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## Photosynthetic glow peaks and their relationship with the free energy changes

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### Abstract

This paper is concerned with relating thermoluminescence to the total free-energy change,  $\Sigma G$ , involved in detrapping a particular electron-hole pair as a photosynthetic sample is warmed from an initial low temperature. It extends a mathematical discussion of four possible mechanisms introduced in an earlier paper [DeVault, Govindjee and Arnold, *Proc Nat'l Acad Sci USA* 80: 983–987 (1983)]; here, particular attention is paid to the dependence of the absolute temperature of the maximum of a glow-peak,  $T_m$ , on the total free-energy change,  $\Sigma G$ . The conclusion from the cases studied is that  $T_m = \Sigma G / (k_B W)$  where  $\Sigma G$  is evaluated at  $T_m$ ,  $W$  is a complicated function of temperature and of thermodynamic parameters in the steps of the mechanism, and  $k_B$  is the Boltzmann constant. If the rate limiting step in the mechanism of detrapping is not preceded by any step in which  $\Delta G$  is appreciably negative,  $W$  is likely to have a value of about 33 and  $T_m$  is approximately proportional to  $\Sigma G$ . Otherwise  $W$  can become much smaller and more strongly dependent on temperature and  $T_m$  is no longer proportional to  $\Sigma G$ . These conclusions are of significance in lending theoretical support to the practice of inferring redox midpoint potential changes from shifts in  $T_m$ .

### Glossary of terms

$B$	Rate of heating, $\text{deg s}^{-1}$	$h$	Planck's constant, $4.13559 \times 10^{-15} \text{ eV s}$
DCMU	3-(3',4'-dichlorophenyl)-1,1-dimethylurea	$\Sigma H$	Defined in Table 2
den	Defined in Table 1	$\Delta H$	Standard enthalpy increase during electron transport
den'	Derivative of den with respect to $T$	$\Delta H^*$	Enthalpy of activation for rate-limiting step
$E_m$	Midpoint redox potential, vs. normal $\text{H}_2/\text{H}^+$ cell	$k_B$	Boltzmann constant, $8.6171 \times 10^{-5} \text{ eV K}^{-1}$
$\Delta E_m$	Increase in redox midpoint potential	$\ln$	Natural logarithm
$ET$	Electron transfer process	$n$	Number of trapped electrons as a function of time or temperature
$F(T)$	Function of $T$ defined by Eq. (2) and Table 1	num	Defined in Table 1
$F$	Faraday constant, $96487 \text{ coulombs mol}^{-1}$	num'	Derivative of num with respect to $T$
$\Sigma G$	$\Sigma H - T \Sigma S$	$\Sigma S$	Defined in Table 2
$\Delta G$	Standard free energy increase during electron transport. $\Sigma H - T \Delta S$	$\Delta S$	Standard entropy increase during electron transport
$\Delta G^*$	Free-energy of activation of rate-limiting step	$\Delta S^*$	Entropy of activation of rate limiting step
		$T$	Absolute temperature

$T_m$	$T$ at maximum intensity of a thermoluminescence band
$W$	Defined in Eq. (6)
$X$	Defined in Table 2

