AN EXPERIMENTAL STUDY OF THE CHARACTERISTICS OF THE CHLOROACETIC ACID ACTINOMETER IN A HELICAL SPIRAL MERCURY RESONANCE LAMP

By

HIROSHI GOCHO

Bachelor of Science
Keio University
Tokyo, Japan
1953

Master of Science
Keio University
Tokyo, Japan
1955

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Thesis Approved:

Earl H. Gilmore
Thesis Adviser

Clarence M. Cunningham

Robert MacVicar
Dean of the Graduate School

430769

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CHAPTER I

INTRODUCTION

Photochemistry is the branch of chemistry that is concerned with chemical changes caused by the action of light on matter. In this usage the word "light" is understood to mean radiation whose wavelength falls within the ultraviolet, visible, and infrared regions of the spectrum although radiation in the last-named region is seldom capable of causing chemical change. A large number of photochemical reactions are known. Among these are syntheses, decompositions, polymerizations, isomerizations, oxidations and reductions, etc. It is noteworthy that many of the reactions known cannot be made to occur by any other means, consequently, the potential for producing chemicals of unusual character by the action of light is an important one. In terms of the quantum concept this fact is understandable since the absorption of light of wavelengths 6000A and 3000A supply energies of 45 Kcal. per mole and 90 Kcal. per mole respectively to the abosrbing species. In addition, the activated molecule does not necessarily reach equilibrium with respect to its internal degrees of freedom before dissociation occurs, therefore, unusual and interesting products can be expected.

The first step in establishing the subject of photochemistry on a quantitative basis was made in 1817 when Grotthus stated the first law of photochemistry; only those radiations which are absorbed are effective in producing chemical change. This law was rediscovered by Draper in 1841 and has since come to be known as the Grotthus-Draper law. Without this principle, the action of light would likely have to be accounted for in terms of a purely catalytic action and consequently the difficulties in postulating photochemical mechanisms would increase considerably. For example, the first law provides a easy explanation for the source of the energy required to make certain observed processes take place.

The Lambert law of absorption (1760), $I = I_o e^{-kl}$, and Beer's modification of this law to include solutes in solution (1846), $I = I_o e^{-\epsilon cl}$, have proved to be of immense practical value in the study of photochemical processes as well as in all processes involving transmission and absorption. The next major advance in the theoretical understanding of the subject came when Einstein formulated the second law of photochemistry early in the present century; one quantum of absorbed energy activates one molecule of the absorbent. This principle came simply as a result of the application of the quantum concept to the process of light absorption. It is important to note that the second law requires nothing specific of the absorbing molecule after it has become activated. The molecule may decompose, give

off luminescence, undergo internal rearrangements, add to another molecule, transfer some or all of its energy to another molecule of the same or of a different kind, etc. A group of molecules similarly activated may undergo any combination of the processes listed, so far as is known. (2, 15, 17).

With the advent of the second law came the concept of the quantum yield or efficiency, which is defined as the ratio of the number of molecules undergoing some specified process to the total number of quanta absorbed. Vavilov was the first to show that although the energy yield of fluorescence from a sodium fluorescein solutions varies as a function of the wavelength of the exciting light, the quantum yield is constant over a very wide range of wavelengths (22). In the study of a photochemical process, a knowledge of the value of the quantum yield helps greatly in the formulation of mechanisms, etc. When a substantial portion of the energy necessary for the initial reaction must come from the light quantum absorbed, the quantum yield seldom exceeds unity, but if the quantum absorbed serves only to initiate a chain reaction such as in the reaction of hydrogen with chlorine, the quantum yield can be as high as 10^6 or even higher.

To obtain quantitative data of any significance on photochemical processes it is necessary to determine the numbers of quanta involved on an absolute basis. Such measurements are called actinometric measurements.

The device used as the primary standard in these measurements is the thermopile. Since its response is linear and non-selective, it would be ideal for direct use in all actinometric work if it were not for its extremely low sensitivity and the awkwardness involved in its use. It is more usual to use the thermopile to calibrate another actinometric device which becomes, in turn, a secondary standard. Photoelectric cells of many sorts are commonly employed as secondary standards because they have high sensitivity and also because they are not as awkward in use as thermopiles. They can be operated in ranges where their response is linear with intensity, but they invariably show wide variations in sensitivity in different regions of the spectrum and therefore require careful calibration.

Another means for measuring numbers of quanta is the chemical actinometer, a device that makes use of a system in which photodecomposition proceeds with a reliable, predetermined quantum yield value. The most universally used of these is an aqueous solution of oxalic acid containing uranyl ions. Uranyl ions absorb the incoming light and cause the oxalic acid to decompose by a photosensitization process as follows (14):

$$h\nu + UO_2^{++} \longrightarrow (UO_2^{++})^*$$

$$(UO_2^{++})^* + H_2C_2O_4 \longrightarrow UO_2^{++} + H_2O + CO + CO_2.$$

The preceeding reaction is recognized as the standard with which quantum intensities can be determined to an accuracy of ± 5 percent. The actinometer responds over the spectral

region from 2000A to 5000A and extensive data are available on the quantum yield as a function of the wavelength (12). These yield values are practically independent of temperature and concentration, but the actinometer is not sufficiently sensitive for all applications. The recently developed ferrioxalate actinometer has a considerably greater sensitivity (8, 16). The primary advantage in the use of a chemical actinometer is that it may be inserted directly into an identical or alternately into the same reaction vessel in which is placed the system under study. Uncertainties regarding reflection, refraction, and absorption effects can therefore be greatly reduced.

Another chemical actinometer that has been used is an aqueous solution of monochloroacetic acid. The compound is hydrolyzed by the action of light as follows:

$$h\nu + H_2O + ClCH_2COOH \longrightarrow H^+ + Cl^- + HOCH_2COOH$$

In general, the uranyl oxalate actinometer is more useful because monochloroacetic acid solutions respond only to wave lengths less than 2600A. This behavior can be advantageous, however, when the photochemical process being investigated is caused to occur by the 2537A mercury line alone. Disadvantages of the latter actinometer are that the quantum yield is strongly dependent upon the temperature, hydrolysis occurs at the rate of about one percent per day at room temperature even in the absence of light. In addition, monochloroacetic acid itself causes painful and slowly healing burns when it comes into contact with the skin.

