3.1 INTRODUCTION:

Luminescence emission which occurs at times greater than the natural fluorescence lifetime i.e. \( \geq 10^{-8} \) sec. is called phosphorescence. It denotes a constrained, partially forbidden or unnatural delay in the radiative return of an excited system to the ground state.

When an electron absorbs radiation it is raised to the excited state or into the conduction band [in the case of photoconducting phosphors]. That electron in the excited state may undergo any one of the two processes:

[a] Recombine with the original centre giving off fluorescence emission.

[b] Fall into a trap [Fig. 3.1]

If the electron falls into a trap, it can escape after a mean life time \( \tau \) and recombine with an empty centre giving rise to phosphorescence emission or it may be retrapped thus causing a delay in phosphorescence emission. The thermal energy \( E \) required to liberate the trapped electron is known as trap depth; this energy may be received by phonon interaction with the surroundings.\(^{1-5}\)

The phenomenon of phosphorescence, besides throwing light on the kinetics involved, also offers valuable information about the population, energy distribution of trapping levels and the time constants of luminescence processes.\(^{6,7}\) The definition of time constant varies with the form of decay. In the case of exponential decay the time required for the intensity to fall to \( 1/e \) times the initial
FIG. 3.1
value is called time constant whereas in the case of power
law decay it is the time in which the intensity falls to half
its initial value.

As regards trap distribution it cannot be
correctly determined without some arbitrary assumptions and
the kinetics involved in decay can also be indicated by some
other experiments such as thermoluminescence. The decay is
measured as a decrease in the afterglow intensity as a
function of time. URBACH et.al.\textsuperscript{7} also studied it by measuring
the decrease in time of the residual light sum which was
determined by observing the stimulated extinction under the
influence of infra-red irradiation.

3.2 **KINETICS OF LUMINESCENCE:** BECQUEREL\textsuperscript{8} distinguished
luminescence decay on the basis of the nature of decay as:

[a] First order kinetics (monomolecular mechanism)

[b] Second order kinetics (bimolecular mechanism)

Generally monomolecular mechanism is characterised
by exponential decay while hyperbolic decay is assigned to a
bimolecular mechanism.

However, it is desirable to distinguish between first
order and second kinetics while discussing the two
mechanisms\textsuperscript{9} because exponential and hyperbolic decay occur
both in fluorescence and phosphorescence.

3.3 **FLUORESCENCE DECAY :**

[A] **FIRST ORDER KINETICS OF FLUORESCENCE :**

When the transitions for luminescence are confined
to within a localised centre only, a monomolecular mechanism
applies. According to this kinetics the number of excited electrons 'n' decreases according to a constant probability law:

\[
\frac{dn}{n} = -p\, dt \quad \text{[3.1]}
\]

where \(p\) is the transition probability. Equation [3.1] on solving, gives:

\[
n = n_0 \exp\left[-p\cdot t\right] \quad \text{[3.2]}
\]

where \(n_0\) is the number of excited electrons at the time \(t=0\).

The luminescence intensity \(I\) is given by:

\[
I = -\frac{dn}{dt} \quad \text{[3.3]}
\]

\[
= p\, n_0 \exp\left[-p\cdot t\right] \quad \text{[3.4]}
\]

\[
I = I_0 \exp\left[-p\cdot t\right] \quad \text{[3.5]}
\]

where \(I_0\) is the intensity at the time when excitation ceases and is given by:

\[
I_0 = p\, n_0
\]

The decay is thus exponential and is independent of temperature and the conditions of excitation. Therefore it occurs in systems of quadrupole and multipole character.\(^{10,11}\)

[B] \textbf{SECOND ORDER KINETICS OF FLUORESCENCE:-}

According to this kinetics the probability of recombination is proportional to the number of excited electrons.

