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AN INVESTIGATION OF COLUMN EFFICIENCY AND THE RELATIONSHIP TO LIQUID PHASE DISTRIBUTION ON ULTRA-LOW LOADED GLASS BEAD GAS CHROMATOGRAPHIC COLUMNS

A Thesis
Presented to the
Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Donald G. Nyberg
May, 1968

This thesis, by Donald G. Nyberg, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the thesis requirement for the degree Master of Science.

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Thanks is extended to the Dow Chemical Company for the assistance generously given on this thesis.

Finally, unbounded love is expressed to my wife, Nancy, whose support and confidence has made the completion of this work possible.

LIST OF NOMENCLATURE

A	Eddy diffusion contribution to the plate height.
B	Longitudinal molecular diffusion contribution to the plate height.
C_g	Plate height term for mobile phase diffusion.
C_l	Mass transfer plate height term for diffusion in the bulk liquid phase.
d	Depth of the bulk liquid phase.
D_g	Molecular diffusion coefficient of a solute in the gas phase.
D_l	Molecular diffusion coefficient of a solute in the liquid phase.
d_p	Average particle diameter.
d_s	Depth of the liquid phase adsorption film.
f	Porosity.
H	Plate height.
H_I	Apparatus contribution to the plate height.
j	Gas phase compressibility factor.
K	Distribution of partition coefficient (liquid phase concentration/gas phase concentration).
L	Column length.
M	Number of contact points per bead.
p	(inlet/outlet) pressure ratio.
P_i	Column inlet pressure.
P_o	Column outlet pressure.

q	Liquid configuration factor.
R	Retention ratio (the fraction of solute in the gas phase).
r_m	Radius of curvature of the gas-liquid interface.
t	Solute retention time.
t_{CH_4}	Methane retention time (unretained sample time).
μ	Average carrier gas velocity.
V_0	Column void volume.
V_i	Liquid phase volume of phase i.
V_L	Total liquid phase volume.
w	Peak width at one-half peak height.
%	Liquid phase percentage (grams of liquid per 100 grams of solid support).
ρ_{GLASS}	Density of glass beads.
ρ_{LIQ}	Density of liquid phase (Tri-o-tolyl-phosphate).
γ	Obstruction factor.

TABLE OF CONTENTS

Page

LIST OF TABLES

Tables VI through XIV below represent data taken on columns run under standard chosen conditions with normal glass beads.

Tables XV and XVI below represent data taken on columns run with Helium carrier gas.

Table

Tables XVII through XIX below represent data taken on columns packed with corning roughened beads.

Tables XX through XXII represent data taken on columns run on original apparatus (before valve change).

LIST OF FIGURES

Figure

I. INTRODUCTION

DYNAMICS OF MIGRATION AND ZONE DISPERSION

The usefulness of quantitative gas-liquid chromatographic (GLC) theory depends upon how well one can relate experimental results to the highly complex underlying array of structural and dynamic parameters.[3,12,28,30,58] Because of the complicated nature of a GLC column, theory is not always reliable or available and the practical application of GLC has been regarded as something of an art.

GLC is a physical method for separating components of mixtures of volatile compounds. The central item in the apparatus for GLC is the column, a long tube packed permeably with a solid which supports a liquid phase.

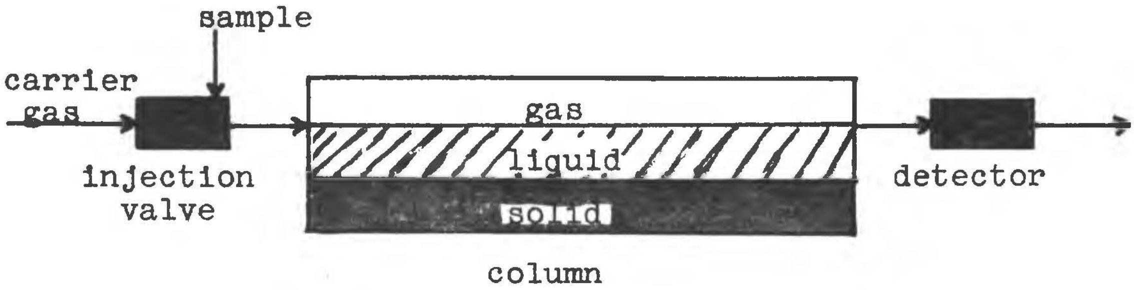

Fig. 1.--Simplified schematic of a gas-liquid chromatographic system.

In the commonest technique of GLC, the Elution method,[65] a solute zone is injected instantaneously into a dynamic inert gas stream which passes continuously through the column. This solute is hence introduced onto the column and begins migrating down the column. Any one molecule remains in the gas phase until 'captured' by the liquid phase. While this particular molecule is retarded, the zone passes by. When the molecule re-enters the gas stream, it is carried along until again immobilized. All of the molecules in the zone undergo this stop-and-go sequence independently of each other and net downstream motion is achieved solely during residence in the mobile gas phase;[28] the result being that the zone migrates smoothly at a fraction, R, of the gas velocity. Thus the R value may be defined as the probability that a solute molecule is in the mobile phase or as a relative migration rate.[29]

Each different type of solute molecule will be retained a different length of time in the liquid phase and this results in a different value of R. Thus, under ideal conditions, all solute types could be separated by differential migration due to even slight variances in physical and chemical properties.

The effectiveness of separation in GLC, however, depends on two important processes.[20,28,29,38,58,61] First and most obvious is the process just discussed; a disengagement of zone centers must be obtained through a difference in migration rates of individual solutes.

This ideal zone separation, unfortunately, is opposed by zone broadening mechanisms which result from the random migration pattern and statistical dispersion of the molecules. This leads to zone overlap, and hence two solutes can only be resolved if the difference in R is sufficiently large to offset the peak broadening effects (see Figure 8).

These two factors are of equal importance in the sense that the separability of a given pair is equally enhanced by either doubling the migration rate difference or halving the spread of the peaks.[29] In practice the relative importance of these two depends entirely on individual circumstances. In some cases a specific liquid phase can be found which yields widely different migration rates and the control of zone spreading is of secondary importance. In other cases--where similar solute structural features exist and it is difficult to enhance a large difference in R values, or with a complex mixture where a liquid phase change might merely reshuffle the peak retention times--zone spreading must be carefully controlled if the peaks are to be resolved.

The development of concepts and mathematical expressions for zone spreading has been one of the major theoretical and practical challenges of GLC and it is to this subject that this thesis pertains. An attempt is made to better understand some of the underlying parameters in hopes of improving the utility and effectiveness of GLC.

GENERAL CONSIDERATIONS

An important requirement for elution of a solute from a GLC column is that the solute have a sufficient vapor pressure to be carried down the column by the inert gas.[59] It was therefore initially felt necessary to operate at column temperatures near the boiling points of the components to be separated.[3,10] This practice limited the usefulness of GLC since most liquid phases will either bleed off at high temperatures (above 300°C) or decompose.[47]

First attempts to extend GLC applications were focused on developing new liquid phases, such as SE-30, which can withstand temperatures up to 375°C. Using high temperatures, however, limits the liquid substrate choice to a few rather exotic substances[3,12,30] and often results in the following additional effects:

1. Decreased column efficiency.[11]
2. Increased instrumental problems.[17]
3. Decreased liquid phase selectivity.[11]
4. Decreased column life.[3]
5. Greater difficulty in stabilizing column temperatures.[59]

6. Increased costs.
7. Greater chance of solute decomposition.[47]
8. Increased tendency for solute-solvent chemical reaction.[11]

Other methods by which high boiling compounds can be eluted more rapidly include:

1. Increasing the carrier gas velocity.
2. Decreasing the column length.
3. Choosing a liquid phase with a smaller partition coefficient.
4. Decreasing the liquid phase percentage.

The first alternative is limited by the finite rate of mass transfer (see Figure 2) and the maximum allowable pressure on the apparatus.

Shorter columns can be used to obtain reasonable retention times, but only at a sacrifice in column efficiency.

Concerning the third method, the large amount of work reported in the literature has been aimed at increasing separability and not at reducing retention times.

The reduction of liquid phase percentages has been discussed by several authors as a possible method of obtaining reasonable elution times.[8,9,16,17,23,31,35,36,48,59,61,71] This follows directly from the basic retention equation

$$t_R = (L/\mu)\left[1 + (V_L/V_0)\,K\right] \qquad (1)$$

where L = column length, μ = average carrier gas velocity, V_L = liquid phase volume, V_0 = carrier gas volume (void space), and K is the partition coefficient.

Dal Nogare and Juvet[11] calculate in one example that to decrease the retention time of a particular sample from 101 minutes to 2 minutes requires either a 400°C increase in temperature or a decrease in the amount of liquid phase from 5cc. to 0.05cc. It is thus proposed that operating the column at a moderate temperature and low liquid phase loading produces the same result as high column temperature, but with the following advantages:

1. Less thermal decomposition of solutes.
2. Increased detector sensitivity and less background noise.[17]
3. Wider choice of liquid phases.
4. Freer flowing column packings.[51,67]
5. Greater difference in solute vapor pressures.[76]

LOW LIQUID LOADS

In general, both experimental and theoretical results show the desirability of reducing the liquid load and column temperature. Hawkes[48] and Giddings[35] suggest that the liquid loading on glass bead columns should be reduced much below what is now customary, to approximately 0.04%, since it is in this region that the liquid can be expected to exist as a thin layer on the beads without pools at the contact points. These predictions need urgent investigation since they radically effect analysis time and column operating conditions.

Column Efficiency Theory

To the best of our present knowledge the plate height of a packed GLC column can be approximated by the highly abbreviated "van Deemter equation" with a velocity dependence roughly of the form[13,25,28]

$$H = \frac{f}{1/A + j/C_g P_o \mu} + \frac{Bjf}{\mu P_o} + C_\ell \cdot \mu + H_I \cdot \mu \qquad (2)$$

flow pattern and gas phase mass transfer	longitudinal diffusion	liquid phase mass transfer	instrument contribution
TERM I	TERM II	TERM III	TERM IV

where A, B, C_g, C_ℓ, and H_I are constants and μ is the carrier gas velocity. Small H values represent efficient columns since H is a measure of the peak spreading which occurs within a column.

Equation (2) can be graphically evaluated, as shown in Figure 2, in order to better illustrate the effects of column variables.

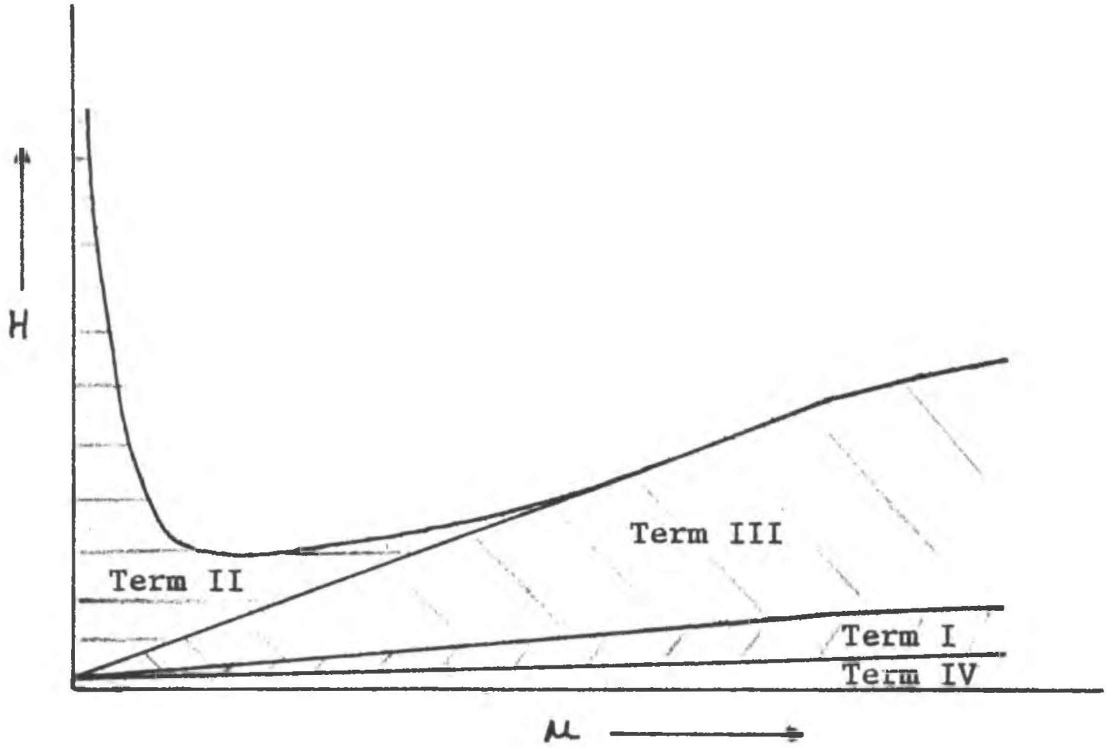

Fig. 2.--Theoretical plot of Eq. (2) showing velocity dependence of theoretical plate height.

Since good column performance is indicated by narrow symmetrical peaks, it is desirable to minimize H by appropriate adjustment of column parameters.

It is apparent from a close examination of Equation (2) and Figure 2 that when the velocity is increased the following occurs:

1. Term I approaches a constant value A.[26,37,46]

2. Term II, which accounts for molecular diffusion of the solute during its residence in the gas phase, decreases and becomes insignificant.
3. Term III, which relates to the time a solute molecule spends in the liquid phase, increases and becomes more meaningful.[33]
4. Term IV slowly increases.[42,43]

Thus, when considering a fast efficient analysis, attention should be focused on factors which affect the constant A term and the velocity dependent H_I and C_ℓ terms. In practice, A is always quite small and can usually be disregarded. H_I on the other hand can and often does significantly affect column efficiency and must be carefully controlled. These two terms will be discussed later.

C_ℓ Term

This thesis will be concerned in detail only with the C_ℓ term which has been expanded by Giddings[25] to the following form

$$C_\ell = \frac{R(1-R)\,d^2}{D_\ell}\cdot q = k\cdot\frac{d^2}{D_\ell} \qquad (3)$$

where D_ℓ is the diffusion of the sample in the liquid phase and d is the liquid film thickness. Thus C_ℓ is dependent upon the time a solute molecule spends in the liquid phase and this time is a function of the following:

1. The film thickness, which is dependent not only upon the amount of liquid, but also upon solid-liquid and liquid-liquid interactions which control the distribution of the liquid on the support.
2. The (inverse) rate at which a solute molecule moves around in the liquid (D_ℓ), since the faster it moves, the greater its chance of hitting the surface and escaping.
3. The sample retention time.

While C_ℓ is just one of several terms contributing to the plate height, it is often the most important (for fast analysis where high gas velocities are used) and most difficult to calculate (since liquid distribution, and hence film thickness, is difficult to predict and D_ℓ values are extremely scarce).

Glass Bead Support

In order to study the effect of liquid loading on column efficiency one needs to use a column whose geometrical characteristics are known. The individual particles of firebrick, celite, and diatomaceous earth, which are frequently used as GLC solid supports, are irregular and porous and therefore not very suitable.[66]

In recent years the glass bead column has shown the best agreement between theory and practice;[25,28,48,51,52] this being due to the well defined geometry,[30] non-adsorptive inert nature,[2] and low porosity of the beads. This allows one to make geometrical calculations and is one important reason that glass beads have been used for this research. In addition, the C_l term is relatively large at normal loadings and hence swamps out the troublesome A and C_g term which is complicated by coupling and other complexities less subject to exact theory.[48] Unfortunately this term cannot be disregarded at the extremely low loadings discussed later in this thesis.

Liquid Phase Distribution

The manner in which liquid accumulates on the surface and in the pore space of the solid support is of obvious importance in view of the direct linearity of H with the thickness squared of the liquid layer. Several early plate height theories,[1,24,40,57,78] of which Equation (3) is representative, did not concern the relationship between plate height, solid support, liquid percentage, and liquid distribution, and thus were seldom able to lead to quantitative prediction of C_l values. For example, the liquid phase on glass bead support was simply assumed to be distributed as an even film around the bead.[13,81] Investigation, however, showed that this was not even an approximate assumption and, in fact, that most of the liquid accumulated around the bead contact points as shown in Figure (3).[1,22,23,51,69]

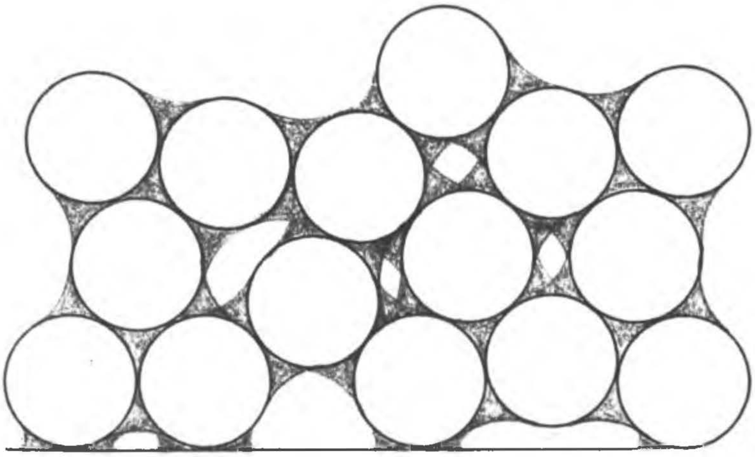

Fig. 3.--Illustration showing liquid accumulation around glass bead contact points as observed microscopically.

