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An experimental study of separation of binary and ternary gas mixtures by parametric pumping

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AN EXPERIMENTAL STUDY OF

SEPARATION OF BINARY AND TERNARY GAS MIXTURES

BY PARAMETRIC PUMPING

BY

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ABSTRACT

An experimental study of gas parametric pumping is
presented which examines the purification of helium using
silica gel to remove the impurity carbon dioxide. Low
gas flow rates are used to allow adequate time for equil-
ibrium to be approached, assuming intraparticle diffusion
is the controlling mass transfer step. By varying the cycle
time, at long cycle times, the effect of penetration length
(a function of dynamic capacity) is indicated. Also, at low
cycle time, the effects during pressure changes become more
significant.

Using low flow rate improves separation effectiveness if
evaluated at equal dynamic capacity. When using low flow rate
and low cycle time, the gas added during repressuring and
removed during blowdown should be used in calculating the
purge to feed ratio. If this is not used then the purge
concentration calculation method will not be accurate. When
operating under conditions where the repressurizing gas makes
up a large percentage of the gas fed, a poor separation efficiency
resulted, due to inadequate regeneration of the purging column.

The system helium, carbon dioxide, and propylene was
evaluated at higher flow rate. Adsorbtion breakthrough curves
from adding carbon dioxide and propylene simultaneously to
silica gel showed the system to be non-ideal. The carbon dioxide

adsorbed to a peak level and then desorbed as additional propylene adsorbed. Using this system, even though more propylene can adsorb than carbon dioxide, the separation of carbon dioxide was more effective than propylene. This apparent departure from theory may be due to insufficient time for the more strongly adsorbed propylene to purge from the column.

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INTRODUCTION

Adsorbtion is a commonly known method of removing impurities from liquid or gas streams. This generally involves a number of columns set up in parallel to allow for regeneration. This is generally a good method to obtain a separation, although it is often not very economical due to the method of regeneration required(chemical reaction, energy input-heat, etc.)

A process which improves the effectiveness of adsorbtion separations was demonstrated for liquid systems by Wilheln and Sweed[4] using temperature to change the adsorbtion of toluene-n-heptane solution on silica gel. The separation process called parametric pumping involves periodic flow direction changed coupled with change of a thermodynamic parameter such as pressure, temperature, pH, etc. which affect adsorbtion equilibrium. Chen and Hill[5] have derived mathematical models for batch, semi-continuous, and continuous parametric pumps in particular as pertaining to liquid systems.

Shendalman and Mitchell[3] have studied adsorbtion of CO_2 from helium using pressure change to cause adsorbtion and desorbtion. In gas separation via parametric pump, adsorbtion occurs at high pressure in one column and desorbtion in a second column at low pressure. A portion of the depleted gas leaving the first column is used to regenerate the adsorbent in the second column. By proper adjustment of the operating

parameters(pressure, feed rate, adsorbent, cycle times, and
flow rates) it should be possible to obtain excellent separation
by this method.

Possible applications of this separation method to commercial
gas separations are many. It is particularly well suited to
situations in which the gas at ambient temperature is already
at high pressure thus avoiding need for compressors. The
alternate separation method for separation of low boiling gases,
cryogenic distillation, requires significantly greater invest-
ment and energy costs.

For evaluation of possible separation schemes using pressure
parametric pump, Shendalman and Mitchell[3] suggest a mathematical
model for prediction of the separation efficiency per stage(cycle)
and also the equilibrium purge gas concentration. The prediction
of the theoretical high pressure product composition after each
stage is based essentially on the pressure ratios and equilibrium
constant, although the data indicate that the purge to feed
ratio significantly affects the actual separation. Another
variable which they showed to have an effect on the separation
was dynamic capacity or as described by Chen and Hill[5] penetration
distance. While the work of Shendalman and Mitchell indicated
many important effects which control separation, they were unable
to match the theoretical separation. Their experiments used
relatively large flow rates and as such may not have attained

equilibrium," which may have reduced their separation efficiency.

The purpose of this thesis is to investigate the effect of lower feed rate(to allow more time for equilibrium) on the separation. By lowering the feed rate at low cycle time we can also examine the effect of pressuring and blowdown. The affect of pressure is also shown. The above experiments were done using 1.05 % CO_2 in helium. Some additional experiments were done to examine separation in the ternary system helium-carbon dioxide,- propylene.

PROCESS DESCRIPTION

Continuous purification of gases by parametric pumps involves use of two adsorbent packed columns at different pressures. The high pressure column is adsorbing while the low pressure column is desorbing. Before the adsorbing capacity of the high pressure column is reached the duties of the columns columns are reversed, that is, the high pressure feed is switched to the regenerated column and the previous adsorbing column is regenerated at low pressure.

The apparatus used for the experiments is shown in Figure 1. The high pressure feed flows from the gas cylinder through a pressure regulator and an open 3 way solenoid valve and into the bottom of column 1. During the adsorbtion half cycle column 1 is maintained at the high pressure P_H. The flow rate F(volume per unit time) is constant during the half cycles but varies during column switching. The columns are packed with silica gel with void fraction ϵ. The volume of the packing V_P is equal $\frac{\pi D^2 h}{4}$, where D is diameter of the column and h is height of the packing. The void volume of the packing ϵV_p is filled with the gas and the more adsorbable gas adheres to the silica gel. Gas at P_H flows out of the top of column 1, through an open solenoid valve. The high pressure(top) product is removed from the system at this point at a constant flow rate Q(volume per unit time). The gas removed as top product is

only part of the amount fed to the column. The remainder of the gas flows through a pressure regulator which reduces it to a low pressure P_L which is the pressure maintained in column 2. The gas flows through a check valve into the top of column 2 and downward picking up desorbing components and leaving the bottom of column 2 through a 3 way solenoid valve. This desorbed gas, designated as purge with flow rate W(volume per unit time), is generally enriched in the desorbing gas as compared with the feed to the system. The flow continues into column 2 until the end of the half cycle at which point the flows are reversed and the next half cycle starts.

During the change of half cycles the system does not follow the continuous constant flows described above. Column 2 at P_L is pressurized quickly to P_H. At this point a feed surge of F^1 (volume of gas) occurs. This pressurization being fast results in negligible variation of the top product flow rate Q. Column 1 at P_H must be vented down to P_L. This results in a higher purge flow rate until P_1 is reached. The time required for the pressure to drop depends on the purge flow rate. While the pressure in column 1 is above P_L the pressure regulator does not allow flow from column 2 into column 1. Since the top product flow doesn't change, the feed during this period is equal to top product flow. Once column 1 pressure drops to P_L , flow from column 2 to column 1 resumes. At this point the conditions are reversed from the previous cycle. The high pressure feed enters.

the bottom of column 2 where adsorbtion is occurring, product
is removed at the top of the column and purge of desorbing
material is from the bottom of column 1. This continues until
the end of $\frac{1}{2}$ cycle when the flows are switched.

Operation of the system in the above manner resulted in
continuous constant flow of the product stream with variations
in the feed and purge streams during column switching due to
pressurizing and depressurizing. Since the objective of this
work was to attempt to obtain data in closer agreement
with theoretical predictions by allowing longer time of contact
for equilibrium to be reached, low flow rates were used. The
low flow rate caused the time required for depressurizing to
be significant. The variations of pressure and flow rate are
shown in fig. 2 through 9. The effects of these variations
will be discueeed further under discussion of results.

Some of the runs used large half cycle times which, dimin
ished the effect of pressure and flow variations. If these
variations are assumed relatively small then the separation
process can be explained simply for binary mixtures, in which
one gas is readily adsorbed and the other is not, by considering
the following. Binary gas mixtures consisting of species α
easily adsorbed component and species β not adsorbed component
with feed composition of α being Y_0 flow into the bottom of
column 1 at high pressure P_H. At the start of the cycling

procedure product at P_H is removed at the top of the column
and composition Y_O and purge is removed from the bottom of
column 2 at low pressure P_L and composition Y_O. When cycling
starts the high pressure feed is changed to column 2 which results
in the gas in the column being adsorbed on the basis of the
relationship $C_j = k_\alpha P_\alpha$. The gas in the top of the column is
now depleted of species α. Gas is removed partially as
top product and part of it is reduced in pressure and used to
pick up desorbing material from the low pressure column. The
larger the percent of the gas which is used for purging, the
greater the amount of component α which is removed from the column
and if more is removed on the desorbtion step than more will be
adsorbed on the next half cycle. Thus the top product comp-
osition should continue to decrease.

EXPERIMENTAL

Apparatus

A diagram of the experimental apparatus is presented in Figure 1. The gas separation occurs within two horizontally mounted columns, each 45 inches, 1 inch OD schedule 40 304 stainless steel. The columns are each filled with 393 cc of 30-60 mesh silica gel. The columns were packed at each end with glass wool to prevent the silica gel from being blown out of the top or bottom of the column.

Feed gas enters under high pressure into the adsorbing column from the bottom through a three way solenoid valve, Automatic Switch type T83146 and the purge gas leaves the desorbing (regenerating) column through a similar valve. At the end of the half cycle the valve is switched so that the feed to the high pressure column is shut off and the outlet from this column to the purge stream is opened. At the same time the valve at the bottom of the other column is also reversed so that purge no longer leaves but rather feed enters. Both three way valves are open from the feed to the column when not energized and open from the column to the purge when energized.

In order to achieve a good separation continuously it is necessary to operate the columns at different pressures. Pressure gauges(0-300psig) from Pall Trinity Micro Corp. are at the top of each column. Gas leaves the top of the adsorbing column through

a two-way solenoid valve, Automatic Switch Type 8262C34. The solenoid valve at the top of the low pressure , desorbing column, is closed to prevent flow of high pressure gas into the low pressure column. A portion of the gas leaving the high pressure column flows through a 1/8" copper tubing to a Gilmont flowmeter(F275) which measures the top product flow. The flow is controlled by a Matheson No. 150 needle valve placed after the outlet of the flowmeter. After the needle valve the gas goes either to atmosphere or to a gas sampling valve attached to a gas chromatograph.

The remainder of the gas leaving the high pressure column flows through a pressure regulator, Fischer Governor Company type 67, to reduce the pressure to the low pressure column conditions. The gas then flows through a Hoke spring ball check valve and then into the top of the low pressure column. The check valve at the top of the low pressure column allows gas to flow in and the check valve at the top of the high pressure column prevents escape of the top product. The purge gas leaves the bottom of the low pressure column through the three way solenoid valve and through a flowmeter. The purge flow rate is controlled by a Gilmont needle valve placed after the exit of the flowmeter. The purge gas goes either to the atmosphere or to the gas sampling valve on

the gas chromatograph. The gas sampling valve and the gas
chromatograph will be discussed further under analytical.

Control of the cycling procedure is done by manual switch-
ing of the solenoid valves by an electrical switch device as shown
in the schematic in Figure 10. Solenoids C and D are open when
not energized and three-way solenoids A and B are open from
the feed to the column when not energized. When circuit 1 is
activated column 1 is purging and feed is entering column 2.
The cycling is controlled by switching the circuits by selector
switch E. Since all cycle times which were used were relatively
large(2-20 minutes) a sweep hand watch was used for timing the
cycles.

Inlet and outlet fittings at the top and bottom of each
column are easily removed to allow removing and replacing the
adsorbent. All pipe fittings are sealed with TFE tape.

Operation

Prior to operation each column was filled with 393 cc
of 30-60 mesh silica gel which had been ground up from large
particles of Type DE5 silica gel and screened to obtain the
30-60 mesh particle size range. The ground up silica gel had
the following sieve analysis.

retained on	Approx vol.	weight
40	730 cc.	565
50	475 cc.	349.8
60	255 cc.	183.5

Before being put into the columns the sieved silica gel was well
blended to make sure that the size range was well mixed by being
put into a half gallon container and rolled on a roller mill for
8 hours. The mixed silica gel was dried for 3 days at 110°C
After the drying of the silica gel is completed it is cooled to
room temperature and quickly put into columns. Glass wool was
put intothe bottom of each column prior to assembly as a
support for the silica gel. After the silica gel is added glass
wool is also put at the top of the columns to insure that the
silica gel doesn't blow out. After the columns are completely
reassembled, the fittings are tightened, and the system is press-
ure tested.

The columns are pressure tested by closing the valves in
the product and purge lines and then with the electrical control
circuits off, so that the feed inlets to both columns are open,
the columns are pressurized with the feed gas up to the highest
pressure which will be used. When the desired pressure is
indicated on the pressure guages the feed is shut off. The
pressure was checked for 15-30 min.and the fittings were checked
for leaks usinf soap solution.

While setting up the column , the gas chromatograph is
turned on to allow it to warm up. At least 2 hours should be
allowed for warmup. Once the gas Chromatograph.is warmed, a sample
of feed gas is injected into it. The analytical procedure will

be detailed in a separate section. Analyses were made on constant volume samples, taken by use of an automatic sample valve. Samples from the feed gas, top product, or purge gas can be directed to the gas chromatograph sample valve by modifying valve arrangements. The feed gas is analyzed by the gas chromatograph at the start in order to make sure that the chromatograph is properly adjusted and also to determine the correct chromatograph detector and attenuation settings in order to obtain the maximum peak height. The feed samples are rechecked until the results are reproduced. When the chromatograph is ready and the columns are leak free, the next step is to saturate the columns with the feed gas.

The columns were saturated using three different methods. One method involved feeding into one of the columns at 60 psia and removing from the other at 20 psia until the analysis of the top product corresponds to the feed gas analysis. An improvement over the first method, the second method is similar to the first method except that the feed continues until the gas leaving the bottom of the low pressure column is also at the feed gas composition. A third method uses high pressure feed gas to saturate both columns until the product is feed gas composition.

Once the columns are saturated the flows must be adjusted. With one column at 60 psia and the other at 20 psia, the purge

flow rate is first adjusted. Since the flow rates used for these experiments were quite low, these flow rates were measured in the following manner. The outlet line after the flow control needle valve is attached to the bottom of a 50 cc. burette. Several drops of soap solution is then added to the burette. The gas after the outlet of the needle valve is essentially at atmospheric pressure. The flow into the bottom of the burette causes the soap solution to form a thin meniscus which rises up the burette at a rate dependent on the flow of gas. The burette being calibrated from 0-50 cc./ min. in 1cc. graduations thus allowing accurate determination of the amount of gas which flows from the column in a minute. For both the purge flow and product flow, flowmeters are available in the lines prior to the flow control needle valves. The flowmeters were used mainly to indicate significant changes in flow.

After the purge flow adjustment is completed, the product flow is adjusted in a similar manner. Here again the flow is measured at atmospheric pressure. After the product rate is set, the purge rate is also rechecked.

As mentioned above both of the flowrates are determined at atmospheric pressure. Knowing the pressures within the column, the flow within the columns may be calculated. Actually, prior to the start of a run the desired feed rate, high and low pressures and purge to feed ratio to be used are picked. From this inform—

ation the required flows at the given pressures can be calculatedby material balance as shown in the sample calculations.Then using pressure ratios the measured flowrates can be calculated. Setting both the purge and product flowrates (assuming no leaks) automatically sets the feed flow rate.

