A PHOTOGRAPHIC STUDY OF EXTRACTION FROM FORMING LIQUID DROPS

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
William Tambo
1960

A PHOTOGRAPHIC STUDY OF EXTRACTION FROM FORMING LIQUID DROPS

By

William Tambo

AN ABSTRACT

Submitted to the College of Engineering
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of
MASTER OF SCIENCE
DEPARTMENT OF CHEMICAL ENGINEERING
1960

A PHOTOGRAPHIC STUDY OF EXTRACTION FROM FORMING LIQUID DROPS

ABSTRACT

A photographic technique was used to investigate the mechanics of extraction from single drops during the period of drop formation.

A toluene drop, saturated with picric acid and water, was formed at the tip of a glass nozzle immersed in stagnant water. The drop formation and the distribution of extracted colored solute in the water surrounding the drop during the formation period were recorded on 16 millimeter film at the rate of 24 and 32 photographic frames per second. The resulting negatives were analyzed by measurement, the use of microphotometer, and observation.

Physical measurements on the resulting film negatives showed that the transfer area generated was nearly identical to the rate which would have been generated if the drop had remained spherical in shape during formation. Optical measurements using a microphotometer and observation indicated that extracted

solute remained in the water film immediately adjacent to the forming drop.

The theories and previous work applying to extraction from single forming drops were reviewed. None of the theories adequately explained why the extracted solute remained close to the drop interface during formation.

Some qualitative and semi-quantitative information was also obtained from the aforementioned photographs and from some additional photographs of drop formation in pulse flow and of drop coalescence which were taken as a supplement to this work. As the drop broke away from the nozzle, the solute, previously in the water film near the drop interface, was dispersed into the bulk water phase. As the drop rose, a vortex action was indicated which drew the extracted solute into a small area behind the rising drop leaving only a small portion of solute behind. Pulse flow over a forming drop rapidly disperses the extracted solvent through-out the bulk water phase. For this system not less than 0.1 percent of the total solute in the drop was extracted during coalescence.

Included in this thesis are appropriate photographs made from the negatives which were analyzed. Miscellaneous information including the hazards of the system studied, and optical theory, is appended.

A PHOTOGRAPHIC STUDY OF EXTRACTION FROM FORMING LIQUID DROPS

By

William Tambo

A THESIS

Submitted to the College of Engineering
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of
MASTER OF SCIENCE
DEPARTMENT OF CHEMICAL ENGINEERING
1960

Approved: Richard A. Zeleny

Acknowledgements

The funds for the project were provided by the Chemical Engineering Department of Michigan State University.

Dr. Richard Zeleny of the Michigan State University Chemical Engineering Department, under whom this project was carried out, suggested this subject, provided some of the background and assisted in the mathematical developments.

The author wishes to extend special thanks to Dr. Zeleny, for being allowed to proceed largely on his own initiative, and to the entire Chemical Engineering Department staff whose interest in the project and willingness to advise, were invaluable.

TABLE OF CONTENTS

Introduction

With the purpose of furthering fundamental concepts of liquid-liquid extraction, several investigators have, in the past, studied extraction from single liquid drops rising or falling in an immiscible stagnant phase.

The techniques which were employed by these investigators were somewhat similar. Briefly, a number of drops formed at the tip of a small nozzle were allowed to rise or fall through a column containing an immiscible stagnant phase of fluid. Solvent, originally present in the drop or the stagnant phase was transferred between phases. Column height was varied for different runs. Data taken included the number of drops rising in an interval of time, the volume of liquid making up these drops, the concentration of the drop fluid at the beginning and end of each run, and the concentration of the immiscible fluid at the beginning and end of each run. These data enabled the calculation of results which could usually be expressed graphically as percent solute extracted vs. column height.

Results of these studies sometimes were in agreement concerning the extraction which took place during the time a drop was rising and enabled investigators to fit assumed mechanisms to the results with fair success. Little agreement, however, was found concerning the extraction which took place during the time a drop was being formed at the tip of a nozzle. The latter information, usually obtained by extrapolation of a percent extraction vs. column height plot back to column height of zero, ranged from a major portion of extraction taking place during drop formation to a negligible portion of extraction taking place during drop formation.

The most recent investigation of extraction from single drops was directed towards obtaining definite information about extraction during drop formation. At least part of the technique employed was novel enough to be given special consideration. In this study, a number of drops were partially formed at a nozzle tip and then "instantaneously" drawn back into the nozzle through a separate channel. By varying formation time and the extent to which a number of the drops were formed in several different runs and then analysing for the solute in the immissible phase, an equation was developed which described the extraction which took place during drop formation as a function of formation rate. In the opinion of the author, however, this equation describes extraction from a number of drops as they were partially formed and withdrawn from the nozzle, not as they were formed with no interference.

From this brief background concerning the study of extraction from single drops, it is apparent that further work in the area of drop formation would not be superfluous. Further study using techniques similar to those previously described would, however, be repetitious and would not add further enlightening facts to those conflicting facts already accumulated.

Preliminary work by Zeleny[17] indicated that photographic methods might be employed to carry out a very exacting study of liquid-liquid extraction from single drops during the formation period. Such methods would allow direct observation of what takes place at any instant and facilitate calculation of extraction rate from the drop at any instant.

The purpose of this paper, then, is to develop the necessary photographic methods and mathematical expressions required to study liquid-liquid extraction from forming single drops and to apply these methods to a suitable system in order that rates and mechanisms may be determined for the drop formation period.

SUMMARY OF RESULTS

Photographic methods have been developed which enable an exacting study to be carried out of liquid-liquid extraction from single drops during the formation period. This development, along with the necessary techniques and mathematical considerations are found in the section of this thesis entitled "Special Techniques and Mathematical Considerations." The mathematics involved in the development have an intrinsic value in that they may be used for other dynamic studies.

The results of a study of the extraction of a colored solute from a liquid drop forming at the tip of a nozzle which is submerged in a stagnant liquid phase immiscible with respect to the drop is presented. This study has been made using the aforementioned methods.

Toluene drops saturated with picric acid and water were formed at the tip of a glass nozzle immersed in distilled water. The drop formation and the distribution of extracted colored solute in the water surrounding the drop during formation were recorded on 16 mm. film at the rate of 24 and 32 frames per second.

Physical measurements on the film negative provided quantitative information regarding the volume rate of drop formation and the rate of transfer surface generation. The transfer surface is generated nearly as if the drop remained spherical during formation.

Optical measurements provide information regarding extraction during the formation period. Within the scope of the methods used, no extraction can be observed during drop formation. It is concluded that the solute which is extracted remains close to the drop interface.

Visual observations indicate that upon break away this solute was dispersed into bulk water phase. Upon rising, a vortex action was indicated which drew the extracted solute into a small area behind the drop leaving only a small trail of solute.

Qualitative and semi-quantitative results concerning extraction from a coalescing drop and a forming drop in pulse flow are presented by photographic prints. Limiting calculations show at least 0.1 percent and probably much more of the total solute present in the drop is extracted during coalescence. Pulse flow over a forming drop rapidly disperses the solute extracted from the forming drop into the water phase.

Photographic prints of all runs are presented on pages 77, 78, 79, 80, 81, 82, 83, 84.

Theory and Literature Survey

The continued need for information concerning the fundamental mechanisms of extraction processes is well illustrated by the remarks appearing in a recent article by Handlos and Baron[6]. The essence of these remarks follows:

> Although rates of mass transfer in an extraction device may be calculated in a manner similar to the calculation of heat transfer rates in a heat exchanger, the evaluation of certain factors in extraction devices presents difficulties.
>
> There is, for example, no simple relationship by which the contact area in an extraction device may be evaluated.
>
> Because, in an extraction device, flow is neither concurrent nor countercurrent, the evaluation of whatever driving force is available also presents problems.
>
> Further, information on transfer coefficients and their use in design calculations is sparce.

With the purpose of obtaining information about some fundamental mechanisms of liquid-liquid extraction, many studies have been carried out of extraction from single liquid drops rising or falling in a stagnant immiscible liquid phase. The value of such studies is based on the very reasonable premise that liquid-liquid extraction basically takes place in a drop-wise fashion and the understanding of extraction from single drops will contribute to the further understanding of all extraction processes.

The value of this work is based on the same premise and therefore space will be devoted to the further elaboration on this concept. If a liquid-liquid extraction process in a packed column could be observed in slow motion, one would see the lighter phase, assuming it is dispersed, enter the bottom of the column in the form of small droplets. These droplets would rise through the continuous phase until restrained by barriers formed by the packing. The barriers referred to act like inverted cups which, as more dispersed phase droplets are restrained or trapped, fill and subsequently overflow. The overflow of light dispersed phase from these barriers probably takes place one or two drops at a time, corresponding to the rate at which the dispersed phase is trapped. As overflow takes place, new droplets are formed which, further up the column, are trapped, repeating the process.

Most likely as a result of a consideration similar to that just presented, it has been proposed[10] that there exists three distinct stages in the life of a drop,

1. Drop formation
2. Drop movement
3. Drop coalescence

In all previous investigations of extraction from single liquid drops rising or falling in an immiscible stagnant liquid phase*, an attempt was made to consider these three stages separately. Experimental means were divised to study each stage, and the resulting data was compared to predicted data based on various assumed mechanisms.

The specific purpose of this work is to obtain quantitative information on the drop formation period in liquid-liquid extraction. The remaining portions of this section are, therefore, confined as much as possible to presenting the theory and previously obtained information concerning extraction from single liquid drops during the formation period. For clarity, the remaining portion of this section is divided into three parts; the first is concerned with theoretical

---

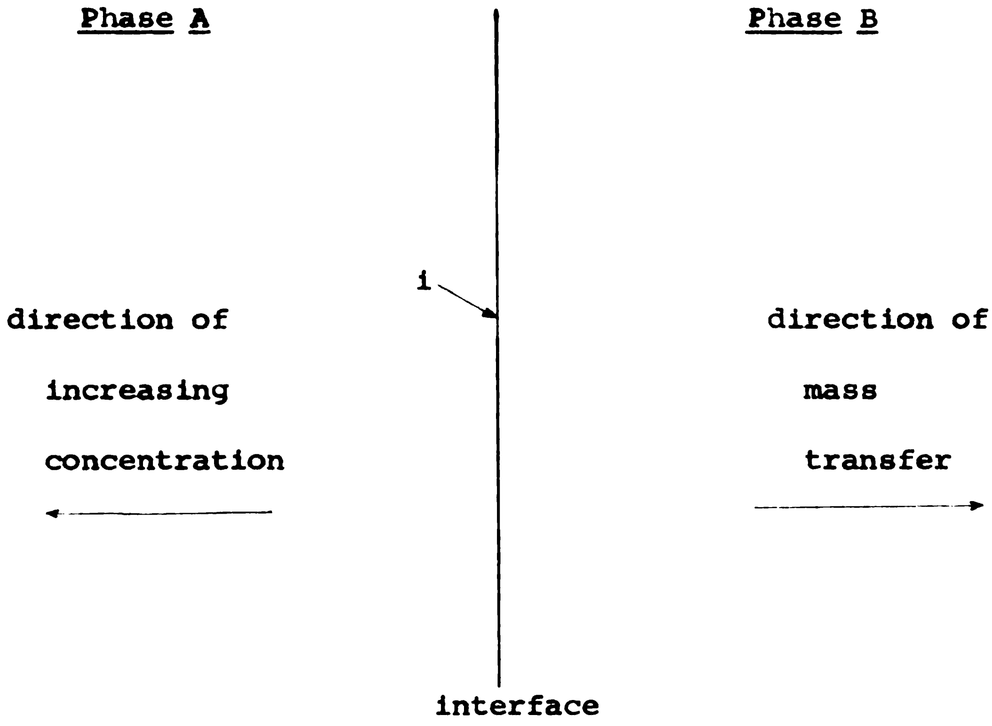
* Hereafter "extraction from single liquid drops" will be understood to mean "extraction from single liquid drops rising or falling in an immiscible stagnant liquid phase".

considerations, the second with previous experimental efforts, and the third with some comments and the basis for continued study. Rather than leave the reader with no background information on extraction in general and extraction from liquid drops in all stages, such information is included wherever it serves the development of the text.

PART I - Theoretical Considerations

A. General

The theoretical development of extraction from single drops is best approached from briefly considering the diffusion of a solute from one solvent to another which is immiscible in the first. In this consideration, the following schematic diagram[4] will be used. The development will be recognized as the two film theory.



In the two phases shown, the concentration of solute in phase B is less than that concentration of solute which would be in equilibrium with phase A. The concentration in the bulk of phase A is greater than the concentration at point i, the interface. The molal rate of diffusion at any instant in the B direction is given by

$$(1) \quad \frac{dN}{dt} = k_A a \, (C_{iA} - C_A)$$

where N = moles

t = time

a = area perpendicular to the direction of diffusion

k_A = transfer coefficient for phase A

C_{iA} = molal concentration of solute at interface in phase A

C_A = molal concentration of solute in the bulk of phase A

If the volume of solvent in A is constant then

$$(2) \quad V_A \frac{dC_A}{dt} = k_A a \, (C_{iA} - C_A)$$

where V_A is the volume of solvent A.

Because the rate of diffusion in both phases must be equal

$$(3) \quad V \frac{dC_A}{dt} = k_A a \, (C_{iA} - C_A) = (C_{iB} - C_B) \, k_B a$$

Now, introducing m, the distribution coefficient so that

$$C_A{}^* = mC_B \text{ and } C^*{}_{iA} = mC_{iB}$$

where $C^*{}_A$ is the concentration of Phase A which would be in equilibrium with the concentration of Phase B and then substituting into (3)

$$(4) \quad V_A \frac{dC_A}{dt} = k_A a \, (C_{iA} - C_A) = \frac{k_B a}{m} \, (C_i{}^*{}_A - C_A{}^*)$$

Then writing an equation considering an over-all transfer coefficient and driving force,

K_A and $(C_A - C_A{}^*)$ respectively

$$(5) \quad V_A \frac{dC_A}{dt} = K_A a \, (C_A^* - C_A)$$

Equating the right hand sides of (4) and (5) and assuming equilibrium at interface or that $C_{iA} = C_{iB} = C_{iB}^*$,

$$(C_A - C_A^*) = (C_A - C_{iA}) + (C_{iA} - C_A^*)$$

Substituting and rearranging

$$(6) \quad \frac{1}{K_A} = \frac{1}{k_A} + \frac{1}{mk_B}$$

or if equilibrium at interface is not assumed

$$(7) \quad \frac{1}{K_A} = \frac{1}{k_A} + (R_i) + \frac{1}{mk_B}$$

where (R_i) is the interfacial resistance.

If m is large and equilibrium at the interface is assumed,

$$(8) \quad \frac{1}{K_A} = \frac{1}{k_A}$$

Going back to equation (5) and assuming C^*_A constant and integrating from $C_A = C_{oA}$ to $C_A = C_{fA}$

where o refers to initial and f to final

$$(9) \quad \ln - \frac{(C_A^* - C_{fA})}{C_A^* - C_{oA}} = \frac{K_A at}{V_A}$$

If the initial concentration of phase B is zero,

$$(10) \quad \ln \frac{C_{fA}}{C_{oA}} = \frac{K_A at}{V_A}$$

and if spheres are considered $\frac{a}{V_A} = \frac{3}{R}$, where R is the radius of the sphere, and

$$(11) \quad \ln \frac{C_{fA}}{C_{oA}} = K_A t \ \frac{3}{R}$$

B. Liquid Drops Already Formed

1. The Dispersed Phase

The above approach was general save for one point where the quantity a/V_A was set equal to 3/R for a sphere. Now the consideration of extraction from single liquid drops already formed will be combined with the above development. For this purpose the equation relating the overall mass transfer to the individual mass transfer coefficients and interfacial resistance will be rewritten

$$\frac{1}{K_d} = \frac{1}{k_d} + (R_i) + \frac{1}{mk_c}$$

where d refers to the dispersed phase or drop and c the continuous phase of the system.

In many systems in which extraction from formed single liquid drop takes place $\frac{1}{mk_c}$ is small enough to be neglected and as a result little effort has been put forth in the determination of k_c. Even though (R_i)

is sometimes thought large enough to be significant, little experimental work has been put forth in its analysis. Further no theory which is adequate has been developed concerning (R_1). Most studies previously made have been directed towards the determination of k_d, and the theory on this subject is plentiful and will therefore be presented first. In all the theory to be presented, whether the drops are formed or forming, the dispersed phase is assumed to be small spherically shaped drops. This should be kept in mind.

The simplest treatment of the dispersed phase is to assume complete mixing of the fluid within the drop right up to the interface. In this way no film can exist and the concentration throughout the drop is uniform. Then, k_c is infinite or $\frac{1}{mk_c}$ is zero. This is an oversimplified consideration and would probably hold true for very few situations in liquid - liquid extraction.

A more reasonable but still extreme treatment is to assume that absolutely no circulation takes place within the drop. Mass transfer from the interior of the drop to the interface would then have to take place by means of pure molecular diffusion. Differential equations have been formulated[4] and solved for this situation. These equations give at any time the concentration at any radius from the center of the drop, the total moles of solute which have crossed the interface of the drop, the average concentration of the drop and, for various size drops, the effective mass transfer coefficient, k_d. The derivations of some of these equations are in Appendix I.

Logically, if the above theorized mechanisms played a major part in extraction from single liquid drops already formed and rising, the actual situation would fall somewhere between, that is, incomplete mixing within the drop. With this reasoning, another treatment of dispersed phase resistance is to consider that the transfer of solvent takes place from elements which always maintain a fixed position with respect to the interface. New elements replace the old ones as the drop rises, and the old elements are dissipated in the center of the drop. Transfer of material from each element is so small that not enough concentration difference exists to cause mass transfer from the center of the drop. The energy required to remove the small surface elements and replace them with new elements is obtained from drag friction. It is interesting to note that this treatment allows for diffusion in the volume close to the surface of the drop and mixing near the center. It would seem, for a rising drop, that the actual situation would involve the opposite physical means of transfer as the inside of the drop would be stagnant and circulation would be at the surface due to drag. The equations derived to describe extraction from a single liquid drop dictated by the above mechanism necessarily includes terms which take into account drop diameter and rate of rise[16]. This is so because frictional forces, a function of diameter, and rate of rise determine the length of time each of the elements is exposed to the interface of the drop.

The film theory has been proposed to explain the mechanism by which extraction takes place from liquid drops. In the simplest treatment of the film theory a thin stagnant film of dispersed phase surrounds the main body of the drop. The film is considered so thin the amount of solute required to establish a gradient across the film is negligible. Mixing takes place within the drop and, $k_d = \frac{Dm}{X}$, where D_m is molecular diffusivity and X is the film thickness.

A modified film theory proposes two films, a laminar one and a turbulent one. A correlation has been worked out on this basis.[13]

An equation has been derived giving the concentration within a drop at any time by predicting the circulation in a moving drop from fundamental equations of hydrodynamics and viscous flow.[5]

The last treatment of any consequence was to consider a "viscous" circulation inside the drop, that is, circulation but no turbulence. A mathematical expression for this physical situation was obtained by considering diffusion from a cylinder of infinite length.[2]

B. Liquid Drops Already Formed

2. The Continuous Phase

The various theories just presented were concerned with dispersed phase resistance. The continuous phase will now be considered.

As previously pointed out, little effort has been set forth to verify any of the theory connected with continuous phase resistance in extraction from single drops. Most investigators have purposely chosen systems in which $\frac{1}{mk_c}$ is so small compared to $1/k_d$ that $\frac{1}{mk_c}$ could be neglected. Some effort has been devoted to analytical and approximate relationships to describe the continuous phase resistance. Some of the considerations are similar to those discussed for dispersed phases resistance.

As might be expected, the simplest treatment of continuous phase resistance is to assume complete mixing of the continuous phase. The resistance to transfer then is zero and k_c is infinite.

The opposite extreme, no circulation of the continuous phase at all, cannot be handled mathematically. By considering diffusion from the drop to a semi-infinite liquid of contact area equal to the surface of the drop, however, an equation has been derived which approximates this physical situation.[14] This equation gives concentration at any point in the continuous phase as a function of time.

A somewhat modified and more realistic model assumes complete mixing of the continuous phase save for a thin film around the drop. This will be recognized as the film theory and it is applicable to the continuous phase in the same way it is applicable to the dispersed phase.

The surface renewal theory may also be applied to the continuous phase. As in the one of the preceeding treatments, however, mathematical development is possible only when approached using the approximation of transfer to a semi-infinite liquid of contact area equal to the surface of the drop.

C. Interfacial Resistance

It is apparent, at this point, that some of the same theories which apply to the dispersed phase are suitable for treatment of the continuous phase. Such is not the case with interfacial resistance (Ri). Interfacial resistance is referred to very little in the literature. In fact, no conclusive evidence of its existence is supplied. Further, there have been found no attempts to treat, analytically or empirically as far as mathematics are concerned, how solute might be transferred across this resistance.

D. Forming Liquid Drops

1. The Dispersed Phase

Thus far the two film theory has been briefly reviewed and this theory has been qualitatively applied to extraction from already formed rising liquid drops. Now, the, same application of the two film theory will be applied specifically to extraction from forming liquid drops.

Beginning with the dispersed phase resistance, again, the simplest treatment is to assume complete mixing of the liquid in the drop and subsequently a uniform concentration throughout. In this case $k_d = \infty$ and $\frac{1}{mk_d} = 0$. This treatment is reasonable as fluid entering the drop might cause complete internal mixing.

If the other extreme is assumed, that is no mixing of the liquid within the drop, then further assumptions must be made regarding what happens to the liquid entering the drop during formation. If it is assumed that this liquid enters the center of the drop, (this assumption is more in error as the drop becomes larger), and pushes old liquid uniformly outward from the center, then the following differential equation, which is derived in the appendix, is obtained.

$$D \frac{\partial^2 C}{\partial r^2} + \frac{2D}{r} \cdot \frac{\partial C}{\partial r} - \frac{U}{4\, r^2} \cdot \frac{\partial C}{\partial r} = \frac{\partial C}{\partial t}$$

No solution for this equation has been obtained. Although the usual approach is to assume a product solution such as $C = R \times T$ where R is only a function of r and T is a function of t, this assumption, however, does not satisfy the boundary conditions of the physical problem. Changing variables in such a manner which allieviate this difficulty has also proven unsatisfactory as the resulting expression is so complicated that attempts to rearrange the equation in such a manner that each term involves one independent variable is impossible.

As a compromise between the aforementioned extremes, complete mixing is assumed within the drop save for a thin film at the surface of the drop. The amount of solute required to effect a gradient across the film is so small that new film generated by drop formation immediately reaches its steady state concentration gradient. Accounting for the variation of surface area, the bulk concentration is given by the equation[4]

$$C = C_o \left\{ \exp \frac{9k_d t}{d} \sum_{n = 0}^{n = 00} \frac{3\,(9k_d t/d)^n}{(Zn + 3)\,n!} \right\}$$

The surface renewal theory, wherein transfer takes place from surface elements which are continually removed and renewed by means of drop circulation can be applied to forming drops. The problem here is to determine an analytical relationship between the element exposure time and the drop formation time. To do this many assumptions regarding drop circulation have been made and these will not be here summarized.

The removal of these surface elements may be assumed to be brought about by means other than circulation... for example frictional drag forces and forces on the surface of the drop.

D. Forming Liquid Drops

2. The Continuous Phase

Although most investigators have eliminated the need for consideration of the continuous phase resistance by choosing a system in which the solute strongly favors the continuous phase, it has been proposed[10] that because of the motion of the incoming liquid in a forming drop, vigorous circulation is maintained within the drop eliminating the dispersed phase resistance entirely. The continuous phase would, on the other hand, remain stagnant and therefore present resistance. The resistance of the continuous phase, thus considered, is controlling. Considering diffusion to a semi-infinite liquid shell and accounting for new surface area by assuming that new surface is formed with a concentration gradient equal to that of the old surface, the following analytical expression for the continuous phase was derived:

$$\frac{C_o - \overline{C}}{C_o - C_i} = 2.34 \; D \frac{(t_f)^{\frac{1}{2}}}{V^{1/3}}$$

E. Coalescence

A word will be said about coalescence. This part of drop life has been most neglected as far as theory and experimental work is concerned. Most investigators have taken steps, though not always successfully, to avoid its effect in their data. When required a qualitative treatment has been given the subject by applying the film theory.

PART II - Previous Experimental Efforts

Now that the various mechanisms for mass transfer from forming drops have been summarized, the most important analytically, the remainder of this section will be devoted to presenting previous studies of extraction from single liquid drops which directly pertain to extraction from single forming liquid drops.

The first study carried out on extraction was presented in a paper prepared by Sherwood, Evans and Longcor[12]. The equipment and experimental procedure involved in this study set the pattern for many following studies, and therefore, a detailed description of the same is worthwhile.

