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Phase Equilibrium of Carbon Dioxide in the Methane-Carbon Dioxide-*n*-Decane System

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Carbon dioxide occurs in varying concentrations in natural gases and crude oils. A knowledge of the phase behavior of carbon dioxide in hydrocarbon systems has applications in petroleum production and refining operations. The methane-carbon dioxide-decane system studied in this work represents a simplified model of natural systems in which carbon dioxide appears in combination with light gases and heavy hydrocarbons.

A chromatographic technique was used in the present study to determine vaporization equilibrium ratios of carbon dioxide at infinite dilution in methane-decane solutions. Since carbon dioxide is often present at low concentrations in natural systems, the state of infinite dilution is not an unrealistic one. Of more importance is the fact that these data yield useful information on interactions of carbon dioxide with methane and decane that, when analyzed in terms of a suitable model, permits predictions of the behavior of carbon dioxide at finite concentrations.

The present authors recently completed a study of the partial volumetric behavior of carbon dioxide at infinite dilution in gaseous methane. Results of that study have been combined with the present data to determine the nonideality of carbon dioxide in carbon dioxide-methane-decane liquid mixtures. Such information rarely has been available for ternary liquid mixtures at elevated pressures. The activity coefficients thus obtained are correlated based on a combined Scatchard-Hildebrand and Flory-Huggins model.

VAPOR LIQUID EQUILIBRIUM BY GAS-LIQUID CHROMATOGRAPHY

Many investigators have obtained equilibrium data at essentially infinite dilution using the gas-liquid chromatographic (GLC) technique (*1* to *8*), including high-pressure systems (*9* to *11*). Equilibrium properties of solutions determined from GLC elution data by previous investigators agreed with those obtained from static methods. A comprehensive review of the nonanalytical uses of chromatograph has been presented by Kobayashi, Chappelear, and Deans (*12*).

Martin and Synge (*13*) and others (*5, 14*) derived the basic relations between vapor-liquid equilibrium at infinite dilution and GLC parameters. One such expression is

$$K_i = \frac{\left(\frac{\rho_L}{\rho_G}\right) V_L}{V_{Ri} - V_G} \tag{1}$$

If the carrier gas is soluble in the stationary liquid and its mole fraction in the liquid phase at equilibrium is x_1, the total moles of the stationary phase, that is, including the dissolved carrier gas, will be

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$$\rho_L V_L = \frac{W_L{}^0}{1 - x_1} \qquad (2)$$

where $W_L{}^0$ is the number of moles of the pure heavy liquid. Substituting Equation (2) into Equation (1), one gets

$$K_i = \frac{W_L{}^0}{(1 - x_1)\,\rho_G(V_{R_i} - V_G)} \qquad (3)$$

From the flow rate of the carrier gas, measured at ambient conditions (T_a and P_a), the retention volume V_{R_i} in Equation (3) is calculated at column conditions by the following relation:

$$V_{R_i} = t_{R_i}\, F_a \left(\frac{P_a}{P}\right)\left(\frac{T}{T_a}\right) Z_G \qquad (4)$$

The retention time t_{R_i} is the time lapse between injection of the sample into the chromatographic column feed stream and detection of the sample in the column effluent as a peak on the recorder chart.

Equation (3) shows that the measured K value is dependent directly upon the value $(V_{R_i} - V_G)$. Consequently, when K values of highly retained components are measured, the accuracy in evaluating V_G is not critical, since for heavy components $V_{R_i} >> V_G$. However, for highly volatile solutes, an accurate knowledge of V_G is required, since $(V_{R_i} - V_G)$ becomes small numerically.

The values of V_G were determined by extrapolation of the measured V_{R_i} of several light gases—helium, neon, argon, etc.—to a hypothetical insoluble gas. Several extrapolation procedures have been reported (*12*). We have found our retention volume data to be most closely linear when plotted by the following scheme. Pierotti (*15, 16*) determined the Henry's law constant of hard sphere gas in a given solvent by plotting the Henry's law constant of real gases in the solvent as a function of the polarizability of the gases and extrapolating to zero polarizability. A smooth curve is defined by noble gases, thus a precise extrapolation is possible. The section of the curve that is defined by helium, neon, and argon is usually a straight line for simple solvents (*17*). A curve of similar characteristics was obtained by plotting the retention volumes of the noble gases helium, neon, and argon in methane–*n*-decane solution versus the polarizability of these gases.

The retention volume of a nonabsorbed component (free-gas volume) will change with pressure due to the change in solubility of the carrier gas in the solvent as well as pressure effects on liquid density. However, such effects may be accounted for if density data are available for the saturated liquid phase of the carrier gas-liquid solvent binary system.