## Introduction

The purpose of this communication is to extend the theoretical treatment of thermoluminescence (glow peaks) of plants presented earlier (DeVault et al. 1981, 1983) in order to find its relationship with the free energies and redox potentials of intermediates involved in the process. In order to appreciate the problem, a brief discussion of thermoluminescence is necessary. Illumination of photosynthetic samples causes charge separation in the reaction center complex. These charges move to other intermediates. Freezing the samples to 77 K freezes the intermediates in their charged states. Upon warming, the charges move back to the initial intermediates as the temperature provides the necessary activation energy. In this fashion, the chlorophyll  $a$  molecule is reexcited chemically, and the light emission (glow) occurs as thermoluminescence. Theoretical treatments were presented by DeVault et al. (1981, 1983) and Vass et al. (1981); the phenomenon in plants has been reviewed by Inoue and Shibata (1982), Sane and Rutherford (1986) and Demeter and Govindjee (1989). A significant success of the analysis by DeVault et al. (1981, 1983) was its ability to explain the non-Randall-Wilkins nature of the glow peaks, discovered by Tatake et al. (1981). A major recent application of thermoluminescence measurements has been in studying effects of ADRY agents (Renger and Inoue 1983) and herbicides on plants and of herbicide resistance in plants (Demeter et al. 1985). The latter authors identified certain glow peaks with particular trapped states and showed that shifts of the peak temperatures,  $T_m$ , are proportional to alterations of the midpoint potential of the secondary quinone acceptor,  $Q_B$ , as estimated by changes of the apparent activation energy obtained by computer assisted fitting of the Randall-Wilkins formula to the glow peak data. In view of the general acceptance of the notion [see also, e.g., Sane and Rutherford (1986) and Demeter and Govindjee (1989)] that changes in peak temperatures of thermoluminescence reflect changes in midpoint

redox potentials ( $E_m$ ) of intermediates and thus, of free energy changes ( $\Delta G = -nF\Delta E_m$ , where  $F$  = Faraday constant), and in response to a need to know to what extent peak temperature shifts are proportional to or otherwise dependent on shifts of redox potentials, we present our current analysis here. If it is not clear from the first paper (DeVault et al. 1983) or from the use of the symbol  $E_m$  above, note that the  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  symbols in this paper all refer to "standard state" values.

Our analysis, at least in the cases examined, supports not only the notion that changes in  $T_m$  are proportional to changes in free energy (and, thus, of changes in midpoint potential) but also that  $T_m$ , itself, is proportional to  $\Sigma G$ , the total free energy required for the detrapping including the free energy of activation,  $\Delta G^*$ , in the rate limiting step. An exception occurs if any step of the detrapping process has  $\Delta G$  appreciably (say, compared to  $k_B T$ ) negative. A detrapping step with negative  $\Delta G$  would be a downhill reaction. In the opposite direction it would be an up-hill step, hindering forward electron transport. At present, we know of no such step in photosynthetic electron transport and we guess that it is probably rare. Thus, we conclude that, for the cases examined,  $T_m$  can usually be considered approximately proportional to  $\Sigma G$ .

## Theory

The temperature,  $T_m$ , at the peak of the glow curve was given by DeVault et al. (1983) as the solution, for  $T$ , of the following differential equation:

$$\frac{dF(T)}{dT} = \frac{[F(T)]^2}{B} \quad (1)$$

where  $T$  is the absolute temperature and  $B$  is the rate of heating.  $F(T)$  is a function of  $T$  whose form depends upon the detrapping mechanism. One must specify a form for  $F(T)$  before one can solve Eq. (1). In the following we will derive an expression for  $T_m$ , given certain forms for  $F(T)$ .

A general form of  $F(T)$  for several different possible mechanisms can be written as:

$$F(T) = \frac{k_B T}{h} \cdot \frac{\text{num}}{\text{den}} \quad (2)$$

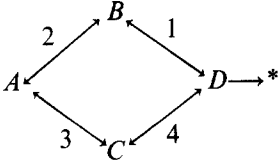
where  $k_B$  and  $h$  are defined in the Glossary of terms. Table 1 exhibits the specific forms of num and den

Table 1. Forms for Eq. (2) for specific mechanisms.

Mechanism No.	Preceding steps	num	den
I.	None (Randall-Wilkins)	$\exp\left[-\frac{\Delta G^*}{k_B T}\right]$	1
II.	One	$\exp\left[-\frac{\Delta G^* + \Delta G_1}{k_B T}\right]$	$1 + \exp\left[-\frac{\Delta G_1}{k_B T}\right]$
III.	Two in series	$\exp\left[-\frac{\Delta G^* + \Delta G_1 + \Delta G_2}{k_B T}\right]$	$1 + \exp\left[-\frac{\Delta G_2}{k_B T}\right] + \exp\left[-\frac{\Delta G_1 + \Delta G_2}{k_B T}\right]$
IV.	Two in parallel each having two in series (# 1 and 2 in one series, 3 and 4 in other; 1 and 4 immediately precede rate limiting step.)	$\exp\left[-\frac{\Delta G^* + \Delta G_1 + \Delta G_2}{k_B T}\right]$	$1 + \exp\left[-\frac{\Delta G_2}{k_B T}\right] + \exp\left[-\frac{\Delta G_3}{k_B T}\right] + \exp\left[-\frac{\Delta G_1 + \Delta G_2}{k_B T}\right]$

