CHAPTER VI

GLOW CURVE ANALYSIS
VI.1. **Introduction**

Thermoluminescence phenomenon demonstrates that during irradiation energy is stored in the sample. The sample cannot release this energy as light as it requires activation energy. Thus glow curves can be used to calculate these activation energies. There are some reports based on Randall-Wilkin's (1945) theory, which deal with the calculation of activation energies of electrons in the trapped states (Augenstein et al., 1961; Weinberg et al., 1962; Kukushkin and Kuznetsov, 1966). No such reports on frequency factors and lifetimes of electrons in the trapped states are available on nucleic acid bases. In the present thesis we have applied the Randall-Wilkin's (1945) theory for investigations on the electron trapping levels in nucleic acid bases and calculated the activation energies, frequency factors and the mean lifetimes of the electrons in the trapped states by the methods of the glow curve parameters as described by Chen (1969).

VI.2. **Theory**

Some of the charge carriers formed due to irradiation of the material with UV, X-rays or gamma-rays are trapped at liquid nitrogen temperature. When the material is warmed at a constant rate $\beta$, the released charge carriers combine emitting light.
Consider the case in which according to Randall-Wilkin theory there is only a single trap, the released charge is not retrapped but is captured by luminescence centres, and the efficiency of luminescence is not dependent on temperature. On the basis of this theory, the intensity of TL glow is proportional to the number of electrons escaping from the trap at a given temperature. The probability $p$ of an electron escaping from a trap of depth $E$ at temperature $T$ is of the form

$$p = g \exp(-E/kT)$$

where $k = \text{Boltzmann constant}$;

$g = \text{preexponential constant with the dimensions of Sec}^{-1}$. It is also called "escape frequency factor" and is considered to be independent of temperature.

Intensity of TL glow is proportional to the number of electrons escaping from the trap at a given temperature, i.e.,

$$I = -\frac{dn}{dt} \text{ at } pn = Cn, \text{ where } C \text{ is constant.}$$

The negative sign indicates detrapping and $n$ is the number of trapped electrons. The solution of the above differential equation is

$$N = n_0 \exp \left[ \frac{-E}{kT} \right] \int_0^T \exp(-E/kT)dt$$

where $n_0 = \text{number of traps originally filled}$. Assuming $C = 1$, we have TL intensity

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It is not possible to obtain $g$ and $E$ from the above equation in a straightforward analytical way. One indirect method employed frequently is to determine $E$ from the early part of the TL curve. The second exponential factor of equation (II) is essentially unity in this region, since the number of filled traps is not greatly changed. The equation of TL intensity as the traps begin to empty is written as (Garlick and Gibbons, 1948)

$$I = \text{constant} \cdot \exp\left(-\frac{E}{kT}\right) \cdot \int_0^T \exp\left(-\frac{E}{kT}\right) dT$$ \hspace{1cm} (II)

A plot of logarithm of the intensity $I$ against $1/T$ gives a straight line (Arrhenius plot), the slope $-E/k$ of which gives the activation energy. One difficulty encountered in the use of this method is experimental: thermoluminescence curves are complex often consisting of several overlapping peaks. Thus it may not be possible to measure the early rise of the curve. Nevertheless this equation provides a very simple means of calculating the activation energy. This method, known as the 'initial rise' method or the 'Arrhenius plot' is valid for first order as well as intermediate order kinetics.

The temperature $T_m$ at which TL emission is maximum may be obtained by differentiating above equation (II) with respect to $T$ and equating the result to zero. This procedure gives

$$\frac{E}{kT_m^2} = \frac{g}{\beta} \exp\left(-\frac{E}{kT_m}\right)$$ \hspace{1cm} (III)
On the basis of thermal vibration period one could estimate the value of $\sigma$ and numerically solve as a transcendental equation for $E$ or by knowing $E$-value $\sigma$ can be calculated by substituting in equation III.