At this point the run is ready to be started. The beginning of the first half cycle starts when the flows are reversed for the first time. The reversing of the flows is controlled by an electrical circuit box with one switch which inputs power to the box and a second switch which selects between two circuits. Thus merely moving the position of one switch causes one column to change from low pressure purge to high pressure feed. and the other column to change from high pressure feed to low pressure purge.

From the start of the cycling, either the top product stream or the purge stream is directed to the gas chromatograph sampling valve. The other stream is vented to the atmosphere through the soap bubble flow measuring device so that the flow could be monitored during the run. The gas leaving the chromatograph sampling valve also vents to the atmosphere. During most of the runs the first two samples taken and the last samples were purge samples. The remainder of the samples ,generally taken every other half cycle were top product.samples. The samples were analyzed at the end of the half cycle, just before the cycle switch.

Data was taken for each experiment on log sheets. Prior to starting the run, the log sheet was made up with the half cycle numbers, the time for cycle switching, and the time for sample taking. The sample analysis, in terms of peak height, was also included in the data sheet. During the run the sample analysis was also plotted in terms of the ratio of sample analysis to feed analysis against half cycle number.

The half cycle time varied from run to run. At the end of each half cycle when the switch is made the following sequence of events occur. The regenerated low pressure column is quickly pressurized. Top product continues to flow at a constant rate and at constant pressure. The column which had been at high pressure must bleed down. Since the purge rate is low compared to the column volume, a significant amount of time (2-4min.) is required before the column reaches its equilibrium. While the depressurizing is occuring the purge flow rate increases but also the purge flow into the column stops. Since the top product rate is constant the feed rate must be different. At the cycle switch, first the feed rate increase quickly in order to pressurize the column and then the feed rate decreases to equal the top product rate until the depressurizing of the other column is complete. This cycle switching procedure is slightly different than that used in Shendalman and Mitchell[1]. Their procedure uses non-continuous top product removal. During repressuring and depressurizing their top product flow is stopped..

After the column conditions are reached and the desired cycle time is reached the columns are once again reversed. This is continued through 10-40 half cycles depending on the half cycle length and the degree of separation which has resulted. Plotting of the dataduring the run helps to if the separation efficiencyis decreasing. When the desired number of half cycles is completed or the separation levelled off or the top product composition decreased past the sensitivity of the chromatograph, the experiment is stopped, by shutting off the solenoid control device, stopping the feed, bleeding the gas out of the column and then closing all valves.

ANALYTICAL

Both top product and purge gas are analyzed by a gas chic
chromatograph. For any particular half cycle only one of
the streams should be analyzed to allow the transfer line
to be adequately purged out. By adjustment of valves either
top product gas, feed gas, or purge gas can be directed
toward the gas chromatograph. After the valves used for
controlling which gas goes to the chromatograph, the gas flows
through 1/8" copper tubing to the gas sampling valve.

Gas continuously flows from the system to the gas
sampling valve. The volume of gas collected in the gas sampling
valve can be changed by replacing the removable tubing used for
collecting. The gas flows continuously into and out of the sample
tube and through a valve to the atmosphere. While the gas is
feeding into the sample valve and out, a second gas stream, the
G.C. carrier gas Helium, is flowing into another section of the
sampling valve and then into the G.C. When the sample is ready to
go into the G.C. the internal shaft of the sampling valve is
moved so that the Helium is now directed through the sample
tube and into the GC. The Helium carrier gas is at 40 psia
and flows at 60 cc./min.

The gas chromatograph is an F&M model 810 equipped with
a Minneapolis Honeywell multispeed recorder. A 1/4"diameter
4 foot long copper column packed with poropak Q is used in the

chromatograph to separate the sample components. A thermal
conductivity detector was used for the analysis. Detector
current 175-185 milliamps was used. For the Helium CO_2 system
25°C was used for injection port, column and detector temperature..
For the ternary system Helium CO_2 C_3H_6 column temp.110°C
detector temp.150°C

Prior to operation of the apparatus, the gas chromatograph
is turned on and allowed 2-4 hours to warm up and for the temper-
atures to stabilize. When the GC is warmed up the carrier gas flow
is turned on, and then the detector current is turned on adjusted
and allowed to stabilize. The linearity of the GC analysis
can be checked by using feed gas and measuring the peak height
resulting from using a constant volume of sample out varying the
pressure.This is shown in Fig. 11.

The sample analyses made during the run were all done
at atmospheric pressure.

Results and Discussion

A total of nine gas separation runs were carried out. One binary mixture consisting of 98.95% helium and 1.05% carbon dioxide and one ternary mixture with 98% helium, 1% carbon dioxide and 1% propylene were used. Also, the breakthrough curves for the ternary helium-CO_2-C_3H_6 system at both 20 psia and 40 psia were determined.

A summary of the test conditions used is included in Table 1. In all cases the purge pressure was 20 psia. The feed pressure was either 40 or 60 psia. The purge to feed ratio varied from 1.2 to 2.2. For all of the binary system experiments the feed rate was 10 cc./minute. The half cycle time varied from 2 minutes to 20 minutes. Experimental results are summarized in Table 2.

The experiments were performed to study the effect of low flow rate on the separation of binary mixtures (Group A) and the effect of purge to feed ratio for the separation of ternary mixtures (Group B).

GROUP A

The experiments, numbers 1 through 7, all used feed rate of 10 cc./min. The reason for using the low flow rate was to insure that equilibrium is attained. At the same time in order to minimize the effect of axial diffusion, the columns used were 4 foot long 1" schedule 40 pipe (ID=.8 inches) as compared to the 1½" x 13" columns used by Wisnosky[2] and the 1½" x 24"

column used by Mitchell and Shendalman.[1]

The parameters studied in this group of experiments include the following:

(1) Half cycle time -Fig. 13, 14, 17

(2) Feed pressure- Fig. 15

(3) Adsorbent column height - Fig. 16

Half cycle time

Experiments one through five varied half cycle times between 4 minutes and 20 minutes. For all of these experiments the feed rate was 10 cc./min. at 60 psia feed pressure, 20 psia purge pressure, and the purge to feed ratio was 2.2. For these experiments,.before beginning the cycling, the columns were saturated by adding feed gas until the top product composition equals the feed composition and the purge composition equals the feed composition. Column 2 was saturated at 60 psia and column 1 was saturated at 20 psia. The starting concentration equals the feed or 1.05% CO_2.

The data from these runs are shown in Tables 3-7 and the results are plotted in Fig. 13 and Fig. 14.

Figure 13 shows the change of top product concentration as a function of the number of half cycles and at various half cycle times. The results are compared to the theoretical separation. The theoretical separation was calculated as shown in sample calculations Table C-3 using the expression derived by Shendalman.[3]

$$Y_n = Y_0 (P_L/P_H)^{(nK(1-\epsilon)/(\epsilon+K(1-\epsilon)))}$$

For $P_H{=}60$ psia and $P_L{=}20$ psia the concentration of the top product should drop to approximately one third per each half cycle and should approach 0 after a large number of cycles.

The data plotted in Fig. 13 as Log (Y_n/Y_0) versus the number of half cycles shows that increasing the half cycle time from 4 minutes to 20 minutes results in a large increase in the separation. For comparison purposes the concentration of CO_2(ppm) after 10 half cycles for each of the runs is listed in Table 2. After 10 half cycles, for 4 minutes and 20 minutes half cycle time, the values were 7350 ppm and 163 ppm respectively as compared to <20 ppm theoretical. This data was also correlated with the dynamic capacity

(cc. feed/cc. adsorbent), which is calculated from the feed rate(F), the half cycle time(θ), and the volume of packing(V_p) by $DC{=}F\theta/V_p$.

Figure 17 is a plot of Log Y_{10} versus dynamic capacity. The data from experiments 1 through 5 result in a straight line when correlated this way. If we were to extend this straight straight line it would indicate that the theoretical separation of <20 ppm would be obtained at dynamic capacity equal to .75. This seems too good to be true, particularly when we consider the results of Shendalman and Mitchell[1] in which at $\theta{=}2.16$, a dynamic capacity of 4.45 resulted in 9 ppm. Other results of Shendalman and Mitchell when plotted in a similar manner also indicate that increasing dynamic capacity improves separation, although the slope is not as great. By

comparing points at the same dynamic capacity but different half cycle time(thus different feed rate) we can see that decreasing the feed rate at the same dynamic capacity improves the separation by allowing longer time for equilibrium to be established.

Figure 14, a plot of $Log(Y_n/Y_o)$ versus half cycle time at various number of half cycles gives a more obvious effect of half cycle time. The data results in reasonably straight lines with slight curvature at low half cycle times. If we extend these lines to the $Y_n/Y_o=1$ line, we find that at approximately 2-3 minutes half cycle time we appear to get no separation. The cause of this is not obvious although there are some factors which may explain it. As mentioned in the process description, when using low flow rates as were used here, the depressurizing of the purge column is slow. During experiment 3 the purge pressure was recorded as a function of time and as shown in Fig. 12 approximately 6 minutes were required for the equilibrium to be obtained. During this time the flow to the purging column stops and therefore the feed to the high pressure column also decreases. For half cycle time less than the depressurizing time there will not be flow of top product gas into the purging column. Thus the column regeneration is limited only to the the amount removed by the depressurizing which will be replaced on repressuring. The ability of this process to continually improve the quality

of the overhead product is dependent primarily on the top
product gas being used to regenerate the upper part of the
column to a lower level of adsorbed component during each
cycle. Thus if the blowdown time does not allow top product
flow into the purge column separation would not be effective.

Pressurizing gas

Another aspect which affects the separation when using
the low flow rate is the fact that at low half cycle times
the gas added to the column by the repressuring makes up
a large percentage of the gas added during the half cycle.
The moles of gas in the column can be calculated by gas law
by $N_p = PV_p \epsilon / RT$. By calculating this for both the feed and
purge pressure we can determine the amount added by press-
urizing or removed by depressurizing. Table 14 shows the
moles of gas input by pressurizing and the moles of gas
fed during various length half cycles. The moles of gas
fed during the half cycle also should be decreased because
of the decreased feed while the purge column is depressurizing.
Based on the above considerations the total moles of flow in
and out of the columns are calculated and shown in Table 15A
(based on 6 minutes blowdown time) and in Table 15B(based on 3
minutes blowdown time). For half cycle time less than ten
minutes(with feed at 10 cc./min.) greater than 50% of the
entering gas is from pressurizing. When such a large portion

of the gas entering and leaving the column is from pressurizing and blowdown the validity of the purge to feed ratio is questionable.

Purge to feed ratio

For experiments 1 to 5 the desired purge to feed ratio was 2.2. Tables 15A and 15B show purge to feed ratios calculated in different ways based on the total flows into and out of the columns. If we discount the pressurizing and blowdown then the actual values range from 0 to 2.0 (assuming 6 minutes blowdown) or 1.4 to 2.1 (assuming 3 minutes blowdown). If we include the pressurizing and blowdown gas then the purge to feed ratio has a range between 2.4 and 2.8.

It has been shown by Shendalman, Mitchell, and others that based on material balance and under equilibrium conditions, that is with n large and $Y_{TP} \to 0$ then the concentration of adsorbed component in the purge gas can be represented by the following:

$$Y_{BP} = \frac{1}{d} (P_H/P_L) \, Y_o$$

This was used to calculate values for $(Y/Y_o)_{BP}$ for each of the purge to feed ratios found in Table 15A and 15B. These values are shown in Table 16 along with the actual measured values of $(Y/Y_o)_{BP}$. For experiments 1 to 5 these data show that for half cycle time less than 10 minutes the calculation which includes the pressurizing gas and blowdown gas gives the best agreement with the actual measured values.

For half cycle time 10 minutes and larger, the σ calculation
which ignores the pressurizing and blowdown gas is better, in
particular the one which uses 3 minutes as the blowdown time.
It is logical that as the half cycle time increases the effect
of the pressurizing and blowdown decreases.

Feed pressure effect

Experiment 6 was used to study the effect of using lower
pressure feed. This run is shown in Table 8 and the results
are compared to experiment 5 in Figure 15. Both run 5 and
run 6 used 20 minute half cycles and feed rate of 10 cc./min.
Run 5 used σ=2.2 but since σ cannot exceed P_H/P_L therefore
for run 6 in which P_H=40 psia and P_L=20 psia, σ would have to
be less than 2. It was therefore decided to adjust σ so that
the same percentage of the feed would be purged in each case.
As would be expected the separation at the lower pressure
was poorer. After 10 half cycles run 5 had only 163 ppm CO_2
whereas run 6 had 2573 ppm CO_2 and run 6 seemed to be leveling
off after 20 half cycles. Also, the purge gas concentration
was slightly lower for run 6 than for run 5. If we compare
the actual separation with the theoretical separation for
both run 5 and run 6 at equal theoretical separation(such as
at (Y/Y_0)theoretical=.1) for run 5 Y/Y_0=.3 while for run 6
Y/Y_0=.48. The larger deviation of run 6 from theoretical
could be due to the lower purge to feed ratio even though
the percent purged was the same because the purge penetration
would be lower.

Adsorbent column height

Run 7 was identical to run 3 except that half of the
silica gel was removed from each column. This experiment
is shown in Table 9 and the results are compared to run 3
and run 5 in Fig. 16. Run 7 uses the same feed rate of
10 cc./min., pressures P_H=60 psia and P_L=20 psia, and purge
to feed ratio 2.2 as runs 1 to 5. We can compare it to run 3
because it uses the same half cycle time(10 minutes), and we
compare it to run 5 because based on the silica gel in the
column it uses the same dynamic capacity as run 5. The figure
shows the separation to be considerably poorer than run 5 and
slightly poorer than run 3. Obviously,.the top half of each
column, being empty, doesn't cause any separation, in fact it
could decrease the separation. The empty space in the column
increases greatly the amount of gas that enters the column
during repressurizing, thus bringing back the problems involved
with short cycle times. Even if we were to use a filled column
half the size we would still have to expect a separation not
as good as run 5, even though the dynamic capacity was the same,
because using the 10 minute half cycle and the same flow rate
the percentage of the feed which is from repressurizing is based
on the ten minute half cycle of run 3 rather than the twenty
minute half cycle of run 5 and also the feed rate per unit
volume of adsorbent is higher.

Group B

In order to quickly study the separation of ternary mixtures as helium-CO_2-C_3H_6, the following things were done.