Note: In IV:  $\Delta G_3 + \Delta G_4 = \Delta G_1 + \Delta G_2$ . See diagrams below Eq. (2) in text for further description of mechanisms.

for the following four possible mechanisms [also considered in DeVault et al. (1983)]:

- I.  $A \rightarrow *$  activation step only.
- II.  $A \xrightleftharpoons{1} B \rightarrow *$  activation preceded by one equilibrium
- III.  $A \xrightleftharpoons{2} B \xrightleftharpoons{1} C \rightarrow *$  activation preceded by two equilibria in series.
- IV.  activation preceded by two parallel paths each consisting of 2 steps in series.

$A$  represents the initial state of the system before beginning to warm it up. It could be, for example,  $S_2 P_{680} Q_B^-$ , where  $S_n$  represents the redox state of the

oxygen evolving complex,  $P_{680}$  is the reaction center chlorophyll of Photosystem II,  $Q_A$  is the one-electron acceptor bound plastoquinone, and  $Q_B$  is the two-electron acceptor plastoquinone that communicates with the plastoquinone pool.  $B$  represents an intermediate state of the system in equilibrium with  $A$ , for example  $S_2 P_{680} Q_A^- Q_B^-$ .  $C$  represents a second intermediate state, say  $S_1 P_{680}^+ Q_A^- Q_B^-$ . An example of  $D$  could be  $S_1 P_{680}^+ Q_A^- Q_B^-$ . The step,  $\rightarrow *$ , represents the rate-limiting activated step which can give rise to the fluorescence with some quantum yield. Radiationless decay would compete. In absolute reaction rate theory  $*$ , the activated state, is also treated as a state mostly in equilibrium with the preceding state.

Except for mechanism I, which is simply the Randall-Wilkins (1945) mechanism, the other three mechanisms assume that the rate-determining step is preceded by one or more faster steps which come to near-equilibrium. They affect the rate by governing the amount of substrate ready for the rate-determining step. To calculate accurately one needs the equilibrium constants or, alternatively the free energy changes, for each step and their dependence on temperature.

From thermodynamics:

$$\frac{\partial \Delta G}{\partial T} = -\Delta S \quad (3)$$

where the  $\Delta S$  is the increase of entropy associated with the same detrapping step to which  $\Delta G$  applies. Thus knowledge of  $\Delta S$  is needed and  $\Delta G$  is not independent of temperature unless  $\Delta S = 0$ . DeVault et al. (1983) used  $\Delta H$  and  $\Delta S$  instead of  $\Delta G$  and considered  $\Delta H$  and  $\Delta S$  to be independent of temperature. The values needed for the  $\Delta G$ 's in Table 1 and for associated  $\Delta S$ 's are the values at  $T_m$ . If  $\Delta H$  and  $\Delta S$  are independent of temperature then  $\Delta G(T_m) = \Delta G(298) + (298 - T_m)\Delta S$ .

Substituting Eq. (2) into Eq. (1) gives:

$$-\ln(\text{num}) = \ln\left(\frac{k_B T_m^2}{hB}\right) - \ln\left[\left(\text{den} \cdot \frac{\text{num}'}{\text{num}} - \text{den}'\right) T_m + \text{den}\right], \quad (4)$$

where the primes indicate derivative with respect to  $T$ . At least for the four mechanisms (Tables 1 and 2), Eq. (4) can be put into a simpler form:

$$T_m = \frac{\Sigma H}{\Sigma S + k_B W} = \frac{\Sigma G}{k_B W} \quad (5)$$

where

$$W = \ln\left[\left(\frac{k_B T_m^2}{hB}\right)\left(1 + \frac{\Sigma H}{k_B T_m} + X\right)^{-1}\right] \quad (6)$$

and the new terms are defined in Table 2 (also see Glossary of terms).  $W$  and  $\Sigma G$  depend to a large or a small extent on  $T_m$  so that Eq. (5) can be solved strictly only by iteration.

