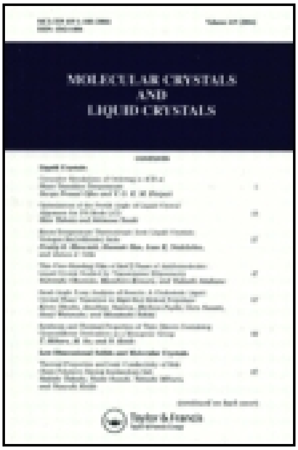

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Luminescence in High-Energy-Irradiated Alkanes at Low Temperature

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Abstract—High-energy bombardment is well-known to produce luminescence in condensed systems which contain suitable scintillators. Such light emission has been observed for weak scintillators like benzene in sufficiently dilute solutions in aliphatic hydrocarbons and, more recently, even in pure liquid benzene. It is not observed in pure liquid alkanes.

However, when suitable alkanes are reduced to sufficiently low temperature (e.g., 77 °K), irradiation with ^{60}Co gammas produces a persistent luminescence, the decay curves of which show peculiar behavior characteristics. This report reviews the decay characteristics and spectra of glassy 2-methylpentane and 3-methylpentane as well as of glassy and crystalline *i*-pentane, reexamines the kinetics and the mechanism of the luminescence process, interprets the applicability of the decay law $I_0/I = 1 + \alpha t$, demonstrates that an excited state of the system (probably a charge-separated state) and not of an individual molecule is involved, presents evidence that the number of available (A and B type) luminescence sites is limited and depends on the history of the system and suggests that the nature of the emitting state may change with temperature. An important aspect of the theoretical considerations is that they suggest that at sufficiently low temperatures such luminescence can be observed even for hydrocarbons as simple as methane.

The most recent work of Janssen, Lang, Hebert, and the authors shows that, although luminescence can be induced in hydrogen and the lower alkanes by irradiation of polycrystalline material at sufficiently low temperature, it appears only when the temperature is raised to certain definite temperatures characteristics of each of the alkanes. Some of these temperatures correspond to known transition points; others may correspond to other solid-state changes.

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1. Introduction

In the course of studies at Notre Dame on the mechanisms of protection and sensitization in radiation chemistry, some of us were stimulated by a suggestion of Maddock[2] that the energy transfer processes were probably similar to those in scintillator solution. Doubtless, in a general and fundamental sense he was correct but we did not know at the time into what areas of activity the stimulation of his remark would lead us. For example, we, as well as others, have developed a great variety of information bearing both on the similarity and on the extreme diversity of photochemistry and radiation chemistry. In an awareness of such diversity, Dillon and Rein, for example, began a study on the effect of temperature of liquid systems on the decay times of luminescence induced by X-rays,[3] to be extended later, and in greater detail, by Amata and Ludwig[4] to ultraviolet induced fluorescence as well. (The essential dissimilarities of the decay curves themselves have since then been revealed in experiments by Ludwig and Huque[5] in which it has been clearly shown that high-energy radiation causes luminescence the characteristics of which are not simply described.) What Dillon and Rein did in their first experiment on glasses was simply to dissolve a typical scintillator in 3-methylpentane (3MP), freeze it to a glass at liquid-nitrogen temperature (in emulation of some aspects of the experiments of Hamill and his co-workers[6]) and look for luminescence in a ^{60}Co-gamma irradiated sample. Of course, they found a very persistent luminescence, as did also Magat and his co-workers,[7] at about the same time, in their studies of frozen cyclohexane containing luminescent impurities. However, one of the present authors was, at the time, more interested in the characteristics of a pure alkane glass than of a solution and out of that interest and the interests and abilities of Dillon and Rein the presently reported work developed.[8]

The most significant result of that early work is that the decay of luminescence does not follow a simple first-order law, nor a second-order law, nor a combination of the two; it can be described by a combination of exponential decays but it is unfortunate for any satisfaction in the exclusive virtue of that result that practically any decay law can be compounded of a mixture of exponential decays. However, the results had certain virtues (e.g., of giving readily interpretable activation energies and, later, activation entropies[9]) which stimulated further study[10] and continued interest and promised to reveal important aspects of the mechanism of the radiation chemistry of condensed systems.

For real understanding of the chemical effects of high-energy radiation in condensed systems it is essential to know the charge distribution at a very early time. Experimental approach to this problem involves studies of luminescence decay processes associated with charge neutralization, the absorption spectrum of the trapped electron and the ESR spectrum of charged species. In the case of liquid systems, the rapidity of charge neutralization limits the experimental method to the study of luminescence decay in the nanosecond range. In the case of organic solids at low temperature the life-time of charged species becomes as long as one hour and consequently the three experimental methods are all feasible. In spite of this apparent advantage in low-temperature studies with organic solids, interpretation of charge neutralization processes in them appears to be more uncertain and more difficult in many aspects than interpretation of the results with organic liquids. Some of these difficulties are enumerated in the following paragraphs.

(1) Decay curves of luminescence or of the absorption spectra of associated trapped electrons cannot be interpreted either as first-order or as second-order. There has been no simple kinetic scheme so far presented which can explain the slow decay of trapped charged species in irradiated organic solids.

(2) Life-times of trapped electrons deduced from optical methods are significantly longer than those obtained by the ESR method.[11]

(3) In solid (glassy) alkanes γ-irradiated for very short periods, the characteristic luminescence cannot be ascribed to impurities or radiolytic products. Both intensity and spectrum of such luminescence are sensitive to the structure of the solid. The mechanism of this luminescence has not been established.[8-10]

In this paper, we review some of the highlights of our presently developed new knowledge of the characteristic luminescence, and also of the absorption spectrum, of the trapped electron in pure alkane glasses and crystals. Also, we propose a kinetic mechanism of charge neutralization which fits experimental luminescence-decay curves.

2. Comment on Experimental Techniques

Details of purification of the alkanes studied and of the techniques of exposure, observation and temperature control are given in the original papers to which reference is made. It is sufficient for the purposes of this review to note that scintillator impurities in any significant concentration were sedulously eliminated, that it was established that oxygen quenches luminescence in all the cases studied and is not itself an emitter, that intrusion of oxygen was prevented, that any effects in windows (when employed) were determined and subtracted, that, in general, concentrations of isomeric alkanes were reduced to $\leqslant 10^{-2}$ M, that benzene, alkene and ketone concentrations were reduced to $\leqslant 10^{-6}$ M, that samples were irradiated for such a short time (generally about 5 min) after glassing or crystallization and at so low dosage (10^{18} eV/g) that the effects of built-up impurities were essentially eliminated, that observation began 20–30 sec after exposure, that annealing effects were taken into account and that the effects of light dispersion by (changes in) polycrystalline structure were likewise noted.

3. Luminescence at About 77 °K

3.1. GENERAL FEATURES

Luminescence from gamma-irradiated pure alkanes at 77 °K decays isothermally to the level of the background luminescence (e.g. of the container) after about 60 min. Approximately an equal amount of *additional* light emission can be produced (thereafter or simultaneously) by continuous long-wavelength (700–1200 nm) irradiation at 77 °K. Figure 1 shows the effect of such IR irradiation, following the isothermal decay, on the luminescence intensity. For the sake of convenience, we call the isothermal part of the luminescence type *A* and the IR-induced part type *B*, respectively.

Continuous IR illumination apparently does not exhaust all the light emission from an irradiated alkane. Subsequent warm-up of the sample produces one or more bursts of light (glow curves); we call the warm-up luminescence type *C*.

