

ENERGY STORAGE STATES OF PHOTOSYNTHETIC MEMBRANES: ACTIVATION ENERGIES AND LIFETIMES OF ELECTRONS IN THE TRAP STATES BY THERMOLUMINESCENCE METHOD

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Abstract—Several methods discussed by R. Chen (1969) were used for the calculation of the activation energies (E), frequency factors (s) and mean lifetimes (τ) of electrons in trap states at glow peak temperatures (T_m) and at room temperature (T_r) from thermoluminescence glow peaks in spinach chloroplasts and *Euglena* cells. Results are presented for E calculated independently, i.e. without any assumptions regarding the frequency factors which were determined subsequently using the activation energy values thus calculated. The most reliable values for E , s , $\tau(T_m)$ and $\tau(T_r)$ for the well-resolved glow peaks Z(118 K), I(236 K), II(261 K), III(283 K), IV(298 K) and V(321 K) are as follows:

Glow peak	E , eV	s , s^{-1}	$\tau(T_m)$, s	$\tau(T_r)$, s
Z	0.58	5.2×10^{23}	11.5	—
I	0.52	2.5×10^9	51.4	0.2
II	0.64	4.5×10^{10}	51.0	1.3
III	0.79	2.4×10^{12}	48.5	7.7
IV	1.10	1.0×10^{17}	38.4	29.0
V	1.32	1.4×10^{19}	37.4	1,062

The present comprehensive study has been compared with the earlier ones and the significance of the observed high frequency factors is discussed. It is concluded that only peaks I and II, related to photosystem II, follow the Randall–Wilkins (RW) theory, whereas peaks IV and V, related to photosystem I, do not.

INTRODUCTION

Thermoluminescence (TL), observed as a burst (or bursts) of light emission when a preilluminated sample is slowly heated, was discovered by Arnold and Sherwood (1957) in dried films of chloroplasts. This phenomenon has also been demonstrated in algal cells, leaves and chloroplasts of higher plants, and photosynthetic bacteria (see e.g. Arnold and Azzi, 1971; Shuvalov and Litvin, 1969; Fleischman, 1974; Sane *et al.*, 1977; Ichikawa *et al.*, 1975; Govindjee *et al.*, 1977). Up to six well-resolved glow peaks are observed when plant photosynthetic cells, frozen to 77 K in light and further illuminated, are slowly warmed in dark (Desai *et al.*, 1975). These glow peaks are observed around 118–120 K (Z); 236 K (peak I); 253–267 K (peak II or A); 275–303 K (peak III or B₁); 290–313 K (peak IV or B₂) and 320–328 K (peak V or C). The Z peak (118 K) is not associated with the

normal functioning of photosynthesis, but, the other peaks are associated with the electron flow in photosynthesis. Most of the peaks involve photosystem II (PSII) but photosystem (PSI) appears to be involved in peaks IV and V (see e.g. Sane *et al.*, 1977).

Using Randall–Wilkins (1945) theory, Arnold and Azzi (1968, 1971), Shuvalov and Litvin (1969), Fleischman (1974), and Lurie and Bertsch (1974a, b) have calculated activation energies for some of the above mentioned glow peaks. In the present paper, we have also applied the Randall–Wilkins theory, but have calculated the activation energies, frequency factors and the mean lifetimes of the electrons in the trap states by several methods based on the glow curve parameters. Our results emphasize the difficulties in using the Randall–Wilkins theory for peaks IV and V that are related to photosystem I.

THEORY AND METHODS OF CALCULATION

Activation energy E

Initial Rise Method. Accurate values of E can be obtained using the Randall–Wilkins (1945) theory

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only if the glow peaks are isolated and uncontaminated with other glow peaks (Bonfiglioli, 1968). Our experimental data (see Results and Discussion) approach this requirement. According to this theory, the intensity (I) of TL glow is proportional to the number of electrons escaping from the trap at a given temperature, i.e.

$$I = \text{constant} \times \left(-\frac{dn}{dt}\right) = \phi \cdot \left(-\frac{dn}{dt}\right) \\ = \phi P n \quad (1)$$

where, the negative sign indicates detrapping, n is the number of trapped electrons, P is the probability per unit time of escape from the trap of energy E and ϕ is the constant of proportionality. The first order rate constant P is given by the Arrhenius expression

$$P = \frac{1}{n} \cdot \left(-\frac{dn}{dt}\right) = s \exp(-E/kT) \quad (2)$$

where k is the Boltzman constant and s is a constant pre-exponential factor with dimensions of s^{-1} and hence is also called 'escape frequency factor' which is considered to be independent of temperature (see e.g. Austin *et al.*, 1974). From Eqs. 1 and 2 we have

$$I = \phi n s \exp(-E/kT) \quad (3)$$

i.e.

