RATE CONSTANTS FOR THE JABLONSKI MODEL OF ESCULIN IN GLUCOSE GLASS

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CHAPTER I

INTRODUCTION

It has long been known that many complex organic compounds in solution in a rigid glassy medium show two distinguishable emission bands at low temperatures when the compounds are excited by the absorption of light. The bands are characterized principally by the differences in their frequencies of maximum intensity and their mean emission lifetimes. The emission at the higher frequency, "fluorescence", is identified by its spectral position and short mean lifetime as the reverse of the lowest energy normal absorption band. On the other hand, the second emission, "phosphorescence", occurs at a lower frequency than the normal fluorescence band and has a relatively long mean emission lifetime. However, the luminescence of complex organic molecules in rigid glass often includes an afterglow spectrally identical with the normal fluorescence band but having a lifetime identical with that of phosphorescence. Wiedmann and Schmidt (54) were first to find that liquid dye solution showing only fluorescence at room temperature showed an afterglow when the viscosity of the solution was increased by the addition of gelatin. The appearance of such new bands has also been observed in various dyes dissolved in rigid glass or adsorbed on gels. Vavilov and Levshin (52) later verified that the afterglow was an emission spectrally identical with normal fluorescence, but having a relatively long mean lifetime.

The existence of these two types of afterglow led Perrin (37) to propose the use of the name "fluorescence of long duration" for this emission to distinguish it from the former type of afterglow, which was named "true phosphorescence". However, Lewis, Lipkin, and Magel (30) preferred to keep the name phosphorescence and avoided implications by speaking of the alpha and the beta process, respectively. These terminologies along with the definitions of phosphorescence and fluorescence themselves have been the subject of much controversy and confusion in the past.*

An important step in the interpretation of the phenomena connected with luminescence of organic compounds was taken by Jablonski (22), who proposed that every molecule having both fluorescence and phosphorescence possesses two excited states of different energies which he called the fluorescence and metastable states. According to Jablonski's theory, molecules in the normal ground state are excited directly to the fluorescent state on absorption of light. A molecule in the fluorescent state, instead of always reverting directly to the ground

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*Opinions on the definition of fluorescence and phosphorescence are given in Trans. Faraday Soc., 35, 2(1939).

Perrin's proposal for the terminology "slow fluorescence" and "true phosphorescence" has been misinterpreted by many workers. Pringsheim (39) and Lewis et al. (30), for example, regarded "true phosphorescence" as the afterglow spectrally identical with fluorescence, and "slow fluorescence" as the lower frequency afterglow, contrary to Perrin's original proposal.

No discussion of the merits of terminologies concerning the two types of afterglow will be given here, and we will follow the terminology used by Lewis noncommittally.

state with the emission of fluorescence, may undergo a radiationless transition to the metastable state of lower energy than the fluorescent state, which might then revert slowly to the ground state with phosphorescent emission of longer wavelength than the fluorescence bands (beta phosphorescence). The molecules in the metastable state might also be activated thermally into the higher fluorescent state, and then return to the normal ground state with the emission spectrally identical with normal fluorescence, but having a lifetime identical with that of phosphorescence band (alpha phosphorescence). In order for alpha phosphorescence to occur, molecules in the metastable state must first absorb heat and be activated to the fluorescent state; therefore, the alpha phosphorescence should be temperature dependent in contrast to the temperature independent beta process.

Lewis, Lipkin, and Magel (30) showed that the alpha phosphorescence of fluorescein in boric acid glass indeed requires an activation energy close to the energy difference between the excited states of the fluorescein molecule, and speculated on the possibility that the "metastable" phosphorescent state might be a triplet state.* Lewis and Kasha (31), basing

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* As in atomic spectra, the multiplicity of the state, i.e., the number of ways in which the total spin angular momentum can combine with the total orbital momentum, is given by (2S+1), where S is the resultant spin. An excited state is derived by removing one of the electrons from the uppermost filled orbital of the ground state (singlet, due to spins of two electrons of opposite sign) to a vacant orbital of higher energy, and if the spin of the excited electron is conserved in this process, the total spin of the excited state is zero, and the multiplicity is again singlet. However, if the spin of the excited electron is no longer opposed to that of the odd electron left in the original orbital, the total spin is unity, the multiplicity of the excited state becomes three, and the excited state is called a triplet state. Triplet states are paramagnetic, whereas singlet states are diamagnetic.

their argument on the existence of two sets of levels between which transition appears to be strongly forbidden for many molecules, and on consideration of the changed configuration brought about in the "metastable" phosphorescent state, identified the phosphorescent state as the triplet state and phosphorescence as a triplet-singlet emission. Support for this identification was provided by Lewis and coworkers (28, 29) who detected the occurrence of paramagnetism in irradiated sample of fluorescein in boric acid glass. Evans (13) provided the further proof that the paramagnetism arises from the excited triplet state by demonstrating the identity of the decay time constants of prarmagnetic susceptibility and the phosphorescence emission upon extinction of the exciting light. Additional, and perhaps the most conclusive evidence, showing that the forbiddenness of the transition from the phosphorescent state is due to the spin-conservation rule, came from McClure (34), whose work dealt with the relation between atomic spin-orbital interaction energies and beta phosphorescence mean lifetime.

In order to understand the electronic natures of molecules, both in their ground states and in their various excited states, a knowledge of the values of the transition probabilities for the processes taking place is of great importance. The first attempts to determine triplet-singlet transition probabilities were made by measuring the beta phosphorescence mean lifetime (34). This was based on the assumption that non-radiative transitions do not occur between these same two states. Quantum yield measurements by Gilmore, Gibson, and McClure (18), however, indicated that non-radiative processes as well as radiative processes may occur to a considerable extent from

the excited singlet state. The work by these authors provided data with which limits could be set on the values of triplet-singlet transition probabilities. Gilmore and Lim (20, 33) devised a procedure for evaluating the individual rate constants (the respective transition probabilities) for all the radiative processes and rate constants for the non-radiative processes of the Jablonski model. The latter rate constants are the sums, respectively, of all non-radiative processes occurring from each of the two excited levels of the model. Data on fluorescence, alpha phosphorescence, and beta phosphorescence emission are required for the calculation.

The principal objective in present research has been to devise an experimental method to obtain the data needed for such a calculation, and subsequently to evaluate the individual rate constants of the Jablonski model for some excited molecular species. In addition to the immediate objective mentioned above, it was felt that the study of this kind might contribute, in an important way, to the better understanding of the processes by which a luminescent molecule dissipates its energy of excitation.

CHAPTER II

THEORY

A. The Relationship Between Rate Constants and Emmission Data.

Figure 1 shows the model used by Gilmore and Lim (20) in devising the procedure for calculating individual rate constants. The model used is the same as that given by Jablonski except that non-radiative processes are premitted to occur from both the singlet and the triplet states. A similar diagram was used by Koizumi and Kato (26) in their studies of quenching of phosphorescence of organic molecules.

The rate equations for the processes occurring during irradiation in the given model are:

$$N_S' = Q - R_S N_S + k_6 N_T \qquad (1)$$

and

$$N_T' = k_3 N_S - R_T N_T \qquad (2)$$

if all processes are considered to be first order*. Symbols used throughout this section are assembled in Table 1.

The steady-state solutions are readily obtained by setting the derivatives in Eqns. (1) and (2) equal to zero, and solving for N_S

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* As long as composition is held constant, higher order processes are pseudo first order, provided that there is only one excited species undergoing the processes.

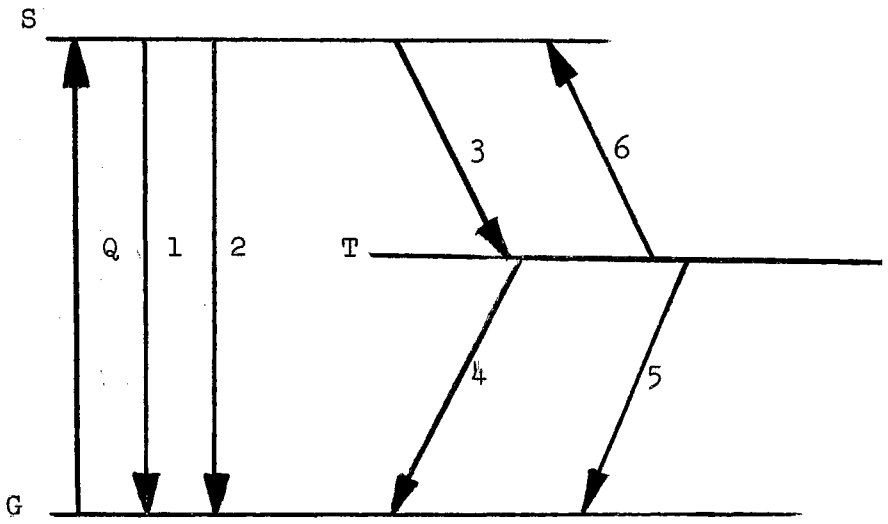

Figure 1

Modified Jablonski model for the electronic transitions of molecules in a rigid glass solution. G, S, and T are the ground, lowest excited singlet, and lowest excited triplet state, respectively; Q is the excitation to the lowest excited singlet state by absorption; 1 and 4 are fluorescence and beta phosphorescence respectively; 2 and 5 are radiationless transition from the lowest excited singlet to ground and the lowest excited triplet to ground respectively; 3 populates T from S; and 6 populates S from T by a thermal process.

Table I

LIST OF SYMBOLS USED

Q = number of quanta absorbed per second.

k_1, k_4 = rate constants for the fluorescence and beta phosphorescence processes respectively

k_2, k_5 = rate constants for the radiationless singlet-ground and triplet-ground transitions, respectively.

k_3 = rate constant for the radiationless singlet-triplet transition.

k_6 = rate constant for the radiationless triplet-singlet transition.

N_S = number of molecules in the lowest excited singlet state.

N_T = number of molecules in the lowest excited triplet state.

t = time, in seconds.

$R_S = k_1 + k_2 + k_3$

$R_T = k_4 + k_5 + k_6$

N_S' = derivative of N_S with respect to t.

N_T' = derivative of N_T with respect to t.

r_1, r_2 = roots of the auxiliary equation.

τ_f = mean lifetime of fluorescence.

$\tau_{\beta P}$ = mean lifetime of beta phosphorescence.

Φ_f = fluorescence quantum yield.

$\Phi_{\alpha P}$ = alpha phosphorescence quantum yield.

$\Phi_{\beta P}$ = beta phosphorescence quantum yield.

P = proportionality constant.

ΔH = heat of activation.

and N_T. The result is

$$N_S = R_T Q \, (R_S R_T - k_3 k_6)^{-1}, \tag{3}$$

and

$$N_T = k_3 Q \, (R_S R_T - k_3 k_6)^{-1}. \tag{4}$$

For the decay process, these equations are reducible to linear, second order, homogeneous differential equations with constant coefficients which can be solved by standard procedures to give for the instantaneous number of molecules in the excited singlet state

$$N_S = Q \left[r_1^{-1}(r_1 + R_T) e^{r_1 t} - r_2^{-1}(r_2 + R_T) e^{r_2 t} \right] (r_2 - r_1)^{-1} \tag{5}$$

and in the excited triplet state

$$N_T = k_3 Q \left[r_1^{-1} e^{r_1 t} - r_2^{-1} e^{r_2 t} \right] (r_2 - r_1)^{-1} \tag{6}$$

where r_1 and r_2 are the roots of the auxiliary equation, and are given by

$$r_1 = -1/2 \left\{ R_S + R_T + \left[(R_S + R_T)^2 - 4(R_S R_T - k_3 k_6) \right]^{1/2} \right\} \tag{7}$$

and

$$r_2 = -1/2 \left\{ R_S + R_T - \left[(R_S + R_T)^2 - 4(R_S R_T - k_3 k_6) \right]^{1/2} \right\} \tag{8}$$

By rearranging the terms within the brackets, factoring the squared terms from the bracket, and applying binomial theorem, the roots may be written as

$$r_1 = -1/2 \left\{ (R_S + R_T) + (R_S - R_T) \left[1 + 2k_3 k_6 (R_S - R_T)^{-2} - 2k_3^2 k_6^2 (R_S - R_T)^{-4} \ldots \right] \right\} \tag{9}$$

and

$$r_2 = -1/2 \left\{ (R_S + R_T) - (R_S - R_T) \left[1 + 2k_3 k_6 (R_S - R_T)^{-2} - 2k_3^2 k_6^2 (R_S - R_T)^{-4} \ldots \right] \right\} \tag{10}$$

Considering the fact that the lifetime of the excited triplet state is usually very much greater than that of the excited singlet state, and since R_S is also greater than R_T by the same factor, it is required that $|r_1| \gg |r_2|$ inasmuch as $r_1 \approx -R_S$ and $r_2 \approx -R_T$ from Eqns. (9) and (10) respectively. The first exponential term in Eq. (5) must therefore be identified with a rapid decay process and the second exponential term

with a slow decay process. For emissions, these processes are the fluorescence and alpha phosphorescence respectively. It is evident that the second exponential term alone is predominant in Eq. (6), and that the emission associated with it is beta phosphorescence.

A measurement of the fluorescence mean lifetime, $\mathcal{T}_f$, gives a good approximation to a value for R_S, since

$$\mathcal{T}_f = -r_1^{-1}, \tag{11a}$$

and

$$r_1 = -R_S. \tag{11b}$$

The constants k_1 and the sum R_T can be found from values for the steady-state quantum yield of fluorescence, alpha phosphorescence, and the beta phosphorescence mean lifetime. Setting $t = 0$ in Eq. (5), one obtains for Φ_f and $\Phi_{\alpha p}$ the following expressions:

$$\Phi_f = k_1(r_1+R_T)r_1^{-1}(r_2-r_1)^{-1} - k_1(r_2+R_T)r_2^{-1}(r_2-r_1)^{-1}, \tag{12}$$

and

$$\Phi_{\alpha p} = -k_1(r_2+R_T)r_2^{-1}(r_2-r_1)^{-1}. \tag{13}$$

Since $|R_T| \approx |r_2| \ll |r_1|$, Eqs. (12) and (13) may be combined to give

$$k_1 = -r_1(\Phi_f - \Phi_{\alpha p}). \tag{14}$$

R_T can then be found by substituting known values of k_1, Φ_f, r_1, and r_2 into Eq. (13), and solving for R_T. The values of r_2 to be used in this operation can be found from the beta phosphorescence mean lifetime by the relationship $r_2 = -\mathcal{T}_{\beta p}^{-1}$.

The root r_2 is approximated more accurately by the use of the first two terms in the bracket of Eq. (10), hence

$$r_2 = -R_T + k_3k_6R_S^{-1} \tag{15}$$

Substitution of the values of r_2, R_T, and R_S into Eq. (15) gives a value for the product k_3k_6. By setting $t = 0$ in Eq. (6), multiplying by K_4

and dividing by Q, one finds for $\Phi_{\beta P}$,

$$\Phi_{\beta P} = k_3 k_4 (r_1^{-1} - r_2^{-1})(r_2 - r_1)^{-1}. \qquad (16)$$

The product $k_3 k_4$ can be calculated by substituting the values for $\Phi_{\beta P}$, r_1, and r_2 into this equation.

One more independent relation required for the evaluation of the rate constants can be obtained if one assumes that the constant k_6 is of the form P. exp(ΔH/ RT), and that the rest of the rate constants are temperature independent.* Differentiating Eq. (15) with respect to reciprocal of the absolute temperature, one obtains

$$dr_2/d(1/T) = (k_6 - k_3 k_6 R_S^{-1}) \Delta H/R. \qquad (17)$$

From a knowledge of ΔH, which is obtainable from spectroscopic data, and a knowledge of the temperature dependence of the beta phosphorescence mean lifetime, one can calculate k_6 with Eq. (17) by using the value for $k_3 k_6$ found from Eq. (15) and the known value for R_S. When k_6 is obtained, solutions for all the rate constants can be found by using the known values of R_S, R_T, k_1, $k_3 k_6$, and $k_3 k_4$.

The aforementioned procedures are summarized in Table 2.