Drops of solvent containing acetic acid were introduced through a nozzle mounted vertically at the bottom end of a glass column filled with water. Drops of this solvent formed at the tip of a nozzle broke away and rose through the water. The solvent feed rate was controlled by maintaining a constant level in a feed tube which was attached to the nozzle. Solvent was fed to this feed tube from a buret so that the amount of solvent used could be recorded.

The top of the aforementioned column consisted of a cork stopper the bottom end of which had been carved out to a conical receptical. A minute quantity of water was forced into the bottom of the column during runs. In this way, the drops which had reached the top of the column were caught in the conical top and carried out with the minute purge water into a glass measuring buret.

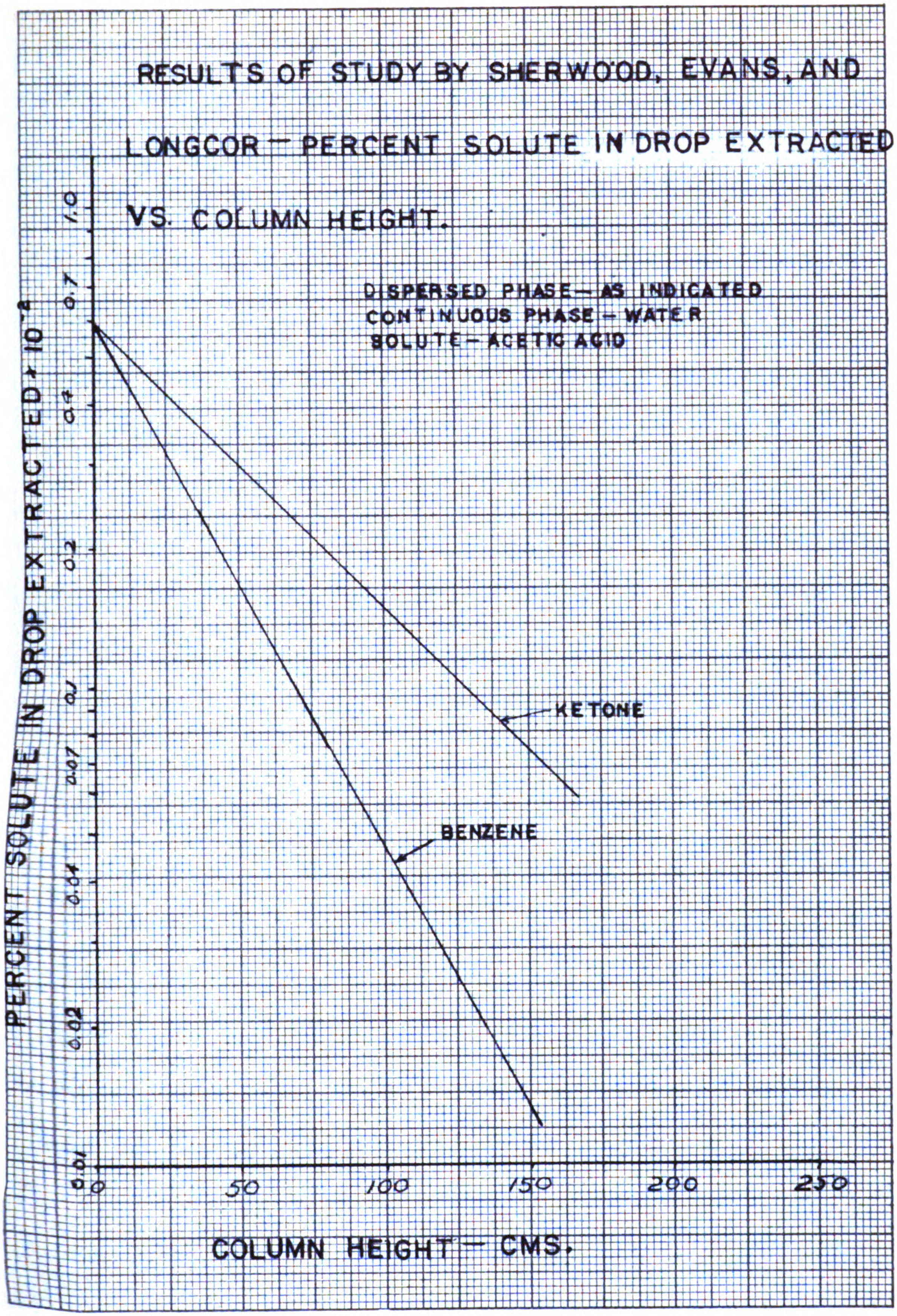
A run consisted of recording the number of drops which rose during a predetermined time interval. After a run was completed, quantities of inlet and outlet solvent and outlet water quantities were determined by buret readings. Acetic acid contained in these solutions was determined by titration. During a run, the number of drops formed was recorded. In this way the time it took a drop to rise and the volume of the drops formed could be calculated.

The solvents used were benzene and methyl isobutyl ketone. Several different size nozzles were used to vary drop size. The column height could be varied by adjusting the position of the stopper in the bottom of the column. The nozzle was inserted through this stopper. All runs were carried out at 22 - 28^{o} C.

In the actual experimental work,drop size, column height, inlet concentration of acid in solvent and solvent feed rate were varied. Drop diameters were calculated on the basis of spherical drops and the amount of solvent fed.

Drop diameter varied slightly compared to nozzle size indicating that the properties of the solution from which the drop was formed are an important factor in drop size.

The most important result of this study is summarized by the graph on page 27, which shows a plot giving percent extracted vs. column height for benzene and ketone. Data for this graph was obtained by changing column height for different runs of the same drop diameter. It will be noted that using a semi-log



RESULTS OF STUDY BY SHERWOOD, EVANS, AND LONGCOR — PERCENT SOLUTE IN DROP EXTRACTED VS. COLUMN HEIGHT.

plot the data appears to fall on a straight line. Extrapolating this line to zero column height would indicate 40 percent of the extraction took place during the time when the drop was forming.

One more word about the study of Sherwood, Evans and Loncor: the method of removing from the column the drop, from which extraction had already taken place, was intended to exclude the effect of extraction in the third stage of the drop life, coalescence. The data, then, are intended to reflect only the extraction taking place during stage one and two, formation and movement of the drop. Later investigators, however, questioned the effectiveness of this method in eliminating effects of coalescence and felt that some error may have been introduced in the data.

A second study of drop-wise extraction was carried out by Kopinsky[8] using a system in which extraction would take place from the continuous phase to the drop. An effort was made to cancel out the effects of the formation period. A detailed summary of this study is omitted because the article was not available.

Farmer[2] carried out a study with acetic acid as the solute in the dispersed phase with several dispersed phase solvents, particularly CCl_4. CCl_4 was heavier than the continuous phase, water, and, therefore, the data pertained to falling drops. Percent extracted was plotted vs. column height and an extrapolation to column height zero showed there was a variation with percent extracted during formation and formation time. No attempt was made to correlate.

Licht and Conway[9] studied falling drops and made an attempt to separate the three stages of drop life by including stop-cocks at various points in the column used. These stop-cocks were closed at the end of a run, thus separating the sections of the column. Data from this study are presented in a plot similar to the that on page 27 . The extrapolation of this plot to column height zero indicated from 10 to 30 percent of the solute was extracted during drop formation. This is lower than Sherwood reported. Further information indicated that drop size or drop formation time had little or no effect on the amount extracted during formation.

Licht and Pasing[10] studied a system of water, acetic acid and methyl isobutanol. Water was the dispersed phase. Similar to the Licht and Conway study, a column was used on which were located stop-cocks to facilitate separation of the amount extracted during the three stages of drop life. In this study no variation of extraction during formation with formation time could be detected which agreed with some of the previous results. It was concluded that some unusual effect was present during formation which caused the amount extracted to be independent of time and drop size. Perhaps, the breaking away of the drop caused this effect. In this study, coalescence is separated from the other stages of drop life and the amount extracted during this stage was found to be independent of size or concentration. The authors also take note that when extrapolating percent extraction-column height curves, several smooth curves could be drawn to column height zero. This would invalidate this method of determining extraction during formation.

Haritatoes and Liberman[7] carried out an investigation in which acetic acid and valeric acid were solutes in a dispersed benzene phase. Water was the continuous phase. The usual extrapolation to column height zero showed an increasing amount extracted during the formation period with an increased formation time. The authors contend that the column purge during coalescence was inadequate in previous studies and this introduced error as the coalescence period was not eliminated. A study of the coalescence period showed that extraction during coalescence was proportional to concentration and diameter. This is contrary to previous results.

Further study of extraction from single drops was carried out at the University of Washington and was reported by West, Robinson, Morgenthaler, Beck and McGregor.[16] Again, a system of Benzene, acetic acid and water was used. The apparatus and experimental methods are so similar to that of Sherwood, Evans and Longcor that description of it would be repetitious. Despite the similarities in the work, results did not agree. The data of West when extrapolated to zero column height show only 14 to 20 percent extraction takes place during drop formation as compared to the 40 percent obtained by extrapolating Sherwood's data to zero.

Further work by West and associates[12] showed that certain impurities in the benzene, acetic acid and water system would affect considerably the amount extracted.

It was concluded that dissolved tygon tubing affected Sherwood's results.

Coulson and Skinner[1] studied a system of benzene and water in which benzene was the dispersed phase. Solvents were used which enabled the experimenters to neglect the continuous phase resistance. This study is important in that the data taken were specifically restricted to the formation period. This was accomplished by partially forming a number of drops at the end of a nozzle and rapidly ejecting these through an alternate opening in the nozzle. By titration of the continuous phase the amount extracted during various periods of formation could be obtained. Though this study was extensive a detailed summary is omitted as the techniques were later improved upon by another investigator and another similar study made.

Gregory[4] carried out a study using acetic acid as the solute with benzene as the dispersed phase and water as the continuous phase. Apparatus similar to that used by Coulson and Skinner was used. The apparatus was improved upon in that ejection was more rapid. Again drops were partially formed at the tip of the nozzle and then instantaneously withdrawn from the tip of the nozzle through an alternate opening in the nozzle. By partially forming a number of drops to different degrees and obtaining data by titration of the immiscible phase, equations were worked up describing extraction during drop formation. The equation which best correlated the data obtained was

$$\frac{k_d}{V} = 3.74\left(\frac{dV\rho}{\mu}\right)^{-0.2}\left(\frac{\mu}{\rho D}\right)^{-1.0}$$

where k_d = dispersed phase transfer coefficient
V = nozzle velocity
d = diameter of the drop
ρ = the density of the drop
D = diffusivity of solute in drop solvent
μ = viscosity of the drop fluid

Gregory concluded that at slow formation rates the extraction mechanism was diffusion and at fast formation rates turbulence carried the solute to the surface of the drop.

It is felt that this study and the resulting equations are concerned with a drop formed and ejected and not a drop formed without interference.

Other studies of drops which do not contain data relative to extraction from forming drops were carried out by Garner and Skelland[3], and Pike, Withers and Beaty[11] and So[14].

PART III - Comments and Basis for Future Study

The equations concerning drop formation are based on rigid assumptions. These assumptions, though necessary to facilitate mathematical development, are extreme. The equations, therefore, pertain to highly idealized mechanisms and probably do not describe actual situations satisfactorily.

Previous investigators, because of limitations of experimental procedure, did not obtain adequate data concerning drop formation. Results conflicted, theoretical equations could not be verified and empirical equations, in most cases, were not formulated. Though further study is indicated, it is apparent that new experimental methods are required if the already existing information is to be added to.

The basis for a new method of studying extraction from single forming liquid drops is found in a study of extraction by Zeleny.[17] In this study the transfer of a colored solute from one phase to another, the phases flowing past each other counter currently in a horizontal extractor, , was studied using photographic methods. As a side light to this study, photographs were taken of rising and forming drops. These photographs indicated that photographic methods could be developed which would make possible a very exacting study of extraction from single drops during the formation period, and, further, such photographic methods would enable visual observations of what is happening at any instant and measurements of extraction at any instant.

This information would enable the formulation of empirical equations which would accurately describe extraction during drop formation. Also, the existing theoretical equations might, with this information, be verified or modified to describe the actual mechanisms of extraction.

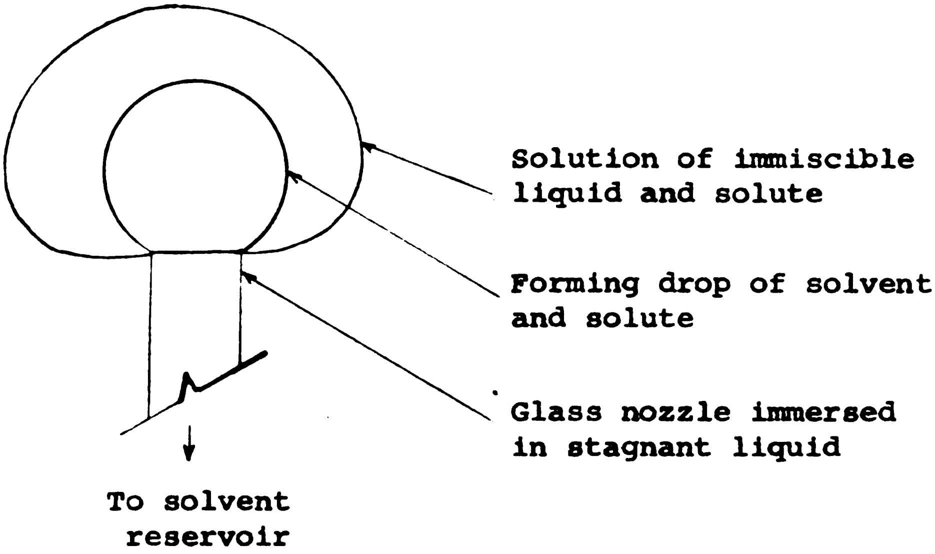
The development of the required photographic methods is found in the following section which is entitled "Special Techniques and Mathematical Considerations".

Special Techniques and Mathematical Considerations

The following section is a description of the means by which quantitative information is to be obtained by photographing, with a motion picture camera, extraction from a drop forming at the tip of a nozzle submerged in a liquid immiscible with respect to the drop. The techniques described and mathematical considerations made have an intrinsic value, in that they may be applied to other types of dynamic studies.

The first stage of extraction from a single drop, as previously mentioned, is the formation of the drop or the generation of transfer interface. In experimental studies of liquid-liquid extraction from single drops this formation takes place at the tip of a nozzle which is immersed in a solute free liquid which is immiscible with respect to the solvent from which the drop is to be formed.

Extraction from the forming drop takes place along the liquid-liquid interface. The extracted solute may logically be assumed to be arranged in a cloud-like fashion in the stagnant liquid surrounding the drop. This is schematically illustrated below.



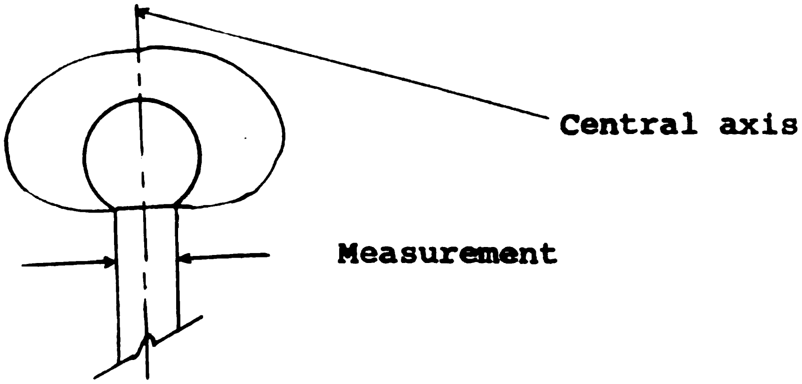
If a colored solute is used, the shape of this cloud may be recorded on a photograph providing, of course, the optimum film, filter, shutter speed, lens opening, and exposure time are used. Obtaining a photograph of the drop during formation, however, provides only qualitative information. If quantitative information on liquid-liquid extraction from single forming drops is desired, the following data must somehow be obtained:

1. the rate of drop formation, $\frac{Vm}{\text{unit time}}$
2. the rate of interface generation, $\frac{\text{area}}{\text{unit time}}$
3. the total extraction which has taken place at any time.
4. the concentration of the solute at any point around the forming drop.

If a motion picture camera is used which takes a known number of frames per second, the first two items are easily determined, providing some type of constant volume feeder is used for the purpose of introducing the solvent.

It might be noted here that it would be no easy task to design a feeder with a calibration fine enough and a timer accurate enough to be sure at what rate the small amount of solvent which makes up the drop had been fed. With a camera, as will be demonstrated, only that the feeder does feed at a constant rate need be known. The camera provides the calibration and the timing device.

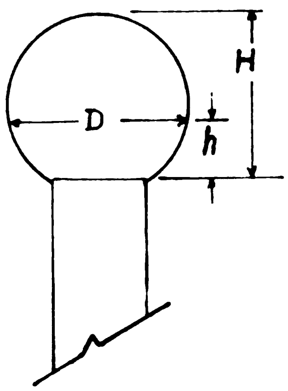
As a drop is formed at the tip of a nozzle immersed in a stagnant liquid, symetry about an axis through the center of the nozzle is observed as illustrated. below.



If one measurement is made on the apparatus, such as shown above, a reference scale is then provided for the photograph which is to be taken and any projection thereof.

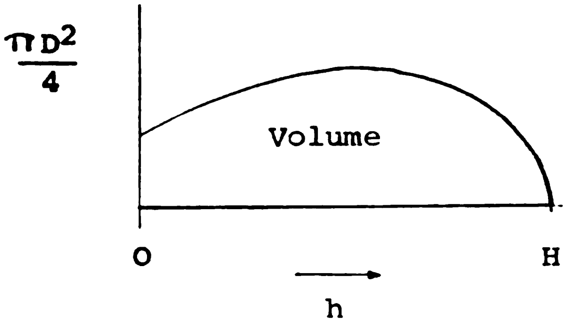
After a film has been developed, several frames could be analyzed, say the fourth, eighth, sixteenth, and thirty-second, counted from the time the drop began to form. These represent, if the camera was taking 32 frames per second, one-eighth, one-fourth, one-half and one second respectively.

The volume of the drop at any time interval may be calculated by assuming symmetry around a central axis and considering the following measurements on a single photographic frame:

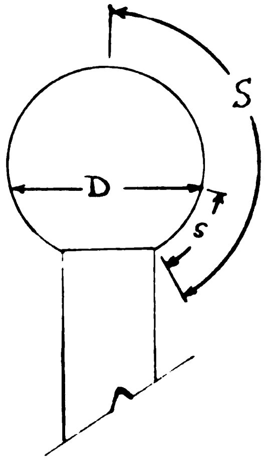


The cross-section of the circle for which D is the diameter $= \frac{\pi D^2}{4}$. If D is a function of height, the volume $= \int_0^H \frac{\pi D^2}{4}\, dh$.

For each frame, the value of the integral may be determined by measurement and graphical integration as shown below:



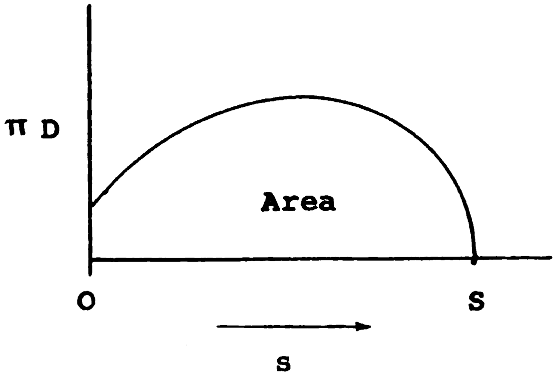
The surface area may be calculated for each frame also. Consider the following measurements:



The circumference of circle for which D is diameter = πD.

If D is a function of s , the area = $\int_0^S \pi D ds$.

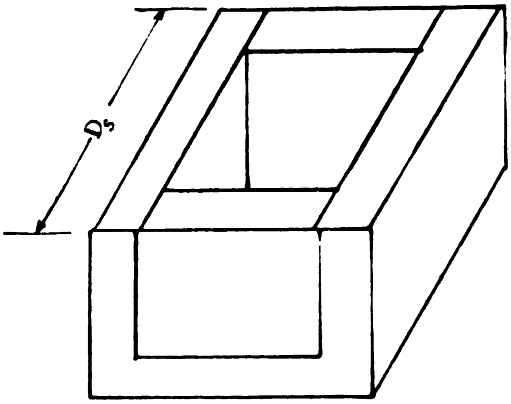
For each frame, the value of the integral may be determined by measurement and graphical integration as shown below:



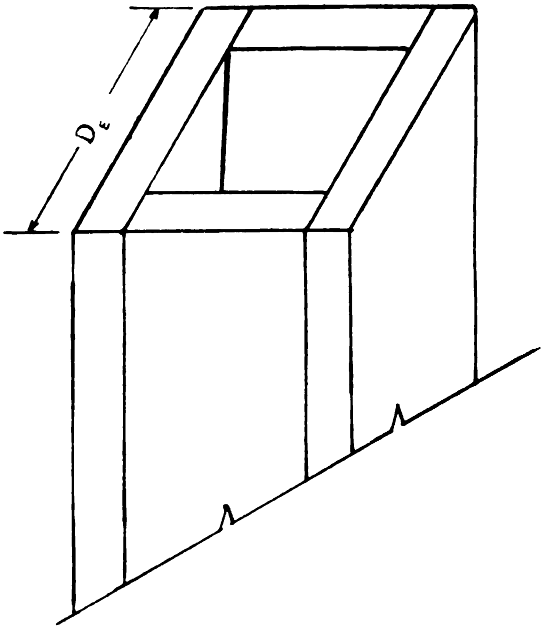
Once the value and surface area of the drop have been evaluated for several frames, a plot may be made and an exact or empirical equation fitted to the data which will represent the surface or volume at any time.

It should be noted that the only assumption made is that of symmetry about a vertical axis passing through the center of the nozzle and drop. This same assumption will also be made in obtaining a concentration distribution of solute in the immiscible phase around the drop.

The figures below show the nature of an extractor and standard cells which will be used for the study.



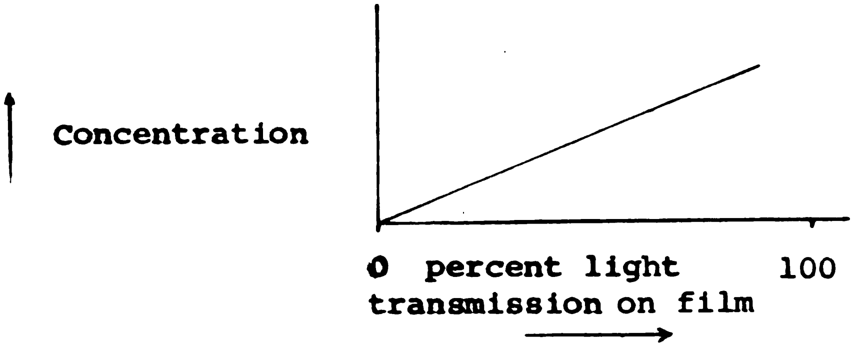
STANDARD CELL



TOP PORTION OF EXTRACTOR

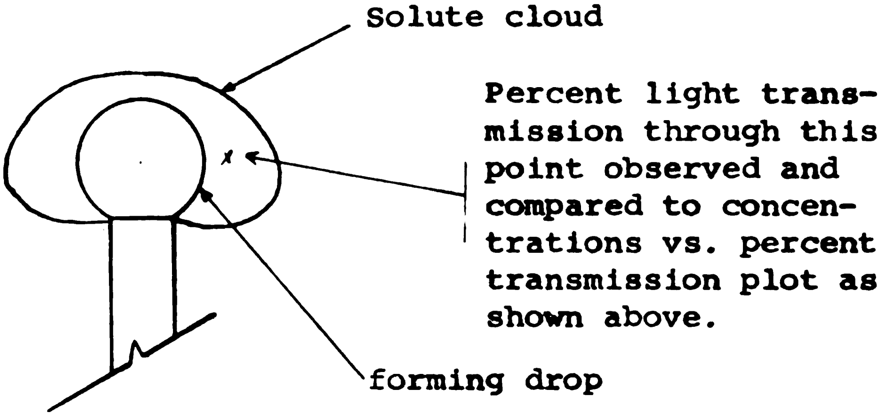
An extractor with a rectangular cross section is shown. Metal sides are used on the extractor. Two parallel glass faces make up the front and back of the unit. Shown next to the extractor is a standard cell. The faces of this cell are constructed of the same type of glass as the extractor, the same thickness and the same distance apart, $D_s = D_e$.

If a colored solute is used, various concentrations of solute and immiscible fluid can be photographed through the standard cell. The density of the film negative will depend on the concentration of solute only as, for each photograph, light source, lens opening, lens speed, film, filter, shutter speed and camera distance will be maintained constant. By comparing these film negatives by use of an optical densitometer a plot can be prepared of concentration vs. light transmission. This plot will look as follows:



where the 0 percent light transmission point is for pure water, and 100 percent for an opague medium.

Now if photographs are taken of a drop forming keeping all previously mentioned variables constant, various points in the immiscible fluid around the drop can be compared for percent light transmission to the standard cell concentrations by means of the optical densitometer. For example see sketch below which represents a certain frame.