$$\ln I = -\frac{E}{k} \cdot \frac{1}{T} + \text{constant.} \quad (3')$$

The activation energy E can therefore be calculated very easily by plotting $\ln(I)$ against $1/T$. This method, known as 'Arrhenius plot' (Lurie and Bertsch, 1974a, b) or the 'initial rise method' (Bonfiglioli, 1968) assumes that n is not appreciably depleted and is valid for first as well as intermediate orders of kinetics (see Chen, 1969). We have used this method in our present studies.

Other methods. The condition of maximum of the TL glow is obtained from Eqs. 2 and 3 as (see Chen, 1969)

$$\frac{BE}{kT_m^2} = s \exp(-E/kT_m) \quad (4)$$

where B is the linear heating rate and T_m the temperature of maximum glow. Assuming a 'reasonable' s value from the work of Randall and Wilkins (1945), Arnold and Azzi (1968) have calculated the values for E (see also Malkin, 1977a). The use of glow curves for calculating the values of E has been viewed with disfavor (Malkin and Hardt, 1973; Malkin, 1977b) since one has to choose the value of s arbitrarily. In the present paper, however, the activation energy is calculated without any assumptions regarding s which is determined subsequently, as described below.

Chen (1969) has described a number of methods for calculating the activation energies without assuming values for s . The basic Eq. underlying them can be written as

$$E = CkT_m^2/\Delta T \quad (5)$$

where, C is a constant specific of the particular method and ΔT denotes the temperature differences as indicated in Table 1 (see footnote to the table).

The value of E according to Chen's modification of Halperin and Braner (1960) equation is given by

$$E = \frac{1.52 kT_m^2}{T_m - T_1} - 1.58 \times 2kT_m \quad (6)$$

A similar equation is used by Grossweiner (1953) and by Lurie and Bertsch (1974a, b). These equations differ from each other in the value of the numerical constant only and it was found that the errors caused due to small errors of measurement of T_m and T_1 much outweighed the differences due to the value of this constant. Hence, in the following calculations, Grossweiner's 1.51 is used as the constant.

Similarly, it is expected that Chen's formula using full width at half height (FWHH) should give more accurate results due to relatively smaller error possible in its determination. Again, if ϵT_m is the error in the measurement of T_m , $\epsilon T_m/T_m$ is relatively small. The term T_m appearing in all the equations in the numerator can therefore contribute only a small additional inaccuracy. Chen's method of using $T_2 - T_1$ thus appears most reliable when the initial rise method cannot be used for some reason (see also Haake, 1957).

The possible proximity of the electron traps and the luminescence centers has led us to assume the applicability of first order kinetics (see for example Halperin and Chen, 1966). This assumption seems justified since the activation energies obtained are in reasonable agreement with the values obtained by the initial rise method (see Eq. 3' above).

The pre-exponential factor, s , and mean life-time, τ

The other important parameter to be determined from the glow curves is the mean life-time, τ , of the electrons in the trap states in view of the possible correlation it might have with the kinetics of delayed light emission (Shuvalov and Litvin, 1969). As a consequence of Eqs. 2 and 4 at T , τ is given by

$$\tau = \frac{1}{P} = \frac{\exp(E/kT_m)}{s} \quad (7)$$

where T is the temperature at which τ is determined (Medlin, 1968). It is observed that, E , T and s need to be determined accurately for obtaining the estimate of τ . In the present paper, we have considered T as the independent variable and determined E , from Arrhenius plots (Augenstine *et al.*, 1969). The values of E are then used to determine the s factors (Eq. 4). We have assumed s to be constant for the same glow peak and independent of temperature and similarly calculated the life-times $\tau(T)$ at room temperature. Such assumption has previously been made in other areas of thermoluminescence for finding out the stability of the electrons in the traps (Fieschi and Scaramelli, 1968).