These two different liquid distribution assumptions (a uniform surface coating and a collection of liquid around the contact points) lead to C_ℓ terms differing by a factor of 3000 for a 0.1 weight percent liquid loading.[25]

One of the steps necessary in the correlation of support and liquid distribution is a study of the forces holding the liquid to the support, since such forces determine the details of the distribution. Any liquid added to a wetable solid is subject to both adsorption and capillary forces.[7,23,25] The intermolecular attraction of solid and liquid leads to adsorption and the liquid-liquid intermolecular attraction is responsible for surface tension and leads to capillary condensation in pores or around contact points.[77] If a liquid is not flooding the support, the adsorption and capillary forces compete with one another for the liquid.

Adsorption forces, to the extent that they predominate in determining liquid distribution, give a rather uniform film thinly distributed over the available surface:[7,23] the C_ℓ term for such a column would be small. Capillary forces, when they predominate, collect the liquid into pools around the contact points.[23] The depth of these pools cause a large C_ℓ term and hence low column efficiency.

At equilibrium we may envisage puddles of capillary liquid at the contact points and a reasonably uniform adsorption layer over the remainder of the bead surface. The immediate question is what is the amount of liquid belonging to each category and how is this ratio affected by a decrease in liquid loading.

Experimental Tests on Liquid Distribution

Analysis of the complex liquid distribution has recently been atempted by several workers at normal liquid loadings. A search of the literature shows that adsorption and condensation theory,[23] the science of porous materials,[24] microscopic investigation,[25,51] and mercury penetration [2] have been applied to determine the relative importance of capillary and adsorption forces.

There is significant evidence to indicate that capillary liquid is predominate (at normal liquid loadings).

1. Giddings[25] has derived an equation for equilibrium between adsorption and capillary forces

$$d_s \cong 10^{-5}\, r_m^{\,1/3} \qquad (4)$$

where d_s is the thickness of the adsorption film and r_m the radius of curvature of the gas liquid interface, a value approximately equal to the depth of the larger liquid pools. It was shown that the formation of capillary liquid is controlling the plate height term

C_ℓ for all conditions investigated.

2. Dal Nogare and Juvet[11] point out that a uniform (adsorption) film on glass bead support would yield a C_ℓ value from 10^2 to 10^4 times smaller than experimental values. Plate height calculations, based on the capillary liquid around the contact points, are in close agreement with experimental results.[22,61]
3. Littlewood[66] has shown that d is reduced with increasing temperature and has suggested that this is most likely due to the lowering of surface tension and the consequent spreading out of the liquid on the support.
4. The capillary liquid collected around glass bead contact points has been observed microscopically by Giddings,[25] Hishta,[51] and Steed.[73] Photographs have been presented.[51,67] The size of the liquid ring was found to be in accord with the amount of liquid load on the column.
5. Janak[55] used an electron microscope and found that film thickness increased unequally with the amount of liquid, indicating an insignificant adsorption effect.

Expanded C_ℓ Term

Based on the above experimentation and theory, a more realistic C_ℓ term can be represented as[30]

$$C_\ell = \frac{\sum R(1-R)\, d_i^2 \cdot q_i \,(V_i/V_L)}{D_\ell} \tag{5}$$

where q_i is a configuration factor which depends on the geometry of the pools of liquid and assumes different values for glass bead columns, uniform films, deep pools, etc.[34] The fraction of the total volume in pools is given by the term V_i/V_L.

For glass bead columns this equation has been further extended by Giddings[22,23] to

$$C_\ell = \frac{R(1-R)\, d_p^2}{120\, D_\ell} \left(\frac{\%\ \rho_{GLASS}}{3m\ \rho_{Liq.}} \right)^{1/2} \tag{6}$$

which is based upon the approximation that the entire liquid mass is distributed in the narrow gaps near the bead contact points.

Deviation From Normal Liquid Loads

Equation (6) has been demonstrated to be capable of predicting meaningful C_ℓ terms for normal glass bead column loadings where the contact point assumption is valid.[35,48] No attempt has been made however to investigate the validity of this equation at ultra-low loadings where this assumption is logically questionable and little is known about liquid distribution.

It is feasible that this 100% capillary liquid assumption may fail completely and that the more desirable uniform film equation[23,25,32]

$$C_\ell = \frac{2}{3} \frac{R(1-R)\, d^2}{D_\ell} \qquad (7)$$

may give more accurate predictions at ultra-low liquid loadings.

This research pertains to ultra-low liquid loadings and attempts to isolate C_ℓ from the other terms in Equation (2), investigate liquid distribution and the effect on C_ℓ, evaluate the lower liquid % limits of Equation (6), and determine how best C_ℓ should be minimized.

II. EXPERIMENTAL

APPARATUS AND PROCEDURE USED

Performance of a GLC column and the reproducibility of data obtained from it is critically dependent on the preparation, modification, and operation of this column; the degree of detail given here is intended to be adequate for duplication of this work by others.

The data for this investigation was obtained by using a highly modified Perkin-Elmer, Model F-11 gas chromatograph with a flame ionization detector. A general scheme of the apparatus used in this study is shown in Figure 4.

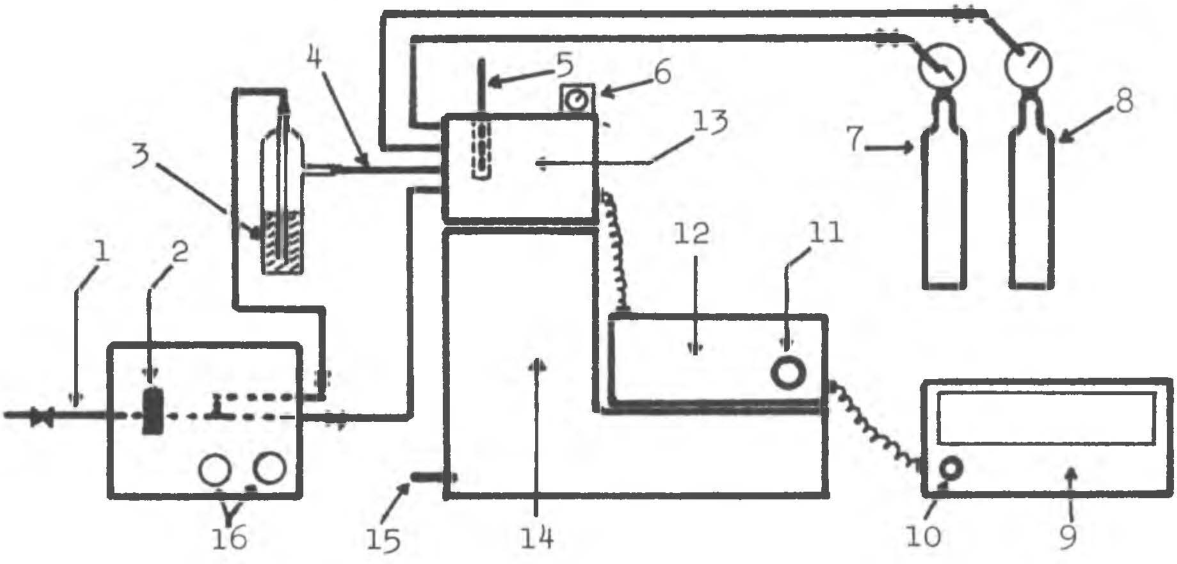

Fig. 4--General scheme of apparatus: (1) Air line, (2) Charcoal air filter, (3) Liquid sample,

(4) Sample inlet, (5) Sample injector valve, (6) Inlet pressure gauge, (7) N or He carrier gas, (8) H gas, (9) Recorder, (10) Chart speed control, (11) Range (detector sensitivity) control, (12) Amplifier, (13) Flame ionization detector, (14) Oven, (15) Temperature control thermistor, (16) Air regulators.

To determine the true performance of the column studied, it is necessary to eliminate contributions due to the apparatus.[3,8,12,21,58,59,61] The original instrument produced extraneous peak spreading, an uncertainty in the retention time, and peak asymmetry. To improve efficiency, the apparatus was disassembled and much of the dead volume was filled with inserted, snugly fitting capillary tubing as shown in Figure 5.

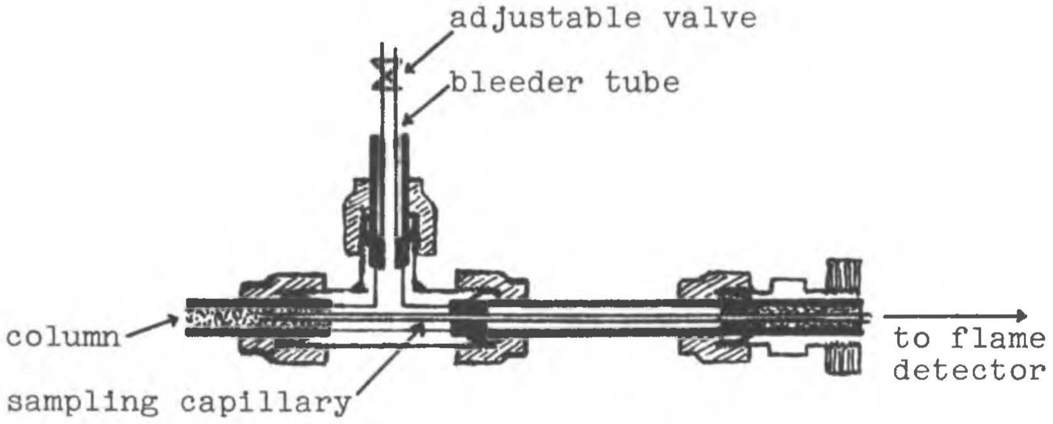

Fig. 5.--Device used to minimize dead volume at outlet and to adjust outlet pressure.

Since the inner capillary diameter was 0.004 inches, a negligible dead volume was obtained and this system largely eliminated peak distortion due to column end effects. In addition, the bleed-off valve could be adjusted to vary sample size and also to prevent flame blow-outs when using high inlet pressures.

A similar splitter was used at the inlet to minimize diffusion of the solute 'plug' and to avoid tailing.

A one millivolt potentiometric recorder manufactured by Texas Instruments Incorporated with a 0.4 second full scale response time was used to obtain all data. This was equipped with ten chart speeds, all of which were checked for accuracy.

Nitrogen was used as the carrier gas due to low cost and its effect on decreasing the longitudinal diffusion plate height term.[4,60,61,68] To minimize instrument noise, all gases were cleaned by passing through an activated charcoal filter.

Column temperature was controlled to 50.5 ± .5° C by an air bath which was temperature regulated by a home made resistor. All gases and solutes entering the column were equilibrated to this temperature by passing through ten feet of coiled empty tubing located within the oven.

The columns employed with this apparatus were constructed of various lengths of three-sixteenth inch outside diameter copper tubing. Before packing, these columns were rinsed several times with ether, chloroform, and acetone.

Glass beads, obtained from the English Glass Company, Leicester, England, was used for the solid support since these beads were found to be much more regularly spherical than beads from several other manufacturers.[48] Seventy and eighty mesh screens were used to size grade the beads. Sieving the beads were difficult, since they clogged the pores of the sieve firmly. Accordingly, the bottom of the sieve needed to be brushed frequently. After sizing, the beads were washed in concentrated nitric acid and then rinsed several times in distilled water, acetone, and ethyl ether. After drying, the mean bead size was determined by counting out several hundred of the beads--with the aid of a magnifying glass--and then weighing these beads on a micro-balance. The mean diameter was found to be 0.0226 centimeters (see Appendix A) which agrees well with the expected 0.0210 centimeters.

Sufficient liquid phase was then dissolved in acetone and added to a measured weight of glass beads. (For example, a 0.5% column required that 500 milligrams of Tri-o-totyl phosphate (TOTP) be dissolved in approximately fifty milliliters of acetone and be evaporated onto 100 grams of beads.) This mixture was stirred, gently, manually until the solvent (acetone) had visibly evaporated.

A 100 mesh copper screen was soldered onto one end of the copper tubing, after which the column was placed inside a suitable length of one-half inch piping--for support--and was packed by pouring beads into the column, and then vibrating and tapping the column until no further settling was observed. A piece of tape was then placed over the open end and the column was coiled into a six inch diameter section. (It should be noted that originally glass wool had been used to plug both ends of the first few columns prepared. During the course of the research however, a literature search revealed an article by Kieselbach[63] which describes a constant plate height term which results when glass wool plugs are used to close column ends. In order to eliminate this extra-column effect, glass wool plugs were discontinued and the plugs from all columns which had been closed by this method were removed. These columns were refilled and data was re-taken.)

After preparing and packing, all columns were conditioned overnight at 100° C and then equilibrated to $50.5 \pm .5^{\circ}$ C for one hour before use.

The sample liquids used were obtained from Phillips Petroleum.

It is impossible to introduce the solute sample onto the column in zero time.[11] Depending on the system used (electromagnetic or pneumatic valves, syringes, etc.) the duration of injection--and hence the original peak width--can vary from a hundredth of a second to several seconds. Furthermore, if a liquid sample is injected, vaporization is not instantaneous. It is therefore obviously desirable to find a way to introduce samples in the vapor phase and to do so as quickly as possible. This is also advantageous from the sample size standpoint since there is less chance of flooding the column; a factor which warrants a considerable amount of attention when working with extremely low liquid loadings.

To accomplish a quick vapor phase injection, air--which had passed through a charcoal filter--was bubbled through the sample; the air-sample mixture then passed through a valve loop (see Figure 6) and then out into the room. A sample was injected onto the column by lifting a plunger up and then down which changed the valve-port-route and directed a sample charge onto the column.

The injection system utilized capillary tubing and a low internal volume valve manufactured by Loenco Inc., Altadena, California.

The system was frequently leak-checked under pressure by pouring a soap solution on all joints and moving parts. When leaks were present, they were easily noticed and were remedied.

SAMPLE INJECTION VALVE--MODIFICATIONS

Due to the many problems mentioned by researchers who have attempted to use relatively low liquid loadings[15,50,52,74] (5% to 0.1%), obstacles were expected to be encountered with the 'extremely' low liquid loadings (0.5% to 0.004%) even though precautions had been taken (see Experimental section) to eliminate the difficulties experienced by others. It was decided, therefore, to attempt to obtain meaningful data from the lowest loaded--and most demanding--column early in the research schedule; knowing that once reliable sample peaks could be obtained from this column that the remaining efforts could be spent collecting data and analyzing results without hinderances.

General apparatus reliability and familiarity were first established by running the less demanding 0.5%, 0.29%, and 0.1% columns. After a few weeks, satisfactory results were obtained for these columns and attention was directed to the 0.004% column: strong tailing effects were observed. This was not a complete surprise since with this low liquid load it is likely that the glass beads are somewhat 'naked' and will tend to adsorb the sample;[27,55] hence possibly causing a non-linear isotherm. This hypothesis was tested by attempting to cover the glass bead adsorption sites with water molecules which are expected to be strongly adsorbed. This was accomplished by bubbling the carrier gas through a water trap before entering the column. Tailing was still observed, thus suggesting that sample adsorption on the beads was not the problem.

In order to substantiate the above conclusion, an empty column was tested and an 'unretained' peak was found to be unsymmetrical. Thus the problem, by elimination, was concluded to originate in the apparatus itself.

Dead volume, the most likely suspect, had already been reduced to a practical minimum and all possible side traps remaining in the system had been made to leak very slightly so as to avoid delayed sample diffusing into the column and causing a tail.

Reasoning thus pointed to the sample injection valve as the only remaining possibility. This valve--schematically illustrated in Figure 6--had been considered for some time a possible cause of tailing due to grease being rubbed off into the valve port hole D when being operated, thus lodging a blob of grease (acting as a liquid phase) in the path of gas flow. Assuming this to be the case, that portion of the sample which became absorbed in the grease would be retained, slowly desorbed, and thus cause a sample tail.