It should be noted that the comparison represents an average concentration which the microphotmeter "sees" compared to the concentration of the standard cell. Analyzing the photographs with the purpose of obtaining point concentrations anywhere around the drop at any time is an involved procedure. Consider Figures

1, 2, 3, and 4 on pages 46 and 47 .

For each photographic frame the area around the drop is to be mapped as shown in Figure 1. The intersections of the lines 1, 2, 3, ..., with the lines A, B, C, ... represents points which will be read on the densitometer for percent light transmission. The mapping lines, in 3 dimensions, represent planes, and Figure 2 shows a cross section of the extractor in isometric represented by plane 4. The lines B, C, D... in Figure 2 represent the intersection of the planes B, C, D..., with plane 4. These lines also represent differential volumes through which percent light transmission will be measured. This is shown in Figure 3. It is clear that any points chosen for measurement can be represented by this mapping method.

What is eventually desired from this analysis is an expression for concentration any point in the "cloud" around the drop. First an expression will be obtained for the concentration at any point on the numbered planes. Consider plane 4 for example, and say this expression can be represented by a series such as

$$(1) \quad C_{4r} = a_o + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4$$

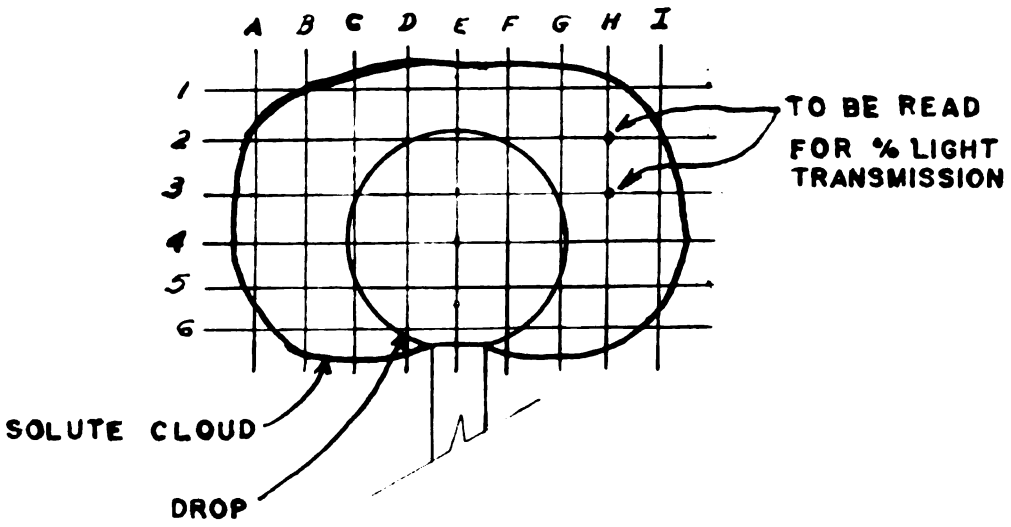


FIGURE 1 — MAPPED DROP

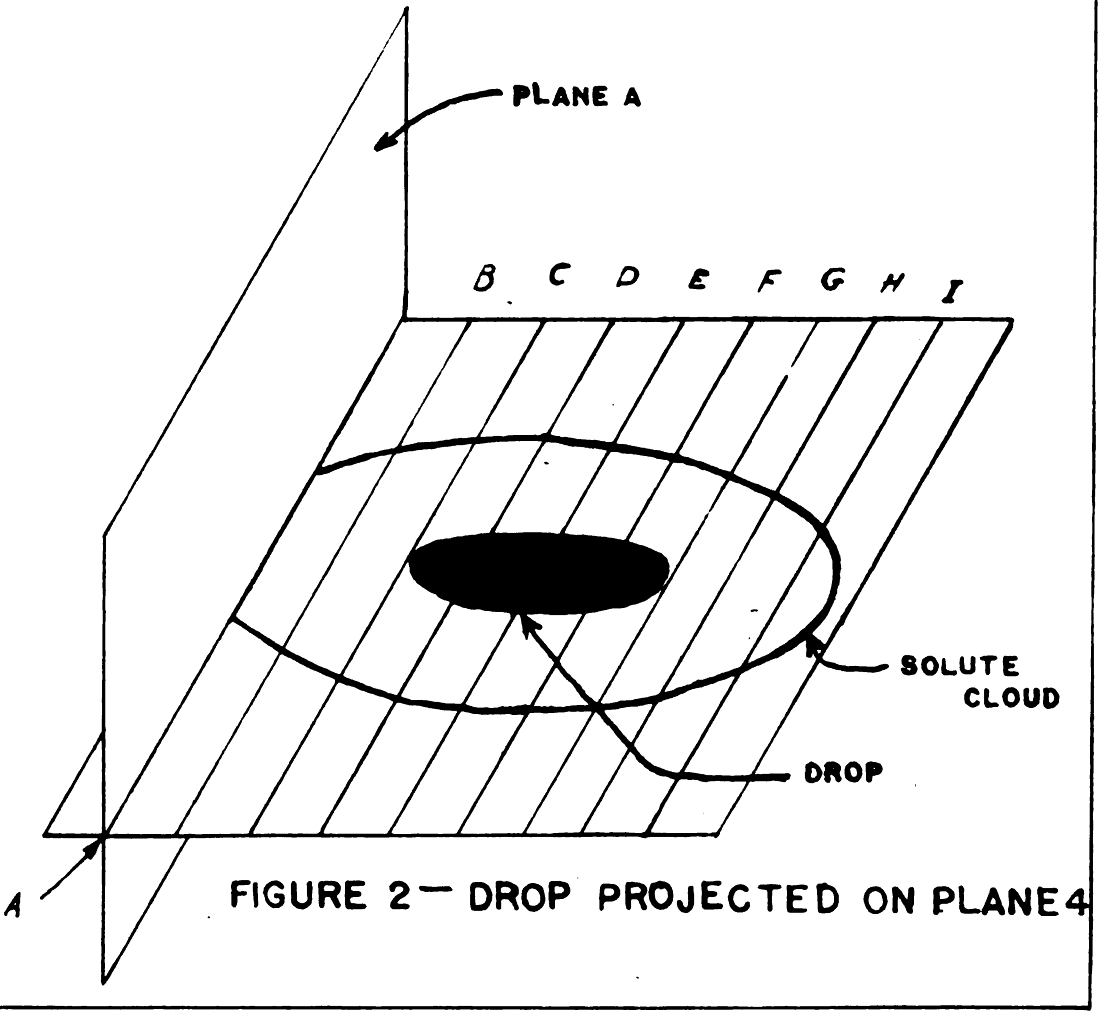
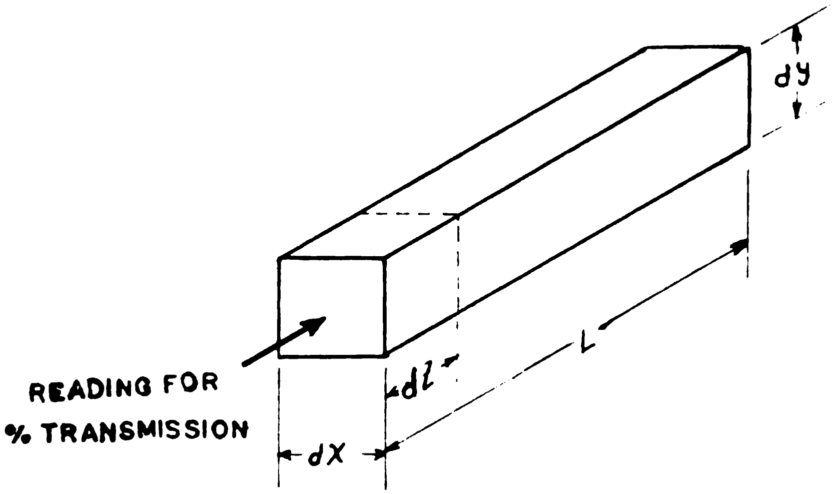


FIGURE 2 — DROP PROJECTED ON PLANE 4

FIGURE 3— ELEMENT



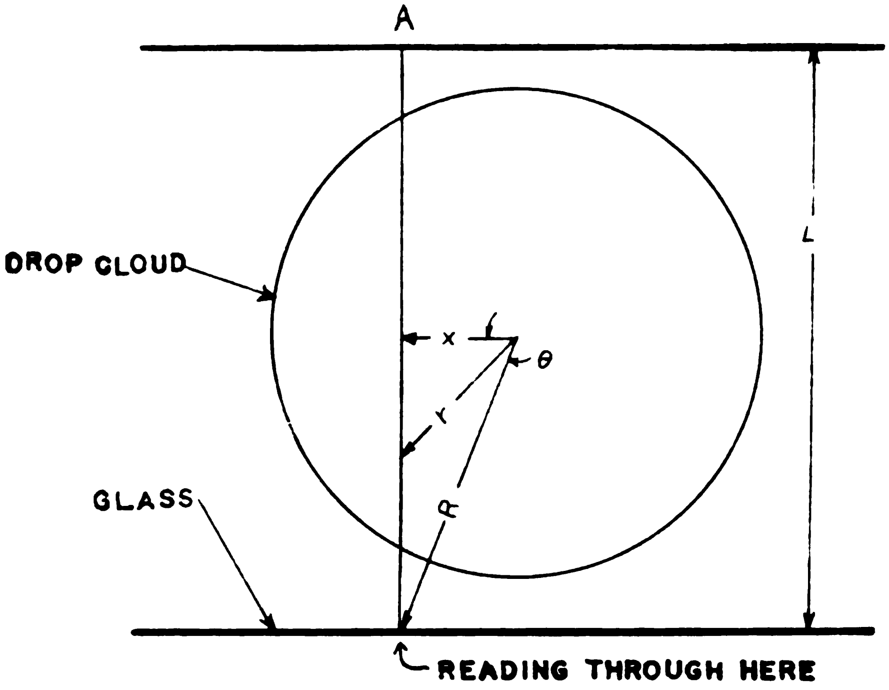


FIGURE 4— VIEW OF DROP CLOUD FROM TOP

where C_{r4} is the concentration on plane 4 corresponding to a distance r away from the central axis as shown in Figure 4. a_o, a,... and a_4 are constants. (Again symmetry with respect to shape and concentration is assumed around the central axis.)

If C_{4A} is the average concentration the densitometer sees through element 4A, using the nomenclature in Figures 3 and 4, then,

$$\bar{C}_{4A} = \frac{\text{total moles of solvent in element LdXdY}}{\text{LdXdY}}$$

or

$$\bar{C}_{4A} = 2\int_0^{L/2} \frac{C_{4r} \quad dXdYdZ}{LdXdY} = (2)\,\frac{2}{L}\int_0^{L/2} C_{4r}\, dZ$$

The trigonometric transformations from Figure 4 give

$$Z = R \sin\theta$$

$$X = R \cos\theta$$

and by division and rearrangement

$$Z = X\frac{\sin\theta}{\cos\theta} = X \tan\theta$$

and

(3) $$dZ = X \sec^2\theta \, d\theta$$

Substituting (1) and (3) into (2)

$$\bar{C}_{4A} = \frac{2}{L}\int_{z=0}^{z=\sqrt{R^2-x^2}} \sum_{i=0}^{i=4} x a_i r^i \sec^2\theta \, d\theta \quad , \quad \text{or}$$

$$\bar{C}_{4A} = \frac{2x}{L}\int_{z=0}^{z=\sqrt{R^2-x^2}} \sum_{i=0}^{i=4} a_i \left(\frac{x}{\cos\theta}\right)^i \sec\theta \, d\theta$$

which upon integration gives

$$\bar{C}_{4A} = \frac{2x}{L}\left\{ a_0 \tan\theta + a_1 x \left[\frac{1}{2}\frac{\sin\theta}{\cos^2\theta} + \frac{1}{2}\cdot\right.\right.$$

$$\left.\log\left(\tan\theta + \frac{1}{\cos\theta}\right)\right] + a_2 x^2\left(\frac{1}{3}\frac{\sin\theta}{\cos^3\theta} + \frac{2}{3}\tan\theta\right)$$

$$+ \quad a_3 x^3\left[\frac{1}{4}\frac{\sin\theta}{\cos^4\theta} + \frac{3}{8}\frac{\sin\theta}{\cos^2\theta} + \frac{3}{8}\log\left(\tan\theta + \frac{1}{\cos\theta}\right)\right]$$

(equation continued on next page)

$$+ a_4 K^4 \left(\frac{1}{5} \frac{\mathrm{Sin}\,\theta}{\mathrm{Cos}^5\theta} + \frac{4}{15} \frac{\mathrm{Sin}\,\theta}{\mathrm{Cos}^2\theta} + \frac{4 \cdot 2}{5 \cdot 3} \mathrm{Tan}\,\theta \right) \Bigg\}$$

Now if 5 readings are taken from the edge of the drop to the point where C = 0, then $a_0 \ldots a_4$ could be determined by solution of 5 simultaneous equations and equation (1) would be representative of the concentration at any point in plane 4.

In a similar manner the concentration at any point in any of the numbered planes can be represented by a series of equations. More than 5 densitometer readings can be taken and more than 5 constants obtained, if more accuracy is desired.

If it is desired to obtain a concentration gradient existing in a certain direction, it is only necessary to calculate data using the aforementioned equations, tabulate and plot this data and put an equation through the points obtained.

The preceding represents an analysis of the drop at a specific time. To make rate considerations, several frames must be analyzed, calculated data combined and tabulated, and equations put through this data. The work involved in the above analysis is voluminous and would best be carried out using a computer.

In Appendix V is a brief discussion on optical theory. Knowledge of optical theory is not required for this study. However, for the reader who may doubt this, a section is included.

Apparatus and Procedure

Figure 5 is a schematic sketch of the equipment used and its arrangement.

The extractor column body was constructed of brass except for two sides which were plate glass. The extractor was held together with screws and the glass was sealed in place with aquarium cement. Openings were provided at the bottom and top of the extractor so water could be pumped into the bottom of the extractor and out of the top. Proper manifold arrangement made it possible to either leave the extractor filled with water or drain it. The important dimension, as far as the extractor is concerned, is the depth or the distance from the outside of one glass side, through the extractor, to the outside of the other glass side. All extractor demensions are shown in Figure 6.

Also shown in Figure 6 is a sketch of the sample cells employed. The standard cell was constructed of the same materials as the extractor. The depth of the sample cells was identical to depth of the extractor. The brass inside faces of the extractor and sample cell were painted a flat black.

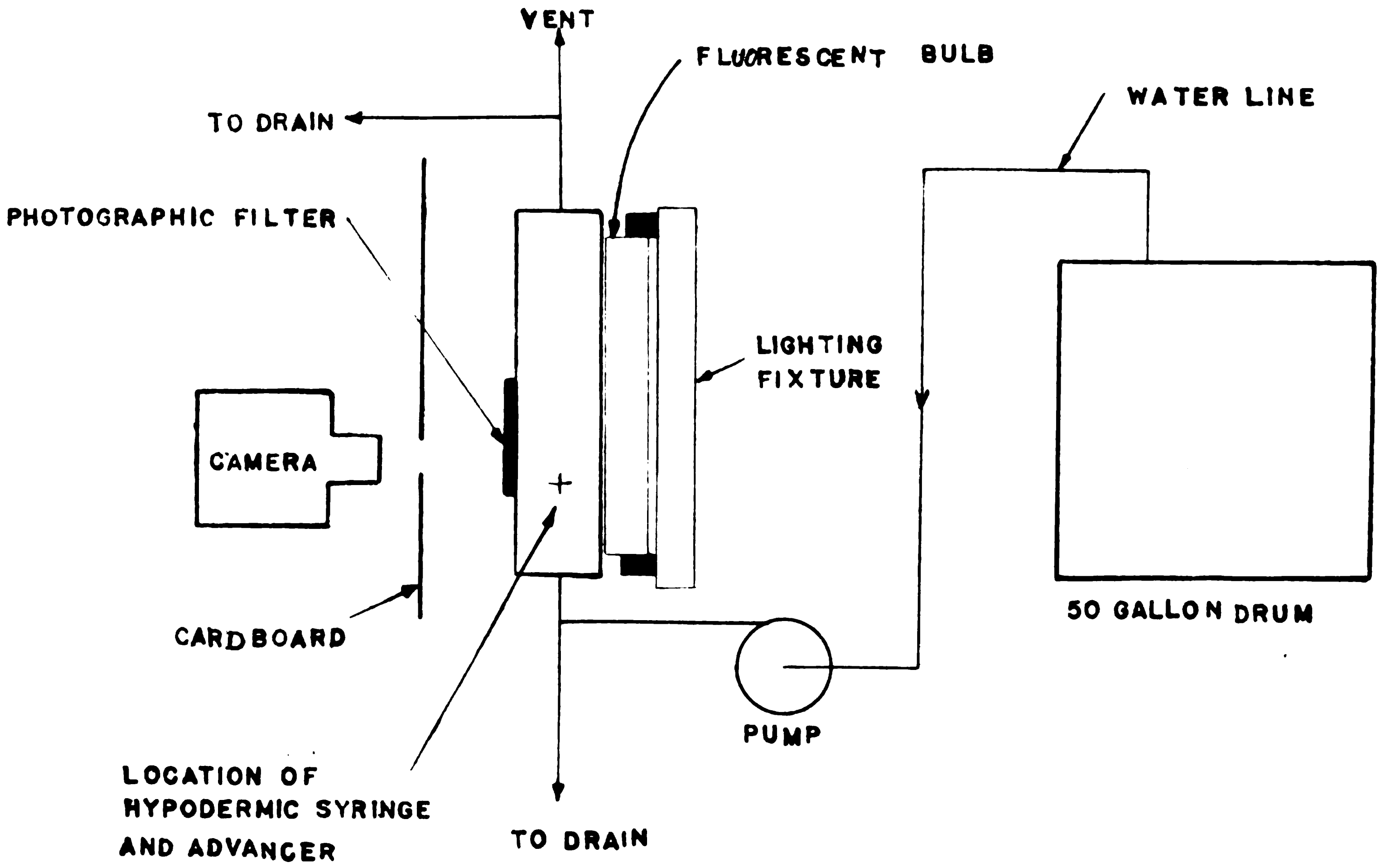
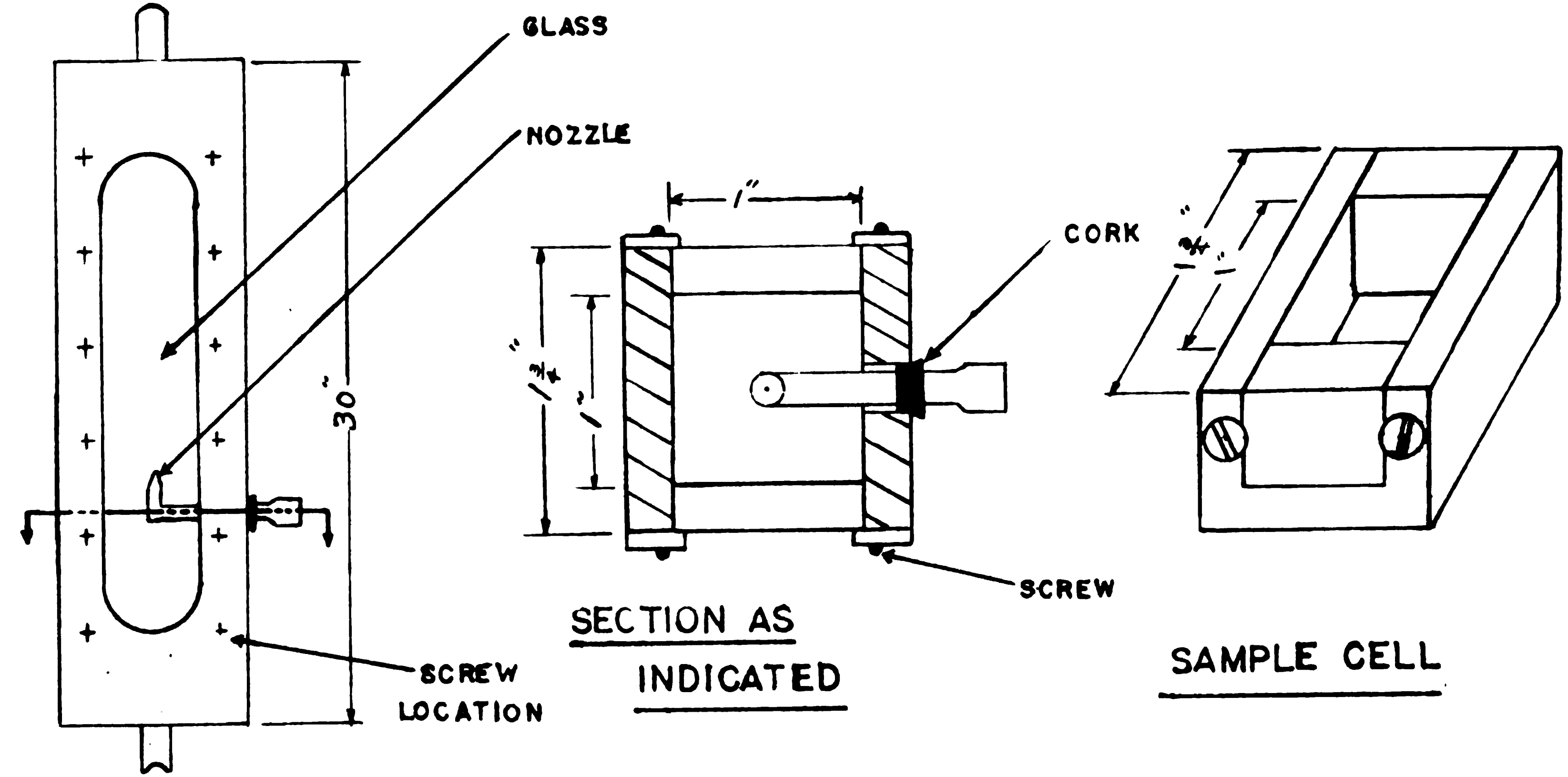


FIGURE 5- EQUIPMENT ARRANGEMENT

FIGURE- 6 EQUIPMENT SCHEMATIC



EXTRACTOR FRONT

SECTION AS INDICATED

SAMPLE CELL

Water came from a clean 50 gallon stainless steel tank. During actual runs this tank contained distilled water cooled or heated to 25^0 C. The heat capacity of this volume of water was large enough that the temperature did not change during the run.

A small centrifugal pump provided head to push the water through the extractor.

A hole one-half inch in diameter was located in one of the brass sides of the column one-third of the way between the bottom and top of the column, exactly half way between the two glass sides. This is shown in Figure 6. The purpose of this hole was to accommodate a rubber stopper through which the drop nozzle was to be inserted in such a manner that the nozzle was vertical and the nozzle tip was equidistant between the glass sides. The drop nozzle was the end of a female pyrex 3-10 glass joint heated and drawn to capillary size. The outside diameter of the nozzle tip was measured so it could be later used as a reference dimension on the photographs. The joint end was cemented with an epoxy plastic to a one cc. hypodermic syringe.

As shown in Figure 5, a micrometer type advancer was located next to the syringe plunger. The purpose of this device was to advance the syringe plunger at a constant and slow rate. The advancer was run by a vari-speed motor. The linkage between the motor and the advancer was through a number of sheaves and a tight thin piece of sash cord. Part of the linkage was through a gear reducer.

Mounted behind the extractor were three blue, 20 watt fluorescent bulbs. These bulbs touched each other and were arranged vertically in the same plane. The foremost parts of the bulbs were one-half inch from the rear glass of the extractor.

Between the lights and the extractor an opaque piece of cardboard was mounted flush with the extractor. A square opening was provided in this cardboard so that light showed through the extractor only in the locality which was to be photographed.

The camera used was on a tripod and the lens was one-half inch from the foremost glass side of the extractor. The camera height and distance from the extractor glass were kept constant during the various runs.

Between the camera and the extractor a suitable photographic filter was mounted flush with the glass side of the extractor.

Before any expefimental runs were made, some preliminary preparation was necessary. First, some standard solutions of picric acid in water had to be made up. The method which was used can be found in Appendix II. In Appendix III will be found a word about the toxic nature of picric acid and toluene and the hazardous nature of metal picrates. Equilibrium data on the picric acid-toluene-water system is found in Appendix IV. The standard solutions were placed in the standard cells which in turn were placed in the same positions as the segment of the extractor where the drop nozzle was located. This positioning was accomplished by means of a "dummy extractor", a piece of wood cut the same size as the extractor and mounted in front of the lights in the same manner as the extractor would be. This piece of wood had a slot in it which would accommodate the standard cells. The slot was located the same height in the "dummy extractor" as the segment of the real extractor in which the nozzle tip was located.

Photographs were taken of the sample cells with solutions in them. Various lens openings, camera speeds and photographic filters were used until a combination was chosen which would give film negative density ranging from no exposure to overexposed over a reasonable concentration range. Finally, using the chosen filter and a camera set-up, photographs were taken of these cells on the same film rolls which were to be used during the actual run.