(1)Breakthrough curves

      (a) CO_2-C_3H_6 at   20 psia   Fig. 18 Table 13

      (b) CO_2-C_3H_6 at   40 psia   Fig. 19 Table 12

(2) Silica gel capacity for CO_2-C_3H_6 at 20 psia and 40 psia

      Fig. 20, Table 17 and 18

(3) Ternary separations run 8 and run 9

      Fig. 21, Table 10 and 11

Figure 18 and 19 show top product analyses which were measured while helium with 1% CO_2 and 1% C_3H_6 is being fed at approx. 334 cc./min. to one silica gel filled column. Prior to running the breakthrough curves in each case, the silica gel was removed from the columns, dried overnight at 110C, and returned to the columns. By knowing that the column is initially empty, and knowing the feed rate and composition and keeping track of the off gas analysis with time it was possible to determine the amount left in the column by material balance. The values of the amount removed from the column are indicated by the peak height and shown in Fig.18 and 19. It was noticed that during the column saturation first a peak was seen for carbon dioxide which initially grew to the size of the corresponding peak in the feed, and then as propylene continued to adsorb the size of the CO_2 peak became larger than the feed indicating that more was

being removed from the column than was being added. Once the
column was saturated with C_3H_6, the exit CO_2 peak decreased back
to the feed composition. Apparently, as propylene is added to
a column saturated with carbon dioxide, the propylene displaces
the carbon dioxide from the silica gel. The saturating of the
column at feed rate of 334 cc./min. required 29 and 32 minutes
to saturate the column with CO_2 at 20psia and 40psia respectively,
while it required 290 and 300 minutes to saturate it with C_3H_6.
The moles of gas added to the column were calculated for each
gas and each pressure and the results plotted versus time are
shown in Fig. 20. The carbon dioxide at first adsorbs to a
high level and then desorbs to a lower equilibrium level as
propylene displaces.it. At 20 psia .0038 moles of CO_2 and
.053 moles of C_3H_6 adsorb on 393.4 cc of silica gel. At 40
psia .0076 moles of CO_2 and .109 moles of C_3H_6 adsorb on
393.4 cc. of silica gel.

Ternary gas separations

Two ternary separations were done in runs 8 and 9 which are
shown in Table 10 and 11 and Figure 21. Each run used feed gas
consisting of 1% CO_2 and 1% C_3H_6 in helium at 340 cc./min. at
40 psia with purge at 20 psia. The half cycle time for each
run was 2 minutes. This corresponds to dynamic capacity=1.73.
The difference between runs 8 and 9 is that for run 8 both
columns were saturated at 40 psia while for run 9 one column
was saturated at 40 psia and the other column was saturated
at 20 psia. Also, run 8 used ϑ=1.5 and run 9 used ϑ=1.2.

Run 9 which had a purge to feed ratio of 1.2 and pressures of
40 psia and 20 psia gave a better separation for CO_2 than run
5 which used higher purge to feed ratio 2.2 and higher pressure
60 psia. We would usually expect the higher pressure and higher
purge to feed ratio to give a better separation, however, runs
8 and 9 used larger dynamic capacity than the previous runs
which probably accounts for the better results. Run 8 also gave
CO_2 separation results as good as run 5 and parallel to the
separation of run 9. The curve for CO_2 separation in run 8 is
shifted one half cycle due to having both columns saturated at
40 psia. For both run 8 and run 9 the carbon dioxide is re-
moved more effectively than the propylene. This was at first
surprizing in view of the higher adsorbtion of C_3H_6 on silica
gel as compared to CO_2 on silica gel as shown by the column
saturation curves of Fig. 20. If we compare the relative
driving force for separation for CO_2 and C_3H_6 as indicated by
the difference in the saturation at high and low pressures
divided by the average saturation at high and low pressure
we find that for the equilibrium situation this value is the
same for both CO_2 and C_3H_6. This should tend to give similar
separation for both the CO_2 and C_3H_6. However, using the two
minute half cycles equilibrium is probably not obtained. If
we consider the greater affinity of propylene for silica gel
which causes it to actually displace CO_2 from the silica gel
we can probably assume that it may take longer time for the
C_3H_6 to desorb than for the CO_2. Thus the deviation from

equilibrium would have a greater affect on the C_3H_6 than the CO_2 purging.resulting in the better separation for the CO_2. The fact that by decreasing the purge to feed ratio between run 8 and run 9 resulted in the separation between CO_2 and C_3H_6 coming closer together would seem to support this because it would decrease the magnitude of the purge effect. From we may suspect that by using lower flow rates to allow more time for equilibrium the relative separation will become equal or possibly favor C_3H_6. Also, by increasing the purge to feed ratio at the high feed rate the separation between CO_2 and C_3H_6 would increase.

CONCLUSION

For the system CO_2 in He using silica gel adsorbent
a high degree of separation is possible. The experimental
data show that when using very low feed rate (10 cc./min.)
with high purge to feed ratio the degree of separation is
improved significantly by increasing the half cycle time in
order to increase the dynamic capacity or penetration length.
Increasing the half cycle time from 4 minutes to 20 minutes
caused a drastic improvement in the separation. The separation
after 10 half cycles when plotted versus dynamic capacity
resulted in a straight line. Comparing this line to the data
of Shendalman and Mitchell(at higher feed rate and higher
dynamic capacity) we can deduce that by increasing the dynamic
capacity(increasing half cycle time) we could approach the
theoretical separation, apparently due to the lower flow rate
used.

At very low dynamic capacity the increase in the separation
with increase in dynamic capacity is large, essentially due to
the effect which pressurizing exerts(at 4 min. half cycle the
pressurizing accounted for 90% of the gas entering the column).
Considering the purge gas analysis as compared to the theoretical
purge gas analysis, we see that for half cycle times less than
ten minutes(at 10 cc./min. feed rate), the purge to feed rate
should be calculated by including the pressurizing gas and blow-
down gas.

Compared at the same 20 minute half cycle time and at
the same percentage purge, lower feed pressure resulted in
lower separation efficiency, as expected.

Use of an adsorbtion column only half filled with
silica gel resulted in a decreased separation efficiency due
to the increased volume of gas added during repressurizing.

Adsorbtion of carbon dioxide and propylene on silica
gel at 20 psia and 40 psia shows that CO_2 adsorbs to one value
and then while C_3H_6 continues to adsorb the CO_2 desorb until
the silica gel becomes saturated with C_3H_6 and then the CO_2
levels off also. Silica gel adsorbs approximately 14 times
more C_3H_6 than CO_2. When operating the column cyclicly at
340 cc./min. feed, 2 minute half cycle and purge to feed
ratio 1.2-1.5 the CO_2 is removed more readily than the C_3H_6
even though more of the C_3H_6 can adsorb. At the high flow
rates used in these experiments it is possible that the C_3H_6
does not desorb quickly enough thus leaving less cites available
for adsorbtion during the next half cycle. Separation between
CO_2 and C_3H_6 is greater at $\phi=1.5$ than at $\phi=1.2$.

Some further experiments which would be helpful in
extending this data include larger cycle times at low flow rate
for the helium-carbon dioxide system. Also, experiments on the
ternary $He-CO_2-C_3H_6$ should include more values of ϕ and also
use of lower feed rates

TABLE 1

SUMMARY OF CONDITIONS

Exp.#	System	Purge to Feed Ratio	Pressure P_H	P_L	$\frac{1}{2}$ cycle Time (min.)	Flow Rates (cc/min.) Feed @P_H	Product @P_H	Purge @P_L
1	98.95%He 1.05%CO_2	2.2	60	20	4	10	2.67	22
2	"	2.2	60	20	6	10	2.67	22
3	"	2.2	60	20	10	10	2.67	22
4	"	2.2	60	20	8	10	2.67	22
5	"	2.2	60	20	20	10	2.67	22
6	"	1.47	40	20	20	10	2.65	14.7
7*	"	2.2	60	20	10	10	2.67	22
8**	98%He 1%CO_2 1%C_3H_6	1.5	40	20	2	340	85	510
9	"	1.2	40	20	2	340	136	408

* This run was made with the columns only half filled with silica gel.

** For this run both columns were saturated at the feed pressure; for all other runs one column was saturated at the feed pressure and the other column was saturated at the purge pressure.

TABLE 2

SUMMARY OF RESULTS

Exp. #	δ	P_H[**]	$\frac{1}{2}$cycle time (min)	Dynamic capacity	ppm CO_2 at 10th half cycle	$\frac{Y_{BP}}{Y_0}$ CO_2	ppm C_3H_6 at 10th half cycle	$\frac{Y_{BP}}{Y_0}$ C_3H_6
1	2.2	60	4	.109	7350	1.1		
2	2.2	60	6	.153	4620	1.22		
3	2.2	60	10	.254	1680	1.45		
4	2.2	60	8	.203	2730	1.31		
5	2.2	60	20	.508	163	1.57		
6	1.47	40	20	.508	2573	1.47		
7	2.2	60	10	.508*	1785	1.36		
8	1.5	40	2	1.73	160	1.915	1160	1.95
9	1.2	40	2	1.73	100	1.404	400	1.667

*Based on packed portion of column only— half of the column was empty.

** P_L= 20 psia

TABLE 3

EXPERIMENTAL RESULTS OF RUN NO. 1

Conditions

P_H= 60 psia $\qquad$ P_L= 20 psia

σ =2.2 $\qquad$ half cycle time =4 min.

Feed 10 cc./min. @ 60 psia $\qquad$ Y_0= 1.05 % CO_2

n	Y_{TP}/Y_0	Y_{BP}/Y_0
4	.88	
8		1.03
12	.664	
16	.522	
20	.448	
24		1.089
28		1.104
30	.373	
34	.313	

Equipment

2 4 foot columns each filled with 393 cc of silica gel

column 1 saturated at 20 psia

column 2 saturated at 60 psia

TABLE 4

EXPERIMENTAL RESULTS OF RUN NO. 2

Conditions

P_H= 60 psia P_L= 20 psia

γ =2.2   half cycle time =6 min.

Feed 10 cc./min..@ 60 psia Y_0= 1.05% CO_2

n	Y_{TP}/Y_0	Y_{BP}/Y_0
2	.766	
4	.586	
6		1.125
8		1.148
10	.461	
12	.394	
16	.352	
18		1.211
20		1.211
22	.336	
24	.319	
26	.308	
30	.281	
32	.269	
34	.266	
36		1.234

Equipment

   2   4 foot columns each filled with 393 cc of silica gel

       column 1 saturated at 20 psia

       column 2 saturated at 60 psia

TABLE 5

EXPERIMENTAL RESULTS FOR RUN NO. 3

Conditions

P_H= 60 psia P_L= 20 psia

∂ =2.2   half cycle time = 10 min.

Feed 10 cc./min. @ 60 psia Y_o= 1.05 % CO_2

n	Y_{TP}/Y_o	Y_{BP}/Y_o
2	.585	
4	.359	
8		1.45
10	.156	
12	.125	
14	.106	
16	.0905	
18		1.48
20	.076	
26	.052	
30	.045	
34	.0367	
38	.0347	
40	.0318	
42	.0312	
46		1.45

Equipment

2   4 foot columns each filled with 393 cc of silica gel

column 1 saturated at 20 psia

column 2 saturated at 60 psia

TABLE 6

EXPERIMENTAL RESULTS OF RUN NO. 4

Conditions

P_H= 60 psia $\qquad\qquad$ P_L= 20 psia

α=2.2 $\qquad\qquad$ half cycle time= 8 min.

Feed 10 cc./min. @ 60 psia $\quad$ Y_0= 1.05 % CO_2

n	Y_{TP}/Y_0	Y_{BP}/Y_0
4	.426	
6		1.235
8		1.265
10	.266	
12	.226	
14		1.31
16	.20	
18	.162	
20		1.31
22	.156	
24	.132	
26	.122	
28	.114	
30	.111	
32		1.29

Equipment

2 $\quad$ 4 foot columns each filled with 393 cc of silica gel

$\qquad$ column 1 saturated at 20 psia

$\qquad$ column 2 saturated at 60 psia

TABLE 7

EXPERIMENTAL RESULTS OF RUN NO. 5

Conditions

P_H= 60 psia P_L= 20 psia

σ=2.2   half cycle time= 20 min.

Feed 10 cc./min/ @ 60 psia Y_O= 1.05 % CO_2

n	Y_{TP}/Y_O	Y_{BP}/Y_O
2	.34	
4	.13	
6	.052	
8	.027	
10	.0155	
12	.0105	
14	.0064	
16	.0044	
18	.0031	
20	.0022	
22	.00165	
24	.00115	
26		1.57

Equipment

2 4 foot columns each filled with 393 cc of silica gel

column 1 saturated at 20 psia

column 2 saturated at 60 psia

TABLE 8

EXPERIMENTAL RESULTS OF RUN NO. 6

Conditions

P_H = 40 psia P_L = 20 psia

α = 1.47   half cycle time = 20 min.

Feed 10 cc./min. @ 40 psia Y_0 = 1.05 % CO_2

n	Y_{TP}/Y_0	Y_{BP}/Y_0
1		1.47
3	.425	
5	.33	
7	.29	
9	.262	
11	.225	
13	.189	
15	.13	
17	.12	
19	.105	

Equipment

2   4 foot columns each filled with 393 cc of silica gel

column 1 saturated at 20 psia

column 2 saturated at 40 psia

TABLE 9

EXPERIMENTAL RESULTS OF RUN NO. 7

Conditions

P_H=60 psia P_L= 20 psia

α =2.2   half   half cycle time= 20 min.

Feed 10 cc./min. @ 60 psia Y_o=1.05 % CO_2

n	Y_{TP}/Y_o	Y_{BP}/Y_o
2		1.36
4	.328	
6	.26	
8	.187	
12	.164	
14	.164	

Equipment

2 4 foot columns each half filled with 200 cc of silica gel

column 1 saturated at 20 psia

column 2 saturated at 60 psia

TABLE 10

EXPERIMENTAL RESULTS OF RUN NO. 8

Conditions

P_H= 40 psia $\qquad$ P_L= 20 psia

σ =1.5 $\qquad$ half cycle time= 2 min.

Feed 340 cc./min. @ 40 psia $\qquad$ Y_o=1 % CO_2
$\qquad$ 1 % C_3H_6

n	CO_2 Y_{TP}/Y_o	Y_{BP}/Y_o	C_3H_6 Y_{TP}/Y_o	Y_{BP}/Y_o
2	.54		.57	
6	.0745		.214	
10	.0159		.116	
14	.0053		.0677	
18	.0026		.0447	
22		1.915		1.95
24		1.915		1.95
36			.012	

Equipment

2 $\quad$ 4 foot columns each filled with 393 cc pf silica gel

column 1 saturated at 40 psia

column 2 saturated at 40 psia

TABLE 11

EXPERIMENTAL RESULTS OF RUN NO. 9

Conditions

P_H= 40 psia P_L= 20 psia

δ =1.2   half cycle time= 2 min.