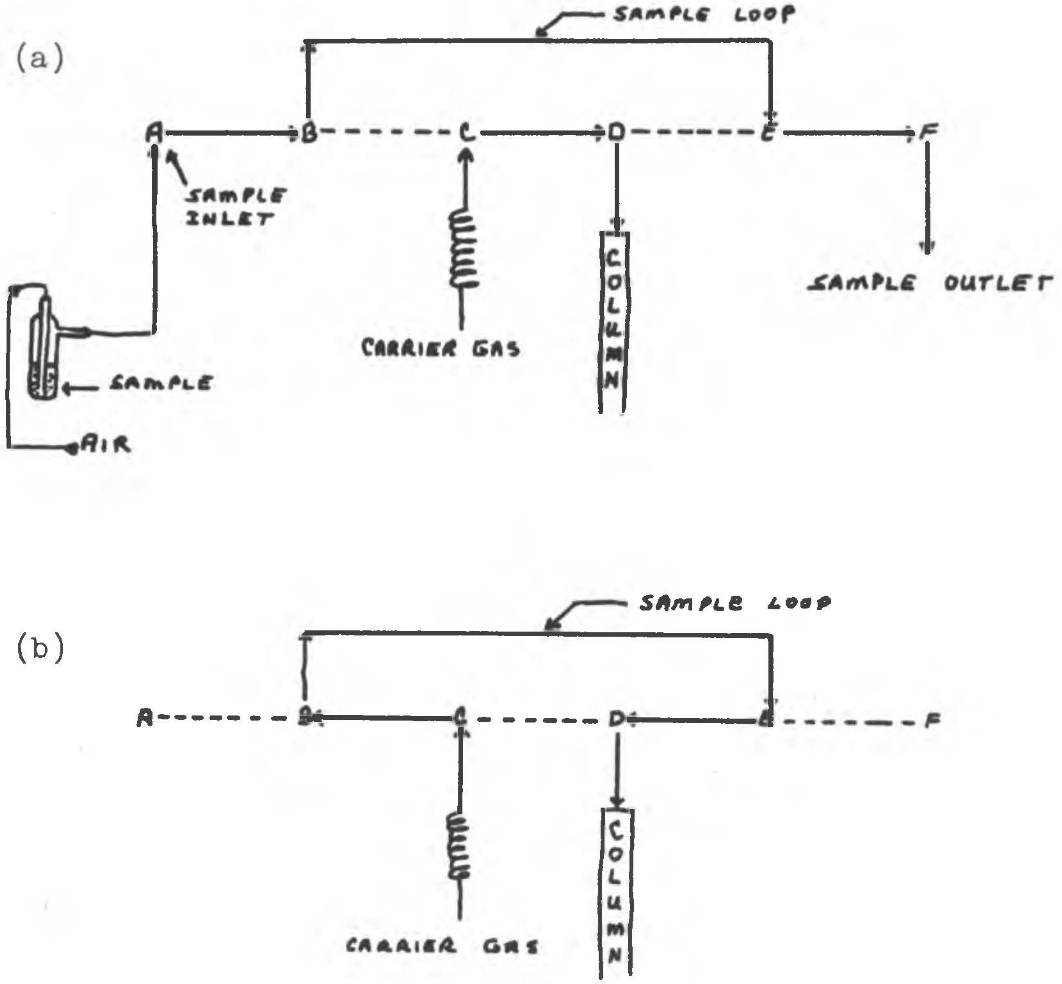

Fig. 6.--Schematical representation of original valve with gas and sample flow paths indicated by solid lines. (a) Closed normal position. (b) Open sample injection position.

This valve was therefore redesigned--as diagramed in Figure 7--to provide a back-flushing after every injection in order to prevent any trailing sample from entering the column.

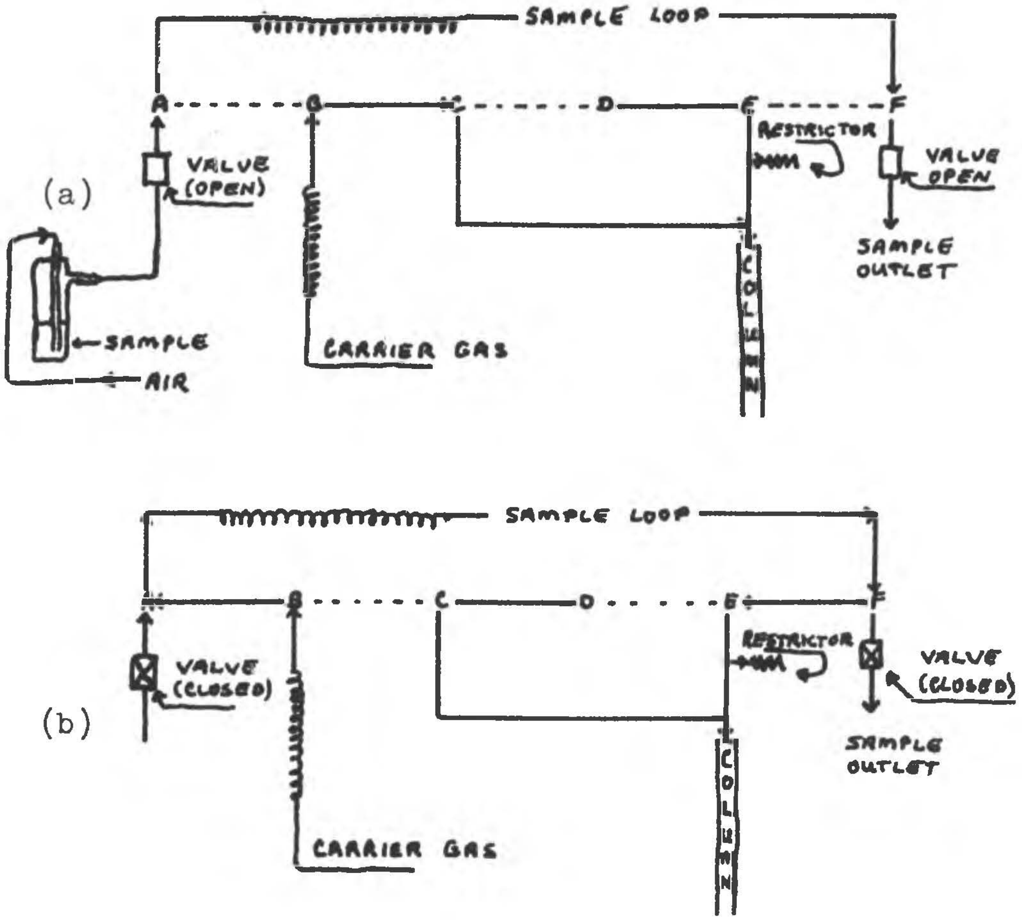

Fig. 7.--Schematical representation of new redesigned valve with gas and sample flow paths indicated by solid lines. (a) Open normal position. (b) Closed sample injection position.

This new valve system was fabricated by the university machine shop and although the end product was a significantly more complicated and delicate valve, experimentation showed that tailing had been eliminated and that a substantial break-through had been accomplished. It was then feasible to proceed with the originally planned study.

MEASUREMENTS AND CALCULATIONS

Data Obtained

A Gaussian shaped curve of concentration versus time (as illustrated in Figure 8) was recorded for each sample run.

The experimental efficiency of a GLC column is quantitatively expressed by[66]

$$H = \frac{L}{5.545} \left(\frac{w}{t_R}\right)^2 \qquad (8)$$

where H is the height (column length) equivalent to one theoretical plate and is directly related to peak width. Ideally a column should be so constructed as to give the lowest H attainable. In order to calculate the H value for each sample run, it is necessary to measure (1) the column length, L, (2) the peak width, w, and (3) the sample retention time, t_R . Figure 8 illustrates the actual measurement of w and t_R values.

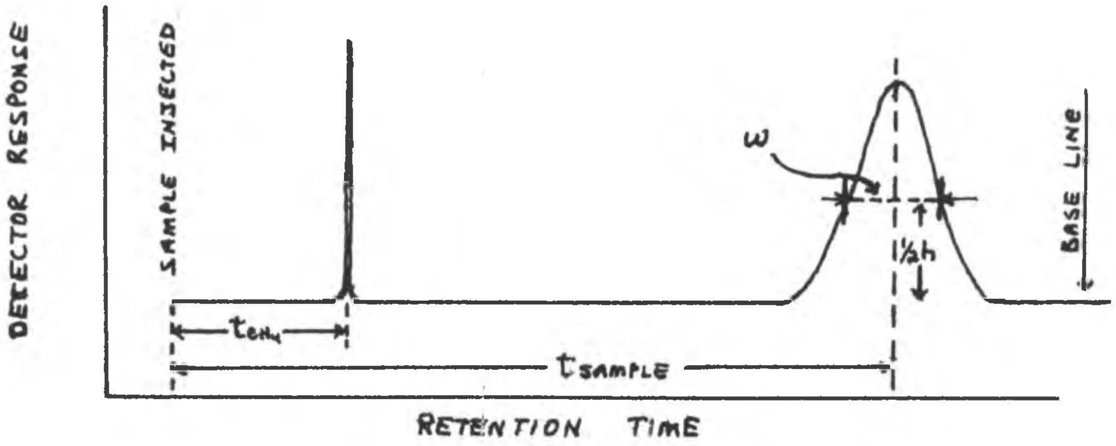

Fig. 8.--Typical chromatogram illustrating dimensions required for the calculation of column efficiency.

The bulk of the data recorded for each run however was used to calculate Term I and Term II in Equation (2) and the C_ℓ (Theoretical) expression represented by Equation (6). This data includes (4) the inlet pressure, P_i , (5) the outlet (atmospheric) pressure, P_o , (6) the methane elution time, t_{CH_4}, (7) the liquid phase percentage, %, (8) the solute diffusivity in the liquid phase, D_ℓ, (9) the solute diffusivity in the carrier gas, D_g, (10) the liquid phase density, $\rho_{Liq.}$, (11) the glass bead density, ρ_{GLASS}, (12) the glass bead diameter, d, (13) the obstructive factor, γ , and (14) the number of contact points per bead, m.

Measurements (2) through (6) must be taken for each run; (1) and (7) need only be found once for each column; (8) and (9) require information for each individual sample; and (10) through (14) data values remain constant in this research and need only be evaluated once.

Measurement of Column Dimensions

The length of each column was measured with a meter stick to within ±0.1 centimeter.

The peak width, sample retention time, and methane elution time were found by measuring to within ±0.01 inch with a ruler calibrated in 0.01 inch gradations and then dividing by the chart speed (inches per second) to get values in centimeters per second.

P_i and P_o values were read from a pressure gauge to a precision of ±0.1 inches of mercury and then converted to dynes per square centimeter.

The column liquid load percentage was found by weighing the liquid to ±0.0001 grams and adding this amount of liquid to a known weight of glass beads.

$\rho_{Liq.}$ and ρ_{GLASS} values were assumed to be 1.18 grams per cubic centimeter and 2.98 grams per cubic centimeter respectively as reported by Hawkes.[48]

Knox[64] has reported a γ value of 0.6 and Giddings[35] approximates m at 6.25 contact points per bead.

The average bead diameter was calculated to be 0.0226 centimeter (see Appendix A).

Diffusion Coefficients

Diffusion coefficients must somehow be obtained before any meaningful calculations can be made. In some cases one can rely on experimental values, although these are scarce for systems of practical interest.

Gaseous diffusion is most amenable to theory. The fairly uncomplicated hard sphere model of Gilliland[39] predicts D_g values for GLC systems within 35%. In addition, a number of experimental values have been reported.[18] Although the precision is less than desired, literature values are reported for the solute-gas systems used in this investigation and thus gaseous diffusion coefficients warrant no further attention.

The theory and measurement of liquid diffusion is much more difficult.[49] Most successful of the semi-empirical equations is that of Wilke and Chang:[79] an average error of 10% is found for "common liquid mixtures". Unfortunately, the solvents used in GLC are not common. In one test of the equation, with Dinonyl phthalate as a solvent, the Wilke-Chang expression is in serious error by a factor of

44.[53] Literature values are extremely rare and hence the only method remaining for obtaining D_ℓ values for conventional GLC systems is an experimental one, such as described in Appendix C.

Calculation of C_ℓ (experimental)

After compilation of the above basic data for each sample run is complete, attention can be focused on obtaining the desired $C_{\ell\,(\text{experimental})}$ value.

If one subtracts Term I and Term II of Equation (2) from Equation (8), the result is Term III as shown below;

$$C_\ell \cdot \mu = \frac{L}{5.545}\left(\frac{\omega}{t_R}\right)^2 - \frac{f}{1/A + j/C_g P_o \mu} - \frac{Bjf}{P_o \mu} \quad , \qquad (9)$$

where

$B = 2\gamma D_g$,

$C_g = C_g^* / D_g$,

$P = P_i / P_o$,

$\mu = L / t_{CH_4}$,

$f = \dfrac{9(P^4-1)(P^2-1)}{8(P^3-1)^2}$, and

$j = \dfrac{3(P^2-1)}{2(P^3-1)}$.

III. PRELIMINARY STUDIES

MINIMIZATION OF EXTRA-COLUMN EFFECTS

Bohemen and Purnell[5,6] have shown that before proceeding to a detailed study of column performance, it is necessary to check that contributions to H from apparatus, detector, injection valve, dead volume, sample size, and solid support adsorption have been reduced to a neglectible value or eliminated. An outline of some recommended procedures has been presented and, to avoid repetition, it is sufficient to state that numerous preliminary experiments and apparatus modifications were made before any of the reported measurements were taken. This part of the work is absolutely essential if meaningful results on column efficiency are to be obtained.

DETERMINATION OF A, C_g, AND D_ℓ VALUES

It is obvious that the solution of Equation (9), and hence the success of this research, depends upon the availability and reliability of A and C_g values (Term I), and D_ℓ data.

It has been suggested that Term I can be neglected when calculating the plate height for most normally loaded glass bead columns.[35,66,75] If this assumption is made, the evaulation of Equation (2) becomes rather straight forward. For the major portion of this research, however, this simplification does not hold (see Table V) and some rather dubious A and C_g data must be relied upon.[24,37,45,62]

Due to time limitations and the fact that the calculation of A and C_g values are currently being attempted by Steed[73] as a separate research project, this author regrets that detailed experimentation in this area could not be carried out. The values determined by Steed of 0.135 and 0.0003 for A and C_g respectively, are considered to be the most reliable data available for the columns used in this work.

As discussed earlier, D_ℓ values for the solute-solvent systems used in this study are not available, cannot be predicted theoretically, and therefore must somehow be found experimentally. For this research, D_ℓ values were calculated using a method suggested by Giddings[35] (see Appendix C).

IV. RESULTS AND DISCUSSION

A complete listing of the measurements made and the results obtained on all columns can be found in Appendix E: this section focuses on averages and trends observed in the Appendix.

EVALUATION OF THE LIMITATIONS OF EQUATION (6)

A close examination of the $C_{\ell(\text{experimental})}/C_{\ell(\text{theoretical})}$ ratios listed in Table I reveals that the predictions of Equation (6) are excellent for columns of 0.5 to 0.1% liquid loading. This agreement was expected and adds weight to the work of Giddings[35] and Hawkes[48] and again substantiates the validity of this theoretical equation with relation to normal liquid loadings on glass bead columns.

It is also obvious however that this equation fails completely to predict the proper C_ℓ values at the lower liquid loadings and, as the ratios indicate, that the columns are actually more efficient than theoretically expected. A feasible cause of this favorable discrepancy is a departure from the 100% capillary liquid assumption upon which Equation (6), and hence the value of $C_{\ell(\text{theoretical})}$,

TABLE I

COMPARISON OF C_ℓ EXPERIMENTAL AND THEORETICAL VALUES

% LIQUID LOADING	C_ℓ (experimental)/C_ℓ (theoretical)		
	n-Heptane	n-Decane	n-Undecane
0.54	1.14	1.09	1.21
0.29	0.86	0.99	0.98
0.20	1.06	0.95	0.99
0.10	--	0.75	0.75
0.048	0.28	0.20	0.22
0.026	0.20	0.05	0.04
0.011	--	0.17	0.20
0.0069	0.72	0.20	0.35
0.0042	0.57	0.30	0.35
0.098*	--	--	0.88
0.023*	--	0.09	0.12
0.0044*	--	0.10	0.13

Temperature 50°C
Particle diameter 0.0226 cm.
TOTP Liquid phase
60-70 mesh glass bead support

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*60-70 mesh Corning "roughened" beads

is based. This assumption, although proven for normal loaded beads, very likely is in error for the ultra-low loadings used in this research. It is suggested that adsorption liquid is always present in some relatively fixed and usually insignificant amount and that this becomes an increasingly larger percentage as the total liquid phase loading is reduced.

It should be noted that the uniform film assumption represented by Equation (7) also fails completely in explaining the results obtained: even at the lowest liquid loading of 0.0042%, which would amount to a uniform film of approximately 5 monolayers, the 100% uniform film assumption is seriously in error.

These conclusions indicate the need for further work and point out the lack of information pertaining to the complex nature of liquid distribution when using ultra-low loaded columns where capillary and adsorption liquid are both significant and neither can be neglected for the simplification of theoretical C_ℓ calculations.

EVALUATION OF EXPERIMENTAL C_ℓ RESULTS

Table II shows the average experimental C_ℓ values obtained for the various n-hydrocarbon—X% TOTP solvent systems studied. Intuitively one would expect the C_ℓ values to decrease <u>significantly</u> with each decrease in

TABLE II

C_ℓ EXPERIMENTAL VALUES FOR VARIOUS LIQUID LOADING PERCENTAGES

N_2 carrier gas
TOTP liquid phase
60-70 mesh glass bead support
50 C column temperature

% TOTP	C_ℓ EXPERIMENTAL					
	n-C_7	n-C_8	n-C_{10}	n-C_{11}	n-C_{12}	n-C_{13}
.54	.087		.022	.013		
.29	.053		.024	.012		
.20	.047		.018	.011		
.10	.035	.036	.018	.011	.0070	.0054
.048	.0040		.0050	.0035		
.026	.0017		.0010	.0004		
.011	.0040		.0040	.0025	.0032	
.0069	.0031	.0021	.0025	.0026	.0036	
.0042	.0027	.0033	.0020	.0011		
.098*	.038	.047	.035	.017	.011	.011
.023*			.0027	.0029		
.0044*	.002		.002	.002		

*60-70 mesh Corning "roughened" beads used for support.

liquid percentage as long as capillary liquid is predominant. As a uniform film is approached, the C_ℓ values should become much less dependent upon liquid percentage; the values at ultra-low liquid loadings should be very small and decrease only very slightly with a liquid load reduction. Table II shows that this prophecy is generally correct except for one deviation: the 0.026% column appears to be super-efficient and gives unexplainably low C_ℓ values.