B. Limitations of the Procedure Devised

The method described in the foregoing section can be applied only to systems in which fluorescence, alpha phosphorescence, and beta phosphorescence are all observed. Since the alpha and the beta phosphorescence are excited by absorption of light in the same absorption bands in which the fluorescence is produced, both processes of afterglow

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* This assumption was made by Lewis, Lipkin, and Magel (30) in their work with the temperature dependence of the intensity of alpha phosphorescence. In some instances, this assumption may not be valid (9).

Table II

SUMMARY OF THE PROCEDURES

PARAMETER SOUGHT	EQUATION USED	REQUIRED DATA
R_S	$R_S = -r_1 = \mathcal{J}_f^{-1}$	$\mathcal{J}_f$
k_1	$k_1 = -r_1(\Phi_f - \Phi_{\alpha p})$	$\Phi_f, \Phi_{\alpha p}$, and $\mathcal{J}_f$.
R_T	$\Phi_{\alpha p} = -k_1(r_2 + R_T)r_2^{-1}(r_2 - r_1)^{-1}$	$\Phi_f, \Phi_{\alpha p}, \mathcal{J}_f$ and $\mathcal{J}_{\beta p}$.
k_3k_6	$r_2 = -R_T + k_3k_6/R_S$	$\Phi_f, \Phi_{\alpha p}, \mathcal{J}_f$ and $\mathcal{J}_{\beta p}$.
k_3k_4	$\Phi_{\beta p} = k_3k_4(r_1^{-1} - r_2^{-1})(r_2 - r_1)^{-1}$	$\mathcal{J}_f, \mathcal{J}_{\beta p}$, and $\Phi_{\beta p}$.
k_6	$dr_2/d(1/T) = (k_6 - k_3k_6R_S^{-1})\,\Delta H/R$	$\Delta H, R, \Phi_f, \Phi_{\alpha p}, \mathcal{J}_f, \mathcal{J}_{\beta p}$, and $dr_2/d(\frac{1}{T})$

The values for all the individual rate constants k_1, k_2, k_3, k_4, k_5 and k_6 can be found from the known values of the above parameters.

are, in many cases accompanied by the emission of the fluorescence during the period of irradiation. Which of the two processes prevails in the afterglow is determined by the nature of the compound and the temperature, and does not depend on the nature of the rigid solvent. As a rule, the alpha phosphorescence prevails at or near the room temperature, while the beta process becomes predominant at lower temperature. Therefore, the analysis is limited in use to intermediate temperatures at which these two types of afterglow appear simultaneously.

Since the method makes use of emission data alone, individual rate constants for the non-radiative processes cannot be determined.

The model allows for excitation to the lowest excited singlet state only, otherwise, exact analysis of the model becomes considerably complicated. Experimentally, this means that it is necessary to use an essentially monochromatic light source capable of effecting only the ground to lowest excited singlet state transition. Singlet-triplet and triplet-triplet transitions are excluded in the model for the same reason. Since the phosphorescence of organic compounds represents the emission accompanying the transition of a molecule from an excited triplet state to the ground state (normal singlet state), it follows that the corresponding absorption process, involving a transition from the normal singlet to the excited triplet state should also be observable. Sklar (47) indeed found a feeble absorption band in benzene corresponding to a singlet-triplet transition. The low intensity of such absorption spectra, however, demands long path lengths of concentrated solutions or of the pure liquid for their observation, and even then the detection of such a forbidden transition is possible only with adequate manipulations. The pioneering work in triplet-triplet absorption for organic molecules

is that of Lewis et al. (30), who found that the absorption of fluorescein in boric acid glass was radically changed when the sample was illuminated by a high intensity mercury arc. With an ordinary light source, the detection of such absorption is possible only in the most favorable of circumstances (35).

Despite these deficiencies in the model it has been found that the luminescence phenomena of fluorescein in boric acid glass are, within the limits of the experimental error, quantitatively explained by the Jablonski model (30).

It is also assumed in the model that a molecule is always in the lowest vibrational level of the electronic state that it happens to occupy. As a result, the possibility that a large number of rate constants exist for processes occurring between any two electronic levels is ignored. The rate constant found is probably a weighted average of these. Such an assumption is necessary, however, if theoretical treatment is not to become too cumbersome.

CHAPTER III

EXPERIMENTAL

The quantum yields of fluorescence, alpha phosphorescence, and beta phosphorescence; mean lifetimes of fluorescence and beta phosphorescence; temperature dependency of beta phosphorescence mean lifetime; and heat of activation are required for evaluating the rate constants. Except for quantum yield measurements of alpha phosphorescence, all of the types of measurements required are described in the literature. However, these measurements had as their objective the studies of specific classes of compounds rather than the acquisition of complete sets of data on the types of systems for which the method of analysis worked out in the preceeding section was developed. These earlier measurements are discussed briefly in the sections describing individual measurements.

The experimental program may be largely divided into three general sections: the design and construction of a recording luminescence spectrophotometer, the search for a system to which the method can be applied, and finally, the acquisition of necessary experimental data on the system chosen.

A. Recording Luminescence Spectrophotometer

With the advent of the photomultiplier tube, the direct photometric determination of luminescent intensities was greatly facilitated. Price, Ferretti and Schwartz (38) were among the first to use a photomultiplier in a fluorescence photometer. Soon afterward, several manually operated instruments were described with which one could obtain spectral distributions of the energy in luminescence. In 1951, Klick, Schumacher, and Stokes (25) described an instrument incorporating a Beckman model DU spectrophotometer that would automatically record

luminescence spectra. Bowen (7) has described an instrument in which the detector circuit is sensitive to a chopped emission, the "chopping" being accomplished by the use of a 60 cycle ac source to excite the emission. Other spectrophotometers capable of automatically recording luminescence spectra have been described, and some of these are commercially available. As yet there has been no report in the literature of the construction of an automatic recording spectrophotometer which can be used to record alpha phosphorescence spectra, although such instruments may have been in use. One of the first problems encountered in the present research, therefore, was that of designing and constructing an instrument that would be suitable for the quantitative study of alpha phosphorescence. Since the instrument designed in connection with this research has some features not found in commercially available instruments, the description will be rather detailed.

As was stated earlier, alpha phosphorescence is an emission spectrally identical with that of the fluorescence. As a consequence, the alpha phosphorescence of a compound cannot be studied conveniently in the presence of the fluorescence. The long lifetime of alpha phosphorescence makes it possible, however, to use a phosphoroscope to block the fluorescence and to permit the passage of the alpha phosphorescence. By such a technique Lewis, Lipkin, and Magel (30) isolated the alpha phosphorescence of fluorescein in boric acid glass, and photographed its spectrum with a Hilger model E-2 medium quartz spectrograph.

In the design of the instrument herein described, it was assumed that the use of a phosphoroscope was unavoidable. Photoelectric rather than photographic detection was used because of its inherently high speed, reliability and greater convenience in practice; consequently,

an electronic system responsive to chopped electrical signal was required. Such a system has the advantage of being unresponsive to both dark current and unmodulated light. Because of the nature of the research program, high sensitivity and short response time of the instrument were desired. High sensitivity was achieved by using a monochromator of high optical speed, a photomultiplier tube as a detector, and a square wave amplifier for the electrical signal from the photomultiplier tube. A rectifying circuit in the amplifier permits the use of a high speed strip chart recorder for automatically recording the spectra. The phosphoroscope was designed so that it might be used unchanged in the instrument to record beta phosphorescence spectra and with minor changes to record fluorescence.

A block diagram of the instrument is shown in Fig. 2. A sample placed between the two discs of the phosphoroscope is illuminated by means of an exciting source. The chopped radiation (square wave) from the sample is detected by a photomultiplier tube mounted at the exit slit of the monochromator. The wavelength drum of the monochromator is driven through a variable speed gear which is, in turn, driven by a synchronous motor. The square wave signal from the photomultiplier tube is first returned to an ac amplifier equipped with a bucking voltage control where compensation for the output voltage resulting from hum and noise pickup is made prior to amplification. The adjusted signal is then amplified, rectified and recorded on the strip chart recorder.

The phosphoroscope is a modified Becquerel type (4). It consists of two slotted discs mounted on a common shaft which is rotated at a constant angular velocity. On either disc are five evenly spaced open slots and each slot subtends an angle from the shaft of 27 degrees. For observing either alpha phosphorescence or beta phosphorescence,

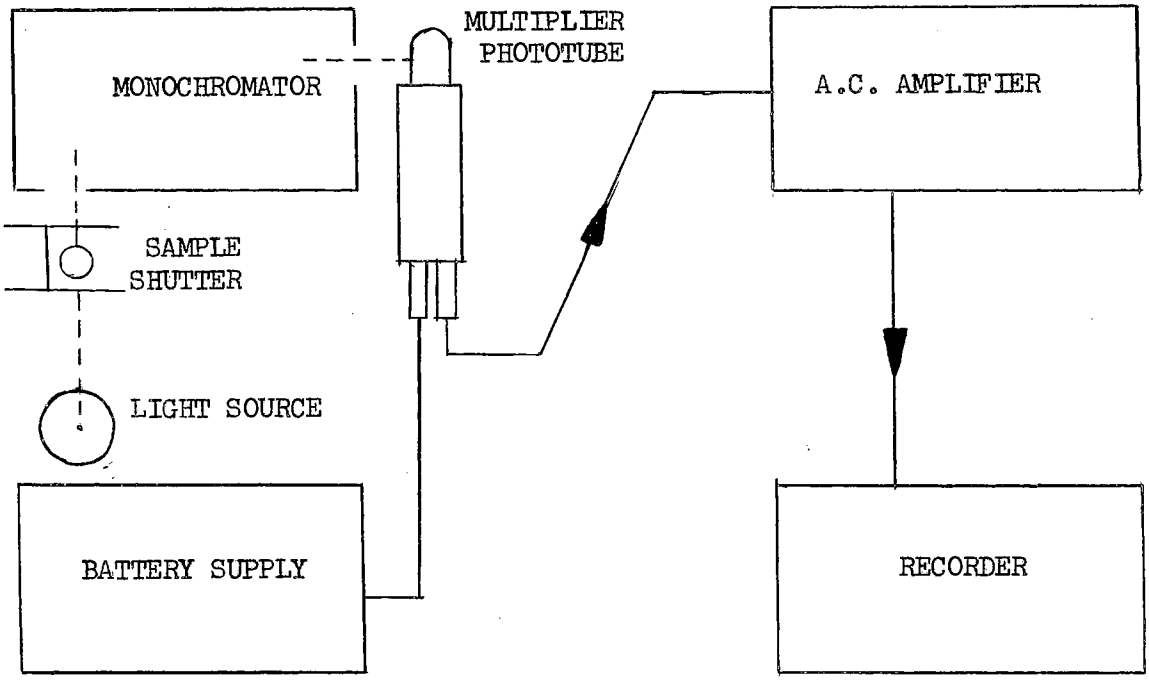

Figure 2

Block diagram of the recording luminescence spectrophotometer.

the discs are so oriented that when the opening in the first disc permits light from the exciting source to strike the sample placed between the two discs, the second does not permit the emission to reach the entrance slit of the monochromator. When the shaft has rotated far enough to permit the luminescence to reach the entrance slit of the monochromator, the sample is cut off from the source by the first slotted disc. In this way, the shutter permits the observation of emission occurring after cessation of the excitation. If it is desired to record fluorescence spectra, the source shutter can either be removed or its slots aligned with those in the second shutter. The phosphoroscope shaft is driven at 1800 rpm by a synchronous motor to give a chopping frequency of 150 cps.

The light source used was a G. E. H85C3 mercury lamp operated on a dc power supply. Light from the capillary was collimated by quartz lenses, filtered by solutions, filter glasses or monochromator when desirable, and then refocused on the sample being studied.

A Bausch and Lomb Model No. 33-86-45 grating monochromator with f:4.4 optics was used without any alteration of its optics. The grating was blazed for maximum efficiency at about 3300A in the ultraviolet.

1P28 and 931A photomultiplier tubes were used as the emission detector in this instrument. Its housing, consisting of a light-tight brass compartment provided with a shutter, is mounted with machine screws to the exit lens mount on the monochromator.

The power supply and switching circuit for the photomultiplier tube is shown in Fig. 3. By means of the selector switch, eight different voltages ranging from 520 to 1180 volts are available to the nine series-connected resistors which divide the voltage for the dynodes.

The circuit diagram for the ac amplifier is shown in Fig. 4. It is two-stage, class A with a diode detector. The output voltage resulting

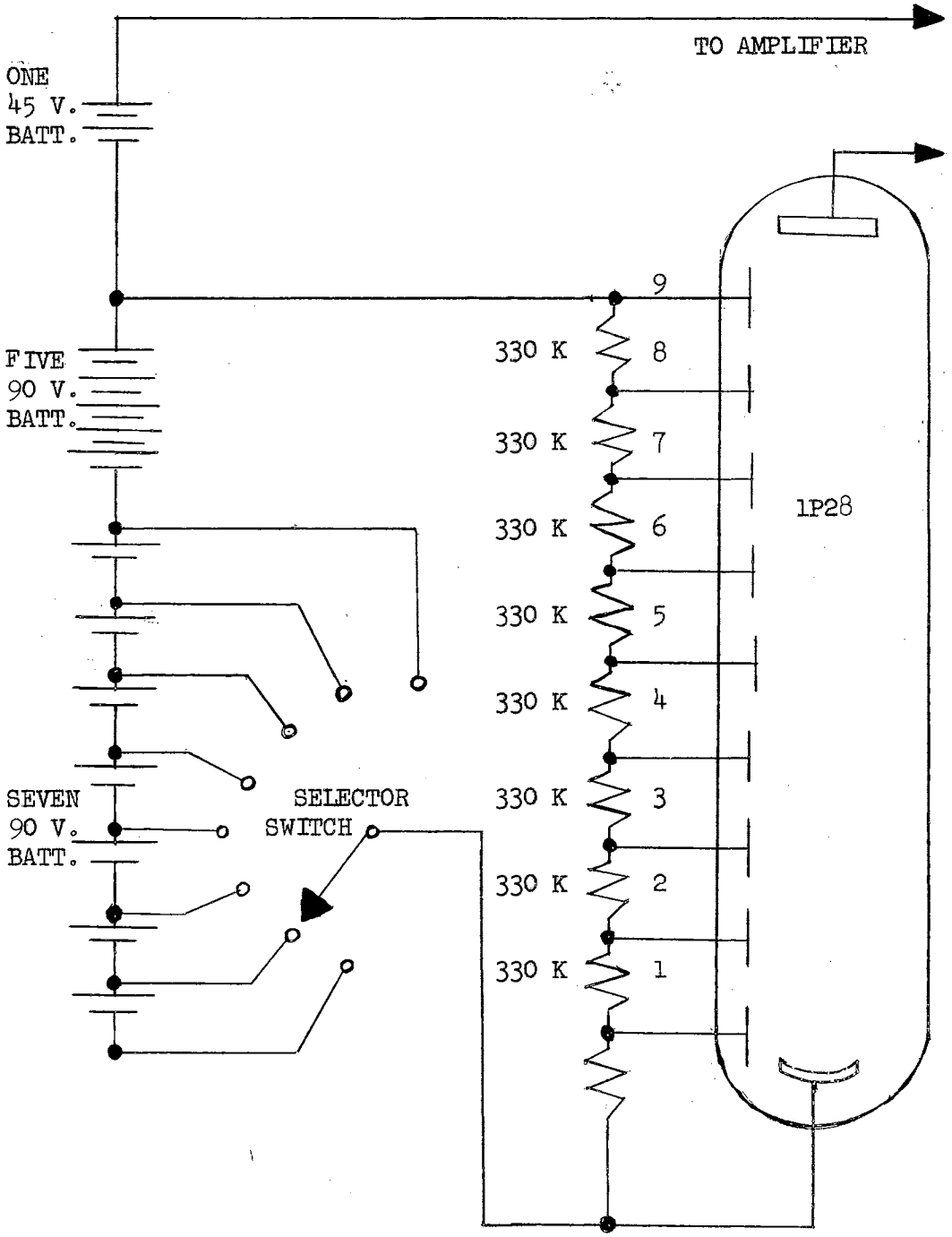

Figure 3

Photomultiplier tube circuit.

