High-Pressure Phase-Equilibrium Studies by Gas-Liquid Partition Chromatography

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An elution gas that might be either a single component or a binary mixture, but which in any case was appreciably soluble in the fixed liquid phase on the column matrix material, was used to form a multicomponent liquid phase within the chromatographic column. Vapor-liquid equilibrium was studied both with the solute of interest at essentially infinite dilution conditions and with the solute present at some finite concentration in both phases. From the elution data vapor-liquid equilibrium ratios, or *K* values, were calculated by expressions relating the solute retention volume to the solute *K* value in the vapor-liquid system maintained within the chromatographic column.

Data were taken for the solutes ethane, propane, and *n*-butane at infinite dilution in the methane-*n*-decane system at 160°, 70°, 40°, 0°, and —20°F from 20 to 2,000 lb./sq. in.; for propane at infinite dilution in methane-*n*-hexadecane at 70°F and 20 to 200 lb./sq. in.; and propane in the system methane-propane-*n*-decane at 40°F from 20 to 460 lb./sq. in. The univariant gas-liquid-solid locus was experimentally determined for the methane-*n*-decane binary system.

The chromatographically determined *K* values for *n*-butane at infinite dilution in methane-*n*-decane were compared with published static equilibrium values and found to be in substantial agreement. Activity coefficients calculated from the data for all the solute isotherms were compared at atmospheric pressure with the results of the Brönsted and Koefoed relation for estimating activity coefficients of hydrocarbons, and close agreement was again found.

This paper presents the results of some investigations designed to increase the scope of gas-liquid partition chromatography (GLPC) as an experimental means for determining phase-equilibrium information. If a GLPC method could be made applicable under a wide variety of conditions, the ease and rapidity in making a GLPC measurement would introduce a method of great application for obtaining phase-behavior data, which at present must be experimentally measured with rather elaborate equipment.

In gas-liquid elution chromatography a nonvolatile liquid phase is fixed on the surface and in the pore space of an inert, porous solid support. This liquid-containing solid support is packed into a column, and a gas phase is caused to flow through the column. A solute which distributes itself between both phases is injected into the column and eluted through by the gas phase. In this way a vapor-liquid system is established within the packed column composed of the mobile elution gas, the immobile liquid on the column packing material, and the solute being eluted through the column.

Martin and Synge (*16*) in their pioneering work on gas-liquid partition chromatography developed an expression relating the retention volume of a solute *k* to its partition coefficient by using a theoretical plate model for the GLPC column. This expression is

$$V_{Rk} = V_g + V_L/H_k \qquad (1)$$

and has been verified by more sophisticated derivations by several authors (*7*, *25*).

That the partition coefficients calculated from Equation (1) by means of GLPC elution data were consistent with partition coefficients obtained from static methods of measurement was established by Porter, Deal, and Stross (*18*). Using a wide range of gas velocity, column length, and amount of nonvolatile liquid on the packing as well as different types of solid support these authors determined partition coefficients chromatographically for *n*-heptane and 2-propanol in diisodecyl phthalate and compared them with partition coefficients determined from static methods of measurement. The agreement between the results obtained by the two methods was good, indicating that column variables within certain limits did not influence the value of the partition coefficient determined by the chromatographic method and that equilibrium results were indeed obtained.

The idea of calculating equilibrium partition coefficients from GLPC elution data was further investigated by Anderson (*1*) and Anderson and Napier (*2*), who found substantial agreement between chromatographic and static values for benzene and cyclohexane in polyethylene glycol.

Other quantities characterizing the behavior of a solute in a vapor-liquid system may be calculated from the partition coefficient for Equation (1).

Several authors (*13*, *24*) have calculated activity coefficients from the GLPC elution data and found these values in agreement with those measured by static means.

Some work has previously been performed in determining vapor-liquid equilibrium ratios, or *K* values, from GLPC elution experiments. Rangel (*20*) measured *K* values for methane and propane in *n*-decane which he found in approximate agreement with values predicted from the DePriester charts (*6*). Preston (*19*) used the partition coefficients obtained by Kwantes and Rijnders (*13*) to calculate *K* values for light hydrocarbons in other paraffin hydrocarbons. Lopez (*14*, *15*) found GLPC *K* values for methane, ethane, propane, and *n*-butane in *n*-dodecane to range from close agreement with values in reference *17* for butane to serious disagreement for methane.

All of the above chromatographic vapor-liquid studies were made with a gas phase such as nitrogen, hydrogen, or helium that was essentially insoluble in the nonvolatile liquid phase. Thus the partition coefficients so determined were for the solute at essentially infinite dilution in the one-component liquid phase. These studies were also made at pressures not greatly removed from 1 atm.

It will be shown in later sections of this paper how the GLPC method for determining *K* values may be extended to include a pure elution gas that is appreciably soluble in the fixed liquid phase and an elution gas mixture whose components are all soluble in the original nonvolatile liquid placed on the column packing. It will also be shown that the GLPC method may be extended to pressures up to 2,000 lb./sq.in. and temperatures in a wide range from 160° to −20°F. with true equilibrium results apparently still being obtained for the *K* value. With these extensions the chromatographic method will be seen to be a useful tool for measuring *K* values as a function of temperature, pressure, and phase composition.

In addition to its applications to vapor-liquid studies the chromatographic method may be useful as a means for determining other types of phase behavior. For instance Rangel (*20*) has investigated the chromatographic measurement of freezing points. It will be shown here how the three-phase solid-liquid-vapor conditions of a binary system may be determined to

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Tabular material has been deposited as document 7352 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

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regions near the critical by gas chromatography.

CALCULATION OF K VALUES FROM CHROMATOGRAPHIC ELUTION DATA

Equation (1) may be used to relate K or y/x values to retention volume in the following manner.

The concentration of a solute k in the mobile elution gas phase may be expressed as

$$C_k = \frac{\pi y_k}{z_M RT} \tag{2}$$

The concentration of solute k in the immobile liquid phase may correspondingly be expressed as

$$w_k = \frac{W x_k}{V_L} \tag{3}$$

where for the moment it will be assumed that the elution gas is not itself soluble in the fixed liquid phase.

