



RICE UNIVERSITY

THE MEASUREMENT AND APPLICATION OF FREE GAS VOLUMES  
IN A GAS-LIQUID CHROMATOGRAPHIC COLUMN  
METHANE K-VALUES AND LIQUID MOLAR VOLUMES  
IN THE METHANE-N-OCTANE SYSTEM

by

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## ABSTRACT

### THE MEASUREMENT AND APPLICATION OF FREE GAS VOLUMES IN A GAS-LIQUID CHROMATOGRAPHIC COLUMN: METHANE K-VALUES AND LIQUID MOLAR VOLUMES IN THE METHANE-N-OCTANE SYSTEM

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The purpose of this research was to investigate an experimental method for determining the free gas volumes in a gas-liquid chromatographic column. Methane K-values and liquid molar volumes in the methane-n-octane system were obtained and compared with known values. Infinite dilution K-values for helium, neon, and argon were also calculated and reported. All data were taken for a system temperature of  $-25^{\circ}\text{C}$  and for a pressure range of 40 to 1028.7 psia.

For a given system temperature the free gas volume inside the column was a function of the system pressure or the methane gas dissolved in the liquid phase. For each pressure, the retention volumes of helium, neon, argon, and tritium-tagged methane were determined. These volumes, measured at atmospheric conditions, were converted to column conditions and were corrected for system dead volume outside the column and for the response of the electronic equipment. The logarithms of the corrected retention volumes of helium, neon, and argon were plotted against the reciprocals of the

reduced temperatures of the respective components. This plot, which was almost linear, was extrapolated to a value of zero for the reciprocal of the reduced temperature. The corresponding value of retention volume was taken to be the free gas volume in the column.

The K-value of methane and the infinite dilution K-values of helium, neon, and argon in the methane-n-octane system were readily calculated. As the pressure was increased, the free gas volume decreased as a result of the swelling of the liquid phase upon dissolution of methane. The molar volume of the pure liquid at its vapor pressure and the composition of the liquid phase at each experimental pressure were obtained. It was then possible to calculate the liquid molar volumes at the various experimental pressures.

The methane K-values and the liquid molar volumes compared very favorably with literature values. The helium, neon, and argon K-values appear to be reasonable, but no literature values are available for comparison.

This method for determining the free gas volume in a gas-liquid chromatographic column appears to be the most reasonable method devised to date.

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## TABLE OF NOMENCLATURE

GLPC	Gas-liquid partition chromatography
$H_i$	equilibrium partition coefficient of the solute between the vapor and liquid phases (moles of component $i$ in the liquid per unit volume of liquid/moles of component $i$ in the vapor per unit volume of vapor)
$K_i$	K-value for component $i$
$P$	total pressure inside the GLPC column
$P_a$	atmospheric pressure
$P_{C_1}$	partial pressure of methane
$P_{H_2O}$	partial pressure of water
$R$	ideal gas constant
$T$	GLPC column temperature
$T_a$	atmospheric temperature
$V_{corr}$	dead volume between ends of GLPC column packing and ends of the column
$V_G$	free gas volume in a GLPC column
$V_L$	total fixed liquid volume in a GLPC column
$V_{ref}$	reference volume
$(V_L)_P$	<u>total</u> volume of liquid inside a GLPC column at pressure, $P$
$(\bar{V}_L)_P$	liquid molar volume at pressure, $P$
$V_{R_i}$	retention volume of component $i$
$V'_{R_i}$	volume of pure methane at atmospheric conditions, $T_a, P_a$

TABLE OF NOMENCLATURE (Continued)

W	moles of fixed liquid in a GLPC column
Z	vapor phase compressibility factor
Lower Case Letters	
$c_i$	moles of component i in vapor per unit volume of vapor
$f_a$	atmospheric flow rate
$n_{C_1}$	number of moles of methane in the liquid
$t_{50}$	time required for a soap film to travel between the reference marks on the bubble meter
$t_{R_i}$	retention time of component i
$w_i$	moles of component i in the liquid per unit volume of liquid
$x_i$	mole fraction of component i in the liquid
$y_i$	mole fraction of component i in the vapor
$(1-x_1-\dots-x_n)$	mole fraction of the fixed liquid in a GLPC column

## I. INTRODUCTION

The gas-liquid chromatograph has been a very useful indirect tool for studying the phase behavior of hydrocarbon systems. One of its more recent applications is the direct determination of vapor-liquid equilibrium K-values using a chromatographic column as the experimental system. A K-value of a given component is defined as the ratio of its mole fraction in the vapor phase to its mole fraction in the liquid phase.

The direct chromatographic method allows the determination of K-values with relative speed and accuracy as compared to classical methods. However, in the past this accuracy has been limited by the fact that  $V_G$ , the free gas volume inside the GLPC column, could not be precisely determined. An accurate value of this parameter is essential to the precise calculation of K-values as well as other useful properties of the system in question.

Previous workers resorted to various methods of calculating or circumventing the calculation of  $V_G$ . Among these are Stalkup,<sup>11</sup> Koonce,<sup>5</sup> and Van Horn.<sup>12</sup>

This work presents an experimental method of determining  $V_G$ . This method is a modification of that proposed by Haydel<sup>3</sup> and has been applied to gas-solid systems by

Masukawa.<sup>9</sup> The system studied is methane and n-octane for which reliable data are available.<sup>4</sup> Since any change in  $V_G$  for different pressures is caused by a corresponding change in  $V_L$ , the liquid volume, the liquid molar volume is also readily determined.

The following data are presented for the methane-n-octane binary at a system temperature of  $-25^{\circ}\text{C}$  and for a pressure range of 40 to 1028.7 psia: K-values for methane; infinite dilution K-values for helium, neon, and argon; and liquid molar volumes.

This work was performed on a modified version of apparatus used by Van Horn.<sup>12</sup> Van Horn made a very thorough search of the literature and found nothing which would indicate that the method employed in this work had ever been successfully utilized previously.

## II. THEORY

### A. Previous Attempts to Determine $V_G$

Stalkup,<sup>11</sup> Koonce,<sup>5</sup> and Van Horn<sup>12</sup> either attempted to calculate  $V_G$  or circumvented its calculation through the relative determination of the K-values. These methods result in K-values of adequate accuracy for components such as ethane, propane, and butane. However, as an examination of the K-value equations (subsequently developed in this section) will show, the relative error associated with each method becomes more significant as the volatility of the component increases.

Stalkup actually measured the void fraction of firebrick and the liquid support. He calculated the density of the liquid on the packing and, subsequently, the volume of the liquid plus the firebrick in the column at column conditions. He then subtracted this volume from that of the empty column which he had measured.

Koonce first utilized Stalkup's method of determining  $V_G$ . For comparison he approached the problem in another way. For given column conditions he measured the retention volume of methane, a component for which he had previously measured its K-value by other means. He then rearranged the K-value equation and solved the resulting expression for  $V_G$ . After comparing his method with that of Stalkup, Koonce decided to

use his own.

Van Horn measured the retention volumes of methane and a reference component, tritium. He then obtained two K-value expressions, one for each component. The three unknowns were: the K-value for methane, the infinite dilution K-value for tritium, and  $V_G$ . He used the Chao-Seader correlation to calculate the K-value of tritium and solved the two equations simultaneously to obtain the K-value for methane.

For determining K-values for ethane and propane, Van Horn used methane instead of tritium as a reference component. He used methane K-values measured by H. L. Chang.<sup>1</sup>

#### B. Experimental Determination of $V_G$

As molecules of a sample in the carrier gas flow through the gas-liquid chromatographic column, they spend a certain amount of time in the liquid phase according to the size of their respective K-values. Their retention volumes vary accordingly. A sample with a large K-value will have a smaller retention volume than a sample with a smaller K-value.

An indication as to whether a component will have a large K-value, and a correspondingly small sample retention volume, for a given set of column conditions might be its reduced temperature. For a series of components having increasingly larger reduced temperatures, the sample retention

volumes would be decreasingly smaller. As the reduced temperature approaches infinity, the retention volumes would then approach a constant value,  $V_G$ . Another way of stating this is that, for a given pressure, as the reciprocal of the reduced temperature approaches zero, the retention volume of the sample approaches  $V_G$ .

In this work a series of three samples was used to determine  $V_G$  for a given pressure - helium, neon, and argon. The three samples were retained in that order, with helium having the smallest retention volume. A plot of the logarithms of the retention volumes versus their respective reduced temperatures was found to be almost linear. Such a plot is presented in Appendix C.

