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I hereby recommend that the thesis prepared under my supervision by William F. Pansing

entitled "Liquid-Liquid Extraction: The Mechanism of Solute Transfer from Single Drops"

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosphy

Approved by:

FORM 668—G. S. & T. C.—500—5-48

LIQUID-LIQUID EXTRACTION:

THE MECHANISM OF SOLUTE TRANSFER

FROM SINGLE DROPS

A dissertation submitted to the
Graduate School of Arts and Sciences
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

1951

by

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Ch.E. University of Cincinnati 1948
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ACKNOWLEDGEMENT

The author wishes to express his sincerest thanks to Dr. William Licht Jr. for his invaluable inspiration and generous help and assistance in the capacity of research supervisor.

Thanks are also due to Professor R. S. Tour for a very enlightening discussion concerning certain findings in the thesis.

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LIST OF SYMBOLS

a	radius of drop (final)
A	interfacial area
B	series coefficient
C	concentration
d	drop diameter
D	molecular diffusivity
E	fraction solute extracted
h	K_d/D_d
I.T.	interfacial tension
k	individual film coefficient
K	over-all film coefficient
n	total solute transferred degree of association index to infinite series
N	rate of solute transfer
Re	Reynold's number
r	radius of drop
t	time
u	variable of integration
U	eigenvalue
v	drop velocity
V	drop volume
x	linear distance from interface
α	constant in series solution

(List of Symbols Continued)

ρ	density
μ	viscosity

Subscripts

a	at outer radius a
b	bulk of phase (uniform)
c	continuous phase
d	dispersed phase
e	equilibrium concentration
f	formation
i	interface
m	mean value
o	initial
t	transient
I	Stage I
II	Stage II
III	Stage III

ABSTRACT

The mechanism of solute transfer from liquid drops was studied. Possible mechanisms in each of three stages (drop-formation, drop-fall, and drop-coalescence) were considered. Theoretical equations were developed to express the amount of extraction during drop-formation and drop-fall. A method for testing experimental data to determine the applicability of each of the possible mechanisms for drop-fall was developed.

The theories developed were tested with data on three extraction systems. Acetic acid was extracted from water with methyl isobutyl ketone, from perchlorethylene with water, and from a mixture of carbon tetrachloride and oil with water. In each case acetic acid was extracted from the dispersed phase.

The amount of extraction occurring during drop-formation was found to be rather small, in accordance with the theoretical equation developed.

In the methyl isobutyl ketone system the mechanism of solute transfer during drop-fall was analyzed on the basis of the conventional two-film theory and a modification of it. At least half of the resistance to solute transfer was found to be in the continuous phase. In the perchlorethylene system, the mechanism was analyzed on the basis of the conventional two-film theory. In this case practically all the resistance

to solute transfer was found to be in the dispersed phase. The difference in behavior of the two systems was attributed to a difference in drop behavior. In the carbon tetrachloride-oil system, the mechanism was analyzed as a gradual approach to a mechanism of pure diffusion within the drop.

The amount of extraction during drop-coalescence was found to be proportional to the concentration of the drop just before entering this stage and to the drop diameter.

INTRODUCTION

In recent years solvent extraction has come into widespread use in the chemical industry. As a result, liquid-liquid extraction has been the subject of many investigations in the literature. However, most of these investigations have been concerned primarily with the overall performance of extraction equipment rather than the fundamental theory of solute transfer. As a result, the performance and design of continuous types of extraction equipment is a rather uncertain and controversial subject.

The spray type of tower is one of the simpler continuous extractors in which the mechanism of solute transfer might be investigated. However, in commercial spray towers, the variation in drop size, the coalescence of drops and the effect of the moving continuous phase complicate the study of the fundamental mechanism of solute transfer. Hence, for the purpose of this investigation spray tower operation has been further simplified to the case of extraction from single uniform size drops passing through a stationary continuous phase.

In an actual spray tower or for the extraction from individual drops, the mechanism of solute transfer will differ in the various stages of the life of the drop. First the drop must be formed in the column, must then pass through the continuous phase and finally must be destroyed as it is collected at the opposite end of the column. Since the

mechanics of these three stages are so different, the individual stages must be studied separately before a correct analysis of spray tower operation can be made.

Licht and Conway[12] recognized these three stages in the life of a drop in a spray tower and designed an experimental extraction column with which an attempt was made to separate the amount of extraction occurring in each stage. Several other investigators have recognized the first stage of extraction from single drops. All of the previous investigators have determined the amount of extraction during drop formation by making a plot of the logarithm fraction unextracted, or an equivalent variable, versus column height. For this plot, Conway[3] obtained data from a column in which the extraction during the last or coalescence stage had been eliminated. The other investigators obtained data from a column in which this stage was either partially eliminated or not eliminated at all.

Since the plot usually gave a relatively straight line, this line was extrapolated back to zero column height. The ordinate intercept was considered to be the fraction of the solute unextracted during drop formation. The amount of extraction obtained in this way varied from ten to fifty percent solute extracted. A surprisingly large amount of extraction occurred during drop formation[6,12,16,18].

However, Conway observed that the amount of extraction occurring in a column three inches high was

relatively independent of drop formation time. It is difficult to see how the apparent amount of extraction during drop formation could be so large without being a function of drop formation time.

In view of the above results, there is an apparent need for a thorough investigation of solute transfer during drop formation. This would prove or disprove the validity of the extrapolation procedure for obtaining the amount of extraction during formation and thus separating the three stages.

Previous investigators have also assumed that the two-film theory applies to the drop moving through the continuous phase. This assumption should also be subjected to investigation.

In view of the above discussion, the objectives of the present investigation are:

1. Check the method used by Conway for separating the three stages of extraction and attempt to verify or explain some apparently contradictory results obtained, particularly the effect of drop formation time.
2. Make a comprehensive study of the possible mechanisms of solute transfer in each stage and attempt to interpret these mechanisms mathematically.
3. Develop methods for testing the experimental

data to identify the various mechanisms.

4. Obtain experimental data with which to check the mathematical solutions and tests obtained above.

PREVIOUS INVESTIGATIONS

A preliminary literature search revealed that very little work of a fundamental nature has been done on extraction from single drops. There have been several investigations[1,2,5,9] concerned with the performance of spray towers. In general, the results are reported in terms of an overall extraction coefficient defined by

$$K = \frac{L(C_2 - C_1)}{A \Delta C_{lm}}$$

where K = overall extraction coefficient (ft./hr.)

L = dispersed phase feed rate (cu.ft./hr.)

C_2, C_1 = solute concentrations of drops at exit and inlet to column (#moles/cu.ft.)

A = total interfacial area of drops in column at any time (sq.ft.)

ΔC_{lm} = log mean driving force based on C_1 and C_2 and the equilibrium concentrations of solute in dispersed phase corresponding to the observed concentrations in the continuous phase (#moles/cu.ft.).

This type of data is generally applicable only under the specific conditions of the experiment and cannot be extrapolated far from the conditions of the experiment.

Sherwood, Evans and Longcor[16] studied extraction from single drops as well as in a packed column. These

investigators extracted acetic acid from benzene and from methyl isobutyl ketone with water. Overall extraction coefficients, based on the total extraction in the column, were determined as a function of drop diameter. They found the coefficient increases with drop size for both systems. Also, for the same drop size the coefficient for the ketone was greater than for the benzene. They extrapolated a plot of the logarithm fraction unextracted versus column height to zero column height. On the basis of this extrapolation they concluded that 40-45% of the solute is extracted during drop formation.

Farmer[6] studied the extraction of acetic acid from a series of organic solvents using water as the extracting and continuous medium. Single drops were used in this investigation. Most of the data was obtained for one drop size. The amount of extraction during drop formation was obtained by extrapolating a semi-log plot of reciprocal fraction unextracted versus fall time to zero fall time. The interface at the terminal end of the column was maintained in a six millimeter connecting tube by continuous withdrawal of the collected dispersed phase. Hence stage three was partially but not wholly eliminated.

Farmer attempted to correlate the results with various systems by the following expression obtained with the aid of dimensional analysis. Any consistent set of units may be used.

$$\frac{K_d d}{D_d} = 0.05 \left(\frac{dv\rho_d}{\mu_d}\right) \left(\frac{\mu_d}{\rho_d D_d}\right)^{0.44} \left(\frac{dv^2\rho_c}{I.T.}\right)^{0.8}$$

where K = overall extraction coefficient based on stages two and three as described above.

d = drop diameter (assumed spherical).

D = molecular diffusivity.

μ = viscosity

ρ = density

I.T. = interfacial tension

v = velocity

subscript d = dispersed phase

c = continuous phase

This expression is supposed to hold only in the turbulent region of fall (Reynold's number $= \frac{dv\rho_d}{\mu_d} >$ 300-350). The resulting transfer coefficient must be multiplied by a correction factor $(\frac{2-n}{n})$ when stripping acetic acid from a dispersed non-polar organic liquid where (n) is the degree of association. This factor represents the fraction of the solute molecules which exist as single molecules in the organic liquid. Farmer postulated that since acetic acid exists in water as unassociated molecules, the rate of extraction is approximately equal to the rate at which single molecules diffuse across the laminar boundary film of the dispersed organic liquid.

Farmer showed that in the systems investigated the resistance to solute transfer in the continuous phase

is negligible compared to the resistance in the dispersed phase. He also obtained the apparent extraction during drop formation by the extrapolation procedure.

West et.al.[18] also studied extraction from single drops. They postulated the existence of transient films around the drops. The essential difference between this theory and the two-film theory is that the time of contact between the material in turbulent motion in the bulk of the drop and the transient film passing around the drop is so short that the film is essentially infinite in extent. This mechanism is considered in detail later in the thesis.

Conway[3], as mentioned previously, studied extraction from single drops and employed a new experimental procedure for separating three stages of extraction in a spray column. He studied the extraction of acetic acid from water (dispersed phase) using methyl isobutyl ketone, isopropyl ether, and ethyl acetate as continuous phases. The primary contribution of Conway's work was the development of the technique for separating the three stages of extraction. This technique is also based on the extrapolation to zero column height to determine the amount of extraction during drop formation.

THEORY

THEORY

As previously mentioned, there are at least three distinct stages in the life of a drop in a spray tower.

Stage I - Drop formation, or the creation of the drop in the continuous phase.

Stage II - Drop passage through the continuous phase.

Stage III - Coalescence of the drop at the interface at the terminal end of the column.

The possible mechanisms of solute transfer in each of these three stages will be considered. For the sake of brevity details of the derivations are omitted but in general may be found in the literature cited. Except where noted, all the equations developed are for any consistent set of units.

Stage I

The conditions under which solute transfer is occurring during drop formation appear to be rather obvious. Since the drop is in the process of being formed, the interior of the drop must be in motion and of relatively uniform concentration. Also, since the drop is growing and new surface is being created, there is little chance for the formation of a relatively stagnant film on the surface of the drop.

The surrounding continuous phase is stagnant except for a small amount of viscous displacement due to the

expansion of the drop. Hence there is no film in the continuous phase surrounding the drop. Actually, a "film" of infinite extent surrounds the drop.

To analyze this mechanism mathematically one pictures a bulk of material of relatively constant and uniform concentration in contact with an extracting medium of infinite extent. The rate of extraction of solute is controlled by the rate of diffusion of solute into this infinite medium.

For convenience, the unsteady state diffusion equation in rectangular coordinates is used, i.e.

$$\frac{\partial c_c}{\partial t} = D_c \frac{\partial^2 c_c}{\partial x^2} \qquad (1)$$

where c_c = point concentration of solute in continuous phase

t = time of contact

D_c = molecular diffusivity of solute in continuous phase

x = linear distance from the surface of contact to a point in the continuous phase.

To solve this problem exactly, the diffusion equation in spherical coordinates should be used but in this case the outer radius of the sphere is considered at infinity, a condition which makes it impossible to obtain a definite solution to the equation. Hence, following the notion used by Higbie[7] who studied gas absorption from bubbles, the problem has been simplified to one of a plane of contact

having an area equivalent to that of a sphere.

The dispersed phase is assumed uniformly mixed and of relatively constant composition, C_{do}. This latter assumption neglects the decrease in the concentration of the drop due to solute transfer during drop formation and hence will only be valid if the total extraction is relatively small. At the interface between the dispersed and continuous phase equilibrium is assumed to be maintained.

Taking the initial concentration of the surrounding medium as zero, the following boundary conditions can be stated:

1. at $t = 0$, $C_c = 0$
2. at $x = 0$, $C_c = \frac{1}{H} C_{do}$

where H is the distribution coefficient (assumed constant) for the solute between the two phases.

The solution is found (4) to be

$$C_c = \frac{C_{do}}{H} \left(1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{D_c t}}} e^{-u^2} du\right) \qquad (2)$$

The instantaneous rate of solute transfer at the boundary $x = 0$, is given by

$$N = -D_c A \left(\frac{\partial C_c}{\partial x}\right)_{x=0} \qquad (3)$$

where the area (A) is a function of time.

Recognizing the fact that $\left(\frac{dV}{dt}\right)$, the volumetric feed rate, is experimentally held constant, the volume of the drop (assumed a sphere) after any time (t) is

$$\left(\frac{dV}{dt}\right) \cdot t = V_F\, t = \frac{4}{3}\pi r^3 \qquad (4)$$

where V_F is the volumetric feed rate.

Combining equation (4) with the formula for the area of a sphere and eliminating the radius, the following expression for the area as a function of time is obtained.

$$A = (4\pi)^{1/3} 3^{2/3} (V_F t)^{2/3} \qquad (5)$$

The total solute lost from the drop is found by integrating the following expression over the total time of drop formation (t_f).

$$n = \int_0^{t_F} N\, dt \qquad (6)$$

Substituting equations (3) and (5) into equation (6), integrating and simplifying, the final result is

$$\begin{matrix}\text{Fraction Solute} \\ \text{Extracted}\end{matrix} = E_F = 2.90 \frac{\sqrt{D_c t_f}}{Hd} \qquad (7)$$

where d is the final drop diameter assuming the drop to be a sphere. Any consistent set of units may be employed. Equation (7) can be used to predict the amount of extraction occurring during drop formation provided a satisfactory value of H and D_c can be obtained.

The derivation of equation (7) has assumed that the drop initially starts from zero volume. This may or may not be the case depending on the design of the tip. In this present investigation, the tips used started each drop at as near zero volume as possible. However, if the tips are designed to permit appreciable wetting of the surface at

See Addendum page 169.

the tip of the nozzle, each drop will not start at zero volume. Actually, as the drop leaves the tip, part of the liquid will remain on this wetted surface to form the initial volume of the new drop. This initial volume will have been subjected to extraction under conditions different from those postulated in the derivation of equation (7). Thus depending on the design of the tip, extraction at the tip may be increased beyond that expected during the formation of the drop itself.

Stage II

General

Many mechanisms or combination of mechanisms of solute transfer may be postulated for Stage II. Before considering any specific mechanisms a general consideration of the mechanism of solute transfer within the drop and in the surrounding medium will be made. The discussion that follows will directly apply only to extraction from drops under the conditions of the present investigation, i.e., single drops falling through a stationary continuous phase.

After the general considerations, the problem becomes one of attempting to express these various mechanisms of solute transfer in terms of mathematical concepts which can be experimentally verified. After the separate mechanisms have been analyzed, an attempt will be made to develop a generalized solution by using an appropriate resistance.

Some of the postulated mechanisms of solute transfer

will undoubtedly be impossible to interpret in rigorous mathematical terms. Therefore, idealized or fictitious conditions will necessarily be assumed.

Survey of Mechanisms

At the end of Stage I the interior of the drop is undoubtedly in motion, hence this condition prevails at the beginning of Stage II. As the drop passes through the continuous phase, the interior of the drop may assume one of several conditions.

1. The interior of the drop may remain in relatively turbulent motion and hence be of uniform but decreasing concentration. At the surface of the drop there will be a gradual transition from turbulent motion to a streamline type of motion. This condition may give rise to a fictitious film which will offer the main resistance to solute transfer within the drop.
2. The initial turbulent state of the drop may change over to a well defined streamline vortex type of motion. That is, the drag of the continuous phase on the surface of the drop may cause the material in the outer portion of the drop to be carried up to the top of the drop. This material will then circulate down through the center of the drop and then back up the outer layers of the drop, thus causing a streamline vortex type of motion. The transfer of solute will occur by pure diffusion between the adjacent streamlines as well as

by transport within the streamlines. This condition within the drop was postulated by Kronig and Brink[10].

3. The interior of the drop may become stagnant and solute will only be transferred by pure diffusion through the drop.
4. The actual conditions in the drop may be somewhere in between these three conditions.

There are also several possible conditions prevailing in the continuous phase surrounding the drop.

1. If the drop is falling in the viscous range of Reynold's numbers, there will be streamlines passing completely around the surface of the drop. The velocity of the continuous phase will go from zero in the bulk of the phase to some maximum velocity at the surface of the drop. Employing the concept of films, there will be an indefinite viscous film around the drop. Theoretically this film might be considered infinite in extent. The rate of transfer of solute through the continuous phase will depend on the rate of diffusion through this film.
2. If the drop is falling in the turbulent range (large Reynold's numbers or velocities) there will be a streamline type of flow over the advancing half of the surface of the drop. However, these streamlines will break into turbulent eddies behind the drop. This turbulent motion in the rear of the drop will probably give way to streamline motion adjacent to the rear surface of the drop.

3. The actual conditions may be intermediate between these two conditions.

The conditions in the continuous phase, as described, can be deduced by analogy to conditions encountered in heat transfer studies. McAdams[13] presents actual pictures of the flow of gases and liquids at various velocities normal to cylinders. Analagous conditions would be expected in the flow of one liquid past a drop of another liquid except for a very important difference between the behavior of a rigid body falling through a liquid and one liquid drop falling through another continuous liquid. A consideration of the hydrodynamics of falling drops elucidates this important difference.

Hydrodynamics

The hydrodynamics of solid spheres falling (or rising) through a liquid medium have been thoroughly investigated and the theory well established. However, the hydrodynamics of liquid drops falling (or rising) through another immiscible liquid have received little more than qualitative treatment, particularly in the case where extraction is occurring from or to the moving drop. The present investigation is not concerned with a theoretical study of the hydrodynamics of falling drops. However, the subject will be considered to an extent necessary to study its effect on the mechanism of solute transfer.

Investigations (3,6,20) of falling (or rising)

liquid drops through another immiscible liquid have led to the following observations.

1. The drop reaches its constant terminal velocity within a very short distance from the tip (about one inch).
2. As the drops fall they tend to assume the shape of an ellipsoid with its major axis horizontal, i.e., the drops tend to "pancake out".
3. The larger the drop, the greater is the departure of its shape from that of a sphere.
4. As the drops fall they oscillate.
5. The larger the drop, the greater the amplitude of these oscillations.
6. For a drop as large as 0.5 cm. in diameter, the error in calculating its area as a sphere of equivalent volume is less than 10%.
7. For drops larger than a critical drop size, the velocity may decrease with increased drop size.

In view of the foregoing observations, it is apparent how the behavior of these liquid drops may alter the mechanism of solute transfer which might otherwise be expected if the drop had behaved like a perfect sphere. This oscillating motion of the drop may tend to increase the eddy currents within the drop thus minimizing the effective resistance of a film on the surface of the drop. Where streamline flow over the advancing half of the drop may be expected, these oscillations may set up eddy currents in the continuous phase surrounding the drop. In this case a fictitious film may exist entirely around the drop.

The Two Film Theory

In studying the over-all effect of mass transfer through two phases, the so called "two-film theory" is customarily used. This theory postulates an interface bounded on each side by relatively non-turbulent layers of fluid which are called the films and which constitute the main resistance to mass transfer. The effect of these two films is assumed to be such that all the material being transferred has to pass through these films in series without accumulating in either film.

This theory has been applied with some success to the study of mass transfer in gaseous-liquid contacting equipment. By analogy, the theory has come into use in liquid-liquid extraction systems. Some of the implications of this theory as applied to liquid-liquid extraction merit some consideration. When a gas is passed over a body of relatively stationary liquid, the bulk of the gas will usually be in turbulent motion. However, the velocity of the gas directly in contact with the liquid will be zero. There will be a transition from zero velocity at the surface to a viscous or streamline type of flow very close to the surface to turbulent flow in the bulk of the gas phase. The break in the velocity gradient from the viscous film to the turbulent mass will be rather sharp.

Totally viscous flow is seldom encountered in industrial liquid-gas contacting systems. However, with liquids, viscous flow may often be encountered. If a fluid

is moving in viscous flow over a surface, then according to the concepts of fluid flow, the velocity increases from zero at the interface to a maximum in the bulk of the fluid. Instead of undergoing a sharp break from viscous to turbulent flow, the velocity gradient is parabolic in shape and hence the concept of a film is meaningless.

The two-film theory also assumes that equilibrium is attained at the interface between the two phases. Obviously, true equilibrium cannot be maintained at an interface for a process involving net mass transfer to or from the interface. However, the displacement from equilibrium may be very slight. In spite of the theoretical shortcomings of the two-film theory, its past usage requires that it be considered as a possible mechanism of solute transfer.

The bulk of the interior of the drop is assumed to be in turbulent motion and of uniform but continuously decreasing concentration. This turbulent motion changes to viscous or streamline motion at the surface of the drop giving rise to a film. A film is also assumed to surround the drop in the continuous phase. If the drop is falling in the range of Reynold's numbers corresponding to viscous fall, then the film is entirely hypothetical, whereas if the drop is falling in the range of Reynold's numbers corresponding to turbulent flow, there will at least be eddy motion in the continuous phase trailing the drop and in all probability the oscillation of the drop will cause eddy motion around the

entire drop. This condition will give rise to a film around the entire drop.

The resistance of this external film may be negligible compared to the resistance in the dispersed phase. This may be due to the fact that since the drop is falling through the fresh continuous phase, the actual time of contact of the drop with the continuous phase at any one point is so short that a concentration gradient cannot build up.

Assuming that the rate of extraction is controlled by the rate of solute transfer across the two films in series, the instantaneous rates of transfer across each individual film may be equated.

$$N = k_d A(C_{db} - C_{di}) = k_c A(C_{ci} - C_{cb}) \qquad (8)$$

where N = instantaneous rate of solute transfer (#moles/hr.)

k = individual film coefficient ($\frac{\#moles/hr\text{-}ft^2}{\#moles/ft^3}$)

A = interfacial area (ft^2)

C = concentration ($\#moles/ft^3$)

subscripts d = dispersed phase

c = continuous phase

i = interface

b = bulk of the particular phase

Equilibrium is assumed to be attained at the interface between the two phases so that

$$C_{di} = H\, C_{ci} \qquad (9)$$

where H is the distribution coefficient, generally a function of concentration.

When allowable, as considered later, a single over-all coefficient, in place of the two film coefficients k_d and k_c, may be employed. These over-all coefficients are defined by the equation

$$N = K_d A(C_{db} - C_{de}) = K_c A(C_{ce} - C_{cb}) \qquad (10)$$

where K_d = over-all coefficient based on dispersed phase

K_c = over-all coefficient based on continuous phase

C_{de} = concentration in dispersed phase which would be in equilibrium with the average bulk concentration of the continuous phase,

C_{ce} = concentration in continuous phase which would be in equilibrium with the average bulk concentration of the dispersed phase.

When equation (9) applies with H constant over the range of concentrations involved, the relation between the over-all and the individual coefficients may be obtained to give

$$\frac{1}{K_d} = \frac{1}{k_d} + \frac{H}{k_c}$$

and (11)

$$\frac{1}{K_c} = \frac{1}{k_c} + \frac{1}{Hk_d}$$

The over-all coefficient can be employed only when $(C_{db} - C_{de})$ remains proportional to $(C_{ce} - C_{cb})$. For this proportionally to hold, equation (9) should apply. The over-all coefficient may also be employed if the resistance of one of the films is negligible compared to the resistance

of the other.

The form of the equation which will be used is

$$N = K_d A(C_{db} - C_{de}) \qquad (12)$$

The over-all coefficient, K_d, may depend on:

1. The nature of the system
2. The viscosity, density and interfacial tension of the phases
3. The diffusivity of the solute in each phase
4. The effective film thicknesses
5. Drop velocity
6. Temperature
7. The value of the distribution coefficient (H)

Several of these variables of the system are obviously interdependent on one another. However, for a given system the over-all coefficient should be constant for a given drop size, if the above variables remain constant. Actually, as the concentration of the drop decreases the interfacial tension may change. More important, the effective film thickness may increase if the turbulence on the interior of the drop decreases. Hence K_d may be expected to remain constant only over a portion of the fall time, if K_d remains constant at all.

Since equation (12) applies to a point in the column, integration over the length of the column is necessary. Using

$$N = -\frac{dn}{dt} \qquad \text{and} \qquad n = VC_{db}$$

where n = quantity of solute present in the drop at any time (#moles)

V = drop volume (assumed constant)(ft^3)

and substituting in equation (12), it follows that

$$V \frac{dC_{db}}{dt} = -K_d A(C_{db} - C_{de}) \qquad (13)$$

The concentration (C_{de}) of the dispersed phase which would be in equilibrium with the average bulk concentration of the continuous phase is assumed to be negligible or zero. This assumption would be valid whenever the continuous phase is initially free of solute and the total quantity of dispersed phase fed to the column is small. Assuming C_{de} to be zero and K_d constant, equation (13) can be integrated to give

$$\log \frac{C_{db}}{C_{do}} = - \frac{K_d A}{2.303V} t \qquad (14)$$

where t = fall time (hrs.)

C_{do} = concentration of solute in the dispersed phase at time $t = 0$ (#moles/ft^3)

Since C_{db}/C_{do} represents the fraction of solute unextracted, equation (14) may also be written, assuming the drop to be a sphere, as

$$\log (1 - E) = -2.61 \frac{K_d}{d} t \qquad (15)$$

where E = fraction solute extracted

d = drop diameter (feet)

Although engineering units have been specified, any consistent set of units may be used since the constant 2.61 is dimensionless. Also, C_{do} and $E = 0$ are values which correspond to $t = 0$, this being not necessarily the start of fall, but any convenient time after detachment of the drop from the tip.

From equation (15) a plot of log (1 - E) versus drop fall time should give a straight line with slope $(-2.61 \frac{K_d}{d})$ over the range for which K_d is constant. Further, if K_d is constant or nearly constant for different drop sizes, the slope of this line should be approximately inversely proportional to the drop diameter.

To investigate this mechanism experimentally, a study of the effect of contact time on the amount of solute extracted from various size drops would be advantageous. For a given system, as the drop size is increased the amplitude of the oscillations of the drop will increase. This will cause increased turbulence within the drop as well as in the continuous phase surrounding the drop. Increased drop size will also increase the drop velocity (up to a certain point) which will reduce the resistance of the film in the continuous phase. Hence K_d will be expected to slightly increase with increased drop size.

Diffusion Within the Drop Controlling

Another type of mechanism which may be considered, results from pure molecular diffusion within the drop. The interior of the drop is assumed perfectly stagnant and the transfer of solute is controlled by the rate of diffusion of solute within the drop. The continuous phase, surrounding the drop, is assumed to offer negligible resistance to solute transfer.

An investigation of this type of mechanism involves

the solution to the diffusion equation in spherical coordinates, i.e.,

$$\frac{\partial C_d}{\partial t} = D_d \left(\frac{\partial^2 C_d}{\partial r^2} + \frac{2}{r}\frac{\partial C_d}{\partial r}\right) \qquad (16)$$

where C_d = point concentration in the dispersed phase

r = radius to any point in the sphere

D_d = molecular diffusivity coefficient in dispersed phase

The boundary conditions imposed are:

1. at $t = 0$, $C_d = C_{do}$
2. at $r = a$, $C_d = HC_{cb} = 0$ (for all times)

where a is the radius of the drop, assumed spherical. Initially, the drop is assumed to be of uniform concentration C_{do}.

The solution to equation (16) with the imposed boundary conditions can be obtained by the application of orthogonal functions or can be found in any of the standard reference works on heat transfer (4). The solution is found to be

$$C_d = \sum_{n=1}^{\infty} \frac{-2\, C_{do}\, a(-1)^n}{n\pi r}\, e^{-\left(\frac{n\pi}{a}\right)^2 D_d t} \sin\frac{n\pi r}{a} \qquad (17)$$

Since C_d, the point concentration at any radius r, cannot be measured, it is desirable to use an integrated mean concentration which may be defined by

$$C_{d\ avg} = \frac{1}{V}\int_0^V C_d dV = \frac{3}{a^3}\int_0^{r=a} C_d r^2 dr \qquad (18)$$

Combining equations (17) and (18),

$$\frac{C_{d\ avg}}{C_{do}} = \sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} e^{-(\frac{n\pi}{a})^2 D_d t} \qquad (19)$$

or

$$(1 - E) = \sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} e^{-(\frac{n\pi}{a})^2 D_d t} \qquad (19a)$$

This infinite series converges sufficiently rapidly so that for large values of t the first term will represent the series. Accordingly, a plot of log (1 - E) versus time should yield a straight line of slope $-\frac{1}{2.303}(\frac{\pi}{a})^2 D_d$, for larger values of t.

With experimental data, this mechanism could be checked in two ways. First, if plots of log (1 - E) versus time are obtained for several drop sizes, after sufficiently long times, straight lines should result with slopes inversely proportional to the square of the radius of the drop. Secondly, by estimating the value of the diffusivity coefficient for the particular solute concerned, equation (19a) could be used to construct a typical curve for a given drop size. This theoretical curve and the actual curve could then be compared.

The straight line portion of the curve represented by equation (19a) should have an ordinate intercept $(\log \frac{6}{\pi^2})$. However since extraction has occurred prior to the stage where this mechanism could apply, t = 0 must be taken as any time after the drop detaches itself from the tip and for which the interior of the drop first becomes stagnant.

Accordingly, at t = 0, (1 - E) will have some value less than one and the ordinate intercept will not be $(\log \frac{6}{\pi^2})$.

The solution to equation (19a) is presented in convenient graphical form in the Appendix.

Diffusion Within the Drop Plus Film Resistance

A third mechanism capable of mathematical analysis is that of pure diffusion within the drop itself plus an additional film resistance around the drop. As will be shown; the mathematical solution is of the same form whether this film is present in the dispersed phase, the continuous phase, or both phases.