The ratio of Equations (3) and (2) is by definition the equilibrium partition coefficient of Equation (1), providing y and x are equilibrium values. If the ratio of (3) and (2) is substituted into Equation (1) for the partition coefficient and the resulting equation solved for y/x, the K value of solute k is expressed in terms of its retention volume. Thus

$$\frac{y_k}{x_k} = K_k = \frac{z_M RTW}{\pi(V_{Rk} - V_g)} \tag{4}$$

Retention volume V_{Rk} is defined as the product of the time the solute spends in traveling from the entrance to the exit of the column and the elution gas volumetric flow rate expressed as column conditions of temperature and pressure. This is the expression used by Preston (*19*), Lopez (*15*), and Rangel (*20*) to calculate K values from elution data when the elution gas was either hydrogen, helium, or nitrogen at a sufficiently low pressure to be insoluble in the fixed liquid phase

If an elution gas, either a pure component or a mixture, is used that is partially soluble in the fixed liquid phase at column conditions of temperature and pressure, Equation (4) would have to be modified to account for this solubility. If an elution gas mixture composed of N components, each of which is soluble in the nonvolatile, fixed liquid on the column packing, is flowed through a chromatographic column until an equilibrium state is reached between gas and liquid, the resulting liquid phase itself will be multicomponent. The expression for the total moles of liquid phase in the column is then

$$\frac{W}{(1 - x_1 - x_2 - \ldots - x_N)} \tag{5}$$

where the x's are the mole fractions in the liquid phase of those components dissolved from the gas phase. This expression should now be used in Equation (3) in place of W alone. The resulting form for Equation (4) is

$$K_k = \frac{z_M RTW}{\pi(V_{Rk} - V_g)(1 - y_1/K_1 - y_2/K_2 - \ldots - y_N/K_N)} \tag{6}$$

where x's have been replaced by y/K's.

Several assumptions are used in the theoretical plate model derivation of Equation (1) which must be approximated experimentally if Equation (1) and consequently Equation (6) are to be used to calculate solution equilibrium properties:

1. The column is equivalent to a large number of equilibrium plates.
2. The partition coefficient is constant throughout the range of concentrations encountered.
3. The sample volume upon introduction into the column occupies only a negligibly small portion of the column volume.
4. The pressure remains constant along the column length, that is there is only a negligible pressure drop.
5. The solute sample molecules are at all times distinguishable from other molecules in the column, and the retention volume in Equation (6) is for the peak in the distribution of the original sample molecules as they emerge from the column.

Experimentally assumption 1 may be approximated by proper choice of column properties and operating conditions. The influence of gas velocity, column size, amount of liquid on the packing, type of solid support, and pressure drop has been discussed in the literature (*9, 18, 24*).

The injected solute band continually changes its composition as it is eluted through the column. Experimental approximation of assumption 2 requires that the concentration of solute introduced to the column be small enough so that as the band of solute travels through the column the partition coefficient is not appreciably influenced by the changing composition of the solute band, if the partition coefficient is sensitive to concentration.

The influence of sample volume on the measured peak retention time has been discussed mathematically in the literature (*18, 25*). Experimentally the sample volume may be decreased until a point is reached where assumption 3 is approximately obeyed, and further decrease of sample volume causes no appreciable effect on the measured solute retention volume.

The assumption of negligible pressure drop may be approximated experimentally by using short, loosely packed columns and low flow rates.

Assumption 5 is of more concern in carrying out experimental determinations. In the derivation of Equation (1) the column is considered not to contain any molecules similar to the sample molecules prior to sample introduction. For example if an elution gas were a mixture of components A and B, Equation (1), and consequently Equation (6), would be valid if a different molecular species C were introduced as a sample, but not if either species A or B were injected at some composition different from the elution gas composition. For this reason Equation (6) would be useful only for calculating the K value of a sample species k that was different from any molecular species present in the elution gas, and the K values under conditions of the experiment for all the molecular species present in the elution gas would be needed from some other source for substitution into the denominator of the right-hand side of Equation (6). If a sample small enough were used such that conditions 2 and 3 above could be approximated, the K value calculated by Equation (6) from elution data would be for component k at infinite dilution in the vapor-liquid system maintained in the chromatographic column before k is introduced.

The possibility of injecting into a chromatographic column a sample composed of a molecular species already present in the elution gas, although differing in composition from the elution gas, has been considered mathematically (*5, 23, 10*). For the case of a constant composition binary elution gas and with the assumptions of point equilibrium and negligible longitudinal diffusion an analytical solution may be derived for the rate at which a concentration perturbation caused by the injection of a negligibly small volume of one of the elution gas components is eluted through the GLPC column (*5*). This expression is

$$\left(\frac{dt}{dx}\right)_{y_1} = \left\{\frac{1}{W_x} + \frac{(1-\epsilon) w_{N+1} K_1 K_2}{W_x \epsilon C} \cdot \frac{(K_1 - 1) y_1 \left[1 - y_2 \dfrac{d \ln K_2}{d y_2}\right] + (K_2 - 1) y_2 \left[1 - y_1 \dfrac{d \ln K_1}{d y_1}\right]}{[K_2 K_1 - K_1 + y_1 (K_1 - K_2)]^2}\right\} \tag{7}$$

where the subscripts 1 and 2 refer respectively to components 1 and 2 of the elution gas.

If now conditions are such that $\left| y_k \frac{d \ln K_k}{d y_k} \right| << 1$, Equation (7) may

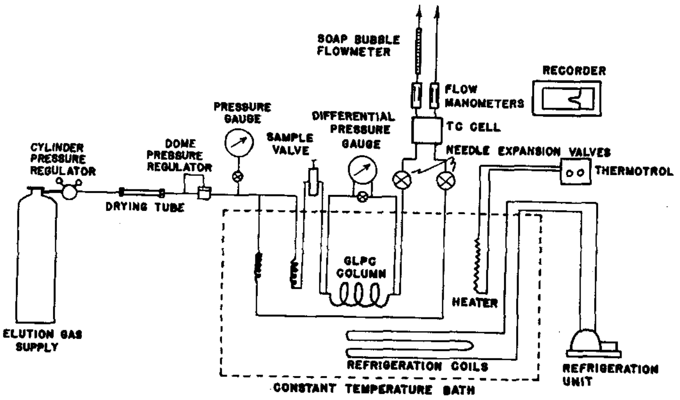

Fig. 1. Schematic diagram of the overall high pressure GLPC apparatus.