### C. Development of Equations Used in Calculations

The basic equation used was presented by Martin and Synge.<sup>8</sup>

$$V_{R_i} = V_G + V_L H_i \quad (1)$$

$V_{R_i}$  = retention volume of component i

$V_G$  = free gas volume in the column

$V_L$  = total fixed liquid volume in the column

$H_i$  = equilibrium partition coefficient of the solute between the vapor and liquid phases (moles of component i in the liquid per unit volume of liquid/moles of component i in the vapor per unit volume of vapor).



The assumptions involved in the derivation are:

1. The column consists of a large number of theoretical plates.
2. Pressure and temperature are constant throughout the column.
3. Instantaneous equilibrium exists between solute (sample) molecules in the vapor and liquid phases.
4. Diffusional effects are negligible.
5. Sample perturbations are small enough that  $H_i$  can be assumed constant throughout the column.
6. Solute molecules are distinguishable from other molecules of the system.

Assumptions 1, 2, and 5 are satisfied by proper choice of experimental conditions.<sup>5</sup> The applicability of assumptions 4 and 5 was demonstrated by Stalkup<sup>11</sup> and Funk and Houghton.<sup>2</sup> Assumption 6 is satisfied for the case of a solute at infinitely small concentrations in the system or for a solute sample made distinguishable by tagging with carbon-14 or tritium.

Since  $V_L$  and  $H_i$  cannot be measured directly, new expressions will be substituted into Equation (1).

By definition

$$H_i = w_i/c_i \quad (2)$$

$w_i$  = moles of component  $i$  in liquid per unit volume of liquid

$c_i$  = moles of component  $i$  in vapor per unit volume of vapor

It is possible to express  $c_i$  and  $w_i$  in terms of the mole fractions of component  $i$ .

moles  $i$ /unit volume = (total moles/unit volume) (mole fraction of  $i$ )

so 
$$c_i = \frac{P y_i}{ZRT}$$

and 
$$w_i = \frac{W x_i}{V_L (1-x_1-\dots-x_n)}$$

where

$W$  = moles of fixed liquid in the column

$(1-x_1-\dots-x_n)$  = mole fraction of the fixed liquid in the column

$P$  = total pressure

$Z$  = vapor phase compressibility factor

$T$  = column temperature

$R$  = ideal gas constant

$x_i, y_i$  = mole fraction of solute  $i$  in the liquid and vapor phases, respectively

By definition

$$K_i = y_i/x_i$$

Substituting into Equation (2)

$$H_i = \left( \frac{ZRT}{P y_i} \right) \left( \frac{W x_i}{V_L (1-x_1-\dots-x_n)} \right) = \left( \frac{ZRTW}{K_i P V_L (1-x_1-\dots-x_n)} \right) \quad (3)$$

Now, substituting Equation (3) into Equation (1)

$$V_{R_i} = V_G + \frac{V_L ZRTW}{K_i P V_L (1-x_1-\dots-x_n)} = V_G + \frac{ZRTW}{K_i P (1-x_1-\dots-x_n)}$$

or

$$V_{R_i} - V_G = \frac{ZRTW}{K_i P (1-x_1-\dots-x_n)}$$

Solving for  $K_i$

$$K_i = \left( \frac{ZRTW}{P (V_{R_i} - V_G)} \right) \left( \frac{1}{(1-x_1-\dots-x_n)} \right)$$

or, in terms of vapor phase compositions

$$K_i = \left( \frac{ZRTW}{P (V_{R_i} - V_G)} \right) \left( \frac{1}{1 - \frac{y_1}{K_1} - \dots - \frac{y_n}{K_n}} \right)$$

Throughout this work, the only component not at infinite dilution is methane. The previous expression simplifies to

$$K_i = \left( \frac{ZRTW}{P (V_{R_i} - V_G)} \right) \left( \frac{1}{1 - 1/K_1} \right)$$

or

$$K_i = \left( \frac{ZRTW}{P (V_{R_i} - V_G)} \right) \left( \frac{K_1}{K_1 - 1} \right) \quad (4)$$

For methane,  $i = 1$  and Equation (4) becomes

$$K_1 = 1 + \frac{ZRTW}{P(V_{R_1} - V_G)} \quad (5)$$

All volumes in the previous development are for methane at column conditions. However, all volumetric data were taken at atmospheric conditions,  $T_a$  and  $P_a$ , for methane saturated with water vapor.

$$P_a = P_{C_1} + P_{H_2O}, \text{ and}$$

$$V'_{R_i} = \left[ V''_{R_i} \right] \left[ \frac{P_{C_1}}{P_a} \right] = \left[ V''_{R_i} \right] \left[ \frac{P_a - P_{H_2O}}{P_a} \right] = \left[ f_a t_{R_i} \right] \left[ \frac{P_a - P_{H_2O}}{P_a} \right]$$

$V'_{R_i}$  = volume of pure methane at atmospheric conditions,  $T_a, P_a$

$f_a$  = atmospheric flow rate

$t_{R_i}$  = retention time of component  $i$

$P_a$  = atmospheric pressure

$P_{C_1}$  = partial pressure of methane

$P_{H_2O}$  = partial pressure of water (its vapor pressure)

$$V_{R_i} = \left[ f_a t_{R_i} \right] \left[ \frac{P_a - P_{H_2O}}{P_a} \right] \left[ \frac{Z P_a T}{P T_a} \right] - V_{\text{ref}} \quad (6)$$

$$V_{\text{ref}} = \left[ f_a t_R \right]_{\text{ref}} \left[ \frac{P_a - P_{H_2O}}{P_a} \right]_{\text{ref}} \left[ \frac{Z P_a T}{P T_a} \right] + V_{\text{corr}} \quad (7)$$

$V_{\text{corr}}$  = dead volume between ends of packing and ends of column

To determine liquid molar volumes, one needs to know the molar volume of n-octane at  $T = -25^\circ\text{C}$  and its vapor pressure (essentially zero psia).

Kohn<sup>4</sup> gives the value

$$(\bar{V}_L)_{P=0} = 154.6 \text{ ml/gm mole}$$

If the liquid and the liquid support (firebrick) inside the column are assumed to be incompressible, then

$$-\Delta V_G = (V_G)_{P=0} - (V_G)_P = (V_L)_P - (V_L)_{P=0} = \Delta V_L$$

$(V_L)_{P=0}$  = volume of liquid inside column at zero pressure

$$(V_L)_{P=0} = (\bar{V}_L)_{P=0} W$$

It follows that

$$(V_L)_P = (V_L)_{P=0} + (V_L)_P - (V_L)_{P=0} = (V_L)_{P=0} + (V_G)_{P=0} - (V_G)_P$$

$$(\bar{V}_L)_P = \frac{(V_L)_P}{W + n_{C_1}} = \frac{(V_L)_P}{\frac{W}{1-x_{C_1}}} = \frac{(V_L)_P}{\frac{K_1 W}{K_1 - 1}}$$

$n_{C_1}$  = number of moles of methane in the liquid

$x_{C_1}$  = mole fraction of methane in the liquid

$$\begin{aligned}
 (\bar{V}_L)_P &= \frac{(K_1 - 1)}{K_1 W} \left[ (V_L)_{P=0} + (V_G)_{P=0} - (V_G)_P \right] \\
 (\bar{V}_L)_P &= \frac{(K_1 - 1)}{K_1 W} \left[ 154.6 W + (V_G)_{P=0} - (V_G)_P \right] \quad (8)
 \end{aligned}$$

### III. EXPERIMENTAL PROGRAM

#### A. Experimental Variables

Equations (5), (6), and (7) contain the experimental variables which were measured. The variables  $T$ ,  $P$ , and  $f_a$  had to be controlled very closely and all the experimental variables  $T_a$ ,  $T$ ,  $P_a$ ,  $P$ ,  $t_{R_i}$ ,  $f_a$ ,  $W$ , and  $V_G$  had to be accurately measured.

A schematic diagram of the experimental apparatus is given in Figure 1.

#### B. Measurement and Control of Experimental Variables

The control and/or measurement of the experimental variables is discussed here in a general manner. More detailed descriptions are given in Appendix A.

##### 1. Temperatures, $T$ and $T_a$

As shown in Figure 1, the GLPC column was suspended in a liquid bath. The bath fluid was low viscosity silicone oil. This oil could be used at a temperature range from room temperature down to around  $-110^\circ\text{F}$ . Its basic advantages over alcohol or hydrocarbon baths were its safety and its low volatility at room temperature. The bath was cooled by a two-stage cascade refrigeration system.

The temperature,  $T$ , was controlled by a Hallikainen proportional-integral controller which regulated heat input to the bath through an electrical heater. A ten junction chromel-constantan thermopile calibrated against a platinum resistance thermometer was used to measure temperature.

The atmospheric temperature,  $T_a$ , was read from a mercury thermometer suspended in the gas stream exhausting to the atmosphere.