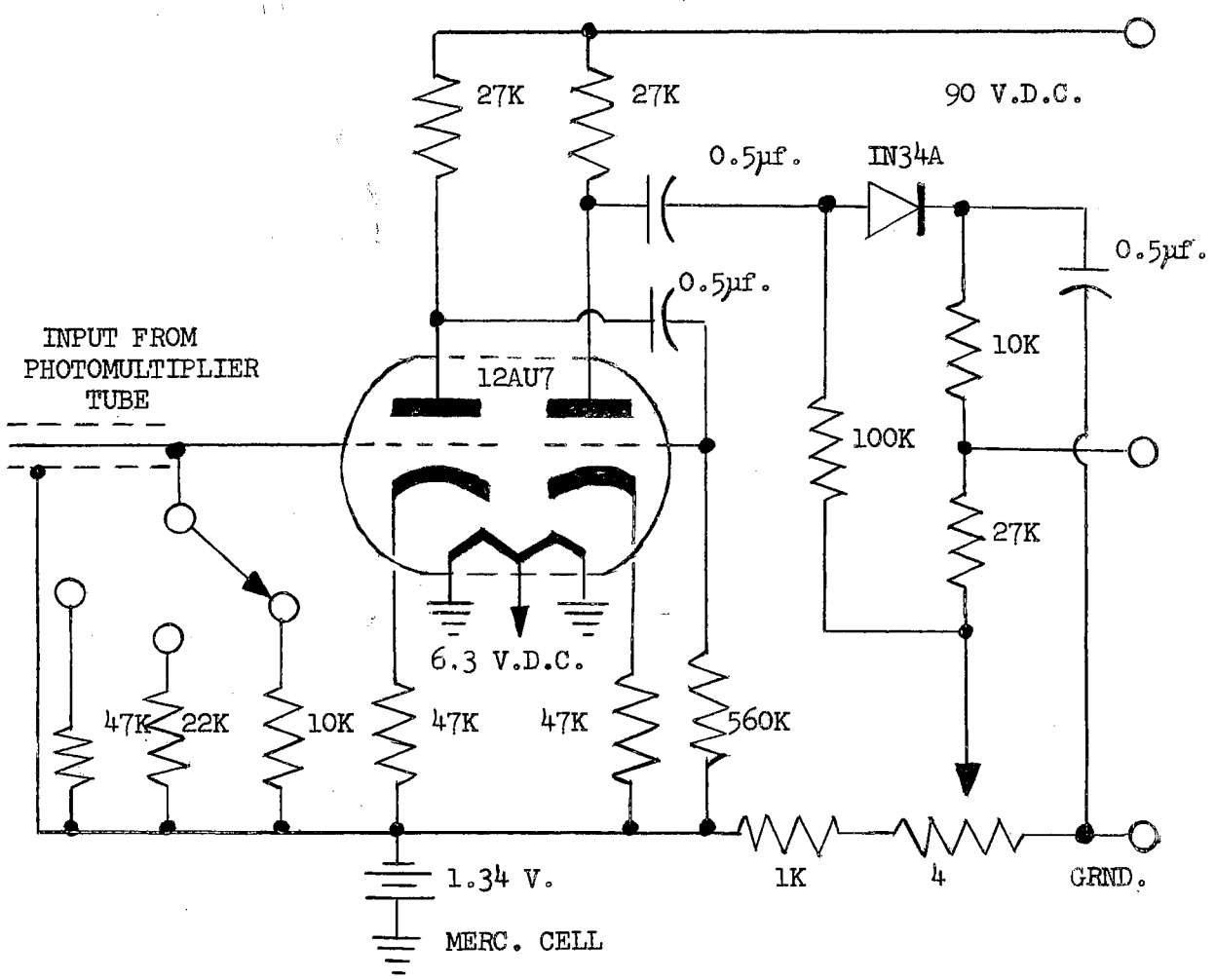

Figure 4

Schematic diagram of ac amplifier.

from hum and noise pickup is cancelled by means of a bucking voltage from the mercury cell applied through the 4 ohm potentiometer. The input selector switch permits the signal voltage to be varied by a factor of three. The amplifier is battery operated throughout and shielded wire is used in the signal circuits to reduce any tendency to pick up 60 cycle hum in the recorder circuitry. It was found that a noisy "B" battery can cause fluctuations of five percent or more in the amplifier output, consquently, periodic checking of noise level in the "B" battery was performed. The tube filament is operated from a 6.3 volt automobile battery. The amplifier gain has shown no measureable variations over a period of two to three months.

The recorder is a Brown "Electronic" high speed potentiometer strip-chart type with a scale span of one millivolt and a two second, full-scale pen travel. The automatic standardizing device and the zero adjust were removed. The amplifier response time has been made less than that of the recorder, so that the recorder limits the rate of response to sudden signal changes.

The dc power supply for the G. E. H85C3 lamp is shown in Fig. 5. The regular lamp ballast is used to step up the line voltage. The circuit shown provides about 250 volts dc at about one ampere. The ac ripple voltage is less than 0.1 percent of the dc output voltage under operating conditions.

The wavelength drive mechanism permits the range from 2000 to 7000A to be scanned in as few as 4 minutes or as many as 160 minutes. Motion is transmitted from a specially constructed gear box through a large brass gear fitted to the monochromator wavelength drive shaft. A simple manual shifting device on the gear box permits one to select the desired

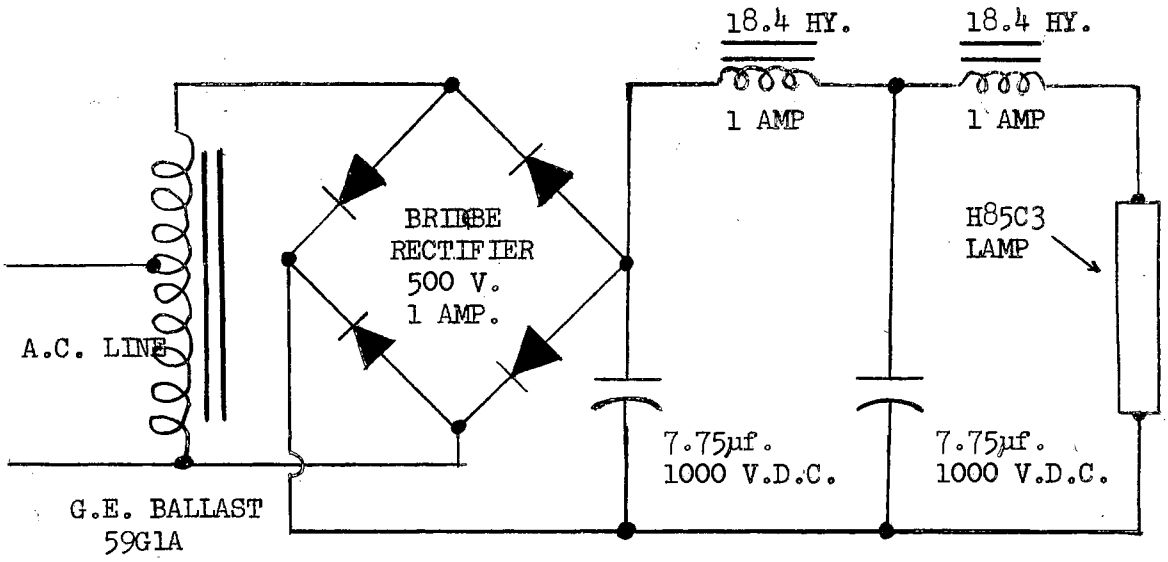

Figure 5

Power supply for the G.E. H85C3 mercury lamp.

scanning rate from the seven rates available. The gear box is driven by a one rpm synchronous motor.

Full scale deflection is obtained on the recorder with a 0.1 millivolt 150 cycle square signal input to the amplifier. The response of the combination amplifier-recorder is linear to within two percent over the entire span of the recorder.

The instrument response to the 3650A group of mercury lines was determined. These lines fall near the wavelength of maximum sensitivity for the 1P28 photomultiplier tube, and near the wavelength of maximum efficiency for the monochromator, so that the measurements provide information on the optimum performance to be expected. Checks were made to see whether infrared radiation was passed by the filter but none was found. The filtered radiation was attenuated by reflection from two diffuse reflector blocks (MgO), the second of which was placed at the focus of the monochromator condensing lens. With 95 volts per dynode stage, it was found that a source emitting $1.5 \pm 0.5 \times 10^7$ quanta per steradian per second would produce a signal of 0.1 millivolts on the recorder with negligible noise.

The instrument is approximately 100 times as sensitive as it is when operated as a detector of unmodulated emission. In the later case, the voltage drop across the anode resistor of the photomultiplier tube is recorded directly by the recorder.

B. Materials Used

The need for a rigid medium cannot be emphasized enough because phosphorescence, usually, is a property characteristic of such media. The function of the rigid glass solution was discussed by numerous workers in the field (23, 30, 34) and the general conclusion drawn

from these discussions is that the rigid medium used as a solvent serves mainly to prevent diffusion-controlled quenching of the triplet states. Lewis and Kasha (32), however, stressed the fact that if the intrinsic mean lifetime of the triplet state were short enough, triplet-singlet emission would be observable even in the liquid and gaseous state. Experimental support for this statement came from the occurrence of strong triplet-singlet emission in biacetyl vapor (1, 32). Robinson (44) also reported luminescence spectra of vapors involving triplet-singlet emission. In such cases, it is believed that short lifetime of the triplet state allows emission to occur without complete quenching.

A large part of the luminescence work at low temperatures has been with a mixture of ether, isopentane, and ethyl alcohol in the ratio of 5:5:2 by volume (E.P.A.) and a mixture of isopentane and methyl-cyclohexane in the ratio of 1:4 by volume (IM_4) as the solvents. These solvents set to rigid glasses at 77°K and have good transmission characteristics. Another popular solvent at low temperatures is glycerol, which becomes rigid at 193°K. At room temperature, boric acid glass and glucose glass have been, by far, the most well known and frequently used solvents. The boric acid glass phosphors are frequently prepared by heating crystalline boric acid previously mixed with the desired amount of phosphorescent compound until about 90% of the combined water is driven off. The glucose glass, whose preparation is to be discussed later, is prepared from anhydrous dextrose by a somewhat similar method. It is known, however, that boric acid glass is not satisfactory because the glass has a faint blue phosphorescence of its own, and because of its high melting point (185°C). Not very many phosphorescent compounds are sufficiently stable to withstand decomposition during preparation of a melt of the compound in boric acid. The use of glucose glass, too, has been limited

because of its poor transmission characteristics in the ultraviolet and its relatively high melting point.

Owing to this circumstance and the fact that no other glass suitable for luminescence study at room temperature has been reported in the literature, it was the full intent from the beginning of this research to spend time on finding suitable solvents which would set to rigid glasses at or near room temperature. It was felt that such a rigid glass was necessary in order to observe alpha phosphorescence.

Since all of the solvents that have been known to form rigid glasses at room temperature contain several hydroxyl groups, it was decided to undertake, first of all, a systematic study of high molecular weight hydroxy compounds and mixtures of these with each other or with other compounds. Experiments indicated that it is relatively easy to obtain compounds or mixtures of compounds that will form satisfactory glasses at temperatures at approximately $0^{\circ}C$ and below, but those forming such glasses at temperatures above $0^{\circ}C$ are not readily available.

It appeared that in order to obtain compounds that would form rigid glasses at room temperature, a considerable amount of organic synthetic work would be necessitated. Since it was impractical to do such synthetic work in our laboratory, it was decided to discontinue the search for such compounds. It was decided to use glucose glass despite the fact that it does not have all the desirable properties.

After the choice of the rigid glass solvent had been made, it was decided to obtain the emission spectra of several different compounds so that proper choices could be made from those for a test of the theory. The necessity for choice does not imply that the theory applies in only a relatively few cases, but rather that the limitations of the apparatus

and of the rigid glass were the controlling factors in these experiments. The Bausch and Lomb monochromator in the recording luminescence spectrophotometer is equipped with a grating which covers the region from 2000 to 7000A in the first order and, therefore, it is necessary that emission bands of the compound fall in this region. Poor transmission characteristic of the glucose glass below 4000A and its high melting property impose still further limitations on the choice of the compound. It is necessary, too, that the compound has the necessary number of measurable emission data, i.e., fluorescence, alpha and beta phosphorescence.

Of several substances tested, the first one found to satisfy the requirements was esculin. At room temperature, this compound showed all three required emissions in the required wavelength range (4000 - 7000A), and its solubility in glucose glass was satisfactory. It was therefore decided to proceed with the experiments by making use of this compound.

C.P. grade esculin from Pfanstiehl Chemical Company was used without further purification throughout this research.

The glucose glass was prepared by the following method. Reagent grade, crystalline, anhydrous dextrose obtained from Baker Chemical Company was purified by the method of Hudson and Dale (21). The purified anhydrous dextrose was heated in a test tube immersed in a paraffin bath until the dextrose crystals melted (m.p. 146°C). The viscous liquid thus obtained was then maintained under a vacuum at 155-160°C. for about two minutes, in order to eliminate bubbles of air or water vapor. When the liquid had become clear, air was admitted and the sample was allowed to cool.

The samples of esculin in glucose glass were prepared similarly from the purified dextrose previously mixed with the desired amount of

esculin by the use of the procedure described above. All the samples of esculin in glucose glass used in the present research were 10^{-3} molal solutions. In our earlier preparations the glucose glass showed very poor transmission at 3650A, owing to a small amount of decomposition at the higher temperatures and numerous minute bubbles in the glass. By the use of a good vacuum line the time required to eliminate bubbles was shortened and decomposition of the dextrose was consequently minimized. In addition, the dextrose was purified immediately before starting the preparation of the glass. With this procedure excellent samples of clear, colorless glass were prepared and transmission characteristics of the glass did not vary from sample to sample, as was the case with the earlier preparations.

The optical density vs wavelength for a typical clear, colorless glucose glass is given in Fig. 6.

