II. If this is true, and our estimate of a System I/System II luminescence yield ratio of ⅓ from the data of Murata et al. is accurate, then the proportion of nonradiative decay in System I cannot be more than three times the proportion in System II.

Furthermore, such a large ratio of System II to System I delayed light would imply that the potential of System II is towards the upper end of the range which gives nearly maximal power storage, while the potential of System I is towards the lower end of the range which gives near maximal power storage. This would suggest a thermodynamically determined lost quantum yield of roughly 10^{-3} for System I, and 0.1 for System II. It may be that System II sacrifices quantum yield in order to develop the chemical potential necessary to oxidize water to molecular oxygen.

Purple Bacteria

We do not know the light intensities used for growing the bacteria whose absorption and fluorescence spectra were discussed in Section III. Even if we did, it is unlikely that the figure would be meaningful, as typical bacterial cultures have a high optical density, so that the mean intensity incident on a bacterium is much lower than the intensity incident on the culture as a whole.

Katz, Wassink, and Dorrestein (1942) found that the rate of photosynthesis of the purple bacterium *Chromatium*, as they cultured it, became half-saturated at 6 to 10 kerg/cm² sec of incident sodium lamp radiation when the optical density of the bacterial suspension was low. One kiloerg from such a lamp represents 0.49 nanoeinsteins of 589 nm light.

Bacterial photosynthesis has a somewhat S-shaped dependence on light intensity,

so that the efficiency of photosynthesis drops at light intensities much below the half-saturation point. For this reason we shall calculate the potential developed for 10 kerg/cm² sec of sodium radiation.

For the present calculation we shall use the absorption and fluorescence spectra of *Chromatium* obtained by Olson and Stanton which were discussed in Section III. The spectrum of the culture used by Katz et al. may have been different because of different growth conditions, but this should not introduce a serious error in the potential calculated.

The information necessary to evaluate the denominator of equation (6) is con-

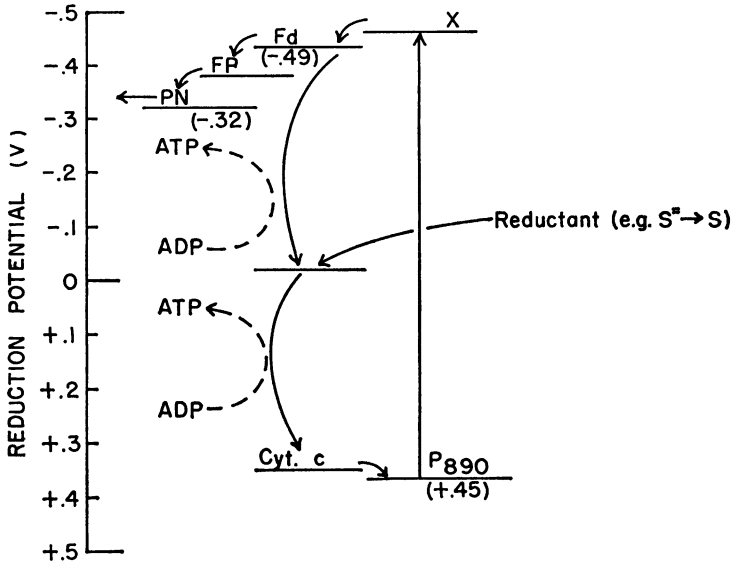

FIGURE 10 Suggested electron flow diagram for bacterial photosynthesis. The potential change indicated for the light-driven step P_{890} to *X* was determined thermodynamically.

tained in the calculations for Fig. 3 b. Combining all of the appropriate factors, we find that μ_{max} is 0.90 ev. The potential for maximum free-energy storage is 0.81 ev and the maximum free-energy storage per photon is 0.79 ev. An α of 3 would lower each of these values by 0.03 ev.

Redox Potentials of Light-Generated Biochemicals

In the previous section we found that the thermodynamic potential generated by the two systems of plant photosynthesis is about 1.2 ev, with the potential of System II being slightly higher than System I. The thermodynamic potential developed in purple bacteria is about 0.8 ev.

When the electronic excitations carrying these potentials are converted into chem-

ical energy, it is thought—at present at least—that the most probable immediate chemical consequence is an oxidation–reduction reaction. It is possible that one might have a conformational change using at least part of the energy relatively early in the process, but an ionization seems to be the most rapid possible, and hence preferable, first step.