Feed 340 cc./min. @ 40 psia Y_o= 1 % CO_2
                                       1 % C_3H_6

n	CO_2		C_3H_6	
	Y_{TP}/Y_o	Y_{BP}/Y_o	Y_{TP}/Y_o	Y_{BP}/Y_o
4	.106		.208	
6	.032		.135	
12	.0053		.0208	
14	.0033		.0182	
28		1.404		1.667
32		1.404		1.667

Equipment

    2   4 foot columns each filled with 393 cc of silica gel

        column 1 saturated at 20 psia

        column 2 saturated at 40 psia

TABLE 12

COLUMN SATURATION WITH CO_2 AND C_3H_6 AT 40 PSIA

Feed to 1 column 48" filled with silica gel at $20^{\circ}C$
Feed flow 334 cc./min. at 40 psia

Time (min)	Moles CO_2 Input	Moles CO_2 Output	Moles CO_2 in column	Moles C_3H_6 Input	Moles C_3H_6 Output	Moles C_3H_6 in column
32	.012090	0	.012090	.012090	0	.012090
35	.013223	.000057	.013167	.013223	0	.013223
37	.013979	.000650	.013329	.013979	0	.013979
39	.014735	.001043	.013692	.014735	0	.014735
41	.015490	.001651	.013839	.015490	0	.015490
45	.017001	.003109	.013892	.017001	0	.017001
50	.018890	.005055	.013835	.018890	0	.018890
70	.026447	.012913	.013533	.026447	0	.026447
90	.034003	.020847	.013155	.034003	0	.034003
110	.041559	.028895	.012664	.041559	0	.041559
120	.045337	.032956	.012381	.045337	0	.045337
260	.098230	.090081	.008149	.098230	0	.098230
270	.102008	.094123	.007885	.102008	0	.102008
280	.105786	.098052	.007734	.105786	0	.105786
290	.109564	.101868	.007696	.109564	.001259	.108305
295	.111453	.103757	.007696	.111453	.002699	.108754
300	.113342	.105646	.007696	.113342	.004385	.108957
305	.115231	.107535	.007696	.115231	.006162	.109069
315	.119009	.111313	.007696	.119009	.009805	.109159
320	.120898	.113202	.007696	.120898	.011739	.109159

TABLE IV

COLUMN SATURATION WITH CO_2 AND C_3H_6 AT 20 PSIA

Feed to 1 column 48" filled with silica gel at $20^\circ C$
Feed flow 334 cc/min at 20 psia

Time (min)	Moles CO_2 Input	Moles CO_2 Output	Moles CO_2 in column	Moles C_3H_6 Input	Moles C_3H_6 Output	Moles C_3H_6 in column
29	.005478	0	.005478	.005478	0	.005478
31	.005856	.000017	.005839	.005856	0	.005856
33	.006234	.000091	.006142	.006234	0	.006234
35	.006612	.000280	.006332	.006612	0	.006612
37	.006989	.000582	.006407	.006989	0	.006989
39	.007367	.000938	.006429	.007367	0	.007367
41	.007745	.001309	.006436	.007745	0	.007745
50	.009445	.003033	.006412	.009445	0	.009445
60	.011334	.004990	.006344	.011334	0	.011334
80	.015112	.008919	.006192	.015112	0	.015112
100	.018890	.012849	.006041	.018890	0	.018890
120	.022668	.016778	.005890	.022668	0	.022668
140	.026446	.020707	.005739	.026446	0	.026446
160	.030224	.024637	.005588	.030224	0	.030224
170	.032114	.026639	.005474	.032114	0	.032114
180	.034003	.028679	.005323	.034003	0	.034003
260	.049115	.045000	.004114	.049115	0	.049115
270	.051004	.047022	.003982	.051004	0	.051004
275	.051948	.048018	.003930	.051948	0	.051948
280	.052893	.049005	.003888	.052893	.000106	.052787
285	.053837	.049983	.003855	.053837	.000600	.053237
290	.054782	.050951	.003831	.054782	.001457	.053325
300	.056671	.052859	.003812	.056671	.003337	.053333
310	.058560	.054748	.003812	.058560	.005226	.053333

TABLE 14

GAS CAPACITIES OF COLUMNS AND FLOWS

MOLES OF GAS IN EACH COLUMN

At 60 psia	.02537	
At 40 psia	.01691	.01691
At 20 psia	.00846	.00845

MOLES OF GAS FED AT 10 cc./min. PER HALF CYCLE

Pressure= 60 psia   F= 0.00168 mole/min.

Pressure= 40 psia . F= 0.00113 mole/min.

Half cycle time(min.)	Moles of gas fed	
	at 60 psia	at 40 psia
4	0.00672	0.00452
6	0.01008	0.00678
8	0.01344	0.00904
10	0.01680	0.0113
12	0.02016	0.01356
20	0.0336	0.0226

Moles of gas fed at 340 cc./min.

2 min half cycle   40 psia   0.07684moles

TABLE 15A

REPRESSURIZATION & FEEDING

Exp. #	Moles fed repressure	Moles fed during** blowdown F_B	Moles fed after blowdown F_{AB}	Total moles fed F_T	% of total feed from repressuring
1	.01691	.00179	0	.01870	90.4
2	.01691	.00269	0	.01960	86.3
3	.01691	.00269	.00672	.02632	64.2
4	.01691	.00269	.00336	.02296	73.6
5	.01691	.00269	.02352	.02312	39.2
6	.00845	.0018	.01582	.02607	32.4
7***	.04606	.00269	.00672	.05547	83.0
8	.00845		.07684	.08529	9.9
9	.00845		.07684	.08529	9.9

BLOWDOWN AND PURGING

Exp. #	Moles blowdown	Moles purge after blowdown W_{AB}	Total moles out purge stream W_T	Purge* / Feed	Purge*+ / feed
1	.01691		.01691	0	2.71
2	.01691		.01691	0	2.59
3	.01691	.00492	.02183	1.568	2.49
4	.01691	.00246	.01937	1.219	2.53
5	.01691	.01724	.03415	1.973	2.37
6	.00845	.01163	.02008	1.32	1.54
7	.04606	.00492	.05098	1.568	2.76
8	.00845	.05768	.06613	1.501	1.55
9	.00845	.04615	.05460	1.201	1.28

* and *+ see calculations   **blowdown time 6 minutes
***only half of the column contained adsorbent

TABLE 15B

REPRESSURIZATION & FEEDING

Exp. #	Moles fed repressure	Moles fed during blowdown F_B	Moles fed after blowdown F_{AB}	Total moles fed F_T	% of total feed from repressuring
1	.01691	.000895	.00168	.019485	86.8
2	.01691	.001345	.00504	.023295	72.6
3	.01691	.001345	.01176	.030015	56.3
4	.01691	.001345	.0084	.026655	63.4
5	.01691	.001345	.02856	.046815	36.1
6	.00845	.0009	.01921	.02856	29.5
7***	.04606	.001345	.01176	.059165	77.8
8	.00845	.	.07684	.08529	9.9
9	.00845		.07684	.08529	9.9

BLOWDOWN & PURGING

Exp. #	Moles blowdown	Moles purge after blowdown W_{AB}	Total moles out purge stream W_T	$\dfrac{\text{Purge*}}{\text{feed}}$	$\dfrac{\text{Purge*+}}{\text{feed}}$
1	.01691	.00123	.01814	1.432	2.79
2	.01691	.00369	.0206	1.734	2.65
3	.01691	.00862	.02553	1.973	2.55
4	.01691	.00616	.02307	1.896	2.60
5	.01691	.02093	.03784	2.099	2.42
6	.00845	.01412	.02257	1.404	1.58
7	.04606	.00862	.05468	1.973	2.77
8	.00845	.05768	.06613	1.501	1.55
9	.00845	.04615	.0546	1.201	1.28

*and *+ see calculations   **blowdown time 3 minutes
*** only half of the column contained adsorbent

TABLE 16

PURGE/FEED RATIO AND BOTTOM PRODUCT CONCENTRATION

Exp.	Planned	P_H	P_L	σ_A	Y_B/Y_o*	σ_B	Y_B/Y_o*	σ_C	Y_B/Y_o*	Actual Y_B/Y_o
1	2.2	60	20			1.43	2.09	2.71	1.1	1.1
2	2.2	60	20			1.73	1.73	2.59	1.16	1.22
3	2.2	60	20	1.57	1.91	1.97	1.52	2.49	1.20	1.45
4	2.2	60	20	1.22	2.46	1.90	1.58	2.53	1.18	1.31
5	2.2	60	20	1.97	1.52	2.10	1.43	2.37	1.26	1.57
6	1.47	40	20	1.32	1.52	1.40	1.42	1.54	1.30	1.47
7	2.2	60	20	1.57	1.91	1.97	1.52	2.76	1.09	1.36

* Calculation from $Y_{BP}/Y_o = (1/\sigma) \times (P_H/P_L)$

σ_A Purge/feed ratio based on moles of purge after blowdown and moles fed after pressuring. Table 15A

σ_B Purge/feed ratio based on moles purge after blowdown and moles fed after pressuring. Table 15B