However, one advantage of this actinometer is that the progress of the photolysis is followed by a direct titration of chloride ion whereas with the uranyl oxalate actinometer one uses the differences in oxalate concentrations between the original and the irradiated solutions.

There has been developed an apparatus in which systems can be subjected to intense radiation of 2537A wave length (9). Because of the usefulness of this apparatus, and because of the fact that there have been no previous studies of the apparatus using monochloroacetic acid solution as the actinometer, the decision was made to investigate the influences of the parameters of major importance on the characteristics of the apparatus. In particular, the concentration of the actinometer and the rate at which it was stirred were varied, reaction vessels of different diameters (also volumes) were used, and the density of the radiation within the helical spiral mercury resonance irradiating lamp was investigated. Linearity of actinometer response and the influence of temperature have evidently been adequately investigated already (13, 19).

CHAPTER II

HISTORICAL

A great advance in the establishment of chemical actinometry as an exact science was made in the classic work of Leighton and Forbes on the photolysis of oxalate ions in solutions containing uranyl oxalate (12). This system had been used as an actinometer prior to the appearance of their work, but the quantum yields of the photolysis at different wavelengths were at best poorly known and at worst were contradictory. Leighton and Forbes established quantum yield values at seven different wavelengths, studied the effects of concentrations of the substituents, investigated linearity of response, and determined the temperature coefficients of the quantum yields at two wavelengths. These workers succeeded in establishing the uranyl oxalate solution as the standard chemical actinometer, and subsequent workers have added more data on its performance and on the techniques of its use (1, 4).

Euler and Cassel apparently gave the first information on the photolysis of monochloroacetic acid in 1913 (3). They stated that the rate of hydrolysis was increased markedly by radiation of wavelength greater than 3000A but shorter than that of visible light. In 1924 Rudberg sought to verify

experimentally the validity of the second law of photochemistry for the photolysis of monochloroacetic acid solutions (18). A value of 1.0, for excitation by the 2537A mercury resonance line, was given for the quantum efficiency as well as the information that ultraviolet radiation of wavelength less than 3000A was required to produce photodecomposition.

Soon after Rudberg's work monochloroacetic acid solutions were used by several workers as chemical actinometers, for which the value of unity for the quantum yield was quite generally accepted. Harris and Kaminsky, who were attempting to develop still another chemical actinometer, remeasured the quantum yield of photolysis for monochloroacetic acid solutions and obtained the value 1.07 ± 0.55 (6). Certain peculiarities in published results from quantum yield studies in which the monochloroacetic acid actinometer was used led Smith, Leighton, and Leighton to reinvestigate the quantum yields of this photolysis (13, 19). A value of 0.31 was found for the yield at 25°C for excitation by the 2537A mercury resonance line. Moreover, it was found that the reaction had a large temperature coefficient, e.g., the yield at 32°C was found to be 0.37. The rate of the dark reaction increased rapidly with temperature, so much so that the system could be of no practical value as an actinometer at a temperature no higher than 69°C. It was found, however, that response was linear with respect to numbers of quanta absorbed, and that

there was no measurable dependency on solute concentration. In a concurrent study by Küchler and Pick, the value of 0.62 ± 0.04 was found for the quantum yield of this photolysis (11).

The rather large temperature coefficient found for the quantum yield of the photolysis by Smith, Leighton, and Leighton causes one to suspect that insufficient attention was given to the control of the temperature in other studies. Only in the work by the last-mentioned authors was a cell used in which the temperature was carefully controlled. In addition, some investigators worked with very low levels of radiant intensities, consequently, the analyses for chloride ion liberated would be more tedious and therefore subject to greater error. In this laboratory, Mr. Norris Smith (20) has found that the value for the photodecomposition yield by wavelength 2537A at 25°C as given by Smith, Leighton, and Leighton check well with results obtained by use of the uranyl oxalate actinometer. Thomas has also confirmed these values (21).

In summary, the following characteristics have been fairly well established for the monochloroacetic acid actinometer:

1. Photolysis is produced only by wavelengths less than 2600-2700A,
2. The response is linear with respect to numbers of quanta absorbed,

3. The quantum yield of photolysis has a large positive temperature coefficient;
4. The rate of the dark reaction is appreciable and increases with an increase in temperature,
5. The quantum yield is independent of the concentration of the monochloroacetic acid.

As indicated in the preceeding paragraph, quantum yield values are not as definitely established as one would like, although it appears that the figure of 0.31 at 25°C is probably correct.

Two problems associated with light sources for use in photochemical investigations are their intensities and spectral purities. All devices used to produce essentially monochromatic radiation decrease intensity by a large factor. In the case of the low-pressure mercury (resonance) lamp, one can obtain radiation consisting of a high percentage of the two mercury resonance lines, 2537A and 1849A. The latter of these is not transmitted by very many materials and consequently it is relatively easy to filter from the 2537A radiation. The resonance lamp is a diffuse source, however, and is generally too weak for use with a monochromator in photochemical work. These lamps can be shaped in such a way that a vessel within them can receive intense radiation. An early example of such a technique is that described by Harris, Ashdown, and Armstrong (7), who used a helical spiral lamp around a vessel for the purpose of exciting Raman spectra. Heidt effected modifications of this lamp so that its emitting portion could be operated in a water bath while

maintaining the electrodes above the water level (9). In a later study Heidt and Boyles investigated quantum output as a function of lamp temperature and of its ageing characteristics (10). These lamps put out on the order of 10^{17} quanta per second at 2537A into the reaction vessel, so that a much higher intensity for photochemical work is available for this wavelength. A sketch of the modified lamp is given in Figure 1.