VI.3. From change in maxima temperatures with heating rates:

(a) Calculation of $\sigma$ by measuring glow peak maxima using two or more heating rates has been suggested by various workers (Booth, 1954; Hoogenstraaten, 1958; Braunlieh, 1963). If $T_m$ and $T'_m$ are the values of glow peak temperatures for heating rates $\beta_1$ and $\beta_2$ and if $\beta_1 > \beta_2$ and $T_m > T'_m$ the value of $E$ can be calculated using relation

$$E = \frac{k}{T_m} \left[ \ln \left( \frac{\beta_1}{\beta_2} \right) \left( \frac{T_m}{T'_m} \right)^2 \right]$$

The value of $E$ can be thus determined by finding the values of $T_m$ at two heating rates.

(b) If $T_m$ is measured at several heating rates then a plot of $\ln \frac{T_m^2}{\beta}$ versus $\frac{1}{T_m}$ will give a straight line (see Hoogenstraaten, 1958). Value of $E$ can be calculated from the slope of this line. Hoogenstraaten has shown that this method holds good for both first and second order kinetics. This method has the advantage of not requiring well isolated peaks, but has experimental limitations in requiring wide range of heating rates to record appreciable changes in $T_m$ with $\beta$. 
VI.4. Methods based on the shapes of the glow curve

There are number of other methods available for calculating activation energies based on glow peak temperature $T_m$ and $T_1$ and $T_2$, the two temperatures on rising side and falling side of glow curve at which TL intensity is half of maximum intensity ($I_m$).

The basic equation can be written as $E = \frac{C T_m^2}{\Delta T}$

where $C$ = constant specific of the particular method;

$\Delta T$ = depending upon the method has values

(a) $\Delta T = \Delta T_1 = T_m - T_1$ i.e., the half width on the low temperature side of the peak

(b) $\Delta T = \Delta T_2 = T_2 - T_m$, the half width on the high temperature side of $T_m$

(c) $\Delta T = \Delta T_\omega = T_2 - T_1$, the total width at half intensity.

According to Chan's (1969) modification of Halperin and Branner equation the value of $E$ is given as

$E = \frac{1.52 K T_m^2}{T_m - T_1} - 1.58 \times 2 K T_m$

Groszewiner (1953) developed another technique for obtaining $E$. He employed the temperature at the glow peak and the temperature $T_1$ on the low temperature side of the peak.

If $E/\chi T > 20$ and $\chi/\beta > 10^7$ then to a good approximation $E$ is given as

$E = \frac{1.51 K T_m T_1}{T_m - T_1}$
Lurie and Bortch (1974) applied correction to Grossweiner's equation. These equations differ from each other only in the value of the numerical constant 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 calculations we have used Grossweiner's 1.51 as the constant. Chen has shown that in using this method the errors would be largest. We agree with this and we believe it to be due to the inaccuracies involved in determining $T_1$ and $T_m$ due to (1) fast rising glow curves or (2) mixing of the adjoining glow peak, if the interfering peak is large. Further, since the difference $\gamma = T_m - T_1$ is smallest of the temperature differences and comes in the denominator, the error involved in $E$ is greatest by this method.

Luschick's (1955) formula as given by Chen is

$$0.976 \frac{K \cdot T_m^2}{d}$$

based on the fall off side of the glow peak which is more gradual in most of the cases. According to Chen's analysis, theoretically less error is involved in the use of Luschick's formula.

Following the same reasoning, it is expected that Chen's formula using the full half width should give more accurate results since the full half-width is in any case greater than either half width and hence the relative error in its determination should be the least. On the basis of these considerations we feel Chen's formula $E = \frac{2.29 K \cdot T_m^2}{w}$
using $T_2 - T_1$ is the most reliable one, if the initial rise method cannot be used for some experimental reasons.

VI.5. Pre-exponential factor $\alpha$ and mean lifetime $I$:

We assume that the pre-exponential factor $\alpha$ is independent of temperature. As a result equation (I) the mean lifetime $I$ is given as

$$I = \frac{\exp \left( \frac{E}{kT} \right)}{\alpha}$$  \hspace{1cm} (IV)

where $T$ is the temperature at which $I$ is determined.