Actual procedure for a run was as follows:

The extractor column was cleaned inside and out. Particular attention was given to the glass, which was cleaned thoroughly with a solution of sulfuric acid and potassium dichromate and rinsed with distilled water. The column was then mounted and the manifolds assembled.

The hypodermic syringe was then carefully loaded with picric acid - toluene solution and the plunger advanced to a point where only the very tip of the nozzle was not filled with toluene - picric acid solution. The nozzle with the loaded syringe attached was inserted through a rubber stopper which in turn was inserted into the column in such a manner that the nozzle was in a vertical position and equidistant from the sides of the extractor.

The column was then flushed with distilled water.

A small air bubble in the tip of the nozzle separated the toluene and water phase. After sufficient flushing of the column to assure that any traces of toluene - picric acid solution on the outside of the nozzle tip were removed and that the column was at the same temperature as the water, the flush water was turned off. The column remained filled with water.

The photographic filter was put into place, the fluorescent lights turned and the camera positioned and set identically to the specifications used for the standard cell photographs.

The camera was set into motion and the vari-speed motor which operated the advancer was turned on an instant after.

The first few bubbles which came out of the drop nozzle were the air which had previously separated the phases. Then the toluene phase came out and formed a drop. After this drop broke away from the nozzle the camera was turned off and the advancer stopped and backed off slightly to draw any partially formed drop back into the nozzle. The column was flushed to assure that all stray picric acid would be washed down the drain and diluted. After the column was drained, the nozzle was removed. Preparation for a second run was the same.

The resulting films (plus x reversible) were developed in a standard Eastman developer for five and one-half minutes in the dark to negative stage. The film densities were determined by a microphotometer and analyzed in the manner described in the previous section.

Several comments are required at this point to round off this section.

First, it should be noted that the only point at which the picric acid and toluene solution touched anything but glass was at the cemented glass joint. Previous examination of the cement showed it to be insoluble in the toluene - picric acid solution.

Secondly, it will be observed that the equipment description is qualitative. The reason for this is not merely to circumvent detailed drawing and description, but rather inherent in the nature of the study. The principles employed are important and not the nature of the equipment. Using entirely different equipment, one should be able to duplicate results providing the consistencies previously noted are followed.

The following table summarizes important equipment, specifications, dimensions and details.

TABLE I

IMPORTANT EQUIPMENT, SPECIFICATIONS, DIMENSIONS AND DETAILS

Item	Specification, Detail or Dimension
Camera	Standard spring wound Eastman special 16 millimeter
Developer	Standard Eastman developer
Developing method	Film developed to negative stage 5½ minutes in dark
Photographic filters	1. Kodak 50 2. Kodak 35 Mounted in B glass
System	Water the continuous phase. Saturated solution of picric acid in toluene, the dispersed phase
Temperature	25° C.
Column depth, sample cell depth	1.75 inches
Plate glass thickness	3/8 inches
Hypodermic syringe	Yale 1 cc.

TABLE I

(Continued)

Light source	Three vertically mounted blue florescent bulbs
Optical measurements	Recording microphotometer Jarrell-Ash model 203 (Optical densitometer)

Several difficulties were encountered in the experimental procedure, and these should be noted.

The extractor design was made without any thought of disassembly. Each disassembly of the extractor required the removal of over 150 screws. Further, reassembly required resealing of the glass extractor with aquarium cement. Because inaccessable portions of the extractor glass had to be cleaned frequently, a great deal of time was consumed carrying out disassembly and reassembling the extractor.

The constant volume feeder used was a hypodermic syringe. The solution of picric acid and toluene used found its way back through the side of the syringe body and the plunger. This caused the plunger to frequently "freeze" in place.

These difficulties are again referred to in the section entitled "Recommendations and Suggestions for Future Work".

Results and Conclusions

This section is divided into three parts. The first part gives a resume of the photographs taken and the conditions under which the photographs were taken. The second part gives qualitative information or the information which was obtained from observation of the aforementioned photographs. The third part presents all the quantitative information obtained from this study.

All photographs referred to are found immediately following this section.

I. Photographs:

A. Drop Formation--Four forming drops were photographed with a 16 millimeter picture camera. Two of these four drops were photographed through a Kodak #35 filter mounted in B glass at the rate of 24 frames per second. The other two drops were photographed through a Kodak #50 filter mounted in B glass at the rate of 32 frames per second. The drop speeds were varied arbitrarily. A sequence of the 16 millimeter negatives were enlarged to 2 inch by 2 inch size and are shown in photograph sets 1, 2, 3, and 4 which follow this section.

B. Drop coalescence and drop formation during pulse flow--As a supplementary project, a drop forming in pulse flow and a coalescing drop were photographed through a Kodak #50 filter mounted in B glass at the rate of 32 frames per second. Again drop speed was varied arbitrarily. A sequence of 16 millimeter negatives were enlarged to 2 inch by 2 inch size and are shown in photograph sets 5 and 6.

C. The Standard Cells--Two sets of standard cells were photographed. One of the two sets was photographed through a Kodak #35 filter mounted in B glass at the rate of 24 frames per second. This set covered a concentration range from 0.0244 grams/liter to 0.000488 grams/liter. The other was photographed through a Kodak #50 filter mounted in B glass at the rate of 32 frames per second. This set covered a concentration range from 0.0975 grams/liter to 0.00249 grams per liter. A sequence of 16 millimeter negatives were enlarged to 2 inch by 2 inch size and are shown in photograph sets 7 and 8.

A summary of the conditions under which all photographs were taken is presented in the following table.

TABLE II

CONDITIONS UNDER WHICH PHOTOGRAPHS WERE TAKEN

Photograph Set	Camera speed - frames per second	Shutter speed - fraction of a second	Filter - Kodak number mounted in B glass	f number	Lighting	Lens distance from glass side of extractor - inches
1,2,7	24	$\frac{1}{45}$	35	5.6	See Apparatus and Procedure	½
3,4,5,6,8	32	$\frac{1}{60}$	50	2.8	See Apparatus and Procedure	½

II. Qualitative Results and Conclusions

A. Drop Formation--The sequence of photographs shown in Photograph Sets 1,2,3, and 4 represent various times, as shown, in the formation periods of drops. Sets 1 and 2 were the best focused drop formation photographs. Certain irregularities appear in these photographs. In set 1 a dirt spot appears in the upper left hand corner of the picture and in the right hand corner stray solute which was not cleaned out of the extractor is apparent. In set 2 the same dirt spots are apparent. In all four sets of photographs the drop is shown from the beginning of formation to a short time after breakaway from the nozzle. In Photograph Sets 1 and 2 no solute cloud can be visibly detected around the drop up to breakaway This would indicate that during drop formation extracted material remains in the water film immediately adjacent to the drop interface and does not move out into the bulk water phase.

In Photograph Sets 1 and 2 it can be observed that break away takes place in a very short time. Obviously, little extraction could take place from the drop during this time. The solute visible behind the drops shown in Photographic Sets 1 and 2 is concluded to be, then, a combination of motion which the camera speed was too slow to stop and the water film, immediately adjacent to the drop during formation, which moves under the drop as a result of break away. As is readily observed in Set 1 at 84/24 of a second, the drop motion not stopped by the camera is small.

The purpose of obtaining Photograph Sets 3 and 4 was two-fold. First, it was desired to use a faster camera speed, a wider lens opening and a less restrictive filter to see if some extraction could be detected which was not observed in Sets 1 and 2 because of conditions which would make the extracted solute appear as part of the drop. Second, it was desired to shift the range of the camera upward and observe more of the breakaway period. Again, in Photograph Sets 3 and 4, irregularities in the glass and dirt spots are apparent. The photographs are also slightly out of focus. While a could does appear around the drop, this is concluded to be from the out-of-focus conditions as the same cloud appears around the nozzle.

An unusual thing is observed during the formation period in Photograph Sets 3 and 4. As mentioned in the procedure, a small amount of air separated the toluene and water before the advancer was set into motion. A bubble of this air was trapped in the drops shown forming in Sets 3 and 4. This probably caused premature breakaway from the nozzle. This did not impair obtaining desired information, however. The slight irregularity in the shape of the forming drop in Set 4 has not been explained.

In this sequence of photographs, Sets 3 and 4, the period just after breakaway is more readily observed. It appears that the solute leaves the drop from the extreme outer portion of the drop, and that only a small trail of solute is left behind the drop. This observation would lead one to believe that a vortex type of action was present which drew the solute into a small area just behind the rising drop and carried the solute with the drop leaving behind only a small portion of solute. The determination of the quantity of the solute in the trail behind the drop was not attempted as it was beyond the scope of this work.

Because of the less restrictive photographic filter used in Photograph Sets 3 and 4, enough light passes through the drop to be seen in the resulting negatives and photographs. One might anticipate from this observation that by measuring light density differences through the drop, extraction from the drop could be measured.

B. Drop Coalescence and Drop Formation During Pulse Flow--The most interesting and informative qualitative photograph sets were obtained as a supplement to this work. Photograph Set 5 shows drop formation photographed in pulse flow. The purpose of this set of photographs was to determine if flow past the forming drop would have an effect on movement of the extracted solute into the bulk water phase. The arrows alongside the photographs show the flow direction. It is most apparent that solute is removed from the drop from the onset of formation and this solute is dispersed into the bulk water phase.

The most fascinating set of photographs is Set 6 which shows the coalescence of a single drop at a water-toluene interface. The interface separating the water, shown in the lower portions of the photographs, and the toluene, shown in the upper portion of the photographs, is clearly visible. Some stray solute is also apparent, but this does not take away from the ease of observation. The drop is seen to press up against the interface for a period of time and suddenly join the toluene phase leaving behind it an appreciable amount of solute. It is concluded that solute left in the water phase was extracted mostly during the time the drop was pressed against the interface. This extracted solute remained in the water film immediately adjacent to the interface. until the motion caused as the toluene drop merged with the bulk toluene phase dispersed it in the bulk water phase. An analysis of mechanism involved was beyond the scope of this work, but using the standard cell plots an estimate was made of the amount of solute which was left in the water phase.

C. The Standard Cells--The standard cells shown in Photograph Sets 7 and 8 are described in the procedure. As the concentration of the picric acid-water solution contained in these cells became greater, less light found its way through the solution and the portion of the resulting photograph which showed the solution became darker. The opposite was true of the negatives from which quantitative information was to be obtained. Two concentration ranges were represented by varying photographic conditions.

The meniscus is clearly visible on the top of these photographs. Irregularities in the glass are apparent at the corner of the solution portion of the photographs. Dirt on the glass shows up as spots.

Except for the irregularities in the glass and dirt spots, optical densities at all points through the standard cells (except the extreme edge of the glass) appeared uniform.

III. Quantitative Results and Conclusions--Quantitative data were obtained by direct and indirect measurement on the film negatives and photographs and by comparison of these negatives and photographs with standard cell negatives and photographs by means of a microphotometer. These data are found in Appendix VI. From these data, certain results were calculated and these results are tabulated in Table Three.

The rate of surface area generation, rate of formation and final drop volume of the drops shown forming in Photograph Sets 1 and 2 were calculated by the means described in the section entitled "Special Techniques and Mathematical Considerations". In order to accurately make the measurements required it was

TABLE III

QUANTITATIVE RESULTS

	Final drop volume-ft^3	Formation time-Secs.	Rate of formation-ft^3/Sec.	Estimate of % total solute in drop which was extracted	Predicted % of total solute in drop which was extracted during formation
Forming Drop-Photograph Set 1	1.85×10^{-6}	3.33	0.55×10^{-6}	> 0.0153	37.4
Forming Drop-Photograph Set 2	1.81×10^{-6}	6.63	0.274×10^{-6}	> 0.0204	46.8
Forming Drop-Photograph Set 3	1.63×10^{-6}	5.32	0.306×10^{-6}	------	31.1
Forming Drop-Photograph Set 4	2.49×10^{-6}	6.09	0.409×10^{-6}	-------	35.1
Forming Drop in Pulse flow-Photograph Set 5	2.49×10^{-6}	4.00	0.625×10^{-6}	-------	34.6
Coalescing Drop-Photograph Set 6	3.26×10^{-6}	5.57	0.586×10^{-6}	$>^{*} 0.144$	----

*During Coalescence

necessary to project the negatives on a microfilm reader. Calculations, graphical integrations and graphical results are found in Appendix VII. The graphical results show that the constant volume feeder was functioning properly and that the surface area of the drop interface was generated nearly at the same rate as if the drop had remained spherical during formation.

The final volume of the coalescing drop, Photographic Set 6, was determined by the means just described. Its rate of formation was determined by dividing its final volume by the number of seconds which elapsed between the beginning of formation and break away from the nozzle. This calculation is shown in Appendix VII.

The final volumes of the drops shown forming in Photograph Sets 3 and 4 and the drop in pulse flow, Photograph Set 5, were determined by direct measurement on the photographs. The rates were determined by dividing the final volume by the time elapsed between the beginning of formation until break away from the nozzle. The accuracy of the measurements involved was poor because of the size of the photographs and the out-of-focus conditions in Photograph Sets 3 and 4. The calculation for this is shown in Appendix VII.

Because the solute remained close to the drop interface and did not form a "cloud" around the forming drop, it was not possible to determine the amount extracted by the means described in the section entitled "Special Techniques and Mathematical Considerations". As an alternative, an estimate was made of the minimum amount extracted in the formation of the drops shown in Photograph Sets 1 and 2 and the coalescence of the drop shown in Photograph Set 6. This was done by measuring the area of the portion of the film representing solute left behind the drop and determining, using the standard cell photographs, the minimum amount of solute in the calculated volumes represented by this area. This is better explained in the calculation shown in Appendix VII. How much more solute than calculated could be in these calculated volumes is undetermined.

No quantitative data on extraction were obtained for the drops shown forming in Photograph Sets 3, 4 and 5.

By using Gregory's[4] formula, page 33 and Equation ten on page 14, the amount of extraction expected from the drops shown forming in all photographic sets was predicted. The use of these equations involved several assumptions which are noted on the pages mentioned. A sample calculation for these predictions is found in Appendix VII.

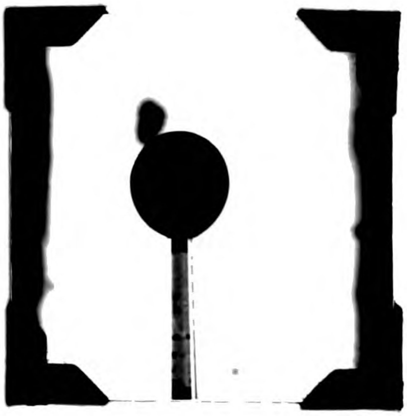
The plots of concentration vs. percent transmission made from the standard cell photographs are presented in Appendix VII. Also in Appendix VII are plots for two standard cell photographs, of percent transmission vs. distance from the side of the standard cell. These plots illustrate that the light source was uniform.

From direct measurement on the photographs in Sets 1 and 2 at 84/24 and 163/24 of a second respectively, the motion during break-away which was not stopped by the camera was calculated. These calculations show that, while the camera shutter was open, (1/45 of a second) each drop moved approximately 0.059 inches upward. Because of the out-of-focus conditions in Photograph Sets 3 and 4, this movement could not be calculated for the drops shown forming in these sets.

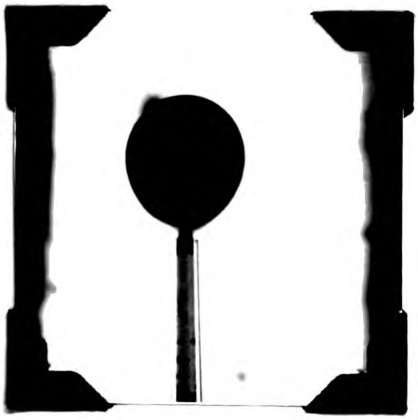
Photograph Set 1 - Forming Drop

Time given in 24ths of a second from beginning of formation.
Camera speed--24 frames per second.
Photographed through Kodak #35 filter
f - 5.6.

$\frac{1}{24}$

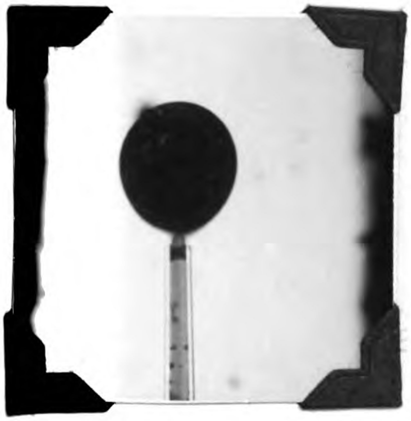


$\frac{48}{24}$



$\frac{72}{24}$

$\frac{78}{24}$

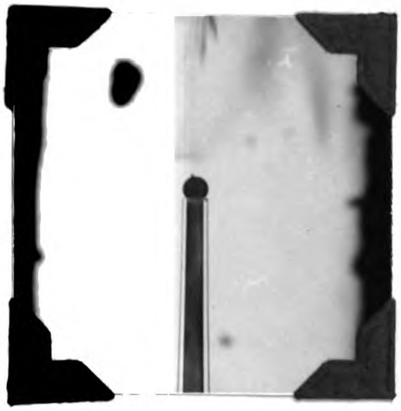


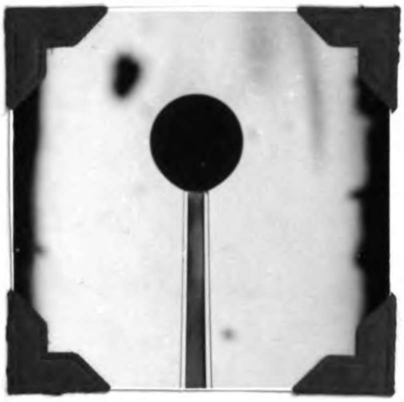
$\frac{80}{24}$

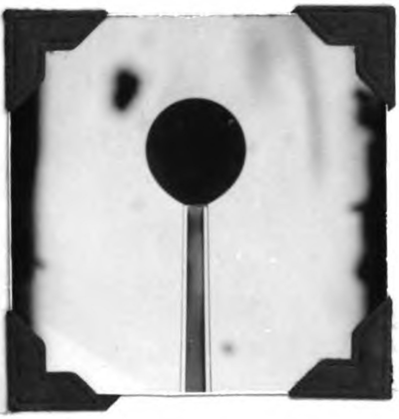
$\frac{84}{24}$

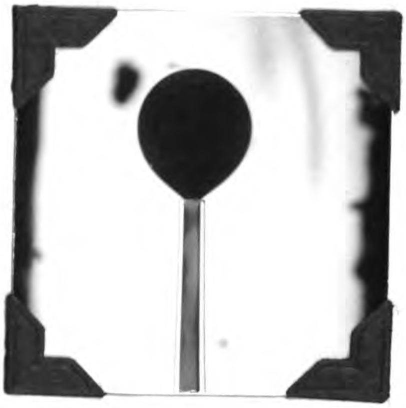
Photograph Set 2 - Forming Drop

Time given in 24ths of a second from beginning of formation.
Camera speed--24 frames per second.
Photographed through Kodak #35 filter
f - 5.6

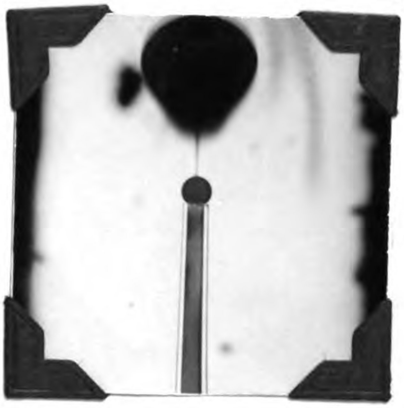

← $\frac{1}{24}$

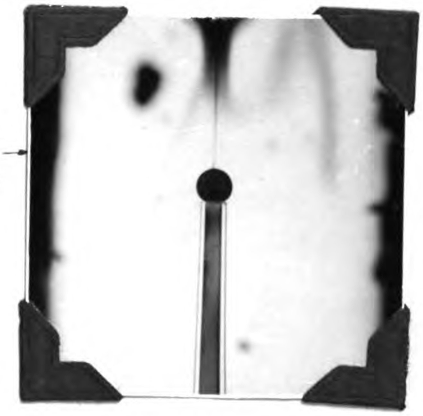

← $\frac{48}{24}$


← $\frac{96}{24}$


$\frac{133}{24}$ →

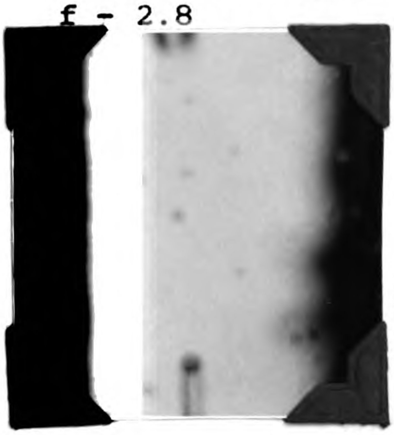

$\frac{159}{24}$ →


$\frac{161}{24}$ →

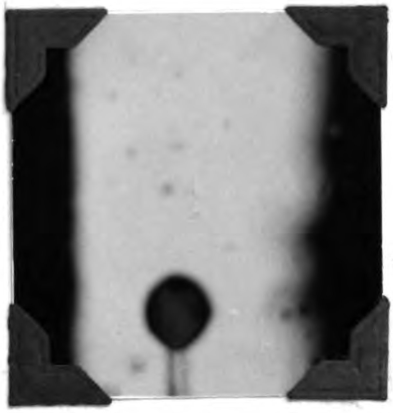

$\frac{163}{24}$ →

Photograph Set 3 - Forming Drop

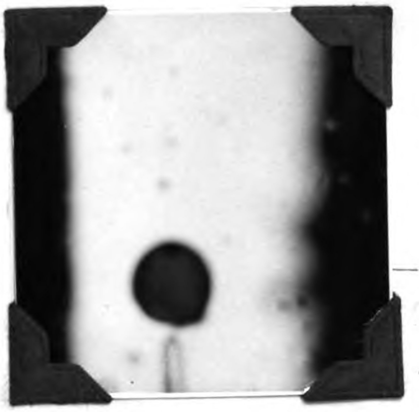
Time given in 32nds of a second from beginning of formation.
Camera speed--32 frames per second.
Photographed through Kodak #50 filter
f - 2.8



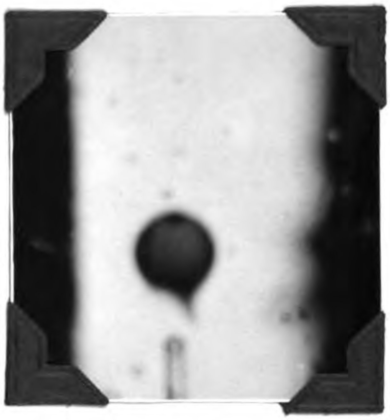
$\frac{1}{32}$



$\frac{96}{32}$



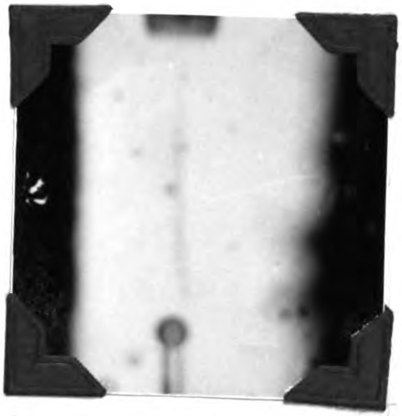
$\frac{169}{32}$



$\frac{170}{32}$

$\frac{173}{32}$

$\frac{177}{32}$

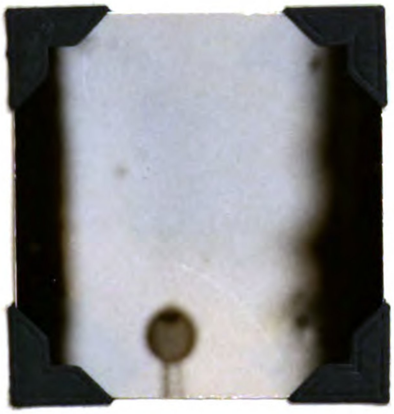


$\frac{179}{32}$

Photograph Set 4 - Forming Drop

Time given in 32nds of a second from beginning of formation.
Camera speed--32 frames per second.
Photographed through Kodak #50 filter
f - 2.8

