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APPLICATION OF RADIOACTIVE TRACERS
IN THE STUDY OF DIFFUSIONAL PHENOMENA

BY

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A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

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ABSTRACT

The study of mass transfer of a solute through a solvent can be greatly facilitated by the use of radioactive tracers.

This experiment was developed to demonstrate that by using radioactive tracers very small quantities of matter that would be very difficult to test chemically, can not only be tested but easily followed without disturbing the apparatus in which the diffusion is taking place.

Oleic Acid tagged with radioactive iodine (I^{131}) was diffused through hexane at constant temperature in a glass column, one inch in diameter and thirty-six inches long.

The diffusion of Oleic Acid was followed by measuring its concentration through its radioactivity at various sections of the column, three inches apart at various intervals.

The results obtained were plotted: concentration at various sections against time. A value of the diffusivity of Oleic Acid in hexane was calculated from data obtained in the early part of the experiment and compared to a theoretical value: the experimental diffusivity is 8.93×10^{-6} cm²/sec, the theoretical value is 13.8×10^{-6} cm²/sec. At later stages of the experiment the data did not seem to indicate true diffusion and was probably adversely affected by factors such as eddy currents caused by inadequate temperature control.

Experiments conducted to study diffusivity between two phases from single drops are also reported in the appendix of this report. Oleic Acid tagged with I^{131} dissolved in a mixture of methanol and glycerol was passed dropwise through a column filled with hexane. The hexane was sampled at various levels and tested for Oleic Acid content through its radioactivity. The technique developed appeared to be satisfactory, but no conclusive results were obtained.

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APPLICATION OF
RADIOACTIVE TRACERS
IN THE STUDY OF
DIFFUSIONAL PHENOMENA

INTRODUCTION

The object of this study is to demonstrate how the use of radioactive tracers can facilitate the study of molecular diffusion in liquids, and to show the advantages of the apparatus and the technique developed over more common methods presently used.

There is hardly a chemical process which does not include as an essential part the transfer of one substance through another, therefore an intimate knowledge of the mechanism of diffusional phenomena and of the quantitative relationship of the factors which control them is of tremendous importance in the solution of many chemical engineering problems.

The transfer of matter from one phase to another or from one point of the same phase to another, can take place by two separate mechanisms: transfer by molecular diffusion and transfer by eddy diffusion. Eddy diffusion occurs in turbulent regions, and is much more rapid than molecular diffusion which occurs through a fluid which is stagnant or in laminar flow. Eddy diffusion is characterized by the bulk transfer of matter often under the driving force of mechanical means; molecular diffusion is characterized by the slow transfer of individual molecules. Both phenomena are encountered at the same time in most chemical processes. Since the molecular diffusion is by far the slowest, it is the controlling factor. It is therefore of tremendous importance to be able

to isolate molecular diffusion from eddy diffusion and make a separate study of it to obtain intimate knowledge of its mechanism.

It is a difficult task to create conditions under which no eddy currents of any nature are present and only molecular diffusion takes place. The major difficulty after convection due to temperature difference and all mechanical disturbances have been eliminated, arises from testing. Many tricks and techniques have been devised. In general, concentrations at different zones of a liquid are determined by sampling and analysis after the diffusion has occurred, or optical or similar means are used by which the course of diffusion is followed without disturbing the liquid. Some experiments become real complex, time consuming and the results obtained only through theoretical assumptions and elaborate calculations.

To eliminate some of the difficulties, apparatus like the following have been devised:

- a. Cohen and Bruins (1) constructed a column by placing several plates in contact with each other, each with a hole through it. A column is formed by lining up the holes. A concentrated solution placed in the hole of one plate can be rotated into contact with the solvent, so creating a minimum of disturbance. At the end of the experiment, various sections of the column can be sampled with a minimum of disturbance by simply slicing them.

- b. Other investigators have resorted to the use of gels to eliminate eddy currents and facilitate the task of sampling.
- c. An elaborate method by which variation in the refractive index can be followed to measure diffusion in volatile liquids systems, the Mach-Zelnder Interferometer, is reported in the October, 1957 Issue (2) of Review of Scientific Instruments.
- d. "Most studies have dealt with fully developed turbulent systems."(3) In these systems molecular diffusion is considered across an inter-
face stagnant film, the area and thickness of which is calculated from the nature of the flow and size and type of equipment used. Concentration differences can be measured at various sections by sampling the two phases.

Without elaborating on their shortcomings, the above mentioned experiments emphasize the need of a better tool in the study of molecular diffusion.

I believe that the biggest problem, testing, can be entirely eliminated by the use of radioactive tracers. Experiments can be set up by which the concentration can be measured accurately at anytime, at any section without ever disturbing the process and without elaborate procedures. It seems strange that with the ever larger use being made of radioisotopes in every field of science and technology, so few applications are found to the study of diffusion. Recent publications (4) show that the "diaphragm cell", and the "capillary cell" are the most popular

devices for measuring diffusivity in liquids, and that a very novel technique developed is the "Carr-Purcell Spin-Echo Method".

Radioisotopes are neither expensive nor dangerous when properly used. Since radioisotopes became available for civilian use in the mid 1940's medicine has made a tremendous use of tracer technique as has industry, agriculture and research. Isotopes are available on the market in various chemical forms, or as pure elements; only applications and techniques have to be developed.

Two examples of applications of radioisotopes to the study of mass transfer are mentioned here:

The first was published by the Atomic Energy of Canada Limited in September 1952 (5). An apparatus is described for studying mass transfer in liquid - liquid extraction under conditions of concentration equilibrium. A small amount of Fe^{59} was dissolved in a solution of ferric chloride in HCL which had previously been contacted with isopropyl ether. The HCL was then passed downward in a spray column and the ether bubbled up. Activity was transferred from one phase to another due to the dynamic equilibrium existing between them. The amount of activity transferred was a measure of the mass transfer coefficient.

The second was published by Helvetic Chemica Acta in 1958 (6). A method for measuring diffusion coefficients in liquids is described. The diffusing substance is radioactively tagged. During the experiment

it diffuses from the bottom of a vessel toward a Geiger-Muller tube. From the total number of counts registered as a function of time, a time lag is determined. The value of the diffusion coefficient is calculated from the time lag and from the thickness of the diffusing medium.

A literature search has revealed that publications on the application of radioactive tracers to the study of mass transfer seem rather scarce. It is the objective of this paper to show that there is a tremendous tool on hand and that it can be sharpened to create that intimate knowledge of mass transfer which is needed. It is a safe, easy to use, and very efficient tool. A straightforward non-complex technique can be developed.

II

EXPERIMENTAL PROCEDURE

This experiment was designed so the rate of diffusion of a solute through a solvent could be followed by periodically measuring the concentration at different sections of the solvent without ever disturbing the apparatus in which the diffusion is taking place. This was accomplished by using a solute tagged with a radioactive element so its concentration could be measured through its activity from a distance. Oleic Acid with I^{131} added to the double bond (Oleotope I^{131} , one of E. R. Squibb and Sons Radiopharmaceutical Products) was used as the diffusing solute. Hexane was used as the diffusing medium.

Apparatus.

The apparatus designed for this purpose consists of: (See Fig. 1)

- a. Glass Column (1" i.d., 3' long)
- b. Glass ampule (about 18 ml)
- c. Rubber tubing with a screw clamp to connect the ampule with the column.
- d. Lead barrier made of $3/4"$ x $3"$ x $6"$ lead bricks stacked one on top of the other and held in place by a wooden rack. A $3/16"$ slot is created between the bricks by placing a small wooden block under both ends of every brick. Through these slots radiation can be measured at every $3-3/16"$ section of the column.
- e. Probe consisting of:
 1. 1" Lead shell

2. Scintillation detector (NaI crystal which converts incident radiation into photons of visible light.
 3. Photomultiplier tube (visible light is converted into bursts of electrons, and these electrons are subsequently multiplied).
- f. Scaler - (electrical pulses are further multiplied and resolved into digital units).

Temperature Control: The temperature is controlled within 1°C.

The column is installed in a corner of a well insulated but not heated room. A well insulated box (1.5' x 1.5' x 3.5') is built around the column with aluminum foil backed by fiber glass. A small electric heating element is placed at the bottom of the box and controlled by a thermostat. The temperature is read on a mercury glass thermometer inserted through a rubber stopper used to seal the top of the column.

Procedure.

The oleic Acid used consisted of a mixture of about 1% Oleic Acid tagged with I^{131} and the rest pure material.

The first step was to determine a relationship between scaler counts and concentration. A solution was prepared of 2 ml of Oleic Acid (about 125 micro-curies) and 248 ml of Hexane, and placed in the column. The column was clamped in a position as close to the lead barrier as possible and not moved from that position until the end of the experiment. The probe was moved from section to section and held in fixed

position on the same wooden rack used for the lead barrier. From this time through the end of the experiment the relative position of the probe to the column remained unchanged for each section. Readings were taken at each section for two minutes. (Readings were always taken for two minutes, so the work "counts" actually stands for "Counts per two minutes".)