3.2. SPECTRA

Luminescence spectra of types *A* and *B* were alone measured. In

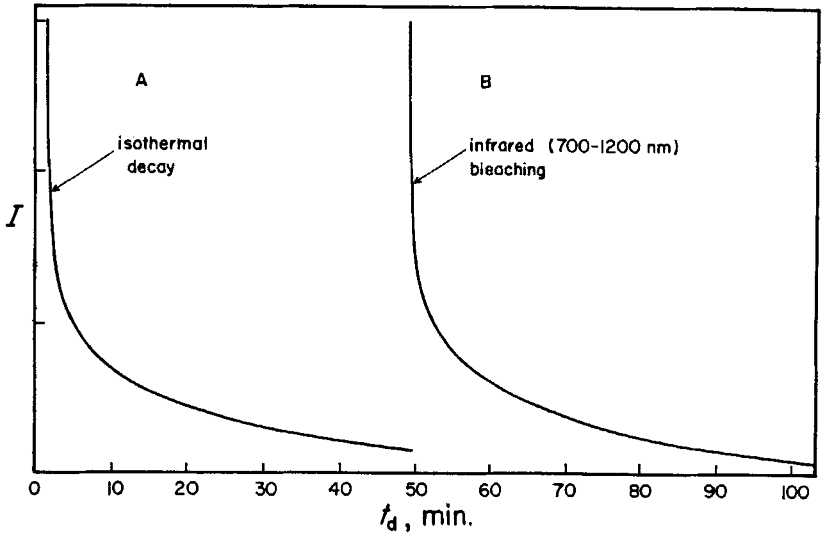

Figure 1. Effect of continuous infrared bleaching after 50 min of isothermal decay on the luminescence intensity of the 425 nm peak for 3MP glass at 77 °K.

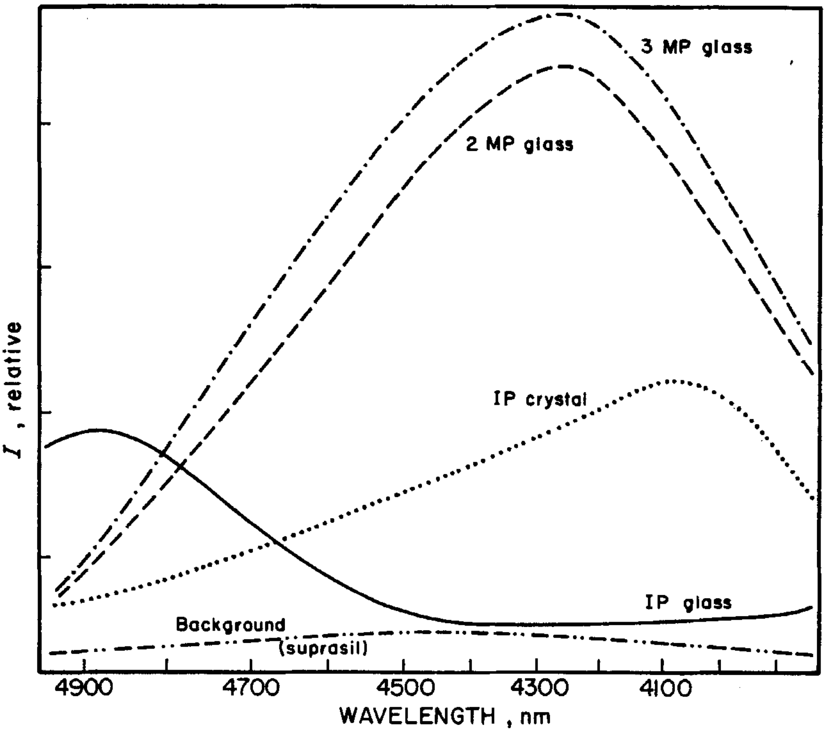

Figure 2. Luminescence spectra of 3MP, 2MP and IP at 77 °K.

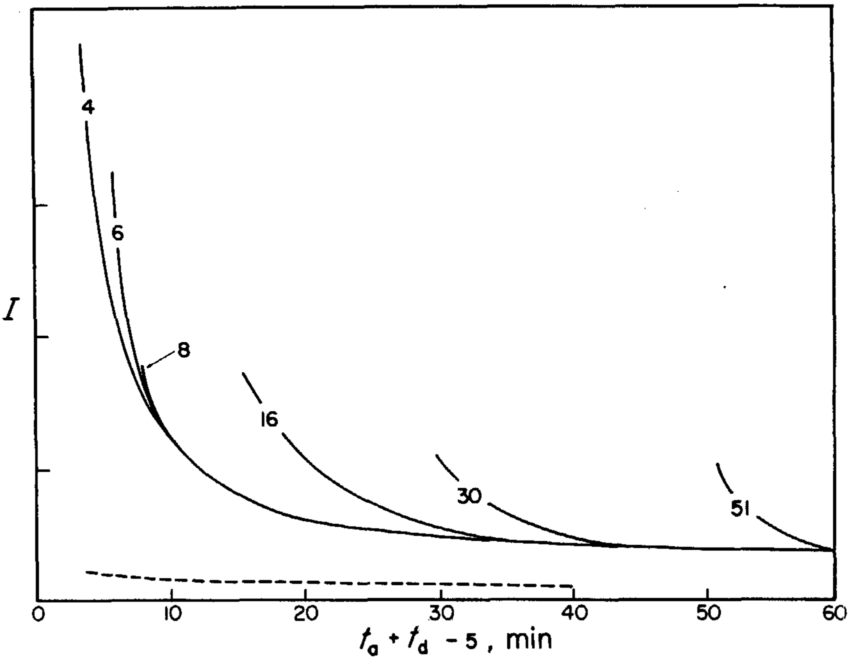

Figure 3. Effect of annealing time, t_a, in liquid nitrogen on 3MP glass; t_d is the decay time. The numbers on the curves indicate the minutes of anneal. The dashed line represents background luminosity of the quartz container. In each case samples were irradiated 5 min after anneal and observation began 20–30 sec thereafter. Times shown on the curves are from the beginning of the " freezing " process.

general, it was difficult to obtain reproducible results for luminescence of type *C* because of poor temperature control during warm-up.

Figure 2 indicates that γ-irradiated 3MP and 2-methylpentane, 2MP, show the same wavelength distribution of luminescence with a broad maximum at about 425 ± 5 nm at 77 °K. The luminescence spectrum of iso-pentane, IP, in the glassy state has a maximum at about 490 nm; in the case of polycrystalline material the maximum is shifted about 80 nm in the direction of shorter wavelength (410 nm).

3.3. ISOTHERMAL ANNEALING

Luminescence intensities of types *A* and *B* *decrease* with the time of isothermal (77 °K) annealing before irradiation. Figure 3 shows

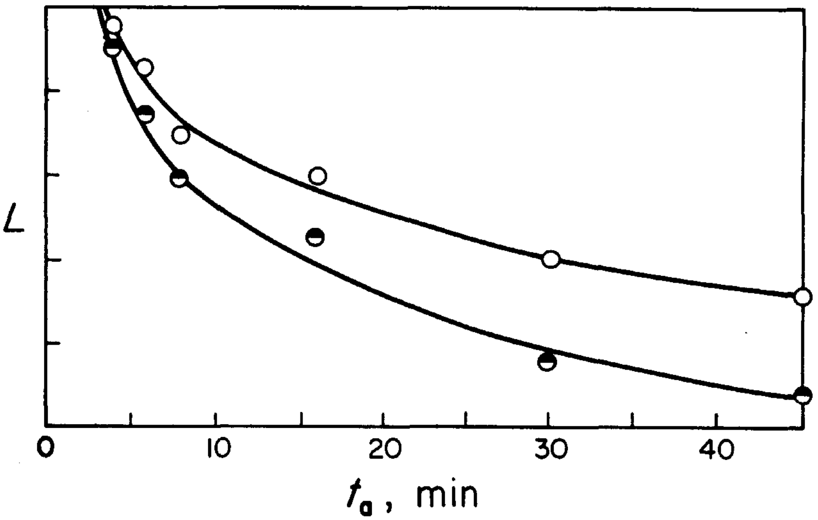

Figure 4. Effect of isothermal preirradiation annealing time on the total luminescence intensity of the 425 ± 5 nm peak for 3MP glass at 77 °K. ○, total luminescence intensity up to 40 min; ◓, total luminescence intensity during period of infrared irradiation thereafter (i.e., up to 90 min).

the effect of annealing time on isothermal luminescence decay of 3MP. Similar results were obtained for type *B* luminescence. Figure 4 shows the effect of isothermal annealing at 77 °K on the *total integrated* luminescence for both types *A* and *B*.

