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1. The Kinetics of Excimer Formation in Fluid Media.
2. Dr. D. Stevens (Sheffield University) - Contractor.
3. Contract No. DA-91-591-EUC-2018.
4. Annual Technical Report.
5. Period covered - November, 1961 - October 31st, 1962.

"The research reported in this document has been made possible through the support of the U.S. Department of Army through its European Research Office."

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ABSTRACT

The observations of delayed fluorescence in the gas phase and in solution, together with the theories proposed to account for its origin and associated phenomena, are reviewed to the date at which the research reported here was started.

It was originally proposed that delayed fluorescence, with a lifetime of the order of milliseconds and a spectrum identical with that of the corresponding fast fluorescence, originates in the dissociation of the excited dimeric species A_2^* , the excimer,



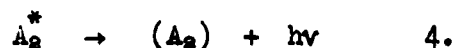
which follows the association of electronically-excited and unexcited molecules A^* and A of an aromatic compound



According to this mechanism the lifetime τ_D of the delayed fluorescence component is given by

$$\tau_D = 1/k_2$$

which requires that the radiative lifetime of the dimer in the vapour phase is considerably longer than τ_D (\sim m secs.) since no dimer emission represented by



is observed.

An analysis of the data presented and previously obtained for anthracene, perylene and pyrene vapours is presented in terms of this (excimer) dissociation mechanism from which it is found that

(i) process 2 has a rate constant of $4 \times 10^2 \text{ sec}^{-1}$ for anthracene at 220°C .

(ii) process 1 has a collisional efficiency of approximately 10% for perylene at 362°C .

(iii) process 4 must be associated with a radiative lifetime of the order of a second.

Although this mechanism gives a qualitative account of the observed phenomena, the extent to which radiative relaxation of the excimer (process 4) is forbidden is difficult to justify on theoretical grounds.

Following the observations of Parker and Hatchard concerning the delayed fluorescence exhibited by solution of phenanthrene and of anthracene, it has been established that the intensity of delayed fluorescence varies as the square of the absorbed light intensity for perylene and pyrene in the vapour phase. This indicates that delayed fluorescence originates in a process involving two electronically-excited molecules for which Parker and Hatchard propose



and which, at the low stationary triplet-state concentrations excited by a constant intensity light source, proceeds to a much lesser extent than the first-order process



A comparison of the expressions obtained for the observed decay of delayed fluorescence and that provided by this mechanism

leads to the relationship

$$\tau_D = 1/2k_9$$

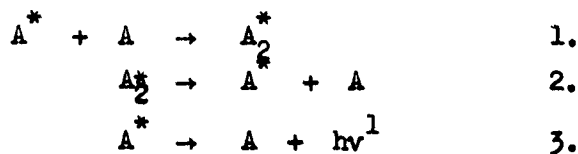
which, insofar as independent estimations of k_9 are available for the vapour phase, appears to be obeyed. Thus the lifetime of delayed fluorescence is determined by the rate of first-order decay of the triplet state and its measurement affords a useful estimate of triplet state lifetimes in the vapour phase.

This mechanism removes the necessity for postulating a long-lived excimer, although during the period covered by this report excimer emission has been reported for some 30 systems and its existence is well-established. A further example, that of acenaphthene, has been observed and is described.

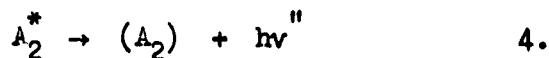
2. RESEARCH REPORT

Introduction

Delayed fluorescence in fluid media was first reported by Kautsky¹ who observed that extremely dilute, carefully outgassed solutions of chlorophyll and related molecules, and of certain dyes, emit a component of fluorescence with the normal spectral distribution but with a lifetime of the order of milliseconds. Kautsky suggested that this was due to the reversible formation of a metastable electronically-excited dimer A_2^* from excited and unexcited aromatic molecules A^* and A respectively i.e. process 1 is followed by 2 and 3.



It is implicit in this mechanism that the radiative relaxation of the excited dimeric species A_2^* (process 4) is very much slower than the competing process 2 which itself must have a rate constant of the order of 10^3 sec^{-1} . Moreover the disappearance of the



delayed fluorescence component with increasing solute concentration remained unexplained.

Some 16 years later Dikun² reported a delayed fluorescence component of similar duration exhibited by the vapours of several aromatic molecules including phenanthrene and carbazole, and concluded that, since the spectra of delayed and normal fluorescence

components are identical, the former is due to the population of an unspecified metastable state which is thermally promoted to the fluorescent state. This work was confirmed and extended by Williams³ who observed delayed fluorescence from the vapours of perylene, pyrene, phenanthrene and anthracene and found that although the intensity of the delayed component is of the order of 1% at low pressures, this increases with pressure up to a maximum of 47% of the total emission intensity in the case of phenanthrene. Since the temperature coefficient for delayed fluorescence intensity was found to be very much lower than that expected for a thermal repopulation of the fluorescent from the triplet state, and since the ratio of delayed to normal component intensities increased with pressure, Williams concluded that the metastable state responsible is unlikely to be the molecular triplet state, and suggested as Kautsky had done, that an excited dimeric species is responsible, i.e. processes 1-3 are operative.

Williams further suggested that a theoretical treatment of the electronic states of the excited dimer might show why process 4 is forbidden; Hoiijtink⁴ subsequently demonstrated that if the dimer has a parallel sandwich-like structure, the wave function for its stable form will be the antisymmetric combination of the product functions of the individual molecules ψ'_i and ψ_i in excited singlet and ground states respectively i.e.

$$\psi_{-}(\text{dimer}) = \frac{1}{\sqrt{2}} (\psi'_1 \psi_2 - \psi_1 \psi'_2)$$

from which radiative transition to the ground state is symmetry-forbidden. However, any deviation from strict coplanarity of the aromatic molecules,

such as might attend interplanar vibrations, would remove the symmetry restriction and emission should be observed.

Such an emission had already been reported by Forster and Kasper⁵ as a broad structureless band some 5000 cm^{-1} to the red of the normal structured fluorescence of pyrene in concentrated solutions. Since they could find no absorptiometric or cryoscopic evidence for molecular association in the ground state, these authors concluded that this new fluorescence band is due to process 4 which follows the photoassociation process 1. This was confirmed by the observation that the concentration at which the dimer band intensity equalled that of the monomer fluorescence increased with increasing viscosity of the solvent at room temperature; moreover Birks and Christophorou⁶, using the low intensity nano-second flash technique have been able to follow the "rise-time" for dimer emission and relate this to the decay constant for the monomer fluorescence measured directly under identical conditions.

If the excited dimeric species responsible for delayed fluorescence in the gas phase and in solution is that which gives rise to a new emission band in concentrated solutions of pyrene, it might be expected that the latter should have a lifetime in the millisecond region. Stevens and Hutton⁷ reported that a component with a lifetime of $1.8 \pm 0.2 \times 10^{-3}$ seconds for 2×10^{-3} molar pyrene in degassed cyclohexane at 20°C , showed that its spectrum is identical with that of dimer fluorescence, and suggested the name 'excimer' be used to distinguish the excited dimeric species formed

in process 1 from that produced by direct light absorption from stable unexcited dimers in concentrated solutions of dyes in solvents of high dielectric constant. Following the failure of Parker and Hatchard⁸ to detect the millisecond component of emission from concentrated solutions of pyrene, Stevens and Hutton⁹, on re-investigating, found that it constituted approximately 1% of the total dimer band intensity.

Meanwhile Stevens, Hutton and Porter¹⁰ observed that the delayed fluorescence spectrum from phenanthrene vapour is identical with the normal fluorescence spectrum of anthracene vapour excited under the same conditions; since absorption measurements placed an upper limit of 10^{-8} moles/lit. on the anthracene concentration in their vapour sample these authors concluded that this could only be sensitised by a metastable state of phenanthrene with an energy at least equal to that of the fluorescent state of anthracene and a lifetime in excess of 10^{-3} seconds, i.e. the phenanthrene excimer. On the grounds that the delayed fluorescence of naphthacene vapour cannot be excited directly but can be sensitised by pyrene vapour Hutton and Stevens¹¹ suggested that in this case also the pyrene excimer is the sensitising species.

In connection with their observation that fluorescence self-quenching in anthracene vapour has a negative temperature coefficient, Hardtl and Scharmann¹² independently suggested that self-quenching proceeds via photoassociation (process 1) followed by internal conversion of the excimer, process 5,



which in this case could lead to the formation of the locally-bonded dimer, dianthracene. If the competing process 2 requires a greater activation energy than process 5, then an increase in temperature will promote excimer dissociation in preference to self-quenching. Stevens and McCartin¹³ confirmed the negative temperature coefficient for self-quenching in this system and showed that, if process 2 is responsible for delayed fluorescence the pressure independence of the self-quenching constant (measured at high pressures) is not inconsistent with the pressure dependence of delayed fluorescence lifetime ($-1/k_2$) observed for low pressures by Williams³, if the unimolecular process 2 follows a Lindemann mechanism, i.e. it is second-order at low pressures and becomes first-order as the pressure approaches the self-quenching region. On the basis of this mechanism, and the assumption that process 1 occurs with unit gas-kinetic collisional efficiency, these authors obtained a difference in activation energies for processes 2 and 5 of

$$E_2 - E_5 \cong 8.0 \text{ kcal/mole}$$

from their own and Hardtl and Scharmann's data.

A review of the available evidence for photodissociation (process 1) based on the criteria of excimer emission, delayed fluorescence, fluorescence self-quenching and sensitised delayed fluorescence, led Stevens¹⁴ to suggest that this is of general occurrence for planar aromatic molecules in fluid media; the absence of self-quenching, excimer emission and delayed fluorescence from such a non-planar molecule as 9,10 - diphenylanthracene being attributed to steric hindrance of photoassociation.

Subsequently excimer emission has been reported for a considerable number of planar aromatic systems including benzene¹⁵, toluene¹⁵ (but, presumably due to steric hindrance, not xylene¹⁵) naphthalene¹⁷, acenaphthene¹⁶, methyl derivatives of 1,2-benzanthracene⁶, 2,5-diphenyloxazole¹⁸, cholanthrene⁶ and 1,2-benzperylene⁶.

Although a qualitative picture of the effects of photoassociation is beginning to emerge, some inconsistencies are evident of which the following demand further attention:-

- a) although there is now no doubt that photoassociation is operative in a number of fluid (and presumably crystalline²⁹) aromatic systems as evidenced by excimer fluorescence, if excimer dissociation is responsible for delayed fluorescence with a decay constant of some 10^3 sec^{-1} , excimer emission in the same or similar systems should have a decay constant of the same order of magnitude; the emission however is very much faster than this (e.g. for perylene 99% of the dimer emission in solution has a lifetime of $< 10^{-7} \text{ sec.}$) and indeed, is observed in aerated solutions^{5,6}
- b) the pyrene excimer fluorescence band has both slow ($\sim 10^{-3} \text{ sec.}$) and fast ($\sim 10^{-7} \text{ sec.}$) components;^{7,9}
- c) excimer emission has not yet been observed in the vapour phase at temperatures in the range of 2-300°C; under these conditions asymmetric interplanar vibrations might be expected to remove the symmetry restriction on radiative relaxation.
- d) if excimer dissociation is responsible for delayed fluorescence it is difficult to reconcile the low rate constant ($\sim 10^3 \text{ sec}^{-1}$)

for this process with the low dissociation energy (~ 8.0 kcal/mole) in the case of anthracene.

The researches described below were carried out with a view to elucidating the mechanism of delayed fluorescence in aromatic vapours, and to obtaining additional examples of compounds exhibiting photoassociation in solution.

Experimental

The principal parameters characterising delayed fluorescence in the vapour phase are

- a) the associated lifetime τ_D or decay constant k_D which are of the order of 10^{-3} sec. and 10^3 sec.⁻¹ respectively.
- b) the ratio of intensities of delayed to normal fluorescence components I_D / I_F .

a) Lifetime measurement

A Becquerel phosphoroscope was used to isolate the millisecond fluorescence component from the normal fast fluorescence of the sample; a plan of the optical arrangement is shown in Figure 1. Light from a d.c. high pressure mercury arc (described below) is focussed by lens L_1 onto one wheel A of the phosphoroscope; when one of the two slots in this wheel coincides with the optical axis, the light beam, after further focussing by lens L_2 , falls on the fluorescent sample in the cylindrical cell M contained in the furnace U. The fluorescence radiation is focussed by lens L_3 onto a photomultiplier tube P (Mazda 27M3) placed directly behind the second wheel B of the phosphoroscope which has two identical slots arranged out of phase with those in wheel A. Thus when the wheels of the

phosphoroscope are rotated by the electric motor E, fluorescence is excited in the sample when wheel A is 'transparent' (at which time B is opaque) whilst the delayed fluorescence is detected only when wheel B is transparent (at which time A is opaque); the phosphoroscope acts as a time filter since the fast fluorescence ($\tau \gg 10^{-6}$ sec.) has completely decayed between the excitation cut-off by wheel A and the onset of detection through wheel B.