In Table 2 it is seen that  $\Sigma S$  and  $\Sigma H$  are simply the entropy and enthalpy respectively in the activated state of the rate-limiting step minus that in the initial state before de-trapping.  $\Sigma G$  ( $= \Sigma H - T\Sigma S$ ) is the total free-energy increase in the de-trapping process including activation for the rate-limiting step.  $\Delta H^*$  (called  $E$  in DeVault et al. 1983) and  $\Delta S^*$  are the activation energy or enthalpy and activation entropy, respectively.

## Results and discussion

Equations (5) and (6) can be used to evaluate the relationship between  $T_m$  and  $\Sigma G$ . In Table 2,  $X$  is the only term that depends in a complicated way on the mechanism. Since it appears as merely an additive part within a logarithm, its influence on  $T_m$  can be minor compared to that of  $\Sigma S$  and  $\Sigma H$  under some conditions. Thus, as an approximation,  $W$ , a logarithmic quantity, may be regarded in these conditions as practically temperature-independent,

Table 2. Definition of terms in Eq. (5)

Mechanism No.	$\Sigma S$	$\Sigma H$	$X$
I.	$\Delta S^*$	$\Delta H^*$	0
II.	$\Delta S^* + \Delta S_1$	$\Delta H^* + \Delta H_1$	$\left(1 + \frac{\Delta H^*}{k_B T}\right) \exp\left(-\frac{\Delta G_1}{k_B T}\right)$
III.	$\Delta S^* + \Delta S_1 + \Delta S_2$	$\Delta H^* + \Delta H_1 + \Delta H_2$	$\left(1 + \frac{\Delta H^* + \Delta H_1}{k_B T}\right) \exp\left(-\frac{\Delta G_2}{k_B T}\right)$ $+ \left(1 + \frac{\Delta H^*}{k_B T}\right) \exp\left(-\frac{\Delta G_1 + \Delta G_2}{k_B T}\right)$
IV.	$\Delta S^* + \Delta S_1 + \Delta S_2$	$\Delta H^* + \Delta H_1 + \Delta H_2$	$\left(1 + \frac{\Delta H^* + \Delta H_1}{k_B T}\right) \exp\left(-\frac{\Delta G_2}{k_B T}\right)$ $+ \left(1 + \frac{\Sigma H - \Delta H_3}{k_B T}\right) \exp\left(-\frac{G_3}{k_B T}\right)$ $+ \left(1 + \frac{\Delta H^*}{k_B T}\right) \exp\left(-\frac{\Delta G_1 + \Delta G_2}{k_B T}\right)$

and then to this approximation  $T_m$  is proportional to  $\Sigma G$ , the total free energy increase required to detrapp an electron-hole pair.

Better than taking  $W$  constant is the approximation of assuming  $X = 0$ . This is exact for the Randall-Wilkins mechanism. In the other three mechanisms it amounts to using the Randall-Wilkins mechanism with  $H^*$  replaced by  $\Sigma H$  and  $S^*$  by  $\Sigma S$ . It ignores the partitioning of  $\Sigma H$  and  $\Sigma S$  into their constituent parts. It is very accurate when  $X$  is actually smaller than either 1 or  $\Sigma H/k_B T_m$ , whichever is larger, because then  $X$  is truly negligible.  $X$  does not have to be much smaller because the logarithm suppresses small differences. When applicable this approximation frees one from considering details of the steps. Table 3 shows how little  $W$  varies with a wide range of the variables needed to calculate  $W$  according to Eq. (6). The range of  $T_m$  and  $\Sigma H$  includes most experimental conditions in photosynthesis research. Increase of  $T_m$  and decrease of  $\Sigma H$  both increase  $W$ , so the choices presented in Table 3 enhance rather than compensate their effects. Thus the values of  $W$  found in Table 3 should cover most cases one can expect if mechanism I applies or if  $X$  is small enough in any of the other mechanisms that it can be neglected.