If \(n\) vacant centres are created by \(n\) excited electrons, the probability of recombination of the electrons and the empty centres will be proportional to \(n^2\). Therefore

\[
\frac{dn}{n^2} = -p\, dt \quad \text{[3.6]}
\]

or

\[
n = n_0 / 1 + n_0\, p\cdot t \quad \text{[3.7]}
\]
The luminescence intensity $I$ is given by:

$$I = - \frac{dn}{dt}$$
$$= p_n^2$$
$$= \frac{I_0}{[1 + \alpha t]^2} \quad [3.8]$$

or

$$\frac{I}{I_0} = \frac{1}{[1 + \alpha t]^2} \quad [3.9]$$

where $\alpha = n_{\infty} p = [I_{\infty} p]^{1/2}$

The decay is hyperbolic in nature and is independent of temperature but depends on the nature and period of excitation.\textsuperscript{12} It can be influenced by altering the intensity of excitation.\textsuperscript{13}

3.4 PHOSPHORESCENCE DECAy :- The phosphorescence decay is assumed to be due to the life time of excited electrons and their subsequent recombination with empty centres. Hence it is a linear function of time. So the kinetics of phosphorescence depends on the spatial location of electron traps and luminescent centres and hence associated with the displacement of the conduction electron.\textsuperscript{14,15}

[A] FIRST ORDER KINETICS :- First order kinetics holds good only if the separation between the trap and centre is less than $10^{-6}$ cm approximately. A short movement of the electron results in recombination. Thus each luminescent centre and trap may be treated as an independent unit giving a recombination constant with time. The system with above mentioned features follows a monomolecular kinetics. In this case the number of electrons recombining with centres is equal to the number of electrons arriving from the traps and

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hence the system obeys an exponential law. The traps of mean life time $\tau$ release electrons according to the relation:

$$n = n_0 \exp \left( -p \cdot t \right)$$

$$n = n_0 \exp \left( -t/\tau \right)$$

[3.10]

where $n_0$ and $n$ are the number of electrons in the metastable state at $t = 0$ and $t = t$ respectively, $p$ is the probability of an electron in the excited state to return to the ground state and is equal to $1/\tau$.

If $d\nu$ be the number of electrons recombining with a centre and $dn$ be the number freed from traps, then

$$d\nu = dn$$

[3.11]

The luminescence intensity is given by:

$$I = -\frac{dn}{dt}$$

$$= -\frac{d\nu}{dt}$$

$$= n_0 /\tau \exp \left( -t/\tau \right)$$

[3.12]

and thus an exponential decay results.

[B] SECOND ORDER KINETICS:

If the traps and centre are spatially independent of each other, the electrons can move over large distances [$\geq 10^{-5}$ cm] and can recombine with any of the available centres. The recombination probability is proportional to the number of empty centres. Hence second order kinetics is applicable and the decay of luminescence is proportional to both the number of empty luminescence centres and to the number of filled traps for this type of kinetics.

Let $n_0$ be the total number of traps per cc out of which $n$ are filled; thus the total number of empty traps per
cc is equal to \( [n_\circ - n] \). Let \( \nu \) be the number of conduction electrons and \( N \) the number of empty centres. If all \( N \) centres are considered to be occupied before excitation we can write

\[ N = n + \nu \]

or

\[ \frac{dn}{dt} = \frac{n}{\tau} - a_c N \nu \quad \text{(3.13)} \]

or

\[ \frac{dn}{dt} = a_t [n_\circ - n] \nu - \frac{n}{\tau} \quad \text{(3.13)} \]

and

\[ I = a_c N \nu \quad \text{(3.14)} \]

Here \( a_c \) = effective cross-section of centres multiplied by thermal velocity of electrons and \( a_t \) is the similar product for traps.

A rigorous analytical solution is possible only for \( a_c = a_t = a \) which corresponds to equilibrium between conduction band and traps. We have \( \nu/n = 1/a.n_\circ \cdot \tau \) where \( 1/a.n_\circ \) is the effective life time for electrons in the conduction band and the differential equation gives \( \frac{dn}{dt} = \frac{n^2}{n_\circ \cdot \tau} \) which has solutions:

\[ n = \frac{n_\circ}{[t + t_\circ]} \quad \text{and} \quad \nu = \frac{1}{a} \frac{t + t_\circ}{[t + t_\circ]} \]

and the luminescence intensity is given by the relation:

\[ I = a [n + \nu]^\nu \]

which decays according to the law:

\[ I = \text{Constant} / [t + t_\circ]^2 \quad \text{(3.15)} \]

where \( t_\circ \) is an integration constant equal to the mean life time of the traps for saturation excitation. This relation holds also for a distribution of traps provided the equilibrium between shallow and deeper traps is assumed. When shallow traps reach equilibrium with the deeper traps, the system behaves as if the mean life time is single valued and
equal to that of the deeper traps. The decay thus tends to the final form \( i \propto t^{-2} \).