Because isothermal annealing sometimes induces cracks in the glass and thereby changes its optical properties, it is necessary to minimize the cracking by careful cooling and proper shape of the container. It was found[9,10] that the observed decrease in luminescence intensity is attributable not to the cracks themselves but to such structural change of the glass which might be accidentally manifested in the cracking phenomena.

Isothermal annealing appears to have little effect on luminescence intensity of type *C*; however, observations concerning type *C* luminescence are not conclusive at this time.

3.4. EFFECTS OF ADDED IMPURITIES

Figure 5 shows that positive charge scavengers 2-methylpentene-1 (2MP-1) and piperidine, as well as the electron scavenger CCl_4, decrease the total luminescence of 3MP at 77 °K. Figure 6 shows the decay curves at the impurity concentration of 5×10^{-3} *M*.

3.5. DOSAGE EFFECTS

Figure 7 shows the effects of dosage on the total luminescence at 425 nm. It can be seen that the total type *A* (isothermal) luminescence reaches a plateau in the dosage region exceeding 4×10^{19} eV/g, whereas there is no indication of a plateau for type *C* luminescence. In general, the *number* of glow peaks of type *C* increases with the dosage. Little can be said about the nature of these peaks at this time, although it is properly suspected that some are associated with first-[7] or second-order transitions and that some are the consequence of the creation of additional trapping centers with increased dosage (i.e., of a chemical effect on the molecules of the glass).

4. Trapped Electrons

Type *B* luminescence (*cf.* Section 3.1) can result, so far as is known, from irradiation anywhere in the absorption spectrum of the γ-irradiated sample. A model for the nature of this process is that the function of the light is to release fairly deeply trapped electrons ($\sim$0.7 eV corresponds to the peak of the absorption) so that they can become available for charge neutralization and related light emission identical with type *A* luminescence. The first problem is to examine the possibility of such electron traps.

At present there appears to be a plethora of evidence that, in the radiation chemistry of aliphatic hydrocarbons, electrons are substantially separated from their sibling positive ions[12,13] and may remain separated in the liquid state for a sufficient time to be detected by their electrical characteristics[12,13] as well as to affect the forms of luminescence decay curves of dissolved scintillator solutes.[5] Further, the existence of type *B* luminescence and the effect of temperature provide evidence that in glasses at low temperature such electrons are held in traps of the order of 0.1 eV deep and may be released from such traps by infrared light (with the usual Franck-Condon restrictions) as well as by heat.[8,9]

Trapped electrons in γ-irradiated organic solids including alkanes

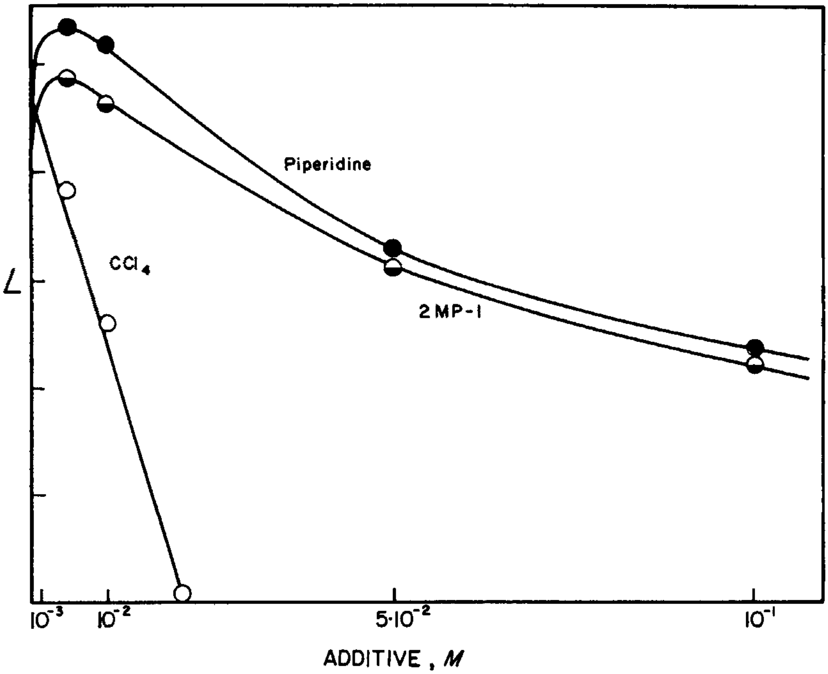

Figure 5. Effects of additives on total A-type luminescence of 3MP at 77 °K.

have been studied by infrared absorption,[14–16] ESR,[17–20] luminescence[8] and electrical conductivity.[21] The absorption spectrum of trapped electrons in 3MP at 77 °K, which is almost identical for γ-irradiated[14] and photo-oxidized[17] systems, and also for systems with[14] and without[8] additives, has the following qualitative features. (1) The spectrum is a broad, structureless one with a peak at about 0.7 eV (*cf.* Fig. 8). (2) In the case of 3MP with additives,[14] the entire spectrum can be bleached with any monochromatic light within that spectrum and also with light of a shorter wavelength. Quantum yield[14–15] of photo-bleaching decreases markedly with the degree of bleaching and is higher if UV light is used. (3) Isothermal bleaching at 77 °K has a half-life time of about 30 min.[9] Decay kinetics for the isothermal bleaching at 77 °K is neither first-order nor second-order.[9]

Because gaseous alkanes have no electron affinity in the ground state, it is generally understood that in the solid state electrons are

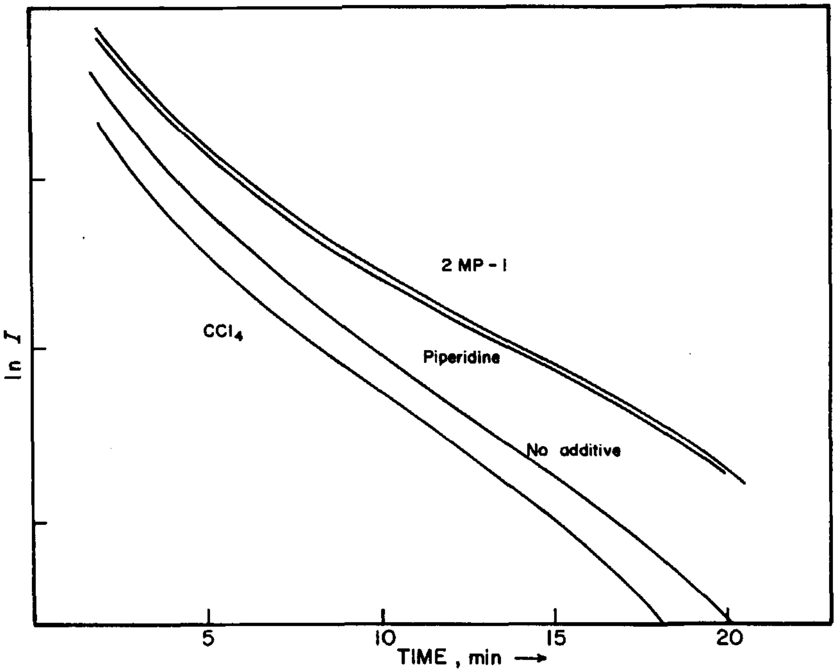

Figure 6. Effect of additives on the luminescence decay curves. The concentrations of the additives are all 5×10^{-3} *M*.