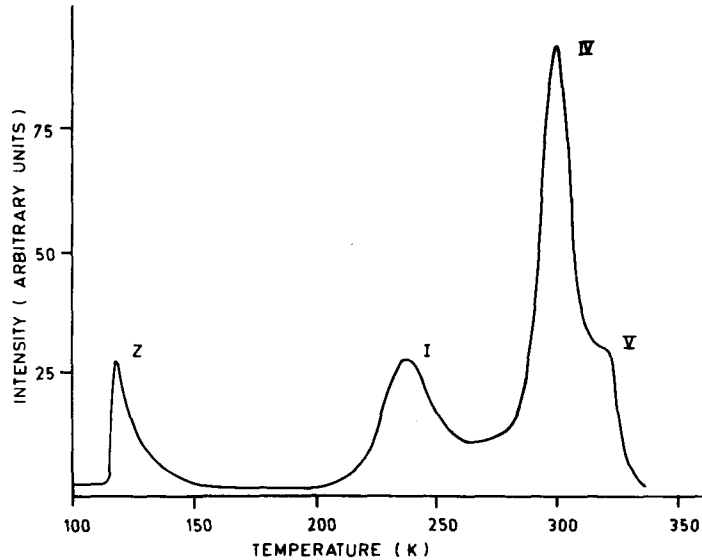


Figure 1. Glow curve of spinach chloroplasts frozen in the presence of intense white light to 77 K.

Limitations of the theory

It is usually assumed that all the parameters in the first order equations above are constant. The photosynthetic membrane, however, is known to undergo structural and conformational changes during electron transport and these changes are temperature dependent. The assumption about the constancy of the parameters such as the activation energy and the frequency factor would therefore be true only in a limited sense (e.g. small or no temperature change). As mentioned in the Introduction, the present paper attempts to bring out the difficulties in using the Randall-Wilkins theory to the photosynthetic membrane

and the values arrived at by the application of the RW theory here may be considered in the light of these limitations.

MATERIALS AND METHODS

Chloroplasts from spinach leaves were isolated according to the procedure of Sane *et al.* (1970). Chloroplast glow curves were obtained as described earlier (Desai *et al.*, 1975). The rate of heating of the sample was $0.18^{\circ}\text{C s}^{-1}$. The untreated chloroplasts give glow curves (Fig. 1) that are ideal for analysis by the Arrhenius procedure, the peaks appearing at 118 K (Z-peak), 236 (peak I) and 298 K (peak IV). A 16 times faster chart speed for recording the Z peak was used to bring out the exponential rise (not shown in

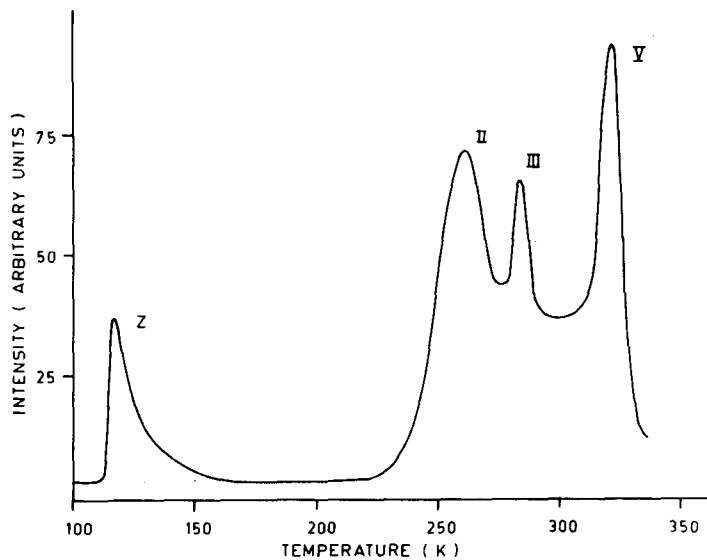


Figure 2. Glow curve of spinach chloroplasts—same as in Fig. 1 except for pretreatment of chloroplasts with $10 \mu\text{M}$ DCMU.