ADIROWITCH\(^{16,17}\) has given an approximate calculation for traps with a single mean life time assuming different capture cross-sections for traps and centres. He has shown that a graph of \( \log I \) vs. \( \log (t + t_o) \) has an inflexion and over an extensive range, \( I \) follows a BECQUEREL type relation.

\[
I = \text{Constant} / (t + t_o)^m \tag{3.16}
\]

where \( m \) depends on the ratio of capture cross-sections of traps and centres respectively. It has been found that this relation holds good for several phosphors except for those which have well separated groups of traps.

MEDLIN\(^{16}\) has discussed the phosphorescence decay of thermoluminescence crystals such as calcite, anhydrite etc., and has pointed out that bimolecular kinetics cannot account for the details of the power law decay shown by equation [3.16] in luminescent materials, except at temperatures well above the thermoluminescence glow peak. He proposed that decay discrepancies can be accounted for by first-order kinetics from a [GAUSSIAN] distribution of trapping levels. The specific values of \( m \) [which can be unity] were determined by the particulars of the trap distribution and by the experimental conditions.

Alternative explanations for the \( t^{-1} \) decay are suggested by studies as those by DELBECQ et.al.\(^{17}\), where a temperature dependent \( t^{-1} \) decay law of luminescence from the combination of trapped electrons and holes in KCl : AgCl and
KCl : TlCl was ascribed to electron tunneling. A simple model, which did not consider the details of the distribution of tunneling centres, was used to show that electron-hole recombination through electron tunneling can, in principle, generate a $t^{-1}$ decay. The approach of using the tunneling phenomenon here is similar to that in other fields, such as semiconductor luminescence and recombination luminescence from irradiated organic molecules in organic glasses, where analogous observations of approximate $t^{-1}$ decays of recombination luminescence have been made and interpreted in terms of electron tunneling.

3.5 SUPERPOSITION THEORIES

Many of the phosphors decay in a manner which does not satisfy any of the equation discussed and usually an attempt is made to fit the experimental curve to any one of the theoretical ones by making suitable assumptions. This discrepancy between theoretical and experimental values may attributed to non-uniform exciting and emitted radiation by a finite thickness of the phosphor which changes the bimolecular decay in its later stage to a power law decay with a power less than two. Different decay constants are associated with the luminescence centres and traps and the overall intensity is due to their combined effect.

Various investigators have suggested different modifications to the bimolecular theory. Many factors such as the distribution of traps, life time,
non-radiative recombination, positive hole migration in the valence band, capture of hole in the activator centres and transfer processes have to be taken into account while dealing with the problem. Hence the complex nature of the mechanism of the phosphorescence can be attributed to a superposition of either a number of monomolecular or bimolecular mechanisms.\textsuperscript{14,15}

[A] **BIMOLECULAR SUPERPOSITION THEORY** :- This theory is favoured by ANTONOV-ROMANOVSKI\textsuperscript{16}, URBACH & OTHERS,\textsuperscript{7} considering two different superpositions. In one case, if there exist fluctuations in the density of the excited state, the decay is expressed as the sum of terms, each representing a bimolecular decay curve. In the other case a continuous distribution of traps of different depths is considered and the superposition is represented by a simultaneous system of different equations of bimolecular type each representing a particular trap depth.

[B] **MONOMOLECULAR SUPERPOSITION THEORY** :-

This theory is based on the distribution of traps of different depths which has been supported by many investigators.\textsuperscript{27-30} The success of this theory is due to RANDALL & WILKINS \textsuperscript{2} who have entirely rejected the bimolecular theory to explain complex hyperbolic decay of sulphide phosphors. They obtained the following relations corresponding to different types of distribution.

Absorption of exciting radiation by a luminescence centre raises an electron into the excited state, F. It may
then either return directly to ground state G with emission of luminescence or it may fall into the metastable state M lying just below F as shown in Fig.10. In the latter case a rearrangement of the atoms of the centre takes place and the transition M → G is usually forbidden. Thus electrons in the metastable state can only return to the ground states if they are first raised into the excited states by receiving sufficient thermal energy or by absorption of long wavelength radiation. For the case of thermal excitation the probability of the transition M → F per unit time is given by:

\[ p = S \exp \left( \frac{-E}{kT} \right) \]

where \( S \) is a constant having the dimensions of frequency, \( E \) is the energy separation between the levels M and F, \( k \) is Boltmann's constant and \( T \) is the absolute temperature. If the transition probability for F → G is high compared with \( p \) above, then the phosphorescence emission depends on the rate at which electrons escape from metastable states and will be given as follows:

1. **SINGLE TRAP DEPTH**

If 'n' is the number of electrons in traps of depth E, then the intensity \( I \) of phosphorescence of traps of depth E is given by:

\[ I = n_0 \cdot S \exp \left( \frac{-E}{kT} \right) \exp \left( -S \cdot t \exp \left( \frac{-E}{kT} \right) \right) \]

or

\[ I = I_0 \exp \left( -S \cdot t \exp \left( \frac{-E}{kT} \right) \right) \]

which is the form of the decay of phosphorescence with time, \( n_0 \) being the number of electrons in M states at the beginning of decay. It agrees with that found experimentally for thallium activated KCl by BUNGER and FLECHSIG.
[ii] UNIFORM DISTRIBUTION OF TRAP LEVELS :-

In most phosphors there are trap levels at many different depths. It is required to find the phosphorescence for a phosphor in which there are an equal number of traps of all depths, that is, the trap distribution is uniform. If \( N_E \) is the number of traps between depths \( E \) and \( E + dE \), then the phosphorescence at time \( t \) is given by

\[
I_t = \int_0^\infty N \exp\left(-\frac{E}{kT}\right) \exp\left(-St \exp\left(-\frac{E}{kT}\right)\right) dE
\]

which on integration gives directly

\[
I_t = n.k.T/t \left[1 - \exp(-St)\right]
\]

when \( St \gg 1 \) that is after a microsecond \( \exp [-St] \) is negligible and

\[
I_t = n.k.T/t \quad [3.17]
\]

The decay of many phosphors approximates to this law. If there is an equal number of traps at all depths, the phosphorescence is at all times proportional to \( 1/t \).

[iii] EXPONENTIAL TRAP DISTRIBUTION :- If the electron trap distribution is exponential in form, that is

\[
N_E = A \exp\left(-E\right)
\]

as is found for many phosphors, the phosphorescence is given by

\[
I_t = \int_0^\infty A \exp\left(-E\right) S \exp\left(-\frac{E}{kT}\right) \exp\left(-St \exp\left(-\frac{E}{kT}\right)\right) dE
\]

putting \( w = St \exp\left(-\frac{E}{kT}\right) \), the equation then becomes

\[
I_t = \int_0^\infty \exp\left(-\frac{St}{kT}\right) dE
\]

As \( St \) is always large \([ > 10^9 ]\), the integration may be taken to infinity.
\[ I_t \approx [St]^{-\alpha T} ASkT/t \int_0^\infty \exp \left[ -w \right] w^{\alpha T} \, dw \]
\[ I_t \approx f[S,kT] \beta t^{-(\alpha T+1)} \]
\[ I_t = \text{constant} \cdot t^{-(\alpha T+1)} \]

under condition \( St \gg i.e. t > 10^{-6} \)

It is clear from equations 3.17 and 3.18 that the decay law of phosphorescence for a phosphor with a distribution of trap depths will be little dependent on temperature.

Equation 3.18 shows that the phosphorescence decays according to a simple inverse power law. For zero, the case of a uniform trap distribution, the reciprocal law holds; this result agrees with equation 3.17. When \( kT \) is unity, an inverse square law results.

3.6 METHODS OF DECAY MEASUREMENT: - Decay is classified into two categories as slow and fast decay. These are discussed below in detail.

[a] FAST DECA Y: - The decay of luminescence lasting for about \( 10^{-9} \) sec. can be measured by an oscillographic method as it provides a direct presentation of decay curves, which is then photographically reproduced.\textsuperscript{31,32} The development of co-axial cables suitable for the transmission of very short pulses\textsuperscript{33} and also colour shifters which convert ultra-violet luminescence to a spectral region more closely matching the spectral response of the detectors have further advanced the scope of this method.

An alternate method of measuring decay of this order is by using an exciting radiation modulated in a
sinusoidal manner with a frequency of a mega-cycle or more and measuring the phase angle between the exciting and emitted radiation. Magnitude of this phase angle depends on the decay constant. This principle has been used to determine decay times of $10^{-9}$ second with high accuracy\textsuperscript{34,35}. Time constants can also be evaluated by measuring the fractional modulation of the exciting radiation and of the luminescence\textsuperscript{32,36}. It is sometimes convenient to measure the luminescence signal relative to the signal from the reflection of the incident radiation by a non-luminescing substance or relative to a luminescence signal of much faster decay rather than comparing the incident and emitted signals. The phase shift is usually determined by electrical circuit techniques\textsuperscript{37,38}. Measurement of decay is also made by methods such as the shorted line technique\textsuperscript{39}.

