

SAMPLING OF THE PHASES WITHIN A LIQUID-
LIQUID EXTRACTION SPRAY COLUMN

by

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ABSTRACT

A study has been made of sampling techniques in a liquid-liquid extraction spray column using first a bell-shaped and a hook-shaped probe for the dispersed phase and for the continuous phase respectively. Later a piston method was attempted for the dispersed phase. The main interest in this research was the point concentration inside the column.

At first, the time to reach steady state was considered in the absence of sampling. Later on, the rate of purging and sampling was varied for the probes up to 14.2 cc./min. for the continuous phase and 28.2 cc./min. for the dispersed phase. These rates were not sufficient to disturb the steady state. The measured point concentration was studied as a function of rate of sampling. Coalescence at the dispersed phase (bell-shaped) probe entrance did not take place.

Finally, a piston sampler was set up and used in conjunction with the continuous phase (hook-shaped) probe as a second way to obtain point concentrations of the dispersed phase to compare with the results obtained with the bell-shaped probe.

From these experiments, it can be concluded that sampling rate, varied from zero to 34.0 cc./min. for the continuous phase and from zero to 28.0 cc./min. for the dispersed phase, does not influence the point concentrations measured for column flows of $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$ and $72.4 \text{ ft}^3/\text{hr.}-\text{ft}^2$ for the water and ketone phases respectively. The point concentration of the dispersed phase measured with the piston do not check definitively the results obtained with the bell-shaped probe; they do indicate that such agreement is fairly probable.

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The production of a covering for the piston, to permit it to operate without leaks, was solely the work of R. Muelchen.

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INTRODUCTION

The last decade has seen the unit operation called liquid-liquid extraction having a rapid growth. These new developments were due firstly to the industrial users asking for more information which showed the need for research. Secondly, the interest of researchers in mass transfer operations caused the spray column type of liquid-liquid extractor to be analyzed by many workers (1,2,3,4,5,6,7,8,9,10,11,12,13).

Mass transfer coefficients were determined in general by using the inlet and outlet concentrations and calculating the logarithmic mean driving force. Several assumptions were made in doing such calculations. One of these was that the two liquids involved were not back-mixing. Another, was that no mass transfer took place during drop formation or during drop coalescence at the end of the column, or in other words, that end effects were absent. It can be pointed out that dilute solutions were assumed also (or constant flows) and constant slope of the equilibrium curve. These were the principal assumptions made before the work of many investigators mentioned later in this survey.

In 1950, Geankoplis and Hixon (1) employed a movable sampling device to remove internal samples of the continuous phase during operation of a spray tower. This sampler consisted primarily of a 5 mm. outside diameter (0.12 in. inside diameter) glass tube, which extended into the extraction section and occupied approximately 1.7% of the column cross sectional area. By means of a hook at the end of the sampler, the descending continuous phase was withdrawn;

the sampler tube touched the wall of the column. These workers determined the continuous phase concentration profile throughout the column and located a large end effect at the inlet of the continuous phase. No end effect was found at the dispersed phase inlet.

Later on, Geankoplis, Wells and Hawk (2), using the same method, found the same large end effects at the continuous phase inlet, and also that these depended neither on the type of system employed, nor the direction of solute transfer. They also proved that the effect of internal sampling is small on the material balances. Also, the effect of internal sampling was small since the deviation in the over-all material balance, calculated as follows:

$$N_w = A L_w (C_{w1} - C_{w2})$$

$$N_t = A L_t (C_{t2} - C_{t1})$$

$$N = \frac{N_w + N_t}{2}$$

$$\% \text{ Deviation} = \frac{N_w - N_t}{N} \times 100$$

averaged 4 % or less for all runs in the tower.

In 1952, Newman (3) entered the discussion and maintained that the end effects found by Geankoplis and Hixson (1) and by Geankoplis, Wells and Hawk (2), were the results of vertical mixing of the continuous phase due to the movement of the drops. He showed that the results of Geankoplis and coworkers (1,2) were midway between the results to be expected for truly countercurrent, unmixed flow of the continuous phase, and the completely uniform concentration in that phase which would be produced by very efficient stirring.

One year later, Geankoplis with Kreager (4) studied the effect of the column height on the mass transfer coefficient. Their conclusions were the same as to end effects at the

continuous phase inlet which Geankoplis and Kreager (4) suggest to be due to the cocurrent flow of continuous phase in the form of "atmospheres" of continuous phase surrounding and travelling with the drops of dispersed phase.

In the same year, Gier and Hougen (5) used two sampling techniques. In the column itself, nine holes were drilled 6 inches apart along the length of a 6 in. I.D. column to provide an entrance for 3 in. hypodermic needles which sampled the continuous phase. Each needle had a thin-walled brass tube bent into a hook shape so that the open end of the hook faced in the direction of drop movement. These sampling needles fitted 29 ml hypodermic syringes. Later, provision was made for sampling the dispersed phase by drilling eight holes along the length of the column, opposite to and midway between the needle holes already mentioned. The dispersed phase samplers each consisted of an inverted 1 in. glass funnel connected by Tygon tubing to a suitably formed length of ¼ in. copper tubing. They found the concentration profiles for the continuous phase similar to those measured by Geankoplis and co-workers (1,2,4) and showed that the material balance equation was not applicable when written as follows:

$$dN = L_c dC_c,$$

although, it was true that:

$$dN = L_d dC_d.$$

(dN being the mass transfer across the interface between phases in a height dh of column). This statement is correct even if the same equations, integrated, both hold for terminal conditions. The reason for the first equation failing is a serious bulk mixing of the continuous phase. The second equation holds because the drops do not back-mix. They also concluded that because of the mixing, the measured height of a transfer unit (as defined later by Miyauchi (6)) must be

determined graphically from internal conditions.

Furthermore, it is pointed out by Smoot and Babb (7) that if longitudinal mixing is extensive, even a graphical integration of the resulting profile to obtain the measured Nox may not yield the "true" Nox. This is equivalent to stating that in the equation:

$$\text{Nox} = (\text{Nox})_M + \text{Correction term}$$

even a graphical integration using the experimental concentration profile and this equation:

$$(\text{Nox})_M = \frac{dx}{x_e - x}$$

will not yield the "true" value of Nox as defined by this equation:

$$\text{Nox} = \frac{K_x a h}{V_x}$$

unless the third term of the first equation mentioned here, is negligible. But this third term is a term which corrects for back-mixing in the x phase. Then, if the x phase is the dispersed phase, Nox and $(\text{Nox})_M$ are identical, since the correction term goes to zero because of no mixing in that phase.

In 1954, Heertjes, Holve and Talsma (8) measured the concentration of the continuous phase of a spray column by draining the column in stages at the end of runs and sampling the effluents. The concentration of the continuous phase appeared to be nearly constant over the column's height. These results appeared to show the existence of good vertical axial mixing but they do not agree with those of Geankoplis and co-workers (1,2,4) where the concentration of the continuous phase was not constant with distance. This difference in the results may be due to mixing, taking place before draining and caused by the currents produced by the final rising of drops after

flow is shut off; perhaps the difference may be also due in part to mixing caused by draining, and also to convection due to density differences.

The foregoing summarizes the information available on sampling techniques before the start of the research in Canada by Cavers and Ewanchyna (9). These workers studied circulation in the continuous phase of a spray column and end effects. Their techniques consisted of using movable vertical probes based on those of Geankoplis and co-workers (1,2,4) and those of Gier and Hougen (5). The first set of internal sampling tubes was constructed of Pyrex tubing, 1/8-in. O.D. and 0.08-in. I.D.. The continuous phase sampling tube had one end curved in the form of a hook with a 3/16-in. I.D. radius. The probe entrance faced upward, away from the rising drops. The dispersed phase sampling tube had one end flared out to 1/4-in. O.D. in order to catch the ketone drops. The maximum percent of the internal cross-sectionnal area of the column occupied by the two probes taken together was approximately 4.2%. (The area of two 1/8-in. diameter circles and one 1/4-in. diameter circle is 4.2% of that of a 1.5-in. diameter circle). These Pyrex sampling tubes did not prove to be very satisfactory because of breakage problems; however, their functioning in other respects was good. A second set of sampling tubes was made out of 1/8-in. O.D. and 0.020-in. wall thickness Type 304 stainless steel seamless tubing. The continuous phase sampling tube had one end curved in the form of a hook with a 3/32-in. I.D. radius. The opening faced the top of the column as before. The dispersed phase sampling tube was fitted into a flared out section of 21/64-in. maximum O.D.. In this case, the maximum percent of the internal column's cross-sectionnal area occupied by the two probes

taken together was 6.2%. These probes were lowered into the column from the top. This approach therefore was similar to that used for the continuous phase only, by Geankoplis and co-workers (1,2,4), but slightly different from that of Gier and Hougen (5). Cavers and Ewanchyna (9) confirmed that the presence of sampling tubes in the column did not change the column operation. They also demonstrated that the direction of sampling (i.e. from top to bottom or bottom to top of the column) did not influence the measured point concentrations. It was also proved that the location of the tubes in the horizontal cross section had no effect on the concentrations of samples withdrawn.

These workers found no end effects where the dispersed phase entered the column, but did find end effects at the continuous phase inlet to the column, i.e. discontinuities in the concentration profiles. For the case of transfer of acetic acid from a continuous aqueous phase to a dispersed, methyl isobutyl ketone (M.I.B.K.) phase, they explained that the discontinuity in the water phase profile could be broken into two parts: one representing the effect of drop agitation at the interface, and the other the effect of back-mixing in the aqueous phase. The discontinuity in the ketone phase concentration profile was attributed to the agitation effect. For transfer of acetic acid in the reverse direction, the discontinuity in the ketone phase profile was absent, and that in the water phase was attributed solely to back-mixing in the continuous phase.

Some years later, the work of Cavers and Ewanchyna (9) was continued by Choudhury (10) who used an apparatus similar to that of Ewanchyna(11). He did work also on the sampling technique. He investigated the minimum purging time required to remove material of the wrong concentration from the probes. Furthermore, he made these

measurements at various rates of flow through the probes. However, he did not get an adequate plot for the minimum purge time, but instead only a few scattered points. Choudhury mentioned also that the drops sometimes coalesced at the ketone sampler's entrance. He had planned to check the effect of such coalescence on the results for the dispersed phase sampler by varying the sampling rate for the dispersed phase.

Also, a material balance has to be made in interpreting the results of analyses of dispersed phase samples. The problem arises as to whether or not the hook probe gives a representative sample of the continuous phase concentration for use in this balance. (Presumably the bell probe, in removing drops, preferentially removes continuous phase from near the drops). Varying the sampling rate of both phases might change the results by changing the average continuous phase concentration taken in by one or both of the probes. Choudhury varied the sampling rate of both phases to measure its influence on the concentrations measured at a point. These experiments were made at a cross-section where the phases were not at equilibrium even if Hawrelak (12) thought so. This statement is made because the point concentrations reported at 6.16 ft from the nozzle were 8.2% from equilibrium* as compared with 19.7%, the maximum deviation between the equilibrium concentration profile (plot of C_{ki}^*) (10) and the concentration profile obtained. Choudhury's results were right, and they did throw light on the problem of C_{wi} being representative for the conditions under study. However, the range of rates covered by Choudhury (10) was too small.

Choudhury (10) found concentration profiles which had the same pattern as those measured by the earlier workers (1,2,4,9,11)

* This percentage is calculated as
$$\frac{(C_{ki}^* - C_{ki})}{C_{ki}^*} \times 100$$

He fixed for himself the maximum permissible purging or sampling rate to be 15 cc./min., without checking the effect on steady state.

Hawrelak (12) designed and constructed a piston-type sampler used in conjunction with hypodermic needles, or with the continuous phase (hook-shaped) probe, to sample the continuous phase, as a second, but not completely independent, way to obtain point concentration of the dispersed phase to compare with the results obtained with the bell-shaped probe. The hypodermic syringes were used to take samples of the continuous phase immediately above and below the piston block; the needles entered the column through the asbestos gaskets sealing the glass column to the piston block. It was discovered later that an appreciable volume of ketone phase was entrained in the continuous phase samples taken by the syringes; the syringe samples were discontinued because of the near impossibility of correcting for transfer between two phases in the continuous phase sample. It was decided that the water phase probe sampler, which showed no ketone entrainment, could be used in place of the syringe samples, if it was assumed that the probe sample gave a representative sample of the water phase. This probe was to be used to sample at the axis of the piston.

A minimum leakage rate around the piston of one to two mls/min. was encountered after a few seconds; but this leakage occurred only when the piston was shoved to the left in the block. Sampling was accomplished by shoving the piston from its right to its left hand position in the block. The 1½-in. I.D. hole in the piston that was to slide into line with the column was filled with either water phase which had leaked from the piston, or with outlet water phase from the column if there was no such leakage. In this way when a piston sample was taken the column continued to operate with no appreciable disturbance.

It was interesting to observe that when a piston sample was taken (portion of column contents removed) a gap in the ketone phase occurred, which appeared to move up the column for one to two feet.

The same difficulty (as specified earlier) arose about the material balance on which the interpretation of the dispersed phase samples depends. To be more specific, does the hook probe give a representative sample of the continuous phase, the concentration of which has to be used in this balance? In addition, analytical difficulties were encountered due to the small dispersed phase holdup obtained. (Holdup = volume percent dispersed phase in the column.) This difficulty arose in using the material balance equation written as follows for the piston sampler:

$$C_{ki} = C_{kf} - \frac{V_w}{V_k} (C_{wi} - C_{wf})$$

It is evident that the volume of the ketone phase in a sample should be large so that the equilibrium concentration of solute in the water phase is considerably different from the initial value. Only then does one avoid the error resulting from having to subtract quantities which are of about the same magnitude in applying the equation. (This approach assumes one analyzes the piston sample at equilibrium. Other possibilities are discussed later.)

The maximum holdup used by Hawrelak (12) was 12.7%, corresponding to a value of $(C_{wi} - C_{wf})^*$ of only $1.2 \text{ lb.-moles/ft}^3 \times 10^3$ where C_{wf} was approximately $40.0 \text{ lb.-moles/ft}^3 \times 10^3$. It is difficult to compare Hawrelak's results with the piston, with those obtained with the bell-shaped probe, because of these analytical difficulties, because of the leakage mentioned earlier, and also because of an error he made

in positioning the continuous phase probe. This was one inch higher than the axis of the piston in several runs. However, the piston method appeared to give the calculated initial ketone concentration always lower than the concentration measured with the bell-shaped probe.

The present work is a continuation of that of Ewanchyna (11), that of Choudhury (10), and that of Hawrelak (12). All three were concerned, at least in part, with sampling of the phases. It was planned to attack the problem by first varying the sampling rate used with both sampling probes and noting any change in the dispersed phase concentration results, and secondly by operating the piston sampler under conditions of very high holdup of dispersed phase in the column, when the analytical problems associated with the piston sampler should be comparatively small. The possibility of the hook-shaped probe not providing representative samples must be considered with respect to both sampling methods, and if these samples were not representative, varying the sampling rates used with each of the probes might produce changes in the results. However, if C_{wi} is considered unrepresentative, and it could only be too high, then C_{ki} comes out too low:

$$C_{ki} = C_{kf} - \frac{V_w}{V_k} (C_{wi} - C_{wf})$$

Hence, $(C_{ki})_{\text{piston}}$ is too low; then it will not check with the probe sampling results which were obtained at high holdup where the correction term, $V_w/V_k (C_{wi} - C_{wf})$, is less important. (Recall that the piston samples were obtained with low holdup).

It is interesting to note that if C_{ki} values were higher, all the water profiles calculated using piston flow (10), would be higher, indicating more backmixing than that assumed present heretofore.

EXPERIMENTAL METHODS

A) Preliminary work.

The apparatus arrangement (Fig. 1) was similar to the one used by previous workers (10, 11, 12, 13) except for a few modifications to be mentioned later.

A general reorganisation of the apparatus and a cleaning were needed because the equipment had been partially disassembled to facilitate the move of the Department of Chemical Engineering into a new building. A rotameter had to be reconditioned.

The aluminum tanks used by Choudhury (10) and Rocchini (13) were corroded. Before replacing them a survey was made of possible materials to contain M.I.B.K. and aqueous solutions of acetic acid. It was found that Pyrex and stainless steel were the only suitable materials which were also readily available at a reasonable price. Taking into account the safety requirements, four stainless steel tanks were chosen and made as specified on Figure 2. To prevent any leakage of M.I.B.K. (flash point 75°F (15)) from the feed and storage tanks, stainless steel tubing and fittings were used to connect both tanks to the pumps. Polyethylene tubing (with some stainless steel fittings and some Saran fittings) was used for the water phase.

Corrosion information was obtained from industrial suppliers of materials for tanks and tubing. The suppliers reported that polyethylene was not recommended to be used with M.I.B.K. except where the M.I.B.K. phase was flowing intermittently. A stagnant M.I.B.K. phase can destroy the properties of polyethylene by taking out the plasticizer.

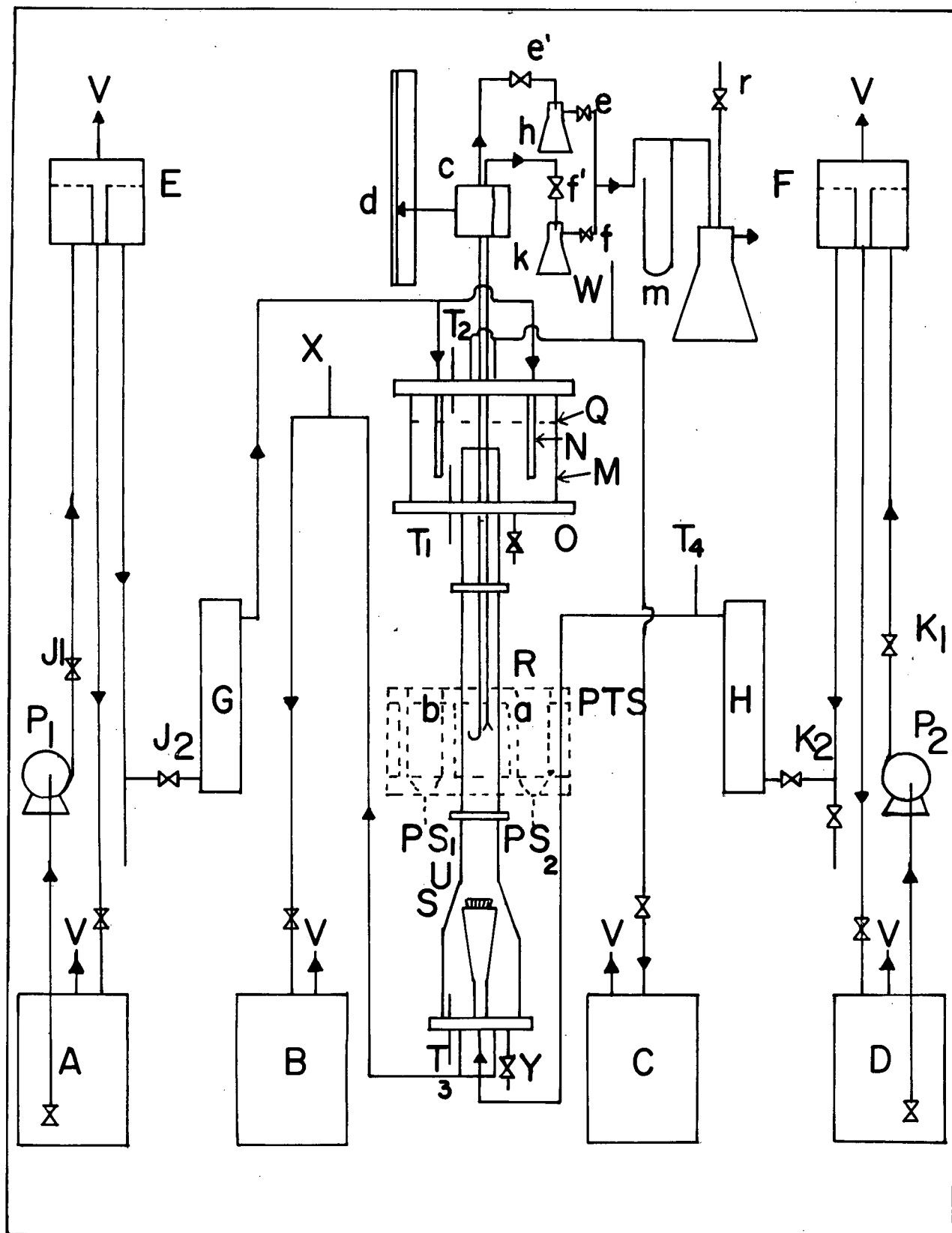


FIGURE 1. SCHEMATIC FLOW DIAGRAM

TABLE 1. KEY TO FIGURE 1

- A - Continuous phase feed tank
- B - Continuous phase receiver and storage tank.
- C - Dispersed phase receiver and storage tank
- D - Dispersed phase feed tank
- E - Continuous phase constant head tank
- F - Dispersed phase constant head tank
- G - Continuous phase rotameter
- H - Dispersed phase rotameter
- I - Continuous phase inlet sample valve
- J_1, J_2 - Continuous phase flow rate control valves
- K_1, K_2 - Dispersed phase flow rate control valves
- L - Dispersed phase inlet sample valve
- M - 6-in. I.D. Pyrex top end section
- N - Continuous phase inlet stainless steel pipes
- O - Drain valve for top end section
- P_1, P_2 - Centrifugal feed pumps for continuous and dispersed phases respectively
- Q - Level of interface
- R - Column proper 1½-in. I.D. Pyrex
- S - Dispersed phase nozzle
- T_1, T_2, T_3, T_4 - Thermometers
- U - Special Pyrex reducer 3-in. I.D. to 1½-in. I.D.
- V - Vent connected to a line going outside building
- W - Pressure equalizing vent
- X - Control for interface level
- Y - Valve for draining the column
- Z_1, Z_2 - Outlet sample valves for continuous and dispersed phases respectively

TABLE 1. CONTINUED

PTS - Piston type sampler

PS₁, PS₂ - Piston sample exit ports

a - Dispersed phase sample probe

b - Continuous phase sample probe

c - Travelling block from which sampling probes are suspended

d - Guide on framework for block "c"

e - Continuous phase sampling rate control valve

e' - Capillary tubing

f - Dispersed phase sampling rate control valve

f' - Capillary tubing

h - Continuous phase sample bottle

k - Dispersed phase sample bottle

m-- Mercury manometer

n - Water aspirator (vacuum controlled by air vent at the bottom of a mercury column and also by "r")

r - Valve for releasing vacuum

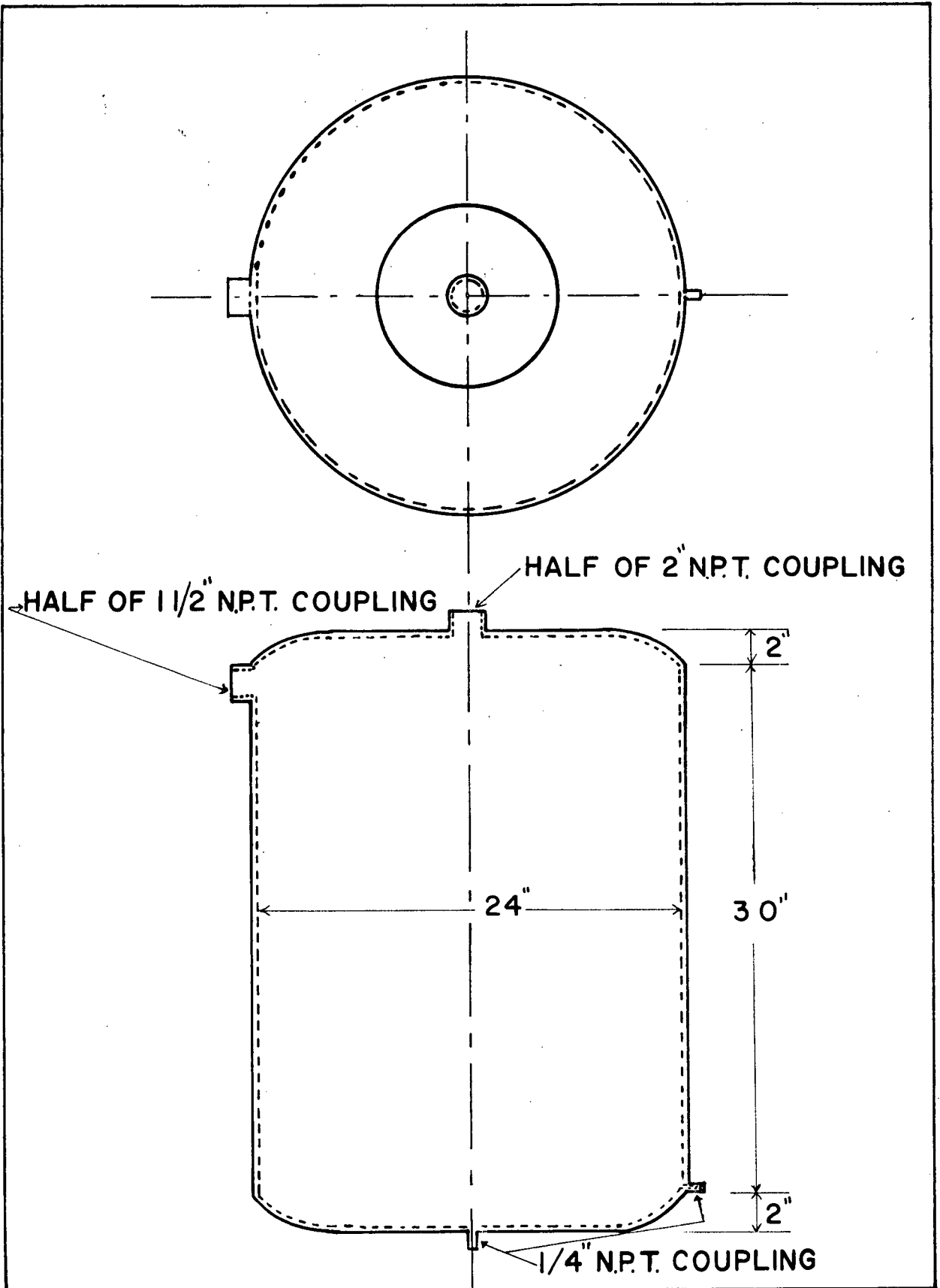


FIGURE 2. STAINLESS STEEL TANK

On the grounds that polyethylene was less expensive than stainless steel, and that polyethylene was probably at least fairly resistant to M.I.B.K., polyethylene tubing was installed to replace Saran tubing which had been attacked by M.I.B.K. (13). However, to prevent mechanical breakage and to give more operating freedom to the author, stainless steel tubing was used later, in places where the M.I.B.K. phase was flowing continuously when the solution were being mixed or recirculated with the column proper not in operation.

All rubber tubing was removed from the sampling lines to prevent any running back of liquid, possibly rubber contaminated, into the column. Finally, polyethylene tubing was installed all the way from the sample receiving flasks to the stainless steel probes.

Initially, the M.I.B.K. had to be distilled as specified by the pamphlet "Ketones" (14) due to pollution from the use of Saran tubing by earlier workers (12,13). Also as specified by the pamphlet, the M.I.B.K. distilled over was collected only between the temperatures of 114°C and 117°C measured just before the vapor left the distilling flask by the side opening. All the available M.I.B.K. was purified in this way. A black precipitate was left in the distilling flask. By doing a chromatograph test, the purity of the distilled material was obtained. Preceding this verification, a chromatographic analysis was run for the M.I.B.K. reserved from the previous drums, specified as being 99.0% pure by the suppliers. One peak exists for the pure material (as received) while three peaks were present for the distilled material, which was composed of M.I.B.K., acetic acid, and distilled water. This result showed that no undesirable impurities were left in the distilled material, if the assumption is made that the observed peaks corresponded to the three substances mentioned. This assumption was not tested.

The repairing of a rotameter was necessary. New stainless steel plates that compress the packing around the tube were made to replace those of mild steel which had been corroded by leaking material. Also, the scales had been shifted relative to the tubes when scales were removed and replaced. Both meters had to be recalibrated and the results are recorded in Appendix I.

The second part of this work was done using a piston sampler designed and constructed by Hawrelak (12) initially. The piston-type sampler, PTS in Figure 1, was flanged to the glass column by means of standard Corning Type I flanges and hard asbestos gaskets. In all cases the piston axis was 1.59-ft. above the nozzle tips. In normal operation of the column, the phases pass through one of the holes in the piston. The principle of this sampling method consists of taking out four inches of the column's phases by cutting through the operating column with the piston which contains vertically drilled passages of the same inside diameter as the column. Piston samples were collected at points PS_1 and PS_2 in Figure 1, into volumetric flasks by slamming the piston from one side to the other of its travel.

Past experience with a hard-chromed phosphor bronze cylinder block and a brass piston coated with soft solder, and also with an aluminum piston, was that there were always leaks (12). An attempt to stop this leakage was made by covering the piston with a polyethylene sheet, holding it mechanically as shown on Figure 3. This approach solved the problem of leaks between the piston and piston block; also this made it unnecessary to consider periodic replacement of the soft solder piston surface due to corrosion or mechanical damage. The polyethylene sheet was attached mechanically because cements can not

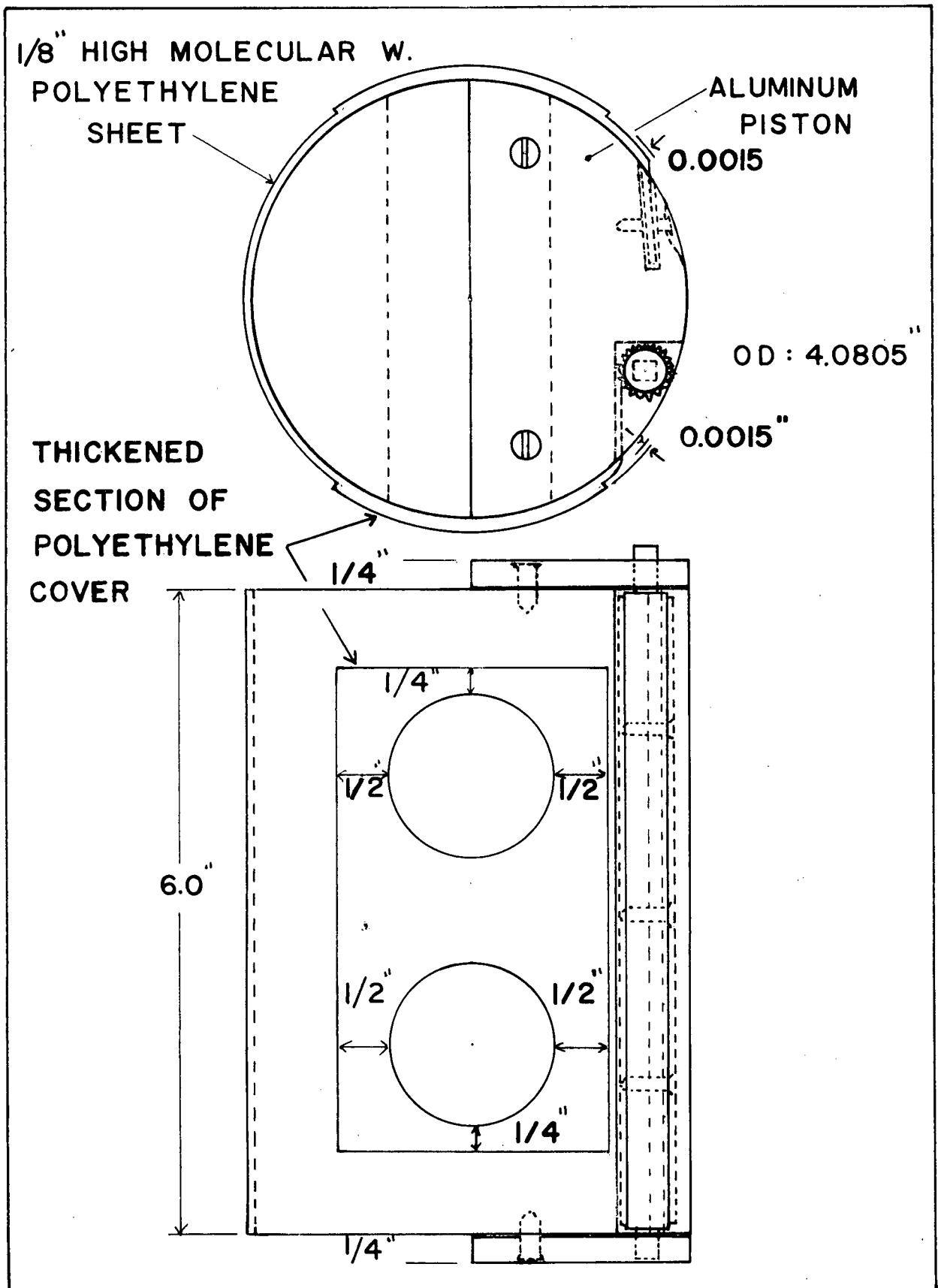


FIGURE 3. PISTON DESIGN

be used due to the danger of solution contamination, particularly with surface-active materials; in addition, most cements are soluble in M.I.B.K. (15).

A lever was built to replace the hand driving handle. The piston diameter tolerances had been reduced by increasing the piston diameter with the polyethylene sheet to help reduce the leaks; but as much friction had to be overcome, a lever mechanism to drive the piston was required. Figure 4 is a sketch representing the lever used to push the piston into the block.

B) Procedure

1- Probe method

In all the runs performed, mass transfer took place from the continuous phase to the dispersed phase. The continuous phase flowed by gravity downward from the top of the column while the dispersed phase was fed to the bottom of the column through chamfered nozzles as droplets.

The required flow rates were set by means of the rotameters; during the time needed to reach steady state, the interface controller was adjusted to hold the interface at one particular level. Throughout all the runs, the interface remained two to four inches below the top of the top plate of the Elgin head. During each run, the interface elevation remained within a range of $\frac{1}{2}$ -in. but varied over one inch range from run to run. Thus the height of the column (nozzle tips to interface) is reported as 7-ft. and $4\frac{1}{2}$ -in. $\pm \frac{1}{2}$ -in. for all runs. Throughout the course of a run, numerous checks were made on the interface height and on the flow meter settings. It was found that little or no readjustment was necessary.