CHAPTER III

EXPERIMENTAL

A. Apparatus

The source used in this work was a fused silica helical spiral mercury resonance lamp manufactured by the Hanovia Chemical and Manufacturing Company. According to the manufacturer, 95 percent of the output of the lamp in the ultraviolet region occurs at 2537A. The lamp was powered by a 5000 volt luminous tube transformer which operated directly from the 110 volt ac supply. The lamp coils were submerged in a water bath in order to achieve temperature control in a manner similar to that described by Heidt and Boyles (10), except that the visible light filter was omitted since the monochloroacetic acid actinometer is insensitive to wavelengths greater than about 2700A. The experimental set-up is illustrated in Figure 1.

Three sizes of irradiation vessels, fabricated by the Corning Glass Works from 9710 Vycor, were used in the experiments. Each vessel had affixed to its top a 29/42 standard taper joint, and was of a total length of about 26.5 cm. The irradiated portions of these vessels were cylindrical and of outside diameters 1.7 cm, 2.5 cm, and 4.6 cm respectively. The vessel with the largest diameter was as large

as could be accommodated conveniently within the lamp coils. In each experiment the vessels were filled with actinometer solution to the same height, 11 cm, thus the smallest vessel contained 18.2 ml, the medium vessel 40.0 ml, and the largest 132 ml. As is illustrated for the medium vessel in Figure 1, the vessels were closed by a glass joint at the top in which was contained the driving device for the stirrer. This assembly reduced the chances that the solutions would be accidentally contaminated or that extensive evaporation of the solvent would occur.

The temperature of the water bath was maintained at 25.0 $\pm$ 0.1°C in all the studies. Operation of the apparatus was far more satisfactory when distilled water was used in the bath instead of tap water. In either case a brown deposit formed on the coils of the lamp and the radiant output at 2537A was thereby reduced, but with tap water in the bath the rate of formation was greatly accelerated. For best results, cleaning at one-week intervals was required even when distilled water was used. Heidt and Boyles report a similar experience (10). A cleaning procedure recommended by Gunning (5) was employed for the lamp which consisted of first allowing hot ethanol vapors to condense on the coils, rinsing with distilled water, then immersing the lamp coils in concentrated nitric acid at 90-100°C for twenty to thirty minutes, and then rinsing with hot distilled water followed by hot ethanol.

B. General Procedure

The vessel chosen for use in a particular experiment was clamped within the coils of the resonance lamp as indicated in figure 1. The clamps were maintained in a fixed position with respect to the lamp coils during every series of experiments except for the last one. The lamp was started and allowed to operate for at least 5 minutes before any irradiation was begun in order to permit its output to become steady. With the shutter in the position shown in figure 1, the solution to be irradiated was added by means of a pipette, the stirring mechanism inserted, the vessel closed and the solution stirred at the rate desired. After 5 minutes of stirring, the shutter was dropped to permit irradiation of the vessel and its contents. All solutions were irradiated for fifteen minute periods, the shutter raised, and the solutions were poured and rinsed from the irradiation vessel and then immediately analyzed for chloride ion.

In most of the series of irradiations there were two irradiations of a reference solution, one at the beginning and the other at the end of a series, to which the responses of the other solutions were compared. This procedure was adopted as a means of monitoring the lamp output because direct monitoring would have required extensive changes in the structure of the water bath, and the latter method would not necessarily have been superior anyway. In some instances a third reference solution was used in the middle of a series.

Occasionally it was deemed necessary to irradiate only one monitoring solution, such as when the lamp and water bath had just been cleaned or when different series of experiments were run in close succession.

Since solutions of monochloroacetic acid in water undergo a dark reaction to produce chloride ion, blank titrations of the solutions were made in some cases and a correction factor was found which was applied to the results of the analyses of the irradiated solutions. The dark reaction was effectively stopped by storing the unirradiated solutions in a refrigerator at 4-5°C.

The quantitative analysis for chloride ion was accomplished by means of a standard potentiometric titration procedure (23). Figure 2 is a block diagram of the apparatus used. A wide range Sargent Potentiometer (S-30260) was used in this set-up. The cell consisted of a saturated calomel electrode connected to an Ag-AgCl electrode by an ammonium nitrate-agar bridge through the solution being analyzed. The performance of the analytical apparatus was checked from time to time by analyzing solutions whose chloride ion concentrations were already known.

C. Specific Procedures

As indicated in the introductory section, the influences of four parameters on the results obtained with the helical spiral fused silica mercury resonance lamp and the chloroacetic acid actinometer were studied. These parameters are

(1) vessel size, (2) concentration, (3) stirring rate, and (4) vessel position.

1) Vessel Size

In the study of all the parameters, except the last-named one, vessels of three sizes given earlier in this section were used. It was not possible to make use of the largest vessel in studying the effect of vessel position because it was too large to permit significant lateral displacement within the lamp coils.

2) Concentration

In general, the influence of concentration was determined in a low and in a high range. Solutions of concentrations 0.1m, 0.3m, 0.6m, and 0.9m were made up and the various series of experiments were run with these solutions. In the higher range the actinometric responses of solutions having concentrations of 1.0m, 1.5m, and 2.0m were determined. A 0.6m solution was arbitrarily chosen as the reference and the responses of all the other solutions were computed relative to its response.

3) Stirring Effect

Various series of experiments were run in which the effect on actinometric response of the rate of stirring was determined. Stirring rates of 0, and about 250, 400, and 600 rpm were used. Only two different concentrations of actinometer solutions were used

in these experiments since extreme effects were being sought. Blank titrations of chloride ion were unnecessary in this series of experiments since identical solutions were being used throughout a given run. Any free chloride ion present would contribute equally to all the results and since any stirring effects would show up as a difference, a knowledge of this constant amount of chloride ion is unnecessary. The results of these studies are collected in table II, and are presented graphically in figure 5.