Various other methods have been used to modulate the light beam. RAU\textsuperscript{40} used nicol prism and kerr cell to which radio frequency voltage was applied. MAERCKS\textsuperscript{41} passed the exciting light through a liquid in which standing supersonic waves were set up and the phase angle was measured by substituting a mirror for the phosphor. BANNET\textsuperscript{42} has described a novel method of obtaining time resolution of the order of $10^{-9}$ second by exciting fluorescence by the flash lamp, observing stroboscopically and gating the photomultiplier.

(b) \textbf{SLOW DECAY} :-) BECQUEREL'S phosphoroscope consisting of two disks mounted on a common rotational shaft and the phosphor
placed in between has been the earliest and simplest method. Alignment of slits cut in the two disks keeps a prescribed phase angle between the exciting and emitted radiations. This arrangement produces a squarewave modulation for the excitation and the adjustment of phase angle permits the determination of luminescence intensity at any prescribed time after excitation. The method allows repeated observation as well as the use of intensity integrating devices such as photographic plates which in turn makes it possible to record very weak phosphorescence.

A modification to the phosphoroscope principle due to R.W. Wood\textsuperscript{43} provides a rotating disk with phosphor in the form of an annulus around the circumference of the disk. Randall and Wilkins\textsuperscript{44} have used a similar arrangement. The excitation takes place at some position fixed in space. The detector can be kept at any desired position and phosphorescence emission is observed at various times after excitation. Besides photographic reproduction, this method facilitates direct observation of colour changes during decay process.\textsuperscript{45}

Oscilloscopic trace with intensity and time as vertical and horizontal components respectively, gives a direct picture of the decay curves which can be recorded photographically.\textsuperscript{12,46} If the luminescence decay is exponential it can be compared with the trace produced by the discharge of a condenser and by adjusting the circuit elements the time constant can be calculated from the circuit
FIG. 3.2 BLOCK DIAGRAM OF EXPERIMENTAL ARRANGEMENT FOR DECAY STUDY
data. The luminescence and discharge signal traces can be mixed oppositely to produce a 'null'. Another useful technique consists of pulsing the power supply of photomultiplier, that is to avoid the overloading and at the same time obtaining the zero reference level as part of the oscilloscope trace.

Also, for an exponentially decaying phosphor, the response of a phosphor to sinuosodial excitation can be used to determine decay time.

Decay of long duration can be studied after cutting-off the exciting radiation by a menhanical shutter. A photomultiplier tube in combination with a galvanometer or an amplifier and a pen recorder forms a very simple system.

3.7 PRESENT METHOD:

1 EXPERIMENTAL ARRANGEMENT: The present arrangement involves the measurement of long period decay of phosphorescence as shown in figure 3.2 (duration > 2 second). The source of excitation was X-rays (X-ray machine type 1104 operated at 32 KV and 12 mA). A photomultiplier Model No. Eu. 701-30 was coupled with the phosphor holder assembly. The output of the P.M. tube was connected with the D.C. Microvoltmeter Model No. PP 9004 PHILIPS.

PHOSPHOR HOLDER ASSEMBLY:

It (Fig. 3.3) consists of a brass cylinder (P1, P2). Two metal tubes of lead were fitted into the openings of the cylinder at right angles to each other.

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\([0_1, 0_2]\). The top of the cylinder consists of an aluminium plate \([A]\) at the center of which a sample mounting plate is fixed. The plate is essentially a rectangular brass sheet \([S]\) and can be raised or lowered and can also be rotated by means of a Knob \([K]\) and its position is indicated by a pointer \([I]\). The plate is provided with a circular cavity \([C]\) in the center to fit a removable brass sample holder with a fine hole to hold a thermocouple \([T]\). A heating element of Kanthal strip \([H]\) was attached behind the sample holder to maintain it at different temperatures. A collimated beam of X-rays through the slit \([SL]\) is allowed to fall on the sample through the tube \([A_1, A_2]\) and the emitted luminescence radiation emerges through another tube. \(T_1, T_2\) and \(T_3, T_4\) are terminals for heater and thermocouple respectively.