C. Heat of Activation

Lewis, Lipkin, and Magel (30) calculated the heat of activation corresponding to the excited triplet-excited singlet transition for fluorescein in boric acid glass to be 8.4 kcal per mole from the slope of the line obtained by plotting the logarithm of the reciprocal of the alpha phosphorescence lifetime against the reciprocal of the absolute temperature. This was in satisfactory agreement with spectroscopic value of 9 kcal found for the difference in energy of the excited singlet and triplet states, which may be derived from the difference between the frequencies of fluorescence and beta phosphorescence band. The results of the two methods, however, do not always agree. The heat of activation obtained from the relation between the logarithm of the

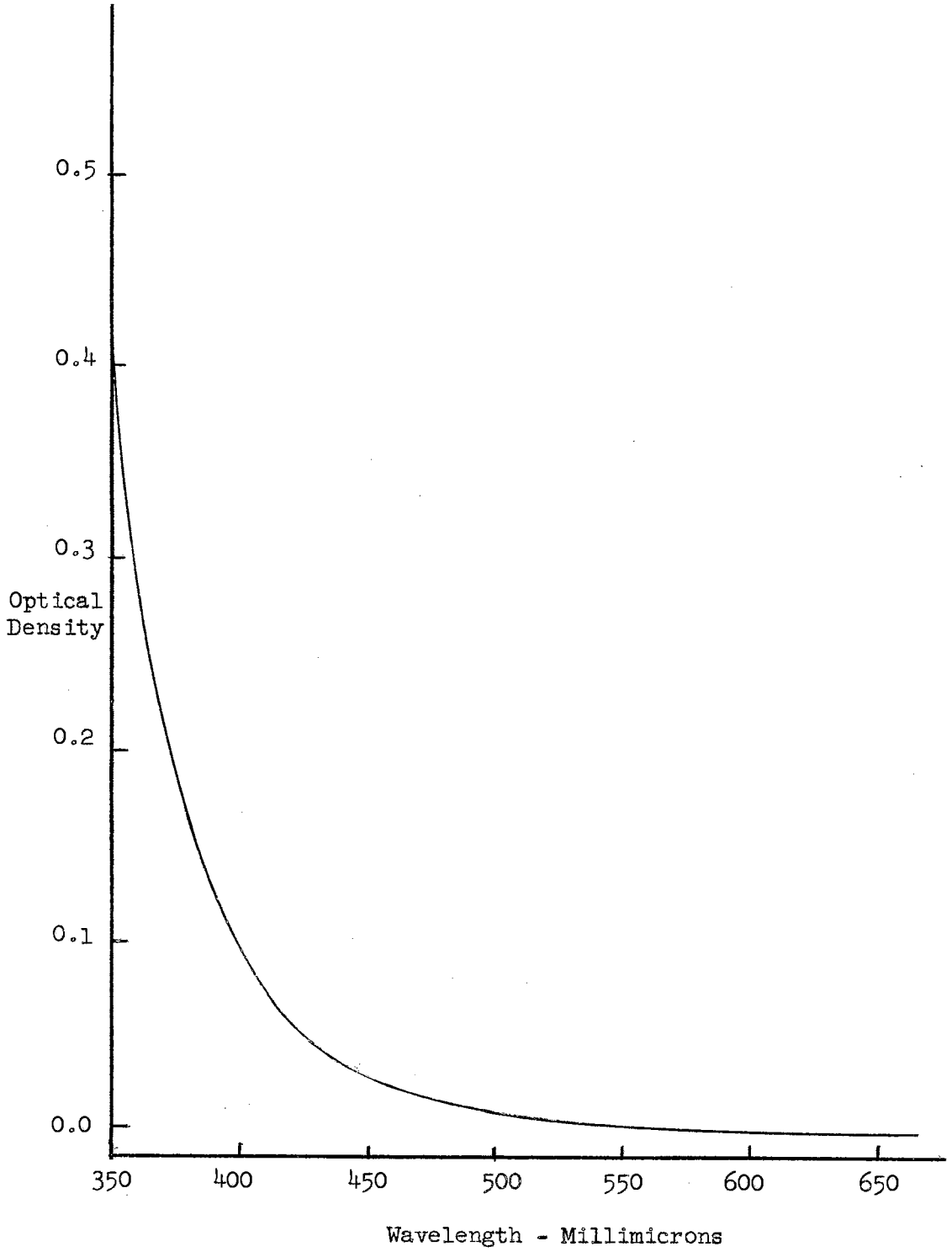

Figure 6

The absorption spectra of glucose glass, taken on DK-1 Recording Spectrophotometer

reciprocal of the alpha phosphorescence lifetime and the reciprocal of the absolute temperature cannot be more than a rough approximation, and there is also some uncertainty involved in the derivation of heat of activation from the difference in the frequencies of fluorescence and beta phosphorescence bands. Values of the heat of activation obtained from spectroscopic data are correct only if the singlet-triplet and the triplet-singlet transitions occur with greatest probability between the nonvibrating level of a singlet state and a vibrating level of a triplet state of the same energy.

Lewis and Kasha (31) reported that the best estimate of the actual energy of the excited singlet state is obtained by averaging the two frequencies corresponding to the first absorption band and the fluorescence band, and multiplying by hc, where h is the Planck's Constant and c is the velocity of light. For the triplet state, however, the spectra corresponding to the singlet-triplet absorption are not, in general, available and an analogous estimation of the energy of the triplet state is not possible for most of the compounds. According to these authors, the best estimate of the energy of the triplet state can be expressed as

$$E_T = hc(\bar{\nu}P + \Delta\bar{\nu}) \qquad (18)$$

where $\bar{\nu}p$ is the frequency at which the phosphorescence band of greatest intensity has its peak and $\Delta\bar{\nu}$ is the half width of that band.* In a similar manner, if the frequency of the fluorescence band alone is known, the energy of the excited singlet state can be best estimated by adding the half-width of the fluorescence band to the frequency at its peak intensity and multiplying by hc.

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* The half-width of a band is defined as the width (in $cm.^{-1}$ usually) between two points whose intensities are half that of the maximum intensity.

In the present study, the heat of activation for esculin in glucose glass was obtained from spectroscopic data by the method of Lewis and Kasha (31).

The recording luminescence spectrophotometer was used unaltered to record the spectra. The light source was a G. E. H85C3 mercury lamp and a quartz monochromator was used to isolate the 3650A mercury line.

D. Beta Phosphorescence Mean Lifetime and Its Temperature Dependency

The first detailed study of triplet-singlet emission lifetimes of complex molecules in a rigid glass solution was published by McClure (34). He measured lifetimes by the use of a mechanical phosphoroscope, a photomultiplier tube as a detector, and a cathode-ray tube as an analyzer. The anode resistor of the photomultiplier tube was connected directly across the vertical plate of a cathode-ray tube. The mean lifetime was calculated by analyzing the photograph of an oscilloscope trace, the vertical component of which is proportional to the phosphorescent light intensity, while the horizontal component consisted of a linear sweep. A comprehensive empirical study of phosphorescence mean lifetimes was subsequently published by Dikun, Petrov, and Sveshnikov (12), and followed by Pyatnitskii (41). Skarsvag (46) and Van Roggen et. al. (49) recently described an improved apparatus for phosphorescence lifetime determinations.

Apparatus and Procedures

In our present study, a method similar to the one used by McClure was employed. Figure 7 shows schematically the geometry of the experimental arrangement together with the photomultiplier circuit.

Since visual observations indicated that the phosphorescence lifetime of esculin in glucose glass is greater than three seconds,

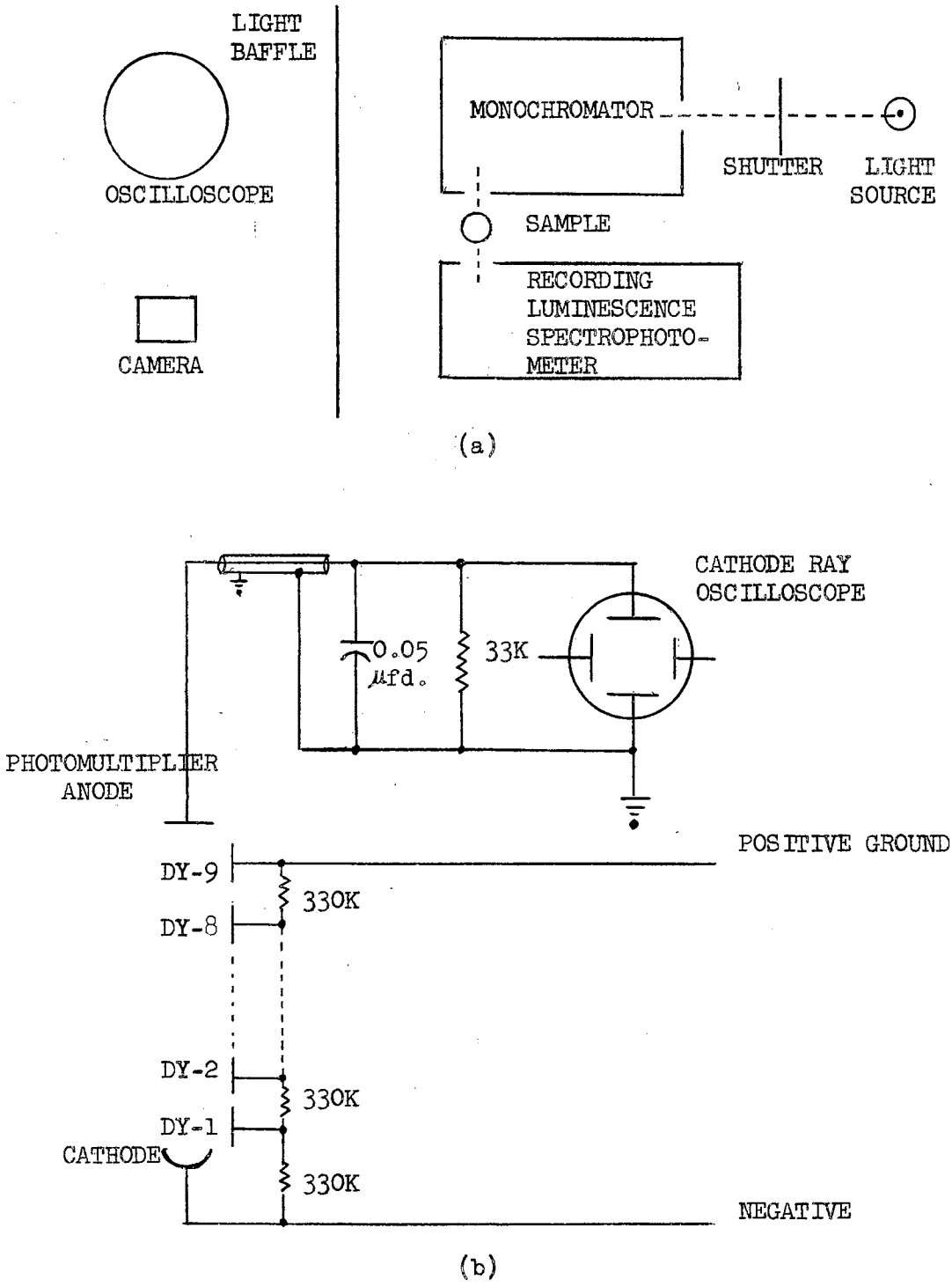

Figure 7

Schematical diagram of the experimental arrangement (a), and the photomultiplier circuit (b), used for the beta phosphorescence mean lifetime determinations.

the phosphoroscope was not employed, and instead, a manually operated shutter was used to block the exciting light during tracings of the decay curves. A Hewlett-Packard cathode-ray oscilloscope, model 130A, was used in observing the photomultiplier tube signal. The oscilloscope has a sweeptime ranging from 1 microsecond per centimeter to as slow as 5 seconds per centimeter, and no special timing markers for the oscilloscope screen were necessary. In all experiments, the exciting radiation was the 3650A group of mercury lines and the wavelength of the receiving monochromator in the spectrophotometer was set at 5500A where the phosphorescent emission has its maximum intensity.

With the shutter open, the spot was set in the lower left-hand corner of the screen on the scope, and the attenuators were adjusted so that the decay curve would cover as much of the screen as possible when the shutter is closed.

Using a small half-silvered pyrex Dewar and a pyrex sample tube, mean lifetimes of esculin in glucose glasses were studied at room temperature, at dry ice-acetone temperature, and at liquid nitrogen temperature.

Glucose glass cracks at temperatures lower than -40°C, but the comparison of mean lifetimes of esculin in cracked and uncracked glasses at room temperature indicated that the mean lifetimes are not affected by cracking of the glass.

E. Fluorescence Mean Lifetime

Experimentally, fluorescence lifetimes have been determined by the use of a fluorimeter. It is, in principle, nothing else than modifications of the Becquerel phosphoroscope. Instead of mechanical shutters used in the phosphoroscopes, the fluorimeters employ

electro-optical shutters. Several types of fluorimeters have been described in the literature (3, 10, 17, 48).

In addition to the development of these fluorimeters, there have also been theoretical equations developed by which the decay period of luminescence may be computed. For two given states, there is a symmetrical relationship between the transition probability for the absorption and that for the corresponding emission process. Thus if the absorption is forbidden, so is the corresponding emission process to an equal extent. In the absorption process, forbiddenness shows up as a low extinction coefficient for the transition in question. Forbiddenness in emission, on the other hand, shows up as a long lifetime for the emission in question provided that there is no alternative to the radiative transition to the lower state. Thus it is to be expected that a relationship should exist between the extinction coefficients for a given transition in absorption and the lifetime for the same transition in emission. Quantitatively, this relationship is

$$\int \epsilon d\bar{\nu} = 3.47 \times 10^8 \frac{1}{\bar{\nu}_A^2 n^2} \frac{g_u}{g_l} \cdot K, \qquad (19)$$

where ϵ is the molar extinction coefficient, $\bar{\nu}_A$ is the wavenumber, in cm^{-1}, of the absorption maximum, n is the refractive index of the medium, g_u and g_l are the multiplicities of the upper and lower states respectively, and k_l is the rate constant for fluorescent emission process and is related to the natural lifetime for the emission, τ_N,* by

---

* The natural lifetime corresponds to the observed mean lifetime of the excited species when emission of radiation is the sole process by which the excited state is deactivated. If other deactivation processes compete with the emission, the observed mean lifetime is shorter than τ_N.

the equation: $\tau_N = 1/k_1$. Eq. (19) is given by Lewis and Kasha (32), and differs only by the refractive index term from the equation derived by Ladenberg (27), who made use of the Einstein theory of equilibrum between radiation and matter. The equation, which was originally deduced for isolated atoms, is valid only when the absorption and emission bands are single, very narrow, and coincide in frequency. The luminescence spectra of organic molecules do not, in general, fulfill these conditions. Nevertheless the equation, when used for the calculation of lifetimes of luminescent organic molecules, is apparently quite reliable (11, 32).

An apparatus capable of measuring fluorescence mean lifetime was unavailable in this laboratory during the period of this research. An alternative plan of using the natural lifetime to calculate R_S from equation (14) was adopted. The natural lifetime was obtained by performing the required integration over the absorption band for the singlet-singlet transition of lowest energy.

Apparatus and Procedures

The intrinsic fluorescence mean lifetime was evaluated from Eq. (19) in the present work. The Beckman Automatic Recording Spectrophotometer, Model DK-1, was used to record the absorption spectra.

Poor transmission characteristics of glucose glasses in the ultra-violet region necessitated the use of a solvent other than glucose glass for the absorption measurement. The use of a solvent

other than glucose glass will undoubtedly lead to error in the calculated lifetime, but this error seems to be much less than the uncertainty introduced when glucose glass was used as the solvent. Glycerol was chosen because its chemical composition resembles that of glucose. Curtin reagent grade glycerol was used.

F. QUANTUM YIELDS

The experimental determination of absolute luminescence yields has proved difficult, and few reliable results have been published.

Vavilov (50) was the first to measure absolute fluorescence yields for dye solutions by the use of a visual photometric method. His technique was to compare the intensity of the fluorescing solution with that of a plate smoked with magnesium oxide, assumed to be a perfect scatterer obeying the cosine emission law. These comparisons were made for small wavelength intervals, covering the entire fluorescence band, and the total fluorescent intensity was obtained by summation. Bowen and Sawtell (8) modified Vavilov's method by introducing a light integrating fluorescent screen, a device which fluoresces with the same intensity when excited by an equal number of quanta, independent of wavelength of the exciting light. The use of this method, therefore, eliminates the necessity for summation over wavelength and simplifies the measurement of the absolute fluorescence quantum yields. Unfortunately, its use, however, is limited to the 2450-4400A region. A more direct method for measuring the absolute yield was that of Almy and Gillette (2), who determined the absolute yield for biacetyl vapor by measuring the light absorbed in a small volume and the fluorescence emitted from this volume in a small solid angle. The total fluorescence was computed by integration over all directions.

In all of the aforementioned measurements it was assumed that the fluorescence was emitted isotropically. It is known, however, that if the degree of polarization of fluorescence radiation differs from zero, the angular distribution is not uniform throughout the solution. Forster and Livingston (14) used an integrating sphere to measure quantum yields of the fluorescence of chlorophyll solutions. Such a sphere is merely a spherical shell coated on the inside with a highly reflecting matt surface. The substance whose energy emission was to be measured was placed in the center of sphere, and the brightness of a portion of the sphere wall was determined by means of a thermopile. It has been demonstrated (45) for such a system that the brightness of the wall is related simply to the total light emitted by the central object. Therefore, the use of an integrating sphere eliminates, in principle, errors due to nonuniform distribution of the fluorescence radiation and avoids the laborious mathematical integrations required in earlier methods.

The first report on the absolute yield of beta phosphorescence was made by Gilmore, Gibson, and McClure (18), who determined absolute quantum yield of fluorescence and beta phosphorescence for a number of organic molecules dissolved in a rigid glass (EPA) at liquid nitrogen temperature. Their method resembled that of Vavilov.

Quantum yield measurements of alpha phosphorescence have not previously been reported in the literature.

The method used in the present research is, in principle, similar to the one used by Forster and Livingston but it differs from theirs in one important respect; namely, a recording emission spectrophotometer was incorporated into the apparatus. In addition to the convenience

brought about, such procedure eliminates some difficulties encountered in the former method, namely, that of finding suitable filters when the fluorescence and absorption bands or the fluorescence and beta-phosphorescence bands overlap. Such overlap occurs with esculin in glucose glass.