σ_C Purge/feed ratio based on total purge and total feed

Figure 1   Experimental Apparatus

Gas Parametric Pump

Parameter Cycles

51

Fig. 2

Pressure

60

40

20

5 10 15 20 25 30 35 40 45 50 55 60

Fig. 3

Feed Flow

25

20

15

10

5

Fig. 4

Purge Flow from Column

20

15

10

5

Fig. 5

Purge Flow into Column

10

5

Fig. 6

Q

1   2
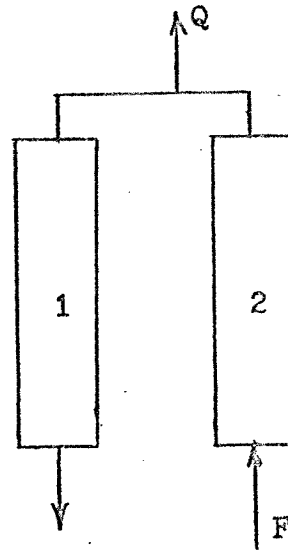
F   W

Fig. 7

Q

1   2

F

Fig. 8

Q

1   2

W   F

Fig. 9

Q

1   2

F
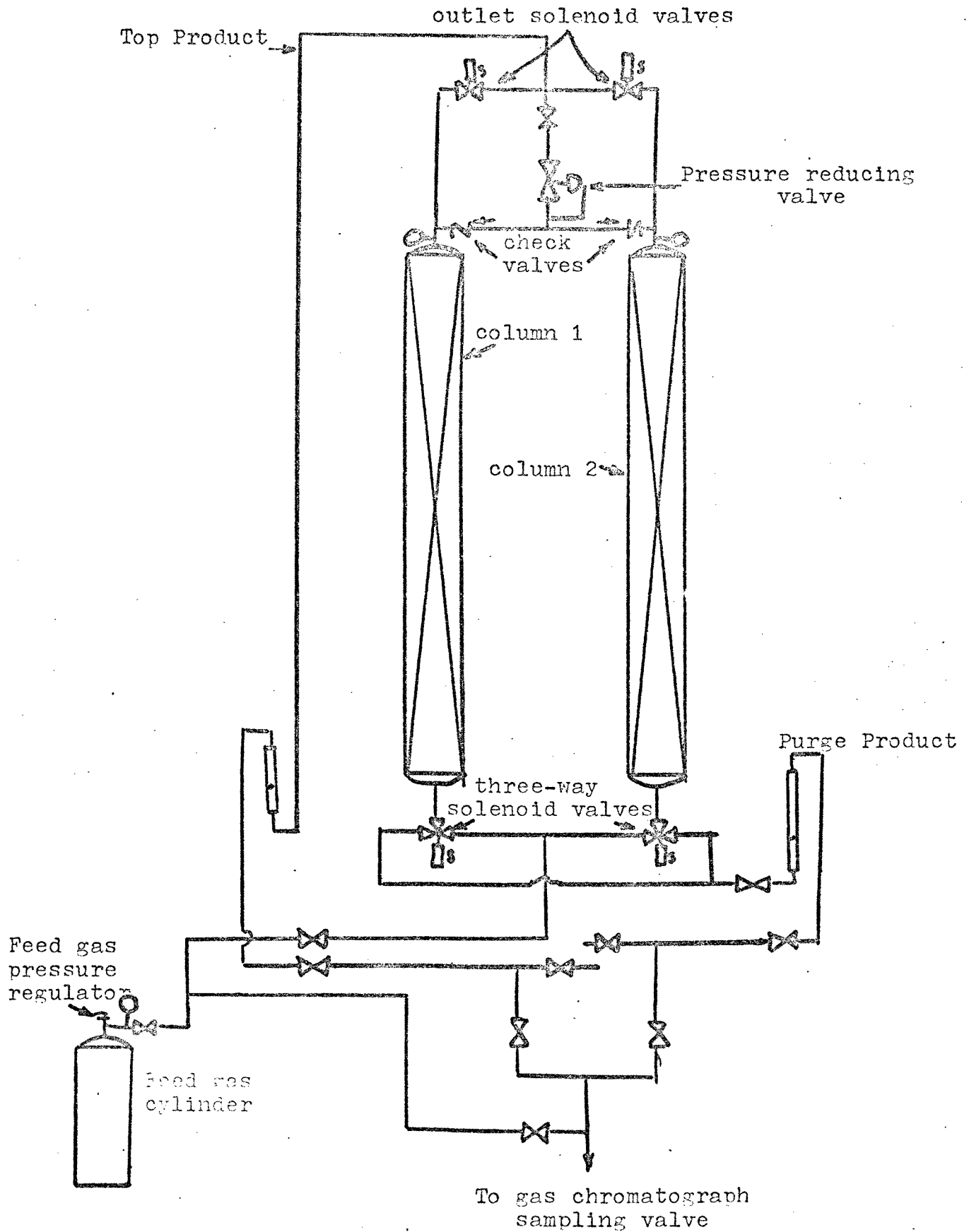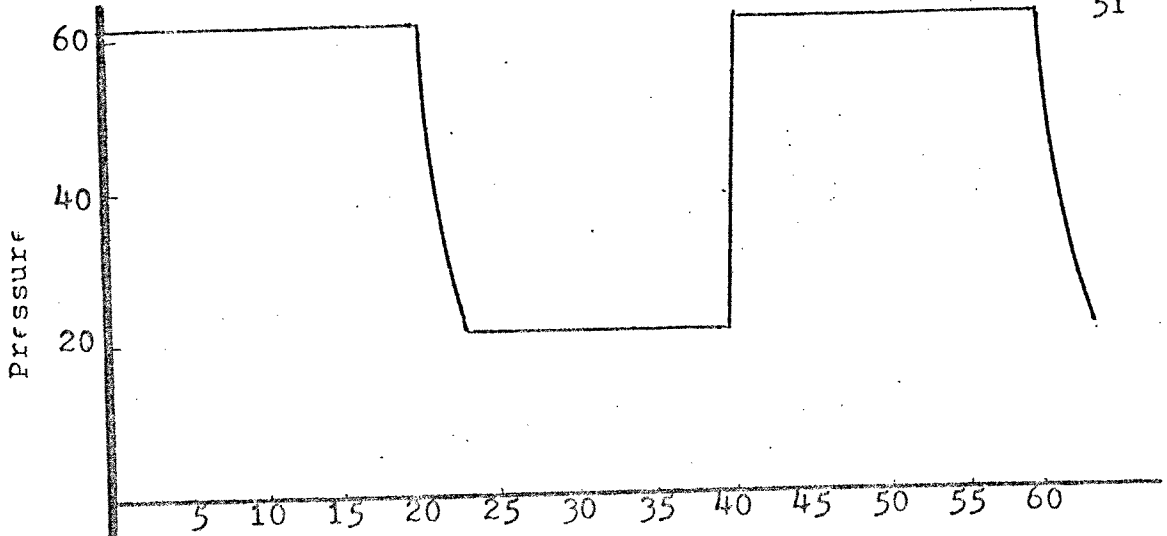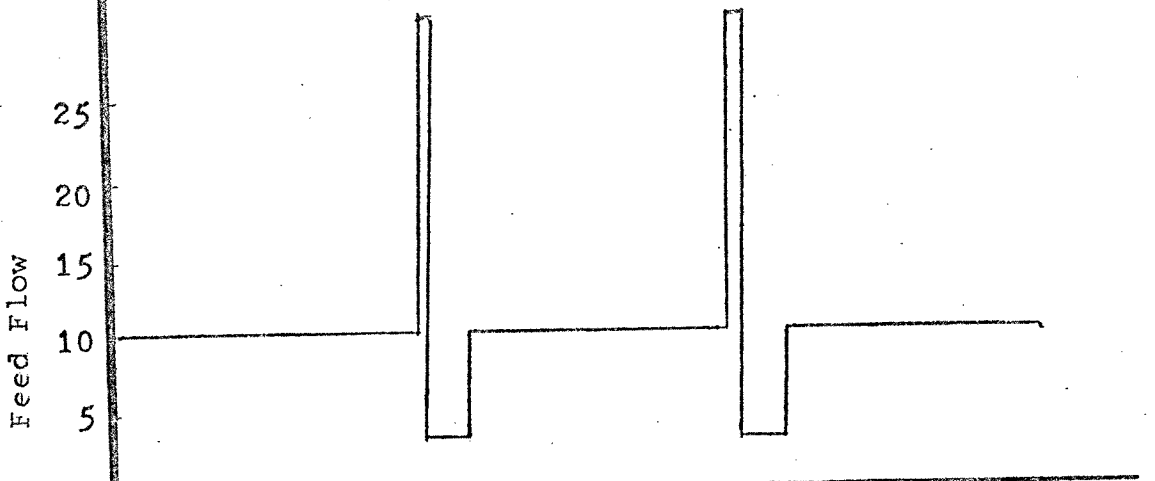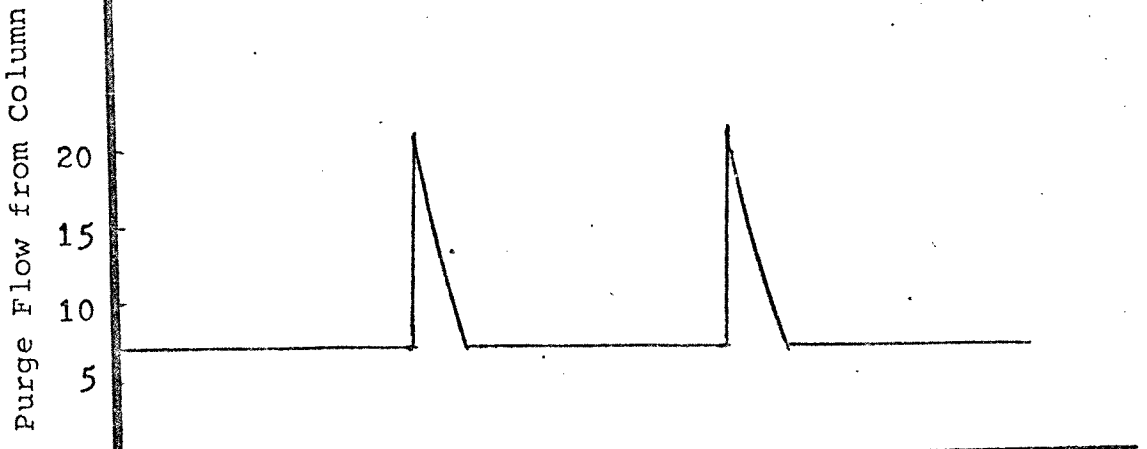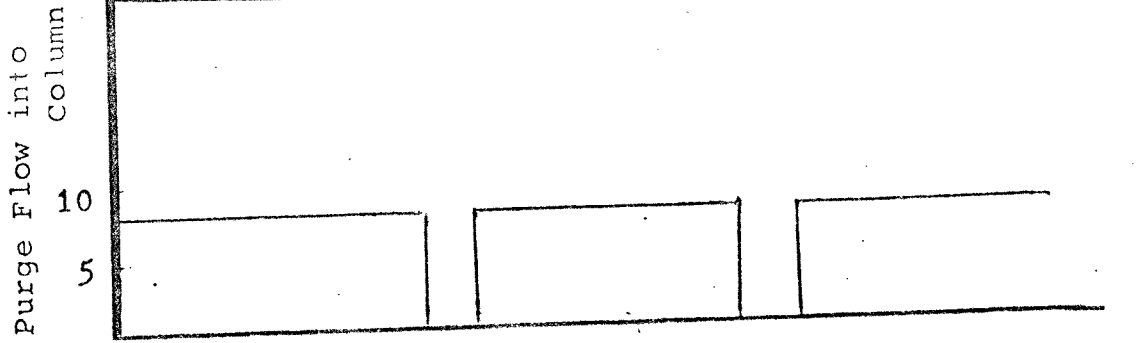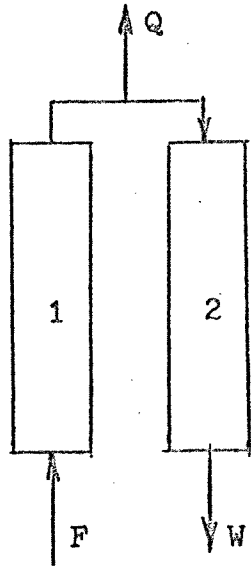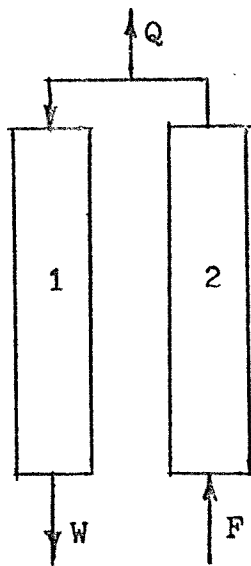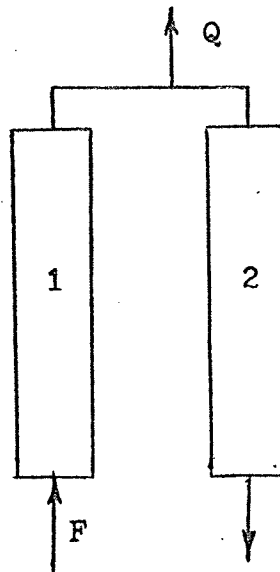
Figure 10

Solenoid Valve Control
Switching Device
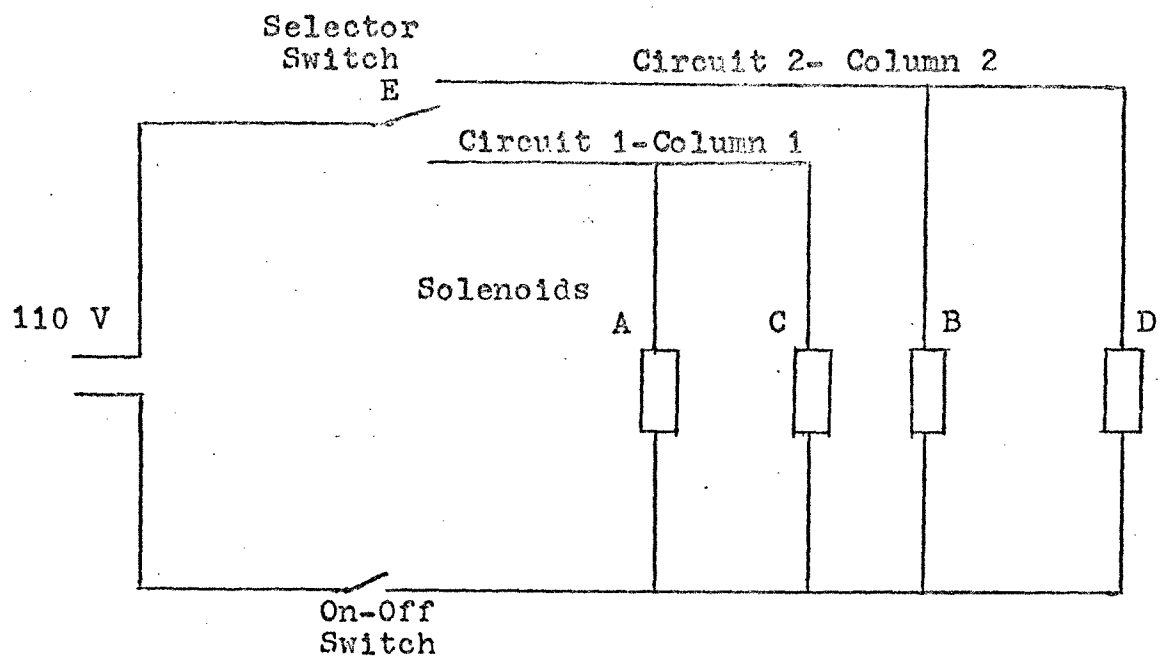
When circuit 1 is activated column 1 is purging.

When circuit 2 is activated column 2 is purging.

Figure 11   Linearity of G. C. Responce

Figure 11   Linearity of G. C. Responce

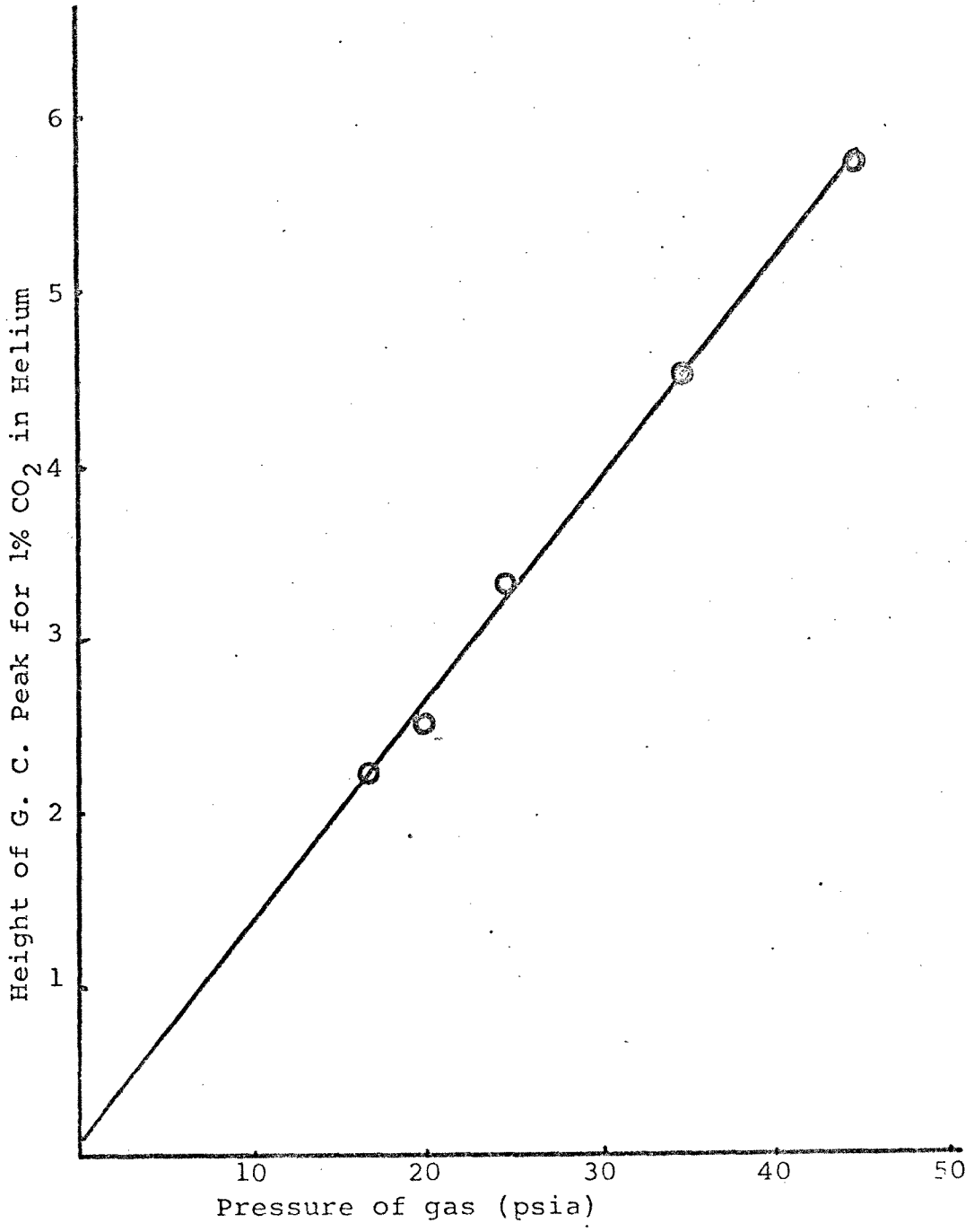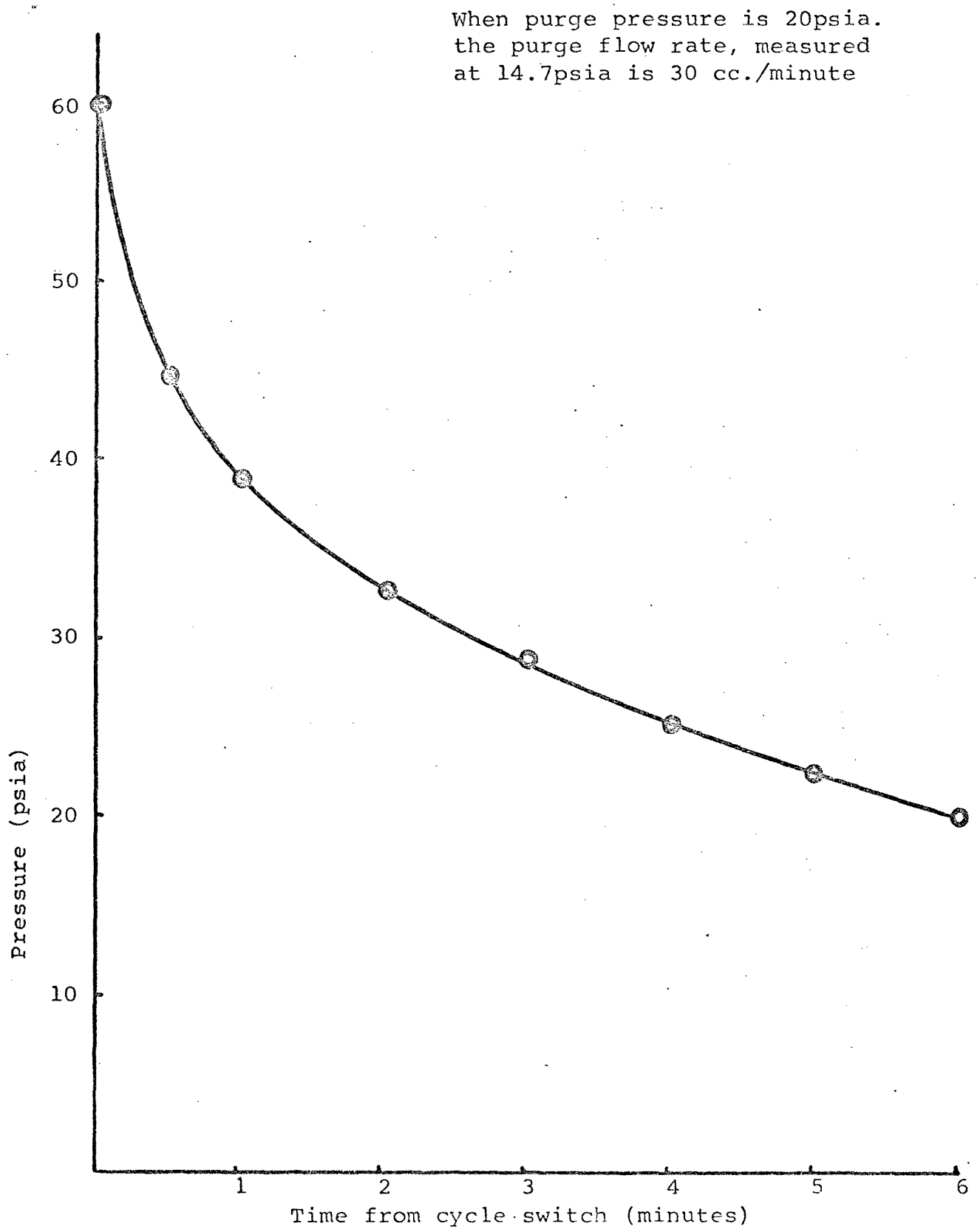Figure 12   Purge Pressure vs. Time