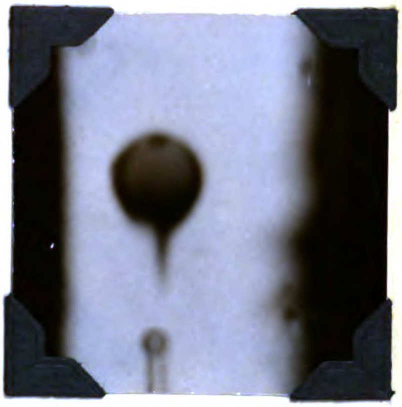
← $\frac{1}{32}$



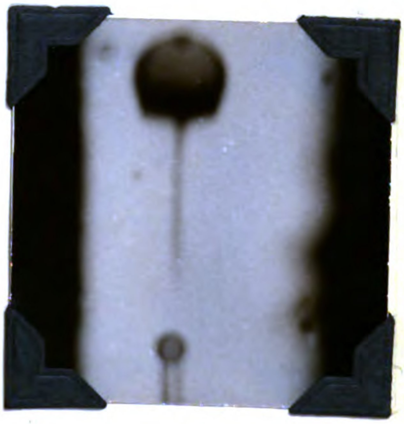
← $\frac{32}{32}$

← $\frac{96}{32}$

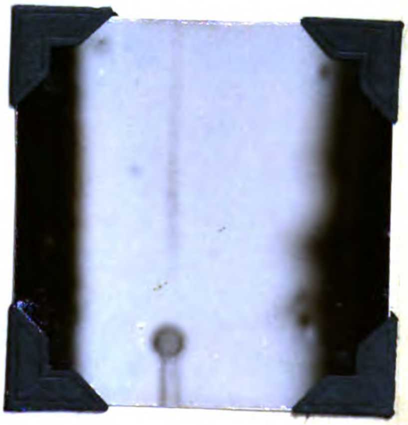
$\frac{197}{32}$ →



$\frac{260}{32}$ →

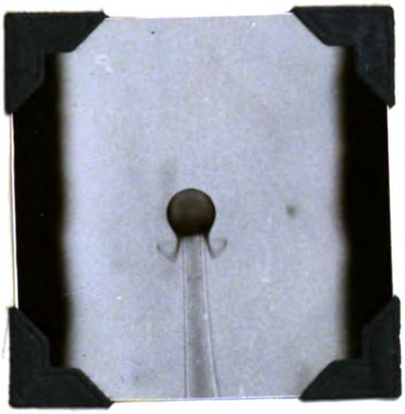


$\frac{203}{32}$ →

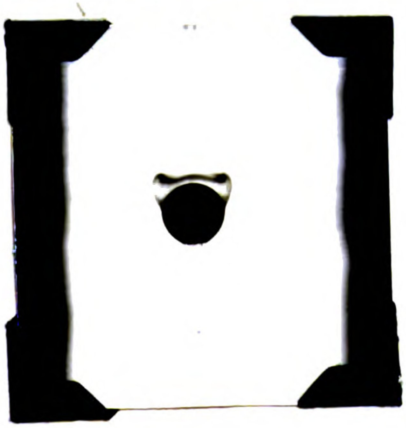


Photograph Set 5 - Forming Drop in Pulse Flow

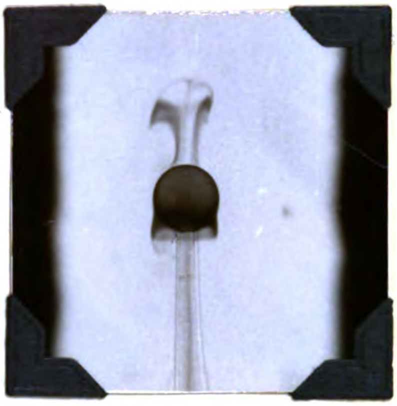
Direction of flow indicated.
Time given in 32nds of a
second from beginning
of formation.
Camera speed--32 frames
per second. Photographed
through Kodak #50 filter
f - 2.8



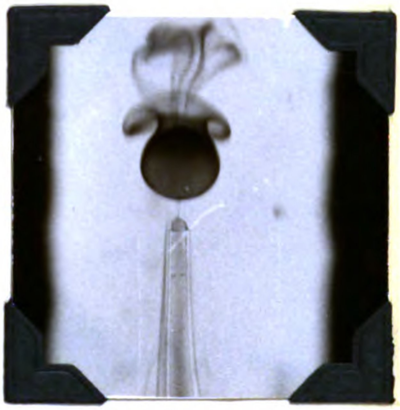
← 32/32 ↓



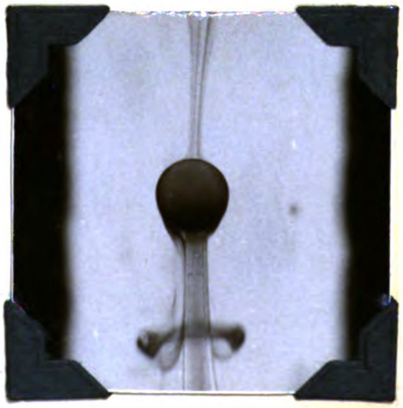
← 66/32 ↑



↓ 96/32 →



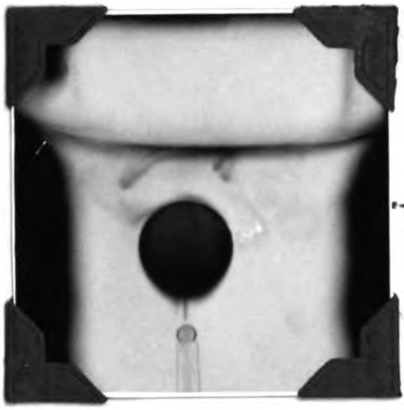
↓ 128/32 →



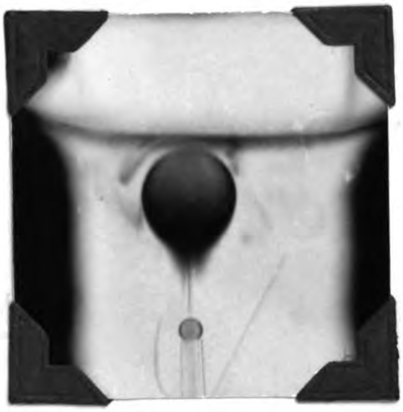
↓ 160/32 →

Photograph Set 6 - Coalescing Drop

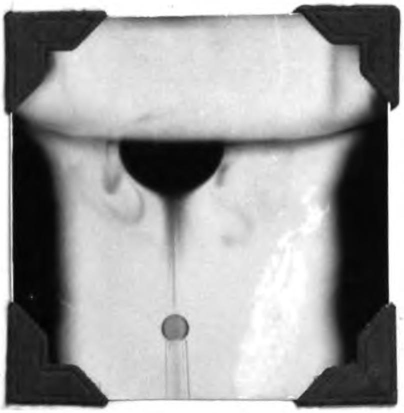
Time given in 32nds of a second from first frame shown. Camera speed--32 frames per second. Time from beginning of formation to break-away (not shown) 178/32 seconds. Photographed through Kodak # 50 filter f - 2.8



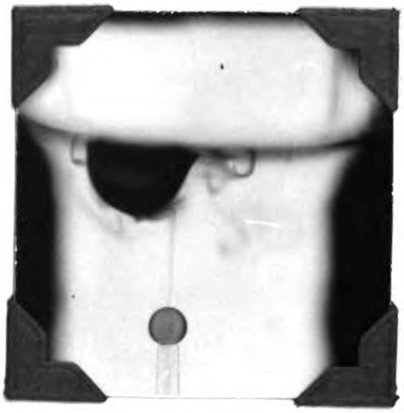
$\frac{0}{32}$



$\frac{3}{32}$

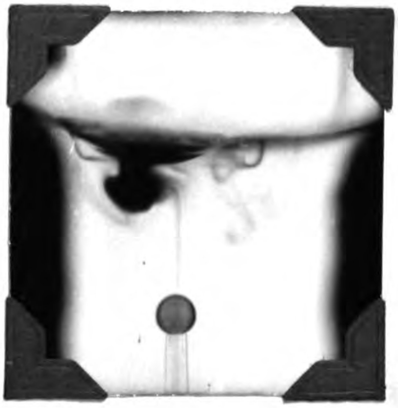


$\frac{6}{32}$

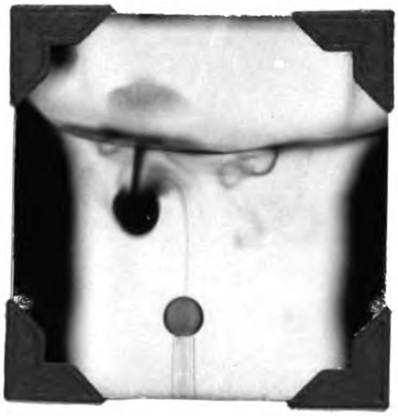


$\frac{19}{32}$

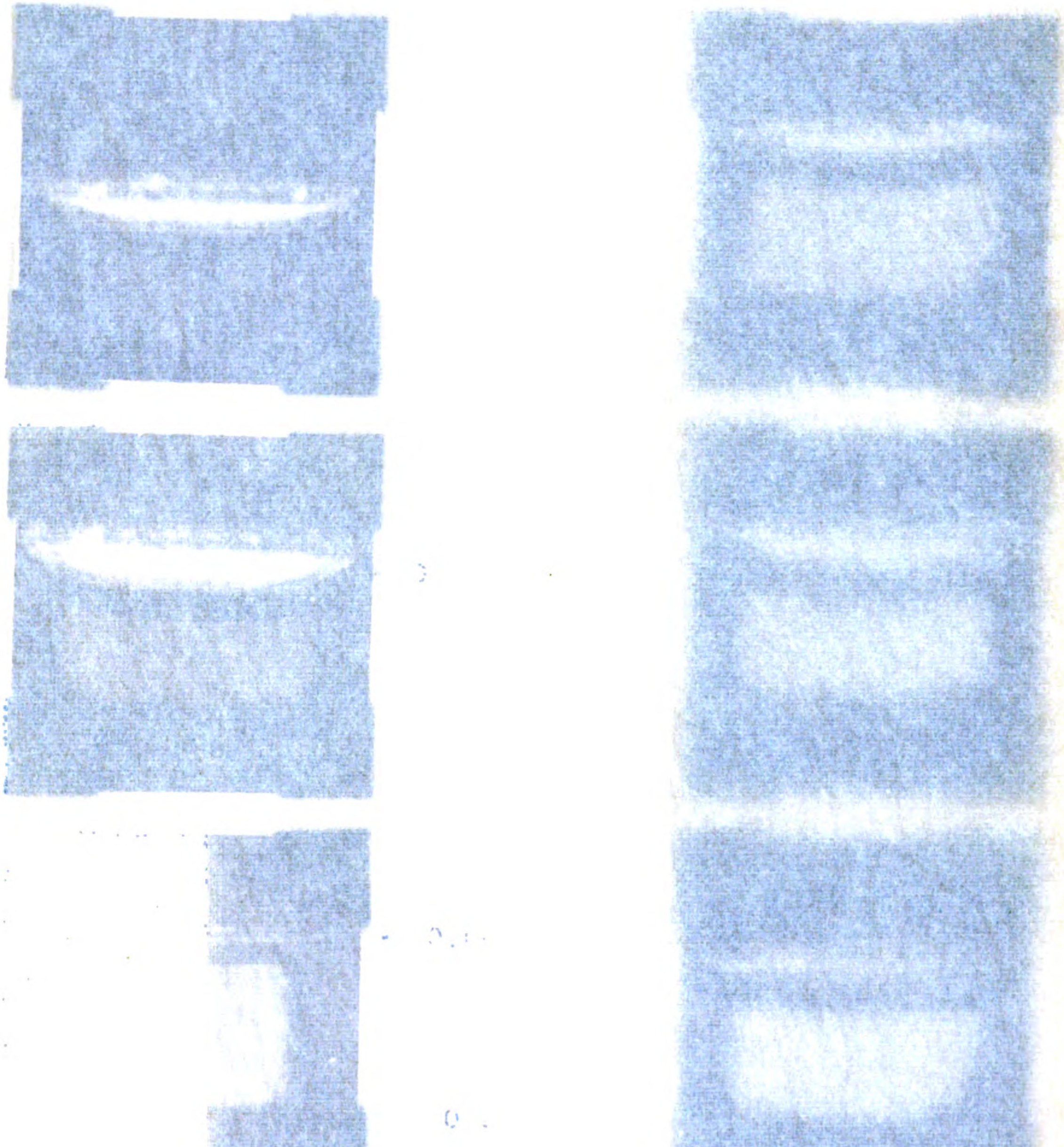
$\frac{20}{32}$



$\frac{21}{32}$

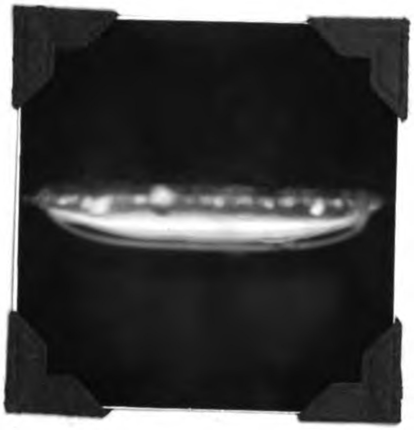


$\frac{22}{32}$

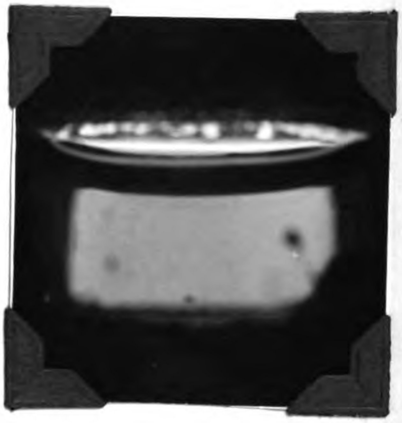


Photograph Set 7 - Standard Cells

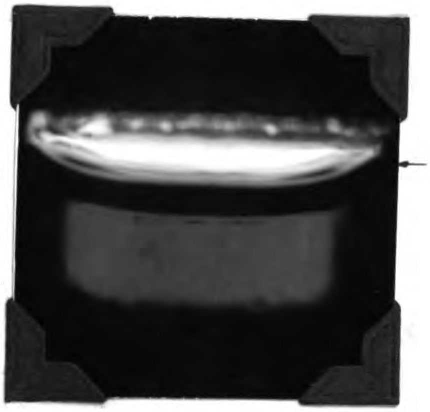
Concentrations given in
grams Picric acid per
liter.
Camera speed--24 frames
per second.
Photographed through
Kodak #35 filter
f - 5.6



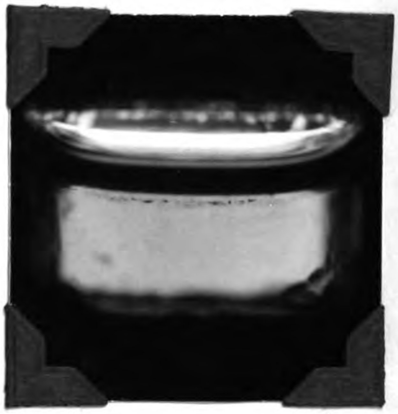
← 0.0244



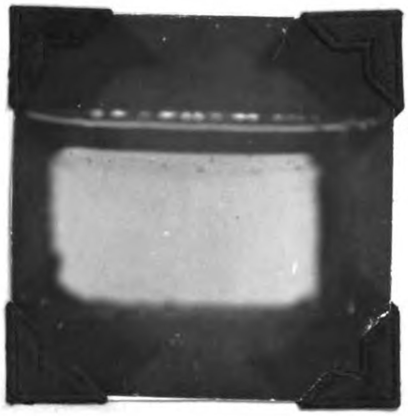
0.00609 →



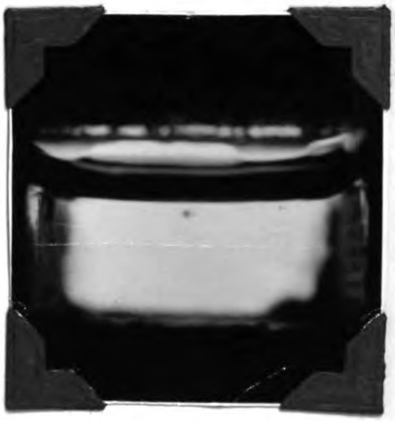
← 0.0122



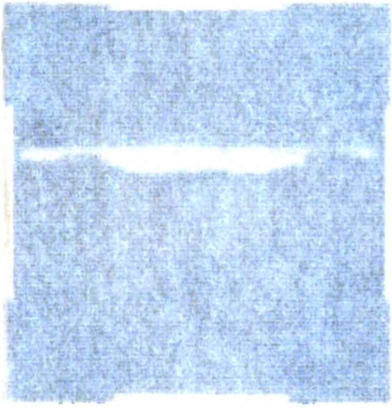
0.00244 →

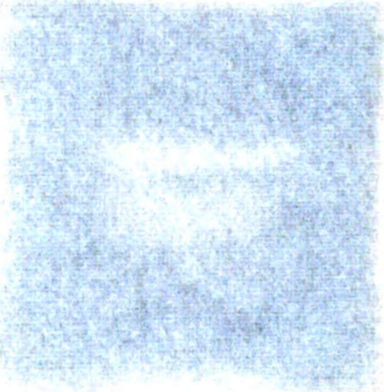


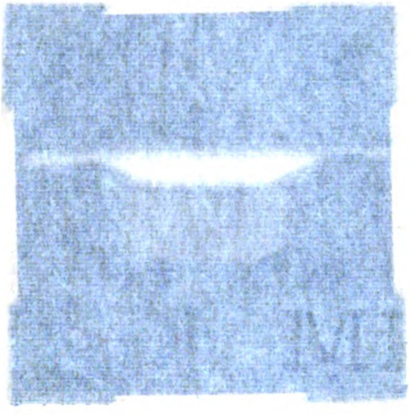
← 0.00975

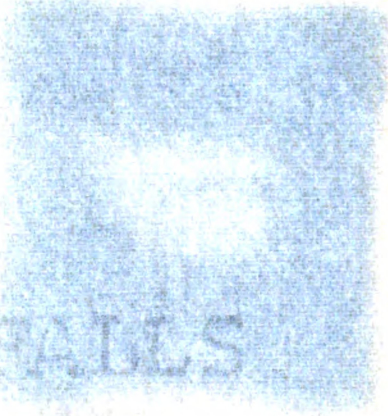


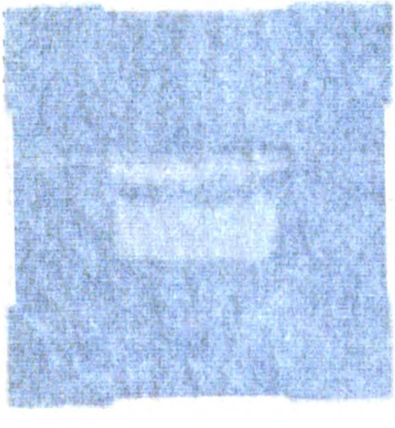
0.000488 →

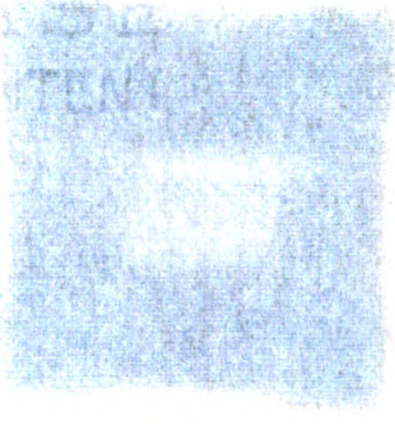






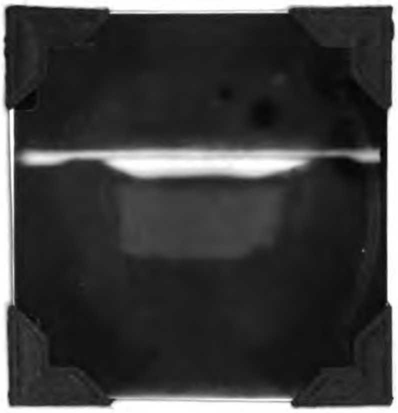




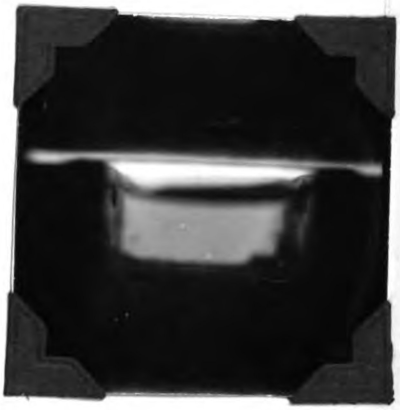


Photograph Set 8 - Standard Cells

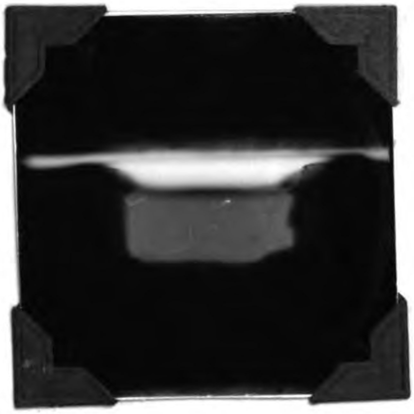
Concentrations given in
grams Picric acid per liter.
Camera speed--32 frames per
second.
Photographed through Kodak #50
filter
f - 2.8



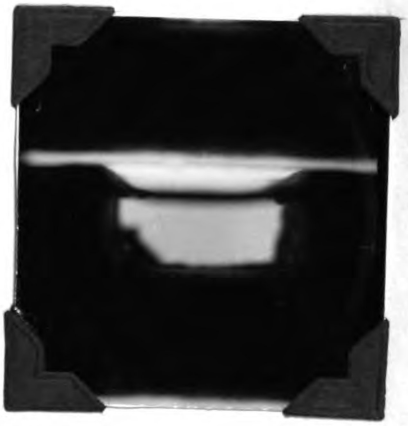
← 0.0975



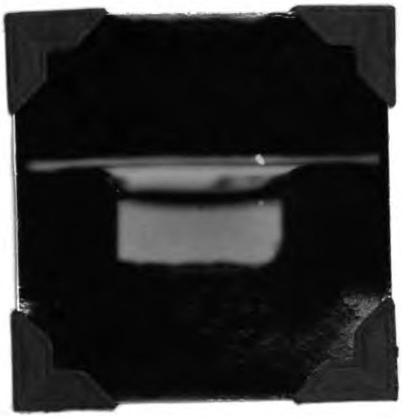
0.0122 →



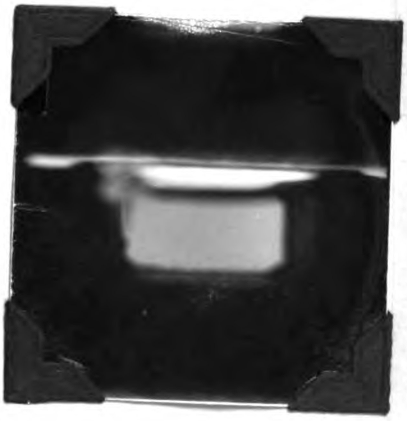
← 0.0488



0.00609 →



← 0.0244



0.00249 →

Recommendations and Suggestions for Future Work

Although the results of this work leave much to be desired, it has been well illustrated that the photographic methods presented are a rigorous means by which studies of extraction from single liquid drops may be carried out. If properly applied, these photographic methods presented leave nothing to speculation. Complete information, qualitative and quantitative, can be obtained on all phases of drop life using these methods. It is therefore recommended that a long range program be initiated in which extensive studies of drop-wise extraction be carried out utilizing the methods presented in this thesis.

An outline of this program based on the experience derived from this work is presented.

Program Outline

A. Equipment Procurement

   1. 35 mm. vari-speed camera on a permanent basis
   2. Film developing facilities in laboratory
   3. Film reader in laboratory

B. Equipment design and fabrication

  1. New extractor (easy to disassemble)
  2. New constant volume feeder with no moving parts (pressure controlled)
  3. Camera mounting or housing

C. Literature Search - A search for systems which are suitable for photographic study

D. Research - Each phase of drop-life for each system should be studied separately. Finally the separate studies should be combined and correlated.

Variables which should be studied in the Research part of the program are listed below.

1. Drop size
   - a. At different rates of formation
   - b. From different size nozzles
   - c. Under different fluid heads
2. Extraction
   - a. During formation
     - (1). At different rates of formation
     - (2). From different size nozzles
   - b. During drop rise
   - c. During coalescence after different distances of rise.

Correlations should be made on the basis of these variables and on the basis of the fluid properties involved.

Another suggested topic of research is the circulation within the drop or the circulation in the continuous phase. This could be studied by photographing systems in which both the drops and the continuous phase have a fine solid dispersed in them. This solid would show up on the resulting negatives and thereby indicate the circulation pattern.

A few words should be said about difficulties encountered in this work. First, when the motion of the drop was stopped and the fluid around the drop was stagnant as in formation and coalescence, the solute did not move out into the water phase as anticipated, but remained in the water layer adjacent to the drop interface. While the principle of obtaining extraction data by comparison using a microphotometer is sound, this phenomenon did not lend itself to analysis and the amount extracted from the drop during these phases of drop life could only be estimated. A different means to determine extraction during these periods is then required. A basis for this means is provided by

Photograph Sets 3 and 4 in which light of varying intensity could be seen through the drops which were forming. It is suggested that this light transmission could be a basis for determining the amount extracted from a drop during a given period. Rising drops might also be studied using this idea.