Readings of about 7000 counts were obtained for each section of the column. Counts vary greatly with the distance from the probe to the column, the dimensions and shape of the slots, the alignment and view of the column from the crystal. Though much care was taken to minimize these effects, it was found that different counts were obtained for the various sections, varying as much as 15%. A correction factor had to be developed for each section. Section C was chosen as the standard section. The correction factor was calculated as follows: 7000 counts at section C, 6140 counts at section D: $7000/6140 = 1.14$. Section E, for instance, had a correction factor of 0.876; all other sections had factors varying from 0.95 to 1.03. These factors were used throughout the experiment.

At this point the column was drained and rinsed with fresh hexane. The ampule was filled with a solution made of 5.8 ml. of Oleic Acid and 12 ml. of hexane; it was installed in place with the clamp closed. Mercury was poured through a rubber tubing into the bottom of the column to a level half way between sections B and C. Then the column was filled

with Hexane to a level half way between sections J and K.

The temperature control set for 27 C was turned on and about half hour allowed for the column to reach the temperature of the surroundings.

At this point the screw clamp was opened and about 10 mls of Mercury allowed to flow down into the ampule, while the Oleic Acid-Hexane solution moved in its place. So by creating a minimum of disturbance a highly concentrated solution was placed in contact with its solvent. Readings were immediately taken at each section and thereafter as often as possible for fifteen days.

At this point it became clear that the solute was evenly distributed throughout the column. Fresh mercury was poured into the bottom of the column to its original level. The experiment was repeated by displacing The remaining Oleic Acid solution from the ampule into the bottom of the column. Counts were taken for five days at 27°C.

At this point the temperature was cut down to 19°C and held for eight days.

At this point the temperature was again raised to 27°C and held for four days.

At this point the activity was evenly distributed throughout the column and the experiment ended.

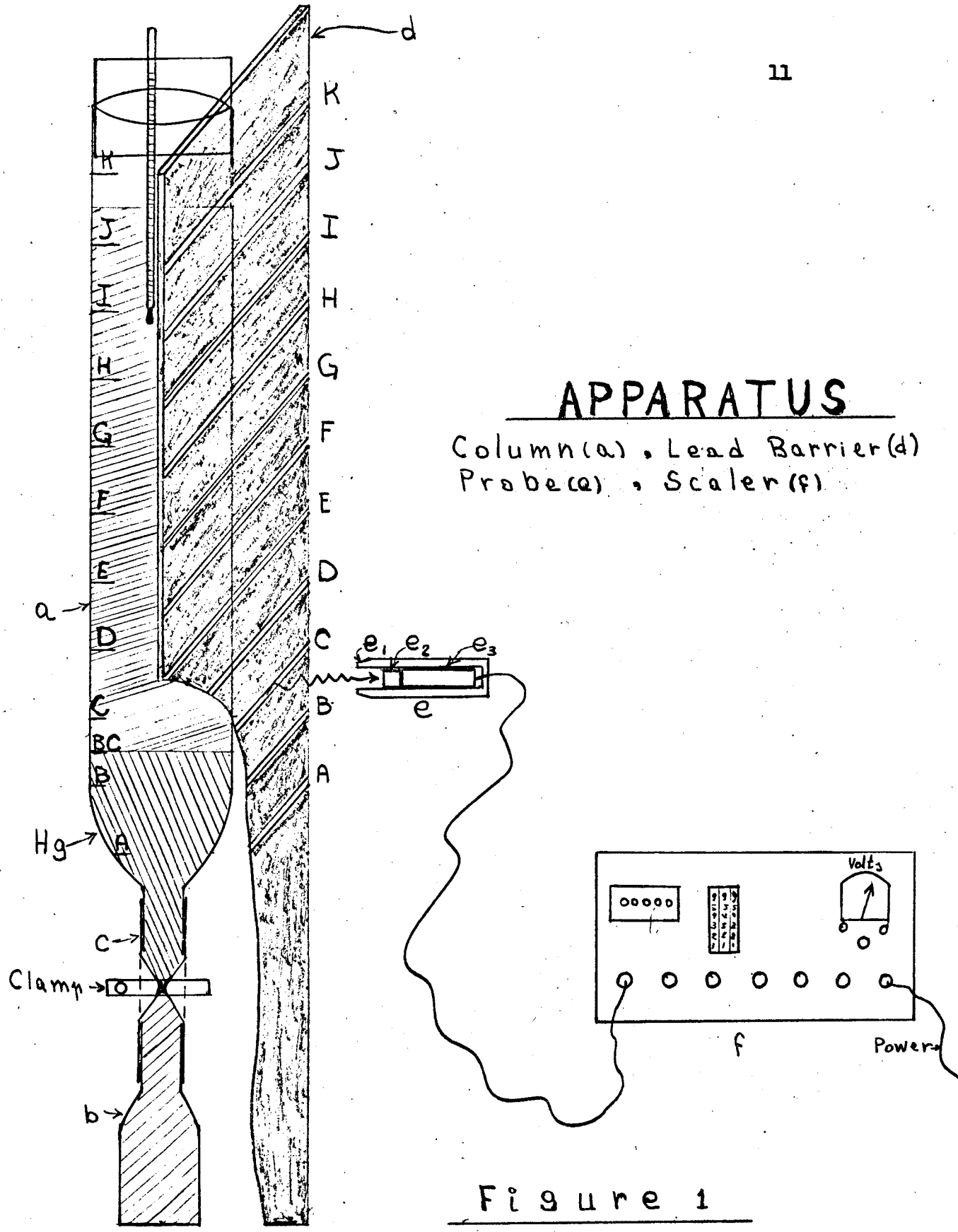


Figure 1

III

CALCULATION AND PRESENTATION OF RESULTS

All counts taken at each section of the column are handled as follows:

1. Background is subtracted from the gross count. Background is considered the count taken at Section K; this section is 1.5 inches above the solution level. A background count is taken every time the regular counts are taken.
2. The net count is multiplied by the section correction factor. Calculation of this factor is described in the previous chapter.
3. This count is then corrected to zero time by dividing by the I^{131} decay factor for the number of hours in question.
4. The corrected counts are converted into mls. of Oleic Acid per ml. of solution by multiplying them by a concentration factor. The concentration factor is determined as follows. The standard solution prepared at the beginning had $\frac{2}{250}$ $\frac{\text{ml. Oleic Acid}}{\text{ml. solution}}$ and it gave 7023 net counts at reference section C at zero time.

$$\frac{2}{250} \frac{\text{ml. oil}}{\text{ml. sol.}} \times \frac{1}{7023 \text{ cnt.}} = 1.14 \times 10^{-6} \frac{\text{ml. oil}}{\text{ml. sol.} \times \text{cnt.}}$$

An example will best illustrate these calculations.

Example: Section E, 468 hours.

<u>Time</u> <u>Hours</u>	<u>Gross</u> <u>Counts</u>	<u>Background</u> <u>Counts</u>	<u>Net</u> <u>Counts</u>	<u>Sect. Correct-</u> <u>ion Factor</u>	<u>Decay</u> <u>Factor</u>	<u>Counts Cor-</u> <u>rected to</u> <u>Zero Time</u>
468	2940	425	2515	0.876	0.1900	11,580

$$11,580 \text{ cnt.} \times 1.14 \times 10^{-6} \frac{\text{ml. oil}}{\text{ml. sol.} \times \text{cnt.}} = 1.32 \times 10^{-2} \frac{\text{ml. oil}}{\text{ml. sol.}}$$

An experimental value of the diffusivity has been calculated for the beginning of the experiment and compared to a theoretical value of the diffusivity for the same system.

Experimental Diffusivity.

$$D = \frac{Na \ l}{\Delta \ c}$$

Since the diffusion rate is constant for many hours at the beginning and the increase in concentration uniform throughout the column, Na can be derived as follows:

$$3.7 \times 10^{-5} \frac{\text{ml. oil}}{\text{ml. sol.} \times \text{hr.}} \times 340 \text{ ml. sol.} = 1.26 \times 10^{-2} \frac{\text{ml. oil}}{\text{hr.}}$$

Where 3.7×10^{-5} is the increase in concentration per hour which can be obtained directly from the plots (part 1, figure 2a), 340 ml. is the measured volume of hexane from section C to JK, and 1.26×10^{-2} is the ml.'s of oil that diffuse per hour through section BC - C.

$$1.26 \times 10^{-2} \frac{\text{ml. oil}}{\text{hr.}} \times 0.9 \frac{\text{gm. oil}}{\text{ml. oil}} \times \frac{1}{282} \frac{\text{gm. oil}}{\text{mole oil}} = 4.02 \times 10^{-5} \frac{\text{mole oil}}{\text{hr.}}$$

$$4.02 \times 10^{-5} \frac{\text{m. oil}}{\text{hr.}} \times \frac{1}{3600} \frac{\text{sec}}{\text{hr}} \times \frac{1}{4.9 \text{ cm}^2} = 2.28 \times 10^{-9} \frac{\text{m. oil}}{\text{sec} \times \text{cm}^2}$$

The distance l through which the diffusion takes place, BC to C is 4 cm.

