

## \* Law of photochemical Equivalence Process

13

M. Bodenstein proposed that photochemical reactions involve two distinct processes—

### (1). Primary process :-

In this process, the light quantum  $h\nu$  is absorbed by a molecule 'A' resulting in the formation of an excited molecule  $A^*$ . Thus,



The molecule which absorbed light may get excited atoms or free radicals. The primary process may also involve loss of vibrational energy of excited molecule by collision with other molecules as well as fluorescence and phosphorescence.

### (2). Secondary Process :-

In this process, the excited atoms or free radicals produced in the primary process react further giving rise to high quantum yields. Some times, the atoms or free radicals initiate a series of chain reactions.

If the secondary reaction is exothermic, the heat of the reaction may activate other molecules thereby causing them to react. This is another reason for high quantum yields.

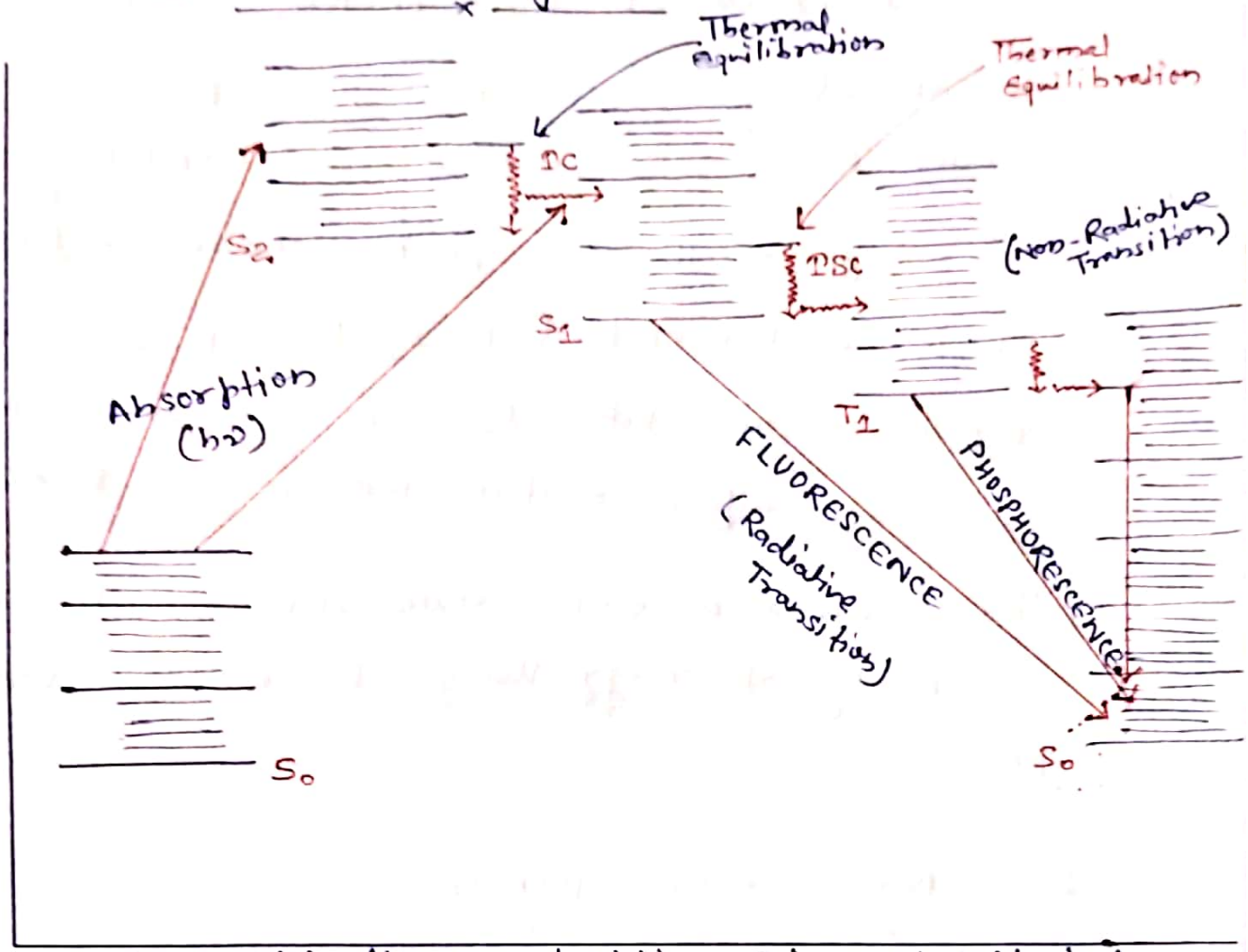
\* Reason for low quantum yields :-

There are following reasons for low quantum yields.

These are:-

- (1). Excited molecules may get deactivated before they form products.
- (2). Collisions of excited molecules with non-excited molecules may cause the ~~former~~ former to lose energy.
- (3). The primary photochemical process may get reversed.
- (4). The dissociated fragments may recombine to form the original molecule.

\* Jablonski diagram



Jablonski diagram depicting various photophysical processes :-

Photophysical Pathways

		<u>Rate</u>
(1)	$S_0 + h\nu \longrightarrow S_1 \text{ or } S_2$ (Electronic excitation)	$I_{abs}$
(2)	$S_1 \longrightarrow S_0 + \text{heat}$ (Internal Conversion)	$k_{IC} [S_1]$
(3)	$S_1 \longrightarrow S_0 + h\nu_f$ (fluorescence)	$k_f [S_1]$
(4)	$S_1 \longrightarrow T_1 + \text{heat}$ (Inter system crossing)	$k_{ISC} [S_1]$
(5)	$T_1 \longrightarrow S_0 + h\nu_p$ (phosphorescence)	$k_p [T_1]$
(6)	$T_1 \longrightarrow S_0 + \text{heat}$ Reverse ISC	$k_{ISC}^T [T_1]$

On absorption of light photon, the electron of the absorbing molecule may jump from  $S_0$  (ground state) to  $S_1$  or  $S_2$  (Excited state) depending upon the energy of the light photon absorbed. For each singlet excited state ( $S_1, S_2$ ) there is a corresponding triplet excited state ( $T_1$ ). The molecule, whether in singlet or triplet excited state is said to be activated.

The activated molecule returns to the ground state by dissipating its energy through the following type of processes—

(1). Non-Radiative Transitions :-

These transitions involve the return of the activated molecule from  $S_2$  to the first excited state  $S_1$  or  $T_1$ .

These transition do not involves the emission of any radiation and called non-radiative transition.

This process is called Internal Conversion (IC) and occurs in less than  $10^{-11}$  sec.

The other transition occurs between states of different spin i.e. different multiplicity i.e.  $S_1$  to  $T_1$  called Inter system crossing (ISC). These are also non-radiative transition.



## (2) Radiative Transition :-

These transition involves the return of the activated molecule from the singlet excited state ( $S_1$ ) and Triplet excited state ( $T_1$ ) to the ground state ( $S_0$ ). Such transitions are accompanied by the emission of radiation.

The transition from  $S_1$  to  $S_0$  state is allowed transition and occurs in about  $10^{-8}$  sec.

The emission of radiation in this transition is called FLUORESCENCE.

The transition from the triplet excited state ( $T_1$ ) to the ground state ( $S_0$ ) is rather slow since, it is a forbidden transition. The emission of radiation in this transition is called ~~phosph~~ PHOSPHORESCENCE.

The lifetime of phosphorescence are much longer i.e.  $10^3$  Sec or greater.

Thus, phosphorescence & fluorescence are called radiative transitions.

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