A second difficulty, which was anticipated but not encountered, was the voluminous work and numerous calculations which would be required for complete analysis of extraction from single drops particularly using the methods described in this work. The use of a computer is vital if progress is to be made in the direction of correlation. Time should be allotted to programing and understanding operational procedure of the computer used before research is to be started.

Third and last was the difficulty in understanding the mathematics and physical considerations involved in extraction from single drops. To alleviate this, the investigator should have a background in the formulation and solution of differential equations, transport processes and viscous and turbulent flow in the boundary layer before attempting a literature search. Part of the degree course work taken should include this subject matter.

BIBLIOGRAPHY

1. Coulson, J. M., and Skinner, S. J., Chemical Engineering Science, 1, 197-211 (1952).

2. Farmer, W. S., "Controlling Variables in Liquid-Liquid Extraction from Signle Drops," CRNL - 635, U. S. Atomic Energy Commission, 1949.

3. Garner, F. H., Skelland, A. H. P., Industrial and Engineering,Chemistry, 48, 51-8 (1956).

4. Gregory, C. F., Jr., "Mass Transfer Between Forming Drops and a Continuous Phase," Ph.D. Thesis in Chemical Engineering, Massachusetts Institute of Technology, June, 1957.

5. Hadamard, J., Comptes Rendus, 152, 1735-8 (1911).

6. Handlos, A. E., Baron, T., A. I. Ch. E. Journal, 127-135, March, 1954.

7. Haritatos, N. J., and Liberman, M., "Liquid-Liquid Extraction in Drops," M. S. Thesis in Chem. Eng., M.I.T., 1953.

8. Kopinski, S., "Mass Transfer in Liquid-Liquid Drop Systems," M. S. Thesis in Chemical Engineering, M.I.T., 1949.

9. Licht, W., Jr., and Conway, J. B., Industrial and Engineering Chemistry, 42, 1151-1157 (1950).

10. Licht, W., Jr., and Pansing, W. F., Industrial and Engineering Chemistry, 45, 1885-1896 (1953).

11. Pike, F. P., Withers, W. T., Jr., and Beatty, K. C., Jr., "Some Mass Transfer Effects inside Drops in a Miniature Liquid-Liquid Spray Tower," North Carolina State College, Raleigh, N. C.

12. Sherwood, T. K., Evans, J. E., Loncor, J. V. A., Industrial and Engineering Chemistry, 31, 1144-1149 (1939).

13. Sherwood, T. K., and Pigford, R. L., Absorption and Extraction, New York: McGraw-Hill Book Company, Inc., 1952.

14. So, W., "Extraction from Single Drops," M. S. Thesis in Chem. Eng., M.I.T., 1955.

15. West, F. B., Herrman, A. J., Chong, A. T., Thomas, L. E., Industrial and Engineering Chemistry, 44, 625-31 (1952).

16. West, F. B., Robinson, P. A., Morgenthaler, A. C., Jr., Beck, T. R., McGregor, D. K., Industrial and Engineering Chemistry, 43, 234-238 (1949).

17. Zeleny, R. A., "A Study of Eddy Diffusion in Liquid-Liquid Extraction," M. S. Thesis in Chemical Engineering, Worcester Polytechnic Institute, June, 1954.

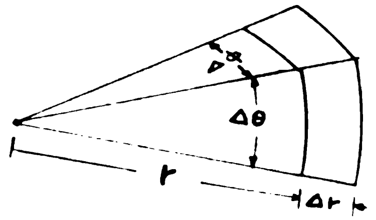
APPENDICES

APPENDIX I

The Derivations and Solutions of Some Differential Equations Pertaining to Extraction from Single Liquid Drops

A. Extraction from a forming liquid drop assuming mass transfer by diffusion only, liquid entering at the center of the drop, equilibrium at the interface and constant interfacial composition.

1. Coordinate system (spherical)



2. Nomenclature

r = radius

D = diffusivity

C = concentration

R' = outer most drop radius

$|_r$ indicates @ r

$|_{r+\Delta r}$ indicates @ $r + \Delta r$

C_i = interface concentration

C_o = initial concentration

t = time

V = drop volume

u = $\frac{dV}{dt}$ = rate of volume change

v = fluid velocity in radical direction

3. Derivation using rate approach

(1) input−output = accumulation

$$(2)\quad \left[(C\mathcal{V} r\Delta\phi\, r\Delta\theta|_{r}) - (C\mathcal{V} r\Delta\phi\, r\Delta\theta|_{r+\Delta r})\right]\Delta t$$

$$+ \left[(-D\frac{\partial c}{\partial r} r\Delta\phi\, r\Delta\theta|_{r}) - (-D\frac{\partial c}{\partial r} r\Delta\phi\, r\Delta\theta|_{r+\Delta r})\right]\Delta t$$

$$= (c\, r\Delta\phi\, r\Delta\theta\Delta r|_{t+\Delta t}) - (c\, r\Delta\phi\, r\Delta\theta\Delta r|_{t})$$

Dividing both sides of equation (2) by $\Delta\phi$, $\Delta\theta$, Δr and Δt and using the definition of derivative,

$$(3)\quad -\frac{\partial}{\partial r}(\mathcal{V} c r^2) + \frac{\partial}{\partial r}\left(D r^2 \frac{\partial c}{\partial r}\right) = \frac{\partial}{\partial t}(c r^2)$$

Carrying out the indicated differentiations in equation (3) and dividing both sides by r^2,

$$(4)\quad -\mathcal{V}\frac{dc}{dr} - \frac{2c\mathcal{V}}{r} - c\frac{\partial \mathcal{V}}{\partial r} + D\frac{\partial^2 c}{\partial r^2} + \frac{2D}{r}\frac{\partial c}{\partial r} = \frac{\partial c}{\partial t}$$

If $U = \frac{\partial \mathcal{V}}{\partial t}$ then $\mathcal{V} = \frac{U}{4\pi r^2}$ and $\frac{\partial \mathcal{V}}{\partial r} = -\frac{U}{2\pi r^3}$

and substituting into (4) and rearranging

$$(5)\quad D\frac{\partial^2 c}{\partial r^2} + \frac{2D}{r}\cdot\frac{\partial c}{\partial r} + \frac{\partial c}{\partial r}\cdot\frac{U}{4\pi r^2} = \frac{\partial c}{\partial t}$$

If C' defined as $C' = \frac{C - C_i}{C_o - C_i}$, the equation may be rewritten

$$(6)\quad D\frac{\partial^2 c'}{\partial r^2} + \frac{2D}{r}\cdot\frac{\partial c'}{\partial r} + \frac{\partial c'}{\partial r}\cdot\frac{u}{4\pi r^2} = \frac{\partial c'}{\partial t}$$

The usual way to solve such an equation is to assume a solution of the form $C' = R \cdot T$ where R is a function of r only and T is a function of t only. This assumption fails to satisfy a boundry condition of the physical problem which is:

$$C' = 0, \quad r = R', \quad t > 0$$

In this boundry condition R', the outer most radius of the drop, is a function of time and this does not fulfill the specification that R be only a function of r.

No solution for this equation has been found.

B. Extraction from a liquid drop assuming mass transfer by diffusion only, equilibrium at the interface and a constant interfacial composition.

1. Coordinate system, same as previous.
2. Nomenclature, same as previous.
3. Derivation using rate approach

(1) Input-output = accumulation

$$(2)\quad \left[\left(-D\frac{\partial c}{\partial r} r\Delta\phi\, r\Delta\theta\Big|_{r}\right)-\left(-D\frac{\partial c}{\partial r} r\Delta\phi\, r\Delta\theta\Big|_{r+\Delta r}\right)\right]\Delta t$$

$$= \left(c\, r\Delta\phi\, r\Delta\theta\,\Delta r\Big|_{t+\Delta t}\right)-\left(c\, r\Delta\phi\, r\Delta\theta\,\Delta r\Big|_{t}\right)$$

Following the same procedure as in previous derivation,

$$(3)\quad D\left(2\frac{\partial c}{\partial r}+r\frac{\partial^2 c}{\partial r^2}\right)=r\frac{\partial c}{\partial t}$$

If C' is defined as $C' = \dfrac{C - C_i}{C_o - C_i}$, equation (3) becomes

$$(4)\quad D\left(2\frac{\partial c'}{\partial r}+r\frac{\partial^2 c'}{\partial r^2}\right)=r\frac{\partial c'}{\partial t}$$

and these equations, (3) and (4), have the boundry conditions

$t = o,\quad c = c_o,\quad c' = 1$

$t = oo,\quad c = c_i,\quad c' = o$

$r = R,\quad c = c_i,\quad c' = o$

Equation (4) may then be solved with the following results

$$(5)\quad c' = \sum_{n=1}^{n=oo} \frac{2(-1)^{n+1}R}{n\pi r}\, e^{-\frac{Dn^2\pi^2 t}{R^2}}.$$

$$\text{Sine}\ \frac{n\pi r}{R}$$

(6)
$$Q = \frac{(C_o - C_i)R}{3} \; (1 - \frac{6}{\pi^2} \sum_{n = 1}^{n = \infty} \frac{1}{n^2} \cdot$$

$$e^{- \frac{Dn^2\pi^2 t}{R^2}}$$

when Q is total moles which have crossed interface.

(7)
$$\bar{c} = C_i + 6 \; (C_o - C_i) \sum_{n = 1}^{n = \infty} \frac{1}{n^2\pi^2} \cdot$$

$$e^{- \frac{Dn^2\pi t}{R^2}}$$

where $\bar{c}$ is the average concentration within the drop at time t.

(8)
$$K = \frac{R}{3t} \; (1-6) \sum_{n = 1}^{n = \infty} \frac{1}{n^2\pi^2} \; e^{- \frac{Dn^2\pi^2 t}{R^2}}$$

Where K is the overall mass transfer coefficient.

APPENDIX II

The Preparation of Standard Picric Acid-Water Solutions

It was desired to prepare a standardized picric acid-water solution which could be diluted as needed to obtain various concentrations of picric acid in water for use in standard cells.

This was done by first weighing out one gram of dried picric acid (Baker reagent grade) and dissolving this in one liter of water.

Using a pipette, 100 mls. of this solution was transferred to a clean 250 ml. Erlemeyer flask along with 10 ml. of wash alcohol. This sample was titrated against 0.02 N sodium hydroxide.

This procedure was repeated three times with the following results:

Titration	Ml. NaOH	Gms./liter picric acid
1	21.30	0.974
2	21.27	0.973
3	21.33	0.975

Sample Calculation

Titration 1

<u>Normality Sodium Hydroxide x Volume Sodium Hydroxide</u> =

Normality of picric acid soln.

$$\text{Normality of picric acid solution} = \frac{0.02 \times 21.30}{100 \text{ ml.}}$$

Equivalent weight of picric acid = 229

$4.26 \times 10^{-3} \times 229$ = gms./liter picric acid =

0.974

APPENDIX III

The Hazardous Properties of Picric Acid and Toluene and Some Advisable Precautions to be Taken When Working with these Compounds

A. Picric Acid

Picric acid is hazardous in two respects.

First, it combines with most metals to form metal picrates which upon impact or rapid heating detonate. Dry picric acid itself will detonate when heated above 300° C. It is therefore advisable to flush thoroughly with water all residue remaining after the acid has contacted metal. Further, any time crystals or a solution of picric acid is discarded, it should be washed down a suitable drain with an abundance of water.

Second, picric acid is toxic in nature. Exposure is usually from two sources, by skin contact with solution or crystals or inhalation of dust particles. Skin contact, particularly on the hands, usually results in transfer of the acid internally as a yellow stain results which is difficult to remove, but comes off slowly when food is transferred to the mouth. A primary symptom of poisoning is dermatitis around the mouth and nose (papules). Extreme poisoning is internally injurious. It is, therefore, advisable to transfer crystals of picric acid with care, and if an extremely dusty variety is being used a dust filter mask should be employed. Contact of a solution of picric acid with the skin should be avoided. If the acid does get on the skin it should be washed off with water and an abrasive soap before the stain sets.

B. Toluene

Toluene is also hazardous in two respects.

First, toluene vapors are flammable and toluene should never be transferred near an open flame.

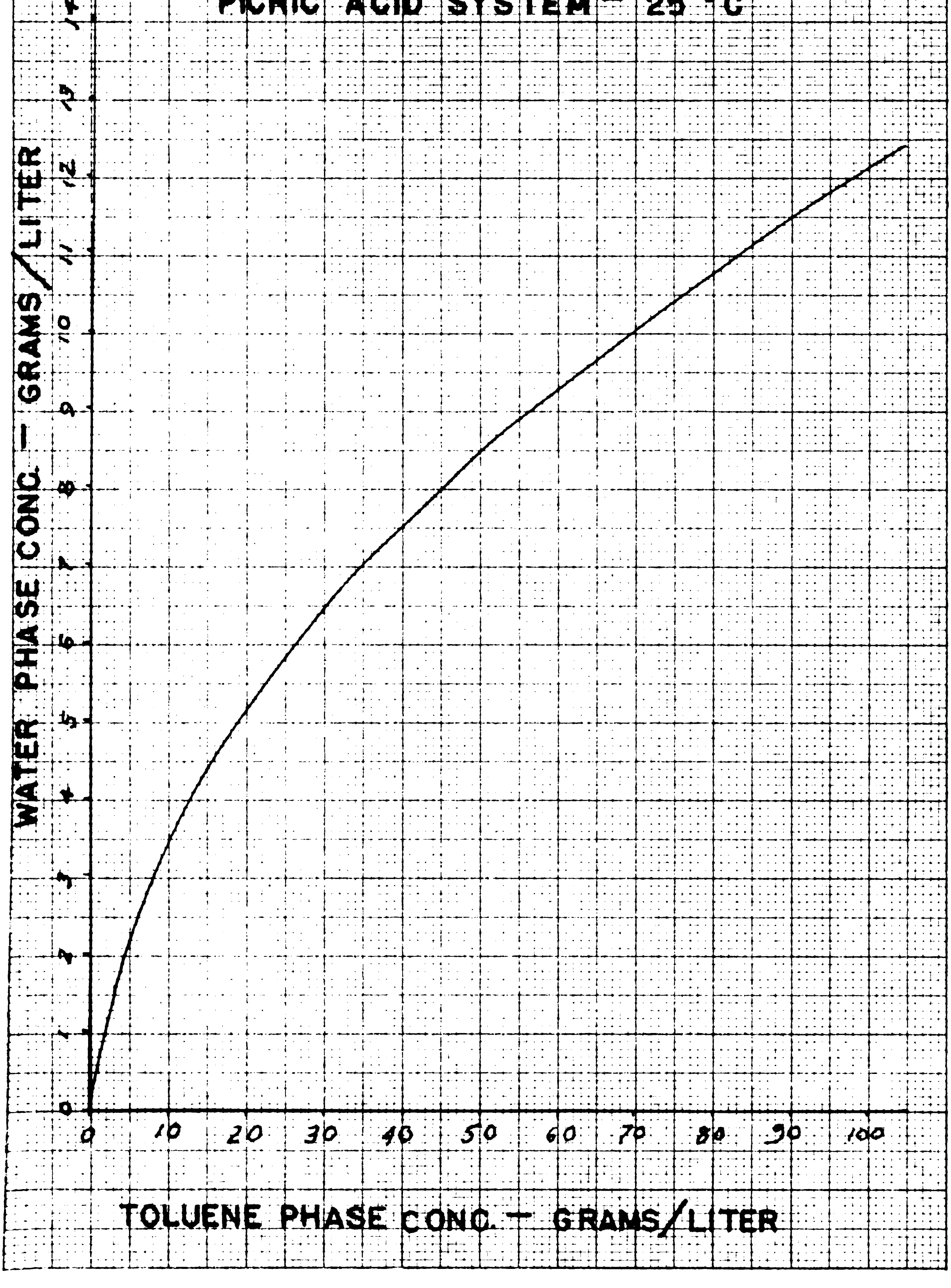
Second, because toluene is very volitile, inhalation is difficult to avoid. An excess of inhaled vapors results in poisoning, the first symptoms of which are similar to alcohol intoxication. Continued exposure results in internal injury. It is advisable to always transfer toluene under a hood or a well ventilated area.

- - - - - - - - - - -

The above information was obtained from the author's experience and <u>Industrial Toxiology</u>, by Laurence Fairhall.

APPENDIX IV

EQUILIBRIUM DATA—TOLUENE, WATER, PICRIC ACID SYSTEM— 25 °C



APPENDIX V

Optical Theory

In this work no actual reference need be made to optical theory as concentrations were to be determined by comparisons.

To make these comparisons easier, certain filters were put in front of the subject. The filters did not transmit light wave-lengths which were transmitted through picric acid-water solutions. For example, the Kodak #35 Filter used would transmit light having wave-lengths of 600 to 680 millimicrons, while a concentrated picric acid-water solution does not transmit light having a wave-length above 500 millimicrons. Thus, a solute cloud around the drop, photographed through a filter would appear light on the negative as little light would have reached the film. This lightness could be compared to a standard cell by means of a microphotometer.

No further knowledge then, is required of optical theory; however, the following is included.

Lambert's law is the basic equation forspectrophotometric - densitometric analysis. For monochromatic light passing through a homogeneous absorbing medium:

$$\frac{dI}{I} = BdX$$

Where

I = Light intensity

dI = Change in intensity after passing through thickness dX of the medium

B = a constant

X = distance through the medium

Upon integration of the above equation between the limits I_o and I, corresponding to length 0 and l, one obtains

$$\frac{I}{I_o} = e^{-Bl} = \frac{1}{t} ,$$

Where t = the fraction transmitted

For a solution,

$$\frac{1}{t} = e^{-\alpha cl}$$

Where c = the concentration of the absorbing solute

and α = a constant

Taking the log of both sides of the last equation

$$\ln \frac{1}{t} = -\alpha cl$$

Now defining $\ln \frac{1}{t}$ as the optical density, D, and α as the extinction coefficient, E,

$$D = Ecl$$

For high accuracy in any analytical determination using optical methods, a high value of E is desirable. This is obtained by varying the light filters in front of the subject until large values of E for any given concentration range exist.

In this work, the use of the Kodak #35 or #50 filter mounted in B glass accomplished this end.

APPENDIX VI

Data:

A. Nozzle Tip Diameter

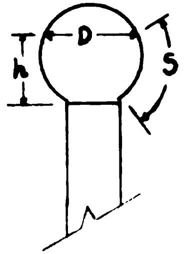
1. Nozzle used for photograph sets 1 and 2

   a. I.D. = 0.027" b. O.D. = 0.041"

2. Nozzle used for photograph sets 3,4,5, and 6.

   a. I.D. = 0.036" b. O.D. = 0.049"

B. Projected Film Negative Measurements for Photograph Set 1

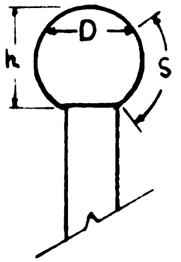


24ths of a second	Dimension as shown in sketch	Measurement - Inches						
2	h	0.00	1.10	0.20	0.30	0.40		
	D	0.350	0.360	0.400	0.350	0		
	s	-----	-----	-----	-----	----		
6	h	0.00	0.20	0.30	0.40	0.60	0.70	
	D	0.350	0.590	0.610	0.610	0.407	0	
	s	-----	-----	-----	-----	-----	----	
12	h	0.00	0.20	0.40	0.60	0.80	0.90	
	D	0.350	0.610	0.790	0.740	0.440	0.0	
	s	0.00	0.35	0.50	0.65	0.95	1.10	
20	h	0.00	0.20	0.40	0.60	0.80	1.00	1.05
	D	0.350	0.290	0.940	0.735	0.561	0.46	0.00
	s	0.00	0.25	0.50	0.70	0.95	1.10	1.35

Projected Film Negative Measurements for Photograph Set 1
(Continued)

32	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20			
	D	0.350	0.810	1.00	1.13	0.99	0.960	0.00			
	s	0.00	0.30	0.55	0.85	1.00	1.12	1.45			
40	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20			
	D	0.350	0.600	1.00	1.31	0.940	0.960	0			
	s	0.00	0.30	0.55	0.80	1.00	1.20	1.5			
52	h	0.00	4.20	0.40	0.00	0.80	1.00	1.20	1.40	1.50	
	D	0.350	0.800	1.11	1.24	1.320	1.260	1.000	0.620	0.000	
	s	0.00	0.30	0.60	0.90	1.00	1.15	1.35	1.60	1.95	
60	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.70
	D	0.350	0.870	1.12	1.29	1.390	1.390	1.240	1.000	0.700	0
	s	0.00	0.15	0.35	0.55	0.90	1.03	1.20	1.50	1.80	2.15
68	h	0.00	-----	----	----	-----	-----	-----	-----	-----	-----
	D	0.350	0.7	1	1.45	1.53	1.53	1.09	0.63	0	
	s	0.00	-----	----	----	-----	-----	-----	-----	-----	-----
78	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.80
	D	0	0.810	1.20	1.40	1.50	1.50	1.46	1.200	0.900	0
	s	0.00	0.40	0.60	0.90	1.00	1.15	1.40	1.55	1.90	2.35

C. Projected Film Negative Measurements for Phorograph Set 2



24ths of a second	Dimension as shown in sketch	Measurement - inches					
2	h	0.00	0.10	0.20	0.32		
	D	0.250	0.350	0.100	0.00		
	s	-----	-----	-----	----		
10	h	0.00	1.10	0.20	0.40	0.50	0.50
	D	0.250	0.470	0.540	0.540	0.450	0
	s	0	0.15	0.30	0.45	0.50	0.70
22	h	0.00	0.20	0.40	0.60	0.80	0.85
	D	0.25	0.78	0.86	0.77	0.40	0.00
	s	0	0.25	0.50	0.70	0.90	1.10

Projected Film Negative Measurements for Photograph Set 2

(Continued)

31	h	0.00	0.20	0.40	0.60	0.80	0.90			
	D	0.250	0.800	1.000	0.950	0.700	0.090			
	s	0.00	0.35	0.55	0.80	1.10	1.35			
40	h	0.000	0.20	0.40	0.00	0.80	1.00	1.05		
	D	0.250	0.720	1.00	1.00	0.900	0050	0		
	s	0.00	0.30	0.55	0.75	0.95	1.30	1.25		
60	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.25	
	D	0.250	0.900	1.150	1.200	1.700	0.950	1.500	0.000	
	s	0	0.35	0.55	0.85	1.10	1.35	1.55	1.8	
50	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20		
	D	0.250	0.900	1.100	1.150	1.100	0.800	0.000		
	s	0.00	0.30	0.550	0.750	0.950	1.20	1.55		
70	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.35	
	D	0.25	0.85	1.120	1.230	1.720	1.110	0.800	0	
	s	0.00	0.40	0.65	0.80	1.05	1.25	1.50	1.90	
80	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.45
	D	0.250	0.900	1.180	1.320	1.320	1.210	1	1.800	1.990
	s	0.000	0.400	0.550	0.900	1.050	1.750	1.150	1.800	1.950

Projected Film Negative Measurements for Photograph Set 2

(Continued)

90	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.50		
	D	0.250	0.900	1.200	1.400	1.600	1.320	1.120	0.600	0		
	s	0	0.350	0.550	0.900	1.050	1.200	1.500	1.800	2.000		
100	h	0.00	0.20	0.400	0.60	0.80	1.00	1.20	1.40	1.60		
	D	0.25	0.90	1.20	1.40	1.45	1.40	1.30	1	0		
	s	0	0.30	0.60	0.80	1.05	1.20	1.45	1.60	2.05		
110	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.65	
	D	0.25	0.90	1.20	1.40	1.50	1.45	1.32	1.10	0.50	0	
	s	0.00	0.30	0.65	0.95	1.05	1.25	1.40	1.65	2.00	2.10	
130	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.75	
	D	0.230	0.800	1.200	1.400	1.520	1.480	1.450	1.270	0.950	0	
	s	0.000	0.30	0.60	0.80	1.00	1.45	1.40	1.70	1.90	2.05	
150	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.80	1.80
	D	0.250	0.700	1.100	1.400	1.520	1.390	1.570	1.400	1.500	1.300	0.840
	s	0.00	0.20	0.55	00.80	0.10	1.25	1.50	1.75	2.00	2.30	2.40
159	h	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.80	1.95
	D	0.0	0.700	1.120	1.400	1.570	1.620	1.600	1.500	1.300	0.840	0
	s	0.000	0.300	0.40	0.55	0.80	1.00	1.20	1.45	1.65	1.95	2.20