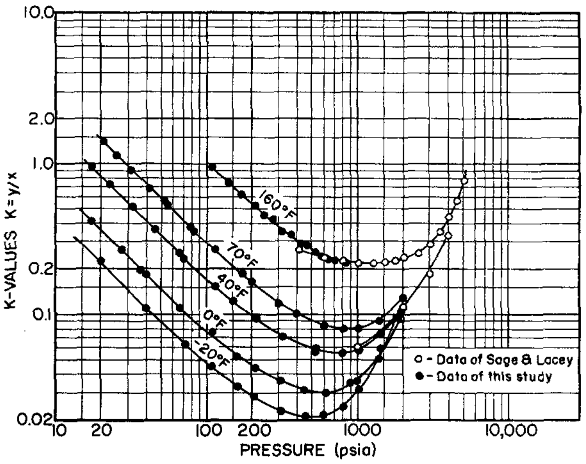

Fig. 2. *K* values for *n*-butane at infinite dilution in the system methane-*n*-decane.

be simplified and related to retention volume to give the expression

$$V_{R_1} - V_g = \frac{z_M\,RT\,W\,K_1K_2}{\pi} \left(\frac{K_2 - 1 + y_1\,(K_1 - K_2)}{[K_1K_2 - K_1 + y_1\,(K_1 - K_2)\,]^2}\right) \quad (8)$$

Equation (8) may be solved for the K value of component 1 in terms of its retention volume V_{R_1} and the K value of component 2. Since only one independent equation is obtained for the case of a binary elution gas, the K value of component 2 must be available from some additional source before K_1 can be calculated from Equation (8).

The restrictions on the terms $y_k \dfrac{d \ln K_k}{d\,y_k}$ in Equation (7) may not be as limiting as might be supposed. For those conditions where $K_2 >> 1$ and $y_1 << 1$ the value of the term $\left[1 - y_2 \dfrac{d \ln K_2}{d\,y_2}\right]$ may vary considerably before more than a negligible error is introduced in the calculation of K_1 (it being here assumed that $K_2 > K_1$). The calculation of K_1 is more sensitive to the value of $\left[1 - y_1 \dfrac{d \ln K_1}{d\,y_1}\right]$. However, as pointed out in the article by Deans and Stalkup (5) for those cases where $y_1 \dfrac{d \ln K_1}{d\,y_1}$ cannot be neglected, experiments may be started at vanishingly small values of y_1 to give an initial value of K_1. Experiments may then be performed by increasing the value of y_1 in the elution gas in small increments and through the use of Equations (7) and (8) and an iteration procedure generate the curve of K_1 vs. y_1.

If y_1 in Equation (8) is allowed to decrease to zero, that is the elution gas becomes pure component 2 into which a solute differing from component 2 is injected, the equation for calculating the K value of this solute becomes

$$K_1 = \frac{z_M\,RTW}{\pi\,(V_{R1} - V_g)\,(1 - 1/K_2)} \quad (9)$$

which is the same result as Equation (6) when it is written for an elution gas composed only of component 2 into which a component 1 is injected.

If now a single component gas is flowed through a GLPC column until a state of equilibrium is reached between it and the nonvolatile liquid and a very small sample of a solute of different molecular species than the elution gas is injected into the column, Equation (9) may be used to calculate the K value of this solute in the vapor-liquid equilibrium system maintained within the column, and this K value would be for the solute at near infinite dilution conditions in the vapor-liquid system at the column temperature and pressure. However some information about the K value of the elution gas must already be known.

On the other hand if a binary elution gas is flowed through the column until equilibrium conditions are attained and a small inlet disturbance of the concentration of one of the components is caused by a sample injection, the K value of this component may be calculated from Equation (8), provided K values for the other gas-phase components are available from some other source and the restrictions on $y_k \dfrac{d \ln K_k}{d\,y_k}$ previously discussed are met.

Since the component whose K value is being calculated by Equation (8) is present at some finite concentration in both the gas and liquid phases, elution chromatography can thus offer a means for studying the influence of composition on K value. For instance at the same temperature and pressure different elution gas mixtures of the same two components could be used to establish a wide range of gas- and liquid-phase compositions within the GLPC column. Equation (8) could then be used to calculate K values in which temperature, pressure, and composition were variables, rather than only for the component at a concentration of near infinite dilution in the system.

It should be mentioned that Equation (6) might offer another means of calculating K values for a solute at other concentrations in the system than infinite dilution. It will be recalled that Equation (6) applies to those cases where the sample molecules that are introduced into the GLPC column are at all times distinguishable from other molecules that are present in the column. That is to say Equation (6) is applicable when the retention time that is measured is the time the original sample molecules spend in the column rather than for the time the perturbation in solute concentration spends in the column. If however a sample were injected that was composed of radioactive isotopes of a component present in the elution gas, and this sample detected as it emerged from the column by a radiation detector, the retention volume calculated from the retention time measured in this manner would be that required by the conditions for using Equation (6). If now for the case of a binary elution gas two samples of one of the components present in the elution gas were injected, one a radioactive isotope and the other nonisotopic, the K value predicted from Equation (6) with the retention time for the isotopic molecules in the column should be the same as the K value predicted by Equation (9) with the retention time for the concentration perturbation caused by injection of the nonisotopic molecules. Agreement in the K values determined by these two methods has been demonstrated (12).