## 2. Pressure, $P$

The methane elution gas was stored at high pressure in gas cylinders. The pressure was reduced to a pressure approximately 100 psi above the desired column pressure by a cylinder pressure regulator. It then was set to the exact pressure desired with the dome loaded diaphragm pressure regulator downstream of the preliminary regulator. At the inlet of the GLPC column the pressure was read from either of two Heise gauges, with respective ranges of 0 - 1000 and 0 - 2000 psia. The pressure drop through the GLPC column was shown to be negligible by Stalkup<sup>11</sup> for typical columns and operating conditions similar to those used in this work.



According to Van Horn,<sup>12</sup> pressure control and measurement was accurate to the stated accuracy of the Heise gauges, 0.1% of their full scale values.

3. Flow rate,  $f_a$

The flow rate of the carrier gas was controlled by the needle valve downstream of the GLPC column. At this point the carrier gas was expanded from column pressure to essentially atmospheric pressure and continued to flow at low pressure through the thermal conductivity cell, the ionization chamber, and water saturator to the bubble meter.

The flow rate was determined by measuring the time for a soap film to travel the 50 cc volume between reference marks on the bubble meter. The flow rate, corrected for water vapor content, was calculated from

$$f_a = \frac{50}{t_{50}} \left[ \frac{P_a - P_{H_2O}}{P_a} \right]$$

$P_{H_2O}$  = vapor pressure of water at temperature,  $T_a$

$t_{50}$  = time required for a soap film to travel between the reference marks on the bubble meter

Normal flow rates were between 50 and 100 cc/min.

## 4. Fixed liquid in column, W

Although n-octane has a very small K-value at column conditions, care must be taken to avoid losing much liquid from the column and to account for any losses which do occur. The initial determination of W has been described by Van Horn.<sup>12</sup> The loss of fixed liquid was accounted for as follows:

1. A reference run was made on each fresh column, measuring the retention time of tagged methane at a pressure of 100 psia. After a series of runs was made, the column was returned to a pressure of 100 psia and another reference run made. An examination of Equation (5) shows that for small liquid losses

$$\frac{W_2 - W_1}{W_1} \approx \frac{[\bar{V}_{R_1}]_2 - [\bar{V}_{R_1}]_1}{[\bar{V}_{R_1}]_1}$$

where the "1"'s refer to the initial reference run and the "2"'s refer to subsequent reference runs.

2. The column was weighed after the experimental pressure range had been covered, and any liquid loss encountered was prorated among the various

experimental pressures according to the results of step "1".

Actually, liquid loss for a given column was of the order of 1% or less.

A presaturator was used to control the liquid loss. This consisted of a column of firebrick soaked in n-octane and located upstream of the GLPC column. This was the same scheme as used by Van Horn.<sup>12</sup>

5. Retention Time,  $t_{R_i}$

A pair of accurate electric timers was used to measure the time between sample injection and emergence of the solute peak. The time desired was that between the sample injection and emergence of the peak centroid. The clocks were started at sample injection by the simultaneous closing of a microswitch in their clutch circuit. They were manually stopped by opening a toggle switch in the clutch circuit. Simultaneously an uncharged capacitor was placed across the input to the recorder, producing a reference mark on the strip chart. The capacitor was then switched out of the circuit.

### C. Experimental Procedure

Three fresh columns were used. For the first column a pressure range of 50 psia to 440.8 psia was covered. Pressure ranges of 40 to 881.8 and 40 to 1028.7 psia were used on columns 2 and 3, respectively. Before a series of runs was made, the temperature was allowed to equilibrate for at least 2 hours. Covering a pressure range usually required a period of about eight hours, during which time the temperature tended to drift somewhat. This was closely watched and corrected at regular intervals.

The first experimental pressure set for a fresh column was 100 psia. The retention volume of methane measured was then used as a reference for determining liquid loss. The following procedure was carried out at each pressure:

1. Read  $P_a$ .
2. Read  $P$ .
3. Inject helium sample.
  - a. measure  $t_{50}$  and read  $T_a$ .
  - b. obtain peak and uncorrected  $t_{R_i}$ .
4. repeat steps 2 and 3 for neon, argon, and tagged methane.

When an experimental pressure range had been covered, the bath was lowered. The column, which was connected to the remainder of the system by Swagelok fittings, was

prepared for removal. Before removal the fittings and tubing adjacent to the fittings were scrubbed with soapy water, carbon tetrachloride, and acetone to remove silicone oil and prevent it from possibly leaking into the column. Upon removal, the ends of the column were plugged, and the entire column was scrubbed with soapy water, benzene, carbon tetrachloride, acetone, and ethyl ether in that order. This cleaning was repeated and the column allowed to dry several hours before weighing to determine liquid loss.

The next step was to make correction runs. The objectives of these runs were to provide correction factors to account for system dead volume outside the column and equipment response time. Obviously, the flow rate for a correction run had to equal that for its corresponding column run.

After the packed column was removed for weighing, the two Swagelok nuts to which it was connected were themselves joined by a Swagelok union. The bath was then raised, the temperature set, and the reference runs made.

It was shown that for these correction runs, helium, neon, argon, and tritium had identical retention volumes for a given pressure, as detected by the thermal conductivity cell. It also was shown that tritium and methane had identical retention volumes as detected by the ionization chamber. For simplicity tritium samples were used for all correction runs.

At each pressure two samples were injected. The retention time of one was recorded from the thermal conductivity cell, and that of the other was recorded from the ionization chamber.

#### D. Experimental Difficulties

A major problem encountered during the course of the experiments was in getting the thermal conductivity cell (TC cell) to operate satisfactorily. A Gow-Mac Pretzel cell (8 filament) model 9285 was first used. It was refilamented with very sensitive W-2X filaments. The noise level was prohibitive and subsequently, the cell became defective. A Gow-Mac diffusion-type cell (8 filament) model 9454 was then used. It gave good results with very low noise level; although this cell did have less sensitive W-2 filaments. It is felt that very low noise levels would have been obtained using moderately sensitive W-2X filaments.

A Microtek liquid injection valve was tried. However, its sample volume was 10  $\mu$  liter as compared to  $\frac{1}{4}$  cc for the Loenco loop-type valve and together with the TC cell troubles its use was prohibited. The Loenco valve would not withstand high pressures as well as the Microtek valve and would start rupturing "O"-rings at around 800 pounds pressure.

Runs made at pressures below 80 psia were plagued by

slight fluctuations in pressure. This caused the flow rates to vary also and considerably increased the time required for each run.

#### IV. DISCUSSION OF RESULTS

##### A. K-Values and Liquid Molar Volumes

Kohn<sup>4</sup> presented smoothed values of P-V-T-X data on the methane-n-octane system. This data appears to be reliable and obviously appears to be consistent within itself. He obtained the data by classical means--separating the vapor and liquid phases in an equilibrium cell and determining the composition of each phase.

Methane K-values were obtained from his data by dividing the mole fraction of methane in the vapor phase by the mole fraction of methane in the corresponding liquid phase. This was done over his pressure range of 147 to 1028.7 psia for a temperature of -25°C. These K-values are plotted in Figure 2.

The methane K-values resulting from this work also appear in Figure 2. These values along with those of Kohn are listed in Table 1. As one can plainly see, they are in reasonable agreement with Kohn's results. The data appear to scatter more at the lower pressures than at the higher pressures. It should be noted that the data points are not equally spaced. Three data points were taken at pressures of 100, 147, 293.9, and 440.8 psia; two data points were



taken at 587.8, 734.8, and 881.8 psia; and only one point was taken at 1028.7 psia. The scatter of the points at pressures such as 100 psia or lower is probably due to the larger relative error in pressure and retention volume measurements. Also as previously stated, the pressure tended to fluctuate at pressures below 80 psia.

Kohn's liquid molar volume data are plotted in Figure 3. He took no data below a pressure of 10 atmospheres, except for the molar volume of pure n-octane. The liquid molar volume data resulting from this work also appear in Figure 3. These values along with those of Kohn<sup>4</sup> are listed in Table 2. Again, the latter data show some scatter at the lower pressures. At the higher pressures the molar volumes resulting from this work tend to be larger than Kohn's. No satisfactory explanation is readily available for this.

The error in reading the lower pressures could be decreased by employing a gauge of smaller range or perhaps a mercury manometer. Obviously, the gauge would be much easier to use and would not pose the threat of contaminating the system with mercury.

Figure 4 shows the infinite dilution K-values of helium, neon, and argon which were calculated from Equation (4). The K-values are also found in Table 3. The data show some scatter but appear to be fairly consistent within themselves.

These K-values are subject to relatively large scatter since the retention volumes of helium and neon are not much larger in magnitude than  $V_G$ .