When purge pressure is 20psia.
the purge flow rate, measured
at 14.7psia is 30 cc./minute

Figure 13 Separation vs. Number of Half Cycles

Feed rate 10 cc./min. @ 60 psia
P_H=60 psia P_L=20 psia δ =2.2
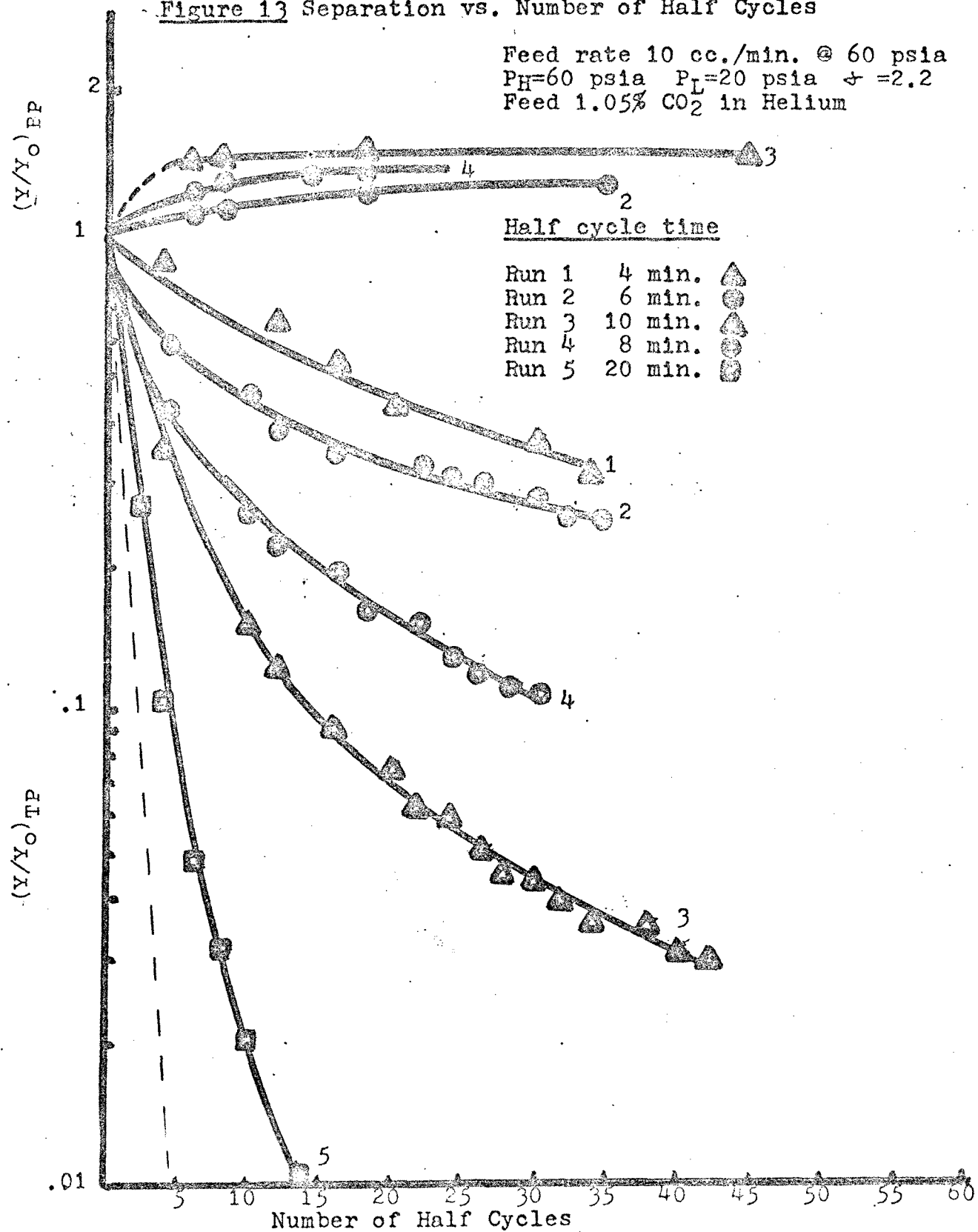Feed 1.05% CO_2 in Helium

Half cycle time

Run 1   4 min.
Run 2   6 min.
Run 3   10 min.
Run 4   8 min.
Run 5   20 min.

Figure 14 Separation vs. Half Cycle Time

Feed rate 10 cc./min. @ 60 psia
P_H=60 psia P_L=20 psia α =2.2
Feed 1.05% CO_2 in Helium

Number of Half Cycles
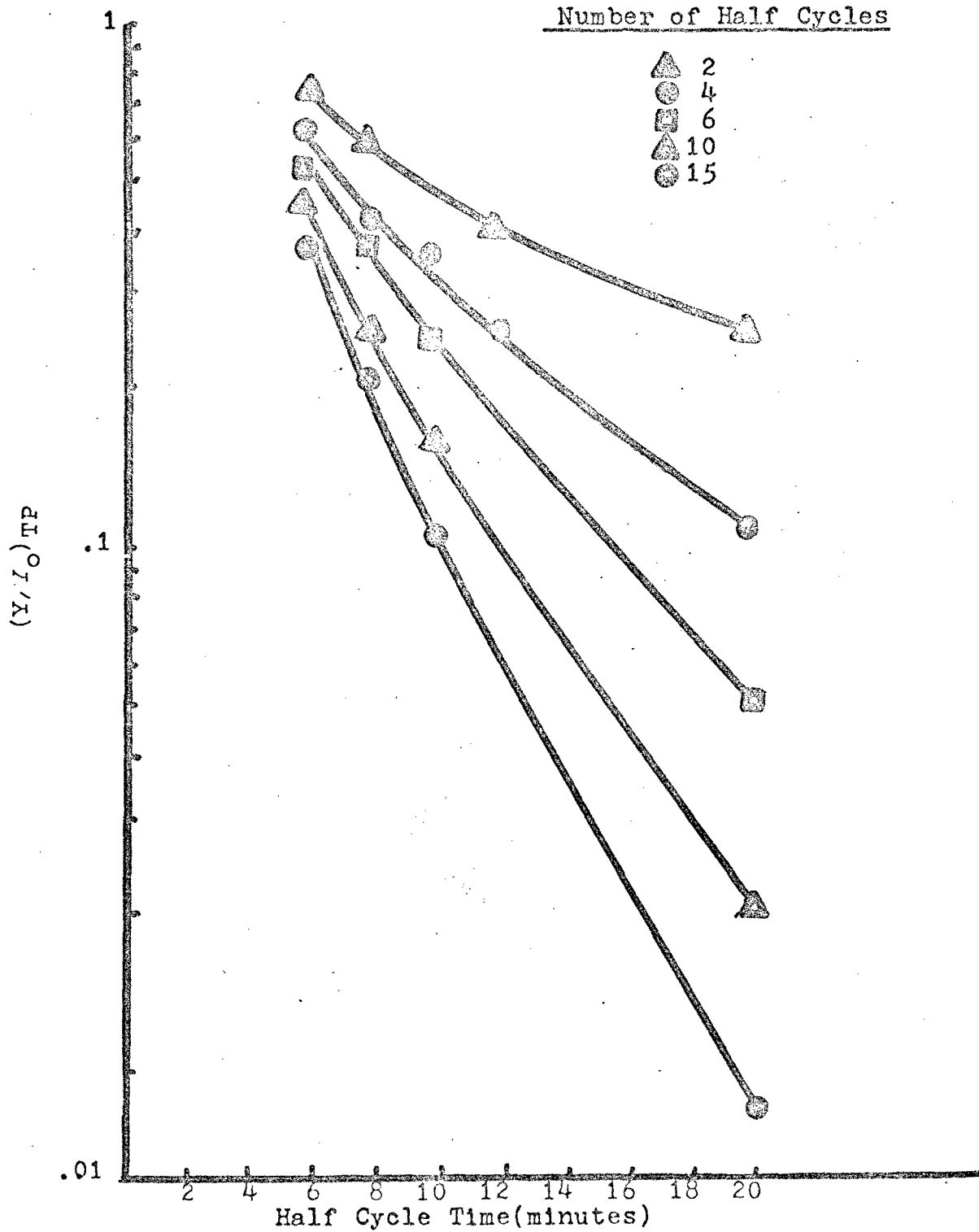
2
4
6
10
15

$(Y/Y_o)_{TP}$

Half Cycle Time(minutes)

Figure 15 Separation vs. Number of Half Cycles
Affect of Feed Pressure
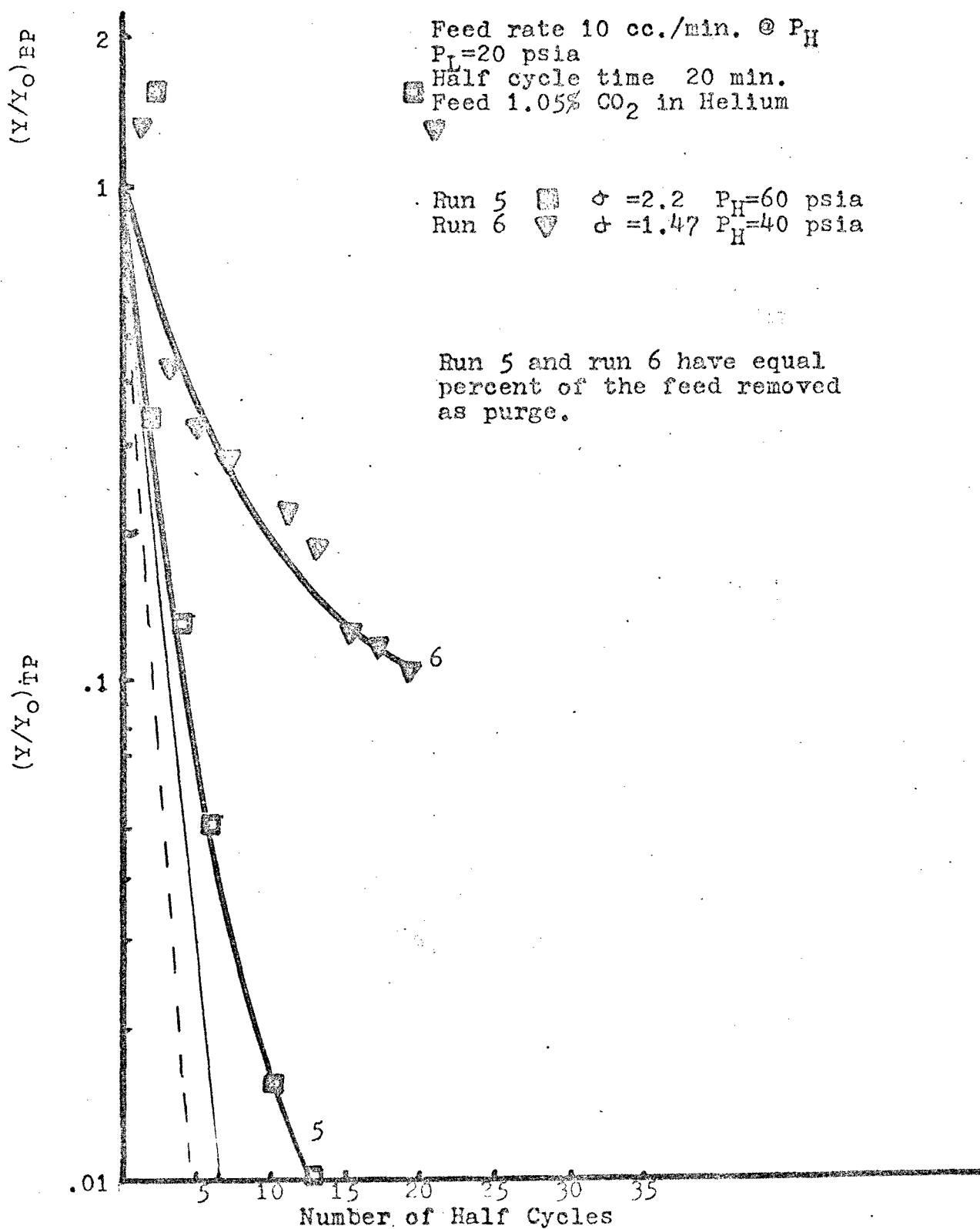
Figure 16 Separation vs. Number of Half Cycles
Use of Partially Filled Columns