DETERMINATION OF FREEZING POINTS FROM CHROMATOGRAPHIC ELUTION DATA

Gas chromatography offers the possibility of studying other phase behavior. It might be possible for example to conveniently determine the solid-liquid-gas equilibrium conditions in this manner. As the elution gas flows through the GLPC column at a near constant pressure (it is assumed that any pressure drop causes a negligible decrease in the total pressure), the temperature of the column may be lowered in small increments, and a small sample of a solute eluted through the column with its retention time being noted. For temperatures above the freezing point of the liquid phase the solute sample would interact only between a gas and a liquid phase, and the retention volume calculated from the retention time measurement would obey the relation of Equation (6) for vapor-liquid equilibrium, if one assumes a solute not present in the elution gas was introduced. For temperatures well below the freezing point no liquid phase would be present in the column. The solute would then interact only between vapor and solid phases, and the retention volume would be expected to obey a relationship different from Equation (6). A plot of retention volume vs. temperature at constant pressure might then be expected to exhibit some discontinuity between the conditions of entirely vapor-liquid or entirely vapor-solid equilibrium prevailing in the column, and this point of discontinuity would be the freezing point of the liquid phase. Rangel (*20*) first investigated this method of measuring freezing points with a column packed with *n*-decane impregnated firebrick through which hydrogen was flowing at low pressures. At the low pressures employed in his experiments the liquid phase was pure decane, and Rangel was able to compare the freezing point determined chromatographically by the procedure outlined above with previously tabulated values. Excellent agreement was found. With very small samples the method should be independent of which solute was used, and plots of retention volume vs. temperature at constant pressure for different solutes should all show a discontinuity at the same temperature, an occurrence which Rangel verified.

EXPERIMENTAL APPARATUS

TABLE 1. COMPARISON OF INFINITE DILUTION, ATMOSPHERIC, LIQUID-PHASE ACTIVITY COEFFICIENTS FOR *n*-BUTANE IN METHANE-*n*-DECANE SYSTEMS

Temperature, °F.	Chromatographic	Brönsted and Koefoed
160	0.898	0.935
70	0.963	0.960
40	0.980	0.973
0	0.987	0.973
—20	0.990	0.976

A schematic diagram of the experimental apparatus used in this investigation is given in Figure 1. The apparatus is quite similar to a conventional GLPC unit used in analytical work except that tubing, fittings, valves, etc. are of stainless steel for use at high pressures and that all connections are for ⅛ in. stock to minimize dead space.

A valve capable of introducing small gaseous samples into the elution gas steam flowing at high pressures was needed. It was constructed of a brass body into which a stem fitted with O-rings was inserted. The O-rings partitioned off various parts in the valve body, and depending on whether the stem was in the up or down position, the gas flow path was either straight through the valve or diverted through a sample tube. The valve as it came from the manufacturer operated satisfactorily up to 500 lb./sq.in. By machining a new stem of 0.0175 in. greater diameter and using hard rubber O-rings one could employ the valve at pressures up to 2,000 lb./sq.in. This valve was found to work more satisfactorily outside the liquid temperature bath in which the column was immersed as small abrasive particles in the bath kept working past the stem to damage the O-rings.

Pressure regulation in the GLPC column was achieved with a sensitive diaphragm pressure regulator placed just upstream from the sample introduction valve. Flow rate through the column and reference side of the system was achieved with stainless steel microneedle valves which served to break the elution gas pressure down to atmospheric pressure as well as control flow rate. These valves were also placed outside the temperature bath, since at some of the lower bath temperatures slight condensation of the elution gas tended to occur upon expansion through the valve.

The thermal conductivity detector used in this work was a conventional hot-wire model. It was mounted in the system past the microneedle flow control and pressure breakdown valves and was operated at atmospheric pressure.

DISCUSSION OF EXPERIMENTAL RESULTS

K Values for the Solute Present at Essentially Infinite Dilution in the Liquid Phase

Equation (9), and thus Equation (6) for the case of a one-component elution gas, was tested experimentally by impregnating firebrick with pure *n*-decane, flowing methane through a GLPC column packed with this material and measuring the retention times of ethane, propane, and *n*-butane as solutes. Some data were additionally taken for propane retention times in a GLPC column containing *n*-hexadecane and through which methane was flowing. The condition of the experiments was such that the assumptions inherent in Equation (9) were observed regarding negligible influence on the peak retention time of amount and volume of sample and negligible influence of pressure drop. Under these experimental conditions the data taken would be for the respective solutes at infinite dilution in the methane-decane or methane-*n*-hexadecane binary systems. The *n*-decane data were taken for 70°, 40°, 0° and —20°F. isotherms for all the solutes and with *n*-butane retention times in decane also being measured at 160°F. Pressure was varied from atmospheric to approximately 2,000 lb./sq. in. The propane in hexadecane retention times were only measured at 70°F.

The free gas volume was both calculated directly by subtracting the nonporous solid firebrick volume and liq-

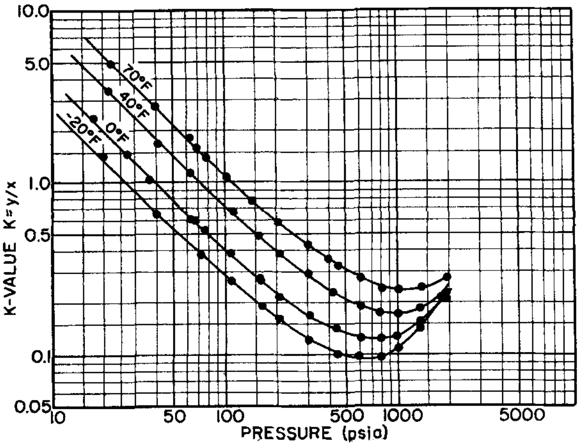

Fig. 3. *K* values for propane at infinite dilution in the system methane-*n*-decane.