D. Projected Film Negative Measurement for Photograph Set 6.

1. Drop diameter - 1.40"
2. Solute cloud diameter - 0.65"
3. Nozzle tip - 0.31"

E. Photograph Measurement for Photograph Set 3.

1. Final diameter - 0.379"
2. Nozzle tip diameter - 0.106"

F. Photograph Measurement for Photograph Set 4.

1. Final diameter - 0.441"
2. Nozzle tip diameter - 0.107"

G. Photograph Measurement for Photograph Set 5.

1. Final diameter - 0.379"
2. Nozzle tip diameter - 0.118"

H. Standard Cell Measurement - Percent Light Transmission through Negatives.

1. Photograph Set 7

Concentration grams/liter	0.0244	0.0122	0.00975	0.00609	0.00488	0.00244	0.000975
Inches from left side of standard cell			Percent transmission				
1/8	--	30.5	17.2	--	--	2.1	--
1/4	84.5	31.0	20.2	9.4	4.4	2.3	1.5
3/8	82.0	29.6	18.1	8.7	5.5	2.7	1.4
1/2	84.5	34.6	18.6	8.5	4.8	2.3	1.3
5/8	--	32.0	21.3	--	--	2.3	--

L 2. Photograph Set 8

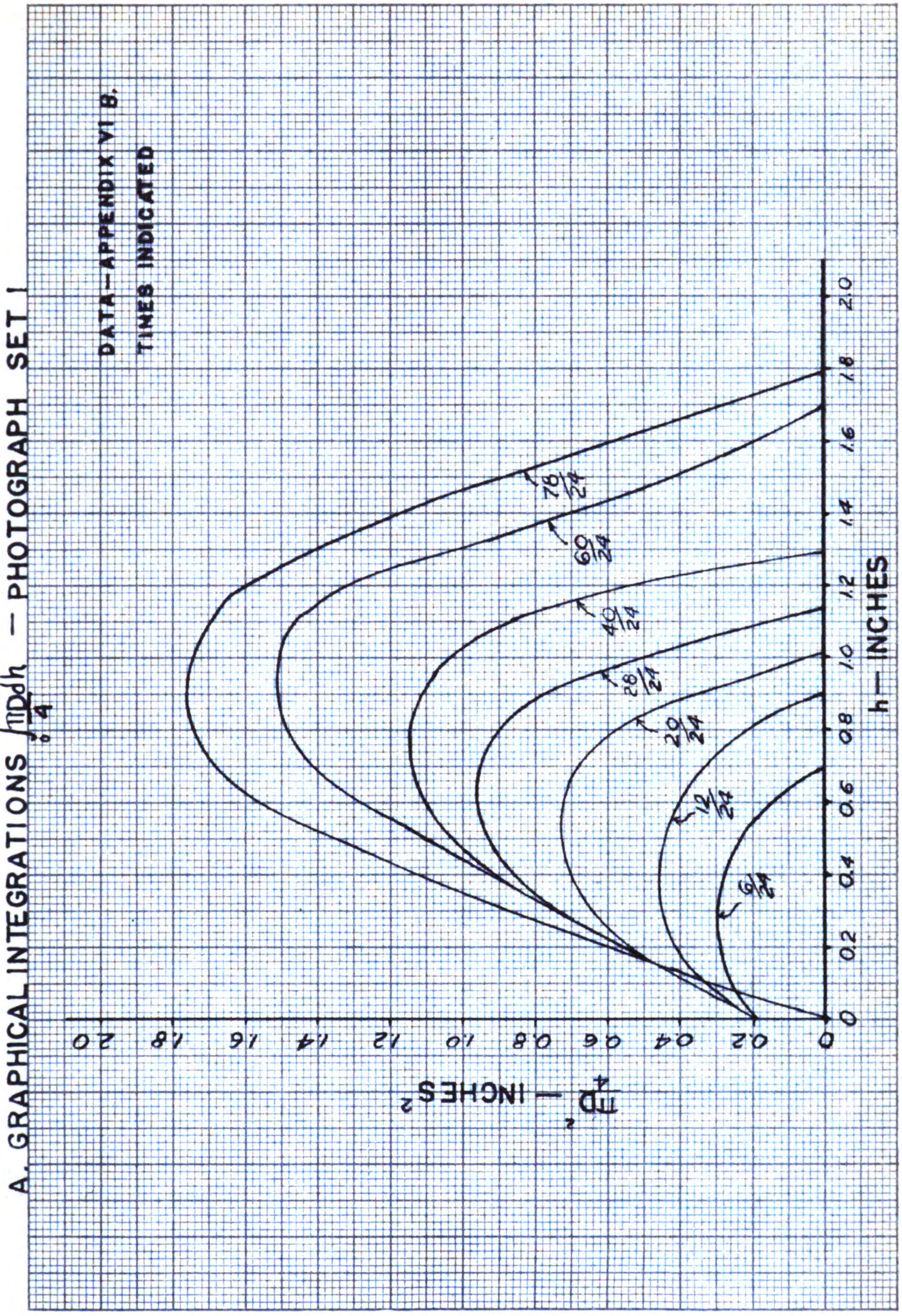
Concentration grams/liter	0.0975	0.0488	0.0244	0.0122	0.00975	0.00609	0.002847
Inches from left side of standard cell			Percent transmission				
1/8	--	19.3	8.3	--	--	2.9	--
1/4"	50.4	20.7	9.2	5.8	3.8	2.7	2.1
3/8'	54.6	20.9	8.3	5.6	4	2.3	1.8
1/2'	51.3	19.2	8.6	5.6	3.8	2.3	2.2
5/8'	--	19.1	7.9	--	--	2.5	--

I. Formation Times

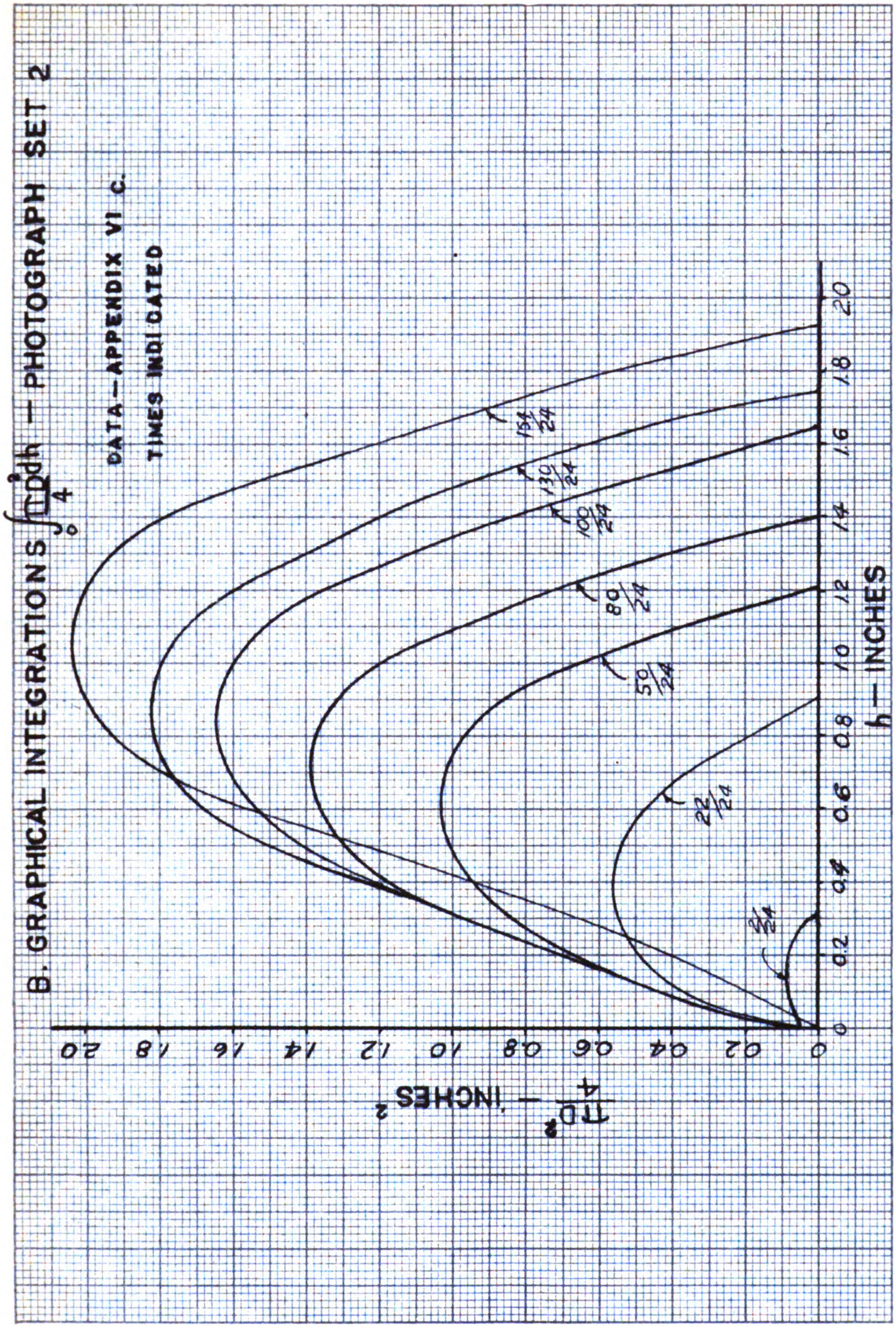
Photograph Set	Formation Time (Seconds)
1	3.33
2	6.63
3	5.32
4	6.09
5	4.00
6	5.57

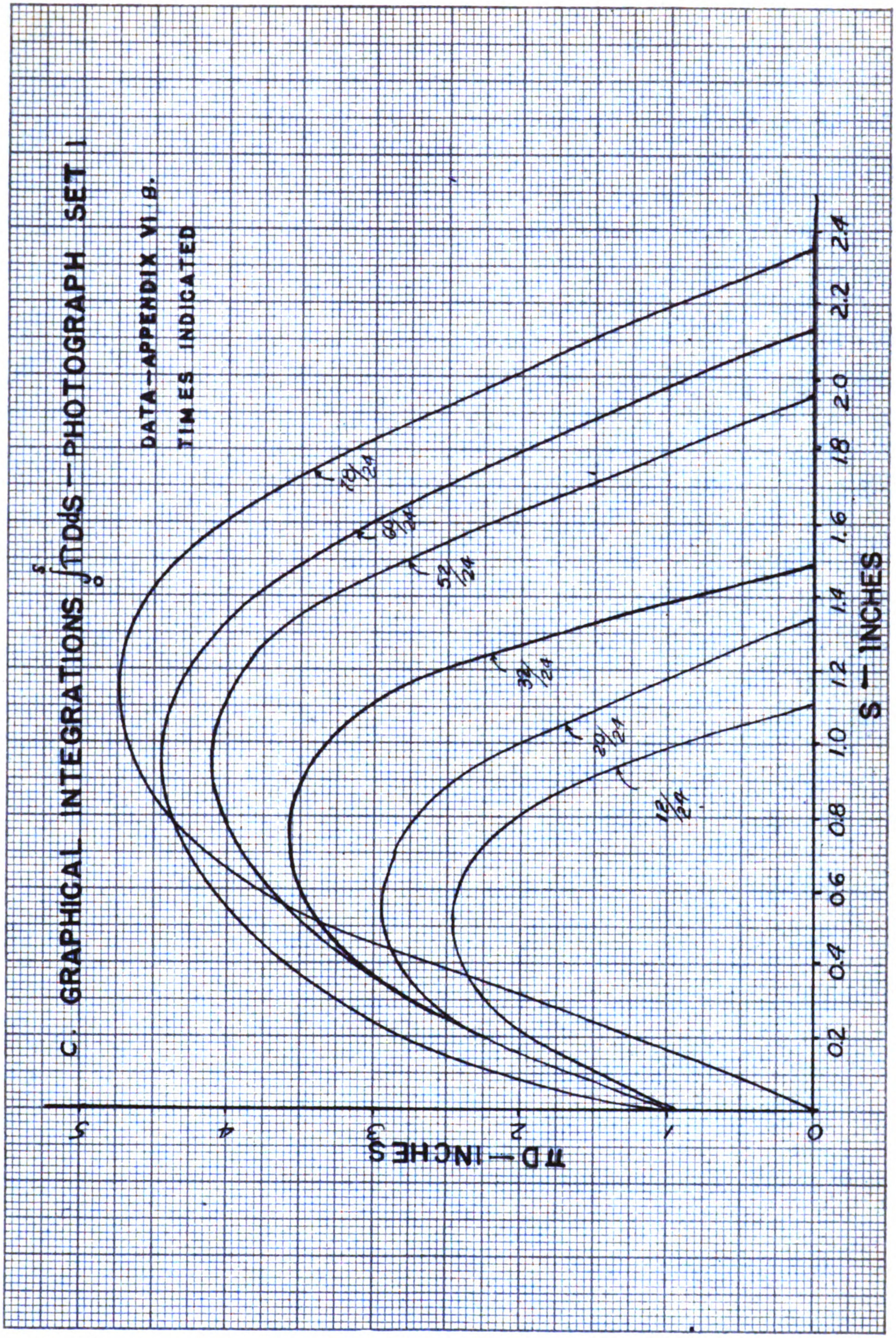
APPENDIX VII

Calculations, Graphical Integrations and Graphical Results

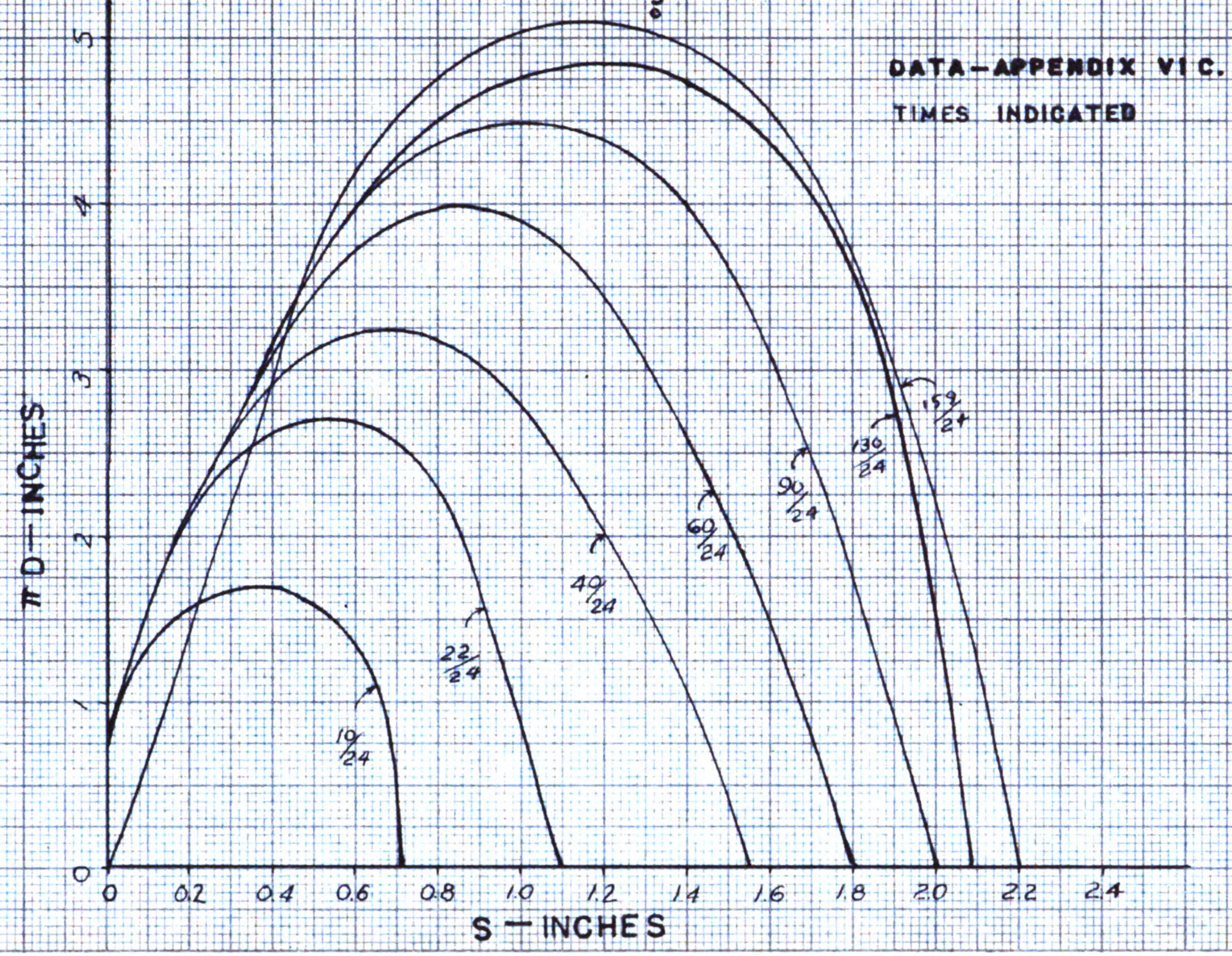


A. GRAPHICAL INTEGRATIONS $\int_0^H \frac{\pi D^2}{4} dh$ — PHOTOGRAPH SET I


B. GRAPHICAL INTEGRATIONS $\int_0^H \frac{\pi D^2}{4} dh$ — PHOTOGRAPH SET 2
DATA — APPENDIX VI C.
TIMES INDICATED
$\frac{\pi D^2}{4}$ — INCHES^2
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
h — INCHES
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
154/24
130/24
100/24
80/24
50/24
22/24
3/24


C. GRAPHICAL INTEGRATIONS $\int_0^s \pi D\,ds$ — PHOTOGRAPH SET I
DATA—APPENDIX VI B.
TIMES INDICATED
70/24
62/24
52/24
32/24
20/24
12/24
S — INCHES
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
πD — INCHES
1
2
3
4
5

D. GRAPHICAL INTEGRATION $S\int_0^S \pi D\,ds$ — PHOTOGRAPH SET 2



E. Data and Calculated Data from Graphs A, B, C and D

1. From Graph A (Photograph Set 1)

Time - 24ths of a second	6	12	20	28	40	60	68	78
in.^{2} measured on graph with planimeter	0.935	1.85	3.17	4.28	8.57	10.31	11.03	12.75
measured in.^{3} times Conversion factor to give actual ft.^{3} of volume	0.136 $\times 10^{-6}$	0.274 $\times 10^{-6}$	0.472 $\times 10^{-6}$	0.634 $\times 10^{-6}$	1.17 $\times 10^{-6}$	1.53 $\times 10^{-6}$	1.63 $\times 10^{-6}$	1.87 $\times 10^{-6}$

2. From Graph B (Photograph Set 2)

Time - 24ths of a second	2	10	22	31	50	60	80	100	130	150
in.^{2} measured on graph with planimeter	0.170	0.794	2.16	3.08	5.28	6.01	18.46	10.06	13.05	15.80
measured in.^{2} times * Conversion factor to give actual ft.^{3} of volume	0.0186 $\times10^{-6}$	0.0895 $\times10^{-6}$	0.244 $\times10^{-6}$	0.348 $\times10^{-6}$	0.595 $\times10^{-6}$	0.678 $\times10^{-6}$	0.946 $\times10^{-6}$	1.20 $\times10^{-6}$	1.26 $\times10^{-6}$	1.81 $\times10^{-6}$

3. From Graph C (Photograph Set 1)

Time - 24ths of a second	12	20	32	52	60	78
in.^{2} measured on graph with planimeter	4.91	7.05	6.61	13.61	17.22	17.98
measured in.^{3} times * Conversion factor to give actual ft.^{2} of surface area	1.86 $\times10^{-4}$	2.68 $\times10^{-4}$	3.64 $\times10^{-4}$	5.18 $\times10^{-4}$	6.47 $\times10^{-4}$	6.82 $\times10^{-4}$

4. From Graph D (Photograph Set 2)

Time - 24ths of a second	10	22	31	40	60	90	130	159
in.^{2} measured on graph with planimeter	2.41	5.41	8.19	8.91	12.55	16.64	18.49	19.59
measured in.^{3} times* Conversion factor to give actual ft.^{2} of surface area	0.766 x10^{-4}	1.72 x10^{-4}	2.60 x10^{-4}	2.84 x10^{-4}	4.00 x10^{-4}	5.29 x10^{-4}	5.88 x10^{-4}	6.22 x10^{-4}

*Conversion factors obtained as illustrated in following example from Graph A at 6/24 ths of a second.

in.^{2} measured on graph = 0.935

One measured in.^{2} on graph = 0.16 in.^{3} as projected (See Graph A.)

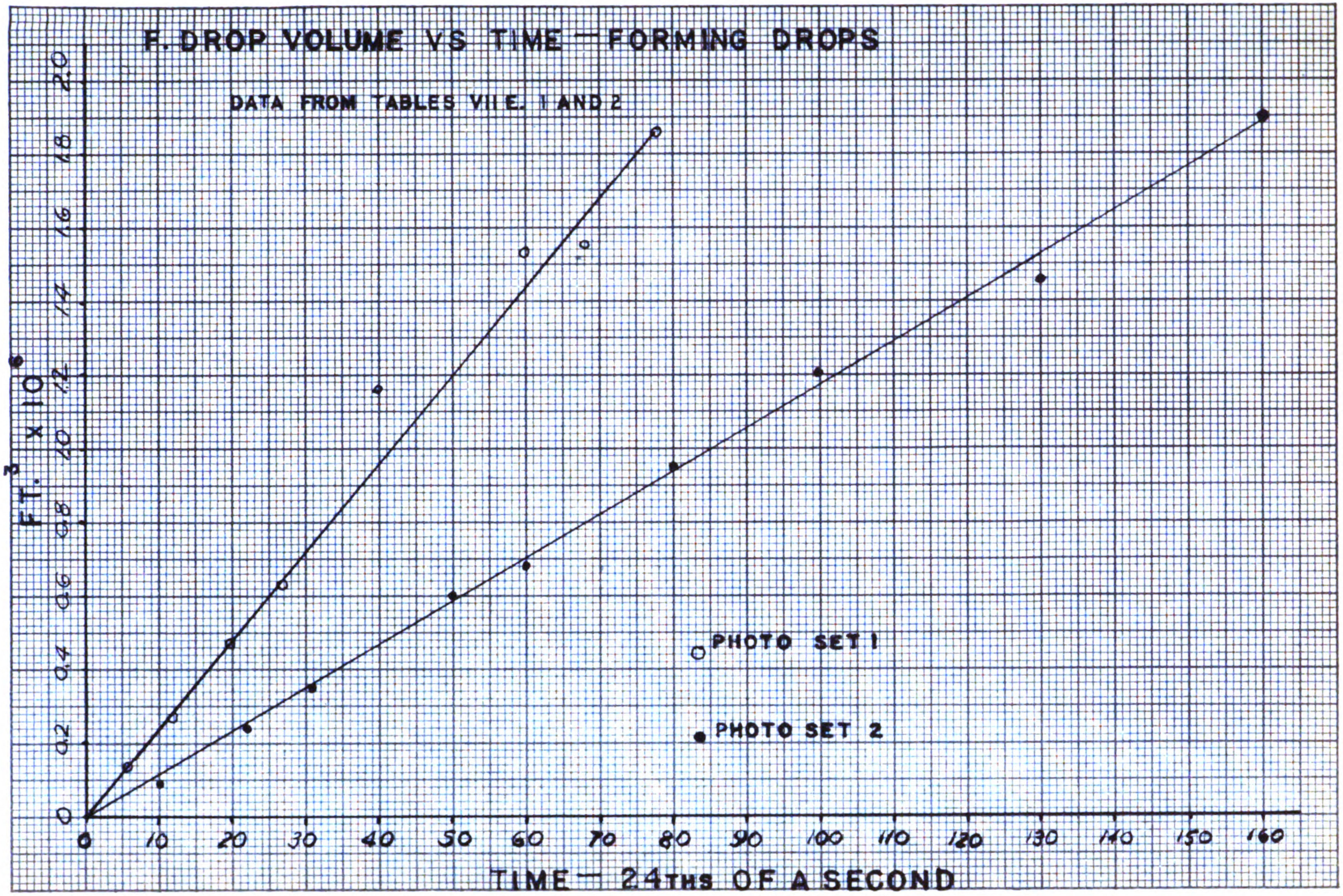
$$1 \text{ in.}^3 \text{ as projected} = \frac{0.041}{0.35} = 1.59 \times 10^{-3} \text{ actual in.}^3$$

where 0.041 is the actual I.D. of the nozzle and 0.35 is the projected measurement.

$$\text{Conversion factor} = \frac{0.16 \times 1.59 \times 10^{-3}}{12 \times 12 \times 12} = 1.45 \times 10^{-4}$$