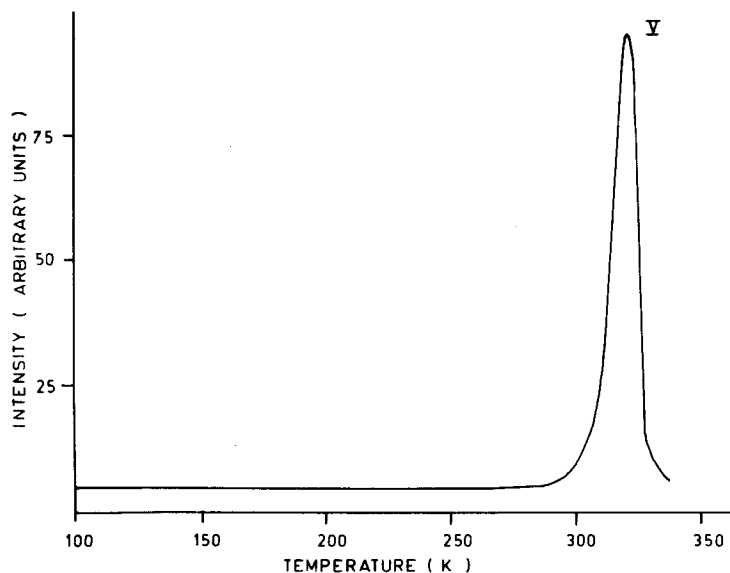


Figure 3. Glow curve of *Euglena* cells relaxed at room temperature for 5 min before freezing in dark to 77 K.

the figure) of the initial portion. However, in Fig. 1 peaks II and V are not resolved. In order to obtain a well resolved peak II, chloroplasts treated with $10 \mu\text{M}$ DCMU [3-(3,4-dichlorophenyl)-1,1-dimethylurea] were used (Fig. 2). Figure 2 was also used for calculating the activation energy for peak III. For peak V preilluminated *Euglena* cells were allowed to relax in the dark for 5 min at room temperature (Fig. 3). This results in the loss of all other peaks.

RESULTS AND DISCUSSION

Activation energies

An analysis of different glow peaks in three different samples by the Arrhenius method is given in

Figs 4 and 5. E values calculated by three different methods (see Eq. 5 and related discussion) and by the Arrhenius method (Eq. 3') as described in the Theory Section are presented in Table 1. In each case mean values of three sets of observations are given. The E values for the various peaks are: 0.29–0.58 eV (Z peak); 0.48–0.68 eV (I); 0.43–0.64 eV (II); 0.79–1.58 eV (III); 0.98–1.44 eV (IV); and 1.32–2.03 eV (V). In most cases, the E value is highest with the Halperin and Braner's procedure and out of line with the other methods. The errors introduced by the use of this method are due to the inaccuracies involved in determining T_1 and T_m due to (1) fast rising glow

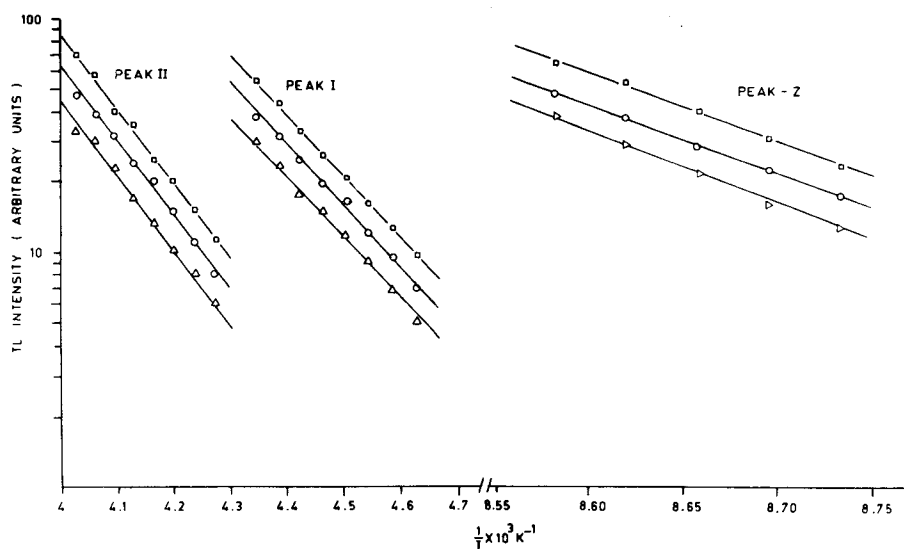


Figure 4. Arrhenius plots for glow curves of Z, I and II peaks. The three plots represent three independent experiments in each case.

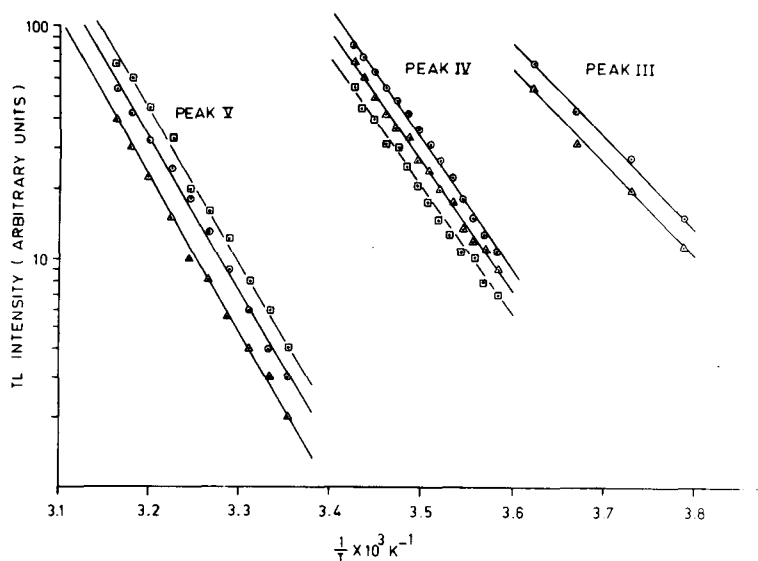


Figure 5. Arrhenius plots for peaks III, IV and V, each line representing an independent experiment.

curves or (2) mixing of the adjoining glow peaks when the interfering peak is large. Furthermore, since the difference $\alpha = (T_m - T_1)$ is smallest of the temperature differences and comes in the denominator, the error involved in E is greatest by this method. We consider the E values obtained by the initial rise method as the most reliable ones. These E values of 0.58 eV (Z); 0.52 eV (I); 0.64 eV (II); 0.79 eV (III); 1.10 eV (IV); and 1.32 eV (V) are compared with those reported by earlier workers for equivalent peaks in Table 2. An

examination of this table shows clearly the similarity and differences of our results with those of the others.

A plot of the calculated Randall-Wilkins (RW) curves for each of the five peaks reported here shows that only peaks I and II follow the RW differential equation (Arnold, personal communication). Furthermore, the Arrhenius plot for peak V gives a value of 1.32 eV, whereas a simple calculation by the 1968 method of Arnold and Azzi using an assumed value of $2.63 \times 10^9 \text{ s}^{-1}$ for the frequency factor gives a value

Table 1. Activation energies in electron volts of different glow peaks

Methods*	Formula	Z (118 K)	I (236 K)	II (261 K)	III (283 K)	IV (298 K)	V (321 K)
Chen's	$E = \frac{2.29 kT_m^2}{\gamma}$	0.31	0.59	0.47	1.21	1.18	1.45
		0.34	0.58	0.48	1.43	1.14	1.40
		0.39	0.52	0.54	1.43	1.12	1.94
		Mean	0.35	0.56	0.50	1.36	1.15
Luschick's	$E = \frac{0.976 kT_m^2}{\beta}$	0.26	0.49	0.41	1.12	1.01	1.25
		0.29	0.49	0.41	1.34	0.97	1.20
		0.33	0.45	0.46	0.96	0.96	1.65
		Mean	0.29	0.48	0.43	1.14	0.98
Halperin and Braner's	$E = \frac{1.52 kT_m^2}{\alpha} - 1.58 (2kT_m)$	0.37	0.71	0.55	1.66	1.49	1.84
		0.42	0.70	0.57	1.66	1.43	1.77
		0.49	0.64	0.64	1.42	1.41	2.48
		Mean	0.43	0.68	0.59	1.58	1.44
Initial rise (Arrhenius Plot)	$I = \phi ns \exp(-E/kT)$ Plot $\ln(I)$ vs $1/T$ (Equation 3) to get E	0.55	0.52	0.64	0.79	1.12	1.31
		0.58	0.54	0.63	0.79	1.10	1.31
		0.61	0.51	0.64		1.09	1.35
		Mean	0.58	0.52	0.64	0.79	1.10

*See text for references to the methods. E = activation energy; k = Boltzmann constant; T_m = temperature of maximum intensity of the glow peak; ΔT (Equation 5) = γ or β or α , where, γ = total width of the glow peak at half intensity; β = half-width of the glow peak on the high temperature side; α = half-width of the glow peak on the low temperature side.

Table 2. Activation energies, E , of glow peaks (eV)

No.	Authors	Z(118 K)	I(236 K)	II(261 K)	III(283 K)	IV(298 K)	V(321 K)	Remarks
1.	Arnold and Azzi (1971)	—	A: 0.52	"DCMU": 0.62	—	B: 0.64	C: 0.64	Heating at "several degrees per second".
2.	Shuvalov and Litvin (1969)	L_1 : 0.067 (nr)	L_2 : 0.35 (r) 0.27 (nr)	—	—	—	L_3 : 0.09 (r) 0.42 (nr)	(r): radiative process following thermal detrapping; (nr): non-radiative. Heating, 0.01 to 1 degrees per second.
3.	Lurie and Bertisch (1974a, b)	—	0.80	0.48	—	—	0.57(?)	Heating: 7 to 12 degrees per second.
4.	Present paper (Arrhenius Plot)	0.58	0.52	0.64	0.79	1.10	1.32	Heating: 0.18 degrees per second.

Note: The different glow peaks reported have been grouped according to our temperature determination, and the classification suggested by their behaviour on DCMU treatment. A, "DCMU", B and C are designations of Arnold; L_1 , L_2 and L_3 are designations of Shuvalov and Litvin; Arrh. Arrhenius plot.

Table 3. Frequency factor (s) and mean life times (τ) of electrons in trap states at glow peak temperature (T_m) and at room temperature (T_r)

Method*	Z (118 K)	I (236 K)	II (261 K)	III (283 K)	IV (298 K)	V (321 K)
Chen's	s $\tau(T_m)$ $\tau(T_r)$	1.9×10^{10} 47.7 s 1.3×10^{-1} s	6.9×10^7 65.3 s 3.6 s	5.9×10^{22} 28.2 s 1.2 s	7.6×10^{17} 37.0 s 27.4 s	4.3×10^{23} 30.8 s 1.8×10^3 s
Luschick's	s $\tau(T_m)$ $\tau(T_r)$	3.2×10^8 55.7 s 3.6×10^{-1} s	2.7×10^6 75.9 s 6.3 s	6.0×10^{18} 33.6 s 2.4 s	8.7×10^{14} 43.4 s 33.6 s	9.0×10^{19} 36.0 s 1.2×10^3 s
Halperin & Braner's	s $\tau(T_m)$ $\tau(T_r)$	8.5×10^{12} 39.2 s 3.1×10^{-2} s	4.5×10^9 55.3 s 1.6 s	5.7×10^{26} 25.3 s 0.6 s	7.7×10^{22} 29.5 s 20.3 s	3.1×10^{30} 24.3 s 4.1×10^3 s
(Chen's modification)	s $\tau(T_m)$ $\tau(T_r)$	2.5×10^9 51.4 s 2.2×10^{-1} s	4.5×10^{10} 51.0 s 1.3 s	2.4×10^{12} 48.5 s 7.7 s	1.0×10^{17} 38.6 s 29.0 s	1.4×10^{19} 37.4 s 1.1×10^3 s
Initial rise method	—	—	—	—	—	—

*See the legend of Table 1.

of 0.71 eV. This also suggests that the simple RW theory does not apply to peak V. However, the activation energies of peaks I–V are thus observed to increase, as might be expected, with the glow peak temperature.

According to our previous assignment (Desai *et al.*, 1975; Sane *et al.*, 1977) peaks IV and V belong to PSI; these have E values greater than 1 eV when calculated by any of the above methods. Peaks I and II, on the other hand, belong to PSII; these have lower E values (0.52–0.64 eV), while peak III, which is related to the intersystem electron transfer chain (Desai *et al.*, 1975) has an intermediate E value of 0.8 eV. These values are consistent with the experimental observation that delayed fluorescence requiring low activation energies in PSII is high at low temperatures, while delayed fluorescence from PSI requiring more activation energy is observable at higher temperatures (Sane *et al.*, 1980).

Frequency factors and mean life times of electrons

Using the E values from Table 1, and Eq. 4, frequency factors and mean lifetimes of the electrons in the trapped state were calculated and are presented in Table 3.

The values for frequency factors, calculated in the present work for Z, and I–V peaks, range from 5.2×10^{23} to $2.5 \times 10^9 \text{ s}^{-1}$. As can be seen in the table, these factors, when calculated by different methods differ by several orders of magnitude. However, the mean lifetimes of electrons in the trap states at the glow peak temperature $\tau(T_m)$ by the Arrhenius method for Z, and I–V peaks range from 11 to 51 s. Values of $\tau(T_m)$ obtained by the other methods are quite similar to those presented above. Finally, the mean lifetimes of electrons in trap states at room temperature $\tau(T_r)$ for I–V peaks were found to be 0.2, 1.3, 7.7, 29.0 and ~ 1000 s, respectively. To a first approximation, the order of magnitudes of $\tau(T_r)$ values by all the methods are comparable.