The concentration difference across BC - C is equal to the original concentration in the prepared solution (0.33 ml. oil per ml solution), minus the concentration in C (about .008 ml. oil per ml. solution).

$$\Delta c = 0.32 \frac{\text{ml. oil}}{\text{ml. sol.}} \times 0.9 \frac{\text{gm. oil}}{\text{ml. oil}} \times \frac{1}{282} \frac{\text{gm. oil}}{\text{m. oil}} =$$

$$= 1.02 \times 10^{-3} \frac{\text{mole oil}}{\text{ml. solution}}$$

$$D = \frac{2.28 \times 10^{-9} \frac{\text{mole}}{\text{sec} \times \text{cm}^2} \times 4 \text{ cm}}{1.02 \times 10^{-3} \frac{\text{mole}}{\text{cm}^3}} = 8.93 \times 10^{-6} \frac{\text{cm}^2}{\text{sec}}$$

Theoretical Diffusivity.

A theoretical value of D has been calculated from a diagram reproduced by R. E. Treybal in "Liquid Extraction", first edition, figure 5.2. The original diagram was developed by C. R. Wilke (#7) and it correlates the solutemolal volume with a quantity F through a parameter ϕ .

The molal volume of Oleic Acid can be obtained by Kopp's Law which states that the molal volume is an additive function of the atomic volumes of the constituents of a molecule.

Oleic Acid: $C_{18}H_{34}O_2$

$$V = 18(14.8) + 34(3.7) + 2(12) = 414 \text{ cm}^3/\text{gm. mole}$$

By using a value of ϕ equal to 0.9 as recommended by Treybal, $F \times 10^{-7}$ is equal to 6.9 for a molal volume of $414 \text{ cm}^3/\text{gm. mole}$.

$$F = \frac{T}{D\mu}$$

Where T = Absolute Temperature ($^{\circ}\text{K}$)

D = Diffusivity (cm^2/sec)

μ = Viscosity (centipoises)

$$F = 6.9 \times 10^7 = \frac{T}{D\mu}, \quad D = \frac{T}{\mu} \frac{10^{-7}}{6.9}$$

$$T = 300^{\circ} \text{K}$$

$$\mu = 0.315 \text{ centipoises (8)}$$

$$D = \frac{300 \times 10^{-7}}{0.315 \times 6.9} = 13.8 \times 10^{-6} \text{ cm}^2/\text{sec.}$$

At the end of the experiment two 10 ml samples of solution were taken after mixing the column content, the hexane was evaporated and the residue weighed.

The residue weighed 0.1209 and 0.1277 gms., for an average of 0.01243 gm. of oil per mol. of solution. Since the volume of the entire

solution is about 360 mls:

$$360 \text{ ml.} \times 0.01243 \frac{\text{gm. oil}}{\text{ml. sol.}} \times \frac{1}{0.9} \frac{\text{gm. oil}}{\text{ml. oil}} = 4.89 \text{ ml. oil}$$

The concentration measurements at the end of the experiment showed an average concentration of $0.01468 \frac{\text{ml. oil}}{\text{ml. sol}}$.

$$0.01468 \times 360 = 5.28 \text{ ml. oil.}$$

These two values of the recovered Oleic Acid are compared to the quantity used in the experiment: 5.8 mls. oil. It must be pointed out here that no specific attempt was made to transfer all of the original solution from the ampule to the bottom of the column.

The results of all the readings are presented in terms of mls. of oil per ml. of solution in Table 1, and they are plotted (concentration against time) in figures 2a, 2b, and 2c.

Table 1

CONCENTRATION CHANGE WITH TIME

Time Hours	Temp. °C	Concentration - ml. oil / ml. solution								
		S	D	E	F	G	H	I	J	
0	27	87.0×10^4	9.4×10^4	5.2×10^4	2.4×10^4	2.3×10^4	1.8×10^4	0.6×10^4	0.2×10^4	
0		88.0	10.8	6.2	4.6	—	—	—	—	
0		86.0	—	—	—	—	—	—	—	
10		79.4	14.0	10.6	9.2	7.6	6.6	6.0	6.2	
12		77.6	15.0	11.8	10.4	9.2	—	—	—	
16		78.0	18.4	16.6	15.0	14.0	14.0	11.6	9.6	
20		77.0	22.0	18.4	17.0	16.6	15.0	13.4	11.0	
35		74.6	27.0	24.4	21.6	21.4	19.4	19.0	17.4	
48		74.8	30.0	28.6	26.0	26.6	22.0	22.4	21.0	
59		74.8	33.0	31.4	29.0	28.0	26.0	26.2	—	
72		75.6	40.8	40.0	38.2	36.4	34.6	34.4	33.6	
84		73.0	44.8	44.4	42.0	40.2	38.6	38.8	36.8	
108		73.8	51.2	50.8	48.4	48.0	43.8	43.4	43.0	
132		76.0	60.6	58.8	55.8	55.6	51.6	51.8	50.8	
136		76.2	64.6	62.6	59.8	60.8	56.4	58.0	54.0	
156		76.6	71.2	70.0	70.6	69.2	66.4	65.2	63.2	
165		74.0	77.2	76.4	75.2	71.6	71.6	72.6	70.0	
188		77.2	75.8	77.2	75.0	77.6	72.6	70.2	68.4	
204		74.8	76.0	76.4	—	—	—	—	—	
214	Y	78.4	75.4	78.6	75.2	77.2	72.8	73.0	71.0	

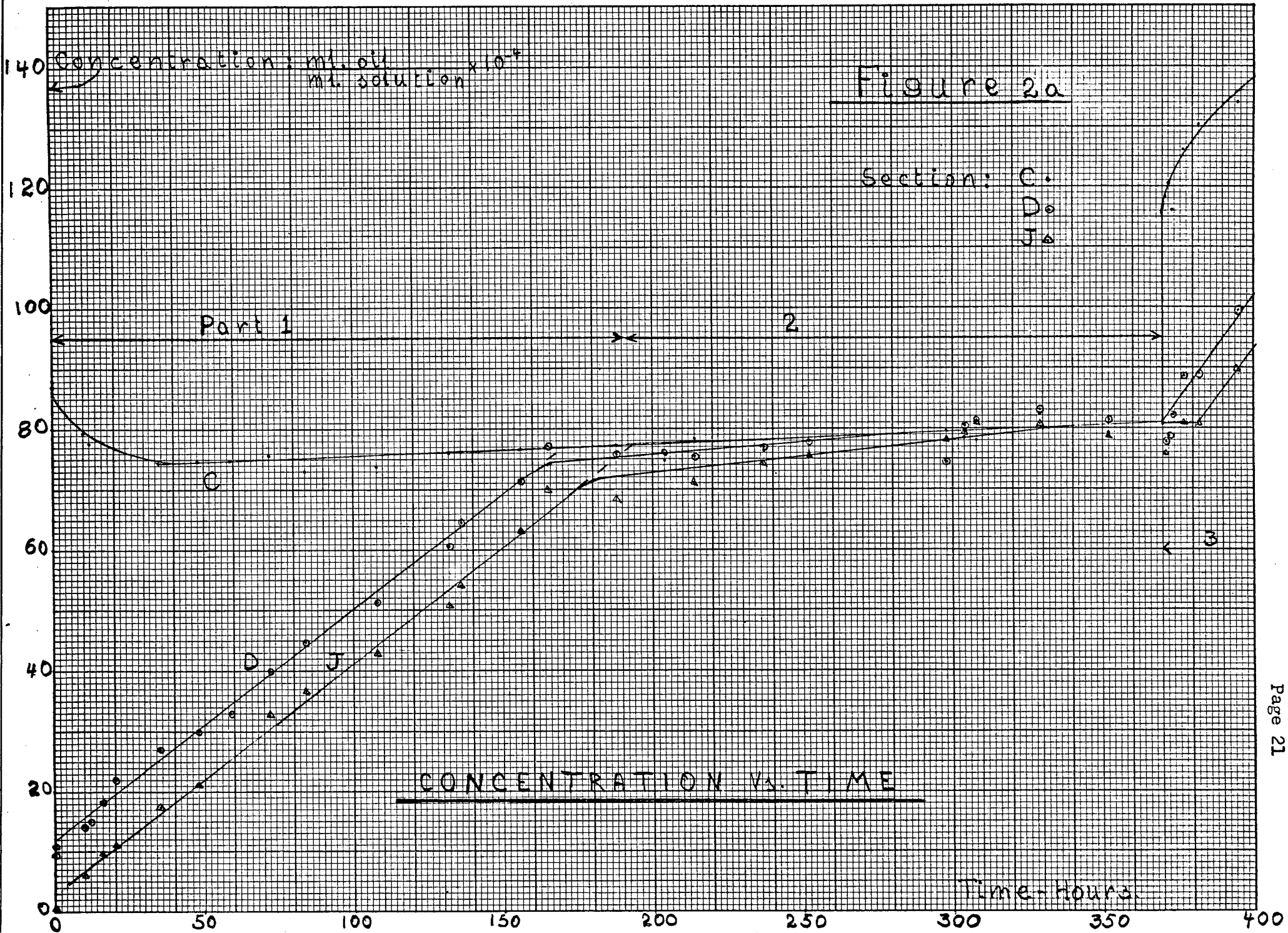
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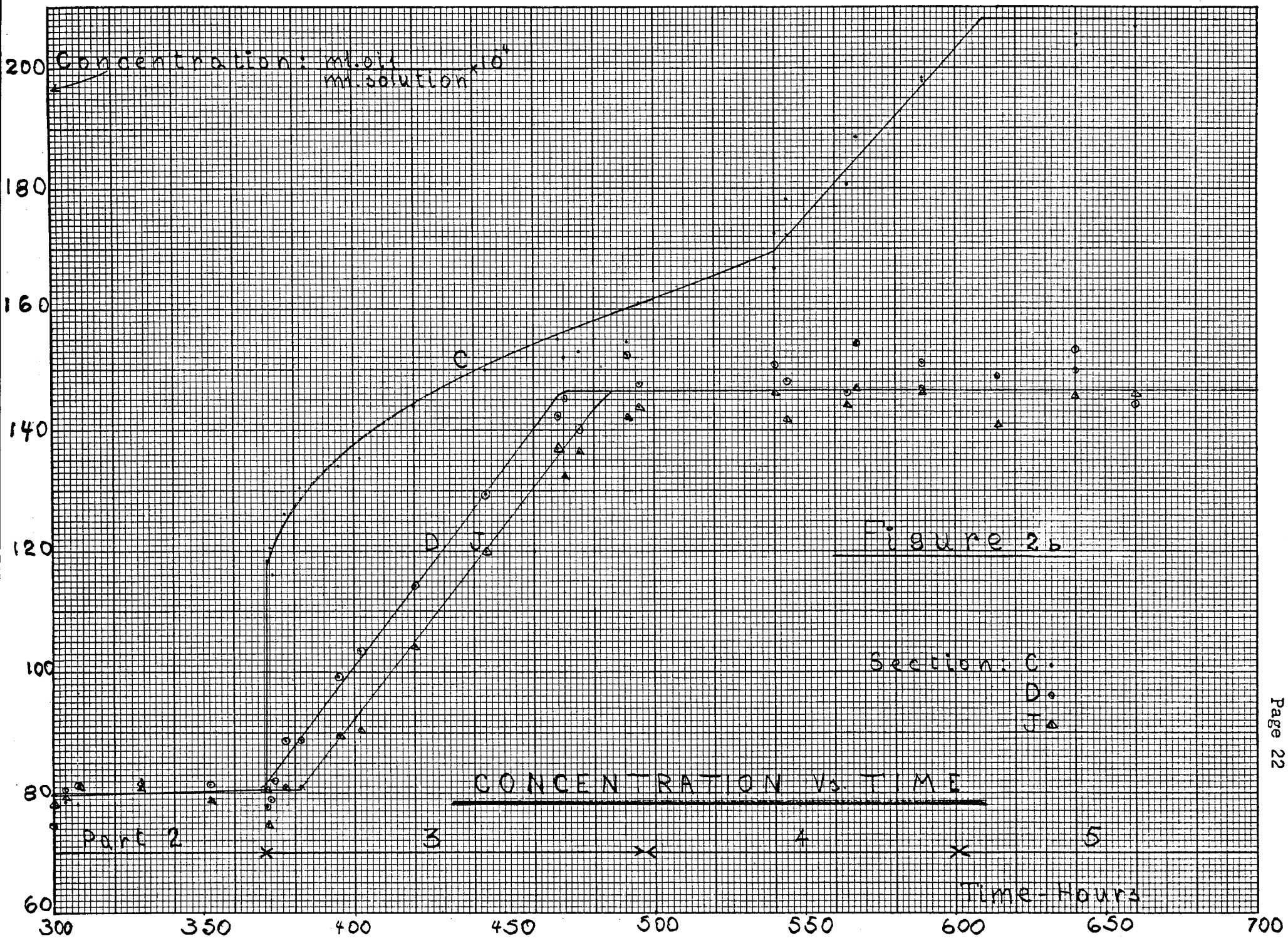
18

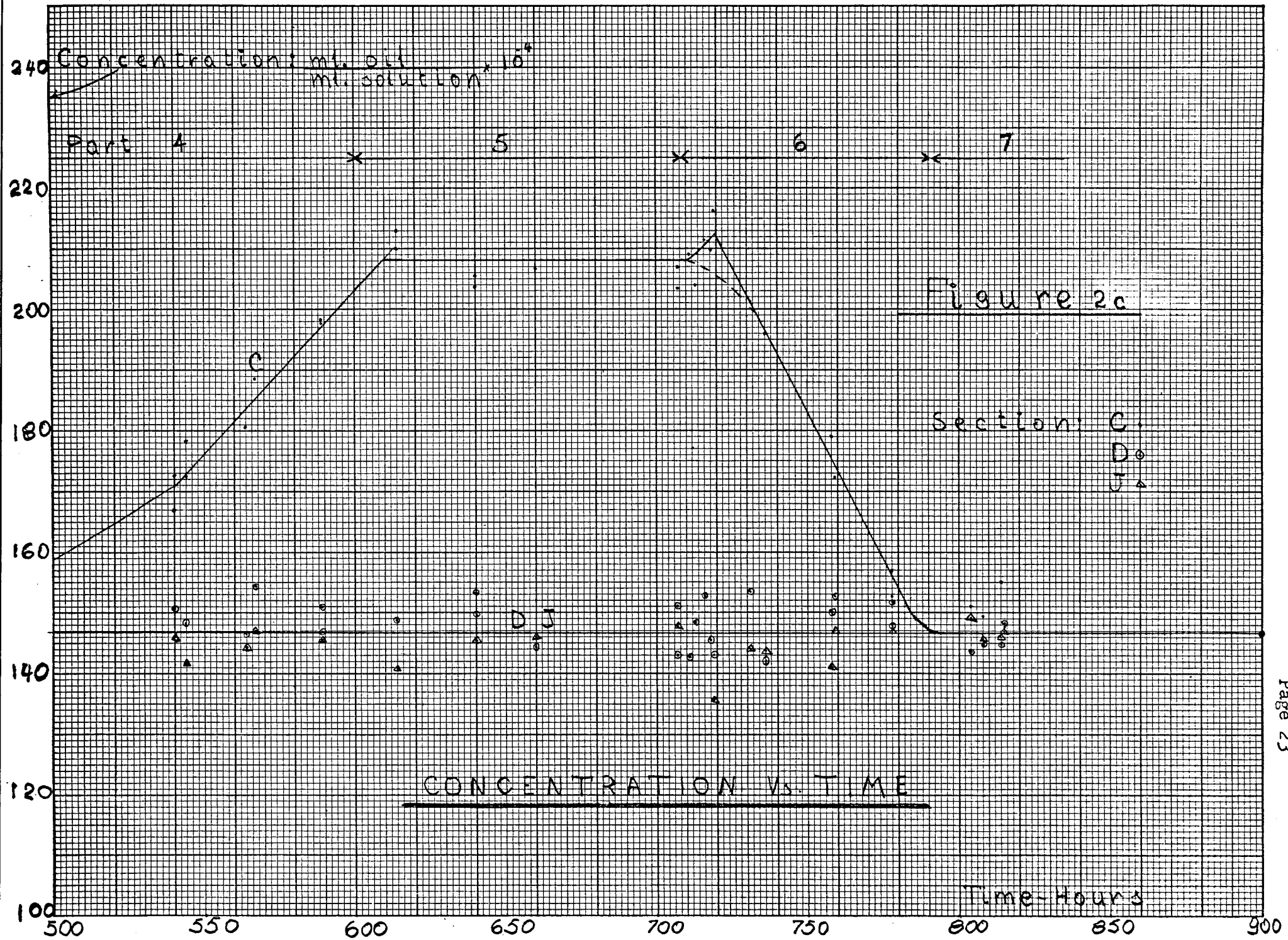
hours	°c	C	D	E	F	G	H	I	J
237	27	76.4×10 ⁴	76.8×10 ⁴	78.0×10 ⁴	76.4×10 ⁴	78.0×10 ⁴	73.0×10 ⁴	74.0×10 ⁴	74.2×10 ⁴
252		75.4	78.0	79.2	77.6	76.4	72.8	73.2	75.2
298		79.8	74.6	79.2	79.0	77.2	75.6	77.0	78.2
304		78.6	80.4	79.8	78.4	79.8	77.0	75.8	79.4
308		78.0	81.2	81.6	76.6	77.6	78.6	79.2	81.2
329		82.4	83.0	83.6	79.6	78.8	77.0	77.4	80.6
352		79.2	81.4	83.6	79.4	79.2	77.4	81.4	79.0
370		80.6	80.6	80.6	80.6	80.6	80.6	80.6	80.6
371		118.4	77.8	75.2	75.6	79.0	76.8	75.4	74.8
372		120.4	78.8	75.2	—	—	—	—	—
373		116.4	82.2	77.2	—	—	—	—	—
377		126.2	88.6	83.2	81.0	81.8	79.4	83.0	81.0
382		130.4	89.0	86.6	81.0	79.6	80.4	81.2	80.8
395		134.0	99.4	95.4	94.8	93.8	90.8	90.0	89.6
402		135.4	105.4	99.0	93.0	96.4	95.0	91.8	90.4
420		144.0	114.4	112.0	110.8	109.0	107.4	107.4	104.2
444		150.0	129.6	131.4	125.4	122.8	115.6	115.6	120.0
468		155.0	142.4	132.0	138.0	137.2	136.8	134.4	137.0
470		152.0	145.2	142.6	132.0	140.0	139.0	139.0	132.2
475		153.0	140.2	143.6	138.4	138.6	136.8	141.0	136.4
491		154.6	152.6	146.8	145.6	143.6	144.0	142.2	142.0
495	Y	161.0	147.6	147.0	144.0	144.8	143.8	140.4	143.6
540	19	167.0	150.6	150.0	—	—	145.2	146.2	146.0

Table 1 cont'd

hours	°C	C	D	E	F	G	H	I	J
540	19	172.8×10 ⁺	—	—	—	—	—	—	—
544		178.4	148.2×10 ⁺	143.6×10 ⁺	139.2×10 ⁺	139.0×10 ⁺	140.2×10 ⁺	140.6×10 ⁺	141.6×10 ⁺
544		172.6	—	—	—	—	—	—	—
564		180.6	146.4	147.6	142.4	143.6	138.0	144.6	144.2
567		188.6	154.6	154.0	147.0	151.0	151.0	148.0	147.0
589		198.4	151.0	150.0	152.2	153.2	143.0	147.6	145.4
589		197.8	146.8	—	149.8	148.0	—	—	—
614		210.0	148.8	151.6	144.4	144.8	139.0	151.0	140.8
614		213.0	—	—	142.2	150.0	—	—	—
640		205.4	153.2	146.4	146.4	150.0	146.6	143.8	145.4
640		203.8	149.8	—	—	—	—	—	—
660		206.8	144.2	156.2	146.8	150.0	143.0	148.2	146.0
707	↓	203.4	143.0	148.8	138.6	139.4	137.4	147.6	147.6
707		207.0	151.0	—	—	—	—	—	—
711	27	209.0	142.6	—	—	—	—	—	—
713		204.0	148.2	—	—	—	—	—	—
716		211.4	152.8	—	—	—	—	—	—
718		209.8	145.4	—	—	—	—	—	—
719		216.6	143.0	140.8	142.8	138.2	134.2	135.6	135.6
731		201.2	153.4	148.2	147.0	147.6	142.6	144.0	144.0
736		196.0	142.0	142.6	138.0	142.0	147.6	143.6	143.6
758		179.0	150.0	144.2	141.4	146.0	144.8	143.8	141.0
759	↓	162.2	153.8	149.4	145.4	147.6	149.4	147.0	147.0







IV

DISCUSSION

No attempt will be made to give any theoretical interpretation of the results, nor to explain them in the light of any theory. More experiments should be conducted before any real conclusions could be drawn. Instead the results obtained will be analyzed and explained so their significance may become clearer. The plots will be sub-divided into seven parts and each part discussed and interpreted separately. A presentation of the type of results expected at the time the experiment was designed will be given to clarify the approach taken and to help explain the results obtained.

Theory Behind The Method

At the time the experiment was designed it was believed that molecular diffusion of a solute through a solvent may take place according to the following mechanism:

As a solute M diffuses through a solvent S, there is always a sharp demarcation line between the solution and the pure solvent. Only pure solvent can be found on one side of the demarcation line, the solution of M in S to be found on the other side. The solution (M + S) is expected to have a concentration gradient varying from almost the original concentration in M at the bottom to zero concentration at the top where it is in contact with pure solvent S. Fig. 3 gives an illustration of this concept.

The experiment was designed so that the course of diffusion could be followed by measuring the concentration of the solution at various

sections of the column at anytime. The results were to be plotted: concentration at each section against time, and concentration at any time against length of the column. The necessary data for the calculation of diffusivity could be obtained from these plots, and also the nature of the diffusion mechanism could be derived from their interpretation.

If diffusion takes place according to the above mechanism, plots similar to Figures 4 and 5 could be expected. An analysis of figure 4 shows that:

1. At time zero, the concentration is zero at all levels.
2. At time t_c the demarcation line has reached the bottom of slot C.
3. At time t_d the demarcation line has reached the bottom of slot D .. and so on.

As time goes on the solute will appear in other sections until it reaches the top of the column (t_j). A concentration gradient is established throughout the column, diffusion will continue to an ever decreasing rate until a uniform distribution is obtained.

Figures 4 and 5 can be plotted from the experimental data and from them the necessary data to calculate the diffusivity can be derived.

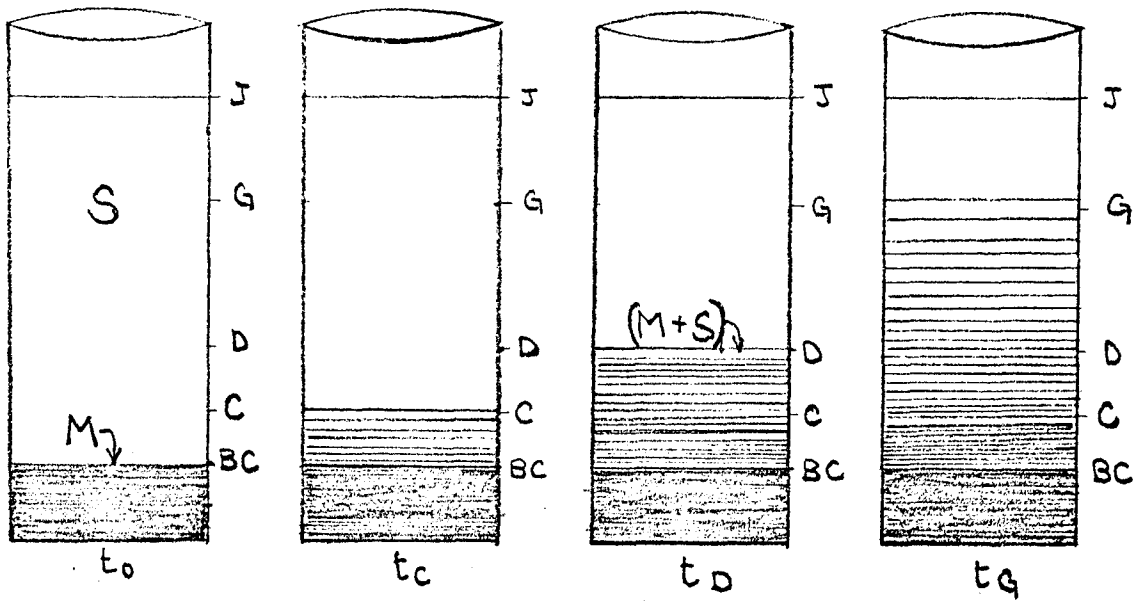


Figure 3: Diffusion of Solute M through Solvent S .

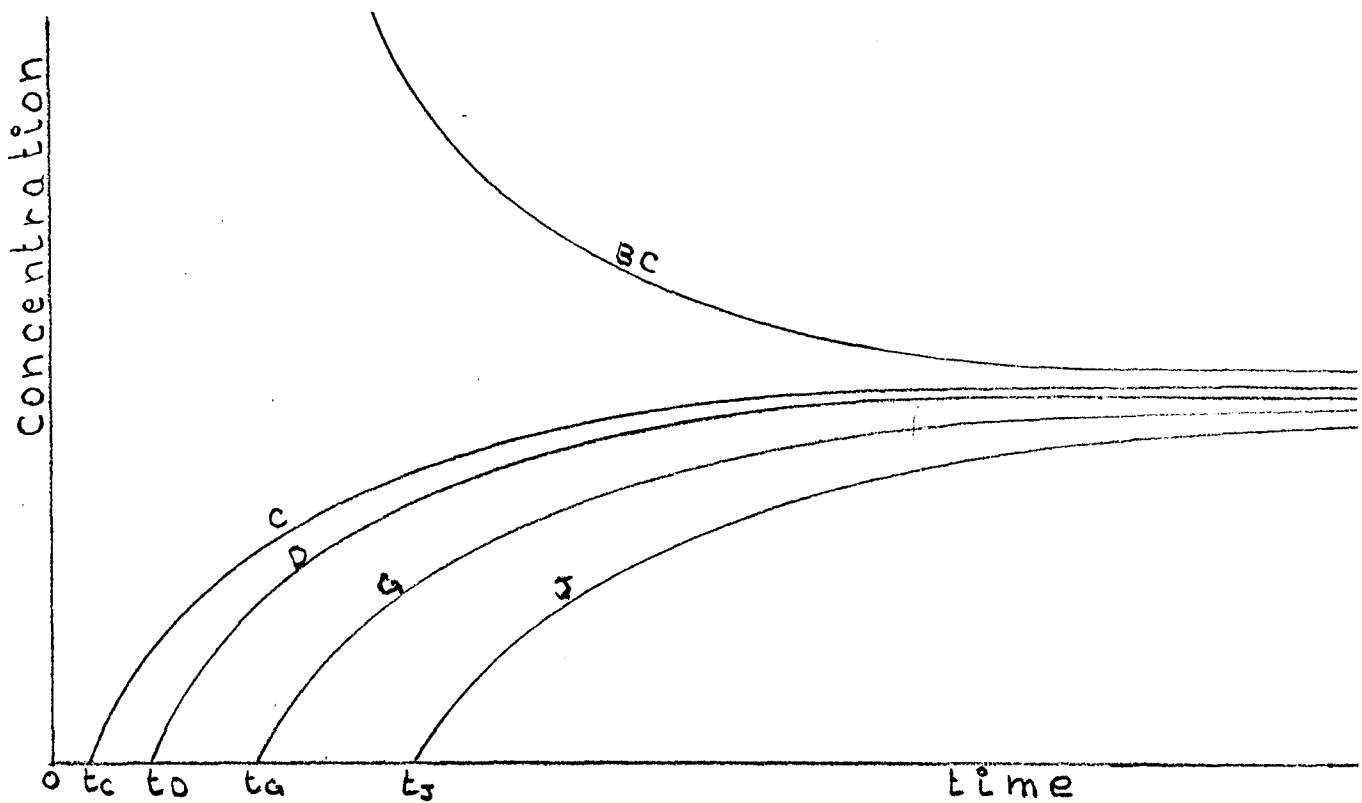


Figure 4: Concentration Vs. Time at Different Column Levels.

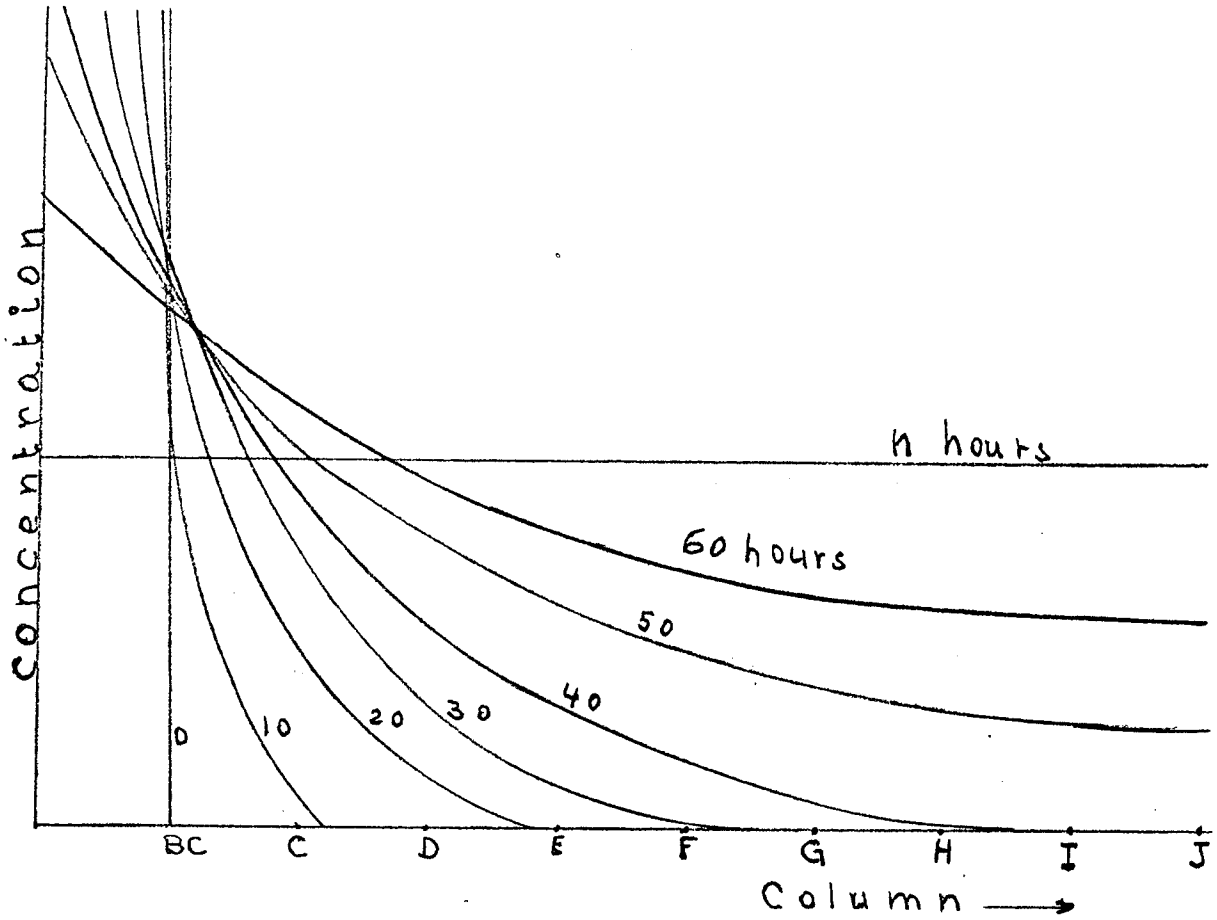


Figure 5: Concentration Vs. Column Length at Different Times.

$$N_a = D \frac{\Delta c}{l}$$

(This formula is a modification of formula 5.13, in "Liquid Extraction" by R. E. Treybal, First Edition.)

Where,

$$N_a \left(\frac{\text{moles}}{\text{sec} \times \text{cm}^2} \right) = \text{moles diffusing per unit time through a unit cross section.}$$

$$l \text{ (cm)} = \text{distance through which diffusion occurs.}$$

$$\Delta c \left(\frac{\text{moles}}{\text{cm}^3} \right) = \text{concentration difference across distance } l$$

$$D \left(\frac{\text{cm}^2}{\text{sec}} \right) = \text{diffusivity}$$

N_a : N_a can be obtained from Figure 5. The area under the curve is the amount of solute in the solution. By calculating the solute content above any chosen section at two chosen times, the amount of solute that diffused through the cross section over that period of time can be obtained.

l : can be chosen as the distance between any two cross sections of the column.

Δc : Concentration at any cross section of the column at any time can be obtained from Figure 4.

Interpretation of the Results

Part 1 : (0 to 190 hours)

An analysis of the plots in this part of the experiment shows that the results do not agree with the results expected at the time the experiment was designed.

The curves for sections D to J are similar to the curves in Figure 4, however they are straight lines for many hours instead of the expected parabolas. The solute diffuses from Section B C at a constant rate instead of at a continuously decreasing rate. Rate would be expected to decrease as the concentration in B C decreases, instead it is uniform for at least 150 to 160 hours, at which time it seems to come down.

Soon after the solute was put in contact with the solvent a concentration gradient was established from one end to the other of the column: a very steep one at the contact end, a very flat one throughout. A small number of molecules soon penetrated the whole system, however, the bulk of the solute remained at the contact end, and it continued to diffuse until a uniform solution was formed. The solute diffused from the contact end into the dilute solution under a high concentration difference, and from one end through the other of the dilute solution under a much smaller concentration gradient.

It is believed that this strange behavior could be explained by the presence of eddy currents caused by small temperature differences. The temperature was controlled within 1°C, and this might not have been enough; also the heating element was situated at a level about 1/4 of the column high, though at least 10 to 12 inches away.

A value of the diffusivity for the period at the very beginning of the experiment was calculated from the obtained data and compared to a theoretical value. The two values of D are of the same order of magnitude,

the experimental results are 64% of the theoretical ones. This value of D was calculated between cross sections B C and C; this is the only section of the column at which a calculation of the diffusivity seems meaningful.

The value of diffusivity across B C - C was calculated by using a value of N_a which was derived from the uniform increase in concentration in the column. Δc was obtained by using a value of the concentration at B C equal to the prepared concentration (one part Oleic Acid, and two parts hexane) minus the measured concentration at section C.

A value of the diffusivity at any other section of the column could not be calculated. A value calculated between sections D and J is about 1000 times higher than a theoretical value; this would substantiate the assumption of the presence of eddy currents above section D. A quick analysis of the results shows that diffusion through cross section D for instance, is about 13/16 of the diffusion through cross section B C, and yet the concentration difference between B C and C is better than 1000 times higher than that between D and E. It seems that the diffusion rate through the column is controlled by the diffusion from section B C.

Another point that remains unexplained is the concentration at Section C: from the very beginning the concentration at this section went up to what turned out to be its final concentration. Maybe a small disturbance at contact time caused eddy diffusion and it was mere coincidence that it turned out to be the same concentration as the final.

However if this was the cause it seems logical to expect that the concentration at C should have soon gone down to a level slightly above the concentration in Section D, and then come up at the same rate as all the other sections in the column. Instead section C seems to act like a transit station only, everything passes through it, but there is no loss of inventory nor accumulation of inventory.

Part 2 : (190 to 370 hours)

During this period no diffusion is taking place because the concentration is uniformly distributed along the column. It was not sure how much solution had been transferred from the ampule to the bottom of the column, so readings were taken for many days just to make sure that the solute was uniformly distributed.

Part 3 : (370 to 495 hours)

At the end of 370 hours the solution in the column was mixed by blowing air through it with a small plastic tubing. The concentration did not change.

More mercury was poured into the column and the experiment repeated as in part 1. The results obtained for sections D through J are the same as in part 1. However for section C two observations are to be made:

- 1) a sharp jump in concentration at start, entirely expected because of some difficulties at beginning which caused even more disturbance than was experienced in part 1;

2) then the concentration in C went up gradually, rather than all at once as was the case in part 1.

Part 4 : (495 to 600 hours)

During this period the temperature was cut down to 19°C. A strange and interesting phenomenon happened: no increase in concentration in sections D through J, while an increase in concentration in C took place. This type of result duplicates the result obtained when the apparatus was given a preliminary test. At that time, for five weeks in October and November 1963, the setup was checked in a nonheated environment where the temperature varied from 18 to 22°C. No temperature control had been devised for the experiment as yet. The results obtained are plotted in Figure 6.

This type of results seem to prove also that the presence of the heating element might have induced small eddy currents. In fact a drop in temperature of even 10°C would not increase the viscosity of the hexane by more than 10% and reduce the diffusivity by the same percent, and yet for the first 200 hours no Oleic Acid had diffused as far as section D. However, it is to be noted here that the experiment of October and November was conducted by using pure Oleic Acid at the contact end instead of a solution of 1 part Oleic Acid and 2 parts hexane.

Part 5 : (600 to 707 hours)

During this period the temperature was held at 19°C. No diffusion

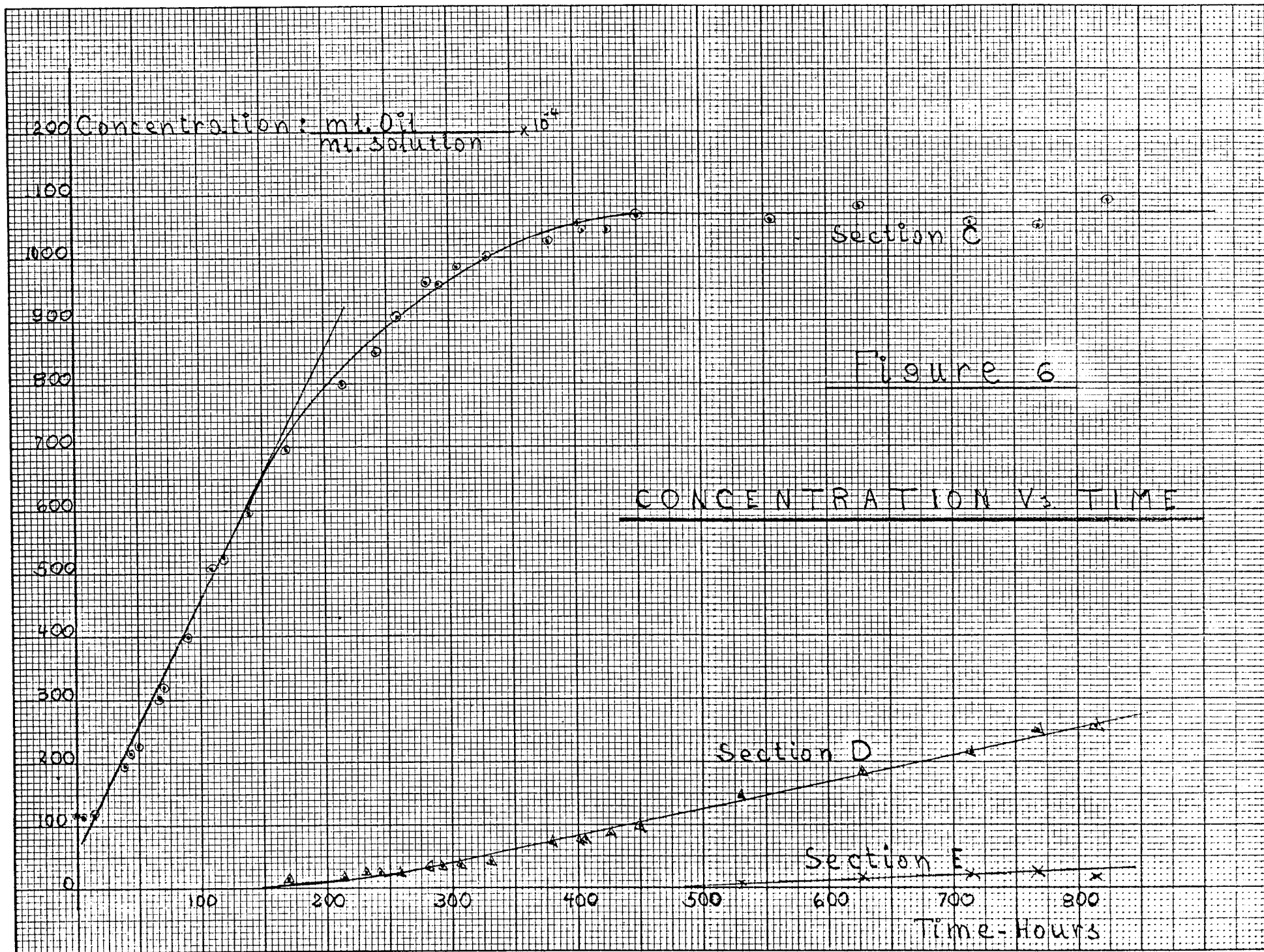
is recorded in any section. No diffusion from B C to C because at this time almost uniform distribution is obtained in this section of the column. No apparent diffusion from C to D because of the slow rate due to low concentrating gradient. The rate was so slow that even the drop in concentration in C could not be detected by the measuring instruments.

Part 6 : (707 to 790 hours)

At this time the temperature was again raised to 27°C. It is interesting to notice that the only thing that was registered was a drop in concentration in section C: the diffusion rate increased, so that the higher concentration in C levelled off with the rest of the column. However, no apparent increase in concentration in D or other sections was detected: the amount of solute that diffused from section C can be estimated at 3 or 4 per cent of the total solute in solution, and this amount falls below the limits of accuracy of the measuring instruments.

Part 7 : (790 to 815 hours)

At this time the solute is uniformly distributed throughout the column, the solution is agitated and a final reading taken to confirm the completion of the diffusion.



Measurements.

To be noted here is the fact that as the experiment progresses the accuracy of the measurements fall off with the decay of the isotope. The number of counts obtained from a certain quantity of radioactive material is reduced at the same rate as its radioactive decay: for instance a quantity of solute tagged with I^{131} that gives 1000 counts per minute at zero time, gives only 60 counts after 800 hours. So that 10 counts more or less at the end of the experiment have more meaning than at the beginning.

It is possible that if counts had been taken for a few more days at the end of the experiment, a trend would have resulted showing a general increase in concentration of 3 or 4 per cent.

The accuracy of the readings can be very good: results could always be repeated within better than $\pm 5\%$. They depend on the efficiency of the electronic instruments used; the instruments should always be checked against a known quantity of the radioactive element used to insure that they are functioning properly.

The reliability of the results depends also on the original standardization of the system. It is very important that the correction factor for each slot be very accurate. Many readings should be taken at the beginning for each slot and averaged to obtain the most accurate correction factor possible. This was not done in this experiment because

The great significance of the correction factor was not realized until the final calculations. A correction factor off by 2 or 3 percent may be very significant when the concentration difference between two adjacent sections is only 1 or 2 per cent. The need of a correction factor was not realized until readings were taken of the standard solution of 2 ml. of Oleic Acid in 248 ml. of hexane to determine a relationship between counts and concentration; at this point it was found that different readings were obtained at different slots for the same solution. If it had been realized, a solution large enough would have been prepared to cover all the slots. A correction factor for the slots H, I and J was derived from the readings at 370 hours when the content of the column was completely mixed.

It is very important also that once the probe and the column have been lined up, the readings be always taken from the same position and distance.

CONCLUSIONS

This experiment revealed that the use of compounds tagged with radioactive tracers can greatly facilitate the study of mass transfer phenomena.

The course of diffusion can be followed without ever having to disturb the set-up. A small, non-elaborate equipment is sufficient. The procedure is very simple.

Very small quantities of solute (one tenth of a milligram of solute per milliliter of solvent) can be accurately followed. It is estimated that if materials with higher per cent of tagged compound were used, the quantity of solute that could be followed may be as low as one part in a million.

The temperature probably must be controlled within a closer range than 1°C. A different arrangement with a more sensitive control should be used; the column could be set in a completely sealed environment if needed and all readings taken from outside. It should be emphasized here, however, that even if this experiment might have been affected by eddy currents the course of the diffusion was followed for many hours.

An experimental value obtained for the diffusivity is in good agreement with a theoretical value, however, no conclusion can be drawn as to the real nature of the diffusion mechanism, because it is hard to tell what part eddy currents played in the experiment. To draw any real

conclusions more experiments should be conducted; this could be done all at once with a series of columns, each with a different solvent, solute, concentration and temperature, and all tested with the same instrument.