#### B. Error Analysis

Experimental variables, their approximate magnitudes, and estimates of the uncertainties involved in their determination are listed in Table 4.

The estimates of the uncertainties were made as follows:

##### Moles of fixed liquid in the column, W

The measurement uncertainty in W was estimated to be  $\pm 0.00002$  g. moles. This corresponded to a margin of uncertainty of  $\pm 0.1\%$ .

##### System temperature, T

Temperature control and measurement were accurate within  $\pm 0.05^\circ\text{K}$ , the limits of measurement uncertainty.

##### System pressure, P

Pressure control and measurement were accurate to the stated accuracy of the Heise gauges,  $\pm 0.1\%$  of their full scale.

##### Atmospheric temperature, $T_a$

Each subdivision of the thermometer used to measure  $T_a$  represented  $0.2^\circ\text{K}$ . The measurement uncertainty was estimated to be  $\pm 0.1^\circ\text{K}$ .

Compressibility factor, Z

The margin of uncertainty in determining Z was estimated to be  $\pm 0.5\%$ . Since the range of magnitude of Z was from 0.7 to 0.98, the range of uncertainty of Z was from  $\pm 0.003$  to  $\pm 0.005$ .

Atmospheric flow rate,  $f_a$ 

Flow rate measurements during the course of a run showed no variation within the accuracy of the measurements. The margin of uncertainty in flow rate measurements was  $\pm 0.3\%$ , the limit of bubble meter accuracy. Since the range of magnitude of  $f_a$  was from 50 cc/min. to 100 cc/min., the range of uncertainty of  $f_a$  was from  $\pm 0.10$  cc/min. to 0.30 cc/min.

Atmospheric Pressure,  $P_a$ 

The margin of uncertainty of  $P_a$  was  $\pm 0.1\%$ . The uncertainty in these pressure measurements was  $\pm 0.03$  in. Hg or  $\pm 0.015$  psia.

Vapor pressure of water,  $P_{H_2O}$ 

The uncertainty of water vapor pressure determinations was estimated to be  $\pm 0.01$  psia.

Retention time,  $t_R$ 

The uncertainty of measurement of  $t_R$  was estimated from the data to be  $\pm 0.003$  min.

Free gas volume,  $V_G$ 

The margin of uncertainty in the determination of

$V_G$  was estimated to be  $\pm 1\%$ . Since a typical value of  $V_G$  was 2.4 cc, the uncertainty of determining  $V_G$  was estimated to be  $\pm 0.03$  cc.

The following is an estimation of the random errors associated with the final results of this work.

Equation (5) was used for calculating methane K-values.

$$K_1 = 1 + \frac{ZRTW}{P(V_{R_1} - V_G)} \quad (5)$$

Expressed in terms of the experimental variables:

$$K_1 = 1 + \frac{RW}{(f_{a t_{R_i}}) \left( \frac{P_a - P_{H_2O}}{T_a} \right)_i - (f_{a t_{R_{ref}}}) \left( \frac{P_a - P_{H_2O}}{T_{a \text{ ref}}} \right) - \frac{PV_{\text{corr}}}{TZ} - \frac{PV_G}{TZ}}$$

For simplicity the following definitions are made

$$A \equiv (f_{a t_{R_i}}) \left( \frac{P_a - P_{H_2O}}{T_a} \right)_i$$

$$B \equiv (f_{a t_{R_{ref}}}) \left( \frac{P_a - P_{H_2O}}{T_{a \text{ ref}}} \right)$$

$$C \equiv \frac{PV_{\text{corr}}}{TZ}$$

$$D \equiv \frac{PV_G}{TZ}$$

The relative errors of these quantities are.

$$\frac{\Delta A}{A} = \frac{\Delta B}{B} = \left| \frac{\Delta f_a}{f_a} \right| + \left| \frac{\Delta t_{R_i}}{t_{R_i}} \right| + \left| \frac{|\Delta P_a| + |\Delta P_{H_2O}|}{|P_a - P_{H_2O}|} \right| + \left| \frac{\Delta T_a}{T_a} \right| \quad (10)$$

$$\frac{\Delta C}{C} = \left| \frac{\Delta P}{P} \right| + \left| \frac{\Delta V_{\text{corr}}}{V_{\text{corr}}} \right| + \left| \frac{\Delta T}{T} \right| + \left| \frac{\Delta Z}{Z} \right| \quad (11)$$

$$\frac{\Delta D}{D} = \left| \frac{\Delta P}{P} \right| + \left| \frac{\Delta V_G}{V_G} \right| + \left| \frac{\Delta T}{T} \right| + \left| \frac{\Delta Z}{Z} \right| \quad (12)$$

Equation (4) was used for calculating helium, neon, and argon K-values.

$$K_i = \frac{ZRTW}{P(V_{R_i} - V_G)} \frac{K_1}{K_1 - 1} \quad (4)$$

The relative error of these K-values is

$$\frac{\Delta K_i}{K_i} = \left| \frac{\Delta \left[ \frac{ZRTW}{P(V_{R_i} - V_G)} \frac{K_1}{K_1 - 1} \right]}{\frac{ZRTW}{P(V_{R_i} - V_G)} \frac{K_1}{K_1 - 1}} \right| + \left| \frac{\Delta K_1}{K_1} \right| + \left| \frac{\Delta K_1}{K_1 - 1} \right| + \left| \frac{\Delta W}{W} \right|$$

$$\frac{\Delta K_i}{K_i} = \left| \frac{2\Delta K_1}{K_1} \right| + \left| \frac{\Delta K_1}{K_1 - 1} \right| + \left| \frac{\Delta W}{W} \right| \quad (13)$$

Equation (8) was used to calculate  $(\bar{V}_L)_P$ .

$$(\bar{V}_L)_P = \frac{(K_1 - 1)}{K_1 W} \left[ 154.6 W + (V_G)_{P=0} - (V_G)_P \right] \quad (8)$$

The relative error of  $(\bar{V}_L)_P$  is

$$\frac{\Delta(\bar{V}_L)_P}{(\bar{V}_L)_P} = \left| \frac{\Delta K_1}{(K_1-1)} \right| + \left| \frac{\Delta K_1}{K_1} \right| + \left| \frac{\Delta W}{W} \right| + \left| \frac{154.6 W + (\Delta V_G)_{P=0} + (\Delta V_G)_P}{154.6 W + (V_G)_{P=0} - (V_G)} \right|$$

(14)

Table 5 gives the limits of uncertainty calculated from Equations (10), (11), (12), (13), and (14).

## V. SUMMARY AND RECOMMENDATIONS

The results of this work indicate that the method used for determining  $V_G$  shows much promise. Not only will it be possible to calculate methane K-values accurately, but also liquid molar volumes. Perhaps, with additional improvements in the existing apparatus and techniques, reliable K-values for helium, neon, and argon can be obtained.

It is recommended that this method be further tested before it is applied to a more general class of systems. Not enough data were taken in this work to be considered an extensive test. A theoretical analysis needs to be made of the concept of the infinite reduced temperature.

The following improvements in the apparatus are recommended:

1. New sample injection valve.

The packing rings in the present valve will not hold up under higher pressures. The valve produces peak tailing in the output due to its inherent dead volume. A sample volume of  $\frac{1}{4}$  cc is recommended.

2. A switching valve to replace the four shut-off valves and two-tees connected to the packed column and the column bypass.

The present layout provides dead volume which can cause sample spreading and result in peak tailing.

3. Smaller ionization chamber.

For operating at extremely low column pressures, low atmospheric flow rates are required to assure phase equilibrium inside the column. The present chamber allows atmospheric flow rates as low as 50 cc/min. to be used. The present chamber volume is 5 cc.

4. A simpler tubing layout.

As much dead volume as possible should be eliminated in the system between the injection valve and the detectors in order to prevent peak spreading.

5. Manometer or narrow range pressure gauge for measuring low column pressures--particularly pressures below 80 psia.

6. Better pressure regulation to eliminate variations at low pressure.

7. A less polar solid for column packing, such as sintered glass beads.

It is recommended that if many data runs are to be made:

1. Calibration curves be made of volumes determined from correction runs. This was done by Koonce.<sup>5</sup>

2. A computer program be written to process the data.

Use of both of the above will result in the saving of much time.



## APPENDIX A

### EQUIPMENT DETAILS AND SPECIFICATIONS

The apparatus used in this work was a slightly modified version of that used by Van Horn.<sup>12</sup> For this reason the only equipment discussed in this section is that which is new or modified.

#### Temperature Measurement

A ten junction chromel-constantan thermopile was used in the measurement of the system temperature. It was calibrated by Harry Lo Chang<sup>1</sup> and used in his work.