It is obvious that efforts to decrease C_ℓ by decreasing the liquid phase percentage become increasingly less effective at loadings less than about 0.03%. It is most fortunate that, as the results to be discussed later indicate, this percent loading also represents the approximate transition at which C_ℓ no longer controls the column efficiency. For example, Table IV shows that at 0.011% liquid loading the C_ℓ term is only 39% of the total plate height and is no longer the dominating peak spreading parameter.

Attention is also directed to the experimental C_ℓ results obtained for "roughened" Corning glass beads. These beads are advertised to have more surface area and a rougher texture, and theoretically should drain away some of the capillary liquid from the bead contact points; thus, C_ℓ values for these beads should be less than for the normal glass beads used throughout this research.

Contrary to expectations, no decrease in C_ℓ values were observed at the ultra-low liquid loadings for which the two types were compared. The importance of this type of bead has not been discredited by these few results however, since at the low loadings evaluated there is very little capillary liquid expected at the bead contact points, even on the regular beads. If comparisons had been made at the 0.5% liquid load level, it is quite likely that the C_ℓ values obtained for the roughened beads would be significantly lower than for the normal beads since capillary liquid definitely predominates (and controls the C_ℓ value) at this higher liquid loading percentage.

It is also significant (as shown later in Figure 12) that the regular beads are much rougher than predicted and **may affect the above comparison.**

CAPILLARY LIQUID AS A FUNCTION OF TOTAL LIQUID LOADING

In previous papers by Giddings[35] and Hawkes[48] the amount of liquid adsorbed on the surface of the beads, $\%_0$, was estimated by plotting

$$\left[\frac{120\,(\%)\,C_{\ell\,(\mathrm{EXP.})}}{R(1-R)\,d_p^{\,2}} \left(\frac{3\,m\,\rho_{\mathrm{LIQ.}}}{\rho_{\mathrm{GLASS}}} \right)^{1/2} \right]^{2/3} \tag{10}$$

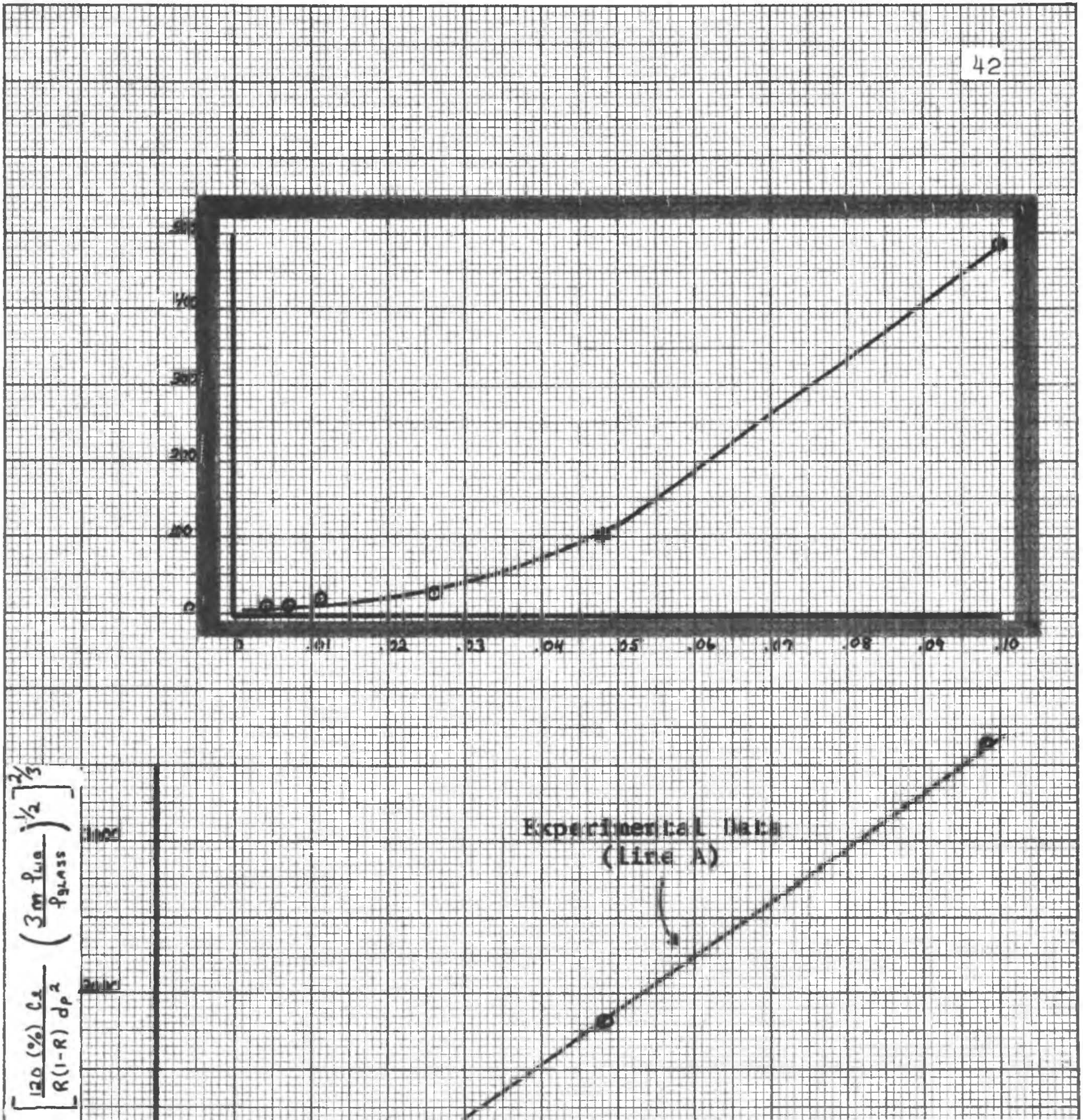
against %. A straight line was drawn through the scattered data points in the 0.1 to 1.0% liquid range examined in their work and extrapolated to a $\%_o$ axis intercept value of approximately 0.04%.

The results can be interpreted as suggesting that at liquid loadings less than 0.04%, the uniform film approximation of Equation (7) should be valid since all the liquid should be adsorption controlled.

This interpretation however is based on an extrapolation from a 0.1% liquid loading and it is felt that an investigation of this graph at lower liquid loadings (especially around 0.04%) would be most appropriate and beneficial to the understanding of actual liquid distribution.

The experimental data of this investigation was therefore plotted according to Equation (10) as shown in Figure 9. As predicted and previously found, a constant slope is observed in the 1.0 to 0.1% liquid loading range and if a line is extrapolated to the % axis intercept, the resulting value for % is approximately 0.04%.

As shown in the expanded portion of the graph, however, the lower liquid percent data points indicate that this line actually curves up and never intercepts either the % axis or the line B(uniform film theory prediction).


0
100
200
300
400
500
0
.01
.02
.03
.04
.05
.06
.07
.08
.09
.10
Experimental Data
(Line A)
$\left[\frac{120\,(\%)\,C_\ell}{R(1-R)\,d_p^{\,2}}\left(\frac{3m\,\rho_{LIQ}}{\rho_{GLASS}}\right)^{1/2}\right]^{2/3}$

The results of this research thus extend the work presented by Giddings and Hawkes and indicate that a uniform film is approached but never reached, even at ultra-low liquid loadings where a uniform film might be expected. It is also important to observe that a liquid load reduction has a significant beneficial result only in the 1.0 to 0.05% range (where the slope of line A in Figure 9 is constant). Additional reductions do little to improve column efficiency and may cause adverse effects such as decreased resolution, increased adsorption effects, and a shorter column life.

ANALYSIS TIME AND COLUMN EFFICIENCY

Another objective of this research was to investigate the relationship between column efficiency and analysis time with respect to various liquid load percentages. Equation (2) shows that the column efficiency is a function of both carrier gas velocity (which determines analysis time) and C_l (which is controlled by the liquid phase quantity and distribution).

A plot of H versus μ for glass bead columns at two different liquid loading percentages, as graphed in Figure 10, is of special interest for two important reasons:

1. The column efficiency is found to be greatly improved (lower H) at the 0.0069% liquid

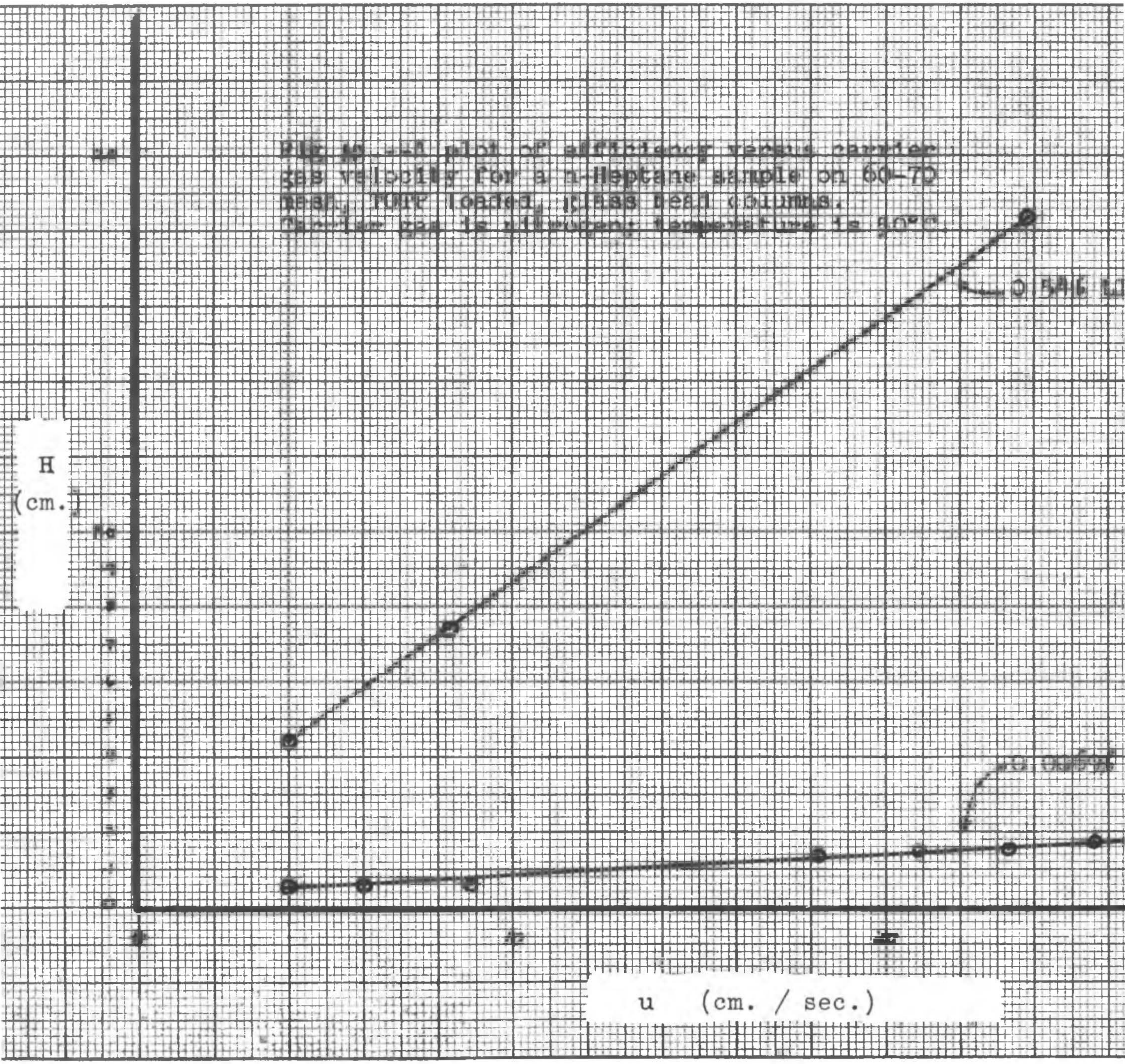


Fig. [illegible] H-u plot of efficiency versus carrier gas velocity for a n-Heptane sample on 60-70 mesh, [illegible] loaded, glass bead columns. The carrier gas is nitrogen; temperature is [illegible]°C loading.

2. The results indicate that greater carrier gas velocities can be used with the low liquid loadings without significantly decreasing the column efficiency as is the result at the higher loading; hence analysis time can be decreased without seriously affecting resolution.

AN INVESTIGATION OF THE SIGNIFICANCE OF EXTRA-COLUMN EFFECTS ON COLUMN EFFICIENCY

Tables 20, 21, and 22 present the efficiency data obtained with the original modified apparatus which was considered to be quite refined and devoid of the usual dead-space found in commercial GLC systems. Tables 6, 12, and 19 show the results obtained from identical GLC columns but with the following technique and valve changes:

1. Glass wool column end plugs were eliminated and columns were filled to the ends with glass beads.
2. The sample injection valve was modified to reduce tailing as discussed in the Experimental Section.

Since H is a function of the carrier gas velocity, before-and-after comparisons must be made at equivalent velocities in order to be meaningful. The comparisons which are valid for the data obtained in this work are summarized in Table III.

It is apparent from this information that a significant decrease in column efficiency, and hence the C_ℓ remainder value, has resulted from the modifications made. This serves to indicate the importance that extra-column effects can have on column efficiency and the results of any investigation. It is obvious that many extra-column effects have been neglected in some published works and that a large quantity of the published data is in error because of apathy in this area.

Needless to say, the data listed in Tables 20, 21, and 22 is included in this thesis only to illustrate this important effect and no reference is made to these Tables for any of the other conclusions of this thesis.

ACCURACY EVALUATION OF THE CALCULATED RESULTS

It is rather important that the C_ℓ term be the predominant plate height parameter since it is measured as the remainder which is left when the other (hopefully much smaller) terms are subtracted from Equation (2). Since the theory of coupling (represented by Term I) is not yet reliably calculable, serious problems can result when this term becomes a significant percentage of the total plate

TABLE III

COLUMN EFFICIENCY BEFORE-AND-AFTER A VALVE AND TECHNIQUE CHANGE

	0.011% COLUMN				0.0044% COLUMN			
	n-Decane		n-Undecane		n-Deacne		n-Undecan	
	before	after	before	after	before	after	before	a
u	15.7	15.0	15.7	15.0	12.2	12.3	12.2	1
H	.197	.091	.177	.106	.192	.074	.123	.
C_ℓ	.0081	.0017	.0066	.0025	.0110	.0012	.0050	.

height.

If we look at the column efficiency for a n-Decane sample as a function of the liquid load percentage at the random constant gas velocity of 27±1.5 cm. per sec., we find data as summarized in Table IV below.

TABLE IV

COLUMN PARAMETER VALUES AT VARIOUS LIQUID LOAD PERCENTAGES

% LIQUID LOADING	u (in cm./sec)	H	TERM II	TERM I	(C_ℓ·u) TERM III	C_ℓ
0.54	27.0	.650	.0020	.083	.5650	.021
0.29	26.3	.688	.0022	.099	.6065	.023
0.10	26.4	.499	.0018	.087	.4106	.015
0.048	25.9	.223	.0014	.097	.1242	.005
0.011	28.3	.165	.0013	.100	.0637	.002
0.0069	25.6	.169	.0013	.103	.0652	.003

If the lower percentages are plotted, as shown in Figure 11, we can visualize the trend which develops as the liquid load decreases. Term II remains at a constant value of approximately 0.002 and is always negligible; Term I remains constant, but at the much larger and more significant value of about 0.10. It is thus obvious that the C_ℓ term is controlling the column efficiency only for

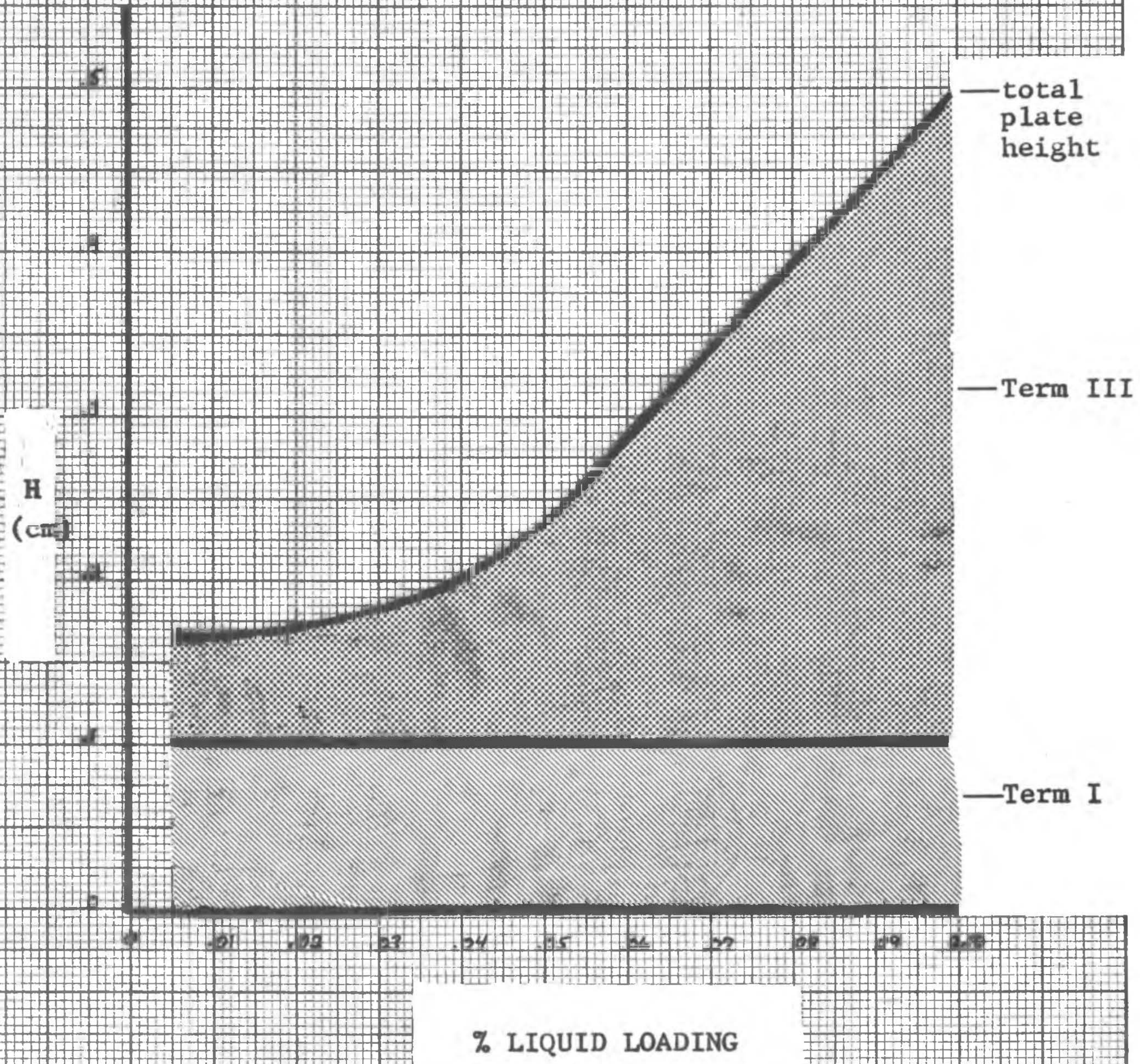


Fig.11.--Contribution of individual peak spreading terms to the total column efficiency as a function of liquid loading percentage.

the more heavily loaded columns, and that a reliable calculation of the C_ℓ term becomes dubious for the lower loadings, where the Coupling term becomes large and eventually predominates.