[2] EXPERIMENTAL PROCEDURE :-

The phosphor was packed into the cavity of the sample holder and kept inside the assembly and was excited by X-rays for 5 minutes. The saturation time for excitation was determined by trial, which came out to be 5 minutes. Hence, each sample was excited for 5 minutes. The excitation was cut-off, the shutter of P.M. tube being kept open. The decaying of luminescence intensity was then recorded as a function of time, every 2 seconds, till the intensity reached an undetectable level. The same amount of phosphor was taken every time. The distance between the phosphor cavity and X-ray window was kept constant throughout the experiment. Two sets of observations were taken for each
sample under similar conditions. They were found to be consistent.

All the measurements were made at room temperature i.e. at 308 K. Decay measurements were also carried out at a higher temperature. The temperature chosen was 383 K which was the average temperature corresponding to the second TL peak.

3.8 Decay Results:

The luminescence decay at room temperature was examined by plotting the afterglow intensity \( I \) as a function of time \( t \). Figs. [3.4] to [3.6] for a few representative samples, show that the curves are hyperbolic. The plot of \( \log I \) vs time \( t \) was drawn to estimate the nature of decay. Some of these are shown in Figs. [3.8] to [3.10]. The non-linearity of the curves rules out the possibility of simple exponential decay with single trap.

Further investigations were done on the basis of a power law decay corresponding to the general equation:

\[
I = I_0 t^b
\]

or

\[
\log I = \log [I_0 t^b]
\]

\[
\log I = \log I_0 + b \log t
\]

taking \( y = \log I \), \( x = \log t \) and \( c = \log I_0 \) one can get

\[
y = bx + c
\]

which is the equation of a straight line.

Fig. [3.7] for a few representative samples shows the plots of \( \log I \) vs \( \log t \). These curves are found to be nearly straight lines suggesting a power law
FIG. 34 DECAY CURVES (AT 308 K) (Simple graph)
FIG. 3.5 DECAY CURVES (AT 308 K) (Simple graph)
FIG. 3.6 - DECAY CURVES (AT 383 K) (Simple graph)
FIG. 3.7 DECAY CURVES (AT 308 K)
Figure 3.7 Decay Curves (At 308 K)

INDEX
1 - Gd$^{3+}$ (10$^{-1}$)
2 - Gd$^{3+}$ (10$^{-2}$)
3 - Gd$^{3+}$ (10$^{-3}$)
4 - Gd$^{3+}$ (10$^{-4}$)

INDEX
1 - Gd$^{3+}$ (10$^3$) Tb (10$^7$)
2 - Gd$^{3+}$ (10$^3$) Tb (10$^6$)
3 - Gd$^{3+}$ (10$^3$) Tb (10$^5$)
4 - Gd$^{3+}$ (10$^3$) Tb (10$^4$)
FIG. 3.7 DECAY CURVES (AT 308 K)
CORRELATION COEFFICIENT: The degree of linearity between log I and log t was estimated by a statistical method. The correlation coefficient 'r' was calculated by using the relation:

\[
r = \frac{m \sum x \cdot y - \sum x \cdot \sum y}{\sqrt{m \sum x^2 \cdot (\sum x)^2} \sqrt{m \sum y^2 - (\sum y)^2}}^{1/2}
\]

where m is the number of sets of observations, 
\[x = \log t\] and \[y = \log I\].

The value of 'r' was found to be very close to unity showing a linear relationship between x and y [Table 3.1]. The sign of 'r' is negative because \(\log I\) decreases as \(\log t\) increases.

DECAY CONSTANT: The hyperbolic character of the decay obeys an equation of the form:

\[I = I_o \cdot t^b\]

where 'b' is known as decay constant. The value of this constant is evaluated by the method of least squares \[^{52,53}\].

\[b = \frac{-\sum x \cdot \sum y - m \cdot \sum x \cdot y}{(\sum x)^2 - m \sum x^2}\]

The values of 'b' computed for all samples are given in table [3.2]. The value varies from 0.58 to 0.81. The sign of 'b' being negative. Hence the decay equation becomes

\[I = I_o \cdot t^{-b}\]

There is no significant variation in the value of 'b' with activator or with concentration.