#### Flow Rate Control

Nupro Model SS regulating valves with vernier handles were used to regulate the flow rates through the column and through the reference side of the thermal conductivity cell. These valves provided fairly good flow control over the pressure range used.

#### Detecting and Recording Equipment

The thermal conductivity cell was a Gow-Mac Model 9454 diffusion type cell. It contained eight W-2 hot wire filaments. This style cell offered good sensitivity with very little dependence on flow rate. Current was supplied by a modified Kepco 40 volt DC power supply. The current was

adjusted so that a cell output range of  $\pm 1$  mv was achieved. This voltage was amplified by a factor of 5 by a Leeds and Northrup Model 9835-B DC linear amplifier.

The outputs of the amplifier and electrometer were hooked through a selector switch to a Leeds and Northrup Speedomax G strip chart recorder with a chart speed of 6 inches per minute. This recorder had a 10 mv range and had a zero center or zero left switch to accommodate the -5 mv to +5 mv output range of the amplifier or the 0 to 10 mv output range of the electrometer.

#### Chromatographic Columns

Columns were prepared from  $\frac{1}{4}$ " O.D. seamless 316 stainless steel tubing with 0.035" wall thickness. They were approximately 36 inches in length.

The research grade n-octane used throughout this work was procured from Phillips Petroleum Company. The stated purity was 99.81 mole %.

The column packing was prepared according to the procedure given by Van Horn.<sup>12</sup>

## APPENDIX B

## SAMPLE CALCULATIONS

Data: Column number 3

$$W = 0.023434 \text{ g. moles}$$

$$P = 147.0 \text{ psia}$$

$$R = 1205.9 \text{ psia cc/g. mole } ^\circ\text{K}$$

$$Z = 0.973$$

$$T = 248.2^\circ\text{K}$$

$$(\bar{V}_L)_{P=0} = 154.6 \text{ cc/g. mole}$$

$$(V_G)_{P=0} = 2.44 \text{ cc}$$

$$(V_G)_P = 2.36 \text{ cc}$$

$$V_{R_{\text{He}}} = 2.375 \text{ cc}$$

$$V_{R_{\text{Ne}}} = 2.513 \text{ cc}$$

$$V_{R_{\text{Ar}}} = 2.944 \text{ cc}$$

$$V_{R_1} = 5.670 \text{ cc}$$

For methane K-values:

$$K_1 = 1 + \frac{ZRTW}{P(V_{R_1} - V_G)} \quad (5)$$

$$K_1 = 1 + \frac{(0.973)(1205.9)(248.2)(0.023434)}{(147.0)(5.67 - 2.36)}$$

$$\underline{K_1 = 15.0}$$

For infinite dilution K-values:

$$K_i = \frac{ZRTW}{P(V_{R_i} - V_G)} \frac{K_1}{K_1 - 1} \quad (4)$$

$$K_{He} = \frac{(0.973)(1205.9)(248.2)(0.023434)}{(147.0)(2.375 - 2.36)} \frac{15.0}{14.0}$$

$$\underline{K_{He} = 3320}$$

$$K_{Ne} = \frac{(0.973)(1205.9)(248.2)(0.023434)}{(147.0)(2.513 - 2.36)} \frac{15.0}{14.0}$$

$$\underline{K_{Ne} = 324}$$

$$K_{Ar} = \frac{(0.973)(1205.9)(248.2)(0.023434)}{(147.0)(2.944 - 2.36)} \frac{15.0}{14.0}$$

$$\underline{K_{Ar} = 85.2}$$

The liquid molar volume is calculated from Equation (8).

$$(\bar{V}_L)_P = \frac{(K_1 - 1)}{K_1 W} \left[ 154.6 W + (V_G)_{P=0} - (V_G)_P \right] \quad (8)$$

$$(\bar{V}_L)_P = \frac{(14.0)}{(15.0)(0.023434)} \left[ (154.6)(0.023434) + 2.44 - 2.36 \right]$$

$$(\bar{V}_L)_{P=147.0 \text{ psia}} = 147.5 \text{ cc/g. mole}$$

## APPENDIX C

## DERIVED DATA

Table 6 shows the derived data for all the runs made. Figure 5 shows a plot of the logarithms of the retention volumes of helium, neon, and argon versus the reciprocals of the reduced temperatures of the respective components for column number 3. This is the plot which was used to determine  $(V_G)_P$ . Figure 6 shows a plot of  $(V_G)_P$  versus P. This plot was used to determine  $(V_G)_{P=0}$  for column number 3.

Table 1  
Methane K-values

P (psia)	$K_1$			
	Kohn <sup>5</sup>	Column #1	Column #2	Column #3
40.0	---	---	91.3	88.9
49.2	---	71.0	---	---
60.0	---	---	44.0	44.3
75.2	---	37.1	---	---
80.0	---	---	30.2	30.0
100.0	---	---	22.9	22.5
101.1	---	24.4	---	---
147.0	15.38	15.5	15.6	15.0
293.9	7.81	7.80	7.91	7.90
440.8	5.35	5.10	5.40	5.41
587.8	4.20	---	4.29	4.25
734.8	3.47	---	3.55	3.50
881.8	2.97	---	3.01	3.00
1028.7	2.68	---	---	2.70

Table 2

## Liquid Molar Volumes

P (psia)	$\bar{V}_L$ (cc/g.mole)			
	Kohn <sup>5</sup>	Column #1	Column #2	Column #3
0	154.6	---	---	---
40.0	---	---	153.8	153.7
49.2	---	153.0	---	---
60.0	---	---	152.0	152.4
75.2	---	---	---	---
80.0	---	---	151.2	151.1
100.0	---	---	150.1	149.8
101.1	---	149.6	---	---
147.0	147.7	147.5	148.1	147.5
293.9	140.6	141.2	140.9	140.9
440.8	134.4	---	134.7	134.7
587.8	128.9	---	129.9	129.4
734.8	123.6	---	124.8	124.1
881.8	118.2	---	119.1	119.1
1028.7	114.1	---	---	114.6

Table 3

## K-Values of Helium, Neon, and Argon

P (psia)	Column #2			Column #3		
	K <sub>He</sub>	K <sub>Ne</sub>	K <sub>Ar</sub>	K <sub>He</sub>	K <sub>Ne</sub>	K <sub>Ar</sub>
40.0	9930	1190	324	11000	1170	313
60.0	7540	841	225	6960	774	208
80.0	6600	680	172	5260	580	158
100.0	4940	540	141	4810	478	127
147.0	3400	366	96.1	3320	324	85.2
293.9	1610	165	43.9	2140	192	48.7
440.8	1310	128	32.9	1480	123	31.8
587.8	1010	108	27.5	1060	101	25.5
734.8	1080	94.5	23.3	752	80.6	21.6
881.8	773	78.6	19.8	692	80.7	18.6
1028.7				651	65.1	16.7



Table 4

Experimental Variables and the Uncertainties Involved  
in their Determination

<u>Variable</u>	<u>Approximate Magnitude</u>	<u>Uncertainties</u>
W	0.02 g. moles	$\pm 0.00002$ g. moles
T	248°K	$\pm 0.05^\circ\text{K}$
P	<1000 psia	$\pm 1$ psia
	$\geq 1000$ psia	$\pm 2$ psia
T <sub>a</sub>	295°K	$\pm 0.1^\circ\text{K}$
Z	$0.7 < Z < 0.98$	$\pm 0.003 < \Delta Z < \pm 0.005$
f <sub>a</sub>	$50 \text{ cc/min} < f_a < 100 \text{ cc/min}$	$\pm 0.10 < \Delta f_a < \pm 0.30$
V <sub>corr</sub>	0.6 cc	$\pm 0.001$ cc
P <sub>a</sub>	29.9 in.Hg	$\pm 0.03$ in.Hg
	14.7 psia	$\pm 0.015$ psia
P <sub>H<sub>2</sub>O</sub>	0.5 psia	$\pm 0.01$ psia
t <sub>R</sub>	1 min.	$\pm 0.003$ min.
V <sub>G</sub>	2.4 cc	$\pm 0.03$ cc

Table 5

## Limits of Uncertainty

P (Psia)	Limits of Uncertainty (%)		
	$K_1$	$K_i$	$(\bar{V}_{L P})$
40.0	$\pm 5.3$	$\pm 16.1$	$\pm 0.82$
100.0	3.8	11.7	0.70
147.0	3.5	10.9	0.51
440.8	3.0	9.5	0.40
881.8	2.9	10.3	0.32