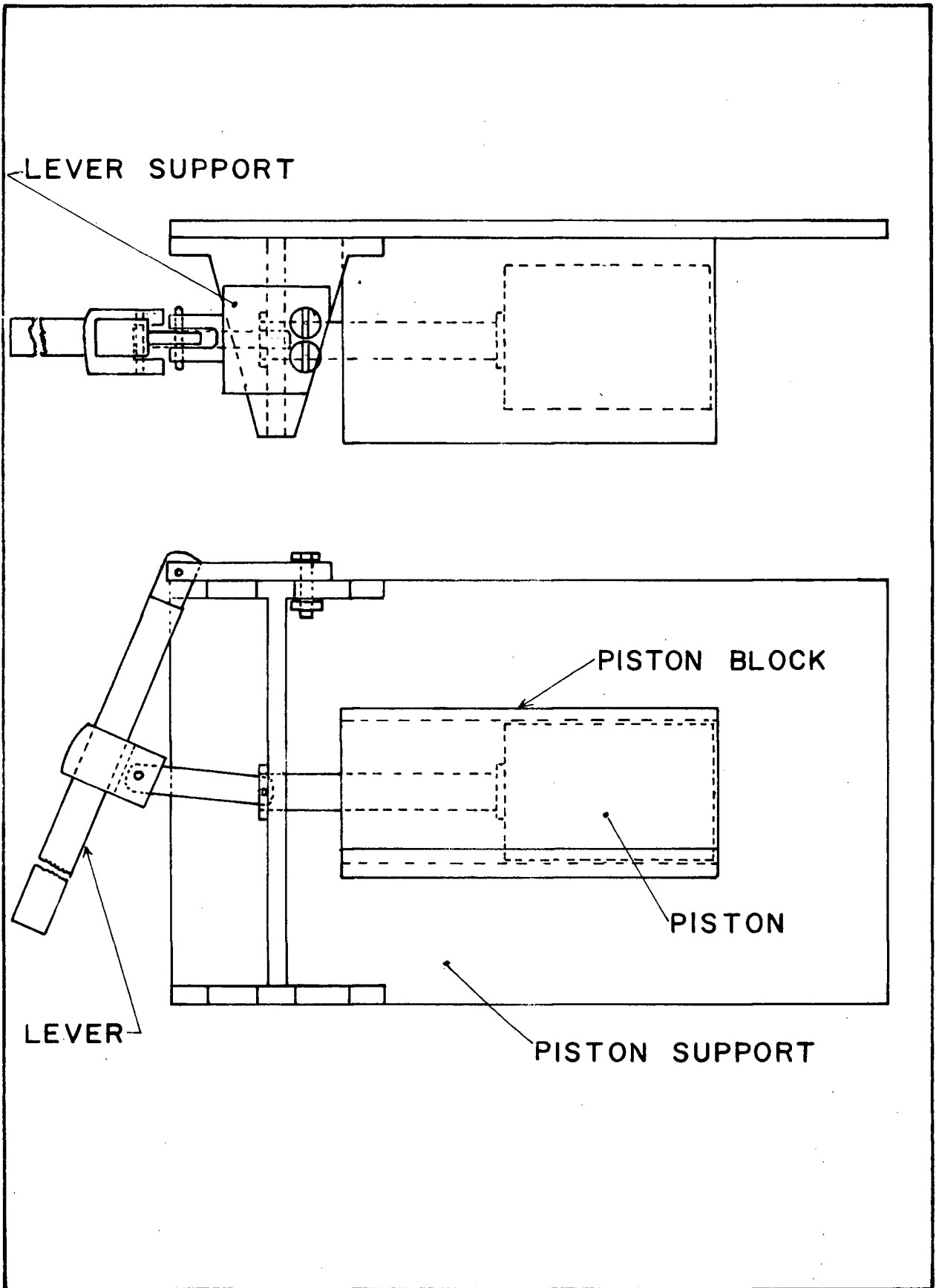


FIGURE 4. LEVER TO PUSH THE PISTON

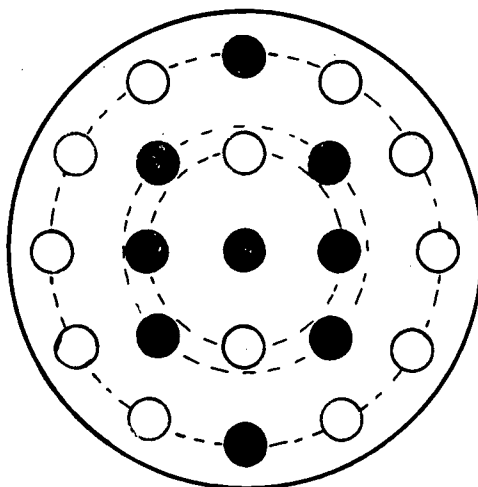
The velocity through each of the nozzle tips was held at a constant value of 0.357 ft./sec., except for a few runs.* To keep this linear velocity of the dispersed phase through the tips constant with varying total ketone flow rates through the column, some of the tips were blocked out by using Teflon caps. Accordingly, the number of open tips changed with ketone flow rate. Figure 5. shows the various tip patterns used. The continuous phase flow rate was held constant throughout this work. The jets of fluid obtained at the nozzle tips would produce uniform drops according to the Johnson and Bliss correlation (16), as reported in Appendix VI. These authors claimed that two different kinds of drop formation can take place at the nozzle depending on the velocity through the nozzle. They mentioned that two regions exist: one region below which drops cease forming at nozzle tips and another above which drops cease being uniform. The correlation of Johnson and Bliss (16) was used as a guide to determine whether the velocity used in this work was low enough to be within the reported region of uniform drop size. However, the work of Rocchini (13), in which a nozzle tip velocity of 0.362 Ft./sec. was used, shows that in the present study various drop sizes must have been present. The distribution was not measured but would be expected to be close to that of Rocchini (13).

The probe method of obtaining point concentrations used by earlier workers (10,11, and 12) needed to be checked. Samples in the present work were taken in the upward direction: from nozzle tips to interface, except when the purging and sampling rate studies were done.

The sampling was done at distances from the nozzle which were the same as those used by Choudhury (10) and shown in Table 2.

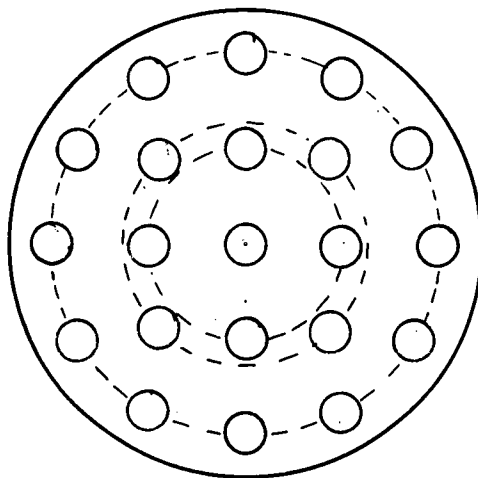
* This velocity was not used for probe samples taken for use with piston samples.

● BLOCK OUT



$$L_K = 72.7 \text{ FT}^3/\text{HR FT}^2$$

$$V^* = 0.357 \text{ FT/SEC}$$



$$L_K = 120.3 \text{ FT}^3/\text{HR FT}^2$$

$$V^* = 0.338 \text{ FT/SEC}$$

FIGURE 5. TIP PATTERNS FOR KETONE NOZZLE.

V^* Linear velocity through tips in ketone nozzle ft./sec.

TABLE 2

LOCATION OF STAINLESS STEEL SAMPLING PROBES (TUBES).

Point number	Distance above nozzle tips, ft.
1	0.078
1A	0.161
2	0.445
2A	1.161
2B	0.911
3	0.755
3A	2.161
3B	1.661
4	1.060
4A	3.161
4B	2.411
5	1.379
5A	1.355
5B	4.161
5C	3.786
6	5.161
7	6.161
8	7.286

This approach was decided on to permit easy comparison with the work of Choudhury (10) which had the object of obtaining concentration profiles.

The probe sample taken were received into clean dry Erlenmeyer flasks. These were closed immediately to prevent as much evaporation as possible. Each sample was analyzed either on the same day as the sample was taken, or, at the worst, not later than the next day. The volumes of the phases were measured by pouring the mixture collected in a volumetric flask into a graduate. From each of the continuous phase samples, a volume of 10 ml. was measured with a pipette and analyzed by titration with approximately 0.1 N sodium hydroxide with phenolphthalein indicator. A similar method was used for the dispersed phase samples, but before titration of 10 ml. from each ketone layer, 25 ml. of SDAG-1K mixture were added. (SDAG-1K mixture is made industrially by mixing 100 gallons of dehydrated ethyl alcohol with 5 gallons of dehydrated methyl alcohol.) The result was a homogeneous, single phase in which the end point could be determined easily (or much more easily than would have been true if two phases had been present). Sometimes after the analysis had been completed, a ketone layer was visible on the surface of the mixture in the flask. Perhaps a larger volume of alcohol should have been used. A blank solution was prepared for the case of the dispersed phase analyses. The blank solution was the same as a typical solution analyzed except that the 10 ml. dispersed phase were not added. Less than a drop of 0.1 N sodium hydroxide was needed to change the color of the blank solution. This amount of titrating agent was considered negligible and not subtracted from the total amount needed to titrate the dispersed phase samples.

Sodium hydroxide and glacial acetic acid were reagent grade

(A.C.S. specification) and were obtained from Nichols Chemical Co., Ltd, Montreal. Laboratory distilled water was used for all runs in this project. The M.I.B.K. was technical grade furnished by the Canadian Chemical Co., Edmonton, except that in the earlier runs (Run 1 up to and including Run 3) the distilled ketone, described in the preliminary work, was used, because the suppliers were not ready to deliver fresh M.I.B.K.. However, as soon as the fresh chemical arrived, the apparatus including the tanks were washed with this M.I.B.K.*.

For all runs, the rate of transfer of acetic acid across the interface in the column was calculated in lb.-moles/hr. by two different equations. One was based on the total change in concentration of the water phase, and the other on the corresponding total change in concentration of the ketone phase.

The equations were:

$$N_w = L_w A (C_{w_1} - C_{w_2}) \quad 1$$

$$N_k = L_k A (C_{k_2} - C_{k_1}) \quad 2$$

These were applied without including the volume of samples taken out by the probes. Values of N_w and N_k were slightly different in general, and an average value was determined by use of the following expression:

$$N = \frac{N_w + N_k}{2} \quad 3$$

This value was estimated to be better than either N_w or N_k for further calculation.

The percentage deviation was calculated for each run as a measure of the quality of the experimental work. The equation used was:

$$\text{Percentage deviation} = \frac{(N_w - N_k)}{N} \times 100 \quad 4$$

* The fresh M.I.B.K. then was used for all runs from and including run 3A.

The point concentrations in the units of lb.-moles/ft³ were readily obtained by titration. With these titration results the following equation was used to calculate back to the dispersed phase concentration at the time of sampling:

$$C_{ki} = C_{kf} - \frac{V_w}{V_k} (C_{wi} - C_{wf}) \quad 5$$

As far as the probe method is concerned, the general calculations stopped at this point because the emphasis was put on the point concentration, rather than on H. T. U. as in previous work.

2. Piston method.

When the piston method was used, the extraction process was the same as mentioned earlier and used with the probe method. But, when the piston sampler was incorporated into the apparatus, the procedure was slightly different. When steady state conditions were achieved, the probes were lowered to the elevation of the axis of the piston where purging and sampling of both phases took place simultaneously. Purging and sampling rates and purging times were used as prescribed by the first part of the present work and recorded on Figure 10. Inlet and outlet samples of both phases were taken regularly from the start to the end of a run and consequently when the probe samples were being taken. When sufficient volumes of both phases had been obtained, the probes were removed from the path of the piston.

The 1½-in. I.D. hole in the piston that was to slide into line with the column was filled with outlet water phase from the column. In this way, when a piston sample was taken, the column continued to operate with no appreciable disturbance. After a piston sample had been taken, sufficient time was allowed to restore the steady state,

which time had been studied as a part of this work.

The principal change made in the extraction process consisted in increasing the dispersed phase flow rate to give a larger holdup of dispersed phase in the column, and, consequently, in the piston sample. Figure 5. shows the setup to the nozzle necessary for this change of flow. It was planned to use the linear velocity of 0.357 ft./sec. as mentioned earlier. However, the flow rate for 21 tips to give this velocity was calculated using the nominal nozzle diameter of 0.10-in. instead of the actual average diameter of 0.1029-in. (10). The actual velocities calculated on the basis of the latter diameter are recorded in Table 10, Appendix II.

An acetic acid material balance has to be made between the initial conditions prevailing in the column at the time of sampling with the piston, and the final concentration existing in the removed piston sample at the time of analysis. The equation used was the same as Equation 5 just given. The quantity C_{wi} is found by using the concentration given by the continuous phase probe at the axis of the piston just before taking a piston sample. When the latter sample is taken, C_{kf} and C_{wf} can be measured and also V_k and V_w . Then C_{ki} can be calculated: the quantity really needed. This calculation is permissible on the basis that:

$$V_{ki} = V_{kf} = V_k$$

and

$$V_{wi} = V_{wf} = V_w .$$

These last two statements probably are very close to the truth, and are assumed to be correct within the experimental error of a run. It should also be understood that the concentration is assumed to vary linearly inside the four inches long piston. This assumption is based on previous results(10,11) which show that the concentration versus the

distance from the nozzle is almost linear over seven feet of the column's length.

RESULTS

A) Steady state requirements:

It was discovered that the concentration inside the column influenced the length of time needed to achieve a steady state in making an extraction run. The concentration of the column filled with the continuous phase feed solution differed from that existing inside the column which had been operated before; this difference was due to the extraction process which took place.

Then, two ways of starting a run needed to be investigated. The first one consisted in using a column filled only with the continuous phase at feed concentration and with no dispersed phase above the interface. (In run 6I₁ (Fig. 6) a slight variation in this procedure took place: some distilled water had been left in the Elgin head from the back-washing operation which preceded). The second way was the start-up of a run using a column filled with the continuous phase left in the column at the end of a previous run and with the corresponding dispersed phase above the interface.

To obtain the time needed to reach a steady state condition for the first way of startup investigated, the column first was filled with continuous phase feed solution only, up to the interface level in the Elgin head. A flow of dispersed phase then was started. Samples of both feed solutions were taken three times during the extracting operation whereas the outgoing solutions were sampled every five minutes. Figure 6 shows the results of a run using an initial continuous phase concentration slightly different from 50.4 lb. moles of acetic acid/ cu. ft. of water due to the presence of distilled water in the Elgin head before the column was filled with

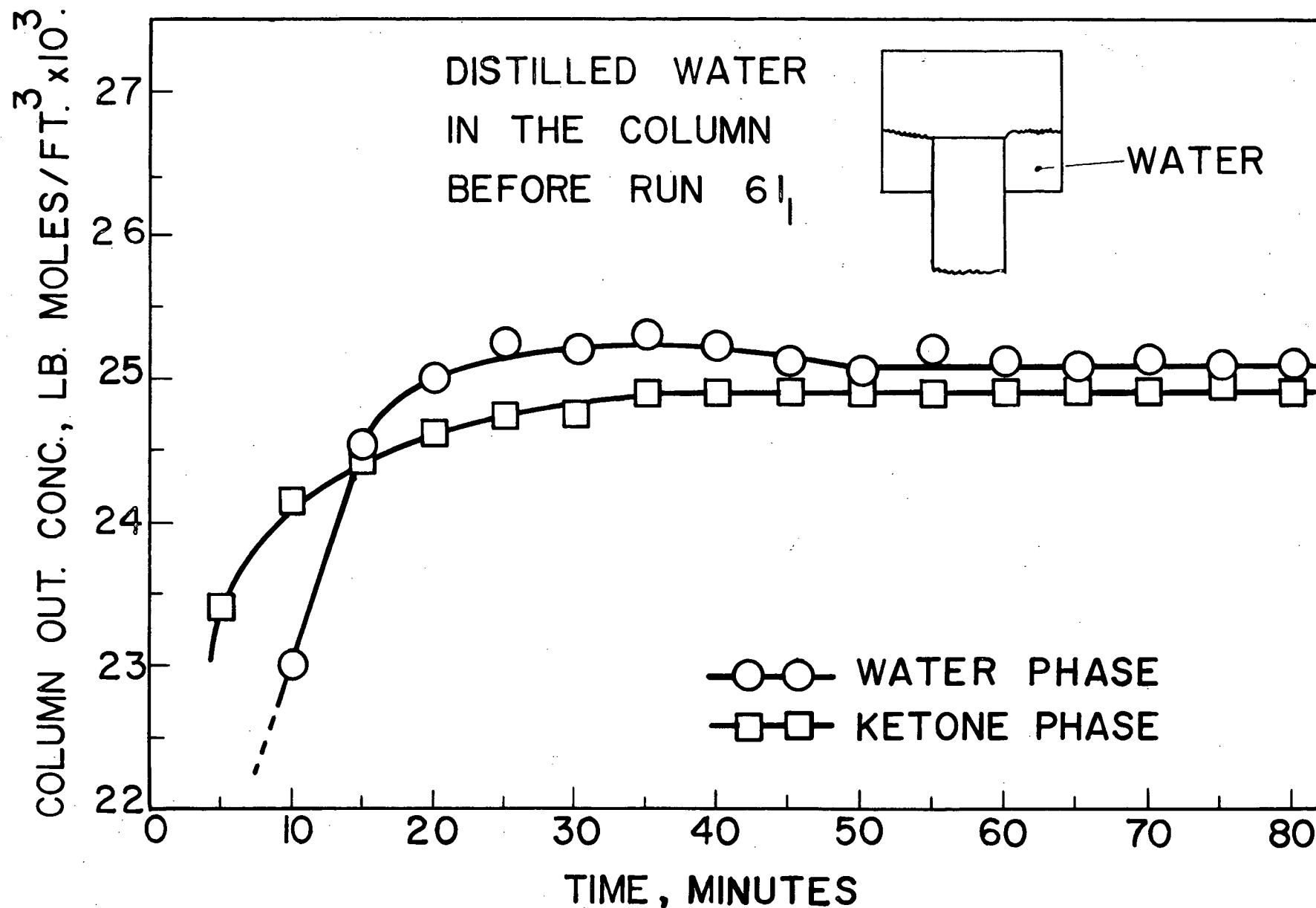


FIGURE 6. Steady state study, Run 6 I₁

continuous phase feed solution. (Consequently, Run 6I₁ is not included in the results given on Figure 8.) The continuous phase feed concentration, of 50.4 lb.-moles/cu. ft. $\times 10^3$, was used in other runs which were done using the same conditions except for the Elgin head which was drained before beginning to fill the column. Figure 6A shows an example of the results of one such run. All these results are recorded in Table 11, given in Appendix III.

To realize the second way of beginning a run (as just mentioned) the column was not operated for one or two days after an earlier run had been completed. This time was allowed to elapse in order to permit the concentrations within the column to approach more uniform and, in addition, lower values than those which applied at the end of the earlier run; extraction continued at a low rate beyond the end of the earlier run. A new extraction run then was started with the object of finding the time required to reach steady state for these new initial conditions. The method of sampling the inlet and outlet solutions was the same as mentioned earlier. Figure 7 refers to a run started with a column where the concentration was lower than 50.4 lb.-moles/cu. ft. $\times 10^3$ due to a previous run. Table 12, given in Appendix III shows the results of four others runs performed using the same procedure.

This investigation was carried out for a constant continuous phase flow rate of 54.8 ft.³/hr.-ft.² while the dispersed phase flow rate was varied from 72.4 ft.³/hr.-ft.² up to 208.0 ft.³/hr.-ft.². Figure 8 summarizes all the results obtained. (Table 13, given in Appendix III, lists the same results.)

These runs were all performed to give the results described without using any internal method of sampling. However, after very long

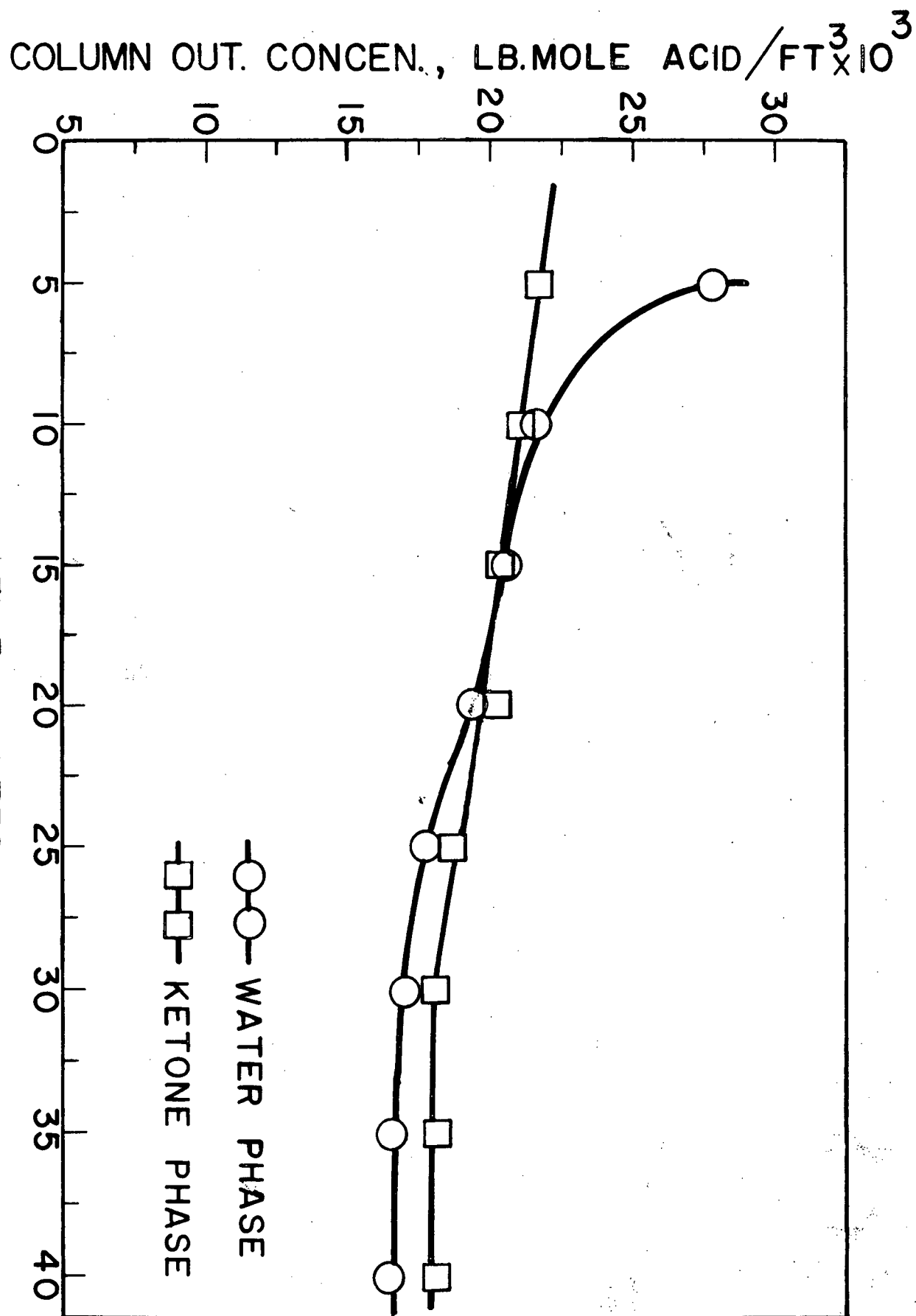


FIGURE 6A. Steady state study, Run 9A.

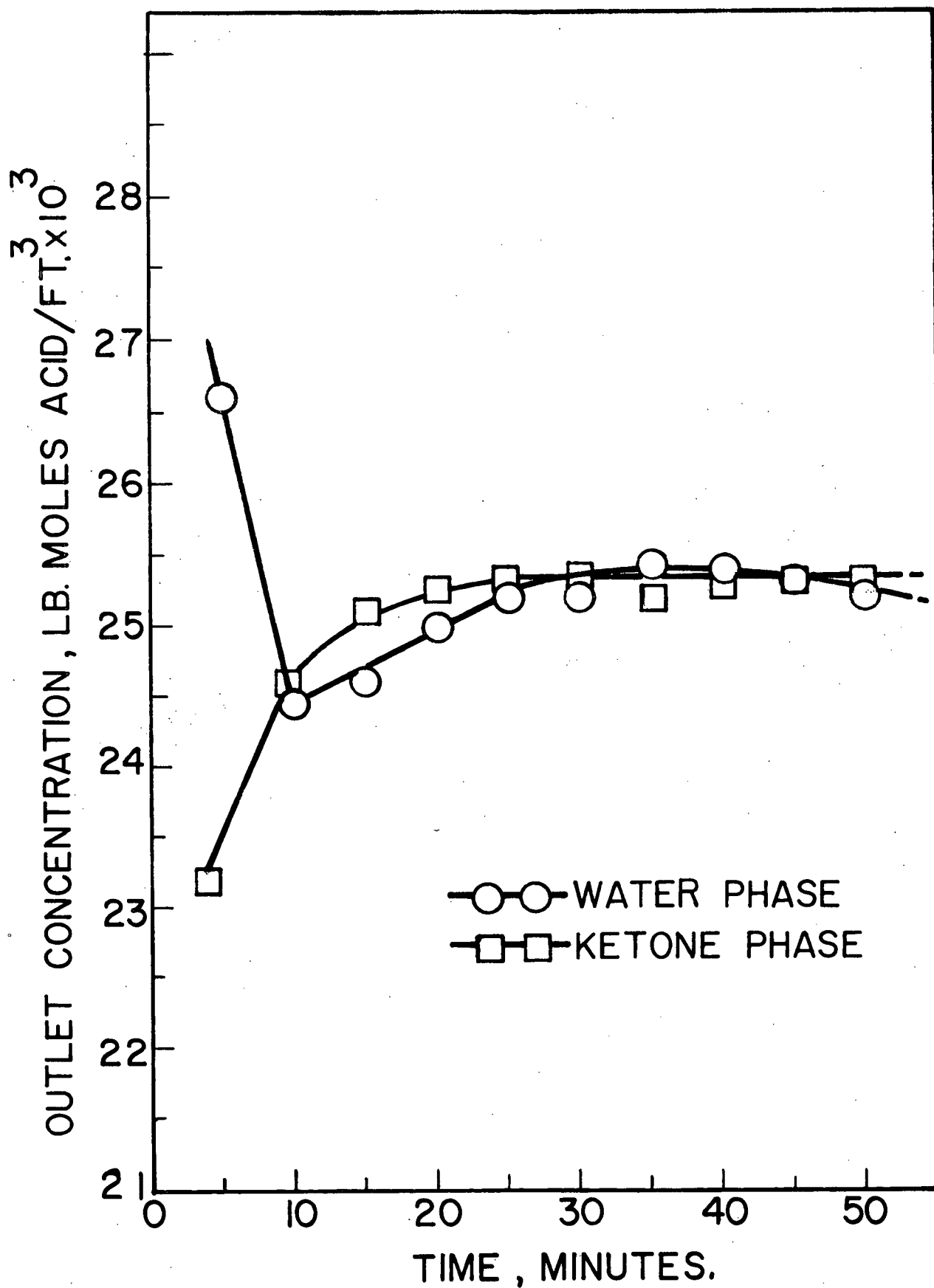


FIGURE 7. Steady state study, Run 6L.

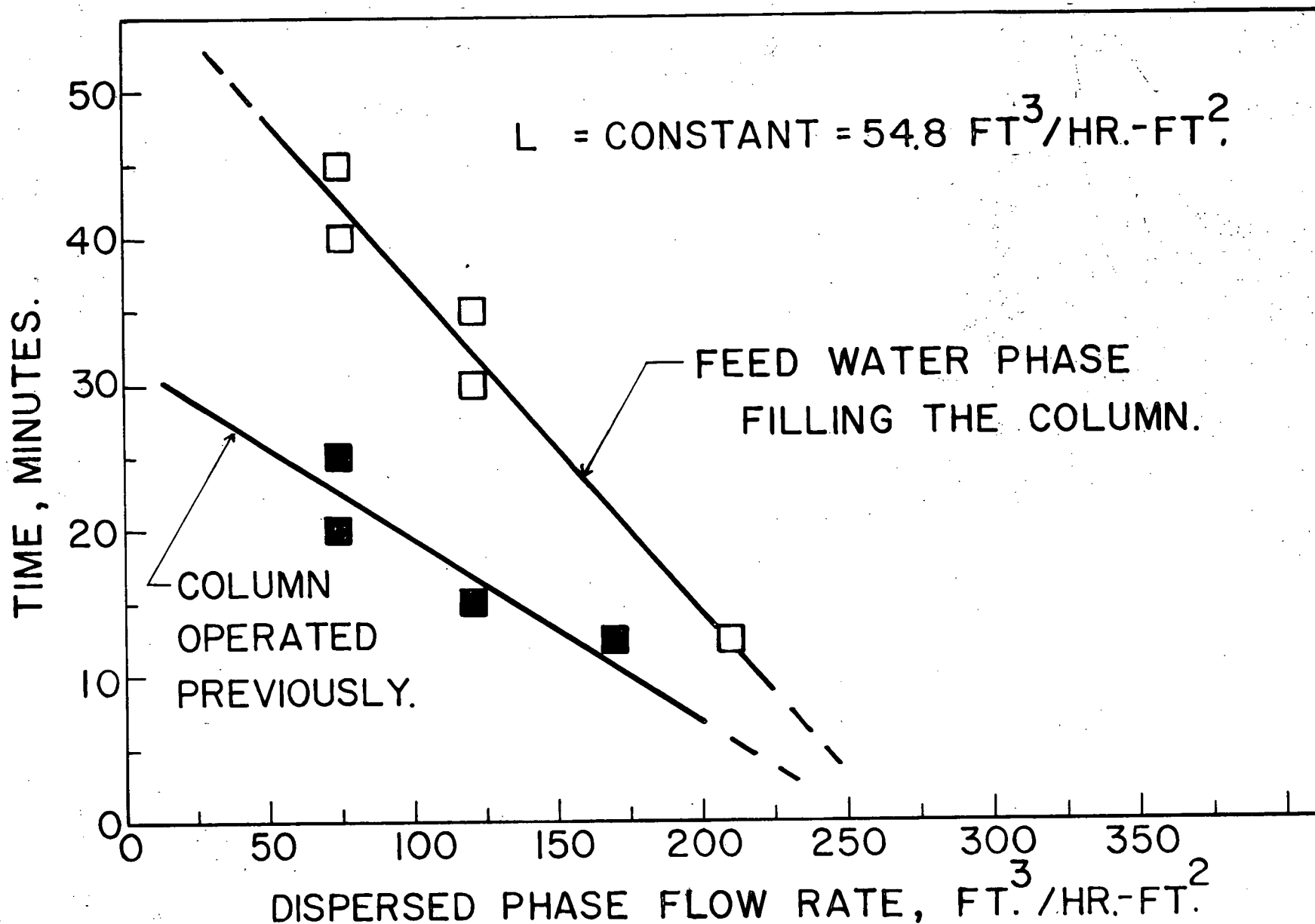


FIGURE 8. Summarizing plot of the steady state results.

times when the steady state had been reached, some of the runs were continued, and internal samples were taken, as part of the study of the effect of such sampling on the steady state.

B) Purging study:

The purging time is the time needed to achieve a uniform concentration after the position of the probes in the column has been changed. The purging time depends on the amount of vacuum applied to the probes, and the resultant rate of purging which is controlled also by the insertion of lengths of capillary tube inside the sampling lines. The vacuum, and these capillaries condition also the rate of sampling, obviously.

The procedure followed was to establish a steady state operation of the extraction column, and then to place the probes at some convenient distance from the nozzle tips. The probes were filled at this position for fifteen minutes at the purging rate to be studied. The probes then were moved to a second position where purging was carried out for measured times. The positions of the probes mentioned here were specifically those of sampling positions 2, 2A, 3B, 4A, and 7 as given in Table 2. (On Figures sampling position is abbreviated to "Position" or "Pos.")

In each run, several samples were taken at various sampling rates. After the probes had been moved to a second (or to a subsequent) position, a sample was taken every minute. The concentration of the samples obtained after sufficient purging in all the runs done for this purpose (Runs 1G, 2, 2A, 2B, 2C, 7, 7B, 7C, and 7D) check within approximately 0.5% at the worst in the respective phase. The sampling rates used for each run in the present work appear in Table 24 (Appendix IV) which also

shows the minimum purging time for each particular value of the purging rate. A typical example of what was obtained for a particular run is shown in Figure 9. All the results obtained for each run concerning the minimum purge time appear in Tables 14, 15, 16, 17, 18, 19, 20, 21, 22, and 23, located in Appendix IV.

A summarizing plot of the results of all these runs is given as Figure 10 following. This Figure shows reasonably accurately the minimum purge time to obtain uniform concentration at various sampling rates. To be on the safe side for normal extracting operations, at least 2 to 3 minutes should be allowed beyond the value of the purge time obtained from Figure 10. Table 24 corresponding to Figure 10 is given in Appendix IV.

C) The influence of sampling rate on point concentrations:

All research work done in the past, using the sampling probe method, appeared uncertain because of the underlying assumption: that the measured water phase probe concentrations, C_{wp} , are representative samples of the aqueous phase for use in the material balance for calculating C_{ki} .

An attempt was made to establish conclusively the continuous phase concentration profile. The method used consisted in placing the probes at various sampling positions in the column where concentrations were reasonably far from equilibrium conditions. Incidentally, Choudhury's equilibrium curve (10), available in the laboratory plotted to a large scale, was used throughout the work for getting equilibrium concentrations. The specific distances used were 1.59 and 1.66 ft. from the nozzle tips. At these locations experiments were made to find any apparent effect of sampling rate on point concentration.

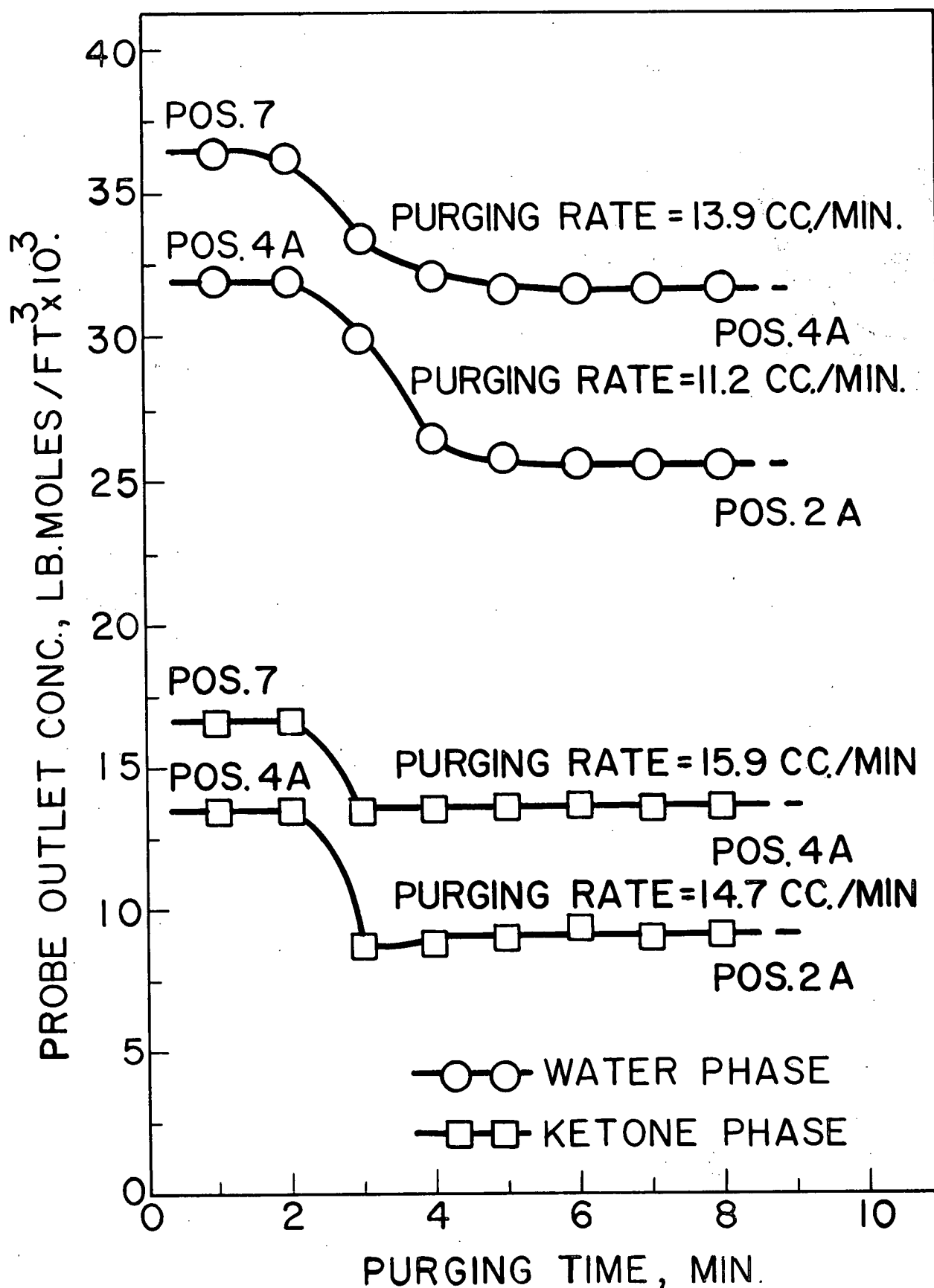


FIGURE 9. Study of the minimum purge time, Run 2.