Nothing can be done to improve this situation until either more reliable Coupling theory can be established, better experimental measurements can be obtained, or the Coupling term can be reduced to a negligible value. In other words, Term I must be diminished or become better defined before more accurate C_ℓ values can be obtained by this subtraction method.

The Coupling term value can be reduced by using a lighter carrier gas--such as Helium--in place of Nitrogen. The need to reduce this term did not become obvious, however, until the research was nearly complete and it would have been inappropriate to change any of the fixed variables at that time. At the conclusion of the scheduled research two of the columns were re-run with Helium in order to examine the actual effect on Term I and Term II.

Table V summarizes results of this exploration which suggest that using Helium as the carrier gas is a feasible way to reduce Term I without seriously affecting Term II; hence, the C_ℓ calculations are more reliable and in addition, the column efficiency has been further reduced.

TABLE V

COLUMN PARAMETER VALUES AS A FUNCTION OF CARRIER GAS CHOICE

	CARRIER GAS	u (in cm./sec.)	H	TERM II	TERM I	$(C_{\ell} \cdot u)$ TERM II
0.0069%						
n-Octane	N_2	25.6	.152	.002	.098	.053
	He	25.8	.094	.005	.057	.032
n-Decane	N_2	25.6	.170	.001	.103	.065
	He	25.8	.106	.003	.069	.034
0.0042%						
n-Octane	N_2	24.4	.168	.002	.092	.074
	He	24.4	.137	.005	.054	.078
n-Decane	N_2	24.4	.127	.002	.098	.027
	He	24.4	.093	.004	.066	.024

SCANNING ELECTRON MICROSCOPIC ANALYSIS OF THE GLASS BEAD SURFACE*

Figure 12 consists of six photographs (of 60-70 mesh glass beads) taken with a Mark IIA, Cambridge Scanning Electron Microscope owned by the Dow Chemical Company. A specimen holder was coated with a thin layer of free-flowing Eastman 910 adhesive, and uncoated glass beads were poured onto the holder. Thus the bottom layer of beads came into contact with the free-flowing liquid (similar to a GLC liquid phase) and were at least partially coated.

A visual inspection gives two types of meaningful information: (1) knowledge of the naked glass bead surface texture, and (2) an indication of how a liquid phase distributes itself on the bead.

As the magnification is increased from 48X, (A), to 4400X, (F), various factors become obvious and merit discussion. (A) illustrates the over-all complexity of a GLC column. This view represents about two thirds of the column diameter and shows the situation facing a typical solute molecule. Note that the beads are quite spherical. (B) focuses on the bead contact points and shows capillary liquid in detail. (C) shows a partially coated bead and (D) is an enlargement of this same bead. This is the first

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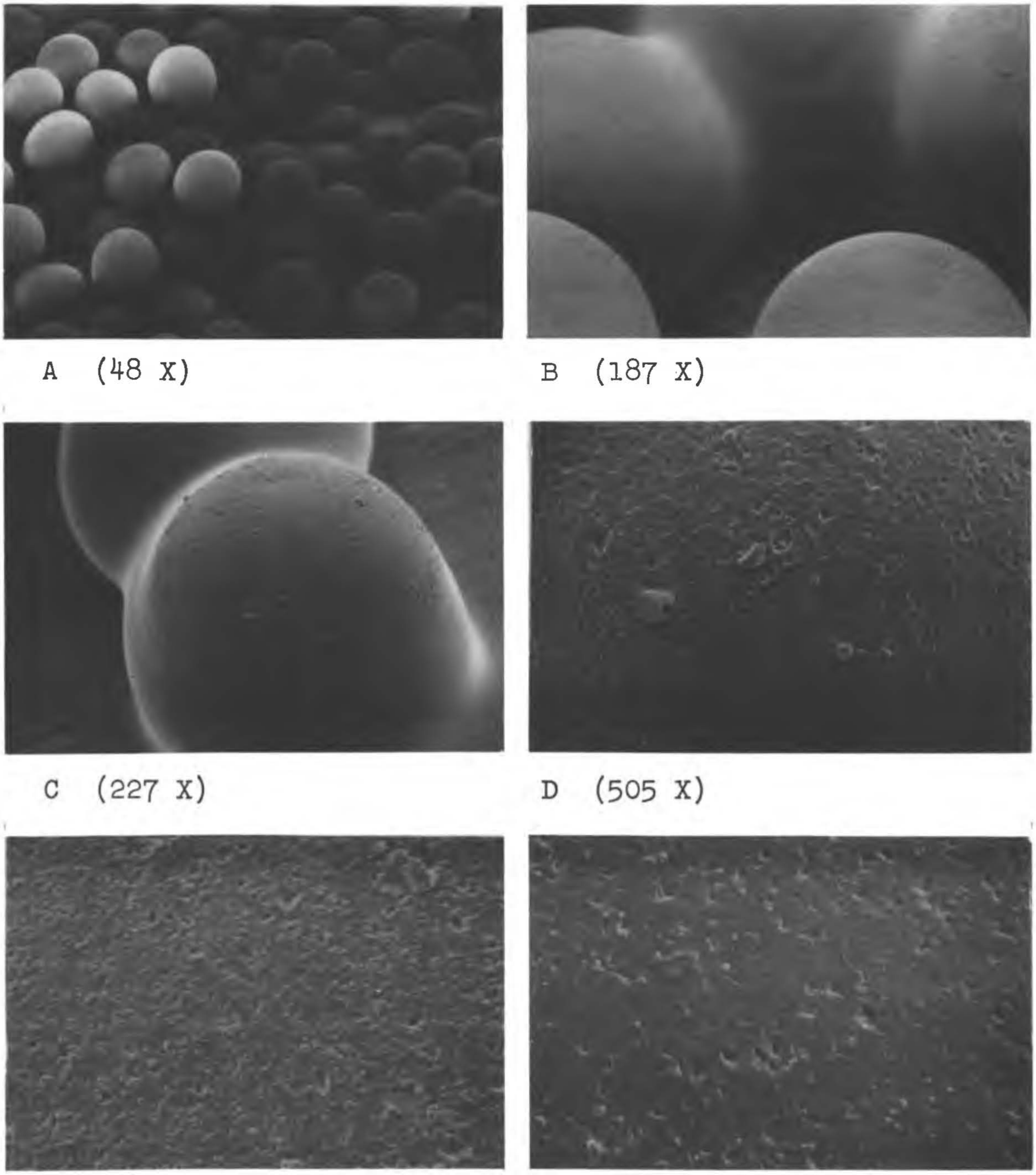
*The opportunity to investigate this subject did not occur until late in the organization of this thesis and thus this section has been tacked on and may appear out of place.



A (48 X)

B (187 X)

C (227 X)

D (505 X)

E (1830 X)

F (4400 X)

Fig. 12 .--Photographs of 60-70 mesh (0.0226 diameter) GLC glass beads taken with a scanning electron microscope.

time, to this author's knowledge, that such surface detail has ever been observed: the experience certainly changes a generally held preconceived conception of a smooth glass surface capable of supporting only adsorption liquid. (E) and (F) represent even further enlargements (of different beads); the latter being a close-up of a bead with a diameter in excess of one meter. The detail shown in these photographs represents a meaningful advancement in the understanding of glass bead surface texture, and thus GLC theory.

V. CONCLUSIONS AND RECOMMENDATIONS

Several interesting conclusions and suggestions for further work have arisen from this study.

1. With further theory improvements, good technique, and refined apparatus, the glass bead column can no doubt be used for the comparatively rapid determination of liquid diffusion coefficients as described in Appendix C.
2. The validity of the theoretical Equation (6) has been substantiated for glass bead columns in the 0.54 to 0.10% liquid loading range. This verification has been attempted only twice before[35,48] and thus the results of this work cast a heavy supporting vote.

   This theory was tested for the first time in the ultra-low 0.10 to 0.004% liquid loading range and was found to be incapable of predicting experimental results. It is postulated that the reason for this discrepancy is a deviation from the 100% capillary liquid assumption upon which Equation (6) is based.

   It was found that the uniform film theory (represented by Equation (7)) also fails to predict the observed C_ℓ values. The actual C_ℓ data obtained lie between the extreme predictions of these two limiting theories and depend critically on liquid configuration.

3. The optimum liquid loading on a 60-70 mesh glass bead column is in the 0.04 to 0.01% range. It is in this range where two important transitions were noticed: (1) C_ℓ ceased to decrease significantly with a liquid load reduction, and (2) the C_ℓ term ceased to be the dominate (efficiency controlling) plate height term.

   Frederick[67] and Hawkes[48] have noticed that glass beads tend to stick together (and become difficult to pack) at liquid loadings greater than about 0.15%. Wilkinson[74] suggests that this phenomenon can serve to indicate the maximum allowable liquid load desired. While this simple test has value, it is clear from the results of this work that smooth flowing beads can still make relatively inefficient columns and that efforts should be made to use the lower liquid loadings.

4. The 0.04% extrapolated uniform film prediction of Giddings[35] and Hawkes[48] is strictly hypo-

thetical; a uniform film is approached with liquid load reduction but it is never realized.

5. A reduction in liquid load is an excellent method of increasing not only column efficiency, but also the sample retention time: in addition, analysis time may be further decreased (when C_ℓ is small) by increasing the carrier gas velocity without significantly affecting the column efficiency. For this work a maximum inlet pressure of about 60 psi. could be used without blowing out the flame of the ionization detector. The maximum gas velocity (minimum analysis time) is limited only by apparatus factors and future work should be based on this knowledge.
6. Throughout the results, the 0.026% column stands out as a super-efficient column. This is unexplainable at the present time and it is recommended that further columns be tested in the 0.05 to 0.01 liquid percent range.
7. For normal liquid loadings, roughened or grooved beads should be an advantageous method of reducing the amount of capillary liquid around the bead contact points; however, there was no advantage gained by using "roughened"

beads with ultra-low liquid loadings.

8. It is recommended that Helium replace Nitrogen as the carrier gas, when further explorations are made pertaining to increased glass bead column efficiency at high carrier gas velocities, in order to decrease Term I to a less significant value.

9. The accuracy of the C_ℓ values reported in this work depends upon the following: (1) the peak spreading resulting from extra-column effects, (2) the accuracy of A, C_g, and D_ℓ data, and (3) the consistency of supposibly fixed variables such as packing technique, column temperature, sample injection time, etc.

The large amount of basic data listed in Appendix E is of considerable value and the results and conclusions of this work will become more valuable if recalculations are made when reliable Coupling theory (Term I) and D_ℓ data are available. The greater majority of any error inherent in the results of this work can be traced to these two factors and the independent calculation of C_ℓ values can only be as successful as the background data available.

10. The advent of newer, high temperature, high pressure instruments and more sensitive detectors with less dead volume, will merely make possible the separation of higher boiling and more difficult compounds when used in conjunction with the lightly loaded (0.04 to 0.01%) columns recommended by this author.

11. Too much attention cannot be drawn to the important role that the apparatus can play in the final result obtained when using a highly efficient column. A poorly designed apparatus can cause considerable loss in the resolution given by a highly efficient column, and since only the overall results are important, it is futile to try to develop more efficient columns when the contributions to peak spreading of the apparatus are of considerable, or perhaps limiting, significance.

In conclusion, let it be noted that a greater portion of time was spent on refining the apparatus and minimizing the often neglected extra-column effects than was spent on gathering the data reported in Appendix E.

VI. POSTSCRIPT--LIMITATIONS TO THE REDUCTION OF LIQUID LOADING

Although these results show that low liquid loadings have many advantages and possible applications, there are limitations to the practicality of this reduction *ad infinitum*.

A few of the more important disadvantages are as follows:

1. A reduced amount of liquid substrate will mean a smaller amount of sample that can be chromatographed to avoid overloading the column.[3,59,71,72]
2. If a smaller sample is used, the detector sensitivity must be increased.[20] Eventually instrument limitations prevail.
3. If a smaller sample is used, important trace components may be missed.[65]
4. A decreased sample size limits the use of GLC for preparative work.
5. If a small weight of liquid phase is removed by evaporation, the proportion so removed is comparatively large, and there can be a significant change in retention times; thus, low loaded columns tend to have short working lives.

6. The solid support of a GLC column is rarely completely inert and thus solute adsorption can become a problem when solid support surfaces are exposed. This can significantly increase peak broadening.[54]
7. Special effort must be made to minimize extraneous peak broadening influences. Such extra-column effects as injection time, dead volume, and detector response time become critical at low liquid loadings.[30,42,58]

In addition to the above considerations, it must be mentioned that the conditions chosen for this investigation were nearly ideal. For example, a polar liquid phase (TOTP) was chosen to cover up any possible polar adsorption sites on the glass bead support. Furthermore, non-polar n-hydrocarbons were used for the solutes to protect against adsorption at the glass bead (or liquid) interface. If a polar sample had been used, the conclusions of this thesis might be less promising.

In summary, the use of ultra-low liquid loadings to increase the column efficiency and decrease sample analysis times demands the development and utilization of high speed valving, low dead volume connectors, fast detectors, precise temperature controls, rapid amplifiers, and inert stationary phases since overall performance is ultimately limited by these extreme conditions.

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APPENDIX

APPENDIX A

CALCULATION OF THE AVERAGE BEAD DIAMETER

The average bead diameter of a 60-70 mesh sieve grading is approximately 0.021 centimeter. However, due to the dependence of Equation (6) on d_p "squared", it is quite important that this parameter be as accurate as possible.