The problem is similar to that of pure diffusion within the drop without a film resistance. The solution begins with equation (16), the diffusion equation in spherical coordinates, i.e.,

$$\frac{\partial C_d}{\partial t} = D_d\left(\frac{\partial^2 C_d}{\partial r^2} + \frac{2}{r}\frac{\partial C_d}{\partial r}\right) \qquad (16)$$

However, in this case the boundary conditions are:

1. at $t = 0$, $\quad C_d = C_{do}$
2. at $r = a$, $\quad N = -D_d A \left(\frac{\partial C_d}{\partial r}\right)_{r=a}$
$\qquad\qquad\qquad\quad = K_d A \left(C_{da} - C_{de}\right)$

Simplifying boundary condition number two, the final second condition becomes:

2. at $r = a$, $\quad \left(\frac{\partial C_d}{\partial r}\right)_{r=a} = -\frac{K}{D_d} C_{da}$

where C_{da} is the concentration of the dispersed phase at the

outer radius a. Thus equation (12), as used in the two-film theory, has been adapted as a second boundary condition. However, note the distinction of C_{da}, the concentration at the surface of the drop, as contrasted to the average concentration of the interior as used in the two-film theory. From the previous discussion of this film mechanism, it is seen that the film may be considered in either or both phases provided K_d, the over-all transfer coefficient remains constant.

The solution to equation (14) can also be worked out or obtained from a standard reference work on heat transfer (4). As compared to the case of pure diffusion alone, the solution is considerably more complicated.

The solution of equation (14) with the stated boundary conditions is

$$C_d = \sum_{n=1}^{\infty} \frac{2C_{do}h\left[\alpha_n^2a^2 + (1-ah)^2\right]}{\alpha_n^2\left[\alpha_n^2a^2 + a^2h^2 - ah\right]} \frac{e^{-\alpha_n^2Dt}}{r} \sin\alpha_n a \sin\alpha_n r \qquad (20)$$

where $h = \frac{K_d}{D_d}$

and the condition on α is that it must be a root of

$$\alpha a \cos \alpha a + (ah - 1) \sin \alpha a = 0 \qquad (21)$$

Since C_d, the point concentration at any radius r, cannot be measured, the integrated mean concentration as previously defined by

$$C_{d\ avg.} = \frac{1}{V} C_d dV = \frac{3}{a^3} \int_o^{r=a} C_d r^2 dr \qquad (18)$$

will again be used.

Combining equations (18) and (20), the following expression can be obtained

$$\frac{C_{d\ avg}}{C_{do}} = (1-E) = \sum_{n=1}^{\infty} \frac{6h^2\left[\alpha_n^2a^2 + (1-ah)^2\right]\sin^2\alpha_n a}{a^2\alpha_n^4\left[\alpha_n^2a^2 + a^2h^2 - ah\right]} e^{-\alpha_n^2 D_d t} \qquad (22)$$

Fortunately, if a plot of log (1 - E) vs. time is made, the series converges so rapidly that for sufficiently long times there should result a straight line of slope

$$\frac{-\alpha_1^2 D_d}{2.303}$$

and of ordinate intercept, obtained by extrapolation of the straight line,

$$\log \frac{6h^2\left[\alpha_n^2a^2 + (1-ah)^2\right]\sin^2\alpha_n a}{a^2\alpha_n^4\left[\alpha_n^2a^2 + a^2h^2 - ah\right]}$$

However, since the drop can't possibly be formed under stagnant conditions, the initial extraction from the drop will be due to some other mechanism. Hence, the value of the ordinate intercept obtained by extrapolation of the straight line will be meaningless. The slope however will still be a criterion of the mechanism.

The value of h, which is directly proportional to the overall film coefficient, will be effected by the operating variables in exactly the same way as the over-all coefficient considered under the two-film theory. Equation (21) predicts that for a given value of the over-all film

coefficient, the value of α decreases as the radius increases. Hence, the absolute value of the slope of the straight line portion of the curve decreases, indicating a slower rate of extraction.

The testing of equation (22) would be difficult since α and the drop radius are not directly related. However, this mechanism should cause a rate of extraction slower than that for diffusion within the drop alone. If a system should actually display this slow rate of extraction, the slopes will be tested as follows. From the slope of the straight line $(-\frac{\alpha_1^2 D_d}{2.303})$ and using a theoretical value of D_d, α_1 could be calculated. For this value of α_1 and the given drop radius (a), equation (21) can be used to find h. If K_d is relatively constant with drop size, then h will be relatively constant. Hence, equation (21) can be used to calculate the value of α_1 corresponding to a new drop size. For this value of α_1 a theoretical slope $(-\frac{\alpha_1^2 D_d}{2.303})$ may be calculated. This theoretical value and the actual value of the slope for the new drop size may then be compared.

Streamline Convection Within The Drop

The fourth type of mechanism to be considered was recently proposed and analyzed mathematically by Kronig and Brink[10]. The interior of the drop is assumed to contain streamline convection currents resulting from the drag of the continuous phase against the drop. These currents will

circulate up the outer portions of the drop and down the center portion of the drop. Solute will be transferred from one streamline to another by molecular diffusion.

The mathematics involved in obtaining the solution is quite complex although the solution is in a usable form. Briefly, Kronig and Brink started with an equation known as "Stokes Current Function" inside the drop. This equation mathematically defines the streamlines within the drop. By combining this equation with another differential equation for the transport of solute between streamlines, the following solution is finally obtained.

$$(1 - E) = \frac{3}{8} \sum_{n=1}^{\infty} B_n^2 \, e^{-U_n \frac{16 D_d t}{a^2}} \qquad (23)$$

where U_n is an eigenvalue and B_n is a coefficient.

Although many physical and mathematical assumptions have been made in the solution, the more important are:

1. Drop is assumed spherical.
2. The resistance to solute transfer in the continuous phase is negligible.
3. The drop radius is greater than 0.10 centimeters.

The first two eigenvalues and coefficients have been evaluated as,

$$U_1 = 1.678 \qquad B_1 = 1.32$$

$$U_2 = 9.83 \qquad B_2 = 0.73$$

From these values, for sufficiently long times, only the first term of the series in equation (23) is needed. Hence a plot of log (1 - E) versus time should give a straight line (for

large times) with a slope

$$-U_1 \frac{16D_d}{2.303a^2} = -46.8 \frac{D_d}{d^2}$$

This mechanism could be checked in the same way as the pure diffusion mechanism. By comparing the length of time required for the solute concentration to decrease to a fraction $\frac{1}{e}$ of its original value by a pure diffusion mechanism and by the streamline convection mechanism, the rate of extraction due to streamline convection is two and one-half times as great as the rate of extraction due to pure diffusion within the drop.

Transient Films

Another type of solute transfer mechanism which can be considered was originally proposed by Higbie[7], who studied the rate of absorption from gas bubbles. He attempted to show that even though a liquid film may exist around the drop, the actual time of contact (penetration period) of the gas with the liquid at any point is so short that the film acts equivalent to an infinite medium with respect to solute transfer.

These transient films might also be expected to exist in liquid-liquid extraction. Thus a film can originate in the continuous phase on the bottom of the falling drop and pass over and disappear on top of the drop. Similarly, a film can possibly be created on the bottom of the drop in the dispersed phase and be carried up around the drop by

the viscous drag of the continuous phase.

Unlike the two-film theory, only one of these two possible films can be considered at any time. Thus if the film is considered to be in the dispersed phase, then due to this film acting as an infinite medium, no solute can possibly reach a film in the continuous phase. Similarly, if the transient film is in the continuous phase, no transient film can exist in the dispersed phase.

The mathematical analysis of this mechanism is similar to that used in analyzing stage one. For this derivation, the film is assumed to be in the dispersed phase. Starting with equation (1), i.e.,

$$\frac{\partial C_f}{\partial t} = D_d \frac{\partial^2 C_f}{\partial x^2} \qquad (24)$$

and imposing the boundary conditions,

1. at $t = 0$, $C_f = 0$
2. at $x = 0$, $C_{fs} = C_{db}$

the following solution is obtained:

$$C_f = C_{db} \left(1 - \frac{2}{\sqrt{\pi}}\right) \int_0^{\frac{x}{2\sqrt{D_d t_e}}} e^{-u^2} du \qquad (25)$$

where C_f = point concentration in the transient film

C_{fs} = concentration at surface of transient film

t_e = time of exposure of bulk of drop to the film

The instantaneous rate of solute transfer at the boundary $x = 0$, is given by

$$N = - D_c A \left(\frac{\partial C_f}{\partial x}\right)_{x=0} \qquad (26)$$

Combining equations (25) and (26) and integrating the rate of extraction over the time of exposure, the following result is obtained,

$$n = 2AC_{db}\sqrt{\frac{D_d t_e}{\pi}} \qquad (27)$$

where n is the total solute crossing the fictitious boundary between the uniform bulk of the drop and the film in the dispersed phase.

At this point, the definition of a film coefficient is introduced by

$$n = K_{dt}A\,(C_{db} - C_{de})\cdot t_e \qquad (28)$$

where K_{dt} is an equivalent over-all coefficient for this infinite transient film and C_{de} is assumed zero.

Equating equation (27) and (28), the following result is obtained,

$$K_{dt} = 2\sqrt{\frac{D}{\pi t_e}} \qquad (29)$$

Introducing equation (29) into equation (15)

$$\log (1 - E) = -2.95\sqrt{\frac{Dv}{d^3}}\ t$$

in which any consistent set of units may be employed and where

v = drop velocity

d = drop diameter (assumed spherical)

D = molecular diffusivity of the solute in the phase in which the film is assumed

Thus a plot of log (1 - E) versus time should give a straight line of slope $(-2.95\sqrt{\frac{Dv}{d^3}})$. This mechanism, like

the two-film mechanism, gives a straight line plot for all values of $t > 0$ provided the other terms remain constant. The mechanisms of "diffusion", "diffusion plus film" and "streamline convection" only give straight lines after some time t sufficiently large, i.e., for low values of t, a curved plot is predicted.

To test this mechanism, the actual slope of the plot can be compared to a calculated theoretical slope. Also, for a given system the slopes of these plots should be directly proportional to the square root of the drop velocity and inversely proportional to the three-halves power of the drop diameter.

West, et.al.[18] have used equation (29) to calculate individual film coefficients for the continuous phase and the dispersed phase by substituting the appropriate diffusivities. They have then combined these individual film coefficients with the distribution ratio to obtain an over-all coefficient in the usual manner. This procedure seems to be illogical since the transient film is equivalent to an infinite film. Certainly two infinite films in series in so far as solute transfer is concerned are impossible.

Generalization

A generalization which could include all the previously developed mechanisms may be of interest. The rate of transfer of any material, whether electrons in electricity, heat in heat transfer or solute in extraction

may be expressed as a ratio of driving force to resistance. The resistance may be one of several types but the driving force is definitely a concentration gradient in this case. This concentration gradient should be taken as the difference between the point of highest concentration and the point of lowest concentration in the system. The lowest concentration occurs in the bulk of the continuous phase which is essentially at zero concentration. If the drop is of uniform concentration, then the highest point concentration is the average concentration. However, if the drop is stagnant, the highest point concentration is the concentration at the center of the drop. Since this concentration cannot be measured, an integrated mean concentration would be used.

Thus, in general,

$$N = \frac{\text{Driving Force}}{\text{Resistance}} = \frac{C_{da} - C_{de}}{R} \qquad (31)$$

This equation can be treated similarly to equation (12) to obtain the following generalization assuming R constant.

$$\log (1 - F) = - \frac{1}{2.3037} \cdot \frac{1}{R} \cdot t \qquad (32)$$

Equations (32) and (14) are practically alike except the over-all transfer coefficient has been replaced by an undefined resistance.

The generalized development has actually analyzed another mechanism. This mechanism assumes the interior of the drop is of uniform concentration and that there is an undefined resistance to solute transfer at the interface between the continuous and dispersed phase. This resistance

may be in the form of a chemical or physical barrier to the transfer of solute molecules. For such a mechanism, a plot of log (1 - E) versus time would give a straight line with slope inversely proportional to drop volume or the diameter cubed.

Summary of Mechanisms

Before considering the experimental work, a general review of the mechanisms and the possibility of actually encountering them will be helpful. The mechanisms which seem to be least likely to be encountered are those of "pure diffusion", "diffusion plus a film", and "streamline convection." These three mechanisms require that the interior of the drop be either perfectly stagnant or in very uniform motion.

Previous observations have shown that the drops are usually oscillating or vibrating. As long as the drops are in this state of oscillation, it is difficult to see how the interior of the drop can be stagnant or even in uniform streamline convection. However, since the amplitude of these oscillations decreases with decreased drop size, smaller drops may tend to exhibit these mechanisms. Also, a dispersed phase with a high viscosity may tend to dampen out the oscillations thereby promoting one of these mechanisms. In general, it appears as though the more nearly the actual drop velocity checks the theoretical drop velocity, assuming the drop a solid sphere, the more likely one of these three types of diffusion mechanisms will hold.

The two-film type of mechanism will be more likely to hold in general since it postulates a turbulent type of motion on the interior of the drop. Further, since the mechanism is semi-empirical in nature, no theoretical value of the over-all transfer coefficient may be calculated and checked with the experimental value. By allowing for the effects of certain variables on the film resistances in the continuous and dispersed phases, most any change in the value of the over-all coefficient with drop size might be explained.

The transient film type of mechanism might be expected to apply to systems in which the major resistance to solute transfer is in the continuous phase since the transient film is more likely to be present in the continuous phase. Any condition promoting streamline or laminar flow around the drop would encourage transient films, e.g., low drop velocities and no oscillations of the drop.

The resistance in the form of retardation of molecules at the interface between the two phases will probably not be encountered in most common systems. However, the addition of a wetting agent which may concentrate at the interface or a rate controlling chemical reaction at the interface may result in such a mechanism.

The various mechanisms and their properties are summarized in the table that follows.

TABLE I

Mechanisms of Solute Transfer in Stage II

Mechanism	Slope log (1-E) vs. t	Resistance (R)	Remarks
1. Two-Film	$-2.61 \frac{K_d}{d}$	$\frac{0.318}{K_d d^2}$	Slope proportional to $\frac{1}{d}$ if K_d constant with drop size.
2. Pure Diffusion Within Drop (no external resistance)	$-17.15 \frac{D_d}{d^2}$	$\frac{0.0485}{D_d d}$	Slope proportional to $\frac{1}{d^2}$
3. Pure Diffusion Within Drop Plus Film Resistance	$\frac{-\alpha_1^2 D_d}{2.303}$	$\frac{1.91}{\alpha_1^2 D_d d^3}$	
4. Streamline Convection Within Drop (no external resistance)	$-46.8 \frac{D_d}{d^2}$	$\frac{0.0178}{D_d d}$	Slope proportional to $\frac{1}{d^2}$
5. Transient Films	$-2.95 \sqrt{\frac{Dv}{d^3}}$	$\frac{0.282}{\sqrt{Dvd^3}}$	Slope proportional to $\sqrt{\frac{v}{d^3}}$
6. Molecular Resistance at Interface	$-\frac{0.83}{Rd^3}$	R	Slope proportional to $\frac{1}{d^3}$

STAGE III

The theory of the mechanism of solute transfer in Stage III is rather obscured. In the first place, the effective interfacial area for solute transfer is unknown. As the drop coalesces at the interface, the area of the drop goes from its relatively constant value in Stage II to zero. In addition the dispersed and continuous phases have a constant area of contact equivalent to the cross-sectional area of the column.

The actual time during which the major portion of the solute is being transferred is unknown. Conway[3] found that the total extraction in a column with the interface maintained at the bottom was independent of how long these two phases were left in contact. This seems to indicate that extraction in Stage III occurs only when a drop actually strikes the interface. The period of time over which this extraction occurs is difficult to define.

Hence, at present no theoretical mechanism will be offered until more extensive data on the stage is present. It seems logical that the entire interface at the terminal end of the column is effective during solute transfer.

EXPERIMENTAL WORK

EXPERIMENTAL WORK

General

The extraction of acetic acid was studied using three different systems. Acetic acid was extracted from water with methyl isobutyl ketone as the continuous phase. The concentration of the acetic acid solution was 0.8123 N or 0.053 lb.moles acid per cu.ft. of water. The acetic acid-water mixture was kept saturated with methyl isobutyl ketone and the methyl isobutyl ketone was kept saturated with water.

Acetic acid was also extracted from perchlorethylene with water as the continuous phase. The concentration of the acetic acid-perchlorethylene solution was 0.9267 N or 0.061 lb. moles acid per cu.ft. of perchlorethylene. The water was kept saturated with perchlorethylene.

Acetic acid was also extracted from a mixture of carbon tetrachloride-mineral oil with water as the continuous phase. The concentration of the carbon tetrachloride-mineral oil-acetic acid mixture was 0.5000 N or 0.032 lb. moles acetic acid per cu.ft. of carbon tetrachloride-mineral oil solution. The acid mixture was prepared by mixing equal volumes of a 1.00 N carbon tetrachloride-acetic acid solution and a heavy mineral oil. The viscosity of the feed mixture was 3.925 centipoises at 25°C. The continuous water phase was kept saturated with carbon tetrachloride and mineral oil.

In the major portion of the experimental work, the amount of extraction occurring over various column heights was measured for a series of drop diameters and given drop formation times. Column heights as short as one-half inch and as long as 79 inches were used. In order to separate the amount of extraction in Stage III, two types of columns were used with the methyl isobutyl ketone system. One column permitted the measurement of the amount of extraction in all three stages while the other permitted the measurement of the amount of extraction in Stages I plus II. With the other two systems, only the second type of column was used for reasons explained later. The experiments were carried out batchwise by allowing a given number of drops to fall through a stationary continuous phase.

Columns

The two columns shown in Figures I and II were essentially the same as those used by Conway[3]. The bottom section of Column No. I was constructed from a six-inch length of 47 mm I.D. pyrex glass tubing to which was joined a burette type stopcock. Additional column heights were obtained by attaching various lengths of tubing to the bottom section with a rubber connecting sleeve. Column No. II, as used by Conway[loc.cit.], was rebuilt in order that the various lengths of 47 mm I.D. tubing as used with Column No. I could be conveniently attached to the bottom section of Column No. II. Other modifications were made and are shown in Figure II.

FIGURE I

COLUMN NUMBER I

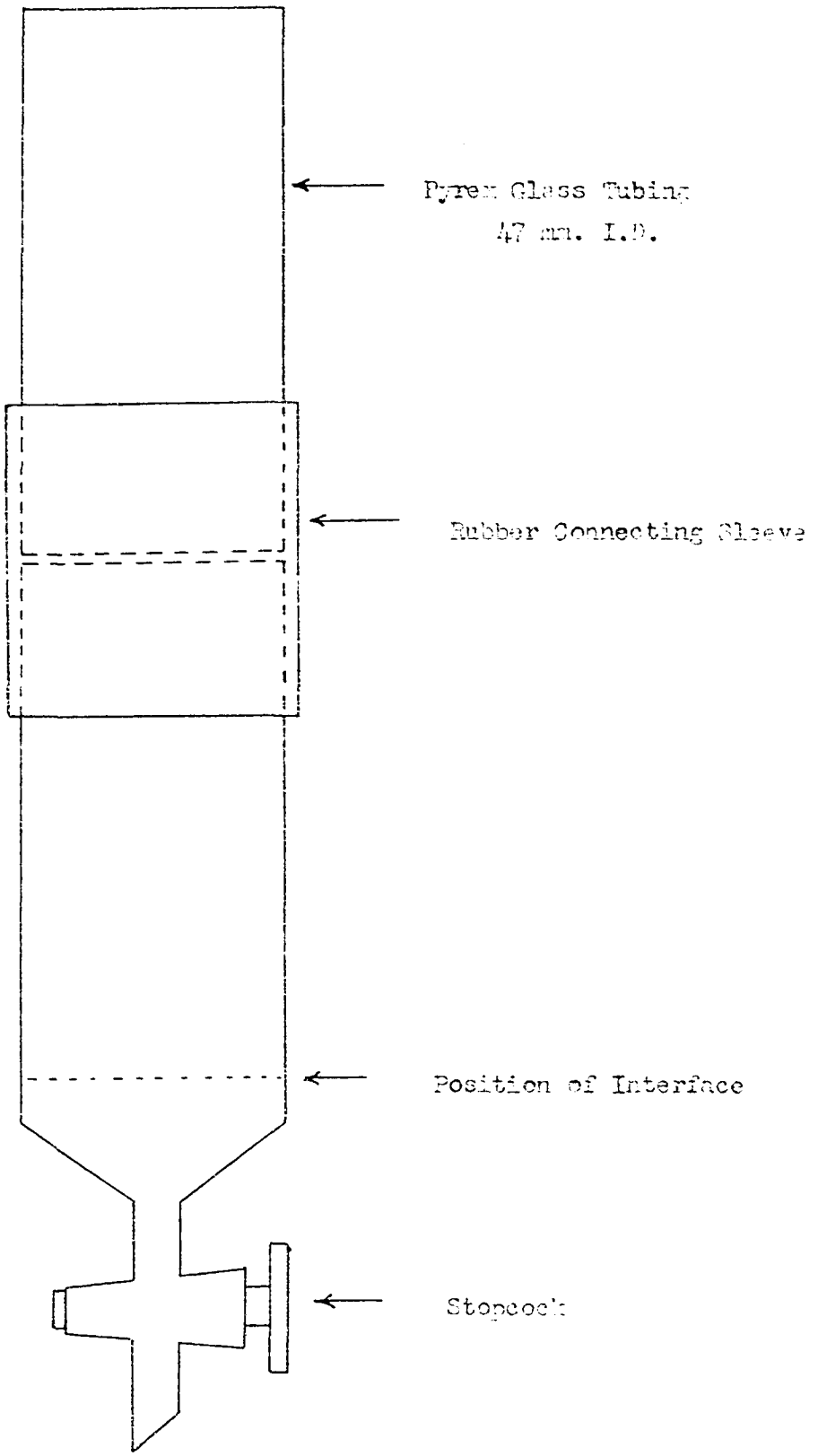
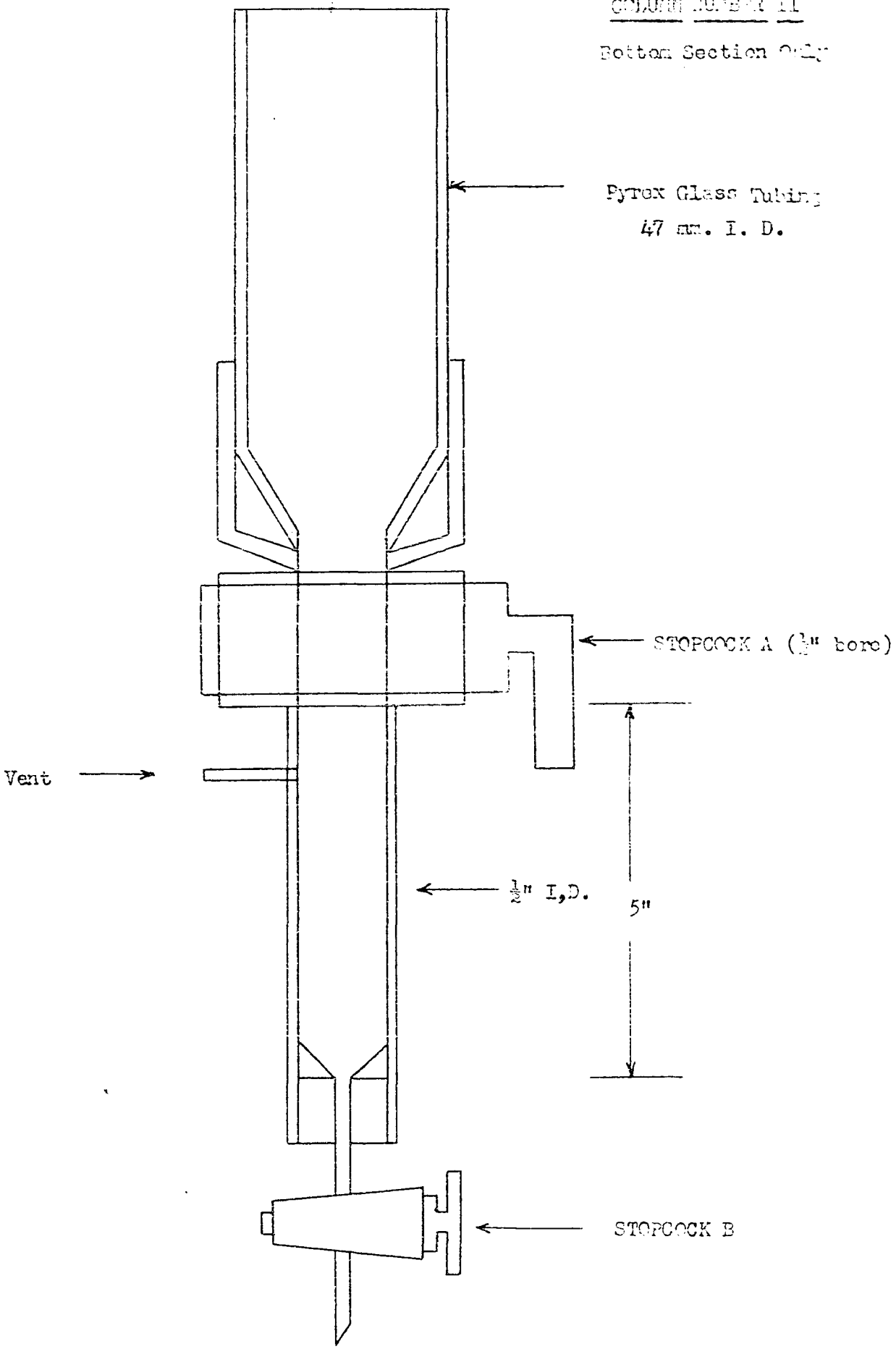


FIGURE II

COLUMN NUMBER II

Bottom Section Only



Feed Device

The feed device consisted of a 10 ml buret, to the delivery end of which was attached a short piece of thermometer capillary (for flow control) followed by a tip. Various size tips were constructed by drawing out five-millimeter pyrex glass tubing in a flame and fire polishing the delivery end. For controlling the rate of feed of the more viscous carbon tetrachloride-oil-acetic acid mixture, a short length of five-millimeter tubing packed with glass wool was used. Coarse control of the feed rate was accomplished by using various lengths of capillary tubing or packed sections. Fine control of the feed rate was accomplished by adjusting the initial level of the liquid in the buret.

Since the total volume of feed delivered during a run was only about 1.5 ml, the slight change in head had no appreciable effect on the rate of drop formation or the drop volume. On the other hand, the volume of feed delivered could be measured with an accuracy of $\pm$0.01 ml.

For a more detailed consideration of the feed device and the tips, the reader is referred to the appendix, page 128.

Materials

The materials used in the research were as follows:

Acetic Acid - Glacial Acetic Acid, C. P. Reagent, E. I. duPont de Nemours, Inc.

Water - Laboratory distilled water.

Methyl Isobutyl Ketone - Technical Grade, Carbide and Carbon Chemical Corp. (Redistilled - first and last portions discarded - Approximate B. P. of portion used 117-119°C)

Perchlorethylene - Technical Grade, Carbide and Carbon Chemical Corp.

Mineral Oil - U.S.P., 100% Petrolatum Liquidum, Trade Name Nujol.

Carbon Tetrachloride - U.S.P. Coleman and Bell Company.

The acidity of the methyl isobutyl ketone, perchlorethylene, carbon tetrachloride and mineral oil was found to be negligible when each of these were shaken with an equal volume of water and the water layer titrated with 0.03 N NaOH using phenolphthalein as an indicator.

Standard base solutions were prepared from sodium carbonate-free sodium hydroxide and preserved in the proper manner. Potassium acid phthalate was used as a standard.

Physical Properties and Constants

Densities and viscosities of the phases were required for various calculations. Densities, except when taken from the literature, were measured with a pycnometer and viscosities were measured with an Ostwald Viscometer. The results are summarized in the Appendix, Table A, page 123. Concentrations and calculated molecular diffusivities are also summarized.

Procedure

Column No. I

With the methyl isobutyl ketone system, runs were

made with Column No. I in the following manner. With a pipet, 50 ml. of distilled water which had been standing in equilibrium with methyl isobutyl ketone were placed in the bottom section. An additional section was attached to the bottom section and the remainder of the column filled with ketone to a point one and one-half inches above the point at which the tip was to be placed. The liquid level in the buret was noted and the feed device was lowered until the tip was submerged in the ketone to a depth of one and one-half inches. The stopcock on the buret was opened and a given number of drops were allowed to fall through the continuous phase. From 50 to 200 drops were used depending on the drop size. A total of from one to two millimeters of dispersed phase were fed. Coincidentally with the detachment of the last drop, the feed mechanism was closed and the liquid level in the buret again noted in order to determine the volume of feed delivered.

After the last drop crossed the interface at the bottom of the column, the aqueous layer was drained from the column and analyzed for acetic acid content by titrating with standard sodium hydroxide solution using phenolphthalein as an indicator. Knowing the volume of feed, the number of drops delivered and the acid content of the aqueous layer, the drop volume and the total solute extracted could be determined. No attempt was made to make a material balance by analyzing the continuous phase for solute.

This procedure was repeated for various column heights and several drop sizes. All runs were made in duplicate or triplicate and the average recorded. Column height was measured from the tip of the feed device to the interface at the bottom of the column. Drop formation time was determined by measuring the total time to deliver the given number of drops. This time divided by the number of drops delivered was taken as the average drop formation time. All runs were made at 25°C ± 1°C.

Column No. II

Runs were made in Column No. II using all three systems. Stopcock A was opened and stopcock B was closed and the column then filled with the continuous phase to the desired height. The feed device was operated as previously described. After the last drop had passed through stopcock A, this stopcock was closed and stopcock B and the vent were opened. The contents between stopcocks A and B were drained and included the collected drops as well as the continuous phase contained between the two stopcocks. The section was washed with distilled water through the vent line and the washings combined with the previous sample. This combined sample was titrated with standard base and phenolphthalein indicator until the first pink color appeared in the aqueous phase.