For a correct estimate of $I$ it is required that $E$, $T$ and $\alpha$ should be determined accurately. Parameter $E$ can be determined by various methods of which the initial rise method is seen to be the most reliable as it does not depend upon the kinetics of the process. A small error in determination of $E$ involves a large error in $\alpha$ and $I$. In the present Thesis we have determined $E$ from Arrhenius plots. The values of $E$ are then used to determine the $\alpha$ factors which in turn are needed to determine the lifetimes $I$ at the glow peak temperature. We have assumed $\alpha$ to be constant and independent of temperature and similarly calculated the lifetimes $I_{77}$ at liquid nitrogen temperature. Such assumption has previously been made by earlier workers (Fieschi and Scaramelli, 1968) for finding out the stability of the electrons in the traps and is also valid in view of the definition of $\alpha$. 
VI.6. Materials and Methods:

To bring out the exponential rise of the initial portion of the glow curve, the glow peak was recorded with a fast chart speed. With those compounds having more than one glow peak, the exponential rise of the glow curve appearing at higher temperature was recorded by allowing the sample to fade at liquid nitrogen temperature. This leads to elimination of peaks appearing at lower temperature. Hence it was not necessary for us to resolve the glow curves by artificial means (such as geometrical constructions). The temperatures $T_1$ and $T_2$ at half intensity of rising and falling side of the glow curve were obtained from the glow curves of different compounds.

VI.7. Results:

Activation energies ($E$-values) of different glow peaks of the compound were calculated by three different methods and the values obtained are presented in the Table VII. In each case mean values of three sets of observations are given. In all the cases, the $E$-value obtained with Halperin and Briner's method was highest. This is the least reliable method. As far as we know, this is the first report where detailed calculations on $E$-values and frequency factors by different methods are reported for all the nucleic acid bases.
## TABLE VII

<table>
<thead>
<tr>
<th>Method</th>
<th>Formula</th>
<th>Adenine 130 K</th>
<th>Guanine 113 K</th>
<th>Cytosine I 132 K</th>
<th>Cytosine II 191 K</th>
<th>Thymine 100 K</th>
<th>Uracil II 110 K</th>
<th>Uracil II 180 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen's</td>
<td>$E = \frac{2.29 \text{K} \text{I}m^2}{\pi}$</td>
<td>0.062</td>
<td>0.068</td>
<td>0.122</td>
<td>0.248</td>
<td>0.056</td>
<td>0.047</td>
<td>0.105</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.059</td>
<td>0.069</td>
<td>0.115</td>
<td>0.239</td>
<td>0.055</td>
<td>0.044</td>
<td>0.098</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>0.061</td>
<td>0.067</td>
<td>0.123</td>
<td>0.237</td>
<td>0.055</td>
<td>0.044</td>
<td>0.100</td>
</tr>
<tr>
<td>Luschick's</td>
<td>$E = \frac{0.976 \text{K} \text{I}m^2}{\sigma}$</td>
<td>0.044</td>
<td>0.045</td>
<td>0.146</td>
<td>0.279</td>
<td>0.036</td>
<td>0.024</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.039</td>
<td>0.046</td>
<td>0.146</td>
<td>0.341</td>
<td>0.032</td>
<td>0.024</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>0.047</td>
<td>0.041</td>
<td>0.183</td>
<td>0.236</td>
<td>0.036</td>
<td>0.025</td>
<td>0.078</td>
</tr>
<tr>
<td>Halperin &amp; Branner's</td>
<td>$E = \frac{1.52 \text{K} \text{I}m^2}{\sigma}$</td>
<td>0.065</td>
<td>0.098</td>
<td>0.091</td>
<td>0.213</td>
<td>0.074</td>
<td>0.102</td>
<td>0.128</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.075</td>
<td>0.108</td>
<td>0.078</td>
<td>0.175</td>
<td>0.118</td>
<td>0.083</td>
<td>0.108</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>0.067</td>
<td>0.104</td>
<td>0.086</td>
<td>0.187</td>
<td>0.091</td>
<td>0.099</td>
<td>0.109</td>
</tr>
<tr>
<td>Initial rise $I = \alpha ns \exp(-E/\text{KT})$</td>
<td></td>
<td>0.058</td>
<td>0.065</td>
<td>0.102</td>
<td>0.136</td>
<td>0.124</td>
<td>0.119</td>
<td>0.101</td>
</tr>
<tr>
<td>(Arrhenius plot)</td>
<td>$\text{Plot } \ln(I) \text{ Vs } 1/T$</td>
<td>0.036</td>
<td>0.068</td>
<td>0.101</td>
<td>0.132</td>
<td>0.127</td>
<td>0.126</td>
<td>0.100</td>
</tr>
<tr>
<td></td>
<td>$I/T$ to get $E$</td>
<td>0.044</td>
<td>0.073</td>
<td>0.105</td>
<td>0.134</td>
<td>0.125</td>
<td>0.119</td>
<td>0.099</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>0.046</td>
<td>0.068</td>
<td>0.102</td>
<td>0.134</td>
<td>0.125</td>
<td>0.121</td>
<td>0.100</td>
</tr>
</tbody>
</table>