4) Position Effects

In all previous experiments, which are numbered 5 through 18 in the tables I and II of data, the axes of the vessels were maintained as nearly coincident with that of the helical spiral of the resonance lamp as was possible. In experiments 19 and 20 in table III, the responses of the actinometer solutions were obtained with the vessel axes laterally displaced distances up to one cm but still with the axis of the vessel and of the lamp maintained paralleled. These experiments were performed with 2.0m actinometer solutions and with the small and medium vessels only. The objectives were to determine the seriousness of improper vessel centering and to learn something about the distribution of the 2537A radiation within the lamp coils.

D. Chemicals

Two samples of monochloroacetic acid were used in the experiments, the first of which was Eastman Kodak White Label purity and which was distilled by Dr. E. H. Gilmore before use. The second sample was Coleman, Matheson, and Bell No. 2793 used directly without further purification. No difference in the results could be detected as long as proper storage procedures were followed and blank analyses were made on the solutions. The silver nitrate used to prepare the solutions used in the analyses was C. P. Reagent Grade.

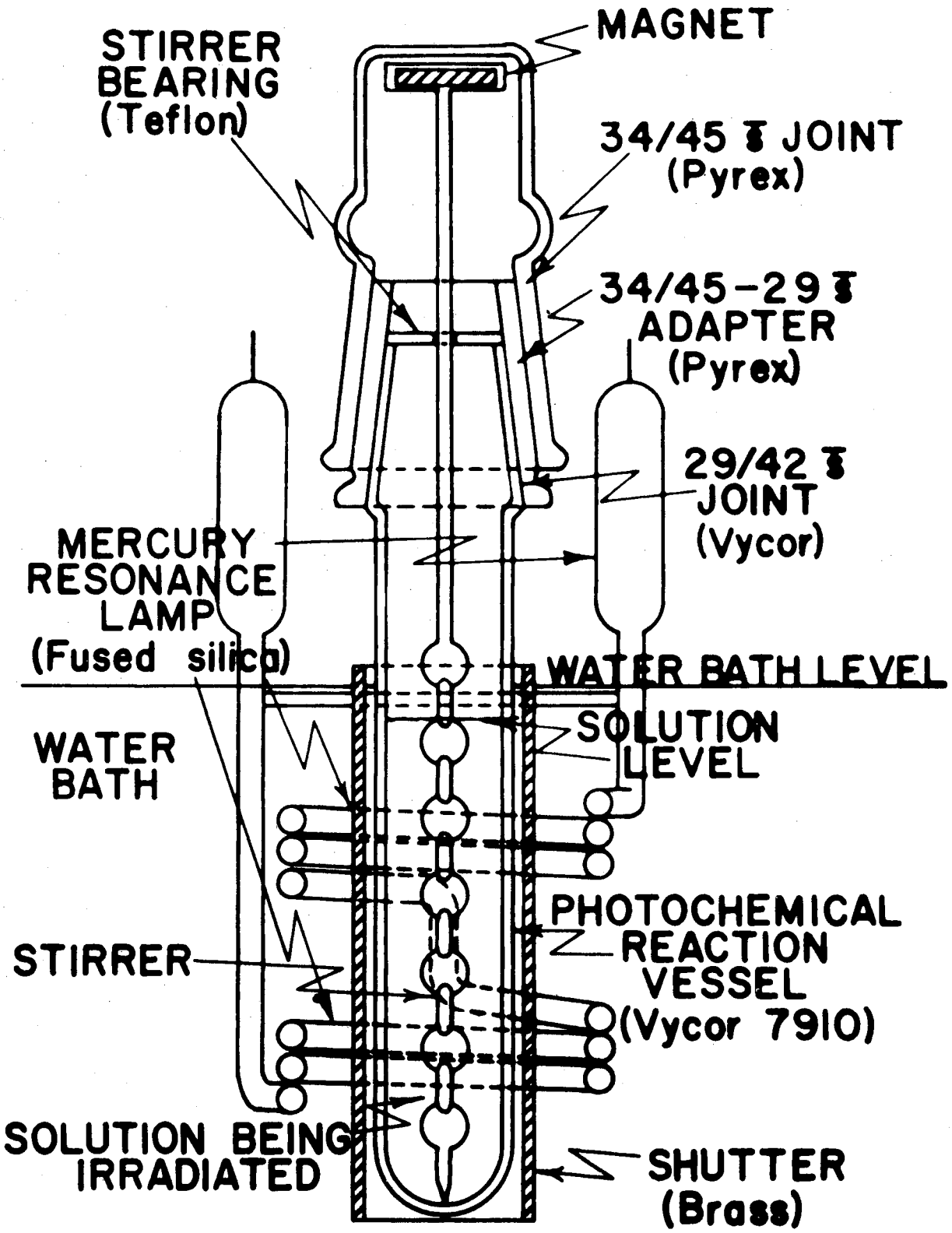

Figure 1. Irradiating Apparatus.