The Theory of the Integrating Sphere

The theory of the integrating sphere, also called the ulbricht sphere, has been extensively treated in the literature (45, 53), and only a brief discussion will be made in this section.

Suppose that a light source of luminous flux F is suspended in a closed sphere of total area S; this luminous flux will then produce an average illumination F/S on boundary surfaces. If the reflection factor of the sphere wall is ρ, a part of the original luminous flux, ρF, will be reflected and distributed over the space, thus producing an average illumination of $\rho F/S$. Again, part of this second incident flux F is reflected, resulting in an illumination of $\rho^2 F/S$, and so on. The total average illumination for multiple reflection is thus found to be

$$E = F/S(1 + \rho + \rho^2 + \ldots) = F/S(1/1-\rho) \ldots (20).$$

In deriving this equation it is assumed that the direct light from the source reaching the wall is not screened. If the direct light from the source should fall on the observation window, the illumination on the window would then depend on the luminous intensity of the light source in the direction of the window and thus on the light distribution of the source and the position of the source with respect to the window. In integrating spheres, therefore, the direct light in the direction of the window is screened off, so that one needs only to consider the illumination produced by light that is reflected at least once

inside the sphere. For the mean indirect illumination symbolized by "E", then, Eq. (20) becomes

$$E_i = F/S(\rho/1 - \rho)... \qquad (21)$$

Now, if we put:

$$\rho/S(1-\rho) = k$$

Eq. (21) becomes

$$E_i = kF \qquad (22)$$

Thus, the indirect illumination measured at the observation window is directly proportional to the total light-flux radiated by the light source in the sphere.

Essentials of the Method

The quantum yield of luminescence is defined as the ratio of the number of quanta emitted as luminescence to the number of quanta absorbed under steady state condition. It follows, therefore, that the determination of the quantum yield requires measurements of the relative numbers of quanta involved in these two processes.

The method employed in the present research can be described on general lines in reference to Fig. 8. I represents the integrating sphere. The cell containing the sample to be studied was placed at C, the center of the sphere. The spherical quartz condensing lens focused the image of the exciting source through an illuminating aperture O_1. Screen S ensures that no light reaches the observation aperture O_2 directly from the cell. Radiation reflected at least once in the sphere before reaching the opening O_2 was chopped by means of a shutter before it entered the recording luminescence spectrophotometer.

In order to measure the luminous flux resulting from absorption of the exciting light in the cell containing the sample, the cell was

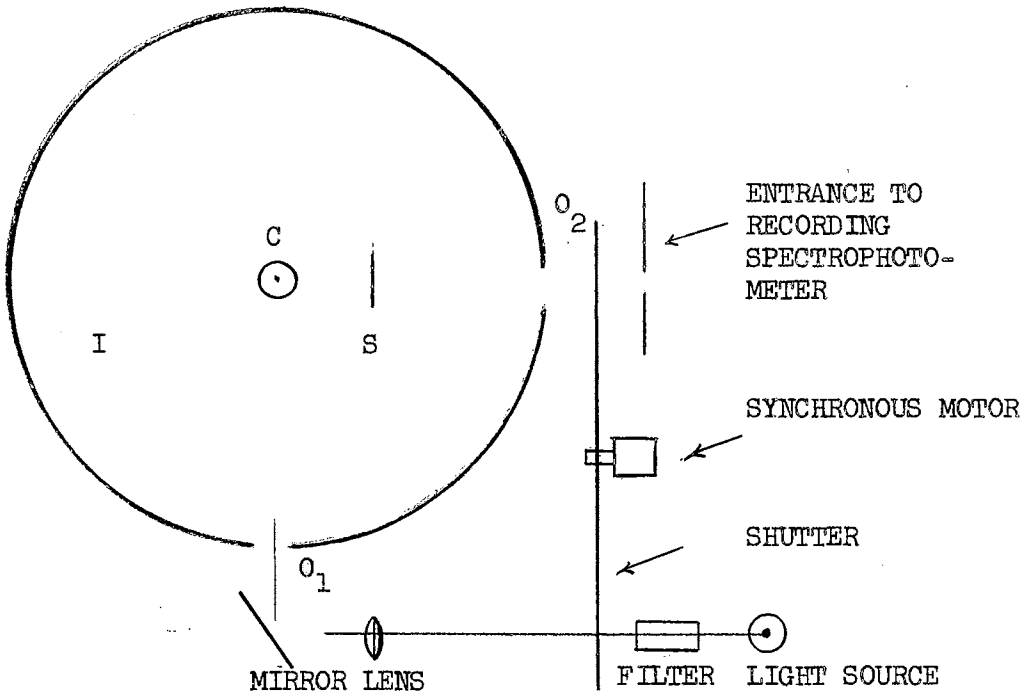

Figure 8

Apparatus for measuring luminescence yields

placed in the center of the sphere and the spectrophotometer response was measured by scanning with the spectrophotometer over the wavelength range of the exciting light. Next, a cell containing only solvent was substituted and the spectrophotometer response again measured. In each case, the exciting light entering the sphere may be divided into two parts; namely, the light reflected by the cell and other fittings in the sphere and the light transmitted through the cell. The amount of light reflected by the cell and other fittings should be the same for both cells when the two cells are of identical dimensions. The difference between the two spectrophotometer responses, therefore, measured the absorption of light by the sample. Since the intensity of the transmitted light will be greater for the cell containing only solvent, the difference in spectrophotometer response may be considered as a light source emitting a negative intensity in the direction toward the rear of the sphere. Thus, it is possible to apply the theory of the integrating sphere to the absorption measurement described above. The difference in the two spectrophotometer responses, R_E, should then be related to the light flux absorbed by the sample, F_E, by

$$R_E = C_E F_E$$

where the subscript E refers to light having the wavelength of the exciting beam. The parameter C_E is not only a function of the reflectance of the sphere wall at a particular wavelength but also a function of the relative spectral response of the recording luminescence spectrophotometer. It is necessary, therefore, to obtain a spectral sensitivity curve for the spectrophotometer - integrating sphere combination before emission data can be used for calculating quantum yields. The relative energy distribution curve is obtained by correcting the spectrophotometer

response at both the exciting and emitting wavelengths by use of the spectral sensitivity curve. The energy, A_E, corresponding to the difference in the two spectrophotometer responses corrected for spectral sensitivity may then be related to the light flux absorbed in the sample by

$$A_E = KF_E$$

where the parameter, K, is independent of the wavelength. The methods used to obtain relative spectral energy distribution curves are described in detail in a later section under the heading of "Calibration of the sphere-monochromator-phototube combination".

To take a measurement of luminescence emission, the cell containing the sample is placed in the center of the sphere and the spectrophotometer response is obtained by scanning over the entire wavelength region of the luminescence spectra. Since the solvent does not have any emission, the spectrophotometer response can be taken as a measure of the radiation coming from the sample. The sample cell may then be regarded as a light source emitting a positive intensity somewhat uniformly in all directions. The total energy, A_L, corresponding to the relative energy distribution curve of luminescent emission may also be related to the total light flux emitted as luminescence by the sample in the following manner:

$$A_L = \int P(\nu)d\nu = KF_L$$

where $P(\nu)$ is the ordinate of the relative energy distribution curve at a particular wave number ν, and the intergration is carried over the entire energy distribution curve.

By definition the energy yield of luminescence φ is

$$\varphi = \frac{F_L}{F_E},$$

$$= \frac{\int_\nu P(\nu)d\nu}{A_E},$$

and the quantum yield $\underline{\Phi}$ then becomes,

$$\underline{\Phi} = \frac{\int_{\nu} \frac{P(\nu)d\nu}{\nu} d\nu}{\frac{A_E}{\nu_E}}$$

Description of the Apparatus

The major pieces of apparatus used to measure luminescence quantum yield are as follows: exciting source, integrating sphere, shutter, and the recording luminescence spectrophotometer.

A G.E. H85C3 medium pressure mercury lamp, filtered by a filter train similar to "combination A" described by Kasha (24) furnished a very narrow band of light with a maximum at 3650A.

The integrating sphere was an aluminum shell 16.3/8 inches in diameter constructed from two hemispherical heater mantle shells.* The two halves meet in butt surfaces which were covered with a strip of 3/8 inch felt, the inside edge of the felt being kept flush with the inside spherical surface. Two 1.3/8 inch holes at 90 degrees from one another were cut in one hemisphere. One hole admitted the exciting light and the other served as a receiving aperture for the spectrophotometer. A white screen placed at about one-third of the distance from the center of the sphere to the wall, and on a line between the sample and the exit aperture, kept direct radiation from the cell from reaching the spectrophotometer. The screen was only of sufficient size to shield the source from the receiving aperture, thus minimizing the error caused by the screen (45). Both the cell holder and the screen were secured to the sphere by thin metal rods and the tightening screws in the sphere permitted adjustment of their position.

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* These are purchased from Glas-Col Apparatus Co.

The sphere wall and all the fittings were painted white with one coat of flat white wall paint, followed by two thin coats of magnesium carbonate. The latter was applied as a water paste and then was allowed to dry in the atmosphere. Because of the ruggedness and portability of the resulting coating, this method was chosen in preference to smoked magnesium oxide.

The shutters were of two kinds. The first set, used for both absorption and fluorescence measurements, is a 25 inch plastic disk with four equally spaced slots. Each slot subtends 40° of arc. The second set, used only for phosphorescence measurements, had three equally spaced slots with each slot subtending 40° of arc. Both shutters were painted flat black and were driven by a 1800 rpm synchronous motor. The exciting source and the spectrophotometer were positioned so that when the first shutter system was used the shutter permitted the exciting light and fluorescence to be received by the spectrophotometer. In the same geometrical arrangement the second shutter served merely as a phosphoroscope.

The recording luminescence spectrophotometer employed a RCA 931-A photomultiplier tube as a detector in this experimental work.

Experimental Procedures

Since the procedure involved in the phosphorescence yield determinations differs a little from that used in the fluorescence yield determinations, the outline of the procedures used for these two types of yield determinations will be presented separately as an outline according to the sequence followed in this work.

1. Procedure for fluorescence quantum yield determinations
   a. About an hour before a run was to be made, the amplifier in the spectrophotometer was turned on.
   b. The exciting lamp was turned on ten minutes before the run and allowed to come to a stable condition of operation.

c. The four-slot shutter was mounted to the motor shaft and the shutter was set into motion.

d. The sample cell was placed in position in the sphere.

e. The photomultiplier tube voltage switch was set at a proper position so that the spectrophotometer response to the exciting light would produce nearly half scale deflection on the recorder.

f. The wavelength of the monochromator was set near the exciting wavelength and the wavelength drive and the recorder were set in operation simultaneously so as to cover the region of the exciting wavelength.

g. Similar operations were made over the region of the spectrum in which fluorescent emission occurs.

h. If the response of the spectrophotometer to the fluorescent emission was small compared to the response obtained from the exciting light, the photomultiplier tube voltage switch was set to a higher voltage and the instrument response to the fluorescent emission repeated. This operation was necessary in almost all cases.

i. The sample cell was removed from the sphere, replaced by the solvent cell and the operation "f" was repeated at the same photomultiplier tube setting. The difference in the response of the instrument to the exciting light is taken as a measure of absorption.

j. If two different photomultiplier tube voltage settings were used to record the responses of the spectrophotometer to the exciting and the fluorescent emission, the relative spectrophotometer response to a given light source was determined at the two voltage

settings in order to compare the responses of the instrument to the exciting and fluorescent emission at the same photomultiplier tube voltage setting.

All of the experiments were carried out in a dark room and light baffles were used whenever necessary. Under these experimental conditions, the amount of stray radiation was of negligible order, and no correction for stray radiation was necessary.

2. Procedure for Phosphorescence Quantum Yield Determinations

The procedure used for obtaining the phosphorescence quantum yields was similar to the one just described for fluorescence quantum yields, except that the measurements of the light absorbed and of the phosphorescent light emitted by the sample were determined separately by the use of the two shutters just described. This procedure was necessary because the phosphoroscope does not allow one to measure the fraction of the exciting light absorbed. First, the difference in the spectrophotometer response to the exciting light, when the solvent cell is substituted for the sample cell, was determined by the procedures outlined in the fluorescence yield meansurements. The four-slot shutter was then replaced by the three-slot shutter and the spectrophotometer response to the phosphorescence emission from the sample determined by scanning over the wavelength region in which the phosphorescence emission occurs.

G. Calibration of the Sphere-Monochromator-Phototube Combination

As was stated earlier, the spectral response of the sphere-monochromator-phototube combination is based on two factors: (1) the effect of non-uniform spectral reflectivity of the sphere wall; and (2) the spectral response of the photomultiplier tube.

In the present work, the total correction for all of these effects was made by calibrating the sphere-monochromator-phototube combination

as a unit. It was obtained in the following manner: a standard tungsten filament lamp, of 2200°K brightness temperature, whose spectral energy distribution could be calculated was placed before the illuminating aperture of the sphere, and the response of the recording luminescence spectrophotometer was obtained as a function of wavelength. During the run, the current through the lamp was regulated to a specified value by means of a carbonpile resistor connected in series with respect to the lamp and the voltage source. The voltage source was two 6 volt automobile batteries connected in parallel and the current through the lamp was read from the voltage drop across a 0.01 ohm standard resistor connected in series between the lamp and the resistor. The lamp was allowed to operate for about ten minutes at the specified current before the determinations of the instrument responses were taken. Fig. 9 gives the instrument response to the emission from the standard lamp at 2200°K brightness temperature along with its spectral energy distribution curve. The latter curve was obtained as follows: the true temperature corresponding to the given brightness temperature was computed from the formula given by Worthing (55) and the spectral energy distribution of the black body at that temperature was computed from the Planck's distribution law and plotted. This curve was then multiplied point by point by the spectral emissivity curve of tungsten filament which was taken from the work of Forsythe and Adams (15). The relative spectral sensitivity curve of the recording luminescence spectrophotometer was obtained from Fig. 9 by dividing the instrument response curve point by point by the spectral energy distribution curve. The resulting curve is shown in Fig. 10. The relative spectral energy distribution curve of the luminescent emission was then obtained by dividing the response of the spectrophotometer to the

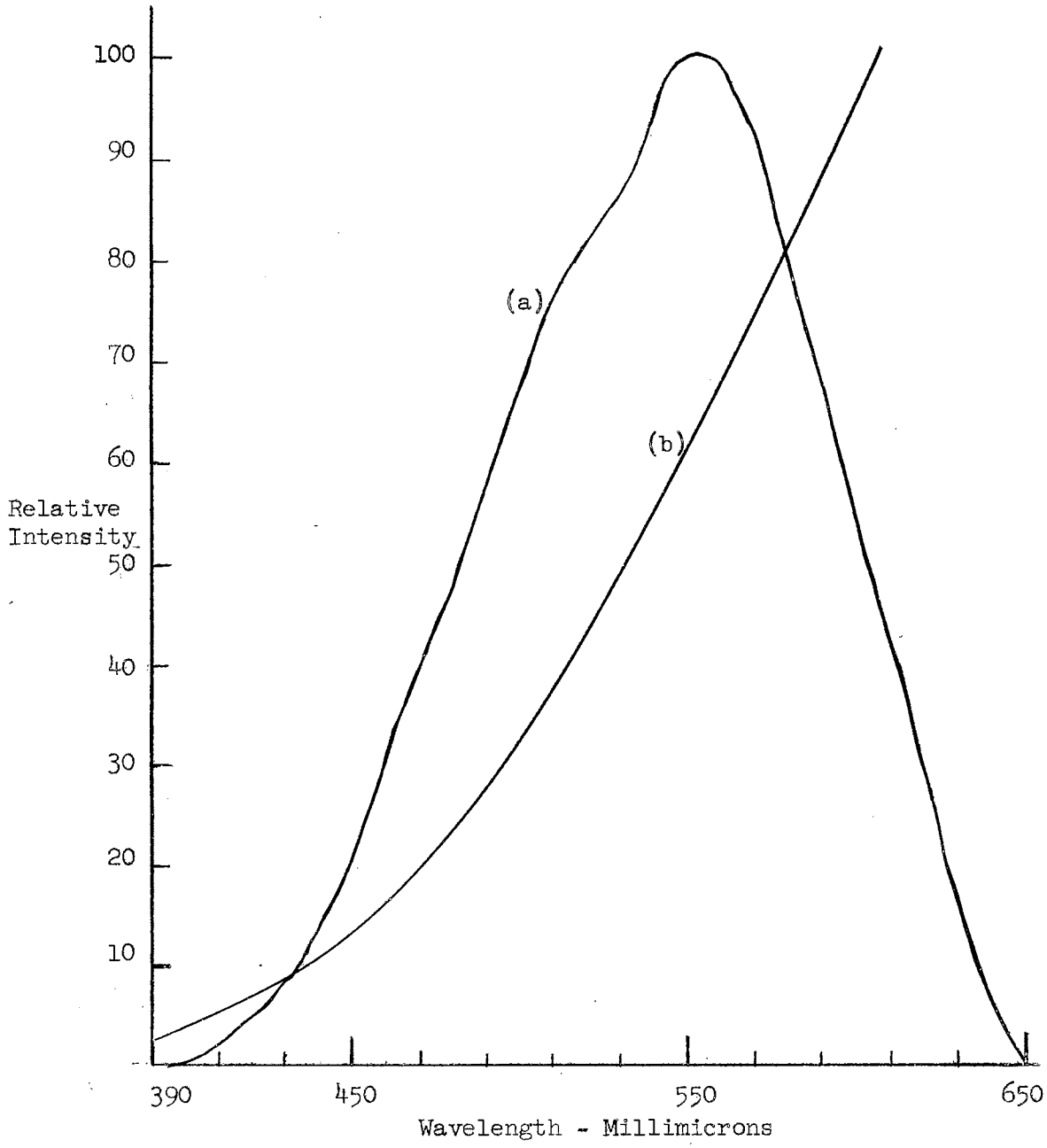

Figure 9

Data for construction of relative spectral sensitivity of the instrument. The instrument response to the emission from the standard lamp at 2200°K brightness temperature (curve a) and spectral energy distribution of the standard lamp at the same temperature (curve b).