Table 6  
Derived Data

P (psia)	Column #1 W = 0.02336 g. moles					Column #2 W = 0.022475 g. moles					Column #3 W = 0.023434 g. moles				
	$V_G$ (cc)	$V_{R_{He}}$ (cc)	$V_{R_{Ne}}$ (cc)	$V_{R_{Ar}}$ (cc)	$V_{R_1}$ (cc)	$V_G$ (cc)	$V_{R_{He}}$ (cc)	$V_{R_{Ne}}$ (cc)	$V_{R_{Ar}}$ (cc)	$V_{R_1}$ (cc)	$V_G$ (cc)	$V_{R_{He}}$ (cc)	$V_{R_{Ne}}$ (cc)	$V_{R_{Ar}}$ (cc)	$V_{R_1}$ (cc)
	0	2.35	--	--	--	--	2.30	--	--	--	--	2.44	--	--	--
40.0	--	--	--	--	--	2.28	2.297	2.422	2.801	4.131	2.42	2.436	2.571	2.982	4.402
49.2	2.34	2.355	2.496	2.937	4.353	--	--	--	--	--	--	--	--	--	--
60.0	--	--	--	--	--	2.28	2.295	2.415	2.787	4.859	2.41	2.427	2.563	2.971	5.079
75.2	2.24	2.247	2.296	2.439	4.782	--	--	--	--	--	--	--	--	--	--
80.0	--	--	--	--	--	2.26	2.273	2.386	2.759	5.103	2.40	2.417	2.554	2.964	5.382
100.0	--	--	--	--	--	2.25	2.264	2.378	2.740	5.269	2.39	2.405	2.541	2.959	5.592
101.1	2.32	2.331	2.452	2.871	5.240	--	--	--	--	--	--	--	--	--	--
147.0	2.28	2.288	2.385	2.783	5.472	2.22	2.234	2.350	2.715	5.277	2.36	2.375	2.513	2.944	5.668
293.9	2.18	2.187	2.221	2.351	5.482	2.15	2.164	2.286	2.662	5.261	2.28	2.292	2.414	2.807	5.527
440.8	2.10	2.105	2.145	2.277	5.617	2.06	2.073	2.193	2.577	5.212	2.19	2.202	2.334	2.747	5.472
587.8	--	--	--	--	--	1.97	1.983	2.092	2.448	5.029	2.10	2.113	2.236	2.638	5.329
734.8	--	--	--	--	--	1.87	1.880	1.984	2.333	4.903	1.99	2.005	2.130	2.512	5.211
881.8	--	--	--	--	--	1.77	1.782	1.888	2.238	4.851	1.88	1.894	2.000	2.400	5.102
1028.7	--	--	--	--	--	--	--	--	--	--	1.80	1.813	1.930	2.308	4.941