trapped physically in cavities rather than at molecules. However, the cavity-model for the trapped electron is at present strictly a matter of speculation. There is neither direct experimental evidence to support this view (such as volume expansion), nor any theory that describes even the qualitative nature of interaction at short distance between an electron and an alkane molecule (i.e., whether it is repulsive or attractive). It is not possible to state at this time whether the traps in 3MP glass, for example, correspond to low (e.g. cavity) or high density (e.g., molecular cluster) regions.[22]

According to Jortner's continuum model,[23] the polarization energy E_p, that is responsible for trapping electrons can be described by either

$$E_p = \frac{1}{2}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) < \psi \mid f \mid \psi > \tag{1}$$

or

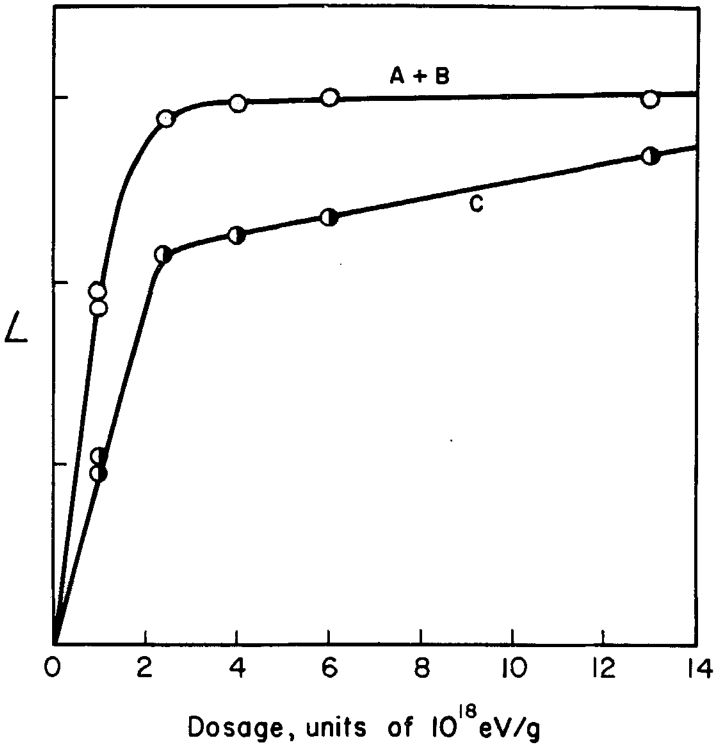

Figure 7. Effect of dosage on total luminescence of 425 nm peak in 3MP glass at 77 °K. ○, isothermal decay (type *A*); ◑, glow curve (type *C*).

$$E_p = \frac{1}{2}\left(1 - \frac{1}{D_s}\right) < \psi \mid f \mid \psi > \qquad (2)$$

where D_{op} and D_s are the optical and static dielectric constants, f the electrostatic potential due to the trapped electron and ψ is the wavefunction. Equation (1) is the result of the adiabatic approximation: the kinetic energy of the extra electron should be negligible in comparison with those of the bound electrons of the normal medium. Equation (2) applies to the case where the kinetic energy of the extra electron is comparable with those of the "medium" electrons. The trapped electrons in alkanes are likely to belong to the first category. Because alkanes are nonpolar, Eq. (1) gives zero polarization energy (no binding). The chief difficulty with Eqs. (1) and (2)

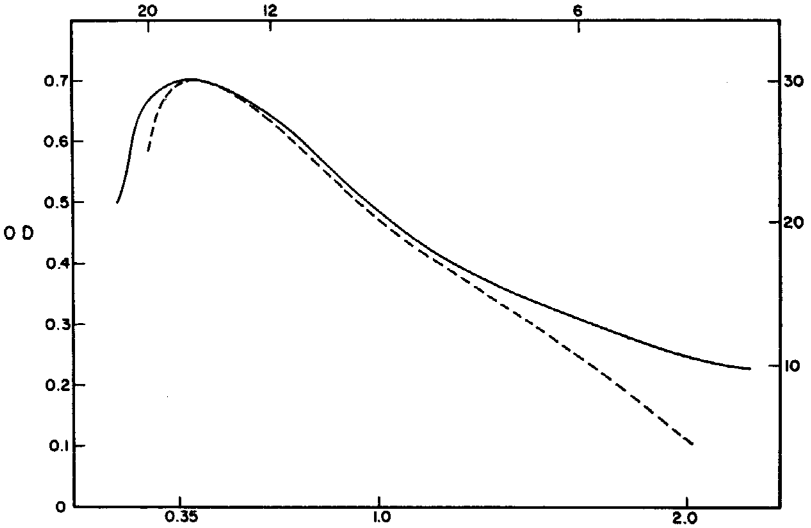

Figure 8. Absorption spectrum of trapped electrons in 3MP at 77 °K. The dotted line is the experimental absorption spectrum and the full line is the theoretical curve which follows from application of the theory of Ohmura and Ohmura.

is that in most cases of interest ψ for the trapped electron is not known very accurately.

Before we proceed to compute the absorption spectrum of the trapped electron we must settle the question of whether light absorption (in the IR) corresponds to a bound-bound or bound-free transition. If light absorption corresponds to a bound-bound (such as $1s \rightarrow 2p$) transition, absorption of light does not necessarily bleach the spectrum. It is also unlikely that potential wells in solid alkanes have enough strength to accommodate an excited state. On the other hand, if light absorption is of a bound-free type of transition, the broadness of the spectrum emerges naturally from the theory.

The problem of a bound-free transiton has been treated by a square-well potential[24] and by the effective range approximation.[25,26] According to Ohmura and Ohmura,[26] the cross section for photoelectric absorption in an electric dipole transition is given by

$$\sigma = \frac{16\pi e^2}{3\hbar c}\left(\frac{2\gamma}{1-\gamma\rho}\right)\left(\frac{k}{\gamma^2+k^2}\right)^3 \qquad (3)$$

where γ and k are defined by the facts that $\frac{\hbar^2\gamma^2}{2m}$ is the threshold energy (binding energy) and $\frac{\hbar^2k^2}{2m}$ is the kinetic energy of the ejected electron, and ρ is the effective range. It is clear from Eq. (3) that the peak in the absorption spectrum corresponds to $\gamma = k$. Because the peak is at about 1650 nm ($\sim$0.75 eV), the binding energy for the trapped electron is about 0.37 eV. Figure 8 shows both an experimental absorption curve[6,8] (dotted line) and the numerical plot of Eq. (3).

The broadness of the absorption spectrum can result also from vibronic coupling[27] and different sizes of the cavities.[28] Bleaching characteristics and the width of the spectrum, however, suggest that the broadness is mainly attributable to the bound-free transition.

Up to the present time interpretations of the absorption spectra in condensed molecular systems have been limited to the physical situation in which incident light is presumed to interact with an isolated trapped electron. In view of the variety of possibilities for the distribution of charged species in a γ-irradiated solid, the applicability of such a model in any one case may be questionable. Interaction of such an electron with positive charges or other electrons could be quite important in understanding the intensity and the shape of the absorption spectrum of " trapped electrons ". This problem is under present investigation.