This procedure was repeated for various column heights and several drop sizes for each system. All runs were made in duplicate or triplicate. Drop formation time

was measured as before. Column height was measured from the tip of the feed device to the bottom of the bore of stopcock A. From the above titration, the total solute extracted in this measured column height was determined. This solute extracted does not include the solute extracted as the drop coalesces just above stopcock B or the solute transferred to the continuous phase by virtue of the prolonged contact at the interface at the terminal end of the column. All the solute transferred by these two latter methods was still trapped between stopcocks A and B at the end of a run.

For a more detailed consideration of various parts of the procedure, the reader is referred to the Appendix, page 132.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

DROP FORMATION TIME

The initial phase of the experimental work was concerned with a preliminary study of the effect of drop formation time on the amount of extraction in Stage I. Using the methyl isobutyl ketone-acetic acid - water system, a series of runs were made in Column No. I. A three-inch column height and three different size tips were used. Drop formation time was varied from 0.4 secs. to 10.0 secs. For a given tip, drop size was a function of drop formation time. Hence a continuous range of drop sizes resulted. The time of fall was approximately 0.6 secs. and relatively constant over the range of drop sizes involved. Fifty drops were used in each case. For drop formation times above approximately three-fourths of a second, secondary drop formation was observed. However, since these secondary drops were very tiny compared to the main drops, this phenomena should have little effect on the results of this preliminary study.

The results are plotted in Figure III, page 51. The total millequivalents of acid fed is plotted against the millequivalents of base required to neutralize the raffinate withdrawn from the column. The drop diameters and drop formation times are separated into given ranges for identification purposes.

Referring to Figure III, the distance (a) divided by the distance (a + b) represents the fraction of solute

FIGURE III

MILLIEQUIVALENTS BASE REQUIRED TO
NEUTRALIZE HARMINE
vs.
MILLIEQUIVALENTS ACID FED

Column - No. I
Column Height - 3 inches
Total Drops - 50
Feed Conen. - 0.8383 N
Base Conen. - 0.1116 N

Drop Diameter (Cm.)	Drop Formation Time (Sec)			
	0-2	2-4	4-6	6-10
0.336-0.347	⊖	⊖	⊖	×
0.337-0.352	⊕	⊕	⊕	
0.352-0.360	⊘	⊘		*

MILLIEQUIVALENTS OF ACID FED

extracted. Since the points lie close to a straight line through the origin, the ratio $(\frac{a}{a+b})$ is constant. Hence the percent solute extracted in a three-inch column is relatively constant and independent of drop size and drop formation time.

The data were plotted in this manner because the effect of drop formation time and drop diameter on the percent solute extracted are clearly shown. Due to the relative error in the value of (a) for each point, the percent solute extracted showed considerable variation from the mean.

From the slope of the line in Figure III, on the average 29.2% solute was extracted. The surprising fact is that not even the points for a 6-10 second formation time show an appreciable variation from the straight line. These results agree with those of Conway[3] who found the percent acetic acid extracted from water with methyl isobutyl ketone (continuous phase) was independent of drop formation times from 0.8 secs. to 3.0 secs. for a 0.342 cm drop diameter in a three-inch Column No. I. He obtained similar results when using isopropyl ether as the continuous phase in an eight-inch Column No. II for a 0.451 cm drop and varying the formation time from 1.2 secs. to 4.5 secs.

The results of the present investigation may be explained as follows. The variation in drop diameter (0.31 - 0.39 cm) is not sufficient to affect the amount of extraction during the relatively short (0.6 secs.) period of fall. The

amount of extraction in Stage III is also relatively constant. Hence the amount of extraction during drop formation is either relatively constant, or so small a portion of the total that the accuracy of the experiments is insufficient to detect it.

It seems entirely out of the question that in a 25-fold variation in drop formation time (0.4 - 10.0 secs.) there should be no variation in the amount of extraction during formation. Equation (7) predicts a 5-fold variation. However, if this portion of the total extraction in a three-inch column is small, then this variation might not show up in the results. The only reasonable conclusion is that the amount of extraction occurring during drop formation is sufficiently small so that the experimental results do not detect the variation of this extraction with drop formation time.

Using equation (7), the effect of drop diameter and drop formation time may be seen by calculating the theoretical fraction of the solute extracted in Stage I for the limits of these variables. The value of D_c, the diffusivity of acetic acid in methyl isobutyl ketone, may be estimated by the method of Wilke[19] as 2.37×10^{-5} $cm^2/sec.$ at 25°C. From Figure XVIII in the Appendix, page 126, the distribution coefficient, H, for an acetic acid solution of concentration 0.053 lb. moles acid/cu.ft. water with ketone is 2.06. The results are summarized as follows:

Table II

Predicted Extraction in Stage I

d (cm)	t_f (sec)	100 E_I
0.300	0.4	1.45%
0.300	10.0	7.25%
0.390	0.4	1.11%
0.390	10.0	5.58%

The theoretical maximum variation in the fraction of the solute extracted during drop formation is from 0.0111 to 0.0725, a difference of about 6% solute extracted. From Figure III, the maximum difference in the percent solute extracted in a three-inch column for the entire range of variables involved is about 10% solute extracted, 4% more than predicted for drop formation alone. However, closer examination of Figure III reveals that this 10% difference doesn't necessarily occur between points representing the extremes of the variables drop formation time and drop diameter. In general, the distribution of points about the straight line is random with no definite trend with drop formation time noted. Hence, considering that the amount of extraction in Stages I and II is not constant with drop size, this 4% difference in solute extracted is a result of experimental error. Thus the actual extraction during drop formation is so small a portion of the total

extraction in the three-inch column that its variation with drop formation time cannot be detected.

No further attempts can be made to verify equation (7) with the data for a three-inch column height.

DROP DIAMETER

The final phase of the experimental work was concerned with the investigation of the effect of drop diameter on the amount of extraction in each of the three stages. The amount of extraction occurring over various column heights was measured for a series of drop diameters and given drop formation times using three different systems. For a given drop diameter, the formation time was chosen so as to prevent the formation of secondary drops, a phenomenon noted when the formation time was above a certain value. In general, the longest possible formation time was used since this permitted accurate counting of the drops.

No secondary drop formation was observed in the carbon tetrachloride - oil system in which drop diameters of 0.237, 0.309, 0.373, and 0.423 cms. were used. The formation time for each of these drop sizes was approximately one second. In the methyl isobutyl ketone system, drop diameters of 0.295, 0.354, and 0.418 cms. were used. Drop formation times varied from 0.53 secs. for the smallest drop to 0.42 secs. for the largest drop. In the perchlorethylene system, drop diameters of 0.209, 0.288, 0.323, 0.338 and 0.394 cms. were used. Drop formation times varied from a minimum of 0.51 secs. for the 0.209 cm. drop to a maximum of 0.58 secs. for the 0.288 cm. drop.

The data for the perchlorethylene system and the carbon tetrachloride - oil system were obtained in Column

No. II only. For the perchlorethylene system, in Column No. I, extraction occurred in Stage III not only when a drop crossed the interface but also as long as the raffinate was kept in contact with the continuous phase. Since the raffinate could not be removed immediately following a run, Stage III was eliminated altogether. However, with the methyl isobutyl ketone system extraction in Stage III apparently occurred only when a drop crossed the interface since the total extraction in the column was independent of how long these two layers remained in contact after a run (up to one-half hour at least).

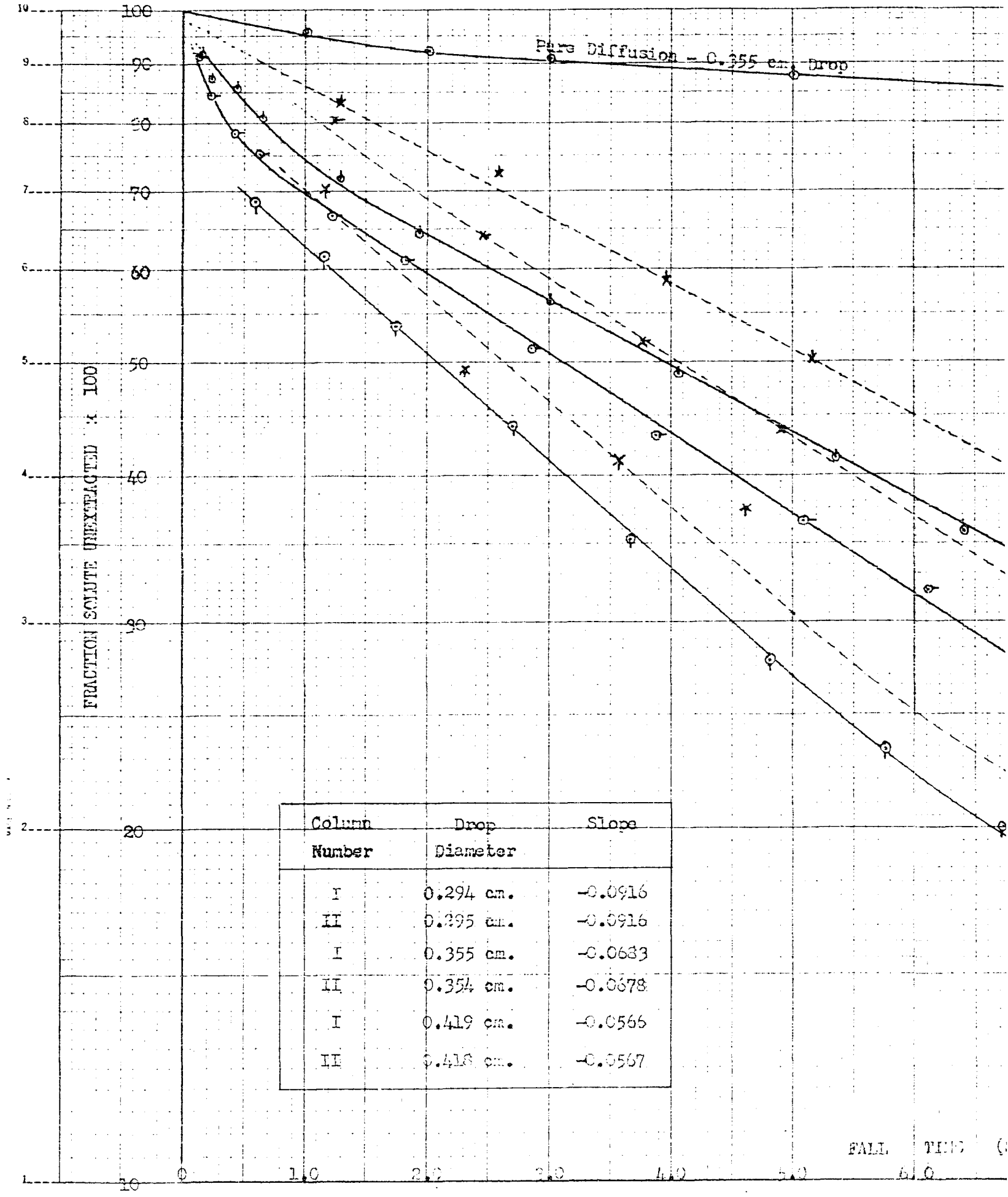
The difference in behavior between the two systems may be explained as follows. With the ketone system the acetic acid molecules had more attraction for the water layer in the bottom of the column than for the ketone in the continuous phase. Hence extraction was not promoted. With the perchlorethylene system the acetic acid had a greater attraction for the water in the continuous phase than for the perchlorethylene layer in the bottom of the column. Hence extraction at the interface was promoted.

In addition, with the ketone system it was observed that when the acetic acid - water drops struck the interface, due to their being slightly denser than the water layer the acid solution tended to sink to the bottom of the column. Refractive index waves due to the difference in densities were actually observed moving toward the bottom of the column after each drop struck the interface. Hence the acid did not

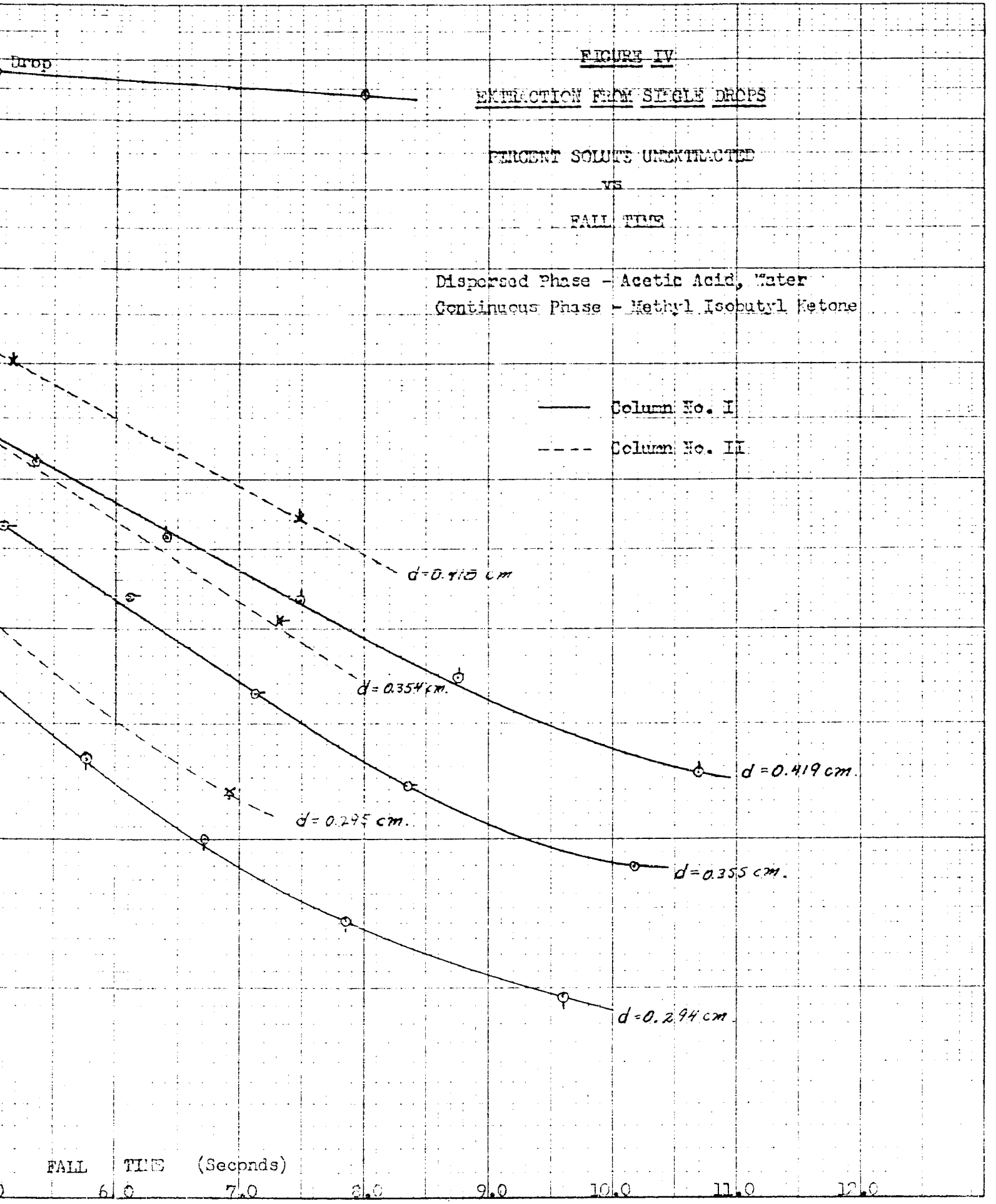
concentrate near the interface. However, with the perchlorethylene system, the solvent - acid drops were a little lighter than the solvent at the bottom of the column and on striking the interface the acid material tended to remain on top of this layer near the interface thereby promoting extraction. Again, due to the difference in refractive indices this lighter acid material could be noticed concentrating near the interface. No attempt was made to investigate Stage III in the carbon tetrachloride - oil system. For the purpose of this investigation Stage III is unimportant provided it can be completely eliminated from the data.

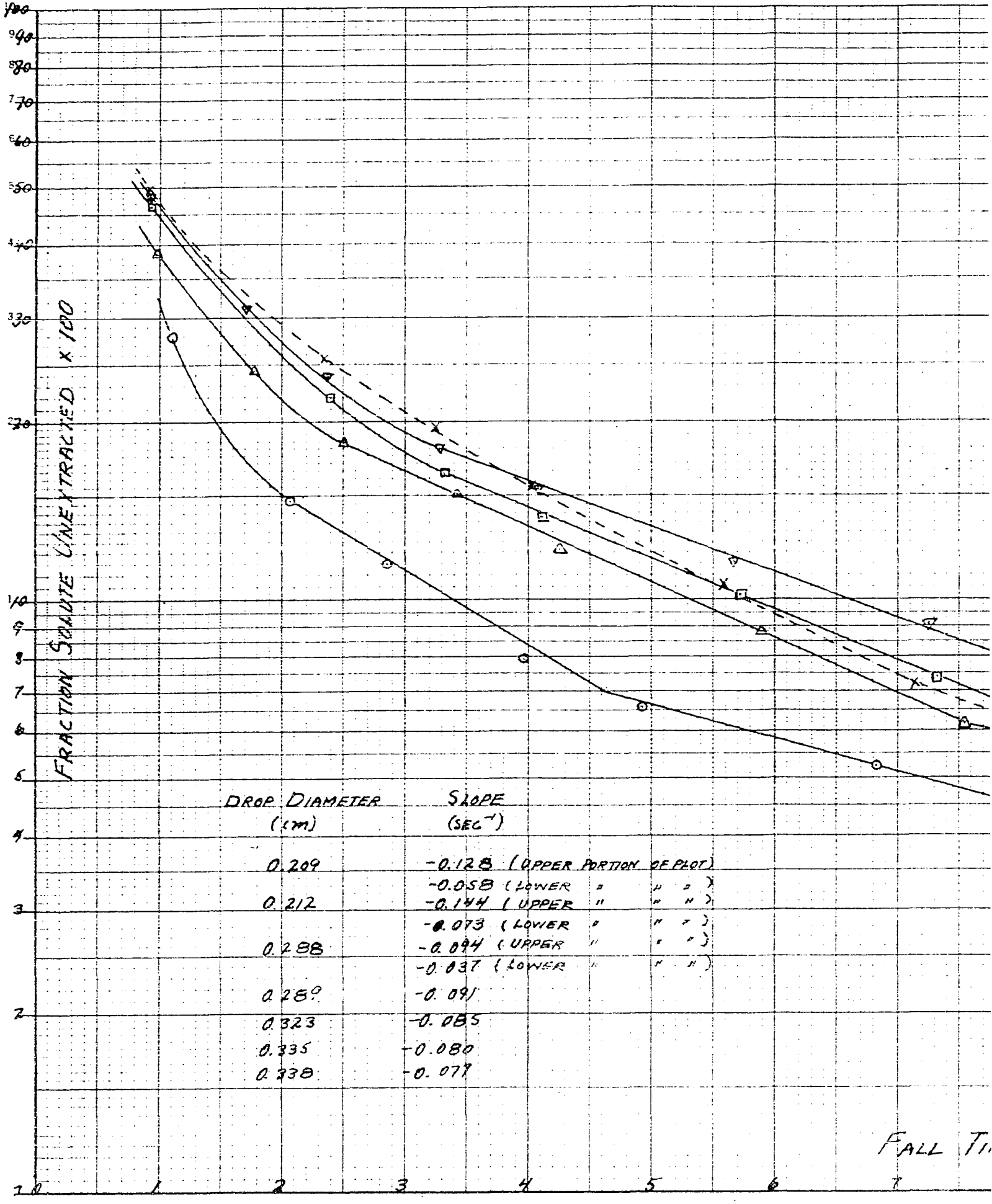
The results of the investigation are presented graphically in Figures IV, V, and VI as logarithm fraction unextracted versus fall time. The data is also tabulated in the Appendix. Data which were obviously inconsistent were discarded. The data for the perchlorethylene system were determined in duplicate and repeated in duplicate. The second set of results is not included in graphical form. The results were plotted, however, and the measurements of the appropriate slopes were made. For the purpose of this investigation, this procedure was preferred to averaging both sets of data to obtain a single plot. This second set of data was obtained as a check because occasionally very inconsistent results were obtained with this system.

For the 0.295 cm. drop diameter in the methyl isobutyl ketone system using Column No. II, the data is



Column Number	Drop Diameter	Slope
I	0.294 cm.	-0.0916
II	0.295 cm.	-0.0916
I	0.355 cm.	-0.0683
II	0.354 cm.	-0.0678
I	0.419 cm.	-0.0566
II	0.418 cm.	-0.0567





DROP DIAMETER (cm)	SLOPE (SEC^{-1})
0.209	-0.128 (UPPER PORTION OF PLOT)
	-0.058 (LOWER " " ")
0.212	-0.144 (UPPER " " ")
	-0.073 (LOWER " " ")
0.288	-0.094 (UPPER " " ")
	-0.037 (LOWER " " ")
0.289	-0.091
0.323	-0.085
0.335	-0.080
0.338	-0.077

FIGURE V

EXTRACTION FROM SINGLE DROPS

PERCENT SOLUTE UNEXTRACTED

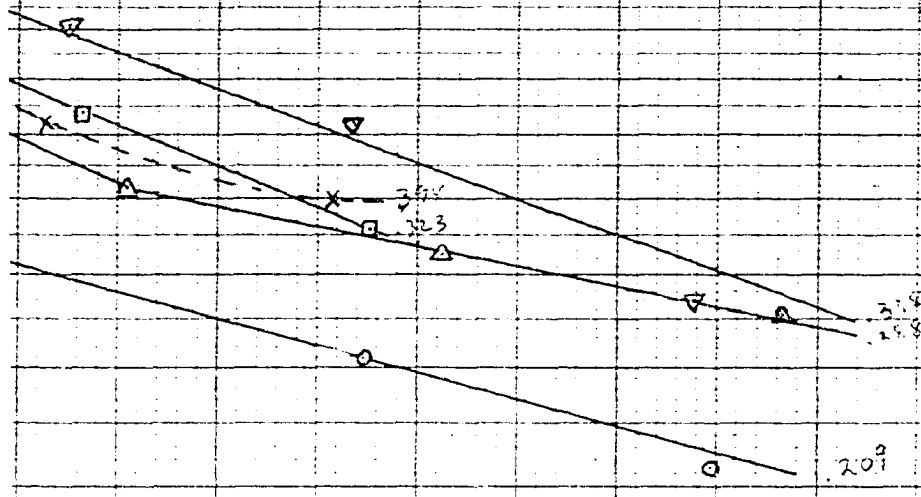
VS.

FALL TIME

COLUMN NO. II

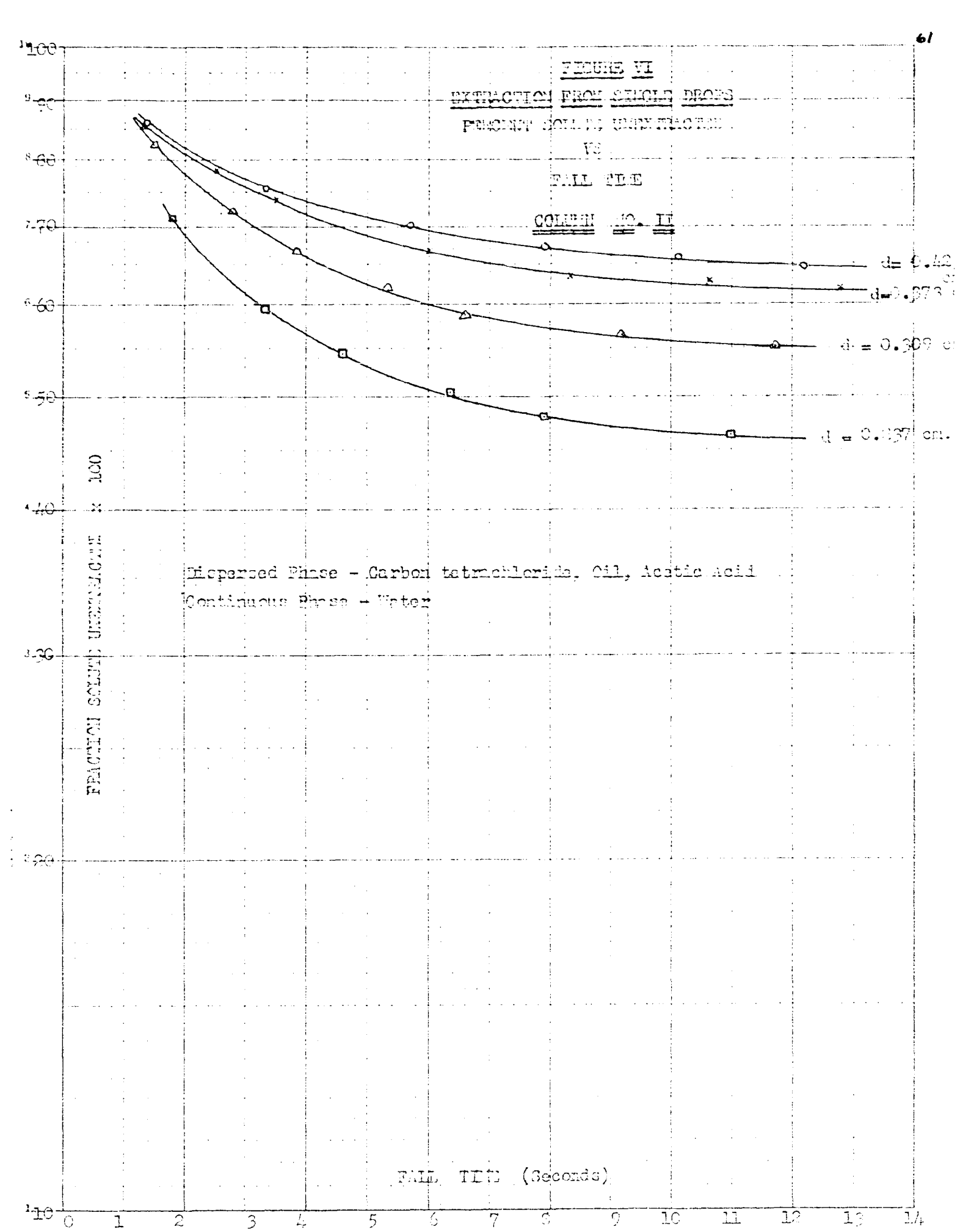
DISPERSED PHASE - PERCHLORETHYLENE - ACETIC ACID

CONTINUOUS PHASE - WATER



FALL TIME (SECONDS)

8 9 10 11 12 13 14 15



scattered. This is due to the adhering of the smaller drops to the bottom of the column before passing through stopcock A.

Reproducibility of Results

In general, the reproducibility of the results was good. For a set of runs at a given drop diameter the maximum variation in drop diameter was about 3%. This, however, was the exception and in general the variation in drop diameter was 1% or less. For a set of runs at a given drop diameter the variation in drop formation time was usually about 2%. Duplicate runs to determine the fraction solute extracted usually checked within 5%.

Drop Velocities

For the methyl isobutyl ketone system, drop velocities were determined by measuring the time of fall at a series of column heights. About twenty readings were taken and averaged for each point. The results for this system are shown in Figure VII, page 65. Since the velocities are constant over the range of column heights, for the perchlorethylene system and the carbon tetrachloride - oil system the velocities were measured at only two column heights of 45 inches and 20 or 6 inches. The shorter heights were merely used as checks and the actual velocity was taken as constant and equal to the velocity measured over the 45 inch column height. Fall times were calculated for the various

column heights using these velocities.

The variation in drop velocity with drop diameter, for the systems investigated, is shown in Figures VIII, IX, and X, pages 66 to 68. In addition, the velocities calculated assuming the drops as rigid spheres are also plotted on the same graphs. These velocities were calculated from the equation (15),

$$u = \sqrt{\frac{4gd(\rho_d - \rho_c)}{3\rho_c f}}$$

where in any consistent units,

u = drop velocity assumed solid sphere

ρ_d = density dispersed phase

ρ_c = density continuous phase

d = drop diameter

f = drag coefficient

g = acceleration of gravity.

A plot of drag coefficient versus Reynold's number was constructed from the data in Perry[15] and is shown in the Appendix, page 127. A complete summary of the drop velocity data including Reynold's numbers, are presented in Table III, page 69.

Wall-effect was not taken into consideration in calculating the drop velocities, assuming the drops to be rigid spheres. For turbulent or near turbulent resistance, Munroe[21] has proposed the following correction factor:

$$f_w = 1 - \left(\frac{d}{d_o}\right)^{3/2}$$

where f_w = correction factor on calculated velocity

d = drop diameter

d_o = column diameter

For the largest drop size used in this investigation (0.423 cm.) the correction factor is only 0.973, hence for the purpose of this investigation the wall-effect can be neglected.

General Observations

A qualitative study of the plots of logarithm fraction unextracted versus fall time in Figures IV, V, and VI, reveals several interesting generalizations.

1. In general, the plots curve toward the origin (100% unextracted) with decreasing contact time. This substantiates the results of the study of drop formation time.
2. For the methyl isobutyl ketone and perchlorethylene systems, at least a portion of each plot is a straight line. Since all of the postulated mechanisms indicate a straight line on this type of plot, perhaps one of the mechanisms will hold in each case.
3. For the carbon tetrachloride - oil system the entire plot is curved in the range investigated. Some of the proposed mechanisms call for a curved plot at low values of time but none predict an entirely curved plot. This may indicate a mechanism not considered under "Theory".