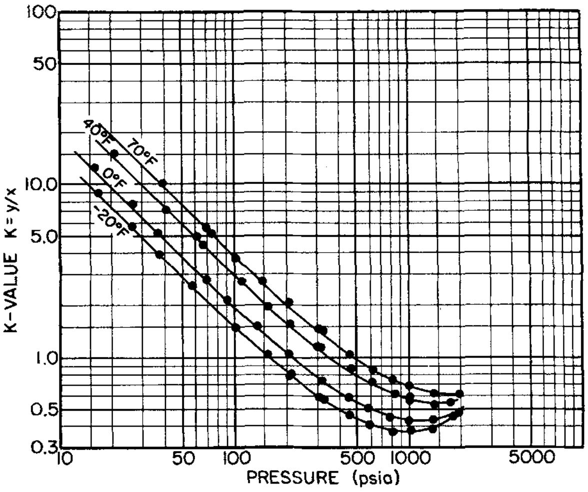

Fig. 4. *K* values for ethane at infinite dilution in the system methane-*n*-decane.

TABLE 2. COMPARISON OF INFINITE DILUTION, ATMOSPHERIC, LIQUID-PHASE ACTIVITY COEFFICIENTS FOR *n*-PROPANE IN METHANE-*n*-DECANE SYSTEM

Solvent	Temperature, °F.	Chromatographic	Brönsted and Koefoed
n-Decane	70	0.933	0.940
n-Decane	40	0.948	0.948
n-Decane	0	0.992	0.962
n-Decane	—20	0.985	0.968
n-Hexadecane	70	0.837	0.810

uid-phase volume from the empty column volume and by measuring the retention volume of some inert gas such as helium which should not be held up by the liquid phase. The density of the nonporous firebrick was measured by displacing kerosene in a centrifuge tube with a weighed amount of firebrick, centrifuging, and observing the volume of liquid displaced. Agreement between these two methods was not very satisfactory, the results of the two methods differing sometimes by as much as 10%, and appreciable error could be introduced into the final calculated result by the uncertainty in the value of V_g, unless the retention volume of the solute were appreciably greater than V_g. Thus the more volatile the solute is, the greater would be the expected error introduced into the final result by the error made in determining V_g. For this work the retention volumes of butane were so great that no significant error in the final result would be introduced by the error made in determining V_g. The retention volumes of ethane however were such that a possible approximate 8% error could have been introduced in the final calculated K value if the error in V_g was as great as the difference in the values given by the two methods for estimating this quantity. The V_g values determined by direct calculation with the liquid, solid, and empty column volumes were used in this work.

It can also be seen from Equation (9) that the compressibility of the elution gas must be known. However the error made in estimating z_M does not actually cause a correspondingly large error in the calculated K value as would be indicated at first glance by Equation (9). The flow rates in these experiments were measured at atmospheric pressure and room temperature and had to be converted to column conditions. Therefore the quantity substituted into Equation (9) for V_{R1} would also contain z_M. This would lead to an effective cancellation of z_M between the numerator and denominator with the term only remaining as the denominator of the V_g term. Then essentially the same remarks made above about V_g would apply to z_M, and for many instances the term could be estimated with sufficient accuracy from generalized correlations.

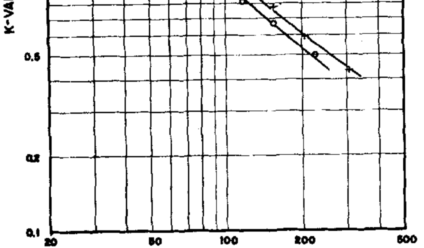

Fig. 5. Comparison of *K* values for propane at infinite dilution in *n*-decane and *n*-hexadecane at 70°F.

The methane K values used in Equation (9) were extrapolated from the methane-*n*-decane data of Sage and Lacey (*22*) with the methane-heptane data of Kohn (*11*) to guide the extrapolation.

One other correction to Equation (9) should be mentioned. At high pressures the amount of methane dissolved in the *n*-decane is appreciable and causes the liquid to swell. This in turn causes a decrease in the value of the free gas volume. Values of the partial molar volume of methane were taken from Sage and Lacey (22) and the liquid volume increase computed. This number was subtracted from the value of V_g determined at low pressures before it was used in Equation (9).

The K values calculated directly from the experimental data are illustrated in Figures 2, 3, 4, and 5.

In Figure 2 at 40° and 160°F. a comparison is made between the K values of *n*-butane at infinite dilution in the methane-*n*-decane system as determined by the chromatographic method and as reported or derived from the published data of Sage and Lacey (*21*) for the methane-*n*-butane-*n*-decane system. This latter data was taken by means of a static equilibrium technique. Sage and Lacey reported their K values as a function of a concentration parameter $x_4/(x_4 + x_{10}) = c$. For 160°F. butane K's were reported as $c = 0$. At 40°F. the Sage and Lacey K's plotted in Figure 2 were those obtained from extrapolating their published 40°F. data to $c = 0$.

It can be seen from Figure 2 that agreement is generally quite good between the data taken by the two methods. At 160°F. and 400 lb./sq.in. there is serious disagreement between the Sage and Lacey point and the chromatographic data. However if the Sage and Lacey curve were extrapolated back to low pressures with this last point, an activity coefficient that is abnormally low for this type of system would be indicated by the K values at low pressures. Also at 40°F. and 1,000 lb./sq.in. there is a slight disagreement in the data taken by the two methods. This is only on the order of 5% however.

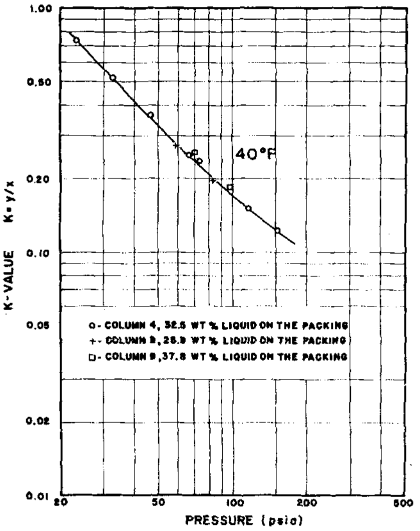

Fig. 6. Comparison of *K* values for *n*-butane at infinite dilution in *n*-decane as determined for several freshly made columns.