Feed rate 10 cc./min. @ 60 psia
P_H=60 psia P_L=20 psia α =2.2
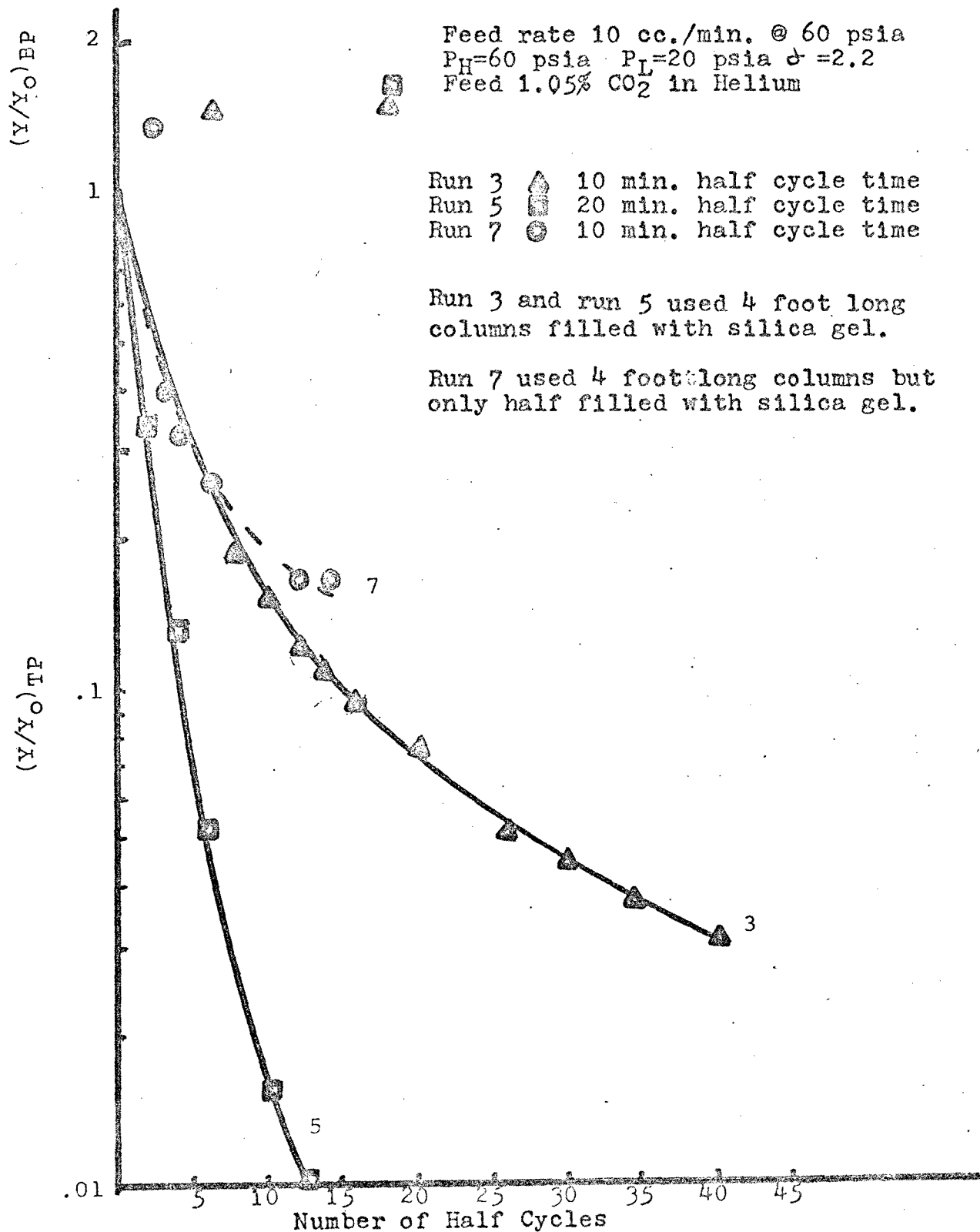Feed 1.05% CO_2 in Helium

Run 3 10 min. half cycle time
Run 5 20 min. half cycle time
Run 7 10 min. half cycle time

Run 3 and run 5 used 4 foot long
columns filled with silica gel.

Run 7 used 4 foot long columns but
only half filled with silica gel.

Figure 17 Effect of Dynamic Capacity on Separation

○ P_H=60psia P_L=20psia σ=2.2
△ P_H=40psia P_L=20psia σ=1.5

*This point from ternary
experiment Run 8

Data of Shendalman & Mitchell
▨ σ=1.5   half cycle time 6 min.
▨ σ=1.5   half cycle time 12 min.

Figure 18

Saturating Silica Gel with CO_2 and C_3H_6

Feed   1% CO_2 1% C_3H_6 in Helium   334 cc./min. @ 20psia
for 1%CO_2 h=50   for 1% C_3H_6 h=21
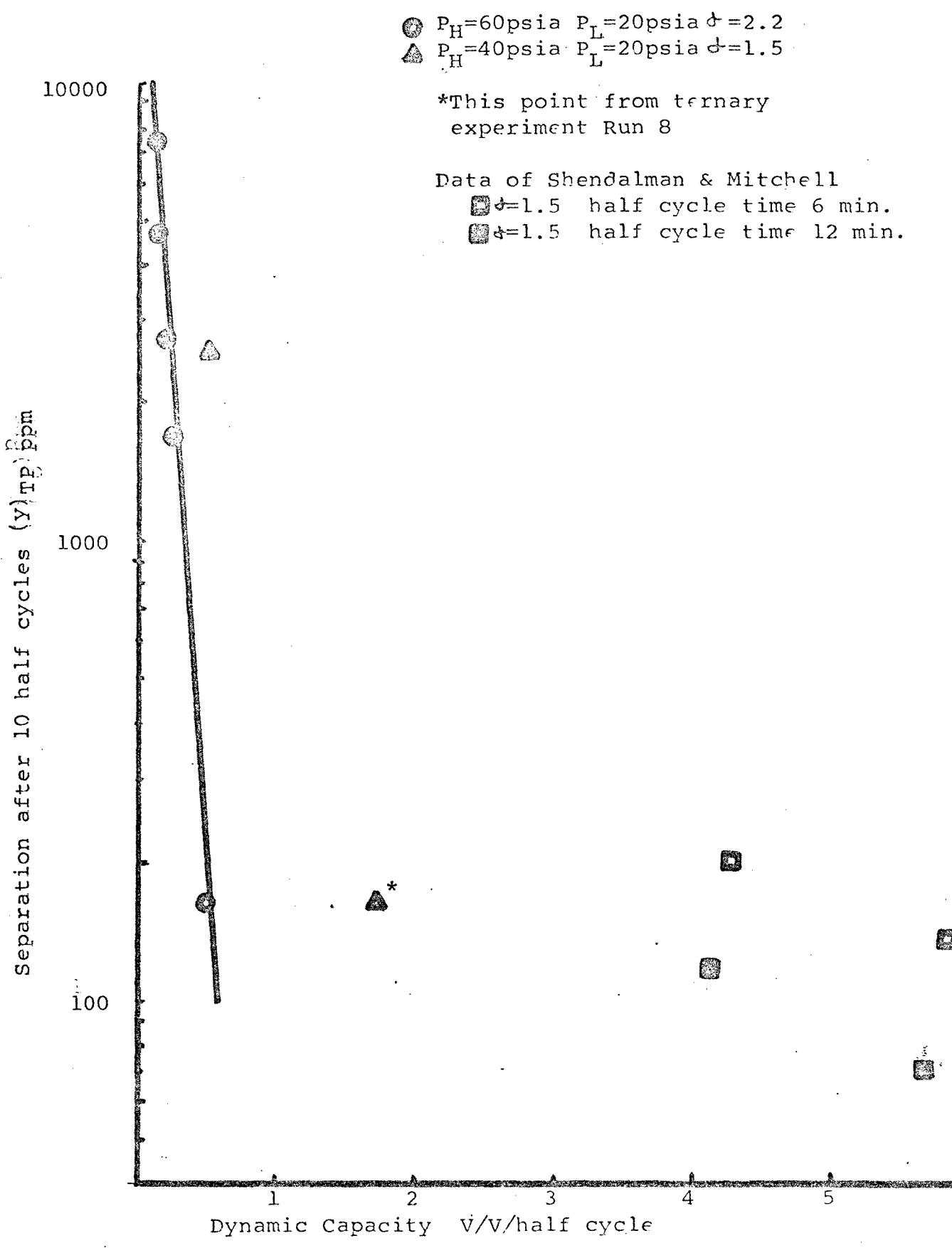
Top Product Sample- No Purge- Feeding 1 Column Only
Gas Chromatograph Peak Height

C_3H_6

CO_2

Time from feed start (minutes)

61

Saturating Silica Gel with CO_2 and C_3H_6

Feed 1% CO_2 1% C_3H_6 in Helium 334 cc./min. @ 40psia
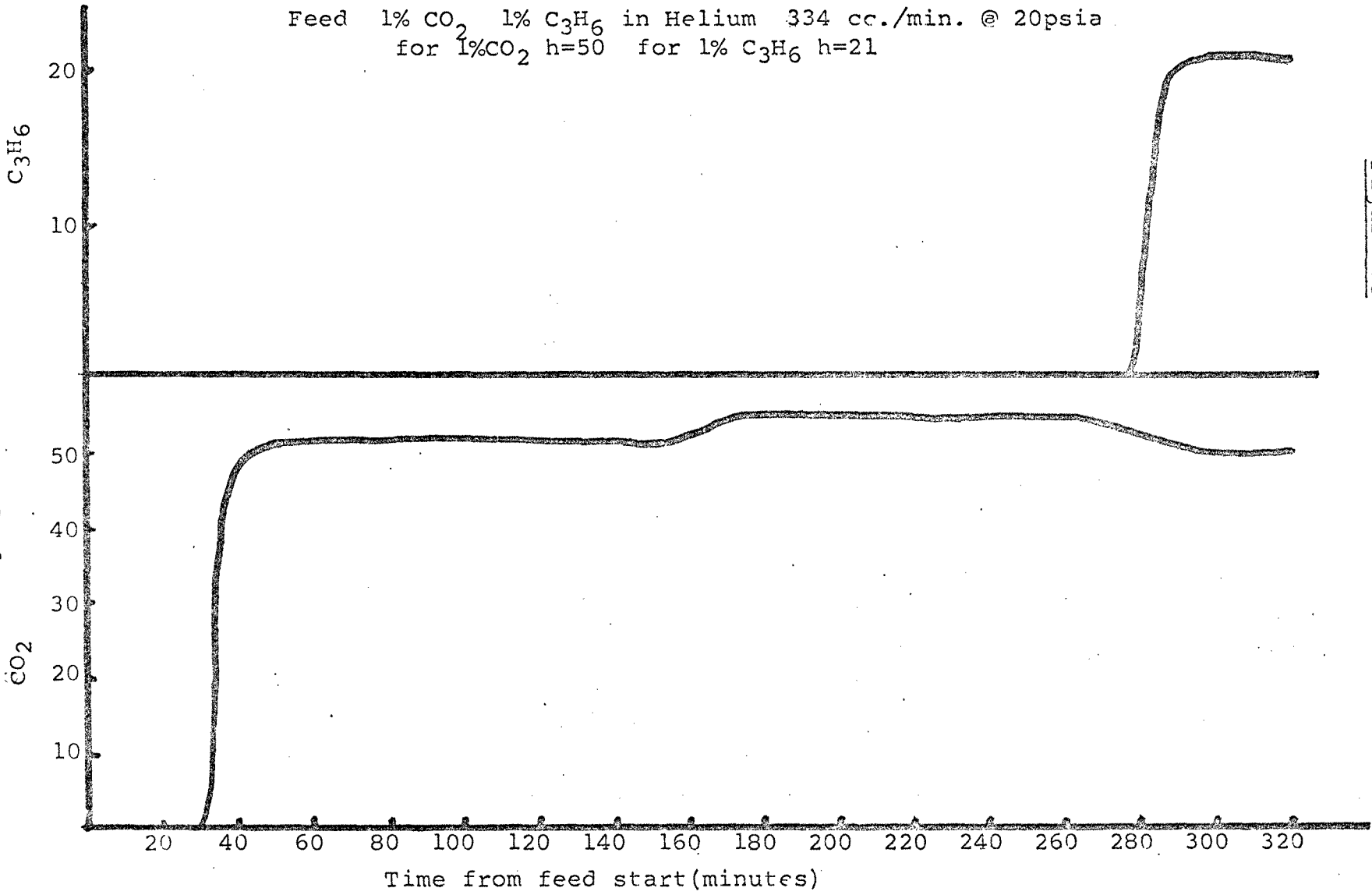for 1%CO_2 h=50 for 1%C_3H_6 h=21

Figure 19

62

Figure 20

Column Saturation with CO_2 and C_3H_6 at 20psia & 40psia
393 cc. of Silica Gel
○ 40psia
▣ 20psia

Moles CO_2 added to column

Moles C_3H_6 added to column

Time from feed start (minutes)