See text for references to the method. $E =$ activation energy; $K =$ Boltzmann constant; $\text{I}m =$ maximum temperature of the glow peak; $\pi =$ total width of the glow peak at half intensity; $\sigma =$ half width of the glow peak on the high temperature side; $\gamma =$ half width of the glow peak on the low temperature side. Initial rise method.
We believe our values to be accurate for the reasons that (a) we have made very accurate measurement of temperatures and (b) our glow curves are well resolved. Arrhenius plots were obtained for nucleic acid bases (Fig. 41 to 45). The activation energies (E-values) calculated from these plots are presented in the Table VII.

VI.8. **Frequency factors and mean lifetimes of electrons**

Using E-values from the initial rise method (Table VII) frequency factors and mean lifetimes of the electrons in the trap states were calculated by substituting the values of E in equations III and IV respectively. These values obtained for lifetimes at $T_m$ and at $77 \, K$ ($T_{77}$) are presented in the Table VIII.

VI.9. **Discussion**

The TL characteristics of a compound are represented by parameters such as activation energy or trap depth, frequency factor and the order of decay kinetics. Number of methods are available for calculating these parameters. However there is considerable inconsistency in the values obtained by different methods for organic and inorganic compounds especially on trap depth and frequency factor (see Stoebe and Watanabe, 1975). If there is preinformation about the defect in the structure of the solid, luminescence efficiency or band structure, then
Fig. 41. Arrhenius plots of the initial rise of glow peak of adenine from three independent measurements.

Fig. 42. Arrhenius plots of the initial rise of glow peak of guanine from three independent measurements.
Fig. 43. Arrhenius plots of the initial rise of glow peak of thymine from three independent measurements.

THYMINE

Fig. 44. Arrhenius plots of the initial rise of glow peak of uracil from three independent measurements.

URACIL
Fig. 45. Arrhenius plots of the initial rise of peak-I and II of cytosine from three independent measurements for peak I and two independent measurements for peak II.


**TABLE VIII**

Frequency factors and mean life times of electrons in trap states at glow peak.

Temperatures ($T_m$) and at liquid nitrogen temperature ($T_{77}$).

<table>
<thead>
<tr>
<th>Method</th>
<th>Adenine</th>
<th>Guanine</th>
<th>Cytosine</th>
<th>Thymine</th>
<th>Uracil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>I</td>
</tr>
<tr>
<td>Initial Frequency factor</td>
<td>0.479</td>
<td>16.66</td>
<td>133.2</td>
<td>36.6</td>
<td>$7.235 \times 10^4$</td>
</tr>
<tr>
<td>rise</td>
<td>Mean life at $T_m$</td>
<td>126.7 s</td>
<td>64.74 s</td>
<td>98.88 s</td>
<td>93.8 s</td>
</tr>
<tr>
<td></td>
<td>Mean life at $T_{77}$</td>
<td>$2.14 \times 10^3$ s</td>
<td>$1.69 \times 10^3$ s</td>
<td>$3.56 \times 10^3$ s</td>
<td>$1.61 \times 10^7$ s</td>
</tr>
</tbody>
</table>
the glow curve analysis becomes simple to some extent. Fortunately these requirements do not come in the way of successful amplification of TL technique in various disciplines as the phenomenon is extremely efficient and reproducible (see Chapter VIII).

