Generalization of Gas-Liquid Partition Chromatography to Study High Pressure Vapor-Liquid Equilibria of Multicomponent Systems

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The use of chromatographic retention volume data to obtain vapor-liquid equilibrium coefficients has been extended to a ternary system with all components present at finite concentrations in the liquid phase and essentially a light binary gas comprising the vapor phase. The data are obtained by observing the retention time of the solute of interest when that solute is eluted by a flowing gas stream through a column packed with an inert porous firebrick on which is impregnated a fixed, relatively nonvolatile liquid. The retention times are used to compute retention volumes which may be related to the K values of the solute.

A previous mathematical description of the elution process is modified to include the case of an N component elution gas, all constituents of which are soluble in the fixed liquid phase. A general solution is derived for the multicomponent elution gas from which K values for each component may be calculated if retention volume data are taken for each, provided molecules of the solute samples used are distinguishable from others of the same species present in the eloution gas. For the case of indistinguishable sample molecules, the rate theory development of Stalkup and Deans is verified for a binary elution gas.

Sufficient retention data were taken to completely define the concentration dependence of the K value for propane in the system methane-propane-*n*-decane at —20°, 0°, 40°, and 70°F. from 20 to 1,000 lb/sq.in.abs. Six methane-propane binary mixtures were used as elution gases, consisting of 2.08, 4.31, 6.90, 9.44, 13.09, 16.27 mole % propane. Retention data were also taken for methane under the same conditions. Distinguishability of sample molecules was achieved by using radioactive solute samples tagged with carbon-14.

Propane retention data were also obtained for the system methane-propane-*n*-heptane at —20° and —40°F. from 100 to 1,000 lb./sq.in.abs. for propane at infinite dilution and for binary elution gases composed of 2.08 mole % propane at —40°F. and 4.31 mole % propane at —20°F.

All K values determined chromatographically were either compared directly with published static equilibrium values or tested for consistency with such values and found to be in substantial agreement.

In this paper the application of gas-liquid partition chromatography (GLPC) to the study of vapor-liquid equilibria is generalized to include multicomponent systems. Establishing the validity of such application greatly increases the spectrum of systems subject to study by GLPC. The rapidity and simplicity of the elution process compared with conventional methods for studying phase behavior make such an increase in applicability desirable.

In the GLPC process a vapor-liquid system is established by passing a gas through a column packed with an inert, porous solid material on the surface and in the pores of which an immobile liquid phase is fixed. A small perturbation with the solute of interest is eluted through the column by the carrier gas. The time required for the perturbation to travel the length of the column is determined by and related to the manner in which the solute distributes itself between the two phases.

GLPC was first introduced by Martin and James (*21*). It was quickly recognized by Martin (*20*) that this technique represented potentially the easiest method of measuring the physical properties of solutes in solvent systems. His suggestion was verified by Porter, Deal, and Stross (*26*) who demonstrated that partition coefficients calculated from experimental elution data were entirely consistent with those obtained from static measurements. These authors observed excellent agreement between chromatographic partition coefficients and equilibrium values for *n*-heptane and 2-propanol in diisodecyl phthalate measured by classical means. They also observed that such variables as gas velocity, column length, quantity of fixed liquid phase, and type of solid support material had no appreciable effect on the value of the GLPC partition coefficient. Further substantiation of the GLPC values as equilibrium properties was presented by Anderson and Napier (*1*) who found good agreement between GLPC and static partition coefficients for benzene and cyclohexane in polyethylene glycol.

Several previous investigators have calculated vapor-liquid equilibrium ratios, or *K* values, from GLPC elution data. Rangel (*29*) used the development of Porter et al.

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(*26*) for partition coefficients to calculate *K* values for methane and propane in *n*-decane at moderate pressures (15 to 60 lb./sq.in.abs.), which were found to be in substantial agreement with values predicted from the DePriester charts. Preston (*27*) calculated *K* values for light hydrocarbons in heavier paraffinic materials from the partition coefficients obtained by Kwantes and Rijnders (*16*). Lopez (*18, 19*) found GLPC *K* values for methane, ethane, ethylene, propane, and *n*-butane in *n*-dodecane to range from serious disagreement with NGAA (*25*) values for methane to substantial agreement for *n*-butane. All of the above used elution gases which were not soluble in the fixed liquid phase such as helium, argon, nitrogen, or hydrogen. Also, these studies were carried out near atmospheric pressure.

Stalkup and Kobayashi (*33*) introduced the use of an elution gas which was appreciably soluble in the nonvolatile fixed liquid and also extended the GLPC technique to high-pressure operation. These authors determined *K* values for ethane, propane, and *n*-butane at essentially infinite dilution in the methane-*n*-decane system over the temperature range −20° to 70°F. and for pressures between 20 and 2,000 lb./sq.in.abs. The results were found to be in substantial agreement with those predicted by NGAA (*25*). The *K* values calculated for *n*-butane at 40° and 160°F. were in close agreement with those extrapolated from the static measurements of Sage and Lacey (*30*). These authors also briefly investigated the use of a binary elution gas, both components of which were appreciably soluble in the fixed liquid, together with thermal conductivity detection of the pulses.

THEORETICAL CONSIDERATIONS

In general all attempts to mathematically describe a chromatographic column can be divided into two categories. The first of these is the theoretical plate theory in which the column is conceived as consisting of a number of plates, much like a packed distillation column. The assumption is made that equilibrium exists at each stage or plate between the average liquid composition on the plate and the vapor leaving the plate. It is further assumed that no transfer of solute by diffusion from one plate to the next occurs. The equations resulting from a material balance around each plate for continuous flow lead to a solution which relates the retention volume of a solute to its partition coefficient.

The second approach to describe the behavior of a chromatographic column is the continuous column rate theory. This treatment attempts to account for the influence of such kinetic phenomena as rate of mass transfer between phases, rate of adsorption, longitudinal and lateral molecular diffusion, and eddy diffusion on the elution history of the solute band.

Theoretical Plate Theory

In their pioneering work on chromatography, Martin and Synge (*22*) developed the following relationship from the theoretical plate analogy:

$$V_{Ri} = V_g + V_L/H_i \tag{1}$$

This expression has been verified by several others (*10, 35*).

Equation (1) relates the equilibrium partition coefficient to properties of the column and the elution process, which are easily measurable. It is desirable to express the partition coefficient itself in terms of the *K* values of the components involved. This is possible if the gas phase concentration for component *i* is expressed by the gas law including the compressibility factor, and the liquid phase concentration is expressed in terms of the moles of fixed liquid on the column. Thus, for the gas phase

$$C_{gi} = \frac{\pi y_i}{Z_M RT} \tag{2}$$

and for the liquid phase

$$C_{Li} = \frac{W x_i}{V_L\,(1 - x_1 - x_2 - \ldots - x_N)} \tag{3}$$

Equation (3) allows the elution gas to be a multicomponent mixture, each component of which is soluble in the fixed liquid with a mole fraction of x_i.