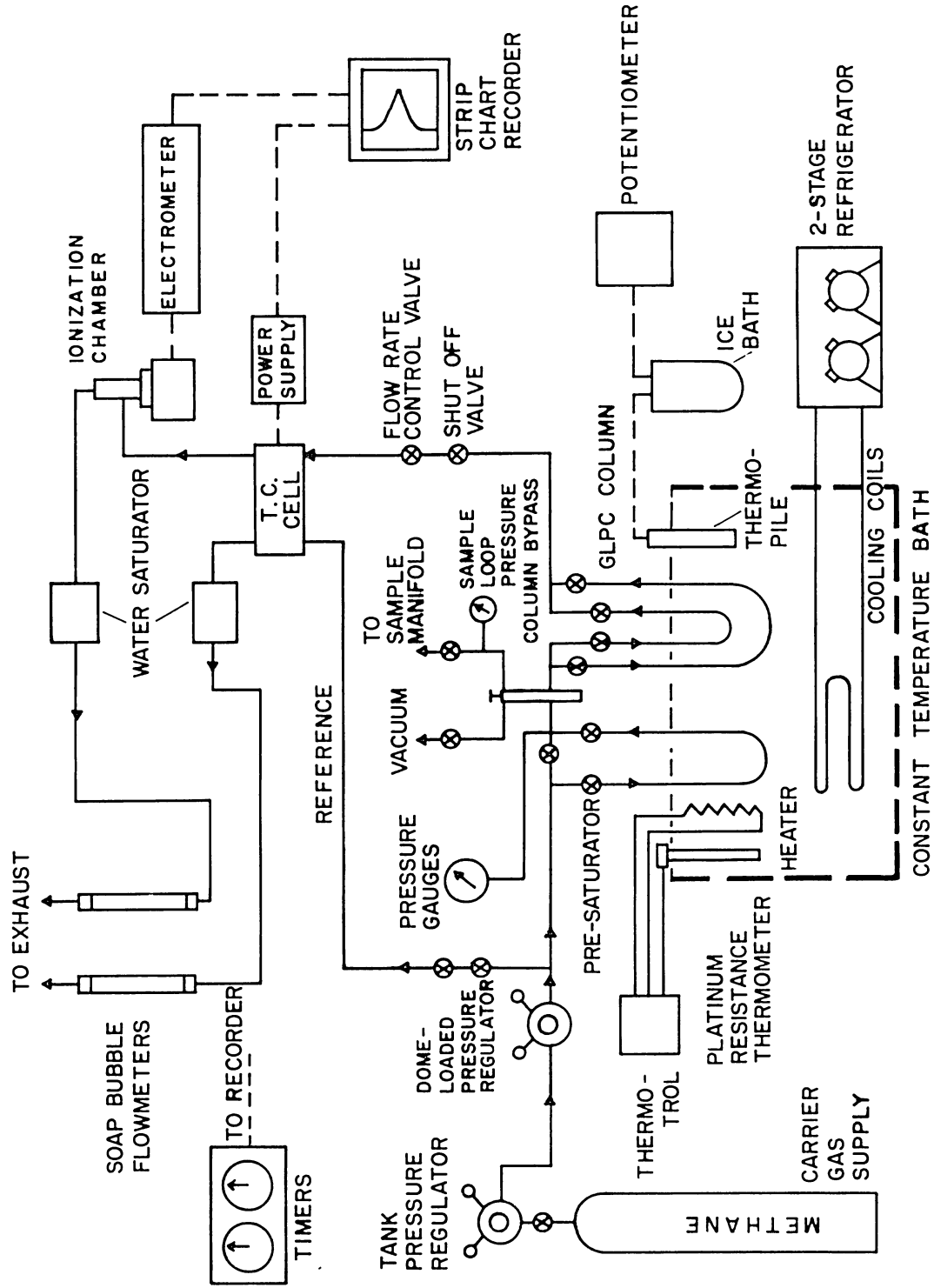


FIGURE I - SCHEMATIC DIAGRAM OF APPARATUS

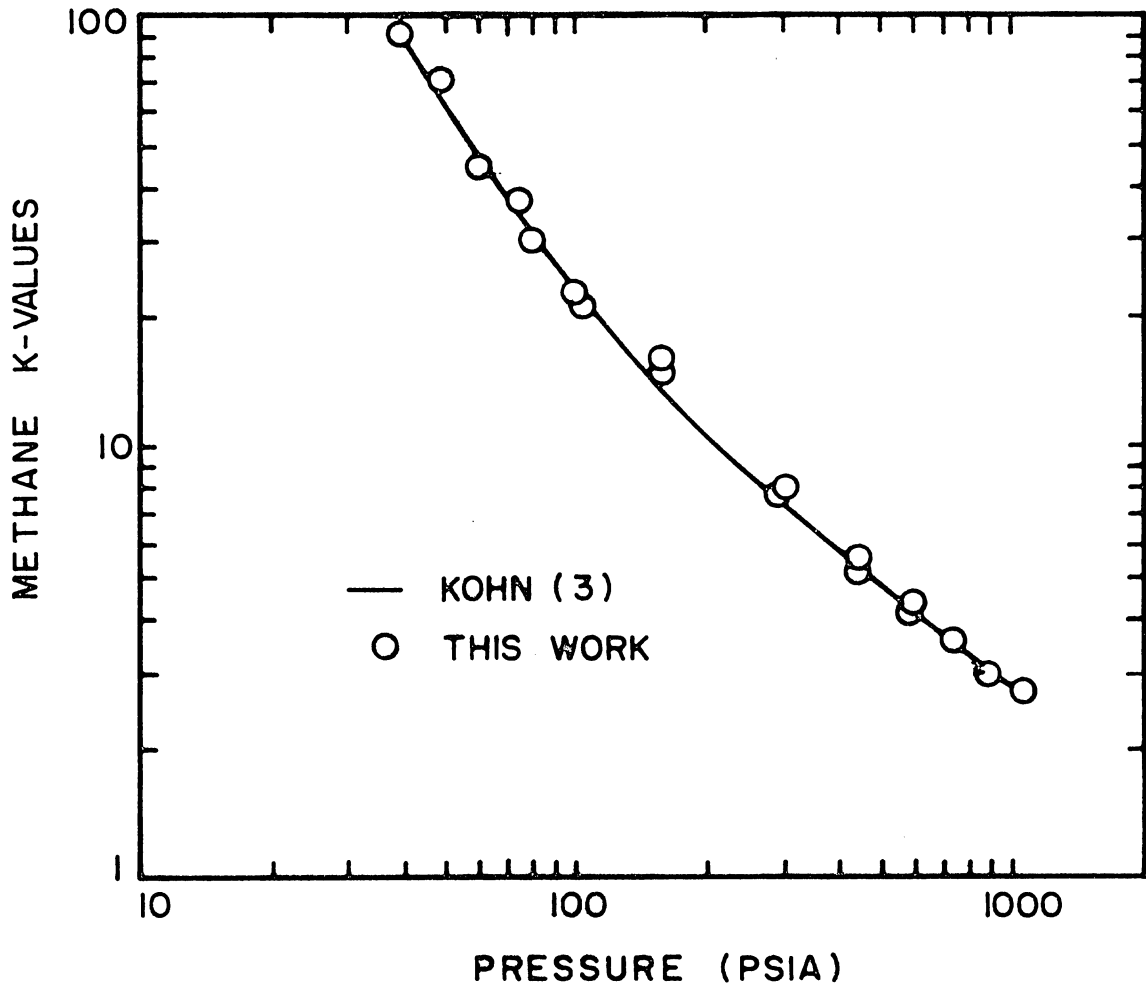


FIG. 2 - METHANE K-VALUE AS A FUNCTION OF PRESSURE AT -25 °C.

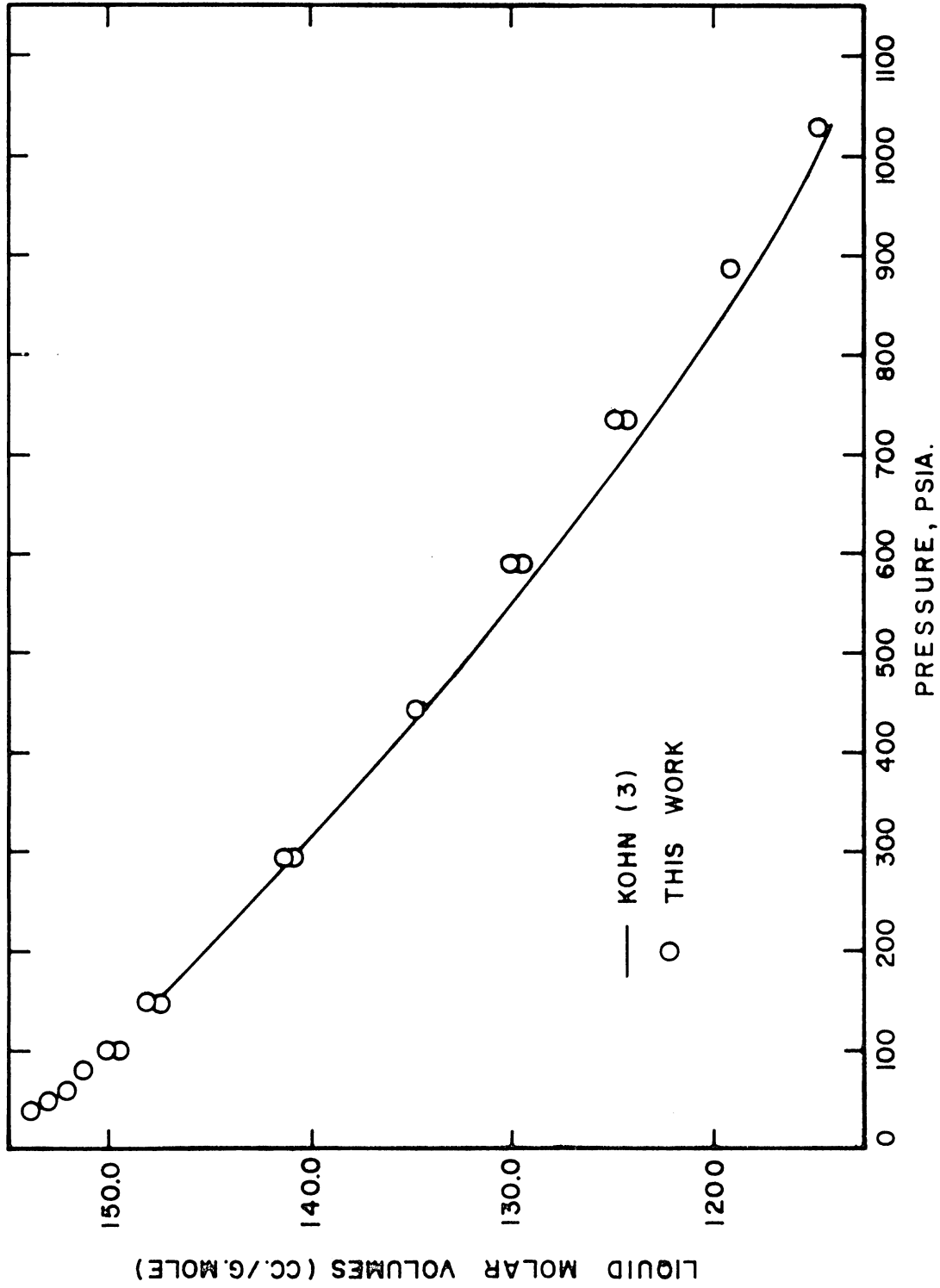


FIG. 3 - LIQUID MOLAR VOLUMES AS FUNCTION OF PRESSURE AT -25°C.

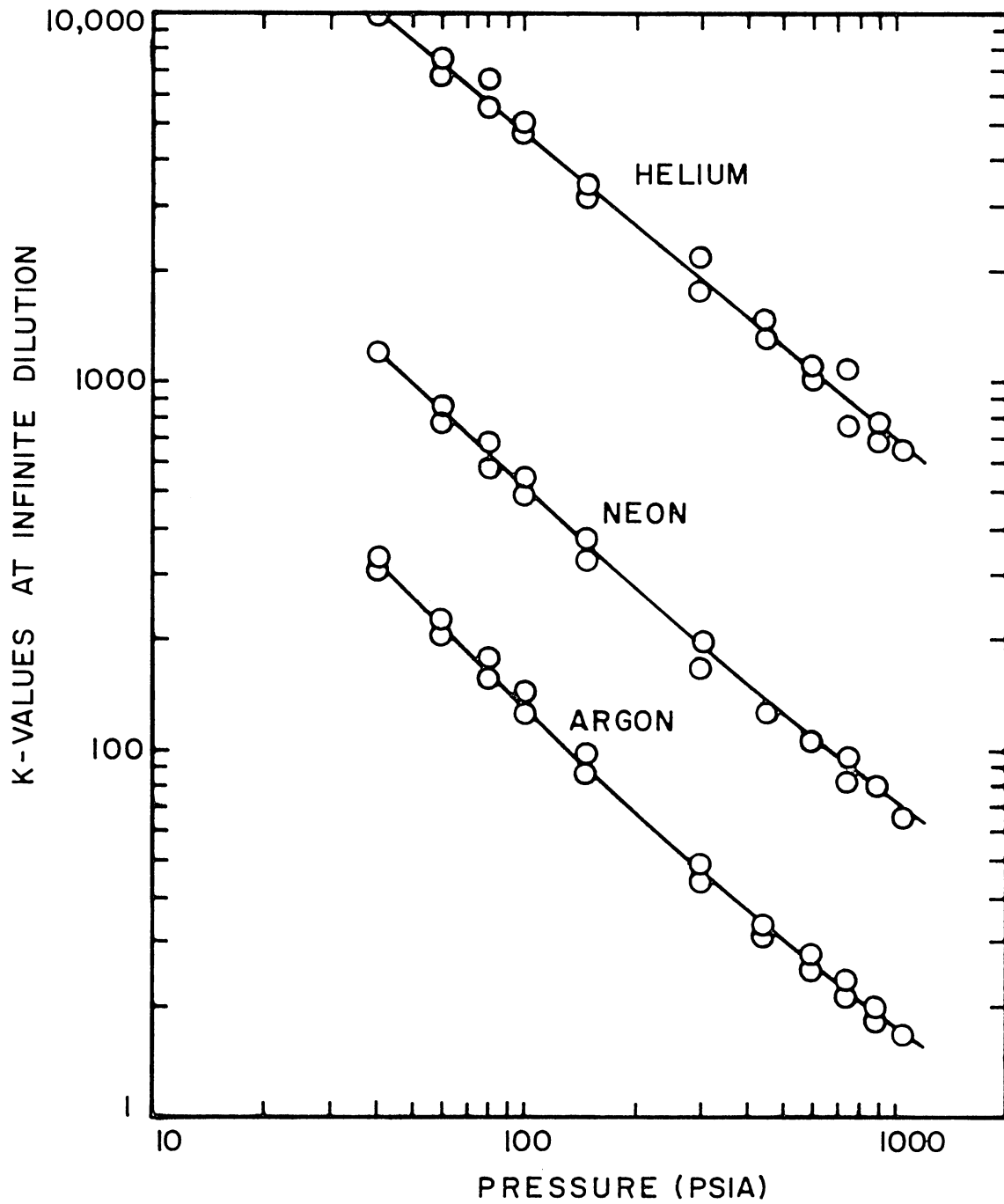


FIGURE 4 - INFINITE DILUTION K-VALUES OF HELIUM, NEON AND ARGON AS FUNCTIONS OF PRESSURE AT -25°C.