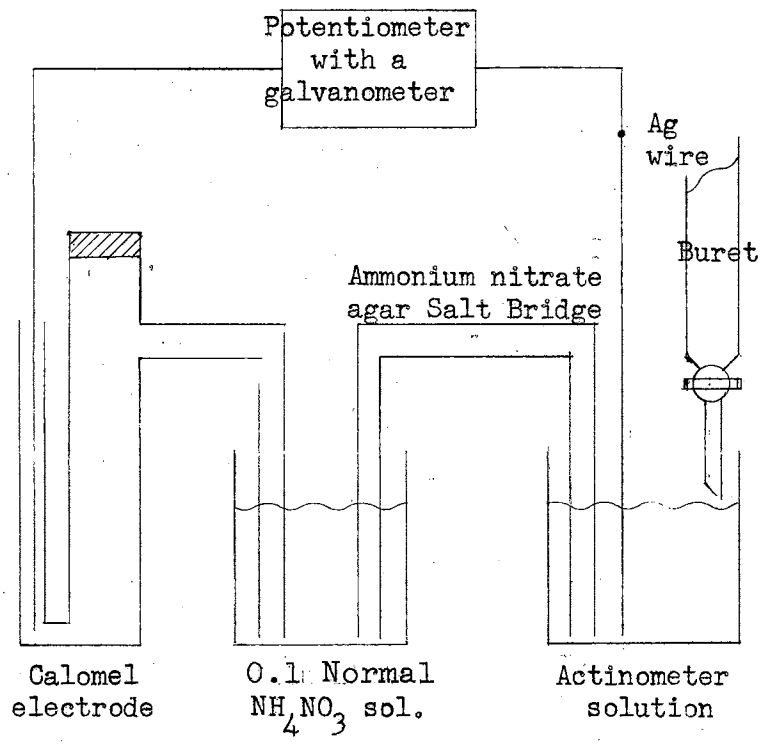

Figure 2

Apparatus used for Titrating Chloride Ion

TABLE I

Concentration and Vessel Size

Exp. No.	Size of Vessel	Conc. of $ClCH_2COOH$	Required $AgNO_3$	Blank	Corr.	Response
5	Small	0.6 m	7.00ml	0.14	6.86	6.86
	"	0.9	7.75	0.20	7.55	7.55
	"	0.3	5.00	0.07	4.93	4.93
	"	0.1	2.80	0.02	2.78	2.78
	"	0.6	7.00	0.14	6.86	6.86
8	"	0.6	6.50	0.14	6.36	6.86
	"	1.0	7.50	0.23	7.27	7.82
	"	1.5	7.80	0.34	7.46	8.03
	"	2.0	8.00	0.46	7.54	8.10
	"	0.6	6.50	0.14	6.36	6.86
6	Medium	0.6	12.30	0.30	12.00	12.00
	"	0.9	13.00	0.45	12.55	12.55
	"	0.3	9.50	0.15	9.35	9.35
	"	0.1	5.40	0.05	5.35	5.35
	"	0.6	12.30	0.30	12.00	12.00
9	"	0.6	12.30	0.30	12.00	12.00
	"	1.5	13.50	0.75	12.75	12.75
	"	1.0	13.30	0.50	12.80	12.80
	"	2.0	13.50	1.00	12.75	12.75
	"	0.6	12.30	0.30	12.00	12.00
7	Large	0.6	28.50	0.99	27.51	27.51
	"	0.9	29.20	1.47	27.73	27.73
	"	0.3	26.00	0.50	25.50	25.50
	"	0.1	18.00	0.17	17.83	17.83
	"	0.6	28.50	0.99	27.51	27.51
10	"	0.6	28.00	0.99	27.00	27.51
	"	1.0	28.30	1.65	26.65	27.10
	"	1.5	28.30	2.48	25.82	26.29

These solutions were exposed for 15 min., stirred at 500 rpm and placed in the center of the lamp coils. The concentration of silver nitrate used was 0.01N.

TABLE II

Stirring Effect

Exp. No.	Size of Vessel	Conc. of $ClCH_2COOH$	Rate of Stirring	Required 0.01N-$AgNO_3$
17	Small	0.3 m	590	5.6
	"	"	0	5.5
	"	"	600	5.7
	"	"	580	5.6
	"	"	280	5.5
	"	"	400	5.6
18	"	2.0 m	470	9.5
	"	"	590	9.4
	"	"	590	9.5
	"	"	0	9.5
	"	"	300	9.4
15	Medium	0.3 m	600	12.2
	"	"	0	12.0
	"	"	600	12.0
	"	"	240	11.9
	"	"	600	12.2
12	"	2.0 m	600	13.3
	"	"	410	13.3
	"	"	600	13.2
	"	"	280	13.3
	"	"	590	13.5
	"	"	0	13.3
14	Large	0.3 m	600	28.0
	"	"	0	27.5
	"	"	400	27.7
	"	"	600	27.6
	"	"	240	27.3
	"	"	600	27.6
11	"	2.0 m	600	28.0
	"	"	400	27.5
	"	"	240	27.0
	"	"	0	26.5

These solutions were exposed for 15 min. and placed in the center of the lamp coil.

TABLE III

Position Effect

Exp. No.	Size of Vessel	Conc. of $ClCH_2COOH$	Rate of Stirring	Position	Require 0.01N-$AgNO_3$
19	Small	2.0 m	470	Center	9.5
	"	"	"	Excentric	9.5
	"	"	"	Center	9.5
20	Medium	2.0 m	600	Center	15.6
	"	"	"	Excentric	15.3
	"	"	"	Center	15.7

These solutions were exposed for 15 min.