When one substitutes $x_i = y_i/K_i$ into Equation (3), the partition coefficient $H_i = C_{gi}/C_{Li}$ becomes

$$H_i = \frac{\pi y_i}{Z_M RT}\;\frac{W x_i}{V_L\,(1 - y_1/K_1 - y_2/K_2 - \ldots - y_N/K_N} \tag{4}$$

Solving for $K_i = y_i/x_i$ one gets

$$K_i = \frac{Z_M RT\,W}{\pi(V_{Ri}^* - V_g)} \cdot \frac{1}{(1 - y_1/K_1 - y_2/K_2 - \ldots - y_N/K_N)} \tag{5}$$

The retention volume V_{Ri}^* is defined as the product of the observed retention time, that is the time the sample is retained by the system before appearing in the effluent, and the volumetric flow rate at column conditions of temperature and pressure. V_{Ri}^* denotes the retention volume for component *i* as measured when the perturbation is effected by a radioactively traced component or when the components of the infinitesimal perturbation do not occur in the elution gas.

Before one uses experimental data in Equation (5) to compute *K* values, the assumptions which underlie its derivation must be considered so that these may be approximated experimentally. The assumptions are:

1. The column is equivalent to a large number of theoretical plates.
2. The sample volume is negligibly small compared with the total column volume.
3. Pressure drop through the column is negligible, or pressure is essentially constant throughout the column.
4. The partition coefficient is constant along the entire length of the column, that is slight local variations in concentration do not affect H_i.
5. Diffusional effects are negligible.
6. Instantaneous equilibrium exists between the two phases on each plate, or the mass transfer coefficient is effectively infinite.
7. The solute sample molecules are completely distinguishable from all other molecules in the system.

The requirement of assumption 1 is met by proper choice of column properties and operating conditions. The effects of such variables as gas velocity, amount of fixed liquid on the packing, type of solid support material, and column size on the number of theoretical plates has been thoroughly investigated and is discussed in the literature (*13, 25, 33*).

Assumption 2 may be satisfied by experimentally reducing the volume of the solute sample until further reduction reflects no change in the measured retention volume.

The use of short, loosely packed columns enables assumption 3 to be easily approximated.

The fourth assumption requires that the concentration of the solute band be such that the partition coefficient is not appreciably affected by the changing composition of the band as it elutes through the column.

The veracity of assumptions 5 and 6 has been demonstrated by Stalkup (*31*). More will be said concerning this verification in the section on rate theory.

Assumption 7 states that in order for Equation (5) to be valid for any solute in a multicomponent gas phase, the sample molecules of that solute must be distinguishable from those of the same component in the elution gas. This has been accomplished in the present work by using radioactive samples of the solutes under investigation. Mathematically, this corresponds to introducing a sample into the elution stream whose physical properties are the same as those of a component in the elution gas, but whose molecules are completely distinguishable from any already present in the equilibrium system. Hence, mathematically the solute sample is at infinite dilution even though its retention volume is characteristic of its physical behavior at a finite concentration. The case of a solute sample which is not originally present in the elution gas is discussed by Stalkup and Kobayashi (33). Thus, none of the assumptions involved in the derivation of Equation (5) are violated, provided distinguishable samples are used to perturb the equilibrium system.

If binary elution gases such as those used in the present study are perturbed with respect to both components in the gas phase, the two equations resulting from Equation (5) may be solved simultaneously to give

$$K_1 = \frac{Z_M\, RT\, W}{\pi(V_{R_1}{}^* - V_g)} + y_1 + \left(\frac{V_{R_2}{}^* - V_g}{V_{R_1}{}^* - V_g}\right) y_2$$

$$K_2 = \frac{Z_M\, RT\, W}{\pi(V_{R_2}{}^* - V_g)} + \left(\frac{V_{R_1}{}^* - V_g}{V_{R_2}{}^* - V_g}\right) y_1 + y_2 \tag{6}$$

Similarly Equation (5) may be solved simultaneously for a N-component elution gas to give

$$K_i = \frac{Z_M\, RT\, W}{\pi(V_{R_i}{}^* - V_g)} + \sum_{j=1}^{N} \left(\frac{V_{R_j} - V_g}{V_{R_i} - V_g}\right) y_j \tag{7}$$

Rate Theory

A very useful rate process development has been presented by Stalkup and Deans (32) for a binary elution gas. By neglecting diffusion and assuming point equilibrium these authors were able to arrive at an analytical solution of the partial differential rate equations describing the GLPC elution process in terms of experimental elution parameters. The result is

$$V_{R_i} - V_g = \frac{Z_M RTWK_1K_2}{\pi} \left\{\frac{(K_1 - 1)y_1\left[1 - y_2\dfrac{d\ln K_2}{dy_2}\right] + (K_2 - 1)y_2\left[1 - y_1\dfrac{d\ln K_1}{dy_1}\right]}{[K_2\ K_1 - K_1 + y_1\ (K_1 - K_2)\,]^2}\right\} \tag{8}$$

The assumptions as stated by Stalkup and Deans for which Equation (8) is valid are:

1. Constant temperature and pressure.
2. Fixed and flowing phases are effectively one dimensional.
3. Total molar concentration is constant.
4. Instantaneous equilibrium at a point in the column.

In this mathematical rate treatment a sample of molecules chemically identical to others already present in the elution gas may be injected into a chromatographic column without regard to their distinguishability.

To check the validity of the assumption of point equilibrium and negligible diffusion effects, the original equations were solved by Stalkup (*31*) numerically for a Peclet number of 2 as suggested by McHenry and Wilhelm (*23*), Aris et al. (*2*), and Carberry (*6*) for a gas in turbulent flow ($Re > 10$) and a wide range of values of the mass transfer term. The Peclet number includes the effects of molecular diffusion, and the mass transfer term accounts for nonequilibrium effects. The calculated retention times were the same for mass transfer values of 10 to 10^6. For elution experiments of the same dimensions as those conducted in this work, Stalkup (*31*) estimated a mass transfer coefficient of about 750, indicating the validity of the instantaneous equilibrium assumption for the experiments reported herein.

Stalkup and Deans (32) also assumed that $y_i(dlnK_i)/(d_{y_i}) << 1$, thus arriving at a simplified version of Equation (8):

$$V_{R_1} - V_g = \frac{Z_M\, RT\, W\, K_1K_2}{\pi} \left\{\frac{K_2 - 1 + y_1\ (K_1 - K_2)}{[\mathrm{K_2K_1 - K_1 + y_1\ (K_1 - K_2}]^2}\right\} \tag{9}$$

Undoubtedly under some experimental conditions the above assumption is valid, but the limits of such conditions had not been established prior to this work.

If Equation (5) is solved for $V_{R_1}{}^* - V_g$ and the ratio of $V_{R_1} - V_g$ as given in Equation (9) to $V_{R_1}{}^* - V_g$ is formed, the result is

$$\overline{R} = \frac{K_2K_1 - K_1 + K_1y_1\ (K_1 - K_2)}{K_2K_1 - K_1 + y_1\ (K_1 - K_2)} = \frac{V_{R_1} - V_g}{V_{R_1}{}^* - V_g} \tag{10}$$

where subscript 1 refers to the solute of interest and subscript 2 is the more volatile component in the elution gas. Since

$$(K_2K_1 - K_1) > 0 \text{ when } K_2 > 1 \text{ and } (K_1 - K_2) < 0, \tag{11}$$

it becomes evident that the following relationships exist between K_1 and $\overline{R}$:

$$\begin{array}{llll} \text{if } K_1 > 1 & \overline{R} < 1 & \text{or} & V_R < V_R{}^* \\ \text{if } K_1 = 1 & \overline{R} = 1 & \text{or} & V_R = V_R{}^* \\ \text{if } K_1 < 1 & \overline{R} > 1 & \text{or} & V_R > V_R{}^* \end{array} \tag{12}$$

These inequalities arise because of the indistinguishability of the sample molecules from those of the same specie already present in the system when a physical property such as thermal conductivity is used to reflect concentration changes. When the sample molecules are tagged radioactively, it is possible to distinguish them from any already present in the elution gas.

This difference in the velocities of the objects inducing a pulse and the pulse itself is similar to the phenomenon in nature of a flood wave traveling faster than the raindrops which induced it, or as another example, traffic stoppage on a freeway actually moving against the direction of movement of the car that originally initiated it (*11*). Helfferich has treated the physical phenomenon with some rigor (*11*).

If tagged solutes are not available, and it is desired to study the phase behavior of a ternary system with a binary elution gas and a fixed nonvolatile component, Equation (9) may be used in connection with Equation (8) to generate the concentration dependence of the solute K value. If it is desired to study an elution gas consisting of more than two components, tagged samples must be used in connection with Equation (7), or the describing rate equations must be solved numerically.

Congruence of the Two Approaches

If a mixture of tagged and untagged molecules of the same molecular species is injected as a sample into a chromatographic column, the retention volume determined from the elution history recorded by a thermal conductivity detector will, under most conditions, be different from that calculated from the trace of an ionization chamber detector. However, the use of the former in Equation (8) and the latter in Equation (5) should result in precisely the same calculated K value. This type of congruence will be demonstrated and discussed in a later section of the paper.

EXPERIMENTAL INVESTIGATION

A schematic diagram of the experimental apparatus used in the GLPC elution experiments is given in Figure 1. Because radioactive materials are used, the entire apparatus was enclosed by a large wooden hood, connected by a 12-in. metal duct to a commercial hood. The elution gases were stored in large high-pressure cylinders as indicated in the diagram. From its source cylinder an elution gas first passed through a moderately sensitive diaphragm pressure regulator before passing through a more sensitive, dome-loaded diaphragm regulator which determines the inlet pressure to the GLPC column. If the elution gas was pure methane, a drying tube of silica gel was inserted between the two regulators. The methane-propane mixtures were dried during preparation, so the drying tube was omitted when a mixture elution gas was used. Beyond the more sensitive regulator, the stream was separated into reference and carrier streams.

The reference gas passed through a coil situated in the constant temperature bath and was expanded through a needle valve before flowing through the reference side of the conductivity cell. The carrier gas passed through a six-way valve through which the flow could be diverted to sweep out a small sample tube containing the solute sample. The carrier gas, now containing solute, passed through the GLPC column which is submerged in the temperature bath. After leaving the column the carrier gas went through a needle valve which reduced the pressure to atmospheric and permitted adjustment of the flow rate. From the valve, the carrier gas passed through the sample side of the thermal conductivity detector and then through an orifice flow meter, across which the pressure drop was carefully measured by means of a mercury manometer and a cathetometer.

The carrier gas then entered the port of a tee where it was joined by a large volume of nitrogen purge gas entering along the straight section of the tee before both passed into and through an ionization chamber. Upon leaving the chamber the carrier gas-purge gas mixture flowed through a soap bubble flow meter to the atmosphere. The bubble meter was used for accurate calibration of the carrier gas orifice flow meter when no purge gas was flowing. During the course of an experiment with purge gas flowing, the cathetometer reading of the orifice differential pressure was used for precise flow rate determination.

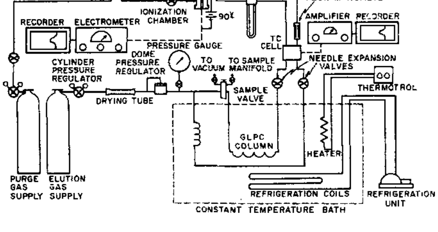

Fig. 1. Schematic diagram of the high-pressure GLPC apparatus.

The signal from the thermal conductivity detector was fed through a d.c. linear amplifier to a chart recorder to give the elution history of the solute.

The ionization current from the ion chamber passed through a preamplifier equipped with a resistance selector where the signal was converted to a voltage. The signal was then monitored by a vibrating read electrometer and recorded on a chart recorder to produce the elution diagram of a radioactive solute sample.

The columns used in this study were 3/16-in. stainless steel tubes from 6 to 18 in. in length. The columns were packed with firebrick on which n-decane or n-heptane had been impregnated by the procedure described by Keulemans (*13*). After several pressure points the column being used was removed, capped at its extremities, cleaned and dried, and then weighed on a large analytical balance to determine the loss of fixed liquid due to evaporation into the flowing gas stream.

Column pressure above 50 lb./sq. in. abs. was measured with a Heise gauge subdivided into 2 lb./sq. in. increments. Below 50 lb./sq.in. abs. a mercury manometer was used for pressure measurement. Temperature was controlled and measured to ±0.1°F.

Briefly, the experimental procedure was to adjust the flow of elution gas, whether pure methane or a mixture of methane and propane, to approximately 70 cc./min. at 760 mm. Hg, 300°K. after the desired column temperature and pressure were established. After sufficient time was allowed for the elution gas to achieve equilibrium with fixed n-decane, a ¼ cc. (760 mm. Hg, 300°K.) sample of gaseous solute was introduced into the column. The samples were mixtures of radioactive methane diluted with nonradioactive methane and radioactive propane diluted with a 50-50 mixture of nonradioactive methane and nonradioactive propane. The time required for

TABLE 1. COMPARISON OF RETENTION VOLUMES AND K VALUES OBTAINED WITH TAGGED AND UNTAGGED SOLUTE SAMPLES

$T = 70$°F. Mole Fraction Propane in Vapor = 0.0690

Press., lb./sq. in. abs.	$\dfrac{V_{R_{C_3}} - V_g}{V_{R_{C_3}}^* - V_g}$	K_{C_3}*	K_{C_3}†	K_{C_3}**
44.0	0.949	2.65	2.65	2.65
74.0	0.986	1.62	1.60	1.60
110	0.990	1.10	1.10	1.10
192	1.011	0.685	0.700	0.695
292	1.043	0.493	0.507	0.499
704	1.077	0.396	0.411	0.400
794	1.144	0.296	0.313	0.298
991	1.193	0.285	0.303	0.286
$T = 0$°F. Mole Fraction Propane in Vapor = 0.0431				
54.0	1.009	0.732	0.737	0.737
107	1.061	0.389	0.394	0.394
203	1.157	0.234	0.238	0.234
302	1.238	0.181	0.186	0.181
402	1.345	0.157	0.160	0.156
605	1.448	0.142	0.145	0.140
795	1.540	0.142	0.147	0.138
$T = 40$°F. Mole Fraction Propane in Vapor = 0.1627				
42.0	0.921	1.96	1.95	1.95
71.5	0.953	1.10	1.12	1.12
102	1.017	0.798	0.812	0.812
200	1.257	0.458	0.468	0.453
300	1.600	0.351	0.354	0.342
402	2.005	0.297	0.302	0.291

* Determined from tagged samples and Equation (15).
† Determined from untagged samples and Equation (9).
** Determined from untagged samples and Equation (8).

the two peak concentrations to appear in the effluent stream was then measured for both detection schemes.

DISCUSSION OF EXPERIMENTAL RESULTS

Equations (6) and (8) were evaluated from retention volume data for methane and propane obtained by eluting samples of these components through a column packed with screened firebrick on which *n*-decane or *n*-heptane had been impregnated. Both pure methane and mixtures of methane and propane were used as carrier gases. The equilibrium established between the fixed liquid phase and the flowing gas phase was perturbed both with respect to methane and propane when a mixture elution gas was used. The time from injection of a sample to the peak of a concentration profile in the effluent stream was measured for both thermal conductivity and radioactive detection schemes.

Elution experiments were used to obtain retention volume data on the system methane-propane-*n*-decane at 70°, 40°, 0°, and —20°F. and pressures between 20 and 1,000 lb./sq.in.abs. The propane vapor phase concentration ranged from 0 to 16.27 mole %.

Phase equilibria data for the system methane-propane-*n*-heptane were calculated for —20° and —40°F. over the pressure range 100 to 1,000 lb./sq.in.abs. and a propane vapor phase concentration range of 0 to 4.31 mole %.

Free Gas Volume

The use of radioactive methane as a solute sample made possible the determination of a retention volume for methane in a pure methane elution gas. It was recognized that if the *K* value for methane in the methane-*n*-decane system were known to a high degree of accuracy, a very accurate determination of the value of V_g, the free gas volume, could be calculated from an experiment with pure methane used as the elution gas. *K* values for methane in the binary system were measured by these authors in independent experiments described in reference *14*. For this system, (5) reduces to

$$K_1 = \frac{Z_M\, RT\, W}{\pi\,(V_{R_1}{}^* - V_g)(1 - 1/K_1)} \qquad (13)$$

which, solved for V_g, becomes

$$V_g = V_{R_1}{}^* - \frac{Z_M\, RT\, W}{\pi\,(K_1 - 1)} \qquad (14)$$

TABLE 2. ESTIMATED UNCERTAINTIES IN MEASURED QUANTITIES

Variable	± Uncertainty limits	Comments
T	0.06°K.	Temperature control limits
π	2 lb./sq. in. abs.	For $p > 50$ lb./sq. in. abs.
	0.01 lb./sq. in. abs.	$p < 50$ lb./sq. in. abs.
Z	0.2%	At low pressure
	0.5 to 1.0%	At high pressure, low temperature
	0.05%	For pure methane
t_r	0.5%	From avg. derivation of 3 t_r's, all points
f_a	0.5%	From avg. derivation of 3 f_a's, all points
W	1.5%	From reproducibility of isotherms on different columns

where now K_1 refers to the *K* value for methane.

All previous investigators (*19, 33*) have indicated a lack of precision in estimating the quantity V_g. If the chromatographic approach to studying vapor-liquid equilibria is to be extended to the very volatile solutes such as methane, an extremely precise knowledge of V_g is required. The accuracy afforded by the experimental evaluation of Equation (14) will be discussed shortly.

In order to maintain an accurate knowledge of the free gas volume, the decrease in V_g due to the dissolution of propane and methane in the fixed liquid had to be carefully estimated. This was accomplished by extrapolating partial molar volumes for both components from the work of Sage and Lacey (*30*) and subtracting the calculated increase in liquid volume from the low pressure value of V_g.

K Values for Methane and Propane in the System Methane-Propane-*n*-Decane

From the radioactive retention volumes calculated for the methane and propane perturbations, the respective *K* values were computed from Equation (6). It was observed that the *K* values for methane obtained in this manner deviated randomly from those for methane in the methane-*n*-decane binary system (*14, 15*) by ± 5 to 10% at moderate or high pressures and even more at the lower pressures.

However, since an error of 10% was undesirable, especially at the higher pressures where the term (y_1/K_1)

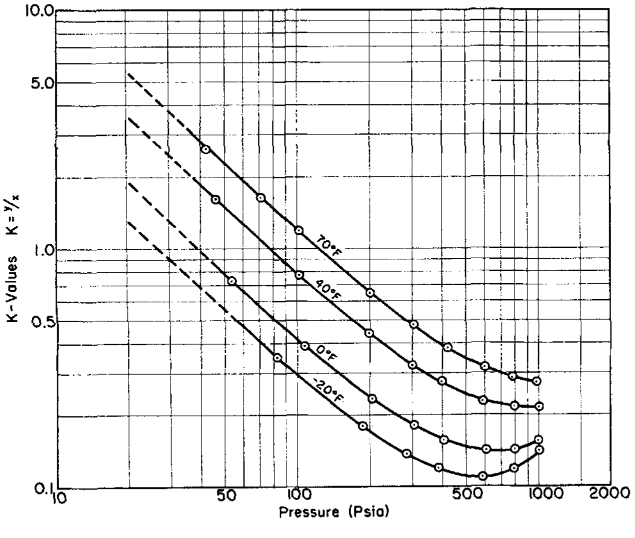

Fig. 2. *K* values for propane in the system methane-propane-*n*-decane with propane vapor composition 0.0431 mole fraction.

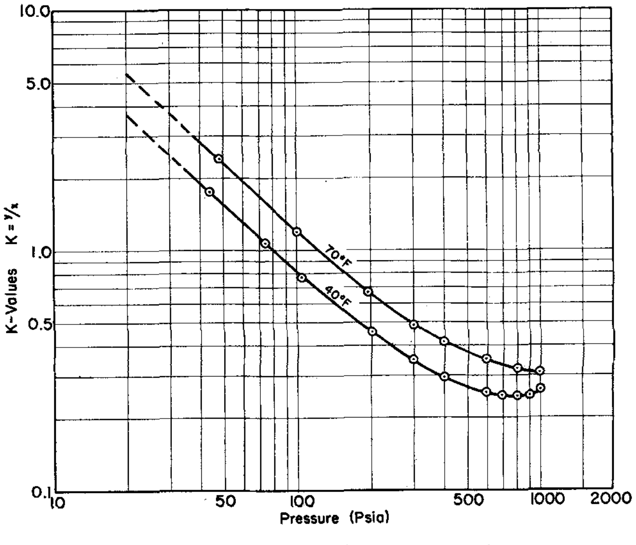

Fig. 3. *K* values for propane in the system methane-propane-*n*-decane with propane vapor composition 0.1309 mole fraction.

becomes appreciable when compared with unity, a decision was made to use the K values for methane predicted by an empirical correlation (3) in connection with Equation (5) to obtain the final values for propane K values. The correlation was based on experimental methane K values collected from numerous sources for a variety of hydrocarbon systems. This correlation includes the solubility data of these authors (*15*), the methane-ethane and methane-propane static data of Price and Kobayashi (*28*), and also the methane-*n*-heptane data of Hurt (*12*). The maximum scatter in the correlation appears to be less than 5% and thus should represent the best source of methane K values in moderately complex hydrocarbon systems.

The final form of Equation (5) used to compute propane K values denoting methane with subscript 1 and propane with subscript 3 is as follows:

$$K_3 = \left[\frac{Z_M R T W}{\pi (V_{R_3}^* - V_g)} + y_3 \right] \left(\frac{1}{1 - y_1/K_1} \right) \qquad (15)$$

A knowledge of the experimental conditions allows a prediction of the methane K value from the empirical correlation.

If the value of $y_i(d \ln K_i)/(d_{y_i})$ is available at every experimental point from an independent source such as the results of the radioactive tracer perturbations in connection with Equation (15), Equation (8) may be solved explicitly for the K value of propane. Similarly, Equation (9) may be rearranged as a quadratic in the K value of propane and solved for K_3 (propane).

Sample isotherms of the data obtained are presented in Figures 2 and 3. A comparison between the propane K values computed from Equation (15) with radioactive retention volumes and those calculated from Equations (8) and (9) with thermal conductivity retention volumes is presented in Table 1.

Agreement between K_3 computed from Equation (9) and K_3 calculated from (15) is good at low and moderate pressures where the effect of composition on K_3 and K_1 is small. However, at the higher pressures where $y_i(d \ln K_i)/(d_{y_i})$ becomes quite appreciable, disagreement as great as 6.5% occurs. Use of (8) decreased the maximum deviation from the K values determined by tracer perturbation for propane to 3.5% and resulted in an average deviation of 1.0% for 125 experimental points. The average deviation with Equation (9) used was 2.8%.

Table 3. Comparison of Measured and Calculated Values of System Free Gas Volume

Column number	Fixed liquid phase	V_g, cc. measured	V_g, cc. calculated	Deviation, %
1	*n*-decane	3.659	3.232	–11.7
2	*n*-decane	4.365	3.851	–11.8
3	*n*-decane	3.745	3.318	–11.4
4	*n*-decane	3.593	2.944	–18.1
5	*n*-heptane	3.276	3.212	– 2.0
6	*n*-heptane	2.862	2.672	– 6.7

It is pertinent to note that V_R (thermal conductivity) for propane in a mixture elution gas under some conditions is greater than twice the corresponding V_R^* (radioactive), and yet use of V_R in Equation (8) results in the same K value as the use of V_R^* in Equation (15). The assumptions made in the derivation of (5) or (15) have been validated by both Stalkup (*31*) and this work. The precise agreement between (8) and (15) serves as an extensive experimental verification of the validity of the rate theory approach to understanding chromatography.

Error Analysis

In estimating expected maximum errors in calculated elution parameters, the familiar technique of totally differentiating an expression and replacing the total derivatives with delta quantities has been applied. This technique assumes the errors to be small enough to allow such a substitution. For example, retention volume is computed from measured quantities by the following equation:

$$V_R = t_r\, f_{HP} = t_R\, f_a \frac{\pi_a}{\pi} \frac{T}{T_a} Z_M \qquad (16)$$

Total differentiation yields

$$dV_R = f_a \frac{\pi a}{\pi} \frac{T}{T_a} Z_M\, dt_R + t_R \frac{\pi a}{\pi} \frac{T}{T_a} Z_M\, df_a + t_R f_a \frac{\pi a}{\pi} \frac{Z_M}{T_a} dT + t_R f_a \frac{\pi a}{\pi} \frac{T}{T_a} Z_M\, d + t_R f_a \frac{\pi a}{\pi} \frac{T}{T_a} dZ_M \qquad (17)$$

Since the cathetometer calibration of the orifice flow meter is corrected to exactly 1 atm. and 300°K., any error in πa and T_a appears in df_a. Also note that the signs have been so chosen as to result in a predicted maximum error.

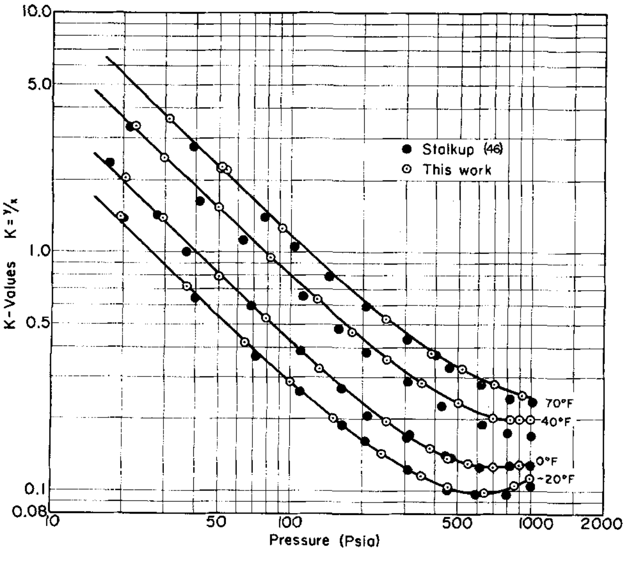

Fig. 4. Comparison of K values for propane at infinite dilution in the system methane-*n*-decane obtained in this work with those of Stalkup (31).

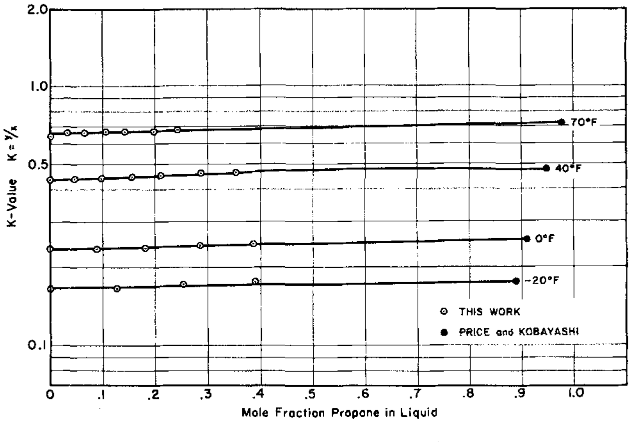

Fig. 5. K value for propane as a function of propane concentration in the liquid phase in the system methane-propane-*n*-decane at 200 lb./sq.in.abs.

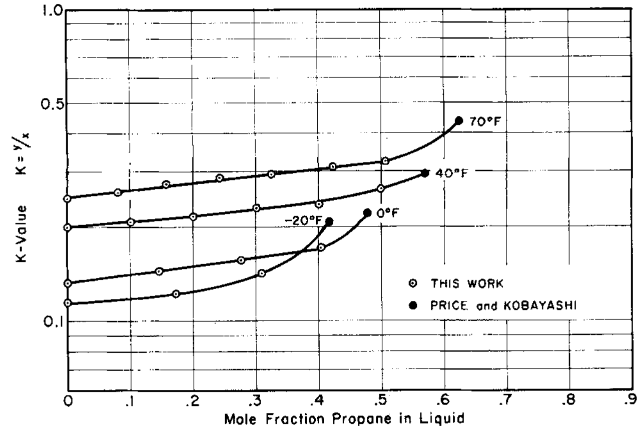

Fig. 6. *K* value for propane as a function of propane concentration in the liquid phase in the system methane-propane-*n*-decane at 1,000 lb./sq.in.abs.

Replacing the differentials with delta quantities and rearranging one obtains

$$\frac{\Delta V_R}{V_R} = \frac{\Delta t_R}{t_R} + \frac{\Delta f_a}{f_a} + \frac{\Delta T}{T} + \frac{\Delta \pi}{\pi} + \frac{\Delta Z_M}{Z_M} \qquad (18)$$

In order to evaluate the maximum probable error in the parameters of interest it was necessary to estimate probable errors in measured quantities. Table 2 lists these uncertainties.

It should be mentioned that the experimentally measured V_g includes both column void space and system dead volume; that is it represents the free gas volume of the entire system. This quantity has also been calculated from the weights and densities of the packing materials and the unpacked volume of the column. When calculated and measured values of V_g are compared, as in Table 3, the calculated value is lower than the measured one. For the *n*-decane column this deviation is substantial, amounting to 11 to 18%. Agreement between the two values is considerably better for the *n*-heptane columns. The densities of *n*-heptane and *n*-decane were taken from the "Handbook of Chemistry" (*17*). The density of the firebrick support was determined by Stalkup (*31*). This comparison indicates that considerable error may be introduced in V_g by attempting to calculate its value. Stalkup also indicated that the use of an inert carrier such as helium did not produce consistent results. Thus, the use of radioactive solutes is proposed as the most accurate technique for the determination of free gas volume to date.

From the analysis and estimation of errors, the following probable errors in the important quantities V_R, V_g, K_1, and K_3 are proposed:

Quantity	Probable % Error
V_R	± 1.0
V_g	± 0.5
K_1	± 5-10
K_3	± 1.5

COMPARISON WITH OTHER INVESTIGATORS

Stalkup *K* Values for Propane at Infinite Dilution in the Methane-Propane-*n*-Decane System

Figure 4 presents a comparison of the chromatographically obtained infinite dilution *K* values of Stalkup with those of this work. Agreement is excellent for the −20° and 0°F. isotherms, especially in the low and moderate pressure regions. However, even in these pressure regions a deviation of about 8% at 40°F. and 4% at 70°F. is observed. For all four isotherms deviation between the two sources is greatest at high pressures, amounting to 7, 3, 15, and 5% at −20°, 0°, 40°, and 70°F., respectively, at 1,000 lb./sq.in.abs. It is significant that when a deviation occurs, the results of Stalkup are always quantitatively less than those of this work.

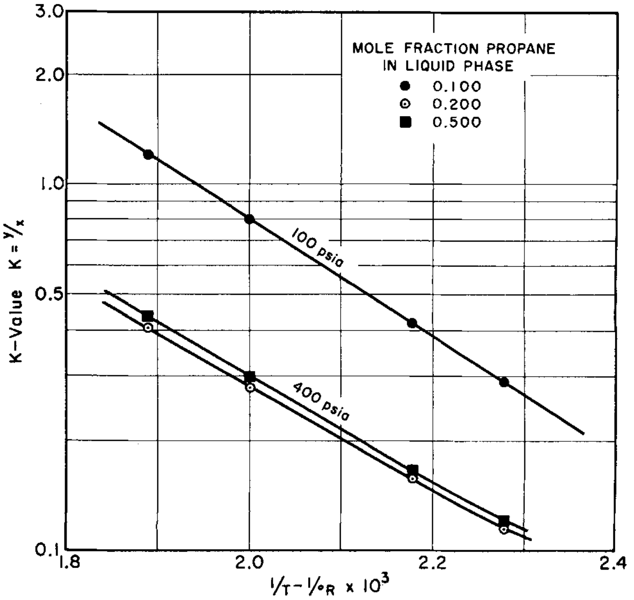

Fig. 7. *K* values for propane in the system methane-propane-*n*-decane as a function of reciprocal absolute temperature at constant pressure and liquid-phase composition.

Two factors contribute heavily to these discrepancies. The first is V_g, which Stalkup determined by direct calculation. Previously, it was demonstrated that this technique results in a value of V_g which is consistently low by 10 to 20%. A low V_g, of course, results in a high $(V_R - V_g)$ and thus a low *K* value which, as stated, is the direction of the observed deviation of Stalkup's work from the present effort. As an illustration of the magnitude of error which might be introduced into K_3 from an error in V_g, the following brief analysis of Stalkup's original data is given. At 800 to 1,000 lb./sq.in.abs. and a temperature

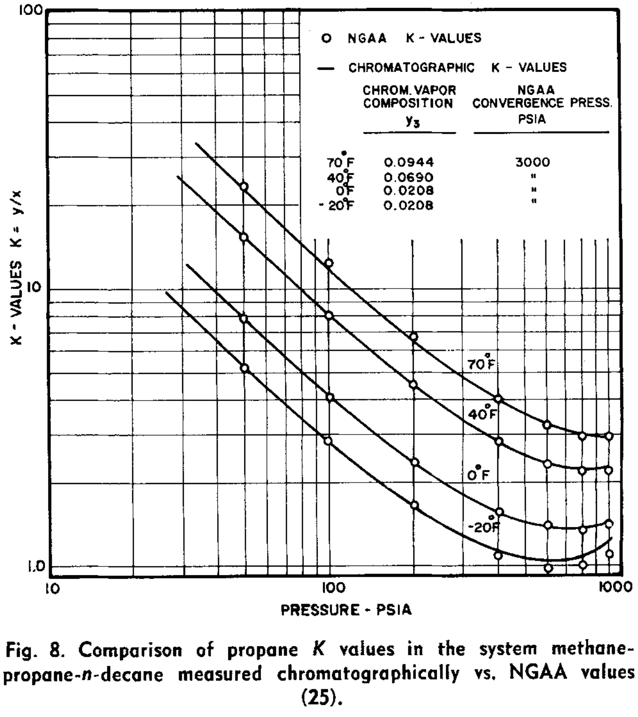

Fig. 8. Comparison of propane *K* values in the system methane-propane-*n*-decane measured chromatographically vs. NGAA values (25).

of 70°F. an error of 20% in V_g produces an error of 7 to 10% in K_3. At 100 to 400 lb./sq.in.abs. the same error in V_g introduces a 3 to 5% error in the K value for propane. Thus, the slight discrepancies that occur between the two sources are virtually explained by considering the free gas volume used in each.

The second factor to be considered is W, the moles of fixed liquid on the column. Stalkup was not equipped to determine the loss of liquid due to evaporation by direct gravimetric techniques. Consequently, a precise knowledge of W at all times was, admittedly, not possible. Errors from this source might affect K_3 in either direction, so its exact contribution cannot be analyzed as directly as that of V_g. Nevertheless, it undoubtedly enters into the discrepancies.

Price and Kobayashi (28): Consistency of *K* Values for Propane in the System Methane-Propane-*n*-Decane

The above investigators have thoroughly studied the methane-propane binary system by a classical vapor recirculation method. Their data furnish a limiting value for the K value of propane as a function of propane composition in the liquid phase. It may be seen from Figures 5 and 6 that the data of this work is quite consistent with that of Price and Kobayashi. The consistency at low pressures is perhaps the most significant, since little or no change in K value with composition is expected in this region. That is to say, essentially the same propane K value should be valid over the entire concentration range and should be that obtained by Price and Kobayashi. This is, in fact, the case, thus further establishing the GLPC K values as true equilibrium information. In Figure 7 cross plots from the K vs. x_3 plots demonstrate the consistency of the data with respect to temperature.

NGAA (25): *K* Value for Propane in the Methane-Propane-*n* Decane System

Figures 8 and 9 are comparisons of propane K values measured chromatographically with those presented by the Natural Gasoline Association of America. Chromatographic values for the cases of propane at an intermediate vapor phase concentration and propane at a fairly high concentration are compared with those corresponding to convergence pressures of 3,000 and 2,000 lb./sq. in. abs. presented by the NGAA. Agreement is seen to be substantial, with no more than 12% deviation between the two sources.

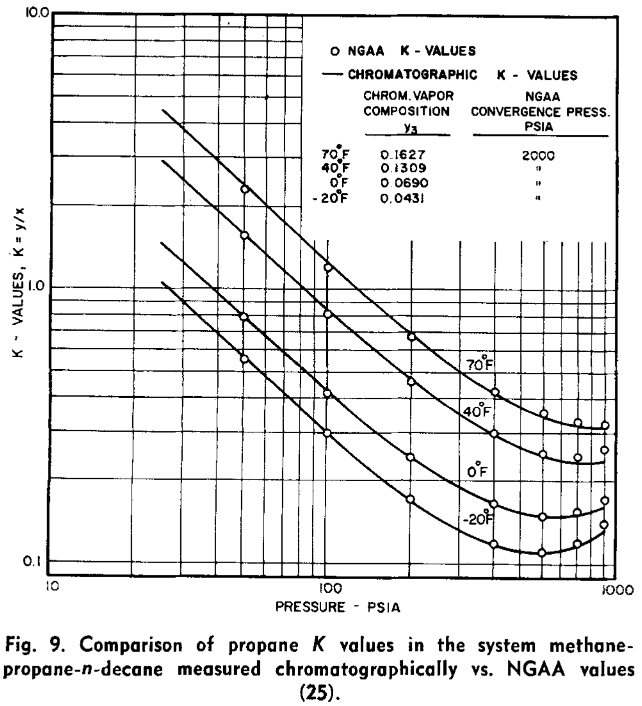

Fig. 9. Comparison of propane *K* values in the system methane-propane-*n*-decane measured chromatographically vs. NGAA values (25).

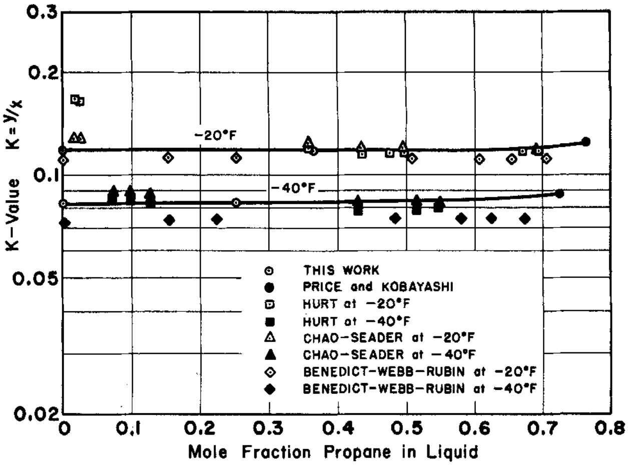

Fig. 10. *K* value for propane as a function of propane concentration in the liquid phase in the system methane-propane-*n*-heptane at 400 lb./sq.in.abs.

Hurt (12), Chao-Seader, and BWR *K* Values for Propane in the System Methane-Propane-*n*-Heptane

The primary incentive for studying the methane-propane-*n*-heptane system was the need to rectify the compositional dependence of the propane K value in the region of low propane concentration in both phases. Hurt has thoroughly investigated this system using the vapor-recycle equilibrium cell followed by sampling and chromatographic analyses. However, in the region of low propane content, Hurt apparently encountered serious sampling and analysis problems, resulting in scattered data. Since the GLPC technique is especially suited to the case of a solute at infinite dilution, it was felt that this approach could be used to establish more firmly the propane K value in the low propane concentration area. Furthermore, by eluting a methane-propane mixture through a heptane GLPC column, a point on Hurt's plot of log K_3 vs. mole fraction propane in the liquid would be generated, thus furnishing for the first time a direct comparison between equilibrium coefficients determined chromatographically and those obtained by a conventional technique.

As a further check on the consistency of the chromatographic data, K values for propane in the methane-propane-*n*-heptane system have been predicted from the Chao-Seader correlation (*8*). The correlation developed by

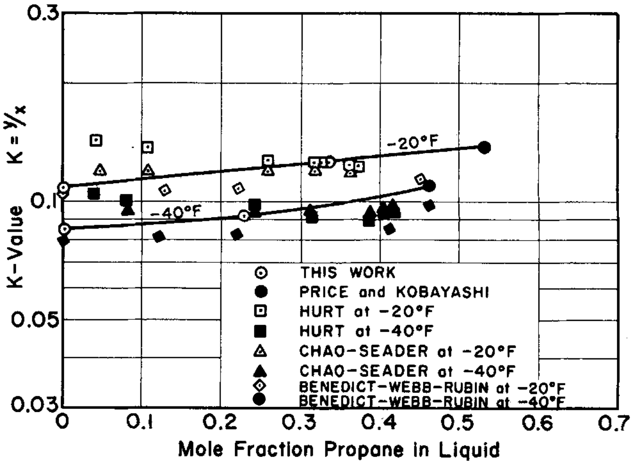

Fig. 11. *K* value for propane as a function of propane concentration in the liquid phase in the system methane-propane-*n*-heptane at 800 lb./sq.in.abs.

Chao and Seader (7) is based upon estimation of the activity coefficient from an empirical solubility parameter. Figures 10 and 11 compare the K value information obtained from the four sources: references *7, 12, 4,* and *28.*

In the region of moderate to high propane concentration in the liquid phase substantial agreement is observed between all three sources. In the region of low propane concentration agreement is best between the data of this work and that of the Chao-Seader correlation. The results of the propane K values obtained by the BWR equation (*4*) with adjusted Co's are somewhat less satisfactory (*36*). Again it is seen that the experimental K values for propane from this study are consistent with the methane-propane tie point from the work of Price and Kobayashi (*28*).

CONCLUSIONS

Validity, Advantages, and Limitations of the GLPC Method

It is strongly felt that the preceding comparisons firmly establish K values obtained by the GLPC technique as actual equilibrium quantities, completely consistent with those obtained from conventional static measurements. Furthermore, the above conclusion holds not only in the region of infinitely dilute solute concentration but also over the entire range of finite solute concentration.

Use of the GLPC technique affords certain advantages over the conventional static methods. An infinite dilution K value may be obtained devoid of the errors inherent in tedious sampling and analysis. Equilibrium studies may be conducted in the finite concentration region with only a single gas-phase analysis and no liquid-phase analyses required. The gas phase may be set at any desired, predetermined concentration. The time required to define an isotherm is reduced by four or five times.

However, the GLPC method is not without limitations. At its present stage of development, the technique still requires the use of a relatively nonvolatile fixed liquid phase. This limits, for the present, the types of systems to which it is applicable. Otherwise, the development of the radioactive tracer techniques presented in this work removes all barriers as to the complexity of the vapor phase. Use of Equation (7) allows the use of an N-component elution gas with radioactive samples of each component.

ACKNOWLEDGMENT

The authors gratefully acknowledge the Petroleum Research Fund of the American Chemical Society for the major financial support of this research. Acknowledgment is also made to the National Science Foundation for its support of the radioactive tracer experiments. The methane used in this study was donated by the Tennessee Gas Transmission Company and the Associated Oil and Gas Company. The propane, *n*-heptane, and *n*-decane were provided gratis by the Phillips Petroleum Company.

NOTATION

C_{gi} = gas-phase concentration of component i, moles/vol.
C_{Li} = liquid-phase concentration of component i, moles/vol.
f_a = volumetric flow rate at 1 atm. and 300°K.
f_{HP} = volumetric flow rate at column conditions of pressure and temperature
H_i = equilibrium partition coefficient, moles/vol. in mobile phase/moles/vol. in liquid phase
K_i = vapor-liquid equilibrium coefficient defined as the ratio of mole fraction in the vapor phase to that in the liquid phase for a given component at equilibrium
N = index number for components in the elution gas
R = gas constant
$\overline{R}$ = ratio of $(V_R - V_g)$ to $(V_R^* - V_g)$
t_R = retention time corrected for equipment response time and low pressure dead volume
T = system temperature (absolute)
T_a = ambient temperature (absolute)
V_L = total liquid phase volume in column
V_{Ri} = correct retention volume measured by thermal conductivity detection for component i, that is the product of the time required for a solute peak to appear in the effluent and the gas flow rate at column conditions
V_{Ri}^* = correct retention volume measured by ionization produced by a radioactive solute of component i
V_g = total system free gas volume
W = total moles of nonvolatile fixed liquid in the GLPC column
x_i = mole fraction of component i in the liquid
y_i = mole fraction of component i in the vapor
Z_M = compressibility factor of elution gas
πa = ambient pressure, atm.
π = system pressure, atm.

LITERATURE CITED

1. Anderson, J. R., and K. H. Napier, *Australian J. Chem.*, **10**, 250-255 (1957).
2. Aris, Rutherford, and N. R. Amundson, *A.I.Ch.E. Journal*, 3, 280 (1957).
3. Baudat, N. P., Brown, and Root, Inc., Houston, Texas, Private communication (July, 1963).
4. Benedict, M., G. B. Webb, and L. C. Rubin, *Chem. Eng. Progr.*, **47**, 419 (1951).
5. Brown, G. G., D. L. Katz, G. G. Oberfell, and R. C. Alden, "Natural Gasoline and the Volatile Hydrocarbons," pp. 32-33, Sponsored by NGAA, Tulsa, Oklahoma (1948).
6. Carberry, J. J., and R. H. Bretton, *A.I.Ch.E. Journal*, 4, No. 3, p. 367 (1958).
7. Chao, K. C., and J. D. Seader, *ibid.*, **7**, 598 (1961).
8. Chao, K. C., Standard Oil Company of California, Richmond, California, Private communication.
9. DePriester, C. L., *Chem. Eng. Progr. Symposium Ser. No. 7,* **49** (1953).
10. Gleuckauf, E., *Trans. Faraday Soc.*, **51**, 34 (1955).
11. Helfferich, P., *J. Chem. Ed.*, to be published.
12. Hurt, L. J., Ph.D. thesis, Rice University, Houston, Texas (July, 1962).
13. Keulemans, A. I. M., "Gas Chromatography," 2 ed., Reinhold, New York (1959).
14. Koonce, K. T., Ph.D. thesis, Rice University, Houston, Texas (Nov., 1963).
15. ———, and Riki Kobayashi, *J. Chem. Eng. Data*, **9**, 490 (1964).
16. Kwantes, A., and G. W. A. Rijnders, "Gas Chromatography," D. H. Desty, ed., Academic Press, New York (1958).
17. Lange, N. A., "Handbook of Chemistry," 8 ed., Handbook Publishers, Sandusky, Ohio (1952).
18. Lopez, Mellado G., M.S. thesis, Rice University, Houston, Texas (Feb., 1959).
19. ———, and Riki Kobayashi, *Petrol. Refiner* (Feb., 1960).
20. Martin, A. J. P., *Soc. for Anal. Chem. Analyst*, **81**, 52 (1956).
21. ———, and A. T. James, *Biochem. J.*, **50**, 679-90 (1952).
22. Martin, A. J. P., and R. L. M. Synge, *ibid.*, **35**, 1358-68 (1941).
23. McHenry, K. W., and R. H. Wilhelm, *A.I.Ch.E. Journal*, No. 1, p. 83 (1957).
24. Mueller, W. H., T. W. Leland, Jr., and Riki Kobayashi, *ibid.*, **7**, No. 2, p. 267 (1961).
25. Natural Gasoline Association of America "Equilibrium Ratio Data Book," Tulsa, Oklahoma (1957).
26. Porter, P. E., C. H. Deal, and F. H. Stross, *J. Am. Chem. Soc.*, **78**, 2999-3006 (1956).

27. Preston, S. T., "Vapor-Liquid Equilibrium Constants from Gas Chromatography Data," Proceedings of NGAA (April, 22-24, 1959).
28. Price, A. Roy, and Riki Kobayashi, *J. Chem. Eng. Data,* 4, No. 1, p. 40 (1959).
29. Rangel, Enrique T., M.S. thesis, Rice University, Houston, Texas (Sept., 1956).
30. Sage, B. H., and W. N. Lacey, "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," Monograph on API proj. 37, American Petroleum Institute, New York (1950).
31. Stalkup, F. I., Ph.D. thesis, Rice University, Houston, Texas (Aug., 1961).
32. ———, and H. A. Deans, *A.I.Ch.E. Journal,* 9, 118 (1963).
33. Stalkup, F. I., and Riki Kobayashi, *ibid.,* p. 121.
34. Stoddart, C. T. H., and P. H. Evertt, *Trans. Faraday Soc.,* 57, 746 (1961).
35. VanDeemter, J. J., F. J. Zuiderweg, and A. Klinkenberg, *Chem. Eng. Sci.,* 5, 271 (1956).
36. Wolf, Frank, Humble Oil and Refining Company, Houston, Texas, Private communication.

Manuscript received February 10, 1964; revision received September 22, 1964; paper accepted September 23, 1964.

An Experimental Investigation of Air Bubble Motion in a Turbulent Water Stream

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The motion of individual air bubbles in a water stream flowing turbulently in a 4 in. × 4 in. vertical conduit is investigated by photographic means. The bulk water velocity ranges from 40.8 to 267 cm./sec., corresponding to a system Reynolds number range of 48,600 to 386,000. Both tap and demineralized water were used at or near room temperatures. Air bubbles range from 0.038 to 0.70 cm. in equivalent radius and the corresponding bubble Reynolds number based on relative velocity ranges from 58 to 4,500.

The results indicated that the bubble relative velocity in a turbulent water stream is similar to the rise velocity of single bubbles through a quiescent liquid. It was found to be practically independent of the system Reynolds number for bubbles having an equivalent radius above 0.3 cm. Large fluctuations in the bubble velocities were noted in all cases. The drag coefficient is, in general, lower for the demineralized water tests than for tap water when the bubble Reynolds number is below 2,000. Above this value, a mergence of the drag coefficients for all tests occur with a peak of approximately 2.0 at a bubble Reynolds number of 3,000, which is lower than the nonflow value of 2.6.

The behavior of bubble motion in a turbulent stream of liquid plays an important role in predicting the characteristics of a boiling reactor system. It also finds its importance in many physical and chemical processes involving mass, momentum, and heat transfer between the liquid and gaseous phase.

Although a great deal of effort has been spent by many investigators in different countries to gain an understanding of the behavior of bubble motion in calm liquids, information on the velocity, drag, and shape is practically nonexistent when the bubble is moving in a turbulent stream (*1*).

The motion of air bubbles in calm liquids has been studied both experimentally and theoretically during the past six decades. Early experiments performed by Allen (*2*) showed that for small air bubbles rising in water and in aniline, good agreement was found with Stokes law when the bubble Reynolds number was less than 2. Miyagi (*3*) studied the motion of single air bubbles in water over a radius range of 0.025 to 0.4 cm. His data on terminal velocity indicated a maximum at a bubble radius of approximately 0.15 cm., followed by a slight drop up to bubble radius of 0.3 cm. Larger bubbles exhibited a terminal velocity independent of bubble radius. Davies and Taylor (*4*) measured the shape and rate of rise of extremely large spherical cap-shaped air bubbles in water

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