CORRELATION OF MASS TRANSFER COEFFICIENTS, PHYSICAL PROPERTIES AND FLOW RATES IN LIQUID-LIQUID EXTRACTION

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INTRODUCTION

Relatively few basic studies of mass transfer rates in continuous countercurrent liquid-liquid extraction columns have been reported in the past, although interest in such studies has steadily increased in recent years, especially on the better design of extraction columns. It is to be understood that the efficiency of extraction is not only influenced by the characteristics of extraction apparatus but is also greatly limited by the physical properties of the systems to be handled. Therefore the selection of a proper solvent and the understanding of the physical properties of the system is just as important. A few investigators have attempted to resolve the overall mass transfer coefficients into individual film values[7,12,17,42] and others have tried to correlate the effects of temperature,[29,36] the Reynolds number,[7,17,42] the Schmidt number,[7,9,12,17] the interfacial tension,[5,6,10,16,20,30] the rates of flow,[1,2,4,12,14,15,20,22,23,37,38,42] the density,[6] the viscosity,[6,7,9,12,17,42] the diffusivity,[7,17,42] the concentration,[4,15,20] and the partition coefficients[32] to the mass transfer rates. However, any of the correlations made has been limited to the relationships within a system itself. Unless a generalized intersystemic relation is derived, it will be almost impossible to design an industrial extraction equipment for a new system without preliminary pilot plant studies. Since this investigation is one of the first to be made in its field, nothing general can be said at the present time about whether the empirical equation developed in this research work is a universal form for all systems. Nevertheless it is reasonable to expect that systems can be classified in certain groups according to their physical and chemical properties. For each of these groups there would be a generalized equation, from which one may predict the relative mass transfer rate when sufficient data on physical properties are available.

THEORETICAL AND EXPERIMENTAL BACKGROUND

A. General

The mass transfer rate of liquid-liquid extraction, in a given equipment, may generally be affected by the viscosity,[6,7,9,12,17,19] the diffusivity,[7,17,42] the density,[6] the concentration,[4,15,20] the rate of flow,[1,2,4,12,14,15,20,22,23,37,38,42] the equilibrium correlation between phases,[32] the interfacial tension[5,6,10,16,20,30] and the interfacial area of the materials handled. Most of these vary further with a change of temperature.[29,36] Therefore the study of mass transfer rate of liquid-liquid extraction of varying systems would be greatly simplified if done at constant temperature. If the two liquid phases should remain the same, and different dilute solutions of similar solutes are employed, the case would be further simplified, because the density, the viscosity, the interfacial tension and thus the interfacial area of the two liquid phases would remain practically identical (the interfacial tension of different dilute acid solutions were experimentally compared and proved to be identical by the double capillary method).[26] Under these restricted conditions the variables may be reduced to: rate of flow, concentration of feed, diffusivity of solute, and partition coefficient; and that is the way in which the experimental work of this paper was carried out.

B. Diffusivity

The diffusion coefficient, D, is defined as the quantity of material that will diffuse across a plane of unit dimensions in unit time under unit concentration gradient, or

$$D = \frac{dQ}{A dt \frac{dC}{dx}} \qquad \text{(III 1)}$$

where, D is the diffusion coefficient, dQ is the quantity which passes across the plane of area A in time dt under a concentration gradient of $\frac{dC}{dx}$.

Various methods are available both for experimental determination[11,13,18,19,21,24,25,28] and for empirical prediction[3,34,43] of diffusivity in liquids. A modified Northrop and Anson Method,[33] using a diffusion cell with sintered glass bottom, was employed in this investigation. The results were compared with values calculated from Wilke's[43] empirical equation. According to Northrop, for general cases,

$$D = \frac{2.3\ K\ V_2 V_1}{(V_1+V_2)t} \quad \log \frac{V_2 S-(V_2+V_1)Q_o}{V_2 S-(V_2+V_1)Q} \qquad \text{(III 2)}$$

where, D = diffusion coefficient,

K = a constant = A/h,

A = area of diffusion,

h = thickness of the sintered glass disc,

V_1 = volume of more concentrated solution =

volume of the cell,

V_2 = volume of dilute solution = volume of liquid in receiving tube,

S = total amount of solute at beginning of experiment,

Q = quantity of solute in dilute solution at any time,

C_1 = concentration of solution in the cell at time t,

C_2 = concentration of solution in receiving tube at time t,

K' = $\frac{2}{2.303KV_1} = \frac{2A}{2.303hV_1}$ = constant for a particular cell, which can be determined by using a solution of known diffusion coefficient,

Q_o = quantity of solute in the dilute solution when t = 0, and

t = time of duration of the experiment.

If at the beginning of the experiment, there is no solute in the receiving tube and V_1 is equal to V_2, equation III 2 can be simplified to:

$$D = \frac{1}{K't} \log \frac{C_1}{C-2C_1} \qquad \text{(III 3)}$$

This equation was used for all of the diffusivity determinations both in water and toluene except that of formic acid in toluene phase. Since formic acid is only slightly soluble in toluene and has a great affinity for water, the amount of the acid that diffused through the sintered glass disc to the toluene had a tendency to escape from the latter to the gaseous phase very easily. This was concluded when the material balance on formic acid was found consistently out of balance. A modification was made by introducing a measured quantity of sodium hydroxide solution of definite strength to the receiving tube at the beginning of the experiment; thus the acid diffused out from the cell, passed to the thin layer of toluene between the cell and the alkali solution, and was instantly removed by sodium hydroxide. Therefore, the concentration of the toluene could be considered constant and equal to zero. A new mathematical relationship was then derived as follows:

Since by definition,

$$\frac{dQ}{dt} = \frac{DA}{h} (C_1 - C_2),$$

and by approximation $C_2 = 0$,

$$\therefore \frac{dQ}{dt} = \frac{DA}{h} (C_1) = \frac{DA}{hV_1} (S-Q),$$

or

$$\int \frac{dQ}{S-Q} = \int \frac{DA}{hV_1} dt ,$$

or

$$2.303 \log \frac{S-Q_o}{S-Q} = \frac{DA}{hV_1} t ,$$

$$\therefore D = \frac{2.3V_1h}{At} \log \frac{S-Q_o}{S-Q} ,$$

$$\therefore D = \frac{2}{K't} \log \frac{S-Q_o}{S-Q} ,$$

and since $Q_o = 0$,

$$D = \frac{2}{K't} \log \frac{S}{S-Q} = \frac{2}{K't} \log \frac{C_1}{C_1-C_2} \qquad \text{(III 4)}$$

where each symbol retains its defined significance except for Q, which, in this case, is equal to the amount of solute that diffused through the sintered glass disc, and the subscript o indicates the initial condition. The experimental results proved to be satisfactory on the material balance.

C. Equilibrium Concentration Distribution

When equilibrium is reached under constant temperature and pressure, the ratio of the concentration of a solute between two contact liquid phases is called the partition coefficient, K_E, or equilibrium distribution constant. This value can be considered as a constant for a range of solute concentration when very dilute solutions are dealt with. For the experimental determination of equilibrium concentration, it is important to assure the approaching of equilibrium state, to avoid disturbance during sampling. The concentration of the solute can be determined by any suitable method of analysis. Since acids were used in this work, direct titration for more concentrated samples, and colorimetric method for more dilute solutions were used.

D. Mass Transfer Rate

Elgin and Browning[16] have shown that for cases where the system does not depart widely from the simple distribution law, and where volume changes, amount extracted, and concentration involved are not large, the rate of mass transfer for extraction may be written:

$$K_W a = \frac{N}{V(\triangle C)_m} \qquad \text{(III 5)}$$

where, $K_W a$ = overall mass transfer coefficient, based on phase W, sec^{-1},

N = gm. moles acid transferred per sec.,

V = volume of packing space, c.c., and

$(\triangle C)_m$ = log mean concentration difference, gm. moles per liter.

APPARATUS

A. Diffusivity Determination

This includes a diffusion cell, three receiving tubes, a constant temperature water jacket and a primary constant temperature water supply bath and auxiliaries, (Figures 1, 2, and 3).

1. Diffusion Cell.--A diffusion cell of the capacity of 31.0028 c.c. at 30° C. with sintered glass bottom, (Figure 1), was used.
2. Receiving Tubes.--Three tubes (Figure 1), made of pyrex glass tubing, were used as receiving tubes. It is of importance that the inner diameter of the lower ends of the receiving tubes should be constructed as close to the outer diameter of the diffusion cell as possible. The narrow gap provides less surface for undesirable evaporation during the process.
3. Constant Temperature Water Jacket and Primary Constant Temperature Water Supply Bath.--Since the accuracy of the diffusivity determination is not only dependent on the least temperature variation but also on the least mechanical vibration, it is essential that direct agitation in the water jacket (Figure 2) should be avoided. A primary constant temperature bath (Figure 2) is thus used as constant temperature water supply for the

water jacket. With this device one can greatly reduce the unnecessary vibration, and at the same time eliminate the effect of temperature rise immediately following the opening of the circuit and due to the residual heat capacity of the heating element. For less temperature disturbances the water jacket is insulated on its side by approximately 1/2-inch felt and 1/4-inch cork sheets at the bottom and top, and the vessel for the immersion-type pump is also insulated with approximately 1/2-inch felt. By using an evaporative type cooler to keep the room temperature between 80-90° F., it is possible to keep the temperature variation within ± 0.01° C. in the water jacket and ± 0.05° C. in the primary constant temperature water supply bath.

4. Auxiliaries

   i. A special pipette of the volume of 31.0028 c.c. at 30° C. was made and used for measuring a definite amount of solvent for the receiving tubes.

   ii. A universal clamp was designed to hold the bottom of the diffusion cell horizontal against the quiescent mercury surface, (Figure 1).

   iii. A 500-watt electric heater was used as the heating element for the primary constant temperature water bath.

   iv. A copper cooling coil made of 10 feet of 1/4-inch copper tubing was used for cooling purposes (tap water was used as cooling medium)(Figure 2).

v. A Fisher Serfass electronic relay coupled with a mercury switch was used for automatic temperature control.

vi. An immersion type pump, 1/30 H.P., mounted on the wooden cover of a 12-inch diameter by 12-inch high pyrex vessel was used for circulating the water. Constant temperature water, siphoned from the primary constant temperature water supply, was pumped to the constant temperature water jacket and was further returned to the primary constant temperature water supply by siphoning action. An immersion type pump was used because a centrifugal type pump introduced a considerable amount of gas which accumulated at the top of the siphon tube and periodically stopped the siphon.

vii. Two calibrated thermometers with 0.01° F. divisions were used in temperature measurements.

viii. A sampling device, with 1/32-inch stainless steel tube, attached to a water suction pump was used to take samples from the diffusion cell.

ix. A framework and base were made (Figure 1) to support the universal joint and water jacket.

B. Equilibrium Concentration Distribution Determination

Three glass tubes with ground glass stoppers and rubber cushions were mounted on the plastic top of the primary constant temperature water supply bath which had originally been used for diffusivity determinations. The tubes were attached to an oscillating device which converted a part of the power of the stirring motor from rotary motion to sliding motion (Figures 4 and 5). The sampling device was the same one as used in diffusivity measurements.

C. Mass Transfer Rate Determinations

The apparatus (Figure 6) for this purpose consists chiefly of an extraction column, a constant temperature (30° C. ± 1° C.) device for the whole system, and the auxiliaries.

1. The Extraction Column

A 4-feet long by 1-1/2-inch diameter pyrex pipe, packed with 34.5 inches 4-mm. glass beads was used as the body of the column (Figure 7). The column was jacketed with a 3-feet 8-inches long by 3-inch diameter pyrex tubing. Inside the jacket space, constant temperature water was circulated to maintain the desired operating temperature.

2. Constant Temperature Device

Constant temperature of the system was maintained by constant temperature water supply from a 20-inch by 20-inch by 36-inch tank, insulated with 2-inch cork sheets on the outside. The temperature of the water inside was automatically controlled by a Fisher Serfass electronic relay coupled with a mercury switch. Tap water at a temperature lower than the controlled temperature was continuously fed into the tank as a cooling source, and a 500-watt electric heater was used as heating element. The larger fraction of the water overflowed from the supply tank to the feed storage bottle jackets, and was then pumped by a gear pump through the column jacket and returned to the supply tank, while a fraction of it was allowed to overflow from the bottle jacket to the drain. The latter part was compensated by the tap water stream to the supply tank. All the connecting lines were well insulated with asbestos cord. The feed storage bottles were further enclosed in a wooden box lined with two inches of cork sheet, and the empty space was filled with excelsior.

3. Auxiliaries

   i. Two inclined manometers filled with mercury were made of glass tubing with capillary glass sections as orifices and used as rate-measuring devices for the feed streams.

   ii. All the lines were made of glass and were connected by saran tubing sections.

   iii. One-quarter inch stainless steel needle valves were used to regulate the feeding rates.

   iv. Two 5-gallon pyrex carboys were used as feed storage bottles.

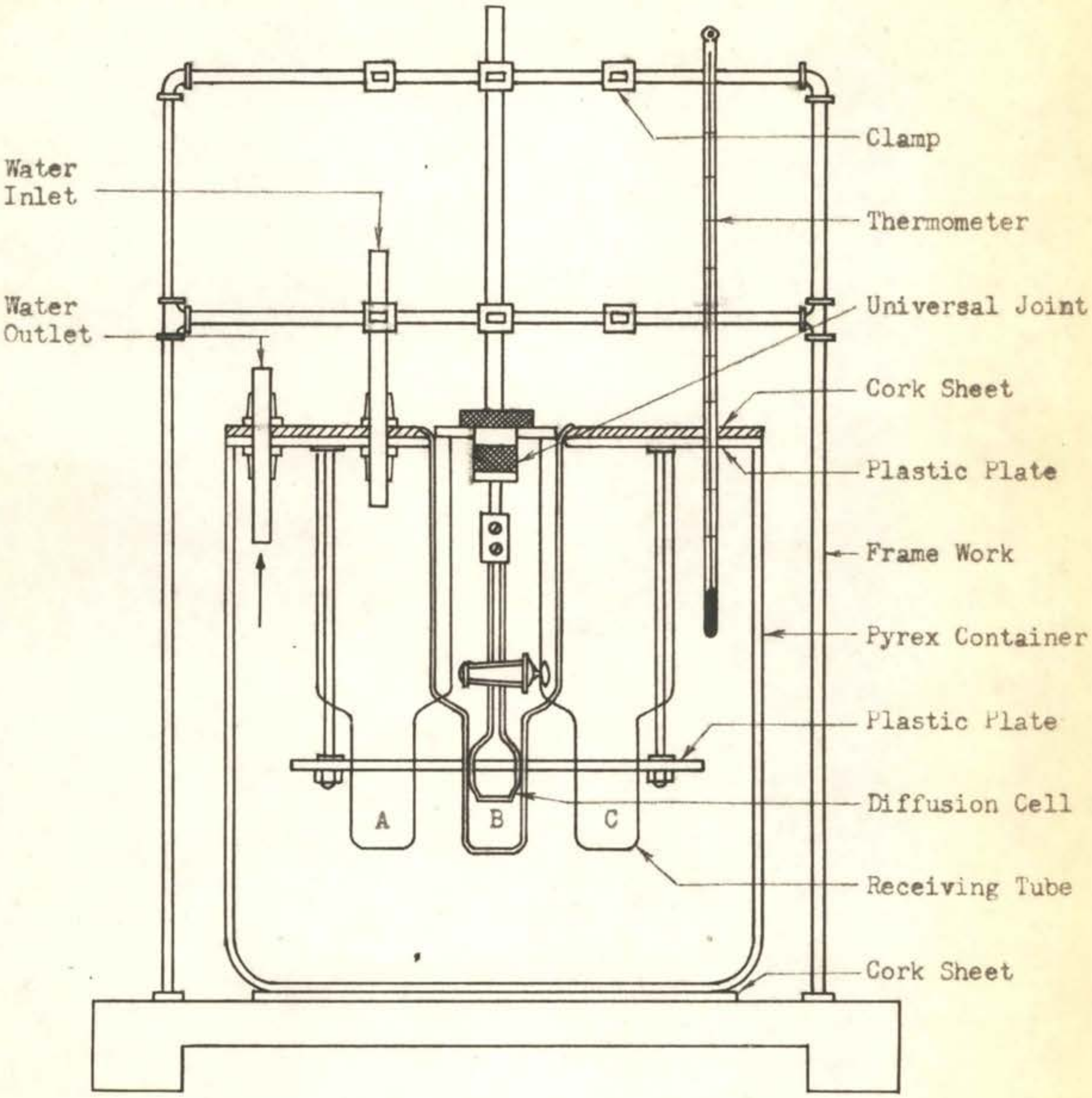
   v. Two 12-gallon pyrex carboys were used as product collectors.

vi. Two 10-gallon garbage cans were used as water jackets for feed storage bottles.

vii. A Caustic agitator for regenerating the toluene was made of a 12-gallon pyrex carboy (Figure 8).

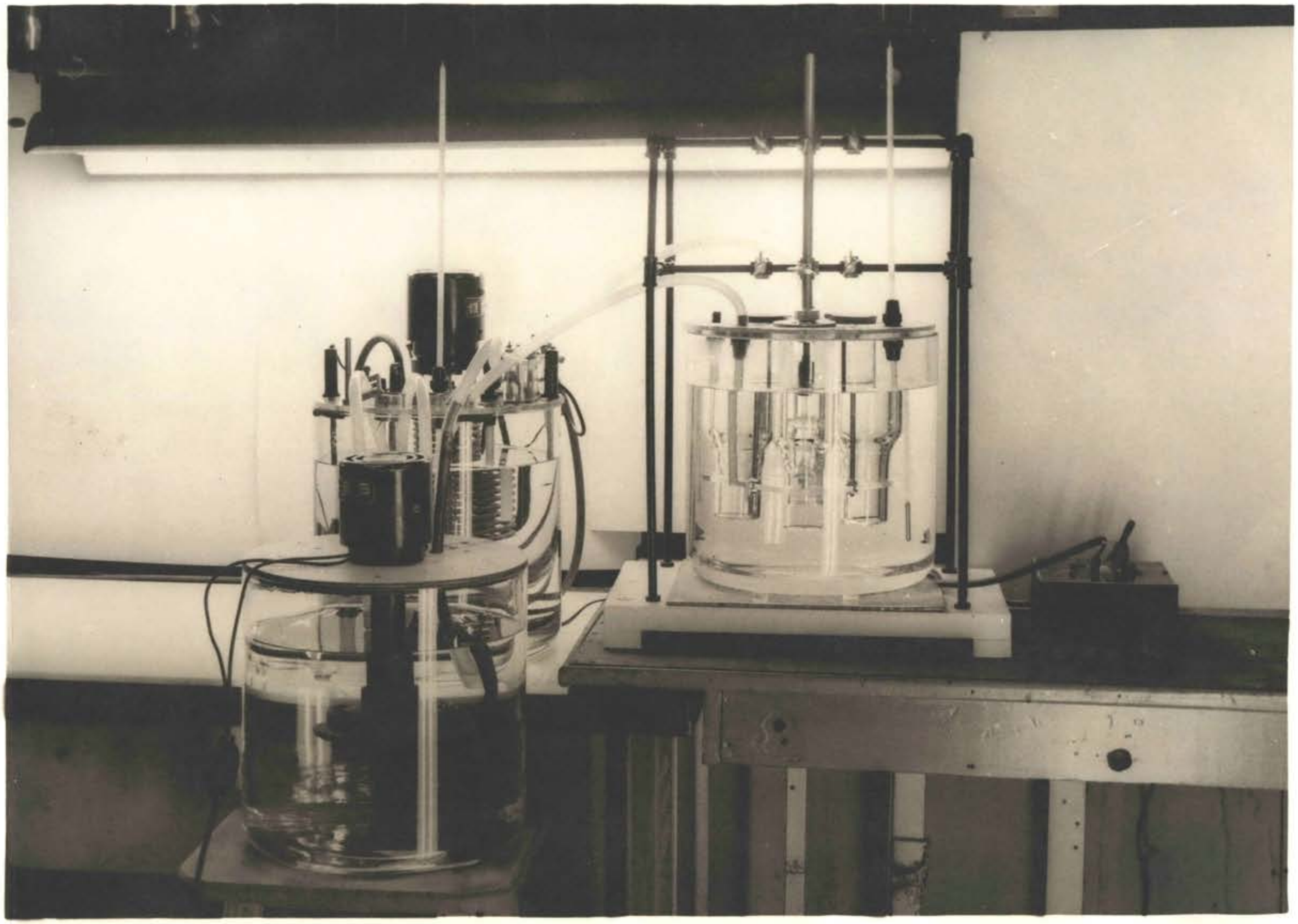
viii. A washing bottle was also made of a 12-gallon pyrex carboy (Figure 9).

Figure 1



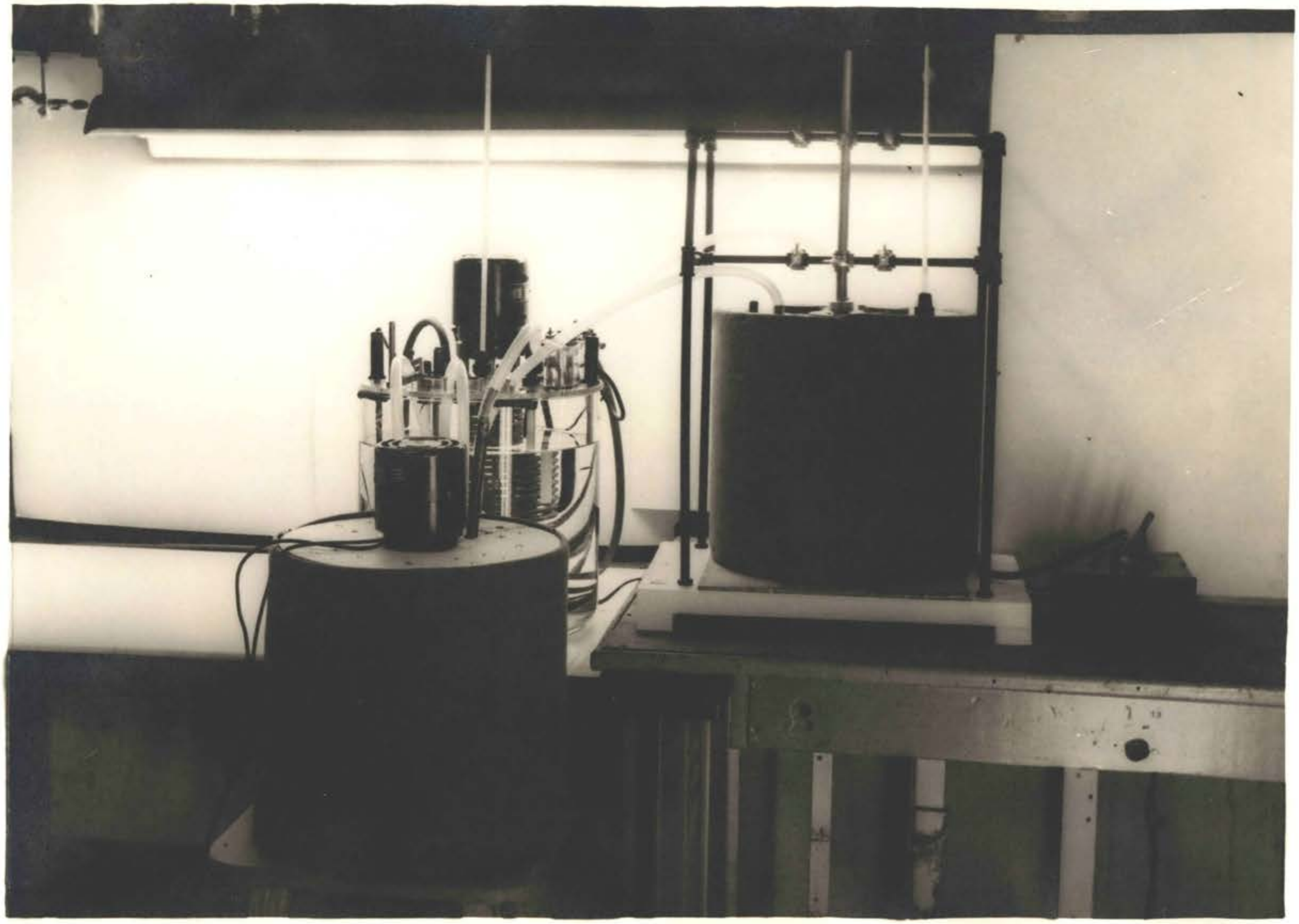
Details of Apparatus for Diffusivity Determinations

Figure 2



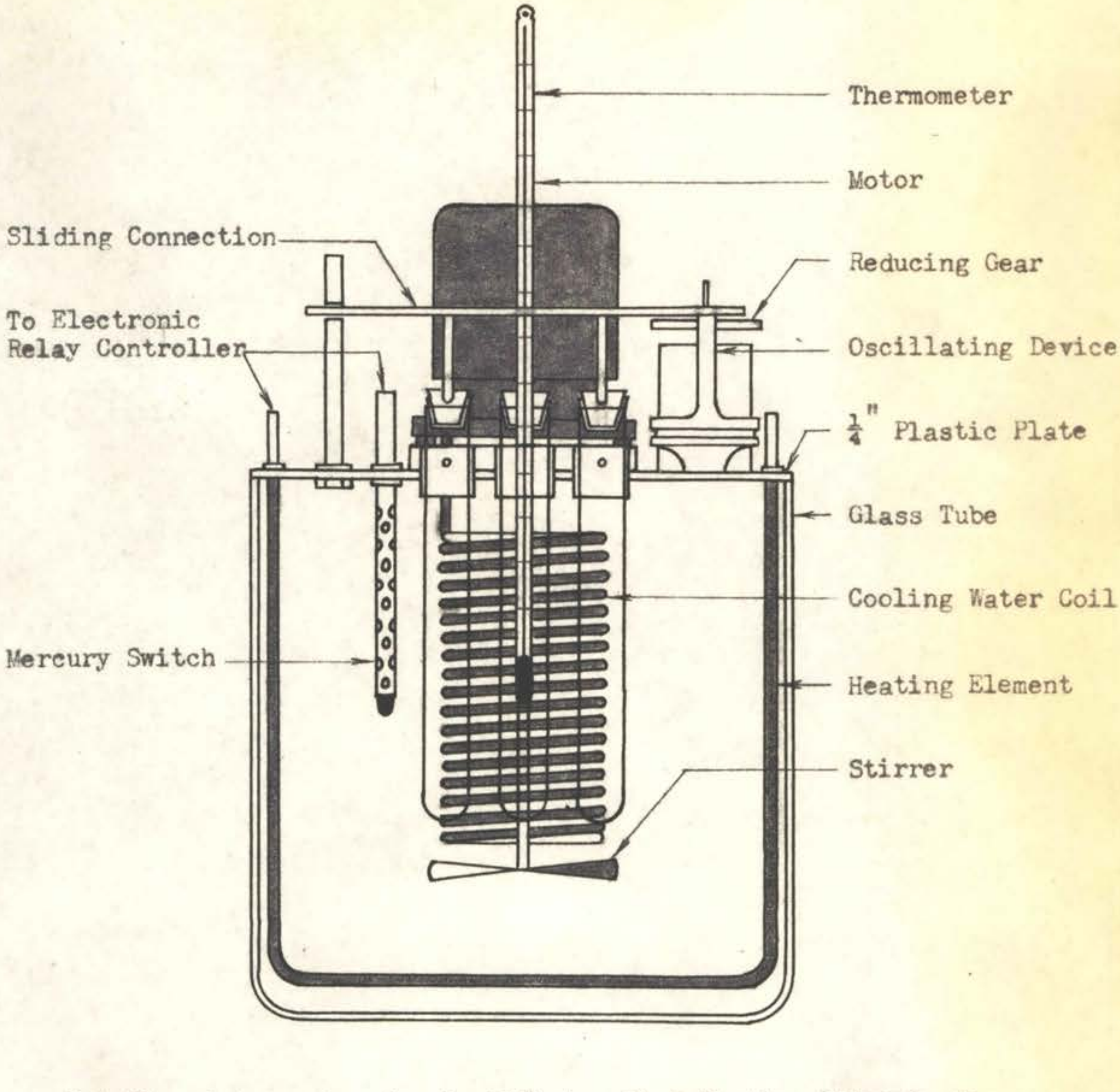
Photograph of Details of Apparatus for Diffusivity Determination

Figure 3



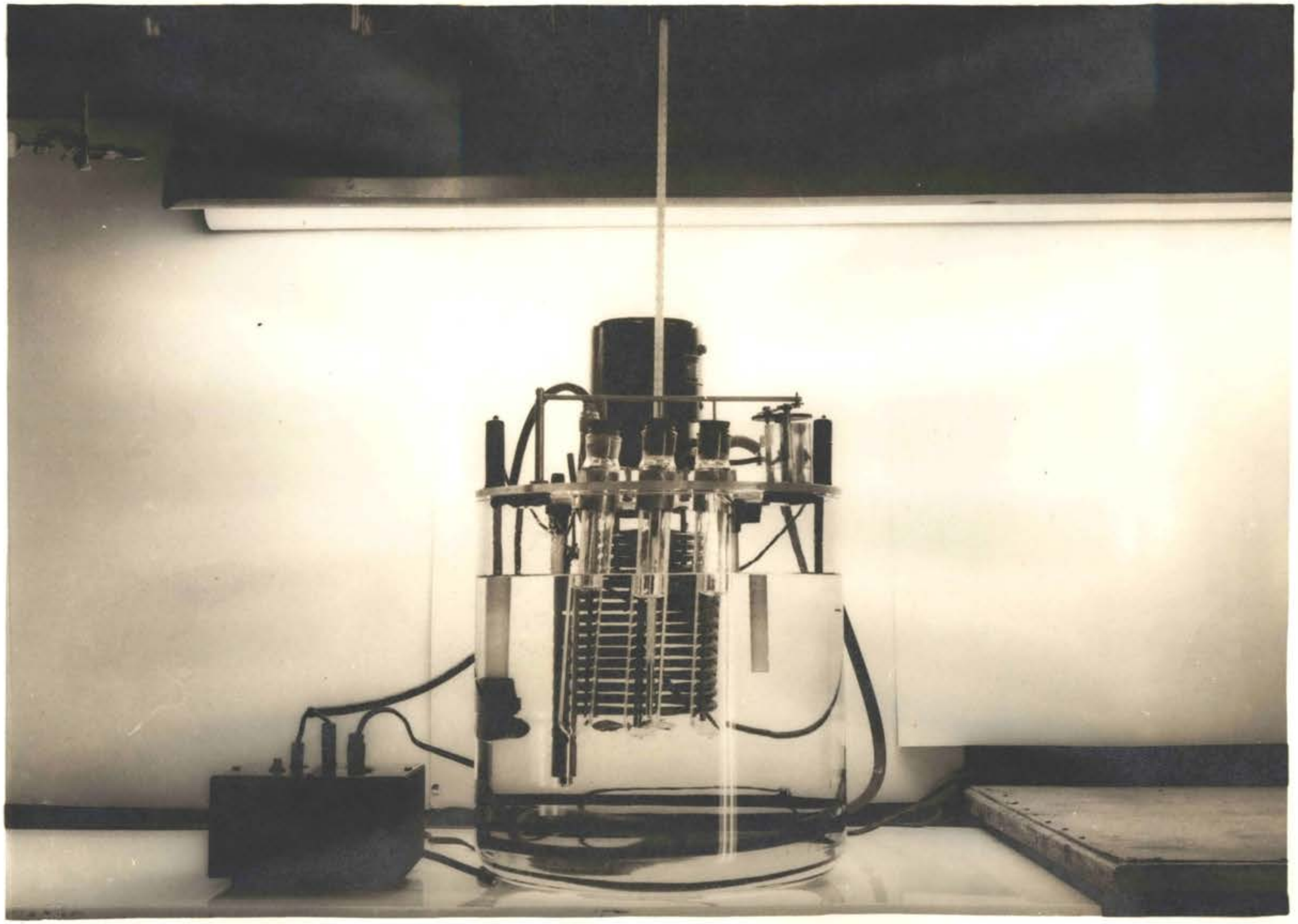
Photograph of Apparatus for Diffusivity Determination in Operation

Figure 4



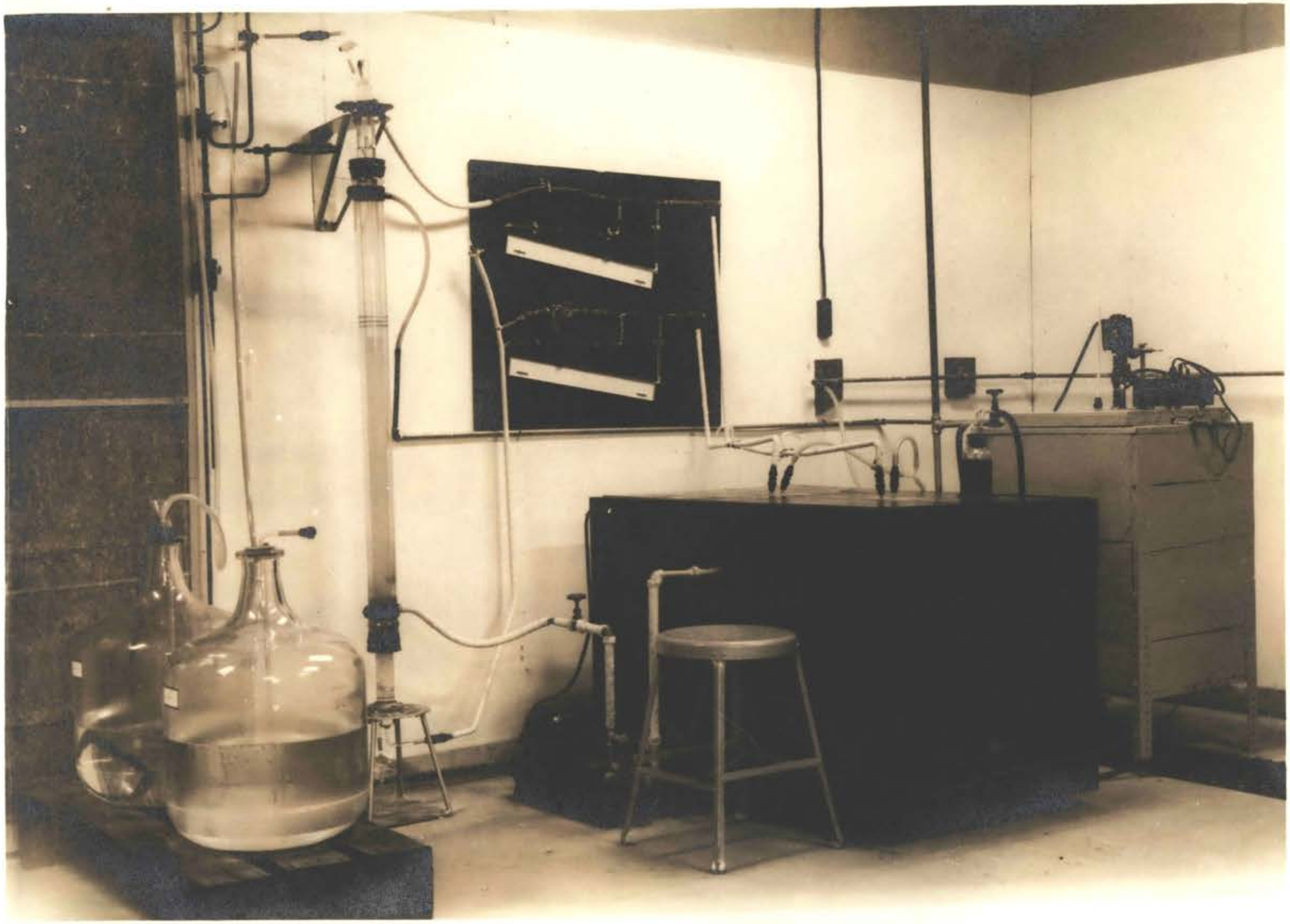
Details of Apparatus for Equilibrium Distribution Determinations

Figure 5



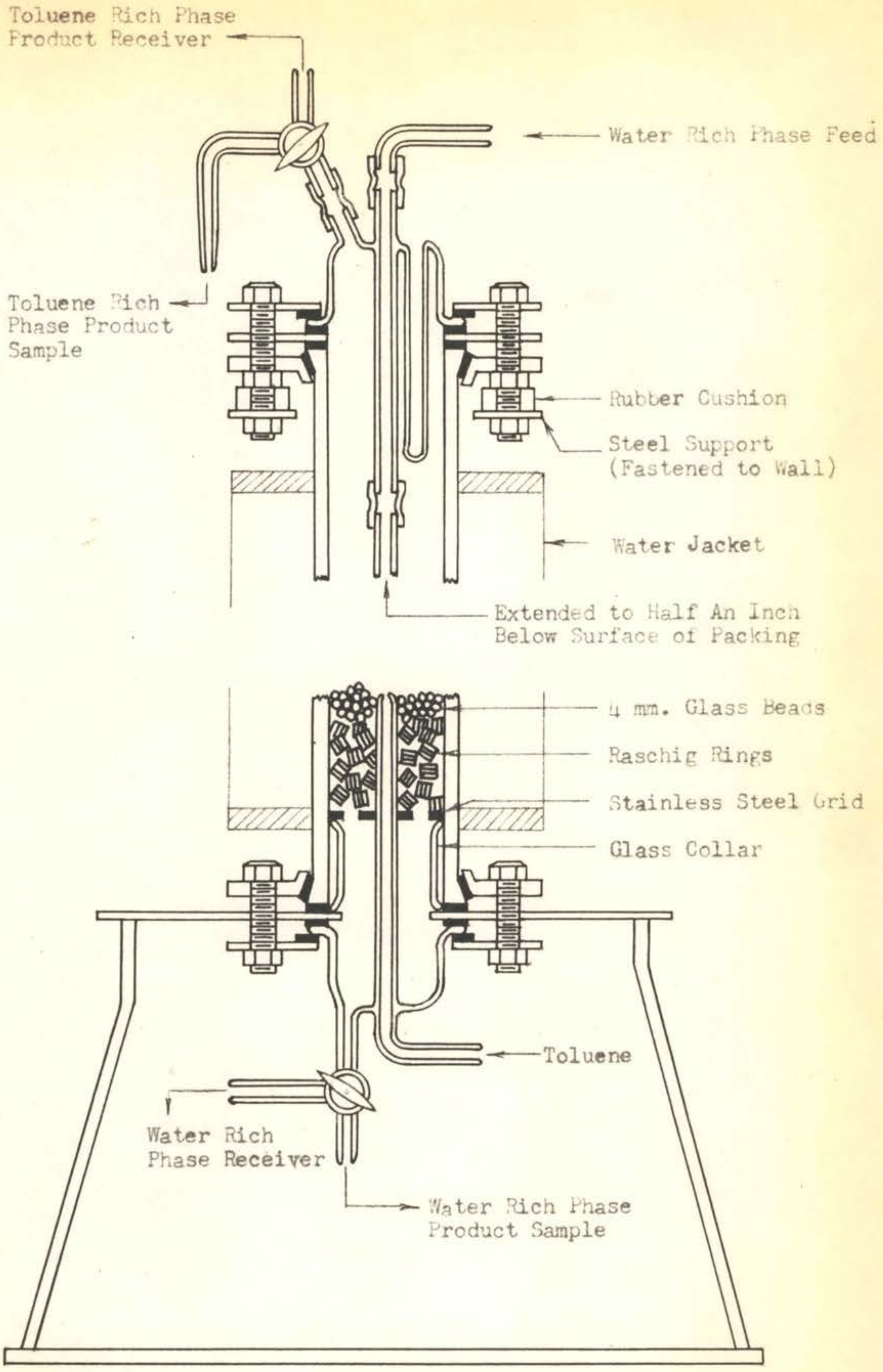
Photograph of Apparatus for Equilibrium Distribution Determination in Operation

Figure 6



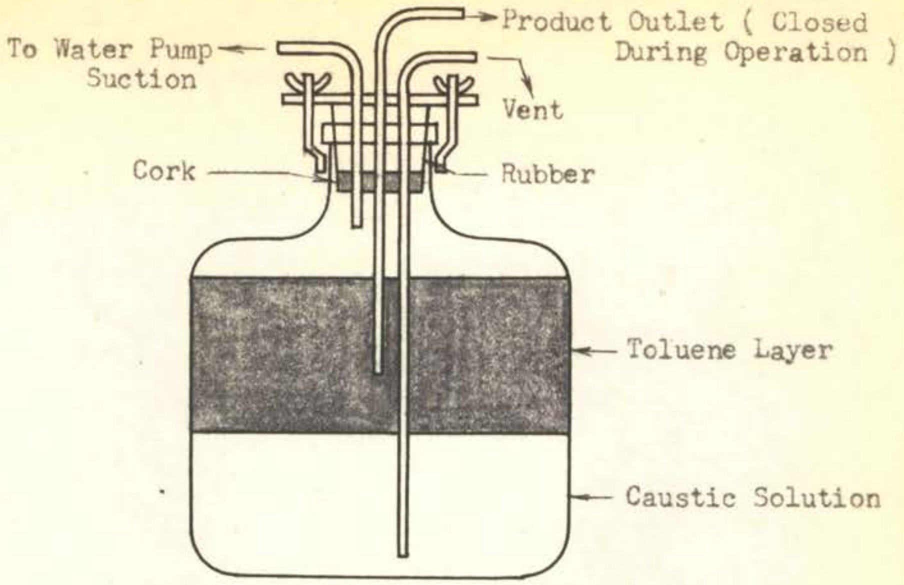
Photograph of Apparatus for Mass Transfer Rate Determination

Figure 7



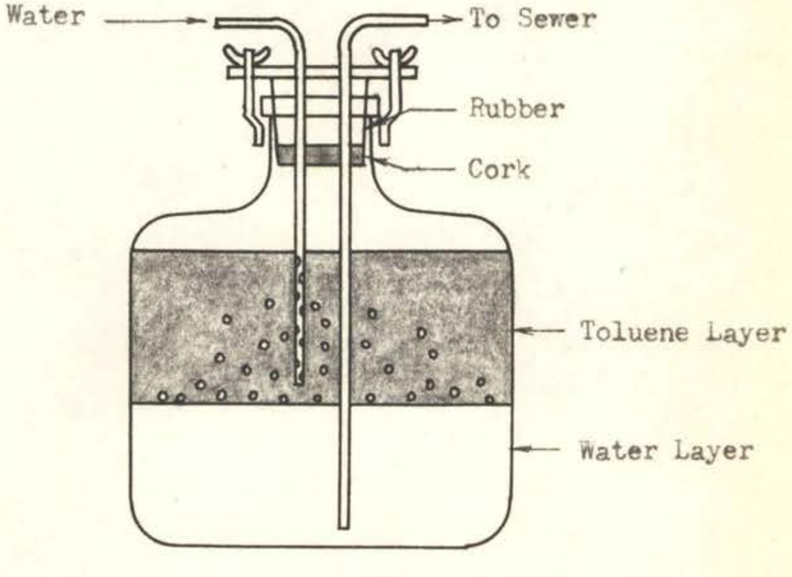
Details of Extraction Column

Figure 8



Caustic Agitator for Toluene Regeneration

Figure 9



Water Washing Bottle for Toluene Regeneration

MATERIAL USED

Reagent grade toluene by Merck and Company, Inc., was used in diffusivity and equilibrium concentration distribution determinations and technical grade toluene by Phillips Petroleum Company was used in rate of mass transfer measurements.

Reagent grade formic acid (98-100%) and valeric acid by Eastman Kodak Company; and reagent grade acetic acid, propionic acid and n-butyric acid by Fisher Scientific Company were used for diffusivity and equilibrium concentration distribution determinations. Ninety per cent formic acid by General Chemical Division; 99.5% acetic acid by Fisher Scientific Company; and n-butyric acid, propionic acid, and n-valeric acid by Eastman Kodak Company were used in rate of mass transfer determinations. Other chemicals used were: reagent grade N_aOH, HCl, KCl, and bromo-cresol green by Merck and Company, Inc. All reagents used in the analytical work met A.C.S. specifications for purity. Distilled water was used in all cases.

PROCEDURE

A. Diffusivity Determination

Before the diffusivity of an unknown solute can be measured, the cell constant must be determined. The procedure for determining the cell constant is exactly the same as that for diffusivity determinations, except that in the former case the cell constant is unknown and in the latter case the diffusivity is unknown.

Cell constants both at 25° C. and 30° C. were determined. The values 1.836×10^{-5} cm.^{2}/sec. for 0.1 N KCl at 25° C.,[18] 2.92×10^{-5} cm.^{2}/sec. for 0.1 N HCl at 25° C. and 3.24×10^{-5} cm.^{2}/sec. for 0.1 N HCl at 30° C. were used in the calibration of cell constants. Diffusivity values for 0.1 HCl were interpolated from James and Gordon's data,[19] (Figures 10 and 11). It was found that small temperature variations cause little change in the cell constant. The general procedure is as follows:

1. The cell is leveled against a quiet mercury surface. Once the universal joint is tightened and the position of the cell is marked, the leveled position can be reproduced easily without further adjustment by using the mercury surface as a reference.
2. Constant temperature water is now circulated through the constant temperature water jacket.
3. The cell is filled with solution by suction applied

at the tube end through the membrane.

4. The outside of the cell is rinsed with pure solvent.
5. Pure solvent is pipetted into the receiving tubes A, B and C.
6. The cell is clamped to the leveled position, and the sintered glass part of the cell is immersed into the solvent in the receiving tube A.
7. The time is noted and diffusion allowed to continue until a desired amount of solute has passed through the membrane. The outside solution is then pipetted off and analyzed, and the cell is transferred to receiving tube B. This process is repeated until the quantity passing through the membrane is constant for equal time intervals; that is, until the system is in steady state. This preliminary diffusion process usually takes four to five hours, the exact time depending on the characteristics of the cell and on the solute and solvent used.
8. The preliminary diffusion was followed immediately by the main part of diffusion. To achieve accurate result, a much longer time period is necessary for this part of the process. The time period would depend on the diffusivity of the particular solute involved for a given solvent. For a solute of large diffusivity less time would be required than for one of small diffusivity.
9. At the end of the diffusion, a sample from the cell

is taken out through a 1/32-inch stainless steel tube inserted through the tube of the cell. The concentration of the sample is determined.

10. A sample of the solution remaining in the receiving tube is also taken and analyzed.

11. In special cases, such as for the determination of the diffusivity of formic acid in toluene, the whole procedure will remain essentially the same, except for a few minor changes. In item 5, besides the pure solvent, a measured amount of sodium hydroxide solution of known concentration is also introduced. A two phase system is therefore formed in the receiving tube. The position of the cell should be so adjusted that the gap between the sintered glass surface and the interface of the two liquid phases would be as close together as practically possible, although they should not be in actual contact with each other. In items 10 and 6, samples of the aqueous solutions are analyzed instead of toluene solutions.

B. Equilibrium Concentration Distribution Determination

1. The temperature of the water bath was adjusted to $30 \pm 0.05^\circ$ C.
2. Twenty-five c.c.'s of acid-water solutions of different concentrations were introduced into three separate glass tubes mounted in the constant temperature water bath.
3. Twenty-five c.c.'s of toluene were added to each

of the three tubes.

4. The apparatus was then assembled properly, and the oscillating device was turned on.
5. Samples from both the aqueous layers and the toluene layers were taken through a 1/32-inch stainless steel tube every three hours until analysis of samples from two consecutive periods indicated no difference in the results.
6. In order to shorten the time required for reaching the equilibrium state, occasional manual shaking of the glass tubing was found very effective.

C. Mass Transfer Rate Determinations

1. Manometers were calibrated by setting a fixed reading of the meter and measuring with a graduated cylinder the amount of fluid collected within a certain time interval. Results were tabulated in tables I and II and plotted in Figures 12 and 13.
2. The capacity of a column is limited by the flooding velocities of the liquid streams that flow through the column. The flooding velocity of the water phase at a fixed toluene phase velocity of 2400 c.c./hr. was determined as 2800 c.c./hr. Since the feeding rate of toluene was held constant at 2400 c.c./hour for all runs, 2800 c.c./hr. should serve as a criterion for the water phase feeding rate.
3. The two feed storage bottles were filled, one with toluene and the other with distilled water.

4. A calculated amount of acid was added to the water. The solution was intimately mixed by bubbling with compressed air.
5. A sample of the water solution was taken and analyzed to see if it was within the desired concentration range.
6. After the concentration was adjusted, constant temperature water was circulated through the system. No measurement was taken before constant temperature was assured.
7. Compressed air, as a lifting means for the feeds, was regulated to 6 psig.
8. The column was first filled with water solution.
9. Toluene was then introduced.
10. The two streams were adjusted to, and maintained at, the exact rates desired by the use of needle valves.
11. The interface was located and adjusted to approximately one inch above the packing by leveling the loop attached to the exit of the water phase product.
12. A steady state condition was approached within one to one and one-half hours for different ranges of flow rates. However, longer time periods were used, and readings were not recorded until identical analytical results of products were obtained on two consecutive periods of half an hour.
13. The whole system was purged every time a new system was used.

14. The water-phase product was collected in a 12-gallon pyrex carboy in which a caustic solution with indicator was originally presented. This was devised to eliminate the unpleasant odor of the higher members of the fatty acids.
15. The toluene was regenerated by first agitating it with caustic solutions for 4 hours and then washing with running water overnight.

ANALYTICAL METHODS

A. The acid concentration of the water phase was analyzed by direct titration against 0.03 N or 0.1 N NaOH solution, using phenolphthalein as an indicator.

B. The acid concentration of the toluene phase was determined by first shaking the sample with ten times its volume of distilled water, and then titrating the whole mixture against 0.03 N or 0.1 N NaOH solution using phenolphthalein as an indicator. However, for the equilibrium concentration distribution determination with formic acid, the colorimatric method had to be used. A Beckman Quartz spectrophotometer was used. The procedure was as follows:

1. Acid-toluene solutions were made to the following concentrations: 0.001, 0.0009, 0.0008, 0.0007, 0.00065, 0.0006, 0.0005, 0.0004, 0.0003, 0.0002 and 0.0001 gram moles/liter.
2. A stock, CO_2-free solution was made consisting of 0.06 gram moles/liter of bromo-cresol green.
3. A 5-c.c. sample was extracted with 25 c.c. of the bromo-cresol green solution.
4. The percentage of transmittance of the solution was plotted against its concentration. The process was repeated, and a percentage transmittance concentration diagram was constructed, (Figure 14).

5. Any unknown acid-toluene solution of a concentration between 0.001 to 0.0001 gram moles/liter can thus be determined by first extracting the toluene with 25 c.c. bromo-cresol green stock solution, and then reading the percentage of transmittance and ascertaining its concentration from the diagram.

C. Standard 0.1 N $AgNO^3$ was used to titrate KCl in the diffusion cell constant evaluation, using potassium chromate as an indicator.

DISCUSSION OF RESULTS AND CONCLUSIONS

A. Diffusivity

The diffusivities of various kind of acids, either in water or in toluene, were determined both experimentally by Northrop's[33] method and empirically by Wilke's[43] equation. In the experimental procedure, the cell constant was first evaluated by using the values of 1.836×10^{-5} cm.^{2}/sec.[18] for 0.1 N KCl solution at 25° C., 2.91×10^{-5} cm.^{2}/sec.[19] for 0.1 N HCl solution at 25° C., and 3.24×10^{-5} cm.^{2}/sec.[19] for 0.1 N HCl solution at 30° C. as standards. Small temperature variations were found not to change the cell constant to a significant extent. The cell constant was found invariably as 0.06142 cm.$^{-2}$ within the experimental temperature range. The results were tabulated in tables III and IV. By plotting diffusivity versus molecular volume on log-log graph paper (Figure 15), a straight line correlation resulted and the following relations were obtained:

$$D_W = 10.9 \left(\frac{1}{V}\right)^{0.487} \qquad \text{(VIII 1)}$$

and, $$D_T = 26.26 \left(\frac{1}{V}\right)^{0.57} \qquad \text{(VIII 2)}$$

where D_W = diffusivity in water x 10^5, cm.^{2}/sec.,

D_T = diffusivity in toluene x 10^5, cm.^{2}/sec., and

V = molecular volume.

B. Equilibrium Concentration Distribution

No particular difficulty was encountered in this part of the experiment. The results were tabulated in tables V, VI, VII, VIII, IX and X and plotted in Figures 14, 16, 17, 18, 19, 20, 21, 22 and 23.

C. Rate of Mass Transfer

K_Wa, the extraction capacity coefficient based on the water phase, was determined experimentally for the extraction of acetic acid, propionic acid, n-butyric acid and n-valeric acid from their dilute aqueous solutions by using toluene at 30° C., (Tables XI, XII, XIII and XIV). The K_Wa for the extraction of formic acid was also attempted. However, due to the exceedingly small amount of acid transferred during the process, no reliable result was obtained. Toluene was the dispersed phase, and water was the continuous phase. The following generalized equation was derived to correlate the extraction capacity coefficient K_Wa with other physical properties of the system:

$$K_Wa = K\ (C)_m^{a}(R)^{b}(K_E)_m^{0.2}D_TD_W \qquad \text{(VIII 3)}$$

where K_Wa = capacity coefficient, based on water phase,

$\frac{\text{lbs./ft.}^3\text{ hr.}}{\text{lbs./ft.}^3}$,

R = rate of flow of water phase, c.c./hr.,

$(C)_m$ = log mean concentration of water phase feed and product, gm. moles acid/l.,

$(K_E)_m$ = partition coefficient corresponding to $(C)_m$,

D_W = diffusivity in water x 10^5, cm.^{2}/sec.,

D_T = diffusivity in toluene x 10^5, cm.^{2}/sec.,

$K = -37.306 + 35.049\,N - 9.924\,N^2 + 0.8835\,N^3$,

$a = -8.50 + 8.085\,N - 2.24\,N^2 + 0.195\,N^3$,

$b = 2.6998 - 2.7265\,N + 0.845\,N^2 - 0.0783\,N^3$, and

N = number of carbon atoms in acid.

The calculated K_Wa was plotted versus the experimentally determined K_Wa in Figure 24, and they are compared in Tables XI, XII, XIII and XIV.

SUMMARY

The extraction of formic acid, acetic acid, propionic acid, n-butyric acid, and n-valeric acid from their dilute water solutions by toluene under constant temperature of 30° C. were studied. A four foot length of 1-1/2 inch pyrex pipe, packed for 34.5 inches with 4-mm. glass beads was used as the extraction column. The diffusivities of each acid, both in toluene and in water, and the equilibrium distribution concentrations for all acids between water and toluene phases were measured. Water was the continuous phase and toluene was the dispersed phase. Mass transfer coefficients at different feeding rates, and various acid concentrations for the water phase, and constant feeding rate and acid-free toluene were determined.* The differences in interfacial tension between the toluene phase and the water phase for the various acids at low concentrations were found to be negligible. Three generalized empirical equations were derived, two of which correlate the molecular volume and diffusivity and the third correlates the mass transfer coefficient, flow rates and physical properties; they are:

$$D_W = 10.9 \left(\frac{1}{V} \right)^{0.487} \qquad \text{(VIII 1)}$$

$$D_T = 26.26 \left(\frac{1}{V} \right)^{0.57} \qquad \text{(VIII 2)}$$

*Note: Except for formic acid-toluene water system. (Reason explained in chapter VIII.)
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and, $K_Wa = K(C)_m^a (R)^b (K_E)_m^{0.2} D_T D_W$ (VIII 3)

where, R = rate of flow of water phase, c.c. per hour,

$(C)_m$ = log mean concentration of water phase feed and product, gm. moles acid per liter,

$(K_E)_m$ = partition coefficient corresponding to $(C)_m$,

D_W = diffusivity in water x 10^5, cm.^{2} per sec.,

D_T = diffusivity in toluene x 10^5, cm.^{2} per sec.,

K = $-37.306+35.049N-9.924N^2+0.8835N^3$,

a = $-8.50+8.085N-2.24N^2+0.195N^3$,

b = $2.6998-2.7265N+0.845N^2-0.0783N^3$,

N = number of carbon atoms in acid, and

V = molecular volume.

SELECTED BIBLIOGRAPHY

1. Allerton, J., B. O. Strom and R. E. Treybal, Trans. Am. Chem. Engr., 39, 361 (1943).

2. Appel, F. J., and J. C. Elgin, Ind. Eng. Chem., 29, 451 (1937).

3. Arnold, J. H., J. Am. Chem. Soc., 52, 3937 (1930).

4. Bergelin, O., F. J. Lockhart and G. G. Brown, Trans. Am. Inst. Chem. Engrs., 39, 173, (1943).

5. Blanding, F. H. and J. C. Elgin, Trans. Am. Inst. Chem. Engrs., 38, 305 (1942).

6. Breckenfeld, R. R. and C. R. Wilke, Chem. Eng. Progress, 46, 187 (1950).

7. Brinsmade, D. S. and H. Bliss, Trans. Am. Inst. Chem. Engrs., 39, 679 (1943).

8. Chilton, T. C. and A. P. Colburn, Ind. Eng. Chem., 27, 255 (1935).

9. Chilton, T. C. and A. P. Colburn, Ind. Eng. Chem., 26, 1183 (1934).

10. Chu, J. C., C. C. Taylor and D. J. Levy, Ind. Eng. Chem., 42, 1157 (1950).

11. Cohen, E. and H. R. Bruins, Z. physik. Chem., 103, 337, 404 (1923).

12. Colburn, A. P. and D. G. Welsh, Trans. Am. Inst. Chem. Engrs., 38, 179 (1942).

13. Cole, A. F. W. and A. R. Gordon, J. Physical Chem., 40, 733 (1936).

14. Comings, E. W. and S. W. Briggs, Trans. Am. Inst. Chem. Engrs., 38, 1943 (1942).

15. Elgin, J. C. and F. M. Browning, Trans. Am. Inst. Chem. Engrs., 31, 639 (1935).

16. Elgin, J. C. and F. M. Browning, Trans. Am. Inst. Chem. Engrs., 32, 105 (1936).

17. Fallah, R., T. H. Hunter and A. W. Nash, J. Soc. Chem. Ind., 54, 49T (1935).

18. Gordon, A. R., J. Chem. Physics, 5, 522 (1937)

19. James, W. A. and A. R. Gordon, J. Chem. Physics, 7, 963 (1939).

20. Johnson, H. F. and H. Bliss, Trans. Am. Inst. Chem. Engrs., 42, 331 (1946).

21. Kegeles, G. and L. J. Gosting, J. Am. Chem. Soc., 69, 2516 (1947).

22. Knight, O. S., Trans. Am. Inst. Chem. Engrs., 39, 439 (1943).

23. Laddha, G. S. and J. M. Smith, Chem. Eng. Progress, 46, 195 (1950).

24. Longsworth, L. G., Ind. Eng. Chem. (Analy.), 18, 219 (1946).

25. Longsworth, L. G., J. Am. Chem. Soc., 69, 2510 (1947).

26. Mack, G. L. and Bartell, J. Chem. Soc., 54, 936 (1932).

27. Meissner, H. P., C. A. Stokes, C. M. Hunter and G. M. III. Morrow, Ind. Eng. Chem., 36, 917 (1944).

28. Miller, C. C., J. Roy. Soc., A 106, 724 (1924).

29. Morello, V. S. and R. B. Beckmann, Ind. Eng. Chem., 42, 1078 (1950).

30. Moulton, R. W. and J. E. Walkey, Trans. Am. Inst. Chem. Engrs., 40, 695 (1944).

31. McBain, J. W. and T. H. Liu, J. Am. Chem. Soc., 53, 59 (1931).

32. Nichols, P. L. Jr., Anal. Chem., 22, 915 (1950).

33. Northrop, J. H. and M. L. Anson, Journal of Gen. Physiology, 13, 543 (1929).

34. Olson, R. L. and J. S. Walton, Ind. Eng. Chem., 43, 703 (1951).

35. Perry, J. H., "Chemical Engineers' Handbook," 3rd. Ed., McGraw-Hill Book Company, Inc., New York (1950).

36. Reeves, E. J., Ind. Eng. Chem., 41, 1490 (1949).

37. Row, S. B., J. H. Koffolt and J. R. Withrow, Trans. Am. Inst. Chem. Engrs., 37, 559 (1941).

38. Sherwood, T. K., J. E. Evans and J. V. A. Longcor, Ind. Eng. Chem., 31, 1144 (1939).

39. Sherwood, T. K. and R. L. Pigford, "Absorption and Extraction," 2nd. Ed., McGraw-Hill Book Company, Inc., New York (1952).

40. Treybal, R. E. and F. E. Dumoulin, Ind. Eng. Chem., 34, 709 (1942).

41. Treybal, R. E., "Liquid Extraction," McGraw-Hill Book Company, Inc., New York (1951).

42. Treybal, R. W. and L. T. Work, Trans. Am. Inst. Chem. Engrs., 38, 203 (1942).

43. Wilke, C. R., Chem. Eng. Progress, 45, 218 (1949).

44. Williams, J. W. and L. C. Cady, Chem. Rev., 14, 171 (1934).

APPENDIX

TABLE I

CALIBRATION OF WATER MANOMETER AT 30° C.

Manometer Reading	Flow Rate, c.c./hr.
3.5	708
4.0	1015
4.5	1265
5.0	1482
5.5	1680
6.5	2030
7.5	2350
9.0	2775
10.0	3042
11.0	3300
12.0	3540
13.0	3780
15.0	4200
17.0	4580
19.0	4980
21.0	5320

TABLE II

CALIBRATION OF TOLUENE MANOMETER AT 30° C.

Manometer Reading	Flow Rate, c.c./hr.
5	1750
6	2215
6.5	2400
7	2590
8	2860
10	3450
12	3950
14	4390
16	4800
18	5180
20	5560

TABLE III

CELL CONSTANT CALIBRATION

Solution Used	Diffusivity x 10^5 cm.^{2}/sec.	Temperature C.°	Cell Constant cm.$^{-2}$
0.1N KCl	1.836	25	0.06168
0.1N HCl	2.910	25	0.06127
0.1N HCl	3.240	30	0.06140
		Average	0.06142

TABLE IV

DIFFUSIVITIES AT 30° C.

D, Diffusivity x 10^5 cm.^{2}/sec.

	in Water, D_W		in Toluene D_T		Molecular Volume
	Experi-mental	Calcu-lated	Experi-mental	Calcu-lated	
Formic Acid	1.684	1.900	2.985	3.140	46.2
Acetic Acid	1.406	1.455	2.392	2.400	68.4
Propionic Acid	1.221	1.220	2.035	2.000	90.6
n-Butyric Acid	1.073	1.065	1.801	1.750	112.8
n-Valeric Acid	0.990	0.946	1.620	1.560	135.0

TABLE V

CONCENTRATION-PERCENTAGE TRANSMITTANCE RELATIVE TO WATER EXTRACT FROM FORMIC ACID-WATER-TOLUENE SYSTEM AT 30° C.

% Transmittance Water Extract	Acid Concentration in Toluene, gm. moles/liter
92.5	0.001
91.0	0.0009
90.0	0.0008
89.2	0.0007
88.0	0.00065
87.1	0.0006
86.1	0.0005
82.2	0.0004
78.0	0.0003
72.5	0.0002
65.4	0.0001

TABLE VI

EQUILIBRIUM DISTRIBUTION OF FORMIC ACID IN TOLUENE-WATER-FORMIC ACID SYSTEM AT 30° C.

% Transmittance of Water Extract	G_T, Concentration of Acid in Toluene Rich Phase, gm. moles/liter	C_W, Concentration of Acid in Water Rich Phase, gm. moles/liter	$K_E = \frac{C_T}{C_W}$
95.5	0.001335	0.5002	0.00267
93.5	0.001065	0.4020	0.00267
90.0	0.000760	0.2850	0.00265
87.0	0.000590	0.2215	0.00267
84.5	0.000465	0.1750	0.00267
77.0	0.000272	0.1000	0.00272

TABLE VII

EQUILIBRIUM DISTRIBUTION OF ACETIC ACID IN TOLUENE-WATER-ACETIC ACID SYSTEM AT 30° C.

C_W, Concentration of Acid in Water Rich Phase, gm. moles/l.	C_T, Concentration of Acid in Toluene Rich Phase, gm. moles/l.	$K_E = \frac{C_T}{C_W}$
0.515	0.00848	0.0164
0.429	0.00599	0.0139
0.366	0.00482	0.0132
0.275	0.00315	0.0115
0.2195	0.002387	0.0109
0.1788	0.001825	0.0102
0.1412	0.001373	0.0097
0.1009	0.0009003	0.0089
0.0500	0.000420	0.0084
0.0000	0.0000	------

TABLE VIII

EQUILIBRIUM DISTRIBUTION OF PROPIONIC ACID IN TOLUENE-WATER-PROPIONIC ACID SYSTEM AT 30° C.

C_W, Concentration of Acid in Water Rich Phase, gm. moles/l.	C_T, Concentration of Acid in Toluene Rich Phase, gm. moles/l.	$K_E = \frac{C_T}{C_W}$
0.4030	0.0960	0.2381
0.3530	0.0764	0.2164
0.3290	0.0669	0.2033
0.2895	0.0539	0.1862
0.2310	0.0364	0.1576
0.1800	0.02315	0.1286
0.1390	0.01580	0.1137
0.1075	0.01010	0.0940
0.0822	0.00769	0.0936
0.0452	0.00293	0.0648

TABLE IX

EQUILIBRIUM DISTRIBUTION OF N-BUTYRIC ACID IN TOLUENE-WATER-N-BUTYRIC ACID SYSTEM AT 30° C.

C_W, Concentration of Acid in Water Rich Phase, gm. moles/l.	C_T, Concentration of Acid in Toluene Rich Phase, gm. moles/l.	$K_E = \frac{C_T}{C_W}$
0.2780	0.6520	2.345
0.2570	0.5650	2.198
0.2260	0.4490	1.987
0.1858	0.3165	1.703
0.1571	0.2300	1.464
0.1327	0.1700	1.287
0.1110	0.1225	1.104
0.0925	0.0877	0.948
0.0770	0.0629	0.816
0.0619	0.0426	0.688
0.0522	0.0313	0.600
0.0431	0.0222	0.515
0.0285	0.0118	0.414
0.01695	0.00509	0.300

TABLE X

EQUILIBRIUM DISTRIBUTION OF N-VALERIC ACID IN TOLUENE-WATER-N-VALERIC ACID SYSTEM AT 30° C.

C_W, Concentration of Acid in Water Rich Phase, gm. moles/l.	C_T, Concentration of Acid in Toluene Rich Phase, gm. moles/l.	$K_E = \frac{C_T}{C_W}$
0.2680	6.340	23.65
0.2165	4.920	22.73
0.1790	3.780	21.11
0.1625	3.295	20.28
0.1321	2.422	18.34
0.1080	1.722	15.94
0.0824	1.080	13.10
0.0580	0.570	9.83
0.0464	0.372	8.017
0.0398	0.2787	7.003
0.0343	0.2100	6.122
0.0258	0.1240	4.806
0.0148	0.0445	3.007
0.0104	0.0231	2.221
0.0077	0.0140	1.818

TABLE XI

DATA AND CALCULATED RESULTS OF MASS TRANSFER RATE FOR ACETIC ACID-TOLUENE-WATER SYSTEM AT 30° C.

	Toluene	Water Solution	Concentration(gram moles acid /liter				N, gram moles acid transferred/sec.			$(\Delta C)_m$, Log Mean Concentration	K_Wa (Experimental) = $\frac{N}{(\Delta C)_m}$		K_Wa (Calculated)	% Error
	Rate	Rate	W_p, Water	T_p, Toluene	W_p, Water	T_p, Toluene	Based on	Based on	Average	Gradient, gram moles acid/liter	gram moles/c.c. sec.	lbs./ft.³hr.	$=KD_WD_T(C)^a_m(R)^b(N_R)^{0.8}_m$	
No. Run	c.c./hr.	c.c./hr.	Phase Feed	Phase Feed	Phase Product	Phase Product	Water Phase	Toluene Phase			gram moles/c.c.	lbs./ft.³	(lbs/ft.³hr.)/(lbs/ft.³)	
1	2400	2030	0.2195	0	0.2170	0.00231	Since the change of acid concentration in water phase is so small it would not be justified to calculate based on its flow rate.	0.00000154	0.00000154	0.03735	0.0000412	0.1485	0.1475	-0.68
2	2400	1680	0.2195	0	0.2161	0.00231		0.00000154	0.00000154	0.03730	0.0000412	0.1485	0.1475	-0.68
3	2400	1265	0.2195	0	0.2158	0.00231		0.00000154	0.b0000154	0.03720	0.0000413	0.1490	0.1480	-0.68
4	2400	1015	0.2195	0	0.2145	0.00231		0.00000154	0.00000154	0.03700	0.0000416	0.1500	0.1480	-1.35
5	2400	2030	0.1788	0	0.1765	0.00176		0.00000117	0.00000117	0.03075	0.0000380	0.1371	0.1380	+0.65
6	2400	1680	0.1788	0	0.1762	0.00176		0.00000117	0.00000117	0.03070	0.0000380	0.1371	0.1380	+0.65
7	2400	1265	0.1788	0	0.1759	0.00176		0.00000117	0.00000117	0.03070	0.0000380	0.1371	0.1380	+0.65
8	2400	1015	0.1788	0	0.1745	0.00176		0.00000117	0.00000117	0.03050	0.0000383	0.1380	0.1370	-0.65
9	2400	2030	0.1412	0	0.1400	0.00132		0.000000881	0.000000881	0.02440	0.0000361	0.1300	0.1285	-1.15
10	2400	1680	0.1412	0	0.1393	0.00132		0.000000881	0.000000881	0.02430	0.0000361	0.1300	0.1289	-0.85
11	2400	1265	0.1412	0	0.1390	0.00132		0.000000881	0.000000881	0.02430	0.0000361	0.1300	0.1289	0.85
12	2400	1015	0.1412	0	0.1388	0.00132		0.000000881	0.000000881	0.02420	0.0000363	0.1310	0.1295	-1.15
13	2400	2030	0.1009	0	0.0997	0.000858		0.000000572	0.000000572	0.01775	0.0000322	0.1160	0.1160	0.00
14	2400	1680	0.1009	0	0.0995	0.000858		0.000000572	0.000000572	0.01770	0.00003225	0.1162	0.1162	0.00
15	2400	1265	0.1009	0	0.0992	0.000858		0.000000572	0.000000572	0.01765	0.0000323	0.1165	0.1162	-0.25
16	2400	1015	0.1009	0	0.0985	0.000858		0.000000572	0.000000572	0.01760	0.00003245	0.1170	0.1168	-0.17

TABLE XII

DATA AND CALCULATED RESULTS OF MASS TRANSFER RATE FOR PROPIONIC ACID-TOLUENE-WATER SYSTEM AT 30° C.

	Toluene	Water Solution	Concentration(gram moles acid /liter				N, gram moles acid transferred/sec.			$(\Delta C)_m$, Log Mean Concentration	K_Wa (Experimental) = $\frac{N}{(\Delta C)_m}$		K_Wa (Calculated)	% Error
	Rate	Rate	W_p, Water	T_p, Toluene	W_p, Water	T_p, Toluene	Based on	Based on	Average	Gradient, gram moles acid/liter	gram moles/c.c. sec.	lbs./ft.³hr.	$=KD_WD_T(C)^a_m(R)^b(N_R)^{0.8}_m$	
No. Run	c.c./hr.	c.c./hr.	Phase Feed	Phase Feed	Phase Product	Phase Product	Water Phase	Toluene Phase			gram moles/c.c.	lbs./ft.³	(lbs/ft.³hr.)/(lbs/ft.³)	
1	2400	2030	0.2197	0	0.1840	0.02945	0.00002015	0.00001968	0.00001992	0.06680	0.000298	1.072	1.083	+1.01
2	2400	1680	0.2197	0	0.1780	0.02915	0.00001950	0.00001944	0.00001947	0.06475	0.000301	1.083	1.064	-1.79
3	2400	1265	0.2197	0	0.1651	0.02870	0.00001917	0.00001916	0.00001916	0.06380	0.000301	1.083	1.025	-5.46
4	2400	1015	0.2197	0	0.1568	0.02805	0.00001775	0.00001871	0.00001819	0.06520	0.000279	1.005	1.004	-0.10
5	2400	2030	0.1795	0	0.1545	0.02100	0.00001420	0.00001400	0.00001405	0.05510	0.000255	0.918	0.903	-1.65
6	2400	1680	0.1795	0	0.1504	0.02080	0.00001358	0.00001388	0.00001373	0.05530	0.000248	0.894	0.892	-0.22
7	2400	1265	0.1795	0	0.1409	0.02053	0.00001355	0.00001366	0.00001361	0.05430	0.000251	0.904	0.853	-4.46
8	2400	1015	0.1795	0	0.1368	0.02028	0.00001206	0.00001352	0.00001279	0.05480	0.000233	0.839	0.835	-0.47
9	2400	2030	0.1385	0	0.1228	0.01380	0.00000887	0.00000921	0.00000904	0.04630	0.000195	0.702	0.709	+0.99
10	2400	1680	0.1385	0	0.1197	0.01370	0.00000879	0.00000913	0.00000896	0.04640	0.000193	0.696	0.704	+1.14
11	2400	1265	0.1385	0	0.1137	0.01360	0.00000873	0.00000906	0.00000890	0.04580	0.000193	0.696	0.680	-2.35
12	2400	1015	0.1385	0	0.1094	0.01340	0.00000822	0.00000892	0.00000857	0.04580	0.000187	0.673	6.670	-0.45
13	2400	2030	0.0954	0	0.0903	0.00800	0.00000514	0.00000534	0.00000524	0.03690	0.000142	0.511	0.522	+2.28
14	2400	1680	0.0954	0	0.0886	0.00797	0.00000505	0.00000531	0.00000518	0.03680	0.000142	0.507	0.526	+3.75
15	2400	1265	0.0954	0	0.0851	0.00792	0.00000503	0.00000528	0.00000516	0.03620	0.000143	0.513	0.502	-2.18
16	2400	1015	0.0954	0	0.0827	0.00783	0.00000472	0.00000523	0.00000498	0.03570	0.000139	0.503	0.495	-1.60

TABLE XIII

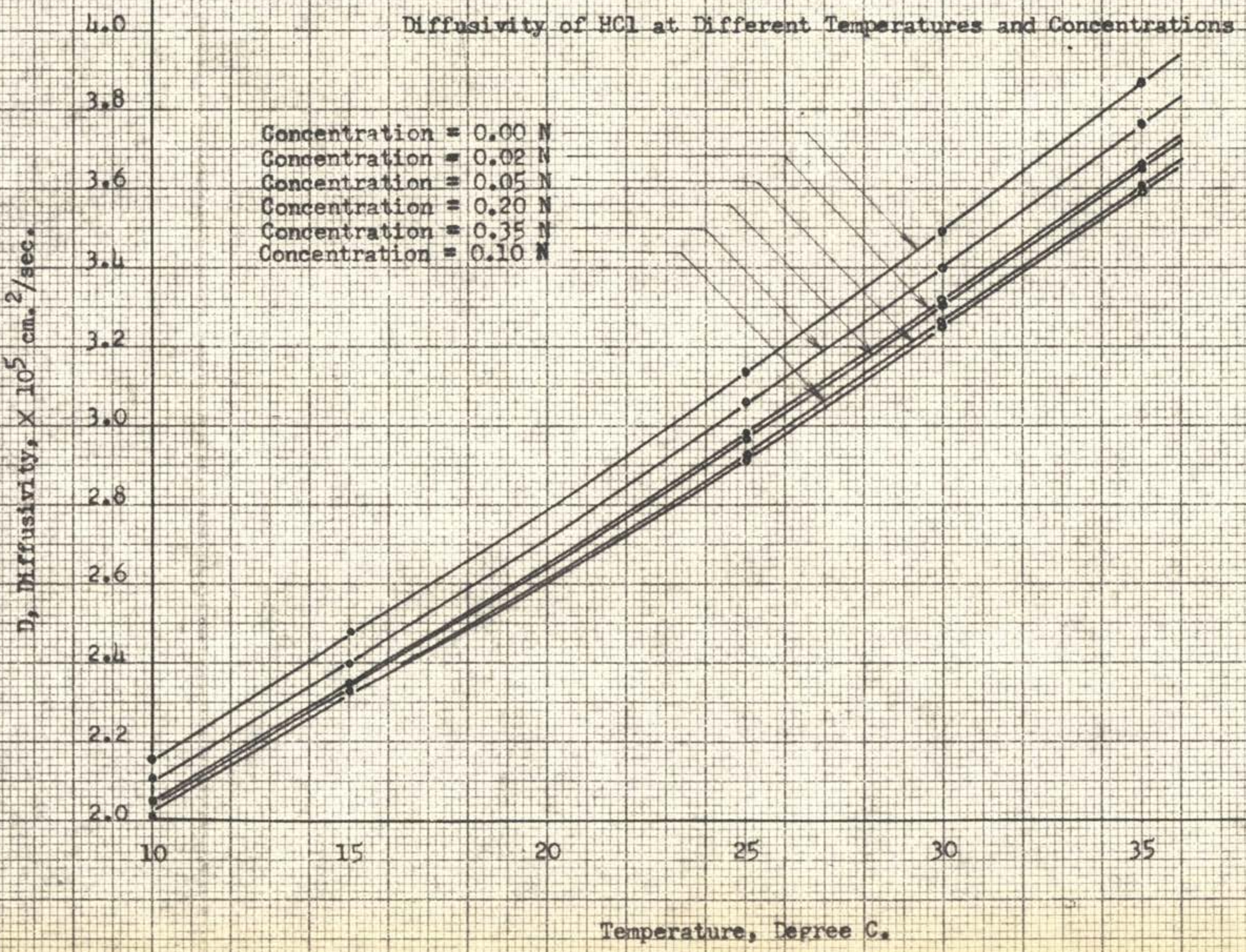
DATA AND CALCULATED RESULTS OF MASS TRANSFER RATE FOR N-BUTYRIC ACID-TOLUENE WATER SYSTEM AT 30° C.

No. Run	Toluene Rate c.c./hr.	Water Solution Rate c.c./hr.	Concentration(gram moles acid /liter				N, gram moles acid transferred/sec.			$(\Delta C)_m$, Log Mean Concentration Gradient, gram moles acid/liter	K_Ga (Experimental) = $\frac{N}{(\Delta C)_m}$		K_Ga (Calculated) $=KD_WD_T(C)^a_m(R)^b(K_E)^{0.2}_m$ (lbs/ft.³hr.)/(lbs/ft.³)	% Error
			W_F, Water Phase Feed	T_F, Toluene Phase Feed	W_P, Water Phase Product	T_P, Toluene Phase Product	Based on Water Phase	Based on Toluene Phase	Average		gram moles/c.c. sec. gram moles/c.c.	lbs./ft.³hr. lbs./ft.³		
1	2400	2030	0.2203	0	0.0567	0.1403	0.0000936	0.0000936	0.0000936	0.0765	0.001222	4.420	4.64	+4.95
2	2400	1680	0.2203	0	0.0478	0.1225	0.0000806	0.0000820	0.0000813	0.0743	0.001093	3.940	4.18	+5.75
3	2400	1265	0.2203	0	0.0352	0.0980	0.0000651	0.0000654	0.0000653	0.0699	0.000934	3.365	3.58	+6.00
4	2400	1015	0.2203	0	0.0280	0.0873	0.0000543	0.0000582	0.0000563	0.0658	0.000855	3.075	3.19	+3.60
5	2400	2030	0.1770	0	0.0519	0.1073	0.0000717	0.0000716	0.0000717	0.0621	0.001152	4.150	4.43	+6.30
6	2400	1680	0.1770	0	0.0445	0.0952	0.0000618	0.0000635	0.0000627	0.0611	0.001024	3.690	3.76	+1.81
7	2400	1265	0.1770	0	0.0324	0.0760	0.0000508	0.0000507	0.0000508	0.0569	0.000893	3.215	3.21	-0.15
8	2400	1015	0.1770	0	0.0255	0.0650	0.0000428	0.0000434	0.0000430	0.0540	0.000797	2.865	2.85	-0.53
9	2400	2030	0.1390	0	0.0481	0.0785	0.0000520	0.0000524	0.0000525	0.0506	0.001037	3.730	3.71	-0.54
10	2400	1680	0.1390	0	0.0418	0.0683	0.0000454	0.0000456	0.0000455	0.0498	0.000913	3.285	3.39	+3.10
11	2400	1265	0.1390	0	0.0302	0.0580	0.0000383	0.0000387	0.0000385	0.0456	0.000845	3.040	2.85	-6.70
12	2400	1015	0.1390	0	0.0239	0.0483	0.0000325	0.00003225	0.0000324	0.04375	0.000740	2.590	2.54	-1.97
13	2400	2030	0.0980	0	0.0440	0.0478	0.00003087	0.0000319	0.0000314	0.0377	0.000832	2.995	3.20	+6.40
14	2400	1680	0.0980	0	0.0386	0.0425	0.00002775	0.0000284	0.0000281	0.0380	0.000739	2.660	2.91	+6.40
15	2400	1265	0.0980	0	0.0280	0.0373	0.0000246	0.00002485	0.0000247	0.0340	0.000727	2.615	2.45	-6.70
16	2400	1015	0.0980	0	0.0225	0.0320	0.0000213	0.0000213	0.0000213	0.0325	0.000656	2.360	2.18	-8.25

TABLE XIV

DATA AND CALCULATED RESULTS OF MASS TRANSFER RATE FOR N-VALERIC ACID-TOLUENE-WATER SYSTEM AT 30° C.

No. Run	Toluene Rate c.c./hr.	Water Solution Rate c.c./hr.	Concentration(gram moles acid /liter				N, gram moles acid transferred/sec.			$(\Delta C)_m$, Log Mean Concentration Gradient, gram moles acid/liter	K_Ga (Experimental) = $\frac{N}{(\Delta C)_m}$		K_Ga (Calculated) $=KD_WD_T(C)^a_m(R)^b(K_E)^{0.2}_m$ (lbs/ft.³hr.)/(lbs/ft.³)	% Error
			W_F, Water Phase Feed	T_F, Toluene Phase Feed	W_P, Water Phase Product	T_P, Toluene Phase Product	Based on Water Phase	Based on Toluene Phase	Average		gram moles/c.c. sec. gram moles/c.c.	lbs./ft.³hr. lbs./ft.³		
1	2400	2030	0.2187	0	0.0109	0.1750	0.0001170	0.0001166	0.0001168	0.0621	0.001882	6.770	6.86	+1.31
2	2400	1680	0.2187	0	0.0079	0.1475	0.0000990	0.0000983	0.0000987	0.0574	0.001719	6.190	6.10	-1.47
3	2400	1265	0.2187	0	0.0055	0.1108	0.0000750	0.0000741	0.0000746	0.0530	0.001407	5.070	5.21	+2.69
4	2400	1015	0.2187	0	0.0044	0.0886	0.0000606	0.0000592	0.0000599	0.0507	0.001180	4.130	4.65	+11.2
5	2400	2030	0.1758	0	0.0109	0.1395	0.0000930	0.0000932	0.0000931	0.0526	0.001170	6.370	6.33	-0.63
6	2400	1680	0.1758	0	0.0079	0.1172	0.0000783	0.0000785	0.0000784	0.0484	0.001620	5.830	5.68	-2.64
7	2400	1265	0.1758	0	0.0055	0.0900	0.0000599	0.0000600	0.0000600	0.0446	0.001345	4.840	4.85	+0.21
8	2400	1015	0.1758	0	0.0044	0.0726	0.0000483	0.0000486	0.0000485	0.0426	0.001138	4.100	4.31	+4.85
9	2400	2030	0.1402	0	0.0109	0.1090	0.0000731	0.0000727	0.0000729	0.0444	0.001640	5.910	5.96	+0.84
10	2400	1680	0.1402	0	0.0078	0.0930	0.0000619	0.0000620	0.0000620	0.0406	0.001528	5.505	5.26	-4.70
11	2400	1265	0.1402	0	0.0055	0.0708	0.0000473	0.00004715	0.0000472	0.0374	0.001260	4.540	4.46	-1.79
12	2400	1015	0.1402	0	0.0044	0.0576	0.0000383	0.0000383	0.0000383	0.03565	0.001073	3.865	3.99	+3.12
13	2400	2030	0.0960	0	0.0109	0.0725	0.00004815	0.0000483	0.0000482	0.0335	0.001438	5.175	5.24	+1.24
14	2400	1680	0.0960	0	0.0077	0.0609	0.00004120	0.0000406	0.0000409	0.0304	0.001345	4.850	4.62	-4.97
15	2400	1265	0.0960	0	0.0055	0.0472	0.00003175	0.0000315	0.0000316	0.02795	0.001131	3.960	3.92	-1.02
16	2400	1015	0.0960	0	0.0044	0.0391	0.00002585	0.0000261	0.0000260	0.0265	0.000982	3.535	3.50	-1.00

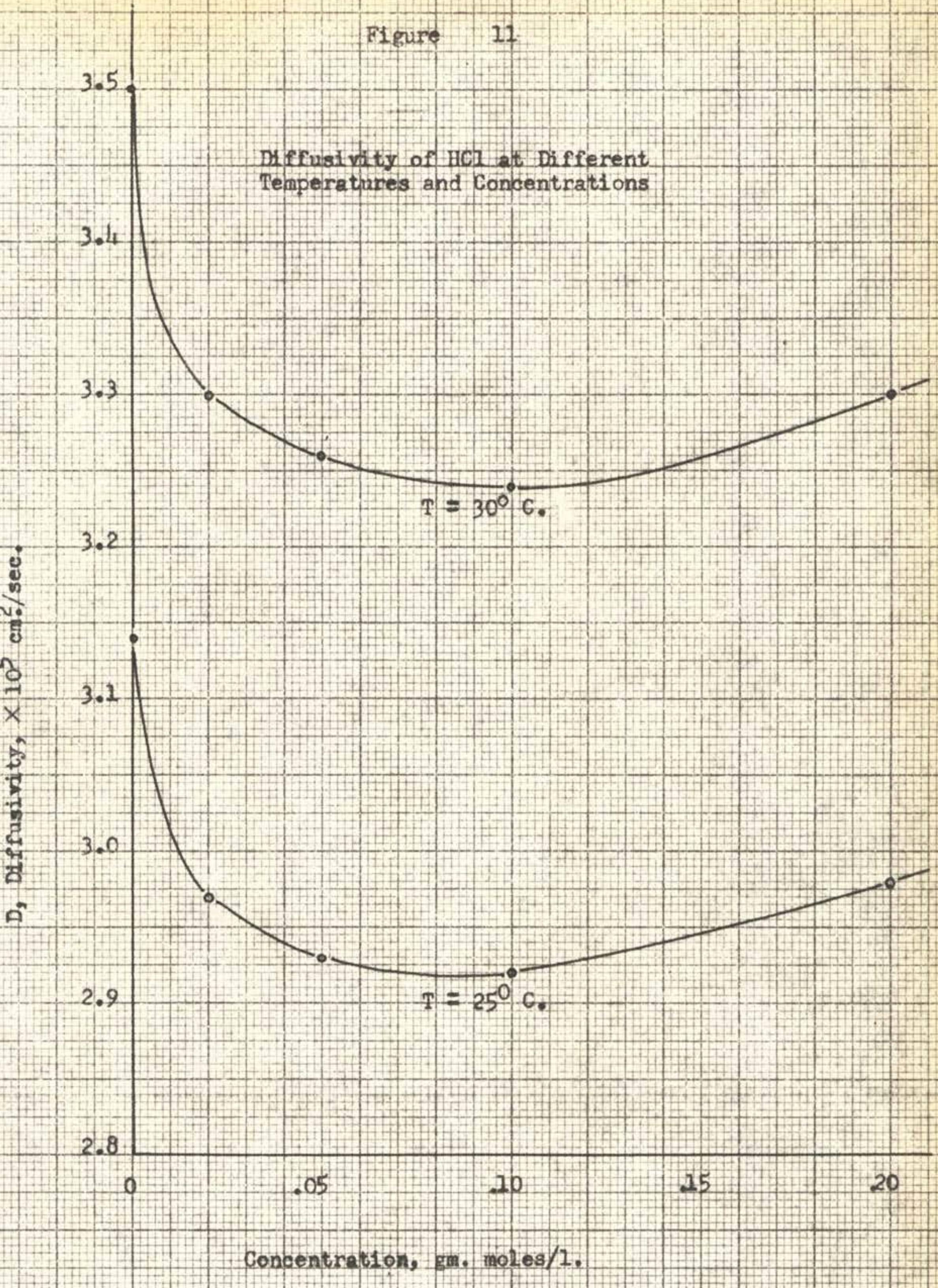


Diffusivity of HCl at Different Temperatures and Concentrations

Figure 10

Figure 11

Diffusivity of HCl at Different Temperatures and Concentrations



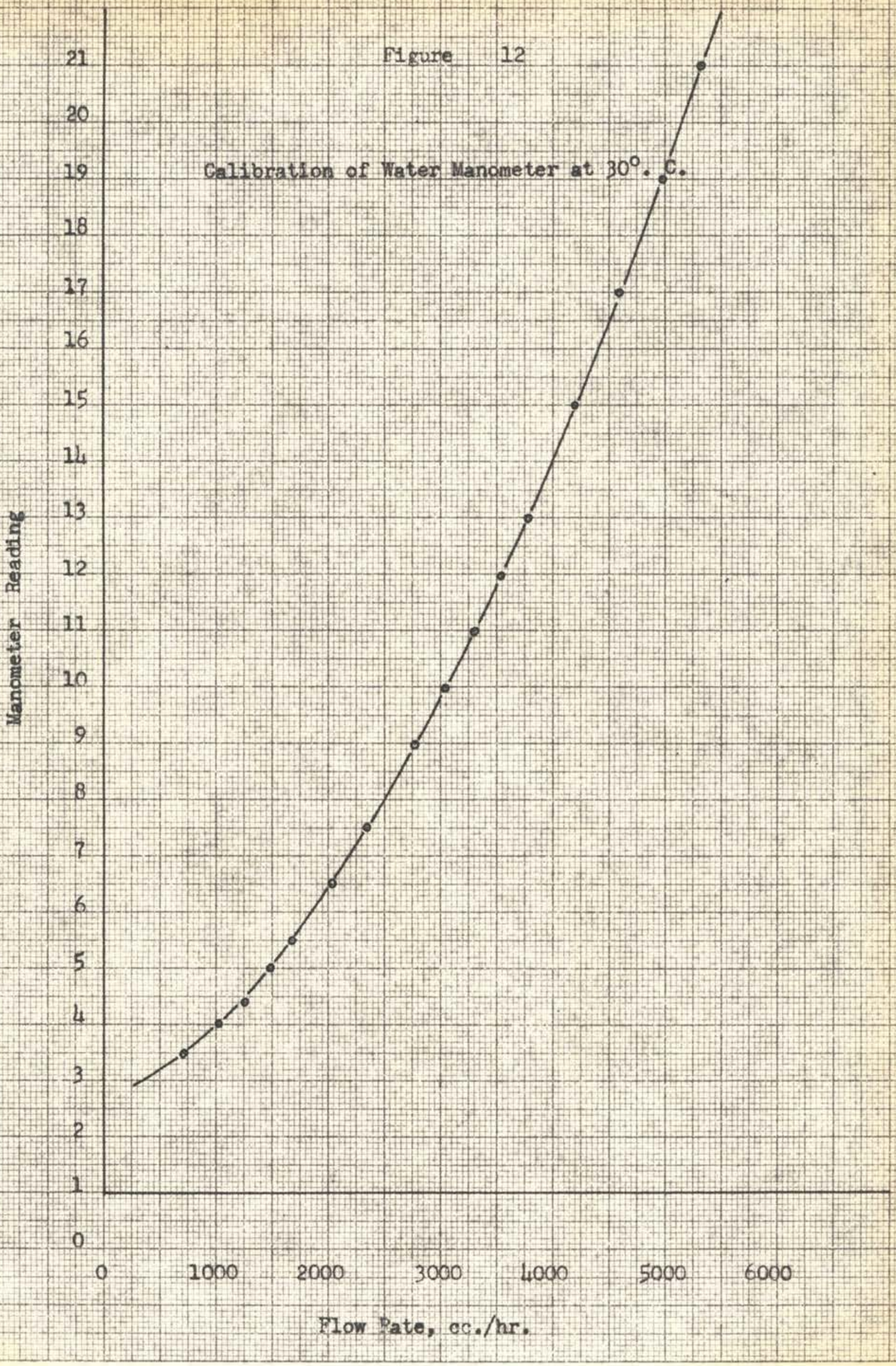


Figure 12

Calibration of Water Manometer at 30°. C.

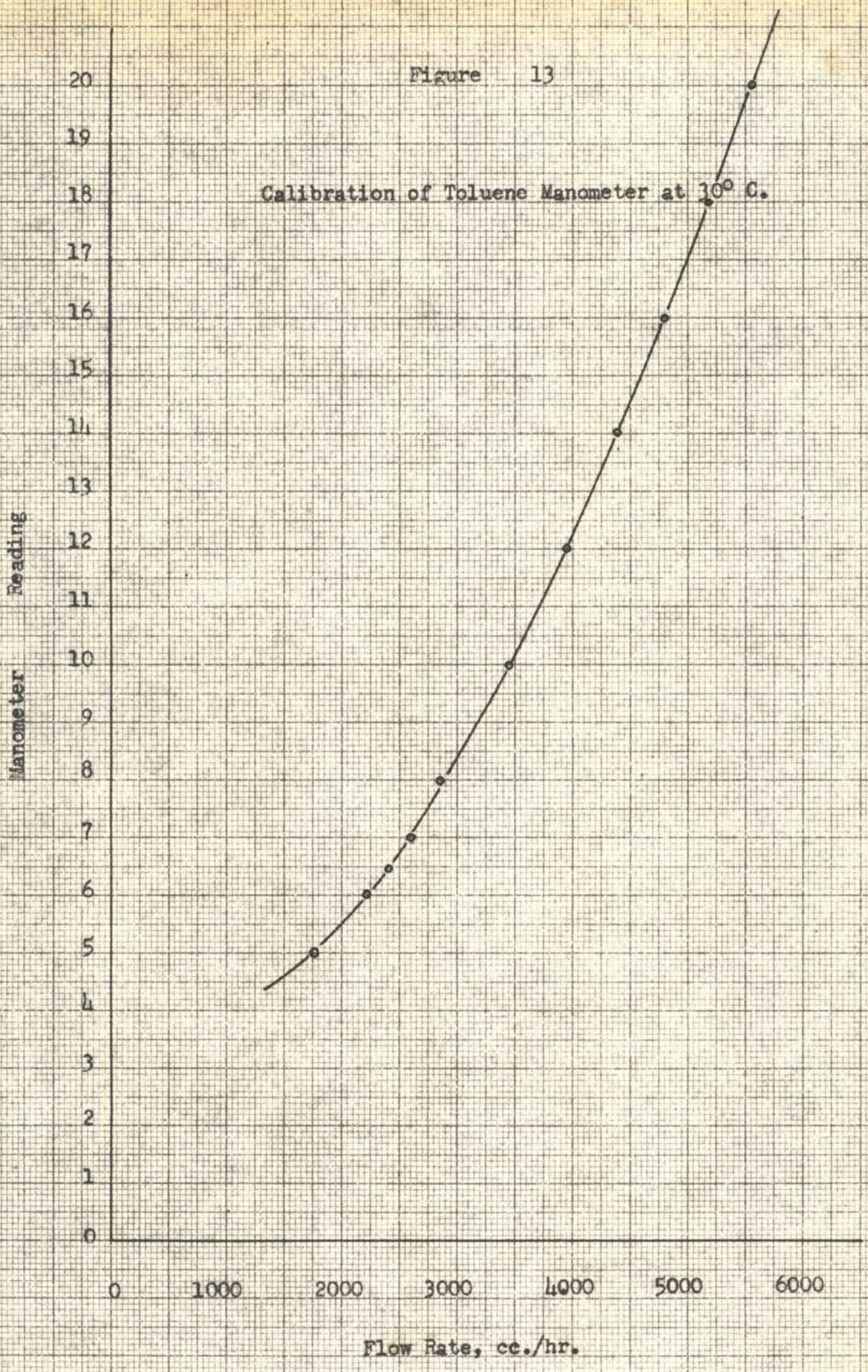
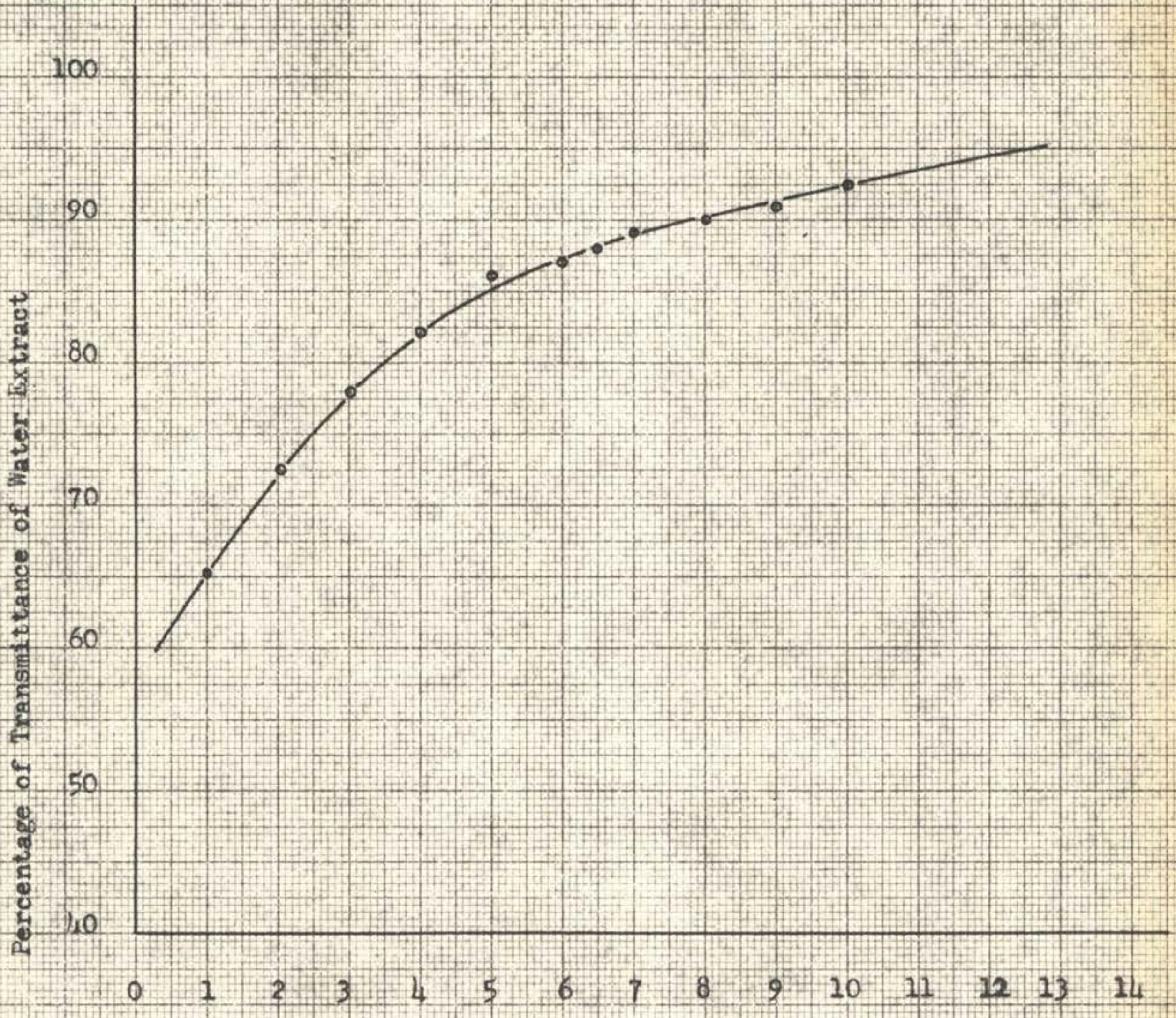


Figure 13

Calibration of Toluene Manometer at 30° C.

Figure 14

Relation of the Concentration of Formic Acid in Toluene Rich Phase to the Percentage of Transmittance in Its Water Extract



Concentration of Formic Acid in Toluene Rich Phase

× 10^4, gm. moles/l.

Figure 15

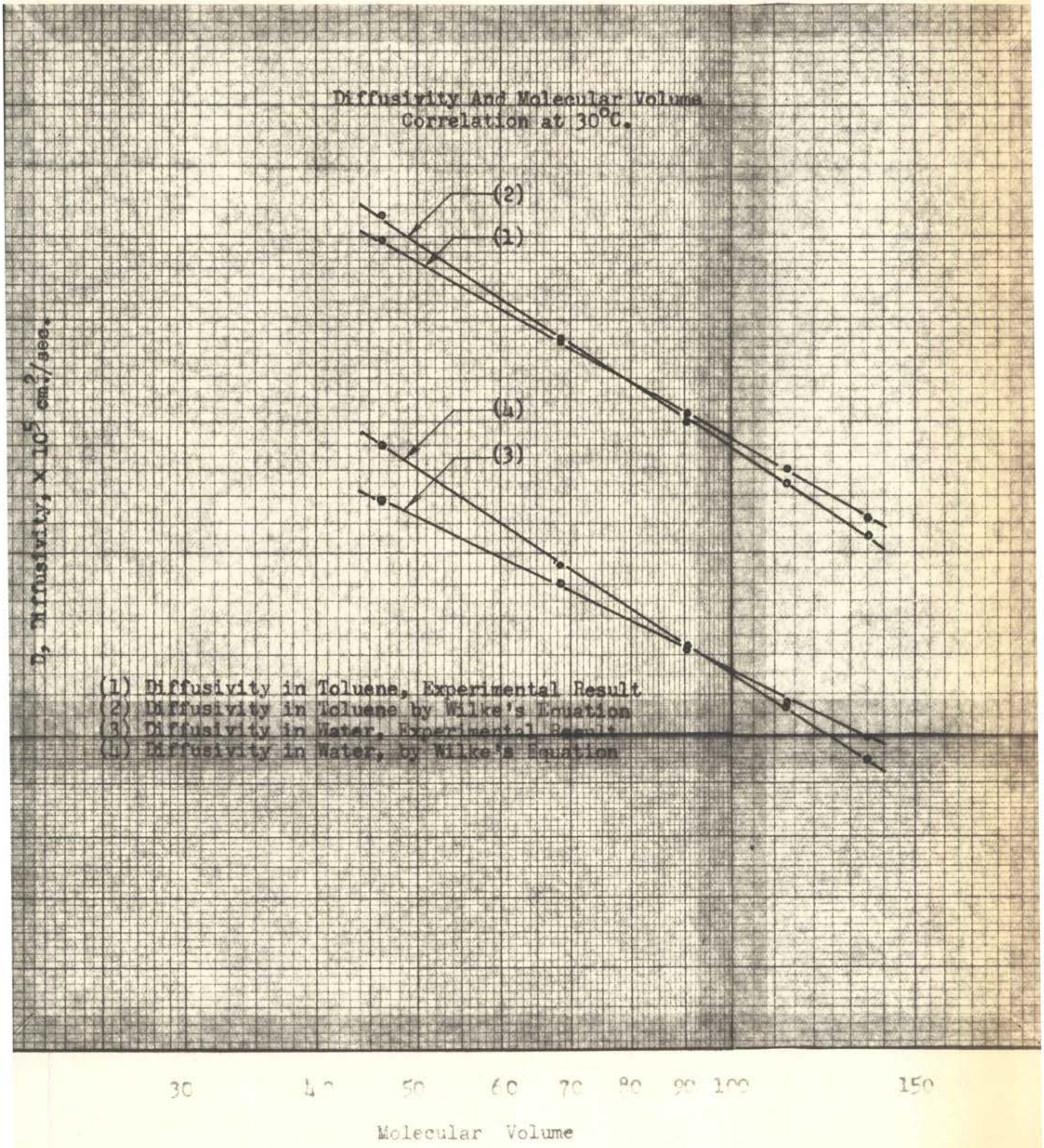
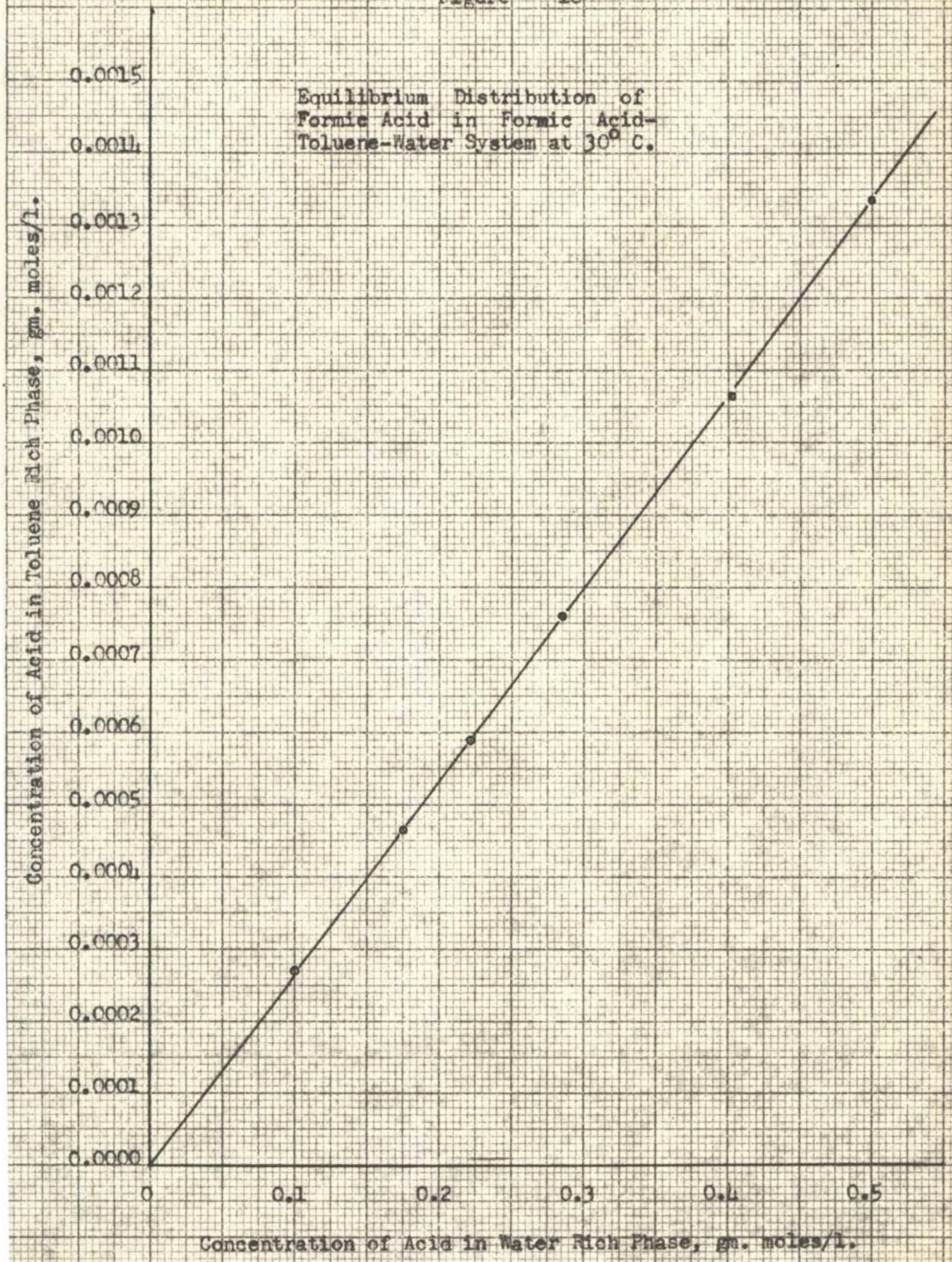

Diffusivity And Molecular Volume
Correlation at 30°C.
(2)
(1)
(4)
(3)
D, Diffusivity, X 10^5 cm.^2/sec.
(1) Diffusivity in Toluene, Experimental Result
(2) Diffusivity in Toluene by Wilke's Equation
(3) Diffusivity in Water, Experimental Result
(4) Diffusivity in Water, by Wilke's Equation
30
40
50
60
70
80
90
100
150
Molecular Volume

Figure 16



Equilibrium Distribution of
Formic Acid in Formic Acid-
Toluene-Water System at 30° C.
Concentration of Acid in Toluene Rich Phase, gm. moles/l.
0.0015
0.0014
0.0013
0.0012
0.0011
0.0010
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
0
0.1
0.2
0.3
0.4
0.5
Concentration of Acid in Water Rich Phase, gm. moles/l.

Figure 17

Equilibrium Distribution of
Acetic Acid in Acetic Acid-
Toluene-Water System at 30°C.

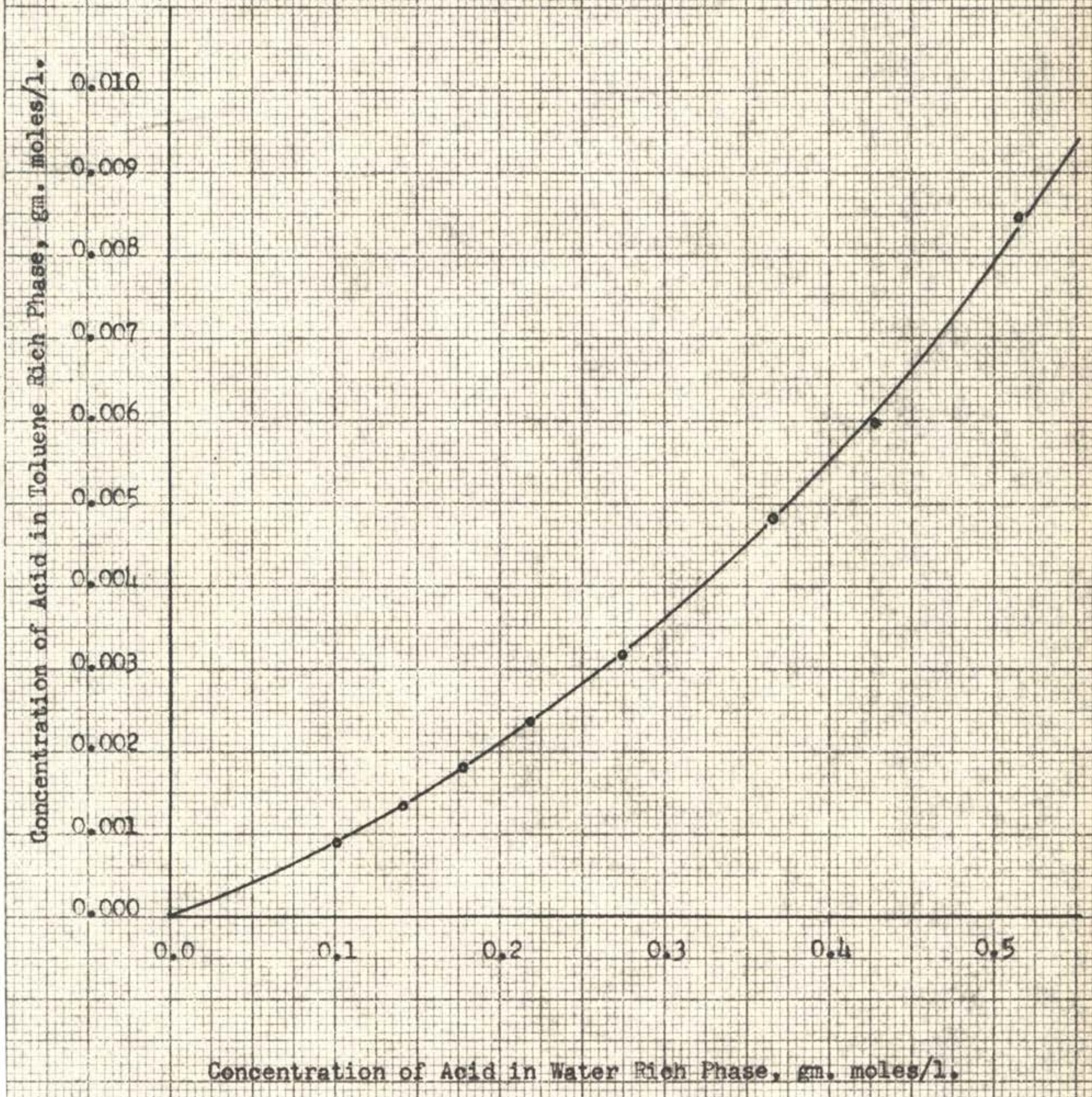
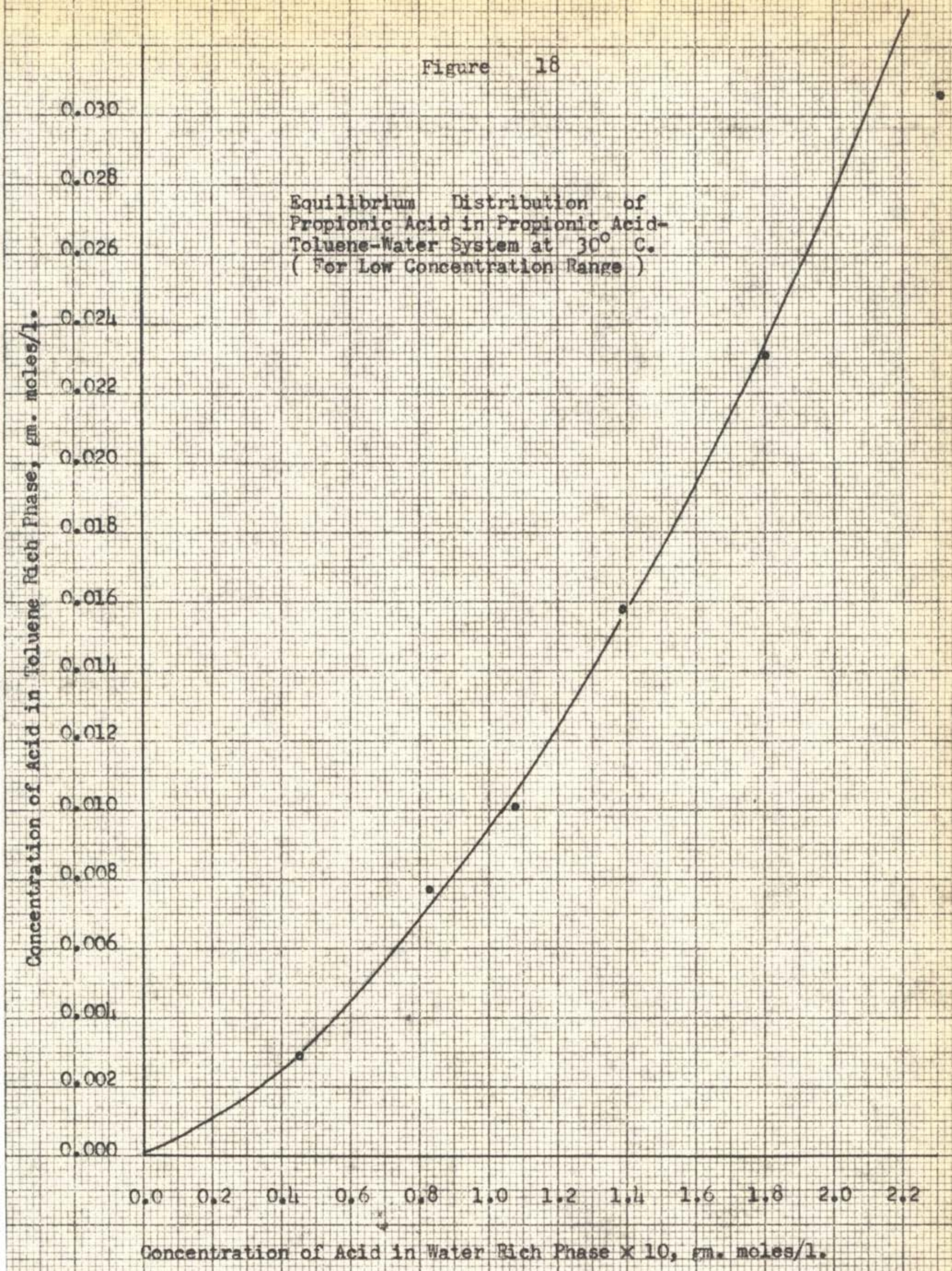


Figure 18



Equilibrium Distribution of Propionic Acid in Propionic Acid-Toluene-Water System at 30° C. (For Low Concentration Range)

Figure 19

Equilibrium Distribution of Propionic Acid in Propionic Acid-Toluene-Water System at 30° C.
(For High Concentration Range)

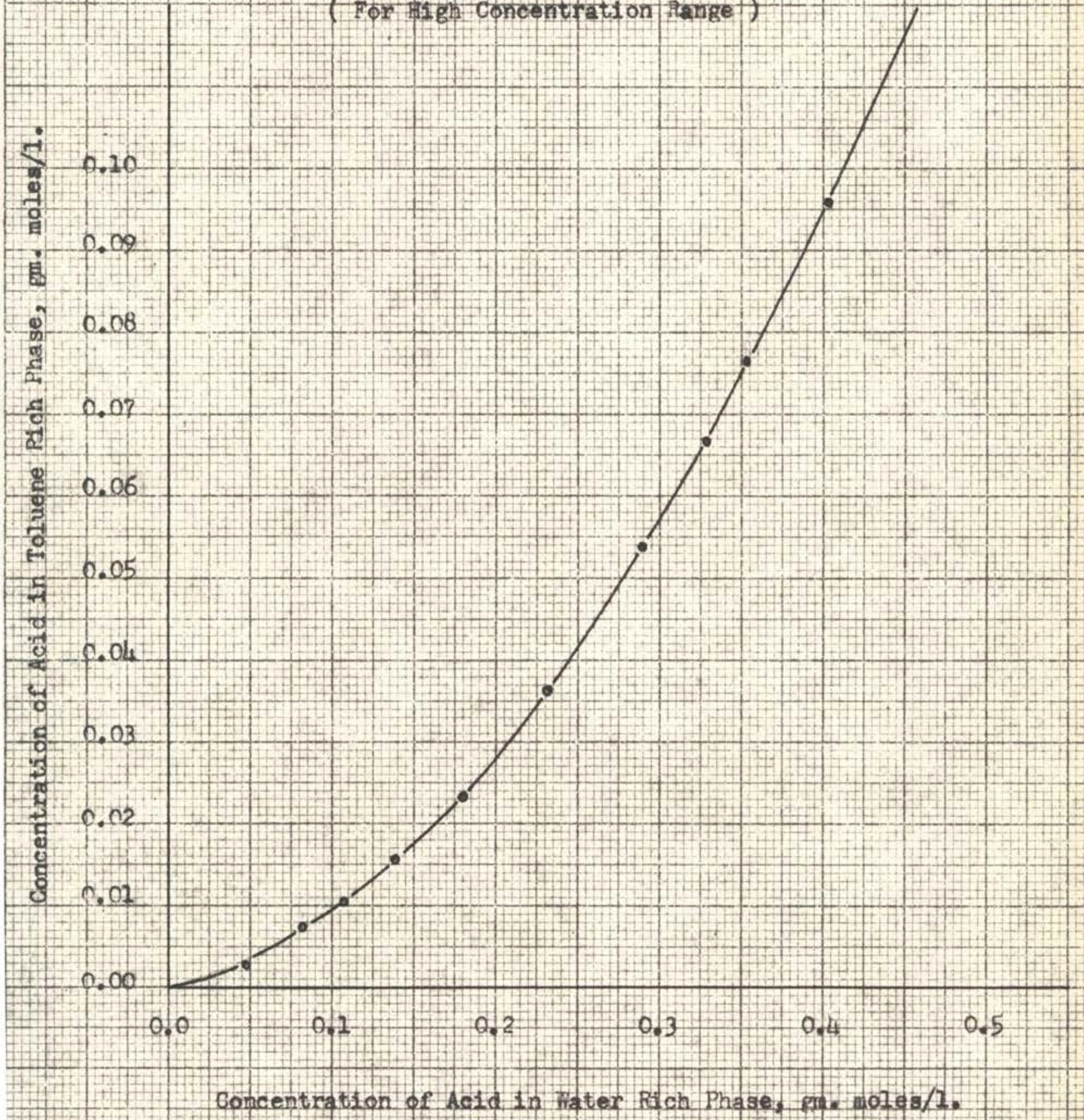


Figure 20

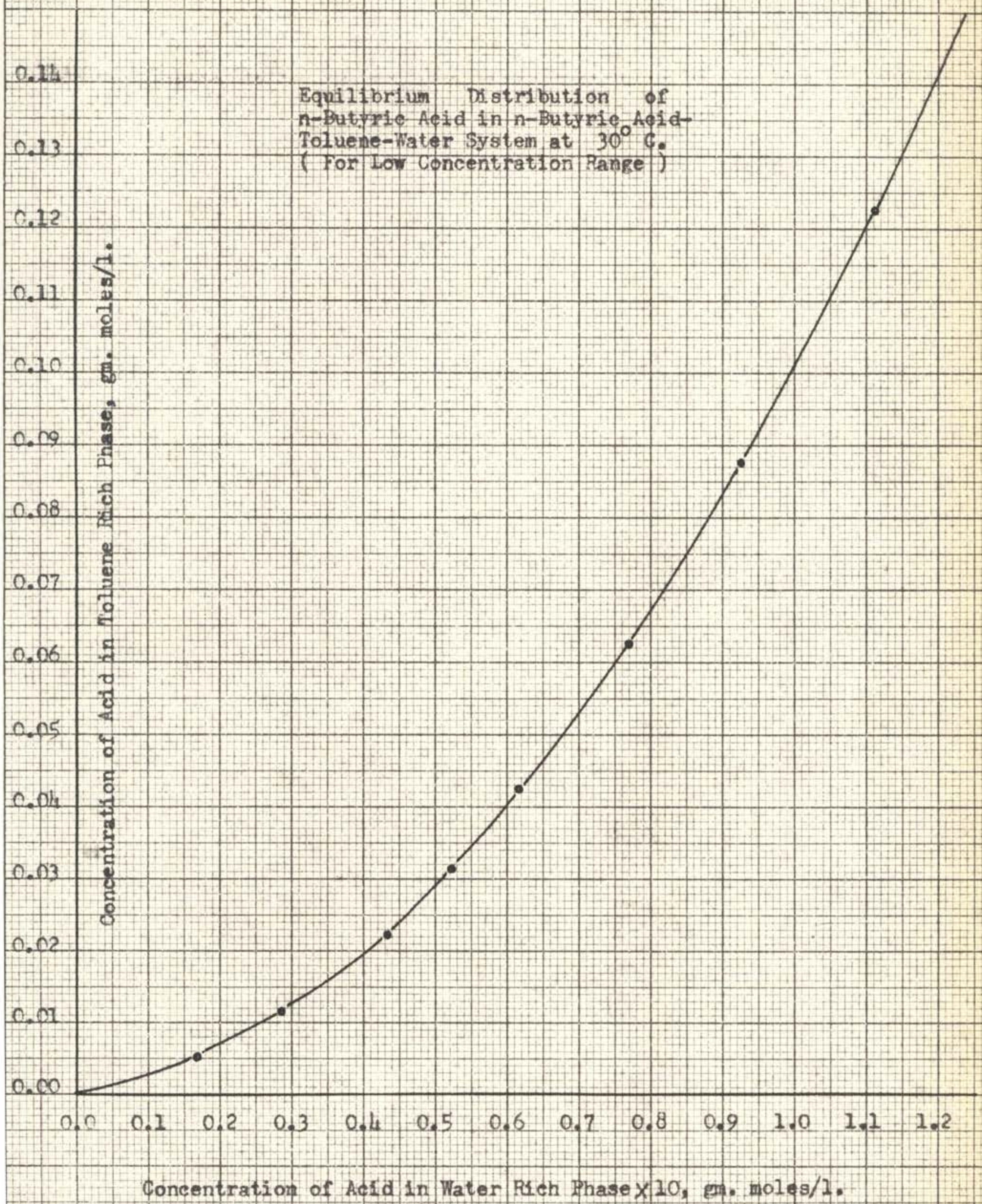
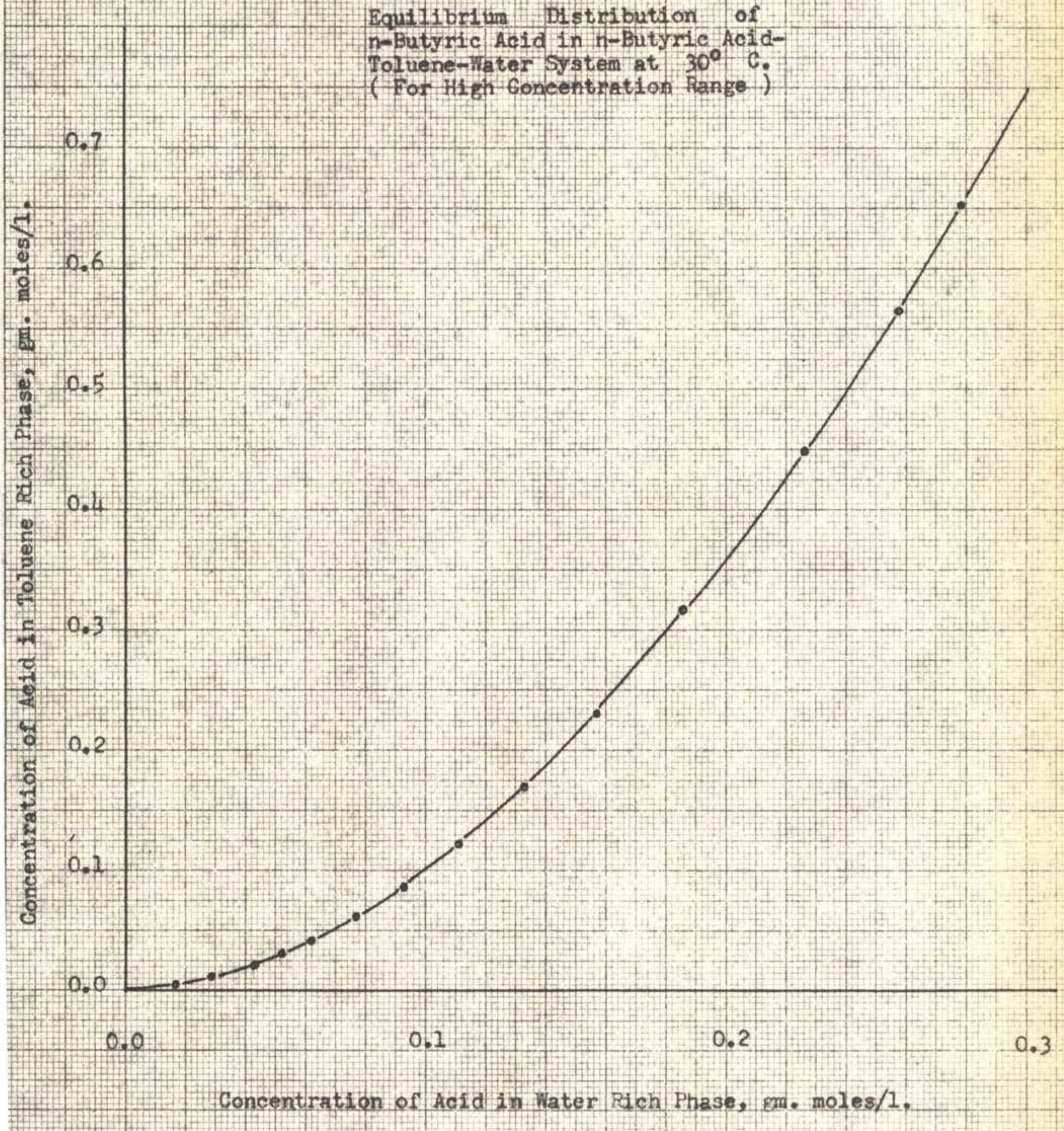

Equilibrium Distribution of
n-Butyric Acid in n-Butyric Acid-
Toluene-Water System at 30° C.
(For Low Concentration Range)
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Concentration of Acid in Toluene Rich Phase, gm. moles/l.
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
Concentration of Acid in Water Rich Phase X 10, gm. moles/l.

Figure 21



Equilibrium Distribution of n-Butyric Acid in n-Butyric Acid-Toluene-Water System at 30° C. (For High Concentration Range)

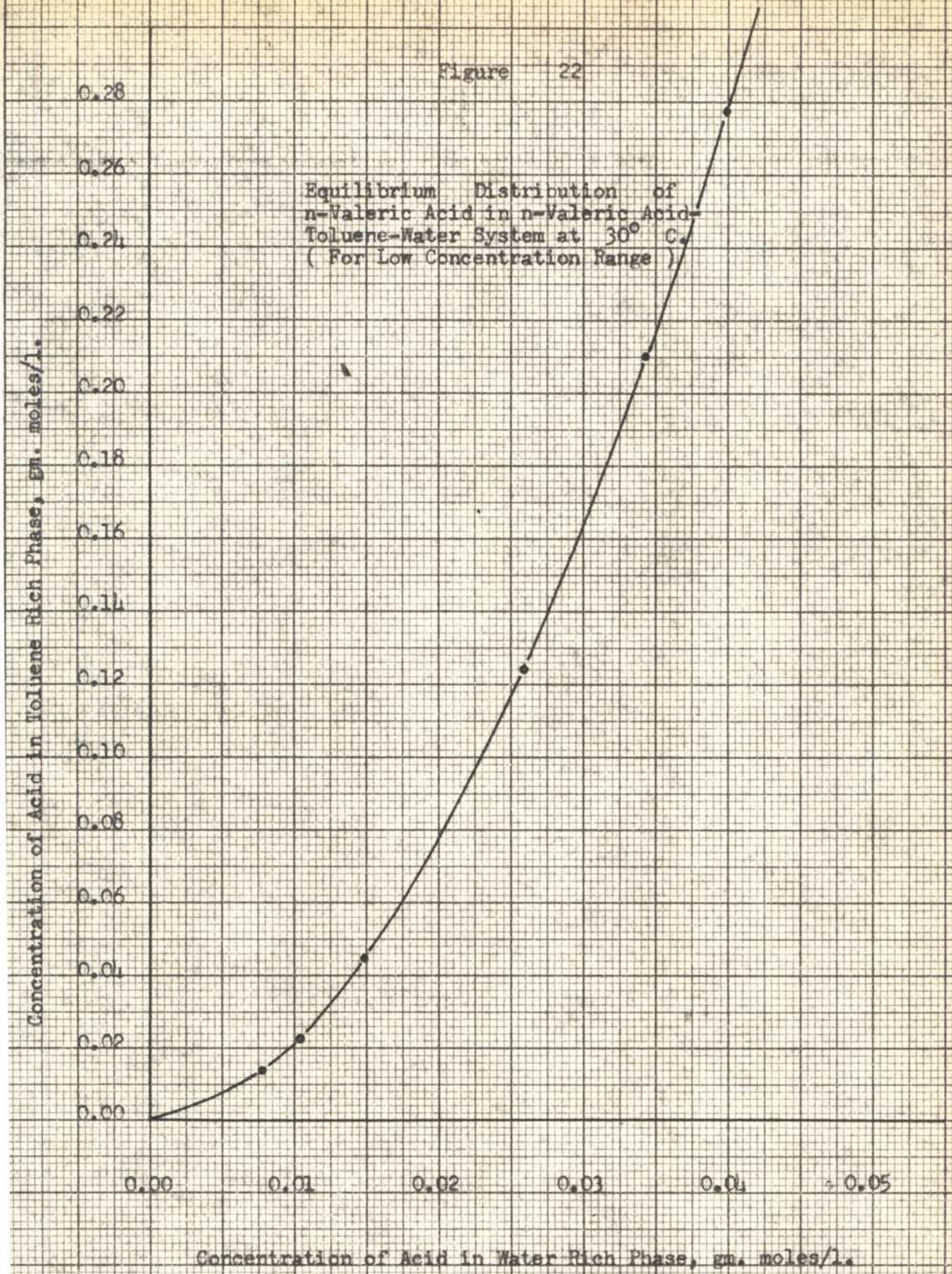


Figure 22

Equilibrium Distribution of n-Valeric Acid in n-Valeric Acid-Toluene-Water System at 30° C. (For Low Concentration Range)

Figure 23

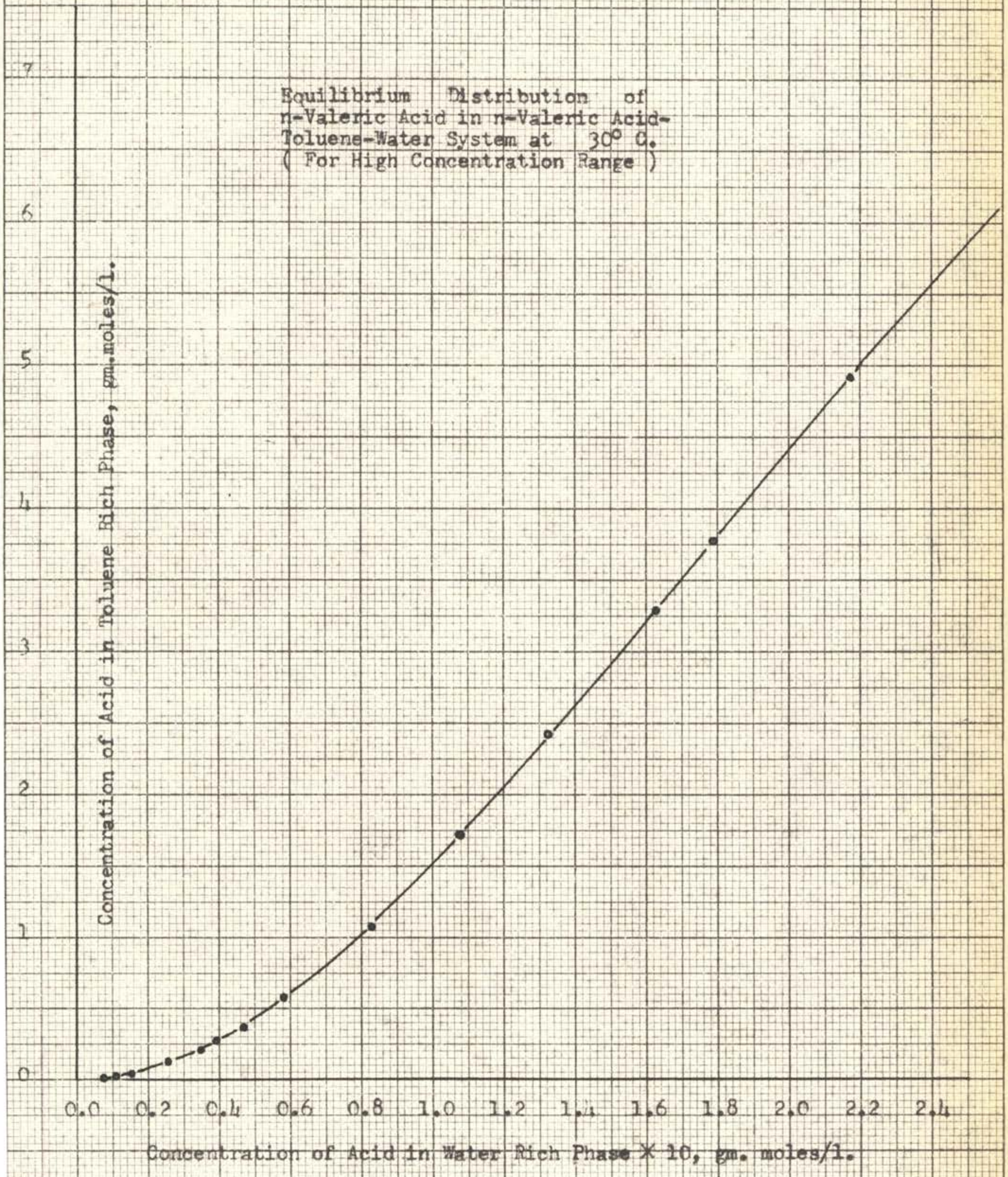
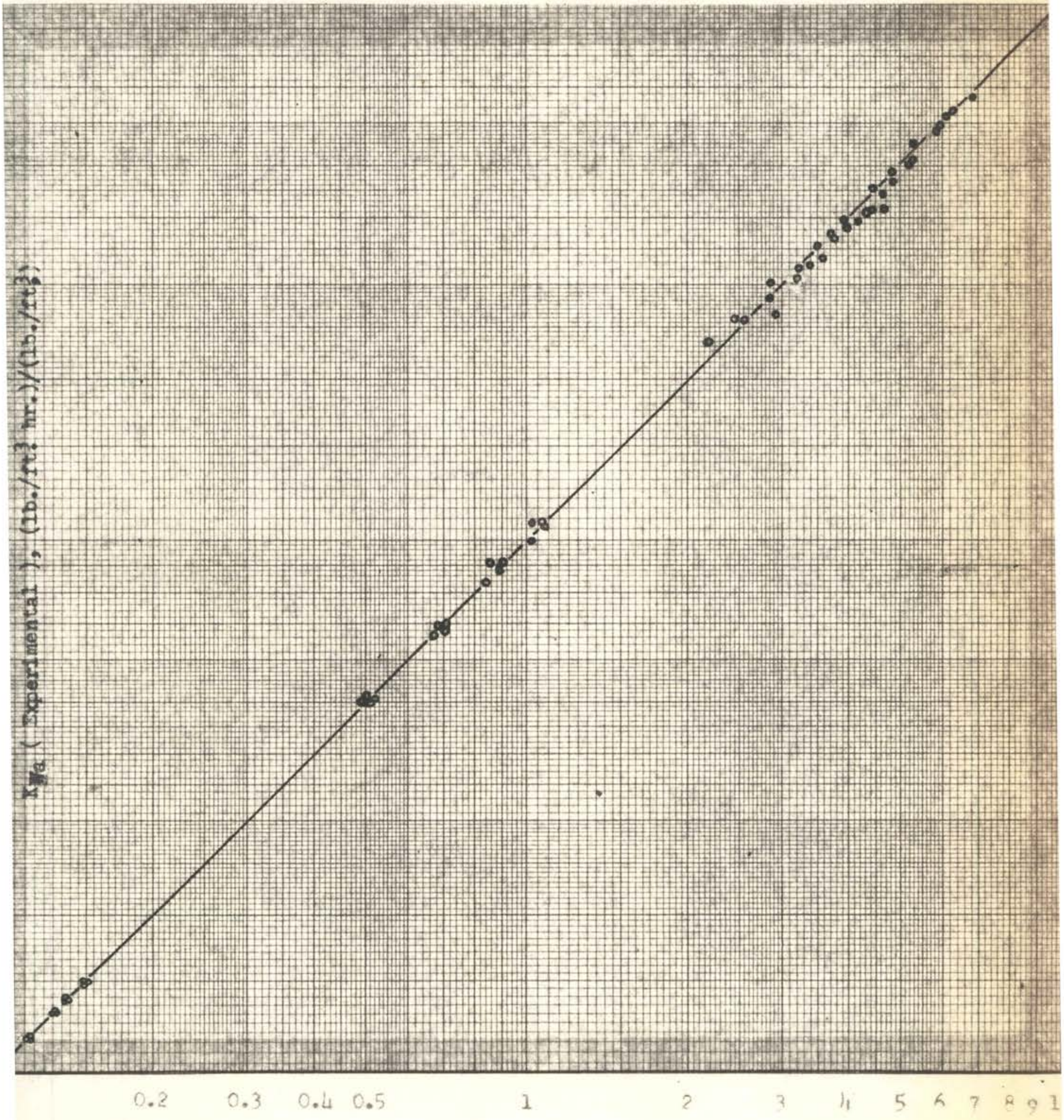

Equilibrium Distribution of
n-Valeric Acid in n-Valeric Acid-
Toluene-Water System at 30° C.
(For High Concentration Range)

Figure 24

Correlation of K_{Wa} (Calculated) to K_{aw} (Experimental)

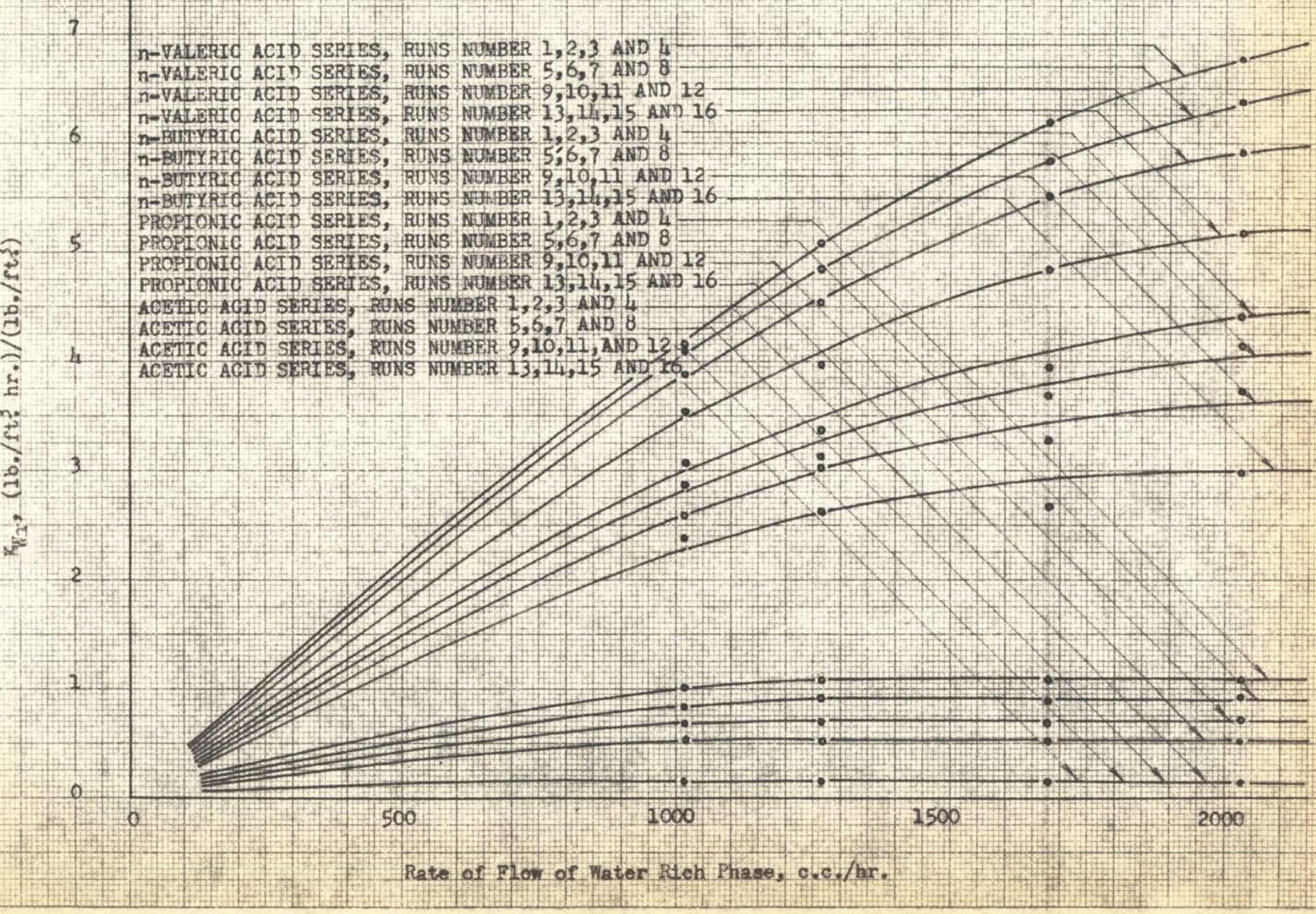
at 30° C.



K_{Wa} (Calculated), (lb./ft.^{3} hr.)/(lb./ft.^{3})

Figure 25

Rate of Flow of Water Rich Phase Versus K_{Wa}



METHOD OF DERIVATION OF THE GENERALIZED EQUATIONS

A. Correlation of Molecular Volume and Diffusivity

1. For the Water Phase.--The diffusivity was plotted versus molecular volume on log-log graph paper, (Figure 15). Since a straight line resulted, an equation of the following form could be written,

$$\log D_W = m \log V + \log C \qquad \text{(IX 1)}$$

where, D_W = diffusivity in water x 10^5, cm.^{2}/sec.,
V = molecular volume, and
m and C = constants.

By substituting two sets of molecular volume and the corresponding diffusivities in equation (IX 1),

$$D_W = 10.9 \left(\frac{1}{V}\right)^{0.487} \qquad \text{(IX 2)}$$

was derived.

2. For the toluene phase, a similar equation was obtained by following the same procedure (Figure 14) as stated in the previous paragraph:

$$D_T = 26.26 \left(\frac{1}{V}\right)^{0.57} \qquad \text{(IX 3)}$$

where, D_T = diffusivity in toluene x 10^5, cm.^{2}/sec.

B. Correlation of Mass Transfer Rate to Physical Properties

It is believed that the mass transfer coefficient for a system in a certain extraction column is a function of D, the diffusivity of the solute in either phase, K_E, the equilibrium concentration distribution constant, C, the concentration of the solute in either phase, $\triangle$, the interfacial tension between the two phases, a, the interfacial area, and R, the flow rate of either phase and the temperature. However, in this particular investigation there are only five significant variables: namely, the concentration in water phase, the diffusivities in both phases, the rate of flow of water phase, and the equilibrium concentration distribution constant. By plotting K_Wa, the capacity coefficient based on the water phase, versus the rate of flow of different acids (Figure 25) at various concentrations, and by drawing curves connecting the points representing the same kind of acid at the same feed concentration, a set of sixteen curves was formed. From these curves the conclusion can be drawn that K_Wa increases with an increase of flow rate of the continuous phase, but decreases with a decrease of feed concentration in the dispersed phase. Despite the fact that the higher members of the fatty acids possess lower diffusivities than those of its lower members, it was noticed that K_Wa increases with an increase in the number of carbon atoms in the fatty acid. This phenomenon can probably be explained by the fact that the distribution constant, which is much greater for the former than that for the latter, is far more significant than the diffusivity in the process of mass transfer.

To correlate the experimental data, this must be carried out stepwise. Theoretically all the variables may be expressed by a general form,

$$K_W a = K(C)_m^{a}(K_E)_m^{c}(R)^{b}(D_T)^{d}(D_W)^{e} \qquad \text{(IX 4)}$$

where $K_W a$ = capacity coefficient based on water phase, hr.$^{-1}$.

$(C)_m$ = log mean concentration of water phase feed and product, gm. moles acid/l.,

R = rate of flow of water phase, c.c./hr.,

$(K_E)_m$ = partition coefficient corresponding to $(C)_m$.,

D_W = diffusivity in water x 10^5, cm.^{2}/sec.,

D_T = diffusivity in toluene x 10^5, cm.^{2}/sec., and

K, a, b, c, d, and e = constants for each acid.

Since all mass transfer rates were measured for dilute solutions with small changes in the concentration range, D_T and D_W can be considered as constant for the same kind of solute, and equation (IX 4) can thus be reduced to,

$$K_W a = (C)_m^{a}(K_E)_m^{c}(R)^{b}\,K' \qquad \text{(IX 5a)}$$

and, at a constant rate of flow, further reduced to:

$$K_W a = (C)_m^{a}(K_E)_m^{c}\,K'' \qquad \text{(IX 5b)}$$

where, K' and K'' are constants only for a single acid. By assuming a value for c, the constant a can be calculated from the experimental data. By trial and error, values of a and c were determined to fulfill each set of different combinations of experimental data. The constant b can be evaluated by substituting the calculated values of c and a, and experimental data into equation (IX 5a). Since a, b, c and K all are constants only for a specified acid, a total of four equations are necessary to make a correlation for each acid. Usually, the physical properties of a series of homologous hydrocarbons can be correlated with the number of carbon atoms present in their structure. Therefore, it would be reasonable to express the constants a, b, c and K in terms of the number of carbon atoms. Since c was found to be universal to all acids and equal to 0.2, only the significance of a, b, and K are to be determined. Let,

$$m_1 + m_2 N + m_3 N^2 + m_4 N^3 = a, \qquad \text{(IX 6)}$$

$$n_1 + n_2 N + n_3 N^2 + n_4 N^3 = b, \qquad \text{(IX 7)}$$

and, $o_1 + o_2 N + o_3 N^2 + o_4 N^3 = K$ (IX 8)

be the general forms,

where, m_1, m_2, m_3, m_4, n_1, n_2, n_3, n_4, o_1, o_2, o_3 and o_4 are constants to be determined, and N is the number of carbon atoms present. By substituting values of a, b, K and N in equation (IX 6), (IX 7) and (IX 8), it was found that with e and d equal to unity,

$$a = -8.50+8.085N-2.24N^2+0.195N^3 \qquad \text{(IX 9)}$$

$$b = 2.6998-2.7265N+0.845N^2-0.0783N^3 \qquad \text{(IX 10)}$$

and $K = -37.306+35.049N-9.924N^2+0.8835N^3$ (IX 11)

Therefore, equation (IX 4) can be used for general cases with the aid of equations (IX 9), (IX 10) and (IX 11), and with d and e equal to unity. The values of calculated capacity coefficient, $K_W a$, and that of the experimentally determined capacity coefficient, $K_W a$, are listed in Tables XI, XII, XIII and XIV, and are plotted in Figure 24. The final form of the generalized equation should be,

$$K_W a = K(C)_m{}^{a}(K_E)_m{}^{0.2}(R)^{b}D_T D_W \qquad \text{(IX 12)}$$

SAMPLE CALCULATIONS

A. Diffusivity Determination

1. Calibration of Cell Constant.

Solution used...................... 0.096973 N HCl

Diffusivity of 0.1 N HCl at 25° C. ....
2.91×10^{-5} cm.^{2}/sec.

Concentration of standard NaOH.......... 0.09867 N

c.c. NaOH for 25 c.c. original solution...........
24.575

c.c. NaOH for 25 c.c. preliminary diffusion sample
0.73

c.c. NaOH for 25 c.c. diffusion sample....... 5.41

c.c. NaOH for 25 c.c. solution remaining inside of the cell at the end of diffusion...... 18.45

Time of diffusion...................... 2455 min.

$$D = \frac{1}{K't} \log \frac{C_1}{C_1 - 2C_2} \qquad \text{(III 3)}$$

$$\text{or } K' = \frac{1}{Dt} \log \frac{C_1}{C_1 - 2C_2}$$

Since the same amount of sample was used for each titration, C_1 and C_2 can be expressed directly in terms of number of c.c. of NaOH required instead of using concentration,

$$K' = \frac{1}{2.91 \times 10^{-5} \times 2455 \times 60} \log \frac{24.575 - 0.73}{24.575 - 0.73 - 2(5.41)}$$

$$= 0.06127 \text{ cm.}^{-2}$$

2. Diffusivity for Unknown Substance

Solution used............. 0.0998 N Propionic Acid

Time of diffusion...................... 4018 min.

Temperature.............................. 30° C.

Cell Constant........................ 0.06142 $cm.^{-2}$

Concentration of standard NaOH......... 0.09867 N.

c.c. NaOH for 25 c.c. original solution..... 24.95

c.c. NaOH for 25 c.c. preliminary diffusion sample................................. 0.35

c.c. NaOH for 25 c.c. diffusion sample....... 4.18

c.c. NaOH for 25 c.c. solution remaining inside of the cell at the end of diffusion...... 20.61

$$D = \frac{1}{K't} \log \frac{C_1}{C_1 - 2C_2} * \qquad \text{(III 3)}$$

$$= \frac{1}{0.06142 \times 4018 \times 60} \log \frac{24.95-0.35}{24.95-0.35-2(4.18)}$$

$$= 1.218 \times 10^{-5} \text{ cm.}^2/\text{sec.}$$

B. Equilibrium Distribution

System used for sample calculation.........Toluene-Water Propionic Acid System

Concentration of standard NaOH............... 0.0326 N

c.c. NaOH for 25 c.c. water rich sample......... 50.45

c.c. NaOH for 25 c.c. toluene rich sample....... 10.25

Temperature................................... 30° C.

* Note: Equation III.4 was used for formic acid in toluene.

$\frac{50.45 \times 0.0326}{5}$ = 0.329 gm. moles acid/liter water rich solution

$\frac{10.25 \times 0.0326}{5}$ = 0.0669 gm. moles acid/liter toluene rich solution

$$K_E = \frac{C_T}{C_W} = 0.2034$$

C. Mass Transfer Rate Determination

System used for sample calculation........ Run No. 1, propionic acid-water toluene series

Acid concentration of water rich feed, W_F ..... 0.2197 gm. moles/liter

Acid concentration of water rich product, W_P .. 0.1840 gm. moles/liter

Acid concentration of toluene rich feed, T_F ... 0.0000 gm. moles/liter

Acid concentration of toluene rich product, T_P 0.02945 gm. moles/liter

Toluene phase feeding rate................ 2400 c.c./hr.

Water phase feeding rate.................. 2030 c.c./hr.

V, effective packing volume.............. 1000 c.c.

N, gram moles acid transferred per second,

$= \frac{2030(0.2197-0.1840)}{3600} = 0.00002015$ (based on water phase)

or, $= \frac{2400(0.02945-0)}{3600} = 0.00001968$ (based on toluene phase)

and, $= \frac{0.00002015+0.00001968}{2} = 0.00001992$ (average)

Equilibrium concentration of acid in water rich phase corresponding to toluene product was found as 0.2068 gm. moles/liter from Figure 19.

Since $K_W a = \dfrac{N}{V(\Delta C)_m}$ * (III 5)

* Note: For acetic acid-water-toluene system $(\Delta C)_m$ was calculated by the following procedure:

$$\Delta C_1 = \frac{1}{M}(T_E - T_P),$$

$$\Delta C_2 = W_F,$$

and, $$(\Delta C)_m = \frac{\Delta C_1 - \Delta C_2}{2.303 \log \dfrac{\Delta C_1}{\Delta C_2}}$$

where, M = slope of equilibrium distribution curve,

T_E = Equilibrium concentration of toluene phase corresponding to W_F,

and, $$(\Delta C)_m = \frac{\Delta C_1 - \Delta C_2}{2.303 \log \dfrac{\Delta C_1}{\Delta C_2}}$$

$$= \frac{(0.2197-0.2068)-(0.1840-0)}{2.303 \log \dfrac{(0.2197-0.2068)}{(0.1840-0)}}$$

$$= 0.0668 \text{ gm. moles/liter}$$

$$K_W a = \frac{0.00001992}{\left(\frac{1000}{1000}\right) 0.0668} = 0.000298 \ \frac{\text{gm. moles/cm.}^3 \text{ sec.}}{\text{gm. moles/cm.}^3}$$

or $$K_W a = 1.072 \ \frac{\text{lb./ft.}^3\text{hr.}}{\text{lb./ft.}^3}$$

NOMENCLATURE

A = area of diffusion.

a = constant, or

a = area of diffusion, or

$a = -8.50+8.085N-2.24\ N^2 + 0.195\ N^3$.

$b = 2.6998-2.7265N+0.845N^2-0.0783N^3$.

c = constant.

C = concentration, gm. moles/liter.

C_T = concentration in toluene phase, gm. moles/liter.

C_W = concentration in water phase, gm. moles/liter.

$(C)_m$ = log mean concentration of water phase feed and product, gm. moles acid/liter.

$(\Delta C)_m$ = Log mean concentration gradient, gm. moles/liter.

C_1 = concentration of solution in the cell at time t, gm. moles/liter.

C_2 = concentration of solution in receiving tube at time t, gm. moles/liter.

$\frac{dC}{dx}$ = concentration gradient.

D = diffusivity, cm.^{2}/sec.

D_T = diffusivity in toluene x 10^5, cm.^{2}/sec.

D_W = diffusivity in water x 10^5, cm.^{2}/sec.

h = thickness of the sintered glass disc.

$K = -37.306 + 35.049N - 9.924N^2 + 0.8835\ N^3$.

K = a constant = A/h.

K' = constant.

K' = cell constant, cm.$^{-2}$.

K'' = constant.

$K_E = \frac{C_T}{C_W}$ = partition coefficient (or equilibrium distribution constant).

$(K_E)_m$ = partition coefficient corresponding to $(C)_m$.

K_Wa = mass transfer coefficient based on water phase (gm. moles/c.m.^{3}-sec.)/(gm. moles/c.m.^{3}), or

K_Wa = mass transfer coefficient based on water phase (lbs./ft.^{3} hr.)/(lbs./ft.^{3})

M = slope of equilibrium distribution curve.

m = constant.

N = gm. moles acid transferred/sec., or

N = number of carbon atoms in acid, or

N = normality.

Q = quantity of solute in dilute solution at any time, gm. moles.

dQ = a differential quantity of material.

R = rate of flow, or

R = rate of flow of water phase, c.m.^{3}/hr.

S = interfacial tension, or

S = total amount of solute at beginning of experiment, gm. moles.

T_E = equilibrium concentration of toluene phase corresponding to W_F.

dt = a differential period of time.

t = time, sec.

V = molecular volume. (c.m.^{3}/gm. moles at boiling point),

V = volume of packing space, liter.

V_1 = volume of more concentrated solution = volume of cell, cm^3.

V_2 = volume of dilute solution = volume of liquid in receiving tube, cm^3.

Subscripts

a = constant.
b = constant.
c = constant.
d = constant.
e = constant.
F = feed.
m = constant.
0 = initial state.
P = product.
T = toluene phase.
W = water phase.
1 = different stage.
2 = different stage.

VITA

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candidate for the degree of
Doctor of Philosophy

Thesis: CORRELATION OF MASS TRANSFER COEFFICIENTS, PHYSICAL PROPERTIES AND FLOW RATES IN LIQUID-LIQUID EXTRACTION

Major: Chemical Engineering

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