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The Experimental Determination of K-Values and Activity Coefficients by Gas-Liquid Partition Chromatography

by

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A THESIS

SUBMITTED TO THE FACULTY

IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Houston, Texas
February, 1959

Riki Kobayashi

ACKNOWLEDGEMENTS

The author wishes to express his deep gratitude to the following persons and institutions:

Dr. Riki Kobayashi for his continuous help and advice in all the phases of this work.

The members of the staff and the graduate students of the Chemical Engineering Department for their suggestions during this research and particularly to Mr. D. Gardner for his assistance in carrying out the computations.

Dr. John E. Parish, Foreign Student Adviser at The Rice Institute.

Mr. Sam Pollard for his assistance in the construction of the apparatus.

The Rice Institute for its hospitality and ecohomic support through the Ora N. Arnold Fellowship.

Phillips Petroleum Co. and Tennessee Gas Transmission Co. for providing the light hydrocarbons and Petrotex Chemical Co. for the furfural donated.

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OBJECTIVES OF RESEARCH

The objectives of this investigation were:

a) To obtain experimental data in a chromatographic unit for several binary systems of light hydrocarbons (methane, ethane, ethylene, propane, butane) on n-dodecane, and derive from them vapor liquid equilibrium constants, (K values).

b) To discuss some of the experimental factors that can affect the parameters which serves as the basis for calculating physical chemical data.

c) To apply the principles of Gas-Liquid Partition Chromatography to determine activity coefficients at infinite dilution, and evaluate from them other thermodynamic data as free energy of solution, heat of solution, entropy of solution, etc., for a system used in extractive distillation. The systems studied were n-butane, the butenes, and butadiene 1, 3 in furfural.

SUMMARY

A brief review of some important theoretical aspects of Gas-Liquid Partition Chromatography is presented, emphasizing in particular parameters connected with solution behavior.

Preliminary to measurements conducted on light hydrocarbon systems, an apparatus was built trying to insure the best possible conditions to obtain physical and thermodynamical data through chromatographic techniques. The apparatus is described in detail.

Experiments were performed with light hydrocarbons methane through normal butane as the solute and normal dodecane as the stationary phase, in a range of temperatures from 0 to 30°C, and pressures from 20 to 40 psia. The experimental equipment and technique were such that the concentration of the solute approached infinite dilution. Vapor-liquid equilibria ratios or K-values obtained from these experiments have been compared with values obtained from static tests. The agreement range from poor agreement in the case of methane to excellent agreement in the case of propane and n-butane.

The study of a system used in extractive distillation (n - butane, butenes, and butadiene 1, 3 in furfural) is presented. Values for the activity coefficients at infinite dilution were obtained, which show inner consistency, and which are in substantial agreement with those reported by Mertes (28). This study covered a range of temperatures from -20 to 40°C and pressures from 20 to 40 psia.

The variation of the activity coefficients with temperature was used to evaluate the differential heats of solution of the hydrocarbons in furfural. Other related thermodynamic properties such as excess free energy of solution, relative volatilities, etc., were calculated and are reported.

INTRODUCTION

Partition chromatography is a technique in which the components of a mixture are distributed between two phases, one stationary supported on a solid bed of large area, and the other phase traveling through the stationary bed. When the moving phase is a gas the process is called: Gas-Liquid Partition Chromatography.

This technique has been widely used for analytical purposes. The possibility of extending its application was pointed out by Martin (24) who refers to gas chromatography "as a means, perhaps the easiest, for studying the thermodynamics of the interaction of a volatile solute with a non volatile solvent."

GLPC makes use of processes of solution and during recent years successful attempts have been made in using this technique to obtain physical chemical data relevant to the solution processes occurring in the column.

Porter et al (35) established the relation of the retention volumes obtained by GLPC with partition coefficients following the plate theory of Martin and Synge (23). They showed the agreement of this partition coefficients with those obtained from equilibrium measurements. Pierotti et al (33) discussed GLPC solvent effects in a quantitative empirical

manner giving attention to the activity coefficients and the structure of solutes and solvents at a given temperature. Littlewood et al (22) introduced the corrected retention volume as a main chromatographic parameter and obtained heats of solution from the variation of retention volumes with temperature.

Anderson (16) established that corrected retention volume is satisfactory only if the heat of solution is required but if the entropy of solution is required also, the evaluation of partition coefficients is more satisfactory.

An expression relating the retention volume and activity coefficients, and a review of the foundations of some empirical relations connected with homologous series was discussed by Herington (14). A review of some theoretical aspects was made by Rock (38) who pointed out the relation of GLPC with extractive distillation. Rangel (36) used the expression obtained by Porter (33) to calculate partition coefficients and obtained some K values for methane and propane on n-decane.

The previous efforts have led to a better understanding of the GLPC as a means of obtaining thermodynamical data.

The close relation between partition chromatography and solution behavior have not yet been completely exploited however, and it is the purpose of this work to study vapor-liquid

equilibria of the light hydrocarbons and the non-ideality of solutions through their activity coefficients.

THEORY REVIEW

Gas-Liquid Partition Chromatography can be used to determine physical constants as well as for analytical purposes. In any case to achieve successful results good understanding of the theory is required. A brief review of the theory will be presented here.

Chromatography involves transport phenomena of several types: gas phase molecular and eddy diffusion, interphase mass transfer, liquid phase diffusion, etc. A complete description of the processes taking place lies beyond mathematical treatment at the present time. Simplifying assumptions have permitted the development of existing theories. Two major assumptions frequently made in theoretical treatments e.g. Van Deemter et al (40) are:

a) That equilibrium concentrations between the two phases are proportional (Linear Chromatography).

b) The exchange process between solute and the stationary liquid phase is thermodynamically reversible and immediately established. Furthermore, longitudinal diffusion and other processes having a similar effect are neglected. As will be seen later, for the case involved in this study (GLPC) the first assumption is valid, but not the second one.

When the condition dictated by assumption (a) obtains, two different approaches can be followed:

(1.) The "plate theory" that considers the chromatographic column in analogy to the distillation columns as consisting of a number of stages or plates, in each of which there is equilibrium between the two phases.

(2) The "rate theory" which considers the kinetic phenomena occurring in the column.

PLATE THEORY

Martin and Synge (23) were the first to exploite the similarity of the chromatographic technique with the process occurring in the distillation and extraction columns. The theory has been reviewed and extended by Mayer and Tompkins (25), Glueckauf (13) and others.

In this model, a packed column (in which equilibrium is not attained at any point) is visualized as a discontinuous medium divided into hypothetical finite segments each of which represents one effective theoretical plate. The height of that segment is called "height equivalent to a theoretical plate", or HETP. The HETP may be defined as a segment of packing along the direction of flow such that the mobile phase leaving it is in equilibrium with the mean concentration of solute in the stationary phase. Further assumptions introduced in order to make the equations manageable are:

a). The diffusion of solute from one plate to another is

negligible.

b). The HETP is small relative to the column length and remains constant throughout the column. (It has been shown (39) that this is true when the ratio of concentrations of the solute entering and leaving the plate is closed to one, that is, when the column has a large number of plates.)

c). At equilibrium, the distribution ratio of a solute between the two phases must be independent both of the absolute value of its concentration and of the presence of other solutes. This partition coefficient is assumed constant throughout the column.

d). The size of the sample and the method by which it is introduced into the column are such that the charge is initially contained in the first plate.

An isolated segment of column consists of a stationary liquid phase of volume V_s supported by a solid of volume V_o, leaving a void space V_m which is available for the flow of gases.

As a solute is eluted through the column, local dissolution of the solute in the stationary phase takes place. Let C_s be the concentration of the solute in the stationary phase and C_m be its concentration in the mobile phase. The ratio of the two concentrations, at the equilibrium, is called the partition coefficient H. This partition coefficient of a solute determines

the rate at which the concentration band of that solute travels down the column and hence determines the position of the elution curve of a solute with respect to the effluent volume.

Consider the advancement through the column of the elution curve of a particular solute in partition chromatography. For a single theoretical plate, after solute breaks through from it, the following relation holds:

$$\underset{\text{Feed}}{F C_o} = \underset{\text{Plate Content}}{V_s C_s + V_m C_m} = \underset{\text{Effluent}}{V C_m} \qquad (1)$$

where:

V_s = volume of stationary phase in a theoretical plate.

V_m = volume of mobile phase in a theoretical plate.

f = feed volume.

C_o = concentration of solute in the feed.

v = effluent volume.

The first term represents the necessary amount of gas for accomplishing the elution process. The maximum concentration in the effluent would be equal to the concentration in the mobile phase, and the effluent volume in those conditions is termed "effective plate volume."

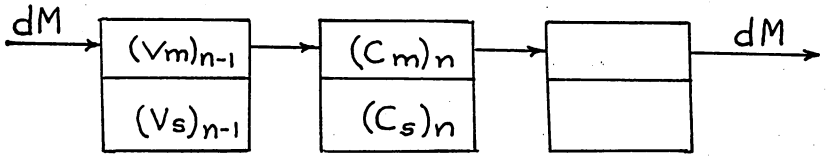
Rewriting (1) $\qquad C_m V_m + C_s V_s = V C_m.$

Dividing by C_m $\qquad V_m + V_s \frac{C_s}{C_m} = V \qquad (2)$

This can be written $\qquad V_m + H V_s = V$

Where $H = \frac{C_s}{C_m}$ is called the partition or distribution coefficient. (3)

The partition chromatography in stages can be represented



Stage No. n-1 n n+1

Representation of General Stages in partition chromatography.

The material balance for the first plate (n=1) if a volume dM of the mobile phase flows throught it is:

$$d(V_m C_m)_1 + d(V_s C_s)_1 = (C_o - C_m)\,dM$$

$$(V_m\,dC_m)_1 + (V_s\,dC_s)_1 + C_{m_1}\,dM = \begin{cases} C_o\,dM & o \le M \le A \\ o & M > A \end{cases} \quad (4)$$

Where M = Total Volume of the Mobile Phase flowed through

A = Feed Volume = Volume of the Mobile Phase while solute concentration $> o$

$C_o dM = 0$ dM for $M > A$ means we are through feeding to first plate.

For any other plate:

$$(V_m\,dC_m)_n + (V_s\,dC_s)_n + C_{m_n}\,dM = (C_m)_{n-1}\,dM \qquad n > 1 \quad (5)$$

Introducing (2) and (3) and with

$$\frac{(C_m)_n}{C_o} = y_n \quad , \quad \frac{M}{V} = \omega \qquad (6)$$

(4) and (5) give rise to the differential equations:

$$\frac{dy_1}{d\omega} + y_1 = \begin{cases} 1 & 0 \leq \omega \leq \frac{A}{V} \\ 0 & \omega > \frac{A}{V} \end{cases} \qquad (7)$$

$$\frac{dy_n}{d\omega} + y_n = y_{n-1} \qquad n > 1 \qquad (8)$$

A boundary condition is given for the initial conditions,

for $$M=0 \quad W=0 \quad Y_1 = Y_2 = \cdots\cdots = Y_n = 0 \qquad (9)$$

The solution of (7) and (8) which are differences differential equations can be worked out for all the stages.

For the first stage with $0 \leq \omega \leq \frac{A}{V}$

$$\frac{dy_1}{d\omega} + y_1 = 1 \qquad (10)$$

Linear differential equation of the type $\frac{dy}{d\omega} + Py = Q$

with general solution $y_1 e^{\int P d\omega} = \int Q e^{\int P d\omega} + C$

Substituting in (10) where P = 1 Q = 1

$$y_1 e^{\omega} = e^{\omega} + C \qquad (11)$$

applying boundary condition (9), $C_1 = -1$

Stage 1 $$y_1 = 1 - e^{-\omega} \qquad (12)$$

For the second stage

$$y_2 e^{\omega} = \int (1-e^{-\omega})\, e^{\omega} d\omega + C_2$$

$$y_2 e^{\omega} = e^{\omega} - \omega + C_2 \qquad \text{with bound. cond. (9)} \quad C_2 = -1$$

Stage II $$y_2 = 1 - (\omega+1) e^{-\omega} \tag{13}$$

For the third stage

$$y_3 e^{\omega} = \int \left[1-(\omega+1)\, e^{-\omega}\right] e^{\omega} d\omega + C_3$$

$$y_3 e^{\omega} = e^{\omega} - \frac{\omega^2}{2} - \omega + C_3 \qquad \text{with b.c. (9)} \quad C_3 = -1$$

$$y_3 = 1 - \frac{\omega^2}{2} e^{-\omega} - \omega e^{-\omega} - e^{-\omega}$$

Stage III $$y_3 = 1 - \frac{1}{2}\left(\omega^2 + 2\omega + 2\right) e^{-\omega} \tag{14}$$

For the stage n

$$y_n = \frac{1}{n-1\,!} \left[\left(\omega^{n-1} + (n-1)\omega^{n-2} + (n-1)(n-2)\,\omega^{n-3} \right) e^{-\omega} \right] \tag{15}$$

Consider the following integral:

$$\int_0^u u^{n-1} e^{-u} du = u^{n-1} e^{-u} + (n-1)\, u^{n-2} e^{-u} + (n-1)(n-2)\, u^{n-3} e^{-u} + \cdots \tag{16}$$

It corresponds with the expression in brackets, and our expression for "y" can take the form:

$$\frac{1}{n-1\,!} \int_0^u u^{n-1} e^{-u} du$$

Let $u = \omega'$ where ω' is a dummy variable. Our final expression for "y" becomes

$$y_n = \int_0^{\omega} e^{-\omega'} \frac{\omega'^{n-1}}{n-1\,!} d\omega' \quad \text{for} \quad 0 \leq \omega \leq \frac{A}{V} \tag{17}$$

For the case $w > \frac{A}{V}$ The general solution corresponds to that treated before.

$$\frac{dy}{dw} + y_1 = 0$$

Stage I $$y_1 = c_1 e^{-w} \qquad (18)$$

For the same column the expression (18) and (12) must be satisfied in the first plate to avoid discontinuity, then at $\frac{A}{V}$

$$1 - e^{-\frac{A}{V}} = C_1 e^{-\frac{A}{V}}$$

$$C_1 = e^{\frac{A}{V}} - 1$$

$$y_1 = \left(e^{\frac{A}{V}} - 1\right) e^{-w} \qquad (19)$$

For the stage II

$$\frac{dy_2}{dw} + y_2 = \left(e^{\frac{A}{V}} - 1\right) e^{-w}$$

$$y_2 e^{w} = \left(e^{\frac{A}{V}} - 1\right) w + C_2 \qquad (20)$$

At w $= \frac{A}{V}$ for continuity

$$y_2 = 1 - (w+1) e^{-w} = 1 - \left(\frac{A}{V} + 1\right) e^{-\frac{A}{V}}$$

$$\left[1 - \left(\frac{A}{V} + 1\right) e^{-\frac{A}{V}}\right] e^{\frac{A}{V}} = \left(e^{\frac{A}{V}} - 1\right)\frac{A}{V} + C_2$$

$$C_2 = e^{\frac{A}{V}} - \left(\frac{A}{V} + 1\right) - \left(e^{\frac{A}{V}} - 1\right)\frac{A}{V} = e^{\frac{A}{V}}\left(1 - \frac{A}{V}\right) - 1$$

$$y_2 = \left(e^{\frac{A}{V}} - 1\right) w e^{-w} + \left[e^{\frac{A}{V}}\left(1 - \frac{A}{V}\right) - 1\right] e^{-w}$$

$$y_2 = \left(w e^{\frac{A}{V}} - w + e^{\frac{A}{V}} - \frac{A}{V} e^{\frac{A}{V}} - 1\right) e^{-w} \qquad (21)$$

The expression in brackets corresponds as before to

$$\int_{w-\frac{A}{V}}^{w} u^{n-1} e^{-u} du$$

Let $u = w'$

Then

$$y_n = \int_{w-\frac{A}{V}}^{w} e^{-w'} \frac{w'^{n-1}}{n-1!} dw' \quad for \quad w > \frac{A}{V} \qquad (22)$$

But from (6)

$$y_n = \frac{C_{m_n}}{C_o} \quad , \quad w = \frac{M}{V}$$

The equations (17) and (22) can then be written

$$C_{m_n} = \frac{C_o}{V} \int_0^M \frac{1}{n-1!} e^{-\frac{M'}{V}} \left(\frac{M'}{V}\right)^{n-1} dM' \quad , \quad 0 \leqslant M \leqslant A \qquad (23)$$

$$C_{m_n} = \frac{C_o}{V} \int_{M-A}^M \frac{1}{n-1!} e^{-\frac{M'}{V}} \left(\frac{M'}{V}\right)^{n-1} dM' \quad for \quad M > A \qquad (24)$$

which express the shape and position of the moving band. The latter equation is particularly important because it represents the situation at the end of the column. The integrand of (24) is analogus to Poisson distribution function:

$$e^{-\mu x} = \frac{(\mu x)^r}{r!}$$

For large μx that means $\frac{M'}{V}$ in equation (24), (that would be a condition fulfilled at the end of the column if the number of plates is not too small), it can be approximated for a Gauss distribution function

$$\frac{1}{\sqrt{2\pi}\,\sigma}\, e^{-\frac{x^2}{2\sigma^2}}$$

Then

$$\frac{1}{(n-1)!}\, e^{-\frac{M'}{V}} \left(\frac{M'}{V}\right)^{n-1} \simeq \frac{1}{\sqrt{2\pi\,\frac{M'}{V}}}\, \exp\left[-\frac{\left(\frac{M'}{V}-n\right)^2}{2\left(\frac{M'}{V}\right)}\right] \qquad (25)$$

This can be further approximated for large $\frac{M'}{V}$ as:

$$\frac{1}{\sqrt{2\pi n}}\, \exp -\left[\frac{\left(\frac{M'}{V}-n\right)^2}{2n}\right] \qquad (26)$$

Introducing (26) for the integrand in equation (24), and replacing for a large number of plates n - 1 by n

$$C_{m_n} = \frac{C_o}{V\sqrt{2\pi n}} \int_{M-A}^{M} \exp\left[-\frac{\left(\frac{M'}{V}-n\right)^2}{2n}\right] dM \qquad (27)$$

The concentration will reach a maximum when:

$$M = nV + \frac{1}{2}A.$$

For small feed volumes $A \ll M$ (27) becomes

$$(C_m)_n = \frac{A C_o}{V\sqrt{2\pi n}} \exp\left\{-\frac{\left(\frac{M'}{V} - n\right)^2}{2n}\right\} \qquad (28)$$

The Retention Volume is defined as the volume of mobile phase passed into the column when C_m is a maximum, and is related to the column geometry and the partition coefficient for the solute in the same way as the effective plate volume is to the volume of mobile and stationary phase.

$$V_R = V_m + HV_s \qquad (29)$$

then

$$V = \frac{V_R}{n}$$

Let $q_o = AC_o$ represent the amount of material charged in the column.

Substituting the relations in (28)

$$(C_m)_n = \frac{q_o}{\sqrt{2\pi n}} \frac{n}{V_R} \exp\left[-\left(\frac{1}{2n}\right)\left(\frac{M}{V} - n\right)^2\right]$$

$$(C_m)_n = \frac{q_o}{\sqrt{2\pi n}} \frac{n}{V_R} \exp\left[-\left(\frac{1}{2n}\right)\left(\frac{Mn}{V_R} - n\right)^2\right]$$

$$(C_m)_n = \frac{q_o}{\sqrt{2\pi n}} \frac{n}{V_R} \exp\left[-\left(\frac{n}{2}\right)\left(1 - \frac{M}{V_R}\right)^2\right] \qquad (30)$$

This equation gives the concentration of the solute in the effluent gas, C_m, as a function of the mobile gas passed into the column, M, the amount of material charged to the first plate, (q_o), the number of plates in the column, n, and the retention volume, V_R, equation (30) was obtained by Porter et al (35) from the earlier work of Martin and Synge (23).

Corrections. The retention volumes directly, or through other parameters derived from them, will be the basis for the estimation of certain physical constants. It is a necessary requirement, therefore, to apply several correction factors resulting from the choice of operating conditions and the experimental apparatus:

a). The pressure drop through the column.

The plate theory was originally developed for the case of liquid partition chromatography (23). James and Martin (17) extended it to the case of a gas in the mobile phase, provided a correction for the fact that the mobile phase is compressible and thus produces a gradient of gas velocity down the column.

The derivation of the equation was made with the assumption that the partial pressures of the substances to be separated are negligible with respect to that of the carrier gas.

The gas volume displaced per unit time is:

$$a u = F \frac{p_o}{p} = K \frac{dp}{dx} \qquad (31)$$

Where:

a = cross section of the column.

u = linear velocity of the gas at the point x

p = pressure of the gas at a point distant x from the outlet

P_o = outlet pressure

F = Volumetric rate of flow at the outlet

K = constant for a given column.

Integrating

$$\frac{K}{P_o}\,\frac{p^2}{2} = Fx + C \qquad (32)$$

At $x = 0 \quad p = P_o \quad$ and $K P_o = C$

Then $$K\,\frac{p^2}{P_o} = 2Fx + KP_o$$

or: $$K = \frac{2Fx\,P_o}{p^2 - P_o^2}$$

$$F = \frac{K(p^2 - P_o^2)}{2x\,P_o} = \frac{KP_o}{2x}\left[\left(\frac{p}{P_o}\right)^2 - 1\right] \qquad (33)$$

In a chromatographic column different solutes travel through it at different rates. The velocity of the solute relative to the velocity of the elution gas is given by the retardation

factor (10)

$$R_f = \frac{\text{movement of position of maximum concentration of solute}}{\text{movement of mobile phase in column over same time interval}}$$

The elution time is given by:

$$t = \int_0^l \frac{dx}{u R_f} \tag{34}$$

Introducing the value of u from the equation (31)

$$u = \frac{F P_o}{a P} \quad \text{and} \quad dx = \frac{K p dP}{F P_o}$$

Rewriting (34)

$$t = \int_{P_o}^{P_1} \frac{\frac{K P dP}{F P_o}}{\frac{F P_o R_f}{a P}} = \int_{P_o}^{P_1} \frac{K P^2 a \, dP}{F^2 P_o^2 R_f} \tag{35}$$

R_f depends only on the nature of the gas, column characteristics, and temperature, but being a ratio of velocities should be independent of pressure because the different components will suffer the same velocity gradient.

Then

$$t = \frac{K a}{F^2 P_o^2 R_f} \int_{P_o}^{P_1} P^2 dP = \frac{K a}{F^2 P_o^2 R_f} \cdot \frac{P_1^3 - P_o^3}{3} \tag{36}$$

But $t F = V_R$

$$V_R = \frac{K a P_o \left[\left(\frac{P_1}{P_o} \right)^3 - 1 \right]}{3 F R_f} \tag{37}$$

Hence, with $x = \ell$, $p = p_i$ and Equation (33)

$$V_R = \frac{Ka\,P_o\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]}{\frac{3KP_oR_f}{2\ell}\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}$$

$$V_R = \frac{2}{3}\,\frac{a\ell}{R_f}\,\frac{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]} \qquad (38)$$

When Pi/Po approaches to unity

$$\frac{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]} \longrightarrow \frac{2}{3} \qquad (39)$$

Then

$$V_R = V_R^\circ = \frac{a\ell}{R_f} \qquad (40)$$

where V_{R° = corrected retention volume for pressure drop.

Substituting (40 in (38)

$$V_R^\circ = V_R\,\frac{3}{2}\,\frac{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]} \qquad (41)$$

This expression has been checked experimentally by James and Martin (17) and Littlewood (22).

(b) Correction for dead volume of apparatus.

The experimental retention time, previously mention represents the average time taken for a molecule of a gas to pass from the injection point to the thermal conductivity cell. This time is the sum of the time spent in the stationary phase and in the gas phase. As the interest lies in the gas-liquid

interaction, it is necessary to correct the retention time for the time spent for the flow of gas through the dead volume of the apparatus, specifically, the dead volume consists of the tube leading from the injection point of the sample to the column, and the tube leading from the column to the detector. The estimation involves the knowledge of these volumes as an apparatus constant and the flow rate of the gaseous phase.

c) Correction for Sample Volume.

The sample size charged to the chromatographic column may affect the apparent retention volume if charged over a significant period of time resulting in a band which spread over an appreciable length of column (35), (40). Porter (35) treated two cases: plug flow, and exponential mixing. Van Deemter (40) obtained the following development. The width of the elution curve was defined as the distance between the points of intersection of the tangents to the elution curve at the points of inflection, with the horizontal axis.

Introducing the dimensionless quantities:

$$m = \frac{M}{v\sqrt{n}} \quad , \quad a = \frac{A}{v\sqrt{n}} \qquad (42)$$

equation (27) becomes

$$\frac{(Cm)_n}{C_o} = \frac{1}{\sqrt{2\pi}} \int_{m-a}^{m} e^{-\frac{1}{2}(m'-\sqrt{n})^2} dm' \qquad (43)$$

From this equation and definition of error function

$$f(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-y^2} dy$$

$$\frac{(Cm)_n}{C_o} = \text{erf} \frac{a}{2\sqrt{2}} \qquad (44)$$

gives the dependence of the height $\frac{(Cm)_n}{C_o}$ to the parameter $a = \frac{A}{v\sqrt{n}}$ Another expression was developed to show the dependence of the width $\Delta m = \frac{\Delta M}{v\sqrt{n}}$ on $\underline{a}$. Plots of Δm vs $\underline{a}$ demonstrated (40) that for $a = \frac{A}{v\sqrt{n}} < .5$ or for sample volumes $\leqslant \frac{.5\, V_e}{\sqrt{n}}$ (45) the width Δm becomes almost independent of the feed volume.

d). Correction for Dead Volume of Detector.

The dead volume of the detector cell affects both retention volume and peak width. The effects are especially pronounced at high detector volumes and low retention volumes. The influence of this factor in the retention volumes must be considered when the highest accuracy is sought. This accuracy is inherently

necessary in the determination of retention volumes and partition coefficients from which physical constants are to be obtained.

Johnson and Stross (19) have developed the theory for detector corrections and used the theory to correlate experimental data reflecting detector dead volume. They assumed that the sample entered the detector exactly as it left the sample injector. Applying a material balance to the plug flow case, the rate of change of amount of sample in the detector with respect to the volume must equal the inflow to the detector minus the outflow:

$$\frac{dx}{dV'} = S - \frac{x}{Z} \tag{46}$$

where:

x = amount of sample in detector chamber, (g)

V' = volume of sample added to the column in plug flow, (c.c.)

S = concentration of sample entering detector (g/cc)

Z = detector volume (cc)

Applying the equation already derived for C_m (30), substituting in the material balance, equation (46)

$$\frac{dx}{dV} = \frac{q_0}{\sqrt{2\pi n}} \frac{n}{V_R} e^{\left[-\left(\frac{n}{2}\right)\left(1 - \frac{M}{V_R}\right)^2\right]} - \frac{x}{Z} \tag{47}$$

The general solution of this differential equation is given as

$$x = e^{-\frac{V}{2}} \frac{q_0 n}{\sqrt{2\pi n}\, V_R}\; e^{\frac{n}{2}\left(\frac{2V_R}{nZ} + \frac{V_R^2}{n^2Z^2}\right)} \int -\frac{n}{2V_R^2}\left[V - V_R\left(1 + \frac{V_R}{nZ}\right)\right]^2 dV + C'' e^{-\frac{V}{Z''}} \qquad (48)$$

In order to simplify, the parameter

$$t = \frac{V - V_R\left(1 + \frac{V_R}{Zn}\right)}{V_R/\sqrt{n}} \qquad (49)$$

is introduced.

Applying the boundary condition that V = 0 at X = 0

$$\frac{x}{q_0 Z} = \frac{1}{Z\sqrt{2\pi}}\; e^{\frac{1}{Z}\left(V_R - V + \frac{V_R^2}{2nZ}\right)} \int_{-\frac{V_R\left(1 + \frac{V_R}{Zn}\right)}{V_R/\sqrt{n}}}^{\frac{V - V_R\left(1 + \frac{V_R}{Zn}\right)}{V_R/\sqrt{n}}} e^{-\frac{1}{2}t^2}\, dt \qquad (50)$$

After this equation the fraction of the measured retention volume that is due to "non-column effects" (19) is plotted as ordinate versus the retention volume measured in units of "effective detector volume" ($Z'/V_{R'}$)

where Z' = effective detector volume

$V_{R'}$ = retention volume corrected for dead volume of apparatus.

This gives different curves for different number of plates, that converge at low values of the detector volume parameter, $Z'/V_{R'}$ (19).

Efficiency of the Column.

Column efficiency has been measured for the height equivalent to a theoretical plate. The HETP has been defined on page -8- . The number of theoretical plates is a measure of the effective number of equilibrations which take place between the fixed and the mobile phase as the gas moves through the column.

James and Martin (17) have proposed two methods for the calculation of the number of theoretical plates from the recorded chromatograms. The first approach, considering the rate of transport of solute corresponding to the plate of maximum concentration lead them to the following equation

$$n = 2\pi \frac{h^2 L^2}{A^2} \qquad (51)$$

where:

h = peak height

L = length of the chromatogram

A = area under the peak

n = number of plates.

The second alternative method of James and Martin (17) which has become the recommended one (11) for the purpose of calculating the number of theoretical plates, has its origin in the consideration that the chromatogram corresponds to

a distribution curve whose shape approaches a normal error curve. The mathematical analysis gives the following equation:

$$n = 16 \frac{L^2}{d^2} \qquad (52)$$

where:

d = peak width distance between the tangents to the inflection points of the distribution curve, measured on the base line.

For a known number of theoretical plates, the HETP is given for the relation

$$H.E.T.P. = \frac{l}{n} \qquad (53)$$

where:

l = length of the column.

The number of plates and the HETP consequently, have been found to be a function of the column characteristics such as length of the column, mesh size of support, ratio of stationary liquid to solid support, and also affected to a certain extent the nature of the mobile and stationary phase (20).

Application of the Theory for Determining Physical Constants.

GLPC has been used not only for analytical purposes but also to determine physical constants (3), (14), (22), (33), (35), (36) and (38). By exploiting the solution processes

taking place in the column GLPC can be used in the study of the non-ideality of solutions. The general pattern followed consists of determining typical parameters as retention volumes and partition coefficients and relating them to the properties of the systems.

For the following development it is convenient to bring out equation (29) which gives the relation of the experimentally determined parameter V_R, the retention volume, or the volume of the mobile phase passed into the column when the concentration is a maximum, as it relates to the characteristics of the column and the partition coefficient.

$$V_R^\circ = V_m + H^\circ V_s \qquad (29a)$$

V_m = volume of the mobile phase in the column.

V_s = volume occupied by the stationary solvent phase in the column.

H° = partition coefficient defined as the ratio of solute per unit volume in the solvent phase to the solute per unit volume of the gas phase taken when the solute concentrations are infinitely dilute.

It must be noted that the retention volume does not depend explicitly on the number of plates in the column but depends only on the column characteristics through V_m and V_s.

In order to use equation (29a) as a basic equation to

obtain other physical and thermodynamical properties it is necessary for partition coefficients as determined to fulfill certain requirements:

a). The coefficients must be consistent if determined in columns of different characteristics and under different flow conditions.

b). They must not be influenced to an appreciable extent by the solid support.

c). They must agree essentially with those determined under well defined equilibrium conditions.

These conditions were found to be substantially fulfilled by Porter (35) who applied equation (29a) to find partition coefficients from retention volumes following the assumptions of the theoretical plate analysis of Martin (23).

Determination of K Values.

The definition of partition coefficient may be alternately expressed as:

$$H = \frac{x}{y} \quad \frac{M_s}{M_m} \tag{54}$$

Where:

x mole fraction of solute in the liquid,

y mole fraction of solute in the gas,

M_s moles of stationary phase per cc of liquid,

M_m moles of mobile phase per cc of gas.

The agreement of the partition coefficients from GLPC with those determined under well defined equilibrium conditions, and the fact that the relation x/y appears in this equation was exploited for Rangel (36) in order to predict K values (vapor-liquid equilibria constants) for hydrocarbons in n-Decane.

Setting $\frac{x}{y} = 1/K$

$$H = \frac{1}{K} \quad \frac{M_s}{M_m} \tag{55}$$

The gaseous phase approaches ideal behavior, so

$$\pi V = nRT \quad \therefore \quad M_m = \frac{n}{V} = \frac{\pi}{RT} \tag{56}$$

and

$$H^\circ = \frac{1}{K} \quad \frac{M_S R T}{\pi}$$

As: $M_S = \frac{\rho_S}{MW_S}$

where:

ρ_s = mass per unit volume of stationary phase,

MW_s = mass of one mole of stationary phase.

$$H^\circ = \frac{1}{K} \quad \frac{\rho_S R T}{\pi \ MW_S} \tag{57}$$

Substituting the value of H in equation (29a) rewritten as

$$H^\circ = \frac{V_R^\circ - V_m}{V_s} \qquad \text{gives} \quad K = \frac{\rho_s RT \ V_s}{(V_R^\circ - V_m)\pi MW_s}$$

But $V_s = W_s/\rho_s$

Then:

$$K = \frac{R T W_s}{(V_R^\circ - V_m)\, \pi\, MW_s} \qquad (58)$$

This equation was found (36) to give reliable K values for hydrocarbons. Its application requires a knowledge of the pressure, temperature, corrected retention volume of the solute, the volume of gas in column, weight of liquid in column, and the molecular weight of that liquid.

Determination of Solution Parameters.

For the study of non-ideal systems, solution behavior may be expressed in terms of deviations from the ideal solution. The development for the liquid phase activity coefficient, a measure of solution non-ideality, follows.

For any ideal solution of a volatile solute in a non-volatile solvent, the ideal behavior obtains in the gas phase, and:

$$\bar{p} = x p^\circ \qquad (59)$$

where $\overline{p}$ = partial pressure

x = mol fraction

p° = vapor pressure in the pure state at the temperature of the solution.

This relation is known as Raoult's law. The liquid phase

activity coefficient is introduced into equation (59) to give

$$\bar{p} = \gamma x p^{\circ} \tag{60}$$

where $\overline{p}$ is partial pressure exerted by an actual system; combining equation (60) with Dalton's law gives:

$$\pi y = \gamma x p^{\circ} \tag{61}$$

where

π = total pressure

γ = activity coefficient.

Rearranging (61)

$$y = \frac{\gamma x p^{\circ}}{\pi}$$

Introducing it in the expression for the partition coefficients (54)

$$H^{\circ} = \frac{x \pi}{\gamma x p^{\circ}} \quad \frac{M_s}{M m} \tag{62}$$

With the assumption of ideal behavior in the gaseous phase

$$\pi = M_m RT$$

where M_m = mole of mobile phase per cc of gas

$$H^{\circ} = \frac{\pi}{\gamma p^{\circ}} \quad \frac{M_s RT}{\pi}$$

$$H^{\circ} = \frac{M_s RT}{p^{\circ} \gamma} \tag{63}$$

Equation 63 was previously derived by Porter (35).

The assumption of constant partition coefficients implies that ideal or infinite dilute solution exists over the whole length of

the column. This is consistent with the situation existing in GLPC which approaches infinite dilute solution.

The following expression can be used for obtaining activity coefficients at infinite dilution from partition coefficients:

$$\gamma^\circ = \frac{M_s R T}{H^\circ p^\circ} \tag{64}$$

This relation which contains a solute dependent factor (p°), a solvent dependent factor (M_s), and a solute solvent dependent factor (γ), has proven useful in the study of solute solvent effects (3), (33), (35) and (36). The expression for the activity coefficients can be set in terms of the directly measured corrected retention volume

$$V_R = V_m + H V_s \tag{29a}$$

Substituting H° from (63)

$$V_R^\circ = V_m + \frac{M_s R T}{\gamma^\circ p^\circ} V_s$$

and therefore

$$\gamma^\circ = \frac{M_s R T V_s}{(V_R^\circ - V_m) p^\circ} \tag{65}$$

The activity coefficient, together with the data for the pure substances can be exploited in many useful ways. Through the application of the activity coefficients established by Equation 65, GLPC can be used to:

1. - Study extractive distillation systems.

2. - Evaluate thermodynamic data.

Application of GLPC to Study Extractive Distillation Systems.

In extractive distillation, a substance not normally presented in the mixture and relatively non-volatile is added in order to increase the difference in volatilities of the most difficultly separable components.

The most convenient measure of the difficulty of separation of two liquids is the relative volatility or relative distribution ratio, defined as the ratio of the compositions of the components in one phase to the ratio of the compositions in the other phase. For a vapor-liquid system:

$$\alpha_{1,2} = \frac{\frac{y_1}{y_2}}{\frac{x_1}{x_2}} \qquad (66)$$

where y_1 and y_2 are the mole fractions of the two components in the vapor, and x_1 and x_2 are the mole fractions of the two components in the liquid.

Writing equation 61 for components 1 and 2,

$$y_1 \pi = \gamma_1 x_1 p_1^\circ$$
$$y_2 \pi = \gamma_2 x_2 p_2^\circ \qquad (61a)$$

introducing the resulting expressions in Equation 66

$$\alpha_{1,2} = \frac{\frac{\gamma_1 x_1 p_1^\circ}{\pi}}{\frac{\gamma_2 x_2 p_2^\circ}{\pi}} = \frac{\gamma_1 p_1^\circ}{\gamma_2 p_2^\circ} \qquad (67)$$

At high pressures, the vapor pressures are replaced by fugacities. α is a constant for a given temperature. The relation γ_1/γ_2 can be varied by addition of a third component to the bynary system; this component (solvent) forms non-ideal solution with one or both of the components and exaggerates the difference in volatility between them. This addition is only effective when the extractive agent appears in large quantities in the liquid phase.

GLPC may be exploited to study extractive distillation because the stationary liquid (solvent) usually has a much higher boiling point than the components of the mixture to be separated, and is presented in comparatively large amount. This fact has been pointed out by Herrington (14) and Rock (38). The resulting relative volatilities at infinite dilution will be indicative of the separation to be achieved by extractive distillation.

Calculation of Thermodynamic Data:

The retention volumes, partition coefficients, or the activity coefficients can be related to other thermodynamic properties connected with the behavior of solutions. In fact this data should be presented as a support of the soundness of those parameters determined from GLPC.

Heats of Solution.

Heats of solution have been calculated from chromatographic

data (3), (22), and (35). Littlewood (22) used the corrected retention volume that is related to the temperature for one expression of the Clausius-Clapeyron type

$$\frac{d \ln V_R^\circ}{dT} = \frac{\Delta H_{s/n.}}{RT^2} + K \qquad (68)$$

K includes terms such as the temperature coefficient of expansion of the phases and $\Delta H_{s/n.}$ = differential heat of solution. Heats of solution may also be obtained from the partition coefficients. Writing Equation 63 in logarithmic form:

$$\ln H^\circ = \ln M_s RT - \ln \gamma^\circ - \ln p^\circ \qquad (63a)$$

Considering the variation with temperature Equation 63a becomes:

$$\ln H^\circ = \ln M_s R - \ln \frac{1}{T} - \frac{\Delta H_s^E}{RT} + \frac{\Delta H_v}{RT} + K \qquad (69)$$

where: ΔH_s^E is the excess partial heat of solution of the solute in the solvent

ΔH_v is the heat of vaporization of the solute.

Since the molecular volume of the solvent is normally not very dependent on temperature, its variation can be neglected.

$$\frac{\partial \ln H^\circ}{\partial \frac{1}{T}} = -T - \frac{\Delta H_s^E}{R} + \frac{\Delta H_v}{R} = \frac{\Delta H_v - RT - \Delta H_s^E}{R} \qquad (70)$$

The plot of logarithm of partition coefficient versus 1/T gives a linear relation which permits the evaluation of ΔH_s^E.

This way was followed by Porter (35) in order to obtain data of heats of solution.

The heat of solution can be obtained from the variation of activity coefficients with temperature. The activity coefficient can be defined as

$$\gamma_1 = \frac{a_1}{N_1} = \frac{f_1}{f_1^\circ N_1} \tag{71}$$

Then

$$\left(\frac{\partial \ln \gamma_1}{\partial T}\right)_P = \left(\frac{\partial \ln f_1}{\partial T}\right)_P - \left(\frac{\partial \ln f_1^\circ}{\partial T}\right)_P \tag{72}$$

As

$$\left(\frac{\partial \ln f}{\partial T}\right)_P = \frac{H_1^* - \bar{H}_1}{RT^2} \tag{73}$$

Therefore

$$\left(\frac{\partial \ln \gamma_1}{\partial T}\right)_P = \frac{(H_1^* - \bar{H}_1) - (H_1^* - \bar{H}_1^\circ)}{RT^2} = \frac{(\bar{H}_1 - H_1^\circ)}{RT^2} \tag{74}$$

This can be written as

$$\frac{d \ln \gamma_1}{d\left(\frac{1}{T}\right)} = \frac{\Delta H_{s/n.}}{2.303\, R} \tag{75}$$

Where $\Delta H_{s/n.}$ = differential heat of solution, BTU/lb.mole

T = temperature absolute°R

R = gas constant, 1.987 BTU/lb. mole°R

The term of the left-hand side of the equation is the slope of the curve when log γ for a hydrocarbon is plotted against 1/T. At infinite dilution log γ° is numerically equal to the Margules binary constant, A_1. As in certain limits A_1 is a straight line function of 1/T, the heats of solution are easily obtained from the relation.

Carlson and Colburn (7) observe that in general if the activity coefficient of a system is less than one the heat of solution is positive, and if larger than one the heat of solution is negative. In either case, an increment of temperature causes the activity coefficients to approach zero.

Some other useful data can be obtained from at infinite dilution. Thus the partial molal excess free energy is obtained (16) from the equation

$$\bar{G}^{E} = RT \ln \gamma^{\circ} \qquad (76)$$

The partial molal excess of entropy can be obtained applying the general relation

$$G = H - TS \qquad (77)$$

That gives

$$\bar{G}^{E} = \bar{H}^{E} - T\bar{S}^{E}$$

$$\bar{S}^{E} = \frac{\bar{H}^{E} - \bar{G}^{E}}{T} \qquad (78)$$

Finally, the Van Laar constant A_1 is related to the activity coefficient at infinite dilution for $A_1 = \log \gamma^{\circ}_{1,2}$

(79)

EXPERIMENTAL

APPARATUS

The apparatus built for this study is shown in Figs. 1 and 2. Fig. 3 is a schematic diagram of the apparatus. It can be described by following the gas stream.

The carrier gas contained in a storage cylinder is supplied at constant pressure through a diaphragm regulator (Hoke-Phoenix) into two coils: a preheater coil, and a coiled column packed with a granular solid which has been properly impregnated with a suitable high boiling liquid. The latter constitutes the chromatographic column.

A sampling system is connected by means of a by-pass arrangement to the carrier gas stream. When the by-pass valve is closed the gas stream is divided into two parts. One stream goes directly through the preheated coil branch while the other pushes the sample from the by-pass through the chromatographic column. These two streams flow through the reference and sample passage of a thermal conductivity cell (katharometer), and respectively, leave the apparatus through different flowmeters. The flow rates are controlled by needle valves located on the downstream side of the katharometer.

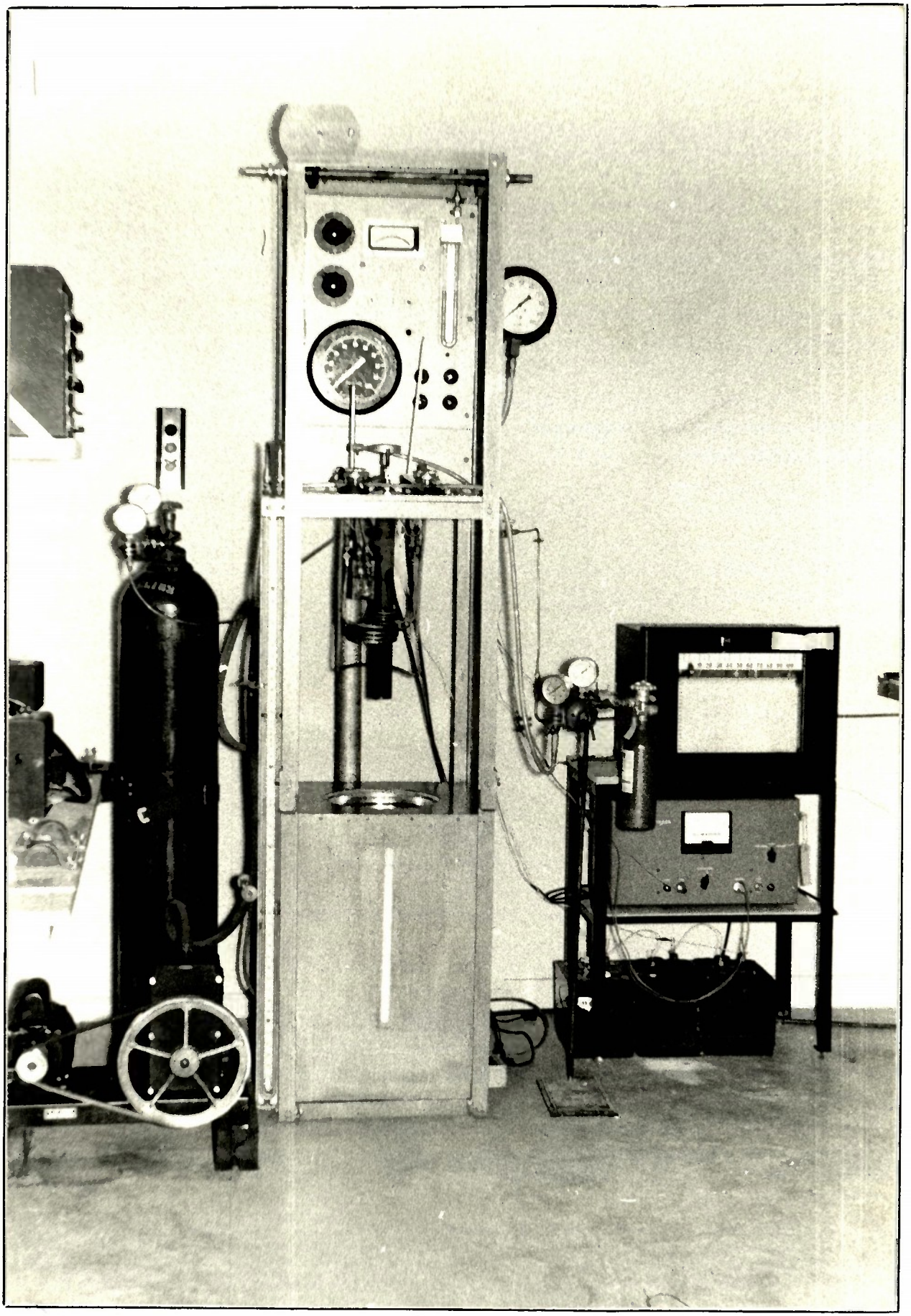


FIG 1.– ASSEMBLED APPARATUS.

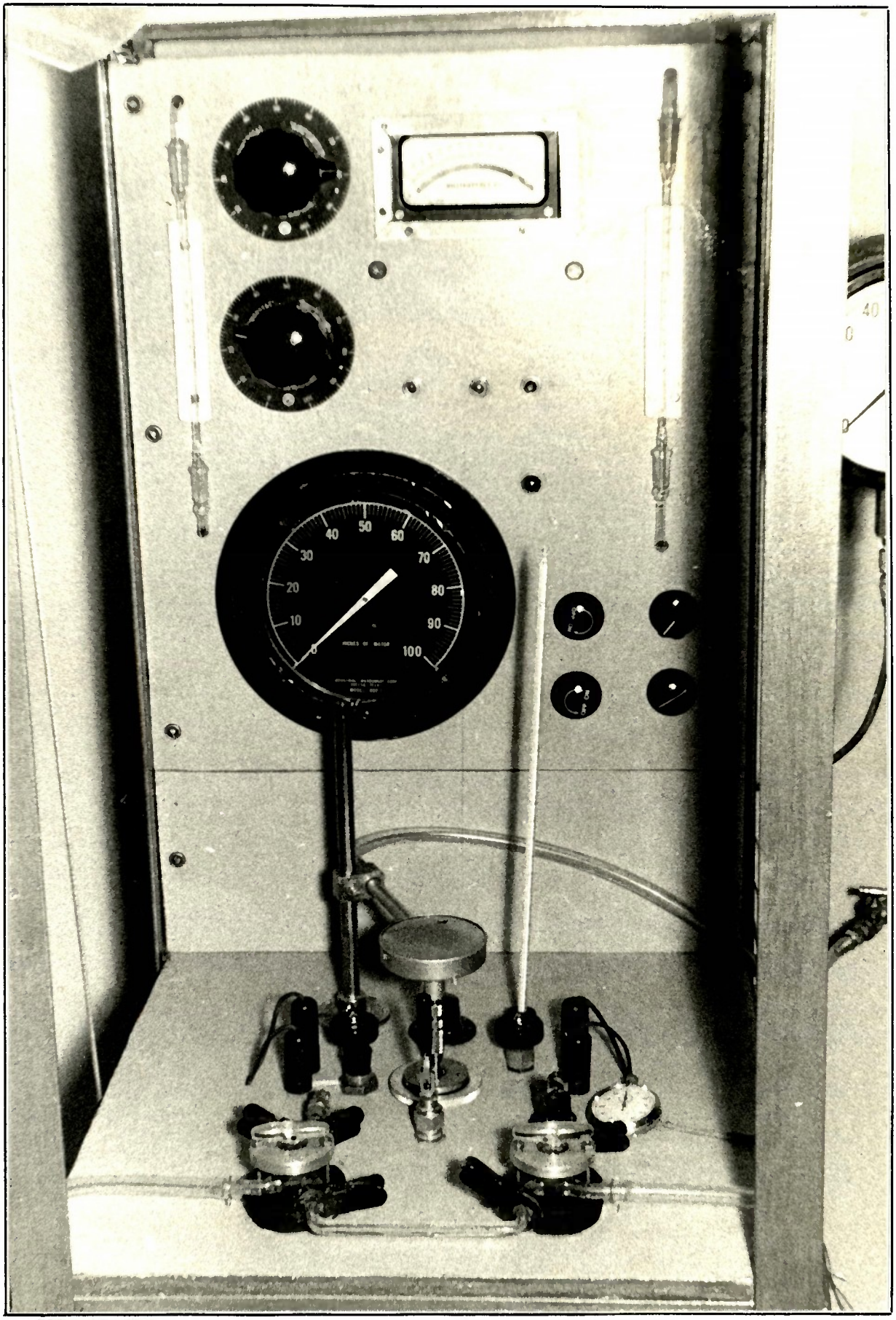


FIG 2.-CONTROL PANEL.

The katharometer, which consists of a Wheatstone bridge with a branch for reference and the other for sample corresponding to the two flow passages, was previously adjusted with carrier gas passing through both sides in such a manner that its output record in a self-balancing potentiometer traces a zero signal. When the by-pass valve is closed the gas sample is displaced with the carrier gas which pushes it through the chromatographic column. When the sample reaches the katharometer, it determines an unbalancing of the Wheatstone bridge which is recorded by the potentiometer over a period of time as a peak.

The apparatus described was designed specifically for use in obtaining physical chemical data from the experimental retention volumes. Some features of the apparatus will be mentioned in the following paragraphs.

Sample System. Sample size and charging technique affect the position and shape of the peaks in a chromatogram. Theory prescribes that the sample must be initially contained in the first plate. That is, the charge must be made as small as possible to avoid the formation of an initial band which overspreads a significant length of column.

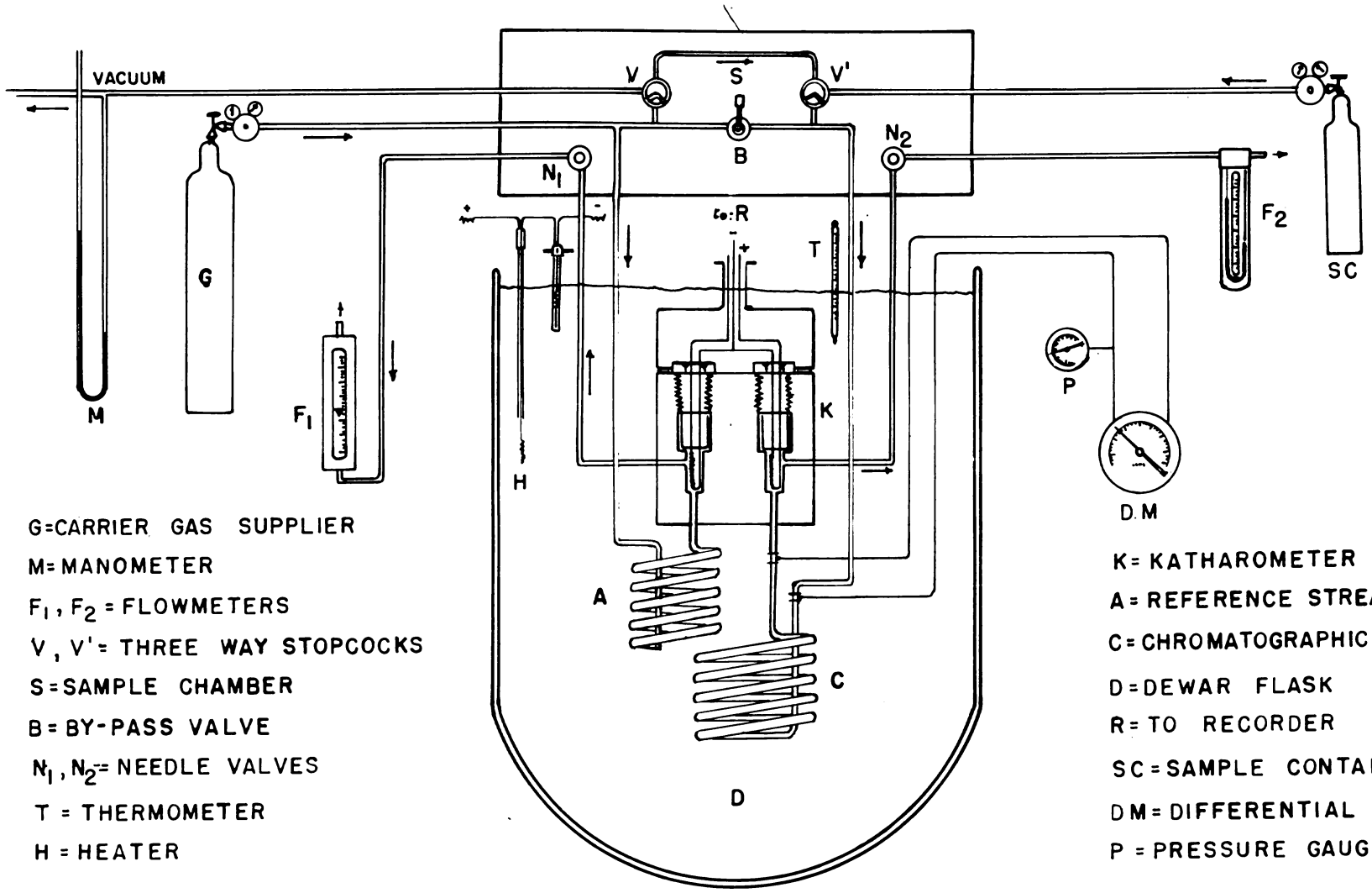


FIG. 3 – SCHEMATIC DIAGRAM OF APPARATUS.

Partition coefficients must be measured at very low concentrations or with small sample volumes in order to approach the infinitely dilute region where the coefficients are constants, i.e. the ratio of concentrations in the two phases is constant.

In the charging technique two cases can be differentiated: plug flow and exponential mixing. In the first case the chromatogram is symmetrical, while the second case is not. The first case represents a better condition for the estimation of the retention volume than the second case when the solute concentration falls to zero exponentially.

The sample system of 1 ml. of gas capacity was made with the chamber connected to two 3-way stopcocks as shown in Figure (3). The sample container was provided with a pressure regulator and a valve to make the samples reproducible. When the valves are correctly operated, the introduction of the sample into the column approaches plug flow.

Columns. Colums were made of 3/8 in. copper tubing, which were coiled after packing. The length was selected to give a low pressure drop while giving retention times long enough for accurate reading.

Dead Volume. In an ideal chromatographic unit there would be

no dead volume between the sample system and the column and no dead volume between the latter and the detector. In the apparatus the dead volume was minimized by using capillary copper tubing whenever possible. The total volume was thereby reduced to 3 ml. before the column and 2.1 ml. after it.

Detector. Some desirable characteristics of detectors are: rapid response, good stability, high sensitivity, low dead volume, linear response with concentration, and relative insensitivity to changes in flow and pressure.

A Pretzell cell T/C 9285 manufactured by the Gow-Mac Instrument Co., Madison, N.J., with 8 filaments incorporates these features to an acceptable degree. The gas volume of the cell is relatively small (4.655 ml.). The cell block design is so that the filaments are on stream giving a time constant practically limited to the pen speed of the recorder. This design, however, increases the sensitivity of such cells to changes in flow which may be overcome by providing a well-regulated flow system. The schematic wiring diagram is given in Fig. 4.

Constant Temperature Bath. The bath consists of a 5-gallon Dewar flask supported in a metal box. The bath is attached to a lifting system. While in upper position, it encloses the

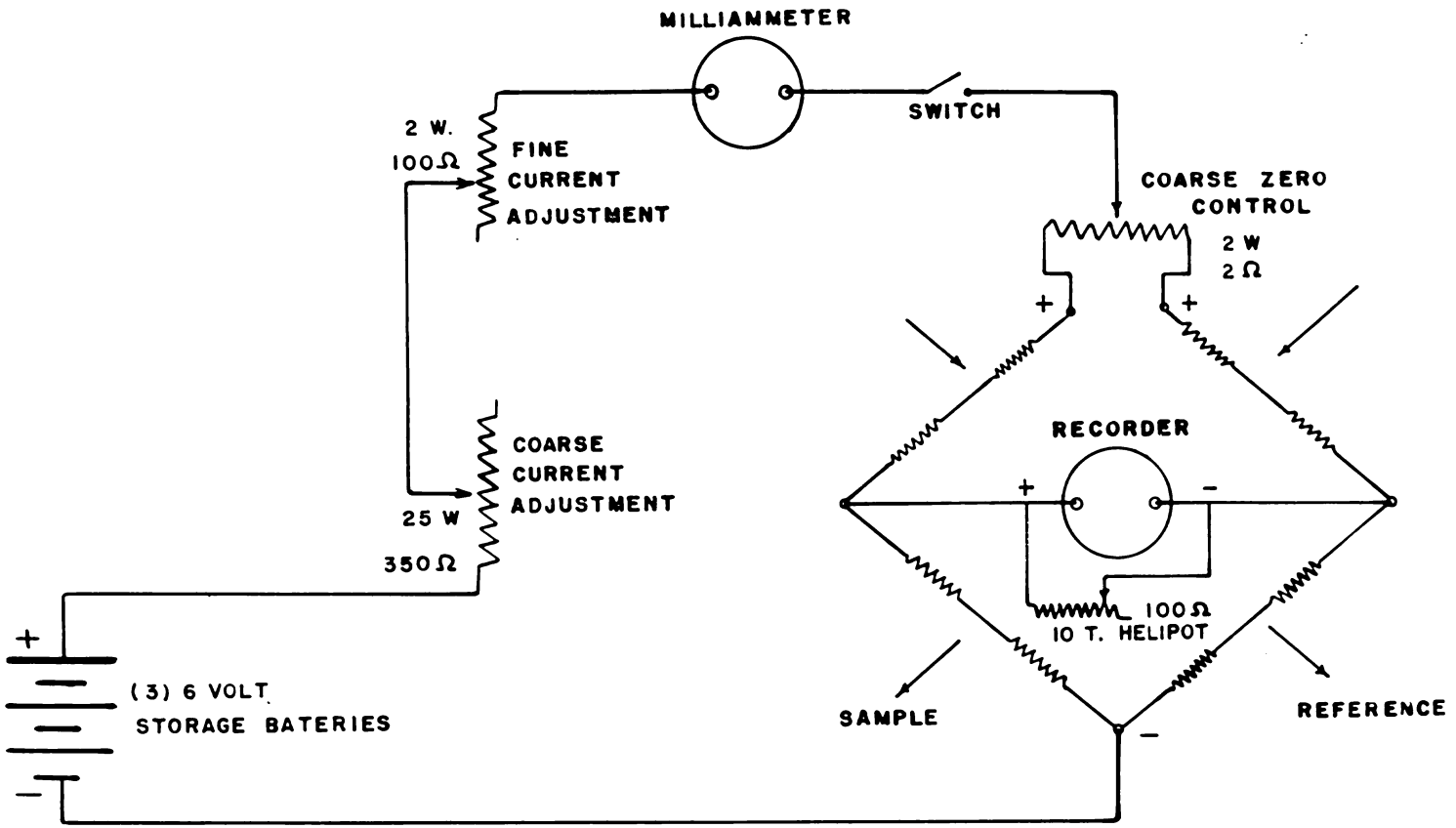


FIG. 4 - SCHEMATIC WIRING DIAGRAM FOR KATHAROMETER.

column, reference coil, katharometer, etc.

The compactness of the column leaves enough room for bath heaters, stirrer and a thermo-regulator. The heating devices are a quick heat unit of 300 watts normal power rating and a 100 watts connected to a Fenwall bimetallic thermo-regulator, for maintaining temperature constant within 0.05°C. Heaters are connected through Powerstats whose position is manually adjusted according to the demands.

Water and ethyl alcohol were used as bath fluids, and ice, dry ice and the heaters were used to obtain the desired temperature.

Flow Control and Measurement. The rate of flow is controlled by the pressure at the head of the column, the pressure drop through it; and it is governed by two needle valves located just after the katharometer, one in the reference stream and the other in the sample stream.

The pressure of the carrier gas was regulated by a Hoke-Phoenix diaphragm regulator. The pressure drop through the column was measured by a differential manometer 0 to 100 in. water (Industrial Instrument Corporation, Odessa, Texas), and the pressure in the column outlet by a test gauge (Jas. P. Marsh Corp., Chicago, Ill.). The flow in the reference side was measured with a flowrator 3 to 170 ml./min.

range (Fisher & Porter), and the flow in the sample side with a calibrated Burrel Flowmeter Mod. 340-70 with range from 0 to 100 ml/min.

Materials.

Methane - Tennessee Gas Transmission Company - 99.6% purity

Ethylene - The Houston Oxygen Co.

Ethane - Phillips Petroleum Co. Research grade - 99.9% "

n-Propane - Phillips Petroleum Co. Instrument grade - 99.5% "

n-Butane - Phillips Petroleum Co. Instrument grade - 99.5% "

Butene-1, cis-Butene-2, trans-Butene-2,

Butadine 1-3 - Phillips Petroleum Co. pure grade - 99% min."

n-Dodecane - Matheson Coleman Co., Inc. - 95% "

Isopentane - Phillips Petroleum Co. Technical grade 95% "

Furfuraldehide - Petro-Tex Chemical Corp. - 99.81% "

Solid Support - Crushed diatomaceous earth firebrick, Curtin C-3.

Preparation of the Column. In order to insure an ever distribution of the stationary liquid phase over the surface of the solid, the stationary liquids, n-dodecane in one case and furfural in another were dissolved in 8 to 10 times their volumes of a low boiling solvent, isopentane and ethyl ether respectively.

TABLE 1

Column Characteristics* V_m

	Length (cu)	Ratio Support/ Solvent	Column Volume (cc)	Support Volume (cc)	Liquid Volume (cc)	"Free" Gas Volume (cc)	Mass Station- ary Phase (gr)	Free Gas Cross Section (cm^2)	Free Liquid Cross Section Cu^2	Mesh Size
				n-Dodecane - Firebrick C-3						
I	183.24	100:25.72	86.18	17.86	13.12	55.20	9.8743	.301	.0716	30-50
II	152.7	100:18.28	71.82	15.29	7.98	48.55 41.54	6.0098	.318	.0523	30-50
III	152.7	100:19.82	71.82	15.29	8.66	47.86 47.86	6.52	.313	.0517	40-60
IV	282.4	100:20.82	132.86	29.87	17.77	85.22 85.21	13.38	.302	.0629	30-50
				Furfural - Firebrick C-3						
V	122.2	100:26.9	57.45	12.78	6.37	38.30	7.39	.313	.0520	30-50
VI	152.7	100:26.9	71.81	16.13	8.05	47.64	9.33	.312	.0528	30-50
VII	152.7	100:26.9	78.82	16.33	8.14	47.35	9.45	.310	.0533	30-50

*All of them were built with copper tubing 3/8"OD and 0.305"ID.

The solid support which was carefully sized and thoroughly dried, is added to this solution at the rate of 100g. of solid for 20 to 30g of stationary liquid to make a loose slurry with it. The low boiling material is slowly evaporated with mild stirring on a steambbath to avoid loss of the solute. The final traces of volatile liquid are eliminated by drying the packing material overnight in an oven at constant temperature (approximately 100°C).

In each step of this preparation quantities of material are weighed carefully. After drying the solid is weighed again in order to know the exact pick-up of stationary phase. The total column volume was determined by filling the empty column with a known volume of liquid.

For filling the column, it is maintained in vertical position, and a glass wool plug is inserted in the bottom. The packing material is added while the column is tapped with a heavy wall hose. This is continued until no further setting of material takes place. Then the upper end is covered with a glass wool plug and the column coiled in 5" diameter coil.

The gas space was estimated from the difference between the total column volume and the volume of the solid and liquid phases. The uncertainties of this method of estimation have been discussed (3). Realizing the importance of these values for the

ultimate accuracy of the thermodynamic data, the determinations were made carefully.

Life of the Chromatographic Columns. The chromatographic columns have a finite life, but the useful life depends on the nature of the stationary phase and the manner in which they are used. Columns of n-dodecane, which has very low pressure at the temperature involved, can be used for a large number of runs without showing any deterioration. This deterioration would show in the form of shorter elution times, but this did not occur in the columns after 100 runs in some cases.

The furfural columns, considering the higher vapor pressure, were used for a small number of runs (15 - 20 each one). After that number of runs none showed any deterioration.

Operation of the Apparatus. With the bath adjusted at the desired temperature, helium was passed at flow rates of 30 to 70 ml./min. through the preheater coil and the chromatographic column. This flow was obtained with inlet pressures ranging from 19 to 40 psia. The two streams were passed through the katharometer and the flow regulated by the needle valves. The current to the katharometer was maintained constant and the potentiometers attached to the recorder adjusted under stabilized conditions to zero output. The sampling

system is evacuated and the sample introduced to a reproducible pressure slightly in excess of the atmospheric pressure. The sample is trapped between the two three-way valves and the lead lines evacuated.

At this point the by-pass valve is closed and the valving system manipulated so as to displace the sample into the column. A stop watch was used to measure the elution time.

Apparent retention volumes are then estimated from the time of sample introduction, the time of efflux of the maximum peak and the flow rate corrected to the operating conditions. This value of the retention volume will be subsequently corrected for dead volume in the apparatus and detector, sample size, pressure drop through the column and will be called corrected retention volume. This parameter will be the basis for the calculation of physical constants.

RESULTS

In order to apply the equation wich relates chromatographic parameters to physical chemical constants, the retention volumes were calculated as the product of the rate of flow times the period elapsed from the injection point to the maximum of the distribution curve, which corresponds to the maximum concentration in the effluent. Those retention volumes were corrected for pressure drop (Equation 41), for the dead volume of the apparatus, for the dead volume of detector using the plot obtained for Johnson and Stross (19) and for the volume of sample (Equation 45). The values obtained were called "corrected retention volumes" and are tabulated in Tables 2 to 6 and Appendix A and B.

Different analyses were conducted on the corrected retention volumes obtained for the system of light hydrocarbons in $n\text{-}C_{12}$ and for the system of C_4 hydrocarbons in furfural. In the first case Equation 65 was applied in order to get information of vapor liquid equilibria ratios (K values). The results are presented in the Tables 2 to 6 and Appendix A and in Figs. 9 to 16. They show in each case, the K values obtained experimentally as a function of pressure and temperature compared with those values reported for similar conditions in the Natural Gasoline Association of America (NGAA) charts. The agreement of the values obtained in this work and the NGAA values was excellent for n-butane but increased in disagreement with decrease in molecular size. The observation of a gradual agreement with

(to page 64)

TABLE 2.

Vapor-Liquid Equilibria (K Values) for the System N-Butane - n Dodecane *

Run Number	Mean Pressure (psia)	Temperature (°C)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromatographic K Values	K Values NGAA	Per cent Deviation
II-452	18.88	0	49	887	0.729	0.76	-4.07
II-453	24.00	0	49	870	0.588	0.605	-2.81
II-454	33.99	0	49	831	0.436	0.43	+1.40
II-455	38.95	0	48	783	0.406	0.39	+4.10
II-456	18.70	10	50	682	1.019	1.09	+6.42
II-457	23.70	10	50	673	0.815	0.88	-7.38
II-458	34.11	10	50	624	0.613	0.635	-3.46
II-459	38.88	10	50	609	0.553	0.565	-2.12
II-460	18.70	20	50	520	1.42	1.52	-6.57
II-461	23.60	20	51	500	1.16	1.22	-4.92
II-462	34.11	20	49	479	0.846	.875	-3.31
II-463	39.28	20	49	459	0.774	.78	-0.77

TABLE 2, continued

Run Number	Mean Pressure (psia)	Temperature (°C)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromatographic K Values	K Values NGAA	Per cent Deviation
II 448	18.85	30	50	408	1.910	1.97	-3.04
II 449	23.67	30	50	388	1.605	1.60	+3.12
II 450	34.04	30	50	371	1.17	1.15	+1.74
II 451	39.00	30	50	376	1.01	1.01	0.0

* This Table presents selected values only. The complete tabulation is included in Appendix A.

TABLE 3

Vapor-Liquid Equilibria Ratios (K Values) for the System Propane - n Dodecane*

Run Number	Mean Pressure (psia)	Tempera-ture (oC)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromato-graphic K Values	K Values NGAA	Per cent Deviation
I-6	19.40	0	70	350.3	3.336	3.45	-3.30
I-9	23.99	0	40	331.0	2.88	2.77	+3.97
I-16	34.11	0	40	322.0	2.09	1.96	+6.63
I-22	39.29	0	40	310.0	1.90	1.71	+11.11
II-161	19.29	10	60	190.5	4.40	4.50	-2.22
II-165	23.94	10	40	183.2	3.73	3.70	+0.95
II-170	34.11	10	30	158.7	3.20	2.60	+23.07
II-175	39.14	10	30	150.3	3.02	2.32	+29.53
II-181	19.71	20	30	159.1	5.72	5.80	-2.07
II-186	24.07	20	30	156.1	4.81	4.7	+2.34
II-191	34.16	20	30	142.1	3.90	3.35	+16.41
II-196	39.10	20	30	132.5	3.79	2.95	+28.47

TABLE 3, continued

Run Number	Mean Pressure (psia)	Temperature (°C)	Flow Rate (cc/min)	Corrected Retention Volume (cc)	Chromatographic, K Values	K Values NGAA	Per cent Deviation
III-289	18.26	30	50	153.6	6.98	7.55	-7.54
III-290	23.31	30	30	144.0	6.24	6.20	+0.64
III-295	33.70	30	30	131.7	4.95	4.25	+16.47
III-300	38.96	30	30	119.7	5.00	3.70	+35.13

* This Table presents selected values. The complete tabulation is included in Appendix A.

TABLE 4

Vapor-Liquid Equilibria Ratio (K Values) For the System Ethane - n-Dodecane*

Run Number	Mean Pressure (Psia)	Tempera-ture (°C)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromato-graphic K Values	K Values NGAA	Per cent Deviation
I-59	20.35	00	60	115.62	15.53	13.00	+19.46
I-63	24.32	00	40	116.44	12.82	10.70	+19.81
I-69	34.36	00	30	108.96	10.33	7.60	+35.92
I-74	39.34	00	30	106.11	9.53	6.70	+42.23
II-140	19.33	10	70	87.28	16.10	16.40	- 4.26
II-144	23.60	10	60	83.97	14.41	13.90	+ 3.67
II-147	34.30	10	30	70.56	15.96	9.70	+64.59
II-152	39.19	10	30	66.89	16.76	8.40	+99.50
II-207	19.04	20	70	81.42	19.93	21.60	- 7.73
II-212	23.52	20	70	80.43	16.63	17.50	+4.97
II-213	34.31	20	30	70.23	16.77	12.00	+39.75
II-220	39.10	20	40	70.79	14.34	10.60	+35.28

TABLE 4, continued

Run Number	Mean Pressure (psia)	Temperature (°C)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromatographic K Values	K Values NGAA	Percent Deviation
III-268	18.34	30	50	84.10	21.06	27.00	-22.00
III-271	22.46	30	50	80.47	20.00	22.00	- 9.09
III-274	33.64	30	30	68.91	19.76	14.90	+32.61
III-280	38.85	30	30	64.33	21.87	12.90	+69.53

* This table presents selected Values. The complete tabulation is included in Appendix A.

TABLE 5

Vapor-Liquid Equilibria Ratios (K Values) for the System Ethylene -n-Dodecane*

Run Number	Mean Pressure (psia)	Tempera-ture (°C)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromato-graphic K Values	K Values NGAA	Per cent Deviation
I-85	19.21	0	70	97.68	23.40	21.00	+ 11.43
I-90	23.71	0	70	95.52	19.90	17.20	+ 15.69
I-91	34.36	0	30	86.08	18.00	12.00	+ 50.00
I-97	39.34	0	30	79.32	20.12	10.50	+ 91.62
II-103	19.59	10	30	74.14	24.03	25.00	- 3.88
II-117	23.94	10	40	69.53	23.99	20.00	+ 19.95
II-121	34.50	10	30	59.82	30.99	14.30	+116.70
II-130	39.03	10	30	59.96	27.05	12.70	+112.99
II-225	19.29	20	70	72.33	27.20	29.00	- 6.20
II-226	24.07	20	30	66.60	28.71	23.50	+ 22.17
II-231	34.31	20	30	58.56	36.38	16.80	+116.19

TABLE 5, continued

Run Number	Mean Pressure (psia)	Temperature (°C)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromatographic K Values	K Values NGAA	Per cent Deviation
II-236	39.10	20	30	54.85	50.64	14.90	+ 239.86
III-247	18.44	30	50	73.59	29.50	34.00	- 13.23
III-250	23.57	30	30	68.44	28.85	27.50	+ 4.91
III-256	33.64	30	30	60.53	32.84	19.50	+ 68.41
III-261	38.79	30	30	57.04	39.31	17.20	+ 128.54

* This Table presents selected values. The complete tabulation is presented in Appendix A.

TABLE 6

Vapor-Liquid Equilibria Ratios (K Values) for the System Methane -n-Dodecane*

Run Number	Mean Pressure (psia)	Tempera-ture (°C)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromato-graphic K Values	K Values NGAA	Per cent Deviation
IV-309	18.98	00	60	105.64	66.74	110.0	- 39.33
IV-315	23.02	00	70	102.82	63.84	90.0	- 29.07
IV-316	34.32	00	30	78.65	—	—	—
IV-321	39.10	00	30	80.87	—	—	—
IV-327	19.60	10	30	103.81	73.59	119.0	- 38.16
IV-333	23.86	10	40	100.65	72.82	94.0	- 22.53
IV-337	34.24	10	30	86.11	—	—	—
IV-342	39.21	10	30	80.10	—	—	—
IV-351	18.47	20	69	108.29	65.16	128.0	- 49.09
IV-352	24.40	20	30	99.83	77.86	97.0	- 19.73
IV-357	34.05	20	30	88.02	—	—	—
IV-363	39.06	20	40	85.26	—	—	—

TABLE 6, continued

Run Number	Mean Pressure (psia)	Temperature (°C)	Flow Rate (cc/min)	Corrected Retention Volume (c.c.)	Chromatographic K Values	K Values NGAA	Per cent Deviation
IV-371	18.23	30	67	110.21	63.02	137.0	- 54.00
IV-376	23.11	30	70	105.23	62.08	108.0	-42.52
IV-377	34.18	30	30	85.01	—	—	—
IV-382	39.05	30	30	80.30	—	—	—

* This table presents selected values. The complete tabulation is presented in Appendix A.

the increase of molecular weight yielded the plot showed in Fig. 17.

The corrected retention volumes obtained for the syetems of C_6 hydrocarbons in furfural were directed to the determination of other solution parameters. For this purpose the corrected retention volumes were introduced into Equation 63 and the partition coefficients were obtained. These values are given in Table Appendix B. The partition coefficients were the basis for the calculation of activity coefficients at infinite dilution from Equation 65 and are presented in Table 7 and in Fig. 18. The only data available for comparison is the work of Horton and Collawn (20), which was carried out at higher temperatures. The observation of the approximate linearity of the log of activity coefficient at infinite dilution versus the reciprocal of the absolute temperature was exploited here to extrapolate the experimental values. The agreement of the activity coefficients obtained from the two sources are demonstrated in Fig. 18. The vapor pressures employed for the calculation of the activity coefficients are presented in the Appendix B.

The consistency of the activity coefficients obtained permitted the evaluation of some other thermodynamic properties: heat of solution, excess free energy of solution, excess entropy of solution, relative volatilities, and Van Laar constants. These results are given in Tables 8 to 11.

Values of heat of vaporization are reported with the values of heat of solution for convenience in estimating the net heat

effect when the hydrocarbons in vapor phase dissolve in furfural in which case the net heat evolved would be the difference between latent heat and heat absorbed on mixing.

Discussion.

The non-linearity of the distribution isotherms is related to the variations of the activity coefficients. An isotherm is linear when Raoult's or Henry's Law applies, in which case = 1.0 or = a constant respectively. Should the activity coefficients be a function of concentration, it follows that parameters related to it may also be expected to vary with concentration.

The departure from linearity may assume the shape shown in Figure 5, b and c. In the case presented in Figure 5b, is smaller and R greater in the more concentrated region. The higher concentration region runs with smaller velocity than the small concentration portion, resulting in a steep drop in the concentration profile and a broad profile in the leading portion of the curve. The reverse consideration is valid for the case of Figure 5c, where is larger and the partition coefficient smaller in the more concentrated region. The slower movement of the lower concentration part of the band causes a steepening of the band front. These effects are more appreciable at the beginning of the column. For longer columns the effect vanishes. These cases are presented in Figure 5 which shows that the measurement of the registered curve becomes difficult and the determination of t_{max} is not accurate.

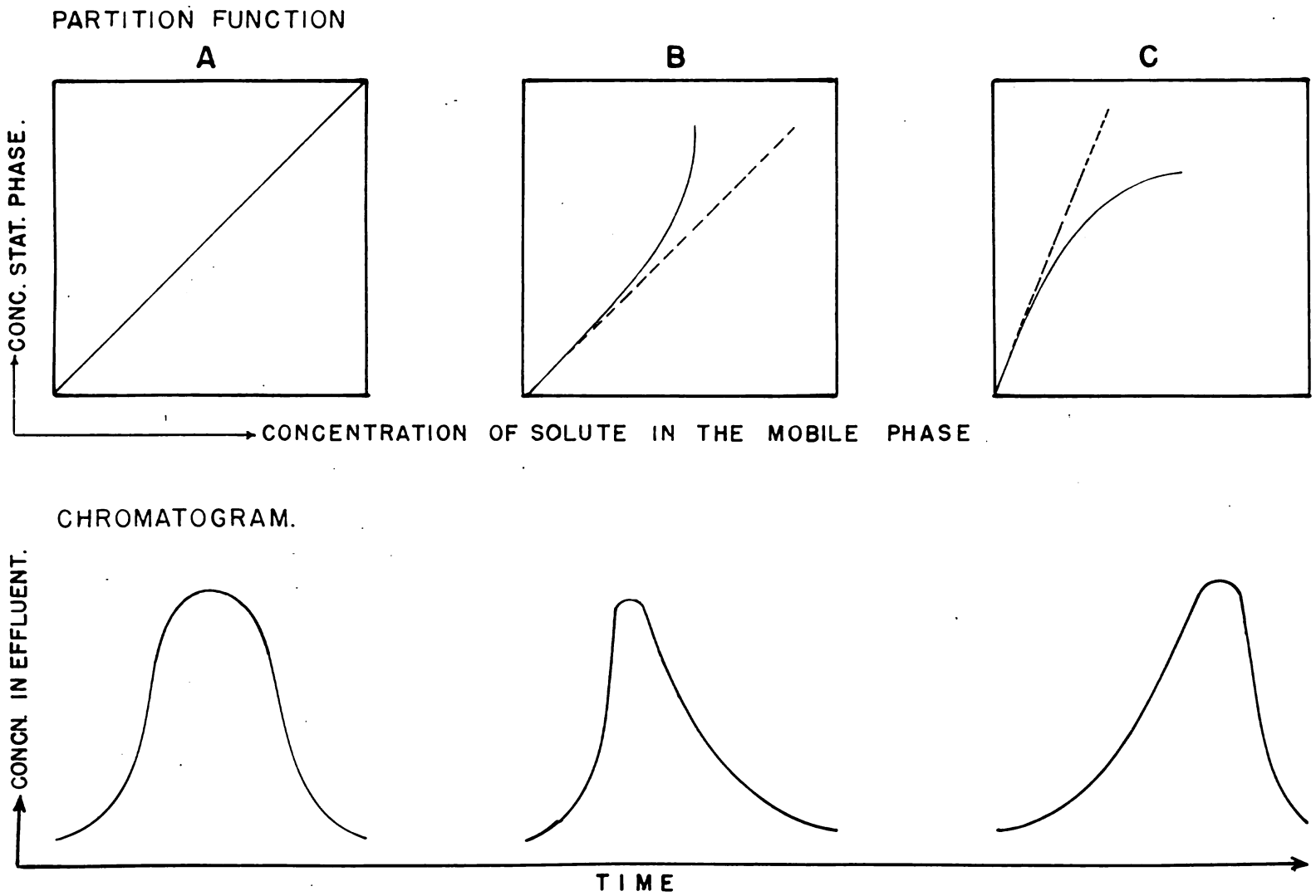


FIG. 5 – SHAPE OF THE ISOTHERMS & CONCENTRATION PROFILE.

In the determinations performed here, however, the columns were long and the concentration was low enough for the isotherms to fall in the linear region, yielding a symmetrical profile in the chromatogram. The cases in which the concentration-time curves registered slight asymmetry were attributed to low flow rates where the diffusion effects can be significant. Asymmetric elution curves will also result if sufficient stationary phase is not placed on the solid leaving sites of varying activity.

Flow Rate. - For the range of flow rate treated, 30 to 70 ml/min., corresponding to a linear velocity from 1.4 to 2.5 cm./sec., the retention volume were found substantially independent of the flow rate.

Fig. 7 shows the variation of the HETP with the flow rate. It shows the normal trend of those reported in the literature (20) and (40), a curve with a flat minimum, which corresponds to the best working conditions. That flat minimum corresponds to flow velocities for which the resistants to mass transfer is very low. K-values determined from the retention volumes corresponding to the points shown in Figure 7 do not exhibit consistent variation with HETP. Apparently the velocities reached were not low enough to introduce longitudinal diffusion in the gas phase to a significant extent.

Solid Support. Throughout the experiments only one type of support, a granulated firebrick, Certin C-3, was used. When coated with stationary liquid it did not tend to form clusters, thus permitting the construction of a uniformly packed column.

F

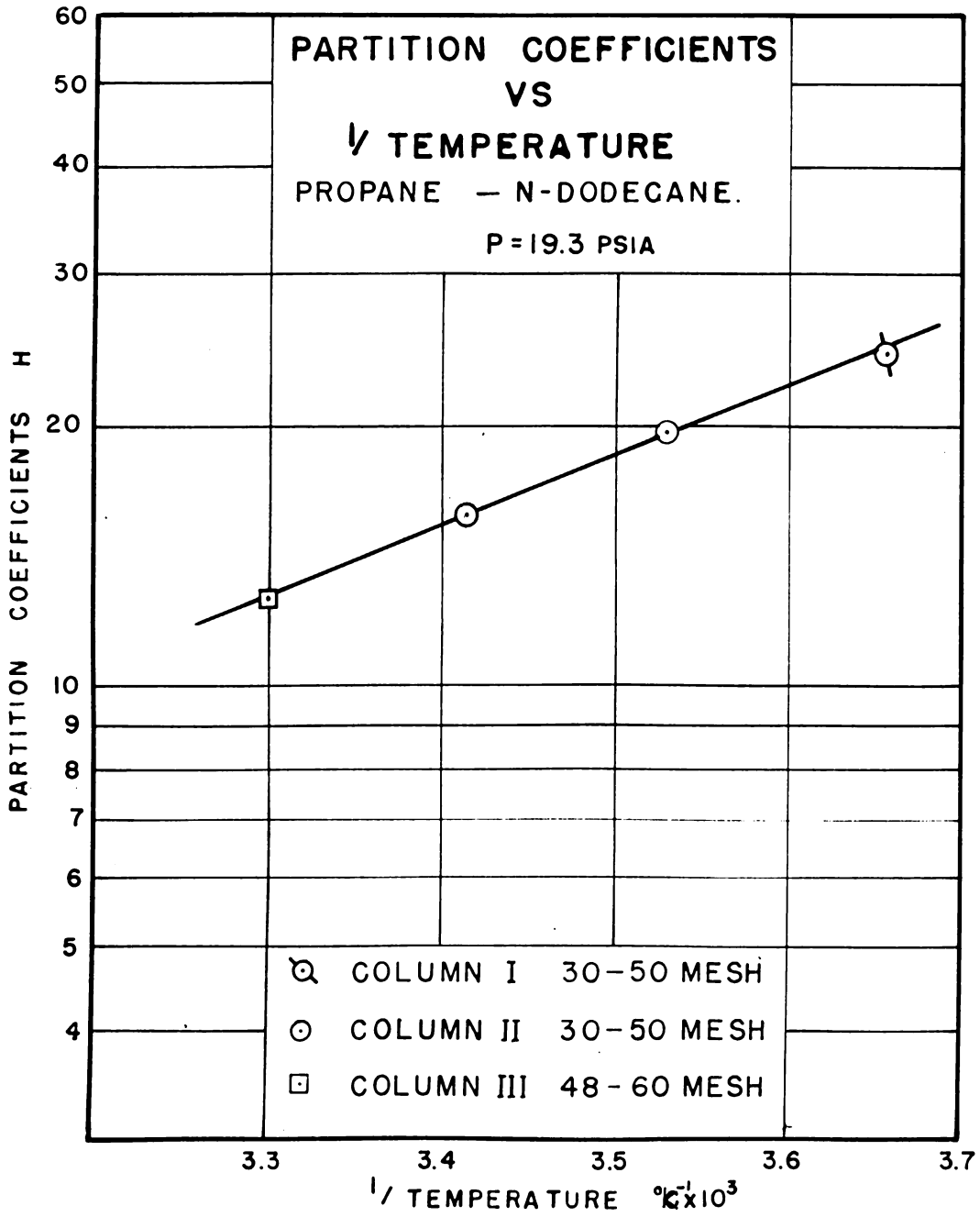

PARTITION COEFFICIENTS
VS
1/ TEMPERATURE
PROPANE — N-DODECANE.
P = 19.3 PSIA
PARTITION COEFFICIENTS H
60
50
40
30
20
10
9
8
7
6
5
4
COLUMN I 30-50 MESH
COLUMN II 30-50 MESH
COLUMN III 48-60 MESH
3.3
3.4
3.5
3.6
3.7
1/ TEMPERATURE °K⁻¹ x 10³

FIGURE No. 6 .

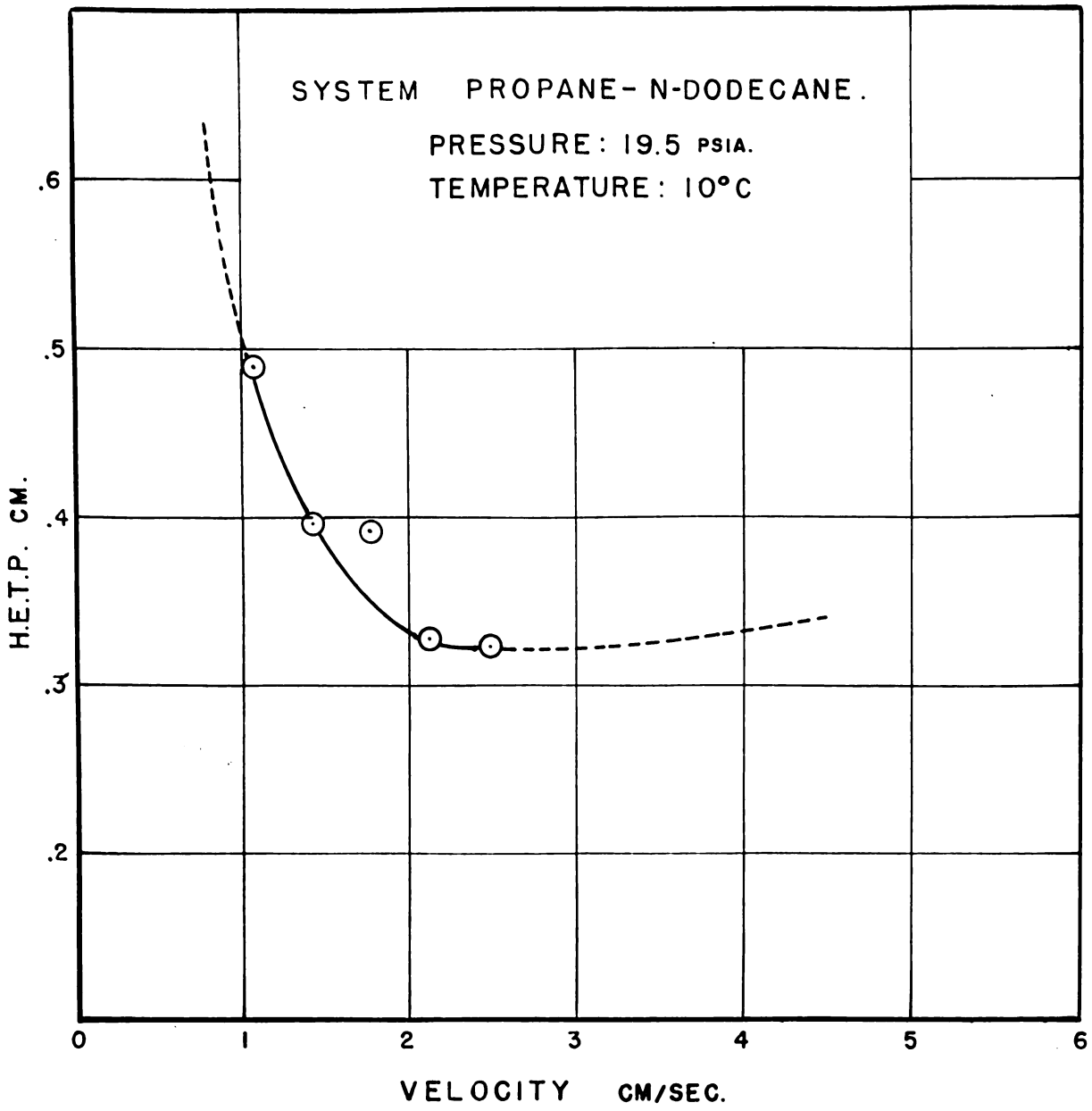


FIG. 7.- VARIATION OF H.E.T.P. WITH THE LINEAR VELOCITY OF THE GAS.

Two different sizes of packing were used 30 to 50 and 46 to 60 mesh. A given solute was eluted through columns with different size of packing. Figure 6, where the log of the partition coefficients are plotted versus the reciprocal of the absolute temperature, shows the linear relationship previously demonstrated (35), even though the runs were made with columns of different packing size.

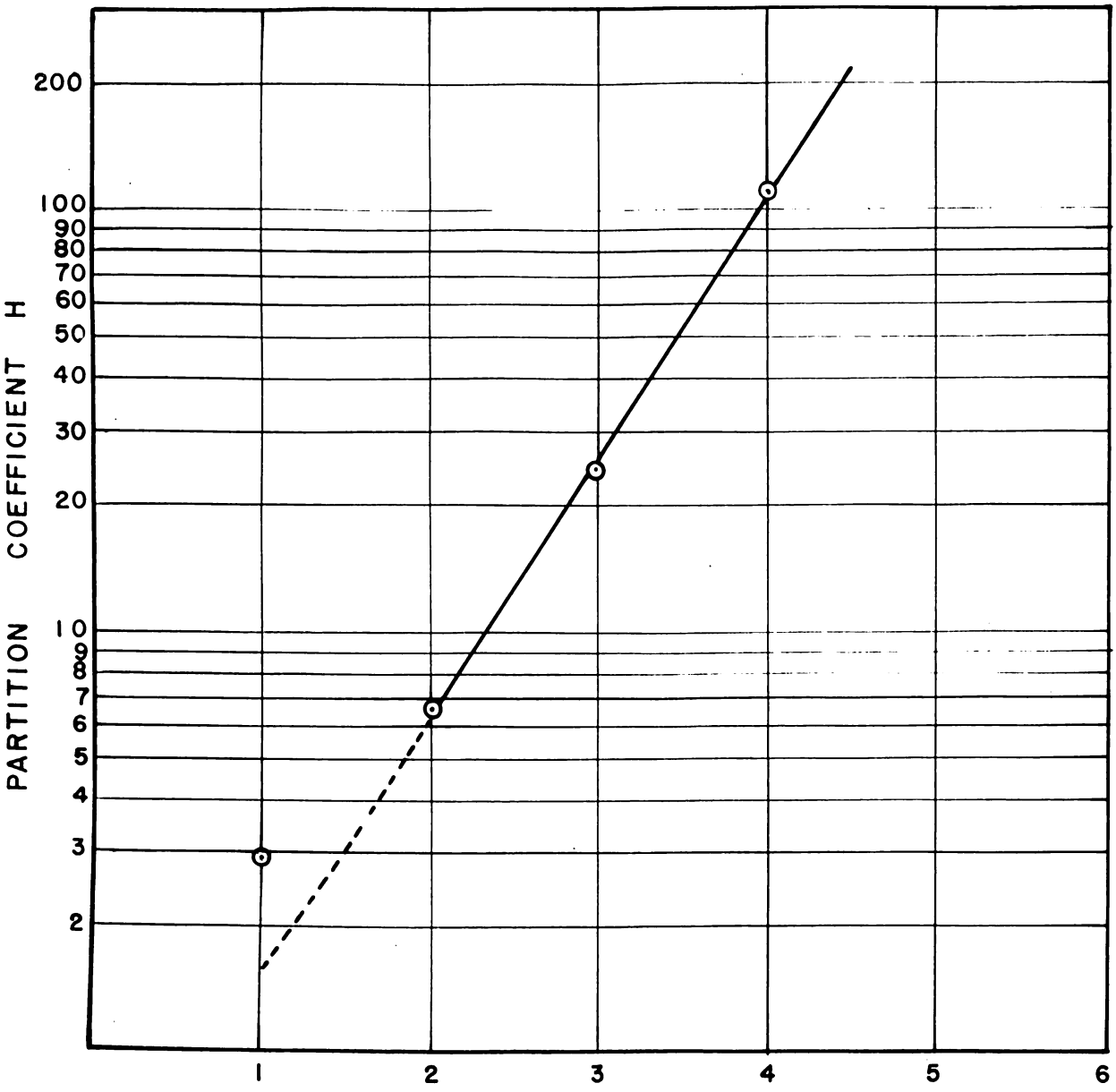
The non influence of diameter size in a certain range can be attributed to the porous nature of the solid with a large specific area where no critical contribution is given for the increase of external area, occasioned by the reduction of particle size. Some authors (21) remark that a more coarse material permits a more regular column packing than a fine that is more liable to lead to channeling and would also occasion a significant pressure drop through the column.

Sample Volume.

The correction to the retention volume for sample volume was shown through the use of Equation 45 (40) to be negligible.

The linear relation of the logarithm of the partition coefficients of the members of an homologous series, as observed for Littlewood (22) was applied successfully to the values obtained in this investigation for ethane through butane and did not hold for methane, Fig. 8.

Vapor liquid equilibrium constants were obtained from the retention volumes. The results are presented in the usual form is isotherms in Figures 9 to 16.



CONDITIONS:

PRESSURE 24 PSIA.
TEMPERATURE: 0°C
FLOW 50 CC/MIN.
SOLVENT: N-DODECANE.

FIG. 8.—CORRELATION OF THE PARTITION COEFFICIENTS OF THE LIGHT HYDROCARBONS.

The values plotted represent averages of several runs at different rates. The NBSA (29) values given for the K in the same conditions are also plotted for comparison. The values determined show a gradual agreement with static values as a function of the molecular size with the methane showing the largest disagreement. The trend of the agreement is presented in Fig. 17 at different temperatures and pressures. From this plot it is observed that better agreement appears at the lower temperatures and pressures.

In the restricted range of temperature, isobaric K values appear almost linear, same as the static determined K values. This characteristic holds better for n butane and decrease to methane. The K values obtained by chromatographic technique show a definite influence of pressure. Values obtained at pressures near the atmospheric agree with those determined by static methods, but increasing the pressure the chromatographic values are high.

The values of the activity coefficients at infinite dilution for the system of C_1 -hydrocarbons in furfural, obtained in this experimental work are presented in Table 7. In Fig. 18 the coefficients are plotted against the reciprocal of the absolute temperature, together with the data obtained by Hortes and Colburn (28). The data of Colburn comes from the extrapolation to zero concentration of a series of values obtained at different concentrations. The experimental values are consistent with those predicted from the data of Hortes and Colburn (28).

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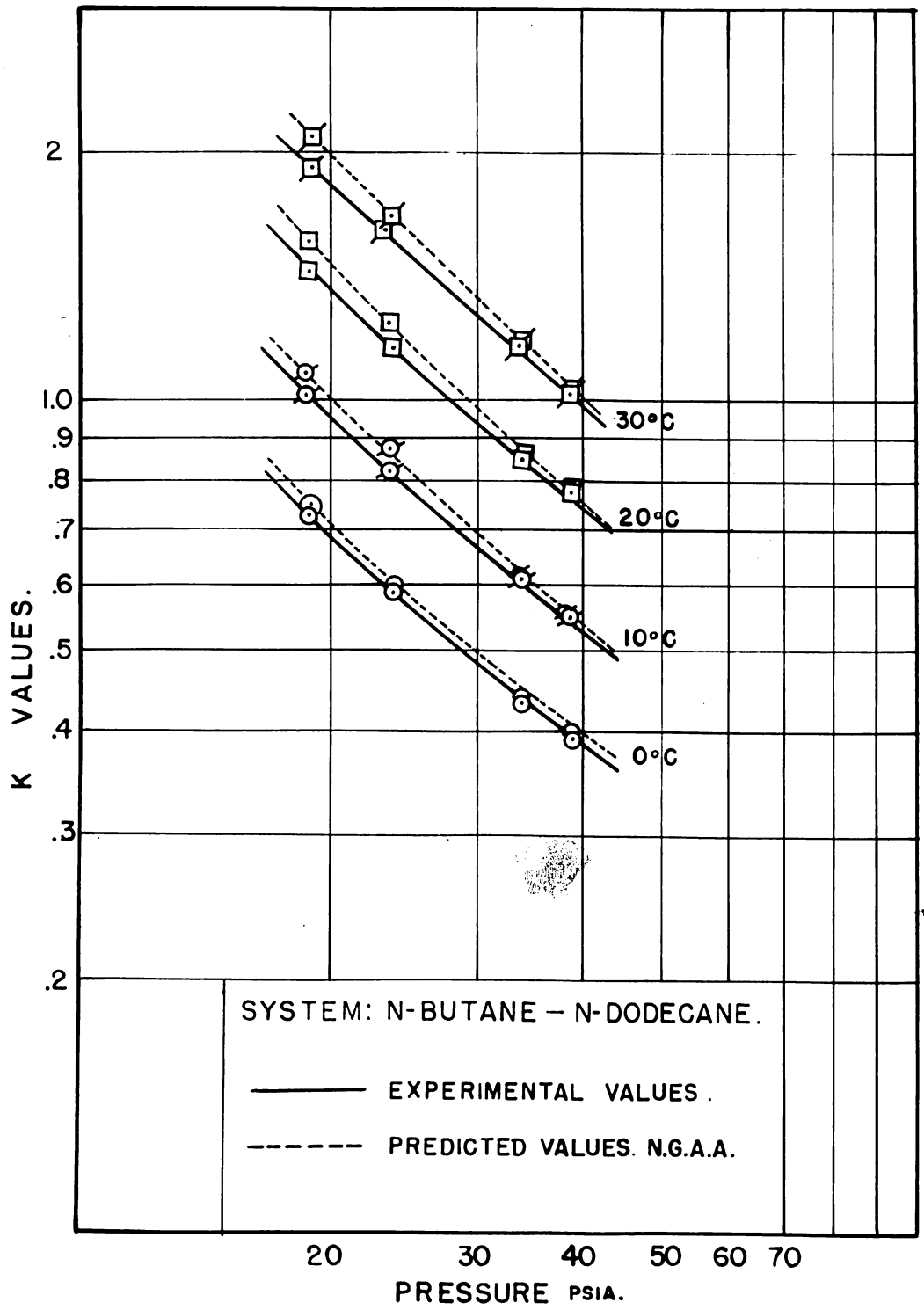

FIG. 9.–COMPARISON OF CHROMATOGRAPHIC K VALUES WITH THOSE FROM STATIC EQUILIBRIUM.

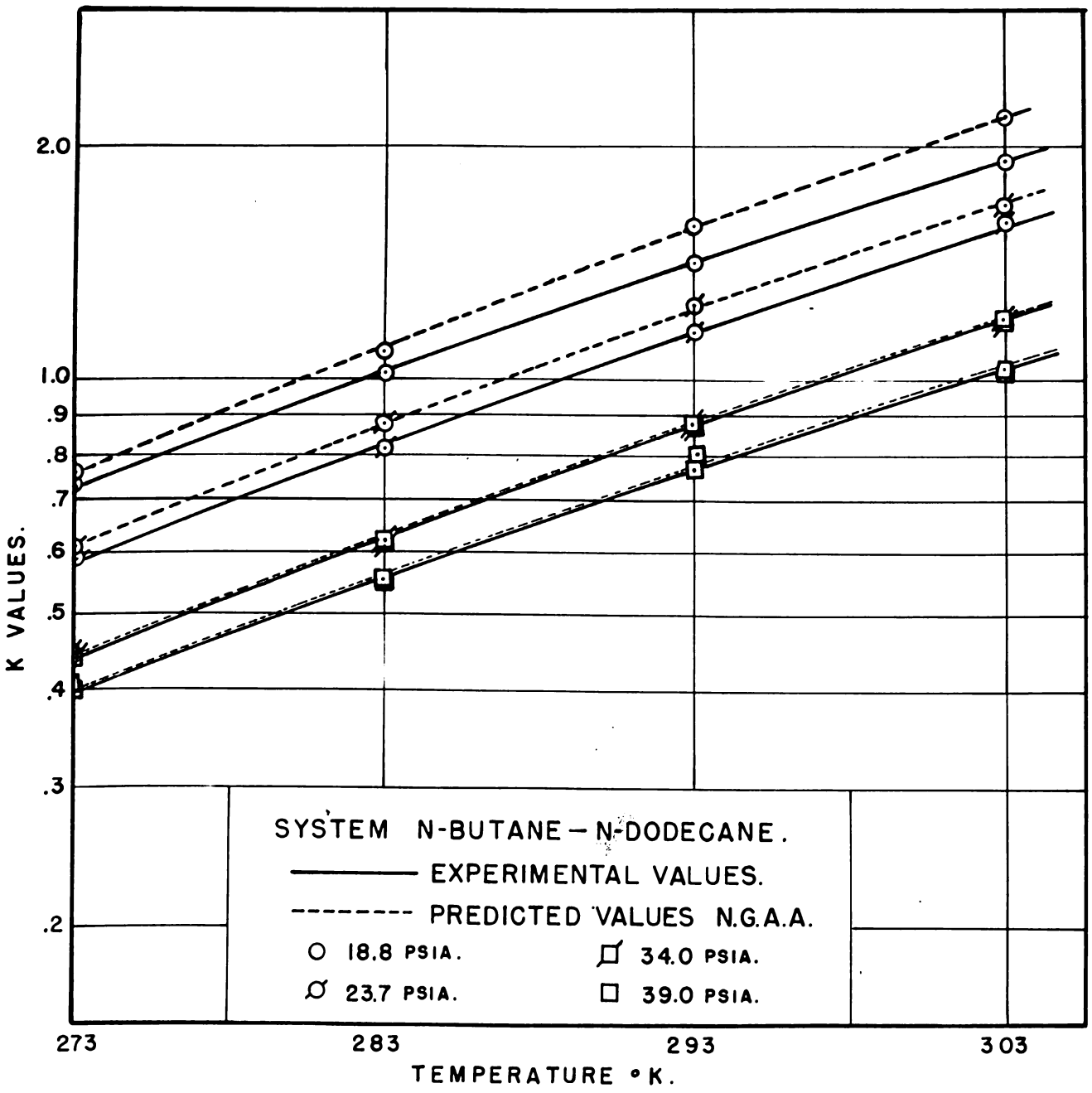

FIG. 10.– COMPARISON OF CHROMATOGRAPHIC K VALUES WITH THE N.G.A.A. VALUES.– CONSTANT PRESSURE.

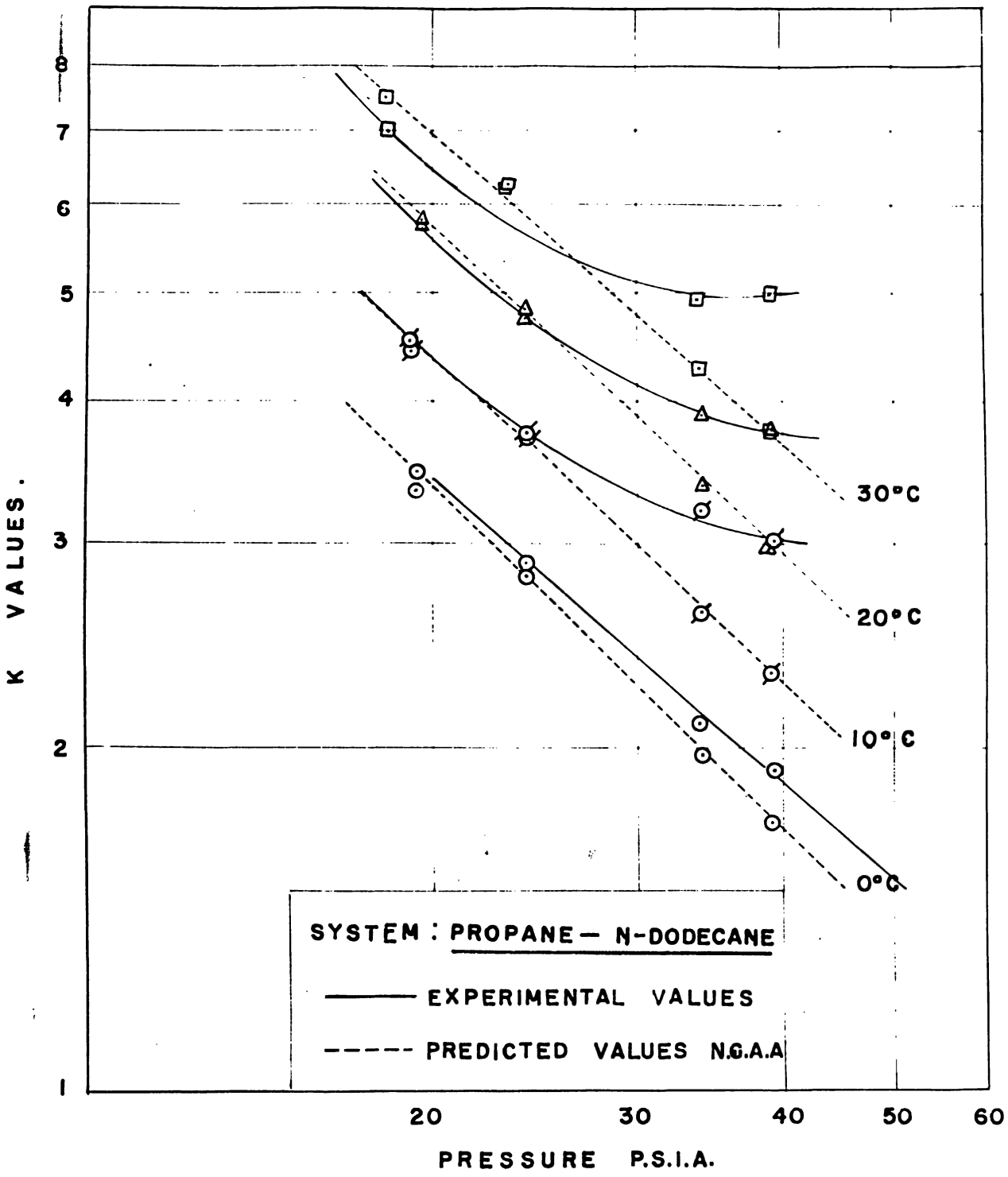

FIG. 11.-COMPARISON OF CHROMATOGRAPHIC K VALUES WITH THOSE FROM STATIC EQUILIBRIUM.

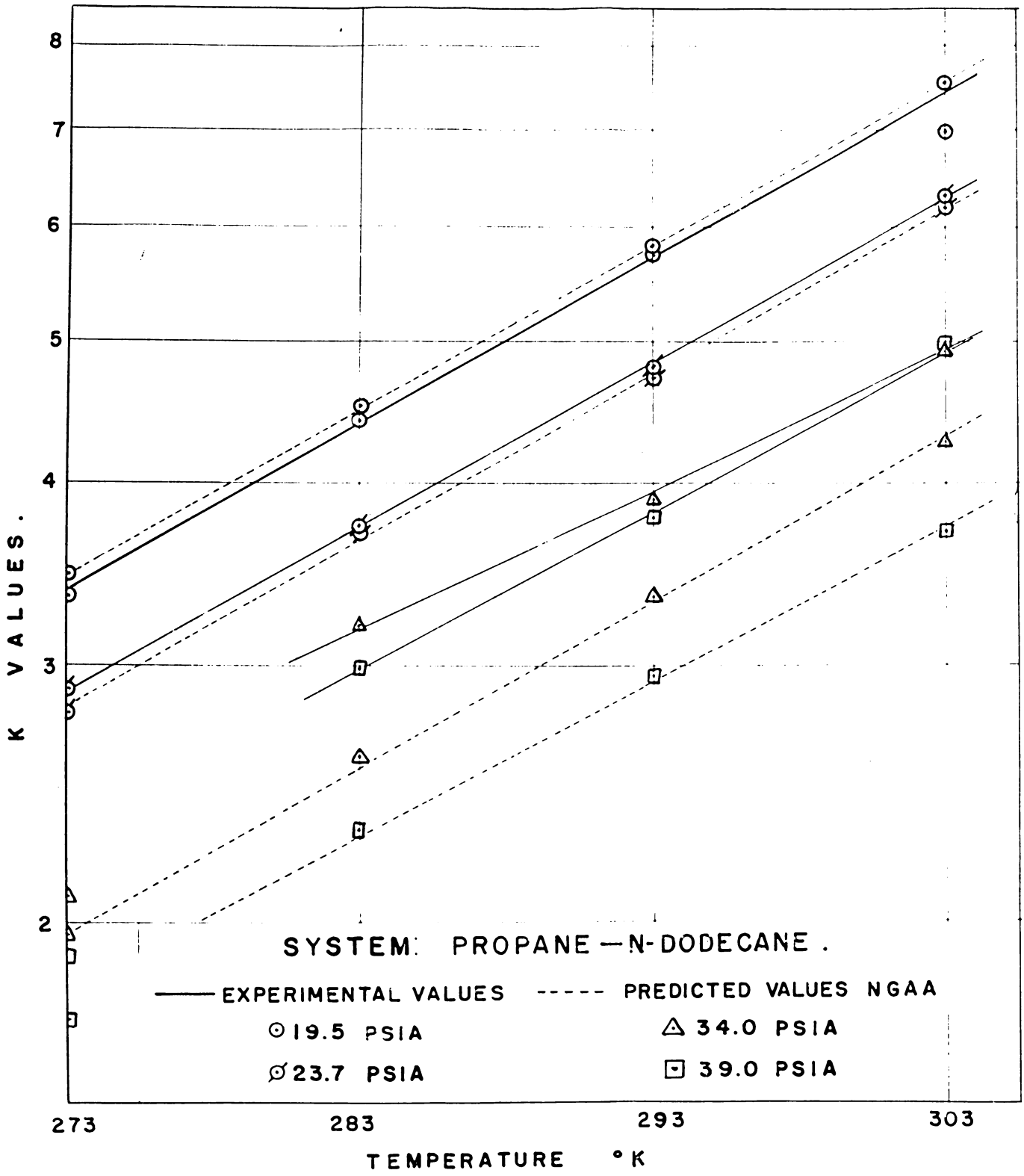

FIG. 12.- COMPARISON OF CHROMATOGRAPHIC K VALUES WITH THE N.G.A.A. VALUES.- CONSTANT PRESSURE.

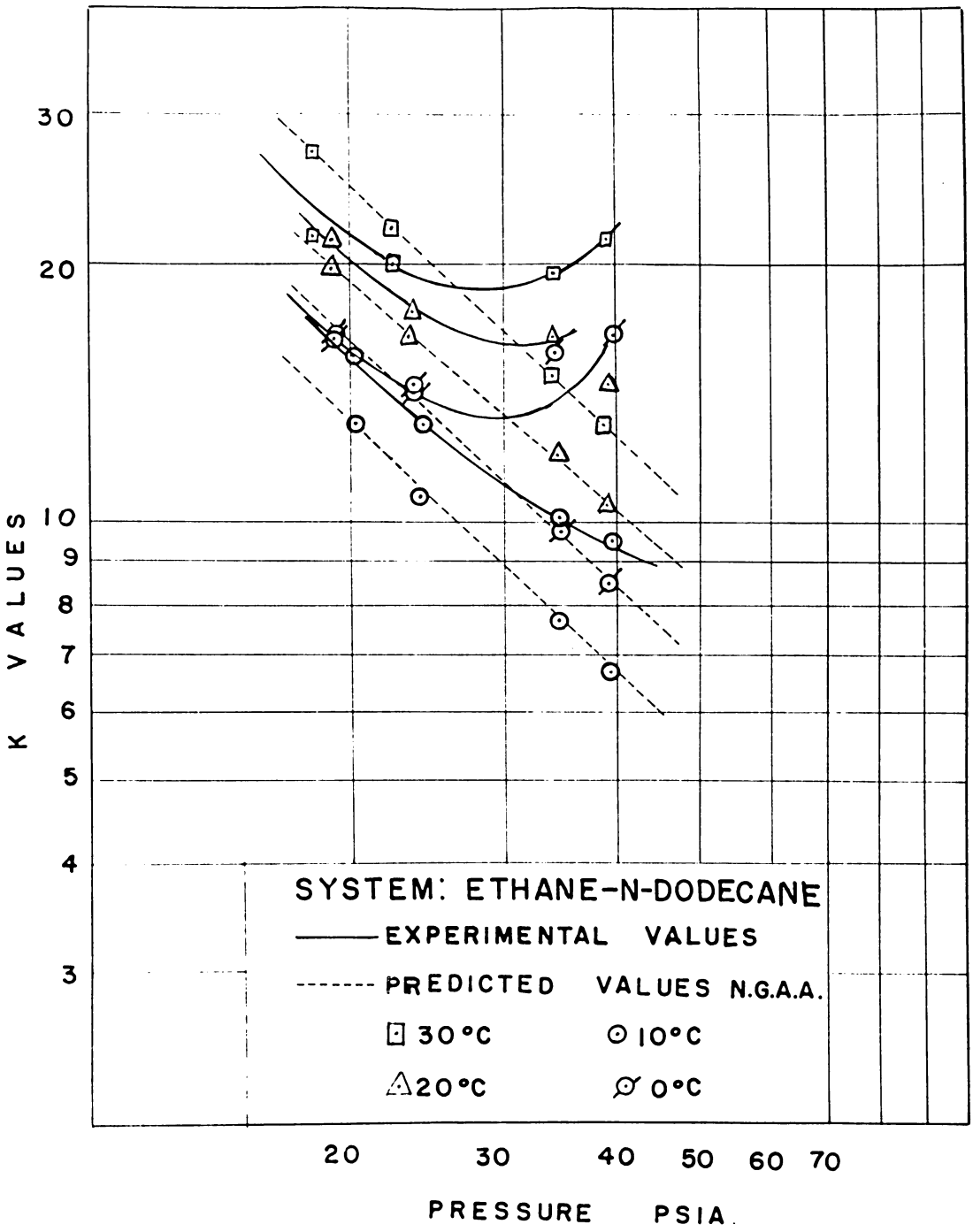

FIG. 13 — COMPARISON OF CHROMATOGRAPHIC K VALUES WITH THOSE FROM STATIC EQUILIBRIUM- N.G.A.A.

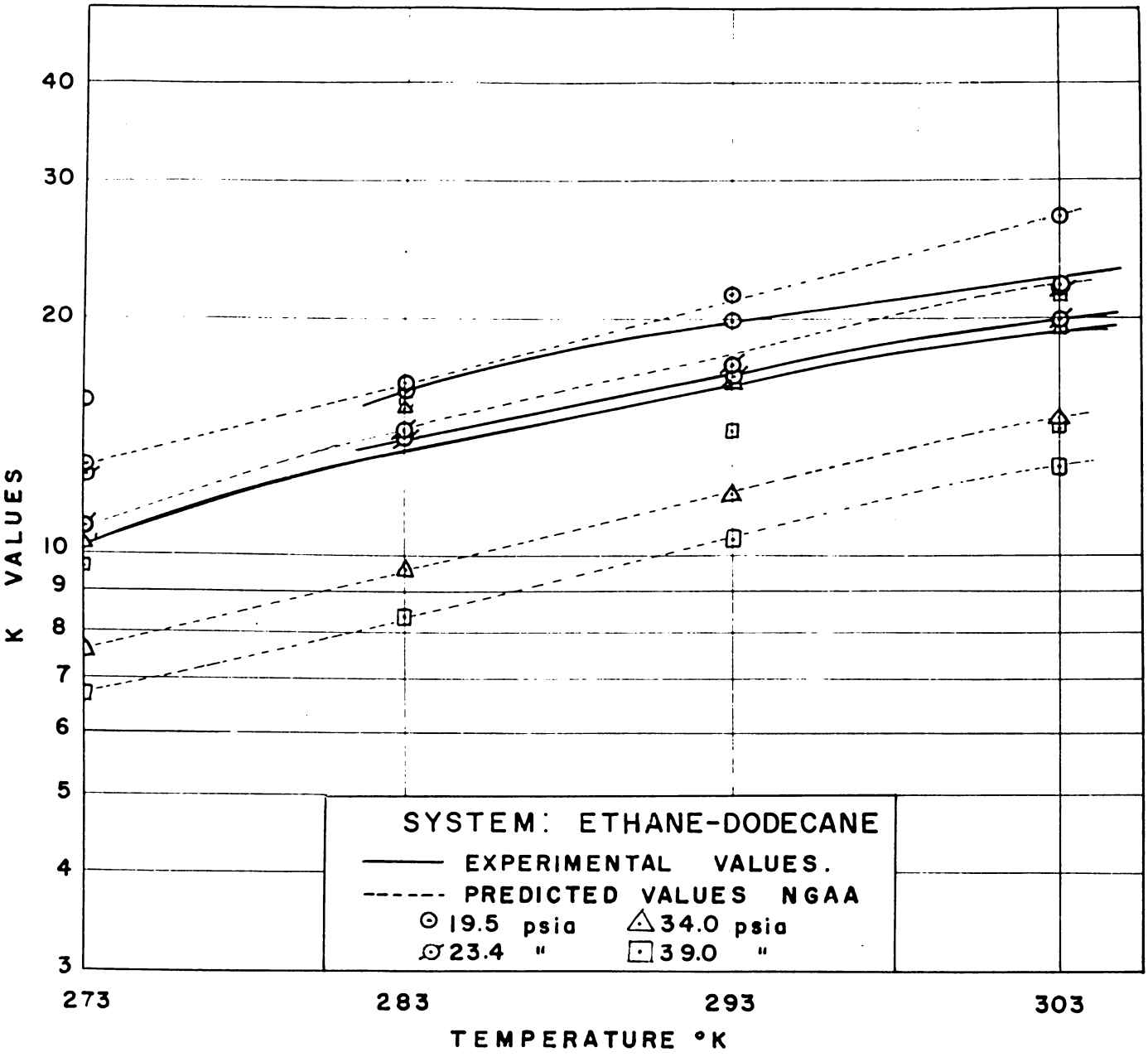

FIG. 14 - COMPARISON OF CHROMATOGRAPHIC K VALUES WITH THE N.G.A.A. VALUES — CONSTANT PRESSURE.

For this reason it is felt that good values of the differential heats of solution could be obtained from the variation of the activity coefficients with temperature. The calculated differential heat of solution for normal-butane from these studies was 3900 BTU/lb. mole from 20 to 40°C, while Horton and Colburn's value was 3180 BTU/lb. mole when evaluated from 38° to 93°C. For 1-butene in furfural the value obtained by chromatographic technique was 2565 BTU/lb. mole while the results from Reference (28) showed a value of 2400 BTU/lb.mole.

The relative volatilities calculated through the equation presented in Table 9 are reasonably close to the values from the literature (6) reproduced in the same Table 9.

It was interesting to notice the separation of cis- and transbutene through the chromatographic technique. The values of the partition coefficients were far enough apart to insure a good separation. This suggests the use of chromatography in the separation of stereoisomers. Some work is reported in diphenyl-polyenes and azobenzene (42) but an explanation of the dependence of absorption and spatial configuration is not available. In this simple case, however, it is reasonable to explain the difference in partition coefficients on the basis that for two substances whose boiling points are nearly equal, the more polar o more easily polarized substance will have the greater solubility in a polar liquid such as furfural. According to the geometrical picture

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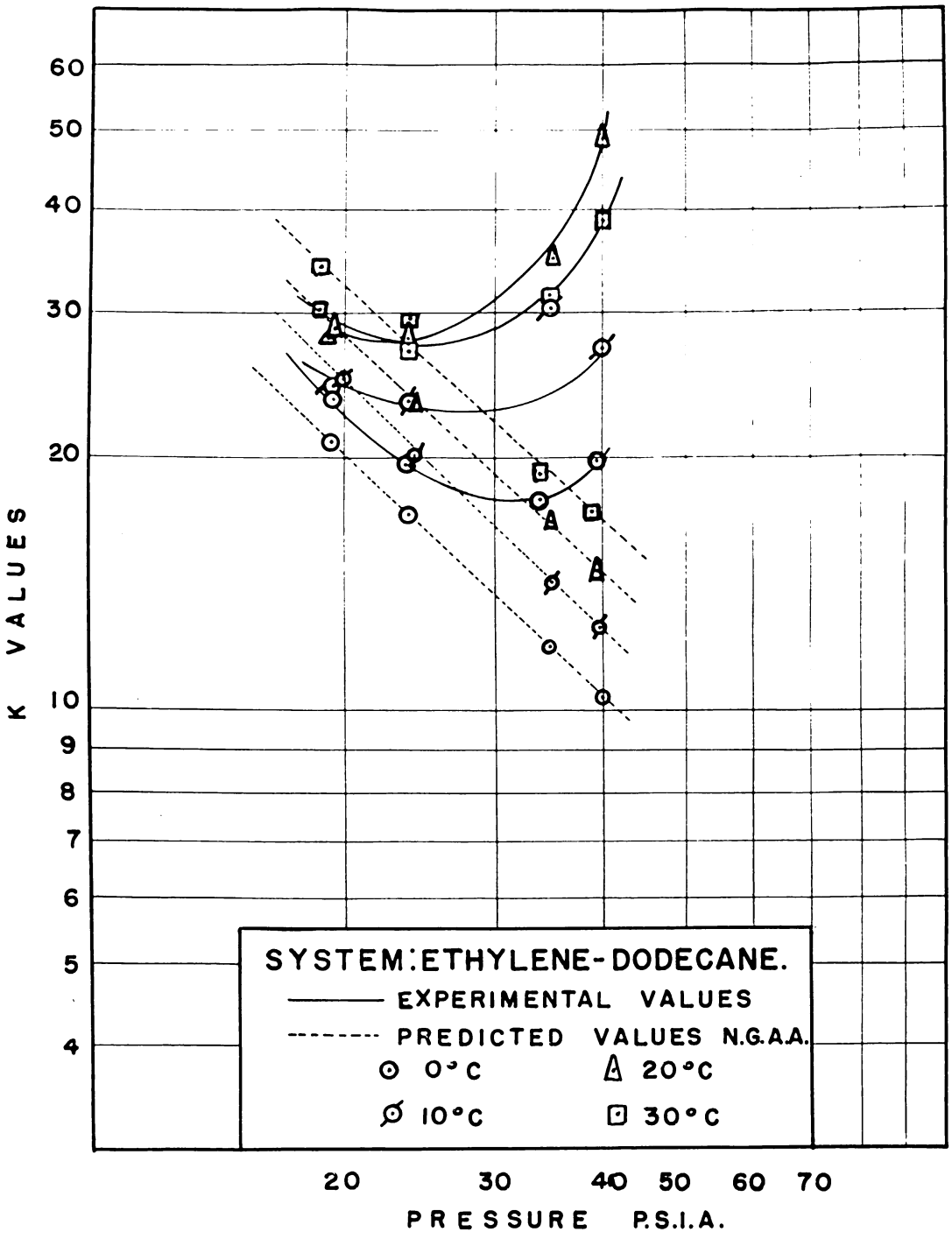


FIG. 15 - COMPARISON OF THE CHROMATOGRAPHIC K VALUES WITH THOSE FROM STATIC EQUILIBRIUM.

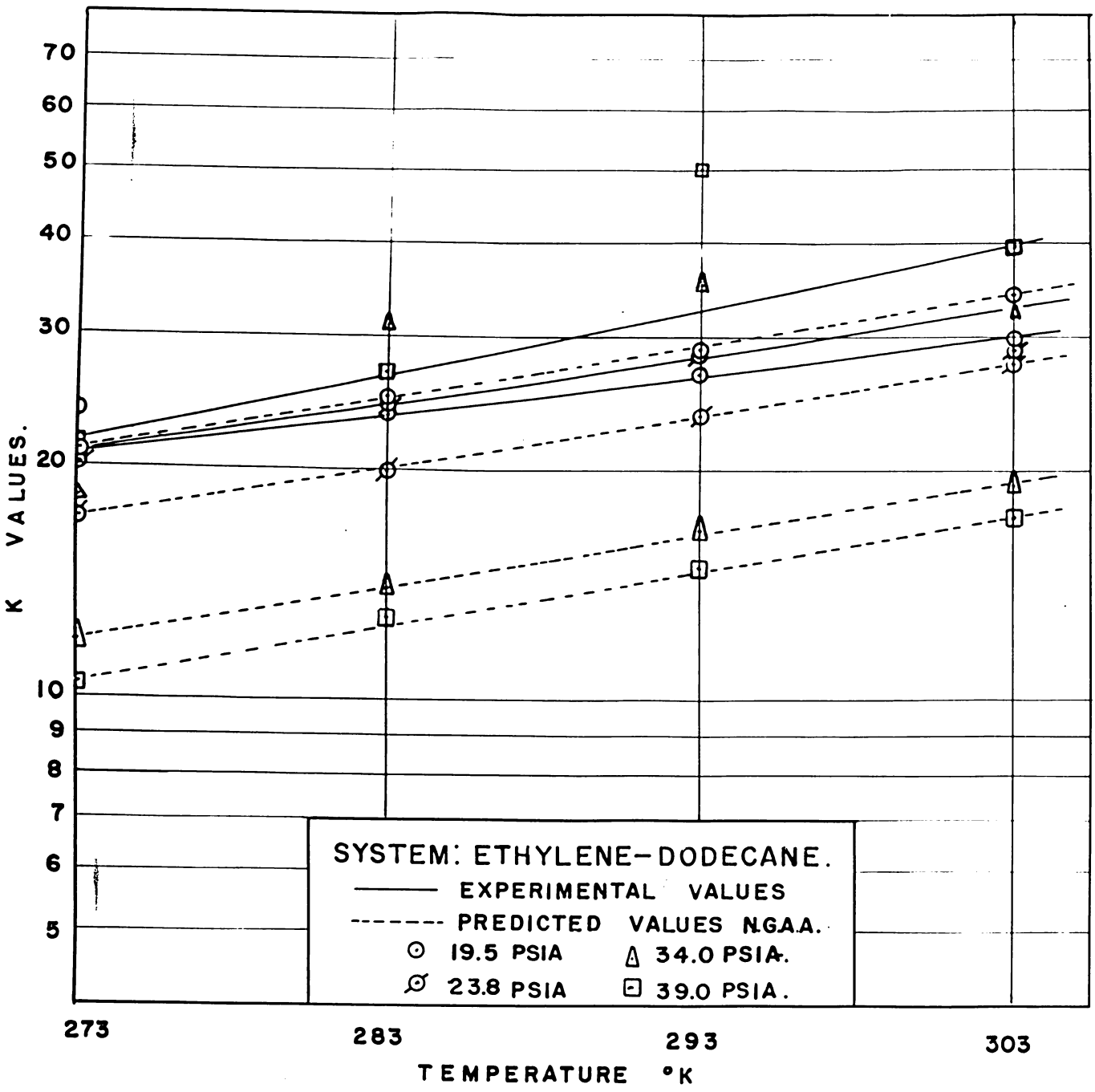


FIG. 16.-COMPARISON OF CHROMATOGRAPHIC K VALUES WITH THE N.G.A.A. VALUES- CONSTANT PRESSURE.

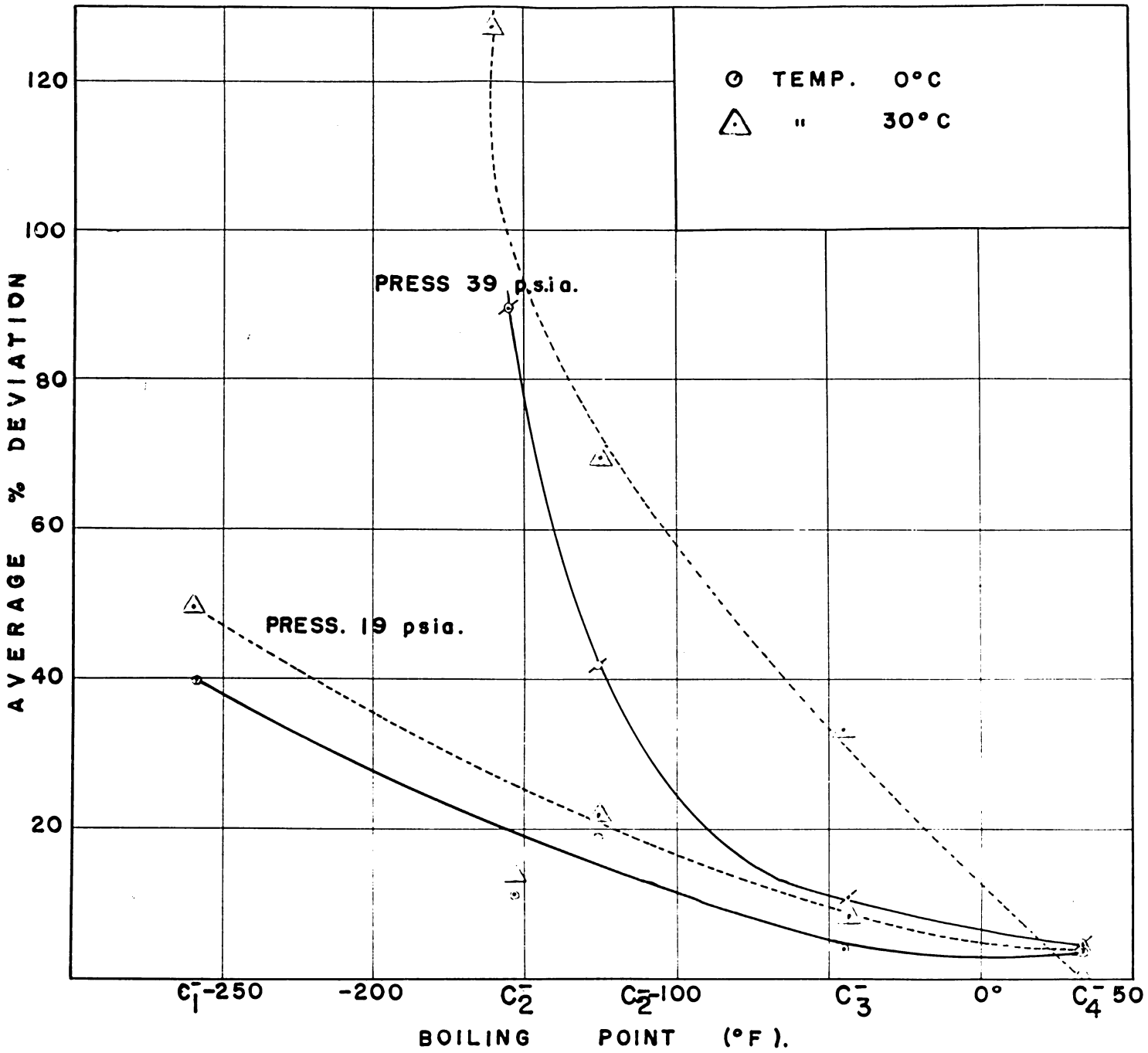
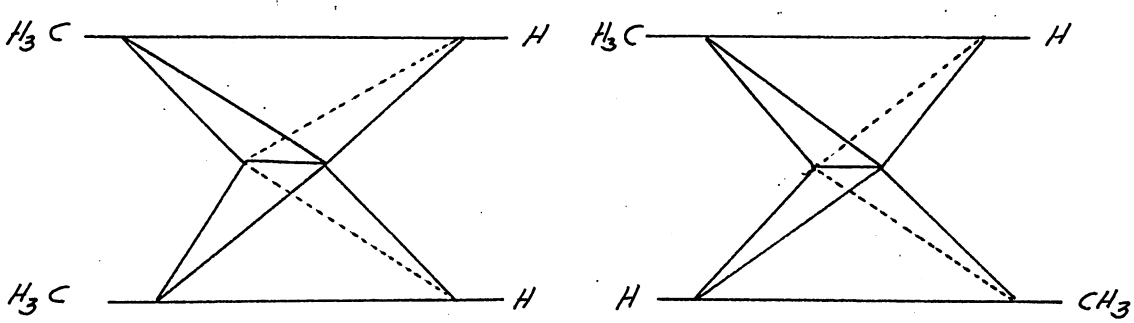


FIG. 17 - AVERAGE PER CENT DEVIATION OF THE CHROMATOGRAPHIC K VALUES RESPECT TO STATIC EQUILIBRIUM K VALUES. (N.G.A.A.)

adopted in organic chemistry.



CIS - BUTENE - 2 TRANS - BUTENE - 2.

the trans form presents the higher degree of symmetry. Therefore, the cis-form would be expected to be more easily polarised in the presence of furfural and is consequently retarded by virtue of its increased solubility.

TABLE 7

Activity Coefficients of C_4 Hydrocarbons at Infinite Dilution in Furfuraldehyde Determined by Chromatographic Methods.

	-20°C	0°C	20°C	40°C
n-Butane	22.20	16.99	13.51	11.55
Butene-1	9.89	8.67	7.36	7.16
Trans-Butene-2	9.18	7.76	7.54	6.48
Cis-Butene-2	8.35	7.36	6.60	6.25
Butadiene, 1-3	4.60	4.22	4.12	3.83

Note:- A complete tabulation for activity coefficients is presented in Appendix B.

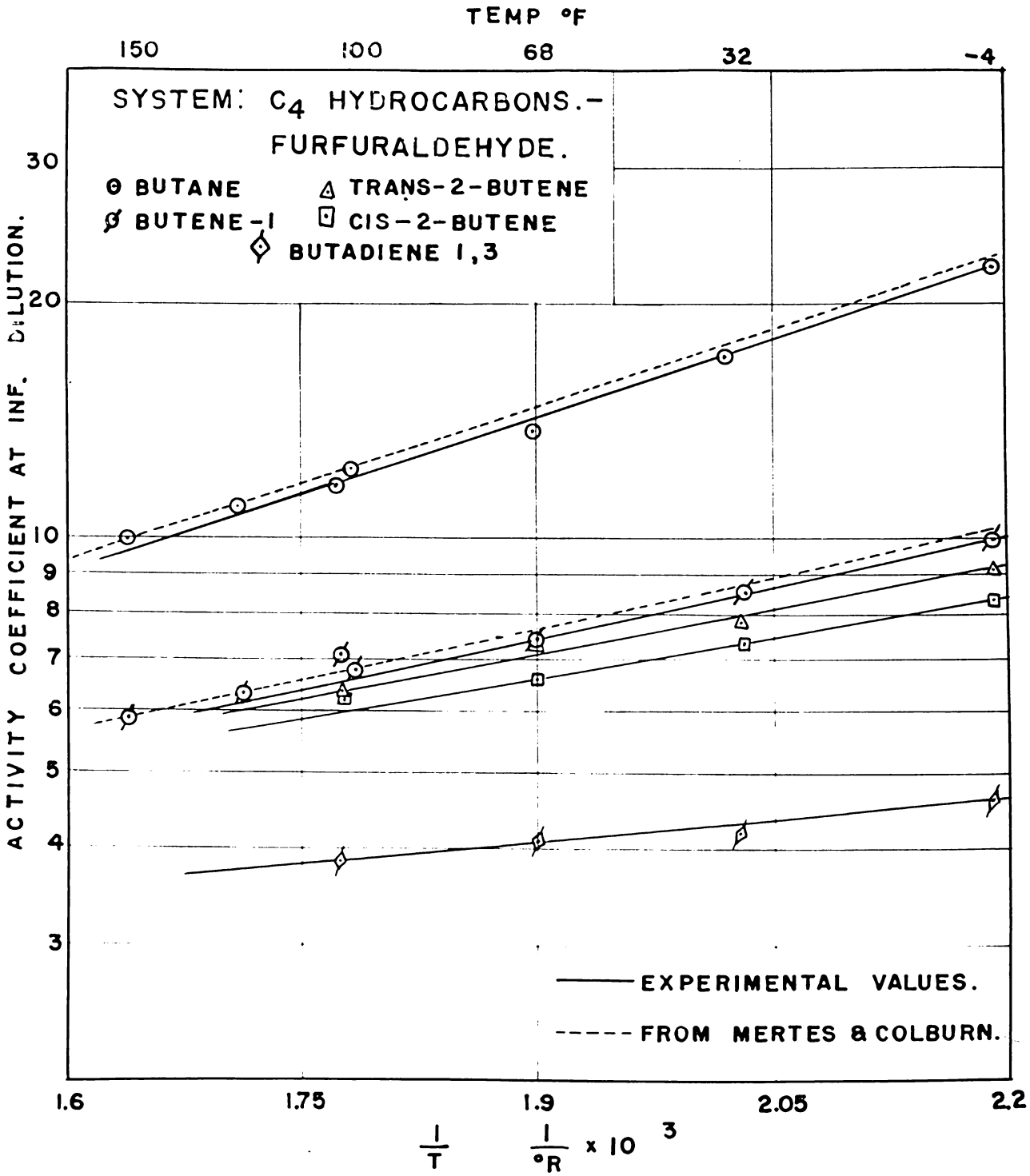


FIG. 18.-ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR C_4 HYDROCARBONS IN FURFURALDEHYDE.

TABLE 8

Heats of Solution of C_4 Hydrocarbons at Infinite Dilution in Furfural and Latent Heats over Range -20°C to 40°C

	Differential Heats of Solution BTU/lb. mole of C_4 Dissolved
n-Butane	3140
Butene-1	2015
Trans-Butene-2	1752
Cis-Butene-2	1558
Butadiene, 1-3	900

Latent Heats of Vaporization	BTU/lb. mole*			
n-Butane	10030	9560	9140	8670
Butene-1	9750	9360	8910	8500
Trans-Butene,-2	10280	9845	9400	8920
Cis-Butene-2	10600	10090	9660	9130
Butadiene 1-3	9950	9520	9090	8630

*When values were not available at the temperature indicated they were calculated from the empirical equation.

Watson K.J., Chem. Soc., 67, 324 (1945)

TABLE 9

Relative Volatilities of individual C-4 Hydrocarbons in Solvent Furfural at Infinite Dilution (pressure 20-40 psia)

Component	Temperature (°C)							
	-20°C		0°C		20°C		40°C	
n-Butane	4.77	4.070	3.985	3.435	3.480	3.015	2.760	2.402
Butene-1	2.15	2.330	2.095	2.245	1.823	1.930	1.687	1.772
Trans-Butene-2	1.933	1.554	1.928	1.570	1.746	1.450	1.592	1.341
Cis-Butene-2	1.762	1.248	1.708	1.256	1.574	1.190	1.492	1.162
Butadiene, 1-3	1.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Reported Values of Volatilities of C-4 Hydrocarbons in Furfural + 4% water

T = 54°C P = 65 psia.

n-Butane	2.02
Butene-1	1.718
Trans-Butene-2	1.19
Cis-Butene-2	1.065
Butadiene 1,3	1.00

TABLE 10

Excess Free Energy For C_4 Hydrocarbons at Infinite Dilution in Furfural, From Data Obtained By Chromatographic Method.

	Excess Free Energy BTU/lb. mol.			
	-20°C	0°C	20°C	40°C
n-Butane	2810	2765	2735	2725
Butene-1	2045	2125	2098	2200
Trans-Butene-2	2015	2010	2120	2090
Cis-Butene 2	1930	1950	1985	2050
Butadiene 1, 3	1387	1417	1487	1500

TABLE 11

Van Laar Constant A

From Data Obtained By Chromatographic Technique

	-20°C	0°C	20°C	40°C
n-Butane	1.346	1.230	1.131	1.062
Butene-1	.978	.938	.867	.855
Trans-Butene 2	.962	.890	.877	.812
Cis Butene 2	.922	.867	.820	.796
Butadiene, 1-3	.663	.625	.615	.583

C O N C L U S I O N S

1. The Aplication of the chromatographic technique to obtain vapor-liquid equilibria ration (K values) gave results which are in "gradual agreement" with those reported from smoothed values of experiments carried under static equilibrium conditions. This agreement ranges from close values for butane to considerable disagreement for methane. The effect of pressure was noticeable. Values obtained at pressures close to the atmospheric pressure were in good agreement but values at higher pressures were found higher than those reported from static methods.

2. The influence of different factors such as flow rate, temperature, etc. upon the experimental parameters in GLPC was found to agree with previous conclusions.

3. The thermodynamic data related to solution behavior in the form of activity coefficients for the C_4 - hydrocarbon system through chromatographic methods was in general agreement with available static results.

4. A practical application is visualized for the GLPC as a means of selecting extractive agents in extractive distillation. The resulting activity coefficients will not only provide the values of the volatilities but will also give information on heat effects so valuable in the design of the towers. The simplicity and speed of the method enable the testing of many possible agents in a minimum of time.

NOMENCLATURE

A = feed volume, (c.c.)

a = gas cross section of column, (cm^2)

A_1 = Van Laar Constant.

A = area of chromatogram, (cm^2)

A, B, C = Constants in Antoine's equation.

c, c" = integration constants.

C = concentration, (suitable unit/c.c.)

C_o = concentration of solute in the feed, (suitable unit/c.c.)

d = peak width, (cm)

e = base of natural logaritms, 2.7183.

F = rate of flow at outlet conditions, (c.c./sec)

f = fugacity

$\overline{G}^e$ = partial molar excess free energy, (BTU/lb. mole)

GLPC = Gas Liquid Partition Chromatography.

H = partition coefficient $= \frac{C_s}{Cm}$ at equilibrium.

h = peak height of the chromatogram, (cm)

H.E.T.P. = height equivalent to a theoretical plate.

H_{sln} = differential heat of solution

$K = \frac{y}{x}$ = vapor-liquid equilibrium constant.

K = constant

L = length of the chromatogram. Distance from the injection point to the maximum of the distribution curve, (cm)

l = column length, (cm)

M = total volume of mobile phase flowed through the column, (c.c.)

M = moles of one phase per c.c.

MW = molecular mass

m = width of the elution curve

n = number of plates in the column

n = number of moles.

p = pressure at any point of the column, (psia).

p_i = pressure of gas applied to chromatographic unit, (psia)

p_o = outlet pressure, (psia).

$\bar{p}$ = partial pressure, (psia)

q_o = amount of material charged to the first plate.

R = gas constant

R_f = retardation factor ratio of traveling velocities of the solute and the solvent.

$\bar{S}^e$ = partial molal excess entropy

t = elution time, (sec)

T = absolute temperature, (°K or °R)

u = linear velocity of gas, (cm/sec)

V = volume of one phase in the column, (c.c.)

V_o = volume of the solid support in column, (c.c.)

v = volume of one phase in one plate, (c.c.)

v = effective plate volume, (c.c.)

V_R = retention volume. Volume of the mobile phase passed through the column when the concentration in the effluent is a maximum, (c.c.)

V'_R = retention volume corrected for dead volume of apparatus, (c.c.)

V°_R = corrected retention volume, (c.c.)

x = amount of sample in detector chamber

x = mole fraction. Mole fraction of solute in the liquid phase.

y = mole fraction of solute in the gas phase.

Z = detector volume (c.c.)

Z' = effective detector volume. Detector volume estimated from the descending portion of the distribution curve, (cc)

Greek Letters.

$\alpha_{1,2}$ = relative volatility of components 1 and 2.

γ = activity coefficient

π = total pressure, (psia)

ρ = density (gr/c.c.)

Subscripts.

m = refers to the mobile phase.

s = refers to the stationary phase.

Superscripts.

° = to indicate reference state or corrected value

* = to indicate ideal state.

Note: The Roman numbers before the serial number of any experiment, corresponds to the column in Table 1.

BIBLIOGRAPHY

1.- Adlard, E.R. "An Evaluation of Some Polyglicols Used as Stationary Phases in Gas-Liquid Partition Chromatography" see Reference (11).

2.- American Petroleum Institute, Project 44. "Selected Values of Physical and Thermodynamical Properties of Hydrocarbons and Related Compounds", Pittsburgh, Pa. (1953)

3.- Anderson J.R. and Napier K.H. "Thermodynamic Data from Gas-Liquid Partition Chromatography" Australian J. Chem., 10, 250 (1957)

4.- Benedict M. and Rubin L.C. "Extractive and Azetropic Distillation" Trans. Am. Inst. Chem. Engrs., 41, 353 (1945)

5.- Bradford B.W., Harvey D., and Chalkley D.E. "The Chromatographic Analysis of Hydrocarbon Mixtures" J. Inst Petrol., 41, 80 (1955)

6.- Buell C.K. and Beathright R.G. "Furfural Extractive Distillation for Separation and Purification of C_4 Hydrocarbons" Ind. Eng. Chem., 39, 695 (1947)

7.- Carlson H.C. and Colburn A.P. "Vapor-Liquid Equilibria of Non Ideal Solutions" Ind. Eng. Chem. 34, 581 (1942)

8.- Coates V.J., Noebels H.J. and Fagerson, I.S., editors. "Symposium in Gas Chromatography". Instrument Society of America, Michigan. August 1957. Academic Press Inc., N.Y. (1958)

9.- Colburn A.P., and Schoenborn E.M. "The Selection of Separating Agents for Azeotropic and Extractive Distillation and for Liquid-Liquid Extraction" Trans. Am. Inst. Chem. Engrs., 41, 421 (1945)

10.- Condsen R., Gordon A.H. and Martin A.J.P.
"Qualitative Analysis of Proteins: A Partition Chromatographic Method Using Paper" Biochem. J., 38, 224 (1944)

11.- Desty D.H., editor. "Vapour Phase Chromatography."
Proceedings of the Symposium sponsored by the Hydrocarbon Research Group of the Institute of Petroleum, London, May/June (1956).
Butterworths Scientific Publications, London (1957)

12.- Gatreaux M.F. and Coates J. "Activity Coefficients at Infinite Dilution" A.I.Ch.E. Journal, 1, 496 (1955)

13.- Glueckauf E. "Theory of Chromatography"
Trans. Faraday Soc., 51, 34 (1955)

14.- Herington E.F.G. "The Thermodynamics of Gas-Liquid Chromatography" See reference (11).

15.-Hildebrand J.H. and Scott R.L. "The Solubility of Non Electrolites" 3rd Edition.
Reinhold Publishing Corporation, New York (1950)

16.- Hougen O.A. and Watson K.M. "Chemical Process Principles" John Wiley and Sons, Inc., New York (1947)

17.- James A.T. and Martin A.J.P "Gas-Liquid Chromatography: The Separation and Microestimation of Volatile Fatty Acids from Formic Acid to Dodecanoic Acid"
Biochem. J., 50, 679 (1952)

18.- James D.H. and Phillips C.S.G. "The Chromatography of Gasess and Vapours, Part II" J. Chem.Soc., 1600 (1953)

19.- Johnson H.W. Jr. and Stross F.H.
"Gas-Liquid Chromatography.-The Determination of Column Efficiency" to be published in Anal. Chem.

20.- Keulemans A.I.M. and Kwantes A.
"Factors Determining Column Efficiency in Gas-Liquid Partition Chromatography" See Reference (11).

21.- Keulemans A.I.M. "Gas Chromatography"
Reinhold Publishing Corp., New York (1957)

22.- Littlewood A.B., Phillips C.S.G. and Price D.T. "The Chromatography of Gases and Vapours. Part V. Partition Analysis with Columns of Silicone 702 and Tritolyl Phosphate" J. Chem. Soc., 1480 (1955)

23.- Martin A.J.P. and Synge R.L.M. "A New Form of Chromatogram Employing Two Liquid Phases" Biochem. J., 35, 1358 (1941)

24.- Martin A.J.P. Symposium in Gas Chromatography. Society for Anal. Chem. Analyst, 81, 52 (1956)

25.- Mayer S.W. and Tompkins E.R. "Ion Exchange as a Separation Method. IV. A Theoretical Analysis of The Column Separation Process" J. Am. Chem. Soc., 69, 2866 (1947)

26.- Maxwell J.B. "Data Book on Hydrocarbons" D. Van Nostrand Co., Inc., New York (1950)

27.- Mellor N. "Factors Affecting Katharometer Sensitivity and Column Efficiency in Vapour Phase Partition Chromatography" See Reference (11).

28.- Mertes T.S. and Colburn A.P "Binary Mixtures of n-Butane, Isobutane and 1-Butane With Furfural" Ind. Eng. Chem. 39, 787 (1947)

29.- Natural Gasoline Association of America "Equilibrium Ratio Data Book" Tulsa, Oklahoma (1957).

30.- Ober S.S. "The Interpretation of Column Efficiency and Resolving Power in Gas-Chromatography" See Reference (8)

31.- Peters W.A. Jr. "The Efficiency and Capacity of Fractioning Columns." Ind. Eng. Chem., 14, 476 (1922).

32.- Phillips C. "Gas Chromatography" Academic Press Inc., Publishers, New York (1956)

33.- Pierotti G.J., Deal C.H., Derr E.L. and Porter P.E. "Solvent Effects in Gas-Liquid Partition Chromatography" J. Am. Chem. Soc., 78, 2989 (1956)

34.- Pollard F.H. and Hardy C.J.
"A Preliminary Study of Some Factors Influencing the Order of Elution of Halogenated Methanes, The Degree of Separation and the Reproducibility of Retention Volumes in GLPC." See Reference (11).

35.- Porter P.E. Deal C.H. and Stross F.H.
"The Determination of Partition Coefficients from Gas-Liquid Partition Chromatography"
J. Am. Chem. Soc., 78, 2999 (1956)

36.- Rangel T.E. "Analysis of Low Temperature Chromatographic Separation of Methane-Propane Mixtures with n-Decane on Celite" M.S. Thesis. The Rice Institute. (1956)

37.- Ray N.H. "Gas Chromatography I. The Separation and Estimation of Volatile Organic Compounds by GLPC"
J. Appl. Chem., 4, 21 (1954)

38.- Rock H. "Gas Chromatography and Extractive Distillation"
Chem. Ing. Tech., 28, 489 (1956)

39.- Sherwood T.K. and Pigford R.L.
"Absorption and Extraction" pp 144-149
2nd edition. McGraw-Hill Book Co., New York (1952)

40.- Van Deemter J.J., Zuiderweg F.J. and Klinkenberg A.
"Longitudinal Diffusion and Resistance to Mass Transfer as Causes of Non-Ideality in Chromatography"
Chem. Eng. Sci., 5, 271 (1956)

41.- Wiebe A.K. "Elution Time and Resolution in Gas Chromatography" J. Physics Chem. 60, 685 (1956)

42. Zechmeister L. "Stereochemistry and Chromatography"
Ann. New York Acad. Sci, 49, 220 (1948).

APPENDIX A

CHROMATOGRAPHIC DETERMINATION OF K VALUES

DATA AND RESULTS FOR THE SYSTEM BUTANE n-DODECANE

RUN No.	TEMP (C)	PRESS INLET (psia)	PRESS OUT (psia)	MEAN PRESS (psia)	FLOW (cc/m)	ELUT TIME m sc.	UNCORRN. RETN VOL (cc)	PRESS CORR FACT	APPTS DEAD VOL (cc)	DETEC CORR $/V_B$	CORRT RETN VOL (cc)	NUM THEO PLAT	K EXP	K NGAA
II 452	0	19.37	18.40	18.88	49	24 05	910.00	1.012	5.21	.006	887.0	564	0.735	.760
II 453	0	24.38	23.60	24.00	49	30 10	890.00	1.010	5.19	.007	870.0	594	0.589	.605
II 454	0	34.28	33.70	33.99	49	41 10	852.00	1.010	5.19	.009	831.0	620	0.437	.430
II 455	0	39.20	38.70	38.95	48	45 51	806.00	1.011	4.84	.0113	783.0	615	0.406	.390
II 456	10	19.20	18.20	18.70	50	17 23	705.00	1.019	5.27	.007	682.0	492	1.017	1.090
II 457	10	24.11	23.30	23.70	50	21 46	688.00	1.008	5.19	.007	673.0	544	0.814	.880
II 458	10	34.41	33.80	34.11	50	29 21	640.00	1.008	5.15	.009	624.0	610	0.614	.635
II 459	10	39.15	38.60	38.87	50	32 38	624.50	1.010	5.15	.010	609.0	645	0.553	.565
II 460	20	19.25	18.20	18.70	50	12 51	539.70	1.019	5.28	.008	520.5	408	1.415	1.520
II 461	20	23.99	23.10	23.60	51	15 33	514.50	1.009	5.21	.009	500.0	484	1.170	1.220
II 462	20	34.42	33.80	34.11	49	22 27	490.35	1.011	5.15	.011	479.5	515	0.850	.875
II 463	20	39.57	39.00	39.28	49	24 44	474.00	1.010	5.15	.012	459.0	543	0.774	.780
II 447	30	19.40	18.30	18.85	50	10 00	439.93	1.029	5.27	.008	408.0	334	1.910	1.970
II 448	30	24.13	23.20	23.67	50	12 06	411.50	1.034	5.21	.010	388.3	413	1.605	1.600
II 450	30	34.37	33.70	34.04	50	17 25	386.00	1.014	5.16	.011	371.0	535	1.170	1.150
II 451	30	39.30	38.70	39.00	50	19 08	390.00	1.009	5.15	.012	376.0	575	1.010	1.010

APPENDIX A

CHROMATOGRAPHIC DETERMINATION OF K VALUES

DATA AND RESULTS FOR THE SYSTEM PROPANE n-OCTADECANE

RUN No.	TEMP	PRESS INLET	PRESS OUT	MEAN PRESS	FLOW	ADJUST TIME	UNCORR RETN VOL	PRESS CORR FACT	APP'PS DEAD VOL	DISSO CORR $/V_R$	CORRT RETN VOL	NUM THEO PLAT	K EXP	K NCAA
	(C)	(psia)	(psia)	(psia)	cc/m	m sec	(cc)		(cc)		(cc)			
I 6	0	19.99	18.80	19.40	70	7 16	369.20	1.032	5.29	.0065	350.32	447	3.356	3.45
I 9	0	24.28	23.70	23.99	40	14 58	344.68	1.012	5.17	.0132	331.00	463	2.880	2.77
I 16	0	34.32	33.90	34.11	40	20 49	335.16	1.006	5.14	.0166	322.50	506	2.090	1.96
I 19	0	34.23	33.50	33.87	70	12 07	345.48	1.011	5.16	.0097	333.36	498	1.970	1.96
I 22	0	39.47	39.10	39.29	40	25 05	322.23	1.005	5.13	.018	309.91	251	1.900	1.71
II 157	10	20.19	19.60	19.90	30	9 06	197.02	1.015	5.19	.018	185.54	307	4.225	4.50
II 161	10	19.65	18.70	19.29	60	4 29	203.48	1.032	5.29	.0078	190.54	469	4.400	4.50
II 165	10	24.28	23.60	23.94	40	8 05	193.79	1.014	5.19	.0145	183.23	465	3.750	3.70
II 170	10	34.32	33.90	34.11	30	13 28	168.57	1.006	5.14	.0226	158.79	643	3.200	2.60
II 175	10	39.36	38.95	39.16	30	14 43	160.53	1.005	5.13	.0266	150.53	369	3.020	2.32
II 181	20	20.02	19.40	19.71	30	7 30	169.69	1.016	5.20	.0185	159.06	510	5.720	5.60
II 185	20	19.65	18.40	19.13	70	3 16	181.99	1.040	5.34	.0070	168.67	396	5.510	5.80
II 186	20	24.33	23.80	24.07	30	9 00	166.15	1.011	5.17	.0199	156.07	363	4.810	4.70
II 191	20	34.37	33.95	34.16	30	11 43	151.62	1.006	5.14	.0235	142.15	434	3.900	3.55
II 196	20	39.30	38.90	39.10	30	12 35	141.74	1.005	5.13	.0297	132.56	498	3.730	2.55
III 286	30	19.01	18.20	19.00	30	6 21	161.15	1.045	5.36	.0175	146.48	259	6.900	7.55
III 289	30	19.60	18.90	18.26	50	3 52	173.24	1.032	5.28	.0090	155.59	324	6.980	7.55
III 290	30	24.04	22.70	25.37	30	7 50	156.78	1.030	5.28	.0209	144.05	279	6.240	6.20
III 295	30	34.22	33.15	33.68	30	10 24	142.53	1.016	5.20	.0254	131.71	352	4.950	4.25
III 300	30	39.47	38.45	38.96	30	11.00	129.97	1.013	5.18	.0280	119.71	359	5.500	5.70

APPENDIX A

CHROMATOGRAPHIC DETERMINATION OF K VALUES

DATA AND RESULTS FOR THE STAGES USING n-BUTANE.

RUN No.	TEMP	PRESS INLET	PRESS OUT	MEAN PRESS	FLOW	RUN TIME	UNCORR RETN VOL	FRACT CORR FACT	APPTS DEAD VOL	RATIO CORR $/V_g$	CORR RETN VOL	SUM THRO PLAT	K EXP	K MCAA
	(C)	(psia)	(psia)	(psia)	(cc/min)	m sec	(cc)		(cc)		(cc)			
I 57	0	20.01	19.35	19.68	40	4 40	151.63	1.017	5.20	.0130	122.57	328	14.40	15.0
I 59	0	20.86	19.85	20.35	60	3 02	125.11	1.026	5.25	.0106	115.62	285	15.55	13.0
I 63	0	24.79	23.85	24.32	40	5 30	125.87	1.020	5.22	.0158	116.44	352	12.82	10.7
I 69	0	34.52	34.20	34.36	30	9 50	117.70	1.005	5.15	.0274	103.96	340	10.35	7.6
I 74	0	39.48	39.20	39.34	30	11 00	114.87	1.003	5.12	.0296	106.11	393	9.53	6.7
II 136	10	20.18	19.60	19.89	30	4 21	94.18	1.015	5.19	.0183	86.09	503	13.65	17.4
II 140	10	20.02	18.65	19.33	70	1 49	96.45	1.037	5.32	.0065	87.28	447	16.10	17.4
II 144	10	24.11	23.10	23.60	60	2 30	91.85	1.022	5.23	.0092	83.97	455	14.41	13.9
II 147	10	34.51	34.10	34.30	30	6 16	77.98	1.006	5.14	.0256	70.56	423	13.96	9.7
II 152	10	39.38	39.00	39.19	30	6 49	74.17	1.005	5.13	.0264	66.89	464	16.76	8.4
II 207	20	19.79	19.30	19.04	70	1 37	90.56	1.041	5.30	.0051	81.42	474	19.93	21.60
II 212	20	24.14	22.90	23.52	70	2 00	89.53	1.027	5.26	.0193	80.43	620	16.63	17.5
II 213	20	34.52	34.10	34.31	30	5 56	76.44	1.006	5.14	.0089	70.23	401	16.77	12.0
II 216	20	39.45	33.65	34.05	60	3 11	83.12	1.012	5.17	.0107	76.20	592	10.59	12.0
II 220	20	39.35	38.85	39.10	40	5 03	77.65	1.006	5.14	.0175	70.79	575	14.34	10.6
III 268	30	19.69	17.00	18.34	50	2 11	97.25	1.031	5.57	.0082	84.10	371	21.06	27.0
III 269	30	24.05	22.70	23.38	30	4 18	86.05	1.030	5.23	.0191	76.90	526	20.06	22.0
III 271	30	23.62	21.30	22.46	50	2 34	91.24	1.055	5.43	.0102	80.47	396	20.00	22.0
III 274	30	34.17	33.10	33.64	30	5 37	76.98	1.016	5.20	.0243	68.91	587	19.76	14.9
III 280	30	39.34	38.85	38.89	30	6 08	72.66	1.013	5.18	.0253	64.93	395	21.87	15.9

APPENDIX A

CHROMATOGRAPHIC DETERMINATION OF K VALUES

DATA AND RESULTS FOR THE SYSTEM STYRENE n-DODECANE

RUN No.	TEMP (C)	PRESS INLET (psia)	PRESS OUT (psia)	MEAN PRESS (psia)	FLOW (cc)	ELUT TIME m sec	UNCORR RETN VOL (cc)	PRESS CORR FACT	APPAR DEAD VOL (cc)	RETN CORR $/V_R$	CORRT. RETN VOL (cc)	NUM THEO PLAT	K EXP	K NGAA
I 84	0	19.87	18.80	19.33	60	2 26	105.97	1.029	5.27	.0071	97.20	451	25.42	21.0
I 85	0	19.83	18.60	19.21	70	2 05	106.99	1.033	5.30	.0074	97.60	390	25.40	21.0
I 90	0	24.22	23.20	23.71	70	2 51	103.61	1.022	5.23	.0076	95.52	461	19.90	17.2
I 91	0	34.52	34.20	34.36	30	7 51	93.96	1.005	5.13	.0263	86.08	499	18.00	12.0
I 97	0	39.49	39.20	39.34	30	8 21	87.20	1.004	5.12	.0300	79.32	399	20.12	10.5
II 103	10	19.88	19.30	19.59	30	3 43	81.72	1.015	5.19	.0166	74.14	310	24.09	25.0
II 107	10	19.73	18.95	19.34	40	3 18	98.53	1.021	5.22	.0098	90.51	446	15.63	25.0
II 117	10	24.28	23.60	23.94	40	3 12	76.72	1.014	5.19	.0139	69.53	380	25.99	20.0
II 121	10	34.69	34.30	34.50	30	5 24	66.80	1.006	5.13	.02444	59.82	390	30.99	14.3
II 130	10	39.22	38.85	39.03	30	6 07	66.81	1.005	5.13	.0231	59.96	460	27.05	12.7
II 225	20	20.02	18.55	19.29	70	1 28	81.05	1.040	5.34	.0063	72.39	392	27.20	29.0
II 226	20	24.34	23.80	24.07	30	4 00	73.84	1.011	5.17	.0191	66.60	375	28.71	23.5
II 228	20	24.18	23.30	23.74	50	2 27	76.99	1.019	5.21	.0105	69.71	437	18.62	23.5
II 231	20	34.52	34.10	34.31	30	5 05	65.49	1.006	5.14	.0257	58.56	427	36.32	16.8
II 236	20	39.30	38.90	39.10	30	5 28	61.74	1.005	5.13	.0259	54.85	450	30.64	14.90
III 242	30	19.79	18.20	19.06	30	3 16	81.54	1.044	5.36	.0151	71.84	317	30.65	34.0
III 247	30	19.79	17.10	18.44	50	1 56	85.61	1.080	5.57	.0064	73.59	465	29.50	34.0
III 260	30	24.23	22.90	23.57	30	3 55	77.04	1.029	5.27	.0182	68.44	399	28.89	27.5
III 256	30	34.19	33.10	33.64	31	4 48	68.08	1.016	5.20	.0214	60.53	419	32.84	19.5
III 261	30	39.27	38.30	38.79	30	5 26	64.45	1.013	5.17	.0254	57.04	418	39.31	17.2

APPENDIX A

CHROMATOGRAPHIC DETERMINATION OF K VALUES

DATA AND RESULTS FOR THE SYSTEM METHANE n-DODECANE

RUN No.	TEMP	PRESS INLET	PRESS OUT	MEAN PRESS	FLOW	ELUT TIME	UNCORR. RETH. VOL	PRESS CORR FACT.	APPTS DEAD VOL	DETRG. COEF. /V_R	CORRT. RETH VOL	NUM THEO PLAT	K EXP	K NGAA
	(C)	(psia)	(psia)	(psia)	(cc/m)	m sec	(cc)		(cc)		(cc)			
IV 309	0	19.97	18.00	18.98	60	2 35	117.50	1.055	5.43	.0049	105.64	759	66.74	111.0
IV 310	0	19.82	17.50	18.66	70	2 12	120.08	1.068	5.50	.0035	106.93	979	63.80	111.0
IV 315	0	24.00	22.05	23.02	70	2 37	113.35	1.045	5.36	.0051	102.82	779	63.84	88.0
IV 316	0	34.54	34.00	34.32	30	7 14	87.09	1.009	5.16	.0310	78.65	345	--	61.0
IV 321	0	39.40	38.80	39.10	30	8 22	88.27	1.008	5.15	.0196	80.87	735	--	55.0
IV 327	10	20.11	19.10	19.60	30	5 05	112.94	1.026	5.26	.0103	103.81	651	73.59	120.0
IV 331	10	19.72	17.30	18.51	70	2 09	123.05	1.071	5.52	.0040	109.24	935	64.60	120.0
IV 333	10	24.41	23.30	23.86	40	4 30	109.27	1.024	5.24	.0091	100.65	790	72.82	94.0
IV 337	10	34.57	33.90	34.24	30	7 29	93.67	1.010	5.16	.0175	86.11	889	--	68.0
IV 342	10	39.53	38.90	39.21	30	8 01	87.45	1.009	5.15	.0108	80.10	769	--	58.0
IV 349	20	19.94	18.20	19.07	50	2 58	119.36	1.048	5.39	.0052	108.13	736	63.50	128.0
IV 351	20	19.73	17.20	18.47	69	2 05	122.39	1.075	5.54	.0094	108.29	788	65.16	128.0
IV 352	20	24.40	23.55	23.97	30	5 48	108.20	1.018	5.21	.0131	99.83	612	77.86	97.0
IV 357	20	34.39	33.70	34.05	30	7 20	95.60	1.010	5.16	.0167	88.02	680	--	70.0
IV 363	20	39.40	38.69	39.06	40	6 06	92.45	1.011	5.16	.0127	85.26	938	--	61.0
IV 367	30	20.01	18.85	19.48	30	4 51	114.94	1.028	5.27	.0098	105.03	570	74.30	137.0
IV 371	30	19.52	16.95	18.23	67	2 05	120.71	1.070	5.55	.0035	110.21	878	63.02	137.0
IV 376	30	24.23	22.00	23.11	70	2 25	116.45	1.051	5.40	.0036	105.23	1060	62.08	108.0
IV 377	30	34.56	33.80	34.18	30	6 53	92.52	1.011	5.17	.0159	85.01	672	--	74.0
IV 382	30	39.40	38.70	39.05	30	7 28	87.66	1.009	5.15	.0178	80.30	705	--	65.0

APPENDIX B

DETERMINATION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION

DATA AND RESULTS FOR THE SYSTEM OF C_4 HYDROCARBONS IN FURFURAL

n-Butane

RUN No.	TEMP (C)	PRESS INLET (psia)	PRESS OUT (psia)	MEAN PRESS (psia)	FLOW (cc/m)	ELUT TIME m sc	UNCORR RETN. VOL (cc)	PRESS CORR. FACT.	APPTS. DEAD VOL. (cc)	DETEC CORR /V_R	CORRT RETN VOL (cc)	PART COEFF	ACTIV. COEFF. ∞DIL.
V 387	0	20.13	19.55	19.84	60	3 44	156.35	1.015	5.19	.0063	148.01	17.22	14.98
V 388	0	29.20	28.80	29.00	60	4 59	146.50	1.007	5.15	.0132	138.10	15.67	16.99
V 389	0	39.22	38.90	39.06	60	6 24	134.70	1.004	5.12	.0144	127.19	13.95	19.02
VII 432	20	20.48	19.65	20.06	60	3 07	139.36	1.021	5.23	.0100	130.02	10.16	13.98
VII 433	20	29.42	28.80	29.11	60	4 17	140.78	1.011	5.16	.0107	132.71	10.49	13.51
VII 434	20	39.40	38.90	39.15	60	5 23	122.61	1.006	5.14	.0132	115.19	8.33	17.04
VI 402	40	19.83	19.00	19.41	60	2 30	123.50	1.022	5.23	.0084	114.75	8.34	9.98
VI 403	40	29.41	28.80	29.11	60	3 29	113.52	1.011	5.16	.0132	105.80	17.22	11.55
VI 404	40	39.36	38.90	39.13	60	4 28	107.78	1.006	5.13	.0131	100.70	6.59	13.82
V 417	-20	20.10	19.60	19.85	60	5 30	212.92	1.013	5.18	.0101	203.01	25.80	21.75
V 418	-20	29.46	29.10	29.28	60	8 00	208.38	1.006	5.14	.0119	199.66	25.33	22.20
V 419	-20	39.38	39.10	39.24	60	10 24	201.83	1.004	5.12	.0125	193.54	24.37	23.05

APPENDIX B.

DETERMINATION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION

DATA AND RESULTS FOR THE SYSTEMS OF C_4 HYDROCARBONS IN FURFURAL

BUTENE-1

RUN No.	TEMP (C)	PRESS INLET (psia)	PRESS OUT (psia)	MEAN PRESS (psia)	FLOW (cc/m)	ELUT TIME m sec	UNCORR. RETN. VOL. (cc)	PRESS CORR. FACT.	APPTS DEAD VOL. (cc)	DETEC CORR /V_R	CORRT. RETN (VOL. (cc)	PART COEFF.	ACTIV. COEFF. ∞ DIL.
V 390	0	20.13	19.55	19.84	60	4 53	204.51	1.015	5.10	.0086	194.72	24.58	8.67
V 391	0	29.25	28.85	29.05	60	7 10	203.38	1.007	5.14	.0016	194.59	24.55	8.65
V 392	0	39.58	39.25	39.41	60	9 08	190.52	1.004	5.12	.0130	182.80	22.60	9.44
VII 435	20	20.18	19.35	19.76	60	4 06	185.80	1.022	5.23	.0094	175.08	15.69	7.36
VII 436	20	29.41	28.80	29.11	60	5 57	178.48	1.011	5.16	.0114	169.52	15.02	7.68
VII 437	20	39.39	38.90	39.14	60	7 30	169.41	1.006	5.14	.0121	161.27	14.00	8.24
VI 406	40	29.51	28.90	29.21	60	4 13	138.96	1.011	5.16	.0124	130.73	10.32	7.16
VI 405	40	20.03	19.20	19.61	60	3 00	146.25	1.022	5.23	.0090	136.77	11.08	6.67
VI 407	40	39.57	39.10	39.33	60	5 31	132.43	1.006	5.14	.0131	124.88	9.59	7.72
V 420	-20	20.30	19.80	20.05	60	8 46	335.96	1.013	5.17	.0078	324.11	44.80	9.89
V 421	-20	29.36	29.00	29.18	60	12 33	353.74	1.006	5.14	.0083	343.56	47.90	9.50
V 422	-20	39.54	39.25	39.39	60	16 03	310.28	1.004	5.12	.0114	300.56	41.22	10.76

APPENDIX B

DETERMINATION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION

DATA AND RESULTS FOR THE SYSTEMS OF C_4 HYDROCARBONS IN FURFURAL

GRAHAM-HOUSE 2

RUN No.	TEMP (C)	PRESS INLET (psia)	PRESS OUT (psia)	MEAN PRESS (psia)	FLOW (cc/m)	ELUT TIME m sec.	UNCORR. RETN VOL (cc)	PRESS CORR FACT	APPRX DEAD VOL (cc)	RETEC CORR $/V_R$	CORR'D RETN VOL (cc)	PART C.COEFF	ACTIV. COEFF. ∞ DIL.
V 393	0	20.18	19.80	19.89	60	6 35	250.39	1.015	5.19	.0097	247.04	32.77	8.54
V 394	0	29.30	28.90	29.10	60	9 53	275.05	1.007	5.14	.0058	267.80	36.03	7.76
V 395	0	39.35	39.00	39.17	60	12 12	260.39	1.004	5.13	.0115	251.29	33.44	8.36
VII 433	20	20.05	19.20	19.61	60	5 04	231.49	1.022	5.23	.0095	219.30	21.12	7.00
VII 439	20	29.27	28.65	28.96	60	7 04	216.47	1.011	5.16	.0114	206.64	19.67	7.54
VII 440	20	39.39	38.90	39.14	60	9 20	210.62	1.006	5.14	.0120	201.95	18.99	7.78
VI 408	40	20.03	19.20	19.61	60	3 34	172.91	1.022	5.23	.0109	162.32	14.24	6.90
VI 409	40	29.40	28.80	29.10	60	5 16	171.64	1.010	5.16	.0128	162.63	14.28	6.48
VI 410	40	39.00	38.47	38.23	60	6 31	156.64	1.006	5.14	.0139	148.50	12.55	7.38
V 423	-20	20.20	19.70	19.95	60	12 33	483.39	1.013	5.17	.0060	469.08	67.65	8.85
V 424	-20	29.46	29.10	29.28	60	17 51	465.44	1.006	5.14	.0077	453.94	65.29	9.18
V 425	-20	39.55	39.25	39.40	60	22 35	470.32	1.004	5.12	.0085	459.49	66.12	9.06

APPENDIX B

DETERMINATION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION

DATA AND RESULTS FOR THE SYSTEMS OF C_4 HYDROCARBONS IN FURFURAL

CIS-BUTENE-2

RUN No.	TEMP INLET (C)	PRESS INLET (psia)	PRESS OUT (psia)	MEAN PRESS. (psia)	FLOW (cc/m)	RETN TIME m sec.	UNCORR. RETN. VOL (cc)	PRESS CORR FACT	APPEN DEAD VOL (cc)	DENSC CORR V_N/V_R	CORRT RETN VOL (cc)	PART C.ESP	ACTIV. COEFF ∞DIL
V 396	0	20.07	19.20	19.78	60	7 50	328.69	1.015	5.19	.0075	317.70	46.60	6.69
V 397	0	29.25	28.85	29.05	60	11 15	318.31	1.007	5.14	.0085	308.37	42.40	7.36
V 398	0	39.91	39.20	39.36	60	14 33	305.80	1.004	5.12	.0101	294.57	40.25	7.75
VII 441	20	19.93	19.10	19.51	60	5 48	266.82	1.022	5.23	.0085	253.01	25.36	6.39
VII 442	20	29.32	28.70	29.01	60	8 29	257.56	1.011	5.16	.0100	247.25	24.55	6.60
VII 443	20	39.49	39.00	39.25	60	10 42	241.07	1.006	5.14	.0113	231.80	22.66	7.15
VI 411	40	20.22	19.40	19.81	60	5 37	190.71	1.021	5.23	.0115	179.60	16.39	6.12
VI 412	40	29.51	28.90	29.20	60	5 28	185.73	1.010	5.16	.0105	176.80	16.04	6.25
VI 413	40	39.66	39.20	39.43	60	7 22	176.39	1.006	5.13	.01052	168.08	14.95	6.70
V 426	-20	20.20	19.70	19.95	60	15 03	582.89	1.013	5.17	.0056	567.26	85.04	8.24
V 427	-20	29.56	29.20	29.38	60	22 02	572.55	1.005	5.14	.0064	560.33	81.95	8.35
V 428	-20	39.48	39.20	39.34	60	27 47	579.35	1.004	5.12	.0063	575.04	84.04	8.10

APPENDIX B

DETERMINATION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION

DATA AND RESULTS FOR THE SYSTEMS OF C_4 HYDROCARBONS IN FURFURAL

BUTADIENE 1,3

RUN No.	TEMP (C)	PRESS INLET (psia)	PRESS OUT (psia)	MEAN PRESS (psia)	FLOW (cc/m)	ELUT TIME m sec	UNCORR. RETN. VOL (CC)	PRESS CORR FACT	APPTS DEAD VOL (cc)	DETEC CORR /V_R	CORRT RETN VOL (cc)	PART COEFF	ACTIV. COEFF ∞DIL.
V 399	0	20.12	19.55	19.84	60	9 44	407.62	1.015	5.19	.0071	393.76	55.80	4.09
V 400	0	29.41	29.00	29.20	60	13 58	393.31	1.007	5.14	.0088	383.38	54.17	4.22
V401	0	39.58	39.25	39.42	60	17 55	373.73	1.004	5.12	.0101	363.33	51.02	4.48
VII 444	20	20.33	19.50	19.91	60	7 15	326.69	1.021	5.23	.0076	312.30	32.55	3.77
VII 445	20	29.31	28.70	29.01	60	10 09	310.75	1.011	5.16	.0091	299.58	29.76	4.12
VII 446	20	39.40	38.90	39.15	60	13 01	294.02	1.006	5.14	.0104	284.04	29.08	4.21
VI 414	40	20.11	19.30	19.70	60	4 44	228.28	1.021	5.23	.0092	216.42	20.97	3.70
VI 415	40	29.34	28.75	29.05	60	6 46	220.64	1.010	5.16	.0105	211.02	20.29	3.83
VI 416	40	39.67	39.20	39.43	60	8 45	209.51	1.006	5.13	.0114	200.83	19.03	4.09
V 429	-20	20.29	19.80	20.04	60	19 18	739.62	1.012	5.17	.0054	721.50	107.22	4.48
V 430	-20	29.46	29.10	29.28	60	27 32	717.93	1.006	5.14	.0069	703.46	104.42	4.60
V 431	-20	39.54	39.25	39.39	60	34 07	665.04	1.004	5.12	.0086	651.81	96.51	4.95

Sample Calculations

For the run V-388* from the data in the Appendix B

$T = 273.2\ ^{o}K$

$F = 60$ cc/min

$P_1 = 29.2$ psia

$P_o = 28.2$ psia

$t = 297$ sec.

mean presure in the column $\pi = \frac{29.2 + 28.8}{2} = 29$ psia

Calculation of corrected flow rate. The orifice flowmeter gives the flow rate at 1 atm and $9^{o}C$ and it must be corrected to the actual working conditions.

For the conditions before the column

$$F = \frac{60}{60} \times \frac{14.7}{29.2} \times \frac{273.2}{282.2} = .486 \text{ cc/sec}$$

For the conditions at the end of the column.

$$F = \frac{60}{60} \times \frac{14.7}{28.8} \times \frac{273.2}{282.2} = .494 \text{ cc/sec}$$

Uncorrected retention volume = 297 sec. x .494 = 146.5 cc.

Correction Factors.

a). For pressure drop

$$\frac{P_1}{P_o} = \frac{29.2}{28.8} = 1.014$$

Applying Equation

$$\frac{V_R}{V_{R^o}} = \frac{2}{3} = \frac{1.014^3 - 1}{1.0142 - 1} = 1.007$$

b). For dead volume of apparatus

Before the column $= \frac{3 \text{ cc}}{.486 \text{ cc/seg}} = 6.17$ sec.

After the column $= \frac{2.1}{.494} = 4.25$ sec.

Total $= 10.42$ sec.

expressed in volume:

$$10.42 \text{ sec.} \times .494 \frac{\text{c.c.}}{\text{sec}} = 5.15 \text{ c.c.}$$

c). For Sample Size.

The number of plates is given by Equation (52)

$$n = \left(4 \frac{L}{d} \right)^2$$

from chromatogram

$L = 12.57$ cm.

$d = 2.74$ cm.

$$n = \left(4 \times \frac{12.57}{2.74} \right)^2 = (18.367)^2 = 337 \text{ plates.}$$

Applying Van Deemter Equation

$$\frac{.5 \times 146.5}{18.367} = 3.99$$

As $3.99 > 1$ cc (sample size volume, no correction for sample

size is necessary

d). Correction for Detector Volume.

From the Chromatogram.

$Z' = 1.865$ cm.

$V_r' = 146.5 - 5.15$ cc. $= 141.35$

$Z'/V_r' = .0132$

In fig. 5 Ref. 19

Z'/V_r' falls in an approximate 45^0 line versus the parameter retention volume due to detector/retention volume. Then retention volume due to detector $= .0132 \times 141.35 = 1.86$ cc

Summary of corrections.

Uncorrected retention volume = 146.50 cc.

- correction for dead volume = 5.15 cc

- correction for detector volume = 1.86 cc = 139.49 c.c.

For pressure drop

$$V_R^o = \frac{139.49}{1.007} = \underline{\underline{138.1 \text{ c.c.}}}$$

V_R^o = corrected retention volume = 138.10 c.c.

Alternative I. - Determination of K values

$V_m = 38.3$

$V_R^o - V_m = 138.10 - 38.30 = 99.80$ c.c.

Introducing in Equation 58

$$K = \frac{84780 \times 273.2 \times 7.3916}{96.08 \times 29 \times 70.3 \times 99.80} = 8.26$$

Alternative II. - Determination of Activity Coefficients

From equation 29a

$$H^0 = \frac{V_{R^0} - V_m}{V_s} = \frac{99.80}{6.37} = 15.68$$

Substituting in Equation 64

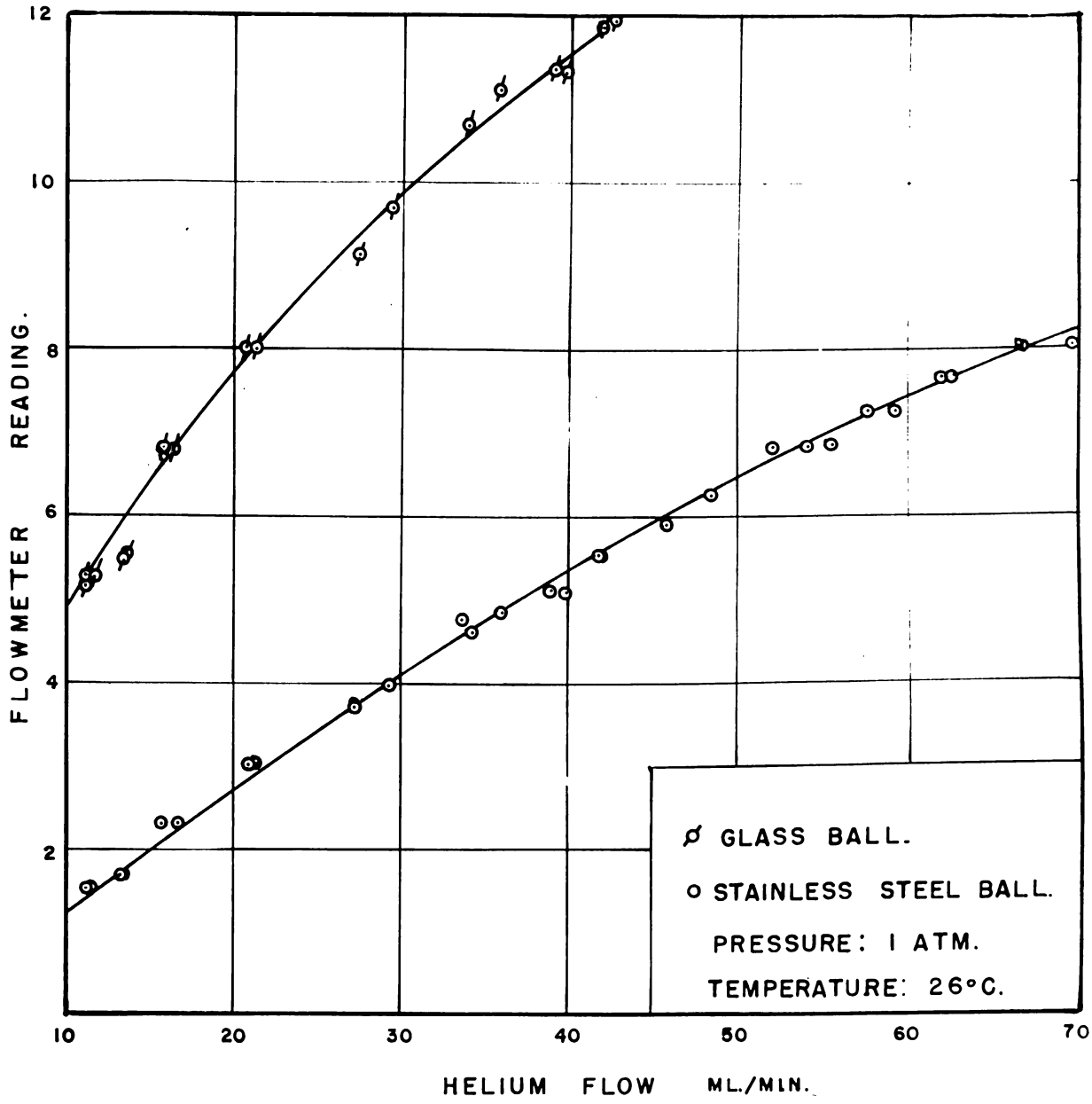
$$\gamma = \frac{M_s RT}{H^0 P^0} = \frac{.01207 \times 62361 \times 273.2}{15.68 \times 774.52} = 11.89$$

Note: The K valve obtained shows the calculation method only. It is necessary to pointed out that it was obtained using furfural as liquid phase. For this reason it is not expected to check with the conventional K values.

VAPOR PRESSURES OF C_4 HYDROCARBONS

Calculated from Antoine's Equation

	Antoine's Equation Constants			Vapor pressures in mm. Hg			
	A	B	C	-20°C	0°C	20°C	40°C
n-Butane	6.83029	945.90	240	339.43	774.52	1556.7	2832
1-Butene	6.84290	926.10	240	429.90	964.15	1909.8	3431
cis-2-Tutene	6.86926	960.10	237	278.50	637.96	1359.7	2530
trans-2-Butene	6.86952	960.80	240	317.87	734.84	1493.3	2742
Butadiene, 1-3	6.85941	935.531	239.55	396.60	899.72	1799	3258



CALIBRATION CURVE FOR THE FLOWMETER.