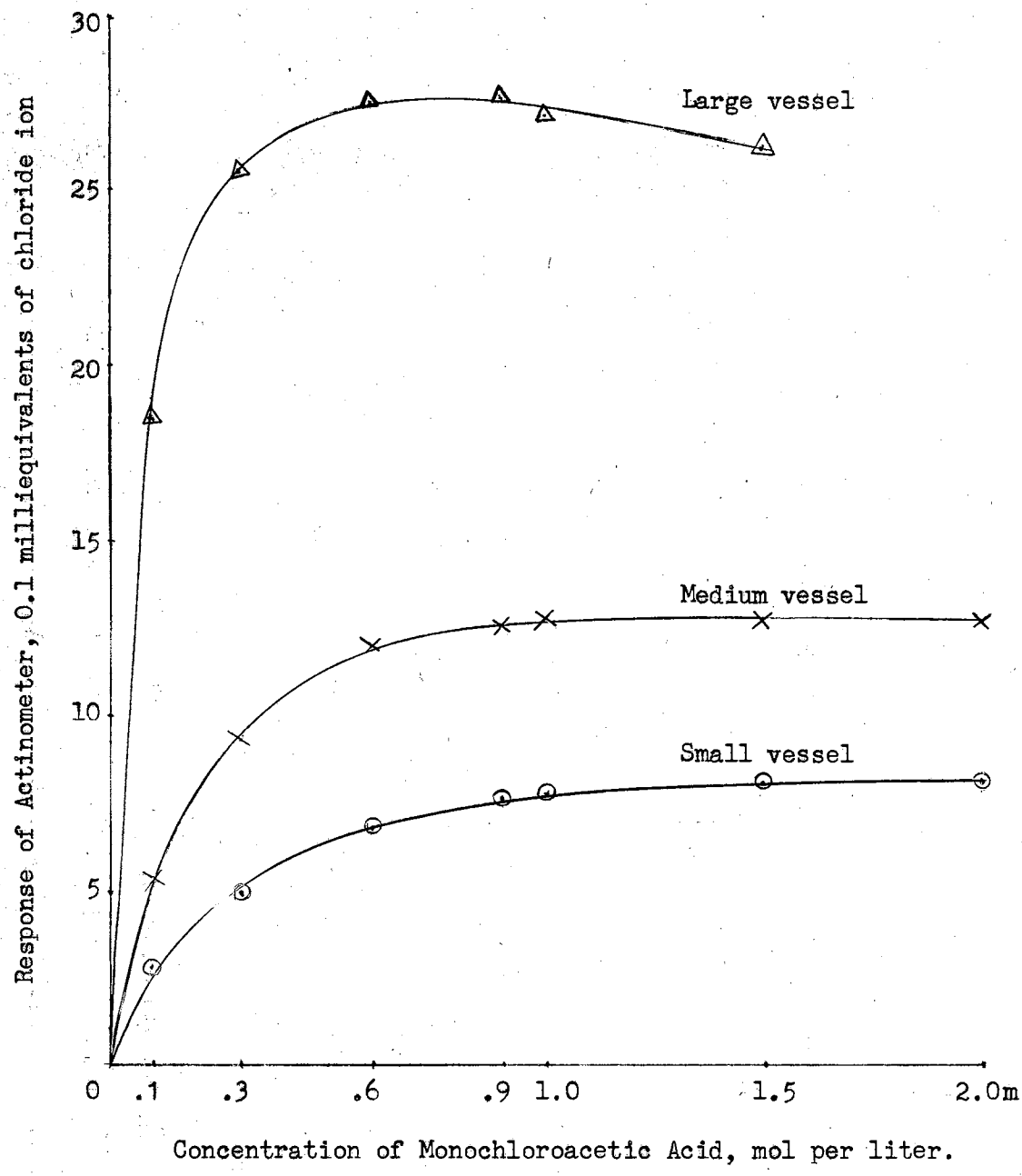

Figure 3

Response of monochloroacetic acid actinometer at differing concentrations for the three sizes of vessels.

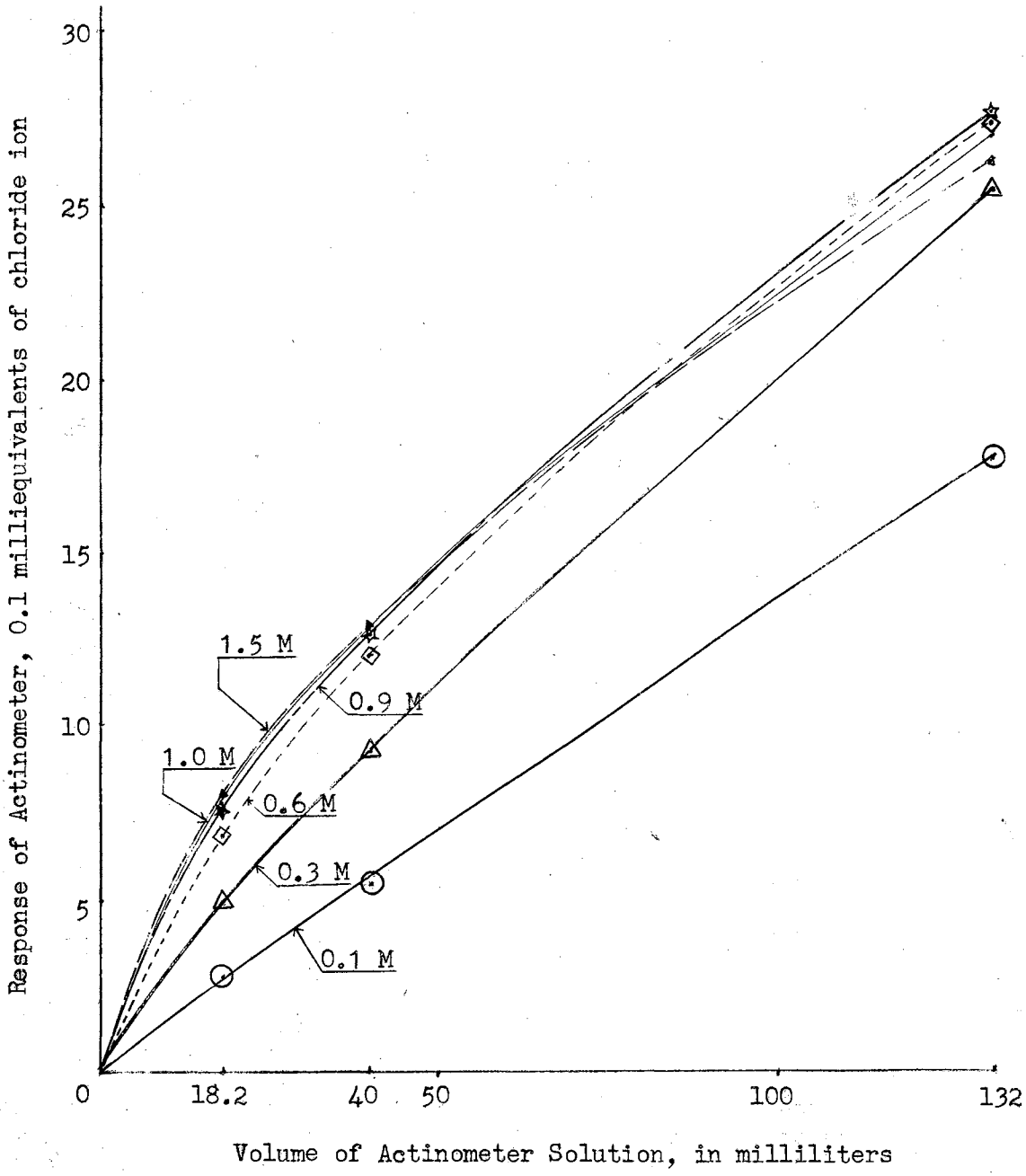

Figure 4

Response of monochloroacetic acid actinometer versus different vessel sizes for the several concentrations studied.