The interval τ_p between excitation cut-off and the beginning of detection is determined by the angular velocity of the wheels and the angle γ between the rear edge of the slot in A and the leading edge of that in B. Thus at its maximum speed of 3000 revolutions per minute τ_p is given by

$$\tau_p = \frac{60}{3000} \times \frac{\gamma}{360} = 5.5 \times 10^{-5} \gamma \text{ seconds}$$

if γ is expressed in degrees of arc. The introduction of slits T_1 and T_2 enabled γ to be reduced to some 2° without introducing effects due to stray light, thus

$$\tau_p \approx 10^{-4} \text{ seconds.}$$

i.e. a luminescence of half-life 10^{-3} seconds would be reduced in intensity by only

$$100 \left\{ 1 - e^{-(10^{-4}/10^{-3})} \right\} \% = 9.5\%$$

before the onset of detection. The voltage supply to the motor was regulated by a Variac (Duratrak, Type V.S.H.M.T.) so that its speed could be varied between 10 and 3000 r.p.m. to obtain maximum intensity of the delayed component; if required, the

the angular velocity of the phosphoroscope could be measured by counting the number of deflections produced by the detector signal on a low speed time-base of the oscilloscope (see below).

Since it was essential that the source should remain at constant intensity for periods of 10^{-6} - 20 seconds, a Mazda 125 watt high pressure stabilised arc (type MBL/D.) was used in conjunction with a bank of twenty 12 volt, 75 ampere-hour accumulators assembled so as to be charged in 10 units of 24 volts and discharged in series to provide 240 volts d.c.

Figure 2 shows the detector circuit. The Mazda 27M3 photomultiplier (with maximum sensitivity in the region 360-500 m μ) was powered by an Ediswan power unit type R1184. The anode was earthed through a 500 K ohm $\frac{1}{2}$ watt resistor, and the potential across this led to the grid of the 6J5 triode in the cathode follower circuit. By feeding the cathode follower signal to the Y plates of the Solartron double beam oscilloscope (CD 71152) through the 16 μ farad condenser it was possible to reduce the time constant of the circuit to a value much lower than the duration of the measured pulse. All leads were screened and the screening carefully earthed to eliminate electrical interference. The oscilloscope was internally triggered by the emission signal to produce repeated traces of the decay curves on the screen and these were photographed on Kodak R60 35 mm. film by means of an attached Cossor oscillograph Camera (model 1428). Times bases in the region 0.2 - 2.0 m sec./c. were used and calibrated by displaying semisoidal waves of accurately predetermined frequency from an Advance signal generator (type J2).

The fluorescent vapour samples were produced in cylindrical Pyrex cells some 5cm. x 2cm. diameter fitted with a narrow lower limb containing the solid or liquid sample, as shown in Figure 3. The same figure shows a plan and elevation of the furnace constructed from two concentrically-bored cylindrical blocks of aluminium wired independently, thermally insulated from each other and equipped with recesses for thermocouples; the upper block equipped with quartz-shielded windows W controls the temperature of the vapour whilst the lower one accommodates the cell limb containing the condensed sample and so controls the vapour pressure.

To eliminate extraneous light, the source, cell, phosphoroscope and detector were housed in a specially-constructed wooden box with an inspection cover, with the controls, power supplies and oscilloscope outside. The apparatus was calibrated by measuring the lifetime of uranyl sulphate luminescence for which a value of 2.54×10^{-4} seconds has been reported; our measured value from an exponential plot of the enlarged photograph of the decay curve was 2.53×10^{-4} seconds from which we conclude that the response time of the apparatus is well below the limit required. Figure 4 shows a typical oscilloscope trace of the delayed fluorescence decay for anthracene vapour.

b) Intensity measurements

To investigate the variation in intensity of delayed fluorescence with incident light intensity, the decay curves produced by a particular vapour sample were photographed under the

same conditions of temperature, pressure, phosphoroscope speed and oscilloscope sensitivity but with Wratten neutral density filters of different optical density between the light source and cell. The height of the decay curve above the base line after a particular decay interval was taken as a measure of the delayed fluorescence intensity since under these conditions the decay constant was found to be independent of the incident light intensity. For these measurements 9 mm of Chance OX1 filter was used to isolate the H α lines at 365 m μ and the optical densities/the neutral density filters at this wavelength were measured on a Unicam SP 700 recording spectrophotometer.

To measure the ratio of intensities I_D/I_F of delayed to fast components of fluorescence the phosphorimeter was modified as shown in Figure 5. The light beam from the same source S is focussed first onto wheel A of the oscilloscope and then onto the vapour sample in the cell M. Fluorescence from the sample is then focussed directly onto the photomultiplier P along an axis at right angles to the excitation beam, F₂ being a filter ($1/8$ M aqueous NaNO₂) to remove scattering exciting radiation, selected by the Chance OX1 filter F but which transmits the fluorescence radiation. The signal generated by the photomultiplier was displayed on the screen of the oscilloscope as previously described.

Under these conditions the fluorescent vapour is subjected to two square pulses of incident light, each of a few milliseconds duration for each rotation of the wheel A. The

fluorescence intensity I_t of the exposed vapour thus increases with time t to a maximum value I_∞ during each pulse according to the equation

$$I_t = I_\infty (1 - e^{-t/\tau})$$

where τ is the fluorescence lifetime. Similarly, after excitation cut-off, the intensity of fluorescence decays according to

$$I_t = I_\infty e^{-t/\tau}$$

so that the square-wave excitation pulse is distorted in the emission signal. This is illustrated in Figure 6 for crystalline uranyl sulphate luminescence the lifetime τ of which was used to check the instrumental response. Vapours exhibiting both fast and slow components of fluorescence distort the square-wave pulse as follows:- the fast component reaches its maximum intensity almost instantaneously and is followed by a much slower increase in the delayed fluorescence component; after excitation cut-off the fast component decays immediately to be followed by a much slower decay of the slow component. Provided the pulse is of sufficient duration ($\sim 4\tau_D$) to allow the slow component to attain its maximum intensity, the ratio of intensities is given by

$$\frac{I_F}{I_F + I_D} = \frac{\text{initial pulse height}}{\text{final pulse height}}$$

whence I_D/I_F can be obtained. In the cases examined I_D/I_F was less than 1% and the following procedure was adopted to measure this with sufficient accuracy:- the emission signal was displayed

on the oscilloscope screen with the Y-plate sensitivity set at 0.1 volts/cm, corresponding to a deflection of several screen diameters, and the horizontal shift adjusted to display the decay of the slow component which was photographed; the Y-plate sensitivity was then reduced to three volts/cm. and the total signal completely displayed on the screen was photographed. Sample traces are shown in Figure 7. The ratio I_D/I_F was obtained from these signal heights by multiplying the total signal by a factor of 30.

c) The Measurement of Fast Fluorescence Lifetimes

During an analysis of the delayed fluorescence data for aromatic hydrocarbon vapours it became necessary to have values for the lifetime of the normal (fast) fluorescence of the same compounds under the same conditions. In the case of perylene vapour, the fluorescence lifetime was estimated from oxygen-quenching measurements using an apparatus described previously¹⁹. The perylene vapour contained in a quartz cell at a pressure determined by the temperature of solid perylene in a lower limit and a temperature equal to that of the furnace housing the cell, was excited by the group of Hg lines λ 365 m μ isolated from a 125 watt high pressure stabilised arc by means of a Hilger quartz prism monochromator. The intensity of fluorescence was measured at right angles to the incident beam, relative to the intensity of the incident beam partially reflected from a quartz plate onto a second photomultiplier; in this way changes due to source fluctuation are minimised. A Hoke packless valve operated at the

cell temperature isolated the cell from a conventional vacuum line and allowed oxygen to be admitted at known pressures; the effect of added oxygen on light absorption by the vapour being measured by a third photomultiplier which intercepted the excitation beam after passage through the cell. The maximum temperature at which the Hoke valve could be operated placed an upper limit on the temperature of the vapour of 244°C .

d) Excimer Fluorescence

As a part of this programme it was decided to continue the search for aromatic compounds which exhibit excimer fluorescence in solution. The instrument used was an Aminco-Keirs spectrophotophosphorimeter adapted for use as a low temperature fluorimeter by removing the rotating cylinder but retaining the dewar holder and assembly. Fluorescence spectra were recorded

- (i) as a function of concentration in toluene at room temperature
- (ii) at room temperature and at -70°C (ethanol-solid Co_2 mixtures) at the maximum concentration consistent with complete dissolution at the lower temperature.

In this preliminary survey no attempt was made to degas the solutions which were examined in the special quartz tubes provided with this instrument for use in conjunction with the dewar vessel. Blank runs were made on the pure solvent in the ethanol-cardice mixture to ensure that observed spectral changes were due to the solute only.

e) Materials

Aromatic hydrocarbons from commercial sources were purified by fractional recrystallisation followed by fractional microsublimation²⁰ in each case. B.D.H. spectroquality solvents were used without further purification and oxygen was taken from a bulb supplied by the British Oxygen Company sealed directly onto the vacuum line.

Results

a) Lifetimes of Delayed Fluorescence in the Vapours of Aromatic Hydrocarbons.

Figures 8 and 9 show the concentration dependence of delayed fluorescence decay constant K_D ($= 1/\tau_D$) for the vapours of perylene and of pyrene under the conditions stated. The decay was found to be strictly exponential over the whole pressure ranges studied and the data obtained in the pressure-independent region (at lower concentrations) are in agreement with previous measurements²¹; however, at higher pressures K_D increases with pressure, an effect not previously noted.

b) The Effect of Absorbed Light Intensity on the Intensity of Delayed Fluorescence

If $I_0(\lambda)$ is the intensity of radiation absorbed by the vapour in the cell is

$$I_A(\lambda) = I_0(\lambda) (1 - 10^{-D(\lambda)})$$

where $D(\lambda)$ is the optical density of the vapour at this wavelength. If now a neutral density filter of optical density

$d(\lambda)$ is placed between the light source and cell the incident light intensity is reduced to

$$I_o(\lambda) 10^{-d(\lambda)}$$

and the vapour absorbs an amount

$$I_A(\lambda) = I_o(\lambda) 10^{-d(\lambda)} (1 - 10^{-D(\lambda)}).$$

The intensity of I_D of delayed fluorescence varies as the n th power of $I_A(\lambda)$ i.e.

$$I_D \propto \left[I_o(\lambda) 10^{-d(\lambda)} (1 - 10^{-D(\lambda)}) \right]^n$$

so that provided $I_o(\lambda)$ and $D(\lambda)$ remain constant

$$\log I_D = \text{constant} - nd(\lambda)$$

Figures 10 and 11, in which $\log I_D$ is plotted against $d(\lambda)$ for the vapours of perylene and pyrene under the conditions stated show that $\log I_D$ varies linearly with $d(\lambda)$ and from the slope of the line

$$n = 1.9 \pm 0.1$$

i.e. within the limits of experimental error the intensity of delayed fluorescence varies as the square of the absorbed light intensity.

Figure 12 shows the variation of I_D/I_F with concentration for perylene vapour under the conditions stated.

c) The Oxygen-quenching of Perylene Vapour (Fast) Fluorescence.