FIGURE VII

TIME OF FALL

vs

COLUMN HEIGHT

Dispersed Phase - Acetic Acid, Water (Density 1.002 g/l)

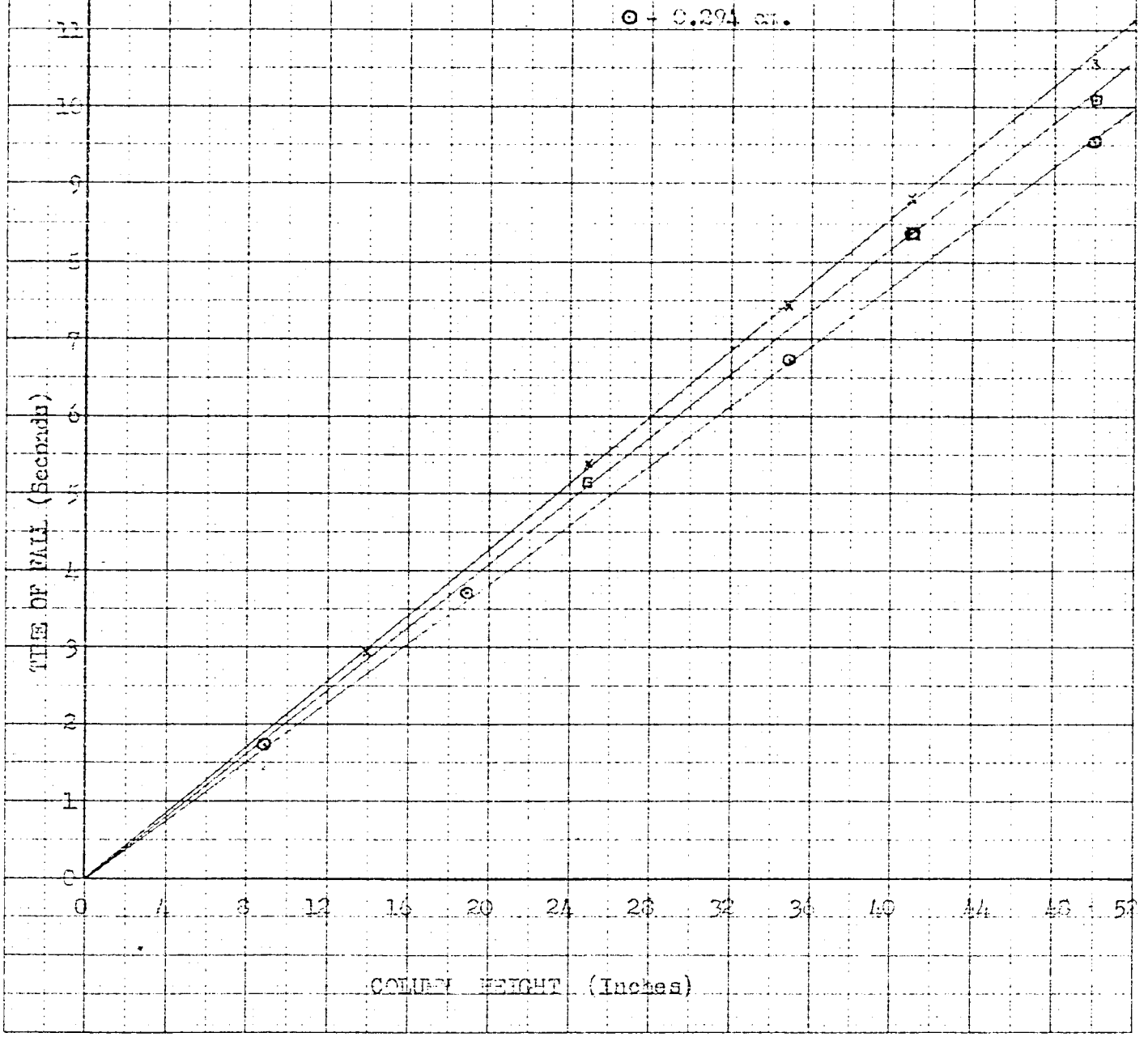
Continuous Phase - Methyl Isobutyl Ketone

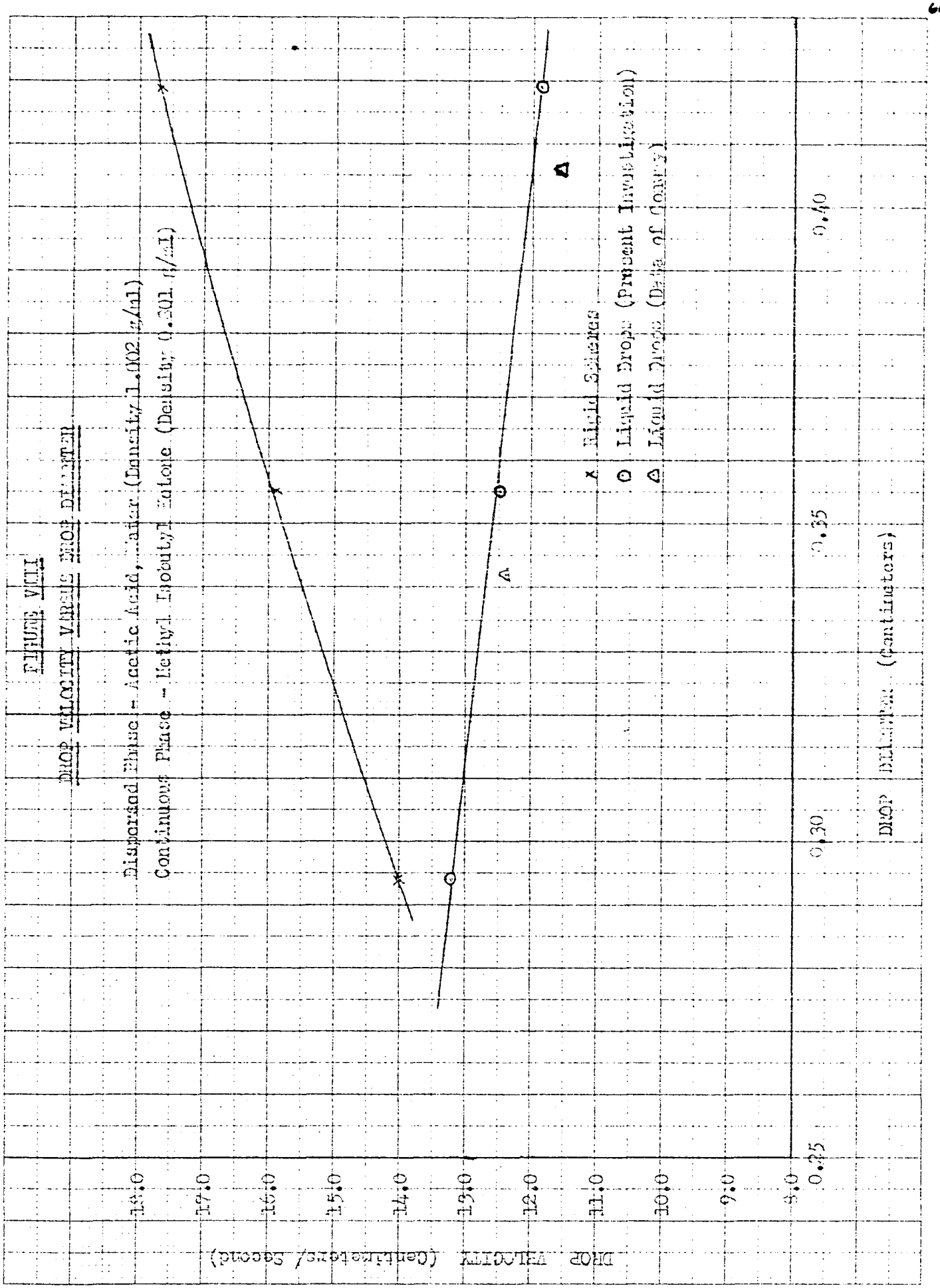
Drop Diameters

x - 0.419 cm.

⊡ - 0.355 cm.

⊙ - 0.294 cm.





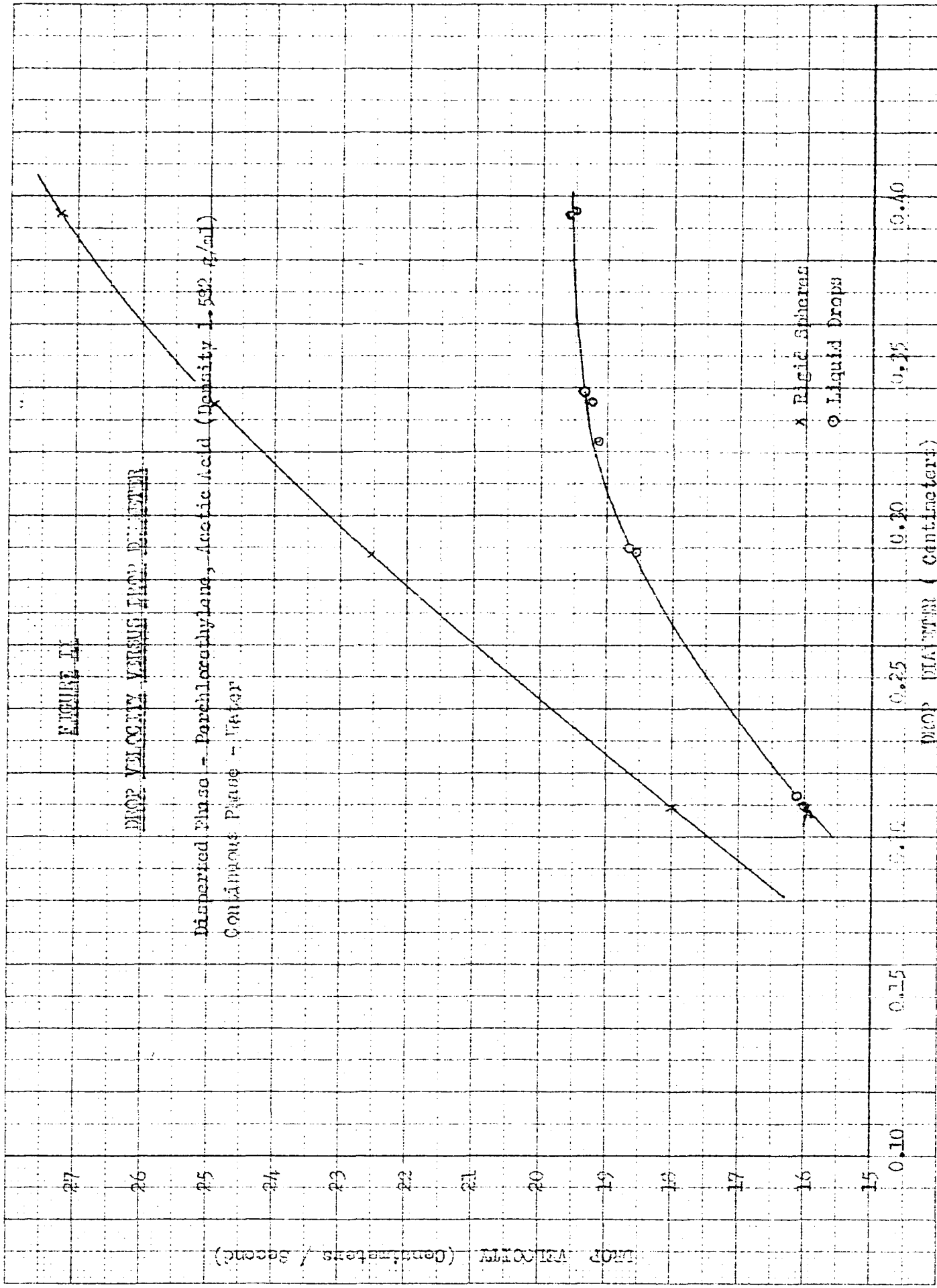


FIGURE X

DROP VELOCITY VERSUS DROP DIAMETER

Dispersed Phase - Carbon Tetrachloride, Oil, Acetic Acid (Density 1.211 g/ml, Vis. 3.925 c.p.)
Continuous Phase - Water

⊙ Rigid Spheres
X Liquid Drops

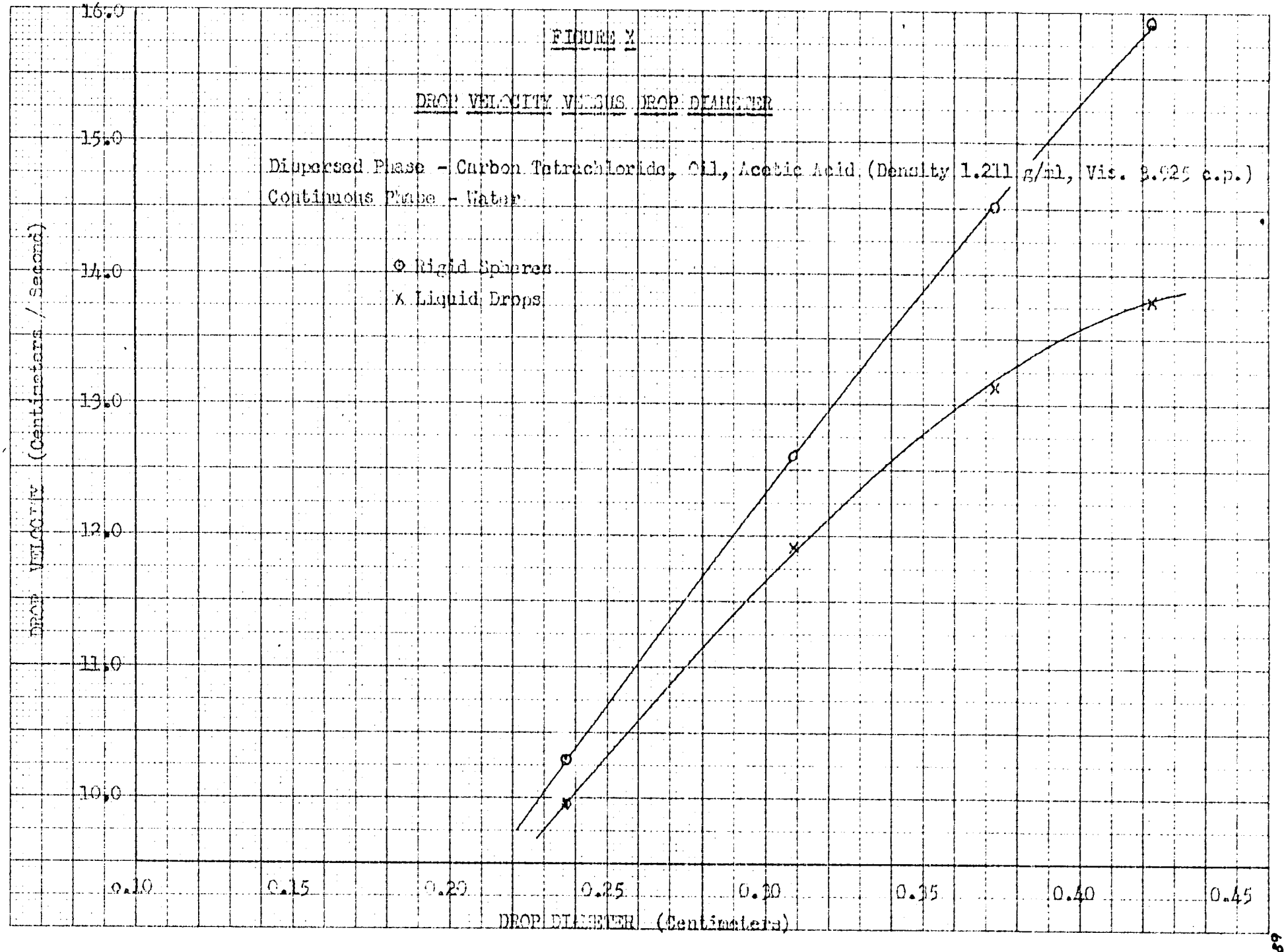


TABLE III

Summary of Drop Velocity Data

Diameter	Velocity Observed (cm/sec)	Velocity Calculated* (cm/sec)	Reynolds Number Observed	Reynolds Number Calculated*
Methyl isobutyl ketone system				
0.294	13.2	14.0	711	753
0.355	12.5	15.9	813	1032
0.419	11.9	17.7	913	1360
Perchloroethylene system				
0.209	15.98	18.0	585	659
0.288	18.52	22.5	954	1155
0.335	19.20	24.9	1165	1608
0.395	19.46	27.2	1300	1932
Carbon tetrachloride - oil system				
0.257	9.96	10.3	327	336
0.373	13.12	14.5	651	720
0.309	11.91	12.6	489	516
0.423	13.79	15.9	791	924

*Calculated assuming rigid sphere.

A study of the plots of velocity versus drop diameter in Figures VIII, IX, and X discloses some interesting results also. For the methyl isobutyl ketone system Figure VIII shows that drop velocity actually decreases with increased drop size, a result just opposite to that predicted for rigid spheres. This is due to the fact that as drop size increases the amplitude of the oscillations increases. The distortion of the drop or the departure of its actual shape from that of a sphere also increases with increased drop size, hence the resistance to fall becomes greater. Below some critical drop size this observed situation would reverse and the drop velocities would decrease with decreased drop size.

From Figure VIII it appears as though the two curves will cross at a drop diameter between 0.25 - 0.30 cms. For this drop diameter the actual velocity and that calculated assuming the drop to be a rigid sphere will coincide. Below this diameter the drops will fall faster than a rigid sphere of equal diameter. West et.al.[16] observed a similar situation in studying the velocity of benzene - acetic acid drops through water.

From Figure IX for the perchlorethylene system as drop size increases, the velocity tends to become constant due to the increased distortion and increased amplitude of the oscillations. The departure from rigid sphere behavior becomes quite large.

From Figure X for the carbon tetrachloride - oil

system, the drops come very close to rigid sphere behavior. Hence, of the three systems investigated this one could possibly display a pure diffusion type mechanism. Since the amplitude of the oscillations is small, the interior of the drop could possibly be stagnant or relatively so.

From Table III it will be noted that all the drops in each system fell in the range of Reynold's numbers corresponding to an intermediate resistance (Re 2-500) or a turbulent resistance (Re > 500 for rigid spheres). Actually, only the smallest drop in the carbon tetrachloride - oil system fell in the intermediate range. The rest of the drops fell in the turbulent range.

In the following sections, a detailed analysis of each stage will be made using the plots obtained.

STAGE I

General

From the accompanying plots, one fact seems certain, That is, in general a plot of the logarithm fraction solute unextracted versus drop fall time is not a straight line all the way back to zero fall time (or zero column height). Hence, in general the amount of extraction occurring during drop formation cannot be obtained by extrapolating the straight line portion of the plot to zero fall time.

The method proposed by Conway(3) for separating the three stages of extraction is based on the validity of this extrapolation procedure. From the results of the present

investigation it must be concluded that Conway's method is incorrect. However, Conway definitely separated the amount of extraction in Stage III. Unless this stage is eliminated from the data, any extrapolation procedure is incorrect since the extrapolated value, whatever its meaning, still includes the extraction in Stage III.

As the drop size increases, the plots show less curvature for short fall times. With the methyl isobutyl ketone system, Column No. I permits the use of column heights as short as one-half inch with which definite curvature in the plot is established. Since the fall times for these very short heights could not be accurately measured, the values were read from the plot of fall time versus column height with the plot going through the origin. These fall times are probably too long since the drop is accelerating for at least the first inch of the column.

With the methyl isobutyl ketone system, the data of Column No. II showed little or no curvature for a minimum of a six-inch column height. However, for drop sizes less than 0.418 cm. diameter, the plots will no doubt show some curvature as they approach zero fall time. The plot for the 0.418 cm. drop can't possibly exhibit much curvature without going through 100% unextracted. Some extraction, even though small, will occur during drop formation.

Comparison of Theoretical Equation with Reported Results

Assuming that solute is lost in Stage I by molecular diffusion into the surrounding medium, equation (7) can be used to predict the fraction of the solute extracted during drop formation.

$$E_I = 2.90 \frac{\sqrt{D_c t_f}}{H\ d} \qquad (7)$$

This equation indicates that the fraction solute extracted should decrease with increased drop diameter. From the plots, this trend is observed.

For the methyl isobutyl ketone system, using the previously obtained values of the constants, the predicted extraction during drop formation has been calculated and compared with the value obtained by extrapolating the straight line portions of Column No. II plots in Figure IV to zero fall time.

TABLE IV

Comparison of Predicted Results with Extrapolated Results

d (cm.)	t_f (secs.)	% Extracted (Calculated)	% Extracted (Straight Line Extrapolation)
0.418	0.42	1.07	1.5
0.354	0.47	1.33	6.0
0.295	0.53	1.69	13.5

With the exception of the 0.418 cm. diameter drop, the value of the percent solute extracted in Stage I obtained by extrapolation of the straight line portion of the plot is much higher than the calculated value. The relative agreement between the two values for the 0.418 cm. drop is good. However, the graphical value can't be greater than 1.5% or less than zero percent, hence the two values necessarily check. This indicates that there may be a drop size above which the plots for Column No. II approach zero fall time without observable curvature.

From the extrapolated values, it is impossible to see how the amount of extraction during drop formation could increase from 1.5% for a 0.418 cm. drop to 6.0% for a 0.354 cm. drop, a difference of 4.5% solute extracted, when the data for a one-inch Column No. I for the same drop sizes show that the percent solute extracted increases from 12.8% to 15.4%, a difference of only 2.6% solute extracted. For the same drop sizes, with a one-half-inch Column No. I, the percent solute extracted increases from 8.41% to 8.67%, a difference of 0.26% percent solute extracted. From Table IV, on the preceding page, the predicted difference in the percent solute extracted during drop formation is 0.26%. Hence, equation (7) predicted the correct result whereas the straight-line extrapolation procedure is no

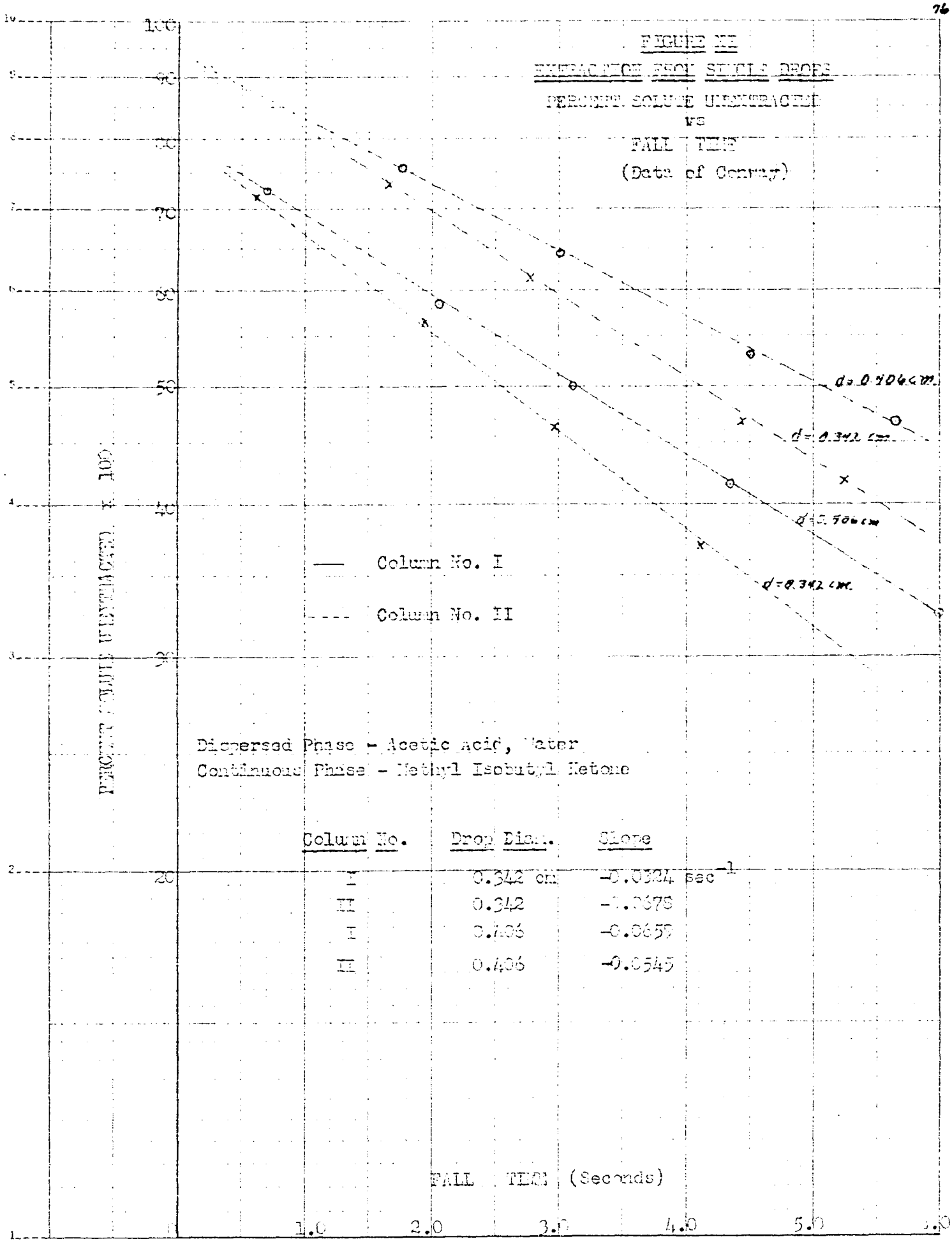
doubt incorrect.

Conway[5] also obtained data on the extraction of acetic acid from water with methyl isobutyl ketone as the continuous phase. He plotted his data as percent acid extracted versus column height, hence the entire plot is slightly curved. On extrapolating the plot for Column No. II to zero column height he concluded that 8% of the solute was extracted in Stage I for both a drop diameter of 0.406 cm. and 0.342 cm. In Figure XI, page 76 , the dataare replotted as logarithm fraction acid unextracted versus fall time. From these plots, the extrapolated value is found to be 5% acid extracted for the 0.342 cm. drop and 6% acid extracted for the 0.406 cm. diameter drop.

Considerable discrepancies are noted between these results and those reported in Table IV, page 73 . However, it will be noted that for similar drop diameters, the slopes of the plots for Column No. II obtained by Conway agree reasonably well with those obtained in the present investigation. Also, the author found for a given drop diameter the slopes of the plots obtained with Columns No. I and II were parallel on a semi-log plot. Conway did not find this to be the case.

A comparison of the procedure used by Conway and the present author reveals several differences.

1. The tips used by Conway did not permit each drop to start from zero volume. His tips were constructed of thick-



walled capillary tubing the end of which was beveled on a grinder. The feed solution constantly adhered to this ground surface, leaving a portion of each drop clinging to the tip. This extracted portion became part of the next drop. Hence, this type of tip would cause more extraction in Stage I than the type of tip used in the present investigation.

2. In using Column No. II, Conway included the solvent in the bore of stopcock A (Figure II) with the continuous phase. Hence, column height was taken from the tip to the bottom of the bore of stopcock A. In the present investigation with the methyl isobutyl ketone system, the solvent in the bore of the stopcock was included with the sample withdrawn from the bottom section of the column. Hence, column height was taken from the tip to the top of the bore of stopcock A. The deformation and slowing down of the drop as it passed through the bore in the stopcock no doubt increased the rate of extraction beyond that which is normally obtained in a length of column equivalent to the length of the bore. Hence, for a given column height, Conway would obtain more extraction than the author.

3. Conway did not mutually saturate the ketone with water or the water with ketone. Hence, due to the solubility of the ketone in water (2% at 20°C) the rate of extraction may be increased by the simultaneous diffusion of acid and water in the same direction. This effect, however,

should be small. (For a more detailed discussion of these differences in procedure, the reader is referred to the Appendix.)

Disregarding the possibilities of errors, the results obtained by Conway by extrapolation to zero column height are incorrect due to the fact that in general the plots do not extrapolate on a straight line to zero column height. Conway did not operate with a sufficiently short range of column heights to detect the curvature in the plots at small values of fall time.

Farmer[6] obtained plots of the logarithm fraction unextracted versus fall time for a given drop diameter and several ternary systems. Column height was varied from 0.3 to 4.88 feet. The fraction of the solute extracted during drop formation was determined by extrapolating the straight line plot back to zero fall time. For the systems used, no curvature was noted in the plots. All of the data were obtained in a column in which an interface at the terminal end of the column was exposed to the continuous phase. However, this interface was maintained in a 6 mm tube leaving the bottom of the column. Since the drops used were larger than 6 mm in diameter, they must have broken or have been other wise distorted before entering the tube. Exactly how effective this procedure was in eliminating or promoting the extraction in Stage III is not known. No doubt some extraction did occur during this final stage in the life of a drop.

The system showing the largest amount of extraction for a given column height was that in which acetic acid was extracted from methyl isobutyl ketone (dispersed phase) with water (continuous phase). Using a value for H (6) of 0.481 and a value of D_c (8) of 0.94×10^{-5} $cm^2/sec.$ corrected to 25°C, equation (7) predicts that 3.4% of the solute would be extracted during the 0.44 sec. formation period of a drop 0.300 cm. in diameter. By extrapolation, Farmer concluded that 33.4% of the solute was extracted during formation.

From the results of the present investigation, for a 0.355 cm. drop in Figure IV, the straight line portion of the solid line (Stage III included) extrapolates back to about 20% extracted at zero fall time. However, in this case acid was transferred from water to ketone whereas in Farmer's work, acid was transferred from ketone to water. Owing to the greater attraction of the acid molecules for the water than for the ketone, this latter direction of transfer would in general be more rapid.

The system showing the smallest amount of extraction for a given column height was that in which acetic acid was extracted from carbon tetrachloride (dispersed phase) with water (continuous phase). For a drop size of 0.398 cm. diameter and a formation time of 0.46 secs., equation (7) predicts that 30.4% of the solute will be extracted during drop formation. By extrapolation, Farmer obtained the value of 16.6%. The calculated result is obviously incorrect.

The error in the calculated result is due to the fact that one of the basic assumptions in equation (7) is not fulfilled. That is true equilibrium is not maintained at the interface between the carbon tetrachloride - acetic acid mixture and the water phase. For the feed concentration (0.01 lb. mols acetic acid per cu.ft. of carbon tetrachloride) used by Farmer, the distribution coefficient[6],

$$H = 0.05 = \frac{\text{concn. HAc in } CCl_4}{\text{concn. HAc in } H_2O}$$

This coefficient is very small indicating greater attraction of the acetic acid molecules for the water molecules than the carbon tetrachloride molecules. However, acetic acid is highly associated in non-polar solvents like carbon tetrachloride. The acid is not associated in methyl isobutyl ketone or water.

Thus the surrounding water will only accept the single acid molecules and true equilibrium is established between the single molecules in the carbon tetrachloride and the single molecules in the water. Since the degree of association of acetic acid (6) is 1.67, only 19.8% of the acid molecules exist as single molecules. Hence the effective concentration of acetic acid in the water phase will be reduced to 19.8% of its expected value. The effective distribution coefficient, H, will be increased to 0.05/0.198 or 0.252. On this basis, the calculated value of the fraction solute extracted during drop formation for Farmer's conditions becomes 0.060. Hence 6.0% of the solute is the

theoretical amount of extraction during drop formation compared to the extrapolated value of 16.6%.