We conclude from Table 3 that when  $X$  is negligible,  $W$  is about 33 (33.2 if the heating rate is  $0.2 \text{ K s}^{-1}$  or about 32.0 if the rate is  $0.67 \text{ K s}^{-1}$ ). One can calculate from Table I of Demeter et al. (1985), who heated at  $0.67 \text{ K s}^{-1}$  that they measured experimentally a proportionality constant between  $k_B T_m$  and  $\Sigma G$  equal to 32.3 and 32.6 for triazine susceptible and resistant biotypes, respectively, of *Erigeron canadensis* and 32.1 when treated with DCMU.

However, a different conclusion is made if  $X$  is large. This is not caused by the terms containing  $\Delta H/k_B T$  in the formulas for  $X$  shown in Table 2. These are always smaller than  $\Sigma H/k_B T$ . It would be

caused by the  $\exp(-\Delta G/k_B T)$  factors if the  $\Delta G$  concerned is negative. Then the factor becomes exponentially large and does not become insignificant by taking the logarithm. The  $\Delta G$  involved would never be  $\Delta G^*$ , however. One needs only to look at the  $\Delta G$ 's for the preceding equilibrium steps. Table 4 presents some hypothetical calculations based on Eqs. (5) and (6) in which  $\Delta G_1$  for the step preceding the activated step is varied from positive to negative. The effects on  $T_m$ ,  $X$  and  $W$  are shown.

It may be of interest to note how the proposed mechanisms affect the practice of estimating apparent  $\Delta H^*$  from the rate of rise of the early part of a glow peak and using this with the observed  $T_m$  to estimate the pre-exponential frequency factor or the related  $\Delta S^*$  as has been done (see e.g., Tatake et al. 1981) assuming Randall-Wilkins mechanism. Of course this only applies to cases in which the glow peak is sufficiently isolated from peaks occurring at lower temperatures so that the rising edge can be observed. In DeVault et al. (1983) it was shown that, on the basis of the proposed mechanisms, before there is appreciable depletion of the traps the intensity of thermoluminescence would be approximately proportional to  $F(T)$ :

$$I_{(\text{rising edge})} \approx \phi n_0 F(T) \quad (7)$$

where  $n_0$  is the initial number of traps contributing to the particular glow peak and  $\phi$  is a proportionality constant. As can be seen in Table 1, at low enough temperature  $\text{den}$  approaches 1 so that  $F(T)$  is proportional to  $\text{num}$ :

$$\begin{aligned} I_{(\text{rising edge})} &\approx \phi n_0 \frac{k_B T}{h} \cdot \text{num} \\ &= \phi n_0 \frac{k_B T}{h} \cdot \exp\left(\frac{\Sigma S}{k_B}\right) \exp\left(-\frac{\Sigma H}{k_B T}\right) \end{aligned} \quad (8)$$

Thus, ignoring the pre-exponential factor of  $T$ , an Arrhenius plot [ $\log(I)$  vs.  $1/T$ ] will yield  $-\Sigma H/k_B$  as the slope of the plot, (instead of  $-H^*/k_B$  as in Randall-Wilkins). This may be combined with the observed  $T_m$  of the peak and Eq. (5) to estimate  $\Sigma S$ :

$$\begin{aligned} \frac{\Sigma S}{k_B} &= \frac{\Sigma H}{k_B T_m} - W = \frac{\Sigma H}{k_B T_m} \\ &\quad - \ln \left[ \frac{k_B T_m^2}{hB} \right] + \ln \left[ 1 + \frac{\Sigma H}{k_B T_m} + X \right]. \end{aligned} \quad (9)$$

Table 3. Values of  $W$  calculated from Eq. (6) (mechanism I or other mechanisms with approximation:  $X = 0$ ).