5. Luminescence Decay Kinetics

5.1. MODEL FOR LUMINESCENT STATE

That the luminescence discussed in this report is associated with charge neutralization is indicated by the quenching effects of added charge scavengers (see Section 3.4). That result does not, however, indicate the nature of the luminescent state. There is, as an example, the possibility that the luminescent state is, or is related to, one of the excited states which can result from charge neutralization. For example,

$$M^+ + e \rightarrow M^* \rightarrow M + h\nu$$

The molecule M can be the solvent molecule or any other molecule which can exist in an irradiated system. The implication of such a mechanism is that M is an apparently normal scintillator molecule with a known emission spectrum. However, in the case of alkanes and their derivatives, no molecule M is known to emit luminescence in the gas phase.[29] In such excited molecules the electronic energy is presumably at once converted to vibrational energy or is dissipated in immediate fragmentation (e.g., in *ca.* 10^{-13} sec). To the best of our knowledge, none of the possible radiolytic products of alkanes are known to luminesce upon excitation in the gas phase. Thus, we are led to conclude that the luminescent state is not an excited state of a molecular entity, but an excited state of the system, such as a charge-separated (or charge-transfer) state. Luminescence phenomena involving charge-separated states have been studied extensively in inorganic semiconductors.[30] Light emission in such cases is the result of the radiative neutralization of electrons trapped on donors by holes trapped on acceptors. The energy of a particular emission act is given in such case as a function of donor-acceptor separation. The emission spectrum reflects the donor-acceptor distribution and varies with decay time. In the case of the characteristic luminescence in γ-irradiated alkane solids the emission spectrum does not change appreciably with time. This observation indicates that either holes or electrons, or both, migrate to form some metastable configuration before emission takes place.

What now is the qualitative picture for the metastable charge-separated state?

The common way of estimating the energy of the charge-transfer state, E_{CT}, as a function of the hole-electron separation R, is

$$E_{\mathrm{CT}} = I - A - \frac{e^2}{\epsilon R} - P_+ - P_- \tag{4}$$

where I is the ionization potential, A is the electron affinity, ϵ the low-frequency[31] dielectric constant of the medium, and P_+ and P_- are the polarization energies of the positive ion and the electron respectively. When R is large the sum of P_+ and P_- is nearly independent of the separation R, and the coulomb energy is the only term that varies with R. On the other hand, when R becomes small, the polarization energy is not a simple sum of the two charges, but that of a dipole which vanishes at zero separation. Thus, the existence of the metastable charge-separated state at a particular separation depends critically upon how the sum of the polarization energies, $P_+ + P_-$, varies with R. It is possible, under certain conditions, to show that E_{CT} has a minimum at a particular R.[32] Eq. (4) may have some validity for aromatic hydrocarbons, the molecules of which have an appreciable electron affinity so that the electron can be regarded as localized at a negative ion, thus justifying the form $\frac{e^2}{\epsilon R}$ approximately.

Application of Eq. (4) to alkanes requires some modification. Because none of the molecules is known to have any appreciable electron affinity and also because the systems are non-polar, the binding energy for the trapped electron, if there is any, is likely to be small or there may even be no bound state in the vicinity of a positive ion. Such a situation means that the point charge approximation required for $\frac{e^2}{\epsilon R}$ is not valid. In order to have some qualitative understanding of this situation, let us consider the electronic energy of an electron in the combined field of a coulomb potential associated with the positive ion and the trapping potential itself (i.e., a " hydrogen-atom-like " system), which is a function of the separation between the positive ion and the trap. The Hamiltonian for this system is given by

$$\mathbf{H} = -\frac{\nabla}{2} + \frac{e^2}{\epsilon r} + v_{\mathrm{R}} \tag{5}$$

where ϵ is the dielectric constant and v_{R} is the trapping potential of a trap located at a distance R from the positive ion. When v_{R} is small in comparison to the coulomb potential, we can expand the eigenfunction for Eq. (5) in terms of the eigenfunctions for

$$\mathbf{H}_0 = -\frac{\nabla}{2} + \frac{e^2}{\epsilon r} \tag{6}$$

i.e., the hydrogen-like wavefunctions.

The energy of the first excited state (of this " hydrogen-atom-like " system) corresponding to the Hamiltonian (5) is plotted against the distance R in Fig. 9. In this calculation the potential v_{R} was taken to have the form

$$v_{\mathrm{R}} = \frac{2\pi\hbar^2}{m} b\delta(r - R), \tag{7}$$

where r alone is variable, m is the electron mass and b is the scattering length for the trap. Such a potential[33] is both oversimplified and fictitious. There is no such thing as a delta-function potential. However, it is useful; it fulfills the essential role that is required of v_R, mixing of the eigenfunctions of $\mathbf{H}_0$. It can be seen from Fig. 9

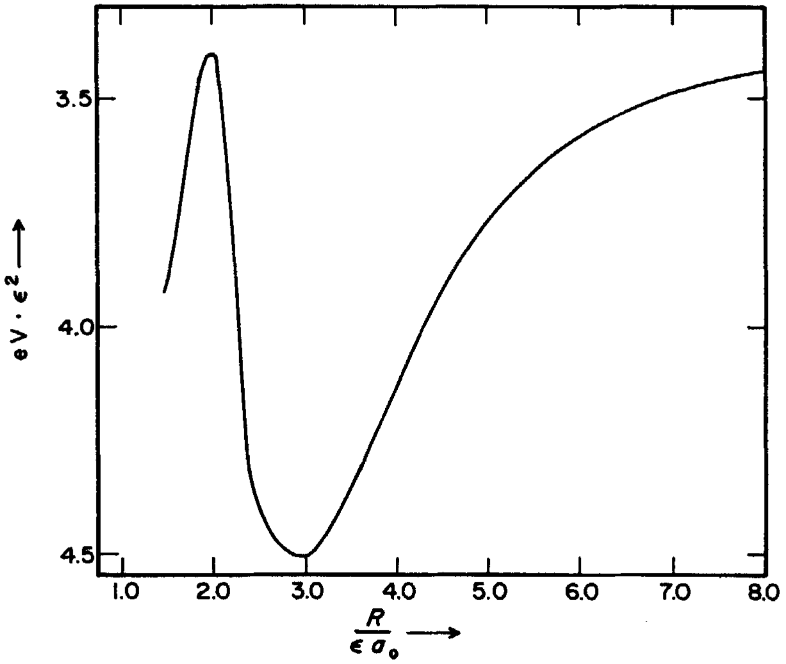

Figure 9. Electronic energy of the charge-separated state as a function of the position of the potential v_R; ϵ is the dielectric constant.

that there is an optimum separation R which corresponds to an energy minimum for the first excited state. The electronic state corresponding to this energy minimum is our qualitative model for the metastable charge-separated state. Figure 10 shows the charge distribution of this state. What v_R does to the zero-th order wavefunctions is something like s-p hybridization; the resultant charge distribution has its centre of gravity away from the positive ion. In order to get the energy of the charge-separated state, the polarization energies must be added on to the eigenvalues of $\mathbf{H}$. The qualitative picture, however, remains the same; namely, there exists