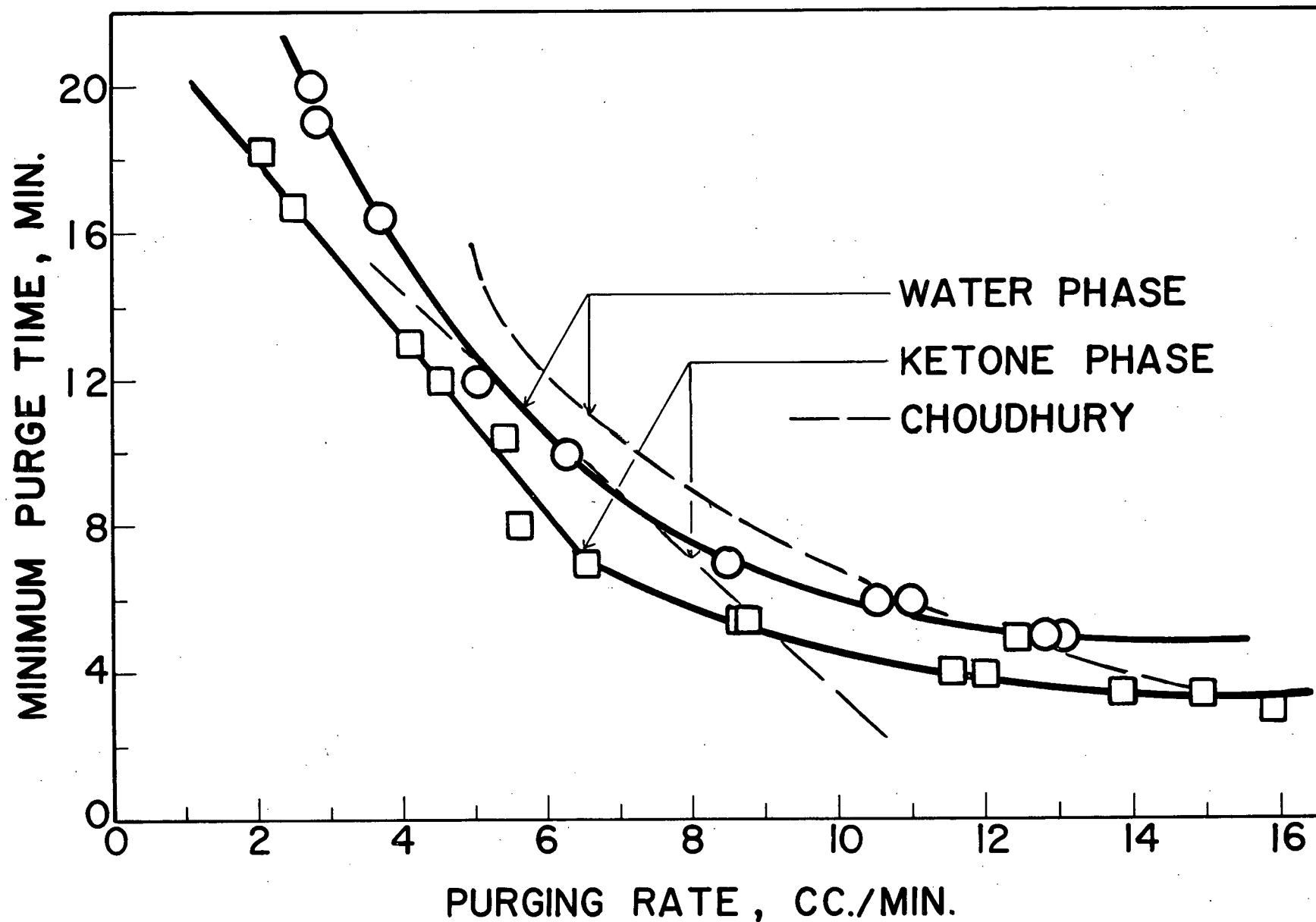


FIGURE 10. Minimum purge time versus purging rate.

Two different kinds of sampling procedure were followed. In one the probes were purged for 10 minutes at a certain rate. Following this period this rate was maintained for an additional period long enough to provide a reasonable volume of sample for analysis. When the sampling ^{rate} was changed, the sampling lines were purged again for 10 minutes at the new sampling rate before taking the new sample. This procedure was ideal* for obtaining concentration values which would differ from each other if the concentration varies greatly with the sampling rate. Run 9H was performed following this sampling procedure for both phases. Figures 11 and 12 (data in Table 25, Appendix V) give the results of this run and show that great differences in point c concentrations do not exist even if the rates varied from 6.2 to 16.0 cc./min. for the water probe and from 8.2 to 15.6 cc./min. for the ketone probe. However, it was discovered later that these samples were taken at a position where the concentrations were only 5% ($\% = \frac{(C_{ki}^* - C_{ki})}{C_{ki}} \times 100$) away from the equilibrium concentrations. Perhaps even in this case, some changes in concentration would be possible for high rates of sampling.

Run 5 G was performed in a manner similar to the method used for Run 9H, except that the purge time was applied as prescribed by Figure 10 in all cases. Other differences were that only the ketone probe was sampled for all the run, and that the concentrations at the sampling position were far from equilibrium concentrations. (This statement is also true for all the other runs, with the possible exception 1D where concentrations were still noticeably away from equilibrium) The water probe sampled just at the beginning and the

* except that in one case a longer purge time would have been required to provide^a safety factor in addition to the requirements of Figure 10.

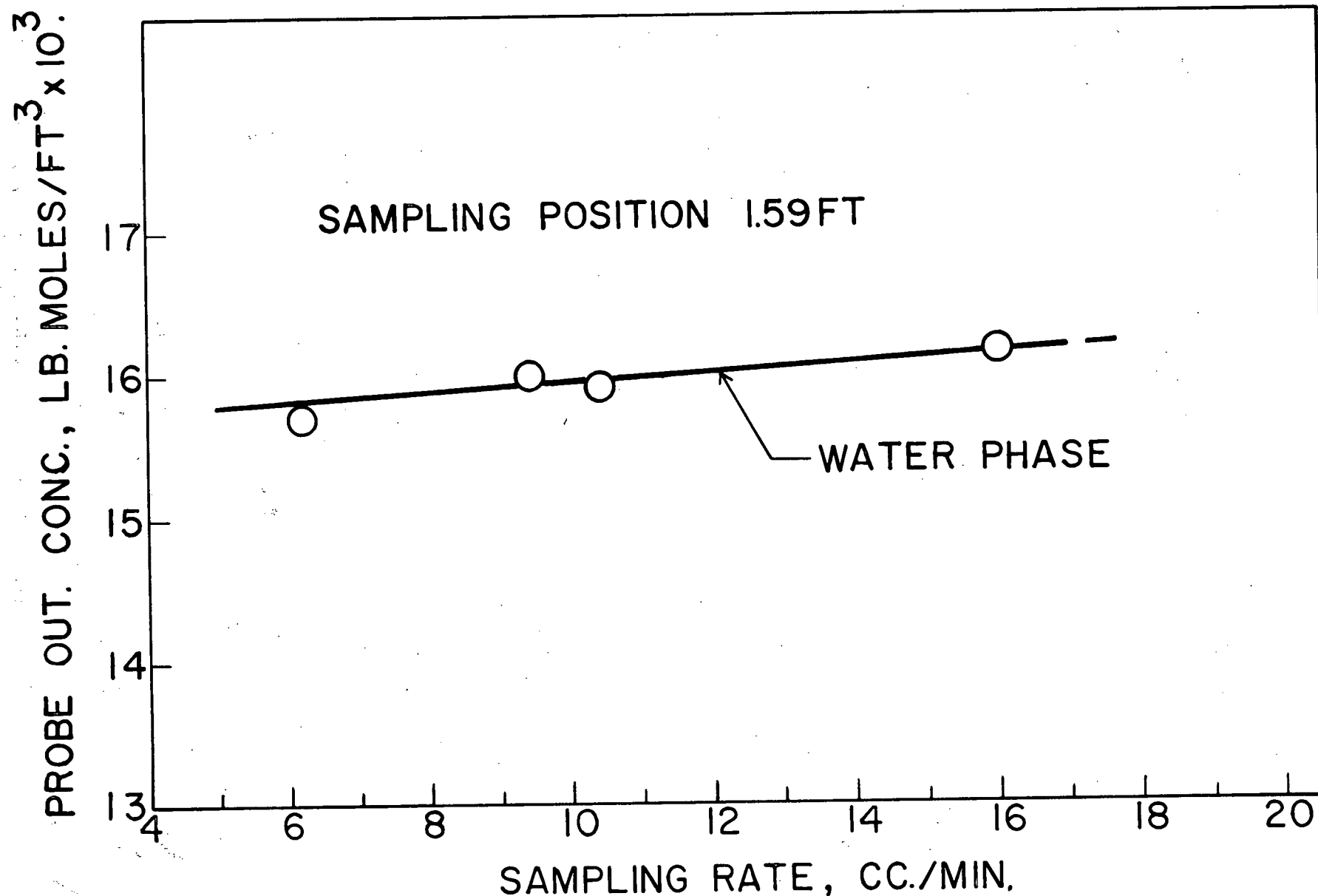


FIGURE 11. Influence of sampling rate on point concentration, Run 9H.

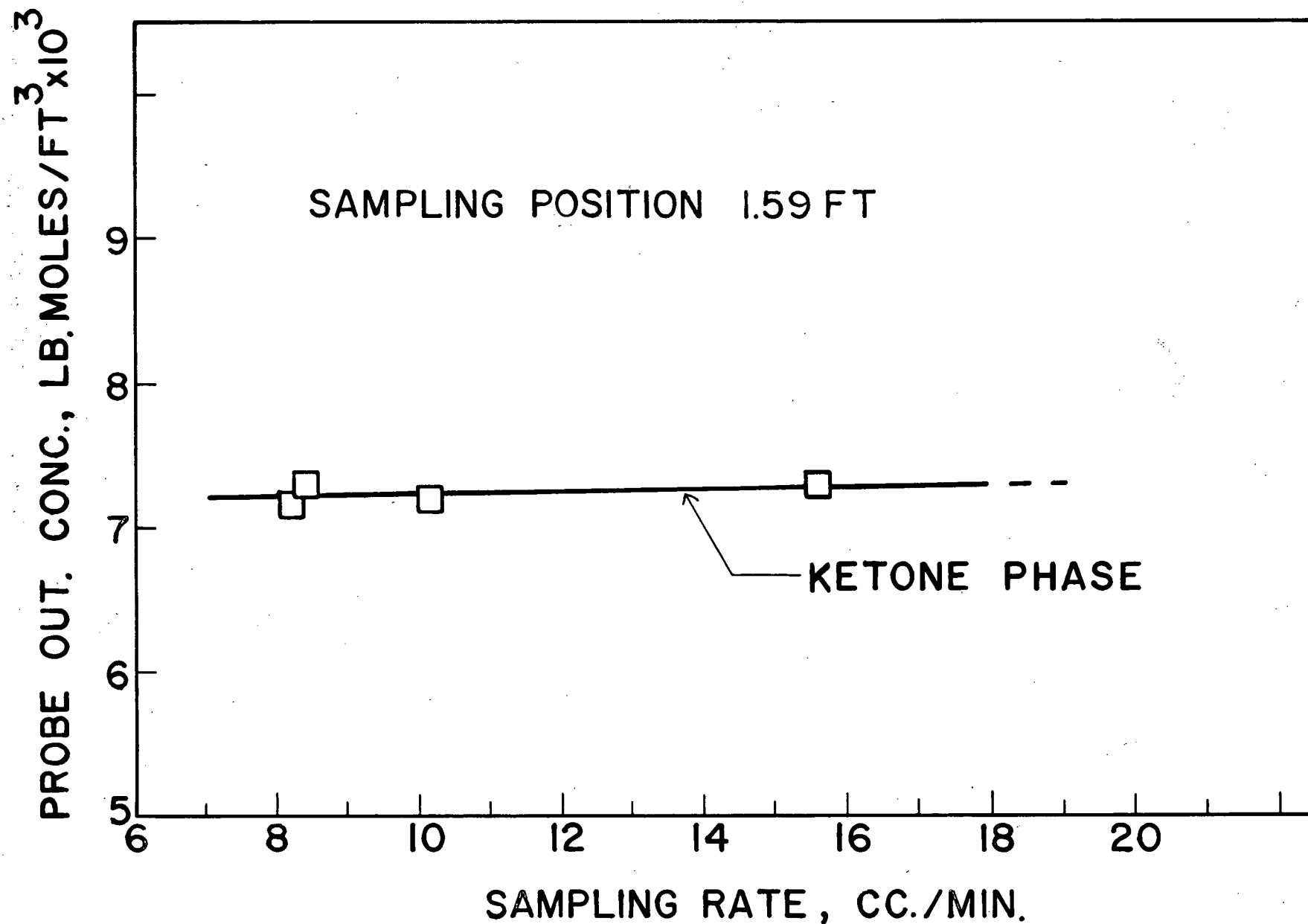


FIGURE 12. Influence of sampling rate on point concentration, Run 9H.

end of the run, and at only one sampling rate. The water probe was not used for the intervening five samples because it was planned to study whether or not the ketone probe concentration varied when samples were not being removed with the water probe. Figure 13 records the results obtained in Run 5G for the ketone probe and Table 25 in Appendix V gives the corresponding data.

Another Run, 5H, was performed to study further the question of any variations in the ketone probe concentration with sampling rate when the water probe did not operate. At the beginning of this Run, the sampling lines were purged for 15 minutes. Then a sample was taken for 3 minutes. The lines were not purged as prescribed by Figure 10 for the next two samples, but were for the remaining three samples. This meant that four samples were obtained according to the first sampling procedure and two according to the second procedure to be described shortly. Figure 14 records the results of Run 5H. (See Table 25, Appendix V for the tabulated results of Run 5H.) The method of plotting this figure is that used for Figure 15 and described when that Figure is presented.

The second sampling procedure consisted in placing the probe at location 3B* (1.66 ft from the nozzle tips) and purging for a sufficient time to purge the probe. After this operation, one sample was taken at the same rate used for purging. Then, instead of purging the probe again, another sampling rate was set, and used to sample at the same location. This sampling procedure was employed in Runs 5B₁, 5F, 7E, 7F and 1D*. Each of these runs must be described here separately.

In Run 5B₁, a purge of nine minutes was carried out before taking the first sample of each phase. Then, without purging, another

* In Run 1D a probe location of 6.16 ft. was used.

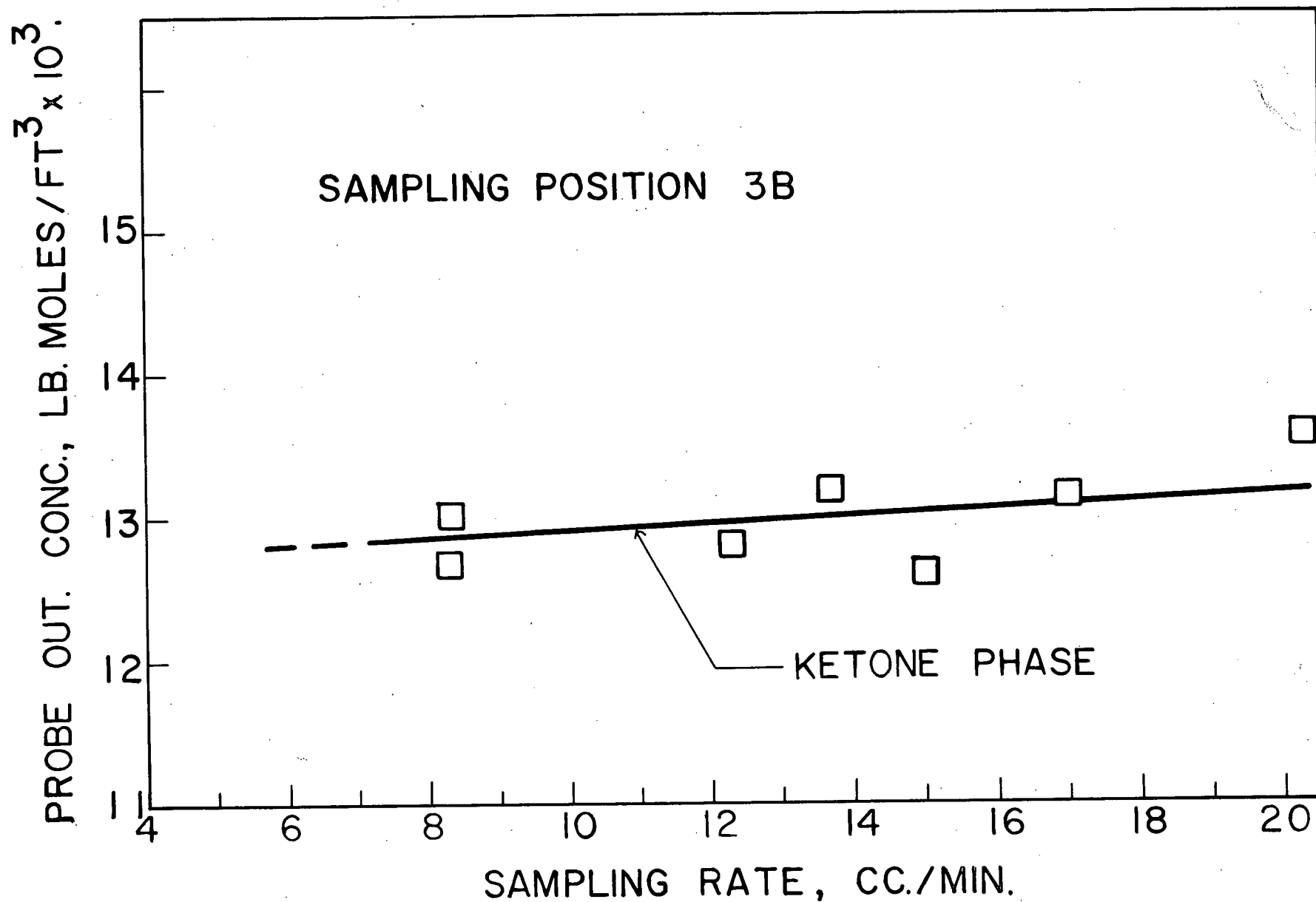


FIGURE 13. Influence of sampling rate on point concentration, Run 5G

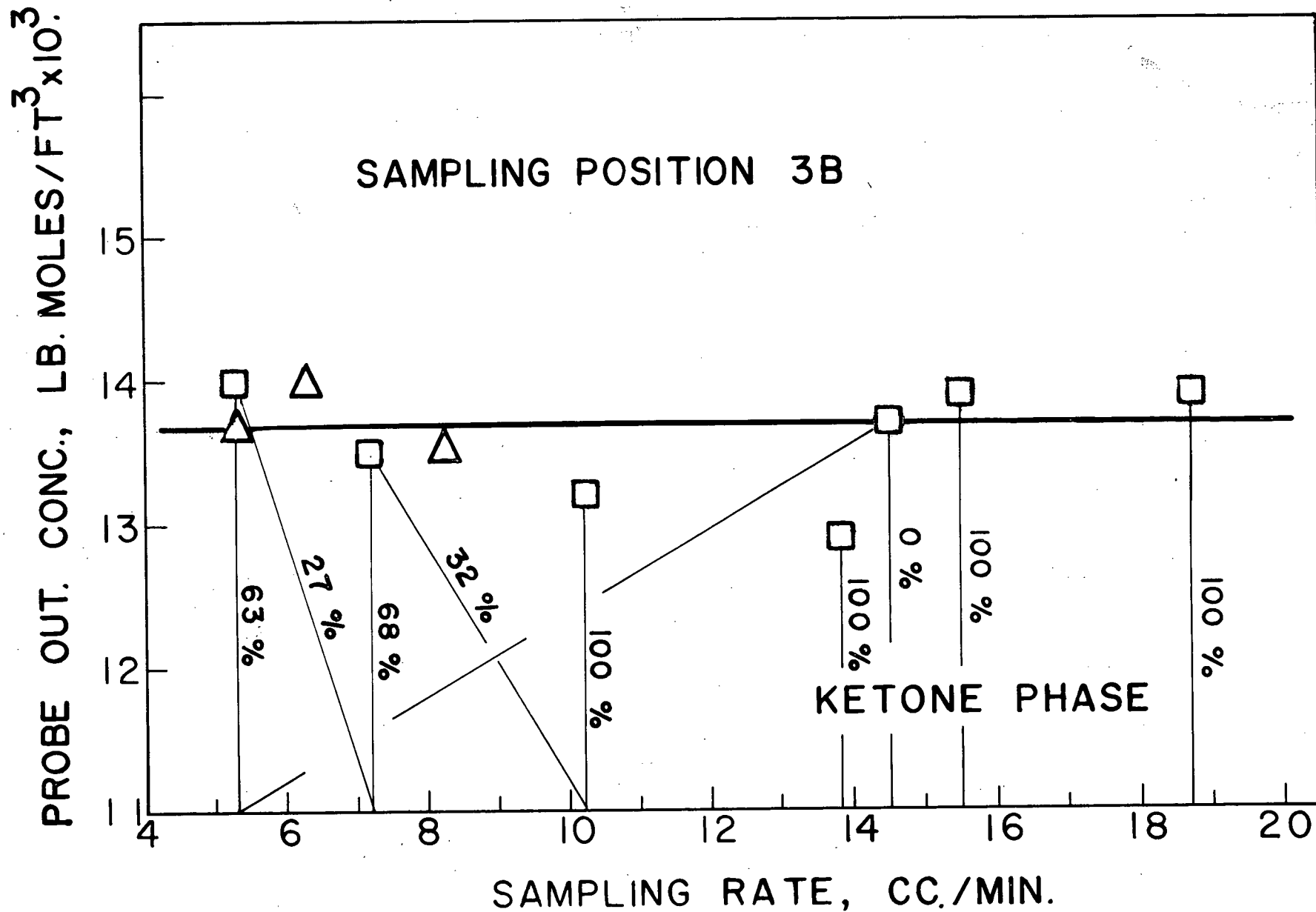


FIGURE 14. Influence of sampling rate on point concentration, Run 5H.

sample was taken at a different rate and only with the ketone probe. Two further samples were obtained in a similar way. Except for the first sample which was done according to the first procedure, those taken after were made up of mixtures of solutions sucked out from the column at different rates. However, if concentration variations due to variations of sampling rate are present, the result of this procedure would be a change in concentration from sample to sample. It is true that concentrations corresponding to definite sampling rates were not obtained; nevertheless, an absence of concentration change would indicate no effect of sampling rate on measured concentrations. Figure 15 shows the results of Run 5B₁. Each square* is plotted at the sampling rate being used when the respective samples passed into the sample flask. The lines drawn from each square* to the axis of abscissas reach that axis at the sampling rates which were in use when the liquids found in the respective sample actually passed into the probe entrance from the column. The percentage marked on each of these lines is the approximate volume percentage of the sample which passed into the probe entrance at the rate indicated by the line. The triangles represent the concentration corresponding to an average rate of passage into the probe entrance. This average rate was obtained by weighting the rate indicated by each of the lines according to the corresponding volume percentage. (These results also are recorded in Table 25, Appendix V.)

Run 5F was performed exactly as Run 5B₁. Figure 16 (and Table 25) shows these results.

The second sampling procedure also was used to perform Run 7E. No purging took place before sampling was begun with the result that the first two samples in Table 25 could not be used. Ten minutes samples of each phase were taken simultaneously at various rates ranging up to

* For Figures 17, and 18 circles are used instead of squares.

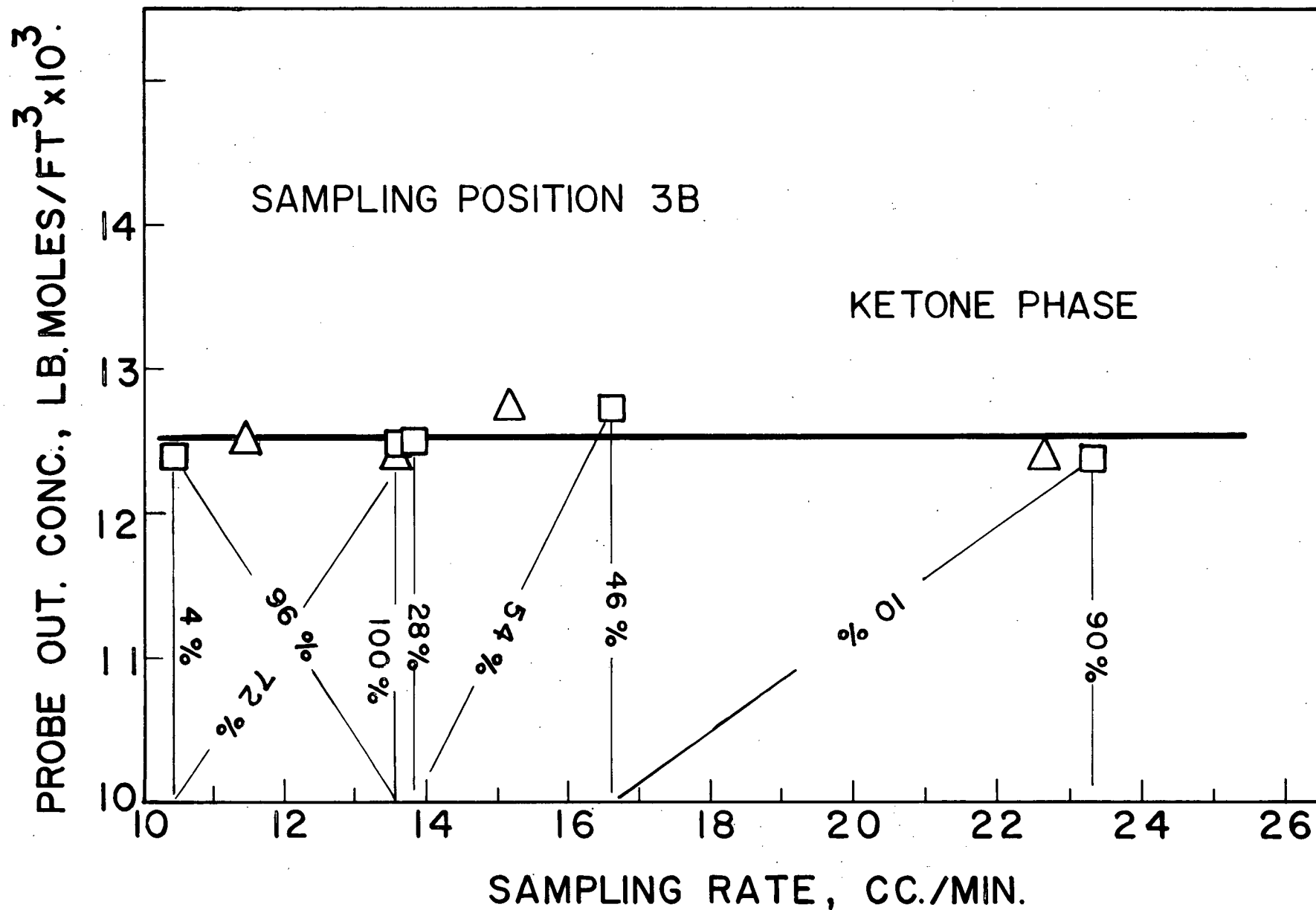


FIGURE 15. Influence of sampling rate on point concentration, Run 5B₁.

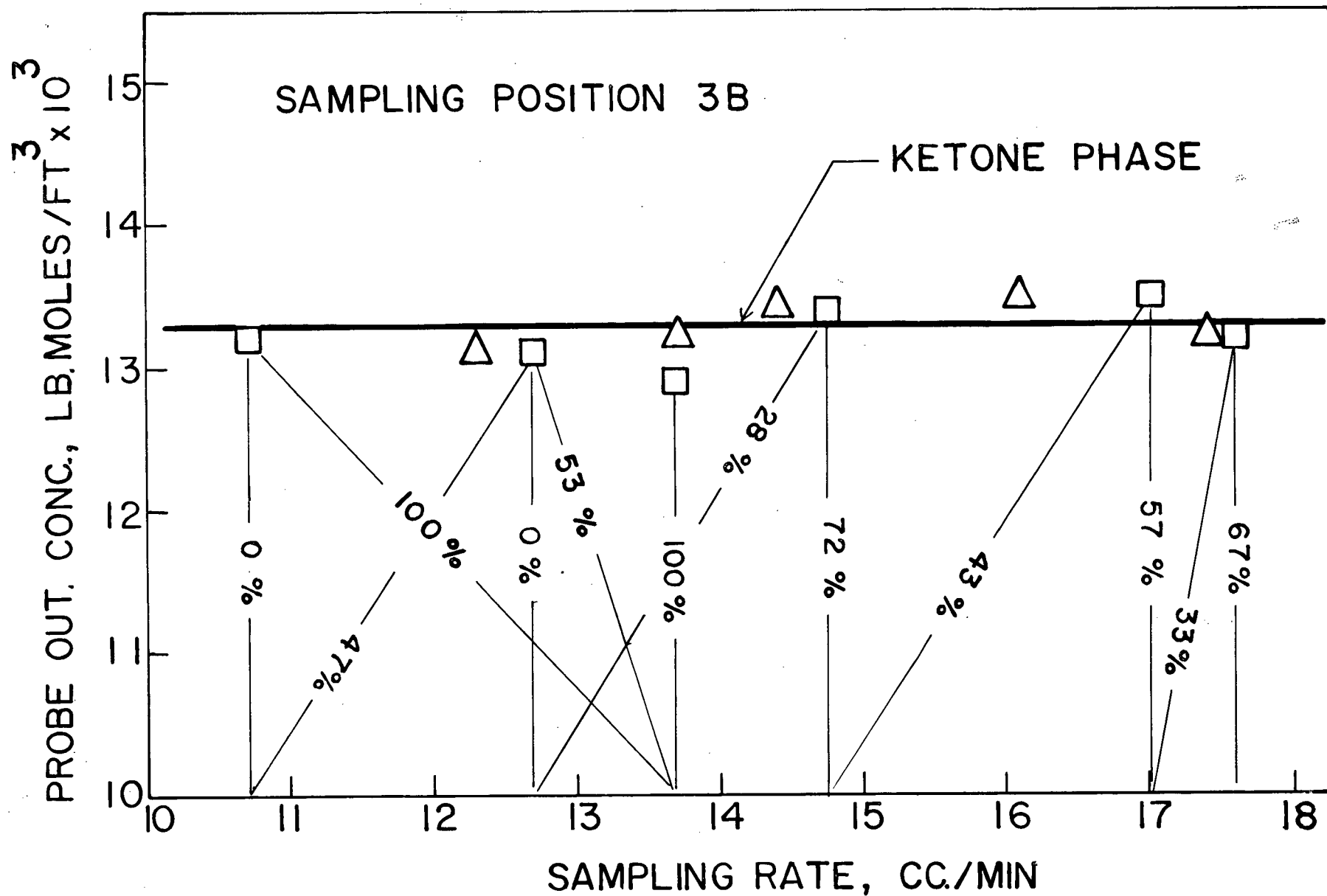


FIGURE 16. Influence of sampling on point concentration, Run 5F.

14.2 cc./min. for the water probe and from 5.4 to 9.8 cc./min. for the ketone probe. Each sample represents the results corresponding to more than one rate of sampling into the probes. Figure 17 shows the results for the continuous phase probe; the same method of plotting was used as Figure 15. Results for both probes appear in Table 25, Appendix V. (The ketone phase results have not been plotted because only a narrow range of ketone sampling rates was investigated.) No significant variations in point concentration were found.

Run 7F was performed as Run 7E. The first two samples in Table 25 could not be used because of failure to purge. Several samples of each phase were taken at various rates ranging up to 28.2 cc./min. for the ketone phase probe. Simultaneous samples were taken with the water probe at a constant rate of 2.8 cc./min.. The results are shown on Figure 17A and recorded in Appendix V, Table 25. (The water phase results have not been plotted because only a single rate of sampling was investigated.)

Another Run, 1D, was done also by using the second procedure (except, of course, that the first sample again was taken, in effect, by the first procedure). In Run 1D, the probes were placed this time 6.16 ft. from the nozzle tips. The sampling lines were purged 20 minutes before taking the first sample of each of the phases. Samples of each phase were taken at the same time at various rates for 5 minutes, again without purging between samples. However, as mentioned earlier, the concentrations measured under these conditions should vary if the sampling rate influenced the point concentration. No significant changes in the concentrations were found even though the water sampling rate was varied from 11 to 34 cc./min. and the ketone sampling rate from 12.9 to 28.4 cc./min.. Figures 18 and 19 record the results for each

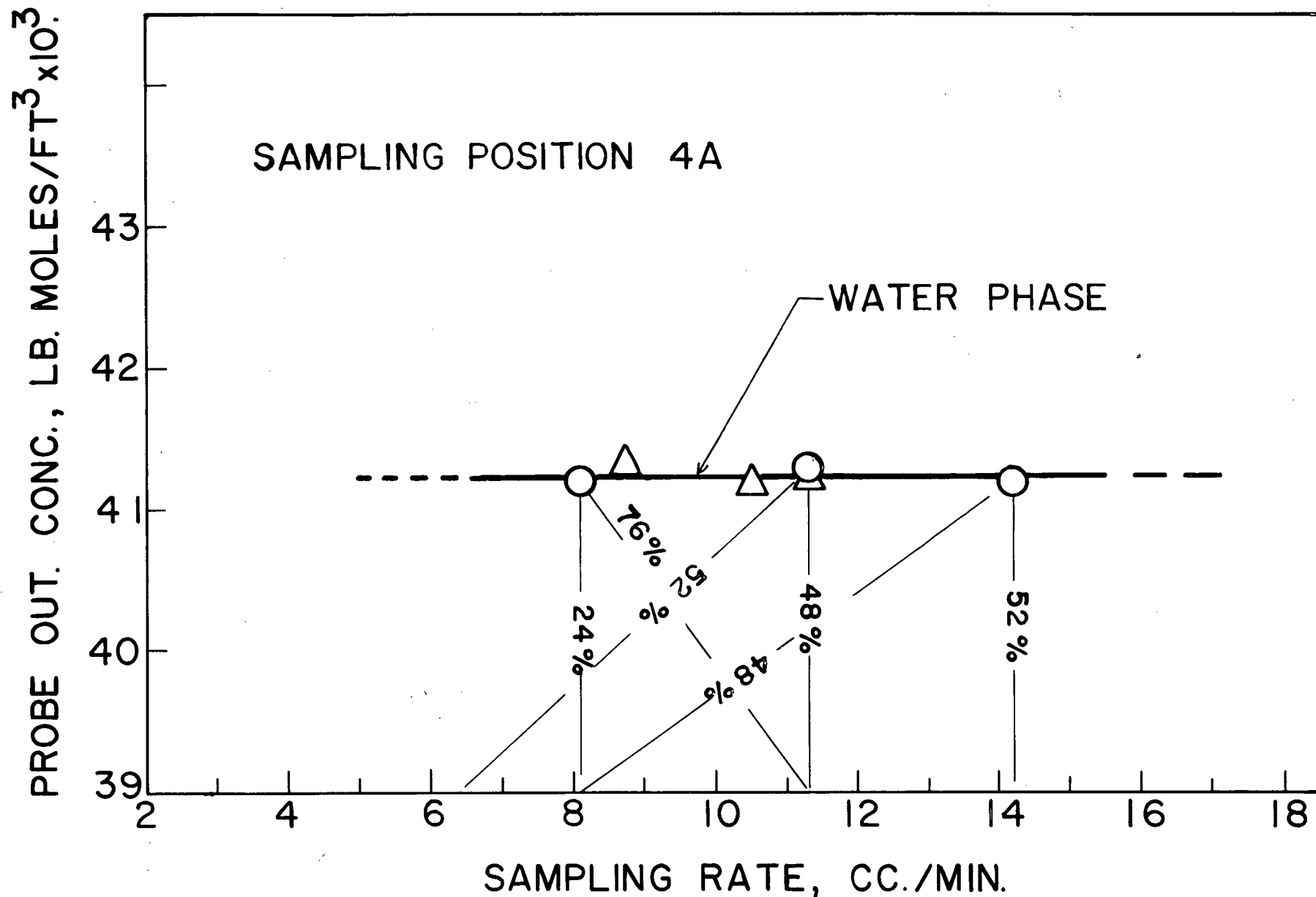


FIGURE 17. Influence of sampling rate on point concentration, Run 7E.

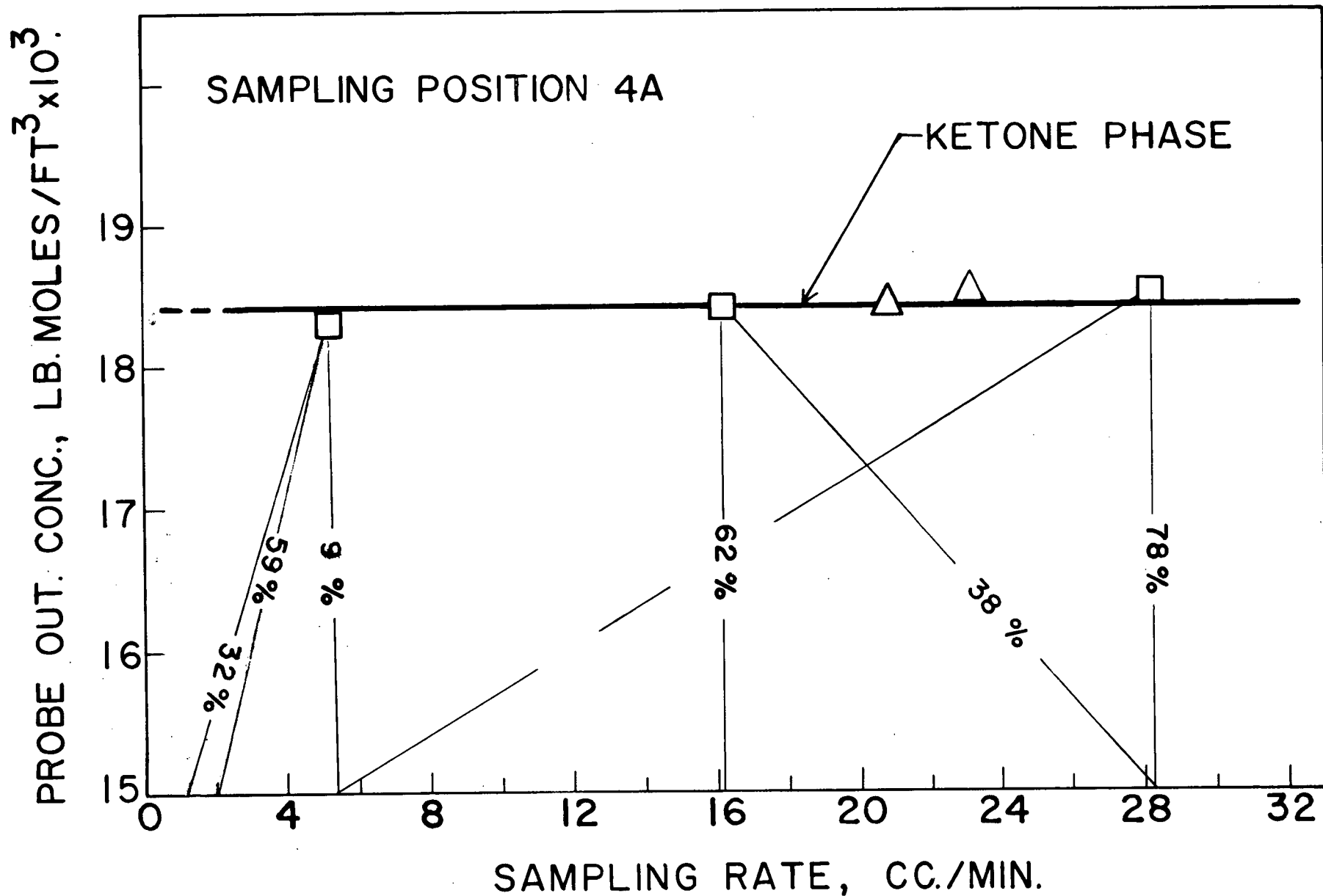


FIGURE 17A. Influence of sampling rate on point concentration, Run 7F.

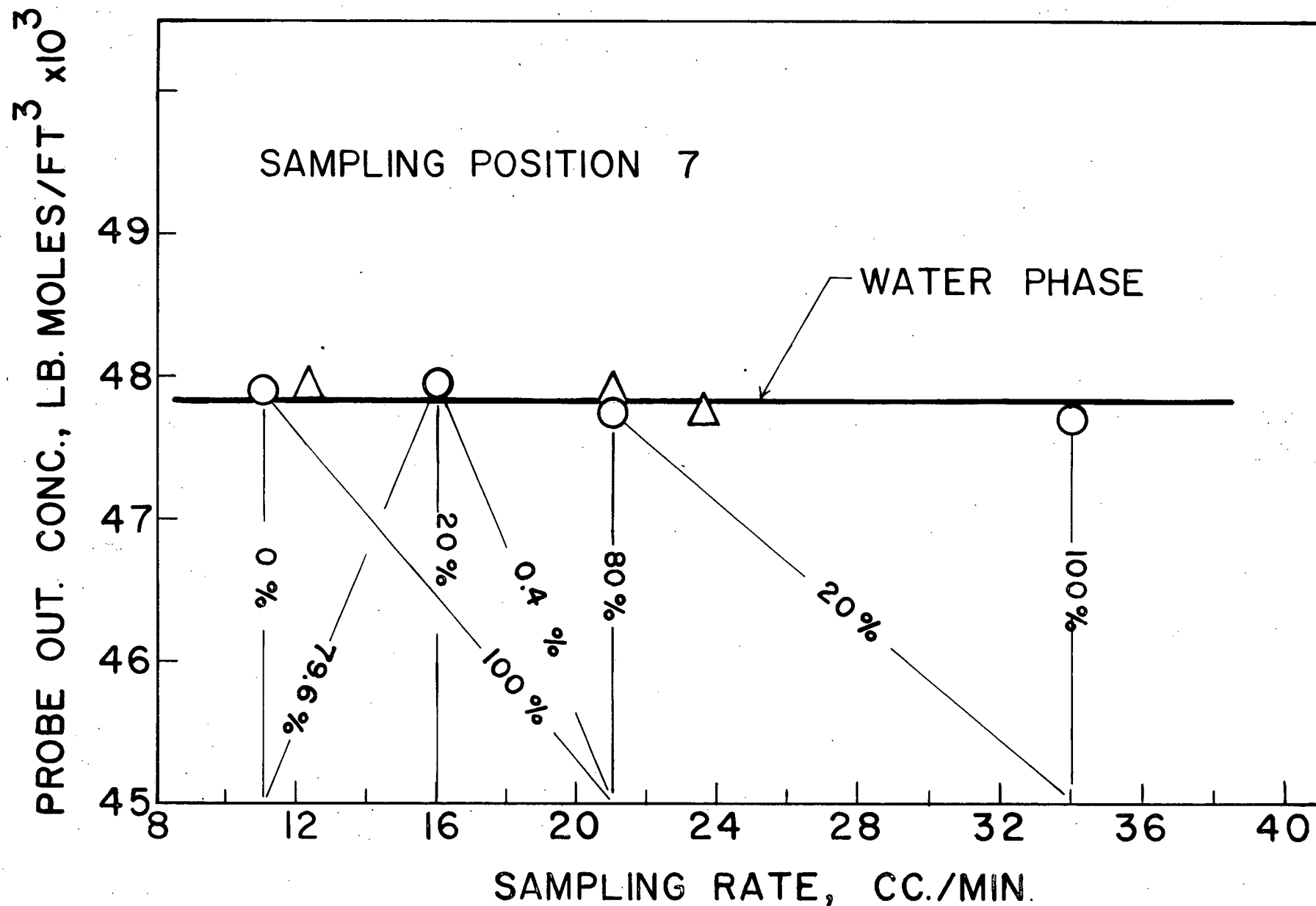


FIGURE 18. Influence of sampling rate on point concentration, Run 1D.

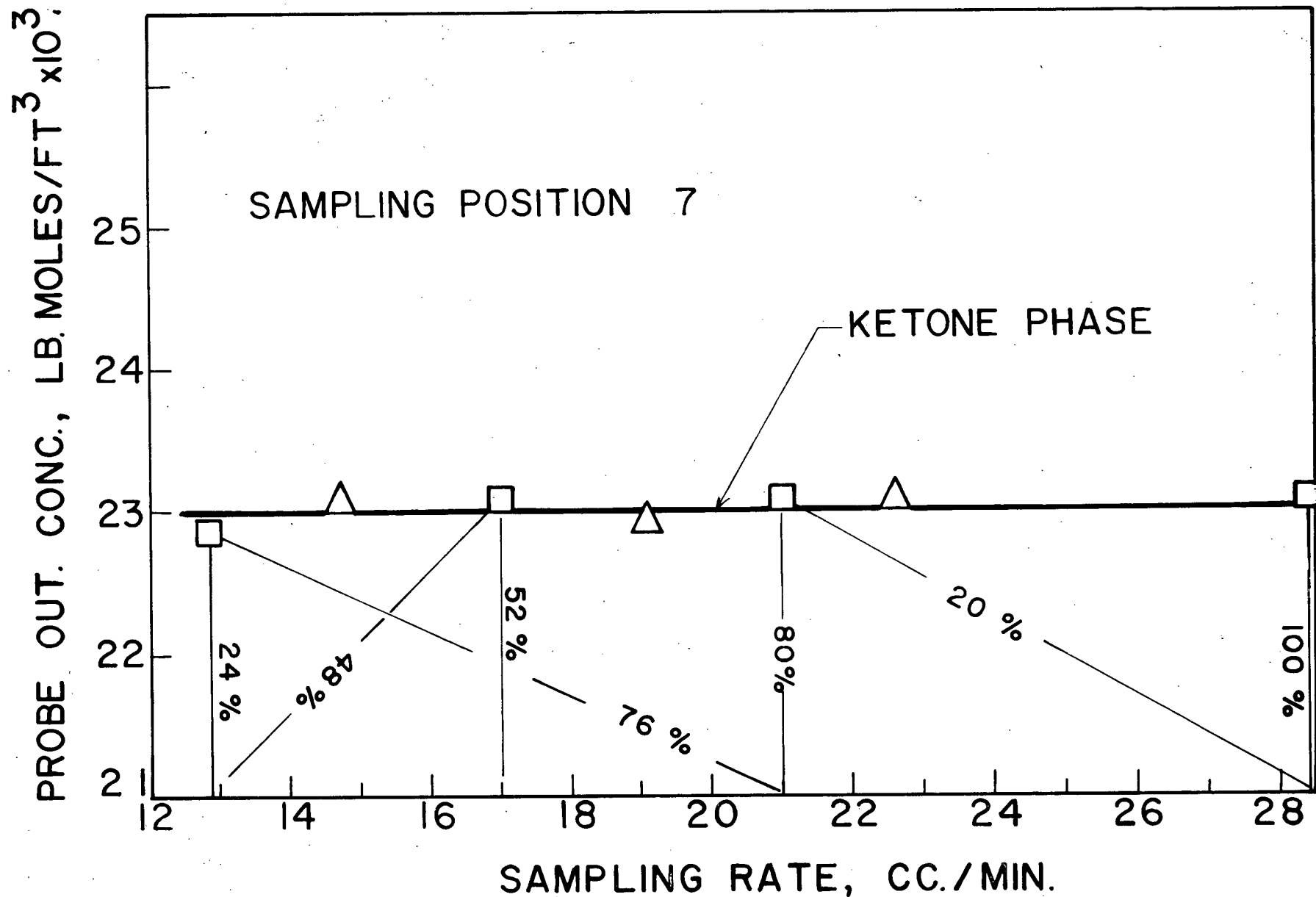


FIGURE 19. Influence of sampling rate on point concentration, Run 1D.

as does Table 25 in Appendix V.

D) The influence of sampling procedure on the steady state concentrations.

During Runs 7E and 7F of the investigation of sampling rate variation for both phases described previously, the column inlet and outlet concentrations were measured. The outlet samples were taken to investigate the influence of the rate of sampling on the steady state concentrations.

At first, the continuous phase sampling rate was kept constant while the dispersed sampling rate was varied over a wide range of rates. Figure 20 records the concentrations obtained in relation to the sampling rate in Run 7F. The next operation consisted in varying the continuous phase sampling rate and holding the other one constant. These results are shown on Figure 21 for Run 7E. The procedure just mentioned was done to study if the concentration profile of either phase would change if either rate is varied with the other one held constant. The concentration profiles were not measured in detail. However, change in the outlet concentration would indicate a change in the profile.

On Figures 20 and 21, the column's length (nozzle tips to interface) has been included, as well as the sampling rate, shown as a percentage of the respective phase flow. A maximum deviation in either run in the outlet concentrations was 2.3% from the mean value. The inlet concentrations were constant because they were fixed before beginning a run. (A maximum rate of 14.2cc./min. was used on the continuous phase probe while the maximum used on the dispersed phase probe was 28.2 cc./min..) (Note also that the probes were in operation only for the times shown. There was no additional purging.)

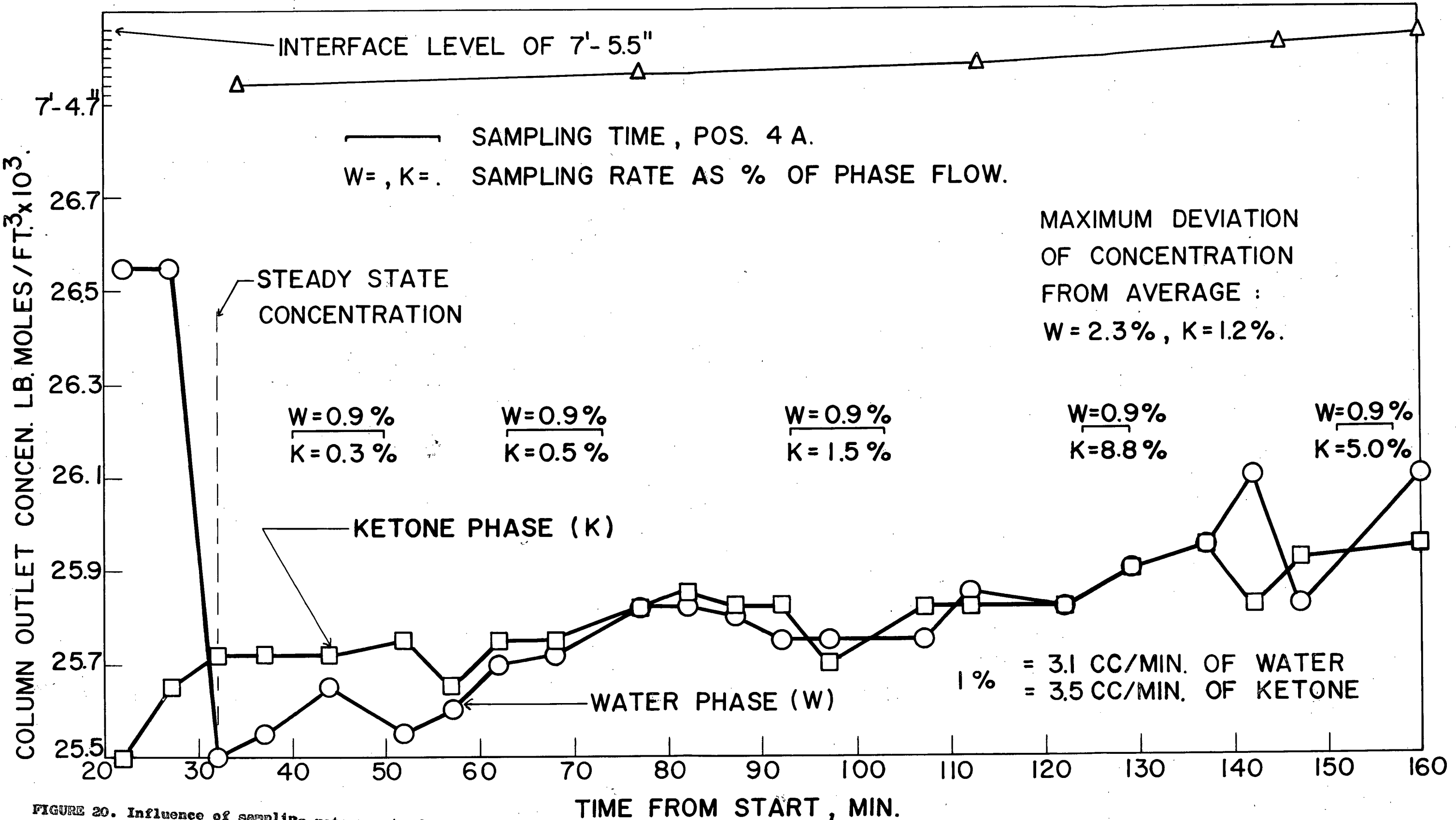


FIGURE 20. Influence of sampling rate on steady state, Run, 7F.

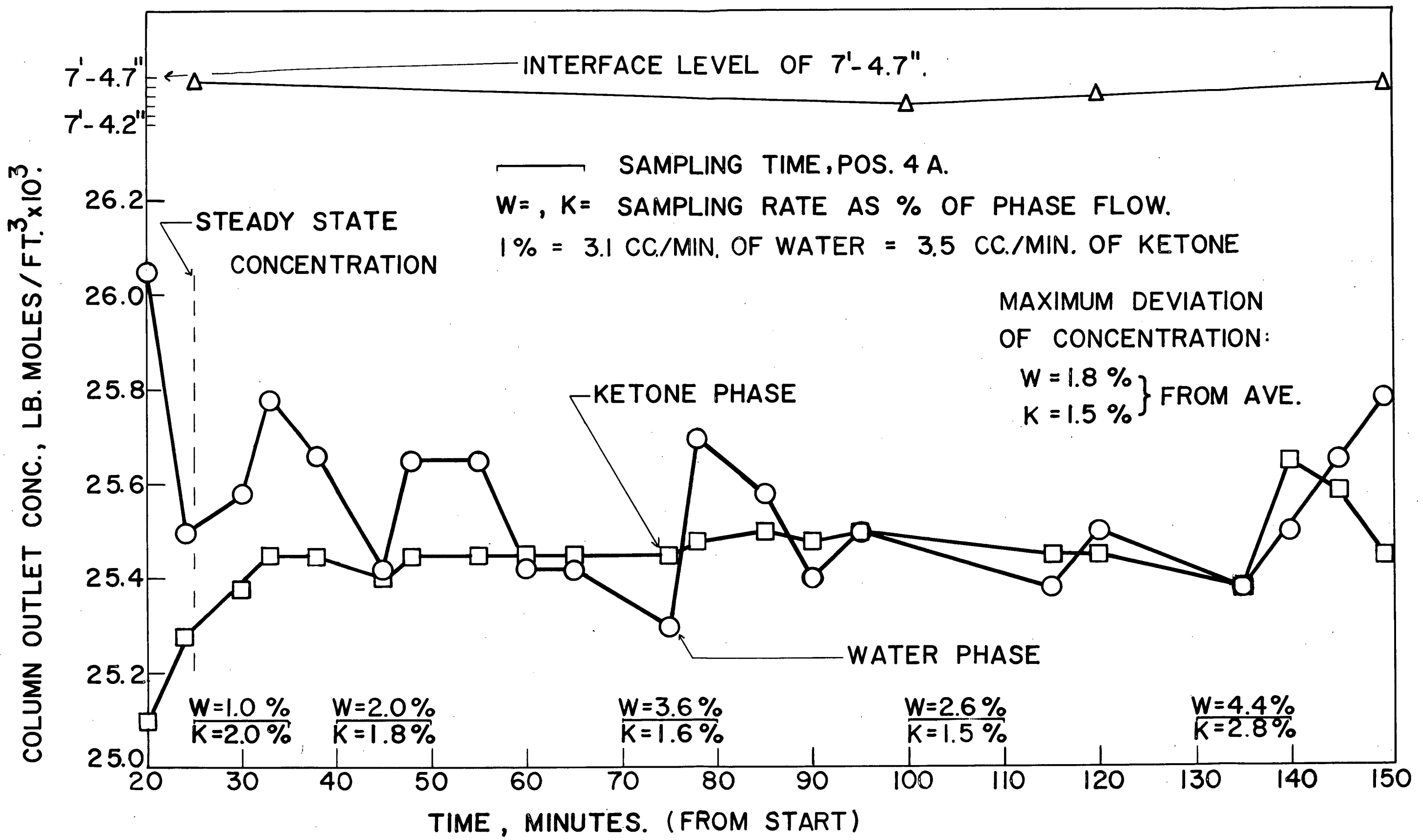


FIGURE 21. Influence of sampling rate on steady state, Run 7E.

E) Concentration profiles:

As mentioned in the literature survey, Choudhury's work did not include the steady state requirements, or an adequate study of the minimum purge time to change the solution inside the probe after a relocation. Furthermore Choudhury assumed that the continuous phase probe sample was representative. The present work was performed to study these effects and consequently it became obvious that the duplication of at least one of Choudhury's runs was a necessity.

The first attempts to duplicate the results obtained by Choudhury were made after knowing the steady state requirements and also the time needed to change the concentration in the probe when relocation took place. Run 65 of Choudhury's thesis (10) was repeated five times.

A comparison of the results obtained with those of Choudhury are shown for Run 5D only, in Figure 22. (Table 10A gives the data of this run.) There was a significant difference in results. It is believed that the difference was caused mainly by an error in analytical procedure made by the present investigator.

At the beginning of the present work, two 10 ml. pipettes were calibrated and used to measure the samples to be analyzed. The calibration of both pipettes showed that the difference in volume from each other and from 10 ml. was negligible. After three months of experiments, a calibrated pipette was broken and replaced by a new one. However, due to the previous experience, the new pipette was not calibrated. However, after long use this pipette was calibrated, and found to deliver 5% more than those used initially. A second cause of error consisted of an evaporation of some dispersed phase from the feed

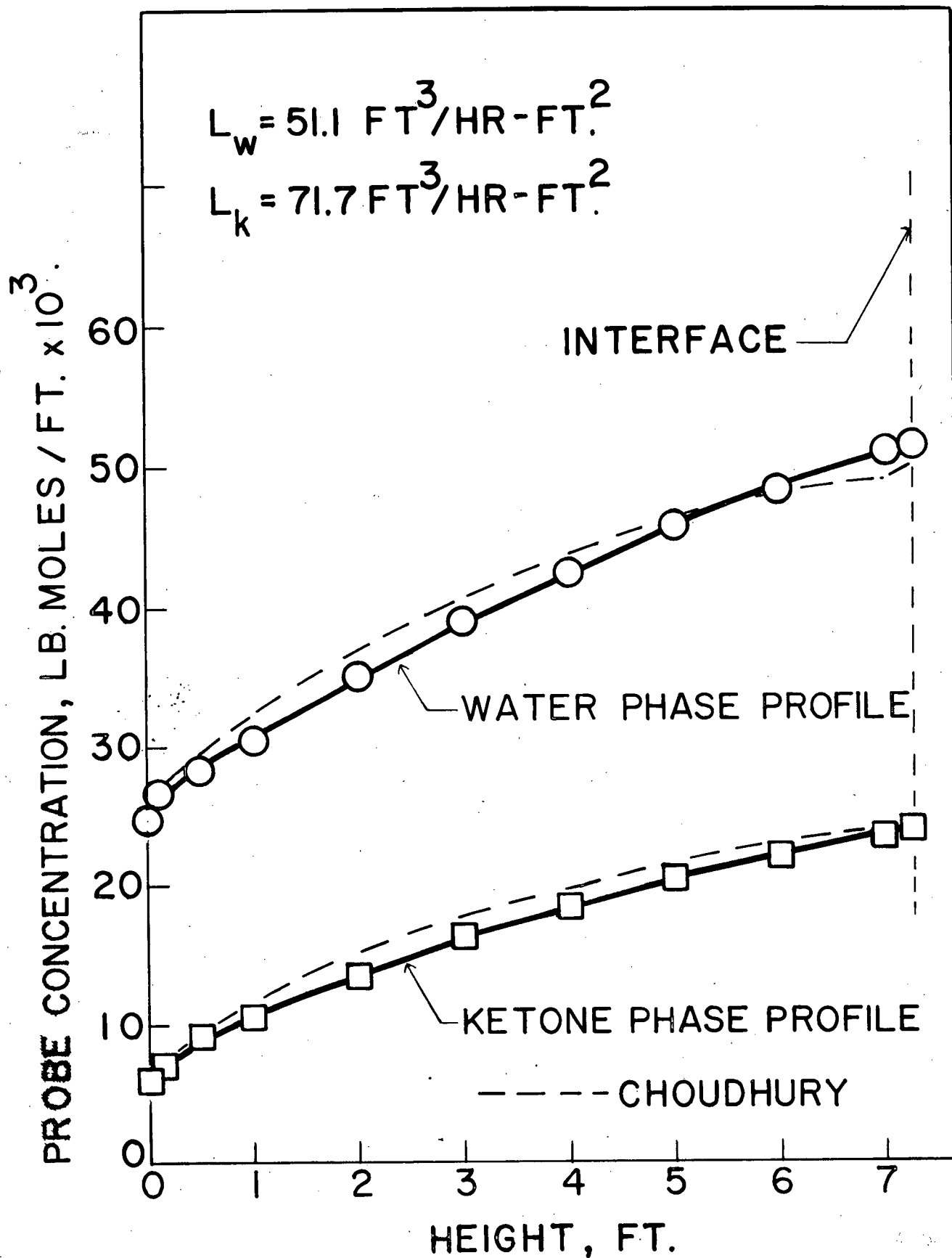


FIGURE 22. Duplication of Choudhury's Run 65, Run 5D.

tank through the vent system. This evaporation caused a gradual increase in the dispersed phase feed concentration.

These errors were readily corrected, and Run 8 was performed to recheck Run 5D and Choudhury's Run 65. Figure 23 shows the results of both Run 8 and of Choudhury's Run 65. These results are given also in Appendix II, Table 10A.

F) Concentration study in the Elgin head:

It should be interesting to mention here an attempt which was made to study solute concentrations in the Elgin head. A glass tube was introduced into a vent line installed on the Elgin head, close to the center of the column. From this location, several samples of water phase and of ketone phase were taken at different distances from the column interface. Table 3 and Figure 24 give the results obtained. Since these concentrations were not related to the point concentrations inside the column, this study was not carried any further.

TABLE 3

Concentration study in the Elgin head.

Height of column. ft.	Distance from nozzle. ft.	Concentration, lb.-moles/ft ³ × 10 ³ .	Located on Figure 24 as:
7'- 3.8"	7'- 0.25"	34.45	A
7'- 3.8"	7'- 3.30"	34.42	B
7'- 3.8"	7'- 3.55"	34.20	C
7'- 3.8"	7'- 4.05"	15.85	D
7'- 3.8"	7'- 4.30"	15.00	E
7'- 3.8"	7'- 6.80"	14.86	F

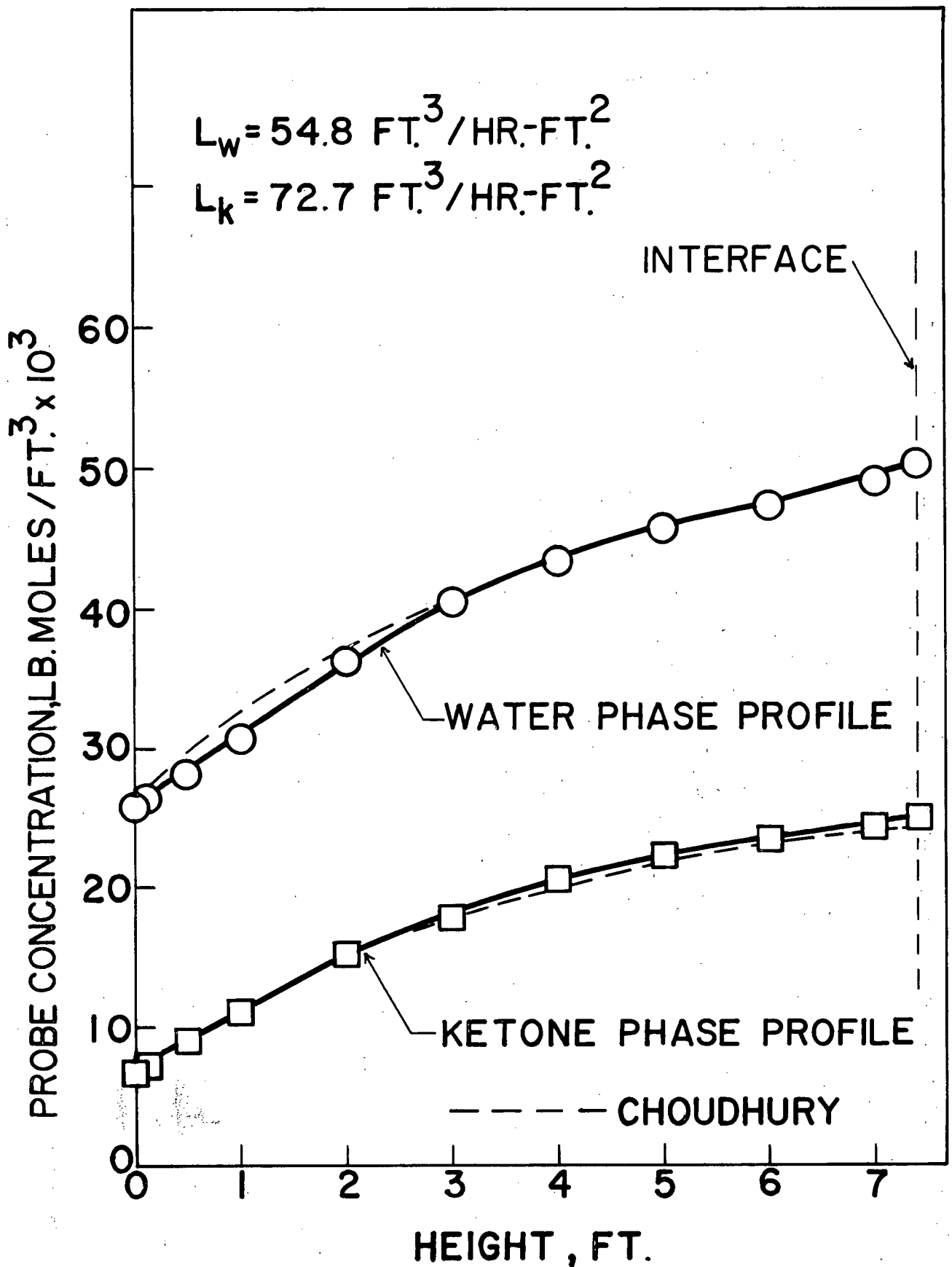


FIGURE 23. Duplication of Choudhury's Run 65, Run 8.

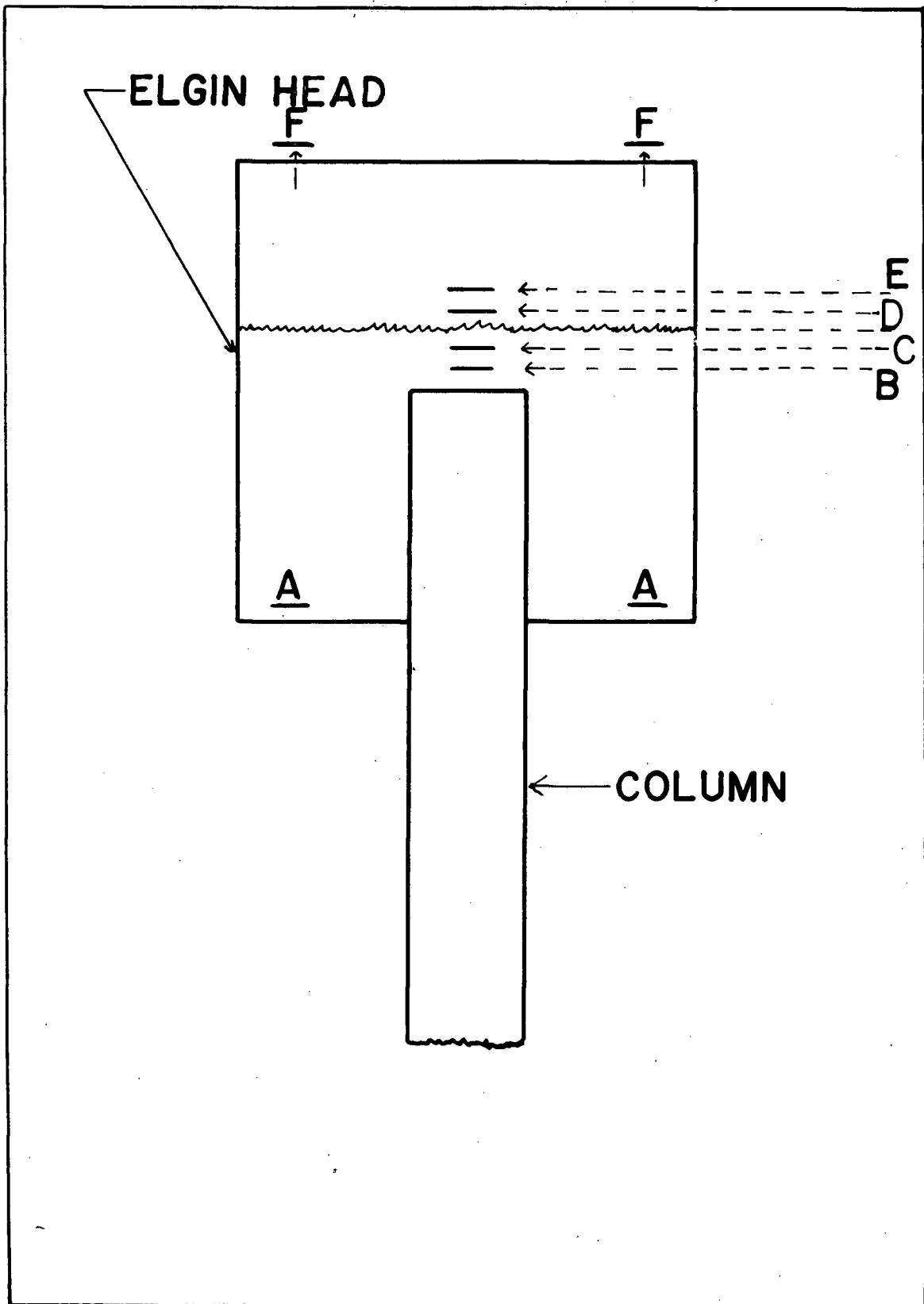


FIGURE 24. Concentration study in the Elgin head.

G) Piston sampling.

1.- Influence on steady state:

Three runs were carried out to determine the length of time required to achieve steady state concentrations under conditions of normal operation using a dispersed phase flow rate of $120.2 \text{ ft}^3/\text{hr.}-\text{ft}^2$ and a continuous phase flow rate of $54.2 \text{ ft}^3/\text{hr.}-\text{ft}^2$. In addition, the influence on steady state was investigated of the removal of a portion of the contents of the column and simultaneous insertion of distilled water, or, on other occasions, of outlet water phase, by means of the piston.

For the first run, the Elgin head was drained completely, the column was filled with continuous phase feed solution, and the extraction process started using the flow conditions just mentioned. Both inlet solutions were sampled three times each during the run, while both outlet solutions were sampled every five minutes from the start. At fifty-two minutes from the beginning of the extracting operation, the piston was operated with distilled water in the hole which was to slide into line with the column proper. Distilled water was used to show the effect of replacing a column section by a water solution which will give the maximum disturbance of the steady state. Just after taking a piston sample, samples of the outlet solutions were taken every two minutes for 10 minutes. Another sample of each outlet solution was taken eighteen minutes after the piston sample had been obtained. Another piston sample was taken 20 minutes after, and the same procedure for sampling the outlet solutions was repeated. From this run, it was found that the time to obtain steady state after the start of the run was comparable to the previous results. Taking a piston sample using distilled water in the piston hole which was moved into line with the

column proper resulted in 15 minutes being required for reestablishing the steady state for the water phase. The dispersed phase outlet concentration was not changed by the piston sample being taken using distilled water to replace the column's section. These results are given in Figure 25.

Run 9D was performed starting with a column which had been operated previously. The flow rates were the same as for Run 9C. A similar procedure was applied to obtain samples of inlet and outlet solutions. At thirty-two minutes from the beginning of the run, a piston sample was taken, resulting in the replacement of a portion of the column by a portion of distilled water. As expected, this run gave a shorter result: for the length of time needed for the column to achieve steady state when samples were not being taken. In this Run some disturbance of the outlet ketone phase concentration apparently took place; however, only one sample showed a deviation from the normal steady value, and the result may not be significant. The disturbance of the water phase exit concentration was much more pronounced (as expected from the previous results). Steady state was restored in a little over 10 minutes. Figure 26 records the results of Run 9D.

Run 9F was performed using exactly the same conditions of flow as those of 9D and 9C. In Run 9F, the probes were used to sample at the piston axis with a purging and sampling rate of 10.0 cc./min. for the continuous phase and 9.4 cc./min. for the dispersed phase. The purging time was 10 minutes. Referring to Figure 10 which specified the minimum purging times for several purging rates, it can be seen that 6.2 minutes were the minimum needed to purge the continuous phase probe at a rate of 10.0 cc./min., and 5.2 minutes were the minimum

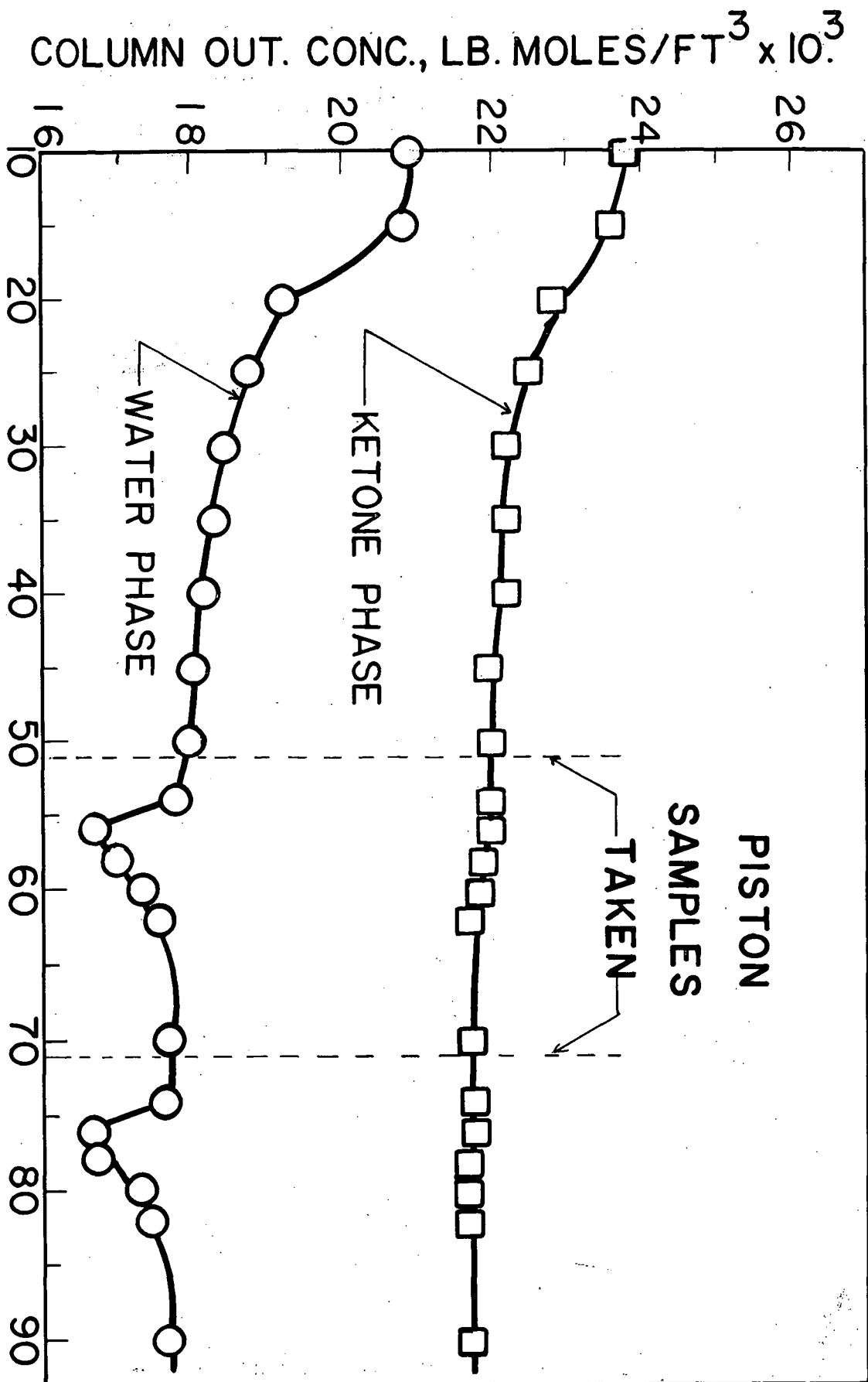


FIGURE 25. Effect of piston sampling on steady state, Run 9C.

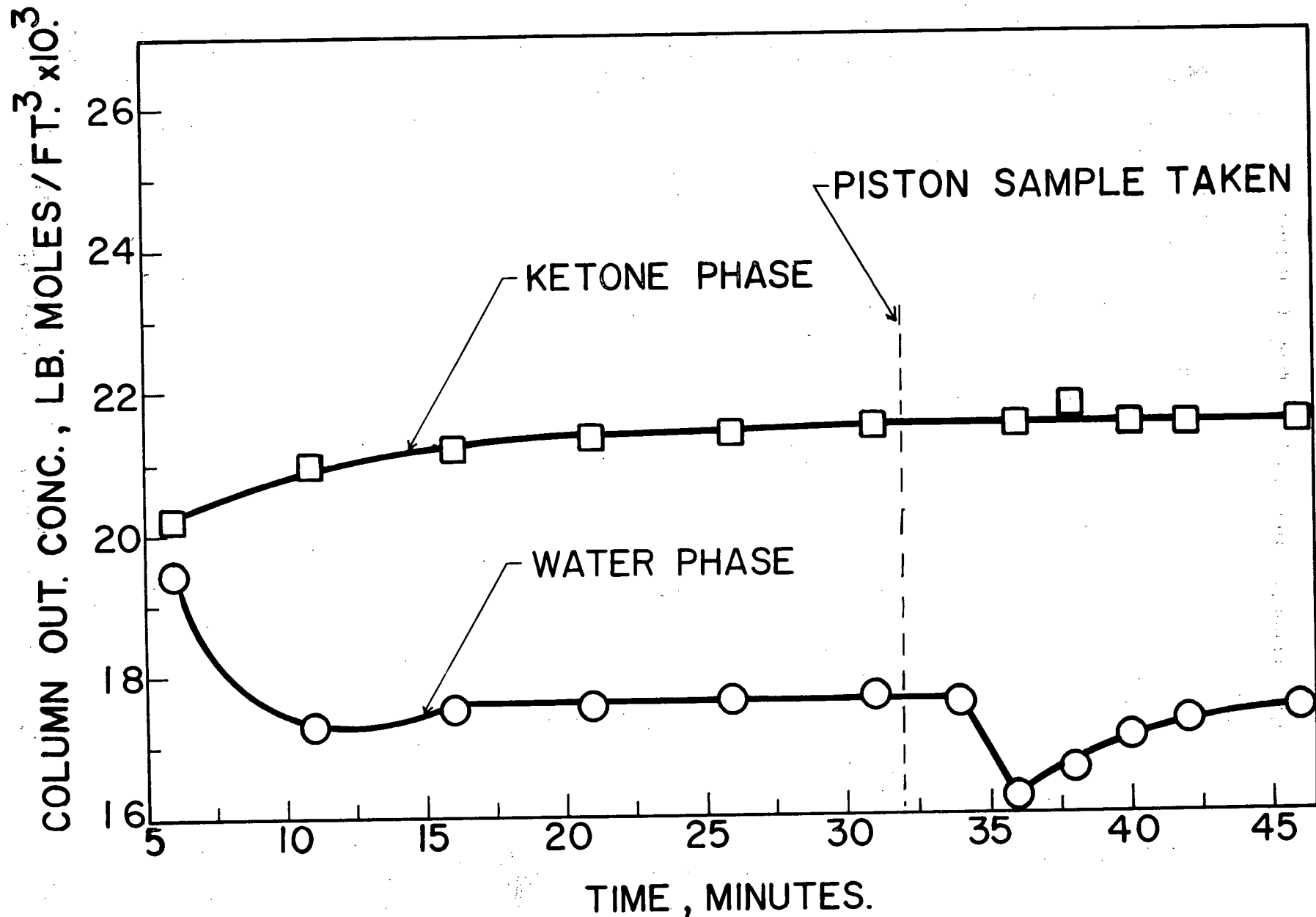


FIGURE 26. Effect of piston sampling on steady state, Run 9D.

needed to purge the dispersed phase probe at a rate of 9.4 cc./min.. It was decided to use 10 minutes to be on the safe side as mentioned earlier. A piston sample was taken half a minute after the probe sample. The piston hole which had to slide into line with the column proper was filled this time with the outlet continuous phase solution. (This was the solution to be used in the dispersed phase sampling runs.) The sampling procedure was repeated three times. Figure 27 shows the results which indicate that the steady state is not disturbed by a piston sample when the piston hole sliding into line with the column is filled with outlet continuous phase solution. The carrying out of probe sampling did not affect the steady state, as would have been expected from the results given under the heading of sampling rate influence on steady state.

2.- Piston point concentrations:

Five runs were performed to obtain information about the sampling procedure by means of a piston sampler.

For the first Run, 9E, flow rates of $120.0 \text{ ft}^3/\text{hr.}-\text{ft}^2$ for the dispersed phase and $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$ for the continuous phase were used. Samples were taken at the axis of the piston by means of the probes; half a minute later a piston sample was taken. Three of these samples were available at the end of this Run. The purging and sampling rates used with the water probe was 12.0 cc./min. and with the ketone probe 13.0 cc./min. The purging time used was 10 minutes as compared with 5.2 minutes and 3.8 minutes required to purge adequately the water and ketone probes respectively according to Figure 10 for the rates just mentioned. The average volume percent ketone in the ketone probe sample was 89.6% while that for the piston sample was 14.5%.

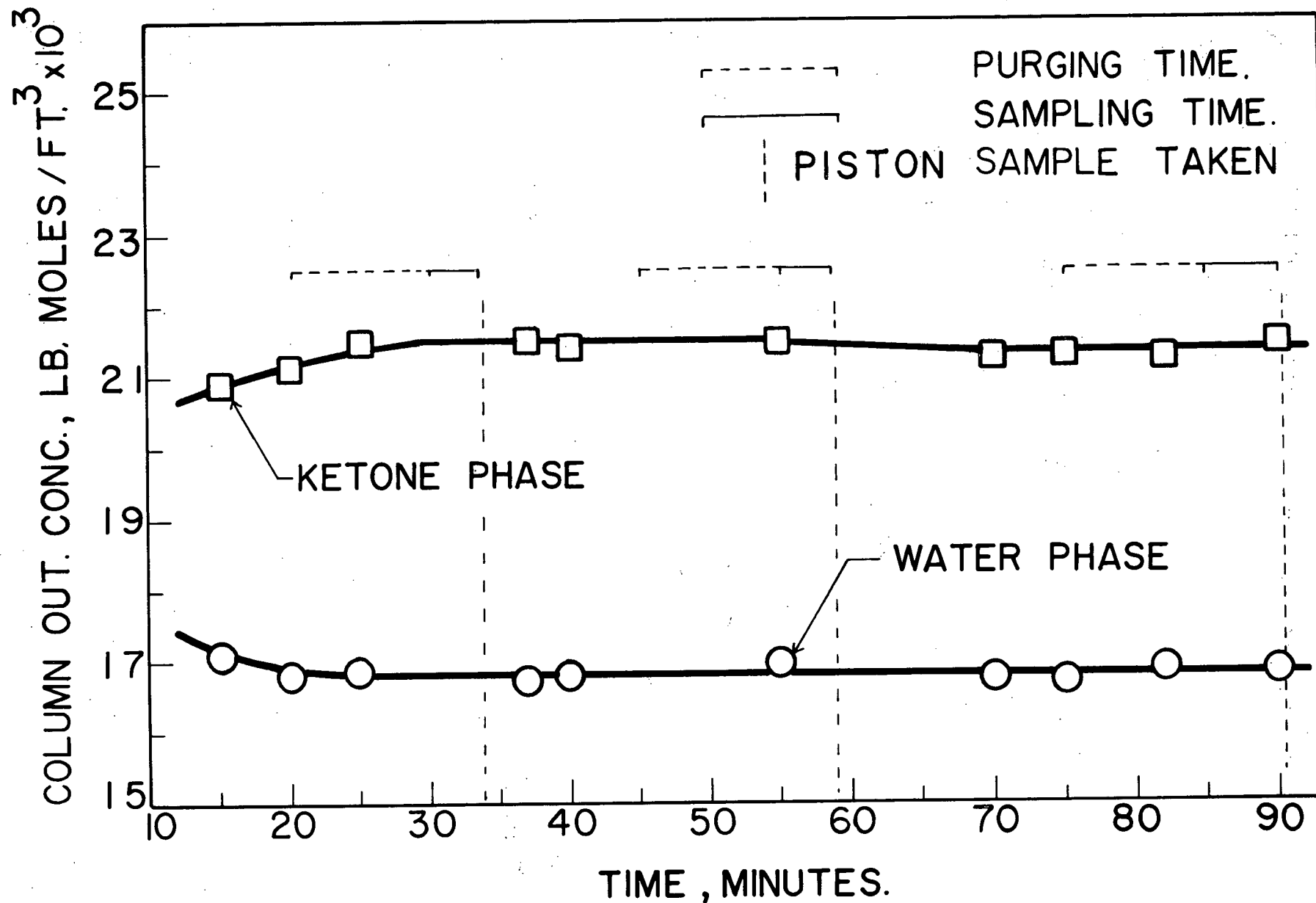


FIGURE 27. Effect of piston sampling on steady state, Run 9F.

A second Run, 9F, was performed to check Run 9E. The dispersed phase flow rate was $119.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$ and the continuous phase flow rate, $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$. As before, the probes were used to sample at the axis of the piston; but, after the second sample had been taken, it appeared desirable to check whether the probes were really at the piston axis when sampling. It was found that they were one inch too low. This meant that the probe samples of run 9E and those of 9F obtained to this point were not suitable for comparison with the piston samples. The error was corrected and Run 9F was continued. The purging and sampling rates used were 10.0 cc./min. for the continuous phase probe and 9.1 cc./min. for the dispersed phase probe. The purging time was 10 minutes whereas the minimum purging time was 5.2 minutes for the ketone probe and 6.2 minutes for the water probe according to Figure 10 for the rates mentioned above. Out of four piston samples taken in Run 9F, the results of the last two were almost exactly the same as those taken with the dispersed phase probe. Run 9E and the part of Run 9F in which the probes were in the wrong position were not discarded. This course was taken because the piston results obtained were comparable with one another and with those of Run 9G which was performed using the same conditions. Table 4 records the results, from which it can be seen that the dispersed phase concentrations of the piston samples of Runs 9E and 9F at the time of analysis, C_{kf} , are equal to close approximation for all the samples.

The next Run to be described, Run 9G, was a repetition of 9F. Run 9G was done to verify the results of the previous runs but with the earlier wrong probe locations avoided. Four piston results were obtained in this Run; they reproduce previous dispersed phase concentrations at time of analysis very closely as shown in Table 4.

All the runs performed to obtain piston results to this point were obtained for a drop velocity through the nozzle tips of 0.338 ft./sec.. Reference to Table 4 shows that a maximum volume percent ketone in the column of 14.8 was found using this dispersed phase linear velocity in Runs 9E, 9F, and 9G. It was suggested that this ketone holdup be increased for the purpose of getting more ketone phase in a piston sample. Other things being equal, the analysis (if done at equilibrium) would be less critical, and, consequently, the piston dispersed phase concentrations would be more accurate. To increase the holdup, it became necessary to increase the velocity in the nozzle tips well above the values used so far.

Run 9H was done using the maximum capacity of the ketone rotameter available at the beginning of the work; 21 nozzle tips were used, and a velocity of 0.475 ft./sec. in them. For Run 9H, the dispersed phase flow rate was $169.5 \text{ ft.}^3/\text{hr.}-\text{ft.}^2$ and the continuous phase flow rate, $54.8 \text{ ft.}^3/\text{hr.}-\text{ft.}^2$. In this Run, the probes were used again to sample at the piston axis. The piston sample was taken half a minute after the probe sample. The purging and sampling rate used with the dispersed phase probe was 8.7 cc./min. and with the continuous phase probe 6.2 cc./min.. The purging time was 10 minutes. Reference to Figure 10 shows that the rates just mentioned require a minimum purging time of 5.4 minutes for the ketone probe and 10 minutes for the water probe. Thus the 10 minutes allowed was ample for the ketone probe but included no safety factor in the case of the water probe. The safety factor was not added in this case because the solutions in the feed tanks were running out very quickly. The volume percent ketone in a piston sample now was 22.2%. (The volume percent ketone for the

corresponding dispersed phase probe samples averaged 92.6%.) The dispersed phase piston concentrations, found at the time of analysis C_{kf} , were lower than previously because of higher dispersed phase flow rate used. These results also are recorded in Table 4.

For the first time some ketone was present with one continuous phase ^{probe} sample out of four as a result of the high ketone holdup. A correction to the water concentration was made by writing Equation 5 for each probe. The value of C_{kf} for the ketone present in the water was taken to be the equilibrium value. The two equations resulting were then solved simultaneously to find the value of C_{wi} . (This calculation is given in Appendix VII.)

A new rotameter was installed and calibrated for the purpose of being able to further increase the dispersed phase flow rate and therefore the column (and piston sample) holdup. The calibration of this rotameter is given in Figure 28, following.

Run 9I was performed using a dispersed phase flow rate of $208.0 \text{ ft}^3/\text{hr.}-\text{ft}^2$ and a continuous phase flow rate of $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$. A velocity of 0.584 ft./sec. was used through the 21 tips of the nozzle. The probes were used to sample at the piston axis using a dispersed phase probe rate of 7.3 cc./min. and a continuous phase probe rate of 6.5 cc./min. Based on Figure 10 minimum purge times of 6.4 minutes and 9.6 minutes were required for the ketone and for the water probe, respectively; however, 10 minutes were allowed as purging time. For the second time, some ketone was present with two continuous phase samples out of a total of five as a result of the high Ketone holdup in the column, in spite of low purging and sampling rates. As done for Run 9H, corrected values were calculated using Equation 5 for each probe. This calculation was done for Samples 3 and 5, but only in

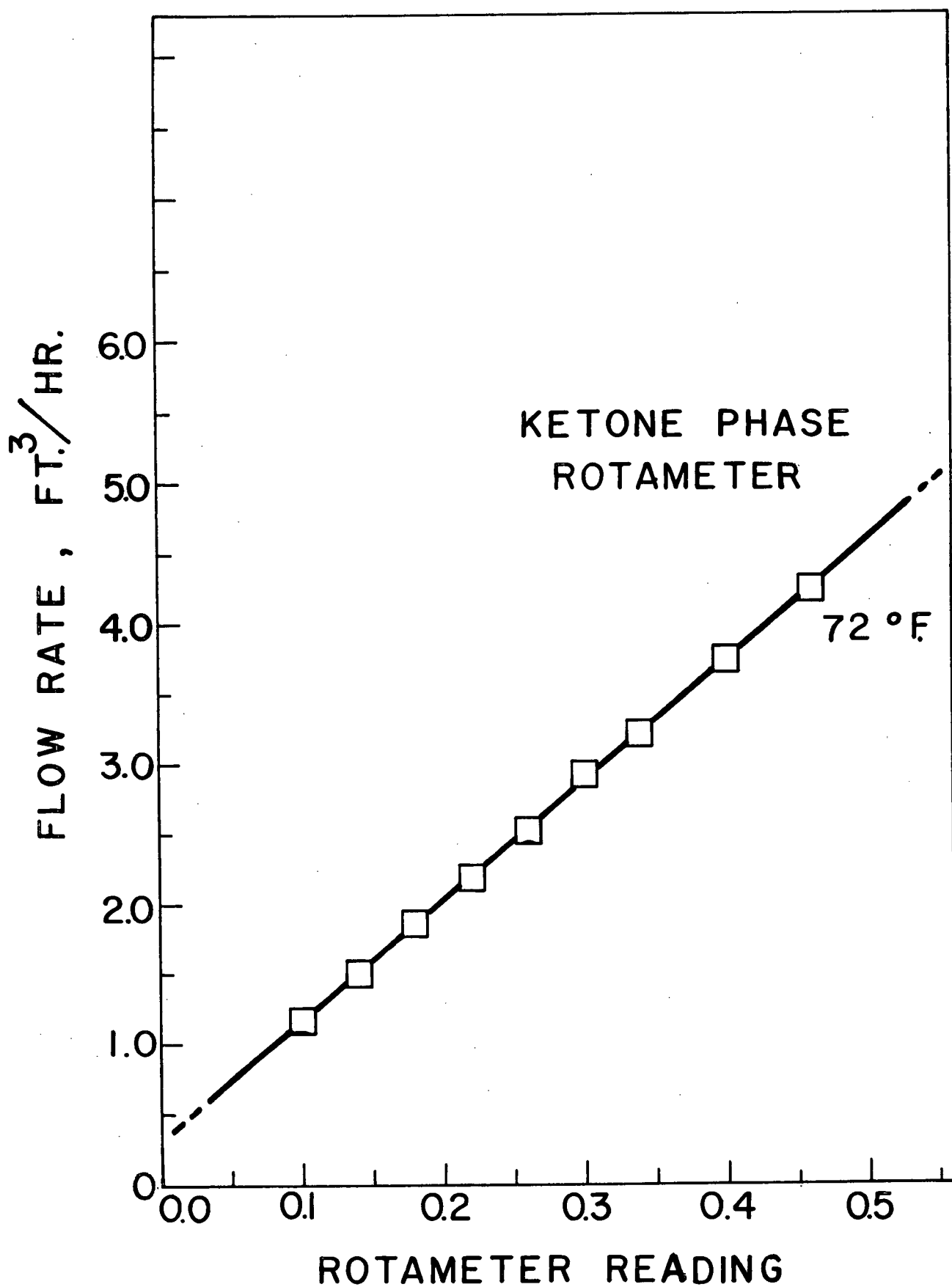


FIGURE 28. Calibration of the rotameter, serial Number 20,789 for a ketone phase having a concentration of 6.43 lb.-moles/ft.³ $\cdot 10^3$

Sample 3 was there any change in the figures* (See Appendix VII) Even in Sample 3 the correction was very small, $+0.03 \times 10^{-3}$ lb.-moles/ft.³ for C_{wi} , and negligible for C_{ki} . The ketone was only 1.2% of the total volume of ^{the} water in Sample 3, and was 0.9% of Sample 5. The highest holdups as measured by the piston sampler were obtained in this Run 9I, the average holdup for five samples being 28.4%. The volume percent ketone in the dispersed phase probe samples for this Run averaged 96.5%. The dispersed phase piston concentrations at time of analysis, C_{kf} , again were found to be lower than before due to the increase in the dispersed phase flow rate. It was found later that the phases were close to equilibrium. This is probably why the initial dispersed phase concentration (determined by using the material balance as applied to the piston samples) checked the probe dispersed phase results within less than 2.0% deviation as defined in connection with Table 4. (For the case of one sample out of five in this Run, the % deviation was higher. The results of this Run appear in Table 4 also.)

Table 5 shows in detail the probe data corresponding to each piston sample. In a few cases there was too little aqueous phase in the dispersed phase sample for it to be possible to obtain C_{wf} by analysis. The value of C_{wf} was then assumed to be the equilibrium value corresponding to C_{kf} , and this equilibrium value was used as C_{wf} in the material balance calculation of C_{ki} . In these cases, the correction applied to C_{kf} to produce C_{ki} was always small, never exceeding 1.5% of C_{ki} .

Subtracting from the C_{wi} values of Table 5 the C_{wf} values of Table 4, produces differences ($C_{wi} - C_{wf}$) which do not increase with increased holdup as was expected; in fact this difference did not change greatly except for Run 9I where it was comparatively low.

* Change or correction from the values obtained if the ketone in the water probe sample was neglected altogether.

Increasing the holdup was supposed to help to make the difference between C_{wi} and C_{wf} bigger, but unfortunately the holdup lowers the mass transfer resistance in the column by increasing the interfacial area between continuous phase and drops. The result is that equilibrium between the phases is approached at the location of the sampler as the holdup increases.

Table 5A records the probe initial results, the piston results at time of analysis, and their corresponding equilibrium values. It also gives the mass transfer driving forces, at the location of the piston calculated from the probe results. Although the holdup was doubled between Run 9G and Run 9I, these driving forces were cut down by a factor of 7.7 for the water phase, and 5.6 for the ketone phase. (These factors should be very close to each other for constant slope of the equilibrium curve.) As shown by Table 5A, this average driving force for the water phase in Run 9I was 0.44, whereas for Runs 9E, 9F, and 9G it was 3.4. The average driving force for the ketone phase in Run 9I was 0.32, whereas for Runs 9E, 9F, and 9G it was 1.8. It should be noted that the values of the ketone phase concentration at time of analysis*, for the piston ($(C_{kf})_{\text{piston}}$, Table 5A) all seem to be approximately 2% beyond the equilibrium values (C_{kf}^*) calculated from $(C_{wf})_{\text{piston}}$ by means of the equilibrium curve. A similar comment can be made, of course, with reference to the values of $(C_{wf})_{\text{piston}}$. These are all less than the equilibrium values (C_{wf}^*) calculated from $(C_{kf})_{\text{piston}}$ again by means of the equilibrium curve.

The probe results of Table 5A show that both phases within the column were almost at equilibrium at 1.59 ft from the nozzle tips

* For the piston samples, the analyses all were done after the phases had reached equilibrium.

for Run 9I. This result was caused by the extraction taking place mainly in the upper part of the column. The large amount of ketone present extracted much more acid from the water entering the column than that removed in the runs at lower holdup. The concentration of acetic acid in the water phase when it reached the piston then was small, and nearly in equilibrium with the concentration in the ketone phase. Further details will be given in the discussion on this subject, later in the thesis.

TABLE 4

Piston results.

Run number.	Volume of sample cc.		Volume percent ketone	Concentrations lb.-moles/ft ³ x10 ³				Average piston and probe results	% deviation of piston results from average.
	V _k	V _w		C _{kf}	C _{wf}	C _{ki}	C _{ki}		
				piston results			probe		
*9E	17.0	100.0	14.5	10.34	20.50	6.22	8.34	7.28	-14.3
*9E	17.0	101.0	14.4	9.87	19.50	9.51	7.98	8.75	+ 8.7
a*9E	17.5	100.0	14.8	9.90	19.68	10.59	7.98	9.29	+14.0
*9F	17.0	100.0	14.5	10.54	20.96	9.48	8.61	9.04	+ 4.8
*9F	17.0	100.0	14.5	10.45	20.79	10.45	8.44	9.45	+10.6
9F	17.0	100.0	14.5	10.34	20.55	8.28	8.43	8.34	- 0.7
9F	16.0	101.0	13.7	10.22	20.55	7.38	8.08	7.73	- 4.5
9G	16.0	101.0	13.7	10.22	20.30	6.45	8.36	7.41	-13.0
9G	16.0	101.0	13.7	10.15	20.35	6.30	8.30	7.30	-13.7
9G	17.0	100.0	14.5	10.15	20.15	7.44	8.33	7.89	- 5.7
9G	17.0	100.0	14.5	10.15	20.30	8.33	8.28	8.31	+ 0.2
a9H	26.0	91.0	22.2	8.00	16.00	8.21	7.20	7.71	+ 6.5
*9H	26.0	91.0	22.2	7.77	15.80	7.25	7.33	7.29	- 0.5
9H	26.0	91.0	22.2	7.65	15.39	6.64	7.05	6.85	- 3.7
9H	26.0	91.0	22.2	7.65	15.53	6.00	7.10	6.55	- 8.4
9I	33.5	83.5	28.6	7.59	15.24	7.02	7.15	7.09	- 1.0
9I	33.5	83.5	28.6	7.09	14.25	5.94	6.74	6.34	- 6.9
*9I	33.0	84.0	28.2	7.09	14.25	6.58	6.76	6.67	- 1.4
9I	33.0	84.0	28.2	7.07	14.39	6.84	6.76	6.80	+ 0.6
9I	33.0	84.0	28.2	7.07	14.39	6.84	6.82	6.83	+ 0.2

* Runs performed with probes 1.-in. below the axis of the piston

a Runs which had a negative ($C_{wi} - C_{wf}$) difference

* Correction was applied for the ketone in the water probe sample.

TABLE 5

Probe results corresponding to piston results of Table 4.

Run number.	Volume of sample cc. (ketone probe)		Volume percent ketone.	Concentrations lb.-moles/ft ³ x10 ³			
	V _k	V _w		C _{kf} ketone	C _{wf} probe	C _{ki}	C _{wi} water
*9E	61.5	37.5	89.2	8.76	17.75	8.34	21.20
*9E	38.0	4.0	90.5	8.29	16.64	7.98	19.56
*9E	31.0	3.0	91.2	8.29	16.35	7.98	19.56
*9E	23.7	1.0	96.0	8.73	#18.20	8.61	21.14
*9F	28.0	2.0	93.4	8.64	#18.00	8.44	20.79
9F	81.0	5.0	94.1	8.64	17.52	8.43	20.90
9F	42.0	5.0	89.3	8.70	15.75	8.08	21.00
9G	40.0	4.0	90.9	8.70	17.51	8.36	20.90
9G	48.5	4.0	92.3	8.58	17.51	8.30	20.96
9G	51.5	4.0	92.8	8.58	17.37	8.33	20.61
9G	53.5	5.0	91.5	8.58	17.37	8.28	20.61
9H	39.0	3.0	95.2	7.30	14.60	7.20	15.94
*9H	15.6	0.4	97.5	7.30	14.95	7.33	15.95
9H	38.0	3.0	92.7	7.15	14.31	7.05	15.68
9H	19.0	1.5	92.7	7.18	#15.00	7.10	16.00
9I	41.5	2.5	94.3	7.18	#15.00	7.15	15.47
9I	36.0	2.0	94.8	6.77	#14.15	6.74	14.71
*9I	28.0	1.0	96.5	6.77	#14.15	6.76	14.45
9I	28.0	1.0	96.5	6.77	#14.15	6.76	14.48
9I	40.0	2.0	95.2	6.83	#14.20	6.82	14.48

* Runs performed with probes 1.-in. below the axis of the piston

: Correction was applied for the ketone in the water probe sample.

C_{wf} results are equilibrium values corresponding to C_{kf}. The volume was too small to be analyzed.

TABLE 5A

Piston and probe results and their corresponding equilibrium values.

Run number.	Piston Results #				Probe Results #				Driving force at probe location.	
	C_{kf}	C_{wf}^*	C_{wf}	C_{kf}^*	C_{ki}	C_{wi}^*	C_{wi}	C_{ki}^*		
	lb.-moles/ft ³ x 10 ³				lb.-moles/ft ³ x 10 ³				$C_{wi}^* - C_{wi}$	$C_{ki}^* - C_{ki}$
9E	10.34	21.30	20.50	9.90	8.34	17.38	21.20	10.25	3.8	1.9
9E	9.87	20.50	19.50	9.50	7.98	16.65	19.56	9.45	2.9	1.5
9E	9.90	20.60	19.68	9.55	7.98	16.65	19.56	9.45	2.9	1.5
9F	10.54	21.70	20.96	10.30	8.61	17.91	21.14	10.25	3.2	1.6
9F	10.45	21.60	20.79	10.00	8.44	17.60	20.79	10.15	3.2	1.7
9F	10.34	21.30	20.55	10.00	8.43	17.60	20.90	10.20	3.3	1.8
9F	10.22	20.90	20.55	10.05	8.08	16.85	21.00	10.20	4.2	2.1
9G	10.22	20.90	20.30	9.85	8.36	17.40	20.70	10.20	3.5	1.8
9G	10.15	20.70	20.35	9.90	8.30	17.30	20.96	10.20	3.7	1.9
9G	10.15	20.70	20.15	9.80	8.33	17.33	20.61	10.00	3.3	1.8
9G	10.15	20.70	20.30	9.85	8.28	17.28	20.61	10.00	3.3	1.7
9H	8.00	16.50	16.00	7.70	7.20	15.00	15.94	7.70	0.9	0.5
9H	7.77	16.15	15.80	7.53	7.28	15.15	15.95	7.65	0.7	0.4
9H	7.65	15.95	15.39	7.38	7.05	14.70	15.68	7.55	1.0	0.5
9H	7.65	15.95	15.53	7.40	7.10	14.80	16.00	7.75	0.6	0.3
9I	7.59	15.80	15.24	7.30	7.15	14.90	15.47	7.40	0.6	0.3
9I	7.09	14.75	14.25	6.80	6.74	14.08	14.71	7.10	0.6	0.4
9I	7.09	14.75	14.25	6.80	6.76	14.09	14.42	6.90	0.3	0.1
9I	7.06	14.70	14.39	6.90	6.76	14.08	14.48	7.20	0.4	0.4
9I	7.06	14.70	14.39	6.90	6.82	14.20	14.48	7.20	0.3	0.4

The starred values are equilibrium values corresponding to the values of the preceeding column of the Table.

DISCUSSION

A) Study of time needed to obtain steady state:

The previous work (10,11,12,13) on a liquid-liquid extraction spray column, did not include an adequate study of the length of time required to reach a steady extracting operation. It is evident that a steady state must be achieved before reliable data can be obtained.

In the present work, an investigation was performed to determine accurately this length of time. As would be expected, there is a relation between the state of the column at the beginning of a run, the dispersed phase flow rate, and the minimum length of time necessary for steady state concentrations to be reached. (The continuous phase flow rate was not varied in this study but would also have an important bearing, of course)

As would have been supposed for the flow rates and the direction of mass transfer studied here, the higher the concentration inside the column at the beginning of a run, the longer is the time needed to achieve steady state. The time required, of course, depends on the dispersed phase flow rate when the continuous phase flow rate is kept constant as summarized in Figure 8 given earlier.

There are two factors which influenced this time to reach steady state. The first one is the initial concentration prevailing inside the column mentioned above. A reduction of approximately 20 minutes in the time to reach steady state at a dispersed phase flow rate of $72.5 \text{ ft}^3/\text{hr.}-\text{ft}^2$ is achieved when the column has been operated before so that low concentrations exist to begin with in the continuous phase. This time reduction is reduced linearly as the dispersed phase flow rate is increased and finally reaches a reduction of two to three minutes as flooding is approached. These results all are for a constant

continuous phase flow rate of $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$. The second factor was the precision of level control at the interface achieved by the interface controller. The length of time to reach steady state is very long when the column as started contains only continuous phase feed solution, perhaps partly because the interface takes between thirty to forty minutes to stabilize at a reasonable level. When the column has been used before, the interface is already at this reasonable level. This second factor was of operational nature and could be solved by the installation of an automatic level controller.

B) Effect of purging rate on the minimum purge time to achieve a uniform concentration in the probe samples:

As expected, the minimum purging time was reduced when the rate of purging was increased as shown in Figure 10 which gave the results obtained from the investigation of the minimum length of time needed to have a uniform concentration in each of the probe samples after relocation of the probes.

On the Figure 10 just mentioned, Choudhury's results were included. These are shown by means of dashed lines. The present study covered a wider range of rates: from 2 to 13 cc./min. for the water phase and from 2 to 16 cc./min. for the ketone phase. A purging rate of 2 cc./min was considered to be the minimum at which sampling could proceed because about 22 minutes purge time is needed even before collection of a sample can begin. The upper ends of the ranges were, respectively, a rate of 13 cc./min. for the water phase, and 16 cc./min. for the ketone phase. These rates were considered to be fairly high because at this time in the research, it was not known if high rates perhaps could influence the point concentration obtained and also disturb

the steady state. After the studies of the rate of sampling versus the point concentration, and of steady state disturbance, it was proved that the rates, just mentioned, were sufficiently high for the purpose of determining concentration profiles.

The present results are similar to those of Choudhury for the continuous phase, but more complete. The present dispersed phase results in Figure 10 are low compared to those of Choudhury. Choudhury's high values for the dispersed phase minimum purge time were probably due to different tube lengths in the sampling lines from those used here. The curves of Figure 10 were used in the present work. For safety, two or three minutes ordinarily were added to the indicated minimum purge time as mentioned earlier. Sometimes by design when feed solution supplies were low, or sometimes inadvertently, this extra amount of time was not always included. However, the purge time was never less than the minimum recommended in Figure 10 except for special cases where the sampling rate was varied to see its influence on the point concentration.

C) Influence of sampling rate on steady state:

The data of Figures 20 and 21, showed that sampling rates from 0.3 to 8.75%* of the dispersed phase flow of 72.8 ft.³/hr.-ft.² and from 0.9 to 4.5%** of the continuous phase flow of 54.8 ft.³/hr.-ft.², caused no real variation of outlet concentration; and therefore no real effect on the steady state.

For most samples the sampling time used was 10 minutes, and, following this, 20 minutes usually was allowed to elapse before beginning to take the next sample. During the ten minutes sampling period the volume of ketone phase in the Elgin head (2.5.-in. of ketone

* 0.3% = 1.1 cc./min. and 8.75% = 28.2 cc./min.

** 0.9% = 2.9 cc./min. and 4.50% = 14.2 cc./min.

in a 6.-in. I.D. cylinder) would be replaced four times, and any changes in outlet concentration (caused by sampling the ketone phase at a given rate) therefore should have shown up, if not in the 10 minutes sampling period, then near the beginning of the time between samples. For the water phase a time of 6.7 minutes is needed to sweep out by piston flow the volume of continuous phase in the column from the level of the probe down to the column bottom plus that in 10 ft. of 3/8.-in. tubing and in the interface controller. The amount in the column was calculated as the volume of the whole empty column below the probe including that of the expanded portion, minus the volume of the nozzle for dispersing ketone, and minus the volumes occupied by the drops. For the flow rates used in Runs 7E and 7F, Choudhury (10) has shown that the value of the driving force factor for back-mixing, F_M (10), is about 0.9, so that, under the conditions of these Runs, back-mixing is not very serious. Therefore during the time of 10 minutes used for sampling, or near the beginning of the period following, before the next sample was taken, any change in concentration caused by sampling would be expected to show up in the analysis of the water leaving the column.

In Runs 7E and 7F the concentration of a water phase in equilibrium with the leaving ketone phase was about 5% different in concentration from the actual entering water phase. Had the phases at the top of the column been in equilibrium little change might have been expected in the outlet ketone concentration as a result of removing samples of the phases within the column.

The small disturbances of the steady state found in the study seem to be caused by the interface controller. The concentrations vary 3 to 4% due to an interface change of 1.-in. This statement is made on the basis of the steady state study, shown in Tables 11 and 12, where

the steady state is not reached if the interface varies by that much. Then smaller interface changes can produce the concentration variations found as part of the work described in the present section. As mentioned earlier, an automatic device should be installed to regulate the interface level and hold it at a fixed distance from the nozzle tips.

It is interesting to remark here that the steady state concentrations can not be disturbed due to the amount of liquid taken out by both probes in Runs 7E and 7F if purging and sampling rate of 14.2 cc./min. is not exceeded for the water phase and 28.2 cc./min. for the dispersed phase. It is to be understood that these sampling rates are conditioned by the phase flow rates, and, as just mentioned only one was investigated for each phase.

The sampling rate of 14.2 and 28.2 cc./min. are safe for these flows. Higher sampling rates than 28 cc./min for the dispersed phase and 14.2 cc./min. for the continuous phase might well have produced noticeable disturbance of steady state conditions. Indeed, increasing either sampling rate indefinitely would be bound to produce this effect at some sampling rate, and beyond this limit the effect on steady state would, of course, be more and more evident. The present results did not extend to values as high as some of those used in studying the influence of the sampling rates on the point concentrations. However, the high sampling rates used to study if the point concentrations vary with the sampling rate, were applied only for that study. These rates were not and should not be used in normal runs because of possible influences on the steady state.

Nevertheless, the present results do show that the steady state condition would not be disturbed by the sampling rates used by the present author in determining concentration profiles in the column, and

in studying the piston method of sampling, in both of which the rates of 14.2 cc./min for the water phase, and that of 28.2 cc./min. for the ketone phase, were not exceeded, or, indeed, approached even closely, in the case of the ketone phase. The present results suggest also that the sampling rates used by Choudhury (10) would have no effect on the steady state in almost all of his runs.

D) Drop coalescence at the dispersed phase probe entrance:

When the column was in full operation the sampling process was carried out using several rates. At the time of sampling, the drops entering the bell-shaped probe were observed carefully. Three modes of behavior can be observed depending on the rate of sampling.

First of all, if the sampling process is not going on, an interface exists at the end of the probe. When the sampling rate is low, drops gather at the entrance and come into the probe slowly. Sometimes two or three drops were pushed out of the way by the drops travelling upward into the probe. However, no coalescence was ever observed during operation of the probe. When the sampling rate is increased, the drops come directly into the dispersed phase probe without touching each other, and without stopping at the probe entrance. This observation was made in answer to Hawrelak's statement (12) that the residence time of ketone drops at the ketone probe entrance is too long. Hawrelak also said that an interface was "sometimes" created there. Figure 29 shows the results of the present study of the behaviour of drops at the ketone probe entrance and shows what really happens there. Never, during purging or sampling was an interface observed. The statement of Hawrelak is not believed by the present worker. Hawrelak apparently did not have detailed information on which

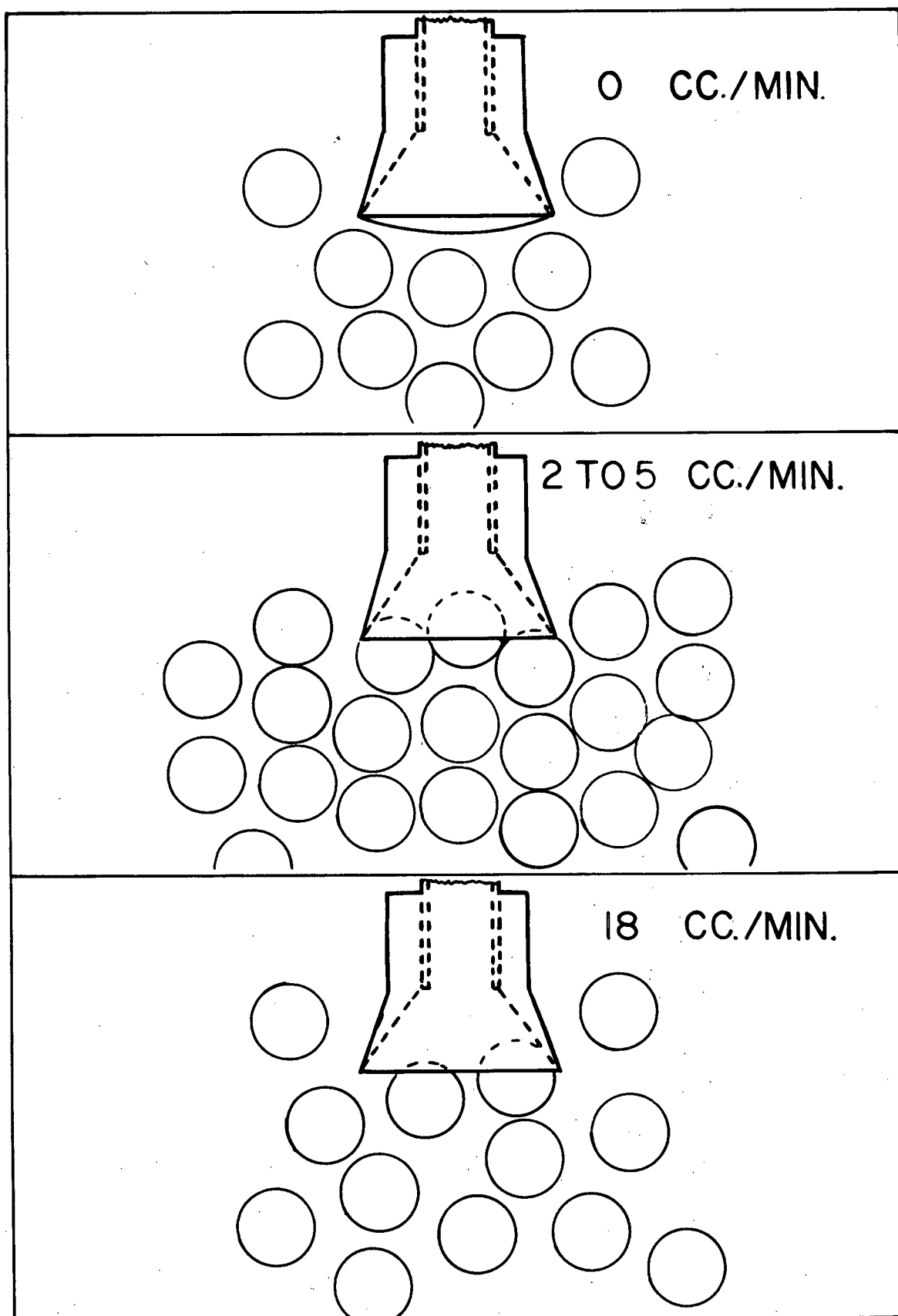


FIGURE 29. Behaviour of the drops at ketone probe entrance at various sampling rates.

to base his statement. Thus he does not say for what conditions an interface was created at the ketone probe entrance. In the present work, observations were made also at much faster rates and consequently over a bigger range of rates than those used by Hawrelak; absolutely no change from the behaviour sketched in Figure 29 occurred at the ketone probe entrance. The difficulty of the residence time being too long, mentioned by Hawrelak, may be something of a problem for the lower rate cases as Figure 29 implies. This problem arises as a result of the accumulation of drops. But drops accumulate only at very low sampling rates i.e. from 2.0 cc./min. up to 5.0 cc./min.; for the range between 5.0 cc./min. and 18 cc./min. a clearing up of accumulated drops is observed and the situation is intermediate between that of the second sketch in Figure 29 and the third sketch (which represents a sampling rate beyond the normal operation). In other words, the residence time of a drop at the ketone probe entrance is not a serious problem as long as the rate is kept above 5.0 cc./min.. As mentioned later, an upper value perhaps would be needed to avoid the problem of false point concentrations due to other liquid coming from above or under the sampling position should this happen. This particular matter will be discussed later.

E) The effect of sampling rate on measured point concentrations:

The effect was studied of changing each of the probe sampling rates on the premise that, if changing either sampling rate produced a change in the corresponding measured concentration, then the results with the corresponding probe would be suspect. (The absence of such a change would not, however, of itself prove that the respective probe was producing the correct result for certain.) Thus such experiments with

the continuous phase probe would result in an apparent decrease in concentration as the sampling rate increased if by increasing the sampling rate the regions near drops made up a larger percentage of the sample. In the case of the dispersed phase probe, increasing the sampling rate would have been expected to lower the concentration if coalescence at the probe mouth had been taking place at low sampling rates with a corresponding mass transfer into the drops during coalescence. (However, coalescence is not observed.) If increasing the dispersed phase sampling rate resulted in continuous phase distant from the drops making a larger contribution to the continuous phase taken into the dispersed phase probe along with the drops, then increasing the dispersed phase sampling rate would have been expected to produce a larger volume of higher average concentration aqueous phase as part of the dispersed phase sample. In the equation used for calculating C_{ki} ,

$$C_{ki} = C_{kf} - \frac{V_w}{V_k} (C_{wi} - C_{wf})$$

the term C_{kf} would have been larger, the factor $(C_{wi} - C_{wf})$ would have been smaller (since C_{wi} , given by the continuous phase probe, presumably would have stayed constant), and the factor V_w/V_k would have been larger. Depending on the relative magnitude of the effects of the changes in these two factors some change in C_{ki} , either up or down, would be expected as a result of the combination of their product with the increased C_{kf} . Partial answers to the questions posed above are given by the results obtained by varying the sampling rates and observing the effects on the measured point concentrations.

Looking at the results presented on this subject shows that little or no variation of concentration occurred even if the sampling

rates were as high as 28 cc./min for the dispersed phase probe and 34 cc./min. for the continuous phase probe.

One interesting aspect of the behaviour of the ketone probe was that, as predicted earlier, the volume percent of ketone contained in a ketone sample (probe) decreases as the sampling rate increases. This effect does not present too serious a problem with the ketone probe rates used in this work, because the volume percent ketone in the ketone sample was always above 90.0% except for some higher rates of sampling where the volume percent ketone was around 85.0% of the ketone sample. The important point is that when the volume percent of ketone is this high, the correction for mass transfer after sampling is only small, and whether the water sample is representative is of comparatively small importance.

As indicated in Table 4 and as discussed later, the dispersed phase concentrations obtained with the piston deviate from the average of the probe and piston results within better than ± 1 per cent for two results obtained, one in each of the Runs 9F and 9G, which Runs were not close to equilibrium conditions. (Runs 9H and 9I were fairly close to equilibrium, 9I more so than 9H.) The other nine results for these two Runs show deviations from the average of up to $\pm 14\%$; however, four results in addition to the two already mentioned exhibit markedly better agreement than this. (The arithmetic average of the percentage deviation is calculated to be -1.24% for Runs 9E, 9F and 9G. If 9H is included also the result is -1.31% .) These results do not prove definitively that the piston results check the probe ones, but they do indicate that such agreement is fairly probable.

If this agreement is assumed for the moment, and if it is recalled that in the probe samples the volume percent water is very low,

so that the problem of whether the water sample is representative is not too important, then agreement between results from the probe, and results from the piston, where the volume percent water is very much higher, does seem to indicate that the water probe gives samples which are representative of the water part of the piston sample.

Furthermore, and as a separate argument, if the results for the piston and for the probe agree with one another, the inference is very strong that the continuous phase probe gives water concentrations which are representative for use in the calculation of $(C_{ki})_{\text{probe}}$. After all, the hook probe preferentially samples the main body of the continuous phase. The values of C_{wi} so obtained would seem to be more appropriate for use with the piston samples, where ketone holdup is low, than with the probe samples, where ketone holdup is high, and where the water phase probably is derived on the average from nearer the drops. Agreement between $(C_{ki})_{\text{probe}}$ and $(C_{ki})_{\text{piston}}$, when the same C_{wi} is used in evaluating each of these, indicates that the region close to the drops does not contribute sufficient solute to the water part of the probe sample to make C_{wi} inappropriate for use in getting $(C_{ki})_{\text{probe}}$.

One should realize that with coalescence at the probe entrance not a problem, the comparison of a piston sample and probe sample where the ketone holdups were the same in each would produce little or no confirmation of either sampling method.

Here it is convenient to mention that the drops are of different sizes and therefore do not all rise at the same rate. Therefore, at any elevation in the column, the concentration of a drop should depend on its size. Fortunately the small drops are only a small percentage of the dispersed phase (13) and the large drops are in a fairly small size range (13), all rising at nearly the same speed.

F) Duplication of Runs:

Figure 23 represents schematically what the author would like to call good reproduction of Choudhury's results considering that feed concentrations are always a bit hard to copy, and reproducibility is rarely perfect when mass transfer is the subject treated.

As mentioned earlier, the duplication appeared to be much better after the small errors of a pipette delivering wrong volume and of evaporation taking place from the contents of the ketone feed tank, had been corrected. Thus, for Run 8, which is most nearly comparable with Choudhury's Run 65, the average deviation of the results from those of Choudhury was 1.6% for the continuous phase concentrations, and 2.2% for the dispersed phase concentrations. (These deviations are given without regard to sign.) Table 6 records the point concentrations obtained in Run 8 and also those of Choudhury. Also included are the deviation and the percent deviation of the results of Run 8 from Choudhury's Run 65, at various distances from the nozzle tips.

G) Concentration study in the Elgin head:

The results obtained in the brief survey of the concentrations in the Elgin head showed that the concentration of the water phase changed from the value applicable at the point of entry of the water phase into the column, to a lower value, before this phase reached the interface or entered the column proper. However, it should be noted that Choudhury (10), and also Ewanchyna (11), assumed that the water entered at its inlet concentration at the interface and that this concentration changed over almost zero height of column to some lower value. These workers also assumed that no further rise in ketone concentration occurred above the interface. Both assumptions are not

TABLE 6

Concentrations in both phases (smoothed values) for Run 8 of this work and Run 65 of Choudhury.

Phase.		Concentration of acetic acid in the phase, lb.-moles/ft. ³ x 10 ³ at distance from nozzle tips (ft.)											Height of column. ft.
		0.0	0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	Inlet	
Run 8	Water	25.93	26.30	28.20	30.80	36.30	40.50	43.50	45.80	47.40	49.00	50.40	7.383
Choudhury Run 65	Water	26.30	27.00	29.60	32.50	36.90	40.40	43.60	46.20	47.70	49.10	50.40	7.383
Deviation of Run 8 from Run 65		-0.37	-0.70	-1.40	-1.70	-0.60	+0.10	-0.10	-0.40	-0.30	-0.10	0.00	
% deviation		1.4	2.6	4.7	5.2	1.6	0.2	0.2	0.9	0.6	0.2	0.0	
Run 8	Ketone	6.75	7.20	9.00	11.10	15.25	17.80	20.50	22.20	23.40	24.30	<u>Outlet</u> 24.96	7.383
Choudhury Run 65	Ketone	6.50	7.10	9.30	11.40	15.00	17.80	19.90	21.60	22.90	24.00	24.30	7.383
Deviation of Run 8 from Run 65		+0.25	+0.10	-0.30	+0.30	+0.25	0.0	+0.60	+0.60	+0.50	+0.30	+0.66	
% deviation		3.5	1.4	3.2	2.6	1.7	0.0	3.0	2.8	2.2	1.3	2.7	

in accord with the present experimental results. In fact, the concentration of the ketone phase appears to decrease above the interface. It appears that both assumptions used by the previous investigators are over-simplifications.

H) Piston results:

1.- Effect of a piston sample on the steady state:

The first operation done with the piston consisted of finding the steady state requirements: mainly the influence of a piston sample on the outlet concentrations. In Figures 25, 26, it can be seen that a piston sample disturbs the steady state for at least 15 minutes if distilled water is used as a liquid for replacing the column liquid taken out by the sampler. Figure 27 shows that little or no disturbances exist when outlet continuous phase is used instead of distilled water. The first test was done to learn the maximum deviation from the steady state likely to be encountered, that occurring when a solution of minimum concentration: distilled water, was put into the piston hole through which the column was not operating. In normal operation of the piston sampling device, the filling up of this piston hole with outlet continuous phase gives a maximum deviation of less than 1% in the exit concentration of the continuous phase and of zero in that of the dispersed phase. With the use of distilled water, the deviation was always 7% for the continuous phase and zero for the dispersed phase (except as already noted for one measurement shown on Figure 26). These deviations were obtained using a continuous phase flow rate of $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$ and a dispersed phase flow rate of $120.5 \text{ ft}^3/\text{hr.}-\text{ft}^2$.

Knowing the effect of a piston sample on the steady state permits one to operate the sampler only when steady state has been

restored after the taking of any preceding sample.

2.- Comparison of piston and probe dispersed phase samples:

Runs 9F, 9F, 9G, 9H and 9I were made with the purpose of getting comparisons between C_{ki} given by the piston and C_{ki} given by the probe. Table 4 shows the results obtained in these Runs. The author would like to mention here that these Runs were made at various dispersed phase flow rates with a view to having a holdup of dispersed phase which increased in a stepwise fashion as runs progressed. The same continuous phase flow rate of $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$ was used for all the runs in Table 4.

But, unfortunately, and as learned later, the last Run, 9I was performed with the solutions near equilibrium conditions in the column at the axis of the piston. Due to this fact, the five results of Run 9I, have not been considered in this discussion. The fact that the flow rate of the dispersed phase was always increased caused the mass transfer resistance in the column to be lowered as a result of the increased interfacial area. The lowered resistance created the equilibrium conditions mentioned above. In the Run preceding 9I, Run 9H, conditions also were not as far from equilibrium as might be desirable.

Run 9I perhaps was close to flooding conditions. According to Sherwood and Pigford (17) (P. 442 Figure 212, curve B) the flooding velocity for the dispersed phase should be roughly $245.0 \text{ ft}^3/\text{hr.}-\text{ft}^2$ for a continuous phase velocity of $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$. The highest dispersed phase flow rate used in this work was $208.3 \text{ ft}^3/\text{hr.}-\text{ft}^2$.

The increase of the holdup, as mentioned earlier, was supposed to make the difference $(C_{wi} - C_{wf})$ bigger. The following example explains why this procedure was adopted.

Suppose two samples are taken with the piston sampler, but

with different ketone flow rates to the column so that the holdups in the column (and in the corresponding sample) are different. Suppose also that the feed concentrations to the column are adjusted so that in both runs the values of C_{ki} and C_{wi} at the sampler location are the same. (Such adjustments were not carried out in the present experiments with the result that in Table 4, C_{ki} , and in Table 5, C_{wi} , are seen to decrease as the holdup increases.) Suppose that the two phases of the piston are allowed to come to equilibrium and are then analyzed. As mentioned earlier, Equation 5 is used,

$$C_{ki} = C_{kf} - \frac{V_w}{V_k} (C_{wi} - C_{wf}) \quad 5$$

Now suppose that of the two samples, numbered one and two respectively, sample 1 has the lower ketone holdup. Hence

$$\begin{aligned} V_{w2} &< V_{w1} \\ V_{k2} &> V_{k1} \end{aligned}$$

and

$$\left(\frac{V_w}{V_k} \right)_2 < \left(\frac{V_w}{V_k} \right)_1$$

The situation is as shown in Figure-29A. For the experiments of this work transfer is out of the water and into the ketone phase. Hence

$$\begin{aligned} C_{wi} &> C_{wf} \\ C_{ki} &< C_{kf} \end{aligned}$$

Now at equilibrium:

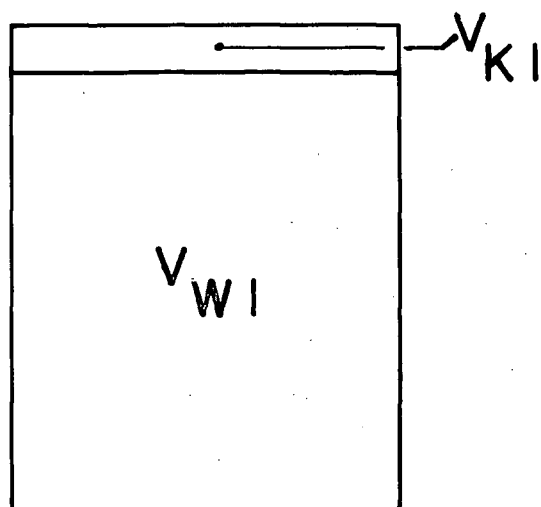
$$C_{wf} \doteq 2C_{kf}$$

Hence

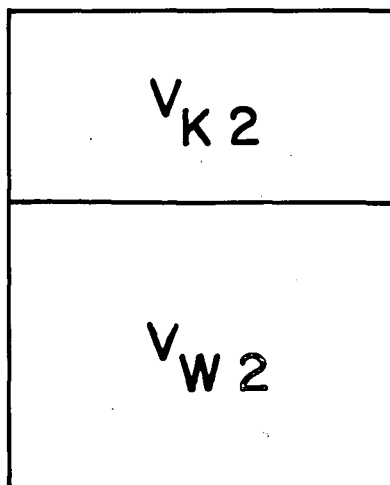
$$C_{wi} > C_{ki}$$

Furthermore, recall that:

$$(C_{wi})_1 = (C_{wi})_2$$



SAMPLE 1



SAMPLE 2

FIGURE 29A. Two piston samples having different holdup.

and

$$(C_{ki})_1 = (C_{ki})_2$$

Considering the relative volumes of water and ketone in samples 1 and 2 shows that there is more total solute available in sample 1 than in sample 2, and, therefore,

$$(C_{wf})_1 > (C_{wf})_2$$

Then

$$(C_{wi} - C_{wf})_1 < (C_{wi} - C_{wf})_2$$

and analysis is less critical for sample 2 where the difference is greater.

Compare now two further runs, one at low holdup and one at high holdup for which the feed concentrations to the column are manipulated so that when the holdup is increased the difference $(C_{wi} - C_{wf})$ is maintained constant. For these two runs, it is evident that the correction term

$$\frac{V_w}{V_k} (C_{wi} - C_{wf})$$

in Equation 5 becomes less important at the higher holdup because $\frac{V_w}{V_k}$ is lower.

As mentioned before the situation as between samples in the present work is not as simple as in either of the two illustrations just discussed. Thus in increasing the holdup, C_{wi} and C_{ki} both decreased and so did their difference. This point will be considered again following a look at the effect on the results of when the analysis is done: before the phases of the piston sample have reached equilibrium, or after they have done so.

Although the piston samples were analyzed at equilibrium as

assumed in the discussion of the last paragraph, the accuracy is not affected if analysis is done before this condition is reached. Suppose that the phases of the piston sample can be separated very quickly, just after the sample has been taken. Then C_{wi} and C_{wf} will be practically identical, and even though the difference ($C_{wi} - C_{wf}$) can be determined only very inaccurately the value of C_{ki} will be known quite accurately, because there is almost no correction to be applied to C_{kf} in determining C_{ki} from it. (Refer to Equation 5.) On the other hand, if equilibrium is reached before the phases are separated and analyzed, ($C_{wi} - C_{wf}$) will be larger, and much more accurately known, as it will have to be in order that the comparatively large correction which is now necessary can be applied to C_{kf} , and an accurate C_{ki} obtained. For intermediate cases where equilibrium has not been reached, but separation of the phases has taken place some time after sampling, the correction will be obtainable with only intermediate accuracy. However, since the correction will be of only intermediate size, such accuracy is appropriate. Evidently, then, and as one would have instinctively assumed, whether or not equilibrium is reached between the phases of the piston sample before they are separated should not affect the accuracy of the final value desired: C_{ki} . But what of the effect of increasing the holdup in the series of piston runs? When one examines the difference ($C_{wi} - C_{wf}$), obtainable from Tables 4 and 5, it becomes apparent that as the holdup increased this difference remained of the same order of magnitude. This result is due to the lower levels of concentrations C_{wi} and C_{ki} mentioned earlier, which correspond in these experiments to the phases in the column being closer to equilibrium than they were at lower holdup. In fact, the phases were almost at equilibrium in the column at the piston location for Run 9I.

The idea of increasing the holdup to decrease the effect of small errors in analysis on the final values of C_{ki} was seized on with enthusiasm but without allowing for other results of increasing the holdup, in particular that whereby the phases come more nearly to equilibrium at the piston location in use. Thus, as the holdup is increasing the mass transfer resistance is decreasing and finally one gets equilibrium conditions in the lower region of the column. (Most of the extraction of acid from the water took place in the upper part of the column as noted earlier.) The present work teaches that as ketone holdup is increased, arrangements must be made to feed the water phase at a concentration high enough so that the phases are not in equilibrium at the sampler location. An alternative would be to move the sampler toward the top of the column. The concentration profiles in the axial direction of the column are not known for the high holdup runs of the present work, and therefore the conditions of the phases with respect to equilibrium toward the top of the column are not known in any detail. However, the water entering the column was not near equilibrium with the ketone leaving the column for Run 9I.

Referring to Table 4, which gives the results obtained with both methods of sampling the dispersed phase: piston and probe, it can be seen that the probe figures and the piston figures are very different indeed in five cases. In these results, the percent deviation, as defined in connection with Table 4, exceeded 10%. But, the arithmetic average deviation of the results for Runs 9E, 9F, 9G and 9H is calculated to be -1.31%. Also, if the dispersed phase concentration at time of analysis, $(C_{kf})_{\text{piston}}$, is observed, it is seen that these results of each Run are in reasonable agreement. The difference between $(C_{ki})_{\text{probe}}$ and $(C_{ki})_{\text{piston}}$ appearing in Table 4 probably are due to

three major errors caused by the manipulations associated with the analyses, as shown in Appendix VIII. An error of 21.3% can be obtained if the errors are supposed to be cumulative. This result explains why some values of the dispersed phase concentrations obtained with both methods are so different.

None of the new values of (C_{ki}) determined with the piston are comparable with those obtained by Hawrelak, because different flow rates were employed by each worker. However, it is possible to compare Hawrelak's deviations and the deviations obtained in this work. The values under ten percent deviation in this work are comparatively numerous (10 out of 15 values if only Run 9I is excluded, or 6 out of 11 values if both of Runs 9H and 9I are excluded). Hawrelak had only 3 values out of 20 in this range of from zero to 10% deviation. Another interesting remark concerning Hawrelak's results as shown in his thesis page 65, is that as many as 6 piston results are compared with a single probe result. In other words, Hawrelak unfortunately did not take a probe sample each time he took a piston sample. (He even uses a probe sample from one run with a piston sample from another run done on a different day.) An examination of his data books confirms these remarks. He was of course operating on the assumptions that he was able to maintain true steady state, that he could reproduce his profiles very accurately, and that he could take probe samples very reproducibly.

However, Hawrelak's Run 84, performed using a water flow rate of 90.0 ft.³/hr.-ft.², and a ketone flow rate of 90.5 ft.³/hr.-ft.², to give a volume percent ketone of 11.6, shows that the average difference ($C_{wi} - C_{wf}$), 1.0 lb.-moles/ft.³ × 10³, was bigger in this run than in his other runs. This average difference is also bigger than those of the

* Should be halved for comparison with the figures of Table 4.

present work. However, the percentage deviation of his piston results from the average of his probe and piston results is generally higher for Run 84 than for his other Runs, (except for Run 79) and also generally higher than the present deviations. (None of Hawrelak's values are below 10% in Run 84.) This is another indication that the difference ($C_{wi} - C_{wf}$) must be made higher (by increasing the inlet concentration of the water phase), but that also the volume ratio, V_w/V_k , in Equation 5 must be smaller.

Considering the present results, the author believes that the check between the two methods of sampling has been put on the right track. It is now known that the difference between C_{wi} and C_{wf} must be increased by increasing the column feed water concentration. Then at high holdups agreement between the two methods of sampling could be expected assuming that the uncertainties of the analysis can be overcome.

SUMMARY

The following statements can be made based on the measurements described in this thesis:

- 1.- A relation was found between the dispersed phase flow rate and the time to reach the steady state. This was done for an average continuous phase flow rate of $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$. The time depended on the initial concentration level inside the column and on whether an interface with ketone above it existed in the Elgin head.
- 2.- A calibration was done to get the relation between the purging rate and the minimum purging time required to change the solution present in the sampling probes.
- 3.- No coalescence can be seen at the dispersed phase probe entrance. Such coalescence takes place only when not sampling.
- 4.- The steady state seems to be influenced more by the interface controller than by the sampling rate used with the probes. No real effect of sampling on the steady state was found for sampling rates up to 8.8% of a dispersed phase flow of $72.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$ and 4.4% of a continuous phase flow rate of $54.8 \text{ ft}^3/\text{hr.}-\text{ft}^2$. (These sampling rates in cc./min. were 28.2 and 14.2 respectively.)
- 5.- The point concentration of either phase as measured by the respective probe did not vary with sampling rate even if rates as high as 34 cc./min. for the water probe and 28.4 cc./min. for the ketone probe were reached.
- 6.- Choudhury's Run 65 was duplicated within 2.2% (average deviation) for the dispersed phase concentrations and 1.6% (average deviation) for the continuous phase concentrations. It should be pointed out that the inlet concentrations were always as close as possible to those of Choudhury, but not exactly the same.
- 7.- The dispersed phase initial concentrations obtained by the piston

method verify those obtained by means of the probes within 2% deviation for three samples (not including Run 9I) and within 10% deviation for ten other results out of fifteen. A final check of the probe sampler by the piston sampler has not been obtained. However, much closer agreement has been demonstrated in the present work than had appeared in the earlier investigation. If a large difference between C_{wi} and C_{ki} can be obtained at the same time as a high holdup of ketone then a check of $(C_{ki})_{\text{piston}}$ and $(C_{ki})_{\text{probe}}$ is expected. But the holdup should not be as high as in the probe sample then, as noted earlier, the methods become identical.

RECOMMENDATIONS

After having worked for almost two years with the apparatus described previously, it can be recommended that an automatic level controller for the interface would result in a great improvement of the operation. Installation of a stripping column would permit work with the spray column to be carried out on a more regular basis. The lengthy back-washing procedure could be carried out while data were being obtained. As far as the apparatus is concerned, these two suggestions would facilitate the research work considerably.

Concerning the theoretical aspect of the research, more study with the piston is needed. A study could be made by varying the continuous phase concentration and flow rate, so that the phases are not in equilibrium at the location of the sampler even if the dispersed phase flow rate is also high. In the light of the previous suggestions, an attempt to increase the holdup of the column would be welcome, in order to get more and more volume percent ketone in a piston sample. However, to do this, new dispersed phase pump would be needed because the maximum capacity of the present pump was reached in Run 9I. It should be borne in mind, however, that the column may have been operating close to the flooding condition in that run, and much higher holdups may not be possible.

Along with these suggestions, a recommendation is made that in measuring the volumes of the phases of the piston samples the procedure of pouring from a flask into a graduate be changed back to the method of Hawrelak, where the phases of each piston sample were collected directly in a graduated flask. Such flasks should be graduated over a larger range than were those of Hawrelak. The larger range is necessary to provide for higher holdups than those encountered

by him. The graduated portion should extend from 0 to 40 ml.

About the analysis technique, it is also recommended that a bigger pipette should be used for purpose of getting the least possible error due to measurement of the volume of the samples.

NOMENCLATURE

Except where noted otherwise, the following nomenclature was used throughout the Thesis:

Symbols

A	Cross-sectionnal area of column, ft^2 .
a	Interfacial area per unit volume of extraction column, ft^2/ft^3 .
C*	Phase solute concentration which could be in equilibrium with the concentration of the other phase, $\text{lb.-moles}/\text{ft}^3 \times 10^3$.
C	Solute concentration, $\text{lb.-moles}/\text{ft}^3 \times 10^3$.
C _{ki}	Initial concentration of solute in ketone phase during internal sampling, $\text{lb.-moles}/\text{ft}^3 \times 10^3$.
C _{kf}	Concentration of solute in ketone phase of ketone sample as measured at time of analysis, $\text{lb.-moles}/\text{ft}^3 \times 10^3$.
C _{wi}	Initial concentration of solute in water phase during internal sampling, $\text{lb.-moles}/\text{ft}^3 \times 10^3$.
C _{wf}	Concentration of solute in water phase of ketone sample as measured at time of analysis, $\text{lb.-moles}/\text{ft}^3 \times 10^3$.
h	Effective height of extraction section of column, ft.. (measured from nozzle tips to interface.)
K	Over-all mass transfer coefficient, $\frac{\text{lb.-moles}}{(\text{hr.})(\text{ft}^2)(\text{lb.-moles}/\text{ft}^3)}$
Ka	Over-all extraction capacity coefficient, hr^{-1} .
L	Phase flow rate, $\text{ft}^3/\text{hr.-ft}^2$.
N	Amount of solute transferred based on inlet and outlet concentrations, $\text{lb.-moles}/\text{hr.}$.
N/A	Not applicable.
N _{ox}	Number of over-all transfer units based on x phase.
V _k	Volume of ketone phase in the ketone sample, cc.
V _w	Volume of water phase in the ketone sample, cc.

\int	Integral sign.
d	Differential sign.

Subscripts

1	Inlet.
2	Outlet.
k	Ketone phase.
w	Water phase.
c	Continuous phase.
d	Dispersed phase.
M	Measured.
x	Phase x.
i	Initial.
f	Final.
t	Toluene.

Superscript

*	Equilibrium value.
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A P P E N D I C E S

I to VIII

APPENDIX I

Rotameters Calibrations.

The rotameters used throughout this work were calibrated after the cleaning and re-assembly of the apparatus at the beginning of the research. The continuous phase rotameter was calibrated using distilled water (saturated with M.I.B.K.) and containing $50.2 \text{ lb.-moles/ft.}^3 \times 10^3$ of acetic acid. For the dispersed phase rotameter, M.I.B.K. (saturated with distilled water) and containing $6.54 \text{ lb.-moles/ft.}^3 \times 10^3$ of acetic acid was used. Both calibrations were carried out at room temperature. The results are given in Table 7 and plotted on Figure 30.

Since the smallest divisions of the scales of the rotameters just mentioned were one quarter of the next largest divisions, it became obvious that a change of scale to cm. and mm. divisions would improve the precision of the readings since then the decimal system could be used directly; in addition, the smallest divisions of the scale would be smaller in actual magnitude than previously. A second calibration was done and the results are shown in Table 8 and plotted on Figure 31.

TABLE 7

Rotameter Calibrations.

Water Rotameter. Serial number 14143.

Room and liquid temperature: 72.5°F

Liquid: distilled water saturated with

M.I.B.K. and containing $50.2 \text{ lb.-moles/ft.}^3 \times 10^3$
of acetic acid.

Rotameter Reading.	Rate of flow, $\text{ft.}^3/\text{hr.}$
0.02	0.1615
0.04	0.3415
0.06	0.5080
0.08	0.6675
0.10	0.8315
0.12	0.9915
0.14	1.1420

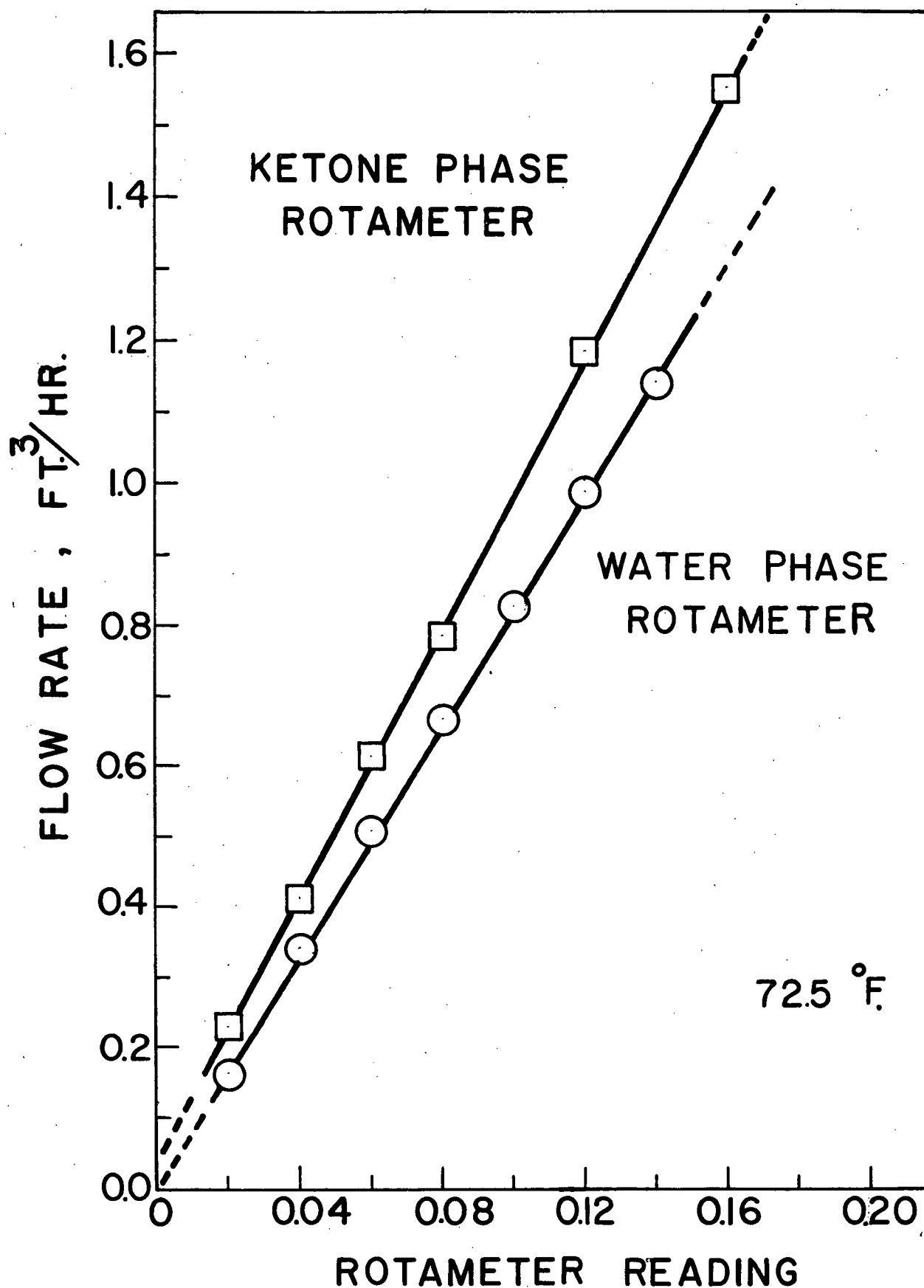


FIGURE 30. Rotameter Calibrations. Rotameter Serial No.: 14143.
No.: 14142.

Ketone Rotameter. Serial number 14142.

Room and liquid temperature: 72.5 °F

Liquid: M.I.B.K. saturated with distilled
water and containing 6.53 lb.-moles/
 $\text{ft}^3 \times 10^3$ of acetic acid.

Rotameter Reading.	Rate of flow, $\text{ft}^3/\text{hr.}$
0.02	0.2320
0.04	0.4150
0.06	0.6150
0.08	0.7850
0.12	1.1850
0.16	1.5510

TABLE 8

Rotameter Calibrations.

Water Rotameter. Serial number 14143.

Room and liquid temperature: 74 °F.

Liquid: distilled water saturated with M.I.B.K.
and containing 50.0 lb.-moles/ $\text{ft}^3 \times 10^3$
of acetic acid.

Rotameter Reading. mm.	Rate of flow, $\text{ft}^3/\text{hr.}$
25	0.0739
50	0.1680
75	0.2682
100	0.3885
125	0.5115
150	0.6273
175	0.7500
200	0.8840
225	1.0200

Ketone Rotameter. Serial number 14142.

Room and liquid temperature: 73 °F.

Liquid: M.I.B.K. saturated with distilled water
and containing 6.53 lb.-moles/ $\text{ft}^3 \times 10^3$
of acetic acid.

Rotameter Reading. (mm.)	Rate of flow, $\text{ft}^3/\text{hr.}$
50	0.2120
75	0.3830
100	0.5800
125	0.7860
150	1.0220
175	1.2780
200	1.5150
225	1.7980

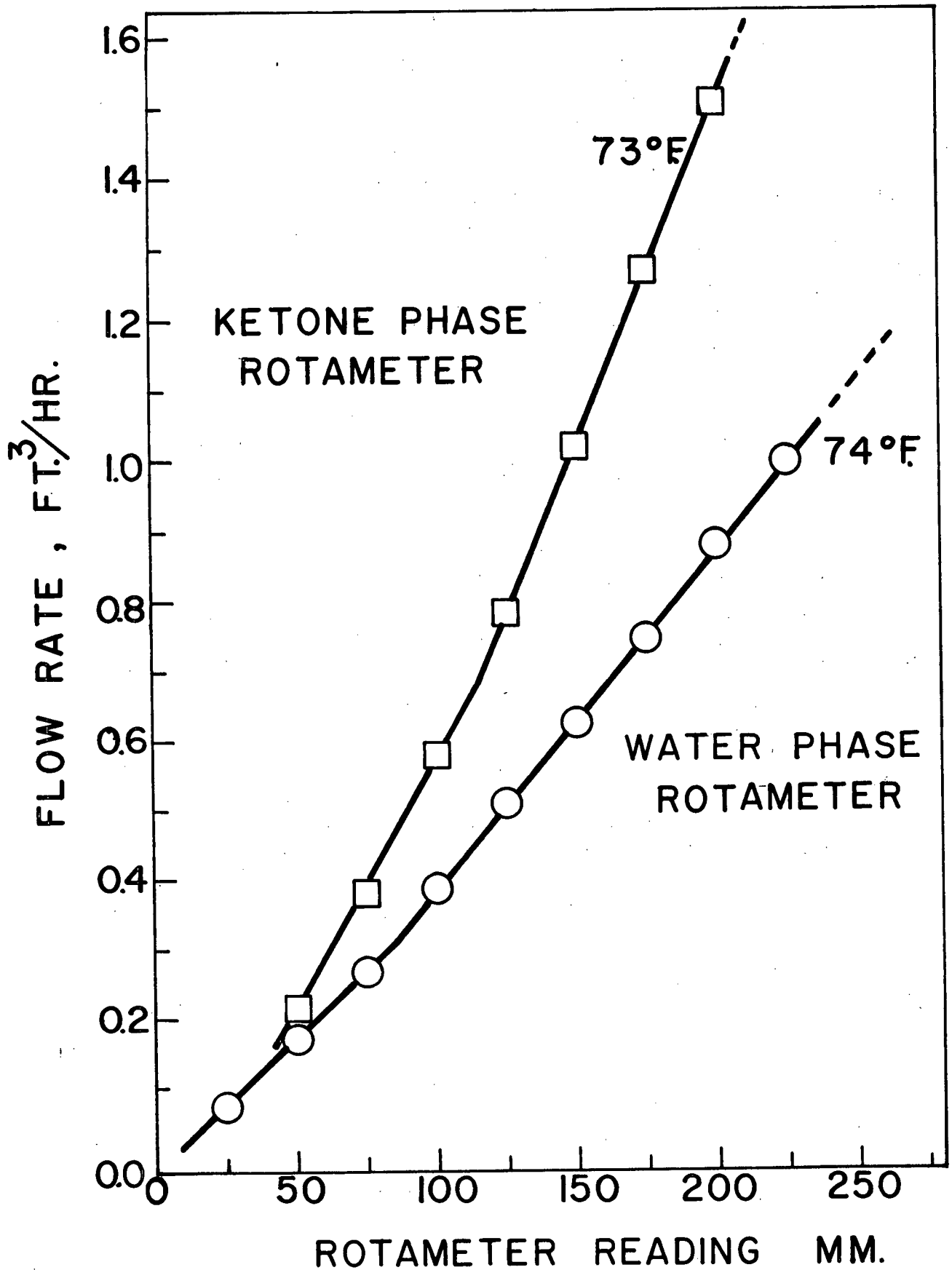


FIGURE 31. Rotameter Calibrations. Mm Scale.

APPENDIX II

Run data.

The following Tables (9 and 10) show the purpose of each of the runs and the over-all transfer data. All Runs done in the present work, which were used to produce the results reported in this thesis are listed here. Also included are the following characteristics which concerned the sampling probes: sampling rate for both phases, the sampling rate as a percentage of the phase flow rate, the purging time, and the temperature at which the run was performed. Also included in Table 10A are the data of Runs 5D and 8 f59m which the concentrations profiles were obtained.

TABLE 9.

Run number.	Purpose of Run.	Sampling rate, cc./min.		Sampling as % of phase flow rate.		Purging time. min.	Temp. °F. (ave.)
		Water phase.	Ketone phase.	Water phase.	Ketone phase.		
*1C	Sampling rate study	V	V	V	V	V	77
1D	Sampling rate study	V	V	V	V	V	78
*1E	Sampling rate study	V	V	V	V	V	78
*1F	Sampling rate study	V	V	V	V	V	77
1G	Sampling rate study	V	V	V	V	V	75
2	Sampling rate study	V	V	V	V	V	76
2A	Sampling rate study	V	V	V	V	V	74
2B	Sampling rate study	V	V	V	V	V	78
2C	Sampling rate study	V	V	V	V	V	78
2D	Sampling rate study	V	V	V	V	V	72
*3	Sampling rate study	V	V	V	V	V	74
*3A	Duplication of Run 65 of Choudhury	9.0	13.0	2.9	3.9	9.0	75
*3B	Duplication of Run 65 of Choudhury	9.0	13.0	2.3	3.3	9.0	75
*3C	Point concentration versus rate	V	V	V	V	V	74
4	Duplication of Run 66 of Choudhury	8.2	12.4	4.1	3.8	8.0	72
*5A	Reproduction of Run 3A	8.0	14.0	2.8	4.2	9.0	72
5B ₁	Duplication of Run 65 of Choudhury	9.3	13.8	3.2	4.2	9.0	76
5D	Duplication of Run 65 of Choudhury	8.9	14.3	3.0	4.3	9.0	76
*5E	Duplication of Run 65 of Choudhury	8.9	13.0	2.9	3.9	9.0	78
5F	Point concentration versus sampling rate	V	V	V	V	V	71
5G	Point concentration versus sampling rate	V	V	V	V	V	74
5H	Point concentration versus sampling rate	V	V	V	V	V	72
6I ₁	Steady state study	N/A	N/A	N/A	N/A	N/A	74
6J ₁	Steady state study	N/A	N/A	N/A	N/A	N/A	73
*6H	Steady state study	N/A	N/A	N/A	N/A	N/A	76
*6I ₂	Steady state study	N/A	N/A	N/A	N/A	N/A	73
*6G ₂	Steady state study	N/A	N/A	N/A	N/A	N/A	72
6K	Steady state study	N/A	N/A	N/A	N/A	N/A	69
6L	Steady state study	N/A	N/A	N/A	N/A	N/A	74
6M	Steady state study	N/A	N/A	N/A	N/A	N/A	73

* Runs which were not used in this thesis.

V = Varied.

N/A = Not applicable.

TABLE 9 Cont..

Run number.	Purpose of Run.	Sampling rate, cc./min.		Sampling as % of phase flow rate.		Purging time. min.	Temp. °F (ave.)
		Water	Ketone	Water	Ketone		
		phase.	phase.	phase.	phase.		
7	Sampling rate study	V	V	V	V	V	75
*7A	Sampling rate study	V	V	V	V	V	75
7B	Sampling rate study	V	V	V	V	V	74
7C	Sampling rate study	V	V	V	V	V	75
7D	Sampling rate study	V	V	V	V	V	72
7E	Steady state versus sampling rate	V	V	V	V	V	75
7F	Steady state versus sampling rate	V	V	V	V	V	75
8	Duplication of Run 65 of Choudhury	10.0	10.0	3.2	2.5	8.0	75
*8A	Point concentration versus sampling rate	7.1	V	2.3	V	10.0	76
*8B	Point concentration versus sampling rate	7.9	V	2.5	V	10.0	75
9A	Effect of a piston sample on steady state	N/A	N/A	N/A	N/A	N/A	76
9B	Effect of a piston sample on steady state	N/A	N/A	N/A	N/A	N/A	76
9C	Effect of a piston sample on steady state	N/A	N/A	N/A	N/A	N/A	76
9D	Effect of a piston sample on steady state	N/A	N/A	N/A	N/A	N/A	74
9E	Piston samples taken	12.0	13.0	3.8	2.3	10.0	76
9F	Piston samples taken	10.0	9.4	3.2	1.7	10.0	76
9G	Piston samples taken	9.6	8.8	3.0	1.6	10.0	75
9H	piston samples taken	6.2	8.2	1.9	1.1	10.0	77
9I	Piston samples taken	6.5	7.6	2.1	0.8	10.0	73

* Runs which were not used in this thesis.

V = Varied.

N/A = Not applicable.

TABLE 10

Over-all transfer data.

Run number	Concentrations, lb.-moles/ft ³ x 10 ³				Flow rates ft ³ /hr.-ft ²		Linear Velocity through the nozzle tips. ft/sec.	Over-all acetic acid transfer rates. lb.-moles/ ft ³ x 10 ³ .		Percent deviation
	Water phase.		Ketone phase.		Water.	Ketone.		N _w	N _k	
	C _{w1}	C _{w2}	C _{k1}	C _{k2}	L _w	L _k				
1C	50.2	26.2	6.3	24.9	55.8	68.7	0.338	16.4	15.7	4.2
1D	50.7	26.5	6.1	24.8	54.6	67.4	0.332	16.2	15.4	5.1
1E	53.7	28.9	6.7	26.3	54.6	67.4	0.332	16.6	16.2	2.4
1F	37.9	21.5	5.4	18.5	54.8	70.6	0.347	11.0	11.3	2.7
1G	39.8	22.5	5.8	17.3	54.1	65.9	0.324	11.5	10.9	5.4
2	37.6	20.4	5.0	18.4	54.6	68.6	0.335	11.5	11.3	1.8
2A	38.3	22.2	5.5	18.8	55.1	68.7	0.335	10.9	11.2	2.7
2B	39.4	20.5	5.2	19.0	54.6	72.7	0.357	12.6	12.3	2.4
2C	40.3	21.8	5.8	19.6	54.6	69.0	0.352	12.4	11.6	6.6
2D	39.5	19.9	4.9	19.1	52.9	71.7	0.352	12.7	12.5	1.6
3	39.7	21.3	5.7	19.3	52.9	71.8	0.353	11.9	12.0	0.8
3A	38.4	19.5	4.8	18.6	52.7	71.7	0.352	12.2	12.1	0.8
3B	38.4	19.5	4.9	18.8	52.4	72.7	0.357	12.2	12.4	1.6
3C	34.7	17.9	4.7	16.4	54.7	71.8	0.353	11.3	10.3	9.3
4	34.4	12.1	4.9	14.9	36.3	71.5	0.352	9.9	8.8	11.8
5A	50.6	25.0	6.6	25.0	52.7	72.7	0.357	16.5	16.4	0.6
5C	50.4	24.8	6.5	24.1	51.2	72.7	0.357	16.1	15.8	1.9
5D	51.6	24.9	6.5	24.5	51.1	71.7	0.352	16.7	15.8	5.5
5E	51.0	24.9	6.5	24.2	51.2	71.7	0.352	16.4	15.6	5.0
5F	51.1	25.6	6.5	24.5	52.9	72.7	0.357	16.5	16.0	3.1
5G	50.3	26.3	6.5	24.4	54.1	72.7	0.357	15.9	15.9	0.0
5H	51.4	25.6	6.4	24.6	52.9	71.7	0.352	16.7	16.0	4.3
6I ₁	49.9	24.4	6.5	24.6	54.9	72.9	0.358	17.1	16.2	5.4
6J ₁	49.9	25.7	6.6	24.8	54.9	73.6	0.362	16.3	16.4	0.6
6H	49.7	24.6	6.5	24.9	54.9	72.9	0.358	16.9	16.3	3.6
6I ₂	49.9	25.1	6.6	24.9	54.9	73.1	0.359	16.0	16.4	2.4
6G ₂	50.1	25.1	6.6	24.9	54.9	72.9	0.358	16.8	16.3	3.0
6K	50.3	25.1	6.8	25.1	54.9	72.9	0.358	16.9	16.4	3.0
6L	50.7	25.3	6.7	25.3	54.8	72.8	0.358	17.1	16.6	3.0

TABLE 10 Cont.

Over-all transfer data.

Run number	Concentrations, lb.-moles/ft ³ x 10 ³				Flow rates ft ³ /hr.-ft ²		Linear Velocity through the nozzle tips. ft./sec.	Over-all acetic acid transfer rates. lb.-moles/ ft ³ x 10 ³ .		Percent deviation
	Water phase.	Ketone phase.	Water.	Ketone.	L _w	L _k		N _w	N _k	
	C _{w1}	C _{w2}	C _{k1}	C _{k2}						$\frac{N_w - N_k}{N} \times 100$
6M	50.7	25.5	6.7	25.5	54.8	73.2	0.360	16.9	16.9	0.0
7	48.7	24.4	6.4	24.3	54.8	72.8	0.358	16.3	16.0	1.9
7A	49.7	24.8	6.9	24.6	54.8	72.8	0.358	16.7	15.8	5.5
7B	49.6	25.0	6.6	24.5	54.8	72.8	0.358	16.5	16.0	3.1
7C.	49.5	25.1	6.7	24.6	54.6	72.8	0.358	16.3	16.0	1.9
7D	50.7	25.9	7.0	25.3	54.8	72.8	0.358	16.6	16.3	1.8
7E	51.3	25.4	6.6	25.5	54.8	72.8	0.358	17.4	16.9	2.9
7F	51.9	25.8	7.0	25.8	54.8	72.8	0.358	17.5	16.8	4.1
8	50.4	25.9	6.8	25.0	54.8	72.7	0.357	16.5	16.2	1.8
8A	51.6	27.2	7.8	25.8	55.0	72.8	0.358	16.4	16.1	1.8
8B	51.5	27.1	8.0	25.7	55.0	73.2	0.360	16.4	15.9	3.1
9A	43.5	16.5	6.8	18.3	54.3	120.0	0.337	17.9	16.9	5.7
9B	43.4	16.7	6.8	18.3	54.2	119.6	0.335	17.7	16.8	5.2
9C	51.4	17.6	6.8	21.8	54.2	120.5	0.338	22.4	22.1	1.4
9D	51.4	17.6	6.8	21.5	54.2	120.5	0.338	22.4	21.7	3.2
9E	49.5	16.5	6.4	21.1	54.8	120.5	0.338	22.2	21.7	2.3
9F	49.9	16.9	6.4	21.3	54.8	119.6	0.335	22.2	21.8	1.8
9G	50.6	17.6	6.5	21.7	54.8	120.5	0.338	22.2	22.4	0.9
9H	50.8	14.4	6.6	18.3	54.8	169.2	0.475	24.4	24.3	0.4
9I	50.5	13.9	6.7	16.3	54.8	208.0	0.584	24.6	24.5	0.4

TABLE 10A.

Data of concentration profiles for Runs 5D and 8. (not smoothed).

Run 5D							Run 8						
Height of the probes. ft.	Volume in a ketone sample.		Concentrations, lb.-moles/ft ³ x 10. ³				Height of the probes. ft.	Volume in a sample.(ketone)		Concentrations, lb.-moles/ft ³ x10. ³			
	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}		V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0.078	0.0	48.0	-	6.57	6.57	26.40	0.078	0.8	32.6	-	7.11	7.11	26.25
0.445	5.4	37.6	18.90	9.24	9.11	27.78	1.161	2.3	29.3	24.50	12.00	11.44	31.60
1.060	5.0	37.0	22.40	12.00	10.78	31.35	2.161	2.2	28.6	31.55	15.90	15.49	37.20
1.661	5.0	36.0	26.85	13.86	12.97	33.32	3.161	2.2	28.2	35.65	18.20	17.81	40.60
2.411	4.8	36.2	30.50	15.90	15.00	37.20	4.161	2.4	28.4	39.90	20.40	20.04	44.15
3.161	4.0	35.5	33.45	17.52	16.80	39.84	5.161	2.0	28.2	41.30	22.08	21.75	46.00
4.161	4.0	34.8	36.45	18.87	18.23	42.00	6.161	2.4	26.4	45.30	23.50	23.28	47.75
5.161	3.8	33.7	40.35	18.87	20.69	46.29	7.286	2.0	26.2	45.15	24.70	24.36	49.60
6.161	4.2	31.4	42.20	23.16	22.25	48.99							
7.286	4.0	30.0	43.50	24.96	23.86	51.72							

Average inlet water concentration: 51.61

Average outlet water concentration: 24.70

Average inlet ketone concentration: 6.50

Average outlet ketone concentration: 24.50

Average inlet water concentration: 50.40

Average outlet water concentration: 25.95

Average inlet ketone concentration: 6.75

Average outlet ketone concentration: 24.96

APPENDIX III

Study of time needed to obtain steady state inside the column.

As mentioned earlier in the thesis, two different concentration profiles exist inside the column before beginning a run. These concentrations depend on the liquid filling the column at that time.

If the column is filled with continuous phase feed before the run starts, and the column hasn't been operated before, the time needed to reach the steady state is longer than it is when the column has been operated before and contains both phases. This result is due to the higher average concentration which exists in the column in the former case and also increased difficulties in steadying out the interface. Table 11 records the results obtained in five runs* where the conditions of the former case applied. The concentrations of both outlet solutions: continuous phase, and dispersed phase, were sampled as functions of time. The height of the column has been noted in the same Table 11. The inlet concentration for the continuous phase feed solution averaged $50.4 \text{ lb.-moles/ft.}^3 \times 10^3$ and, for the dispersed phase, $6.6 \text{ lb.-moles/ft.}^3 \times 10^3$.

As just mentioned, if the concentration profiles inside the column resulted from a previous run, the time needed to reach the steady state is shorter, due to the smaller average concentration existing at the start of the run, and due to the existence of a liquid-liquid interface at the start of the run. Table 12 records the results obtained for this case.

* All the runs of this sort.

TABLE 11.

Steady state study.

Time, min.	*Run 6I ⁺ .				Column height, ft.	*Run 6J.				Column height, ft.
	Concentrations, lb.-moles/ft. ³ x10 ³					Concentrations, lb.-moles/ft. ³ x10 ³				
	C _{w1}	C _{w2}	C _{k1}	C _{k2}		C _{w1}	C _{w2}	C _{k1}	C _{k2}	
0	49.90	-	6.53		-	49.8	-	6.50	-	
5		19.2		23.4			29.1		25.3	
10		23.0		24.2			29.1		25.3	
15		24.6		24.5			27.2		25.1	
20		25.0		24.6			26.7		25.0	
25		25.3		24.8		49.9	26.3	6.6	24.9	7.46
30		25.2		24.8			26.4		24.9	7.44
35		25.3		24.9			25.9		24.8	7.43
40		25.2		24.9	7.46		25.7		24.8	7.42
45		25.1		24.9	7.44		25.7		24.8	7.41
50	49.9	25.1	6.53	24.9			25.7		24.8	7.38
55		25.2		24.9	7.43		25.5		24.7	7.38
60		25.1		24.9		49.9	25.4	6.6	24.7	7.38
65		25.1		24.9	7.43		25.2		24.6	7.37
70		25.1		24.9	7.43		25.3		24.6	7.36
75		25.1		24.9	7.42					
80		25.1		24.9						
85										
90	49.9	24.9	6.47	24.8	7.43					

* Runs started with continuous phase feed filling the column.

In the blank spaces no readings were taken.

+ In this run there was distilled water in the annular space of the Elgin head.

TABLE 11 Cont.

Steady state study.

Time, min.	*Run 6M				Column height, ft.	*Run 9A				Column height, ft.
	Concentrations, lb.-moles/ft. ³ x10 ³ .					Concentrations, lb.-moles/ft. ³ x10 ³ .				
	C _{w1}	C _{w2}	C _{k1}	C _{k2}		C _{w1}	C _{w2}	C _{k1}	C _{k2}	
0	50.5		6.6							
5		31.9		26.3			27.9		21.8	
10		28.3		26.2			21.6		21.0	
15		27.3		-		43.6	20.6	6.7	20.4	7.29
20		26.7		25.9			19.4		20.2	7.24
25		26.3		25.7		43.3	17.7	6.8	18.7	7.24
30	50.7	26.2	6.8	25.3	7.46		17.0		18.2	7.25
35		26.2		25.5	7.45		16.6		18.2	7.27
40		25.9		25.7			16.5		18.3	7.28
45		25.7		25.5	7.43		16.5		18.3	7.29
50		25.5		25.5			16.5		18.3	7.30
55		25.3		25.5	7.42	43.4		6.8		
60		25.5		25.5						
65		25.2		25.5	7.41					
70		25.7		25.2	7.41					
75	51.0		6.7							

* Run started with continuous phase feed filling the column.

The blank spaces mean that no reading was taken.

TABLE 11 Cont.

Steady state study.

Time, min.	*Run 9C.				Column height, ft.	*Run 9I.				Column height, ft.
	Concentrations, lb.-moles/ft ³ x 10 ³					Concentrations, lb.-moles/ft ³ x 10 ³ .				
	C _{w1}	C _{w2}	C _{k1}	C _{k2}		C _{w1}	C _{w2}	C _{k1}	C _{k2}	
0										
5	51.3	28.9	6.8	25.2			14.2		14.6	
10		20.9		23.9			13.9		16.0	
15		20.8		23.6		50.4	14.0	6.7	17.2	
20		19.2		22.9			14.2		17.6	
25	51.5	18.8	6.8	22.5			14.2		17.4	
30		18.5		22.2	7.46		13.9		16.3	<u>a7.28</u>
35		18.3		22.2			13.9		16.1	
40		18.2		22.2	7.42		13.8		16.2	7.29
45	51.4	18.0	6.8	22.0			13.9		16.3	
50		18.0		22.0	7.40		13.9		16.2	
55							13.8		16.3	
60							13.8		16.3	
65							13.9		16.2	
70							13.9		16.4	
75						50.4	13.9	6.7	16.4	7.37

* Run started with continuous phase feed filling the column.

a Interface controller raised l.-in. after this reading.

The blank spaces mean that no reading was taken.

TABLE 12.

Steady state study.

Time, min.	**Run 6K.					**Run 6L.					Column height, ft.
	Concentrations, lb.-moles/ft ³ x10 ³ .				Column height, ft.	Concentrations, lb.-moles/ft ³ x 10 ³ .					
	C _{w1}	C _{w2}	C _{k1}	C _{k2}		C _{w1}	C _{w2}	C _{k1}	C _{k2}		
0	50.1		6.5		7.45	50.8		6.5			
5		26.4		23.6	7.45		26.6		23.2	7.40	
10		24.8		24.4	7.45		24.5		24.6	7.39	
15		24.8		24.8	7.45		24.6		25.1	7.39	
20		25.0		25.0	7.40		25.0		25.3		
25	50.3	25.0	6.8	25.0	7.40		25.2		25.3	7.38	
30		25.2		24.9	7.40	50.6	25.2	6.7	25.4		
35		25.1		25.0	7.40		25.5		25.2	7.38	
40		25.0		25.2	7.40		25.4		25.3		
45		25.1		25.1	7.41		25.3		25.3	7.38	
50	50.3	25.1	6.8	25.1	7.41	50.5	25.2	6.7	25.3	7.38	

** Run started with a column which operated before.

Blank space means that no reading was taken.

TABLE 12 Cont.

Steady state study.

Time, min.	**Run 9B				Column height, ft.	**Run 9H				Column height, ft.
	Concentrations, lb.-moles/ft ³ x 10 ³ .					Concentrations, lb.-moles/ft ³ x 10 ³ .				
	C _{w1}	C _{w2}	C _{k1}	C _{k2}		C _{w1}	C _{w2}	C _{k1}	C _{k2}	
0										
5	43.5	16.6	6.8	18.2	7.33	50.6	18.4	6.6	17.6	<u>a 7.37</u>
10		16.7		18.3			14.7		17.5	
15		16.6		18.3	7.34		14.1		18.4	
20		16.6		18.3						
25		16.5		18.3	7.35					
30	43.4	16.6	6.8	18.3						
35		16.7		18.3	7.37		14.4		18.7	
40	43.2		6.8							
45		17.0		18.5	7.38		14.4		18.7	
50		16.5		18.4						
55		16.5		18.5	7.38		14.4		18.4	7.37
60										
65						50.9		6.6		7.37

** Run started with a column which had been operated before.

a Interface controller lowered 1.-in. after this reading.

Blank spaces mean that no reading was taken.

Table 13 summarizes the results obtained in all these runs.

This Table shows, for each different way of starting a run, the time in minutes which one should wait to get steady state using the dispersed phase flow rate mentioned. The continuous phase flow rate used was at a value of $54.8 \text{ ft}^3/\text{hr.}\cdot\text{ft}^2$.

TABLE 13.

Summary of the time needed to obtain steady state depending on the concentration in the column .

$$L_w = \text{constant} = 54.8 \text{ ft}^3/\text{hr.}\cdot\text{ft}^2$$

Continuous phase feed filling the column before the start of a run and no dispersed phase present.

Runs started from a column which had been operated before.

Run number.	Time, min.	Dispersed phase flow rate, L_k	Run number.	Time, min.	Dispersed phase flow rate, L_k
6J	40.0	73.60	6K	20.0	72.90
6M	45.0	73.20	6L	25.0	72.80
9C	30.0	120.00	9B	15.0	120.20
9A	35.0	120.00	9H	12.5	169.40
9I	12.5	208.00			

Note: The time values were taken from graphs made of the results given in Table 11 and 12. For safe operation, 5 minutes more should be added.

Run 6 I₁ has not been included; this run was begun with distilled water in the Elgin head.

APPENDIX IV

Study of the minimum purge time for changing the concentration of the solution in the probes using various rates.

The following Tables, 14 to 23, give the results of eleven Runs (1G, 2, 2A, 2B, 2C, 2D, 7, 7B, 7C and 7D) performed to study the time required to change the concentration of the material in the probes using various rates of purging.

It can be remarked that in these Tables (14 to 23), for some Runs a complete analysis of the ketone sample is not given; this was due to the presence of only a small volume of water in the ketone sample. The smallness of this volume was caused by the low purging rate which collected 90 to 95% by volume of ketone phase in the dispersed phase sample. The effect of such a small volume of water on the results would be less than 2% at the worst.

A summarizing Table (number 24) is given at the end of this Appendix. The purge time was found to fall as the purging rate increased as would be expected.

TABLE 14.

Study of minimum purge time.

Run 1G.

Note: Probe filled with liquid at sample position 4A and
moved at zero time to sample position 7.

Average continuous phase probe sampling rate 4.9 cc/min.

Average dispersed phase probe sampling rate 13.7 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	2.2	11.3	27.9	16.2	15.2	32.8
1	2	2.2	12.0	27.5	15.7	14.7	33.7
2	3	2.3	11.8	33.1	18.1	18.1	-
3	4	1.9	11.8	34.2	19.0	18.5	37.2
4	5	2.1	11.6	34.8	19.0	18.5	37.8
5	6	2.4	11.4	34.1	19.1	18.3	37.8
6	7	2.1	11.8	34.5	19.0	18.5	-

TABLE 15.

Study of the minimum purge time.

Run 2

Note: Probe filled with liquid at sample position 7 and
moved at zero time to sample position 4A.

Average continuous phase probe sampling rate: 13.8 cc./min.

Average dispersed phase probe sampling rate: 15.7 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	2.4	13.3	33.1	18.0	16.6	36.4
1	2	2.4	13.3	32.3	17.5	16.7	36.2
2	3	2.4	13.2	27.3	14.6	13.5	33.4
3	4	2.6	13.3	27.2	14.5	13.5	32.1
4	5	2.4	13.6	27.0	14.4	13.6	31.7
5	6	2.5	13.4	27.2	14.5	13.7	31.7
6	7	2.6	13.8	26.4	14.5	13.5	31.7
7	11	7.4	38.0	27.6	14.4	13.6	31.8

(a) one minute sample.

TABLE 15 Cont.

Study of the minimum purge time.

Run 2

Note: Probes filled with liquid at sample position 4A and moved at zero time to sample point 2A.

Averaged continuous phase sampling rate: 10.7 cc./min.

Averaged dispersed phase sampling rate: 14.5 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	2.4	12.0	26.9	14.6	13.6	32.0
1	2	2.4	12.6	27.6	14.7	13.5	31.9
2	3	2.3	13.0	19.5	10.4	8.6	29.9
3	4	2.4	12.4	19.7	10.1	8.8	26.4
4	5	2.4	12.8	20.2	10.1	9.1	25.8
5	6	2.0	12.0	20.5	10.2	9.4	25.6
6	7	2.5	12.2	19.6	10.3	9.1	25.6
7	12	11.0	62.5	20.2	10.1	9.2	25.6

TABLE 16.

Study of the minimum purge time.

Run 2A.

Note: Probes filled with liquid at position 2A and moved at zero time to position 4A.

Averaged continuous phase probe sampling rate: 3.8 cc./min.

Averaged dispersed phase probe sampling rate: 8.7 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	1.1	8.2	25.55	10.45	10.45	25.32
1	2	1.2	8.0	-	10.13	10.13	25.10
2	3	1.0	8.3	-	10.39	10.39	25.50
3	4	1.1	8.0	-	13.62	13.62	25.52
4	5	1.1	8.1	-	14.35	14.35	25.70
5	6	1.0	7.3	-	14.48	14.48	26.50
6	7	1.0	7.3	-	14.10	14.10	26.25
7	8	0.9	7.8	-	14.55	14.55	29.68
8	9	0.9	7.4	-	14.55	14.55	29.72
9	10	0.8	7.6	-	14.61	14.61	31.10
10	11	0.8	7.5	-	14.61	14.61	31.00
11	12	0.9	7.4	-	14.54	14.54	31.10
12	13	0.9	7.5	-	14.54	14.54	30.65

TABLE 16 Cont.

RUN 2A cont.

Note: Probes filled with liquid at sampling position 4A and moved at zero time to sampling position 7.

Averaged continuous phase probe sampling rate: 10.5 cc./min.
Averaged dispersed phase probe sampling rate: 11.7 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft. ³ x 10 ³ .			
From	to	V _w	V _k	(b) C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	1.8	9.6	-	15.40	15.40	32.4
1	2	1.8	10.2	-	15.55	15.55	32.3
2	3	1.6	10.4	-	16.18	16.18	33.6
3	4	1.4	10.1	-	18.20	18.20	34.4
4	5	1.6	10.0	-	18.20	18.20	36.7
5	6	1.4	10.1	-	18.20	18.20	36.7
6	7	1.4	10.6	-	18.32	18.32	36.8
7	8	1.7	10.1	-	18.15	18.15	36.6
8	9	1.5	9.8	-	18.83	18.83	36.4

(a) one minute sample

(b) Not enough water in the ketone sample for analysis.

TABLE 17.

RUN 2B.

Study of the minimum purge time.

Note: Probes filled with liquid at sampling position 4A and moved at zero time to sampling position 7.

Averaged continuous phase probe sampling rate: 8.5 cc./min.
Averaged dispersed phase probe sampling rate: 7.0 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft. ³ x 10 ³ .			
From	to	V _w	V _k	(b) C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	0.7	5.2	-	14.7	14.7	31.8
1	2	1.0	9.0	-	14.4	14.4	31.4
2	3	1.2	7.9	-	14.6	14.6	31.9
3	4	0.7	7.8	-	15.2	15.2	33.9
4	5	0.4	4.8	-	18.0	18.0	35.9
5	6	1.0	8.7	-	18.5	18.5	36.5
6	7	0.5	5.1	-	18.3	18.3	37.2
7	8	0.5	3.5	-	18.3	18.3	37.2
8	9	0.3	3.5	-	19.0	19.0	37.3

(a) One minute sample.

(b) Not enough water in the ketone sample for analysis.

TABLE 18.

Study of the minimum purge time.

RUN 2C

Note: Probes filled with liquid at sampling position 4A and moved at zero time to sampling position 2A.

Averaged continuous phase probe sampling rate: 7.7 cc./min.

Averaged dispersed phase probe sampling rate: 11.97 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft. ³ x 10 ³ .			
From	to	V _w	V _k	(b) C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	1.3	10.2	-	14.2	14.2	32.4
1	2	1.3	11.2	-	13.6	13.6	31.6
2	3	1.0	11.1	-	12.4	12.4	31.0
3	4	1.2	11.2	-	9.5	9.5	29.1
4	5	1.2	11.2	-	9.5	9.5	26.6
5	6	1.4	11.4	-	9.6	9.6	25.3
6	7	1.2	10.2	-	9.6	9.6	24.6
7	8	1.2	9.5	-	9.7	9.7	24.4

(a) One minute sample.

(b) Not enough water in the ketone sample for analysis.

Note: Probes filled with liquid at sample position 4A and moved at zero time to sampling position 4A.

Averaged continuous phase probe sampling rate: 1.6 cc./min.

Averaged dispersed phase probe sampling rate: 5.6 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft. ³ x 10 ³ .			
From	to	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	0.1	3.9	-	18.7	18.7	35.9
1	2	0.0	3.8	-	18.9	18.9	36.3
2	3	0.0	7.0	-	18.5	18.5	34.7
3	4	0.0	6.2	-	18.6	18.6	36.9
4	5	0.0	4.4	-	19.0	19.0	34.9
5	6	0.3	5.8	-	17.6	17.6	36.0
6	7	0.1	6.2	-	15.6	15.6	36.6
7	8	0.5	6.0	-	14.8	14.8	36.4
8	9	0.2	5.6	-	14.9	14.9	36.3
9	10	0.2	6.6	-	14.9	14.9	36.0

(a) One minute sample.

(b) Not enough water in the ketone sample for analysis.

TABLE 18 Cont.

RUN 2C cont.

Note: Probes filled with liquid at sampling position 2A and moved at zero time to sample position 4A.
 Averaged continuous phase sampling rate: 9.0 cc./min.
 Averaged dispersed phase sampling rate: 11.5 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	(b) C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	1.2	10.4	-	10.8	10.8	27.3
1	2	1.2	10.4	-	11.0	11.0	27.4
2	3	1.2	10.4	-	11.8	11.8	28.2
3	4	0.0	3.8	-	15.8	15.8	30.7
4	5	0.8	7.2	-	15.5	15.5	32.9
5	6	1.6	11.6	-	15.8	15.8	33.9

(a) One minute sample.

(b) Not enough water in the ketone sample for analysis.

TABLE 19.

Study of the minimum purge time.

RUN 2D

Note: Probes filled with liquid at sampling position 4A and moved at zero time to sampling position 2A.
 Averaged continuous phase sampling rate: 10.4 cc./min.
 Averaged dispersed phase sampling rate: 12.4 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	(b) C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	1.4	11.6	-	13.6	13.6	-
1	2	1.1	9.9	-	13.8	13.8	29.9
2	3	1.4	10.6	-	12.7	12.7	29.1
3	4	1.4	10.4	-	9.3	9.3	26.7
4	5	1.6	11.2	-	9.2	9.2	24.9
5	6	1.5	11.3	-	9.2	9.2	24.0
6	7	1.6	11.7	-	9.5	9.5	24.3
7	8	1.6	11.6	-	9.4	9.4	24.3

(a) One minute sample.

(b) Not enough water in the ketone sample for analysis.

TABLE 19 Cont.

RUN 2D cont.

Note: Probes filled with liquid at sampling position 2A and moved at zero time to sample position 4A.

Averaged continuous phase sampling rate: 1.9 cc./min.

Averaged dispersed phase sampling rate: 6.5 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	(b) C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	1	1.0	5.2	-	10.9	10.9	22.2
1	2	1.2	5.2	-	10.9	10.9	24.4
2	3	1.0	5.4	-	10.8	10.8	23.7
3	4	1.0	5.0	-	10.8	10.8	20.2
4	5	1.1	4.8	-	10.1	10.1	24.2
5	6	0.8	6.6	-	12.3	12.3	26.3
6	7	0.4	6.9	-	14.0	14.0	24.0
7	8	0.6	6.4	-	14.0	14.0	24.5
8	9	0.5	6.3	-	13.9	13.9	24.1
9	10	0.0	6.8	-	14.0	14.0	24.3
10	11	0.8	6.0	-	14.0	14.0	25.1

(a) One minute sample.

(b) Not enough water in the ketone sample for analysis.

TABLE 20

Study of the minimum purge time.

RUN 7.

Note: Probes filled with liquid at sampling position 4 and moved at zero time to sampling position 4A.

Averaged continuous phase probe sampling rate: 2.8 cc./min.

Averaged dispersed phase probe sampling rate: 5.4 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	(b) C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	3	0.8	16.2	-	11.7	11.7	29.8
3	6	0.8	16.4	-	12.2	12.2	29.6
6	9	0.8	15.1	-	17.7	17.7	29.7
9	12	0.8	14.8	-	17.7	17.7	32.5
12	15	0.8	15.0	-	17.7	17.7	36.4
15	18	2.0	24.0	-	17.4	17.4	38.9
18	21	2.0	26.0	-	17.4	17.4	38.7

(a) Three minutes sample.

(b) Not enough water in the ketone sample for analysis.

TABLE 21.

Study of the minimum purge time.

RUN 7B.

Note: Probes filled with liquid at sampling position 1A and moved at zero time to sampling position 4A.
 Averaged continuous phase probe sampling rate: 2.8 cc./min.
 Averaged dispersed phase probe sampling rate: 2.1 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft. ³ x 10 ³ .			
From	to	V _w	V _k	(b) C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	3	2.6	3.1	-	12.4	12.4	30.8
3	6	0.4	6.4	-	12.4	12.4	30.5
6	9	0.0	7.3	-	11.8	11.8	30.9
9	12	0.0	6.8	-	11.5	11.5	32.6
12	15	0.3	5.7	-	12.4	12.4	38.1
15	18	0.0	4.2	-	17.0	17.0	38.8
17	19	0.0	4.0	-	18.0	18.0	39.3
19	21	0.0	4.0	-	18.0	18.0	39.3
21	23	0.0	3.8	-	18.0	18.0	39.4

(a) Three or two minutes samples.

(b) Not enough water in the ketone sample for analysis.

TABLE 22.

Study of the minimum purge time.

RUN 7C.

Note: Probes filled with liquid at sampling position 4A and moved at zero time to sampling position 1A.
 Averaged continuous phase probe sampling rate: 5.0 cc./min.
 Averaged dispersed phase probe sampling rate: 4.8 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft. ³ x 10 ³ .			
From	to	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	3	0.6	8.2	-	18.0	18.0	39.6
3	6	0.8	10.8	-	18.2	18.2	38.6
6	9	0.6	13.2	-	17.5	17.5	33.0
9	11	0.3	8.4	-	16.0	16.0	30.9
11	13	0.4	8.8	-	11.7	11.7	30.6
13	15	0.3	7.9	-	11.8	11.8	30.6
15	17	0.6	8.2	-	11.8	11.8	30.6
17	19	0.3	8.0	-	11.8	11.8	30.8

(a) Three or two minutes sample.

(b) Not enough water in the ketone sample for analysis.

TABLE 22 Cont.

RUN 7C cont.

Note: Probes filled with liquid at sampling position 1A and moved at zero time to sampling position 4A.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	3	0.6	12.8	-	11.9	11.9	30.7
3	6	0.6	13.5	-	11.7	11.7	33.8
6	10	0.8	16.0	-	15.7	15.7	39.0
10	12	0.6	7.4	-	18.0	18.0	39.0
12	14	0.6	9.6	-	17.7	17.7	39.7
14	16	0.5	9.7	-	18.0	18.0	39.7
16	18	1.0	20.2	-	18.0	18.0	39.7

(a) Four, three and two minutes samples.

(b) not enough water in the ketone sample for analysis.

TABLE 23.

Study of the minimum purge time.

RUN 7D.

Note: Probes filled with liquid at sample position 1A and moved at zero time to sample position 4A.

Averaged continuous phase probe sampling rate: 3.7 cc./min.

Averaged dispersed phase probe sampling rate: 2.5 cc./min.

Time, min. (a)		Volume of phases in ketone sample cc.		Concentrations, lb.-moles/ft ³ x 10 ³ .			
From	to	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
0	3	0.6	6.6	-	12.1	12.1	31.2
3	6	0.7	7.8	-	12.2	12.2	31.5
6	9	0.0	4.8	-	12.1	12.1	34.1
9	11	0.0	4.8	-	12.8	12.8	38.7
11	13	0.0	4.9	-	12.8	12.8	40.1
13	15	0.0	5.2	-	17.1	17.1	40.4
15	17	0.0	4.5	-	18.8	18.8	40.7
17	19	0.0	5.0	-	18.8	18.8	40.7
19	21	0.0	4.9	-	18.8	18.8	40.7

(a) Three or two minutes sample

(b) Not enough water in the ketone sample for analysis.

TABLE 24.

Summary of all results to determine the minimum purge time. (Smoothed values).

Run number.	<u>Continuous phase.</u>		<u>Dispersed phase.</u>	
	Sampling rate, cc./min	Minimum purge time, min.	Sampling rate, cc./min	Minimum purge time min.
1G	12.8	5.0	13.8	3.5
2	11.0	6.0	15.9	3.0
2	13.0	5.0	14.9	3.5
2A	3.8	-*	8.7	5.5
2A	10.5	6.0	11.7	4.0
2B	8.5	7.0	8.8	5.5
2C	7.7	-*	12.0	4.0
2C	9.0	5.0	11.5	4.0
2C	1.6	-*	5.6	8.0
2D	1.0	-*	6.5	7.0
2D	10.4	7.0	12.4	5.0
7	2.8	20.0	5.4	9.0
7B	2.8	19.0	2.1	18.3
7C	5.0	12.0	4.1	13.0
7C	6.3	10.0	4.5	12.0
7D	3.7	16.0	2.5	16.8

* The minimum purge time was not obtained in these runs; the time was too short for the concentration curve to flatten out.

APPENDIX V.

Point concentration versus sampling rate.

The following Table, 25, represents the results of the runs done to demonstrate that the sampling rate did not influence the point concentration.

TABLE 25.
Point Concentration Versus Sampling Rate.

Run number.	Purge time, min.	Sampling time, min.	Minimum Purge Time according to Figure 10. min.		Rate of Sampling, cc./min.		Volume of phases in ketone sample. cc.		Concentrations, lb.-moles/ft. ³ x 10 ³ .				Probe location.
			Water phase.	Ketone phase.	Water phase.	Ketone phase.	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}	
<u>9H</u>	10	5	6.0	5.6	10.4	8.4	3.0	39.0	14.6	7.3	7.2	15.8	1.59
	10	5	4.0	3.0	16.0	15.6	7.0	69.0	15.0	7.3	7.2	16.2	1.59
	10	5	10.0	5.6	6.2	8.2	3.0	38.0	13.3	7.2	7.1	15.7	1.59
	10	2	6.4	4.8	9.4	10.3	1.5	19.0	15.0	7.2	7.1	16.2	1.59
<u>7F</u>	0	10	18.6	25.0	2.8	1.1	0.6	10.4	28.4	19.1	18.9	41.4	4A
	0	10	18.6	18.6	2.8	2.0	1.8	17.8	28.0	18.8	18.4	41.2	4A
	0	10	18.6	9.4	2.8	5.2	2.0	50.0	27.7	18.4	18.3	41.3	4A
	0	4½	18.6	1.0	2.8	28.2	24.0	103.0	28.6	18.4	18.5	41.3	4A
	0	8	18.6	3.0	2.8	16.2	19.0	111.0	28.5	18.1	18.4	41.4	4A
<u>7E</u>	0	10	18.6	6.8	2.9	7.0	14.0	56.0	29.2	19.6	16.6	41.2	4A
	0	10	9.8	7.4	6.4	6.2	4.0	58.0	27.7	18.6	17.7	41.2	4A
	0	10	5.2	8.6	11.3	5.7	3.0	54.0	27.7	18.6	17.8	41.3	4A
	0	10	7.6	9.2	8.1	5.4	3.0	50.5	27.7	18.6	17.7	41.2	4A
	0	10	4.3	5.0	14.2	9.8	6.0	82.0	27.3	18.3	17.3	41.2	4A
<u>5H</u>	15	5	6.8	3.6	9.0	13.8	5.0	64.0	26.7	13.5	12.9	33.3	3B
	5	5	13.8	4.8	4.5	10.2	4.0	47.0	27.0	13.8	13.2	34.8	3B
	5	5	*	6.6	-	7.2	2.5	33.3	27.0	14.0	13.5	-	3B
	8	6	*	9.4	-	5.3	0.0	26.5	-	14.0	14.0	-	3B
	7	3	10.6	3.4	6.0	14.5	5.0	38.5	28.2	14.4	13.7	35.0	3B
	10	3	*	3.0	-	15.5	5.5	41.0	28.6	14.5	13.9	-	3B
	5	3	*	2.0	-	18.7	7.0	48.2	28.6	14.5	13.9	-	3B

TABLE 25 Cont.

Run number.	Purge time, min.	Sampling time, min.	Minimum Purge Time according to Figure 10.		Rate of Sampling, cc./min.	Volume of phases in ketone sample.		Concentrations, lb.-moles/ft ³ × 10 ³ .					Probe location.
			min.	min.		Water phase.	Ketone phase.	V _w	V _k	C _{wf}	C _{kf}	C _{ki}	C _{wi}
<u>5G</u>	18	3	6.6	3.6	9.3	13.7	4.0	37.0	27.3	14.1	13.2	35.4	3B
	7	3	*	4.1	-	12.3	3.8	33.2	27.1	13.8	12.8	-	3B
	8	3	*	5.6	-	8.3	2.0	23.0	25.5	13.9	13.0	-	3B
	9	3	*	5.6	-	8.3	2.0	23.0	23.4	13.7	12.7	-	3B
	5	3	*	3.2	-	15.0	5.8	39.2	25.8	14.1	12.6	-	3B
	5	3	*	2.6	-	17.0	7.0	44.0	28.0	14.3	13.1	-	3B
	6	2	6.4	0.5	-	20.3	5.0	35.5	27.3	14.7	13.6	35.7	3B
<u>5F</u>	9	3	7.0	3.6	8.8	13.7	4.0	37.0	26.1	14.0	12.9	35.5	3B
	0	3	13.2	4.6	4.7	10.7	3.0	29.0	27.6	14.0	13.2	35.6	3B
	0	3	*	4.0	-	12.7	3.0	35.0	26.7	13.9	13.1	-	3B
	0	9½	*	3.2	-	15.0	14.0	125.0	28.4	14.1	13.4	-	3B
	0	6	*	2.6	-	17.0	9.0	109.8	28.1	14.2	13.5	-	3B
	0	7.	*	2.3	-	17.6	17.0	105.2	29.0	14.3	13.2	-	3B
5B ₁	9	3	6.6	3.7	9.3	13.6	5.5	36.3	24.6	12.6	12.5	32.1	3B
	0	5	13.4	4.8	4.6	18.4	6.0	46.0	24.6	12.5	12.4	32.2	3B
	0	5	*	2.7	-	16.6	11.3	71.0	25.9	12.8	12.7	-	3b
	0	5	7.0	*	8.9	-	-	-	-	-	-	32.0	3B
	0	5	*	0.5	-	23.3	20.0	96.6	27.4	13.3	12.4	-	3B
	0	5	6.6	*	9.2	-	-	-	-	-	-	32.7	3B
<u>1D</u>	4	5	0.5	1.0	34.0	28.4	27.7	104.3	45.7	23.8	23.1	47.7	7
	0	5	1.0	1.0	21.0	21.0	25.0	80.0	45.6	23.8	23.1	47.8	7
	0	5	5.2	3.8	11.0	12.9	10.2	54.0	44.2	23.5	22.8	47.9	7
	0	5	4.0	2.6	16.0	17.0	12.2	72.6	45.1	23.5	23.1	47.9	7

a = Equilibrium value, not analyzed.

* = Not sampled.

+ = Average water concentration was used to calculate these values.

= First concentration of water used to do the calculations.

APPENDIX VI

Jet characteristic data. (Jonhson and Bliss).

Reference to Rocchini's thesis (13) page 63, showed that he used a velocity through the nozzle of 0.3623 ft./sec. However, Choudhury (10) used a velocity of 0.357 ft./sec. as reported in his thesis, page 26. It was discovered that this difference was caused by the use of slightly different flow rates of dispersed phase.

After recalculating the velocity of these previous workers (10,13) and checking the above values to close approximation, it was decided to use a value of 0.357⁺ ft./sec. based on the average diameter of the nozzle tips presently available. This is 0.1029.-in. (10).

It became necessary to check if this velocity through the nozzle would be expected to give uniform drops. Referring to Jonhson and Bliss (16), it was discovered that the velocity used in this work was high enough so that the drops would have ceased forming at the nozzle tips* but not so high that the drops would have ceased being uniform. In other words, the velocity of 0.357 ft./sec. utilized would give uniform drops.

Although a linear interpolation of Table II of the paper by Jonhson and Bliss (16) indicates that drops should, for a nozzle of 0.103.-in. I.D., cease being uniform when the velocity in nozzle tips reached 0.350 ft./sec., according to their curve in their Figure 3, the velocity plotted at 0.11-in. I.D. appears to be too low. (This plotted velocity is the one from the Table.) In fact, at 0.111-in. I.D. nozzle diameter they draw their curve considerably above the plotted point. It is on the basis of this fact that the statement is made that the tip velocity of 0.357 ft./sec. should produce uniform drops

+ Not always used.

* It was observed that the drops formed straight (not sinuous) jets except for one tip; at this tip the jet was sinuous. All jets were app. 1½-in. in length.

according to Jonhson and Bliss(16).

APPENDIX VII

Sample calculation of the material balances used in connection with Run 9H water Sample no. 2 which contained ketone.

As a result of a high flow rate of dispersed phase and perhaps of too high a sampling rate for such a flow, the following calculations have to be made to correct for the presence of ketone in the water probe sample.

Equation 5 is applied first to the sample obtained with the water probe:

$$(C_{ki})_{\text{probe}} = (\epsilon_{kf})_{\text{water probe}} - (V_w/V_k)_{\text{water probe}} (C_{wi} - (C_{wf})_{\text{water probe}})$$

The same equation is applied also to the ketone probe sample:

$$(C_{ki})_{\text{probe}} = (C_{kf})_{\text{ketone probe}} - (V_w/V_k)_{\text{ketone probe}} (C_{wi} - (C_{wf})_{\text{ketone probe}})$$

Where the volume of one phase in the sample is small, as compared with the volume of the other phase, an equilibrium value is taken instead of making use of analysis. In the two equations only two unknowns, C_{ki} and C_{wi} , are left. These, of course, can be solved for.

In Run 9H, Sample number 2, the water probe sample contained 2.6 cc. of ketone and 10.2 cc. of water. From the values listed in Table 5 the following are obtained after substitution:

$$(C_{ki}) = 7.62 - 10.2/2.6 (C_{wi} - 15.88)$$

$$\text{and } (C_{ki}) = 7.36 - 0.4/15.6 (C_{wi} - 14.95)$$

Solving for C_{wi} , it was found that:

$$C_{wi} = 15.95 \text{ lb.-moles/ft}^3 \times 10^3$$

Using this initial value for the water probe gives a values of 7.33 for C_{ki} for the probe dispersed phase. Using C_{wi} of 15.95 in the material balance for the piston sample produces a C_{ki} of 7.25.

APPENDIX VIII

Possible sources of errors causing discrepancies between piston and probe dispersed phase results.

Problems arising in the analysis of the solutions in the piston samples were suspected by Hawrelak (12) as being the sources of much error in the values of $(C_{ki})_{\text{piston}}$. In Equation 5, the factor $(C_{wi} - C_{wf})$ appears in the second term to the right of the equal sign. The concentrations involved are of about the same order of magnitude as mentioned earlier, and subtracting them tends to make analytical errors important. An example would illustrate better the difficulty just mentioned.

In Sample no. 2 of Run 9G done with the piston, the phase concentrations at time of analysis were $(C_{wf})_{\text{piston}}$; and $(C_{kf})_{\text{piston}}$, 20.35 lb.-moles/ft.³ x 10³ and 10.15 lb.-moles/ft.³ x 10³ respectively. This sample contained 101 cc. of continuous phase and 16 cc. of dispersed phase. The analysis of the continuous phase taken with the probe, or $(C_{wi})_{\text{probe}}$, was 20.96 lb.-moles/ft.³ x 10³. Now, substitution in Equation 5:

$$(C_{ki})_{\text{piston}} = (C_{kf})_{\text{piston}} - V_w/V_k((C_{wi})_{\text{probe}} - (C_{wf})_{\text{piston}})$$

produces,

$$(C_{ki})_{\text{piston}} = 10.16 - 101/16(20.96 - 20.35)$$

$$(C_{ki})_{\text{piston}} = 6.30 \text{ lb.-moles/ft.}^3 \times 10^3.$$

This concentration has to be compared with the one obtained by the probe method which was 8.30 lb.-moles/ft.³ x 10³, for which the volumes were 4 cc. of water and 48.5 cc. of ketone.

$$(C_{ki})_{\text{probe}} = 8.58 - 4/48.5(20.96 - 17.52)$$

It seems logical now to consider if it is possible that the dispersed phase concentrations obtained by the two methods do not check because of possible manipulative errors in analysis. For example, what can be the effect of a pipetting error on the final results? Based on the calibrations of the 10-ml. pipettes, a possible error of $\pm 0.4\%$ in the volume delivered can be expected. What can be the effect of errors in measuring the volumes of the phases in a piston sample? At the worst, ± 0.5 cc. of water can be taken as possible errors in V_w , and corresponding to these errors, ± 0.5 cc. in V_k . Finally, what can be the effect of adding one drop past the end point in the titrations of the probe and of the piston samples? Calculations have been done to reveal the effects of the possible errors mentioned above.

First of all, to be able to really see their influence on some of the analysis values, the effect of each error has been considered separately; the results are presented in four cases:

First case:

suppose that in pipetting 10 ml. of water from the continuous phase of the probe sample, 10.04 ml. actually was delivered, and, similarly, 9.96 ml from the water phase of the piston sample. All other quantities measured in the analysis were assumed to have the values used to calculate the results of Sample 2 of Run 9G given earlier in this Appendix. Replacing in Equation 5 for the piston sample:

$$C_{ki} = 10.16 - 101/16 (20.88 - 20.43)$$

A value of $7.32 \text{ lb.-moles/ft.}^3 \times 10^3$ is found for $(C_{ki})_{\text{piston}}$ as compared with 6.30 as given earlier. (The difference is 16.4% of 6.30.)

Replacing in Equation 5 for the probe sample:

$$C_{ki} = 8.58 - 4/48.5 (20.88 - 17.52)$$

A value of $8.30 \text{ lb.-moles/ft.}^3 \times 10^3$ is found for $(C_{ki})_{\text{probe}}$ as compared

with 8.30 calculated earlier.

Second case:

suppose that in pipetting 10 ml. of water from the continuous phase of the probe sample, 9.96 ml. actually was delivered, and, similarly, 10.04 ml. from the water phase of the piston sample. As before all other quantities measured in the analysis are taken to be unchanged. In Equation 5, for the piston sample, then:

$$C_{ki} = 10.16 \div 101/16 (21.04 - 20.27)$$

Then a value of $5.30 \text{ lb.-moles/ft.}^3 \times 10^3$ is found for $(C_{ki})_{\text{piston}}$ as compared to 6.30. (The difference is 15.9% of 6.30) Equation 5 for the probe sample then is

$$C_{ki} = 8.58 - 4/48.5 (21.04 - 17.52)$$

A value of $8.29 \text{ lb.-moles/ft.}^3 \times 10^3$ is found for $(C_{ki})_{\text{probe}}$ as compared with 8.30 calculated earlier.

Third case:

suppose that the volume of water in the piston sample was actually 100.5 cc. instead of 101.0 as measured and suppose that the corresponding volume of ketone was really 16.5 cc. instead of 16.0 cc.. All other quantities measured in the analysis were as used in the calculation given at the beginning of this Appendix.

Equation 5 for the piston sample becomes for these conditions:

$$C_{ki} = 10.16 - 100.5/16.5 (20.96 - 20.35)$$

The resulting $(C_{ki})_{\text{piston}}$ would have been $6.44 \text{ lb.-moles/ft.}^3 \times 10^3$ instead of 6.30 the original value. (The difference is 2.2% of 6.30.)

Fourth case:

suppose that the titrations of each phase of the piston sample, one drop was added past the end point in each analysis. (In the titration, it would be much easier to overrun the end point than to add too little

sodium hydroxide.) Once again, all the other measurements involved in the basic calculations are assumed correct. In Equation 5, then:

$$C_{ki} = 10.13 - 101/16(20.96 - 20.32)$$

Then the resulting $(C_{ki})_{\text{piston}}$ would have been $6.09 \text{ lb.-moles/ft.}^3 \times 10^3$ as compared with 6.30 obtained originally. (The difference is 3.3% of 6.30.)

A calculation was made of the effect of several errors of the sort discussed in cases 1 to 4 taking place at the same time in connection with one piston sample and the probe sample corresponding to it.

An error of 21.3% over the original value of $6.30 \text{ lb.-moles/ft.}^3 \times 10^3$ for $(C_{ki})_{\text{piston}}$ is calculated if due to pipetting error, the volume analyzed for the probe continuous phase had been 10.04 ml. instead of the 10 ml. assumed and, if both phases of the piston sample analyzed had been 9.96 ml. instead of the 10 ml. assumed and, if the measured volume of the phases of the piston sample had been measured too low by -0.5 cc. and too high by +0.5 cc. for the water and ketone phases respectively, and finally if 1 drop of 0.1 N NaOH had been added past the end point in the titration of the water of the continuous phase sample. Equation 5 for this case is (for the piston sample):

$$C_{ki} = 10.20 - 100.5/16.5(20.85 - 20.43)$$

For the probe sample an error of 0.4% over the original of $8.30 \text{ lb.-moles/ft.}^3 \times 10^3$ is cumulated in this way:

- a) if the volume analyzed had been 10.04 ml. instead of the 10 ml. assumed for the probe continuous phase sample.
- b) if the volume analyzed had been 9.96 ml. instead of the 10 ml. assumed for the ketone of the probe dispersed phase sample.

c) if the volume of water of the continuous phase probe had been titrated one drop past the end point. Equation 5 for this case is:

$$C_{k_i} = 8.61 - 4/48.5(20.85 - 17.52)$$

If one can eliminate these possible errors by analyzing bigger volumes and by using the highest accuracy to measure the volumes of the phases of a piston sample, then it would appear that analysis difficulties should no longer be a problem.