The addition of quenching species at concentration Q reduces the yield of a fluorescent compound in the gas phase or in solution from γ_o to γ which are related to the quenching constant K_Q by the Stern-Volmer equation:-

$$\gamma_o/\gamma = 1 + K_Q [Q]$$

Thus if F_0 and I_0 are the measured fluorescence intensity (in arbitrary units) and absorbed light intensity due to perylene in the absence of added oxygen, and F and I are the corresponding quantities in the presence of oxygen at concentration $[O_2]$ this relationship becomes

$$\frac{F_0/I_0}{F/I} = 1 + K_{O_2} [O_2]$$

For perylene vapour at 244°C and 0.2 mm Hg pressure excited by the Hg lines at 365μ , the oxygen quenching data are plotted according to the Stern-Volmer equation in Figure 13; from the slope of the line and the relationship

$$K_{O_2} = p Z \tau$$

where p is the collisional quenching probability (assumed to be unity) and Z is the collision frequency at unit concentration, it is found that the lifetime of the potentially fluorescent perylene molecule is given by

$$\tau = 0.56 \times 10^{-9} \text{ sec.}$$

under the conditions stated (values of 5.0 \AA and 1.7 \AA are taken for the collision radii of perylene and oxygen respectively).

d) Fluorescence Spectra

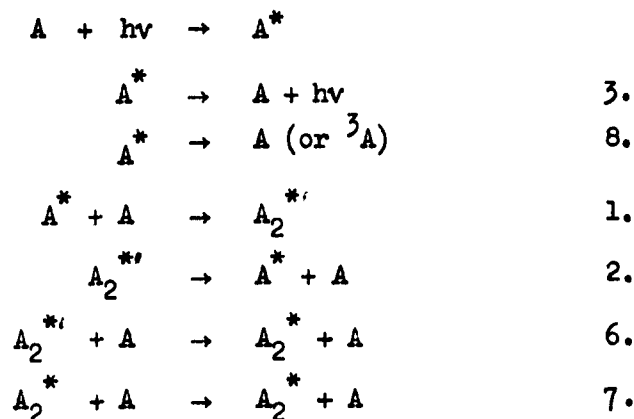
During a search for new compounds exhibiting excimer fluorescence evidence was obtained for this behaviour in the case of acenaphthere. No concentration dependence of the emission spectrum could be detected at room temperature but on cooling a moderately dilute (10^{-3}M) solution in toluene to -40°C the excimer band was observed. Figure 14 shows the recorded fluorescence spectra of this solution at -40°C and at

room temperature.

Discussion

a) The Excimer Dissociation Mechanism of Delayed Fluorescence

The mechanism of delayed fluorescence proposed by Williams³ for delayed fluorescence in the vapour phase is summarised by the following processes:-



Stevens and McCartin¹³ introduced the additional process



to accommodate overall self-quenching of fluorescence of the monomer. Here again the asterisk denotes an electronically excited species and the superscript indicates sufficient vibrational energy for excimer dissociation. Under the non-photostationary conditions following excitation cut-off the rate of excimer disappearance is given by

$$- \frac{d \left([A_2^{*'}] + [A_2^*] \right)}{dt} = k_2 [A_2^{*'}] + k_5 [A_2^*]$$

$$\text{or } k_D = - \frac{d \ln ([A_2^{*'}] + [A_2^*])}{dt} = \frac{k_2 [A_2^{*'}] + k_5 [A_2^*]}{[A_2^{*'}] + [A_2^*]} \quad 22.$$

where k_D is the rate constant for delayed fluorescence i.e.

$$k_D = 1/\tau_D$$

and since the decay is exponential

$$\frac{dk_D}{dt} = 0$$

Thus

$$- \frac{d [A_2^{*'}]}{dt} = - \frac{d [A_2^*]}{dt}$$

or

$$\frac{[A_2^{*'}]}{[A_2^*]} = \frac{k_5 + 2k_7 [A]}{k_2 + 2k_6 [A]}$$

and

$$\begin{aligned} k_D &= k_2 \left\{ \frac{1 - [A_2^*]}{[A_2^{*'}] + [A_2^*]} \right\} + \frac{k_5 [A_2^*]}{[A_2^{*'}] + [A_2^*]} \\ &= k_2 + \frac{(k_5 - k_2) [A_2^*]}{[A_2^{*'}] + [A_2^*]} \\ &= k_2 + \frac{(k_5 - k_2) (k_2 + 2k_6 [A])}{k_2 + k_5 + 2k_6 [A] + 2k_7 [A]} \end{aligned}$$

I

where k_n is the rate constant of process n and the square brackets denote concentration of the enclosed species.

At high pressures I reduces to

$$k_D^{\infty} \approx \frac{k_2 k_7 + k_5 k_6}{k_6 + k_7} \quad \text{II}$$

and becomes

$$k_D^0 \approx \frac{2k_2 k_5}{k_2 + k_5} \quad \text{III}$$

as the pressure approaches zero. Moreover the initial slope S of the plot of k_D against pressure is given by

$$S = \left\{ \frac{dk_D}{d[A]} \right\}_{[A] \rightarrow 0} = \frac{2k_6 (k_5 - k_2)}{k_2 + k_5} \quad \text{IV}$$

so that S may be negative or positive depending on the relative magnitudes of k_5 and k_2 .

Anthracene

An examination of the concentration-dependence of k_D for anthracene vapour obtained previously²¹ (given by Figure 15) shows that

$$\begin{aligned} k_D^0 &= 8 \times 10^8 \text{ sec}^{-1} \text{ at } 220^\circ\text{C} \\ S &= 1.4 \times 10^7 \text{ lit. mole}^{-1} \text{ sec}^{-1} \text{ at } 220^\circ\text{C} \\ k_D &\geq 3.0 \times 10^3 \text{ sec}^{-1} \text{ at } 220^\circ\text{C} \end{aligned}$$

Since these three experimental parameters are related to four rate constants k_2, k_5, k_6 and k_7 by equations II, III and IV it is necessary to make an assumption concerning one of these if the other three are to be estimated. If we assume that the rate of collisional activation (process 7) of the dissociating species is very much less

than the rate of collisional activation (process 6) i.e.

$$k_7 \ll k_6$$

then from II

$$k_D^{\infty} \approx \frac{k_2 k_7}{k_6} + k_5$$

or since S is positive (whence $k_5 > k_2$)

$$k_D^{\infty} \approx k_5 > 3.9 \times 10^3 \text{ sec}^{-1} \text{ at } 220^\circ\text{C.}$$

If $k_2 \ll k_5$ equation III becomes

$$k_D^0 \approx 2k_2 = 8 \times 10^2 \text{ sec}^{-1} \text{ at } 220^\circ\text{C}$$

i.e. k_2 is an order of magnitude less than k_5 as assumed.

By defining

$$[A_{\frac{1}{2}}] = [A]$$

$$\text{when } k_D - k_D^0 = (k_D^{\infty} - k_D^0)/2 \quad \text{V}$$

we show that

$$k_D - k_2 \left\{ \frac{2 [A_{\frac{1}{2}}] + [A]}{[A_{\frac{1}{2}}] + [A]} \right\} \approx \frac{S [A]}{1 + [A]/[A_{\frac{1}{2}}]} \quad \text{VI}$$

and with $k_2 = 4 \times 10^2 \text{ sec}^{-1}$ plot the L.H.S. of VI against

$[A] / (1 + [A] / [A_{\frac{1}{2}}])$ for various values of $[A_{\frac{1}{2}}]$ to obtain

curves of slope S. It is found that

$$S = 1.4 \times 10^7 \text{ lit.mole}^{-1} \text{ sec}^{-1}$$

in agreement with the experimental value when

$$[A_{\frac{1}{2}}] = 4 \times 10^{-4} \text{ mole. lit}^{-1}$$

At this concentration

$$k_D = 3.5 \times 10^3 \text{ sec}^{-1}$$

whence from V

$$k_D^{\infty} = 6.2 \times 10^3 \text{ sec}^{-1} \text{ at } 220^\circ\text{C}$$

Finally from IV and the approximate values for k_2 and k_5 we obtain

$$k_6 \simeq 8 \times 10^6 \text{ lit. mole}^{-1} \text{ sec}^{-1} \text{ at } 220^\circ\text{C.}$$

The curve through the experimental points in Figure 15 is drawn according to I with

$$\begin{aligned} k_2 &= 4 \times 10^2 \text{ sec}^{-1} \\ k_5 &= 6.2 \times 10^3 \text{ sec}^{-1} \\ k_6 &= 8 \times 10^6 \text{ lit. mole}^{-1} \text{ sec}^{-1} \\ k_7 &= 0. \end{aligned}$$

Perylene and Pyrene

According to Figures 8 and 9, k_D is independent of vapour pressure for perylene and pyrene except at higher pressures. The absence of fluorescence self-quenching in these vapours¹³ indicates that

$$k_5 \ll k_2$$

in which case

$$k_D \simeq k_2$$

or

$$\begin{aligned} k_2 &\simeq 3.7 \times 10^2 \text{ sec}^{-1} \text{ for pyrene at } 260^\circ\text{C.} \\ &\simeq 1.3 \times 10^3 \text{ sec}^{-1} \text{ for perylene at } 362^\circ\text{C.} \end{aligned}$$

The absence of excimer emission in the vapours of anthracene, perylene and pyrene shows, on the basis of this mechanism that

$$k_4 \ll k_2$$

i.e the radiative lifetime of the excimer must be in the region of

0.1 - 1.0 sec; this is extremely difficult to justify on theoretical grounds unless the excimer is in a triplet state, in which case its formation from singlet excited and ground state molecules (process 1) infringes the requirement of spin conservation.

The Efficiency of Excimer Formation in Perylene Vapour.

In the absence of self-quenching¹³, and under photostationary conditions the photokinetic scheme outlined above leads to the following expressions for the quantum yield γ_D of delayed fluorescence:-

$$\gamma_D = \frac{k_1 [A]}{k_3 + k_8 + k_1 [A]} \times \frac{k_3}{k_3 + k_8 + k_1 [A]}$$

and for the quantum yield γ_F of fast fluorescence

$$\gamma_F = \frac{k_3}{k_3 + k_8 + k_1 [A]}$$

Thus the ratio of intensities of slow to fast fluorescence is given by

$$I_D/I_F = \frac{\gamma_D}{\gamma_F} = \frac{k_1 [A]}{k_3 + k_8 + k_1 [A]}$$

and the limiting slope of the curve obtained by plotting I_D/I_S against $[A]$ is

$$\left\{ \frac{d(I_D/I_S)}{d[A]} \right\}_{[A] \rightarrow 0} = \frac{k_1}{k_3 + k_8} = k_1 \tau$$

where $\tau = 1/(k_3 + k_8)$ is the lifetime of the excited monomer in the same concentration region.

For perylene vapour it is seen from figure 12 that

$$\frac{d(I_D/I_S)}{d[A]} = k_1 \tau = 37.2 \text{ lit. mole}^{-1} \text{ at } 362^\circ\text{C.}$$

τ measured by oxygen-quenching of fluorescence at 244°C has the value of 5.6×10^{-10} sec. which is unlikely to be exceeded at 362°C. The temperature of the O₂-quenching measurements was limited by that at which the Hoke packless valve could be safely operated. Thus with

$$\tau \leq 5.6 \times 10^{-10} \text{ sec.}$$

$$k_1 = \frac{37.2}{\tau} \geq 6.6 \times 10^{10} \text{ lit. mole}^{-1} \text{ sec}^{-1}$$

Under these conditions and using a value of 5.0 \AA for the collision radius of perylene the simple kinetic theory expression provides the value

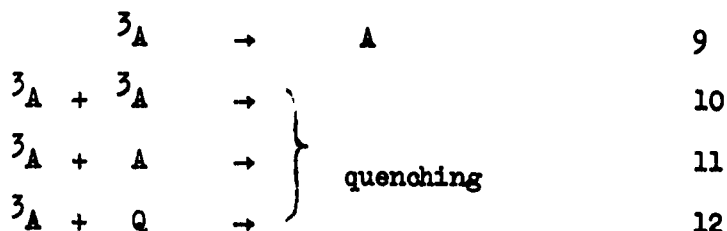
$$Z_1 = 6.2 \times 10^{11} \text{ lit. mole}^{-1} \text{ sec}^{-1}$$

for the collisional rate constant. Thus either

- (i) the lifetime of the excited perylene molecule at low pressures is shorter at 362°C than at 244°C by a factor of 10 and process 1 occurs with unit collision frequency, or
- (ii) τ is independent of temperature (which is unlikely) and one collision in 10 leads to excimer formation.

b) The Triplet-Triplet Annihilation Mechanism of Delayed Fluorescence

In fluid media the radiative relaxation (phosphorescence) of triplet states of aromatic molecules is not usually observed since the competing processes 9,10,11 and 12 are very much faster



and flash absorption experiments^{22,23} have shown that the rate of triplet decay is given by

$$-\frac{d[{}^3A]}{dt} = k_9 [{}^3A] + k_{10} [{}^3A]^2 + k_{11} [{}^3A][A] + k_{12} [{}^3A][Q]$$

where Q is any quenching species present.

For aromatic hydrocarbons it is found that²²

$$k_{11} \ll k_{10}$$

so that in carefully deoxygenated systems and in the absence of added quenchers

$$-\frac{d[{}^3A]}{dt} = k_9 [{}^3A] + k_{10} [{}^3A]^2$$

If $k_{10} [{}^3A] \gg k_9$

the triplet decay is second-order; this condition prevails

- (i) in solution immediately following flash excitation which produces a high instantaneous population of triplet states;
- (ii) in the gas phase following flash excitation²⁴ since the collision frequency is some orders of magnitude faster than the diffusion rate in solution, i.e.

$$k_{10}(\text{vapour}) \gg k_{10}(\text{solution}).$$

The final stage of triplet decay following flash excitation in solution is virtually first-order since the triplet state concentration is reduced to the level.

$$[{}^3A] \ll k_9/k_{10}$$

and values of k_9 can be obtained from the experimental curves in this region.