To obtain this value, a number of beads were weighed on a microbalance after which they were carefully dumped onto a black surface and counted with the aid of a magnifying glass. With the average weight per bead determined and the glass density known,[48] the bead diameter can be calculated as follows:

WEIGHT OF BEADS = 0.015767 g

NUMBER OF BEADS = 883

GRAMS PER BEAD = 1.8×10^{-5}

VOLUME PER BEAD = $\frac{4\pi r^3}{\text{cm.}^3}$

BEAD DENSITY = 2.98 g/cm^3

$$\frac{4\pi r^3}{3} = \frac{\text{wt./bead}}{\text{density}}$$

$$r^3 = \frac{1.8 \times 10^{-5} g \cdot 3}{2.98\ g/cm^3 \cdot 4 \cdot 3.14} = 1.45 \times 10^{-6} cm^3$$

$$r = 0.0113\ cm$$

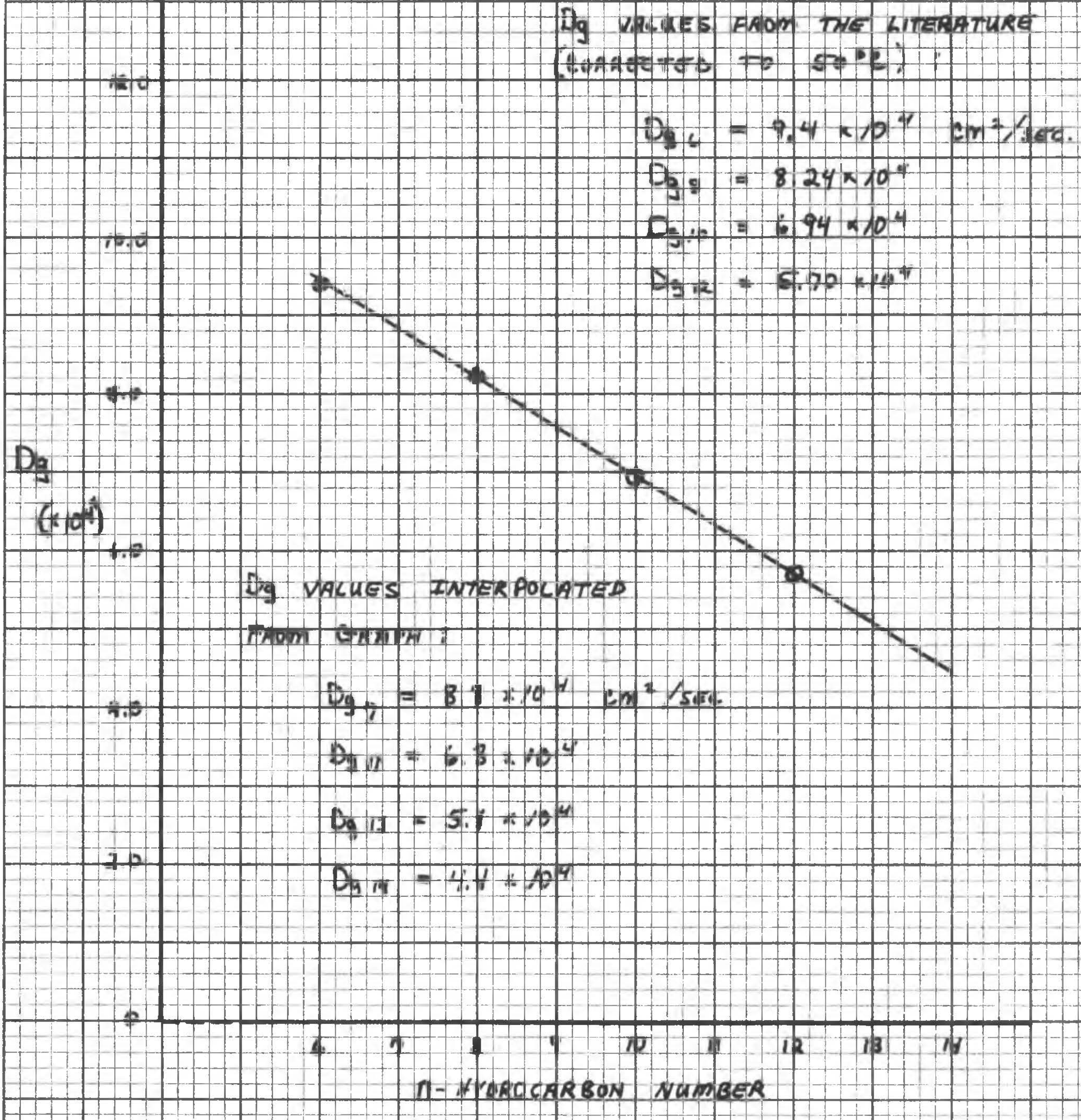
$$d_p = 2r = 0.0226\ cm$$

APPENDIX B

INTERPOLATION OF D_g VALUES FROM LITERATURE DATA

For many of the solute-carrier gas systems used in this experiment, D_g values can be found in the literature.[18] Some are not available however, and none are listed at the temperature used for this research. The available D_g values were thus corrected to 323°K by multiplying by $\left[\frac{323}{T}\right]^{1.75}$.[18]

If these values are graphed, as shown in Figure 13, a straight line is observed which allows for an interpolation of the missing D_g values.



Dg VALUES FROM THE LITERATURE (CORRECTED TO 50°C)

$D_{g_6} = 9.4 \times 10^{4}$ cm²/sec.
$D_{g_8} = 8.24 \times 10^{4}$
$D_{g_{10}} = 6.94 \times 10^{4}$
$D_{g_{12}} = 5.70 \times 10^{4}$

Dg VALUES INTERPOLATED FROM GRAPH :

$D_{g_7} = 8.8 \times 10^{4}$ cm²/sec.
$D_{g_{11}} = 6.3 \times 10^{4}$
$D_{g_{13}} = 5.1 \times 10^{4}$
$D_{g_{14}} = 4.4 \times 10^{4}$

Fig. 13.—a plot of the D_a values of various n-hydrocarbons in nitrogen gas at 50°C.

APPENDIX C

DETERMINATION OF D_ℓ DATA

In separate experiments Giddings[35] and Hawkes[48] have obtained results which indicate that Equation (6),

$$C_{\ell\,(\mathrm{THEORETICAL})} = \frac{R(1-R)\,d_p^{\,2}}{120\,D_\ell} \cdot \left(\frac{\%\ \rho_{\mathrm{GLASS}}}{3m\ \rho_{\mathrm{LIQ}}}\right)^{1/2}$$

is capable of predicting theoretical C_ℓ values to within 10% of measured experimental C_ℓ values for normal loaded glass bead columns. The solute-solvent systems used were benzene-0.1% TOTP and n-Heptane-1.05% TOTP respectively, thus suggesting that a feasible way of calculating D_ℓ values is to assume that $C_{\ell\,(\mathrm{experimental})}$ (Equation (9)) is equal to $C_{\ell\,(\mathrm{theoretical})}$ (Equation (6)) in the 1.0 to 0.1% liquid loading range. It then follows that

$$D_\ell = \frac{R(1-R)\,d_p^{\,2}}{120\,C_{\ell\,(\mathrm{EXP.})}} \cdot \left(\frac{\%\ \rho_{\mathrm{GLASS}}}{3m\ \rho_{\mathrm{LIQ.}}}\right)^{1/2}, \qquad (11)$$

and diffusivity values can be calculated from experimental column efficiency results.

A 0.54% TOTP column was prepared and the n-hydrocarbon solutes employed in this research were eluted to obtain the necessary $C_{\ell\,(\mathrm{experimental})}$ values.

Figure 14 which follows shows the D_ℓ values calculated by this method.

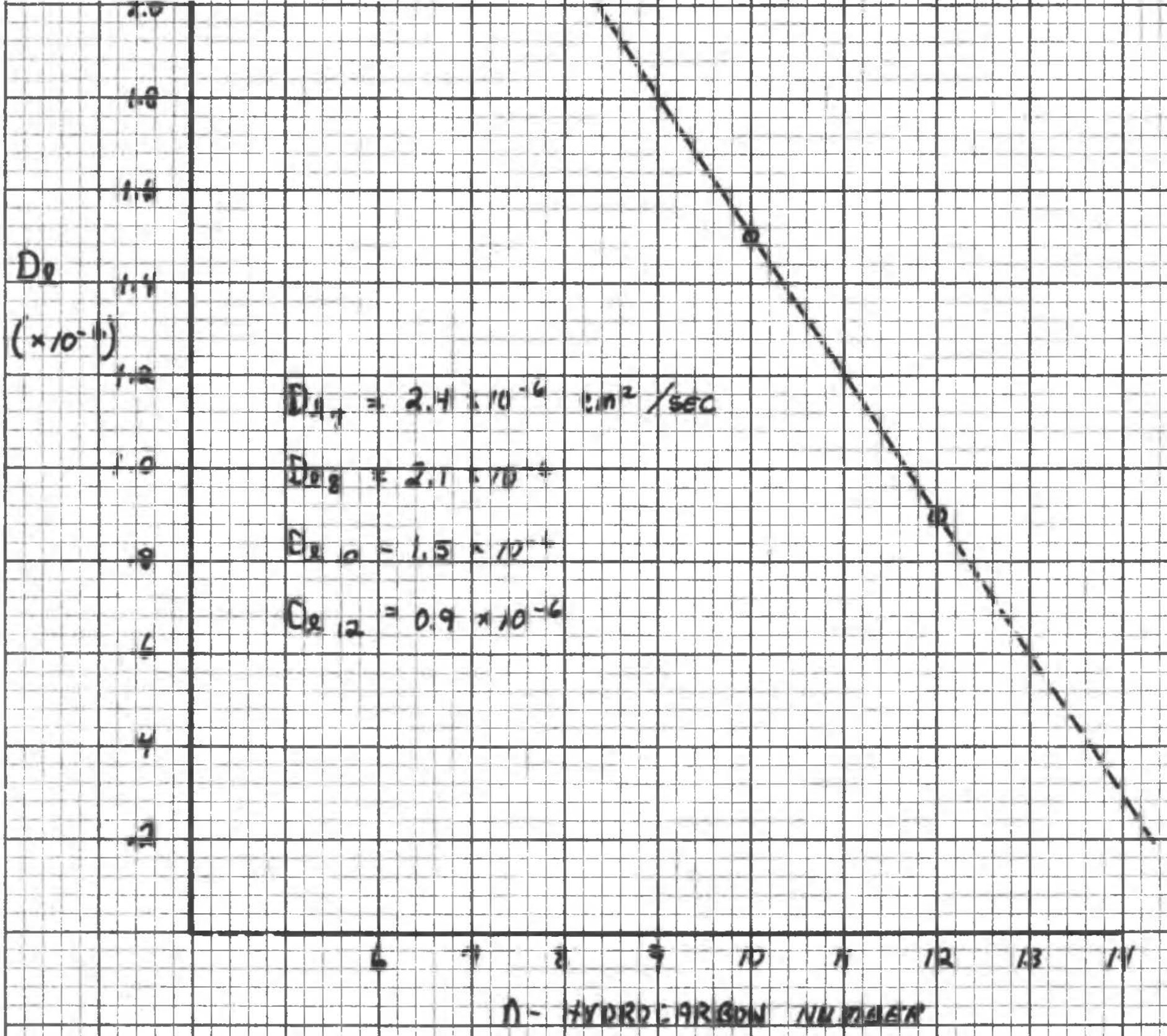


Fig. 14 --a plot of the D_g values obtained from a 0.54% TOTP column at 50°C.

APPENDIX D

COMPUTOR PROGRAM FORMAT USED FOR THE CALCULATION OF COLUMN PARAMETERS

The Fortran IV program which follows is designed to solve Equation (9) and (6) for $C_{\ell(\text{experimental})}$ and $C_{\ell(\text{theoretical})}$ values respectively.

Fig. 15.--Fortran IV computor program used to calculate the results listed in Tables VI through XXII from the experimental data obtained.

```
 CALCULATION OF CL (EXPERIMENTAL AND THEORETICAL)
 NGAS = 1 FOR HE AND 2 FOR NITROGEN
 PI AND PO ARE IN INCHES OF HG  TCH4,TS,AND W ARE IN SECS.
    INTEGER C,Y
    REAL L
    REAL J
    LOGICAL XCLTHE,XCLRAT
    EQUIVALENCE (XCLTHE,CLTHE),(XCLRAT,CLRAT)
    DIMENSION DC(20,3)
    DC(1,1)=791588.
    DC(6,1)=371958.
    DC(7,1)=300290.
    DC(8,1)=281026.
    DC(10,1)=200000.
    DC(11,1)=160000.
    DC(12,1)=120000.
    DC(13,1)=80000.
    DC(1,2)=200000.
    DC(6,2)=94000.
    DC(7,2)=88333.
    DC(8,2)=82268.
    DC(10,2)=69467.
    DC(11,2)=63333.
    DC(12,2)=56912.
    DC(13,2)=50833.
    DC(14,2)=44666.
    DC(7,3)=.0000033
    DC(8,3)=.0000026
    DC(10,3)=.0000020
    DC(11,3)=.0000017
    DC(12,3)=.0000014
    DC(13,3)=.0000011
    DC(14,3)=.0000005
    DIMENSION  TCD(12)
    COMMON L,DP,PCNT,NGAS,Y,PI,PO,TO,TS,W,C
    DIMENSION CGAS(2,2)
    DATA CGAS/6HHELIUM,1H ,8HNITROGEN/
100 CALL CTINP (L,TCD,K)
    WRITE(4,900)L,DP,PCNT,CGAS(1,NGAS),CGAS(2,NGAS)
    WRITE (2,900) L,DP,PCNT,CGAS(1,NGAS),CGAS(2,NGAS)
900 FORMAT(///1H1,10X,16HLENGTH          =,F6.1,4H  CM/1H ,10X,
   116HBEAD DIAMETER  =,F7.4,3H CM,/1H ,10X,16HPERCENT LIQUID =,
   2F7.4/1H ,10X,17HCARRIER GAS     = ,A6,A2)
    WRITE(4,902)
902 FORMAT(///1H ,10X,6HCARBON,3X,1HU,6X,2HPI,5X,2HPO,3X,6HSAMPLE,
   11X,7HMETHANE,1X,4HPEAK,2X,9HRETENTION/1H ,12X,3HNO.,24X,4HTIME,
```

```
   23X,4HTIME,3X,5HWIDTH,3X,5HRATIO)
    WRITE (2,905)
905 FORMAT(///1H ,9X,6HCARBON,2X,1HU,4X,4HHETP,4X,1HB,3X,8HCOUPLING,
   12X,2HCL,7X,2HCL,5X,2HCL,/1H ,11X,3HNO.,8X,4HEXP.,3X,4HTERM,3X,
   24HTERM,3X,4HTERM,5X,4HEXP.,2X,6HTHEORY,2X,5HRATIO)
    WRITE(2,903)
    WRITE(4,903)
903 FORMAT(1H ,10X,61(1H*))
101 CALL CTINP (Y,TCD,K)
    IF (K.GT.1) STOP
    IF(Y.EQ.99) GO TO 100
    H = L/5.5452*((W/TS)**2)
    P=PI/PO
    J=3.0*(P**2-1.0)/(2.0*(P**3-1.0))
    F=J**2*(P**2+1.0)/2.0
    U=L/TO
    POD=PO*33860.0
    R=TO/TS
    B=2.0*0.6*DC(C,NGAS)/POD
    BTERM = B*J*F/U
    CPTERM=F/(1.0/.135+(J/(.00030*POD*U/DC(C,NGAS))))
 **********
 FOR THIS RUN I HAVE USED PAULS NEW VALUES FOR (A) AND (CG)
 **********
    CLTERM = H-BTERM-CPTERM
    CLEXP = (H-BTERM-CPTERM)/U
    CLTHE = R*(1.0-R)*DP**2*SQRT(0.1347*PCNT)/(120.0*DC(C,3))
    CLRAT=CLEXP/CLTHE
    IF(XCLTHE)XCLTHE=.FALSE.
    IF(XCLRAT)XCLRAT=.FALSE.
    WRITE(2,906)C,U,H,BTERM,CPTERM,CLTERM,CLEXP,CLTHE,CLRAT
906 FORMAT(1H ,10X,I2,F7.2,1X,4F7.4,2X,2F7.4,2X,F5.2)
    WRITE(4,904)C,U,PI,PO,TS,TO,W,R
904 FORMAT(1H ,12X,I2,F7.2,1X,2F7.2,F8.2,2F7.2,F8.3)
    GO TO 101
    END
```

APPENDIX E

COLUMN PARAMETER RESULTS

Tables VI through XIV represent data taken on columns run under standard chosen conditions with normal glass beads.

Tables XV and XVI represent data taken on columns run with Helium carrier gas.

Tables XVII through XIX represent data taken on columns packed with corning roughened beads.

Tables XX through XXII represent data taken on columns run on original apparatus (before valve change).