The chromatographic K values at atmospheric pressure taken from Figures 2, 3, 4, and 5 were used to calculate liquid phase activity coefficients by the expression

$$\gamma_{L^\circ k} = \frac{\pi \gamma_{k\pi} K_k}{P_k^\circ \gamma_{k,P^\circ k}} \qquad (10)$$

The vapor pressures used in Equation (11) were taken from Brown, Katz, Oberfell, and Alden (*4*) and the fugacity coefficients from Hougen and Watson, part II (*8*).

Activity coefficients at these temperatures were also calculated with the empirical relation of Brönsted and Koefoed (*3*). This relation is

$$\log \gamma_{L^\circ k} = D\,(n_{\text{solvent}} - n_{\text{solute}})^2$$

The above relation was proposed by Brönsted and Koefoed after studying a few binary hydrocarbon systems.

The chromatographic activity coefficients and those calculated from the Brönsted equation are compared in Tables 1, 2, and 3. The agreement is seen to be quite good.

TABLE 3. COMPARISON OF INFINITE DILUTION, ATMOSPHERIC, LIQUID-PHASE ACTIVITY COEFFICIENT FOR ETHANE IN METHANE-*n*-DECANE SYSTEM

Temperature, °F.	Chromatographic	Brönsted and Koefoed
70	0.945	0.922
40	0.937	0.935
0	0.994	0.950
—20	0.980	0.960

As a check on the reproducibility of the results from one freshly prepared GLPC column to another and also on the influence of the amount of liquid on the column packing on the final results, K value data were taken at 40°F. for n-butane over a small pressure range from three different, freshly prepared columns. These results are shown in Figure 6. The reproducibility indicated here is readily acceptable, although there is an indication that a limit on the amount of liquid that may be placed on the packing material to give satisfactory data may have been reached for the column containing 37.8 wt. % liquid on the firebrick, since the K values for this column appear slightly higher than those for the other columns.

The data taken were quite consistent internally. Figure 7 is a cross plot of the n-butane data and shows little scatter of the points.

Figure 8 compares the chromatographic K values at 1,000 lb./sq.in. with the values taken from reference *17*. At 70°F., where the disagreement in all cases is the worst, the per cent difference in the chromatographic and reference *17* K values at 1,000 lb./sq. in. is roughly 48, 18, and 10% for butane, propane, and ethane respectively.

Equation (6) was further verified by flowing a 12.1% propane in methane elution gas through the GLPC column and introducing an ethane sample. The K value used for propane in the right-hand side of Equation (6) was taken from Figure 3, and the methane K value was taken from the source mentioned previously. Although the liquid phase was in this case a ternary methane-propane-n-decane, rather than the binary methane-n-decane, for which the propane K value was measured, it was felt any compositional effect on the K values would be negligible at the low pressure at which the data were taken. The K value of ethane determined with the methane-propane mixture flowing through the column at 36.5 lb./sq. in. abs. and 40°F .was 8.2 compared with a K value of 8.0 taken from Figure 4. The close agreement verifies Equation (6) for use with elution gas mixtures as long as the retention time of the original sample molecules is used.

In summary the main experimental errors in the application of Equation (9) are in the measurement of the effective moles of nonvolatile liquid on the packing and the determination of V_g/z_M as well as the estimation of K_2, the K value of the elution gas. In the present work it is felt that the moles of original liquid placed on the packing that were effective was probably known to within 5%. Of course the longer a given column is used, the greater is the danger of error caused by solvent evaporation. In more recent investigations the weight of fixed liquid phase on the packing is being determined by removing the column from the system periodically and weighing it. The difference between the total weight and the solids involved is taken to be the liquid weight.

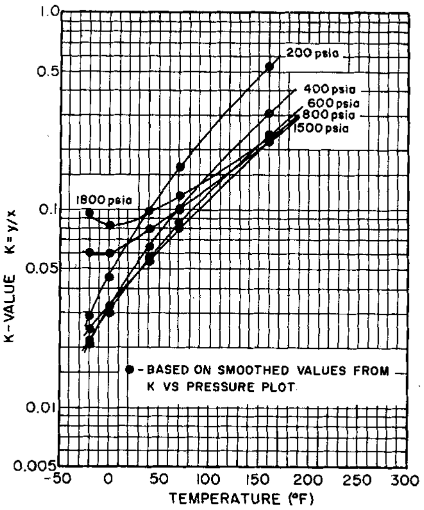

Fig. 7. K values for n-butane at infinite dilution in the system methane-n-decane.

It was mentioned previously that the error caused in the K value calculated with Equation (9) from the error in determination of V_g was probably minor for n-butane and possibly a maximum of 8% for ethane. At high pressures, where the compressibility factor may start to appreciably effect the value of V_g/z_M, the error made in estimating this combined term may cause a few per cent error in the calculation of butane K's and as high as 10 to 12% error in the calculation of ethane K's.

The influence of the error made in estimating K_2 becomes larger at higher pressures as the value of K_2 becomes smaller. However if $K_2 \geqq 10$, an error of 20% in its estimation would cause an error of less than 3% in the calculated value of K_1.

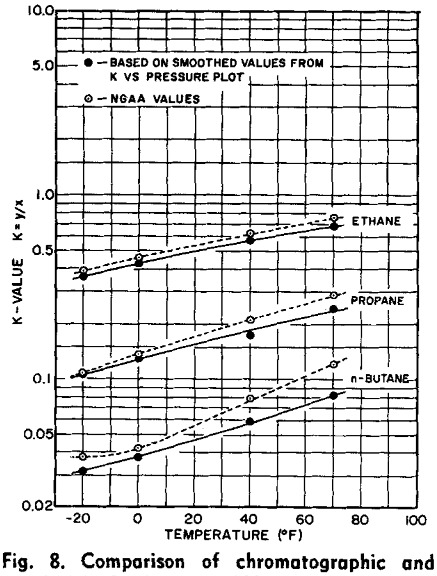

Fig. 8. Comparison of chromatographic and NGAA K values at 1,000 lb./sq. in. abs.

The other quantities V_{R_1}, T, and π may be measured as accurately as desired depending on the elaborateness of the experimental setup, and the error caused from measurement of these quantities may be kept below some desired value.