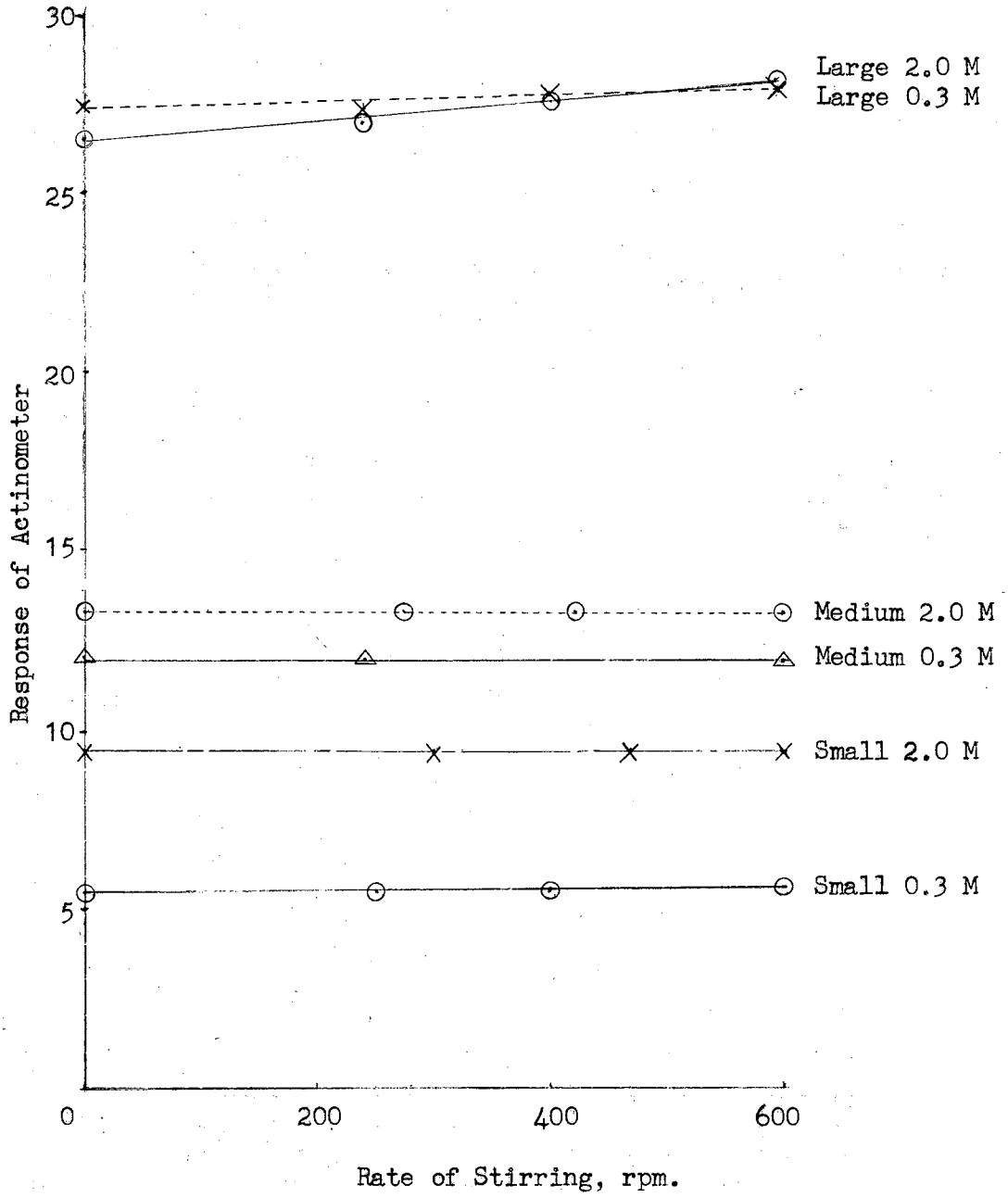

Figure 5

The influence of the stirring rate on the actinometer response at different concentrations and for the three sizes of vessels. The ordinate is in units of 0.1 milliequivalents of chloride ion.

CHAPTER IV

INTERPRETATION OF THE DATA

In general, information from three of the four series of experiments was intended to provide information on the relation of the actinometer response to certain geometric and optical properties associated with the actinometer and its containing vessel. The last series of experiments was designed to give information on the nature of the distribution of actinic radiation within the coils of the fused silica helical spiral mercury resonance lamp.

The data obtained in the study of concentration dependence and vessel size are given in experiments 5-10 of table I. Graphs of these data illustrate several interesting features of the inter-relations of these variables. Figure 3 shows actinometer responses to a constant number of absorbed quanta as a function of the concentration. The separate curves are for the three different sized vessels as indicated. Response for the largest vessel rises most rapidly to its maximum value with increasing concentration whereas the rate of rise is least in the smallest vessel. Such behavior could be explained on the basis that absorption becomes essentially complete in the larger vessel at lower concentrations because of the longer optical paths involved.

In figure 4 the data from experiments 5-10 are plotted with actinometer response as the ordinate, and volume of the solution as the abscissa. Since the actinometer solution vessels were filled to constant heights, the volumes are almost directly proportional to the cross-sectional area. It is seen from the figures that with the most dilute solution studied, the response is a linear function of the volume of actinometer used with the solution heights maintained constant. At higher concentration of the actinometer solutions, the curves show a definite downward curvature.