This correction on H for non-polar solvents is similar to a correction factor used by Farmer. In studying the extraction of acetic acid from a series of solvents with water as a continuous phase, he found that in order to correlate the values of the overall transfer coefficients for the non-polar solvents with those for the polar solvents a correction factor $\frac{2-n}{n}$ had to be applied where n is the degree of association. This factor is actually the fraction of the acid molecules existing as single molecules in a non-polar solvent.

Subject to further proof, it may be stated that in general equation (7) will require a correction factor of $\frac{2-n}{n}$ when applying the equation to the extraction of a solute from a dispersed phase in which the solute is associated.

The distribution data for the perchlorethylene - acetic acid - water system and the carbon tetrachloride - oil - acetic acid - water system are not available and were not determined. Hence equation (7) was not applied to these systems. However, from Figure V the actual amount of extraction during drop formation is much less than the value which would be obtained by extrapolating the straight line portion of the plots to zero fall time.

The curves in Figure VI very definitely curve toward the 100% unextracted mark as fall time decreases indicating a very small amount of extraction during drop formation.

Unfortunately, the present experimental methods do not permit the determination of the actual amount of solute lost during drop formation. Using Column No. II, data for a column height less than seven inches was thought to be undesirable since the drop is required to pass through the narrow opening (1/2 inch bore) in stopcock A (Figure II). This no doubt causes some end effects which are not detected in the seven inch length column but which may become quite serious if shorter column lengths are used.

STAGE II

Various possible mechanisms of solute transfer in Stage II have been considered and methods for testing the experimental results, to identify the various mechanisms, have been developed. In this section the experimental data will be tested in an attempt to determine the prevailing mechanism in each system investigated. For convenience, each of the systems will be considered separately.

Property of Plots

The analysis of the mechanism of solute transfer in Stage II depends upon an important property of the type of plots employed. That is, the slope of the straight line portion of a plot of logarithm fraction unextracted versus fall time is

$$\frac{\log \frac{C_1}{C_o} - \log \frac{C_2}{C_o}}{t_2 - t_1} = \text{slope}$$

where C_1 and C_2 are the concentrations of the drop corresponding to any times t_1 and t_2 and C_o is the initial concentration of the drop. This slope reduces to the form

$$\frac{\log \frac{C_1}{C_2}}{t_2 - t_1}$$

Thus, the slope of the plot is independent of the initial concentration of the drop. Hence, regardless of the previous history of the drop, if a given mechanism is established after any time t_1, the slope of the plot will be

the same as if this mechanism had controlled throughout the life of the drop.

Methyl Isobutyl Ketone System

Figure IV shows that there is about an eight second range of fall time over which the plot is definitely a straight line for all drop sizes. This corresponds to a net column length of about 40 inches. For the data of Column No. I the initial portion of the plot is curved and after a total fall time of about 9-10 seconds, curvature is again noticed. Hence it may be assumed that one distinct mechansim exists for at least 40 inches of fall of the drop. After approximately 40 inces of fall, either the mechanism again changes or the acid in the drop reaches equilibrium with the acid in the surroundings. This latter possibility will be considered later.

Three of the mechanisms investigated give mathematical solutions in the form of infinite series. Numbered as in Table I, page 39 , these mechanisms are,

2. Molecular diffusion in the drop. No resistance in continuous phase.
3. Molecular diffusion in the drop. Film type of resistance surrounding drop in the dispersed phase or the continuous phase.
4. Streamline convection within the drop. No resistance in continuous phase.

Each of these mechanisms indicate that a plot of the logarithm

fraction unextracted versus fall time will give a straight line after a sufficient length of time while for short contact times the plot will curve to the origin, 100% unextracted. Hence the possibility exists that the initial curvature of the plot is not due to a change in mechanism but is merely the normal situation expected when one of these three mechanisms applies.

Figure IV shows the theoretical shape of the curve for a mechanism of pure diffusion alone controlling the rate of extraction. The value of the diffusivity of acetic acid through water (D_d) is 0.94 x 10^{-5} $cm^2/sec.$ corrected from 12.5°C to 25°C (8). A drop diameter of 0.355 cm. was used. The shape of this theoretical curve is very similar to that of the actual curves but the slope of the theoretical curve is much too small to represent the true mechanism. Also, since the drop is formed under dynamic conditions, a mechanism of pure diffusion couldn't apply at time zero.

Mechanisms numbers 2 and 4 indicate a definite theoretical value of the slope of the plot. Hence, the actual slope may be compared to the theoretical slope. This comparison is summarized below.

TABLE V

Comparison of Diffusion Type Mechanisms

d (cm.)	Actual Slope (sec^{-1})	Pure Diffusion Slope (sec^{-1})	Streamline Convection Slope (sec^{-1})
0.295	-0.0916	-0.00185	-0.00505
0.354	-0.0678	-0.00128	-0.00349
0.418	-0.0567	-0.00093	-0.00254

The actual slopes are very much greater than the theoretical slopes. Hence these two types of mechanisms indicate a rate of extraction much too slow compared to the actual rate. A theoretical value for the slope of mechanism number three cannot be obtained. However, this mechanism would be expected to cause a rate of extraction even slower than that predicted for pure diffusion. Hence the theoretical slope of the plot would be smaller than that for the two previous mechanisms. On this basis, all three of the above mechanisms may be eliminated.

Since even the mechanism for streamline convection in the drop indicates much too slow a rate of extraction, obviously the interior of the drop must be in relatively turbulent motion. Thus, the two film type of mechanism of solute transfer will be considered next. No theoretical value of the slope of the plot can be predicted. However, if K_d, the over-all transfer coefficient, remains relatively constant with drop size, the slopes of the plots of logarithm fraction unextracted versus fall time should be inversely proportional to the drop diameter.

In Figure XII, the logarithm of the slope has been plotted against the logarithm of the drop diameter. The slope of this plot is (-1.34). Hence the slopes of the plots of the logarithm fraction unextracted versus fall time are inversely proportional to the drop diameter to the 1.34 power.

Notice that if mechanisms 2, 3, or 4 had applied,

the slopes of the plots of logarithm fraction unextracted versus fall time would have necessarily been inversely proportional to the drop diameter squared. Conceivably, a relatively large fictitious diffusivity coefficient could be used to make one of the diffusion equations fit the data for a given drop diameter. However, since the slopes of the plots are not inversely proportional to the drop diameter, the fictitious diffusivity coefficient could not be constant. Hence, any further analysis based on these types of equations would be purely empirical and would shed little light on the true mechanism of solute transfer.

From Figure XII the ratio of the slopes of the plots of logarithm fraction unextracted versus fall time has been found to be inversely proportional to the drop diameter to the 1.34 power. The slope of any one of these plots is equal to $(-2.61 \frac{K_d}{d})$. Hence,

$$K_d \propto \frac{1}{d^{0.34}}$$

The value of K_d has been calculated from the slope of each of the plots for the various drop diameters. The results follow.

FIGURE XII

ANALYSIS OF STOKE'S LAW EXPONENT

Methyl Isobutyl Ketone System

$S \propto d^n$

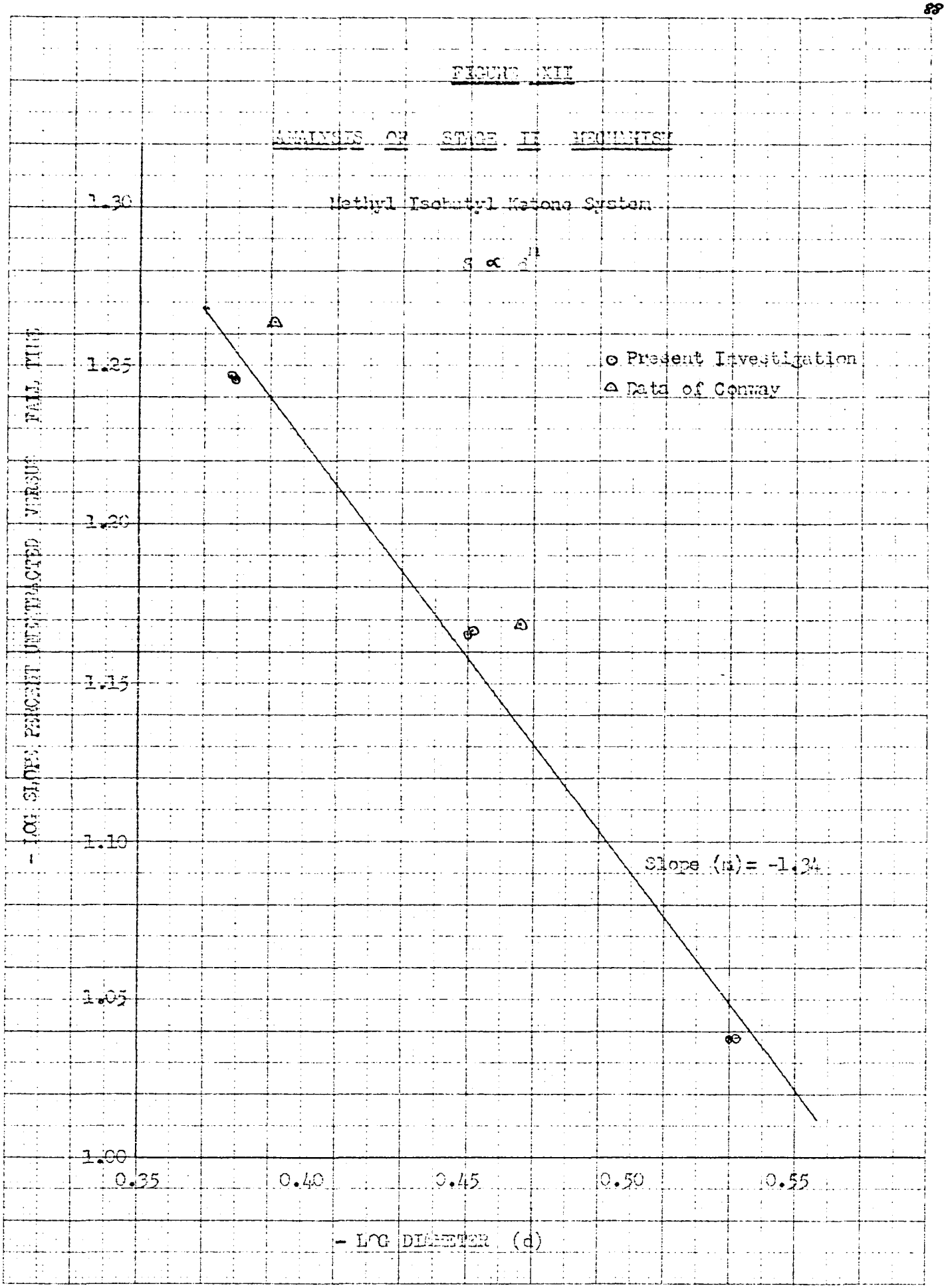


TABLE VI

Values of K_d for Methyl Isobutyl Ketone System

d (cm)	K_d (cm/sec)	K_d (ft/hr)	$K_d d^{0.34}$ (ft-hr)
0.294	0.01032	1.22	0.251
0.295	0.01037	1.22	0.251
0.354	0.00919	1.08	0.236
0.355	0.00929	1.10	0.240
0.418	0.00910	1.07	0.248
0.419	0.00909	1.07	0.248

From the above table the value of the over-all transfer coefficient, K_d, decreases slightly as the drop diameter increases. However, the value of $K_d d^{0.34}$ is relatively constant as predicted.

The drops in this system were observed to be appreciably deformed and in a continuous state of oscillation. As the drop size increases the deformation and the amplitudes of the oscillations increase. One would expect this larger amplitude of the oscillations to increase the turbulence in the drop and thus reduce the effective resistance of the film in the dispersed phase. Hence K_d would be expected to increase as drop diameter increases. However, K_d actually decreases with increased diameter.

The only possible explanation is that some or all of the resistance to solute transfer actually exists in a film in the continuous phase surrounding the drop. Experimentally, for the range of drop sizes used in this investigation, the drop velocity actually increases as the drop size

decreases. (See Figure VIII) Hence as the drop size is decreased; the faster rate of fall reduces the resistance of the film surrounding the drop in the continuous phase.

Equation (11) may be used to estimate that fraction of the resistance actually due to the continuous phase.

$$\frac{1}{K_d} = \frac{1}{k_d} + \frac{H}{k_c} \qquad (11)$$

Theoretically, the film coefficient for the continuous phase may be considered a function of the drop velocity, i.e.,

$$k_c = pv^m$$

where p and m are constants. Inserting this in equation (11) the following is obtained.

$$\frac{1}{K_d} = \frac{1}{k_d} + \frac{1}{Hp} \cdot \frac{1}{v^m} \qquad (33)$$

According to this equation a plot of $\frac{1}{K_d}$ versus $\frac{1}{v^m}$ will be a straight line with intercept $\frac{1}{k_d}$ provided k_d is not a function of drop velocity or in other words not a function of drop diameter.

Trial and error plots were made until the exponent m, which gave a straight line for a plot of $\frac{1}{K_d}$ versus $\frac{1}{v^m}$, was found. This value of m was approximately 0.9. The results are summarized below.

TABLE VII

$1/K_d$ versus $1/v^{0.9}$

d (cm.)	$\frac{1}{K_d}$ (ft/hr)	v (ft/hr)	$\frac{1}{v^{0.9}}$
0.294	0.820	1560	0.00134
0.355	0.909	1476	0.00141
0.419	0.935	1403	0.00147

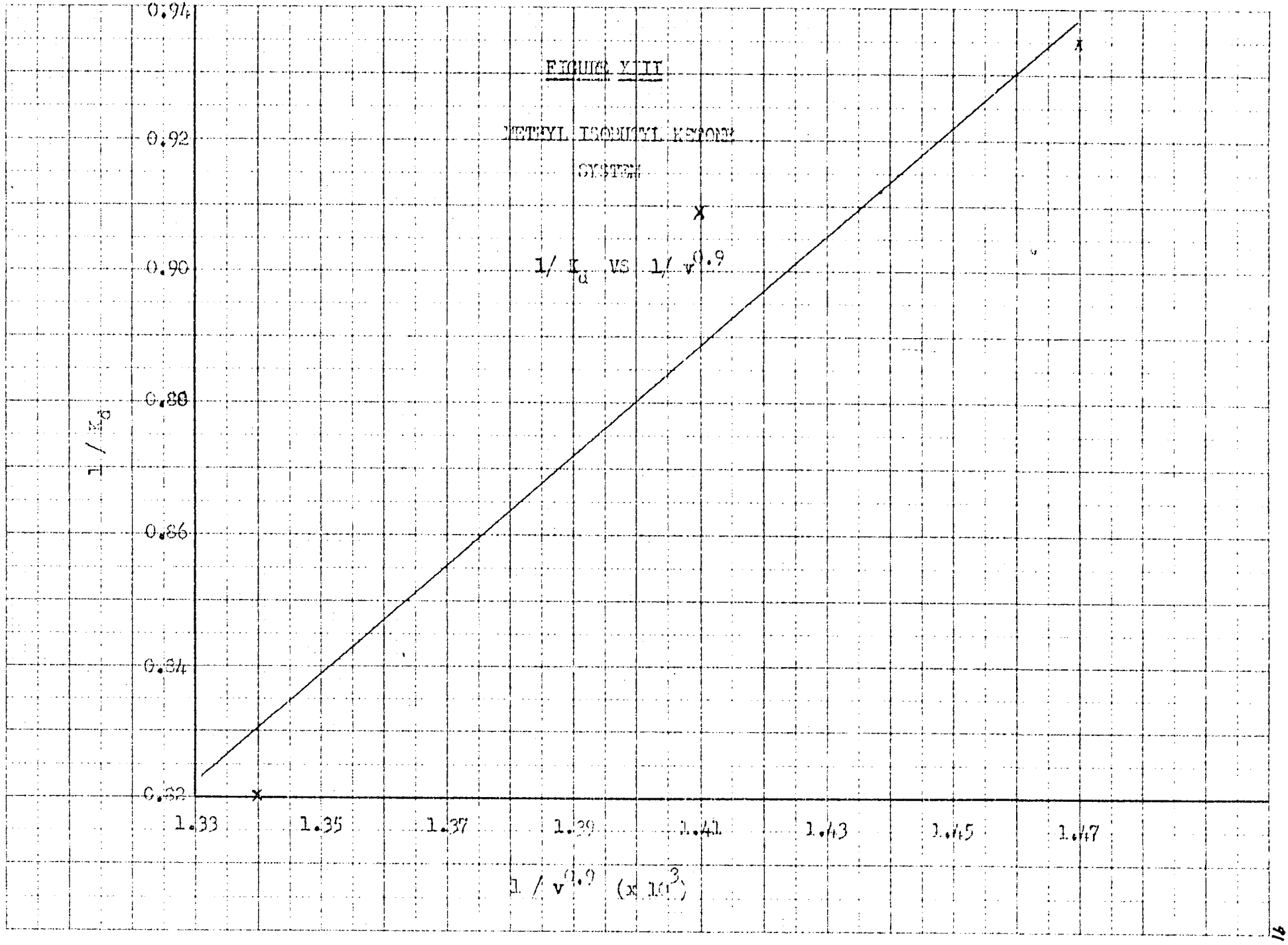
BOSTON MASS
LITHOGRAPHED IN U. S. A.

FIGURE XIII

METHYL ISOBUTYL KETONE

SYSTEM

$1/I_d$ VS $1/v^{0.9}$



The plot of $\frac{1}{k_d}$ versus $\frac{1}{v^{0.9}}$ is shown in Figure XIII, page 11 . From the slope of this line the value of $\frac{1}{H_p}$ = 834. The ordinate intercept $\frac{1}{k_d}$ is found to be (-0.29). Since the value of $\frac{1}{k_d}$ cannot be negative, it must evidently be zero. Hence this analysis predicts that all of the resistance to solute transfer is in the continuous phase.

Most of the resistance to solute transfer in a spray tower is usually assumed to be in the dispersed phase. Farmer[6] stated and attempted to prove that all the resistance to solute transfer is in the dispersed phase for the extraction of acetic acid from a series of solvents with water as a continuous phase. He attempted to prove this by substituting various concentrations of a sodium hydroxide solution for water as the continuous phase when extracting acetic acid from carbon tetrachloride as the dispersed phase. He observed negligible effect on the rate of extraction and thus assumed the resistance to solute transfer is not in the continuous phase. Actually, this may be a false deduction. The results do indicate that there is not a rate controlling reaction occurring between the acid and the water. However the sodium acetate formed at the interface must diffuse through the film away from the drop and the sodium hydroxide must diffuse through the film toward the drop. Actually this process may be just as slow as diffusion of acetic acid through the water film.

As previously noted, the drops in this system fell with oscillations of relatively large amplitude. These

oscillations will keep the interior of the drop well mixed and tend to prevent the formation of a film in the dispersed phase. At the same time the drop will be carrying with it a laminar layer of the continuous phase. It is entirely possible that all the resistance to solute transfer will be in this film in the continuous phase.

The values of the Reynold's numbers for these drops correspond to turbulent flow as defined for rigid spheres. (See Table III) However, there isn't any experimental verification for the assumption that for a given Reynold's number, conditions will be the same for a rigid sphere and an oscillating drop. Hence the conditions in the continuous phase may actually not be as turbulent as expected.

Another mechanism which may elucidate the mechanism of solute transfer is the transient film type of mechanism. If this mechanism applies, the slopes of the plots of logarithm fraction unextracted versus fall time should be proportional to $\sqrt{\frac{v}{d}}$. The theoretical value of the slope is $-2.95\sqrt{\frac{D_c v}{d}}$. The analysis of this mechanism is summarized below where the transient film is assumed in the continuous phase. The value of D_c has been taken as before as 2.37×10^{-5} cm^2/sec.

TABLE VIII

Test of the Transient Film Mechanism

d (cm.)	v (cm/sec)	Actual Slope ($cm.^{-1}$)	Theoretical Slope ($cm.^{-1}$)	Actual Slope / $\sqrt{\frac{v}{d^3}}$
0.294	13.2	-0.0916	-0.327	0.00402
0.355	12.5	-0.0683	-0.240	0.00409
0.419	11.9	-0.0566	-0.182	0.00445

From the above table, the ratio of the actual slope to $\sqrt{\frac{v}{d^3}}$ is not quite constant as the mechanism calls for although the disagreement is not sufficient to completely eliminate the mechanism. However, a comparison of the actual slope with the theoretical slope is sufficient grounds on which to eliminate the mechanism. In each case, the theoretical value of the slope is about three times as large as the actual value. If the transient film is assumed to be in the dispersed phase, the diffusivity of acetic acid in water is used in calculating the slope. This value, as previously used, is 0.94×10^{-5} cm^2/sec. This would make the theoretical slope only a little smaller. Thus, the transient film mechanism predicts a faster rate of extraction than is actually observed.

Before completely eliminating the transient film mechanism, it is interesting to note how this mechanism can be combined with the two film theory to provide a logical correlation of the experimental results. The consideration of a transient film in the dispersed phase seems to be

illogical. This film would originate at the bottom of the drop, pass up the outer surface of the drop and be deposited in the top of the drop. If this film behaves like an infinite film then the solute could never be actually transferred through the film to the surrounding continuous phase. Hence it would be impossible for solute to be transferred from the drop.

However, the film in the continuous phase surrounding the drop may actually act as an infinite film with respect to solute transfer. Conditions favoring this situation are short contact times with the surrounding film or a thick laminar layer around the drop. Hence, the possibility of a transient film in the continuous phase plus a fictitious film in the dispersed phase will be considered. The consideration of this additional resistance in the dispersed phase may account for the fact that the transient film mechanism alone predicts too rapid a rate of extraction.

From equation (29), for the transient film mechanism, the value of the individual film coefficent in the continuous phase is

$$k_c = 2\sqrt{\frac{D_c}{\pi t_e}}$$

Replacing t_e by its value in terms of drop velocity and drop diameter, the following is the result,

$$k_c = 1.13\sqrt{\frac{D_c v}{d}} \qquad (33)$$

This equation may be combined with equation (11) to give

the value of the over-all transfer coefficient, i.e.,

$$\frac{1}{K_d} = \frac{1}{k_d} + \frac{H}{1.13}\left(\frac{d}{D_c v}\right)^{1/2} \qquad (34)$$

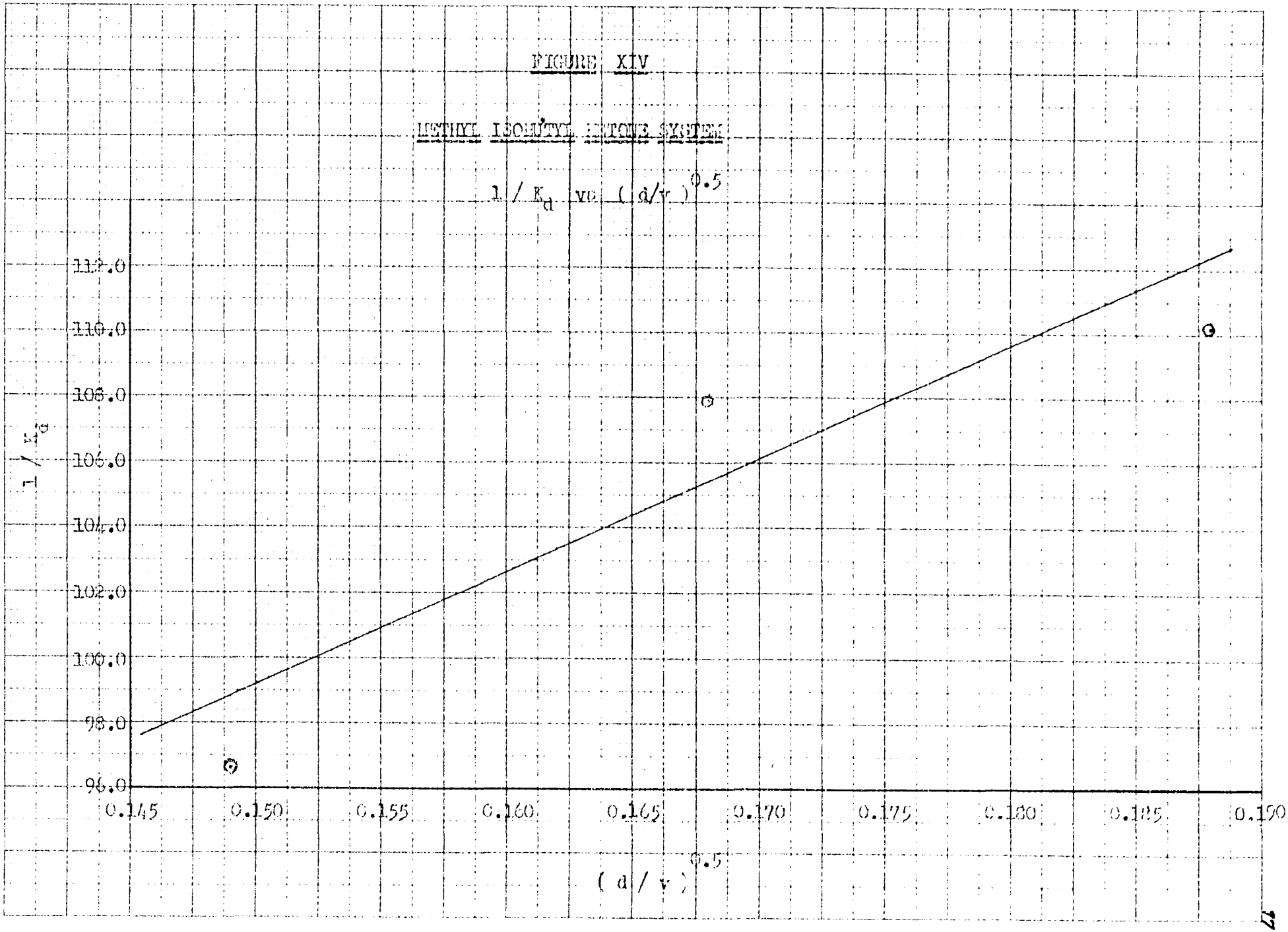
Assuming k_d constant over the range of drop sizes investigated, a plot of $\frac{1}{K_d}$ versus $(\frac{d}{v})^{1/2}$ should produce a straight line with intercept $\frac{1}{k_d}$ and slope of $\frac{H}{1.13\ D_c^{1/2}}$. The results are tabulated below.

TABLE IX

$1/K_d$ versus $(\frac{d}{v})^{1/2}$

d (cm.)	v (cm/sec)	$\frac{d}{v}$ (sec.)	$(\frac{d}{v})^{1/2}$	$1/K_d$ (sec./cm)
0.294	13.2	0.0223	0.149	96.7
0.355	12.5	0.0284	0.168	107.8
0.419	11.9	0.0352	0.188	110.0

In Figure XIV page 97 , a plot of $1/K_d$ versus $(d/v)^{1/2}$ is shown. The slope of the straight line drawn is 343. Using values of D_c and H as previously used, the calculated value of the slope is 375. Considering that only three points were used, the agreement is excellent. The value of the ordinate intercept, $\frac{1}{K_d}$, is 47.8 or k_d is 0.021 cm/sec. Hence, depending on drop size, about one-half of the resistance to solute transfer is in the dispersed phase and the other half is in the continuous phase. As drop size increases that portion of the total resistance which is in the continuous phase increases from 51% for the smallest drop (0.294 cm. diameter) to 57% for the largest



drop size (0.419 cm. diameter). Hence as drop velocity increases the resistance in the continuous phase decreases.

The results of this analysis do not check the results obtained with the previous analysis based on the two film theory. However both analyses definitely show that a large part of the resistance to solute transfer is in the continuous phase. The analysis based on a transient film in the continuous phase seems to provide a more reliable result. No assumptions have been made other than assuming the type of mechanism involved. The agreement between the theoretical value and the actual value of the slope of $1/K_d$ versus $(\frac{d}{v})^{1/2}$ justifies the mechanism, to a certain extent.

In the analysis based on the two film theory, the continuous film coefficient was assumed to be proportional to some power of the drop velocity. Such a relation has never actually been established for liquid-liquid extraction from drops although the relation is well established in gas absorption. Actually, up to the present time, no one has separated the film resistances in dropwise extraction.

From Figure XI, page 76 , in which the data of Conway[3] have been replotted, using the slopes of the plots for Column No. II, K_d for the 0.342 cm. diameter drop is 1.05 ft./hr. and for the 0.406 cm. drop is 1.00 ft./hr. These results are in good agreement with those of the present investigation.

Sherwood, Evans, and Longcor[16], when extracting

acetic acid from methyl isobutyl ketone with water as a continuous phase, found for a 0.178 cm. drop, K = 1.6 ft/hr and for a 0.356 cm. drop K = 2.0 ft./hr. These values are much larger than those obtained by either Conway or the author. However, the direction of extraction is different. As explained by Conway, the extraction of acetic acid from water is more difficult than the extraction of acetic acid from ketone due to the formation of hydrogen bonds between the acetic acid and the water. In addition, the values of K increase with increased drop size whereas in the present investigation the values of K decrease with increased drop size. However, in Sherwood's investigation, drop velocity increased with increased drop size, hence K would be expected to increase also. Due to the large increase in K, a large portion of the resistance to solute transfer no doubt lies in the continuous phase. However, Sherwood explains the results by assuming that the oscillations in the larger drop cause increased turbulence within the drop.

The next step in the analysis is to consider the mechanism of solute transfer during the initial one second time interval. The plots of data from Column No. I show definite curvature toward the 100% unextracted mark. Initially, the rate of extraction appears to be very rapid but then tapers off to the straight line portion of the plot.

This rapid initial rate of extraction is due to the oscillations of large amplitude of the drop just after leaving the tip. As the drop starts to leave the tip, the

liquid "necks down" until the drop actually breaks away. The elongated drop "springs" into a spherical shape and then immediately "pancakes out" as the resistance to fall in the continuous phase is met. Hence, there is a short period during which the drop is accelerating and oscillating. Consequently, the initial resistance to solute transfer in the continuous phase is small. Evidently, these abnormal effects are dampened out within the first second of fall after which steady conditions are reached.

As the drop size increases, the impact of the necked down portion against the drop does not produce oscillations as large as with small drops. Hence, the initial rate of extraction is less in the larger drops.