As mentioned earlier, activation energies calculated by initial rise method have number of advantages and it is most reliable. The E-values calculated by this method had shown interesting results with nucleic acid bases. Purines have shown lower values of E compared to pyrimidines (Table VII) while they need much higher energy for free radical formation (see Tatske, 1965). Jelinek and Pospisil (1969) calculated E-values for nucleic acid bases. They reported the E-values to depend on how the sample was prepared. Adenine sample prepared by evaporating water (in which it was dissolved) at 70°C showed glow peak at 129 ± 3 K with activation energy of 0.125 ± 0.005 eV. However, when evaporated at room temperature the glow peak appeared at 155 ± 3 K with activation energy of 0.234 ± 0.009 eV. Similar results were obtained with guanine (see Jelinek and Pospisil, 1969). On the basis of these results they concluded that the traps correspond to the properties of the crystalline structure as a whole rather than with the structure of the molecule forming the molecular crystal. We feel that crystals of different sizes might have formed in the samples prepared by evaporating at 70°C and at room temperature.
This could have resulted into glow peaks appearing at different temperatures in the samples with different activation energies. In our studies on activation energies of nucleic acid bases, the pellets were made from amorphous powder. The glow peak temperature (Table II) and E-values (Table VII) calculated were lower than those obtained by Jelinek and Pospisil. We believe this difference could be due to different procedures adopted in the preparation of samples which might be providing different sites for electron traps. However, there is no report on change in emission quality of TL due to different procedures followed in the preparation of the sample. This is expected since the method of preparation might be providing different sites for electrons to get trapped. However, when it is released thermally or optically it is expected to go to the excited states of the molecule. Its return to ground state will lead to fluorescence or phosphorescence type TL emission which would depend on the location of trap in the energy level diagram (see Fig. 25).

Gill and Weissbluth (1964) reported E-values for amino acids and proteins. Lower E-values were obtained for proteins compared to amino acids. Further they noticed that proteins unlike amino acids do not follow monomolecular kinetics. Nikol’skii and Ruben (1960) and Tochin and Nikol’skii (1969) obtained high E-values (1.26 to 2.8 eV) for one of the glow peak (γ peak) of polyethylene. They felt the high value of
frequency factor \((10^{61}\text{ sec}^{-1})\) could not be associated with any real physical processes. In contrast, Caserta et al. (1969) obtained low values of frequency factor for the glow curves of some plant seeds. They felt that the significance attached to frequency factor in Randall and Wilkin theory could not be given to these values. Thomas et al. (1968) using initial rise method obtained continuous range of \(E\)-values from 0.12 ev at low temperature to 0.59 ev at higher temperature. An excellent review on \(E\)-values obtained from glow peak temperatures and shapes of glow curve is presented by Fleming (1968). Activation energies calculated by different methods were reported earlier for amino acids and proteins (see Weinberg et al., 1962; Kubushkin and Kuznetsov, 1966; Thomas et al., 1968; Partridge, 1972).

These studies have shown that the \(E\)-values and frequency factors obtained by different workers even for the same compounds do not agree. In spite of number of reports none of them have really dealt with the significance of these values and their role in TL. However, some of them tried to explain the kinetics involved. In spite of the fact that the \(E\)-values calculated by different methods differ, still they could give some information about crystal structure (see Jelinek and Pospisil, 1969), defects in the crystal etc. However their role will be known better if they could be accurately calculated. The values of mean lifetime obtained by us at room temperature and at 77 K for nucleic acid bases are given
in Table VIII. These values are too high to be associated with the phosphorescence life time of the compound. We feel that 'they might agree with the life times of ITL. A great deal of systematic work is necessary for understanding the significance of these values.