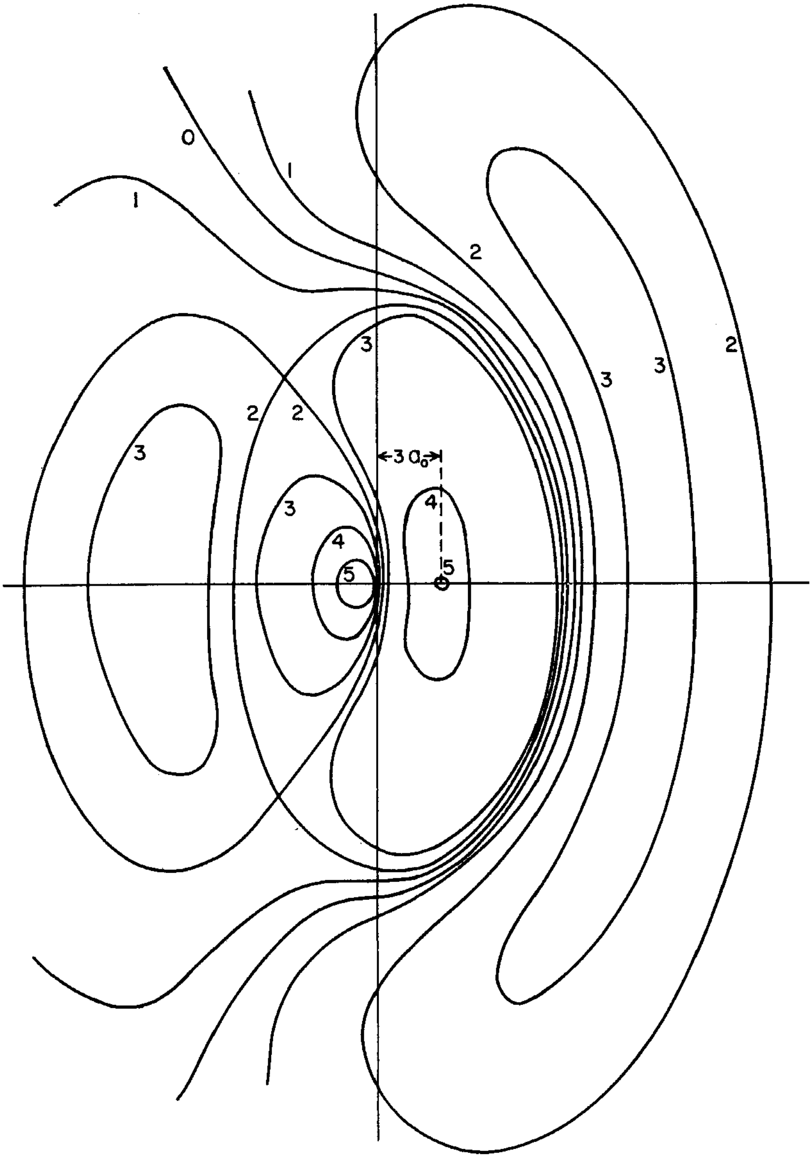

Figure 10. Contour diagram for electron distribution for the configuration corresponding to the minimum in Fig. 9 in units of probability.

0 : 0 3 : 0.0001
1 : 0.000004 4 : 0.01
2 : 0.000036 5 : 0.04

a metastable charge-separated state at a certain separation R with energy below that of the first excited state of the molecule in the dielectric medium without the potential v_R. According to this model, stability of the metastable charge-separated state depends upon the existence of the trapping potential which mixes the molecular excited states. In order to have efficient mixing, the electronic orbitals corresponding to the molecular excited states must have appreciable amplitudes at the trap site. These orbitals may correspond to the Rydberg states of some molecular entity which could exist in γ-irradiated solid alkanes. It is not possible to identify the nature of the positive ion at this time. In view of the dominant role of N-V transitions in alkanes,[34] it is unlikely that the unconverted alkane positive ion is involved in the stable charge-separated state.

5.2. LUMINESCENCE DECAY

When an empirical (experimental) law of luminescence decay is combined with a theoretical model for charge transport, one can derive the charge distribution function corresponding to a specified time. Debye and Edwards[35] used the diffusion-kinetic model to obtain the electron distribution function for the case that the luminescence decay is proportional to t^{-m}.

None of the luminescence decay curves that we studied could be fitted with an inverse power law (t^{-m}), or a simple exponential or a second-order law. Such a result is, of course, not totally unexpected; the decay law must be a combined result both of reaction mechanism and of initial charge distribution.

If G for trapped electrons is assumed to be about unity, then the average separation between the electrons (for a dose of 10^{19} eV/g) becomes about 200 Å, and the corresponding Coulomb-interaction energy (~ 0.03 eV with $\epsilon = 2$) exceeds the thermal energy, kT, at 77 °K (~ 0.006 eV). This result means that on the average the motion of the electrons cannot be described by random-walk. On the other hand, it is unlikely that the initial charge distribution is that of highly correlated ion-pairs; consequently the decay law must involve successive unimolecular cascades.

Figure 11 shows that a variety of decay curves obtained in our present work (see Fig. 5) are best fitted with the equation

$$I_0/I = 1 + \alpha t, \tag{8}$$

where I_0 and I are the luminescence intensities at " time zero " and t, respectively, and α is a constant.[36] It is worthy of note not only that α is independent of presence of added quencher but that the decay law is independent of the value of I_0, which is arbitrarily established by the degree of anneal which the system has established before irradiation, by the speed with which the first observation happens to be made and by the concentration and properties of added quencher. One feature clear from the steadiness of α is that the added quencher is a so-called " static " quencher. Because the system is solid the quencher molecule acts only on potential luminescence emitters in its immediate neighborhood and does so as soon as they are formed in the initial irradiation act. It thus decreases the amount of possible luminescence. Because the quencher does not diffuse, it does not interfere with any process which occurs at a later time. Consequently, the coefficient α cannot be affected by the nature of the quencher.

The decay law of Eq. (8) was first recognized by Bagdassarian and his coworkers[37] in a study of low-temperature luminescence of gamma-irradiated organic glasses with aromatic additives. It is remarkable that so simple a decay law as represented by Eq. (8) is able to fit luminescence decay curves both with and without additives. The most desirable procedure for understanding of the law would seem to be the derivation of the initial charge distribution which would generate Eq. (8) assuming, of course, that the kinetic scheme for charge recombination is known. This procedure is not followed in this work. Instead of trying to derive the charge distribution function, we attempt to " explain " that decay law from a more elementary viewpoint using the concept of concentration. It should be emphasized that use of concentration ideas such as are characteristic of the kinetics of homogeneous chemical reactions is itself a questionable procedure in a study of the kinetics of a radiation chemical process. However, at the moment we are still searching for an adequate approximation to the kinetics of reaction in what may be a rather heterogeneous medium. Several theoretical investigations in this area of radiation chemistry are now being conducted in the Radiation Laboratory at Notre Dame. The first mechanism herein presented was suggested originally by Bagdassarian and his co-workers.[37] The key concept in this mechanism is the charge-separated state or complex, which in the cases under immediate discussion has an extraordinary stability at 77 °K. In the view they propose, approach of a free electron or hole perturbs the system and diminishes the stability of what is essentially a charge-separated state; neutralization (and light emission) ensue. The proposed mechanism involves competitive processes

$$M^+ + e^- \xrightarrow{k_1} \text{neutralization} \tag{i}$$

for well separated solvent ion and electron and

$$(P^+, e^-) + e^- \xrightarrow{k_2} P + h\nu + e^- \tag{ii}$$

where P is a radiolytic product (either initial or secondary) which forms a stable charge-separated complex (P^+, e^-).[33] In step (ii) it is assumed that the perturbing charge carrier is the electron, but the latter can be replaced by M^+ without changing the kinetics. The luminescence intensity is given from step (ii) as

$$I = \mu k_2 x y, \tag{9}$$

where μ is the probability of light emission on charge neutralization, x is the concentration of the stable complex (P^+, e^-) and y is the concentration of the mobile " free " electron (or positive hole).

The concentration of " free " electron (or hole) experiences changes as a consequence of reaction i according to a very simplified law

$$\frac{dy}{dt} = -k_1 y^2 \tag{10}$$

Simultaneously, the concentration of the complex changes in this simplified view according to

$$\frac{dx}{dt} = -k_2 x y \tag{11}$$

From Eqs. (9), (10) and (11) the luminescence intensity can be written as

$$I = I_0(1 + k_1 y_0 t)^{-(1+k_2/k_1)} \tag{12}$$

where y_0 is the initial concentration of the free electron (or hole) and I_0 is the initial luminescence intensity. A reasonable assumption[37] is $k_1 \gg k_2$ in (12). The empirical law represented by Eq. (8) thus follows.

The fact that the mechanism selected by Bagdassarian and his co-workers yields the rate law shown by Eq. (8) does not, of course, establish the reality of the mechanism. One is reminded of the similarity of Eq. (8) to the steady-state law for luminescence in presence of quencher

$$\frac{I'_0}{I'} = 1 + \gamma[D] \tag{13}$$

where the prime signs indicate steady-state luminescence intensities, $[D]$ is quencher concentration and $\gamma = k_q/\sum r$; in the last expression k_q is the specific rate of the quenching process and $\sum r$ is the summed specific rates of disappearance of the luminescent species by all other processes.

Specifically, we consider four important reactions in the type of luminescence discussed in Section 6.

$S \rightsquigarrow S^*$ initial excitation

$S^* \longrightarrow X^*$ transfer to emitting state

$X^* + D \longrightarrow X + D$ quenching

$$\begin{tikzcd} & X + h\nu \\ X^* \arrow[ur] \arrow[r] \arrow[dr] & X \\ & \text{etc.} \end{tikzcd}$$

luminescence

The initial excitation reaction (initiation) is complete before observation begins. For Eq. (8) to follow from these reactions it is necessary that S^* be produced in such large concentration that the transfer reaction appears to be zero order. It is further necessary not only that $[D]$ be a linear function[39] of t but also, as shown in Fig. 11, that, in the relationship $[D] = \kappa t$, κ remains constant in all cases studied at a particular temperature. We can imagine that such a requirement might be met if quencher were also introduced in a zero order process the specific rate of which does not depend upon prior treatment of the system. The type of process which can give constancy of κ from case to case is not immediately apparent.

A third mechanism suggested in the course of discussions of the processes involved notes that a decay law of this kind can be obtained

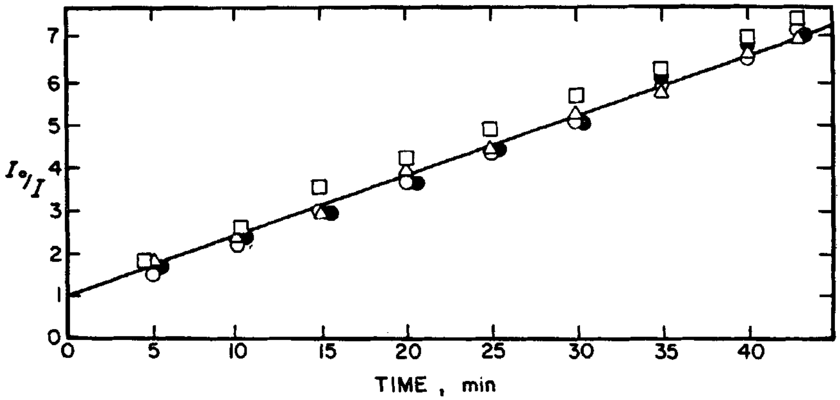

Figure 11. Decay Law for isothermal luminescence in four different studies

☐	3MP, 10^{-2} M CCl_4	○	3MP, 5×10^{-3} M 2MP-1
△	3MP, no additive	●	3MP, 10^{-3} M piperidine

by a combination of processes in which second-order decay predominates. Consider a glass in which a concentration of potentially luminescent species X^* is produced initially. That species may be considered to disappear by two processes

$$X^* \xrightarrow{k_e} X + h\nu \quad \text{emission} \tag{iii}$$

$$2X^* \xrightarrow{k_q} 2X \quad \text{quenching} \tag{iv}$$

If $k_q \gg k_e$, the concentration of X^*, and consequently the light intensity at that time, follow the second order law

$$I_0/I = 1 + k_q t$$

The simple fact which must not be neglected is that the luminescence decay processes shown in Fig. 11 seem to follow a single, second-order law. This statement does not mean that other more complicated laws are automatically eliminated. It does, however, mean that we must examine the situation in order to determine what factors can yield such a simple law in spite of the heterogeneity of the situation. One cannot take the view that the second-order kinetics is wholly accidental. On the other hand, it can be incidental to the phenomena involved.

The earlier report by Herley and the present authors[9] contains two curves for the decay of luminescence of 2MP, one at 77 °K and the other for data at 90 °K. The data there represented are not considered as complete as those of the present work. However, the first points over a 10 minute range for the decay of luminescence of 2MP at 77 °K can be fitted to a Bagdassarian equation precisely (there is some departure from such an equation at longer times). The data for the 90 °K case cannot be fitted to such an equation. It is notable that the data of the 77 °K case do *not* yield the same value of α as do the data for the 3MP luminescence described by Fig. 11 in this work. It is reasonable to expect (or, at least, not to find too surprising) the fact that, determined by the various combinations of (iii) and (iv) (or (i) and (ii)), α may very well be different depending on what the reacting species actually is. It is not too surprising to discover that 3MP and 2MP do not yield the same species of (P^+, e^-) and that the specific rates of the ractions of (P^+, e^-) depend on what P actually is. The spectrum of type A luminescence should also depend on the precise nature of P. As Fig. 2 shows, the difference between 3MP and 2MP, if any, is small but the difference from the two IP cases is very large.

5.3. NATURE of (P^+, e^-)

Figure 3 clearly shows that the time of anneal of the sample of 3MP glass before irradiation definitely affects the maximum intensity that can be observed and also seems to affect the rate at which the luminescence intensity decreases. Such a result would suggest in a tentative sort of way that the number of sites at which the luminescent species (P^+, e^-) can be formed is decreased by the pre-annealing. However, something more than this purely numerical phenomenon is involved. We have not been able to prepare crystalline 3MP or 2MP. However, both glassy and crystalline *iso*pentane have been prepared. Figure 2 shows that there is a considerable difference between the emission spectra of glassy IP and crystalline IP. Both show type A luminescence. However, the type A luminescence is different depending upon the treatment of the IP. The conclusion is that (P^+, e^-) in that case is not by any means to be confused with a simple, excited state of an IP molecule (i.e.,M^*).

The excited state (P^+, e^-) is a state which belongs to the system and is characteristic of the system and not of a particular molecule. We show it as a charge-separated state and we conclude (from the

IP work) that this charge-separated state must be different depending on the structure of the system.

There is one point in connection with the nature of (P^+, e^-) in 3MP and 2MP glasses which may have considerable significance. That point is that the luminescence spectra of those two glasses are very similar. The suggestion is that in the considerably disordered condition characteristic of glasses the precise location of the methyl group on the chain of 5-carbon atoms does not seem greatly to affect the nature of the upper and lower levels (or at least the energy difference between those levels) of the charge-separated state.