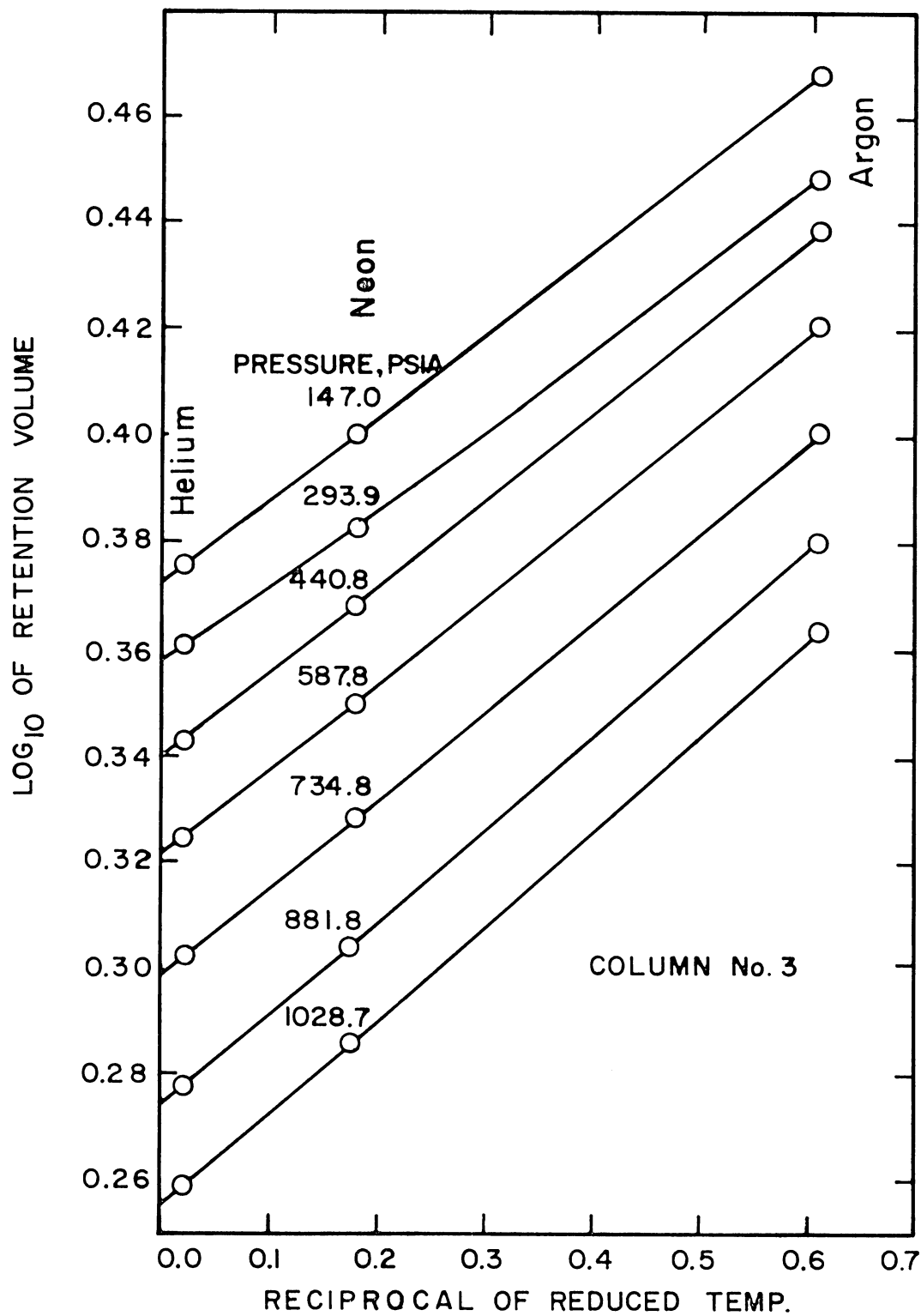


FIG.5 - LOGARITM OF RETENTION VOLUME AS A FUNCTION OF RECIPROCAL OF REDUCED TEMPERATURE



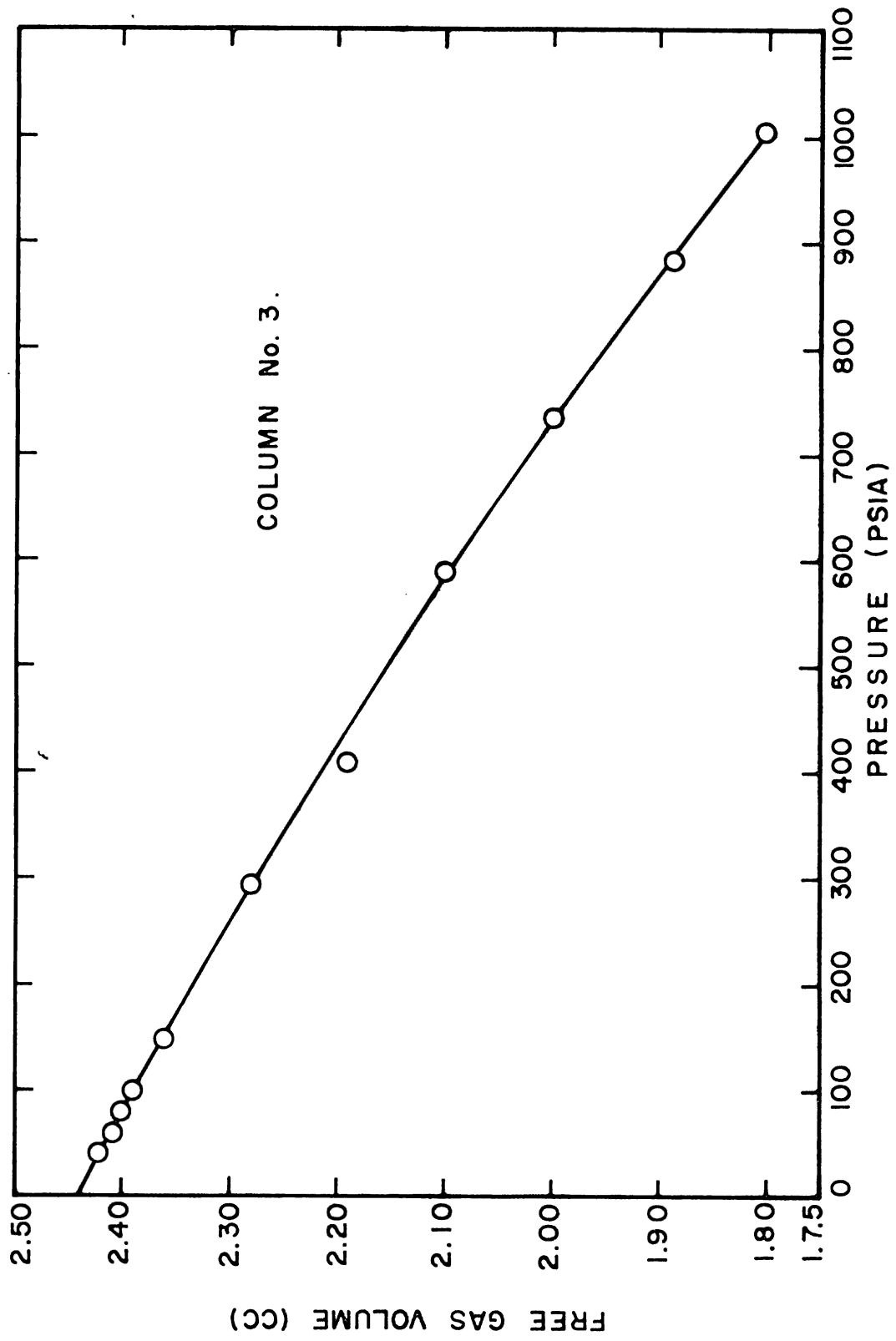


FIG. 6 - FREE GAS VOLUME AS A FUNCTION OF PRESSURE

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