The method of determining the chromatograph column void volume is illustrated in Figure 1. The value of $(V_{R_i} + \Delta V)$ is plotted as a function of the polarizability of the solute gas, where ΔV is the change in stationary liquid solution volume between the system pressure P, and the lowest system pressure P_0 used in the experiment. Values of ΔV were taken from volumetric data on the methane–*n*-decane system (*18*).

In principle, all the curves in Figure 1 for various isobars should intersect at a common point (V_{R0}, α_0), where V_{R0} is the free-gas volume at pressure P_0 and α_0 is the polarizability of a nonabsorbed or nonretained hypothetical component. In general α_0 is not equal to zero, since substances for which $\alpha = 0$ have finite solubilities (*15, 16*).

Corrections for the change in V_R with pressure were made using the values of ΔV.

The K values of carbon dioxide reported here are essentially independent of the procedure of extrapolation, since V_{R_i} is much greater than V_G.

EXPERIMENTAL APPARATUS AND PROCEDURE

Experimental Apparatus

The apparatus built for this study consisted of a chromatograph designed for high-pressure systems and equipped with a sensitive detector cell. A wide range of operational conditions, under close control, was possible. A schematic diagram of the experimental apparatus used in this investigation is shown in Figure 2.

The following are salient features of the experimental apparatus. Chromatograph detector: The detector cell was equipped with two glass-coated 30,000 Ω thermistors (Victory Engineering Corporation, Catalog No. AX 1243). The 0.285-mm. bead diameter thermistors were located in the gas flow path. The detector cell internal volume was 0.02 cu.cm., permitting rapid rate of response. One of the two thermistors sensed the carrier stream containing the sample and the second was placed in the reference carrier gas stream for balancing. The two thermistors were connected to opposing arms of a Wheatstone bridge powered by two 12-v. storage batteries. Recorder: The output signal from the detector was fed to a Minneapolis-Honeywell recorder for a visual representation of the chromatogram. The recorder has 1 mv. full scale deflection. Sample valve: The solute sample was injected into the high-pressure carrier gas by a sample valve with a sweep-out configuration. Chromatograph column: The chromatograph column was made of 15 to 18 in. of ¼-in. copper tubing packed with 30/60 mesh size firebrick column support and impregnated with pure *n*-decane. The liquid load was about 30% wt. (wet basis). Presaturator: The function of the presaturator was to saturate the carrier gas with *n*-decane before it entered the chromatograph

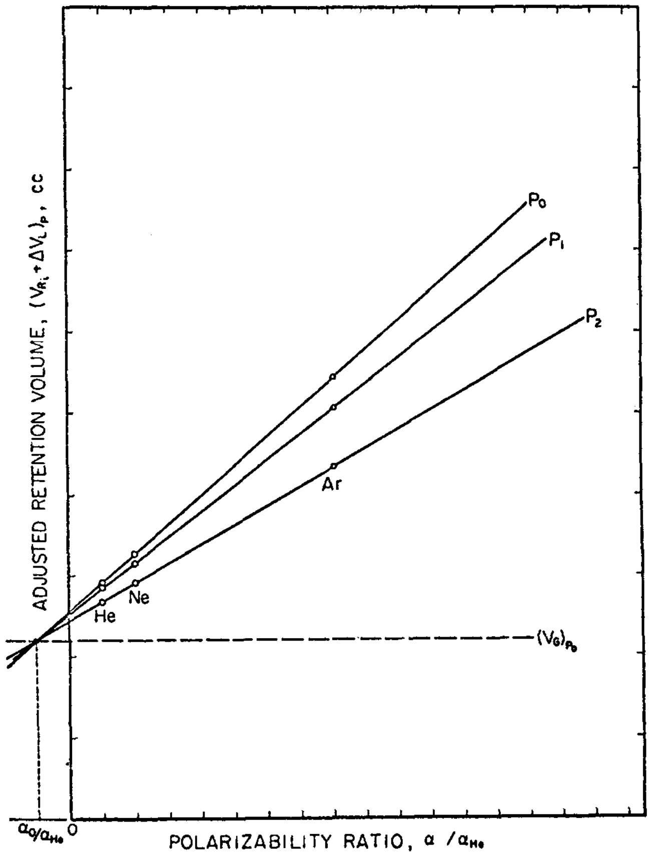

Fig. 1. Method for determination of chromatograph column void volume.