The above discussion offers a reasonable explanation for the initial curvature of the data taken with Column No. I. However, further examination of the plots reveal that the data of Column No. 2, for the two largest drops, show much less curvature for short fall times. Actually, the plot for the 0.418 cm. drop shows negligible curvature. The vertical distance between the plots for Columns No. I and II for approximately the same drop size, represents the amount of extraction in Stage III. As will be shown in the next section, for the range in which these plots are parallel, the extraction in Stage III is proportional to the concentration of the drop just before entering Stage III.

For short fall times, the plots for Columns No. I and II are no longer parallel but tend to converge. Hence the extraction in Stage III is no longer proportional to the concentration of the drop before entering Stage III but is actually decreasing. For the smaller drop sizes, part of the curvature in the plots for Column No. I may be due to the fact that as the column height becomes very short, the amount of extraction in Stage III decreases. This could be due to the fact that for very short column heights, the drop does not have sufficient time to reach its maximum velocity. Hence the impact of the drop at the interface is not as great as when the drop has reached its terminal velocity before striking the interface. Consequently, for very short column heights, one might expect less extraction in Stage III. This stage is considered in more detail later in the thesis.

As previously noted, after a fall time of about 9-10 seconds, the plots again show curvature. The shape of this portion of the curve indicates a gradual decrease in the rate of extraction as compared to that observed in the straight line portion of the plot. Since the plot is on a logarithmic scale, theoretically the curves must not become asymptotic.

One of the assumptions in all the theories is that the concentration of the continuous phase is negligible. This assumption can be checked by means of a material balance. The concentration of the acid feed is 0.0531 lb.moles acid/

ft^3 water. For an average volume of feed of 1.5 ml. and assuming 100% extraction the concentration of acid in a 50 inch column would be only 3.62×10^{-5} lb. moles acid/ft^3 ketone. Since the distribution coefficient (H) is about 2.0, the concentration of acid in the drop couldn't possibly be approaching equilibrium with that in the continuous phase. Hence the final curvature in the plots must be due to a change in the mechanism.

A possible explanation is that the turbulent motion within the drop is beginning to calm down or become more uniform. In effect, a diffusional type of mechanism may be beginning to control the rate of extraction from within the drop.

Stage 3

The vertical distance between the two plots for Columns No. I and II for approximately the same drop size, represents the amount of extraction in Stage III. The slope of the straight line portion of the plot for Column No. II may be expressed by

$$\frac{\log \frac{C_1}{C_2}}{t_2 - t_1}$$

where C_1 and C_2 correspond to any set of points on the straight line portion of the plot. For a similar drop size and Column No. I, at the same values of t each of the concentrations will be reduced by the amount of extraction occurring in Stage III. Hence the slope becomes

$$\frac{\log \frac{C_1 - x}{C_2 - y}}{t_2 - t_1}$$

where x and y represent the decrease in concentration of the drop due to the extraction in Stage III.

The only possible way in which these two slopes can remain equal is for x and y to be proportional to C_1 and C_2 respectively. In addition, the proportionately constant must be the same. Hence for the range in which the plots for Column No. I and II are parallel the equation for Stage III may be represented by

$$E_{III} = MC_{III}$$

where E_{III} is the fraction solute extracted in Stage III and C_{III} is the concentration of the drop before entering Stage III.

Since C_{III} is proportional to the amount of solute unextracted in Stages I and II, this equation may be written as

$$E_3 = M^1 (1 - E_{1-2})$$

where E_{1-2} is the fraction solute extracted in Stages I and II and M^1 is a new constant.

This equation has been checked at various points and the results tabulated below.

TABLE X

Analysis of Stage III

d (cm.)	t (sec)	E_3	$(1-E_{1-2})$		M^1	$\frac{M^1}{d}$
0.418	2	0.115	0.760		0.151	
	4	0.086	0.583		0.148	
	6	0.067	0.450		0.149	
				Avg.	0.149	0.356
0.354	2	0.095	0.690		0.138	
	4	0.070	0.505		0.139	
	6	0.052	0.370		0.141	
				Avg.	0.139	0.393
0.295	2	0.060	0.569		0.106	
	4	0.040	0.374		0.107	
	5	0.033	0.303		0.109	
				Avg.	0.107	0.362

The proportionality constant is found to increase with drop size. A comparison of the values of $\frac{M^1}{d}$ shows this quantity to be relatively constant. Hence the proportionality constant is directly proportional to the drop diameter. Thus the amount of extraction in Stage III is proportional to the drop diameter and to the concentration of the drop as it enters Stage III. However, for very short column lengths, this proportionality no longer exists. Apparently the extraction in Stage 3 decreases as we approach zero column height.

Actually, the amount of extraction in Stage III would be expected to be a function of column diameter which

was not a variable in this investigation. However, out of curiosity, a small amount of chalk dust was suspended in the interface between the water phase in the bottom of the column and the methyl isobutyl ketone on top of the water phase. As the individual drops struck the interface, the dust particles accelerated rapidly to the wall and were reflected back toward the center of the column. Just before the particles reached their original position, the next drop struck the interface and the process was repeated. This indicates that the entire area of the interface will be effective in transferring solute in Stage III.

Conway[3] found that the amount of extraction in Stage III was constant and independent of drop size and column height (or drop concentration). These results are impossible to explain.

PERCHLORETHYLENE SYSTEM

The perchlorethylene system was chosen for the investigation of Stage II because of the large value of the density of perchlorethylene (1.61 gm/cc). These dense drops fell rapidly and with little distortion. Actually, no visible vibrations were noticed except for the 0.394 cm. diameter drop. Hence, this system was expected to produce a good correlation of the data with the theoretical mechanisms.

Figure V shows that there is a considerable range of fall time over which the plot is definitely straight. Unfortunately, the change in slope of the plots with drop

diameter is very small. The plots for the 0.209 cm. drop and the 0.288 cm. drop exhibit a definite break. The portions of the curves before and after the breaks appear to be straight lines. For the purpose of checking mechanisms, only the first straight line portion of the plots will be used. This portion is more likely to represent the same type of mechanism which is controlling the rate of extraction from the larger drops.

The procedure used in checking the various mechanisms is identical with that previously used for the methyl isobutyl ketone system. The mechanisms of pure diffusion or streamline convection within the drop may be eliminated by comparing the actual slopes with the theoretical slopes. The results are summarized below. The value of D_d, the diffusivity of acetic acid in perchlorethylene was estimated by the method of Wilke[19] as 1.47×10^{-5} cm^2/sec.

TABLE XI

Comparison of Diffusion Type Mechanisms

d (cm.)	Actual Slope	Pure Diffusion Slope	Streamline Convection Slope
0.209	-0.126 (Upper portion) -0.058 (Lower portion)	0.00576	0.0157
0.288	-0.094 (Upper portion) -0.037 (Lower portion)	0.00304	0.00830
0.338	-0.077	0.00221	0.00604

Thus, not even the lower straight line portion of the plot corresponds to a rate of extraction as slow as predicted by the diffusion types of mechanism.

An additional check can be made by observing whether the slopes of the plots are inversely proportional to the square of the drop diameter. From Figure XV, the slope is inversely proportional to the diameter to the first power. Hence the diffusion types of mechanisms **are** definitely eliminated from consideration.

The transient film mechanism may be similarly eliminated by comparing the actual slope with the theoretical slope. In addition the slope should be inversely proportional to the quantity $\sqrt{\frac{v}{d^3}}$. The results are tabulated below. The film is assumed to be in the continuous phase.

TABLE XII

Test of the Transient Film Mechanism

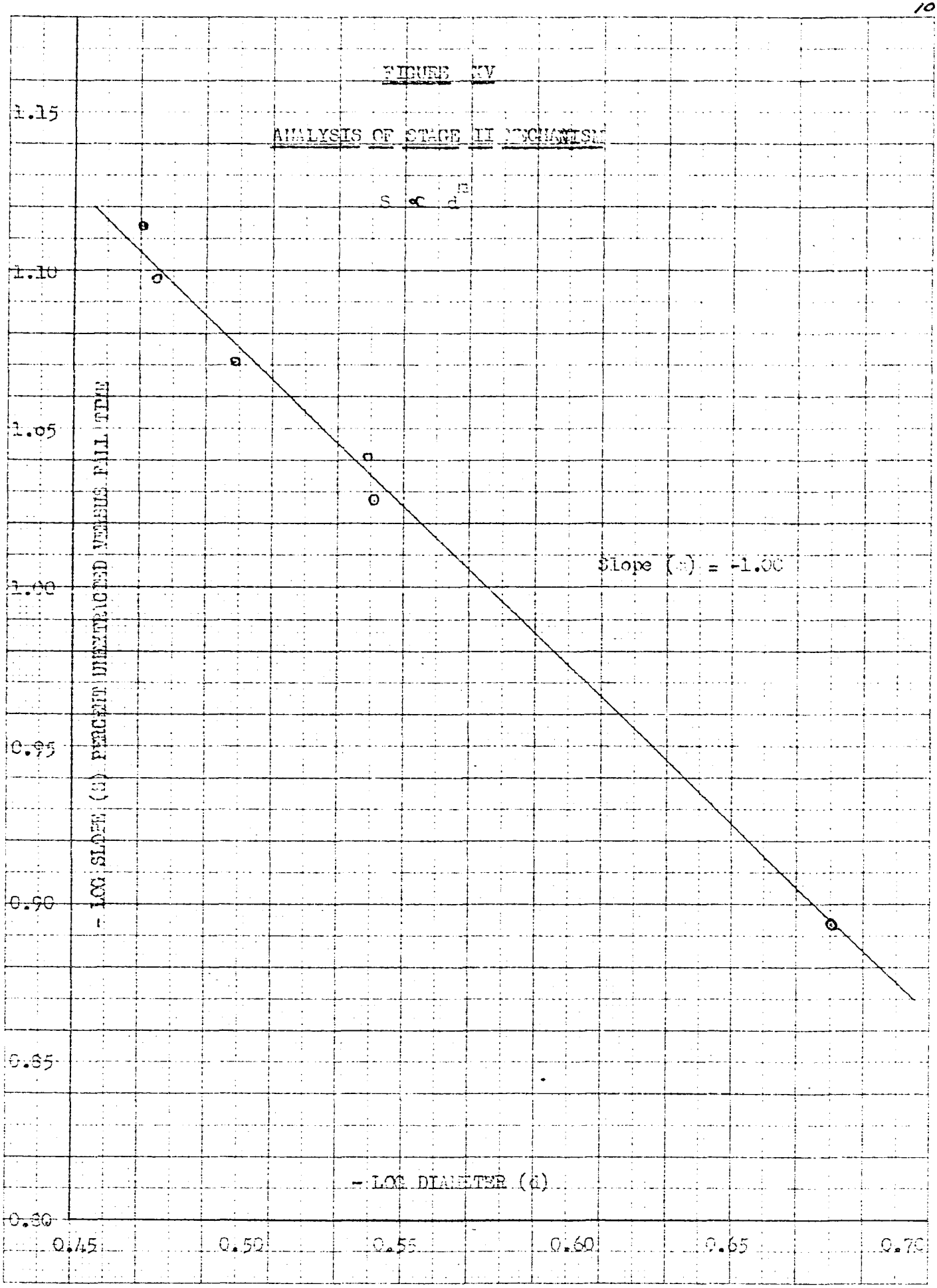
d (cm.)	Actual Slope (sec^{-1})	Theoretical Slope (sec^{-1})	v cm/sec	Actual Slope / $\sqrt{\frac{v}{d^3}}$
0.209	-0.128	-0.378	15.98	0.00306
0.212	-0.144	-0.372	16.10	0.00350
0.288	-0.094	-0.251	18.52	0.00338
0.289	-0.091	-0.251	18.62	0.00328
0.323	-0.085	-0.215	19.08	0.00357
0.335	-0.080	-0.204	19.20	0.00354
0.338	-0.077	-0.202	19.30	0.00346

Before leaving this mechanism, the relative constancy of the values in the last column should be noted.

FIGURE IV

ANALYSIS OF STAGE II MECHANISM

$S \propto d^{\beta}$



This mechanism could possibly be forced to apply by introducing a correction factor in the form of an increased time of contact between the drop and the transient film. Since the theoretical slope of the plot is $-2.95/\frac{D_c v}{d\delta}$, this increased time of contact would result in a fictitious velocity less than the actual velocity. That is, the actual time for this transient film to pass over the surface of the drop may be increased due to the dragging of the continuous phase along with the drop. A correction factor (f^2) may be defined as the ratio of the velocity of the film over the drop relative to the center of the drop to the actual velocity of the drop relative to the stagnant continuous phase, i.e.,

$$f^2 = \frac{v_f}{v}$$

The theoretical slope is then $-2.95/\frac{D_d v_f}{d\delta}$ or $-2.95\, f/\frac{D_d v}{d\delta}$.

The value of f^2 necessary to correct the theoretical slope was found to be about 0.15. Thus the film is moving at a velocity about two-tenths of the actual velocity of the drop.

West et.al.[18] have used a correction factor identical with that above but found the mechanism not to hold for extraction of acetic acid from benzene with water as a continuous phase. However, they obtained data for only three column heights and did not establish a straight line relation on a logarithmic plot or a ratio of slopes to drop

diameter. Hence their results are inconclusive.

Although f has been given a physical meaning, the value may be fictitious. One of the assumptions in deriving the analytical expression for this mechanism is that the time of contact of the drop with the film is so short that insofar as solute transfer is concerned, the film is infinite. However if the actual time of contact is increased to ten times the expected time of contact, the film may no longer act infinite in extent.

In conclusion, this mechanism has neither been proved or disproved. It does have its merits, however, and could do much to establish the theory of extraction from drops in some cases. Further work on this type of mechanism is needed. The present investigation has at least established a method for preliminary testing of data to see if the mechanism can possibly hold.

The established two-film theory provides a logical basis for analyzing the data. From Figure XV the slope of the plot of logarithm fraction unextracted versus fall time is found to be almost inversely proportional to the drop diameter. If the lower point on the plot is neglected, within experimental error the slope of the plot is -1.00. This indicates that, K_d, the overall transfer coefficient is independent of drop diameter.

The values of K_d are summarized as follows.

TABLE XIII

Values of K_d for Perchlorethylene System

d (cm.)	v (cm/sec)	K_d (cm/sec)	K_d (ft/hr)
0.209	15.98	0.01025	1.21
0.212	16.10	0.01170	1.38
0.288	18.52	0.01038	1.22
0.289	18.62	0.01009	1.18
0.323	19.08	0.01051	1.24
0.335	19.20	0.01028	1.21
0.338	19.30	0.00997	1.18

From the above table, the values of K_d are seen to be relatively constant and independent of drop velocity. Since the value of K_d is independent of drop velocity, all the resistance to solute transfer must be in the dispersed phase. Hence $K_d = k_d$ over the range of drop sizes employed.

For the drop sizes from 0.209 cm. to 0.338 cm. diameter, the drops fell calmly with very little distortion and no visible vibrations. Additional data, not included so far in the study of the mechanisms, were obtained for a 0.394 cm. drop. This curve is indicated as a dotted line in Figure V. This size drop, in contrast to the smaller drops, was extremely distorted and was definitely oscillating. The result is that this curve shows a rate of extraction entirely unpredicted from the trend observed with the smaller drops. The gradual decrease in the rate of extraction with increased drop size has been completely reversed until the rate is about equal to that for the 0.209 cm. drop.

The explanation of this increased rate of extraction can be found in the difference in behavior of the drop as noted above. The oscillations of large amplitude have set up stronger eddy currents within the drop as well as in the surrounding medium. The velocity (19.55 cm/sec) is not out of line with those found for the smaller range of drop sizes, hence the change in the rate of extraction cannot be credited to this.

Since the velocity has not abnormally increased, most of the increased extraction rate is due to the stronger eddy currents within the drop and the consequent reduction in the effective film thickness. Further study of this reversal in the rate of extraction should be quite fruitful. Commercially, this is important since increased drop size would produce increased throughput without sacrificing extraction efficiency. Whether all systems exhibit such a phenomenon is not known. However, no one has ever reported such a phenomenon.

Since all of the data in Figure V were obtained with Column No. II, the initial curvature of the plots cannot be attributed to any effects in Stage III. Since the drops fell relatively fast and a minimum of a six inch column was used, the shape of the plots below one second fall time is unknown. However the plots do show definite curvature toward the 100% unextracted mark. This is some justification for the use of equation (7) to predict extraction during drop formation.

The reason for the breaks in the straight line portion of the plots for the two smallest drop sizes is not too certain. The only explanation that may be offered is that the eddy currents have decreased within the drop and the effective resistance to mass transfer has consequently increased. The fact that the break appears to be very sharp is difficult to explain. These breaks were actually reproduced in the two sets of data for the smallest drop size. Perhaps that this break appears to occur at the intersection of two straight lines is merely a fortuitous result and the true plot is actually curved.

CARBON TETRACHLORIDE - OIL - SYSTEM

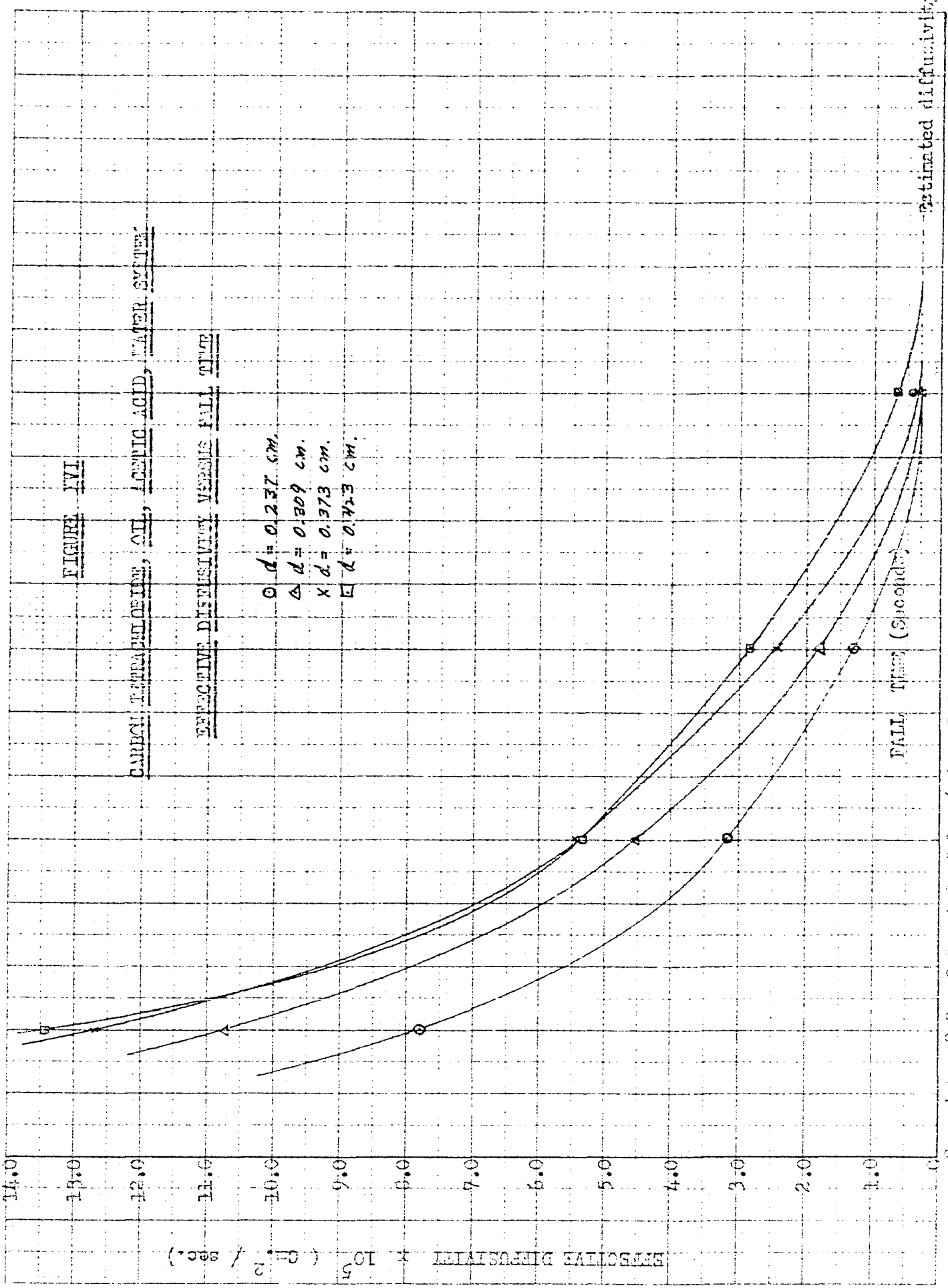
From the first two systems investigated, pure diffusion mechanisms were evidently not going to be encountered with the normal type of systems. To determine what effect increased viscosity of the drop may have on the mechanism, this present system was investigated. The results are plotted in Figure VI and were obtained in Column No. II. The viscosity of the carbon tetrachloride -oil - acetic acid mixture was 3.93 centipoises.

Notice that no portion of the curve is a straight line. Hence it is impossible to attempt to analyze this data as before. The only types of mechanisms producing any type of curved plot are the diffusion types of mechanisms. On this basis, an attempt was made to fit the pure diffusion mechanism to the data.

Regardless of the value of the diffusivity used, the curves could not be reproduced with the diffusion equation. The plot of the theoretical diffusion equation invariably straightens out within two seconds of fall time. Hence, it must be concluded that the curvature of the plots is due to a continuously changing mechanism. From the shape of the curves, a logical assumption is that the initial rate of extraction is due to the convection or eddy currents remaining in the drop after formation. Due to the viscosity of the drop, dampening of these currents takes place as the drop falls. Eventually the interior of the drop becomes stagnant and pure diffusion within the drop controls the rate of extraction.

If this mechanism just cited is the correct one, then the slope of the curves should gradually approach the slope for pure diffusion. To check this, the slope of each of the curves was measured at a given time, for a series of time intervals. Since the slope is directly related to the diffusivity, the diffusivity was calculated for each slope and designated an "effective diffusivity." These effective diffusivities were then plotted in Figure XVI against the corresponding fall times.

From the plot, the effective diffusivity very definitely approaches the estimated molecular diffusivity, 3.30×10^{-6} $cm^2/sec.$, estimated by the method of Wilke[19]. Hence, the proposed mechanism is probably the true mechanism.



The drops in this system fell very calmly with no visible distortions, a condition no doubt necessary for pure diffusion to eventually control the mechanism. In addition, from Figure X, the actual values of the drop velocities are similar to the values predicted for rigid spheres. This, no doubt, is also a necessary (but not sufficient) condition for pure diffusion to control the rate of extraction from a liquid drop.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The mechanism of solute transfer from drops was studied using three different systems. Possible mechanisms in each of three stages (drop formation, drop fall and drop coalescence) were considered and investigated mathematically. During drop formation (Stage I) the rate of extraction was assumed to be controlled by the rate of molecular diffusion through a relatively stagnant continuous phase surrounding the drop. The equation developed for this stage indicated a relatively small amount of extraction should occur during drop formation.

Experimentally, from a study of drop formation time in the methyl isobutyl ketone system, it was found that the total amount of extraction occurring in a three-inch column (including all three stages) was independent of drop formation times from 0.4 to 10.0 seconds. This indicated that the amount of extraction during drop formation was so small a portion of the total extraction in the column that the amount of solute transferred was obscured within experimental error.

Further, plots of logarithm fraction solute unextracted versus fall time, showed definite curvature toward the 100% unextracted mark, indicating a relatively small amount of extraction during drop formation. On the basis of these plots, it was shown that the procedure of extrapolating the straight line portion of a semi-log plot of fraction solute

unextracted versus fall time to obtain the extraction during drop formation is generally incorrect.

When applying the theoretical equation for Stage I to the extraction of acetic acid from non-polar solvents, it was found necessary to apply a correction factor $\frac{2-n}{n}$ where n is the degree of association. This factor represented the fraction of the total acid molecules existing as single molecules.

Several distinct mechanisms for the transfer of solute during Stage II (drop fall) were postulated. Mathematical equations were developed to express the amount of extraction. A method for testing experimental data to determine the applicability of each of the possible mechanisms was developed and its application illustrated in each case.

For the extraction of acetic acid from water with methyl isobutyl ketone (continuous phase), the mechanism of solute transfer was found to be definitely not one of pure diffusion within the drop. Two possible mechanisms for Stage II were found to explain the experimental results. The analysis based on the two-film theory, showed all the resistance to transfer to be in the continuous phase. The analysis based on a fictitious film in the dispersed phase and a laminar layer of solvent surrounding the drop (a "transient film") in the continuous phase, showed that one-half of the resistance to solute transfer is in the dispersed phase and the other half in the continuous phase. Hence, it was concluded that a large portion of the total resistance to solute transfer is in

the continuous phase.

For the extraction of acetic acid from perchlorethylene with water (continuous phase), a pure diffusion mechanism was again found to be impossible. The analysis based on the two-film theory showed that all the resistance to solute transfer must be in the dispersed phase. The value of the over-all transfer coefficient was found to be constant with variations in drop size or drop velocity.

The extreme difference in behavior between the methyl isobutyl ketone system and the perchlorethylene system can be partly attributed to the difference in drop behavior. In the ketone system, the drops were very distorted or "flattened out" and vibrating. This evidently caused a laminar portion of continuous phase to be "dragged" along with the drop. This can be verified by the fact that the larger drops fall slower than the smaller drops, a very definite departure from the behavior of rigid spheres. Due to the vibrations, the interior of the drops were kept thoroughly mixed, and no film could be formed in the dispersed phase. Hence all the resistance to solute transfer was found to be in the continuous phase.

However, for the perchlorethylene system, the drops fell rapidly with very little distortion and no visible vibrations. Hence, these drops tended to "glide" through the continuous phase. Therefore, the continuous phase offered negligible resistance to solute transfer while the dispersed phase offered all the resistance.

The semi-log plots (perchlorethylene system) for the two smallest drops showed a definite decrease in slope with fall time indicating an apparent decrease in the overall coefficient. This was probably due to the interior of the drop approaching stagnant conditions. However, the investigation of one large drop size in this system showed a rate of extraction very much greater than was expected from the normal trend noticed with the smaller drops. This was no doubt due to conditions as observed in the ketone system. That is, this large drop was very distorted and noticeably vibrating. Thus the interior of the drop was kept thoroughly mixed and a film in the dispersed phase could not be formed. Hence, part of the resistance to solute transfer had probably shifted from the dispersed phase to the continuous phase.

In conclusion, it might be expected that the degree of distortion and the amplitude of the oscillations of the drop have a large influence on whether the resistance to solute transfer will be found in the continuous phase or the dispersed phase. This suggests the important need for a thorough investigation of drop behavior in relation to the properties of the system.

For the extraction of acetic acid from a mixture of carbon tetrachloride and a heavy mineral oil with water (continuous phase), over the range of column heights investigated, no one mechanism was found to apply. However, it was shown that the initial turbulence in the drop was "dampening out"

and a process of pure diffusion within the drop was starting to control the rate of solute transfer. The drops in this system were found to fall undistorted without vibrating.

The mechanism of solute transfer in Stage III (drop coalescence) was investigated with the methyl isobutyl ketone system. The amount of extraction in this stage was found to be proportional to the concentration of the drop before entering this stage and the diameter of the drop. It was also demonstrated, but not definitely shown, that the entire interfacial area between the two phases is effective in transferring solute in this stage.