TABLE VI

```
LENGTH          = 200.0  CM
BEAD DIAMETER   = 0.0226 CM
PERCENT LIQUID  = 0.5400
CARRIER GAS     = NITROGEN
```

```
CARBON  U    HETP    B   COUPLING  CL       CL     CL
  NO.        EXP.   TERM   TERM   TERM     EXP.  THEORY   RATIO
 *************************************************************
  1   8.26  0.1041 0.0276 0.0121 0.0644   0.0078 0.0000   0.00
  7   4.03  0.4405 0.0273 0.0121 0.4011   0.0995 0.0769   1.29
  7   8.26  0.7441 0.0122 0.0246 0.7072   0.0856 0.0767   1.12
  7  23.81  1.8351 0.0032 0.0650 1.7668   0.0742 0.0752   0.99
  7  27.03  2.3849 0.0025 0.0750 2.3074   0.0854 0.0794   1.08
  7  35.09  3.3746 0.0017 0.0889 3.2839   0.0936 0.0775   1.21
  7  40.00  3.8938 0.0013 0.0986 3.7938   0.0948 0.0799   1.19
 10  23.81  0.5618 0.0025 0.0734 0.4858   0.0204 0.0182   1.12
 10  27.03  0.6504 0.0020 0.0834 0.5650   0.0209 0.0208   1.01
 10  35.09  0.8149 0.0014 0.0968 0.7167   0.0204 0.0196   1.04
 10  40.00  1.1141 0.0011 0.1059 1.0072   0.0252 0.0209   1.20
 11  35.09  0.5279 0.0012 0.0997 0.4270   0.0122 0.0101   1.20
 11  40.00  0.6463 0.0010 0.1084 0.5368   0.0134 0.0109   1.23
```

```
LENGTH            = 200.0  CM
BEAD DIAMETER     = 0.0226 CM
PERCENT LIQUID    = 0.2900
CARRIER GAS       = NITROGEN
```

TABLE VII

```
CARBON   U     HETP     B     COUPLING   CL        CL       CL
 NO.           EXP.    TERM     TERM    TERM      EXP.    THEORY   RATIO
*****************************************************************************
  1    4.07   0.1127 0.0614 0.0057 0.0456    0.0112 0.0000    0.00
  1    8.10   0.0851 0.0284 0.0118 0.0450    0.0056 0.0000    0.00
  1   17.09   0.1686 0.0119 0.0256 0.1311    0.0077 0.0000    0.00
  1   17.09   0.1029 0.0113 0.0271 0.0646    0.0038 0.0000    0.00
  7    4.07   0.3164 0.0271 0.0122 0.2771    0.0682 0.0636    1.07
  7    8.10   0.5506 0.0125 0.0241 0.5140    0.0635 0.0636    1.00
  7   17.09   0.7827 0.0053 0.0470 0.7304    0.0427 0.0565    0.76
  7   17.09   1.0060 0.0050 0.0491 0.9518    0.0557 0.0636    0.88
  7   22.73   1.2727 0.0034 0.0633 1.2060    0.0531 0.0637    0.83
  7   29.63   1.5163 0.0023 0.0781 1.4359    0.0485 0.0637    0.76
  7   36.36   2.0410 0.0017 0.0903 1.9490    0.0536 0.0637    0.84
  7   40.00   2.2542 0.0014 0.0958 2.1570    0.0539 0.0636    0.85
 10   26.32   0.6878 0.0022 0.0791 0.6065    0.0230 0.0238    0.97
 10   32.26   0.9091 0.0016 0.0921 0.8155    0.0253 0.0252    1.00
 10   36.04   1.0087 0.0013 0.0977 0.9096    0.0252 0.0247    1.02
 10   40.00   1.0320 0.0011 0.1032 0.9277    0.0232 0.0245    0.95
 11   26.32   0.4028 0.0020 0.0823 0.3185    0.0121 0.0127    0.95
 11   32.26   0.5304 0.0014 0.0951 0.4339    0.0135 0.0135    1.00
```

TABLE VIII

```
LENGTH           = 200.0  CM
BEAD DIAMETER    = 0.0210 CM
PERCENT LIQUID   = 0.2000
CARRIER GAS      = NITROGEN


CARBON   U      HETP     B    COUPLING  CL        CL       CL
 NO.            EXP.   TERM    TERM    TERM      EXP.   THEORY   RATIO
*************************************************************************
  1    3.42   0.1183 0.0732 0.0048 0.0403    0.0118 0.0000    0.00
  1    4.26   0.1104 0.0576 0.0060 0.0467    0.0110 0.0000    0.00
  7    4.26   0.2527 0.0255 0.0129 0.2143    0.0504 0.0456    1.10
  7   19.23   0.9233 0.0040 0.0574 0.8619    0.0448 0.0456    0.98
 10   10.31   0.2391 0.0071 0.0379 0.1941    0.0188 0.0208    0.91
 10   19.23   0.4556 0.0031 0.0657 0.3867    0.0201 0.0209    0.96
 10   35.71   0.7324 0.0013 0.0994 0.6317    0.0177 0.0196    0.90
 10   41.67   0.8816 0.0010 0.1080 0.7726    0.0185 0.0198    0.93
 10   42.55   1.0423 0.0009 0.1117 0.9298    0.0218 0.0218    1.00
 11   10.31   0.1625 0.0065 0.0405 0.1155    0.0112 0.0112    1.00
 11   19.23   0.2645 0.0029 0.0690 0.1927    0.0100 0.0112    0.89
 11   35.71   0.4703 0.0012 0.1022 0.3669    0.0103 0.0107    0.96
 11   41.67   0.5446 0.0009 0.1105 0.4331    0.0104 0.0108    0.96
 11   42.55   0.7040 0.0008 0.1141 0.5891    0.0138 0.0118    1.17
```

TABLE IX

```
LENGTH            = 248.0  CM
BEAD DIAMETER     = 0.0210 CM
PERCENT LIQUID    = 0.1000
CARRIER GAS       = NITROGEN


CARBON    U      HETP      B     COUPLING   CL          CL        CL
  NO.            EXP.    TERM     TERM     TERM        EXP.    THEORY   RATIO
********************************************************************************
   7    1.71   0.1238  0.0682  0.0051  0.0505      0.0295  0.0278     1.06
   7   30.62   1.5723  0.0018  0.0889  1.4816      0.0484  0.0300     1.61
   8    1.71   0.1284  0.0635  0.0055  0.0595      0.0348  0.0408     0.85
   8   30.62   1.2019  0.0017  0.0914  1.1089      0.0362  0.0405     0.89
  10    5.82   0.1448  0.0139  0.0221  0.1087      0.0187  0.0233     0.80
  10   26.38   0.4994  0.0018  0.0869  0.4106      0.0156  0.0227     0.69
  10   30.62   0.6508  0.0014  0.0969  0.5525      0.0180  0.0239     0.76
  11    8.86   0.1491  0.0076  0.0360  0.1055      0.0119  0.0133     0.89
  11   26.38   0.3592  0.0017  0.0901  0.2675      0.0101  0.0131     0.77
  11   15.12   0.2098  0.0038  0.0591  0.1469      0.0097  0.0133     0.73
  12   15.31   0.1714  0.0033  0.0633  0.1047      0.0068  0.0072     0.95
  12   25.83   0.2745  0.0015  0.0931  0.1799      0.0070  0.0074     0.95
  13   15.12   0.1553  0.0030  0.0667  0.0856      0.0057  0.0040     1.42
  13   25.83   0.2379  0.0014  0.0967  0.1398      0.0054  0.0041     1.33
```

TABLE X

```
LENGTH            = 350.0  CM
BEAD DIAMETER     = 0.0210 CM
PERCENT LIQUID    = 0.0480
CARRIER GAS       = NITROGEN


CARBON   U      HETP     B     COUPLING   CL         CL       CL
 NO.            EXP.    TERM     TERM    TERM       EXP.    THEORY   RATIO
******************************************************************
  1     0.94   0.4242 0.2781 0.0013 0.1448     0.1535 0.0000    0.00
  7    16.67   0.1088 0.0039 0.0603 0.0446     0.0027 0.0147    0.18
  7    20.35   0.1536 0.0029 0.0720 0.0788     0.0039 0.0158    0.25
  7    20.35   0.1491 0.0028 0.0725 0.0738     0.0036 0.0145    0.25
  7    25.18   0.2184 0.0021 0.0846 0.1318     0.0052 0.0171    0.31
  7    25.93   0.2092 0.0018 0.0893 0.1181     0.0046 0.0133    0.34
 10    16.67   0.1556 0.0030 0.0688 0.0838     0.0050 0.0246    0.20
 10    20.35   0.1648 0.0022 0.0806 0.0820     0.0040 0.0244    0.16
 10    20.35   0.1849 0.0022 0.0812 0.1015     0.0050 0.0246    0.20
 10    25.18   0.1988 0.0016 0.0929 0.1043     0.0041 0.0236    0.18
 10    25.55   0.2394 0.0015 0.0966 0.1414     0.0055 0.0255    0.22
 10    25.93   0.2230 0.0014 0.0974 0.1242     0.0048 0.0253    0.19
 10    30.17   0.2763 0.0011 0.1065 0.1686     0.0056 0.0253    0.22
 10    33.02   0.2817 0.0009 0.1117 0.1691     0.0051 0.0255    0.20
 11    20.35   0.1545 0.0020 0.0838 0.0687     0.0034 0.0155    0.22
 11    25.55   0.1945 0.0014 0.0995 0.0936     0.0037 0.0164    0.22
```

```
LENGTH             = 400.0  CM
BEAD DIAMETER      = 0.0210 CM
PERCENT LIQUID     = 0.0260
CARRIER GAS        = NITROGEN
```

TABLE XI

```
CARBON   U      HETP     B     COUPLING   CL        CL      CL
 NO.            EXP.    TERM    TERM     TERM      EXP.   THEORY   RATIO
*************************************************************************
  1    1.11   0.3404 0.2322 0.0015 0.1067    0.0963 0.0000     0.00
  1    1.42   0.2629 0.1782 0.0020 0.0827    0.0582 0.0000     0.00
  1   12.12   0.0954 0.0127 0.0257 0.0570    0.0047 0.0000     0.00
  1   16.33   0.0868 0.0080 0.0377 0.0411    0.0025 0.0000     0.00
  1   17.70   0.0794 0.0070 0.0419 0.0305    0.0017 0.0000     0.00
  1   19.51   0.0841 0.0060 0.0472 0.0309    0.0016 0.0000     0.00
  1   25.32   0.1040 0.0038 0.0638 0.0364    0.0014 0.0000     0.00
  7   16.33   0.0959 0.0035 0.0641 0.0282    0.0017 0.0084     0.21
  7   17.70   0.0913 0.0031 0.0694 0.0188    0.0011 0.0086     0.12
  7   19.51   0.1112 0.0026 0.0758 0.0327    0.0017 0.0085     0.20
  7   22.22   0.1312 0.0021 0.0846 0.0446    0.0020 0.0083     0.24
 10   12.12   0.0823 0.0044 0.0553 0.0226    0.0019 0.0219     0.09
 10   17.70   0.0987 0.0024 0.0781 0.0182    0.0010 0.0219     0.05
 10   19.51   0.1135 0.0021 0.0844 0.0270    0.0014 0.0219     0.06
 10   22.22   0.1021 0.0017 0.0930 0.0075    0.0003 0.0220     0.02
 10   25.32   0.1279 0.0013 0.1012 0.0254    0.0010 0.0221     0.05
 10   27.21   0.1109 0.0011 0.1061 0.0037    0.0001 0.0223     0.01
 11   27.21   0.1214 0.0010 0.1088 0.0115    0.0004 0.0157     0.03
 11   12.12   0.0719 0.0040 0.0584 0.0094    0.0008 0.0151     0.05
 11   16.33   0.0816 0.0025 0.0761 0.0030    0.0002 0.0152     0.01
 11   25.32   0.1264 0.0012 0.1041 0.0211    0.0008 0.0155     0.05
```

LENGTH = 325.7 CM
BEAD DIAMETER = 0.0210 CM
PERCENT LIQUID = 0.0110
CARRIER GAS = NITROGEN

TABLE XII

CARBON NO.	U	HETP EXP.	B TERM	COUPLING TERM	CL TERM	CL EXP.	CL THEORY	RATIO
7	2.42	0.0673	0.0455	0.0075	0.0143	0.0059	0.0046	1.29
7	4.45	0.0728	0.0227	0.0144	0.0356	0.0080	0.0043	1.88
7	9.41	0.0643	0.0089	0.0325	0.0228	0.0024	0.0045	0.54
7	15.01	0.0780	0.0046	0.0533	0.0200	0.0013	0.0046	0.29
10	2.42	0.0637	0.0358	0.0094	0.0186	0.0077	0.0153	0.50
10	4.45	0.1113	0.0179	0.0178	0.0756	0.0170	0.0174	0.97
10	9.41	0.0821	0.0070	0.0389	0.0362	0.0038	0.0155	0.25
10	15.01	0.0909	0.0036	0.0615	0.0257	0.0017	0.0156	0.11
10	21.57	0.1315	0.0021	0.0829	0.0465	0.0022	0.0155	0.14
10	28.32	0.1650	0.0013	0.1000	0.0637	0.0023	0.0156	0.14
10	32.57	0.2100	0.0010	0.1085	0.1005	0.0031	0.0157	0.20
11	2.42	0.0669	0.0326	0.0103	0.0241	0.0100	0.0109	0.91
11	4.45	0.0914	0.0163	0.0193	0.0558	0.0125	0.0126	1.00
11	9.41	0.0775	0.0064	0.0415	0.0296	0.0031	0.0112	0.28
11	15.01	0.1062	0.0033	0.0647	0.0381	0.0025	0.0115	0.22
11	21.57	0.1101	0.0019	0.0861	0.0220	0.0010	0.0114	0.09
11	28.32	0.1771	0.0012	0.1029	0.0730	0.0026	0.0115	0.22
11	32.57	0.1705	0.0009	0.1111	0.0584	0.0018	0.0117	0.15

LENGTH = 400.0 CM
BEAD DIAMETER = 0.0210 CM
PERCENT LIQUID = 0.0069
CARRIER GAS = NITROGEN

TABLE XIII

CARBON NO.	U	HETP EXP.	B TERM	COUPLING TERM	CL TERM	CL EXP.	CL THEORY	RATIO
1	0.42	0.9778	0.6457	0.0006	0.3315	0.7972	0.0000	0.00
1	0.99	0.3997	0.2621	0.0014	0.1363	0.1373	0.0000	0.00
1	1.88	0.1994	0.1313	0.0027	0.0655	0.0349	0.0000	0.00
1	3.29	0.1122	0.0695	0.0051	0.0376	0.0114	0.0000	0.00
1	6.71	0.0658	0.0287	0.0121	0.0250	0.0037	0.0000	0.00
1	9.32	0.0612	0.0183	0.0185	0.0244	0.0026	0.0000	0.00
1	13.11	0.0700	0.0111	0.0290	0.0299	0.0023	0.0000	0.00
1	16.81	0.0815	0.0074	0.0403	0.0338	0.0020	0.0000	0.00
1	18.18	0.1490	0.0066	0.0442	0.0983	0.0054	0.0000	0.00
1	20.83	0.1101	0.0052	0.0523	0.0526	0.0025	0.0000	0.00
1	23.26	0.1195	0.0043	0.0591	0.0561	0.0024	0.0000	0.00
1	25.16	0.1398	0.0037	0.0647	0.0714	0.0028	0.0000	0.00
1	25.64	0.1252	0.0036	0.0657	0.0559	0.0022	0.0000	0.00
1	26.49	0.1378	0.0034	0.0684	0.0660	0.0025	0.0000	0.00
1	27.78	0.1425	0.0031	0.0716	0.0678	0.0024	0.0000	0.00
7	3.98	0.0582	0.0245	0.0136	0.0201	0.0050	0.0040	1.27
7	6.02	0.0589	0.0146	0.0217	0.0226	0.0037	0.0040	0.93
7	8.85	0.0591	0.0087	0.0338	0.0166	0.0019	0.0040	0.47
7	18.18	0.1353	0.0029	0.0723	0.0601	0.0033	0.0039	0.84
7	20.94	0.1451	0.0023	0.0817	0.0611	0.0029	0.0042	0.70
7	23.26	0.1461	0.0019	0.0887	0.0555	0.0024	0.0041	0.58
7	25.64	0.1783	0.0016	0.0952	0.0815	0.0032	0.0040	0.79
8	15.75	0.0935	0.0034	0.0653	0.0248	0.0016	0.0090	0.18
8	20.94	0.1206	0.0021	0.0843	0.0342	0.0016	0.0089	0.18
8	23.26	0.1490	0.0018	0.0911	0.0561	0.0024	0.0089	0.27
8	25.64	0.1518	0.0015	0.0976	0.0527	0.0021	0.0088	0.23
8	27.78	0.1733	0.0013	0.1028	0.0693	0.0025	0.0089	0.28
10	3.98	0.0490	0.0193	0.0168	0.0130	0.0033	0.0111	0.29
10	6.02	0.0496	0.0115	0.0265	0.0117	0.0019	0.0111	0.17
10	15.75	0.1204	0.0029	0.0714	0.0462	0.0029	0.0111	0.26
10	18.18	0.1246	0.0023	0.0810	0.0414	0.0023	0.0112	0.20
10	18.35	0.1190	0.0023	0.0812	0.0355	0.0019	0.0112	0.17
10	20.94	0.1448	0.0018	0.0902	0.0527	0.0025	0.0112	0.23
10	22.73	0.1481	0.0015	0.0960	0.0505	0.0022	0.0114	0.19
10	23.26	0.1486	0.0015	0.0969	0.0502	0.0022	0.0113	0.19
10	25.64	0.1695	0.0013	0.1030	0.0652	0.0025	0.0113	0.23
10	27.78	0.1890	0.0011	0.1079	0.0800	0.0029	0.0114	0.25
10	30.08	0.1897	0.0009	0.1125	0.0762	0.0025	0.0114	0.22
11	18.35	0.1410	0.0021	0.0845	0.0544	0.0030	0.0075	0.40
11	22.73	0.1537	0.0014	0.0991	0.0532	0.0023	0.0077	0.30
12	22.73	0.1863	0.0013	0.1024	0.0826	0.0036	0.0044	0.84

TABLE XIV

```
LENGTH          = 400.0  CM
BEAD DIAMETER   = 0.0210 CM
PERCENT LIQUID  = 0.0042
CARRIER GAS     = NITROGEN


CARBON   U     HETP     B    COUPLING   CL        CL      CL
 NO.           EXP.   TERM    TERM     TERM      EXP.   THEORY   RATIO
*****************************************************************************
  1     0.79  0.5005 0.3353 0.0011 0.1642     0.2089 0.0000    0.00
  1     1.47  0.2630 0.1728 0.0021 0.0881     0.0598 0.0000    0.00
  1     2.12  0.1784 0.1161 0.0031 0.0593     0.0280 0.0000    0.00
  1     2.55  0.1517 0.0943 0.0038 0.0537     0.0211 0.0000    0.00
  1     3.88  0.1088 0.0576 0.0061 0.0450     0.0116 0.0000    0.00
  1     4.60  0.0916 0.0470 0.0075 0.0372     0.0081 0.0000    0.00
  1     5.56  0.0838 0.0370 0.0094 0.0373     0.0067 0.0000    0.00
  1     5.86  0.0715 0.0346 0.0101 0.0268     0.0046 0.0000    0.00
  1    13.99  0.0432 0.0102 0.0311 0.0019     0.0001 0.0000    0.00
  1    14.11  0.0440 0.0101 0.0314 0.0025     0.0002 0.0000    0.00
  1    19.90  0.0446 0.0058 0.0485-0.0096    -0.0005 0.0000    0.00
  7     7.02  0.0407 0.0121 0.0257 0.0029     0.0004 0.0043    0.10
  7    14.04  0.0670 0.0045 0.0554 0.0071     0.0005 0.0044    0.11
  7    20.62  0.1342 0.0025 0.0784 0.0534     0.0026 0.0048    0.54
  7    24.39  0.1561 0.0018 0.0899 0.0644     0.0026 0.0048    0.55
  7    28.17  0.1803 0.0014 0.1004 0.0785     0.0028 0.0044    0.63
  8     7.02  0.0662 0.0112 0.0272 0.0278     0.0040 0.0082    0.48
  8    14.04  0.0966 0.0042 0.0578 0.0345     0.0025 0.0082    0.30
  8    20.62  0.1551 0.0023 0.0809 0.0719     0.0035 0.0083    0.42
  8    24.39  0.1681 0.0017 0.0923 0.0741     0.0030 0.0083    0.37
  8    28.17  0.1788 0.0013 0.1027 0.0749     0.0027 0.0081    0.33
 10     7.02  0.0570 0.0095 0.0311 0.0164     0.0023 0.0057    0.41
 10    14.04  0.0907 0.0035 0.0638 0.0234     0.0017 0.0058    0.29
 10    20.62  0.1209 0.0019 0.0869 0.0320     0.0016 0.0057    0.27
 10    24.39  0.1267 0.0014 0.0980 0.0272     0.0011 0.0058    0.19
 10    28.17  0.1264 0.0011 0.1078 0.0175     0.0006 0.0060    0.10
 10    27.78  0.1738 0.0011 0.1074 0.0653     0.0024 0.0064    0.37
 11    28.17  0.1425 0.0010 0.1105 0.0310     0.0011 0.0032    0.35
```

TABLE XV

```
LENGTH             = 400.0   CM
BEAD DIAMETER      = 0.0210  CM
PERCENT LIQUID     = 0.0069
CARRIER GAS        = HELIUM


CARBON    U      HETP      B    COUPLING   CL          CL       CL
 NO.             EXP.    TERM    TERM     TERM        EXP.    THEORY   RATIO
*************************************************************************
  1    16.60   0.0795  0.0284  0.0133  0.0377      0.0023  0.0000    0.00
  1    23.53   0.1055  0.0156  0.0232  0.0667      0.0028  0.0000    0.00
  7     8.10   0.0628  0.0323  0.0111  0.0194      0.0024  0.0041    0.58
  7    16.60   0.0751  0.0108  0.0305  0.0338      0.0020  0.0040    0.51
  8    16.60   0.0617  0.0101  0.0321  0.0194      0.0012  0.0090    0.13
  8    18.78   0.0749  0.0081  0.0383  0.0284      0.0015  0.0088    0.17
  8    21.05   0.0826  0.0067  0.0444  0.0315      0.0015  0.0088    0.17
  8    25.81   0.0937  0.0047  0.0565  0.0324      0.0013  0.0091    0.14
 10     8.10   0.0582  0.0215  0.0160  0.0207      0.0026  0.0110    0.23
 10    16.60   0.0775  0.0072  0.0414  0.0288      0.0017  0.0111    0.16
 10    18.78   0.0814  0.0058  0.0486  0.0270      0.0014  0.0112    0.13
 10    21.05   0.0941  0.0048  0.0556  0.0338      0.0016  0.0112    0.14
 10    23.53   0.1054  0.0040  0.0626  0.0388      0.0016  0.0111    0.15
 10    25.81   0.1056  0.0034  0.0687  0.0335      0.0013  0.0110    0.12
 11    16.60   0.0768  0.0057  0.0484  0.0227      0.0014  0.0073    0.19
 11    18.78   0.0881  0.0046  0.0561  0.0273      0.0015  0.0074    0.20
 11    21.05   0.1029  0.0038  0.0635  0.0356      0.0017  0.0074    0.23
 11    23.53   0.0924  0.0032  0.0707  0.0185      0.0008  0.0073    0.11
 11    25.81   0.1007  0.0027  0.0770  0.0210      0.0008  0.0073    0.11
```

TABLE XVI

```
LENGTH          = 400.0  CM
BEAD DIAMETER   = 0.0210 CM
PERCENT LIQUID  = 0.0042
CARRIER GAS     = HELIUM


CARBON   U     HETP     B     COUPLING   CL        CL      CL
 NO.           EXP.    TERM    TERM     TERM      EXP.   THEORY   RATIO
**************************************************************************
 1     1.36  0.7917 0.7390 0.0005 0.0521    0.0383 0.0000    0.00
 1     1.91  0.5939 0.5099 0.0007 0.0833    0.0436 0.0000    0.00
 1     2.31  0.4437 0.4122 0.0009 0.0306    0.0133 0.0000    0.00
 1     3.56  0.2878 0.2494 0.0015 0.0370    0.0104 0.0000    0.00
 1     4.24  0.2538 0.2014 0.0018 0.0506    0.0119 0.0000    0.00
 1     5.15  0.2108 0.1580 0.0023 0.0505    0.0098 0.0000    0.00
 1    12.90  0.1689 0.0437 0.0087 0.1165    0.0090 0.0000    0.00
 8    17.09  0.1154 0.0098 0.0328 0.0728    0.0043 0.0082    0.52
 8    21.28  0.1109 0.0067 0.0444 0.0599    0.0028 0.0080    0.35
 8    24.39  0.1374 0.0051 0.0541 0.0783    0.0032 0.0076    0.42
10    12.90  0.0540 0.0110 0.0292 0.0137    0.0011 0.0062    0.17
10    18.26  0.0686 0.0063 0.0456 0.0167    0.0009 0.0061    0.15
10    21.28  0.0682 0.0048 0.0555 0.0079    0.0004 0.0063    0.06
10    24.39  0.0933 0.0036 0.0662 0.0235    0.0010 0.0066    0.15
```

LENGTH = 250.0 CM
BEAD DIAMETER = 0.0226 CM
PERCENT LIQUID = 0.0980
CARRIER GAS = NITROGEN

TABLE XVII

CARBON NO.	U	HETP EXP.	B TERM	COUPLING TERM	CL TERM	CL EXP.	CL THEORY	RATIO
7	1.86	0.1404	0.0626	0.0055	0.0722	0.0388	0.0289	1.34
8	1.86	0.1523	0.0583	0.0059	0.0881	0.0473	0.0469	1.01
10	1.86	0.1375	0.0493	0.0069	0.0813	0.0437	0.0331	1.32
10	6.41	0.2228	0.0127	0.0239	0.1862	0.0291	0.0334	0.87
11	6.41	0.1581	0.0115	0.0257	0.1208	0.0189	0.0201	0.94
11	10.50	0.2158	0.0064	0.0409	0.1685	0.0160	0.0199	0.81
12	10.50	0.1651	0.0058	0.0441	0.1153	0.0110	0.0111	0.99
12	18.38	0.2631	0.0028	0.0696	0.1907	0.0104	0.0107	0.97
12	33.33	0.4691	0.0012	0.1009	0.3670	0.0110	0.0102	1.08
13	35.71	0.4995	0.0009	0.1105	0.3881	0.0109	0.0065	1.68

TABLE XVIII

```
LENGTH            = 300.0  CM
BEAD DIAMETER     = 0.0226 CM
PERCENT LIQUID    = 0.0230
CARRIER GAS       = NITROGEN


CARBON   U      HETP      B     COUPLING   CL          CL       CL
 NO.            EXP.    TERM     TERM     TERM        EXP.   THEORY   RATIO
**********************************************************************
  1    1.97   0.1982 0.1306 0.0027 0.0649    0.0329 0.0000    0.00
 10   28.30   0.1818 0.0016 0.0921 0.0881    0.0031 0.0280    0.11
 10   37.04   0.1935 0.0010 0.1081 0.0844    0.0023 0.0281    0.08
 10   40.00   0.2181 0.0009 0.1128 0.1044    0.0026 0.0284    0.09
 11   28.30   0.1808 0.0015 0.0951 0.0842    0.0030 0.0226    0.13
 11   37.04   0.2038 0.0009 0.1107 0.0922    0.0025 0.0229    0.11
 11   40.00   0.2398 0.0008 0.1152 0.1238    0.0031 0.0233    0.13
```

TABLE XIX

LENGTH = 400.0 CM
BEAD DIAMETER = 0.0226 CM
PERCENT LIQUID = 0.0044
CARRIER GAS = NITROGEN

CARBON NO.	U	HETP EXP.	B TERM	COUPLING TERM	CL TERM	CL EXP.	CL THEORY	RATIO
7	3.57	0.0596	0.0284	0.0118	0.0194	0.0054	0.0016	3.38
7	12.35	0.0755	0.0057	0.0464	0.0234	0.0019	0.0014	1.34
7	14.29	0.0658	0.0046	0.0539	0.0072	0.0005	0.0018	0.28
7	19.05	0.0944	0.0030	0.0698	0.0215	0.0011	0.0030	0.38
7	29.41	0.1681	0.0014	0.0997	0.0670	0.0023	0.0018	1.25
10	3.57	0.0509	0.0223	0.0146	0.0140	0.0039	0.0127	0.31
10	4.88	0.0484	0.0154	0.0204	0.0126	0.0026	0.0127	0.20
10	8.66	0.0593	0.0074	0.0377	0.0142	0.0016	0.0127	0.13
10	12.35	0.0735	0.0045	0.0542	0.0148	0.0012	0.0127	0.09
10	14.29	0.0673	0.0036	0.0622	0.0015	0.0001	0.0127	0.01
10	19.05	0.0814	0.0024	0.0784	0.0006	0.0000	0.0129	0.00
10	23.53	0.0840	0.0016	0.0939	0.0114	0.0005	0.0126	0.04
10	29.41	0.1416	0.0011	0.1071	0.0334	0.0011	0.0127	0.09
11	4.88	0.0695	0.0141	0.0220	0.0334	0.0068	0.0139	0.49
11	8.66	0.0687	0.0068	0.0403	0.0217	0.0025	0.0140	0.18
11	12.35	0.0786	0.0041	0.0573	0.0171	0.0014	0.0140	0.10
11	14.29	0.0967	0.0033	0.0654	0.0280	0.0020	0.0139	0.14
11	19.05	0.0983	0.0022	0.0817	0.0144	0.0008	0.0136	0.06
11	23.53	0.1317	0.0015	0.0969	0.0334	0.0014	0.0141	0.10
11	29.41	0.1649	0.0010	0.1098	0.0541	0.0018	0.0141	0.13

```
LENGTH          = 200.0  CM
BEAD DIAMETER   = 0.0226 CM
PERCENT LIQUID  = 0.5400
CARRIER GAS     = NITROGEN
```

TABLE XX

```
CARBON    U     HETP     B    COUPLING   CL          CL      CL
 NO.            EXP.    TERM    TERM    TERM        EXP.  THEORY   RATIO
******************************************************************
  7    4.03  0.4407 0.0278 0.0119 0.4010     0.0995 0.0755    1.32
  8    4.03  0.3263 0.0259 0.0127 0.2877     0.0714 0.0598    1.19
 10    3.64  0.1227 0.0243 0.0134 0.0850     0.0234 0.0182    1.29
 10    6.90  0.1931 0.0120 0.0249 0.1562     0.0227 0.0182    1.25
 10    6.41  0.2168 0.0125 0.0242 0.1801     0.0281 0.0231    1.22
 10   10.00  0.3625 0.0069 0.0393 0.3164     0.0316 0.0279    1.14
 10   10.87  0.4453 0.0059 0.0445 0.3949     0.0363 0.0321    1.13
 11   10.31  0.1752 0.0068 0.0388 0.1296     0.0126 0.0095    1.33
 12   14.71  0.1850 0.0039 0.0570 0.1241     0.0084 0.0050    1.69
 12   25.00  0.2714 0.0019 0.0848 0.1848     0.0074 0.0052    1.41
 12   39.22  0.4768 0.0010 0.1081 0.3678     0.0094 0.0051    1.85
 12   50.00  0.5194 0.0007 0.1188 0.3999     0.0080 0.0048    1.66
 13   25.00  0.2613 0.0017 0.0886 0.1710     0.0068 0.0029    2.37
```

LENGTH = 350.0 CM
BEAD DIAMETER = 0.0210 CM
PERCENT LIQUID = 0.0110
CARRIER GAS = NITROGEN

TABLE XXI

CARBON NO.	U	HETP EXP.	B TERM	COUPLING TERM	CL TERM	CL EXP.	CL THEORY	RATIO
7	7.68	0.0454	0.0114	0.0269	0.0072	0.0009	0.0047	0.20
7	8.33	0.0695	0.0102	0.0295	0.0299	0.0036	0.0048	0.75
8	7.68	0.0593	0.0106	0.0284	0.0203	0.0026	0.0106	0.25
8	8.33	0.0863	0.0095	0.0311	0.0457	0.0055	0.0105	0.52
8	15.70	0.2272	0.0038	0.0613	0.1622	0.0103	0.0104	1.00
10	1.93	0.0866	0.0449	0.0076	0.0341	0.0176	0.0150	1.18
10	5.65	0.1221	0.0130	0.0237	0.0853	0.0151	0.0155	0.97
10	7.68	0.0786	0.0089	0.0324	0.0372	0.0048	0.0151	0.32
10	8.33	0.0889	0.0080	0.0354	0.0455	0.0055	0.0153	0.36
10	15.70	0.1971	0.0032	0.0672	0.1267	0.0081	0.0156	0.52
11	8.33	0.1238	0.0073	0.0379	0.0786	0.0094	0.0109	0.86
11	10.00	0.0890	0.0057	0.0454	0.0378	0.0038	0.0108	0.35
11	15.70	0.1769	0.0029	0.0705	0.1035	0.0066	0.0114	0.58
12	16.99	0.1354	0.0023	0.0785	0.0546	0.0032	0.0066	0.49
12	23.03	0.1607	0.0015	0.0963	0.0629	0.0027	0.0064	0.42
12	28.00	0.2104	0.0011	0.1058	0.1034	0.0037	0.0061	0.61
13	28.00	0.2232	0.0010	0.1091	0.1132	0.0040	0.0034	1.17

TABLE XXII

```
LENGTH            = 400.0   CM
BEAD DIAMETER     = 0.0226  CM
PERCENT LIQUID    = 0.0044
CARRIER GAS       = NITROGEN


CARBON   U      HETP      B     COUPLING    CL          CL       CL
 NO.            EXP.     TERM    TERM      TERM        EXP.    THEORY    RATIO
******************************************************************************
  7    3.01   0.0768  0.0347  0.0098  0.0323     0.0107  0.0017    6.40
  7   12.20   0.0858  0.0058  0.0458  0.0342     0.0028  0.0017    1.65
  8    3.01   0.0729  0.0323  0.0104  0.0302     0.0100  0.0042    2.40
  8   12.20   0.1016  0.0054  0.0480  0.0482     0.0040  0.0042    0.93
 10    3.01   0.0748  0.0273  0.0122  0.0354     0.0118  0.0127    0.92
 10   12.20   0.1917  0.0046  0.0535  0.1336     0.0110  0.0127    0.86
 11   12.20   0.1229  0.0042  0.0566  0.0621     0.0051  0.0138    0.37
```

ABSTRACT

AN INVESTIGATION OF COLUMN EFFICIENCY AND THE RELATIONSHIP TO LIQUID PHASE DISTRIBUTION ON ULTRA-LOW LOADED GLASS BEAD GAS CHROMATOGRAPHIC COLUMNS

An Abstract of
A Thesis
Presented to the
Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Donald G. Nyberg
May, 1968

ABSTRACT

Studies have been made of column efficiencies, extra-column effects, the liquid phase mass transfer term (C_ℓ), and liquid phase distribution at ultra-low liquid loadings on glass bead gas-liquid chromatographic columns. The advantages of using lightly loaded columns are described in detail along with a critical evaluation of the limitations of this liquid phase reduction ad infinitum.

Theories have been presented by Giddings[22,23,25,30,32] which predict the mass transfer term (C_ℓ) as a function of two extreme liquid phase distributions. The first equation assumes 100% "capillary" liquid held at the glass bead contact points and represents a very inefficient column. This prediction is known to be valid for normal loaded columns in the 1.0 to 0.1 liquid percentage range[35,48]. The second equation assumes a uniform liquid "adsorption" film around the glass bead which represents a very efficient condition. This equation has never been experimentally verified, but Hawkes[48] and Giddings[35] suggest that this condition is approached when the liquid phase is reduced and that a uniform film exists at loadings less than approximately 0.04%.

The results of this research show that although a uniform film is approached with liquid load reduction, it is never reached, even at loadings as low as 0.004%. Data show that the capillary liquid assumption is valid for glass bead columns with liquid loadings greater than 0.05%, but fails to

predict the proper efficiency term at the lower loadings.

Two important transitions occur at about 0.03% liquid loading: (1) C_ℓ ceases to decrease significantly with a liquid load reduction, and (2) C_ℓ ceases to be the predominant (plate height controlling) efficiency parameter. Reductions below 0.03% do little to improve column efficiency and may cause adverse effects such as decreased resolution, increased adsorption, and a shorter column life.

Data collected before and after some apparatus and procedure changes indicate the importance of minimizing extraneous peak broadening sources. It is suggested that a large amount of the literature is in error because of apathy in this area.

The results suggest that a reduction in liquid load is an excellent method of increasing the column efficiency and reducing the analysis (sample retention) time.