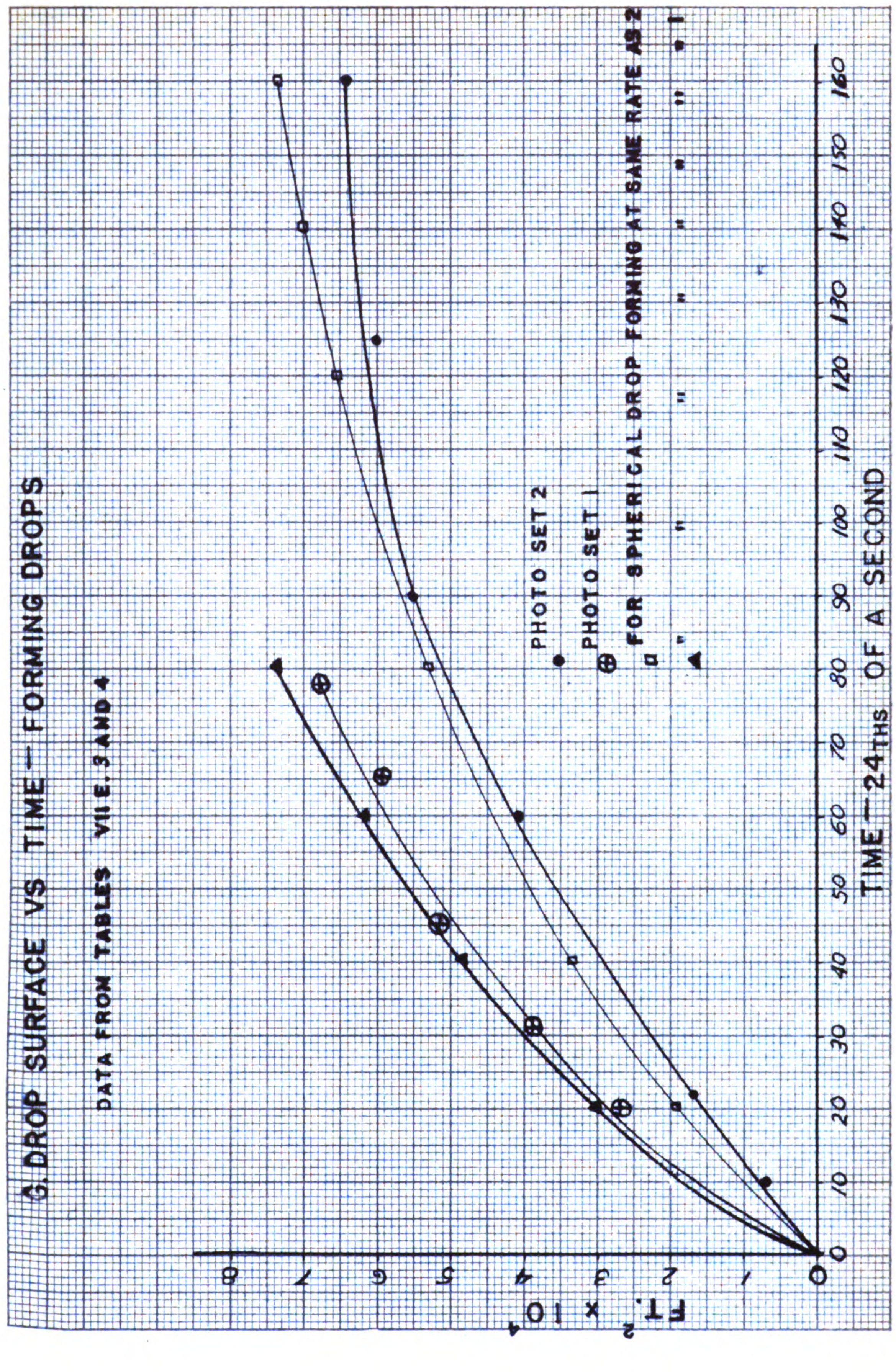
$$\frac{\text{actual ft.}^3}{\text{measured in.}^2}$$

$$0.935 \text{ measured in.}^2 \times 1.45 \times 10^{-4} \frac{\text{actual ft.}^3}{\text{measured in.}^2} = 0.136 \times 10^{-4} \text{ actual ft.}^3$$



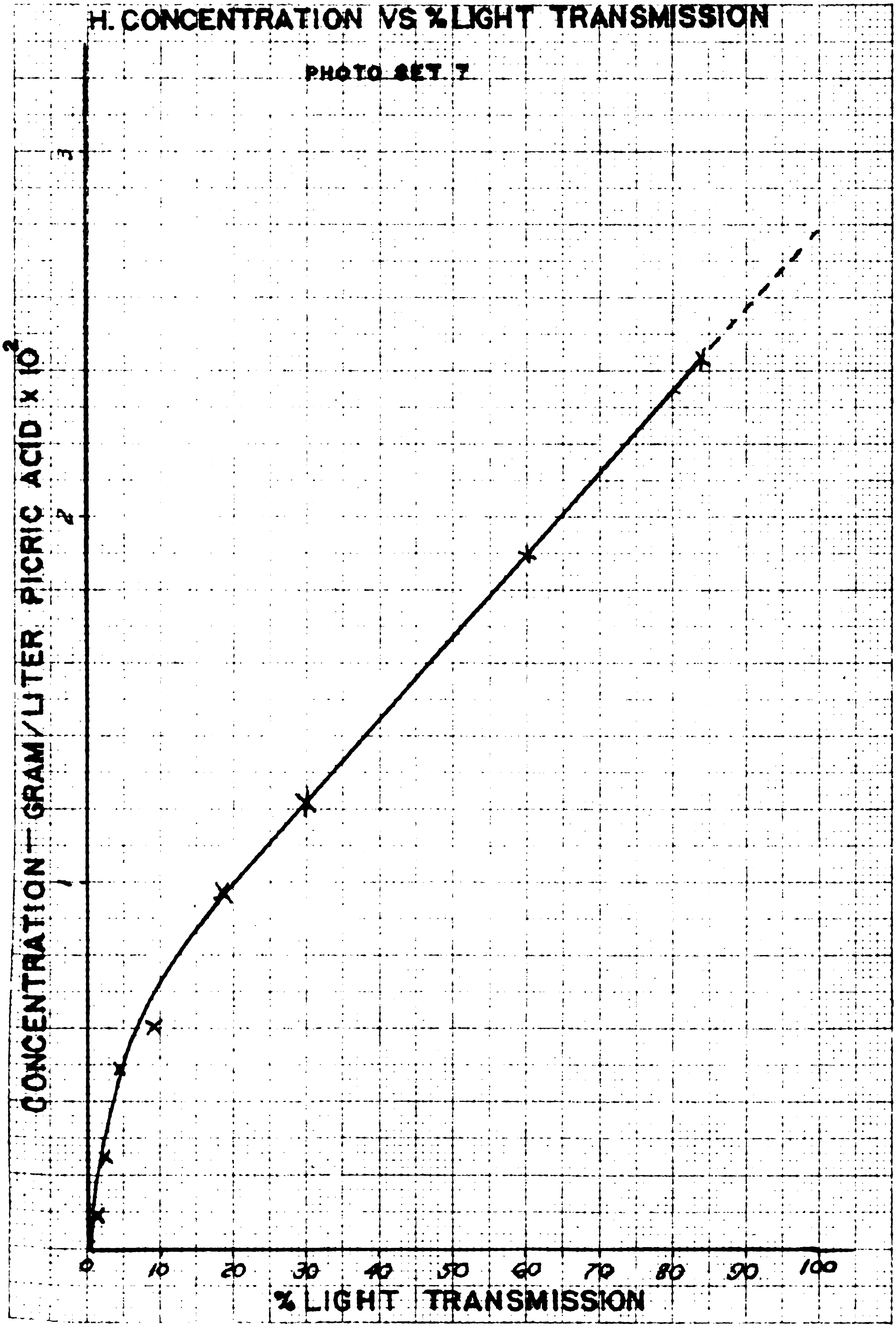
F. DROP VOLUME VS TIME — FORMING DROPS

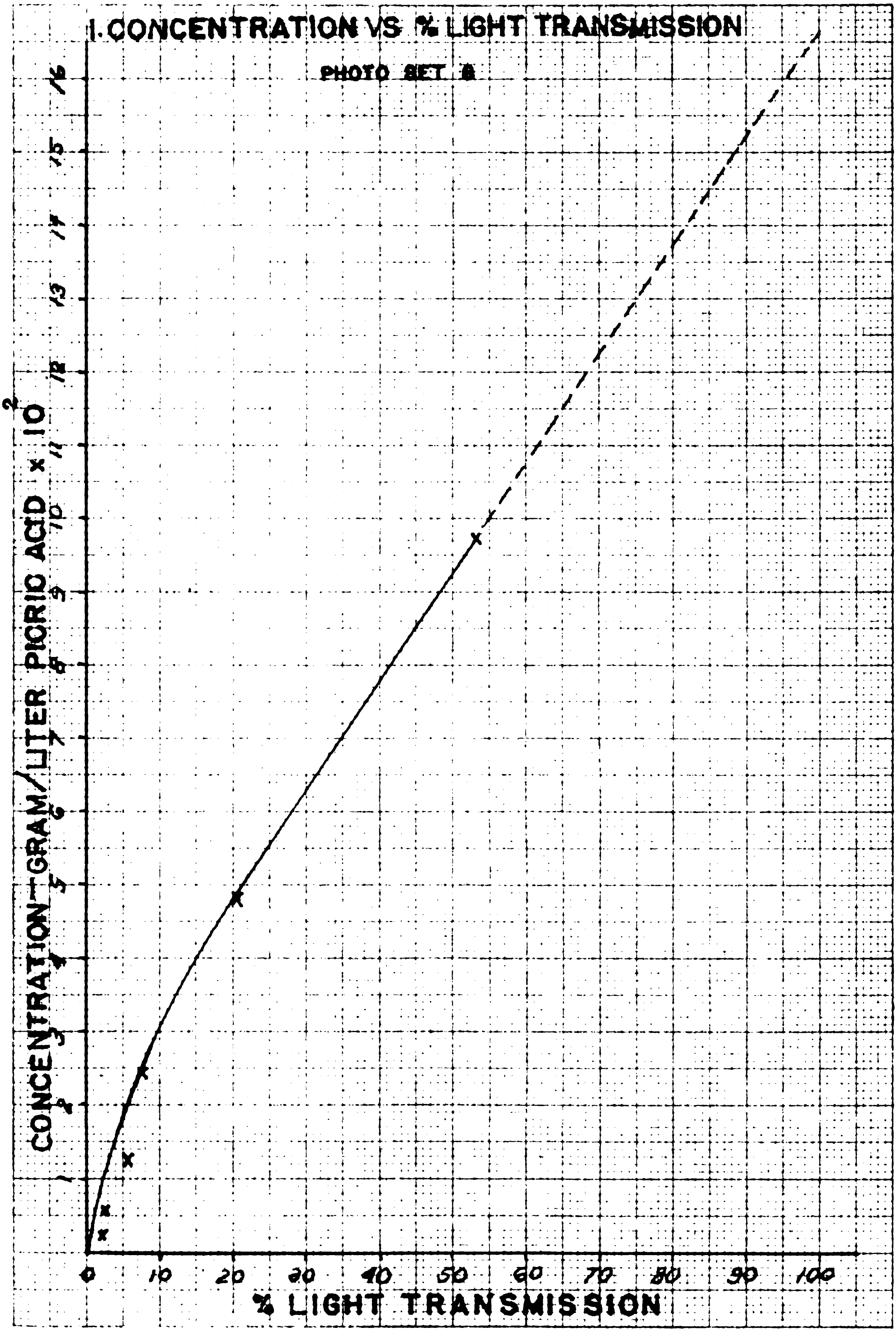
DATA FROM TABLES VII E. 1 AND 2



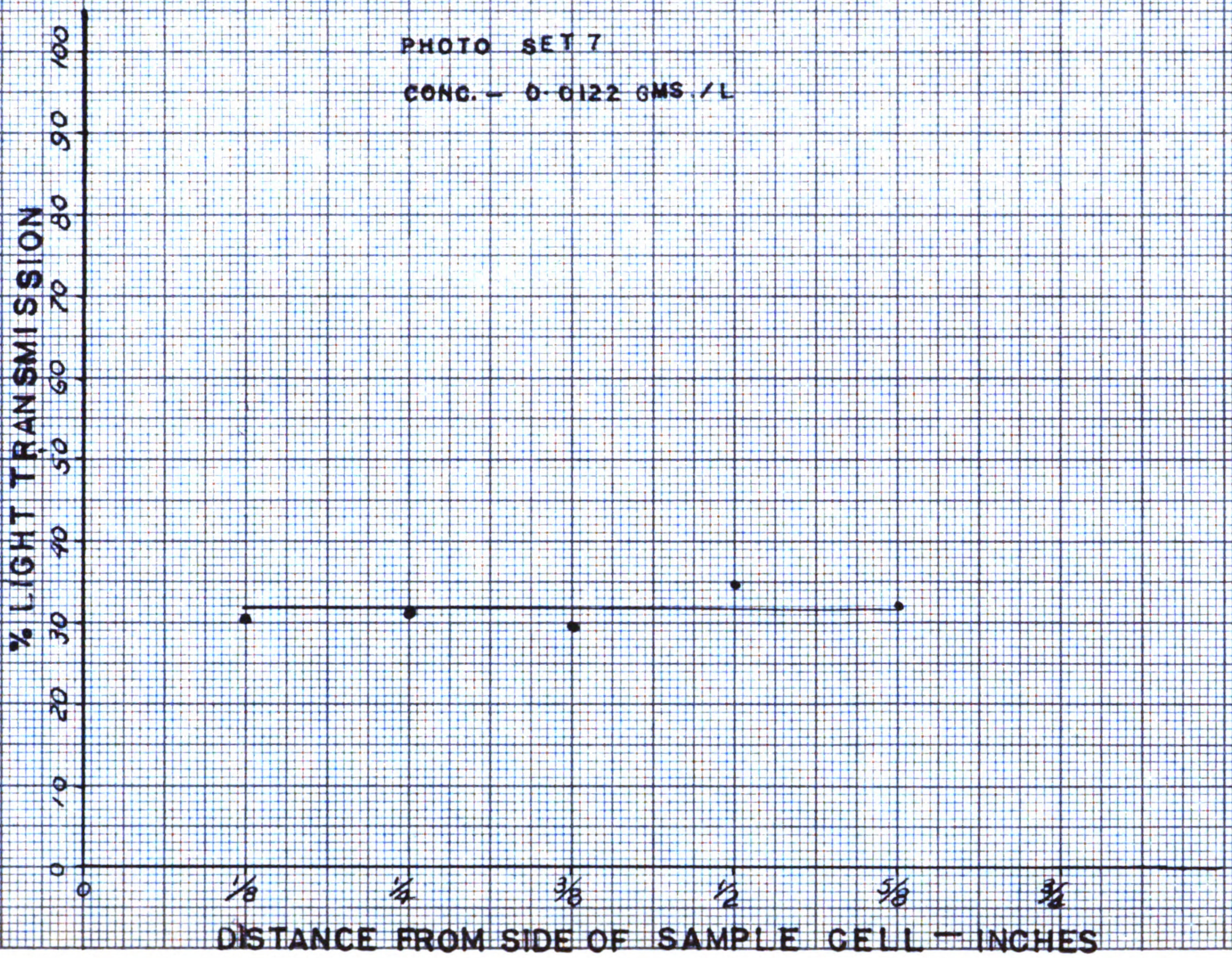
G. DROP SURFACE VS TIME — FORMING DROPS

DATA FROM TABLES VII E. 3 AND 4

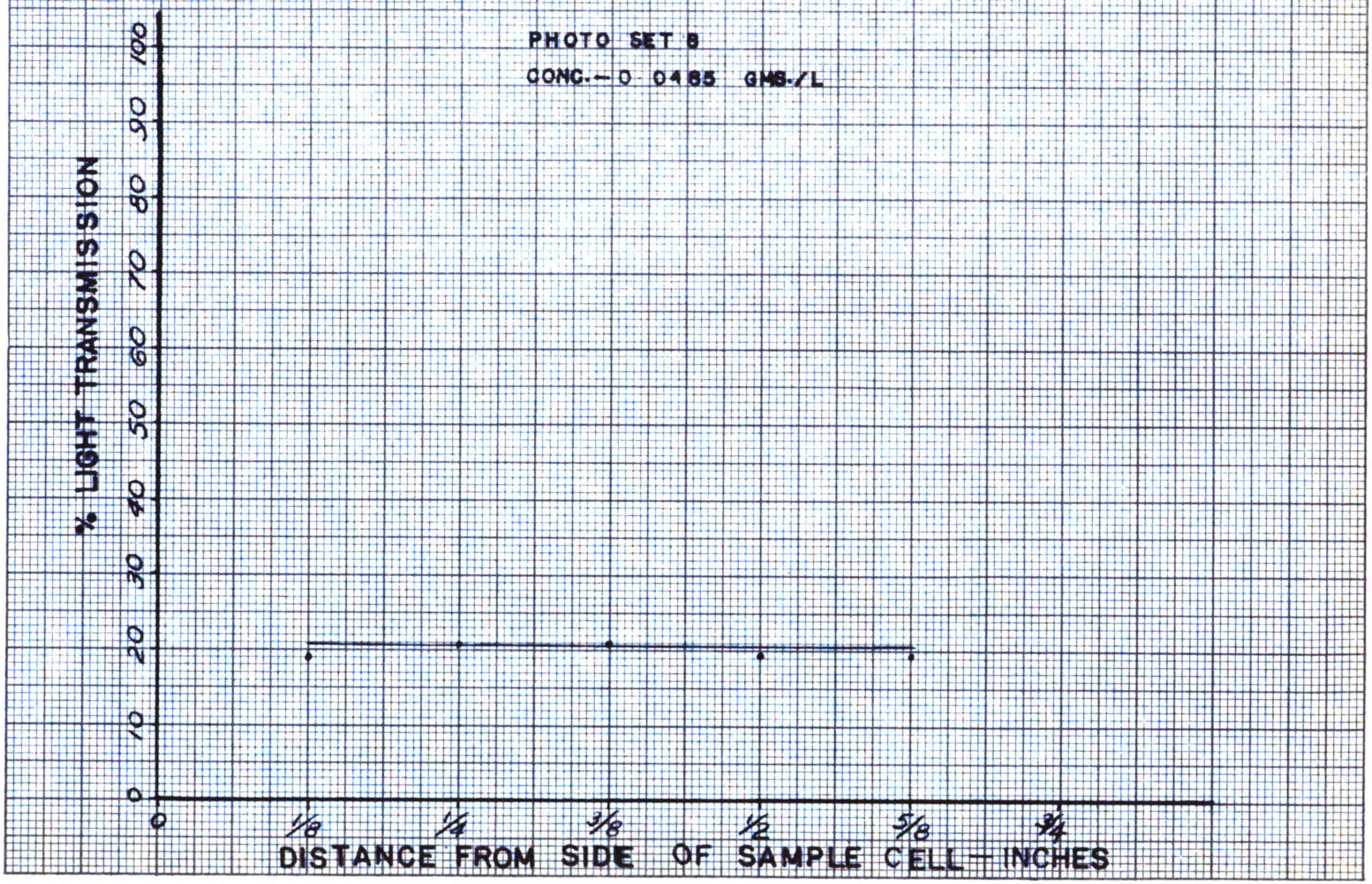

H. CONCENTRATION VS % LIGHT TRANSMISSION
PHOTO SET 7
CONCENTRATION — GRAM/LITER PICRIC ACID x 10^2
3
2
1
0
10
20
30
40
50
60
70
80
90
100
% LIGHT TRANSMISSION


1. CONCENTRATION VS % LIGHT TRANSMISSION
PHOTO SET B
CONCENTRATION—GRAM/LITER PICRIC ACID × 10^2
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0
10
20
30
40
50
60
70
80
90
100
% LIGHT TRANSMISSION

J. % TRANSMISSION VS INCHES FROM SIDE OF CELL



K. % TRANSMISSION VS DISTANCE FROM SIDE OF CELL



L. Sample Calculations

1. The estimation of percent of total solute extracted from the coalescing drop, Photograph Set 6.

a) Projection Factor

0.31 measured inches = 0.049 actual inches

$$1 \text{ measured inch} = \frac{0.049}{0.31} \text{ actual inches}$$

1 measured inch = 0.158 actual inches

b) Drop volume

Diameter of drop = 1.40 measured inches

$$\text{Drop volume} = \frac{1}{6}\pi d^3 = \frac{1}{6} \times \pi (1.40 \times 0.158)^3$$

Drop volume = 0.00580 cubic inches

c) Grams of solute in drop

Grams of picric acid in one liter of toluene saturated with water and picric acid, - 121

$$121 \frac{\text{grams}}{\text{liter}} \times \frac{\text{liter}}{61.2 \text{ in.}^3} \times 0.0058 \text{ in.}^3 = 1.15 \times 10^{-2} \text{ grams}$$

d) Grams of solvent in solute cloud

Volume of cylinder which has a length equal to inside width of extractor and a diameter equal to the actual diameter of the solute cloud.

$$\frac{\pi D^2 \times 1}{4} = \frac{(0.65 \times 0.158)^2}{4} \times 1 = 0.00826 \text{ cubic inches}$$

e) Concentration of solute in this volume as determined from the standard cell Photograph Set 8 -

> 0.0975 gms/liter

f) Grams extracted from drop, $> 1.31 \times 10^{-5}$ gms.

g) Percent of total solute in drop which was extracted.

$$\frac{>1.31 \times 10^{-5}}{1.15 \times 10^{-2}} \times 100 = > 0.114\%$$

2. The determination of the final drop size and rate of formation of the drop shown in Photograph Set 3.

a) Enlargement factor

0.106 measured inches = 0.049 actual inches

$$1 \text{ measured inch} = \frac{0.049}{0.106} \text{ actual inches}$$

1 measured inch = 0.462 actual inches

b) Drop volume

Diameter of drop = 0.379 measured inches

$$\text{Drop volume} = \frac{1}{6}\pi d^3 = \frac{1}{6}\pi (0.379 \times 0.462)^3$$

$$\text{Drop volume} = 0.00279 \text{ in.}^3$$

$$= 1.63 \times 10^{-6} \text{ ft.}^3$$

c) Rate of formation

$$\frac{1.63 \times 10^{-6} \text{ ft.}^3}{5.32 \text{ Sec}} = 0.306 \times 10^{-6} \frac{\text{ft.}^3}{\text{Sec}}$$

3. Calculation of percent of total solute in drop extracted during formation for Photograph Set 1 using Gregory's formula, page 33 and formula 10 on page 14.

a) Date and nomenclature

μ = viscosity of drop fluid - 3.76×10^{-4} $\frac{\#\ \text{mass}}{\text{ft.} - \text{Sec}}$

V = nozzle velocity ---- 0.132 ft/Sec

d = final drop diameter - 1.52×10^{-2} ft.

ρ = density of drop fluid - 54 $\#/\text{ft.}^3$

D = Diffusivity of picric acid in toluene --- 5.59×10^{-5} $\frac{\text{ft.}^2}{\text{hr.}}$

The viscosity and the density of the drop fluid is taken as the viscosity and density of toluene at 25°C, from the 36th edition of The Handbook of Chemistry and Physics. The diffusivity of picric acid in toluene was calculated from formula (23) on page 21 of Absorbtion and Extraction by Sherwood and Pigford, 2nd edition; k_1 in this formula was taken for benzene. The nozzle velocity was obtained by dividing the formation rate by the nozzle channel cross section.

b) $K_d = 3.74\ V \left(\frac{dV\rho}{\mu} \right)^{-0.2} \left(\frac{\mu}{\rho D} \right)^{-1.0}$ (p. 33)

$$k_d = 0.132 \, \frac{\text{ft.}}{\text{Sec}} \times 3600 \, \frac{\text{Sec}}{\text{hr}} \times 3.74 \times$$

$$\left(\frac{1.52 \times 10^{-2} \text{ ft.} \times 0.132 \, \frac{\text{ft.}}{\text{Sec}} \times 54 \, \frac{\#}{\text{ft.}^3}}{3.76 \times 10^{-4} \, \frac{\#}{\text{ft.-Sec.}}} \right)^{-0.2} \times$$

$$\left(\frac{3.76 \times 10^{-4} \, \frac{\#}{\text{ft.-Sec}} \times 3600 \, \frac{\text{Sec.}}{\text{hr.}}}{54 \, \frac{\#}{\text{ft.}^3} \times 5.59 \times 10^{-5} \, \frac{\text{ft.}^2}{\text{hr}}} \right)^{-1.0}$$

$$k_d = 1.28 \, \frac{\text{ft.}}{\text{hr}}$$

c) **Percent of total solute extracted:**

$$\text{In} \, \frac{CfA}{CoA} = \frac{Kt3}{R}$$

$$K = k_d \qquad \text{(p. 14)}$$

$$\ln \frac{C_{fA}}{C_{oA}} = -\frac{k_d t3}{R} = -1.28 \, \frac{\text{ft.}}{\text{hr.}} \times \frac{3.34}{3600} \text{ hr.}$$

$$\times \frac{3 \times 2}{1.52 \times 10^{-2} \text{ ft.}}$$

$$\ln \frac{C_{fA}}{C_{oA}} = -0.496, \qquad \frac{C_{fA}}{C_{oA}} = 0.626$$

$$\% \text{ extracted} = (1 - 0.626) \times 100 = 37.4\%$$