$T_m$	$\Sigma H$	$B$	$X$	$W$
260 K	1.3 eV	$0.2 \text{ K s}^{-1}$	0	32.4
290	0.8	0.2	0	33.2
320	0.5	0.2	0	34.0
260	1.3	0.67	0	31.2
290	0.8	0.67	0	32.0
320	0.5	0.67	0	32.8

Table 4. Effect of  $\Delta G_1$  on mechanism II.

Calculation No.:	1	2	3	4	
<i>Assumed values</i>					
$\Delta H^*$	0.31	0.71	0.91	1.11	eV
$\Delta S^*$	-0.0004	-0.0004	-0.0004	-0.0004	eV K <sup>-1</sup>
$\Delta H_1$	0.49	0.09	-0.11	-0.31	eV
$\Delta S_1$	+0.0003	+0.0003	+0.0003	+0.0003	eV K <sup>-1</sup>
<i>Calculated</i>					
$\Sigma H$	0.80	0.80	0.80	0.80	eV
$\Delta G^* (T_m)$	0.426	0.828	1.055	1.285	eV
$\Delta G_1 (T_m)$	0.403	0.002	-0.219	-0.441	eV
$\Sigma G (T_m)$	0.829	0.830	0.836	0.844	eV
$T_m$	289.7	294.8	362.8	437.1	K
$\Sigma H/k_B T_m$	32.0	31.5	25.6	21.2	
$X$	$1.30 \times 10^{-6}$	27.2	$3.3 \times 10^4$	$3.7 \times 10^6$	
$W$	33.2	32.7	26.7	22.4	

Note: Because we assumed  $\Delta H$  and  $\Delta S$  values to be independent of temperature,  $\Delta G$  depends on temperature and the value at  $T_m$  cannot be calculated until  $T_m$  is found.  $T_m$  is found by reiterating Eq. (5) ( $\Sigma H$  part) with different trial values for  $T_m$  until consistency is achieved. Values were chosen so that  $\Sigma G$  is approximately constant, which, if  $W$  had been constant, would have given a constant value for  $T_m$ . Calculations #1 and #2 show very little effect of  $\Delta G_1$  which is positive in both, and less than  $\Sigma H/k_B T_m$ . Calculation #3 and #4, which have negative  $\Delta G_1$ , show significantly increased  $T_m$ , huge values for  $X$ , and significantly decreased values for  $W$ . The values of  $\Sigma H/k_B T_m$  are given for comparison with  $X$ . Rate of heating,  $B = 0.2 \text{ K s}^{-1}$ .

If the glow curve is fitted by computer to a Randall-Wilkins type curve as done by Demeter et al. (1985) one would expect the same considerations to apply: The apparent activation energy would estimate  $\Sigma H$  and the apparent activation entropy would estimate  $\Sigma S$ .

### Concluding remarks

In conclusion, if  $X$  in Eq. (5) and Table 2 is smaller than 1 or  $\Sigma H/k_B T_m$ , then  $X$  is negligible and  $W$  has only small dependence on  $T_m$  so that  $k_B T_m$  is approximately proportional to  $\Sigma G$  with proportionality constant equal to  $1/W$ . This is expected to be the case if  $\Delta G$  for each step preceding the rate limiting step of detrapping is positive. If any detrapping step has negative  $\Delta G$ , then  $X$  and  $W$  can have large dependence upon  $T_m$  and this must be taken into account in estimating  $T_m$  from Eq. (5).

We do not now know of any step in photosynthetic reversed electron transport in which  $\Delta G$  is negative but we are not in position to say that such will never be found.

Equation (2) and most of the conclusions which follow depend upon examination of a limited number of mechanisms. To the extent that they are representative of the actual mechanisms this paper

provides the rationale and the mathematical limitations for the relation between thermoluminescent peak temperatures and thermodynamic parameters of detrapping.

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