During the course of the work described in this report, Parker and

Hatchard²⁵ published their findings concerning the delayed fluorescence of phenanthrene and anthracene in solution. To explain their important observation that the intensity of the delayed component varies as the square of the absorbed light intensity, these authors suggested that delayed fluorescence originates in the two quantum process 10 which produces an excited singlet state of the molecule i.e.



Under conditions of low intensity (non-flash) illumination

$$k_{10} [{}^3A] \ll k_9$$

so that the triplet decays essentially by the first-order process 9 and after excitation cut-off its concentration is given by

$$[{}^3A]_t = [{}^3A]_0 e^{-k_9 t}$$

The delayed fluorescence component decays according to

$$\begin{aligned} - \frac{d I_D}{dt} &= k_{11} [{}^3A]^2 \\ &= k_{11} [{}^3A]_0^2 e^{-2k_9 t} \end{aligned}$$

which may be compared with the experimental observation

$$- \frac{d I_D}{dt} = e^{-t/\tau_D} \times \text{constant}$$

$$\text{to give } \tau_D = 1/2k_9 = 1/k_D$$

i.e. the decay constant of delayed fluorescence is exactly twice the first-order decay constant of the triplet state. The evidence presented by Parker and Hatchard supports this statement.

Figures 10 and 11 show that the intensity of delayed fluorescence in the vapour phase also varies as the square of the absorbed light intensity. It thus appears that process 10 is responsible for delayed fluorescence in the vapour phase as in solution; if this is the case then a method is available for measuring the triplet state lifetimes of aromatic hydrocarbons in the vapour phase. Values of these lifetimes ($= 1/k_9$) together with values of τ_D collected from this and previous work are given in Table 1.

Table 1. Delayed Fluorescence (τ_D) and Triplet State ($1/k_9$) lifetimes of Aromatic Hydrocarbons in the Vapour Phase ($\tau_D = 1/2k_9$) $\lambda_{ex} = 365\mu$.

Molecule	T°C	$10^3 [A]$ m./l.	$10^3 \tau_D$ sec.	$10^3/k_9$ sec.
Anthracene	220	0*	1.2	2.4
"	220	2	0.4	0.8
"	220	4	0.3	0.6
"	220	8	0.26	0.5 ₂
"	250	4	0.2 ₇	0.5 ₄
"	300	4	0.2 ₆	0.5 ₂
"	350	4	0.2 ₄	0.4 ₈
Perylene	362	0-1.6	0.77	1.54
Pyrene	260	0-0.8	2.7	5.4
Anthanthrene	362	0.05-0.25	1.2	2.4
1,12-benz-perylene	362	?	0.53	1.06

* extrapolated value

A strict first-order decay of triplet states has not been observed following the flash-excitation of aromatic hydrocarbon vapours since by the time the triplet state concentration has been reduced to satisfy the inequality

$$[{}^3A] \ll \frac{k_9}{k_{10}}$$

it is too small to be detected reliably in absorption. However by analysing the composite first and second-order decay curves obtained in this way for the triplet state of anthracene vapour, West²⁴ estimates that

$$k_9 = 1.08 \pm 0.20 \times 10^3 \text{ sec}^{-1} \text{ at } 160^\circ\text{C}$$

consistent with

$$\tau_D = 0.5 \pm 0.1 \times 10^{-3} \text{ sec.}$$

which is in agreement with the experimental values obtained at 220°C.

c) Excimer Fluorescence in Acenaphthene

Since by definition the ground state of the excimer is dissociated it is not observed in absorption and the only direct evidence for its formation is the appearance of its characteristic structureless fluorescence spectrum to the red of the molecular fluorescence spectrum. Dissociation (process 2) and internal conversion (process 5) compete with excimer emission (process 4) which has a quantum yield γ_D given by

$$1/\gamma_D = \left\{ 1 + \frac{1}{\tau k_1 [A]} \right\} \left\{ 1 + \frac{k_2 + k_5}{k_4} \right\}$$

Thus conditions favouring excimer emission are

- (i) a long lifetime τ of the excited monomer from which

it is formed,

- (ii) a low viscosity solvent in which the diffusion-controlled rate constant k_1 is as large as possible,
- (iii) a high concentration $[A]$ of the aromatic solute,
- (iv) low rate constants k_2 and k_5 for dissociation and internal conversion compared with the rate constant k_4 for emission.

Unfortunately these conditions cannot always be met simultaneously, since the solubility of the hydrocarbon may be low in a low viscosity solvent whilst γ and k_5 are parameter characteristic of the system. However it is possible to reduce the rate of process 2, which requires an activation energy equal to the enthalpy of excimer formation, by lowering the solution temperature although this advantage is to some extent offset by an increase in viscosity and a reduction in solubility; thus Döller and Förster¹⁷ have demonstrated the appearance of the naphthalene excimer band by cooling a solution in toluene to -62°C . According to Figure 14 solutions of acenaphthene in toluene behave similarly.

It is not possible to estimate the enthalpy of excimer formation from the emission spectra of monomer and dimer since, as shown in Figure 16, the position of the latter is determined by the repulsive energy of two ground state molecules at the same interplanar distance, and the absence of structure removes the possibility of assigning a $0'' - 0'$ band. However by measuring the temperature dependence of the rate of monomer to dimer bands in a solvent for

which the temperature coefficient of viscosity is known, it should be possible to estimate the activation energy for dissociation which is equal to the enthalpy of excimer formation. Such measurements are in progress.

3. IMPLICATION OF THE RESULTS FOR POSSIBLE FUTURE WORK

If the dependence of delayed fluorescence intensity on the square of absorbed light intensity reported here for the vapours of perylene and pyrene is indeed due to triplet-triplet annihilation then for the first time a method is available for measuring triplet state lifetimes of aromatic molecules in the vapour phase. Moreover similar measurements in solution can be compared with data obtained by the flash absorption technique under the same conditions.

Flash photometric measurements show^{22,26} that the triplet state lifetimes ($= 1/k_0$) increase with increasing solvent viscosity and approach the radiative (phosphorescent) decay time in rigid media. Moreover the measured lifetime appears to decrease with increasing temperature, an effect which may in part be due to a simultaneous lowering of viscosity. Vapour-phase measurements should provide limiting zero-viscosity values for triplet state lifetimes and enable their temperature-dependence to be investigated without changing the viscosity of the medium; this may contribute to an explanation of the puzzling viscosity dependence of the first-order decay of the triplet state in solution.

A possible future application of process 10, in which the energy of two long-lived excited electronic states is accumulated in one molecule, is the conversion of light of low to higher frequencies if the low frequency radiation can be used to populate the triplet state indirectly by energy transfer²⁷. Such a process has

long been suggested by James Franck²⁸ in connection with the physical aspects of photosynthesis.

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ANNEX

1. Personnel utilised during the reporting period:-
 - a) Principal Investigator, Dr. B. Stevens, from Nov. 1st 1961.
 - b) Dr. Chizuko Tanaka from May 1st, 1962.
 - c) Dr. Miklos I. Ban, from October 1st, 1962.
 - d) Mr. Michael S. Walker, from July 1st, 1962.

2. Unofficial summary of man-hours:-
 - a) Principal Investigator450
 - b) Post-Doctoral.....1400
 - c) Post-Graduate.....800

Expenditure on materials - £150.

No important property acquired during the contract period
at contract expense.

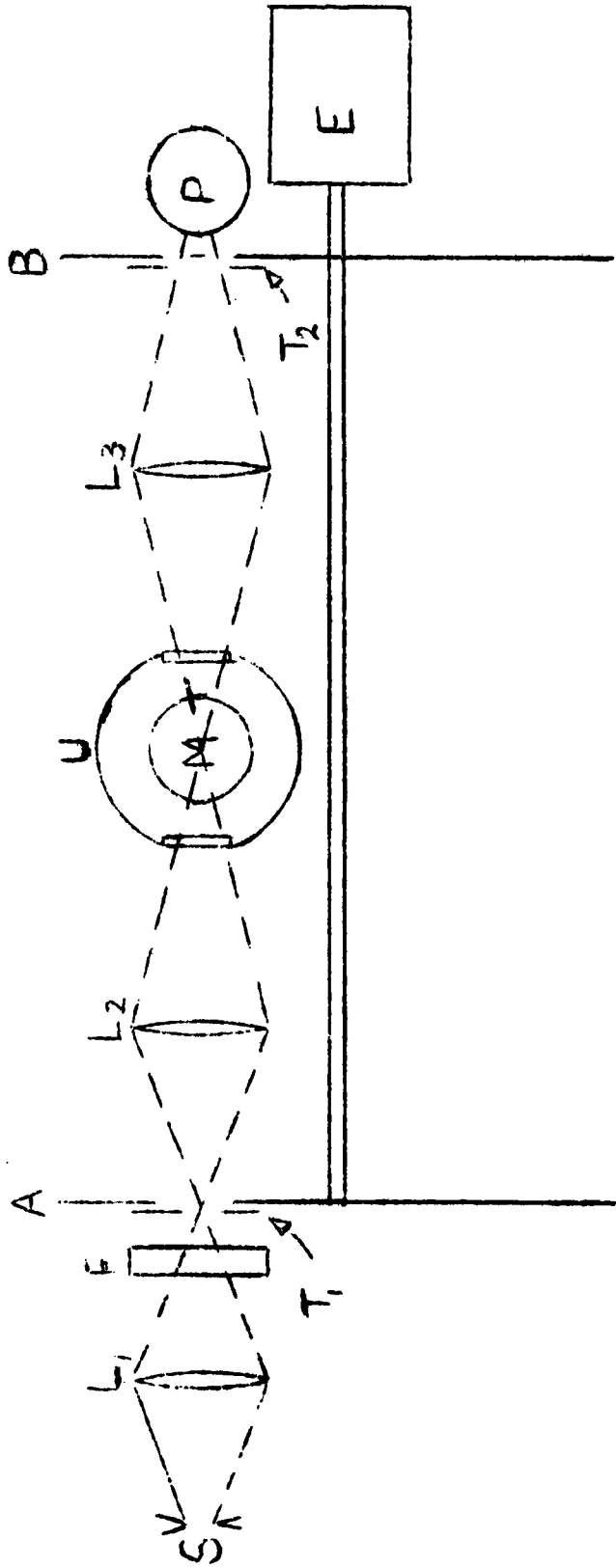


Figure 1. Diagram of apparatus used to measure lifetimes of delayed fluorescence.

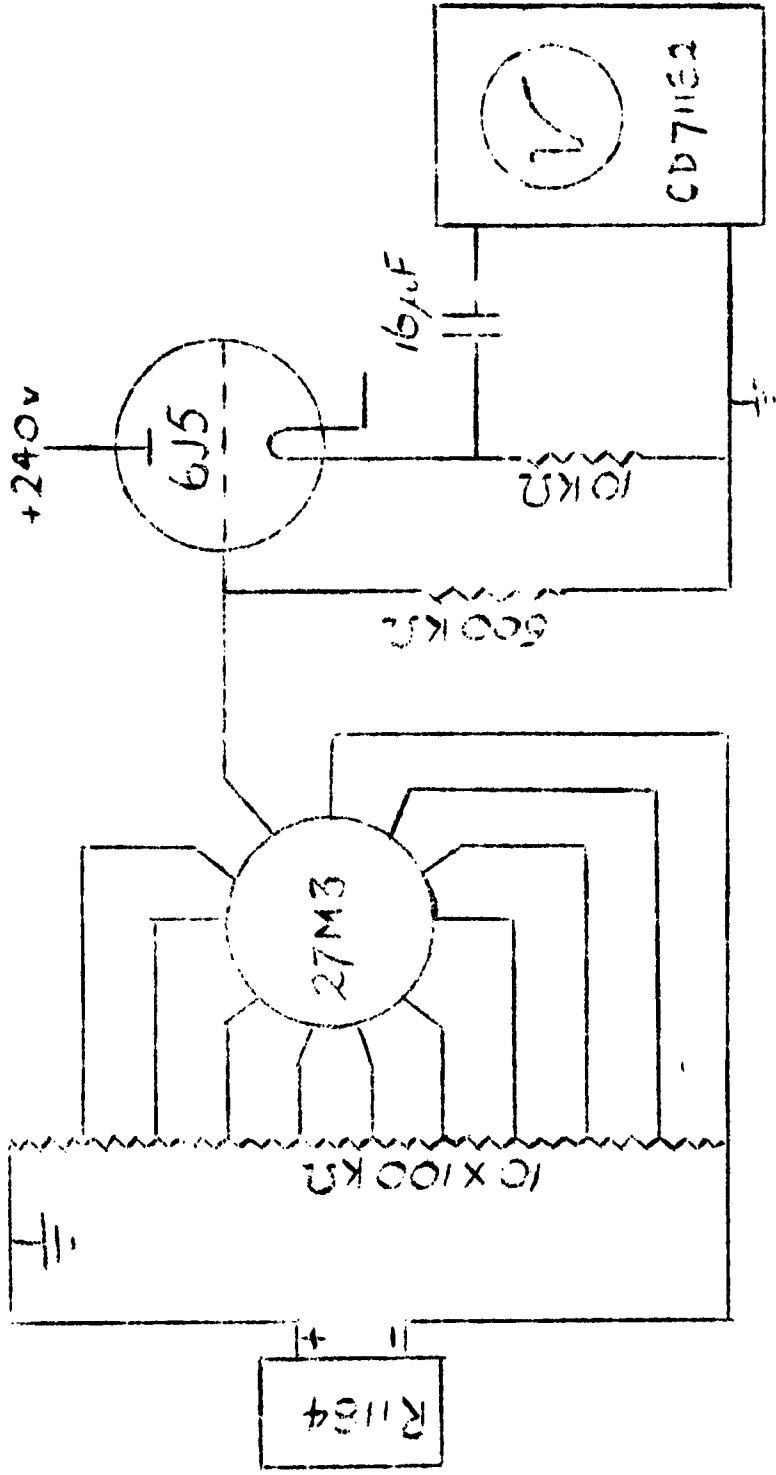


Fig. 2 . . . Detector Circuit

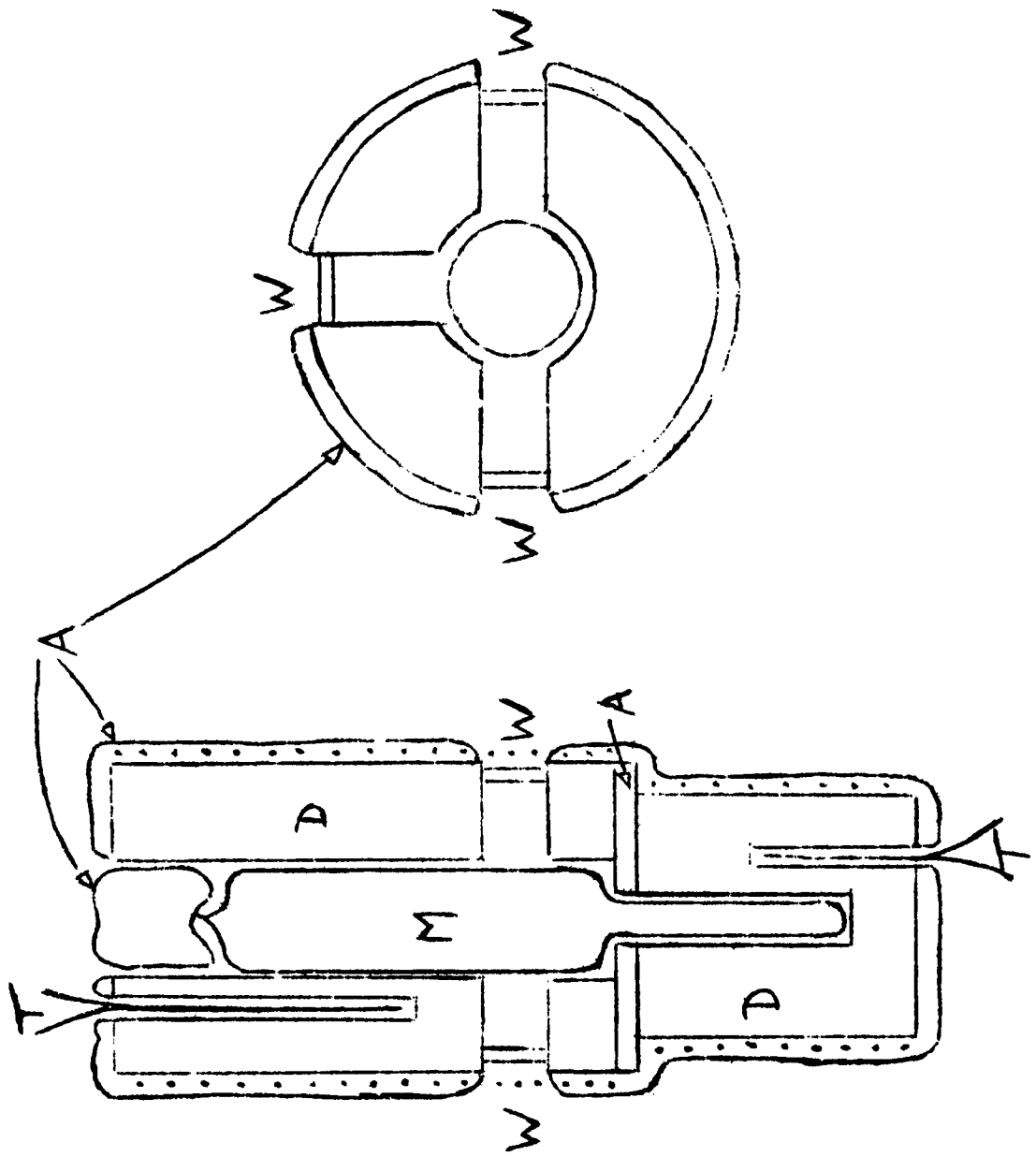


Figure 3. Elevation and plan of fluorescence cell M and furnace
W - windows; A - asbestos lagging; D - aluminium
block; T - thermocouples.

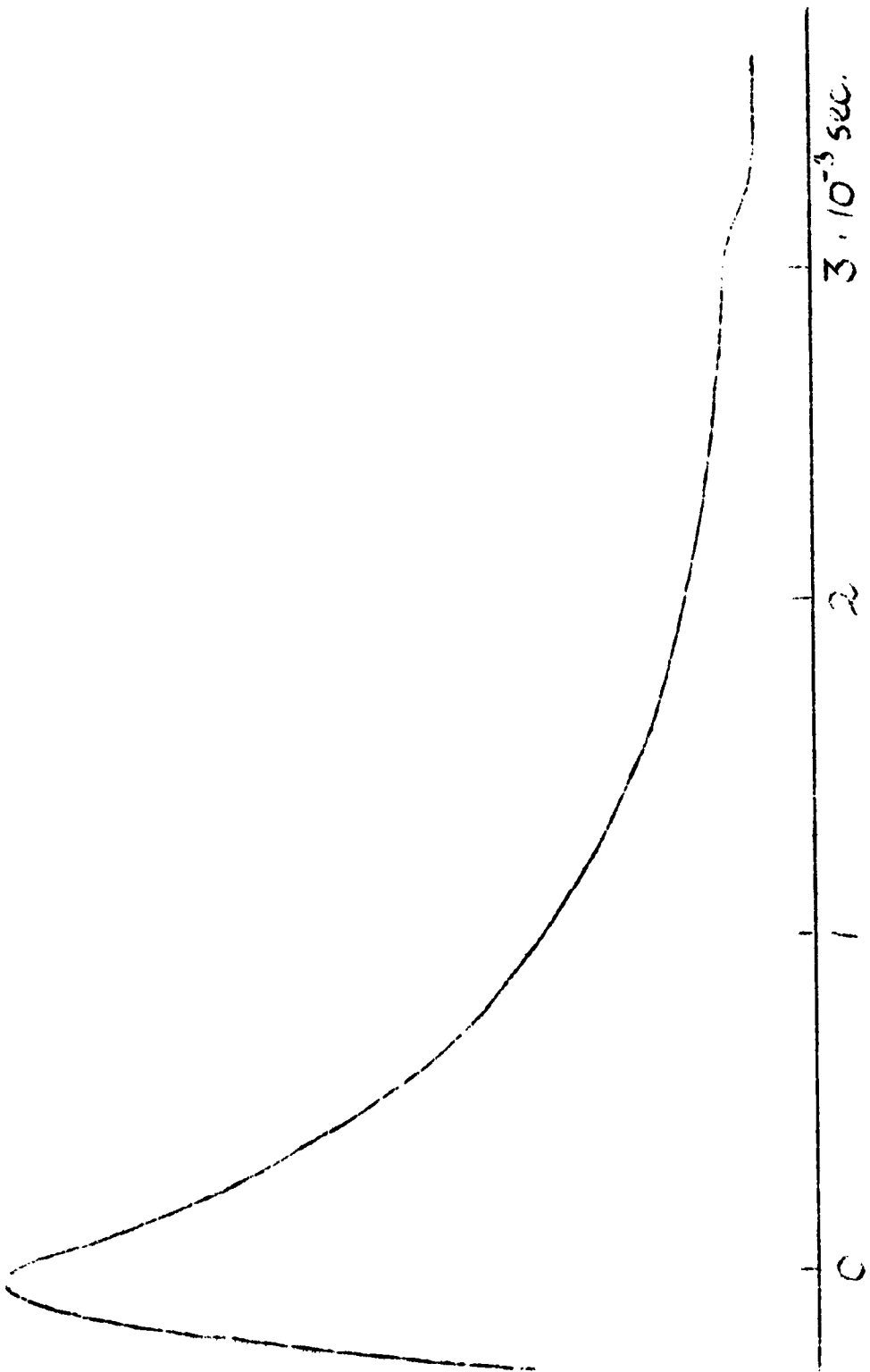


Figure 4. Typical oscilloscope trace of delayed fluorescence decay (from perylene vapour).

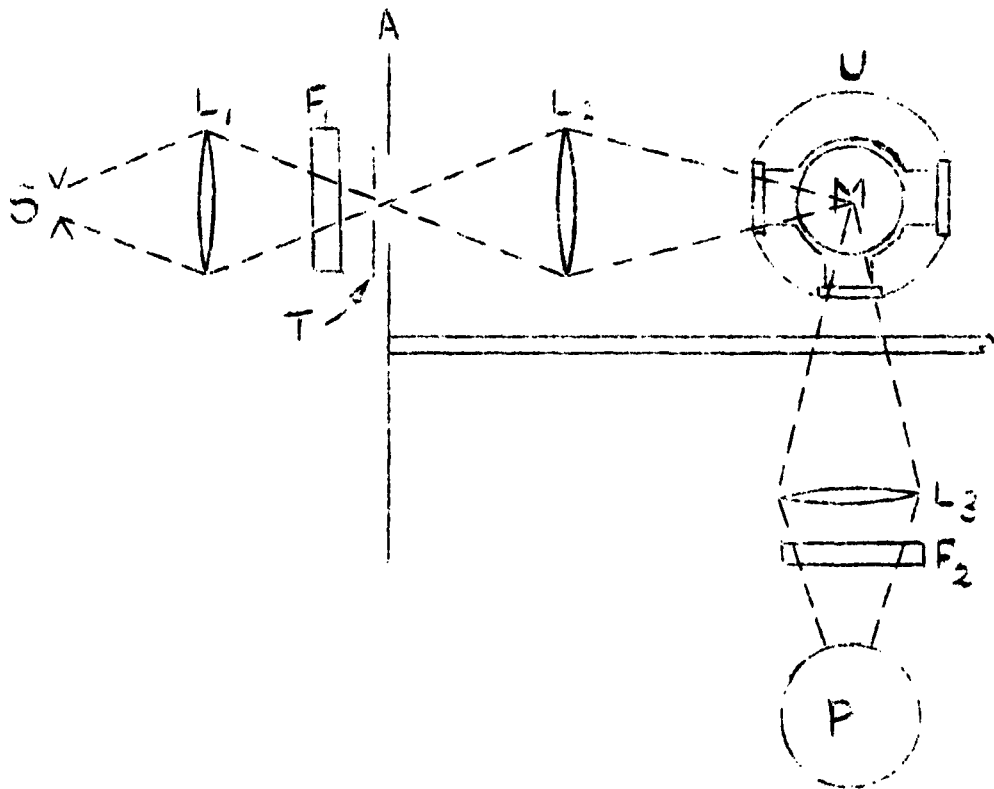


Figure 5. Plan of experimental arrangement used to measure ration I_D/I_F of delayed to fast fluorescence intensities.

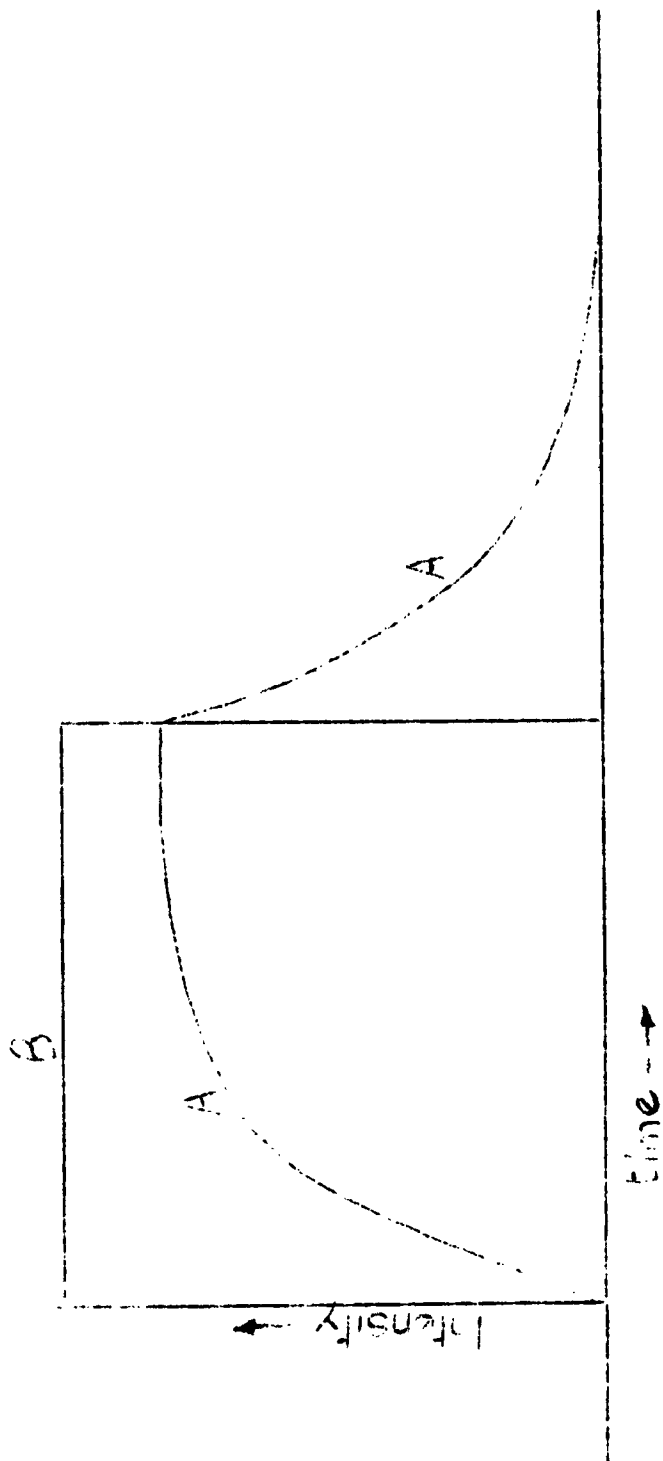


Figure 6. Rise and decay of uranyl sulphate crystal luminescence ($\tau = 2.5 \times 10^{-4}$ sec.) A excited by light pulse B of 1 m sec. duration.

Figure 7. Oscilloscope traces of distorted square-wave fluorescence pulse
A-decay of Delayed Fluorescence with Y sensitivity = 0.1 volts/cm.
B-Total Delayed Fluorescence with Y sensitivity = 3 volts/cm.

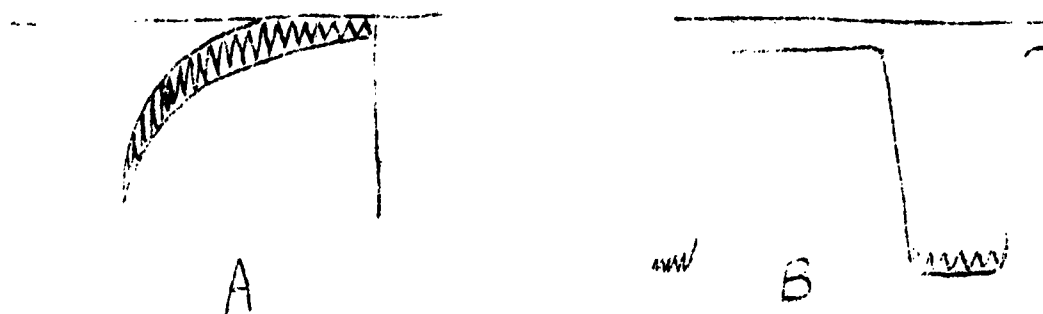
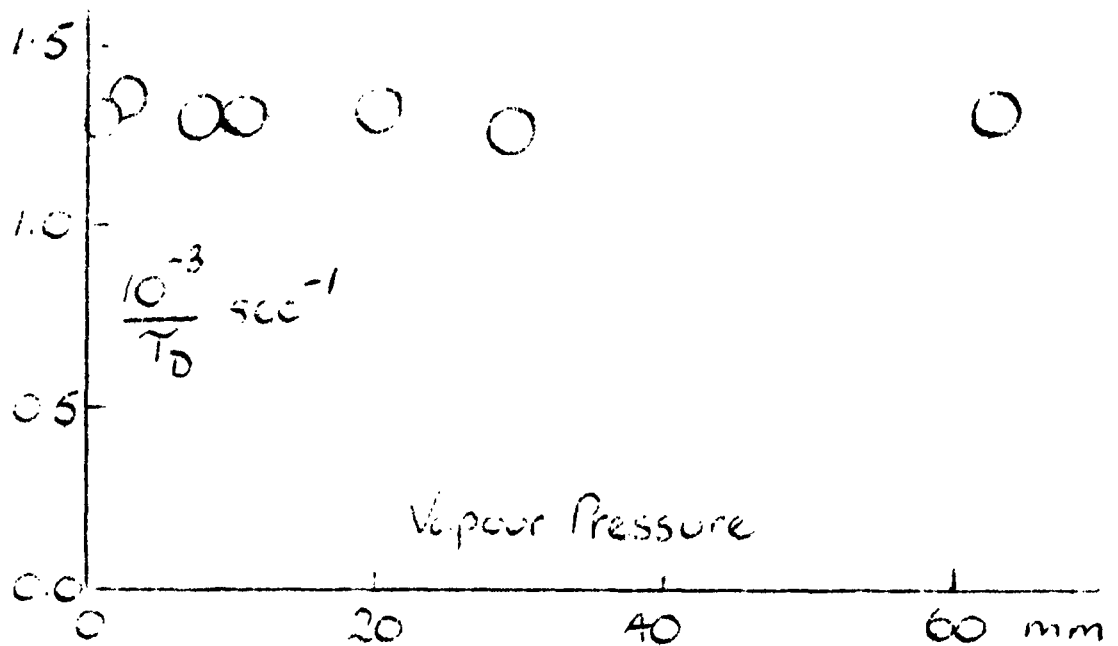


Figure 8. $1/\tau_D$ for perylene vapour
as a function of pressure
at 362°C.



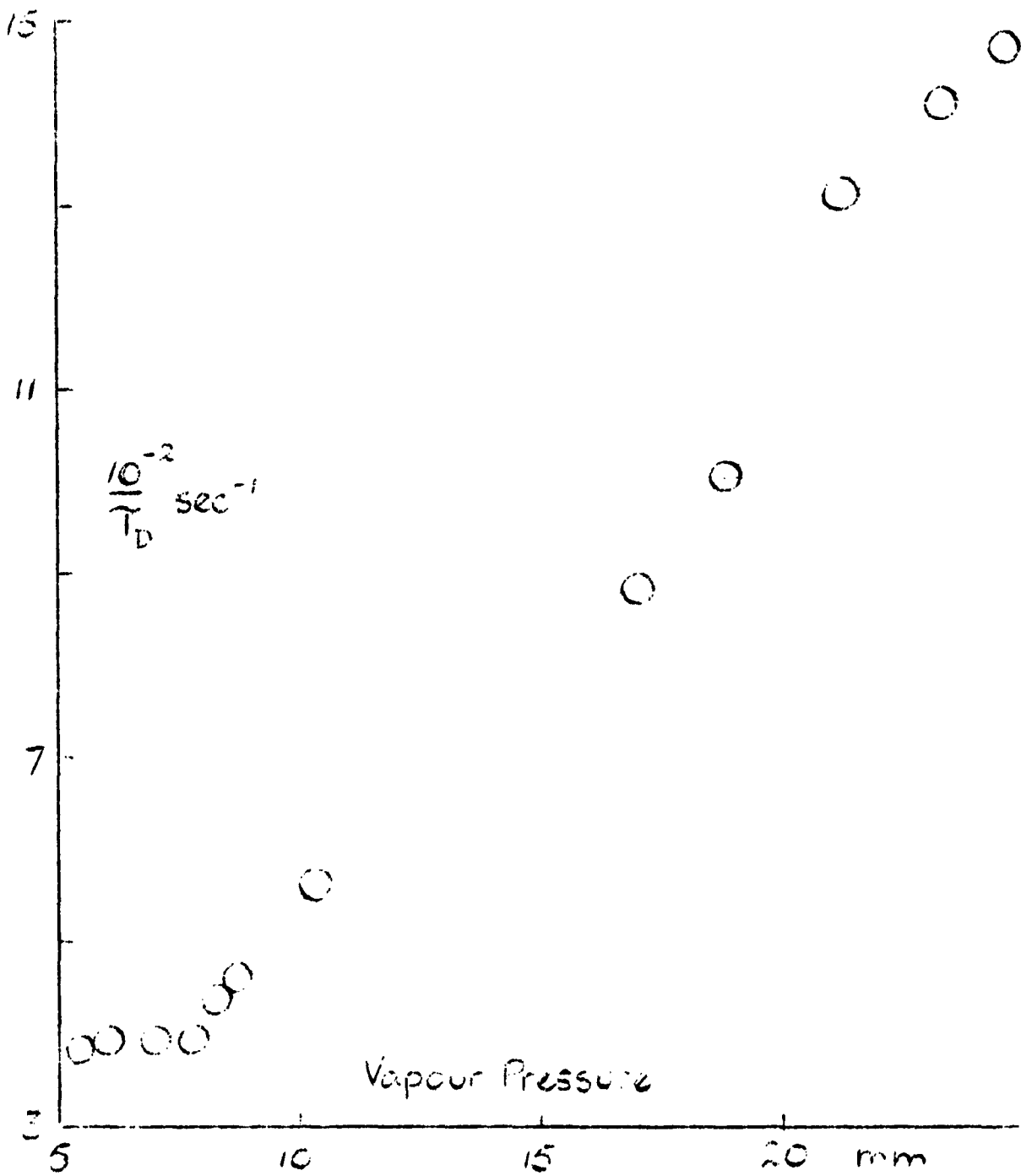
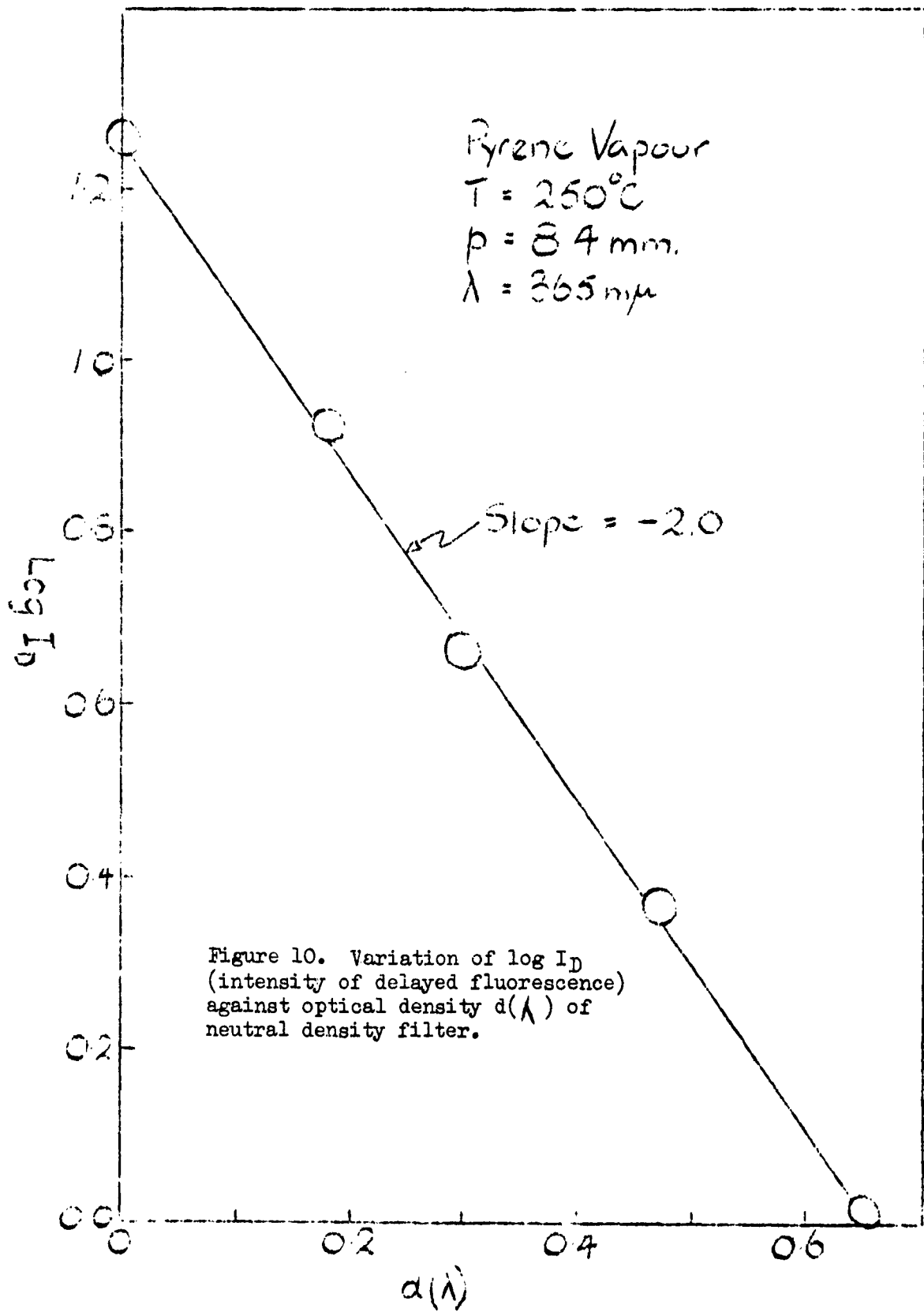
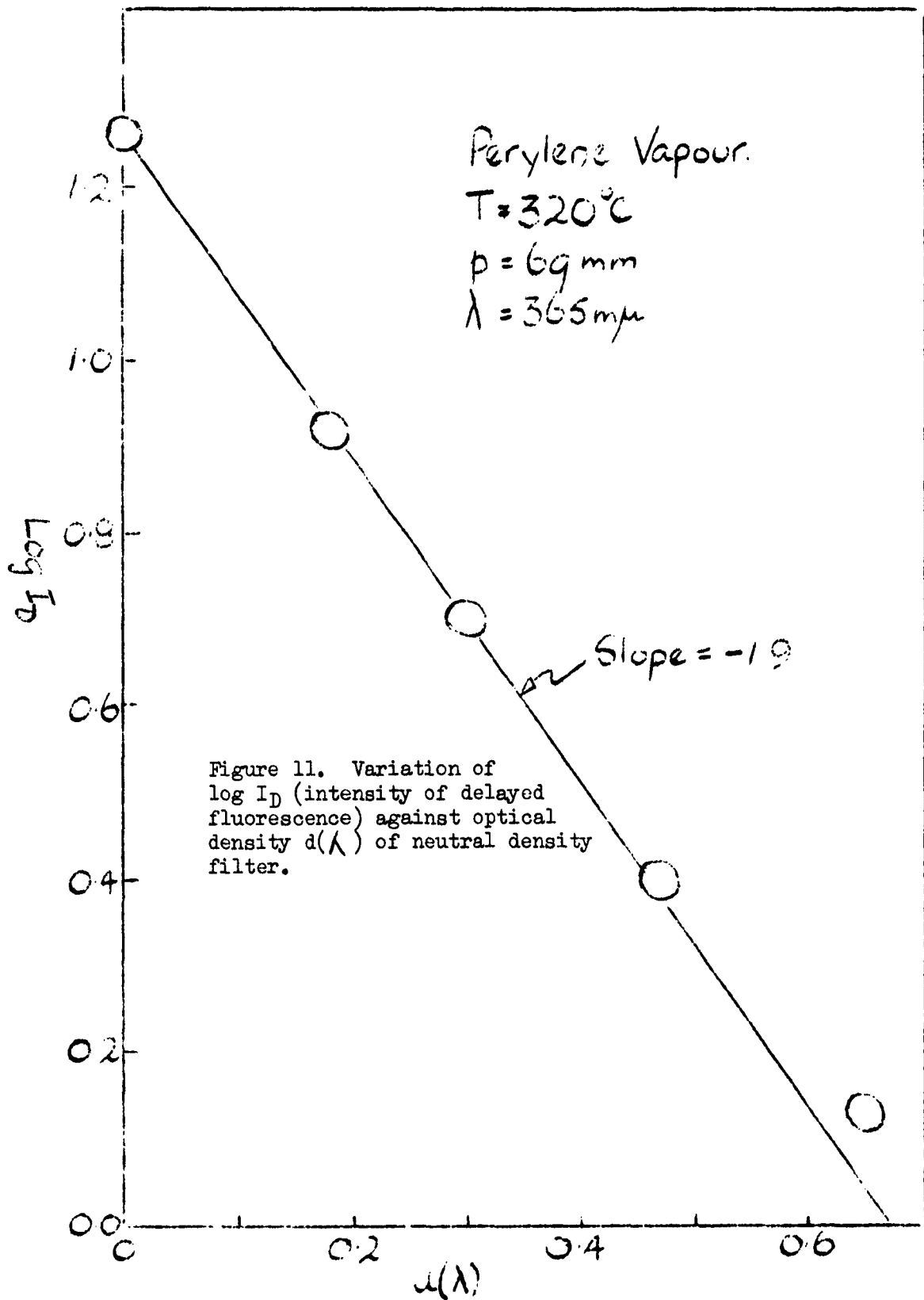


Figure 9. $1/\tau_D$ for perylene vapour as a function of pressure at 250°C.





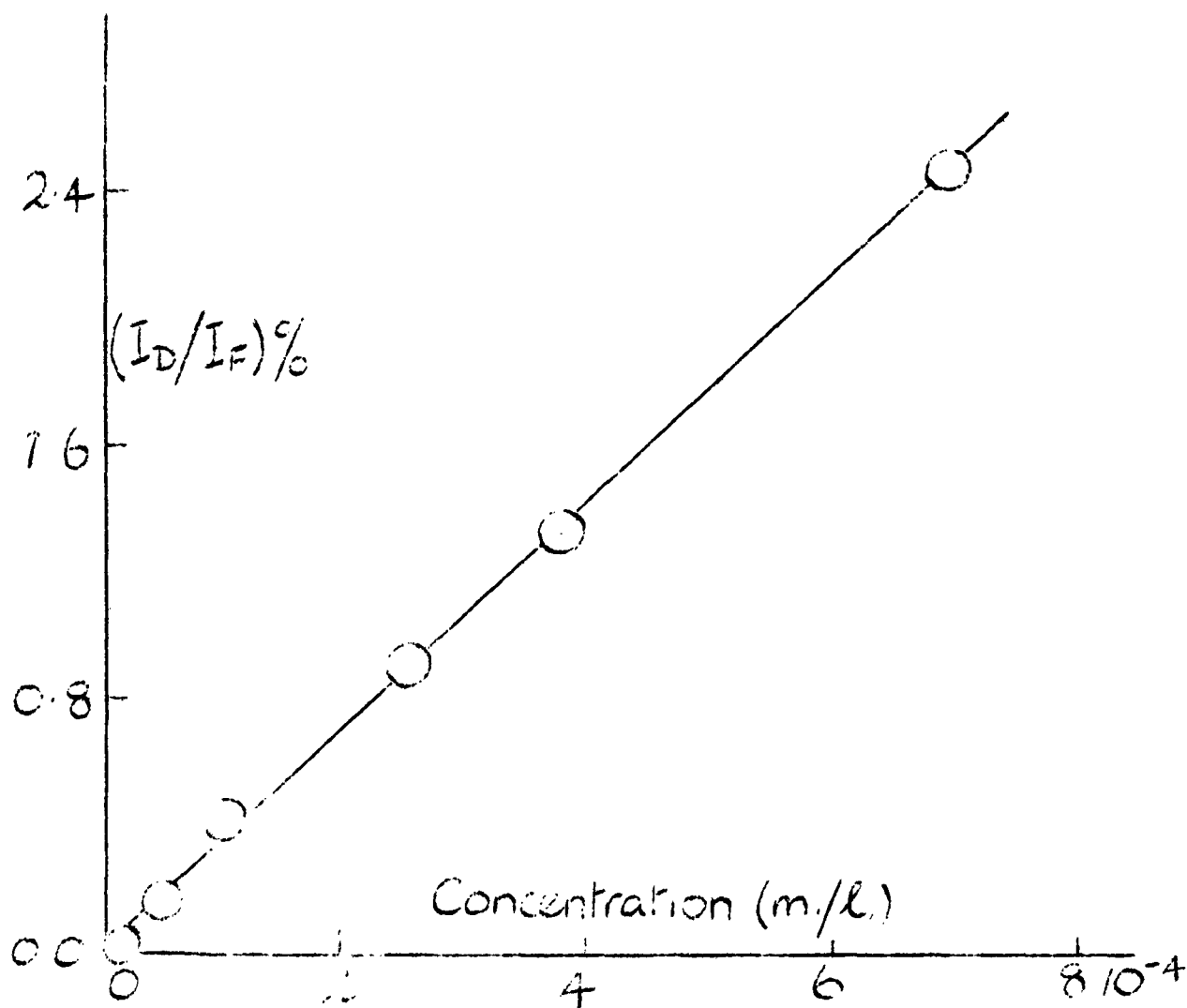


Figure 12. Plot of I_D/I_F against concentration of perylene vapour at 262°C . $\lambda = 365 \text{ m}\mu$.

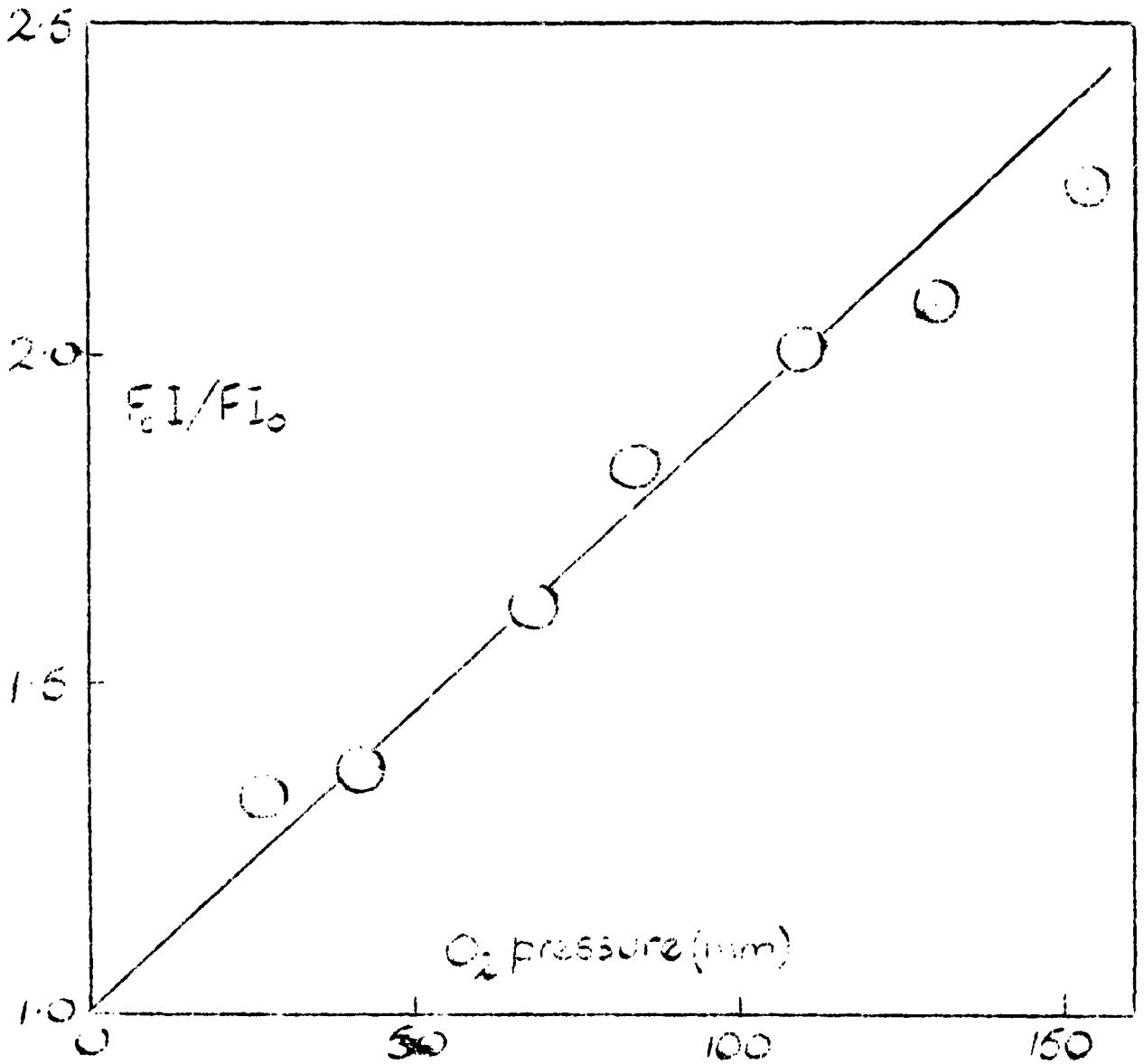


Figure 13. Stern-Volmer plot for quenching of perylene vapour fluorescence by O_2 at 244 °C and 0.2 mm. $\lambda = 365m\mu$.

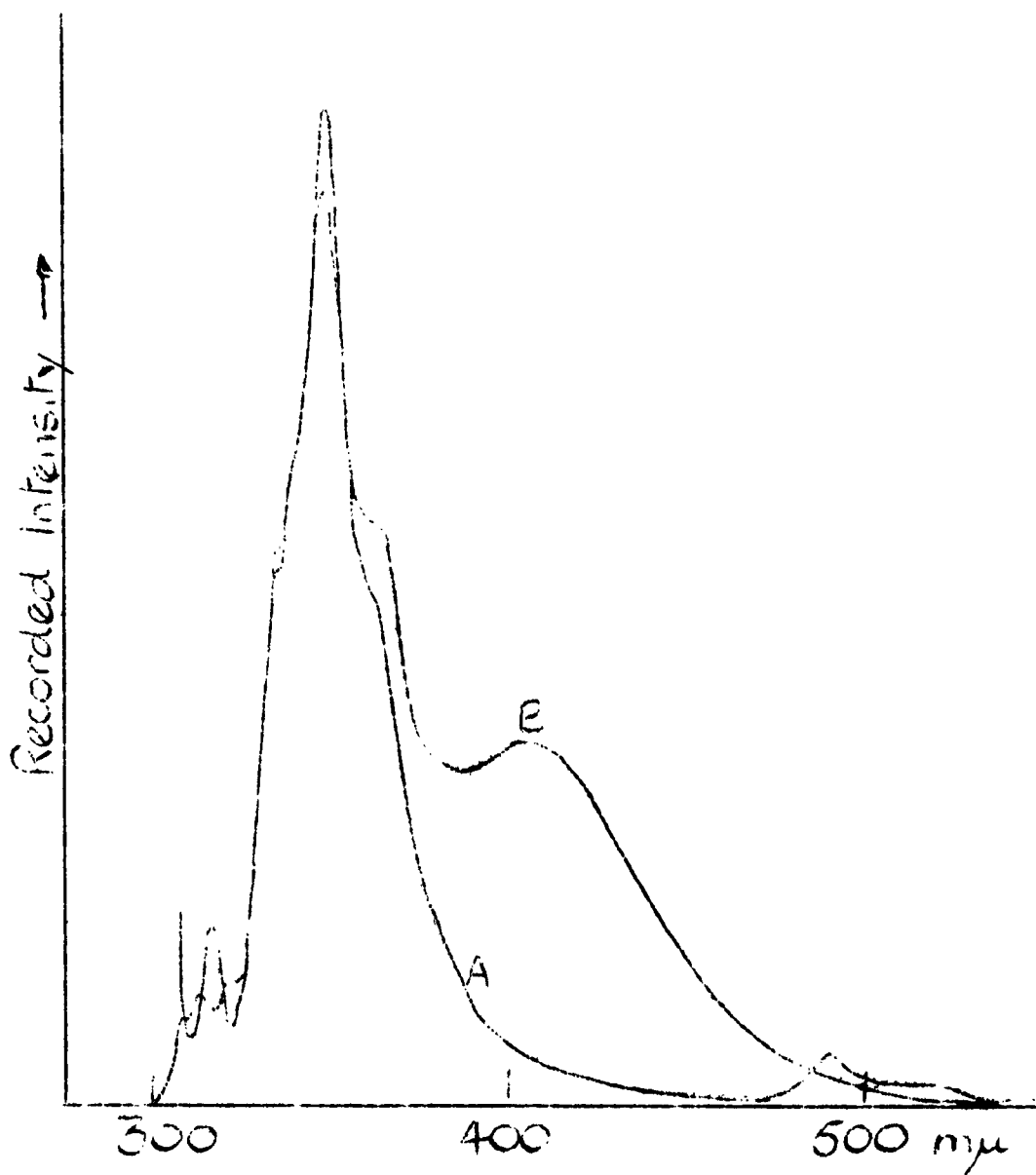


Figure 14. Fluorescence signal recorded for 10⁻³ molar solution of acenaphthene in toluene. A- at room temperature; B- at -40°C.

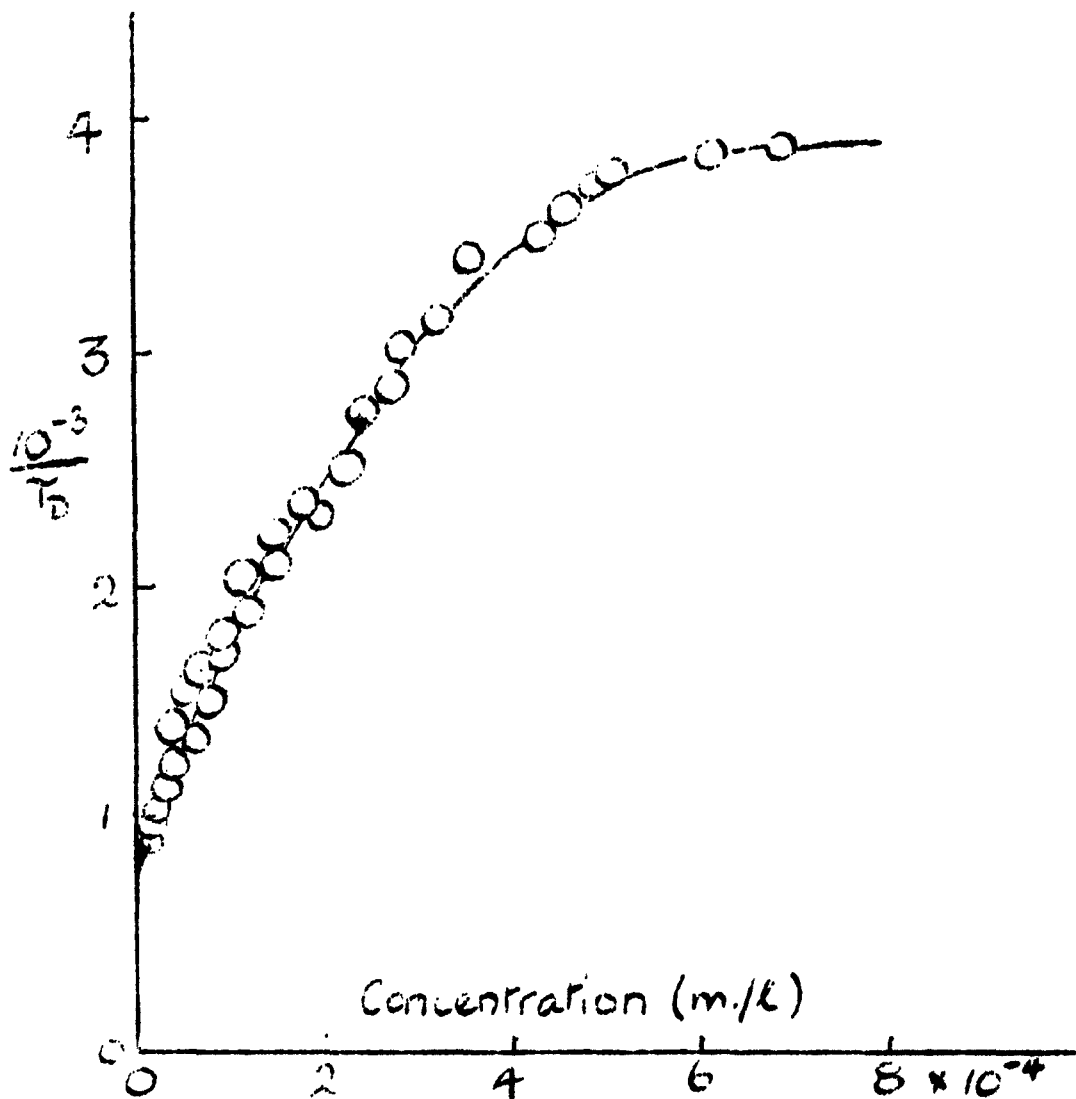


Figure 15. Variation of γ_D with concentration for anthracene vapour at 220°C.

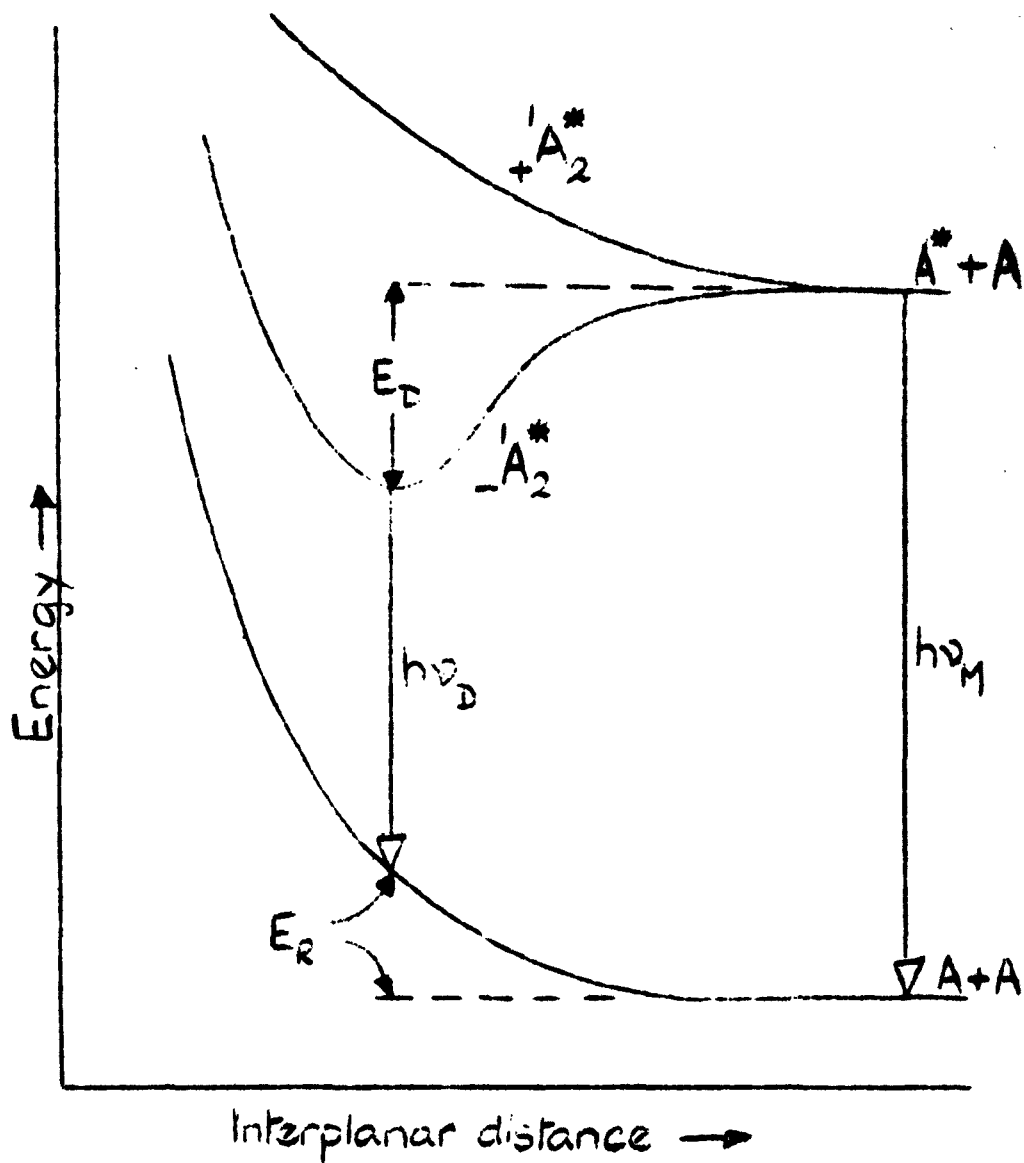


Figure 16. Potential energy diagram for interaction of planar aromatic molecules in ground and excited singlet states. $h\nu_M - h\nu_D = E_D + E_R$, with E_R unknown. $+^1A_2 + ^-1A_2$ are dimeric states described by symmetric and antisymmetric combinations of molecular wave functions for A^* and A .