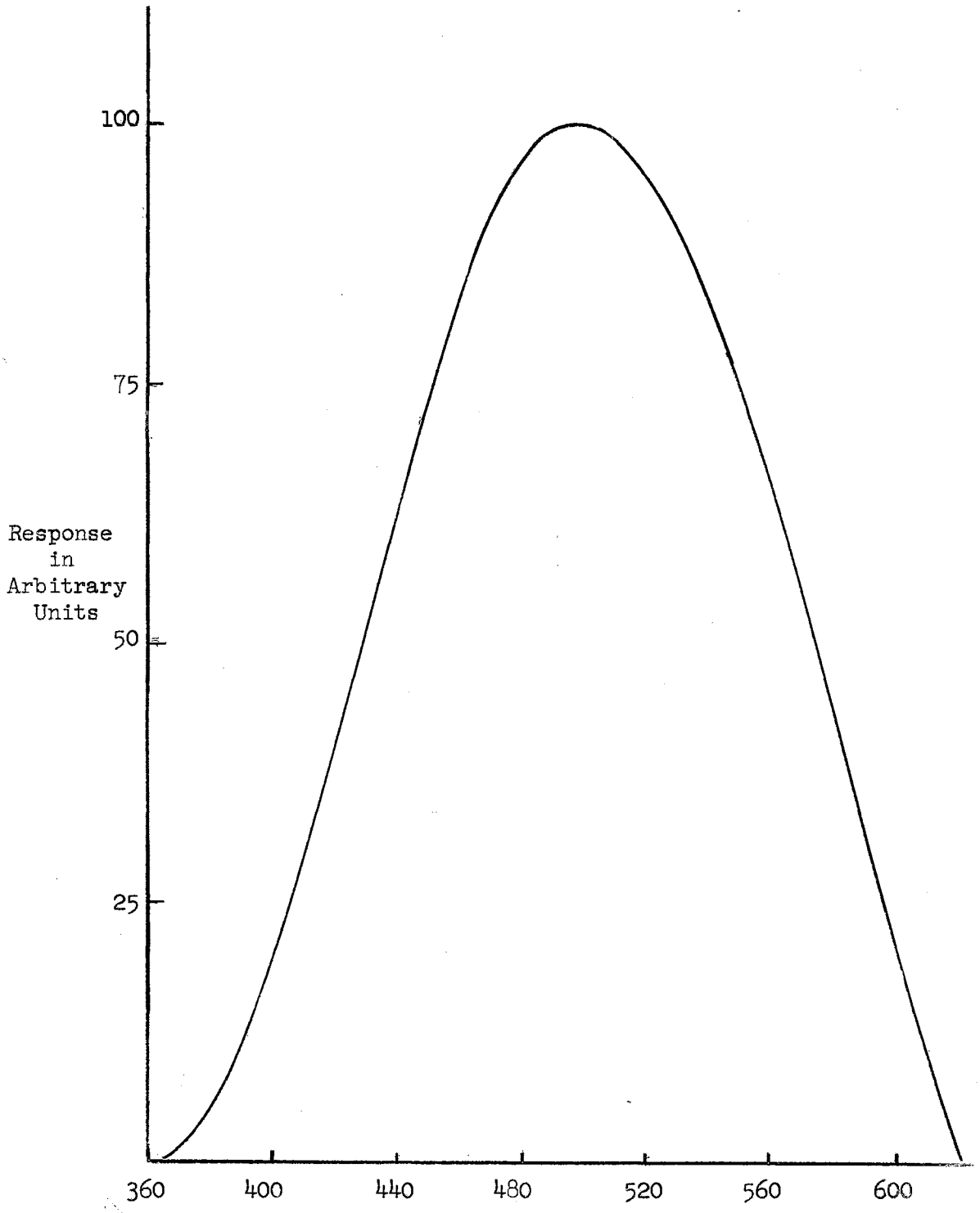

Figure 10

Relative spectral sensitivity of the instrument

luminescent emission by appropriate value of the relative spectral sensitivity of the instrument.

Since the standard lamp used for the calibration has no appreciable emission below 3900A, the procedure just described cannot be used in determining the relative spectral sensitivity of the sphere-monochromator-phototube combination at the exciting wavelength. A relative method, essentially the same as the one described by Gilmore and Knipe (19), was used in order to circumvent this difficulty. The calibration was carried out by comparing the response of the instrument to the response of a thermopile to two different mercury lines. A vacuum thermopile was placed in front of the illuminating aperture of the sphere to intercept the incident beam entering the sphere, and its responses to 4360A and 3650A mercury lines were recorded. The light source was the G.E. H85C3 lamp and a quartz monochromator served to isolate these lines. The thermopile was then moved away and the recording luminescence spectrophotometer response to the same two lines were determined. Under this condition, the sensitivity of the instrument at one wavelength relative to that at the other wavelength can be written

$$S_{4360:3650} = P_{4360} \cdot T_{3650} : P_{3650} \cdot T_{4360}$$

where T refers to the thermopile response and P refers to the instrument response. The result thus obtained showed that the relative spectral sensitivity of the sphere-monochromator-phototube combination was 3.2 times as sensitive at 4360A than at 3650A. Such a difference is to be expected because the response of the entire instrument to a light flux of any given wavelength is proportional to the product of the light flux reaching the phototube and of the spectral response of the photomultiplier tube. The light flux reaching the phototube is proportional to

$$\rho / 1 - \rho$$

where ρ is the reflectivity of the sphere wall.

The 931-A photomultiplier tube has what is designated as S-4 response, and the responses at 3650A and 4360A are the same within five percent (43).

Therefore, the responses of the instrument at these two lines depend chiefly on their relative values of $\rho/1-\rho$. Benford, Lloyd, and Schwarz (5, 6) reported that the reflectance of magnesium carbonate is 0.965 at 4360A and 0.890 at 3650A. On application of the formula, $\rho/1-\rho$, to the result of Benford et al., it was found that the ratio of the instrument sensitivities at these two lines should be about 3.4, in close agreement with the experimental result.

CHAPTER IV

RESULTS AND ANALYSIS OF THE DATA

A. Heat of Activation

The recording spectrophotometer trace of the fluorescence and beta phosphorescence spectra of esculin in glucose glass at room temperature is shown in Fig. 11. Maxima are indicated by pips on the tracing.

In contrast to the result obtained by Pringsheim and Vavilov (40), the lower frequency beta phosphorescence band is greater in its intensity than that of higher frequency band even at room temperature. At the liquid nitrogen temperature, the lower frequency band acquires a higher intensity while the intensity of the higher frequency band diminishes. At this low temperature, the phosphorescent emission undoubtedly occurs from or near the zero-point vibrational level of the lowest triplet state. The higher frequency band observed in the beta phosphorescence spectra must therefore be due to the emission from vibrational levels of the lowest triplet state. Consequently, the energy of the triplet state was calculated from the frequency of the lower frequency band. Since the two beta phosphorescence bands overlap each other appreciably, the half-width of the stronger band was estimated from an exponential curve fitted to the higher frequency side of the stronger band and extrapolated into the region of the weaker band.

In table 3 are given the maximum frequencies of the fluorescence and beta phosphorescence bands, $\bar{\nu}$, along with values of the half-width, $\Delta\bar{\nu}$, from which the energy of each state is calculated. Heat of activation for esculin in glucose glass is given in the last row of Table 3.

Alpha phosphorescence of esculin in glucose glass was found to be spectrally identical with normal fluorescence as expected.

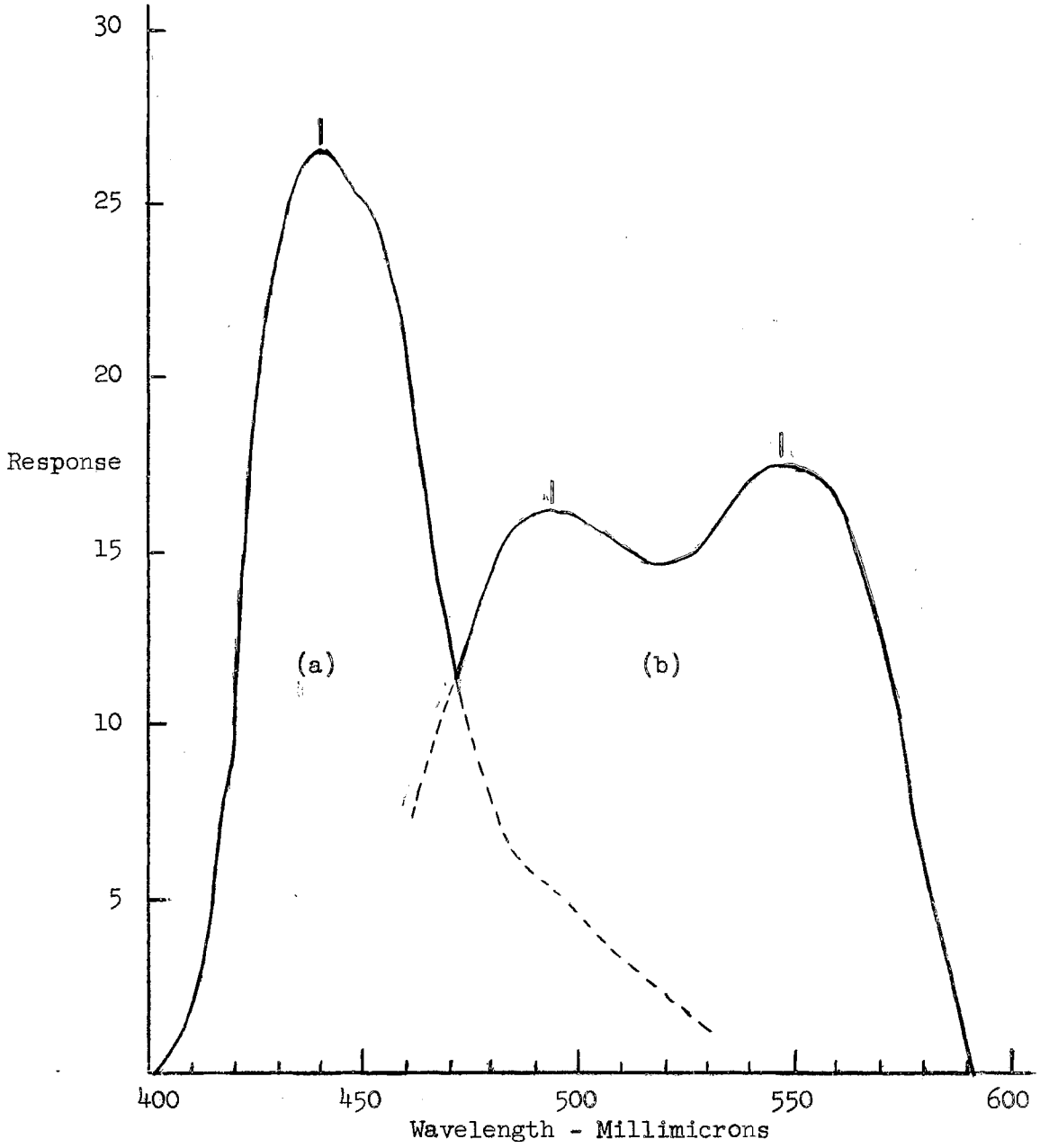

Figure 11

The recording luminescence spectrophotometer tracings of the fluorescence (curve a) and beta phosphorescence (curve b) spectra of esculin in glucose glass at room temperature. The ordinates are in arbitrary units and are not the same for curves (a) and (b).

Table III.

ANALYSIS OF THE ESCULIN EMISSION DATA

	Fluorescence Band	Beta phosphorescence Band
Maximum Frequency, cm^{-1}	22,730	18,250
Half-width, cm^{-1}	2,310	2,120
Energy of the State, Kcal	71.5	58.2
Heat of Activation, Kcal	13.3	

B. Beta Phosphorescence Mean Lifetime and Its Temperature Dependency

Oscilloscope tracings of beta phosphorescence decay curves of esculin in glucose glass at three different temperatures are shown in Fig. 12. Sweep speed of the oscilloscope was set at 0.5 sec. per centimeter.