63
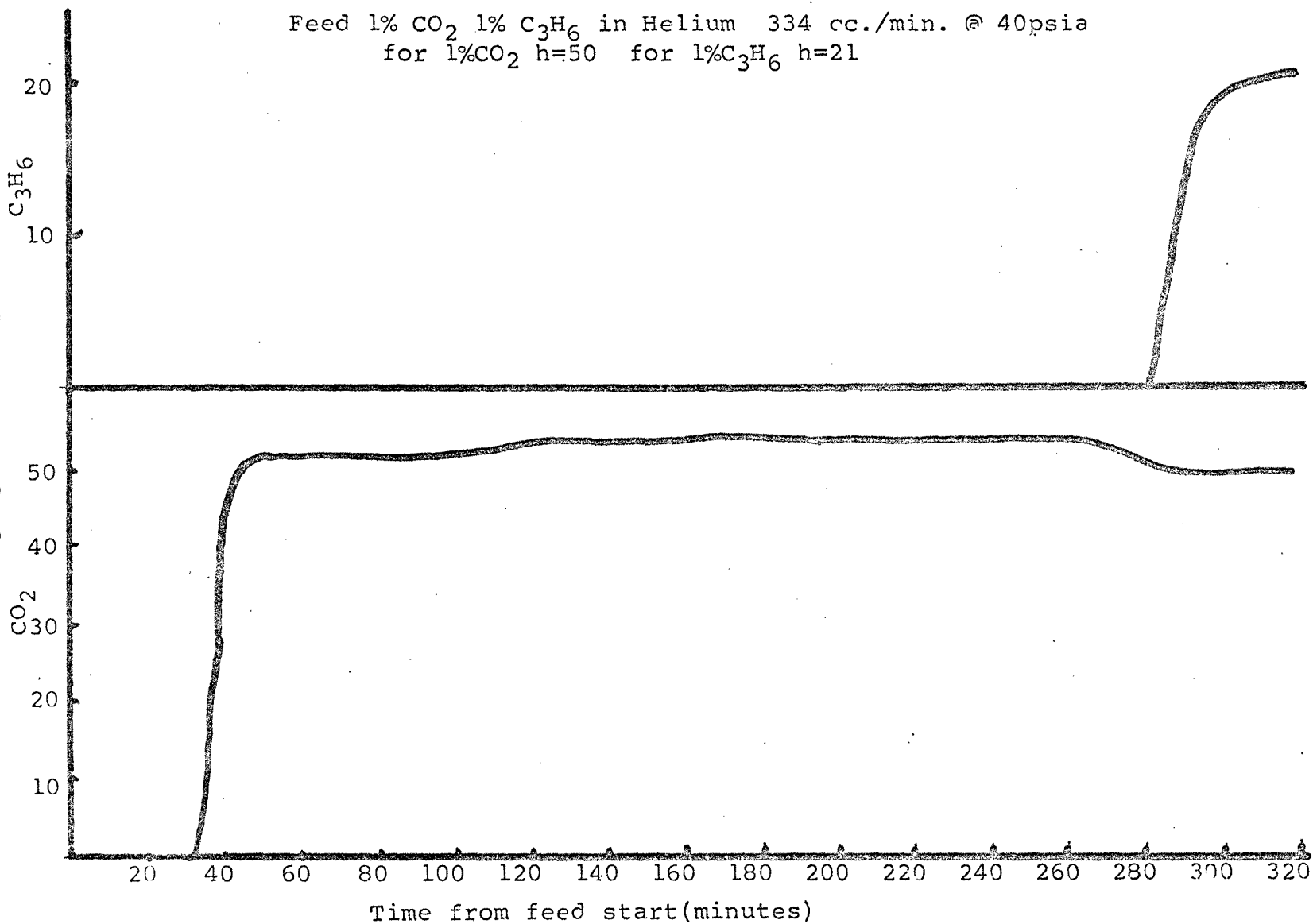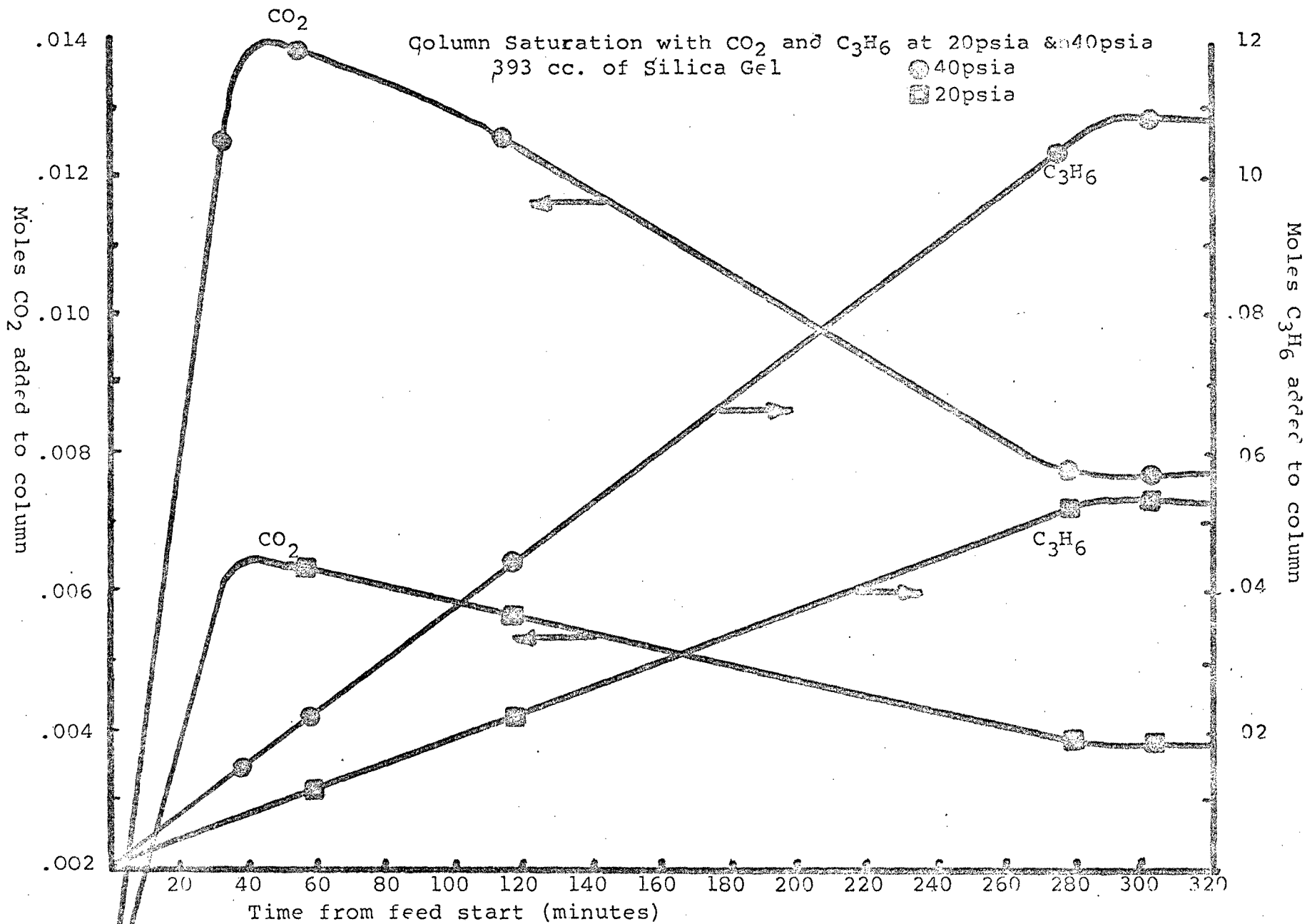
Figure 21 Separation vs. Number of Half Cycles
Ternary System- Helium-CO_2-C_3H_6

Feed rate 340 cc./min. @ 40psia
Half cycle time 2 minutes
P_H=40psia P_L=20psia
Feed 1% CO_2 1% C_3H_6

Run 8 ∂=1.5
      ⊙ CO_2 ▣ C_3H_6
Run 9 ∂=1.2
      ⊙ CO_2 ▣ C_3H_6

For run 8 both columns were
saturated at 40psia.
For run 9 one column was
saturated at 40psia and the
other at 20psia.

$(Y/Y_0)_{TP}$

Number of Half Cycles
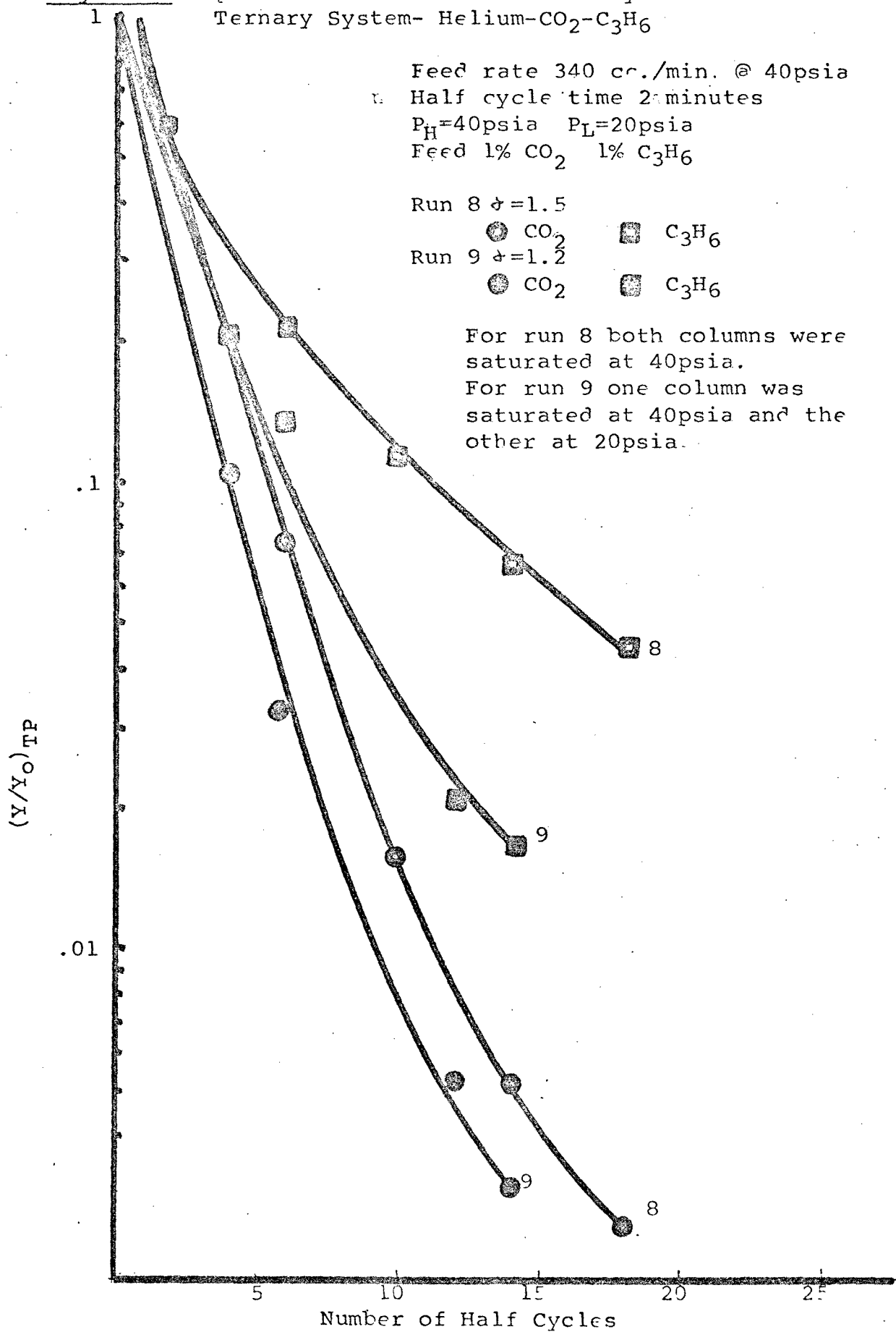
CALCULATIONS   C-1

VOLUME OF EACH COLUMN

Column diameter	ID=	.824 inches
Packed height	h=	45 inches
Volume of packing	$V_p=$	$\dfrac{\text{II } D^2}{4}$ (h)

$$\frac{\text{II }(.824 \text{x} 2.54)^2}{4}(45 \text{x} 2.54) = 393.4 \text{cc}.$$

Volume of Voids $\qquad V_g = \epsilon V_p$

$\epsilon = .38$ For 30-60 mesh silica gel (Chem. Eng. Handbook- Perry)

$\qquad V_g = .38(393.4) = 149.5$ cc.

This would be the maximum flow per half cycle to avoid breakthrough if no adsorbtion was occuring.

Calculations of σ for Table 15 A&B

Purge/feed# = $W_{AB}(P_H/P_L)/(F_B + F_{AB})$

Purge/feed# = $W_T(P_H/P_L)/F_T$

SAMPLE CALCULATION   C-2

GIVEN CONDITIONS

Feed pressure P_H= 60 psia   Purge pressure P_L= 20 psia

Feed rate F= 10 cc./minute at 60 psia

$\dfrac{\text{(Purge rate at 20 psia)}}{\text{(Feed rate at 60 psia)}} = \sigma = 2.2$

PURGE RATE

Purge flow rate W at 20 psia = σ (F)

W= 2.2 (10) = 22 cc./min.

TOP PRODUCT RATE

By material balance at equal pressure $F=Q+W^1$

Converting purge flow W to W^1 (flow at feed pressure)

$W^1 = \dfrac{P_L(W)}{P_H} = \dfrac{20}{60} (22) = 7.33$ cc./min.

Then Q= $F-W^1$ = 10-7.33 = 2.67 cc./min.

FLOW RATE ADJUSTMENT

Since the flow was actually measured at 14.7 psia the above rates were adjusted as below.

Wmeas. =WxP_L/ 14.7= 22x20/14.7 =29.9 cc./min.

Qmeas. =QxP_H/ 14.7= 2.67x60/14.7 = 10.9 cc./min.

MOLES OF GAS IN THE COLUMN

$N=PV_g/RT$ at 60 psia $=\dfrac{(60)(149.5)}{(14.7)(82.057)(293.16)} = .02537$

DYNAMIC CAPACITY (As defined by Shendalman and Mitchell)

Volume fed per volume of adsorbent.

$$DC = FO/V_p = 10\ (20)/393.4\ = .508$$

CALCULATION OF CO_2 CONTENT   After n/2 cycles or n half cycles

by the equilibrium theory expression derived by Shendalman[3]

$$Y_{n/2} = (P_L/P_H)^{(nK(1-\epsilon)/(\epsilon+K(1-\epsilon)))}$$

For P_L= 20 psia P_H = 60 psia O= .38 Using He with 1.05% CO_2

Since He is essentially not adsorbed and at equilibrium

X= KY or 1= K(.0105) Therefore K= 95.24

$K(1-\epsilon)/(\epsilon+K(1-\epsilon))$ = 95.24(.62)/(.38 + 95.24(.62))=

$$59.05/59.43 = .9936$$

$$Y_2 = 1.05(20/60)^4(.99360)\ = .0134$$

$$Y_2/Y_0 = .0127$$

NOMENCLATURE

D   diameter of column, inches

DC   dynamic capacity, V/V/half cycle

ϵ void fraction of column packing

F   feed rate in cc./min. at feed pressure

F' feed moles fed during repressure

F_B moles fed during blowdown

F_{AB} moles fed after blowdown

h   height of packing, inches

K   distribution coefficient

N   number of moles of gas in the column

n   number of half cycles

P_H pressure of feed, high

P_L pressure of purge, low

Q   top product flow rate cc./min. at feed pressure

R   gas law constant

V_p volume of packing

V_g void volume of packing gas volume

W   bottom product flow rate cc./ min. at purge pressure

W_{AB} moles of purge after blowdown

W_T total moles purge

θ half cycle time (minutes)

δ purge/feed Ratio = $\dfrac{\text{(purge flow) at purge pressure}}{\text{(feed flow) at feed pressure}}$

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1. Mitchell, J. E. and L. H. Shendalman, "Study of Heatless Adsorbtion in the Model System CO_2 in He: Part II" AIChE Symposium Series, No. 134, Vol. 69

2. Wisnosky, C.J., Masters Thesis, Newark College of Engineering, Newark, N. J. (1974)

3. Mitchell, J. E. and L. H. Shendalman, "A Study of Heatless Adsorbtion in the Model system CO_2 in He: Part I" Chem. Eng. Sci., Vol 27, (1972)

4. Wilhelm, R. H. and N. H. Sweed, "Parametric Pumping Separations of Mixtures of Toluene and n- Heptane" Science 159, 522(1968)

5. Chen, H. T. and F. B. Hill, "Characteristics of Batch, Semi-continuous, and Continuous Equilibrium parametric Pumps". Separation Science, 6, 411(1971)