The τ values for the electrons in the trap states, at room temperature, obtained here (in the ms and in the second region for peaks I and II, respectively) agree with those obtained by other workers. These two peaks assigned by us previously to PSII probably represent the two major components of delayed light emission which have been demonstrated to originate in PSII (see reviews by Lavorel, 1975a; Malkin, 1977a). The peaks IV and V apparently associated with PSI are distinct from other peaks in having relatively large (seconds and minutes) τ values. Our τ values (37 s for peak IV and ~ 1000 s for peak V) do not agree with those obtained by Shuvalov and Litvin (1969) and Lurie and Bertsch (1974a, b) who obtained a value of 1.6 s for both peaks IV and V. Our values must be correct because the complete relaxation of the chloroplast or leaf (i.e. loss of all glow peaks) requires 4–5 min. The relationship of these high temperature glow peaks to DLE at high temperatures

from PSI has recently been strengthened by the data of Sane *et al.* (1980). This means that the energy storage states associated with PSI are far more stable as compared to those associated with PSII. The charge separation in PSI thus seems to be well stabilized and hence prevents recombination of oxidized and reduced entities produced during the functioning of PSI.

The high values of pre-exponential (frequency) factors in the Arrhenius equation require further comment. The frequency factor corresponding to a vibrational quantum of energy, kT ($f = kT/h$) is $\approx 6 \times 10^{12} \text{ s}^{-1}$ where h is the Planck's constant and $kT = 0.0252 \text{ eV}$ at 20°C . kT/h is the well known frequency factor(s) appearing in the absolute reaction rate theory (Eyring, 1935a, b). Values of s higher than 10^{12} s^{-1} , ranging from 10^{17} to 10^{23} s^{-1} , indicate that the Randall–Wilkins theory may not be adequate to explain all the glow peaks from photosynthetic membranes. DeVault (1980) states that if the frequency factor is appreciably less than 10^{13} s^{-1} , for the first order reaction, then electron tunneling is the rate determining step. The values of s for peaks I, II and III therefore suggest electron tunneling. However, the high values of this factor for peaks IV and V suggest that electron tunneling is not rate limiting here.

The pre-exponential factor is also defined by the equation.

$$s = \nu_0 \exp(S/k) \quad (8)$$

where ν_0 is the characteristic trap frequency and S is the vibrational entropy associated with the trapped electron (Mott and Gurney, 1940; Beall-Fowler, 1968). The occurrence of large frequency factor would then mean large changes in the phonon modes of ions neighboring the electron trap. Modifying Eq. 7, we have

$$\tau = \frac{1}{P} = \frac{\exp(E/kT)}{\nu_0 \exp(S/k)} \quad (7')$$

where S would be the entropy associated with the filled electron trap specified by the temperature T . Considering the mean lifetimes of the electrons in the trap states at the two temperatures $\tau(T_m)$ and $\tau(T_r)$ given in Table 3, the change in the entropy ΔS involved in the release of the electrons from the traps is given by

$$\Delta S = k \ln \left(\frac{\tau(T_m)}{\tau(T_r)} \right) - \frac{(T_r - T_m)E}{T_r T_m} \quad (9)$$

Using the $\tau(T_m)$ and $\tau(T_r)$ values from Table 3 for the glow peaks the ΔS values are found to be: 3.49×10^{-7} (Z), -1.89×10^{-7} (I), -6.15×10^{-7} (II), -9.88×10^{-9} (III), 1.02×10^{-8} (IV) and -3.32×10^{-7} (V). These values are thus seen to be extremely small and, when substituted in Eq. 7, do not materially affect the value of s . It thus appears that the applicability of the Randall–Wilkins theory to the photodynamic structure like a chloroplast is

limited and that we have to look elsewhere for the interpretation of the high pre-exponential factor for peaks IV and V, related to PSI. Nevertheless, the analysis of the glow peaks carried out above brings out, for the first time, two distinct groups of trapped electrons associated with the two photosystems, the

PSII peaks following the Randall–Wilkins theory and the PSI ones not without further modifications.

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