VI

APPENDIX

The experiment described in this chapter was actually conducted about one year before the experiment described in Chapter II. Eight runs were made, but it had to be discontinued and about six months later, new ideas on the applications of radioisotopes to the study of diffusion led to the design of the other experiment. However, it is considered worth-while describing the experiment here as an example of a different application of radioactive tagged chemicals to the study of diffusional problems, and because it may be of interest to the chemical engineer.

Object of the Experiment

The object of this experiment was to study the effect of drop size on the rate of mass transfer between two phases, and also to prove the results of several investigators which show that in a spray column about 40% of the diffusion takes place at the dispersed phase inlet (9, 10, 11).

Apparatus

The apparatus used consists of: (see Figure 7)

- (A) One ml. pipette
- (B) Rubber tubing with a clamp which is used to manually and easily control the flow of the drops.
- (C) One inch glass column.
- (D) Sampling device: (a) four tygon tubings of about 1 mm in diameter which reach four different levels in the column; (b) small clamp with each tubing; (c) hypodermic needles; (d) rubber stopper through which the needles reach into small test tubes (e) inside of a bottle (f).

Samples from any level of the column can be easily obtained by opening the appropriate clamp and drawing with syringe (g).

Materials Used

In this case two immiscible solvents are needed which are at the same time solvents of Oleic Acid. After investigating all the common solvents it was impossible to obtain a pair that would do. The problem was solved by using hexane as one solvent and a combination of 80% methanol and 20% glycerol (MG) as the second solvent. MG is a fair solvent of Oleic Acid (up to about 5%) and does not mix with hexane.

Procedure

Solvent MG plus Oleic Acid (MGO) is passed dropwise from the pipette through the column filled with hexane. The number of drops is visually counted. Drops of different volume can be obtained by using pipettes with different tip openings.

The sampling device is inserted in the column before the experiment starts. As soon as the flow of drops is stopped, a sample (4 to 5 mls) is drawn from the top level; this brings at the same time the pipette tip above the hexane level. The samples from the other levels are immediately drawn one after the other.

Some difficulties were experienced in trying to obtain drop formation below the hexane surface. As the tip of the pipette filled with MGO

was lowered below the surface, hexane would start moving upward through the pipette displacing the heavier liquid MGO downward in a small stream. This situation could be eliminated with a trick: The pipette was set in place with the tip just above the surface, a few mls. of hexane added to the column to bring its level just above the pipette's tip and the flow of drops immediately started.

Difficulties were also experienced with the shape of the drops, some were perfect round, some were distorted. Some drops broke into two as soon as they started moving downward: A large drop (about 90%) would be followed by a much smaller one.

Experiment #1

A solution (10 mls) of I^{131} tagged Oleic Acid in solvent MG was prepared: 2.0 ml. glycerol, 0.1947 gms. Oleic Acid (about 50 microcuries), methanol to 10 mls. Two samples (0.045 and 0.065 mls.) were taken and counted in gamma ray spectrometer for one minute giving respectively 665,000 and 975,000 counts. A standard is calculated from the average counts and the average volume:

$$820,000 \text{ cnt.} \times \frac{1}{0.01947 \text{ gm/ml} \times 0.055 \text{ ml}} = 7.66 \times 10^8 \text{ cnt/gm. oil}$$

80 drops of above solution (for a total of 1.415 mls.) were passed through the column as fast as they could be counted. Samples of the hexane were taken at four levels, 1 inch apart, starting about 0.5 inch from the top.

One ml. from top level gives 74600 counts per minute.

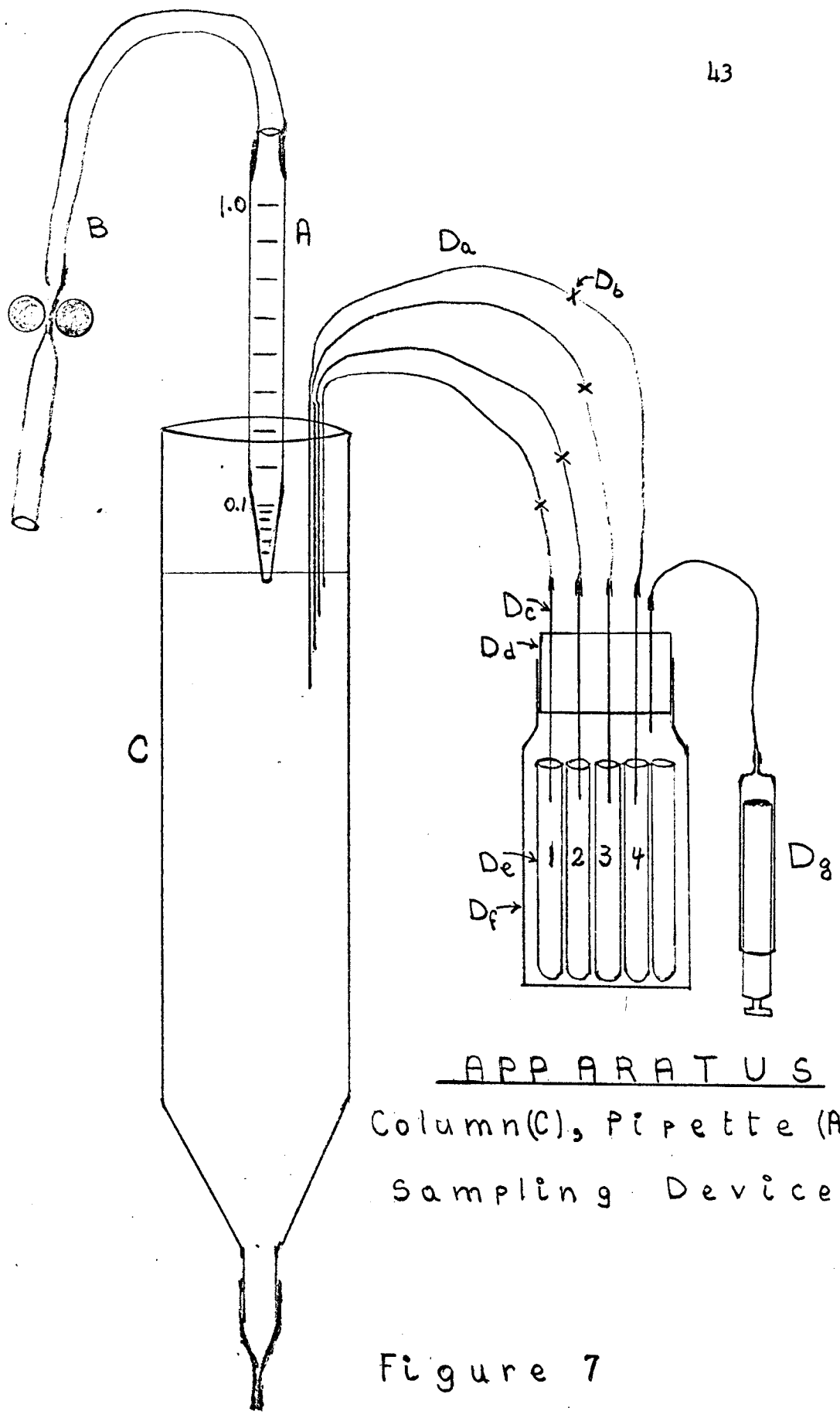
$$74600 \text{ cnt/ml.} \times \frac{1}{7.66 \times 10^8} \text{ cnt/gm. oil} = 9.75 \times 10^{-5} \text{ gm.oil/ml.}$$

The results of two experiments are shown in Table 2.

Conclusions

1. Mass transfer between two phases can be studied at very low concentrations. Very minute traces of a solute are sufficient for an experiment. The diffusion taking place from a few drops can be easily detected and accurately measured. Solutions containing one part in a million or even less can be quickly and accurately tested.

2. A very small apparatus is needed, drop size can be accurately measured, the number of drops can be counted. Contact between the drops and the solvent takes place with a minimum of mixing, only the laminar flow of the drops is present in the system. A non-agitated solution can be sampled at the desired spot with a minimum of disturbance.



APPARATUS

Column(C), Pipette (A),
Sampling Device (D).

Figure 7

Table 2
Concentration Found at Four Column Levels.

Solution Used						Results		
$\frac{\text{gm. Oil}}{\text{ml. MGO}}$	$\frac{\text{Standard counts}}{\text{gm. Oil}}$	Experiment #	MGO used ml's	Number of Drops	$\frac{\text{ml's}}{\text{drop}}$	Level	counts ml	$\frac{\text{gm. Oil}}{\text{ml}}$
0.01947	7.66×10^8	1	1.415	80	0.0177	1 (top)	74,600	9.75×10^{-5}
						2	75,300	9.82×10^{-5}
						3	74,500	9.73×10^{-5}
						4	71,200	9.28×10^{-5}
0.01947	7.66×10^8	2	0.878	51	0.0172	1 (top)	52,000	6.78×10^{-5}
						2	50,000	6.52×10^{-5}
						3	52,000	6.78×10^{-5}
						4	49,600	6.47×10^{-5}

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