As was stated earlier, observations show that the phosphorescence intensity of a molecule decays according to the exponential law:

$$I = I_o \exp (-t/\tau_m)$$

where I is the intensity at time t after the removal of the exciting light, I_o is the intensity of the phosphorescent light during excitation, and τ_m, the mean lifetime, is the time required for the intensity to fall to 1/e of its initial value. Thus the intensities at time t_1 and t_2 after the withdrawal of the exciting light can be expressed as

$$I_1 = I_o \exp (-t_1/\tau_m),$$

and

$$I_2 = I_o \exp (-t_2/\tau_m)$$

respectively. From these two equations, the mean lifetime, τ_m, can be

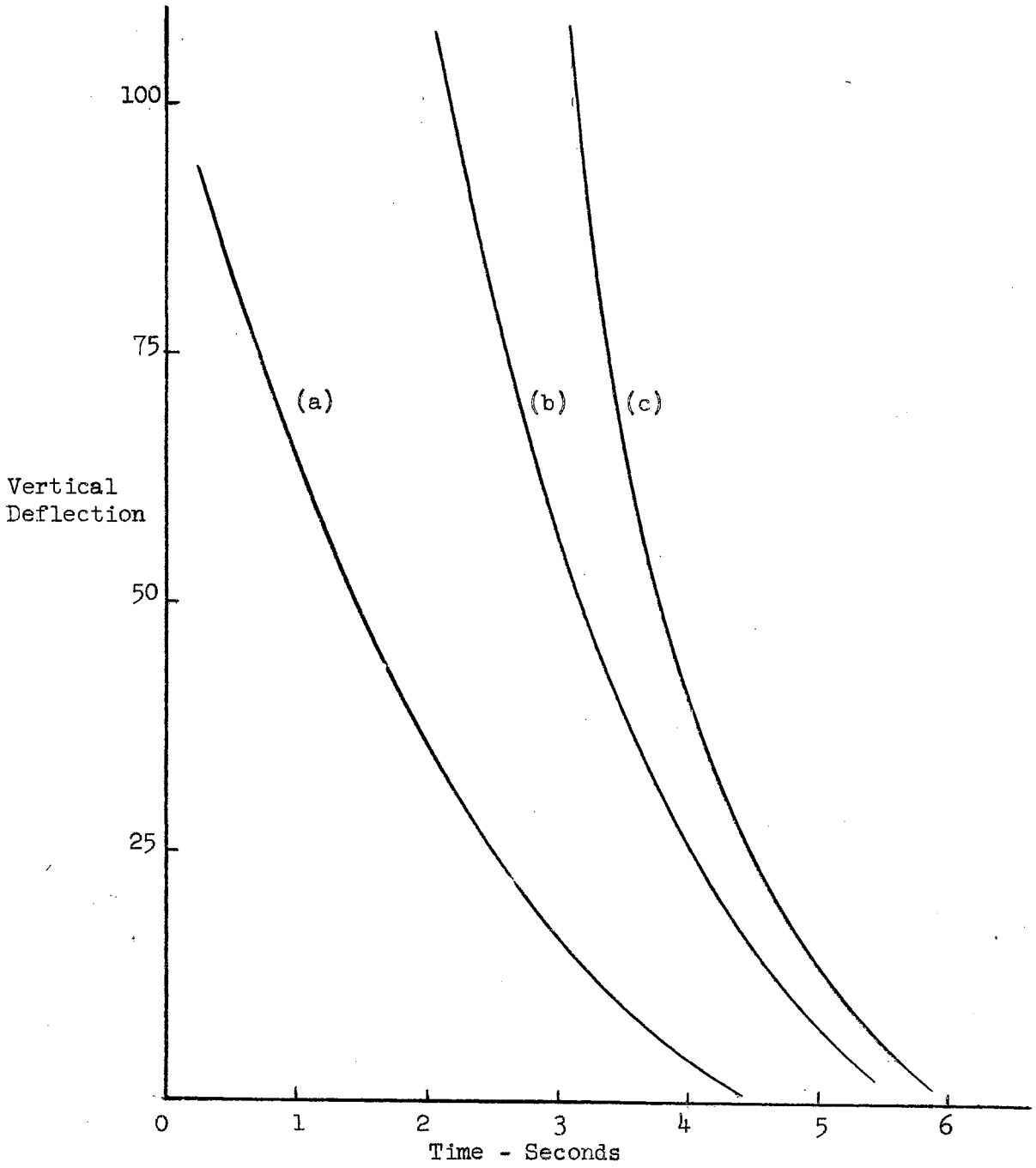

Figure 12

Emission decay curve of the beta phosphorescence of esculin in glucose glass at (a) 77°K, (b) 200°K, (c) 298°K. The ordinates are in arbitrary units.

obtained as a function of the time t_1, t_2, and respective intensities I_1 and I_2, i.e.,

$$\tau_m = t_2 - t_1 / 2.303 \log I_1/I_2$$

Therefore, it is only necessary to know intensities at two different times in order to compute the mean lifetime of phosphorescence emission from a decay curve.

In the present study, the mean lifetime was calculated from the best straight-line fit to the decay curve plotted on semilogarithmic coordinates. Most of the decay curves gave straight lines, indicating an exponential decay law. By measuring the slopes of these straight lines, the beta phosphorescence mean lifetime of esculin in glucose glas was determined for the three temperatures. These are 0.68 sec. at 298°K, 0.85 sec. at 200°K, and 1.12 sec. at 77°K. These mean lifetimes are estimated to have a precision of about six percent.

There has been some disagreement on the relationship between the observed mean lifetime of the beta phosphorescence and the temperature. Lewis, Lipkin, and Magel (30) found the lifetime to be nearly independent of temperature for fluorescein dissolved in boric acid, whereas Pyatnitskii and Vinokurova (42) reported that the phosphorescence lifetime of biphenyl varied from 1 to 0.4 second when temperature ranged from 90° to 130°K. It should be emphasized, however, that the observed increase in mean lifetime at lower temperatures is by no means a proof of a change in the transition probability of the corresponding electronic transition, but that it is merely an indication of a decrease in the efficiency of the competing radiationless transition (for instance, the triplet to singlet excitation process). If there were no such competing processes, both the intensity and the lifetime of phosphorescence should be independent of

temperature. The lifetime referred to by Lewis et al. is the intrinsic mean lifetime in the absence of such competing process. Since the intrinsic mean lifetime in the absence of competing processes is a true measure of the corresponding probability, their report merely suggests an invariant transition probability. Examination of their published data indicates an increase in observed mean lifetime occurs as the temperature decreases. Their results are in agreement with these obtained in the present study.

In Fig. 13, the reciprocals of the mean lifetimes are plotted against the reciprocals of the corresponding absolute temperatures. The value of $dr_2/d(\frac{1}{T})$ at room temperature is obtained from the slope of the tangent to the curve at the point, P, and is found to be 280.

C. Fluorescence Mean Lifetime

Figure 14 shows the recording spectrophotometer tracing of the absorption spectra of esculin in glycerol at room temperature.

The rate constant for the fluorescence process, k_1, was evaluated from equation (19). The value of the integral was evaluated from a plot of the molar extinction coefficient vs wavenumber by the use of an Ott planimeter. The refractive index for glycerol was obtained from the Handbook of Chemistry and Physics and redetermined as an additional check. $\bar{\nu}_A$ was obtained from the absorption curve and the multiplicities for the upper and lower states are taken as unity. The values thus obtained are as follows:

$$\bar{\nu}_A = 29850 \text{ cm}^{-1}$$

$$n = 1.47$$

$$g_u = g_l = 1$$

$$\int \epsilon d\bar{\nu} = 7.78 \times 10^7$$

From these values, the rate constant k_1 is found to be 4.27×10^8 and the intrinsic fluorescence mean lifetime, i.e., the reciprocal of this rate

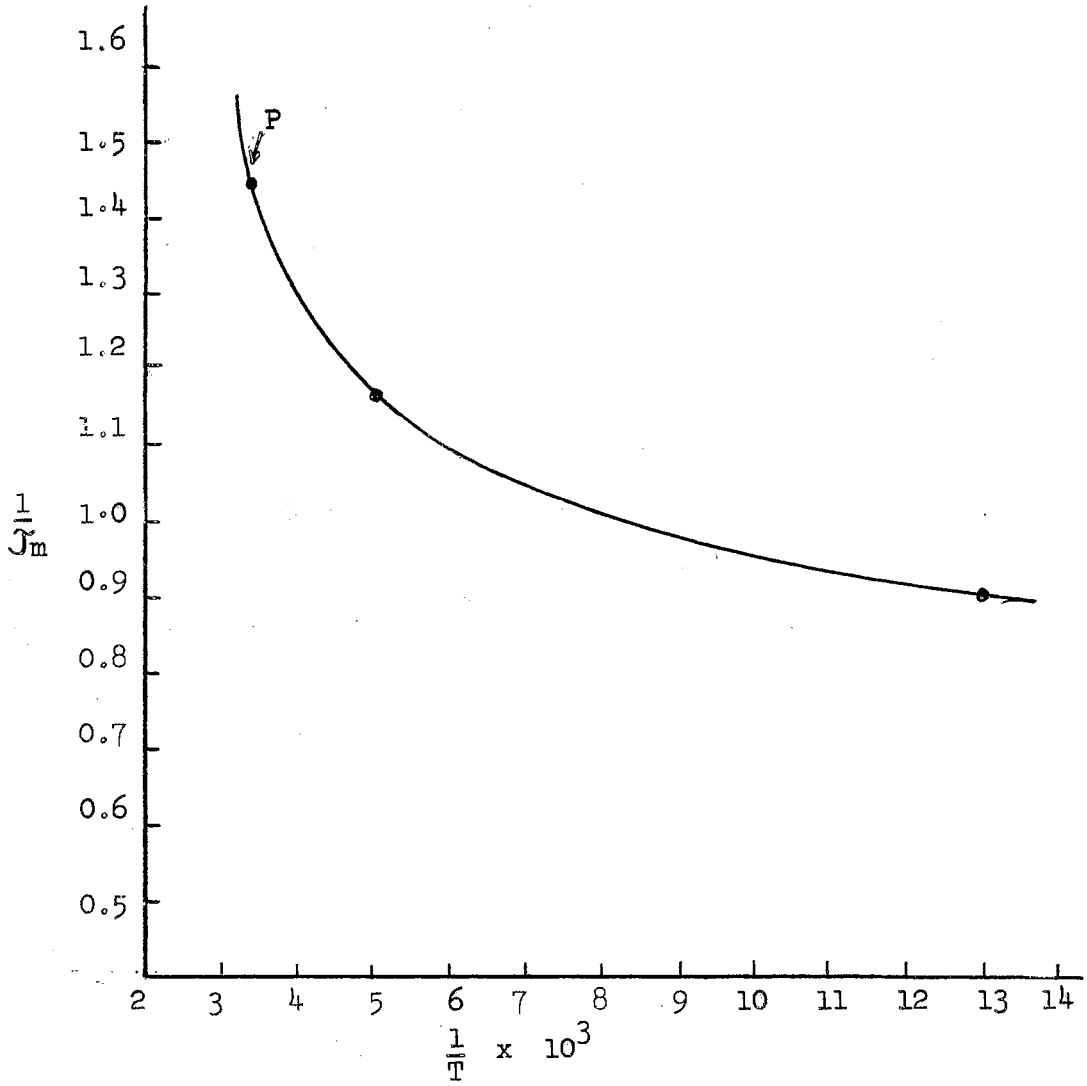

Figure 13

The reciprocal of the beta phosphorescence mean lifetime as a function of the reciprocal of the absolute temperature.

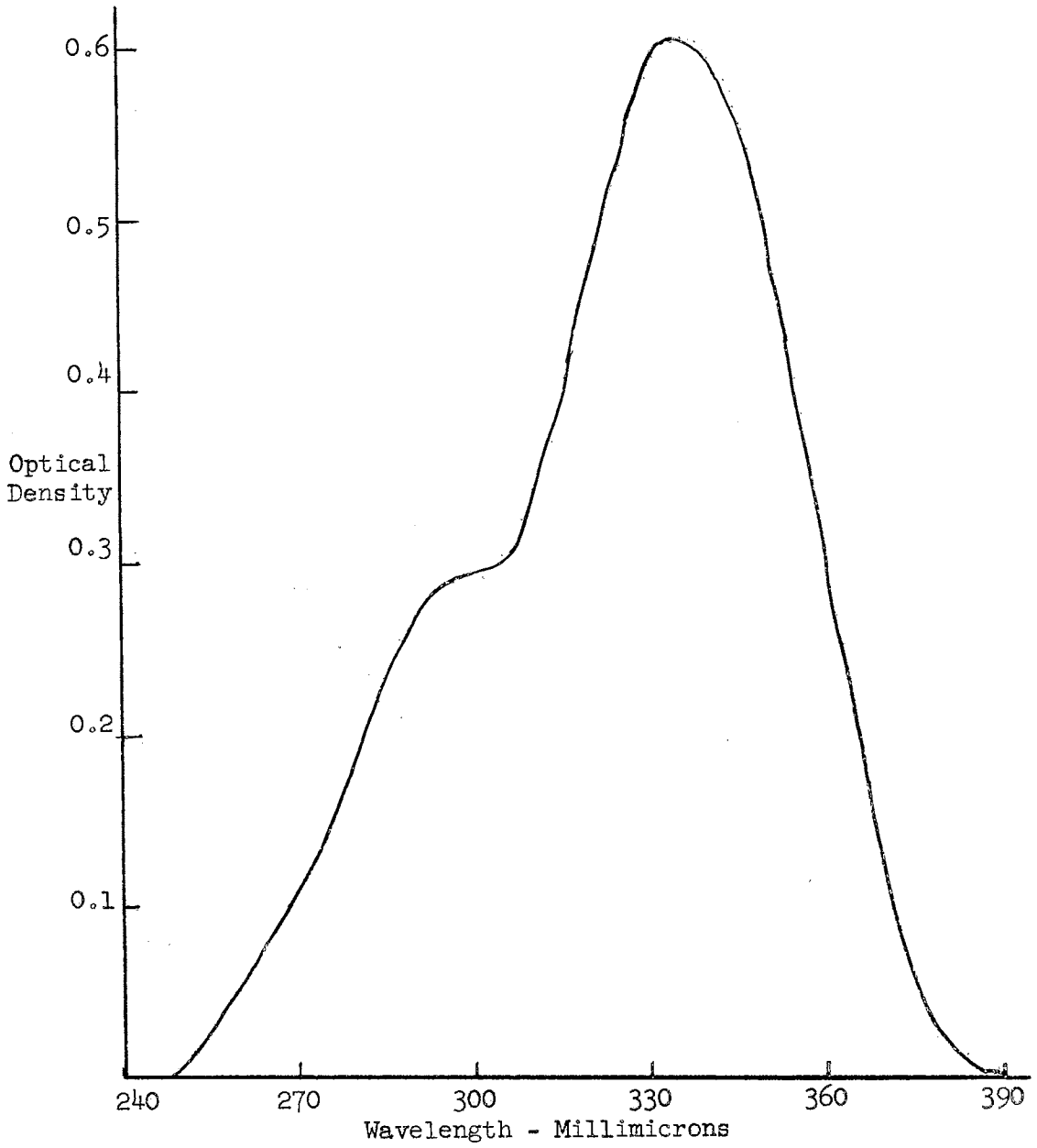

Figure 14

The absorption spectra of esculin in glycerol.

constant, is calculated to be 2.34 mμsec. The intrinsic mean lifetime agrees well with the measured lifetime of 2.5 mμsec. (16). It is quite probable that the intrinsic fluorescence mean lifetime of esculin in glucose glass does not differ very much from this value.

D. Quantum Yields

Redetermination of the Absolute Fluorescence Yield of Aqueous Dye Solutions

The quantum yields of the fluorescences of esculin and fluorescein in aqueous solutions were determined as a check on the reliability of our apparatus and experimental method. The results obtained are summarized in Table 4. The absolute fluorescence yields of these aqueous solutions found in this study agree satisfactorily with the most reliable values previously obtained by other methods (51).

Quantum Yields of Esculin in Glucose Glass

(1) The values of $\int_\nu \frac{P(\nu)}{\nu} d\nu$ and A_E/ν_E along with the calculated quantum yields for 1 x 10^{-3} molal solution of esculin in glucose glass are given in Table 5.

(2) The determination of the integral $\int_\nu \frac{P(\nu)}{\nu} d\nu$ for fluorescence and phosphorescence was accomplished by the use of a plot of relative number of quanta emitted, $\frac{P(\nu)}{\nu}$, versus wavenumber. The areas contained in the integrals were evaluated with an Ott planimeter, and are expressed in arbitrary units. The relative number of quanta absorbed by the sample, A_E, was also evaluated with an Ott planimeter and A_E/ν_E is expressed in the same arbitrary units as those for $\int_\nu \frac{P(\nu)}{\nu} d\nu$. Since the overlap of the absorption and fluorescence (or alpha phosphorescence) band is negligible for esculin in glucose glass, none of the fluorescence and alpha phosphorescence yields determined here has been corrected for autoabsorption. These yields, however, are believed to be smaller than the actual yields

Table IV.

ABSOLUTE FLUORESCENCE YIELDS OF ESCULIN AND FLUORESCEIN AQUEOUS SOLUTIONS

Dye	Concentration	Exciting Wavelength	Quantum Yield
Esculin	10^{-3} g/ml	Hg 3650	0.93
Fluorescein	10^{-3} g/ml	Hg 3650	0.64

Table V.

ANALYSIS OF THE QUANTUM YIELD DATA

Emission	ν_E	$\int_\nu \frac{p(\nu)}{\nu} d\nu$	A_E	Φ
Fluorescence	3650A	4.17	30	0.14
Alpha Phosphorescence	3650A	0.093	62	0.0015
Beta Phosphorescence	3650A	0.44	62	0.0073

because of the partial opaqueness of the glucose glass to the fluorescent and alpha phosphorescent emission.