In Reactions (iii) and (iv), X^* is identified with (P^+, e^-). The approach of these species to each other causes quenching. If we envisage these species as triplet,[40] their interaction results in an allowed transition. The more easily they move, the more frequently they approach each other and the more rapidly the allowed transition (to the ground state) occurs. Annealing results in improved crystallinity and freer movement of the Wannier exciton. Thus, as Fig. 3 shows, the greater the annealing of the glass (and presumably the greater the regions of crystallinity), the more rapidly the states interact and the lower the initial intensity of luminescence which can be observed. In the relatively few seconds which precede observation after irradiation, those exciton states near each other interact sufficiently rapidly so that they annihilate (i.e., self-quench). In such cases, it is only the Wannier excitons which must move a considerable distance (and therefore through less well-organized material) which enter into the observable fraction of reaction (iv). Added to this effect on luminescence intensity is an effect much more controlling: annealing decreases the number of sites at which (P^+, e^-) can be formed. This fact is clearly shown in the effect of annealing on type *B* luminescence, which is likewise decreased.[9]

5.4. Number of Available Sites

For trapped electrons, both Willard[42] and Williams[11] have concluded from their work that the number of available sites for trapped electrons in glasses (containing added impurities) is limited. These results with pure glasses lead to the same conclusion.

The plateau shown in Fig. 7 for type *A* luminescence indicates that beyond a certain irradiation no more sites for storage of energy, later to appear as type A luminescence, are available. Furthermore, the experiments on the effects of isothermal annealing seem to indicate that the number of such sites is reduced by the annealing process.

5.5. TYPE B LUMINESCENCE AND THE EFFECT OF QUENCHERS

Type B luminescence is the kind that appears when, after type A luminescence has decreased to a very low value, the system is irradiated with light in the presumable region of its absorption spectrum. A simple picture of the process involves the existence of (P^+, e^-) states. If such states are formed relatively far from each other or in completely disorganized glass, the probability of their interaction (as a result of diffusion) is decreased to a point where resultant type A luminescence becomes of very low intensity. However, the species (P^+, e^-) has its own absorption spectrum (irrespective of the distance from other (P^+, e^-) sites) and, when irradiated, the charges in (P^+, e^-) become separated and can diffuse. In such event, what happens to the (P^+, e^-) state is well indicated by Reaction (ii) of the Bagdassarian treatment. Any charge which approaches such a " triplet " state may likewise cause either light emission or non-radiative destruction of the state (*cf.* also Reaction (i) of the Bagdassarian treatment). More detailed kinetic study of this type luminescence is required.

Incidentally, it may be noted that, in a glass or crystalline solid, *primarily introduced quenchers* are frozen into position. It is only the quenchers near the (P^+, e^-) states initially which can quench those states; thus the static nature of the quenching, to which allusion is made in Section 5.2, is explained.

5.6. EFFECTS OF TEMPERATURE

In our consideration of the applicability of the Bagdassarian equation to the work herein reported, we note that the Herley data[6] on the luminescence of 2MP at 90 °K do not fit such a law. This result probably reflects some of the difficulties in maintenance of even temperature during the observations in the neighborhood of the softening point of the glass. Figures 12 and 13, selected from some current, as yet unreported, work of Janssen, Lang, Hebert and the present authors, show possible reasons for some of the difficulties involved. Luminescence can be caused in solid hydrogen. In these more recent experiments solid hydrogen is exposed to γ radiation at 4 °K. Thereafter, the temperature is permitted to rise by the simple device of allowing free distillation of the liquid helium in the cryostat.

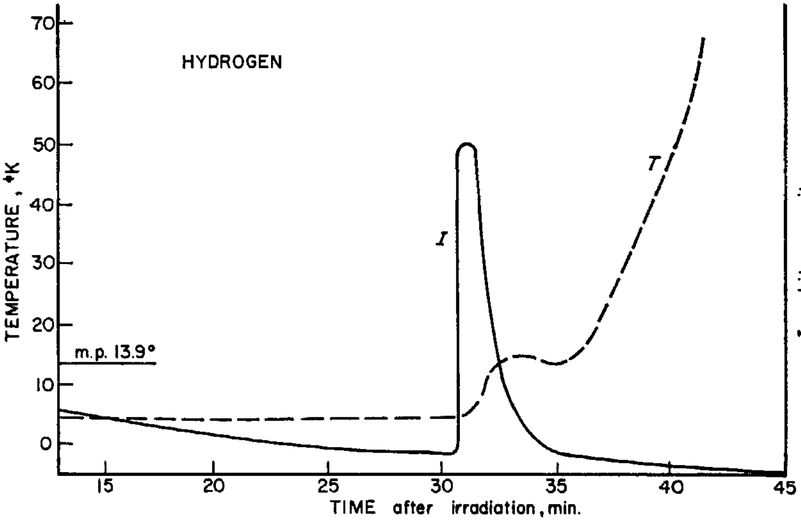

Figure 12. Thermoluminescence of γ-irradiated solid hydrogen.

Figure 12 shows that the only luminescence first observed comes from the walls of the containing vessel itself. Suddenly, as the temperature continues to rise, but below the melting point of the solid hydrogen, a sharp luminescence peak appears and the temperature rises abruptly, attaining the melting point at about the same time as the luminescence decreases to a value corresponding to that of the container itself. This is the simplest type of curve we have observed. It is obtained under conditions, and is of a form, unsuitable for studies of luminescence decay. The principal characteristic is the association of the luminescence with the melting point. Exactly the same curve has been obtained repeatedly.

Slightly more complicated curves have been obtained with methane. In that case, a sharp luminescence peak, preceded by a small preliminary peak, appears in the neighborhood of the transition point at 21°K. Figure 13 shows one of the more interesting cases we have studied. It represents the relationship between time, temperature and luminescence for ethane irradiated at 4 °K. The sharp peak of luminescence occurring near 55 °K without a correspondingly significant halt in the temperature curve suggests the occurrence of a second-order transition, not previously reported, at that temperature in the case of ethane. The double peaks just before the melting point are not understood. They have been found repeatedly in the study of ethane and they do show the difficulty of obtaining much information concerning the activation processes from studies of luminescence even at most carefully controlled temperature conditions. Thus, failure to find a Bagdassarian law for the luminescence of 2MP at 90 °K (studied in the earlier work) may represent the intrusion of an essentially different process near that temperature with, perhaps, corresponding lack of temperature control. The new results clearly show that maintenance of precise temperature control in the various (temperature) regions of luminescence is essential to studies of the kinetics. They also reflect the possibility that different elementary phenomena may be responsible for the luminescence at such considerably separated temperatures[41]

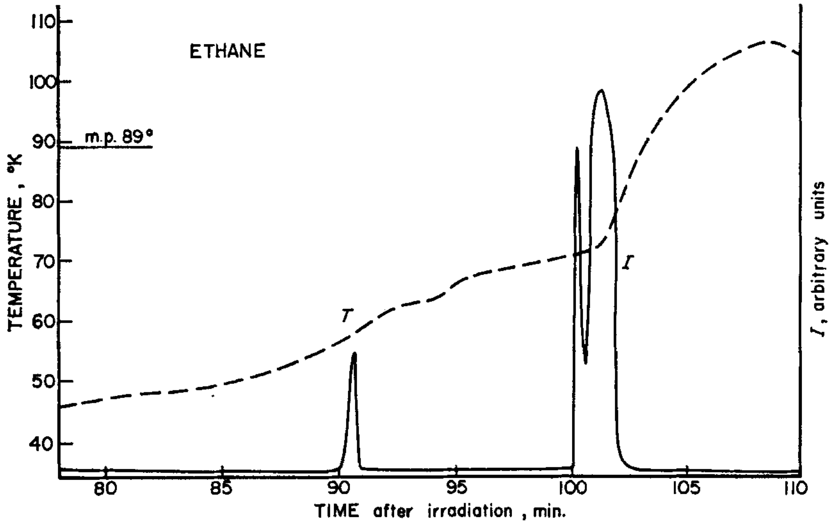

Figure 13. Thermoluminescence of γ-irradiated solid ethane.

so that our previous conclusions, from such data, regarding activation energy and activation entropy may be invalid.

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