PEELING-OFF OF THE DECAY CURVES: RANDALL and WILKINS \[^6\].
FIG. 3.8 "PEELING-OFF" OF THE DECAY CURVES (AT 308K)
FIG 3.8 "PEALING OFF" OF THE DECAY CURVES (AT 308 K)
Fig. 3:8 "Pealing Off" of the Decay Curves (at 308 K)
**FIG. 3.9** "Pealing off" of the decay curves (at 308 K)
FIG. 3.9 "PEALING OFF" OF THE DECAY CURVES (AT 308 K)
Fig. 3.9 "Pealing off" of the decay curves (at 308 K)
FIG. 3.10 "PEELING-OFF" OF THE DECAY CURVES (AT 383 K)
FIG. 3.10 "PEALING OFF" OF THE DECAY CURVES (AT 383 K)
FIG. 3.10 "PEALING OFF" OF THE DECAY CURVES (AT 383 K)
FIG. 3.10 "PEALING OFF" OF THE DECAY CURVES (AT 383 K)
considered the hyperbolic decay as a result of superposition of exponentials corresponding to different traps. Such a decay can be expressed by an equation of the type:

\[ I_0 = I_0 e^{-b} \]

\[ = I_{0_1} e^{-p_1 t} + I_{0_2} e^{-p_2 t} + \ldots + I_{0_n} e^{-p_n t} \]

where \( I_{0_n} \) is the phosphorescence intensity due to electrons in the traps of energy \( E_n \) and \( p_n \) is the transition probability of an electron escaping from a trap of depth \( E_n \). All the decay curves were "peeled off" into a set of three exponentials by the method of successive subtraction as has been followed by BUBE\(^{30}\). Some of them are shown in Figs [3.8] to [3.10]. The trap depth corresponding to each exponential was determined by the following formula.

\[ E = 2.3026 k T \left( \log_{10} S + \log_{10} t - \log(2.3026 (\log_{10} I_0 - \log_{10} I)) \right) \]

The value of \( S \) was taken to be \( 10^9 \) per second, a value used by earlier workers\(^{6,54-56}\). The trap depth corresponding to different exponentials for the various samples at 308 K lie between 0.58 to 0.67 eV and are shown in Table 3.2.

Fig [3.10] shows the decay curves obtained at higher temperature, that is 383 K. The nature of decay curves was found to be the same as that obtained at room temperature (308 K). The only difference in the two was that the intensity in the latter case falls to negligible values much faster. These curves were also peeled off into three exponentials by the same procedure. The trap depths corresponding to the three components were calculated and found to lie between 0.70 to 0.83 and are shown in Table 3.3.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Conc. of Tb$^{3+}$ mole %</th>
<th>Conc. of Gd$^{3+}$ mole %</th>
<th>Initial Intensity [Arb.Units]</th>
<th>Decay Constant *</th>
<th>Correlation Coefficient *</th>
</tr>
</thead>
<tbody>
<tr>
<td>SJT</td>
<td>[10$^{-1}$]</td>
<td>-</td>
<td>88.9</td>
<td>0.81</td>
<td>1.00</td>
</tr>
<tr>
<td>Series</td>
<td>[10$^{-1}$]</td>
<td>-</td>
<td>101.2</td>
<td>0.72</td>
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</table>

$ = Below Optimum Conc., $ = Optimum Conc., $ = Values are negative
TABLE - 3.2

ACTIVATION ENERGIES AS OBTAINED FROM THE ANALYSIS OF 'PEELING OFF' OF THE DECAY CURVES [AT 308 K].