The behavior of the curves in figure 4 bears a resemblance to what one would predict from an application of Beer's law to the problem of light absorption in a cell. If one takes Beer's absorption law in the form

$$I = I_o \, e^{-2.303\epsilon cl} \qquad (1)$$

and symbolizes the fraction absorbed by f_a, then it readily follows that

$$f_a = 1 - e^{-2.303\epsilon cl}. \qquad (2)$$

If the photolysis is first order with respect to exciting quanta, then the response of the actinometer should be proportional to the fraction of quanta absorbed, hence

$$R = kf_a$$

or

$$R = k(1 - e^{-2.303\epsilon cl}) \qquad (3)$$

if R represents the actinometer response. When the exponent in equation (3) is sufficiently small, the response will

become linear with respect to both concentration and path length. This result can be obtained by expanding e^{-x},

$$e^{-x} = 1 - x + x^2/2! - x^3/3! + \cdots$$

and for sufficiently small values of x

$$1 - e^{-x} \doteqdot x,$$

therefore

$$R = k2.303\epsilon cl,$$

and the approximation becomes more accurate the smaller the value of the exponent.

The optical arrangement for the irradiation experiments described herein is considerably different from that which is required for a straightforward application of Beer's law.

It is possible to develop an empirical equation that will reproduce with reasonable success the curves of figure 4. If the linear distance "l" of equation (3) is replaced by the volume of solution irradiated, and an empirical constant "a" is introduced into the exponent, one obtains

$$R = k\,(1 - e^{-2.303a\epsilon CV}), \qquad (4)$$

from which the various curves of figure 4 can be reproduced satisfactorily by different choices for the value of "a". Equation (4) may be modified further by raising the concentration term to the power "b" and solving for "b" by utilizing data from the separate curves of figure 4. The equation obtained is

$$R = 34.6\,(1 - e^{-0.0125C^{0.39}V}) \qquad (5)$$

which satisfactorily predicts responses for the actinometer as a function of volume at constant solution height and

concentration. A comparison of the experimentally determined and the calculated responses is given in talbe IV.

TABLE IV

Exp. No.	Volume of $ClCH_2COOH$	Conc. of $ClCH_2COOH$	Observed Response	Calculated Response
5	18.2 ml	0.1 M	2.78	3.02
6	40	0.6	12.00	11.5
10	132	1.5	26.3	29.6

It should be emphasized that although there may be theoretical justification for the form of equation (5), it is strictly empirical in character. Three empirically determined constants appear in the equation, consequently it is not surprising that reasonably good agreement if sound with the experimentally determined actinometer responses. Major differences exist between the optical systems involved for the experiments described herein and that required for a straightforward application of Beer's law. For example, the actinometer vessel is cylindrical in shape and radiation enters from many different directions Beer's law applies strictly when a cell with plane parallel faces is irradiated at normal incidence.

The results from experiments 11-18 of table II are plotted in figure 5. It is immediately evident that in the medium and small vessels the stirring rate has no effect on the actinometer response. In the largest vessel, the response increases slowly with increase in stirring rate. The only

explanation for the latter case is that a resonance lamp may emit the 1849A mercury line as well as the 2537A line. If the 1849A mercury line should produce by photolysis a substance opaque to either the 1849A or 2537A line, the actinometer response would be lowest when there is no stirring. When the large vessel is in place, its walls lie within 5-10 mm of the lamp coils, but with the smaller vessels, at least 20 mm separates the coils from the vessel walls. Heidt reports that 10 mm of water is sufficient to remove all the 1849A line (10). Hence, the smaller vessels were unlikely to have received and of this line whereas it is possible that the largest one may have. The amount of the 1849A line received in any event would be quite small because of the low transmission of Vycor 7910 in this spectral region.

The results of the experiments in which the two smaller vessels were deliberately displaced from the axis of the resonance lamp are given in experiments 19 and 20 of table III. It is evident that the actinometer vessel does not require critical positioning in order to give reproducible results. With the available data, it is possible only to speculate concerning these results. One of two conditions may exist inside the coils of the lamp. The number of quanta entering any specific area of the vessel may change as the position of the vessel is changed, but the sum of such changes must be zero, otherwise, the total response would be a function of position. Alternatively, the density and orientational distribution of the quanta inside the helix

may be constant, hence, no matter how much the vessel is laterally displaced within the coils, any unit area of the vessel would receive the same number of quanta. Additional experiments would be required to decide between these alternatives.

One may readily conclude, from the fact that vessels of different diameters have different limiting values of actinometer response, that the radiation from inside the lamp coils travels in all conceivable directions through the interior of the helical spiral. It would be a dangerous procedure to assume for any purpose that the quanta are all directed toward the central axis of the lamp.

CHAPTER V

SUMMARY

The response of the monochloroacetic acid actinometer used in the apparatus as shown in figure 1 is a function of both concentration and vessel size. The response attains a maximum value as actinometer concentration is increased, and one may use figure 3 to determine whether the actinometer solutions probably is absorbing all quanta entering.

An empirical equation was found with which one can satisfactorily predict actinometer responses in the type of experiment performed in this research. The variables in the equation are concentration and volume for constant height of the actinometer solutions.

It appears that stirring is not essential in obtaining proper performance of the actinometer, particularly when the smaller solution vessels are used, neither is it necessary to place the vessels in precisely the same position within the coils of the lamp.

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VITA

Hiroshi Gocho

Candidate for the Degree of

Master of Science

Thesis: AN EXPERIMENTAL STUDY OF THE CHARACTERISTICS OF THE CHLOROACETIC ACID ACTINOMETER IN A HELICAL SPIRAL MERCURY RESONANCE LAMP

Major Field: Chemistry

Biographical and Other Items:

Born: April 6, 1930, at Tokyo, Japan, the son of Kiichiro and Kimi Gocho.

Undergraduate Study: Keio University, Tokyo, Japan, 1949-1953.

Graduate Study: Keio University, Tokyo, Japan, 1953-1955

Oklahoma State University, 1956-1958

Experience: Teaching Assistant, Department of Chemistry, Oklahoma State University, 1956-1958

Date of Final Examination: