MEASUREMENT OF THE TRIPLET-TRIPLET

ANNIHILATION RATE CONSTANT

FOR AROMATIC VAPORS

BY

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ABSTRACT

A survey of the literature shows that inspite of the enormous bulk of material on fluorescence and phosphorscence many "quantitative" problems still exist. Among these is the determination of γ/c, γ being the rate constant of triplet-triplet annihilation and c the fraction of the triplets undergoing bimolecular collisions with each other leading to excited singlets.

The expression for γ/c has been derived in the present paper assuming a triplet-triplet annihilation mechanism for the delayed fluorescence. One of the unknown terms in this expression is BQ where B is an instrumental constant and Q the quantum efficiency of the fluorescence.

The relation $BQ = \frac{h\nu F}{P_0 - P_1}$ derived from certain theoretical considerations forms the basis of the experimental method followed. Where F is the prompt fluorescence signal and P_0 and P_1 the powers transmitted at "zero" and "P_1" vapour pressures, respectively.

The effect of vapour pressure, temperature, and wavelength of the exciting light on BQ was studied. The results obtained thereof lead to the conclusion that BQ is independent of vapour pressure and temperature over the ranges studied (0.23 - 0.91 torr, 145 - 360^{0}C.) while it shows an unexpected dependence on the wavelength of the exciting light.

The lack of dependence on vapour pressure is thought to be due to

the very low pressures employed (maximum 1 mm Hg) so that none of the pressure-induced phenomena which could affect B & Q such as reabsorption, collisional deactivation, and pressure-broadening could be operating.

The lack of dependence of BQ on temperature is explained by the lack of sufficient energy in the exciting beam so that even a temperature increase of 200°C. doesnot raise the molecules much higher than the first vibrational level of the excited singlet state, thus leaving the rate constants of the various transitions unaffected.

Finally the significance of BQ for further research is discussed briefly.

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INTRODUCTION

In 1935, Jablonski[1] attempted an explanation for the phenomena of fluorescence and phosphorescence by suggesting a metastable state to exist between the ground and an upper short-lived excited state. The molecule in the latter state could either return directly to the ground state or could cross over to the metastable state from which radiative transition to the normal state could occur.

Lewis and Kasha,[2] accepting the scheme proposed by Jablonski in its basic form, tried to elucidate the nature of the metastable state. They proved experimentally that each substance had only one metastable state from which emission to ground occurred and that evidences cited contrary to this conclusion were cases where impurities, species formed by photooxidation, or other processes such as isomerisation could be shown to be responsible for the observation of more than one long-lived luminescence. Furthermore, they suggested that the long lifetime of the phosphorescent state as compared with that of the fluorescent state was due to the forbiddenness of transition between states of different multiplicities and the positive results of some chemical reactions designed to check the presence of unpaired electrons in the metastable molecule led them to the conclusion that the metastable state was the triplet state.

A more convincing evidence for Lewis' and Kasha's suggestion came from Lewis and Calvin[3] who observed that a fluorescein-containing bar suspended horizontally in a magnetic field showed a deflection in the expected direction when illuminated, thus demonstrating the magnetic nature of the metastable state and establishing that the phosphorescent state was the triplet state.

It is now accepted, after Lewis and Kasha[2], that the term "phosphorescence" indicates radiative transition between states of unlike multiplicities while "fluorescence" denotes the radiative transition between states of like multiplicities.

While phosphoresence and fluorescence and the mechanisms leading to their occurrence were attracting the main portion of attention, people were observing two kinds of "afterglow" which Lewis and Kasha[2] had designated as α and β . Jablonski had explained this in 1935[4] using the scheme referred to before. According to him molecules which could cross over from the excited singlet to the metastable state, now known to be the triplet state, could either return to the ground state by emission of radiation, the process being designated as the β afterglow by Lewis and Kasha[2], or they could rise to the original excited state by thermal activation and then return to the ground level. This process, if radiative, was called the α afterglow by Lewis and Kasha.[2]

It had also been noticed that these two processes were characterized by different spectral features meaning that they involved different electronic transitions, the spectral features of the α pro-

cess being identical to that of normal fluorescence.[4] Also, while the α process was tempaerature dependent in lifetime and intensity, the β process appeared to be constant.

In an attempt to clarify the mechanism of the α process, which is now called the delayed fluorescence, Williams[5] carried out a series of experiments on anthracene, perylene, and pyrene in the vapour phase. He found that the decay process for the delayed fluorescence was exponential, that the lifetime of the delayed fluorescence changed slightly with temperature, that there was a strong dependence of lifetime on the vapour pressure, and that the delayed fluorescence yield increased with pressure. These results led him to propose a mechanism whereby an excited dimer is formed between an excited singlet and a normal molecule. The excited dimer can dissociate later to give an excited singlet and, so, lead to delayed fluorescence.

Parker and Hatchard distinguished between two types of delayed fluorescence which they called the E-type and the P-type.[6] The E-type fluorescence was observed by them in the case of eosin[7] and other dyestuffs, where the temperature dependence of the intensity of the delayed fluorescence band relative to that of the phosphorescence band and the small energy difference between the triplet and the first excited singlet states in these molecules led them to postulate the mechanism whereby molecules in the triplet state were raised thermally to the original excited singlet state, from which transition to the ground state could occur in the normal manner.

In further study of the delayed fluorescence, using solutions of

anthracene and phenanthrene, the above scientists observed that ϕ_d/ϕ_f, ratio of the delayed fluorescence efficiency to the prompt fluorescence efficiency, was dependent on the light intensity in a linear fashion.[8] This result led them to the conclusion that a dimer formation, similar to that proposed by Williams for vapours,[5] could not explain the observation and a mechanism was required whereby triplet-triplet quenching gave rise to an excited species which would then result in an excited singlet molecule from which delayed fluorescence would occur.

Thus, for the first time in the course of development of a mechanism for delayed fluorescence, triplet-triplet annihilation was held responsible for the phenomenon.

Although in their proposed mechanism the authors postulated an excited species formed through triplet-triplet interaction, they also mentioned that the delayed fluorescence could be due to direct triplet-triplet quenching, basing this conclusion on their observation that the lifetime of the delayed fluorescence was half that of the triplet state.[8] In later experiments they observed that the delayed emission intensity was proportional to the square of the rate of light absorption and concluded that triplet-triplet quenching was the only way of explaining the experimental results.[9]

Azumi and McGlynn, arguing that the above observation by Parker and Hatchard indicated the biphotonic nature of the delayed fluorescence, without indicating what species were actually involved in the process, measured the intensities of phosphorescence and of delayed

fluorescence at different light intensities and found that the ratio of the intensity of the latter to the square of the intensity of the former was a constant and concluded that the delayed fluorescence was definitely due to triplet-triplet annihilation.[10]

Thus, by 1963, the scientists in the field had succeeded in solving many of the puzzles that they had been encountering. Among other things, they had established finally that the phosphorescent state was the triplet state and that the delayed fluorescence could be brought about by two different mechanisms. In compounds with a small energy difference between the triplet and the excited singlet thermal activation could cause repopulation of the excited singlet from the triplet state while in compounds with a large energy difference between those two states triplet-triplet annihilation would be the direct cause of reproducing excited singlets. Parker and Hatchard designated the first mechanism as the E-type[7] and the second as the P-type[6] delayed fluorescence.

Although the mechanism of the delayed fluorescence had been elucidated, quantitative problems, such as the magnitude of the rate constants of the different steps involved in the P-type mechanism,[11] continued to attract the attention of the scientists.

The present study also is an attempt to help in clarifying some of these "quantitative" problems. Since this study has been done on anthracene, whose delayed fluorescence falls in the P-type class, a triplet-triplet annihilation mechanism has been assumed.

THEORY

It was mentioned in the "introduction" that the delayed fluorescence of anthracene was due to triplet-triplet annihilation. The main conversions and reactions of the different species involved are represented in Figure 1, where the solid lines represent radiative, and the broken lines non-radiative, transitions. The other symbols will be defined shortly.

Figure 1, though a great visual aid to the understanding of the processes, cannot be used to illustrate all the possible reactions. Therefore, one has to resort to the conventional signs and symbols for representing a reaction or transition. The following is the set of all reactions and transitions that could occur in an anthracene-vapour-containing cell illuminated with a light of an appropriate wavelength.

$S + h\nu$	$\longrightarrow$	S^*	1
S^*	$\xrightarrow{k_s}$	S + heat	2
S^*	$\xrightarrow{k_f}$	$S + h\nu$	3
S^*	$\xrightarrow{k_{ST}}$	T	4
$S^* + S$	$\longrightarrow$	$2S$	5
$S^* + S^*$	$\longrightarrow$	P	6
$S^* + T$	$\longrightarrow$	P	7

$T + S$	$\xrightarrow{k_A}$	$2S$ + heat	8
$T + T$	$\xrightarrow{c\gamma}$	$S^* + S$	9
$T + T$	$\xrightarrow{b\gamma}$	$T + S$ + heat	10
$T + T$	$\xrightarrow{(1-c-b)\gamma}$	$2S$ + heat	11
T	$\xrightarrow{\beta}$	$S + h\nu$ or heat	12

The symbols used above represent the following:

S : a molecule in the ground state

S^* : a molecule in the first excited singlet state

T : a molecule in the lowest triplet state

P : products

$h\nu$: emission or absorption of radiation

It should be mentioned that reactions with molecularity greater than two have been assumed to have almost zero probability.

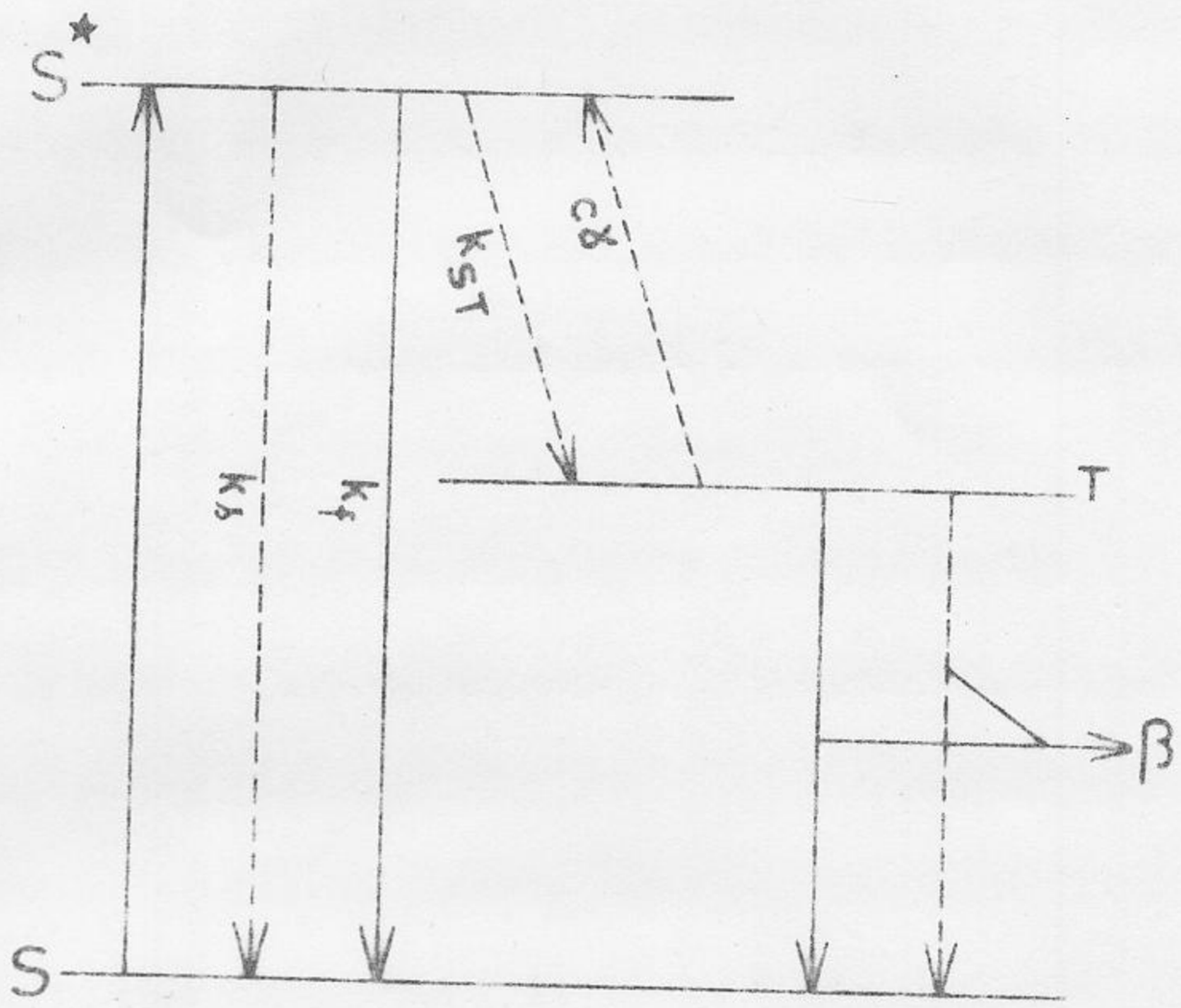

Fig. 1 Schematic diagram of radiative and nonradiative transitions in anthracene vapour

The kinetic analysis presented here follows closely that of Zahlan et al.[11] This analysis can be greatly simplified if one considers the reactions 5,6 and 7. While the lifetime of an excited singlet is of the order of 10^{-8} sec. the bimolecular collision rate, at the pressures employed in our case, is much smaller and therefore they can be ignored.

Considering the rest of the equations, the rate of production of triplets, when the sample is illuminated by a flash lamp of high intensity and very short duration, about 2 μ sec., can be written as

$$\frac{dn_T}{dt} = k_{ST}n_S^* - (\beta + k_A n_S)n_T - (2-b)\gamma\, n_T^2 \qquad 13$$

At constant pressure n_S can be assumed to remain unchanged and equation 13 can be written as

$$\frac{dn_T}{dt} = k_{ST}n_S^* - Dn_T - (2-b)\gamma\, n_T^2 \qquad 14$$

where $D = \beta + k_A n_S$.

Considering the period immediately after the flash, the number of the excited singlets can be assumed to be sustained in a steady state by triplet-triplet annihilation. Thus, one can write

$$\frac{dn_S^*}{dt} = c\gamma\, n_T^2 - kn_S^* = 0 \text{ or,}$$

$$n_S^* = \frac{c\gamma}{k}\, n_T^2 \qquad 15$$

where $k = k_s + k_f + k_{ST}$, i.e., the total decay constant of the singlets, and n_S and n_T are the number of molecules of singlets and triplets, respectively, per unit volume.

Substituting for n_{S}^{*} in equation 14, the latter becomes

$$\frac{dn_T}{dt} = \frac{c\gamma k_{ST}}{k} n_T^2 - Dn_T - (2-b)\gamma n_T^2 \text{ or,}$$

$$\frac{dn_T}{dt} = -An_T^2 - Dn_T \qquad 16$$

where $A = \left[(2-b) - \frac{ck_{ST}}{k}\right]\gamma$

Equation 16 is a "Bernoulli" equation which can be transformed into a linear differential equation

$$\frac{du}{dt} - Du = A \qquad 17$$

by making use of the substitution

$$u = n_T^{-1} \qquad 18$$

The differential equation 17 can be solved by using e^{-Dt} as the integrating factor. Multiplying both sides of "17" by this factor and integrating from t = 0 to t = t gives

$$n_T^{-1} e^{-Dt} = \frac{-A}{D} e^{-Dt} + \frac{A}{B} + IC \qquad 19$$

The integrating constant IC can be determined by noting that $n_T = n_{T_0}$ at t = 0, whereby $IC = n_{T_0}^{-1}$.

Substituting $n_{T_0}^{-1}$ for IC, multiplying by e^{Dt}, and inverting both sides tranforms equation 19 to

$$n_T = \frac{Dn_{T_0}}{(An_{T_0} + D)e^{Dt} - An_{T_0}} \qquad 20$$

Since $D = \beta + k_A n_S$ is the first order decay constant of the triplets, i.e., the reciprocal phosphorescence lifetime and this is

known to be of the order of 10^{-3} sec, the "Dt" term in equation 20 can be safely considered much smaller than unity for time intervals of the order of 10^{-5} second. The series expansion of e^{Dt} can then be approximated to (1 + Dt) and equation 20 can be written as

$$n_T = \frac{n_{T_o}}{(An_{T_o} + D)\ t + 1} \qquad 21$$

Since the delayed fluorescence originates from the first excited singlet state, S^*, the delayed fluorescence signal should be proportional to the number of excited singlets. Obviously the greater the overall decay constant of the excited singlets the larger the delayed fluorescence signal is expected to be, since the latter phenomenon contributes to the overall decay. However, only a fraction of all the excited singlets produced by direct light absorption return to the ground state by radiative transition, the rest undergoing internal conversion or intersystem crossing. Designating this fraction as Q one can write:

$$F(t) \propto QkV\, n_{S^*}(t) \qquad 22$$

where F(t) is the fluorescence signal at time t

Q is as defined above and can be expressed as $\frac{k_f}{k_f + k_s + k_{ST}}$

$Vn_{S^*}(t)$ is the number of excited singlets at time "t", V being the volume and n_{S^*} the excited singlet density in molecules per unit volume.

k is the overall decay constant of the excited singlets, i.e.,

$$k = k_f + k_s + k_{ST}$$

$\propto$ denotes proportionality.

The proportionality sign in equation 22 can be changed into an equality by introducing a proportionality constant expressing the efficiency of the detector. The following factors contribute to this constant.

1. Geometry of the setup is critical. A change in the geometry could change the light path, thus affecting the amount of the fluorescence light "seen" by the detectors.

2. Filters used for either selecting a narrow band or for decreasing the intensity of the fluorescent beam cut down the observed fluorescent signal by a factor determined by their transmission properties.

3. Temperature and pressure changes may alter the spectral features of the fluorescent signal, causing an unreal change in the observed signal. For example, a line filter chosen to transmit a narrow fluorescence band would transmit the fluorescence signal only partially when the latter is pressure-broadened.

4. Finally, the energy-to-current conversion factor of the detectors and the current-to-voltage conversion factors of the measuring devices used in our case come in.

So, equation 22 can be written as

$$F(t) = BQkV\, n_{S^*}(t) \qquad 23$$

where B is the proportionality constant consisting all the above factors.

Using equation 15, equation 23 becomes

$$F(t) = BQc\gamma V n_T^2 \qquad 24$$

which upon substituting for n_T from 21, inverting, and taking square roots of both sides, becomes

$$\left[F(t)\right]^{-\frac{1}{2}} = \frac{1}{\left[BQVc\gamma\right]^{\frac{1}{2}}} \left[\frac{1 + (An_{T_o} + D)t}{n_{T_o}}\right] \qquad 25$$

Since D is the triplet decay constant and is known to be of the order of 10^3, it can be ignored with respect to An_{T_o} and equation 25 can be written as

$$\left[F(t)\right]^{-\frac{1}{2}} = (BQVc\gamma)^{-\frac{1}{2}} \left[\frac{1 + An_{T_o} t}{n_{T_o}}\right] \qquad 26$$

Thus, a plot of $\left[F(t)\right]^{-\frac{1}{2}}$ versus time should give a straight line with a slope which, upon substitution for A, can be expressed as

$$S = \left[\frac{\gamma}{VBQc}\right]^{\frac{1}{2}} \left[(2-b) - \frac{ck_{ST}}{k}\right] \text{ volt}^{-\frac{1}{2}} \text{ sec}^{-1} \qquad 27$$

from which can be derived

$$\frac{\gamma}{c} = \frac{S^2 VQB}{\left[(2-b) - \frac{ck_{ST}}{k}\right]^{\frac{1}{2}}} \qquad 28$$

An accurate knowledge of γ/c is important because it throws more light on triplet-triplet annihilation mechanism since γ is the overall rate constant of the triplet-triplet annihilation and c is the fraction of triplets undergoing bimolecular collisions with each other leading to excited singlets.

The present study was undertaken in an attempt to take a step

forward in arriving at a reliable value for γ /c by developing and carrying out a method for determining the value of BQ as a single quantity. The following is the theory upon which this method was based.

Equation 26 was derived assuming the sample to have been illuminated by a light of high intensity and of very short duration.

Suppose the flash lamp were replaced, after the end of the experiments, by a lamp with a steady output operated continuously and that otherwise the arrangement and the components remain identical with those in the flash experiments.

Under such condition a steady state is expected to be reached soon so that the rate of formation of the excited singlets will be equal to the rate of singlet decay.

The fluorescence observed in this case, i.e., the prompt fluorescence would then be proportional to the rate of emission of photons which, in turn, would be proportional to the rate of absorption of photons.

The rate of absorption of photons can be expressed as $\frac{P_0 - P_1}{h\nu}$ where P_0 and P_1 are the power transmitted at "zero" and at "P_1" vapour pressure, respectively, so that $P_0 - P_1$ is the light energy absorbed per second.

The above term, i.e., $\frac{P_0 - P_1}{h\nu}$, would also be the rate of emission of photons, assuming steady state, if the excited singlet decay were exclusively radiative. However, since only a fraction, Q, of the excited singlets formed decay by radiative transition the rate of

emission of photons would be $Q \frac{P_0 - P_1}{h\nu}$

The fluorescence signal can then be written as

$$F_p \alpha Q \frac{P_0 - P_1}{h\nu} \qquad 29$$

If all the factors contributing to B in equation 23 were maintained constant in the shift from the "flash" to the "steady state" experiment equation 29 can be assigned the same proportionality constant which will then lead to

$$F_p = BQ \frac{P_0 - P_1}{h\nu} \text{ , or,} \qquad 30$$

$$BQ = \frac{F_p h\nu}{P_0 - P_1} \qquad 31$$

It will be explained in the following pages how the above equation can be, and was, used to determine BQ.

EXPERIMENTAL

The theoretical considerations in the previous section clearly showed that a measurement of γ /c ratio required a knowledge of the value of BQ. It was also shown that

$$BQ = \frac{F_p h\nu}{P_0 - P_1} \qquad 31$$

where B is an instrumental constant

F_p is prompt fluorescence signal

h is Planck's constant

Q is quantum efficiency of fluorescence

ν is frequency of exciting radiation

P_0 is power transmitted at "zero" vapour pressure

P_1 is power transmitted at "P_1" vapour pressure

Equation 31 suggests that BQ can be determined once one has ways of determining ν, P_0-P_1, and F_p. For clarity purposes the steps taken will be presented in the following separate sections in the same order as they were performed.

I. Preliminary Steps

Prior to setting up the actual experimental setup, it was necessary to chose the proper measuring devices for each of the three quantities mentioned above, i.e., ν, P_0-P_1, and F_p. Besides, it was necessary to have sufficient information on the behaviour of each of

these measuring devices. For these purposes the following steps were taken.

A. Selection of "ν"

For isolating a desired wavelength a Carl Leiss monochromator was used. It was necessary, however, to calibrate this instrument so that the wavelength corresponding to each drum reading would be known.

The calibration was done using a mercury and a cadmium-mercury lamp, one at a time, as the light source. The radiation from these sources was passed through the monochromator and fed into a photo-multiplier placed at the exit slit. The signal from the photo-multiplier was displayed on a microammeter and the peak current values with the corresponding drum readings were recorded. Comparison of the data thus obtained with wavelength and intensity of mercury and cadmium lines recorded in the literature made the calibration possible. The curve obtained is reproduced in Fig. 4 in the next section.

B. Measurement of $(P_0 - P_1)$

Since P_0 and P_1 are transmitted powers any device capable of measuring radiation of low intensities, such as were employed in our case, could be used. The device used in this study was a vacuum type Eppley thermopile Serial No. 5827 which was capable of developing a mean emf of 0.060 microvolts per microwatt per sq.cm. with the front face fully exposed. This calibration factor could have been used to obtain the transmitted power if the area of the sensing surface illuminated by the transmitted beam were known. However, an accurate

measure of the area would have been sufficient only if one were certain that the thermopile response changed uniformly over all the areaof the sensing surface.

In order to obtain the above information the dependence of the Eppley thermopile response on the height and the width of the beam was studied. In both cases an ordinary projector lamp was used as the light source, with a filter to cut down the intensity. The beam was passed through a slit of variable height or width, depending on the dimension being studied, keeping the other dimension fixed. This beam was then centered on the thermopile window and the response measured using and L & N model 9834 DC null detector and an L & N type K-3 potentiometer, capable of reading to the nearest 0.1 μ volt. In each case a reading was also obtained with the thermopile window fully illuminated, a condition used by the Manufacturer for calibrating the thermopile.

Figure 5 and Figure 6 show typical results of these measurements.

II. Experimental Setup

Once the preliminary steps were completed the apparatus was assembled as shown in Figure 2.

The light source "L" was a one-kw GE BH_6 lamp operated continuously. The radiation from the lamp was focussed, by means of a concave and a plane mirror both being components of the monochromator, on the entrance slit of the Carl Leiss monochromator. The 3663$\mathring{A}$ mercury line from the exit slit was rendered nearly parallel, using a quartz lens "l", pased through the cell unit "C" and finally received by the

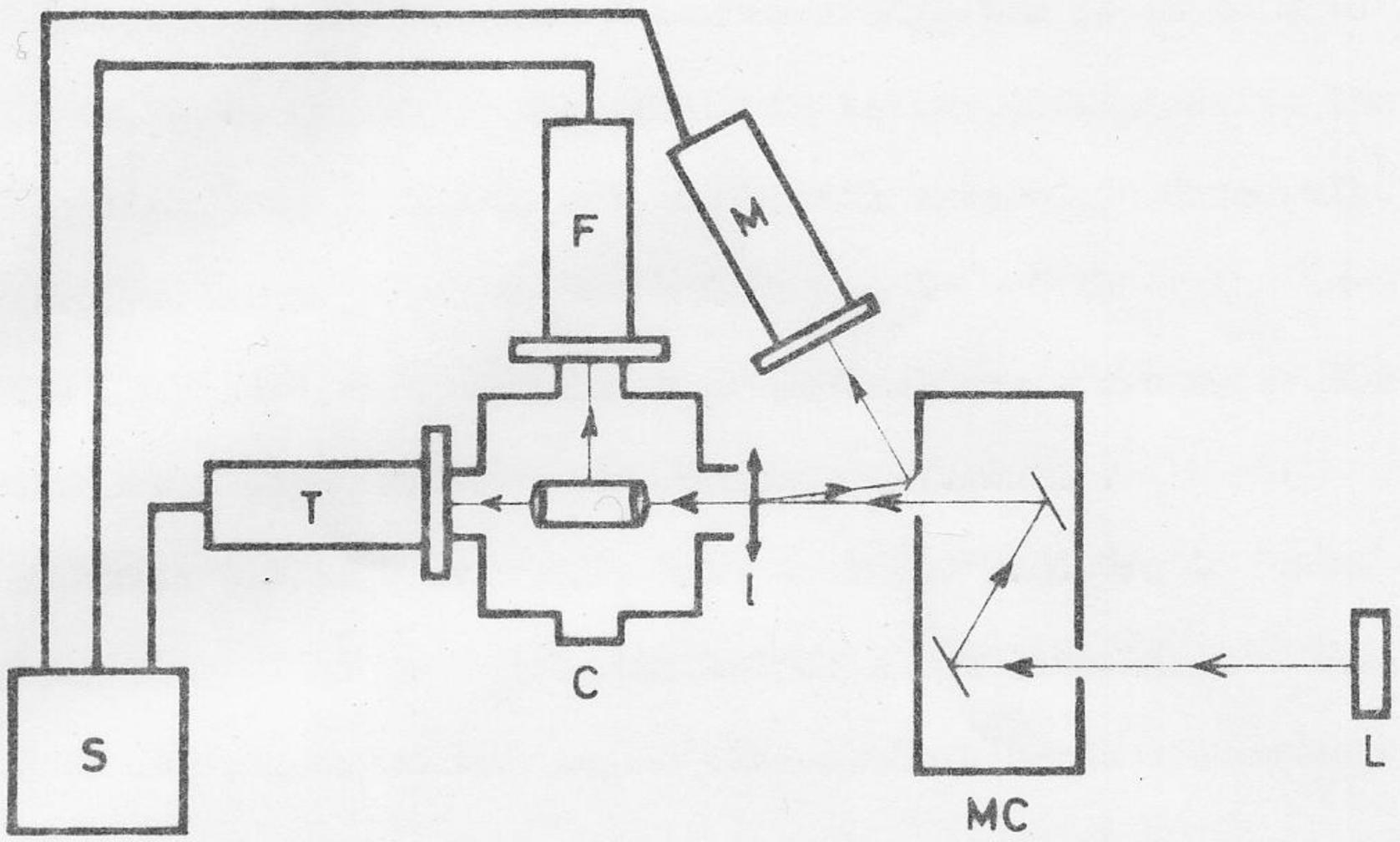

Fig. 2 Schematic Diagram of the Experimental Set Up

L : Light Source

MC : Monochromator

M : Monitor

I : Lens

F : Fluorescence Receiver

C : Cell Unit

T : Transmittance Receiver

S : Oscilloscope

"T" sensing device. "F" received the fluorescence light.

The entrance and the exit slits were adjusted so as to give an image on the exit window of the cell unit having dimensions in the region of linearity of the Eppley thermopile response. This will be referred to later.

The cell unit, "C", consisted of several parts the main ones being the cell, the oven, and the cooling devices.

The cell was made of silica with an inner diameter of 18 mm and an optical path of 41 mm. It consisted of a cylindrical part with an opening in the center of the curved surface leading to a long tapered part. The cylindrical part was designed to contain the vapour and the tapered part the solid. Figure 3 shows a drawing of the cell.

The cell was placed in an oven consisting of two aluminium blocks separated by a thin asbestos sheet. The oven, was designed in this manner in order that the temperature of the two blocks could be varied independently of each other. In this way the temperature of the lower block would indicate the vapour pressure while the temperature of the upper block would simply be the temperature of the vapour.

The upper block was designed to contain the cylindrical part of the cell while the tapered part fitted into a well drilled through the asbestos sheet and the lower block. Four circular quartz windows of one inch diameter were located on the four sides of the upper block, close to the bottom, so that both the flat and the curved surfaces of the cell could be viewed.

A narrow channel drilled in the lower block provided the

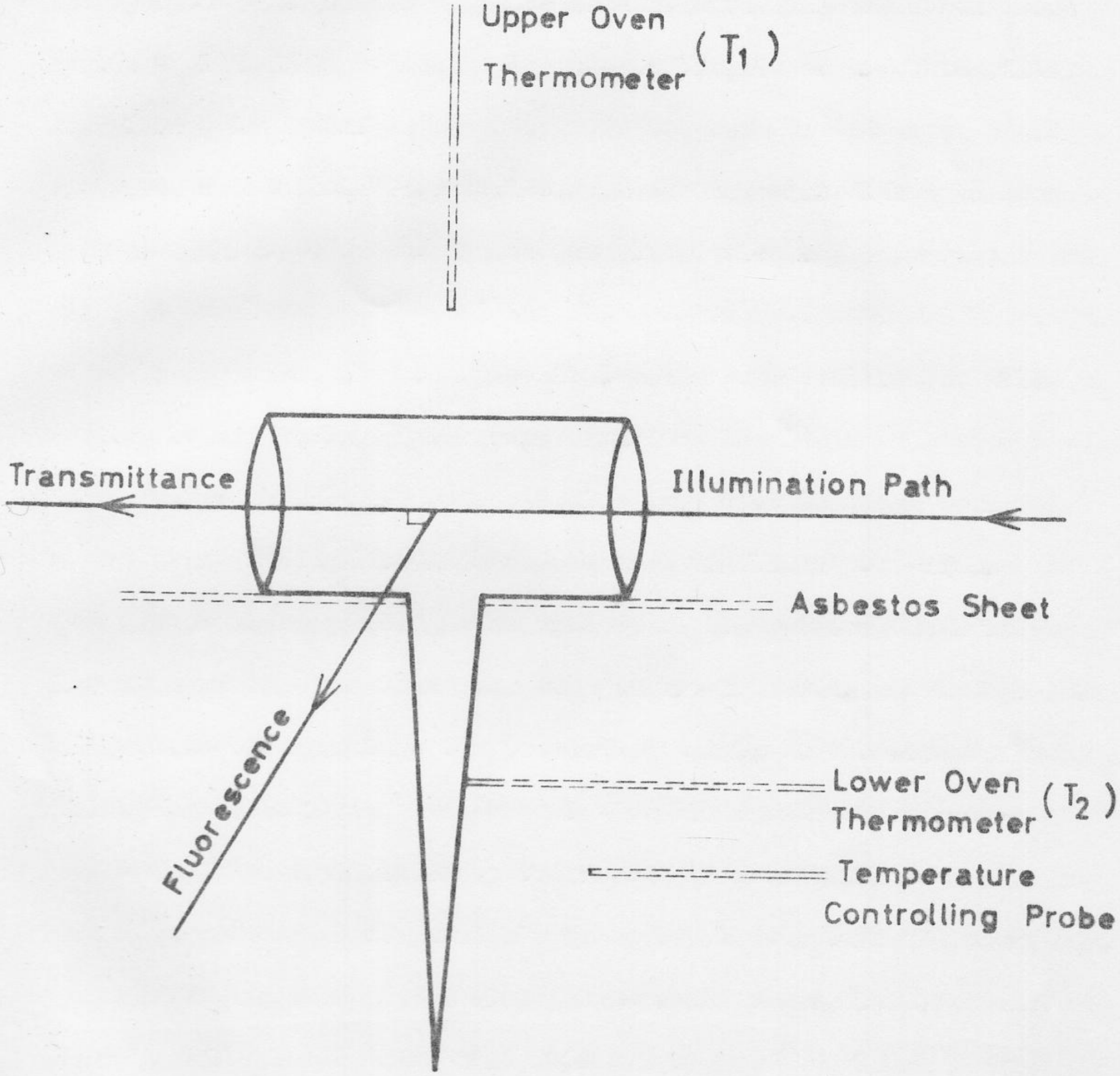

Fig. 3 Drawing of the cell

necessary space for a thermometer which touched the tapered surface of the cell, thus giving the vapour pressure-controlling temperature. An adjacent shallow well was used for thermostating the lower block by using a thermistor temperature sensor coupled to a servomechanism controlling the oven heater power. In the case of the upper block no thermostating was used and the thermometer was placed in a shallow well so that there was no direct contact between the thermometer and the cell.

In each of the two blocks three wells were drilled for three heating resistors connected in parallel.

The two blocks with the asbestos sheet between them were made to fit closely in an asbestos case having wall thickness of one inch. Four hollow metallic cases were mounted on the asbestos case at the positions of the quartz windows and water was circulated through them. The cooling was necessary for preventing damage to the sensing devices mounted on these cases.

Since the insulation was found not to be sufficient to prevent heat leak from the upper to the lower block a copper tubing was passed through the lower block for water circulation. This also permitted rapid cooling of the lower oven when necessary.

The cell unit "C" with the exception of the cell was made in the Machine Shop of the Physics Department.

The fluorescence sensing device, "F", was an IP28 photomultiplier mounted on the side facing the curved surface of the cell, i.e., perpendicular to the exciting beam. For isolating the fluorescence band

and cutting down the interference from the exciting wavelength the 3-73, 3-74, and 5-58 Corning Glass filters were used.

The transmittance sensing device, "T", was the Eppley thermopile at first. However, it was noticed that thermal radiation contributed to the Eppley reading to a large extent and that, therefore, two readings were necessary at each temperature, one with the cell illuminated and the second with the exciting light shut off.

Since this was rather inconvenient and also reduced the accuracy of the readings at high temperatures it was decided to use a photomultiplier with 7-37 filter chosen so as to transmit the exciting light as exclusively as possible.

Since the Eppley thermopile would be "seeing" a volume of the cell with a cross section equal to the narrow opening of its front surface, a blackened metallic sheet with a slit at its center of the same dimensions as that of the Eppley window was placed in front of the filters of the transmittance photomultiplier. This was to make certain that conditions were the same for both devices.

Since measurements could be compared only when the intensity of the exciting light were the same for all those measurements a knowledge of the variation of the light source intensity during each set of measurements was important. For this purpose an IP28 photomultiplier, "M", was positioned facing a small mirror attached to the exit slit. The mirror would reflect the exciting light, which was reflected from the lens, on the photomultiplier.

The signals from the three photomultipliers were displayed on a

Tektronix 555 double beam oscilloscope. Attenuating resistors of 1×10^6 ohms were used for the "F" and "T" photomultipliers and one of 1×10^3 ohms for the "M" photomultiplier.

III. Measurements

The actual every day measurements involved several operations which are listed and discussed below in, roughly, the order of performance. These were setting of the photomultiplier power supplies to the desired voltages, focussing of the lamp, setting of the monochromator drum reading, controlling the temperatures, calibrating the transmittance photomultiplier, and, finally, reading the voltages displayed on the oscilloscope and the Eppley response on the potentiometer.

The power supplies were set at the proper values using their meters. However, it was suspected that the meter setting was not reproducible with a high enough degree of accuracy and it was decided to resort to potantiometric measurement. This was done by using a resistive voltage devider to feed about one volt of the total power supply output to the same potentiometer as used for measuring the thermopile response. The power supply was then set, before each reading, to reproduce the potentiometer setting first obtained. This potentiometric modification was emplyed only in the last few experiments.

Refocussing of the lamp was found to be necessary at the start of each experiment. This was done by using the mirrors of the monochromator to focus the lamp image on the entrance slit.

The next step in each experiment was the setting of the mono-

chromator drum reading. Although a calibration curve had been obtained, as discussed previously, an irreproducibility was noticed with time. Therefore, the calibration curve was used to give the approximate drum setting corresponding to a desired wavelength. The actual setting was done by rotating the drum, in a narrow range around the point given by the calibration curve, and locating the setting for the maximum response as indicated by the monitor's signal on the oscilloscope.

The drum setting was followed by temperature control. The lower block was maintained at a constant temperature using the thermistor-servo mechanism while the temperature of the upper oven was controlled by manipulating the voltage supplied to the heating resistors. The lower oven temperatures used were 125°C, 135°C, and 142°C and for the upper block the range 140°C to 360°C was covered. These temperatures were chosen after a set of preliminary measurements.

As mentioned before, in later experiments the Eppley was replaced by a photomultiplier. However, since the Eppley was calibrated to give the power transmitted, it was necessary to calibrate the photomultiplier against the Eppley thermopile. This was done by obtaining an Eppley reading for the transmittance followed immediately by a photomultiplier reading. The temperatures chosen for these measurements were below 80°C for the lower block, i.e., "zero" vapour pressure, and about 140°C for the upper block. These temperatures were chosen to obtain a large reading for the Eppley with a low contribution from thermal radiation.

The final step was reading the signals as they appeared on the

scope, at the proper lower and upper oven temperatures. In the usual case the lower oven temperature was held constant, i.e., a constant vapour pressure was maintained, while the upper oven temperature was allowed to rise at an appropriate rate and readings were taken when a desired upper oven temperature was reached. In some special cases the upper oven temperature was held constant and that of the lower varied. The former was achieved by supplying enough voltage to the heating elements so as to compensate for the cooling of the oven, once it had been brought to the proper temperature.

The results of these measurements are presented in the following section.

DATA AND RESULTS

The data obtained are presented in the following pages in the same order as the corresponding experiments were performed.

Calibration of the Monochromator

The procedure for this calibration is described on page 17. The data obtained are presented graphically in Figure 4.

Dependence of the Eppley Thermopile Response on the Dimensions of the Light Beam

The method for obtaining this information is described on page 18. Figure 5 and Figure 6 show the dependence of the thermopile response on the height and the width, respectively, of the beam striking the sensing surface of the thermopile.

"BQ" Determination

The above two steps were the preliminary steps for the determination of BQ. The actual experimental setup for this determination and the detailed procedure are described on pages18 - 26.

1. Measurement with the Eppley Thermopile

It is mentioned on page 23 that the Eppley thermopile was used as the transmittance sensing device in the early series of experiments. The only other condition which was changed in the later experiments

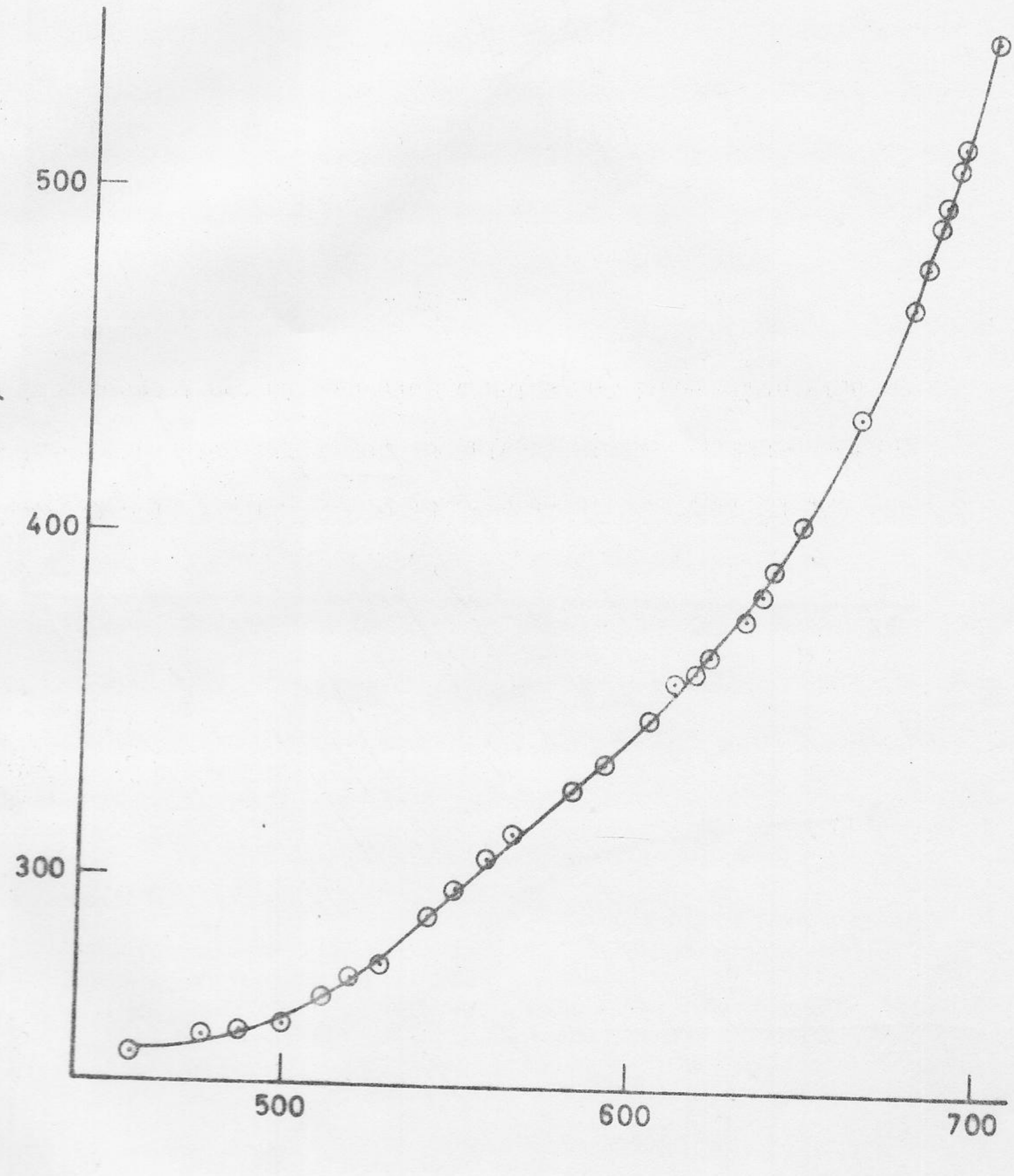

Fig. 4

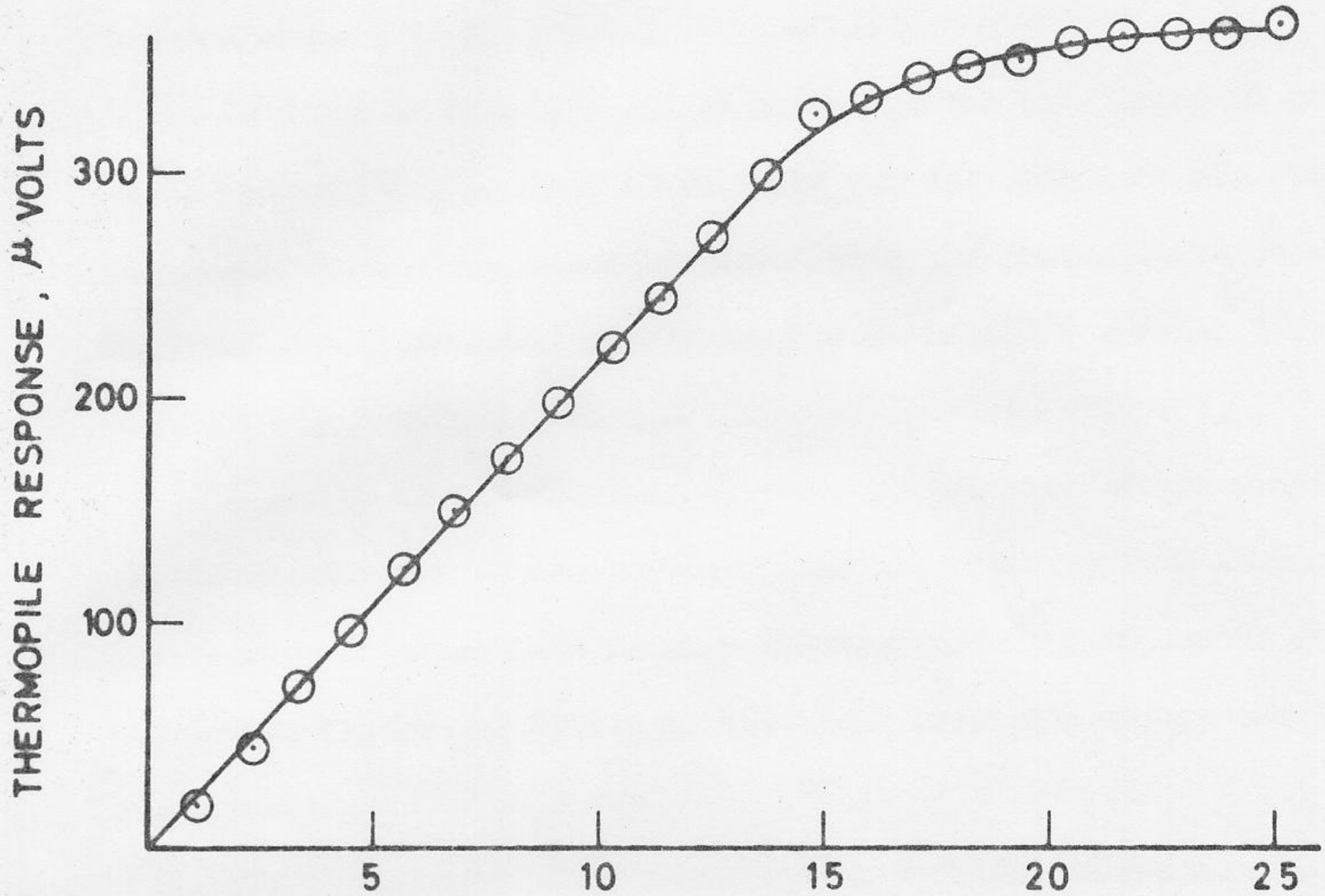
THERMOPILE RESPONSE, μ VOLTS
300
200
100
5
10
15
20
25
IMAGE HEIGHT, m.m.

Fig. 5

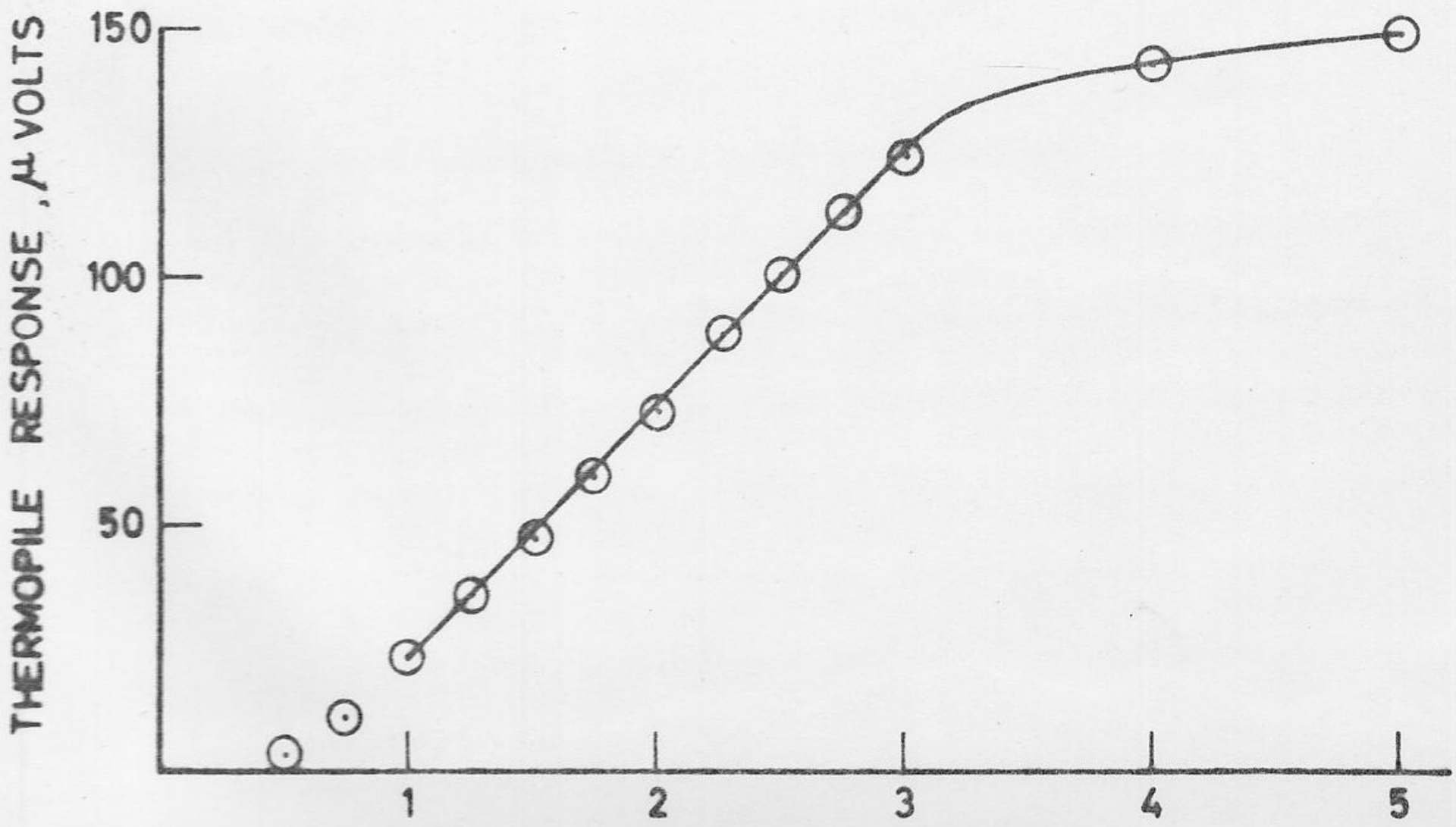
RESPONSE, μ VOLTS
150
100
50
1
2
3
4
5
IMAGE WIDTH, m.m.

Fig. 6

was the voltage of the fluorescence sensing photomultiplier. This was decreased from 1500 volts to 1150 volts.

In order to have a means of comparing the data obtained at these two voltages a calibration curve was determined by observing the change in the fluorescence signal with the photomultiplier voltage at fixed upper and lower oven temperatures of 180°C and 141.5°C, respectively. This calibration curve is shown in Figure 7.

A change in the voltage, filters, or position of the monitor from one to another set of measurements does not interferewith comparing the results of these sets because the monitor was designed to give a correction factor for drifts in the light intensity during one set of measurements.

The BQ resulting from measurements with the thermopile are listed below in Table 1. The fluorescence signals were converted to values corresponding to a voltage setting of 1150 before performing the calculations.

2. Measurements using a photomultiplier

For reasons mentioned on page 23, the Eppley thermopile was replaced by an IP_{28} photomultiplier, calibrated against the thermopile for each set of measurements, and the above experiments were repeated. All these measurements were made at the fluorescence photomultiplier voltage of 1150 and a transmittance photomultiplier voltage of 750 volts.

The BQ values obtained are tabulated in Tables 2, 3, and 4.

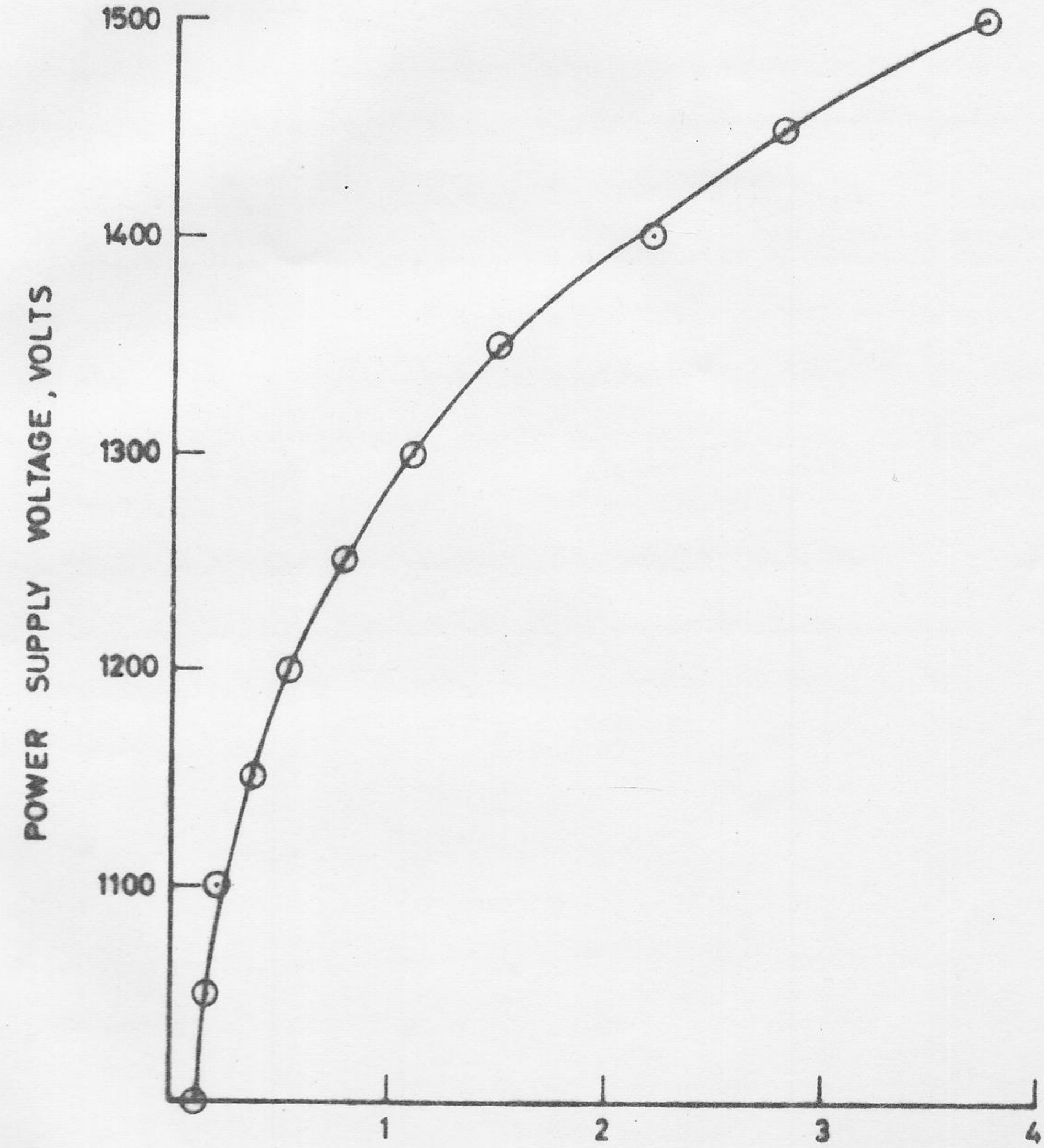
1500
1400
1300
1200
1100
POWER SUPPLY VOLTAGE, VOLTS
1
2
3
4
FLUORESCENCE SIGNAL, VOLTS

Fig. 7

Table 1 - "BQ" determined from measurements at vapour pressures of 0.17 - 0.19, 0.40 - 0.42, and 0.57 - 0.63, and vapour temperatures ranging from 135°C - 359°C. The Eppley thermopile was used as the transmittance sensing device.

Lower Oven Temperature °C	Vapour Pressure mm	Vapour Temperature °C	BQ, volt sec. Mean	Standard Deviation	Number of Measurements
125.5±0.5	0.17-0.19	135-360	3.15×10^{-13}	2.43×10^{-13}	14
135.5±0.5	0.40-0.42	145-359	4.18×10^{-13}	1.51×10^{-13}	15
141.5±0.5	0.57-0.63	161-360	4.17×10^{-13}	0.567×10^{-13}	10

Table 2 -

BQ measurements at lower oven temperature 125.5 ± 0.5°C.

Vapour Temperature °C.	BQ volt sec.
136	1.11×10^{-13}
158	1.13
183	1.45
203.5	1.08
222.5	1.25
242	1.08
265	1.16
282	1.23
301	1.18
321	1.06
337	1.23
357	1.16
359	1.16

Mean = 1.17×10^{-13}

Standard Deviation = 0.098×10^{-13}

Table 3 -

BQ measured at a lower oven temperature of 135.5±0.5°C.

Vapour Temperature °C.	BQ volt sec.
150	1.11×10^{-13}
165	1.40
180	1.37
195	1.33
210	1.35
226	1.45
246	1.62
268	1.49
289	1.54
307	1.47
334	1.45
361	1.37

Mean = 1.41×10^{-13}

Standard Deviation = 0.124×10^{-13}

Table 4 -

BQ measurements at lower oven temperature of 142±0.5°C.

Vapour Temperature °C.	BQ volt sec.
161	1.64×10^{-13}
173	1.57
173	1.59
184	1.57
185.5	1.47
187	1.71
189	1.49
193	1.69
201	1.67
211	1.69
221.5	1.57
235	1.69
246	1.54
252	1.59
273	1.52
293	1.54
311	1.47
328	1.37
338	1.42
357	1.37

Mean = 1.51×10^{-13}

Standard Deviation = 0.116×10^{-13}

3. Dependence of BQ on Vapour Pressure

In this part the lower oven temperature was varied keeping the upper oven at a constant temperature. The experiments were performed at two different upper oven temperatures. The BQ values obtained are tabulated in Table 5. All the experimental determinations are tabulated as an example. R_0 and R_1 are transmitted signals at zero and P_1 vap. pressures.

Table 5 - Dependence of BQ on Vapour Pressure. The mean and the standard deviation for BQ (see eq. 31) are calculated ignoring the first four and the last two of each set. (see p. 40 for explanation). R_0 values were obtained using the relation $R_0 = \frac{P_{00}}{M_0} M_1$ where P_{00} is the transmitted signal at zero vapour pressure, M_0 is the monitor signal at zero vapour pressure and M_1 is the monitor signal at P_1 pressure.

Lower oven temp. °C	Vapour pressure mm	Vapour temp. °C	M_1 volts	R_1 volts	R_0-R_1 volts	F volts	BQ volt sec
102	0.027	188	0.245	0.70	0.002	0.035	35.2×10^{-13}
107	0.039	188	0.245	0.69	0.012	0.056	9.36
115.5	0.076	187	0.240	0.65	0.039	0.092	4.76
125	0.17	187.5	0.240	0.508	0.181	0.160	1.78
129.5	0.23	188	0.235	0.675	0.173	0.205	2.38
135	0.40	188	0.230	0.460	0.201	0.230	2.30
142	0.63	188	0.230	0.360	0.301	0.340	2.27
146.5	0.91	188.5	0.230	0.300	0.361	0.410	2.28
150.5	1.0	188.5	0.235	0.230	0.445	0.450	2.03
155	1.6	188	0.230	0.190	0.471	0.480	2.05
103	0.027	290	0.295	0.85	0.053	0.046	1.75
116	0.083	290	0.280	0.77	0.086	0.120	2.79
108.5	0.048	290	0.290	0.81	0.077	0.069	1.80
124.5	0.16	290	0.270	0.70	0.126	0.200	3.20
130.5	0.25	290	0.270	0.60	0.226	0.270	2.40
135	0.40	290	0.270	0.53	0.296	0.340	2.30
142	0.63	290	0.270	0.41	0.416	0.460	2.22
146.5	0.91	290	0.260	0.33	0.466	0.530	2.29
150.5	1.0	290	0.260	0.27	0.526	0.580	2.25
155	1.6	290	0.260	0.20	0.596	0.620	2.09

Mean = 2.30×10^{-13}

Standard Deviation = 0.058×10^{-13}

4. Dependence of BQ on Temperature

In principle all the figures in Tables 1, 2, 3, and 4 can be regarded as results of studies on the temperature dependence of BQ. However, only one experiment was done with this object specifically in mind. The BQ obtained thereof are recorded in Table 6.

Table 6 - Dependence of BQ on Temperature. Measurements were made at a lower oven temperature of 142.0 ± 0.5°C.

Vapour Temperature °C.	BQ volt sec
145	2.03×10^{-13}
158	1.98
182	1.82
187	1.98
201	2.09
204	1.93
209	2.09
215	1.93
236	2.09
256	2.02
271	2.02
293	2.13
311	2.07
326	2.17
340	2.07
358	2.17

Mean = 2.04×10^{-13}

Standard Deviation = 0.085×10^{-13}

5. Dependence of BQ on Drum Position

Since it was necessary to know whether a slight change in the monochromator drum setting affected the resulting BQ to any considerable degree an experiment was carried out at fixed lower and upper oven temperatures and different drum settings. The BQ values are given in Table 7. The wavelength range covered in this experiment was 358 - 374 mμ, as obtained from the calibration curve of the monochromator.

Table 7 - Change of BQ with drum settings 358 - 374 mμ at an upper oven temperature of 180 and a lower oven temperature of 140.5°C. The symbols have been defined previously.

Drum reading	Wavelength mμ	R_o volt	$R_o - R_1$ volt	F volt	BQ volt sec
615	358	0.090	0.020	0.040	2.74×10^{-13}
616	360	0.182	0.107	0.046	0.59
617	361	0.119	0.034	0.058	2.34
618	362	0.159	0.058	0.085	1.95
619	363	0.245	0.139	0.135	1.33
620	364	0.378	0.128	0.198	2.12
621	365	0.480	0.140	0.250	2.45
622	366	0.615	0.165	0.290	2.41
623	367.5	0.728	0.208	0.305	2.01
624	369	0.796	0.196	0.300	2.10
625	370	0.796	0.136	0.279	2.81
626	371	0.815	0.135	0.240	2.44
627	372.5	0.695	0.075	0.170	3.11
628	374	0.536	0.006	0.100	22.9

6. Effect of Very Close Control of the Power Supplies on the Value of BQ

For reasons mentioned on page 24 the L & N type K-3 potentiometer was used to control and reproduce precisely the output of the photo-multiplier power supplies. The procedure is described on the same page.

The first set of measurements using this method of output control was obtained at a fixed vapour pressure and different vapour temperatures. The BQ values obtained are tabulated in Table 8.

Table 8 - BQ determined at different upper oven temperatures and at a lower oven temperature of 142 $\pm$ 0.5°C. The voltages of the power supplies were set potentiometrically before each reading.

Vapour Temperature °C.	BQ volt sec	Time min.
147	1.28×10^{-13}	0
159	1.20	20
180	1.24	45
200	1.47	55
213	1.37	
230	1.50	94
253	1.37	110
271	1.38	125
297	1.37	
311	1.43	150
325	1.50	165
342	1.42	178
354	1.35	186

Mean = 1.38×10^{-13}

Standard Deviation = 0.093×10^{-13}

The gradual increase in the values of BQ observed in Table 8 was thought to be a temporal effect due to the time needed for the power supplies to stabilize and for the resistors to heat up to a constant temperature. This guess was encouraged by the previous knowledge of the lack of dependence of BQ on temperature.

To test the above hypothesis it was decided to repeat the experiment at fixed upper and lower oven temperature for a long enough period, as determined by the experiment represented in Table 8. The power supplies would then be left on overnight for maximum stabilization and the experiment would be repeated the following day.

The results are given in Table 9 and Table 10.

Table 10 indicates that after sufficient time has been allowed the values obtained for BQ tend to attain a constant level as indicated by the random distribution and the small standard deviation.

Assuming that with this last modification, i.e., close control of the power supplies, the important variables in BQ determination had come under control the absolute value of BQ at vapour pressure corresponding to $140.5 \pm 0.5^{\circ}C$. and vapour temperature of $202 \pm 1^{\circ}C$. with the fluorescence photomultiplier voltage at 1150 and the transmittance photomultiplier at 700 volts is $(1.24 \pm 0.066) \times 10^{-13}$ volt-sec, where the limits indicate the standard deviation.

Table 9 -

BQ determined at an upper oven temperature of 202.5 ± 0.5°C. and a lower oven temperature of 141 ± 0.5°C.
The voltages of the power supplies were set potentiometrically.

BQ, volt sec
0.910×10^{-13}
1.01
0.98
1.05
1.08
1.11
1.13
1.33
1.25
1.20
1.21

Mean = 1.11×10^{-13}
Standard
Deviation = 0.159×10^{-13}

Table 10 -

BQ determined at upper and lower oven temperatures of 202 ± 1°C. and 140.5 ± 0.5°C., respectively. The power supplies had been left on over night after the data in Table 9 were obtained.

BQ, volt sec
1.20×10^{-13}
1.25
1.24
1.20
1.11
1.21
1.33
1.27
1.30
1.28

Mean = 1.24×10^{-13}
Standard
Deviation = 0.066×10^{-13}

CONCLUSION AND DISCUSSION

1. Characteristics of BQ

From the data obtained in Tables 5 and 6 we can conclude that BQ is independent of pressure and temperature of the anthracene vapour, respectively.

The vapour pressure range for which this conclusion holds is 0.23 mm - 0.91 mm corresponding to a lower oven temperature range of 129.5°C to 146.5°C., the lower limit being imposed by the small size of the fluorescence signal, of $P_o - P_1$, or of both, leading to a large error in the calculated BQ. The upper limit was imposed by a decrease in the absorption depth at higher pressures, or by selfabsorption, causing a decrease in BQ, as seen in Table 5.

The vapour pressures corresponding to different lower oven temperatures were obtained from Figure 8. This plot was prepared from data found in the literature.[12]

The temperature range over which BQ is found to be constant is 145 - 360°C. In this case the lower limit was imposed by the experimental necessity that the upper oven temperature had to be higher than that of the lower oven to avoid condensation of the vapour in the cylindrical part of the cell. The upper limit was chosen to avoid damage to the seal of the cell.

An increase in vapour pressure is expected to cause several

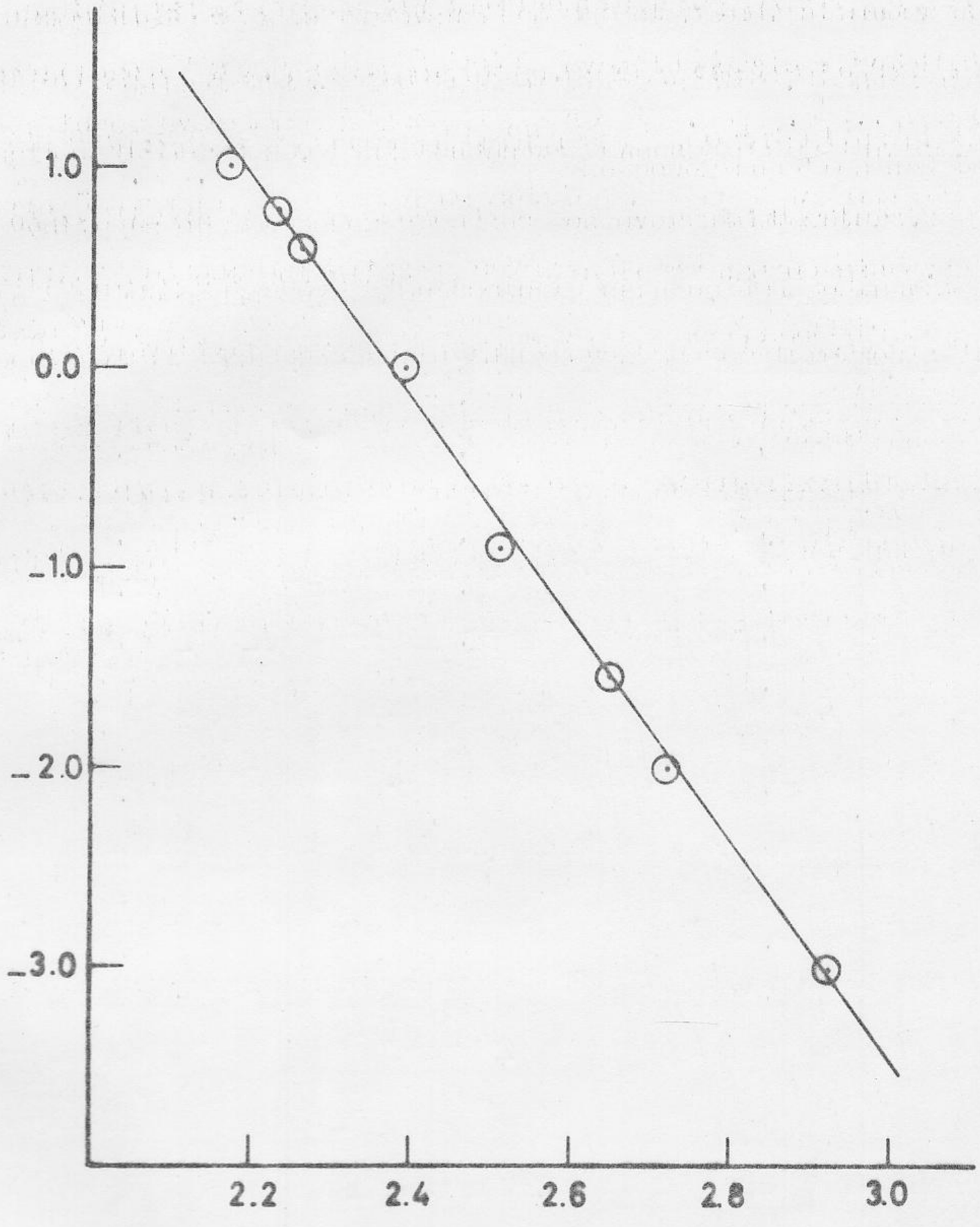

Fig. 8 _ Vapour Pressure _ Temperature Plot

of Anthracene (Ref. 12)

phenomena each affecting B & Q. Among these are reabsorption, collisional deactivation of the excited molecules, and pressure-broadening.

Reabsorption is a process whereby an emitted photon is absorbed in the vapour before it has a chance of leaving the illuminated sample. This process becomes important at pressures high enough to decrease the absorption depth sufficiently, and is expected to cause a decrease in Q, where $Q = \frac{k_f}{k_f + k_s + k_{ST}}$ is the fraction of the excited singlets decaying by radiative transition.

Another consequence of increasing the vapour pressure of the sample is that the rate of collision of an excited singlet molecule may exceed the rate of fluorescence. Thus, the excited singlet will be quenched before it has the chance to fluoresce. This process, like reabsorption, causes a decrease in Q.

A factor that could affect B is pressure-broadening, whereby the fluorescence bands become broader due to high pressure, retaining the same total area. The effect of this phenomenon on B can be seen in Figure 9.[13] While the transmission of the $2.5 \times 10^4 cm^{-1}$ band is not expected to change much by a slight pressure-broadening, the transmission of the $2.6 \times 10^4 cm^{-1}$ band will be influenced greatly because the latter falls on the steep portion of the filter absorption curve so that a slight broadening of the band places it in the high-transmission region of the filter. Thus, in our case, pressure broadening is expected to increase the fluorescence signal and, therefore, lead to a larger B value.

Since B & Q are expected to change in different directions due to

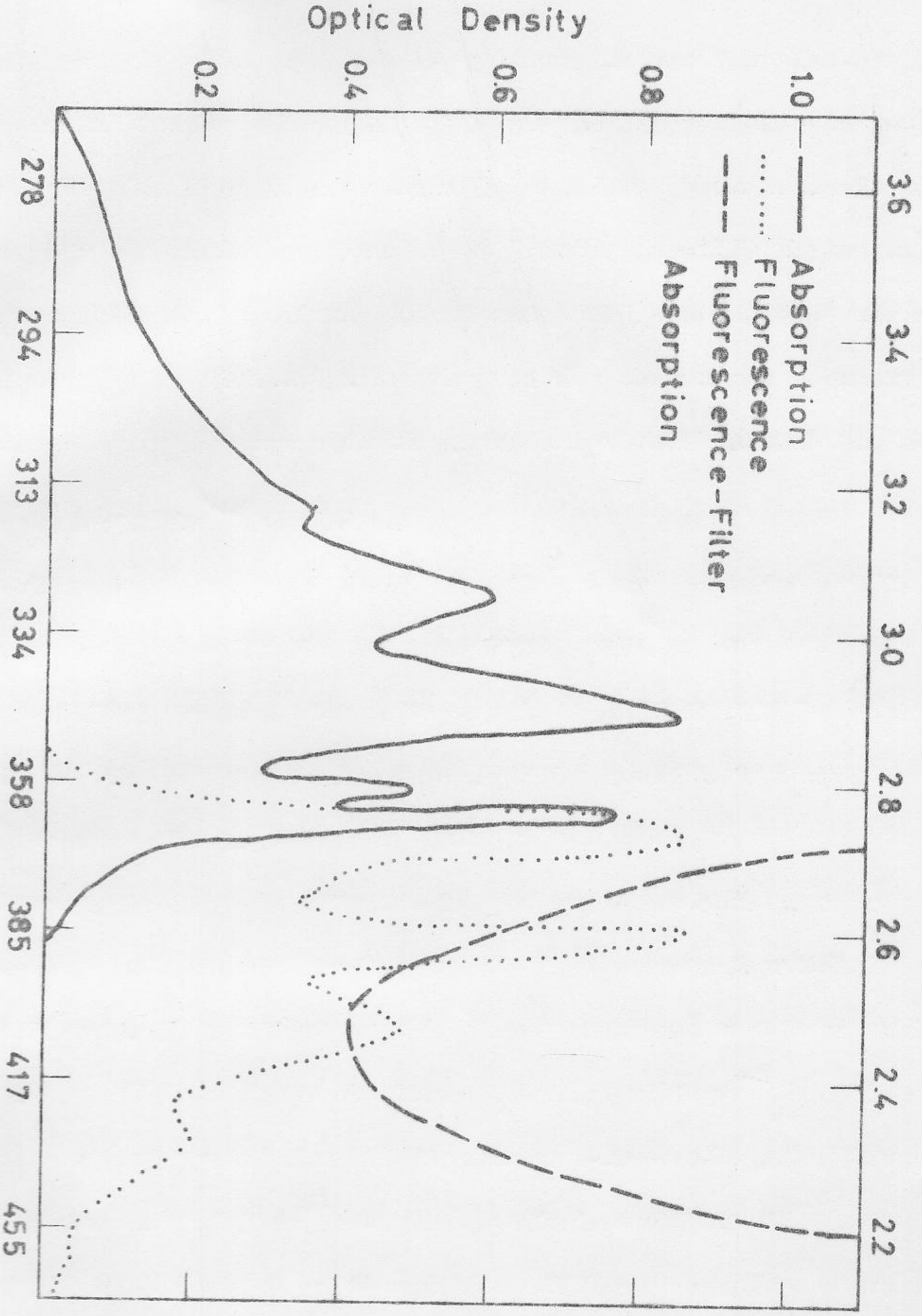

Fig. 9 - Absorption & Fluorescence Spectra of Anthracene (Ref. 13), & Fluorescence-Filter Absorption Curve

increasing pressure and since it is improbable that the rate of change of B & Q with pressure be equal one should expect a variation in BQ as the pressure is increased. However, the maximum pressure employed in the present study is about one mm Hg. At this pressure the collision frequency of a molecule is calculated to be of the order of 10^6 sec^{-1}, for the volume and the maximum temperature used in our case. Comparing this with the lifetime of an excited singlet, i.e., 10^{-8} to 10^{-9} sec it is reasonable to expect that the pressure-induced factors listed above do not operate in the pressure range utilized. So, the experimental result that BQ is constant over the pressure range used is not unreasonable.

The effect of temperature on BQ can be discussed qualitatively with the aid of Figure 10. At a temperature T_1 absorption of light raises the molecule to a certain vibrational level of the excited state. The excited molecule undergoes rapid radiationless conversion to the lowest, or nearly the lowest, vibrational level of the excited state and subsequently returns to the normal state by radiative or nonradiative transition.

When the temperature is raised to T_2 a higher vibrational level of the normal state is occupied by the molecule. Absorption of the exciting light raises the molecule to a higher vibrational level of the excited state, compared with the first case at temperature T_1. The molecule again undergoes rapid radiationless conversion to a lower vibrational level of the excited state but, due to the additional energy in the molecule, the population of the lowest vibrational state will differ. In other words the excited molecule will retain some vibrational energy after its vibrational "cascade", and returns to the ground state from this level

directly.

Several factors can be considered here which might affect BQ.

The rate constant for radiative and nonradiative transition to the ground state could be affected by the starting vibrational level of the excited state. In other words, k_f & k_s could change depending on the vibrational level from which transition to ground occurs. Since

$$Q = \frac{k_f}{k_f + k_s + k_{ST}}$$ a temperature change could, therefore, alter Q.

A second possibility is a change in k_{ST} with temperature. Figure 10 shows two triplet states. If the second triplet were higher than the lowest singlet an increase in temperature would be expected to increase the rate of cross over from the singlet to the triplet level due to the increasing probability of overlap of the vibrational levels of the two states. If this hypothesis were true Q would be expected to show a decrease with an increase in temperature.

The above speculations can be given a more realistic form by the following semiquantitative analysis.

The 0-0 band of anthracene is about 27450 cm^{-1}, as found in the literature.[14] This can also be seen in Figure 9. A comparison of this 0-0 energy with the wave number 2.73×10^4 cm^{-1} of the exciting light used in the experiments shows that the molecules get less than enough energy to be raised to the zero vibrational level of the excited state. However, the band width of the excited light and the thermal excitation of the normal anthracene molecules is large enough to cover the 0-0 gap.

Referring to Figure 9, if the second longest-wavelength absorption

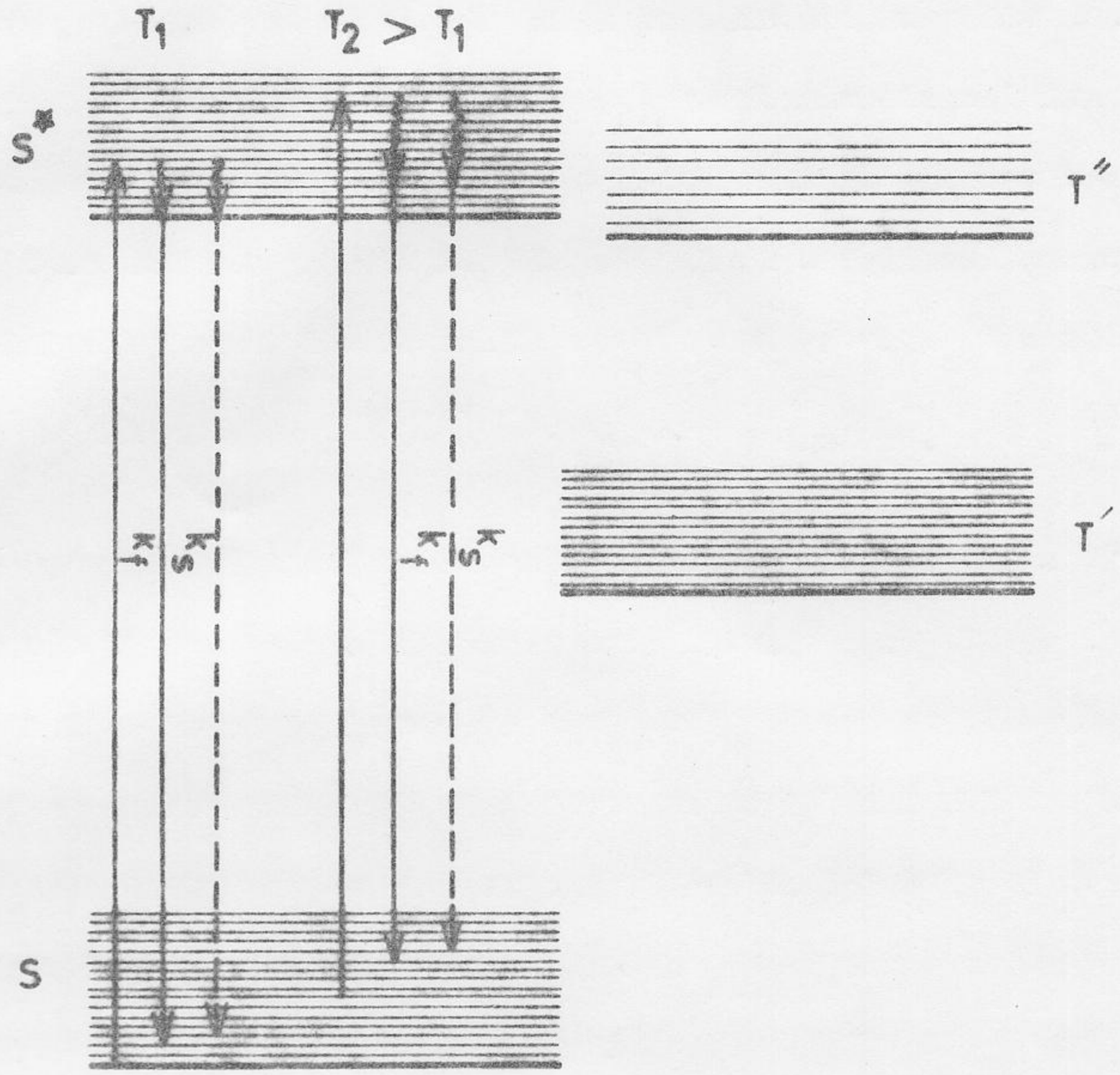

Fig. 10 _ Effect of Temperature on Various Transitions

band is assumed to be due to the transition to the second vibrational level of the excited state, this requires additional energy of about 450 cm^{-1} corresponding to the excited state vibrational level spacing. From this energy difference the relative population of the two levels at certain temperatures can be calculated using the Boltzman equation $\frac{n_2}{n_1} = e^{-\epsilon/kt}$. The value for $\frac{n_2}{n_1}$ is found to be 0.234 at 150°C. and 0.375 at 350°C. This means that an increase of 200°C in temperature raises the fraction of the excited molecules in the first vibrational level from 18% to 27.5%.

Since the temperature range is about the maximum range covered in our case it can be concluded that only the first vibrational level of the excited singlet state gets populated to any appreciable degree as the temperature is raised.

This suggests, therefore, that in the temperature range employed in our experiments almost all transitions to ground are from the lowest vibrational level of the excited state so that k_s & k_f will remain essentially the same over the temperature range.

Considering the factors contributing to B, which are listed in the "Theory" section, the experimental result that BQ is independent of temperature suggests that Q is constant over the specified range, since B is unlikely to change. Since $Q = \frac{k_f}{k_f + k_s + k_{ST}}$, the above conclusions suggest that k_{ST} is independent of temperature as well.

The 3rd conclusion that can be drawn concerning BQ is that it varies with wavelength. This result, givenin Table 7, is surprising because neither B nor Q is expected to change with wavelength. How-

ever, some difference of opinion seems to exist in the literature found on the subject. While Pringsheim[15] mentions that fluorescence yield is independent of wavelength Noyes and Harter report a distinctive dependence of triplet yield of benzene vapour on wavelength.[16] The latter result means, of course, that k_{ST} is strongly wavelength dependent and, hence, so is Q.

However, although its interpretation must be left uncertain pending further information, the above result led to the practice of setting the monochromator drum reading at the maximum intensity of the exciting line at the beginning of each experiment to ensure that the same wavelength was used in all experiments.

2. Factors Affecting BQ

It is explained on page 18 that the dimensions of the light beam should be chosen so as to be in the region of linear response of the Eppley thermopile. Figures 5 and 6 show the thermopile response with height and width of the light beam, respectively. The deviation from linearity observed in both figures for very small dimensions can be attributed to the difficulty of accurate measurement of such dimensions. In Figure 5 another reason could be that since the thermocouple junctions are arranged vertically the height of the beam could be small enough to miss a junction.

Figures 5 and 6 show the limit of linearity of the thermopile response to be 15 mm for the height and 3 mm for the width of the beam, respectively. The actual light beam employed had a height of 16.1 mm and a width of 2.4 mm. Although the height of the beam was somewhat

larger than what it should have been the error induced thereby is negligible since the height used was very close to the linear portion.

Another factor affecting the resulting BQ is the output of the power supplies. This can be seen more clearly when one compares Tables 4 and 6 on one hand with Tables 9 and 10 on the other. The results in the former pair were obtained under similar conditions except that the experiments were performed on different days, the output of the power supplies being controlled by their meters. The data in Tables 9 and 10 were obtained using the potentiometer for controlling the output of each of the power supplies. Also, sufficient time was allowed for the power supplies to stabilize and for the resistors to heat up to a constant temperature.

While the mean BQ values of Table 4 and Table 6 differ from each other by as much as 0.5×10^{-13}, the mean of the BQ values obtained from the last four readings of Table 9 is the same as that of Table 10 which suggests that the exact control of the power supplies, other things being under control, enables one to obtain a reproducible BQ. The fact that only the last four readings of Table 9 attain the mean value obtained in Table 10 can be explained by assuming that only by the end of the experiment had the power supplies achieved stability.

3. Significance of BQ Value Obtained for Further Experiments

In the light of what was said above it can be concluded that although BQ can be determined reliably and reproducibly in a set of experiments its numerical value is subject to so many conditions that no "absolute" value can be determined. It is only under very strict

control of the geometry of the setup, the output of the power supplies and the wavelength of the exciting light that a BQ value can be reproduced from one experiment to another.

Thus, for arriving at reliable values for γ/c, the "flash" and the "steady state" experiments should be performed under identical, or else, calibrated conditions if the BQ determined in the latter is to have any value for calculating γ/c.

BIBLIOGRAPHY

1. C. Reid, Excited States in Chemistry and Biology, Butterworths Scientific Publications, London, 1957, p. 86.

2. Gilbert N. Lewis and M. Kasha, J. A m. Chem. Soc., 66, 2100 (1944).

3. Gilbert N. Lewis and M. Calvin, J. Am. Chem. Soc., 67, 1232 (1945).

4. Peter Pringsheim, Fluorescence and Phosphorescence, Interscience Publishers Inc., New York, N.Y. 1949, p. 435.

5. Richard Williams, J. Chem. Phys., 28, 577 (1958).

6. C.A. Parker and C.G. Hatchard, Trans. Faraday Soc., 59, 284 (1963).

7. C.A. Parker and C.G. Hatchard, Trans. Faraday Soc., 57, 1894 (1961).

8. C.A. Parker and C.G. Hatchard, Proc. Roy. Soc. (London), A 269, 574 (1962).

9. C.A. Parker and C.G. Hatchard, Proc. Chem. Soc., 147 (1962).

10. T. Azumi and McGlynn, J. Chem. Phys., 38, 2773 (1963).

11. A.B. Zahlan, S.Z. Weisz, R.C. Jarnagin, and M. Silver, J. Chem. Phys., 42, 4244 (1965).

12. a) Hans H. Landolt and Richard Bornstein, Zahlenwerte und Functionen aus Physik, Chemie, Astronomie, Geophysik, Technik, Vol. II, Part 2, pp. 100, 152, Springer-Verlag, Berlin, 1950.

. b) C.W. Sears and E.R. Hopke, J. Am. Chem. Soc., 71, 1632 (1949).

13. William R. Ware and Paul T. Cunningham, J. Chem. Phys., 43, 3826 (1965).

14. Hans H. Landolt and Richard Bornstein, Zahlenwerte und Functionen aus Physik, Chemie, Astronomie, Geophysik, Technik, Vol. I, Part 3, p. 65. Springer-Verlag, Berlin, 1950.

15. Peter Pringsheim, Fluorescence and Phosphorescence, Interscience Publishers, Inc., New York, N.Y., 1949, p. 309.

16. W. Albert Noyes, Jr., and D.A. Harter, J. Chem. Phys., 46, 674 (1967).