$ = \text{BELOW OPTIMUM CONC.,} \ # = \text{OPTIMUM CONC.}

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<th>SAMPLE</th>
<th>CONC.</th>
<th>CONC.</th>
<th>SLOWEST</th>
<th>MIDDEL</th>
<th>FAST</th>
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<td>No. of Tb$^{3+}$</td>
<td>mole %</td>
<td>of Gd$^{3+}$</td>
<td>exponential</td>
<td>exponential</td>
</tr>
<tr>
<td>SJT</td>
<td>[10$^0$]</td>
<td>-</td>
<td>0.65</td>
<td>0.62</td>
<td>0.59</td>
</tr>
<tr>
<td>Series</td>
<td>[10$^{-1}$]</td>
<td>-</td>
<td>0.68</td>
<td>0.64</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>[10$^{-2}$]</td>
<td>-</td>
<td>0.68</td>
<td>0.64</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>[10$^{-3}$]</td>
<td>-</td>
<td>0.65</td>
<td>0.63</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>[10$^{-4}$]</td>
<td>-</td>
<td>0.65</td>
<td>0.63</td>
<td>0.59</td>
</tr>
<tr>
<td>SJG</td>
<td>-</td>
<td>[10$^0$]</td>
<td>0.66</td>
<td>0.63</td>
<td>0.59</td>
</tr>
<tr>
<td>Series</td>
<td>-</td>
<td>[10$^{-1}$]</td>
<td>0.66</td>
<td>0.62</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>[10$^{-2}$]</td>
<td>0.65</td>
<td>0.62</td>
<td>0.59</td>
</tr>
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<td></td>
<td>-</td>
<td>[10$^{-3}$]</td>
<td>0.64</td>
<td>0.61</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>[10$^{-4}$]</td>
<td>0.64</td>
<td>0.61</td>
<td>0.58</td>
</tr>
<tr>
<td>SJTG</td>
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<td>[10$^{-7}$]</td>
<td>0.65</td>
<td>0.61</td>
<td>0.59</td>
</tr>
<tr>
<td>Series</td>
<td>[10$^{-3}$]</td>
<td>[10$^{-6}$]</td>
<td>0.66</td>
<td>0.62</td>
<td>0.59</td>
</tr>
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<td>[10$^{-5}$]</td>
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<td>0.62</td>
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<td>[10$^{-4}$]</td>
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<td>0.63</td>
<td>0.60</td>
</tr>
<tr>
<td>SJGT</td>
<td>[10$^{-7}$]</td>
<td>[10$^{-3}$]</td>
<td>0.66</td>
<td>0.62</td>
<td>0.59</td>
</tr>
<tr>
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<td>[10$^{-3}$]</td>
<td>0.66</td>
<td>0.62</td>
<td>0.59</td>
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<td>0.59</td>
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<td>[10$^{-7}$]</td>
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<td>[10$^{-6}$]</td>
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</tr>
<tr>
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<td>[10$^{-5}$]</td>
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<td>0.63</td>
<td>0.59</td>
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<tr>
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<td>[10$^{-4}$]</td>
<td>0.67</td>
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<td>0.60</td>
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<td>[10$^{-2}$]</td>
<td>0.67</td>
<td>0.63</td>
<td>0.60</td>
</tr>
<tr>
<td>Series</td>
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<td>[10$^{-2}$]</td>
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<td>0.62</td>
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<td>[10$^{-2}$]</td>
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<td>[10$^{-2}$]</td>
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<td>0.62</td>
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<td>[10$^{-2}$]</td>
<td>0.67</td>
<td>0.62</td>
<td>0.60</td>
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</table>
### TABLE - 3.3.

**ACTIVATION ENERGIES AS OBTAINED FROM THE ANALYSIS OF 'PEELING OFF' OF THE DECAY CURVES [AT 383 K].**

<table>
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<tr>
<th>SAMPLE</th>
<th>CONC. No. of Tb$^{3+}$ mole %</th>
<th>CONC. mole % of Gd$^{3+}$</th>
<th>SLOWEST exponential $E_1$ [eV]</th>
<th>MIDDLE exponential $E_2$ [eV]</th>
<th>FAST exponential $E_3$ [eV]</th>
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<td>SJT</td>
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<td>-</td>
<td>0.82</td>
<td>0.74</td>
<td>0.68</td>
</tr>
<tr>
<td>Series</td>
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<td>$[10^{-1}]$</td>
<td>0.83</td>
<td>0.77</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$[10^{-2}]$</td>
<td>0.83</td>
<td>0.74</td>
<td>0.71</td>
</tr>
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<td>$[10^{-3}]$</td>
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<td>0.76</td>
<td>0.71</td>
</tr>
<tr>
<td>SJG</td>
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<td>0.76</td>
<td>0.72</td>
</tr>
<tr>
<td>Series</td>
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<td>$[10^{-2}]$</td>
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</tr>
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<td>$[10^{-3}]$</td>
<td>0.80</td>
<td>0.74</td>
<td>0.70</td>
</tr>
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<td>SJTG</td>
<td>$[10^{-3}]$</td>
<td>$[10^{-6}]$</td>
<td>0.80</td>
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<td>0.71</td>
</tr>
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<td>$[10^{-3}]$</td>
<td>$[10^{-5}]$</td>
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<td>$      $</td>
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<td>$[10^{-5}]$</td>
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3.9.

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