Of course the assumptions used in deriving Equation (9) such as point equilibrium, small sample volume, and a low enough sample concentration such that the partition coefficient is essentially constant throughout the range of compositions encountered must be fulfilled.

It is felt by the authors that the butane data represented by Figure 2 may have an experimental error of 3 to 5% with the higher error more likely at higher pressures. The ethane data in Figure 4 may be in error as much as 10 to 15% at the high pressures due to experimental errors.

Since the error in the butane K's extrapolated from the data of reference *20* is probably on the order of 5%, the disagreement between the chromatographic data of this work and the values extrapolated from the work of reference *21* is felt to be within the experimental error.

K Values for the Solute Present at a Finite Concentration in the Liquid Phase

Elution data were taken for propane as a solute for a number of methane-propane elution mixtures. Such mixtures contained 6.89, 12.10, and 25.55 mole % of propane. At equilibrium between the elution gas and fixed liquid phase a ternary equilibrium system would be attained in the GLPC column.

Equation (8) was used to calculate propane K values from the elution data. Several rough values for $y_2 \dfrac{d \ln K_2}{d y_2}$ in Equation (7)were estimated with the methane-n-butane-n-decane data of reference *21* as a guide. For the system studied in this work the influence of this term appears to be entirely negligible. In fact for the data reported in Figure 9 the term $\left[1 - y_2 \dfrac{d \ln K_2}{d y_2}\right]$ could be varied from 0 to 1 without causing an appreciable change in the calculated K value of propane. From the data of Figure 9 an estimate was also made of the term $\left[y_1 \dfrac{d \ln K_1}{d y_1}\right]$ in Equation (7). Under the conditions of these experiments this term also contributed only a negligible effect to the calculated K of propane represented in Figure 9.

At pressures not greatly removed from atmospheric very little influence of the K value of propane due to the presence of a finite propane concentration in the liquid phase would be ex-

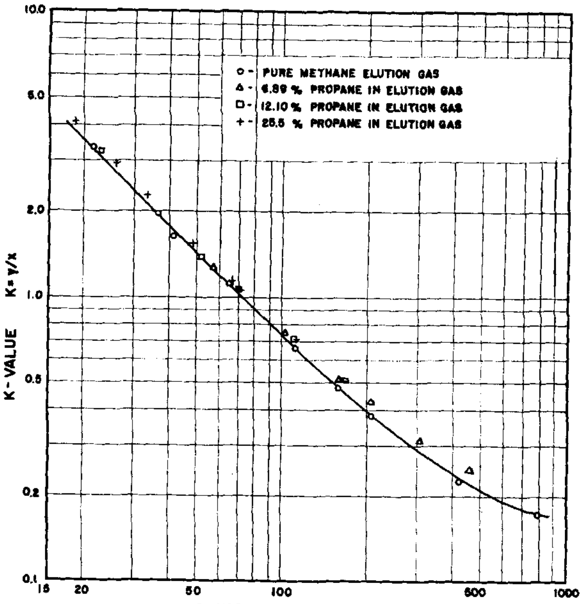

Fig. 9. *K* values for propane in the system methane-propane-*n*-decane.

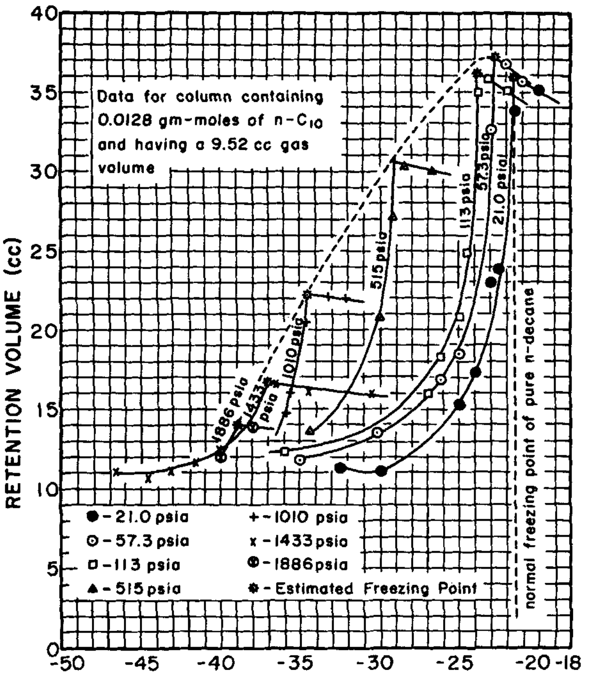

Fig. 10. Effect of temperature on retention volume at constant pressure of ethane in a methane-*n*-decane system.

pected. The propane *K* values calculated for the cases of gas phases that are mixtures would then be expected to coincide with the *K* values at infinite dilution. From Figure 9 this can be seen to be the case within a small limit of error. The *K* values calculated for the case of the 25.5% propane elution gas mixture seem to lie very slightly higher than the infinite dilution *K*'s. Since this deviation is only of the order of 4 to 5%, it approaches the limit of experimental error and may be caused by an inaccurate determination of the moles of *n*-decane on the packing material.

At pressures in the neighborhood of 150 lb./sq.in. the *K* values calculated for the 6.89% propane elution gas appear to be diverging from the infinite dilution values and to be greater than these values. This could be due to the liquid-phase composition beginning to exert an influence on the *K* value of propane. Unfortunately there appear to be no data with which to make a direct comparison to decide if this diverging from the infinite dilution values is due to liquid-phase compositional effects or should be attributed to some other source.

Determination of S-L-G Line for Binary System

Freezing point as a function of pressure was determined for the methane-*n*-decane binary system by eluting ethane samples through a GLPC column at different temperatures but the same constant pressure, plotting retention volume vs. temperature, and taking the point of discontinuity in these plots as the freezing temperature. The retention volume-temperature plots for a series of constant pressures are shown in Figure 10.

It can be seen from Figure 10 that for a constant pressure the plot of retention volume vs. temperature is nearly linear in the vapor-liquid region up to the point of discontinuity. Then one observes at first a rapid, followed by a more gradual, decrease in retention volume as temperature is lowered. Finally, if the temperature were lowered enough, a gradual, almost linear increase in the retention volume with decrease in temperature would be observed, as reported by Rangel (*20*), in the region of vapor-solid equilibrium only.

The region of rapid then gradual decrease of retention volume with temperature occupies a temperature range of roughly 4° to 5°F. and appears to be a region in which both vapor-liquid and vapor-solid equilibrium are occurring within the column. Thus the liquid phase apparently does not all freeze at the same temperature, even though very long times were allowed for thermal equilibrium to be attained. This transition region was also approached from both high temperatures and temperatures well below the freezing point to rule out metastability as the cause of this observed phenomenon. The results were the same in both cases. One possible explanation for this effect is that the liquid phase is contained in pores of various sizes in the firebrick and this pore size distribution is creating a freezing point lowering due to surface tension effects on the liquid in the very small pores. The liquid in the very large pores should freeze first at the freezing point of the liquid on a plane surface.

That the point of discontinuity gives the true freezing point is seen by the curve for 21 lb./sq.in. At this pressure the amount of methane dissolved in the decane is quite negligible, and the point of discontinuity gives the freezing point of pure decane, −21.5°F.

The S-L-G line for the methane-*n*-decane system derived from the points of discontinuity in the curves of Figure 10 is plotted in the phase diagram of Figure 11. The S-L-G line does not form a continuous path from the triple point of decane to the quadruple point of the binary system but rather rises rapidly to the critical locus of the system and intersects with and divides the critical locus. There is probably another S-L-G line rising from the quadruple point in the neighborhood of the methane-triple point and intersecting the critical locus starting from the methane critical. However the determination of

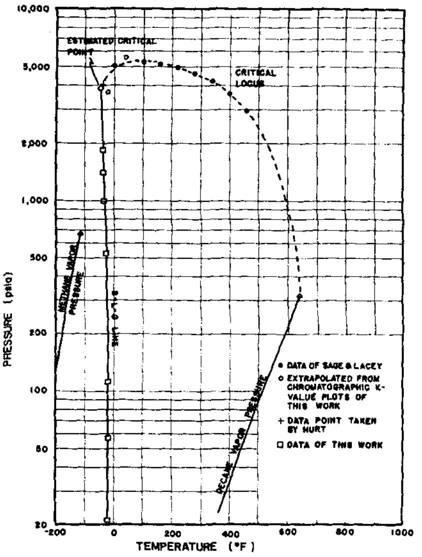

Fig. 11. Phase diagram for the methane-*n*-decane system.

this latter three-phase line was beyond the temperature limits of the experimental apparatus used in this investigation.

CONCLUSIONS

From the results of previous investigations in this field and from the comparisons made here between K values measured experimentally by the gas chromatographic method and values either measured by static equilibrium means or derived from such measurements, the hypothesis that partition coefficients, activity coefficients, or K values determined by gas-liquid partition chromatography are true equilibrium values seems to be established for the case of a solute being eluted at essentially infinite dilution in the vapor-liquid system. This is the case at pressures as high as 2,000 lb./sq.in. as well as at atmospheric pressure. Moreover from the limited amount of data taken the chromatographically determined K values for propane at some finite concentration in the liquid phase appear also to be equilibrium values, although no known static equilibrium data is available for direct comparison. The influence and evaluation of the $y_k \frac{d \ln K_k}{d y_k}$ terms in Equation (7) may pose a restriction on this method for studying the variation of K with composition under many conditions. For the foregoing study however these effects appear to be smaller in magnitude than the other experimental errors outlined in the paper.

In addition the chromatographic technique apparently offers a reliable method for measuring such phase behavior as the solid-liquid-gas line. The scant information available for direct comparison of freezing points substantiates this approach.

Thus it appears that the chromatographic method offers a relatively easy and rapid method under many sets of conditions for obtaining vapor-liquid equilibrium information for liquid phases containing at least one nonvolatile component. The method is seen as a complement to the established methods, such as the vapor recycle method, of obtaining this information.

The chromatographic technique has certain advantages over the static methods in that it offers a direct way for measuring infinite dilution data; it is inherently suited for nonvolatile liquids (the other methods are best suited for volatile liquid since, requiring an analysis of the liquid phase, care usually must be taken to completely vaporize a liquid sample); the gas phase can be set easily to the desired composition, and only one analysis, that of the gas phase, need be performed.

At present however the chromatographic method has certain disadvantages in that it is not suited for studying highly volatile solutes because of the error present in the measurement of column void volume; K value information from another source need be available for the lightest component of the elution gas mixture, at least if thermal conductivity detection is used; solvent evaporation can lead to errors; and detection problems arise when the solute sample must be made very small to ensure the condition of constant partition coefficient under the solute band as it travels down the column.

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NOTATION

C = total molar concentration in the gas phase
C_k = concentration of component k in the gas phase
D = constant in Brönsted and Koefoel equation for a given temperature
H_k = partition coefficient of component k (concentration of k in the liquid phase)/(concentration of k in gas phase) at equilibrium
K_k = equilibrium y_k/x_k value for component k
n = carbon number
P_k° = vapor pressure of component k at T
R = gas constant
t = time
T = absolute temperature
$(V_k)x$ = velocity of component k in the flowing phase
V_L = volume of liquid phase on column packing
V_{Rk} = retention volume of component k
V_g = free gas volume or volume available to gas flow
W = total moles of the nonvolatile liquid component
W_x = molar average velocity of the flowing phase
w_{n+1} = concentration of nonvolatile liquid component
w_k = concentration of component k in the stationary phase
X = distance along column
x_k = mole fraction of component k in the liquid phase
y_k = mole fraction of component k in the gas phase
z_M = compressibility factor of elution gas mixture

Greek Letters

ϵ = void fraction of column
π = total column pressure
$\gamma_{k \cdot \pi}$ = fugacity coefficient of component k in gas phase at T and π
γ_k, P_k° = fugacity coefficient of saturated component k in the gas phase at T, P_k°
$\gamma_{L^\circ k}$ = activity coefficient of component k in the liquid phase

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