If the primary oxidation and reduction reactions are one-electron processes, then

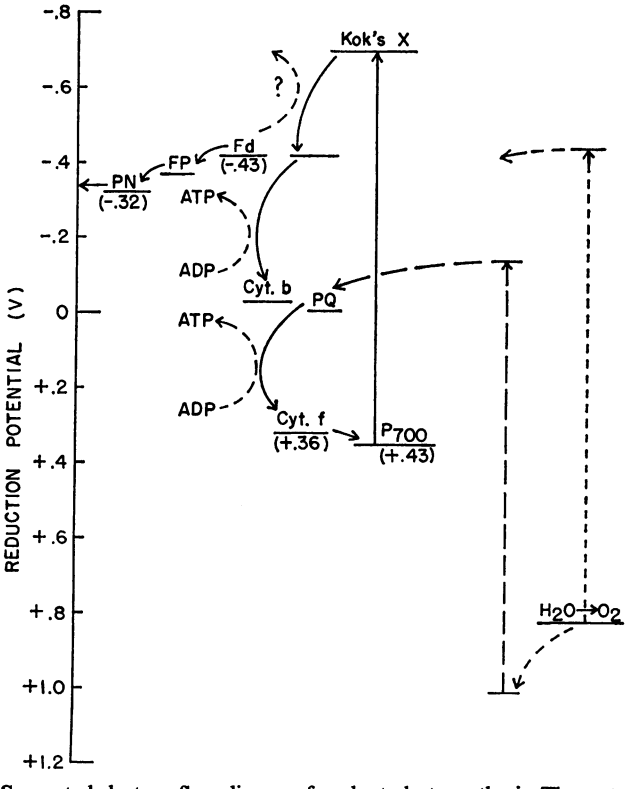

FIGURE 11 Suggested electron flow diagram for plant photosynthesis. The potential changes for the light-driven steps were determined thermodynamically. The solid line indicates the light act of System I and the vertical dashed lines indicate two possible positions for System II.

the difference between the redox potentials of these two half-reactions should be equal to the thermodynamic potentials just calculated.

One can attempt to represent the electron transport chains of bacterial and plant photosynthesis by the potential diagrams shown in Figs. 10 and 11.[4] Here the vertical arrows represent the input of free energy in the light-driven reactions, while

[4] For a review of what is known about the electron transport chain of bacterial photosynthesis, see Vernon (1964); for plants, see Clayton (1965 *b*). For a more recent review of both, see Vernon and Ke (1966).

downward arrows indicate spontaneous, or "dark" reactions. Points at which this electron transport process is thought to be coupled to energy-storing phosphorylation are indicated with the curved dotted lines.

Chemicals which have been identified as participating in the electron transport pathway are indicated by their initials, and placed according to our estimate of their redox potential when the organism is illuminated. If the primary molecules to be oxidized and reduced are largely in their "acceptor" oxidation states, then the actual potential will be shifted from the midpoint potential, which is indicated in parentheses.

Fd stands for ferredoxin; FP for flavoprotein; PN for pyridine nucleotide; Cyt. for cytochrome; PQ for plastoquinone; and P_{890} and P_{700} for molecules having absorption peaks at 890 and 700 nm which can be bleached by light, and also reversibly bleached chemically with the midpoint potentials indicated.

In the case of bacteria, the available free energy would be adequately explained by the difference in redox potentials between the well-characterized *c*-type cytochromes and P_{890}, and bacterial ferredoxin. The thermodynamics is also in accord with a proposal by Loach (1966) that a two-electron/photon oxidation–reduction occurs with midpoint reduction potentials of -0.02 and $+0.44$ v.

In System I of plants, shown as the solid vertical arrow of Fig. 11, the available energy significantly exceeds the potential difference between spinach ferredoxin, and cytochrome *f* and P_{700}. On the basis of the reduction of viologen dyes by illuminated chloroplasts, Kok, Rurainski, and Owens (1965) have proposed the existence of a System I chemical having a reduction potential in the vicinity of -0.7 v. The thermodynamic calculations support this hypothesis.

Less is known about System II, which oxidizes water to molecular oxygen in order to generate a reductant. The usual assumption that the upper end of System II terminates near plastoquinone is reasonable if one assumes that a powerful oxidant with a potential of greater than $+1.0$ v is generated, and some losses are incurred in the oxidation of water. It is also thermodynamically possible that electrons removed from water at pH 7 could be brought to the potential of ferredoxin with a single quantum of light, but this could not be done with a simultaneous phosphorylation as has been suggested by Arnon (1966); this process is indicated by the dotted line to the far right of Fig. 11. Kok and Datko (1965) have recently suggested that the reductant produced by System II has a potential of $+0.18$ v; a two-electron/photon process between this potential and the water/oxygen potential would be in accord with the thermodynamics.

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