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TABLE A

Summary of Properties

	System					
	Methyl Isobutyl Ketone - Acetic Acid - Water		Perchlorethylene - Acetic Acid - Water		Carbon Tetrachloride - Oil - Acetic Acid - Water	
Dispersed Phase	Acetic Acid - Water		Perchlorethylene - Acetic Acid		Carbon Tetrachloride - Oil - Acetic Acid	
Continuous Phase	Methyl Isobutyl Ketone		Water		Water	
Property	Dispersed Phase	Continuous Phase	Dispersed Phase	Continuous Phase	Dispersed Phase	Continuous Phase
Concentration (#mols/ft^3)	0.053	0	0.061	0	0.032	0
Density (gm.ml) (25°C)	1.002	0.801	1.582	0.997	1.211	0.997
Viscosity (25°C) (centipoises)	---	0.546*	---	0.894	3.925	0.894
Diffusivity x 10^5 (cm^2/sec) (25°C)	0.94***	2.37**	1.47**	0.94***	0.330**	0.94***

* Reference (3)

** Estimated by method of Wilke[19]

*** Reference (8) - corrected to 25°C

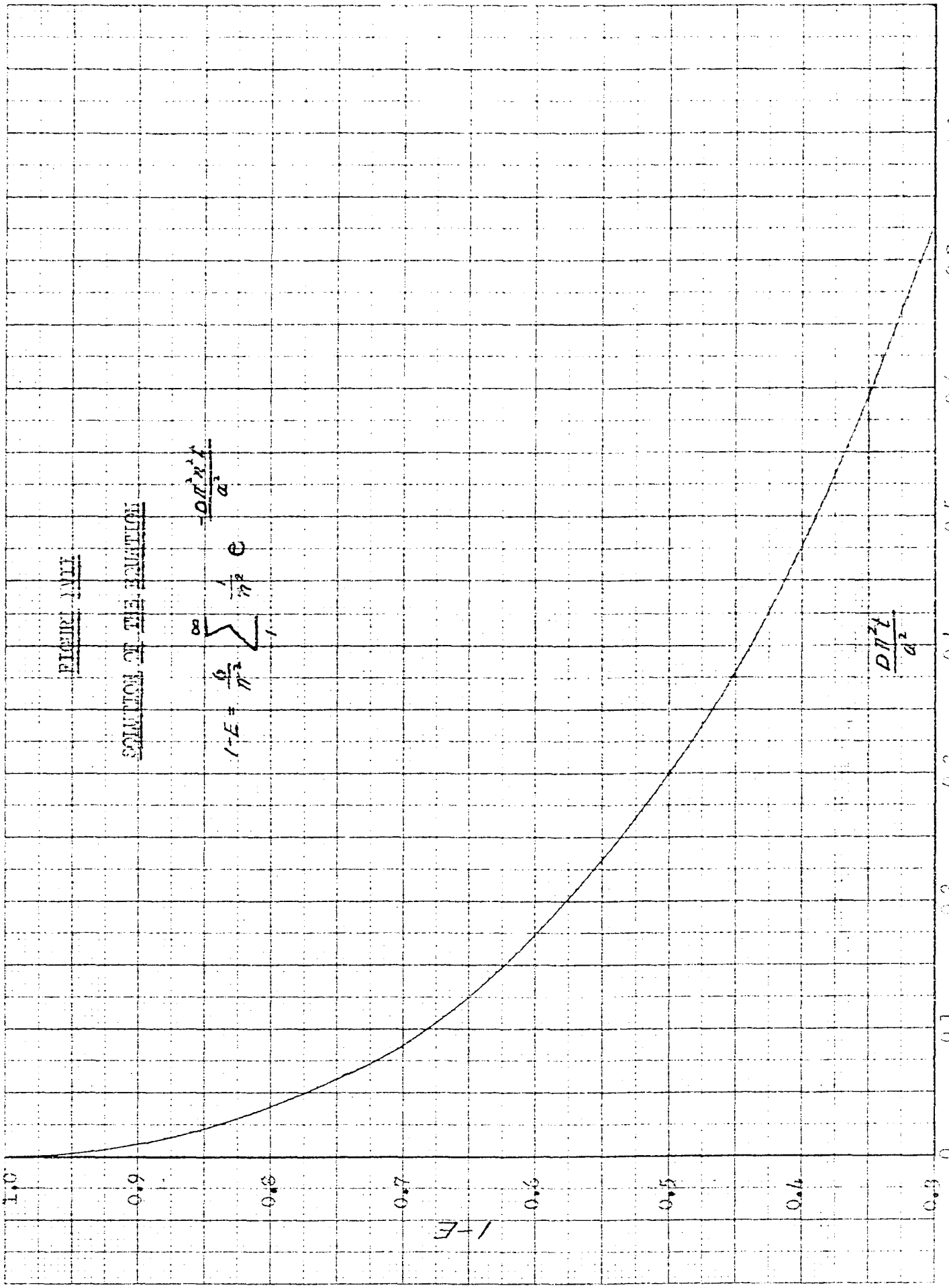


TABLE 1

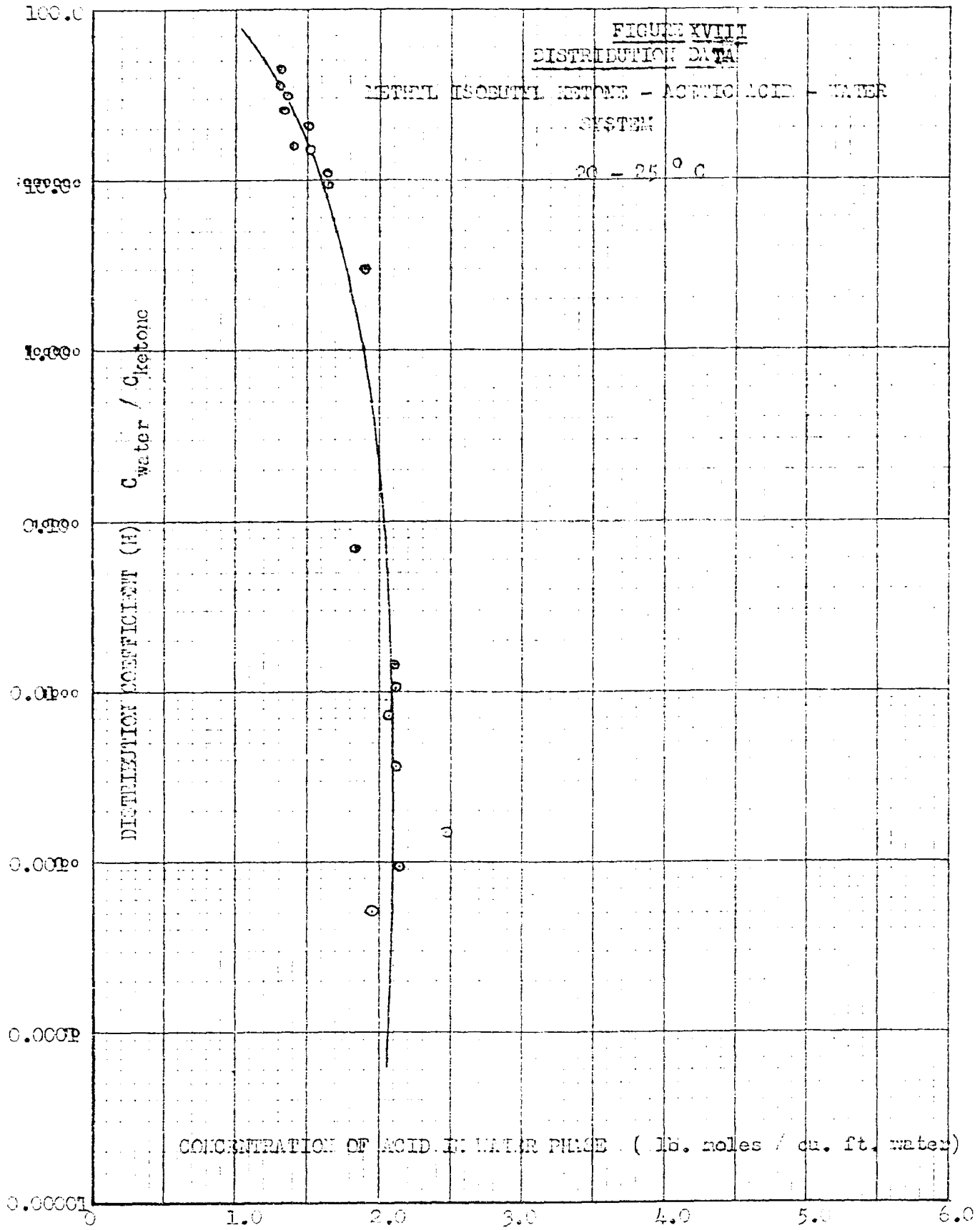
Distribution Data For Methyl Isobutyl Ketone - Acetic Acid - Water System

Concentration of Acetic Acid (lb. moles/cubic foot)				
C_M	C_W	H	Temp.(°C)	Literature Reference
5.7	9.43	1.65	22.0°C	(14)
10.5	15.9	1.51		
19.1	26.7	1.40		
22.9	31.3	1.37		
25.6	33.6	1.31		
27.0	35.1	1.30		
0.0377	0.0694	1.84	21.0°C	(6)
0.0069	0.014	2.11		
0.0052	0.011	2.11		
0.00352	0.0073	2.07		
0.00178	0.00377	2.11		
0.000623	0.00155	2.48		
0.000436	0.000935	2.14		
0.000262	0.000511	1.95		
1.56	2.96	1.9	25°C	(16)
7.4	12.2	1.65		
14.4	21.5	1.5		
20.5	27.2	1.33		
25.6	34.1	1.33		
27.9	36	1.29		

C_M = conc. of acid in ketone

C_W = conc. of acid in water

MODEL DATE



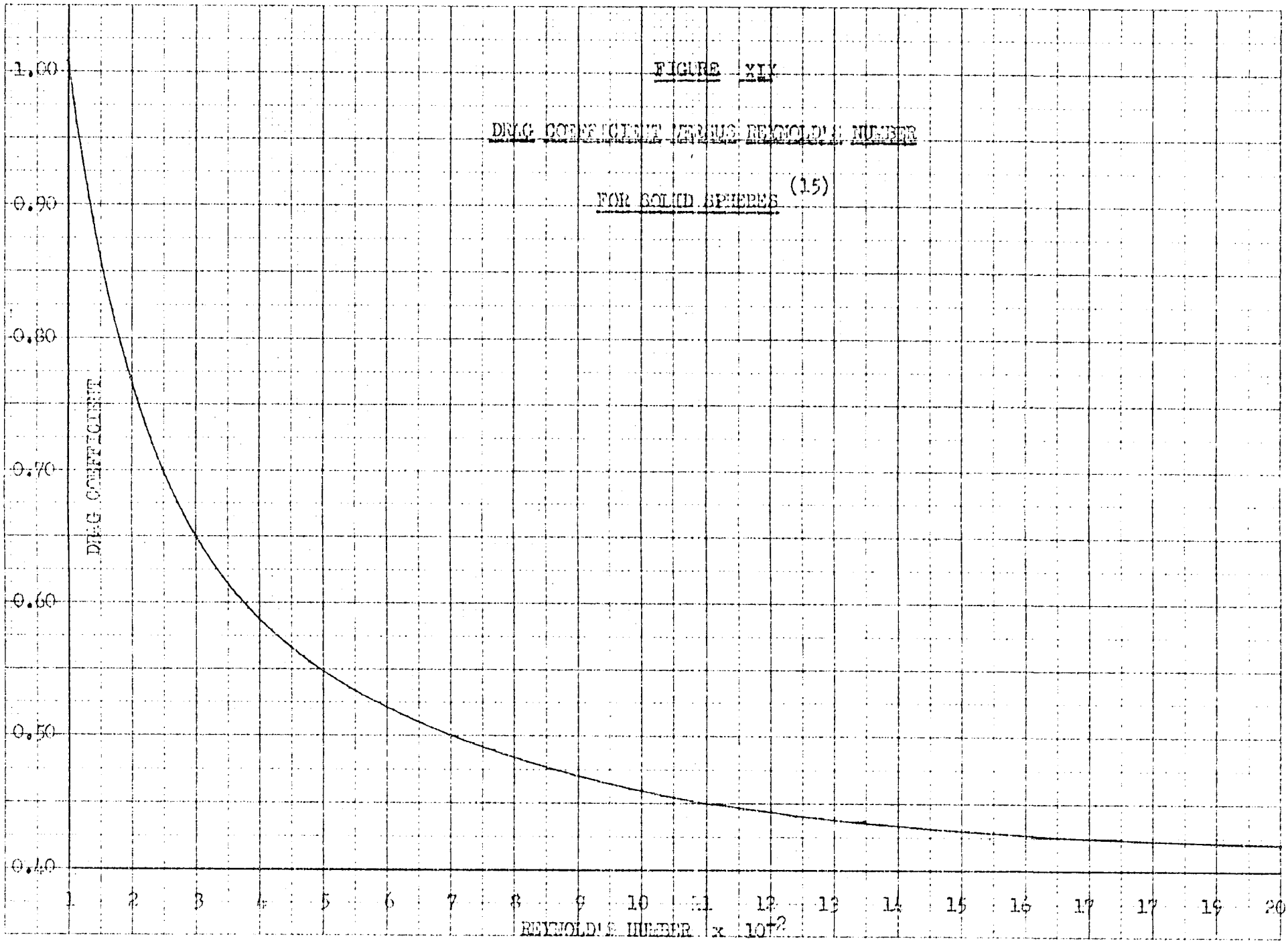


FIGURE XIV

DRAG COEFFICIENT VERSUS REYNOLDS NUMBER

FOR SOLID SPHERES (15)

APPENDIX

FEED DEVICE

(Supplemental Information)

The feed device was designed to permit accurate determination of the total volume of feed delivered. In order to feed drops at a uniform rate, a constant head type of feed device would be desirable. Much time was spent in investigating all types of constant head feed mechanisms. Since the experiments are carried out as a batch type of extraction, the total quantity of dispersed phase introduced into the column should be small to prevent an appreciable build up of solute in the continuous phase.

No practical constant head feed device permitting accurate measurement of a very small quantity of liquid could be devised. Hence, a feed device of the type used by Conway(loc.cit.) was employed. This consisted merely of a standard, ten-milliliter glass stopcock burette to which was attached a feed rate control device and a delivery tip. This assembly was then supported by a system of clamps which held the entire device securely but yet permitted raising or lower of it on the column support by manipulation of only one clamp.

This type of feed device did not permit constant head delivery of the feed since the head was continuously decreasing as the liquid level fell. However, the distance the liquid level fell in the burette during a given run was only from one to two inches (about one to one and one-half

milliliters of liquid delivered). This slight change in head had a very small effect on the rate of drop formation over a given run and hence could be tolerated.

Various designs of delivery tips or nozzles were tested. Conway[3] used tips constructed of thick walled capillary tubing. The outside diameter of the delivery end of the tube was reduced by beveling off the end of the tube on the wet grinder but still leaving some flat area exposed. The length of capillary tube used to construct the tip was chosen so as to provide sufficient pressure drop to properly regulate the rate of flow or feed.

With this type of tip, the feed liquid actually wets the entire ground surface including the beveled surfaces. Hence, instead of the drop forming at the opening, the drop forms around the entire ground surface of the tip. When this globule of liquid becomes sufficiently large to pull off the tip, the liquid actually "necks down" from the ground beveled surface. When the drop has left the tip, a considerable amount of it still clings to these wetted surfaces to become part of the next drop. Since conditions for extraction are favorable during this formation process, it seems desirable to have each drop start from zero volume.

Conway also had considerable difficulty in obtaining uniform drop sizes unless the tip was very clean. This was no doubt due to the fact that the ultimate drop size depends on the amount of ground surface wetted by the feed solution. If a dirt or grease film prevents the wetting of

part of this surface, variations in drop size will result.

The author constructed a series of delivery tips from standard five-millimeter pyrex glass tubing. The tubing was drawn out to a fine capillary in a flame. The tip was then cut off to produce a given size opening. In this way a series of tips with various size openings were made. Each tip was then carefully ground to give a smooth, flat opening and then lightly firepolished to remove any ground surfaces.

These tips were simple to construct and gave excellent reproducibility of drop sizes. The drops formed only at the opening and did not wet up the outer walls of the tip. The maximum drop size was limited by the original diameter of the tubing used without drawing to a tip. The minimum drop size was limited by the size of opening of the tip which would still permit liquid feed to flow through it under the maximum head obtainable in the buret. Each tip was approximately three inches in length.

In order to regulate the rate of flow of feed liquid to the tip some sort of reproducible feed rate control was needed. Much of the work was done using various lengths of thermometer capillary tubing inserted ahead of the tip to restrict the rate of flow. Relatively short lengths (about one-half inch) were required depending on the drop size and rate of drop formation desired. This gave very satisfactory results except that great care had to be taken to prevent any lint or foreign matter from clogging this very fine

capillary in the middle of a run. Later in the work it was found more desirable to replace the capillary tubing by a short section of standard glass tubing packed with glass wool. By varying the amount of packing and the degree of packing any desired flow rate could be obtained without the difficulty of clogging. Fine control of the feed rate was obtained by adjusting the initial level of the feed in the burette. To eliminate any possible errors due to the adsorption of acetic acid by the glass wool, the packed section was thoroughly soaked with the feed solution before use.

PROCEDURE

(Supplemental Information)

The column height was measured from the tip of the nozzle to the interface of the water and methyl isobutyl ketone at the bottom of the column. The one and one-half inches of solvent above the tip was sufficient so that upon draining the water layer from the bottom of the column, the tip remained submerged in the solvent. This was necessary since upon cutting off the feed at the end of a run, a small portion of a drop usually remained on the tip. If the solvent layer was allowed to fall below the tip while draining the bottom layer from the column, this portion of a drop detached itself and fell to the bottom of the column.

The tip, capillary length and burette were carefully washed and dried before use. In addition, the tip was placed in a warm cleaning solution for about fifteen minutes to insure uniform wetting by the feed solution and hence uniform drop sizes from day to day. After cleaning and assembling, the burette was filled with the acetic acid - water mixture and the feed assembly placed on the support above but not over the column. The feed device was swung to one side and a small beaker of solvent was placed on a platform below the tip. The tip was immersed in the solvent and allowed to feed drops until a burette full of feed had been used. Care was taken to make sure that all air pockets were excluded from the tip and capillary. This insured

thorough flushing of the device and permitted checking of the desired drop formation time and drop size before actually making a run. After a run, the feed device was returned to its original position with the tip immersed in the small beaker of solvent.

The number of drops fed depended on the size of the drops. A total of about one or one and one-half milliliters of feed was used. This amount of feed did not cause an excessive variation in drop formation time due to changing head during the run. This total quantity of feed also prevented the concentration of solution in the continuous phase from building up above a negligible value (0.03% acetic acid).

After the last drop had crossed the interface at the bottom of the column, a two hundred and fifty milliliter Erlenmeyer flask was placed beneath the stopcock at the bottom of the column and the acetic acid - water layer was drained from the column. By careful manipulation of the stopcock, this layer could be completely removed without removing any of the continuous solvent phase in the column.

The drop formation time was obtained in one of two ways. In the initial phases of the work, the time of formation of the drop formed at the midpoint of the total drops to be formed was recorded by a stopwatch. This procedure was used through most of the work on the methyl isobutyl ketone system. In subsequent work, the total time

to deliver all the drops was measured and this time divided by the number of drops delivered was taken as the average formation time. This latter method gave more consistent results and was more accurate since the timing of a fraction of a second process with a stopwatch is rather inaccurate.

The temperature in the column was checked at frequent intervals. However, practically all runs were made at 25°C ± 1°C, the normal range of room temperatures. Considerable difficulties were encountered with cooling of the laboratory. This cooling caused "cloud points" to occur in the methyl isobutyl ketone saturated with water. The only practical way to remove this cloudiness was to cool the solvent down with ice, shake thoroughly to coalesce some of the larger cloud droplets, then warm back up to room temperature.

After an experimental run was completed, the solvent was drained from the column. For the shorter column heights (three and six inches) the solvent was only used once while for larger column heights, the same solvent was used for making a check run. The solvent was never used more than twice. This procedure kept the acid concentration well below 0.03%.

After use, the solvent was recovered by placing it in a large separatory funnel and shaking with a dilute sodium hydroxide solution. The solvent was then washed with distilled water three or four times or until the wash water showed no pink color with phenolphthalein indicator. One

extra wash was then given to insure neutrality. It was noticed that the solvent, which is normally colorless, acquired a faint tint of yellow color after continued use and recovery. The material, however, exhibited no differences in its extractive properties. Nevertheless, at the first sign of a yellow color, the solvent was distilled. This yellow color was probably due to the sodium hydroxide treatment which catalyzed a condensation type reaction resulting in a yellow polymerized product.

Considerable difficulty was had in obtaining a sharp end point when titrating the two phase methyl isobutyl ketone - acetic acid - water mixture withdrawn from Column No. II. This was caused by the solvent being in excess and not dissolving the phenolphthalein, hence the red color appeared only in the water phase. On shaking, the dispersed solvent obscured a sharp end point. This difficulty was overcome by adding two drops of a powerful wetting agent (50% Roccal from the Hilton-Davis Chemical Company) to the two phase mixture and thoroughly shaking. On titrating this emulsion a sharp pink end point could be obtained. A negligible blank on this mixture was obtained.

The column height in Column No. II was measured in one of two ways. When the methyl isobutyl ketone - acetic acid - water system was used, the rather large size acetic acid - water drops tended to slide down the walls of the stopcock A after being funneled into its opening. Several drops actually stuck in this stopcock. To avoid undesirable

end effects due to this action, when Stopcock A was closed, the entire column was removed from the stand and the continuous solvent phase was poured out of the top of the column. The column was then replaced on the stand and stopcocks A and B opened allowing the contents of both the collecting chamber and the bore of the cylinder of stopcock A to drain into the sampling flask. When using this procedure, the column height was measured from the delivery end of the tip to the top of the cylinder of stopcock A.

The drops of the other two systems employed showed no tendency to stick to the glass stopcock but passed through stopcock A without being interrupted. Hence for these systems the more convenient method of draining only the liquids between stopcocks A and B was used. Hence in this case, the column height was taken as the distance from the delivery end of the tip to the bottom of the cylinder of stopcock A.

When using water as the continuous phase in the latter two systems, the water in the column at the end of each run was drained and discarded. This simplicity of operation was one reason for switching to systems with water as the continuous phase.

A slight difference in the handling of the feed device was required with the perchlorethylene and carbon tetrachloride systems. As previously mentioned, with the methyl isobutyl ketone system the tip of the feed device was kept submerged in a beaker of methyl isobutyl ketone between

runs. This solvent was in equilibrium with a rather large amount of feed which had accumulated while making the necessary trial measurements of drop size and formation time. Hence little or no extraction occurred out of the opening in the tip while it remained submerged in the beaker of solvent. Even if extraction had occurred, the tip was flushed out with several milliliters of fresh feed before making the next run. This should insure no dilution of the feed due to a premature extraction from the tip.

When using the perchlorethylene - acetic acid - water system, the tip was kept submerged in a beaker of water between runs. However in this case the acetic acid is so much more soluble in the water than in the perchlorethylene that appreciable extraction occurred through the opening in the tip. However, the tip was flushed with several milliliters of feed before the next run and hence the feed concentration from the tip should have been standard. Nevertheless, poor checks in the amount of extraction were obtained at a given column height. When the tip was kept submerged in its own feed solution (perchlorethylene plus acetic acid), consistent results were obtained. The errors probably were due to this extraction from the tip between runs. Even though the tip was flushed out with several milliliters of fresh feed, it is possible that flow through the entire length of the tip merely flushed out the center portion of the tip leaving some diluted feed in the tip to eventually be fed into the column.

A study of the formation of the drops revealed that there was a definite limit on the drop formation time for most systems. With the methyl isobutyl ketone-acetic acid - water system and the perchlorethylene - acetic acid - water system, it was observed that when the drop formation time was increased above a certain value, a tiny trailer drop was formed directly behind the larger drop. From the standpoint of the experimental work, these secondary drops are very undesirable and must be avoided. The approximate maximum formation time permissible with the two systems mentioned above was three-fourths of a second. To operate in a safe range, drop formation times of about one-half second were used. The drop formation time had to be short enough to prevent secondary drop formation but long enough to permit accurate counting of the individual drops. No secondary drop formation was observed with the carbon tetrachloride - oil - acetic acid - water system.

Although tip design determines the ultimate size of the drop, other factors limited the drop size with the methyl isobutyl ketone system. The interfacial tension between methyl isobutyl ketone saturated with water and water was relatively small. This was noticed by observing the foaming which occurred on shaking a mixture of the two phases in a bottle. This low interfacial tension evidently resulted in the drops having had a tendency to stick to the glass of the column if conditions were favorable. It was

noticed that when the drops left the tip they had a rather erratic type of motion but definitely followed a curved path for a distance of about two inches from the tip. Beyond this distance the drops fell rather calmly. With the methyl isobutyl ketone system, the smaller size acetic acid - water drops actually curved into the wall of the column and stuck there. Hence it became necessary to limit the size of the drops to the smallest size which showed no tendency to curve all the way into the wall and stick.

This curving motion of the drop immediately after leaving the tip was thought to be due to the tip design. A thorough investigation of the tip design showed that all types of tips produced drops which had a definite curved path after leaving the tip. This curvature could have been caused in two ways. First, the curvature of path could be due to the interior of the drop acquiring a definite uniform rotation in a particular direction during formation. Then on starting to fall through the continuous phase the drop would tend to curve (much like a thrown baseball) until this definite direction of rotation was unbalanced. The second cause could be due to the fact that when a drop falls from a tip, the drop initially "pancakes" out due to the sudden resistance offered by the continuous phase. This pancaked shaped drop may then tend to "slide off" the perpendicular path. That is, the drop would tend to take the path of least resistance which would not be in the direction of the flattened out surface of the drop. When the drop

contacts and oscillates about a spherical position, it can then fall in a relatively vertical path.

With the perchlorethylene - acetic acid - water system and the carbon tetrachloride - oil - acetic acid - water system this curving action was not so great and the drops did not reach the wall of the column. The fact that the curving action was not so pronounced in these latter two systems may add weight to the second reason given above for the drops curving. The increased interfacial tension of these latter two systems resulted in small amplitude oscillations of the drops and hence less curving motion caused by the flattened drop sliding off to one side.

TABLE 2

System: Methyl Isobutyl Ketone - Acetic Acid - Water
Continuous Phase: Methyl Isobutyl Ketone (saturated with water)
Dispersed Phase: Acetic Acid - Water (saturated with ketone)
Drop Diameter (avg.): 0.294 cm.
Number of Drops: 100
Column: No. I
Acetic Acid: 0.8123 N
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
1	1.34	3.0	0.58	0.60	25.8	6.74	30.90	
2	1.31	3.0	0.58	0.55	26.0	6.55	31.30	
3	1.36	3.0	0.58	0.68	26.0	6.78	31.51	31.24
4	1.33	6.0	1.15	0.55	25.8	6.01	37.92	
5	1.34	6.0	1.15	0.77	26.0	5.99	38.59	38.26
6	1.34	9.0	1.70*	0.65	26.0	5.29	45.76	
7	1.33	9.0	1.73	0.73	26.0	5.18	46.49	46.13
8	1.33	14.0	2.69		25.8	4.25	56.10	
9	1.33	14.0	2.69	0.66	26.0	4.30	55.58	55.84
10	1.34	19.0	3.70*	0.60	25.8	3.46	64.53	
11	1.31	19.0	3.65	0.55	25.8	3.46	63.72	
12	1.35	19.0	3.65	0.65	25.0	3.38	65.62	64.62
13	1.34	25.0	4.80	0.65	25.8	2.70	72.32	
14	1.33	25.0	4.80	0.62	25.0	2.72	71.90	72.11
15	1.34	30.0	5.76	0.72	25.8	2.32	76.21	
16	1.34	30.0	5.76	0.63	25.0	2.25	76.93	76.57
17	1.32	35.0	6.72*	0.55	25.8	1.92	80.01	
18	1.35	35.0	6.72	0.64	25.0	1.96	80.06	80.04

(continued)

Table 2 (continued)

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
19	1.35	41.0	7.86	0.63	25.8	1.63	83.41	
20	1.31	41.0	7.86	0.55	26.2	1.76	81.54	
21	1.32	41.0	7.86	0.56	28.0	1.64	82.93	
22	1.35	41.0	7.86	0.66	25.0	1.59	83.82	82.93
23	1.32	50.0	9.53*	0.45	25.8	1.42	85.22	
24	1.33	50.0	9.60	0.58	26.2	1.42	85.33	85.28

*Experimental values. Other fall times obtained from plot.

TABLE 3

System: Methyl Isobutyl Ketone - Acetic Acid - Water
Continuous Phase: Methyl Isobutyl Ketone (saturated with water)
Dispersed Phase: Acetic Acid - Water (saturated with ketone)
Drop Diameter (avg.): 0.355 cm.
Number of Drops: 50
Column: No. I
Acetic Acid: 0.8123 N
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
25	1.16	0.5	0.10	0.48	27.5	7.70	8.81	
26	1.17	0.5	0.10	0.48	27.5	7.79	8.52	8.67
27	1.18	1.0	0.20	0.48	27.5	7.49	12.79	
28	1.18	1.0	0.20	0.48	27.5	7.05	17.91	15.35
29	1.17	2.0	0.41	0.48	27.5	6.61	22.38	
30	1.18	2.0	0.41	0.48	27.5	6.80	20.82	21.60
31	1.19	3.0	0.61	0.48	27.5	6.51	24.84	
32	1.19	3.0	0.61	0.48	27.5	6.43	25.76	
33	1.17	3.0	0.61	0.48	24.5	6.55	23.09	
34	1.18	3.0	0.61	0.48	23.5	6.44	25.02	24.68
35	1.17	6.0	1.22	0.48	24.5	5.68	33.30	
36	1.17	6.0	1.22	0.47	24.5	5.71	32.95	33.13
37	1.18	9.0	1.83	0.48	24.5	5.27	38.64	
38	1.17	9.0	1.83	0.47	24.5	5.19	39.06	38.85
39	1.17	14.0	2.85	0.47	24.5	4.42	48.10	
40	1.18	14.0	2.85	0.46	24.5	4.37	49.12	48.61
41	1.18	19.0	3.87	0.47	24.5	3.68	57.15	
42	1.17	19.0	3.87	0.47	24.5	3.73	56.20	56.68
43	1.17	25.0	5.09	0.47	24.5	3.10	63.59	
44	1.17	25.0	5.13*	0.47	24.5	3.13	63.25	63.42

Table 3 (continued)

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
45	1.17	30.0	6.11	0.47	24.0	2.75	67.71	
46	1.17	30.0	6.11	0.46	25.2	2.67	68.64	68.18
47	1.16	35.0	7.13	0.46-	24.0	2.27	73.12	
48	1.18	35.0	7.13	0.46	25.2	2.23	74.03	73.58
49	1.16	41.0	8.35	0.47	24.0	1.90	77.50	
50	1.18	41.0	8.38*	0.46	25.2	1.88	78.11	77.81
51	1.16	50.0	10.19	0.47	24.0	1.54	81.76	
52	1.17	50.0	10.08*	0.47	25.2	1.66	80.50	81.13

*Experimental values. Other fall times obtained from plot.

TABLE 4

System: Methyl Isobutyl Ketone - Acetic Acid - Water
Continuous Phase: Methyl Isobutyl Ketone (saturated with water)
Dispersed Phase: Acetic Acid - Water (saturated with ketone)
Drop Diameter (avg.): 0.419 cm.
Number of Drops: 50
Column: No. I
Acetic Acid: 0.8123 N
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
53	1.92	0.5	0.11	0.30	26.0	13.02	6.84	
54	1.92	0.5	0.11	0.40	26.0	12.58	9.98	8.41
55	1.92	1.0	0.21	0.35	26.0	12.35	11.62	
56	1.94	1.0	0.21	0.34	26.0	12.16	13.88	12.75
57	1.93	2.0	0.43	0.36	26.0	12.16	13.43	
58	1.92	2.0	0.43	0.35	26.0	11.90	14.85	14.14
59	1.92	3.0	0.55*	0.32	26.0	11.24	19.57	
60	1.94	3.0	0.64	0.33	26.0	11.58	18.00	
61	1.92	3.0	0.64	0.42	24.5	11.24	19.56	19.04
62	1.90	6.0	1.20*	0.40	25.7	10.08	27.12	
63	1.90	6.0	1.28	0.40	25.7	9.92	28.27	
64	1.92	6.0	1.28	0.42	24.5	9.89	29.23	28.21
65	1.94	9.0	1.80*	0.40	25.7	9.22	34.70	
66	1.91	9.0	1.93	0.40	25.7	8.89	36.06	
67	1.93	9.0	1.93	0.42	24.5	9.06	35.50	35.42
68	1.90	14.0	3.00	0.40	25.7	7.69	44.40	
69	1.92	14.0	2.90*	0.42	24.5	7.86	43.75	
70	1.92	14.0	3.00	0.42	25.0	7.98	42.89	43.68
71	1.90	19.0	4.06	0.42	24.5	6.66	51.84	
72	1.92	19.0	4.06	0.42	25.0	6.87	50.83	

(continued)

Table 4 (continued)

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
73	1.92	19.0	4.06	0.42	25.0	6.95	50.26	
74	1.93	19.0	4.01*	0.42	25.0	6.89	50.95	
75	1.92	19.0	4.06	0.42	25.0	6.75	51.70	51.12
76	1.95	25.0	5.35	0.35	25.8-	5.82	59.00	
77	1.93	25.0	5.27*	0.38	25.8	5.62	60.00	
78	1.87	25.0	5.35	0.42	24.0	5.94	56.35	
79	1.92	25.0	5.35	0.42	24.0	5.70	59.21	
80	1.92	25.0	5.38*	0.42	24.5	5.86	58.06	58.52
81	1.94	30.0	6.41	0.35	25.8	5.04	64.31	
82	1.93	30.0	6.41*	0.45	25.8	5.02	64.27	64.29
83	1.94	35.0	7.49	0.35	26.2	4.50	68.13	
84	1.91	35.0	7.44*	0.45	26.2	4.41	68.28	
85	1.92	35.0	7.49	0.42	24.5	4.40	68.51	
86	1.94	35.0	7.49	0.42	25.0	4.45	68.49	68.35
87	1.94	41.0	8.76	0.45	26.0	3.87	72.59	
88	1.94	41.0	8.76	0.35	26.0	3.81	73.02	
89	1.91	41.0	8.81*	0.42	24.5	3.80	72.66	72.76
90	1.93	50.0	10.60*	0.35	26.0	3.11	77.86	
91	1.93	50.0	10.70	0.35	26.0	3.12	77.79	
92	1.93	50.0	10.70	0.42	24.5	3.33	76.29	77.31

*Experimental values. Other fall times obtained from plot.

TABLE 5

System: Methyl Isobutyl Ketone - Acetic Acid - Water
Continuous Phase: Methyl Isobutyl Ketone (saturated with water)
Dispersed Phase: Acetic Acid - Water (saturated with ketone)
Drop Diameter: 0.295 cm.
Number of Drops: 100
Column: No. II
Acetic Acid: 0.8123 N
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall* Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
93	1.35	6.0	1.15	0.54	25.5	6.97	29.06	
94	1.33	6.0	1.15	0.53	25.5	6.80	29.76	29.41
95	1.34	12.0	2.30	0.54	25.5	4.95	49.25	
96	1.34	12.0	2.30	0.53	25.5	4.69	51.92	50.59
97	1.35	18.5	3.55	0.53	25.5	4.12	58.07	
98	1.35	18.5	3.55	0.53	25.5	3.99	59.39	58.73
99	1.34	24.0	4.61	0.52	25.5	3.70	62.07	
100	1.33	24.0	4.61	0.52	25.5	3.61	62.71	62.39
101	1.35	36.0	6.91	0.52	25.5	2.04	79.24	
102	1.33	36.0	6.91	0.52	25.5	2.21	77.18	78.21

*Fall times read from plot of data in Table 2.

TABLE 6

System: Methyl Isobutyl Ketone - Acetic Acid - Water
Continuous Phase: Methyl Isobutyl Ketone (saturated with water)
Dispersed Phase: Acetic Acid - Water (saturated with ketone)
Drop Diameter: 0.354 cm.
Number of Drops: 50
Column: No. II
Acetic Acid: 0.8123 N
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall* Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
103	1.15	6.0	1.22	0.48	25.8	6.73	19.59	
104	1.15	6.0	1.22	0.47	25.8	6.74	19.47	19.53
105	1.15	12.0	2.44	0.48	25.8	5.36	35.96	
106	1.15	12.0	2.44	0.47	25.8	5.38	35.72	35.84
107	1.17	18.5	3.76	0.48	25.8	4.45	47.75	
108	1.16	18.5	3.76	0.47	25.8	4.38	48.13	47.94
109	1.15	24.0	4.89	0.48	25.8	3.67	56.15	
110	1.15	24.0	4.89	0.47	25.8	3.65	56.40	56.28
111	1.15	36.0	7.33	0.46	25.8	2.55	69.53	
112	1.16	36.0	7.33	0.47	25.8	2.57	69.56	69.55

*Fall times read from plot of data in Table 3.

TABLE 7

System: Methyl Isobutyl Ketone - Acetic Acid - Water
Continuous Phase: Methyl Isobutyl Ketone (saturated with water)
Dispersed Phase: Acetic Acid - Water (saturated with ketone)
Drop Diameter: 0.418 cm.
Number of Drops: 50
Column: No. II
Acetic Acid: 0.8123 N
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall* Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
113	1.92	6.0	1.28	0.42	25.5	11.61	16.92	
114	1.90	6.0	1.28	0.42	25.5	11.52	16.70	16.81
115	1.90	12.0	2.57	0.42	25.5	9.99	27.76	
116	1.90	12.0	2.57	0.42	25.5	10.11	26.90	27.33
117	1.94	18.5	3.96	0.42	25.5	8.25	41.58	
118	1.92	18.5	3.96	0.42	25.5	8.27	40.82	41.20
119	1.93	24.0	5.14	0.42	25.5	7.02	50.03	
120	1.90	24.0	5.14	0.42	25.5	6.98	49.53	49.78
121	1.96	35.0	7.49	0.42	25.5	5.29	62.92	
122	1.93	35.0	7.49	0.42	25.5	5.20	62.98	62.95

*Fall times read from plot of data in Table 4.

TABLE 8

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter:(avg.): 0.209 cm.
Number of Drops: 200
Column: No. II
Acetic Acid - Perchlorethylene: 0.9267 N
Standard Base: 0.0278 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
123	0.97	7.0	1.11	0.50	23.8	8.95	72.32	
124	0.97	7.0	1.11	0.51	23.8	8.94	72.36	72.34
125	0.92	13.0	2.07	0.50	25.0	4.52	85.26	
126	0.91	13.0	2.07	0.50	25.0	4.41	85.46	85.36
127	0.97	18.0	2.86	0.51	23.8	3.73	88.46	
128	0.97	18.0	2.86-	0.51	23.8	3.68	88.62	88.54
129	0.92	25.0	3.97	0.51	25.0	2.37	92.27	
130	0.91	25.0	3.97	0.50	25.0	2.45	91.92	92.10
131	0.97	31.0	4.93	0.51	23.8	2.12	93.45	
132	0.97	31.0	4.93	0.51	23.8	2.13	93.41	93.43
133	0.97	43.0	6.83	0.52	24.0	1.69	94.77	
134	0.98	43.0	6.83	0.53	24.0	1.70	94.79	94.78
135	0.98	55.0	8.74	0.50	24.0	1.33	95.93	
136	0.98	55.0	8.74	0.50	24.0	1.33	95.93	95.93
137	0.99	66.0	10.49	0.51	25.0	1.03	96.88	
138	0.99	66.0	10.49	0.51	25.0	1.03	96.88	96.88

19.5" Fall time = 3.04 sec.
45.0" Fall time = 7.15 sec.

Velocity = 6.29 in./sec.

TABLE 9

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter: 0.212 cm.
Number of Drops: 200
Column: No. II
Acetic Acid: Perchlorethylene - 0.8879N(average)
Standard Base: 0.0278 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
139	0.97	7.0	1.10	0.51	23.5	8.40	72.89	
140	0.97	7.0	1.10	0.52	23.5	8.69	71.95	72.42
			(1.00 ml. Acid Req'd.			31.80 ml. Base)		
141	1.03	13.0	2.05	0.56		5.30	83.89	
142	1.00	13.0	2.05	0.54		5.22	83.66	83.78
143	1.00	18.0	2.84	0.53	24.0	3.79	88.13	
144	1.00	18.0	2.84	0.52		3.88	87.85	87.99
145	1.00	25.0	3.94	0.53		2.70	91.54	
146	1.00	25.0	3.94	0.53		2.63	91.77	91.66
			(0.50 ml. Acid Req'd.			15.92 ml. Base)		
147	1.00	31.0	4.89	0.53		2.07	93.52	
148	1.00	31.0	4.89	0.53		2.06	93.55	93.54
149	1.00	43.0	6.79	0.53		1.52	95.24	
150	1.00	43.0	6.79	0.53		1.46	95.43	95.34
			(0.50 ml. Acid Req'd.			16.01 ml. Base)		

(continued)

Table 9 (continued)

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
151	1.05	55.0	8.68	0.55		1.18	96.48	
152	1.00	55.0	8.68	0.54		1.10	96.55	96.52
153	1.00	66.0	10.41	0.54		0.83	97.40	
154	1.00	66.0	10.41	0.54		0.85	97.34	97.37

(0.50 ml. Acid Req'd. 16.05 ml. Base)

20.0" Fall time = 3.15 sec.
45.0" Fall time = 7.10 sec.

Velocity = 6.34 in./sec.

TABLE 10

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter (avg.): 0.288 cm.
Number of Drops: 100
Column: No. II
Acetic Acid - Perchlorethylene: 0.9267 N
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
155	1.27	7.25	0.99	0.58	24.9	4.03	61.79	
156	1.25	7.25	0.99	0.57	24.9	3.99	61.56	61.68
157	1.25	13.0	1.78	0.54	24.8	2.50	75.92	
158	1.24	13.0	1.78	0.55	24.8	2.53	75.43	75.68
159	1.25	18.25	2.50	0.58	24.9	1.87	81.98	
160	1.23	18.25	2.50	0.56	24.9	1.91	81.29	81.64
161	1.24	25.0	3.43	0.56	24.8	1.55	84.94	
162	1.24	25.0	3.43	0.59	24.8	1.55	84.94	84.94
163	1.24	31.0	4.25	0.58	24.8	1.26	87.76	
164	1.24	31.0	4.25	0.66	24.8	1.23	88.05	87.91
165	1.24	43.0	5.89	0.62	24.9	0.89	91.36	
166	1.24	43.0	5.89	0.60	24.9	0.92	91.06	91.21
167	1.24	55.0	7.54	0.65	24.9	0.65	93.69	
168	1.23	55.0	7.54	0.73	24.9	0.61	94.03	93.86
169	1.25	66.5	9.12	0.62	24.9	0.55	94.70	
170	1.25	66.5	9.12	0.57	24.9	0.50	95.18	
171	1.25	66.5	9.12	0.57	24.8	0.58	94.41	94.76
172	1.25	79.0	10.83	0.54	24.8	0.48	95.37	
173	1.25	79.0	10.83	0.55	24.8	0.47	95.47	95.47

19.5" Fall time = 2.67 sec.
45.0" Fall time = 6.17 sec.
Velocity = 7.29 in./sec.

TABLE 11

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter: 0.289 cm.
Number of Drops: 100
Column: No. II
Acetic Acid - Perchlorethylene: 0.9271N (average)
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
174	1.25	7.0	0.95	0.57	24.8	4.08	60.71	
175	1.25	7.0	0.95	0.53	24.8	4.15	60.04	60.38
176	1.27	13.0	1.77	0.52		2.51	76.21	
177	1.26	13.0	1.77	0.53		2.58	75.35	75.78
			(0.9 ml. Acid Req'd. 7.47 ml. Base)					
178	1.27	18.0	2.46	0.52		2.00	81.04	
179	1.24	18.0	2.46	0.53		1.92	81.36	81.20
180	1.26	25.0	3.41	0.54		1.50	85.67	
181	1.26	25.0	3.41	0.55		1.49	85.76	85.72
			(0.9 ml. Acid Req'd. 7.46 ml. Base)					
182	1.28	31.0	4.23	0.54		1.28	87.97	
183	1.27	31.0	4.23	0.53		1.28	87.87	87.92
184	1.26	43.0	5.86	0.53		0.96	90.83	
185	1.27	43.0	5.86	0.54		0.95	91.00	90.92
186	1.27	55.0	7.50	0.54		0.75	92.89	
187	1.27	55.0	7.50	0.54		0.72	93.17	93.03
			(0.9 ml. Acid Req'd. 7.50 ml. Base)					

(continued)

Table 11 (continued)

Run No.	Vol. acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
188	1.27	66.0	9.00	0.55		0.51	95.17	
189	1.27	66.0	9.00	0.55		0.51	95.17	95.17

45.0" Fall time = 6.14 sec.

Velocity = 7.33 in./sec.

TABLE 12

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter: 0.323 cm.
Number of Drops: 75
Column: No. II
Acetic Acid - Perchlorethylene: 0.9300 N (average)
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
190	1.33	7.0	0.93	0.51	25.5	5.17	53.35	
191	1.32	7.0	0.93	0.52	25.5	5.05	54.09	53.72
			(0.9 ml. Acid Req'd.		7.52 ml.	Base)		
192	1.32	18.0	2.40	0.53	25.5	2.45	77.73	
193	1.33	18.0	2.40	0.52	25.5	2.38	78.53	78.13
			(0.9 ml. Acid Req'd.		7.51 ml.	Base)		
194	1.33	25.0	3.33	0.51	25.5	1.81	83.67	
195	1.33	25.0	3.33	0.50	25.5	1.81	83.67	83.67
196	1.33	31.0	4.12	0.50	25.5	1.54	86.10	
197	1.34	31.0	4.12	0.50	25.5	1.51	86.48	86.29
198	1.33	43.0	5.72	0.51	25.5	1.11	89.98	
199	1.32	43.0	5.72	0.54	25.5	1.13	89.73	89.86
			(0.9 ml. Acid Req'd.		7.44 ml.	Base)		
200	1.33	55.0	7.31	0.53	25.5	0.86	92.24	
201	1.32	55.0	7.31	0.53	25.5	0.77	93.00	92.62

(continued)

Table 12 (continued)

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
202	1.32	66.0	8.78	0.53	25.5	0.63	94.27	
203	1.32	66.0	8.78	0.53	25.5	0.59	94.64	94.46

(0.9 ml. Acid Req'd. 7.53 ml. Base)

45.0" Fall time = 5.99 sec.

Velocity = 7.51 in./sec.

TABLE 13

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter (avg.): 0.335 cm.
Number of Drops: 75
Column: No. II
Acetic Acid - Perchlorethylene: 0.9176 N
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
204	1.51	7.0	0.93	0.53	25.5	6.07	51.11	
205	1.53	7.0	0.93	0.53	25.5	5.77	54.13	52.62
206	1.51	13.0	1.72	0.53	25.5	3.88	68.75	
207	1.52	13.0	1.72	0.53	25.5	3.76	69.92	69.34
208	1.52	18.0	2.38	0.53	25.5	2.97	76.23	
209	1.52	18.0	2.38	0.53	25.5	2.87	77.04	76.64
210	1.51	25.0	3.31	0.53	25.5	2.57	79.30	
211	1.49	25.0	3.31	0.52	25.5	2.32	81.06	80.18
212	1.50	31.0	4.10	0.53	25.5	1.95	84.19	
213	1.50	31.0	4.10	0.53	25.5	1.88	84.76	84.48
214	1.51	43.0	5.69	0.52	25.5	1.47	88.16	
215	1.51	43.0	5.69	0.53	25.5	1.47	88.16	88.16
216	1.50	55.0	7.27	0.53	25.5	1.28	89.63	
217	1.50	55.0	7.27	0.53	25.5	1.24	89.94	89.79
218	1.52	66.0	8.73	0.53	25.5	0.82	93.44	
219	1.52	66.0	8.73	0.53	25.5	0.88	92.96	93.20

19.5" Fall time = 2.64 sec.
45.0" Fall time = 5.95 sec.

Velocity = 7.56 in./sec.

TABLE 14

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter: 0.338 cm.
Number of Drops: 75
Column: No. II
Acetic Acid - Perchlorethylene: 0.9216 N (average)
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
220	1.53	7.0	0.92	0.52	25.0	6.15	51.33	
221	1.52	7.0	0.92	0.53	25.0	5.97	52.43	51.88
			(0.9 ml. Acid Req'd. 7.44 ml. Base)					
222	1.53	13.0	1.71	0.53	25.0	3.90	69.13	
223	1.51	13.0	1.71	0.53	25.0	3.90	68.73	68.93
224	1.51	18.0	2.37	0.53	25.0	2.99	76.02	
225	1.51	18.0	2.37	0.53	25.0	2.93	76.50	76.26
			(0.9 ml. Acid Req'd. 7.42 ml. Base)					
226	1.51	25.0	3.29	0.53	25.0	2.29	81.63	
227	1.51	25.0	3.29	0.53	25.0	2.19	82.44	
228	1.51	25.0	3.29	0.53	25.0	2.20	82.36	82.14
229	1.51	31.0	4.08	0.53	25.0	1.97	84.20	
230	1.51	31.0	4.08	0.53	25.0	1.86	85.08	84.64
231	1.52	43.0	5.66	0.53	25.0	1.44	88.53	
232	1.51	43.0	5.66	0.53	25.0	1.44	88.45	88.49
			(0.9 ml. Acid Req'd. 7.44 ml. Base)					

(continued)

Table 14 (continued)

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
233	1.51	55.0	7.24	0.53	25.0	1.14	90.86	
234	1.51	55.0	7.24	0.53	25.0	1.12	91.02	90.94
235	1.51	66.0	8.69	0.53	25.0	0.90	92.79	
236	1.51	66.0	8.69	0.53	25.0	0.89	92.86	92.83
			(0.9 ml. Acid Req'd. 7.43 ml. Base)					
237	1.51	79.0	10.40	0.53	25.0	0.59	95.27	
238	1.51	79.0	10.40	0.53	25.0	0.58	95.35	95.31

45.0" Fall time = 5.92 sec.

Velocity = 7.60 in./sec.

TABLE 15

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter: 0.394 cm.
Number of Drops: 50
Column: No. II
Acetic Acid - Perchlorethylene: Used average of normalities before and after series of runs.
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
239	1.64	7.0	0.91	0.50	25.0	6.59	50.52	
240	1.63	7.0	0.91	0.51		6.60	50.13	50.23
			(1.0 ml. Acid Req'd.		6.12 ml.	Base (0.9062 N)		
241	1.59	18.0	2.34	0.52		3.35	74.08	
242	1.59	18.0	2.34	0.53		3.29	74.55	74.32
			(1.0 ml. Acid Req'd.		6.14 ml.	Base (0.9084 N)		
243	1.60	25.0	3.25	0.53		2.53	80.36	
244	1.60	25.0	3.25	0.52		2.51	80.51	80.44
245	1.57	31.0	4.03	0.51		1.92	84.51	
246	1.57	31.0	4.03	0.54		1.94	84.65	84.58
			(1.0 ml. Acid Req'd.		7.96 ml.	Base (0.8883 N)		
247	1.59	43.0	5.59	0.54		1.36	89.33	
248	1.60	43.0	5.59	0.55		1.34	89.56	89.45
			(1.0 ml. Acid Req'd.		8.08 ml.	Base (0.9017 N)		

(continued)

Table 15 (continued)

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
249	1.62	55.0	7.15	0.54		0.95	92.77	
250	1.54	55.0	7.15	0.51		0.89	92.88	92.83
251	1.61	66.0	8.58	0.54		0.78	94.03	
252	1.61	66.0	8.58	0.55		0.78	94.03	94.03

(1.0 ml. Acid Req'd. 8.15 ml. Base (0.9056 N)

45.0" Fall time = 5.85 sec.

Velocity = 7.69 in./sec.

TABLE 16

System: Perchlorethylene - Acetic Acid - Water
Continuous Phase: Water (saturated with Perchlorethylene)
Dispersed Phase: Acetic Acid - Perchlorethylene
Drop Diameter: 0.395 cm.
Number of Drops: 50
Column: No. II
Acetic Acid - Perchloretnylene: Used average of normalities before and after series of runs
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
253	1.62	7.0	0.91	0.52	25.2	6.66	49.13	
254	1.61	7.0	0.91	0.53	25.2	6.60	49.28	49.21
255	1.60	13.0	1.70	0.53	25.2	4.38	66.13	
256	1.60	13.0	1.70	0.53	25.2	4.30	66.75	66.44
			(0.9 ml. Acid Req'd.			7.17 ml. Base (0.8891 N)		
257	1.61	18.0	235	0.53	25.2	3.37	74.10	
258	1.61	18.0	2.35	0.53	25.2	3.30	74.64	74.37
			(1.0 ml. Acid Req'd.			8.07 ml. Base (0.9006 N)		
259	1.62	25.0	3.26	0.54	25.2	2.45	81.29	
260	1.62	25.0	3.26	0.55	25.2	2.49	80.98	81.14
			(1.0 ml. Acid Req'd.			8.03 ml. Base (0.8961 N)		
261	1.60	31.0	4.05	0.54	25.2	1.87	85.54	
262	1.61	31.0	4.05	0.53	25.2	1.87	85.63	85.59
263	1.61	43.0	5.61	0.54	25.2	1.25	90.39	
264	1.61	43.0	5.61	0.53	25.2	1.29	90.08	90.24
			(1.0 ml. Acid Req'd.			8.24 ml. Base (0.9196 N)		

(continued)

Table 16 (continued)

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
265	1.62	55.0	7.19	0.54	25.2	0.97	92.59	
266	1.61	55.0	7.19	0.53	25.2	0.91	93.00	92.80
		(1.0 ml. Acid Req'd. 8.10 ml. Base (0.9040 N)						
267	1.63	66.0	8.62	0.53	25.2	0.75	94.31	
268	1.60	66.0	8.62	0.53	25.2	0.71	94.51	94.41
		(1.0 ml. Acid Req'd. 8.20 ml. Base (0.9151 N)						

45.0" Fall time = 5.88 sec.

Velocity = 7.66 in./sec.

TABLE 17

System: Carbon Tetrachloride - Oil - Acetic Acid - Water
Continuous Phase: Water (saturated with carbon tetrachloride and oil)
Dispersed Phase: Carbon Tetrachloride - Oil - Acetic Acid
Drop Diameter (avg.): 0.237 cm.
Number of Drops: 200
Column: No. II
Dispersed Phase: 0.5063 N (average)
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
			(1.00 ml. acid feed required 4.60 ml. base)					
269	1.38	7.0	1.78	0.99	26.0	4.49	28.28	
270	1.38	7.0	1.78	0.99	26.0	4.43	29.24	28.76
271	1.39	13.0	3.31	1.01	26.0	3.72	41.01	
272	1.38	13.0	3.31	1.00	26.0	3.75	40.10	40.56
273	1.38	18.0	4.59	1.00	26.0	3.40	45.70	
274	1.38	18.0	4.59	1.00	26.0	3.42	45.37	45.54
			(1.00 ml. acid feed required 4.52 ml. base)					
275	1.38	25.0	6.36	0.99	26.0	3.14	49.85	
276	1.38	25.0	6.36	1.00	26.0	3.18	49.21	49.53
277	1.38	31.0	7.90	1.00	26.0	3.00	52.08	
278	1.37	31.0	7.90	0.99	26.0	3.00	51.73	51.91
279	1.38	43.0	10.98	0.99	26.0	2.89	53.84	
280	1.38	43.0	10.98	0.99	26.0	2.91	53.51	53.68
281	1.38	55.0	14.01	0.99	26.0	2.83	54.80	
282	1.44	55.0	14.01	1.07	24.6	2.99	54.23	
283	1.39	55.0	14.01	0.92	26.0	2.86	54.65	54.56
284	1.43	66.0	16.82	0.97	26.0	2.91	55.14	55.14
			(1.00 ml. acid feed required 4.49 ml. base)					

8.0" Fall time = 1.86 sec
45.0" Fall time = 11.48 sec.
Velocity = 3.92 in./sec.

TABLE 18

System: Carbon Tetrachloride - Oil - Acetic Acid - Water
Continuous Phase: Water (saturated with carbon tetrachloride and oil)
Dispersed Phase: Carbon Tetrachloride - Oil - Acetic acid
Drop Diameter: 0.309 cm.
Number of Drops: 100
Column: No. II
Dispersed Phase: 0.5000 N (average)
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
285	1.55	7.0	1.49	1.08	24.0	5.70	17.92	
286	1.51	7.0	1.49	0.97	24.0	5.60	17.22	17.57
287	1.54	13.0	2.78	0.97	24.0	4.98	27.82	
			(1.00 ml acid feed required 4.48 ml. base)					
288	1.55	13.0	2.78	0.96	24.0	5.02	27.72	27.77
289	1.55	18.0	3.84	0.99	24.0	4.63	33.33	
290	1.55	18.0	3.84	0.99	24.0	4.64	33.19	33.26
291	1.53	25.0	5.33	0.97	24.0	4.24	38.14	
292	1.55	25.0	5.33	1.03	24.0	4.30	38.08	38.11
293	1.55	31.0	6.62	0.97	24.0	4.09	41.11	
			(1.00 ml. acid feed required 4.48 ml base)					
294	1.54	31.0	6.62	0.97	24.0	4.04	41.44	41.28
295	1.55	43.0	9.17	1.00	24.0	3.90	43.85	
296	1.55	43.0	9.18	1.01	24.0	3.95	43.12	43.49
297	1.54	55.0	11.73	0.96	24.0	3.81	44.78	
298	1.55	55.0	11.73	1.00	24.0	3.83	44.85	44.82
299	1.55	66.0	14.10	1.02	24.0	3.80	45.28	
300	1.55	66.0	14.10	1.02	24.0	3.80	45.28	45.28
			(1.00 ml. acid feed required 4.48 ml. base)					

45.0" Fall time = 9.60 sec.
Velocity = 4.69 in./sec.

TABLE 19

System: Carbon Tetrachloride - Oil - Acetic Acid - Water
Continuous Phase: Water (saturated with carbon tetrachloride and oil)
Dispersed Phase: Carbon Tetrachloride - Oil - Acetic Acid
Drop Diameter: 0.373 cm.
Number of Drops: 50
Column: No. II
Dispersed Phase: 0.5015 N (average)
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
301	1.35	7.0	1.36	0.94	24.2	5.21	14.12	
302	1.35	7.0	1.36	0.98	24.2	5.23	13.78	13.95
			(1.00 ml. acid feed required 4.51 ml. base)					
303	1.35	13.0	2.52	0.98	24.2	4.73	22.02	
304	1.35	13.0	2.52	0.99	24.2	4.77	21.37	21.70
305	1.35	18.0	3.48	0.99	24.2	4.50	25.82	
306	1.36	18.0	3.48	1.00	24.2	4.49	26.52	26.17
307	1.36	25.0	4.84	0.99	24.2	4.24	30.62	
308	1.36	25.0	4.84	0.99	24.2	4.10	32.90	31.76
309	1.36	31.0	6.00	0.99	24.2	4.04	33.89	
			(1.00 ml. acid feed required 4.48 ml. base)					
310	1.36	31.0	6.00	1.00	24.2	4.11	32.74	33.31
311	1.36	43.0	8.33	0.99	24.2	3.89	36.35	
312	1.36	43.0	8.33	0.99	24.2	3.87	36.67	36.51
313	1.35	55.0	10.63	1.00	24.2	3.82	37.03	
314	1.38	55.0	10.63	1.00	24.2	3.89	37.28	37.16
315	1.36	66.0	12.78	1.00	24.2	3.77	38.31	
316	1.36	66.0	12.78	0.99	24.2	3.80	37.82	38.07
			(1.00 ml. acid feed required 4.49 ml. base)					

8.0" Fall time = 1.51 sec.
45.0" Fall time = 8.71 sec.
Velocity = 5.16 in./sec.

TABLE 20

System: Carbon Tetrachloride - Oil - Acetic Acid - Water
Continuous Phase: Water (saturated with carbon tetrachloride and oil)
Dispersed Phase: Carbon Tetrachloride - Oil - Acetic Acid
Drop Diameter (avg.): 0.423 cm.
Number of Drops: 40
Column: No. II
Dispersed Phase: 0.5050 N (average)
Standard Base: 0.1116 N

Run No.	Vol. Acid Fed (ml.)	Column Height (inches)	Fall Time (sec)	Formation Time (sec.)	Temp. (°C.)	Vol. Base Required (ml.)	Percent Extracted	Average Percent Extracted
317	1.60	7.0	1.29	0.98	25.0	6.26	13.54	
318	1.59	7.0	1.29	0.98	25.0	6.11	15.08	14.31
			(1.00 ml. acid feed required 4.52 ml. base)					
319	1.59	18.0	3.32	1.00	25.0	5.39	25.09	
320	1.58	18.0	3.32	0.92	25.0	5.45	23.77	24.43
321	1.60	25.0	4.60	1.01	25.0	5.21-	28.04	
322	1.58	25.0	4.60	0.95	25.0	5.20	27.27	27.66
			(1.00 ml. acid feed required 4.54 ml. base)					
323	1.58	31.0	5.71	0.98	25.0	5.04	29.50	
324	1.59	31.0	5.71	0.99	25.0	5.04	29.95	29.73
325	1.59	43.0	7.92	1.01	25.0	4.85	32.59	
326	1.60	43.0	7.92	1.01	25.0	4.87	32.74	32.67
			(1.00 ml. acid feed required 4.53 ml. base)					
327	1.59	55.0	10.12	0.97	25.0	4.74	34.12	
328	1.59	55.0	10.12	0.98	25.0	4.72	34.40	34.26
329	1.60	66.0	12.18-	0.99	25.0	4.58	36.75	
330	1.58	66.0	12.18	1.00	25.0	4.68	34.54	
331	1.59	66.0	12.18	0.96	25.0	4.71	34.55	35.28
			(1.00 ml. acid feed required 4.51 ml. base)					

20.0" Fall time = 3.67 sec.
45.0" Fall time = 8.29 sec.
Velocity = 5.43 in./sec.

ADDENDUM

It should be pointed out that in deriving equation (7), the volumetric feed rate was eliminated by replacing its value in terms of the drop diameter and drop formation time. This leads one to conclude that the extraction in Stage I is proportional to the one-half power of the drop formation time, other things being equal. However, this elimination was arbitrary and the drop diameter could have been eliminated just as well. The resulting equation in terms of the volumetric feed rate and drop formation time leads one to conclude that the extraction during drop formation is proportional to the one-sixth power of the drop formation time, other things being equal. Mathematically, both forms are correct; however for determining the effect of variables one of the three variables, volumetric feed rate, drop diameter, or drop formation time, should be held constant during the experimental work. In this investigation, for runs at various drop sizes, all three variables were varied. Hence, the equation cannot be checked other than by calculating absolute values of the amount of extraction during Stage I.