The ratio of the fluorescence yield to the alpha phosphorescence yield, $\Phi_f / \Phi_{\alpha p}$; and the ratio of the beta phosphorescence to the alpha phosphorescence yield, $\Phi_{\beta p} / \Phi_{\alpha p}$, were next examined as a function of the intensity of the exciting radiation. The intensity of the exciting radiation was varied with neutral filters (Corning No. 5860) and the ratios of the quantum yields are calculated from the values of $\int_\nu \frac{p(\nu)}{\nu} d\nu$ for the

individual luminescence bands. The results obtained indicate that the ratios of the quantum yields, as well as individual quantum yields, are independent of the intensity of the exciting radiation within the limit of experimental accuracy.

Estimation of Errors

The principal sources of error involved in the present quantum yield measurements are the errors inherent in the use of the integrating sphere, and the errors due to uncertainty in the calibration of the sphere-monochromator-phototube combination.

In the derivation of equation (22), it was assumed that the reflection from the sphere wall is perfectly diffuse and it is independent of the light distribution of the light source. In practice, however, there are certain departures from these ideal conditions, viz.:

1. The reflection from the sphere wall is never perfectly diffuse.
2. A part of the reflected light falls on the objects in the sphere, and is partly absorbed by these objects.
3. The screen masks not only the light source, but also a part of the sphere wall.
4. The illuminating and receiving apertures are not subject to the cosine law.

The effects of these deviations from the ideal sphere will be discussed separately.

The error due to an imperfect diffuser is known to be pronounced when two light sources with different light distribution are to be compared. This is the situation encountered in the present quantum yield measurements. McNicholas (36) has demonstrated that deviation from the cosine law causes errors that do not exceed one percent for highly reflecting

substances such as magnesium carbonate. Therefore, the error resulting from the first deviation is for all practical purposes negligible. The maximum error that arises from the absorption of the reflected light by the objects in the sphere depends on the fraction of the total reflected light falling on the objects and the absorption coefficient of the objects. Since the screen and all the other fittings are painted with magnesium carbonate, and since less than five percent of the total reflected light falls on these objects, the error resulting from this source is also negligible on the final values of the quantum yields. The screen in the sphere masks not only the receiving aperture but also a part of the sphere wall directly opposite to the receiving aperture. Rosa and Taylor (45) gives an expression for this error when the substitution method of photometry is used.

$$\% \text{ error} = \frac{(f_1 - f_2)\, a}{1 - f_1\, a}$$

where f_1 and f_2 are the fractions of total light flux incident on screen and screened area for the light source L_1 and L_2 respectively, and a is the absorption factor of the sphere wall. For the absorption source at hand, f_2 is approximately zero and for the fluorescence source, f_1 is less than 0.1. The absorption factor of the sphere surface, a, is less than 0.1 for the present sphere. Upon substitution of these values into the above expression, it is found that the error due to the presence of the screen in the sphere is less than one percent. An additional source of error arises from the presence of apertures in the sphere wall. Such apertures must be considered as areas of zero reflection coefficient. According to Walsh (53), the error due to the presence of such apertures is given by:

$$\% \text{ error} = \frac{A\{\theta + \rho(1-\theta)\}}{1-\rho} \times 100,$$

$$A = \frac{\text{area of aperture}}{\text{area of sphere}}$$

$$\theta = \frac{\dfrac{\text{energy falling directly on aperture}}{\text{area of aperture}}}{\dfrac{\text{energy falling on remainder of sphere}}{\text{area of sphere}}}$$

Since the receiving aperture is screened from the light source, only the illuminating aperture need be considered in the present case. For the absorption source, θ is almost zero because the light flux is directed toward the rear of the sphere opposite the aperture in consideration. For the luminescence source, on the other hand, θ is unity or nearly unity because the luminescent emission is distributed fairly uniformly in all directions. The reflection coefficient of the sphere wall is about 0.95 for the wavelength region in which the luminescent emission occurs. A is about 0.005 for the present sphere. Substituting these values into the above expression, it is found that the error in the absorption measurement is 4.5 percent, while the error in the luminescent measurement is five percent. Thus, the measured luminescence yield would then be about one-half percent too low, which is well under the experimental error one would expect.

The principal errors in the calibration of the instrument arise from the uncertainty in the temperature of the calibrating lamp, the accuracy to which the spectral emissivity of tungsten are known, and the random fluctuations in the thermopile-galvanometer circuit. Forsythe and Adams (15) estimate the accuracies of the spectral emissivity to be from five to eight percent. The degree of variation of the lamp temperature during calibration is not known, but the lamp current is accurately controlled during the calibration; consequently, the error incurred in the values of

the quantum yields due to the lamp temperature variation is assumed to be less than ten percent. The error due to the random fluctuations in the thermopile-galvanometer circuit is estimated to be of the order of ten percent.

Taking into account these and other sources of error, the absolute quantum yields quoted are believed to have a precision of about ten percent.

E. Evaluations of the Rate Constants

The data taken in the experiments of the preceding sections are utilized in the present section to calculate the individual rate constants for the processes occurring in esculin dissolved in glucose glass. Calculations are carried out by the procedures outlined in Chapter II. The results are listed in Table 6, and the modified Jablonski model is reproduced in Fig. 15 for the purpose of showing relative magnitude of the individual rate constants. Since the rate constant k_1 was calculated from the theoretical intrinsic mean lifetime of fluorescence, the values of the other rate constants quoted also have the uncertainty inherent in the value of k_1.

Table VI.

RATE CONSTANTS FOR THE ELECTRONIC TRANSITIONS
OF ESCULIN IN GLUCOSE GLASS
AT 298 °K

Rate Constant	Unit, in sec^{-1}
k_1	4.27×10^8
k_2	1.81×10^9
k_3	8.55×10^8
k_4	0.0385
k_5	1.34
k_6	0.0578

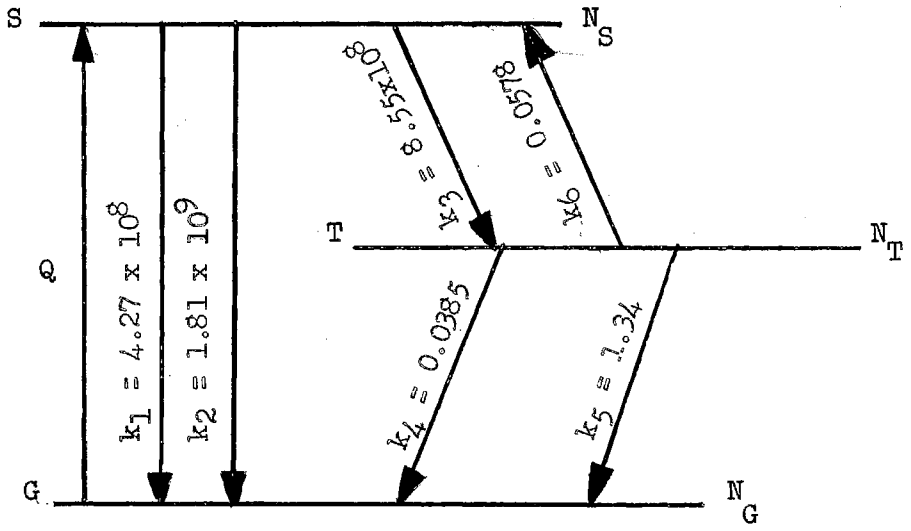

Figure 15

The rate constants for the electronic transitions of esculin in glucose glass. Q is excitation to lowest singlet state by absorption, k_1 and k_4 are rate constants for the fluorescence and beta phosphorescence processes respectively; k_2, k_5 are rate constants for the radiationless singlet-ground and triplet-ground transitions, respectively; and k_3 and k_6 are rate constants for the radiationless singlet-triplet and triplet-singlet transitions, respectively.

CHAPTER V

DISCUSSION OF RESULTS

If the Jablonski model describes the luminescence phenomena of molecules in rigid glass correctly, it can be shown from Eqns. (12), (13), and (16) that the ratio of any two of the three emission quantum yields should be independent of the intensity of the exciting radiation and depend only on the relative values of the rate constants charateristic of the quantum yields. The result obtained in the present work shows that the ratios are actually independent of the intensity of the exciting radiation within the limits of the experimental accuracy.

In devising the procedure for evaluating the rate constants, it was assumed that only the rate constant for the triplet to singlet excitation process is temperature dependent. According to Eq. (17), a plot of the logarithm of $dr_2/d(\frac{1}{T})$ values against the reciprocal of the corresponding temperature must give a straight line if this assumption is correct. When such a plot was made by the use of the data taken from Fig. 14, it was found that the plot gives a straight line within the limit of the accuracy of the mean lifetime values.

Examination of the rate constants obtained reveals that the transitions originating from the triplet state are highly forbidden in accordance with the electronic selection rule forbidding intercombinational transitions. It is very interesting to note, however, that the same selection rule does not impede the radiationless singlet-triplet transition to any great extent. The rate constants for the radiationless processes occuring from the singlet or the triplet state are much greater in magnitude than that of the respective raidative process for the system at hand. As may

be seen from Eqns. (3) and (4), the ratio of the number of the excited molecules stored in the triplet state to that in the singlet state during irradiation is determined by the ratio, k_3/R_T, and is of the order of 6×10^8. Therefore, most of the excited molecules are stored in the triplet state during irradiation. Comparison of the ratio of the number of excited molecules stored in each state during irradiation and the rate constants for the radiationless transitions from these two states indicates that the number of molecules undergoing radiationless transition from the singlet state is greater than that from the triplet state by the factor of 20. This is in accord with the conclusion, reached by Koizumi and Kato (26), that the state related with the quenching process is chiefly singlet state. Furthermore, comparison of the fluorescence quantum yields of esculin in water and in glucose glass supports this conslusion.

Another result of considerable interest is that the sum of all quantum yields for processes terminating at the ground state is close to unity. This is a condition that must be satisfied provided that the Jablonski model correctly describes the system under study. Substitution of arbitrary values for the emission data gives almost invariably negative rate constants, and moreover, the sum of the quantum yields for the processes terminating at the ground state does not add up to unity.

The alpha phosphorescence of esculin in glucose glass is spectrally identical with normal fluorescence in agreement with the observations made by previous workers.

The results discussed above indicate that the Jablonski model is a correct representation of the system under study.

SUMMARY AND CONCLUSIONS

A method was described whereby the rate constants for the electronic processes postulated in the Jablonski model can be calculated from emission data.

Experimental apparatus and procedures were then devised for the purpose of acquiring emission data required by this method.

From the emission data obtained, it has been possible to calculate a set of rate constants for the electronic transitions of esculin in glucose glass at 298°K.

The following conclusions were reached from the results obtained:

1. A large fraction of the quenching occurring in the system studied occurs from the excited singlet state.
2. Nonradiative processes occur from either the excited singlet or the excited triplet state of a molecule.
3. The transitions originating from the triplet are all highly forbidden in accordance with the electronic selection rule forbidding intercombinational transitions.
4. The Jablonski model correctly describes the system.

BIBLIOGRAPHY

1. Almy, G. M., and Anderson, S., J. Chem. Phys., 8, 805 (1940).
2. Almy, G. M., and Gillette, P. R., J. Chem. Phys., 11, 188 (1943).
3. Bailey, E. A., and Rollefson, G. K., J. Chem. Phys., 21, 1315 (1953).
4. Becquerel, H., Ann. Chim. et Phys., 27, 539 (1871).
5. Benford, J. R., Lloyd, O. P., and Schwarz, S., J. Opt. Soc. Am., 38, 445 (1948).
6. Benford, J. R., Schwarz, S., and Lloyd, O. P., J. Opt. Soc. Am., 38, 964 (1948).
7. Bowen, E. J., Photoelectric Spectrophotometry Group Bulletin, No. 6, P. 124, September, 1953.
8. Bowen, E. J., and Sawtell, J. W., Trans. Faraday Soc., 33, 1425 (1937).
9. Bowen, E. J., and Stebbins, D. M., J. Chem. Soc., 360 (1957).
10. Brody, S. S., Rev. Sci. Instr., 28, 1021 (1957).
11. Brody, S. S., Ph. D. Thesis, University of Illinois (1956).
12. Dikun, P. P., Petrov, A. A., and Sveshnikov, B. Ya., Zhur. Eksptl. Teort. Fiz., 21, 150 (1950); via C. A. 45, 8357i (1951).
13. Evans, D. F., Nature, 176, 777 (1955).
14. Forster, L. S., and Livingston, R., J. Chem. Phys., 20, 1315 (1952).
15. Forsythe, W. E., and Adams, E. Q., J. Opt. Soc. Am., 35, 108 (1945).
16. Galanim, M. D., Doklady Akad. Nauk S.S.S.R., 925 (1950); via C. A. 45, 60626 (1951).
17. Gaviola, E., Z.f. Phys., 42, 853 (1927).
18. Gilmore, E. H., Gibson, G. E., and McClure, D. S., J. Chem. Phys., 20 829 (1952).
19. Gilmore, E. H., and Knipe, R. H., J. Opt. Soc. Am. 42, 481 (1952).
20. Gilmore, E. H., and Lim, E. C., Unpublished work.

21. Hudson, C. S., and Dale, J. K., J. Am. Chem. Soc., 39, 320 (1917).

22. Jablonski, A., Z. Physik, 94, 38 (1935).

23. Kasha, M., Chem. Revs., 41, 401 (1947).

24. Kasha, M., J. Opt. Soc. Am., 38, 929 (1948).

25. Klick, C. C., Schmacker, J. G., and Stokes, R. G., Rev. Sci. Instr., 22, 776 (1951).

26. Koizami, M., and Kato, S., J. Chem. Phys., 21, 2088 (1953).

27. Ladenberg, R., Z. Physik, 4, 451 (1921).

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

29. Lewis, G. N., Calvin, M., and Kasha, M., J. Chem. Phys., 17, 804 (1949).

30. Lewis, G. N., Lipkin, D., and Magel, T. T., J. Am. Chem. Soc., 63, 3005 (1941).

31. Lewis, G. N., and Kasha, M., J. Am. Chem. Soc., 66, 2100 (1944).

32. Lewis, G. N., and Kasha, M., J. Am. Chem. Soc., 67, 994 (1945).

33. Lim, E. C., M. S. Thesis, Oklahoma State University, (1956).

34. McClure, D. S., J. Chem. Phys., 17, 905 (1949).

35. McClure, D. S., J. Chem. Phys., 19, 670 (1951).

36. McNicholes, H. J., Nat. Bur. Stand., R.P. 3, Vol. I (1938).

37. Perrin, F., Ann. de Phys., 12, 169 (1929).

38. Price, G. R., Ferretti, R. J., and Schwartz, S., U.S. Atomic Energy Commission, AECD-2282, June, 1945.

39. Pringsheim, P., Fluorescence and Phosphorescence, Interscience, New York (1949).

40. Pringsheim, P., and Vavilov, S. J., Z. f. Phys., 37, 705 (1926).

41. Pyatnitskii, B. A., Izvest. Akad. Nauk. S.S.S.R., 15, 597 (1951); via C. A. 46, 8972 (1952).

42. Pyatnitskii, B. A., and Vinokurova, T. P., Doklady Akad. Nauk. S.S.S.R., 68, 281 (1949); via C. A. 44, 444b (1950).

43. R.C.A. Tube Handbook, HB-3

44. Robinson, G. W., J. Chem. Phys., 22, 1147, 1384 (1954).

45. Rosa, E. B., and Taylor, A. H., Nat. Bur. Stand., Sci paper 447 (1922).

46. Skarsvag, K., Rev. Sci. Instr., 26, 397 (1955).

47. Sklar, A. L., J. Chem. Phys., 5, 669 (1937).

48. Szymanowski, W., Z. f. Phys., 95, 450 (1935).

49. Van Roggen, A., and Vroom, R. A., J. Sci. Instr., 32, 180 (1955).

50. Vavilov, S. J., Z. f. Phys. 22, 266 (1924).

51. Vavilov, S. J. Z. f. Phys. 42, 311 (1927).

52. Vavilov, S J., and Levshin, W. L., Z. f. Phys., 44, 539 (1927).

53. Walsh, J. W. T., Photometry, Constable, London (1926).

54. Wiedman, E., and Schmidt, G. C., Ann. d. Phys., 56, 201 (1895).

55. Worthing, A. G., Phys. Rev., 10, 377 (1917).

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