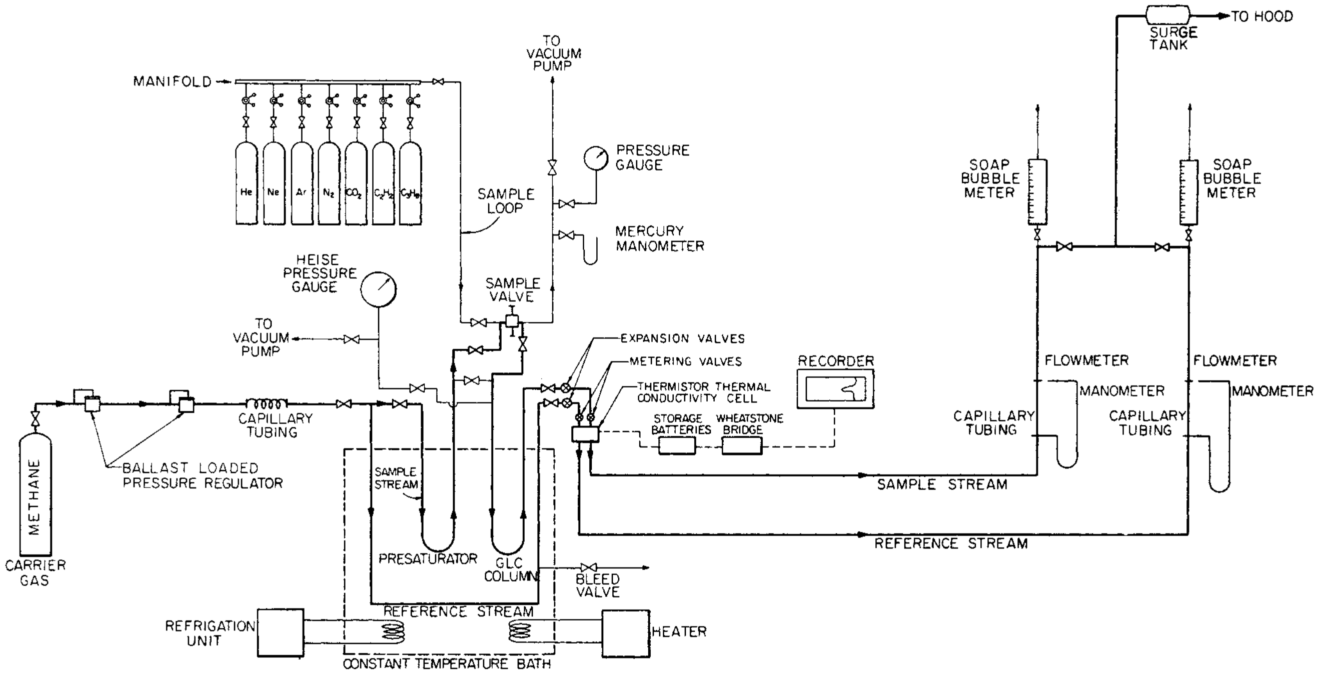

Fig. 2. Schematic diagram of the chromatographic apparatus.

column. It was made of a 35 to 50 in. of ¼-in. stainless steel tubing packed with material identical to that of the chromatograph column. Longer presaturators were used for higher system temperatures.

The system temperature and the temperature of the detector cell were measured by copper-constantan thermocouples and controlled by Hallikainen temperature controllers. The system pressure was measured at the column inlet by a Heise bourdon pressure gauge and controlled by two ballast-loaded pressure regulators connected in series. The flow rate of the carrier gas was measured at ambient conditions by a calibrated soap bubble meter and controlled by a fine needle metering valve.

The following chemicals were used during the course of this study:

Chemical	Purity	Supplier
Methane	99.05 mole %	Phillips Petroleum Co.
Carbon dioxide	99.8	Matheson Co.
n-Decane	99	Phillips Petroleum Co.

Experimental Procedure

A typical experimental run consisted of the following steps. A column and presaturator packed with firebrick column support impregnated with pure *n*-decane were installed in the system. The weight of the *n*-decane in the column had been accurately determined.

System temperature and pressure were set and controlled at the specified conditions for the run. The system temperature was measured with an accuracy of ± 0.04°F. and the system pressure was measured with an accuracy of ± 1 lb./sq.in. Methane carrier gas flow through the presaturator and column was begun at a specified flow rate until a steady state was reached. The stability of the detector output signal served as a criterion for steady state conditions of the chromatographic system. The flow rate of the sample stream was measured at ambient conditions by a calibrated soap bubble meter. The flow rate of the reference stream was kept close to that of the sample stream. Both flow rates were monitored with an orifice flowmeter equipped with glass manometers containing triethylene glycol.

The sample loop and the sample cavity of the sample valve were evacuated before being flushed and charged with the solute gas to be injected. The solute sample was trapped inside the sample cavity at a known pressure. The solute sample was injected into the high-pressure carrier gas and the electrical timer was turned on simultaneously. The retention time t_{R_i} of the solute sample was taken as the time lapse between the sample injection and the visual detection of the peak on the recorder chart. The retention time was recorded to the nearest 0.01 sec.

Samples of helium, neon, argon, and carbon dioxide as well as the other solutes were injected successively. The retention times of the light gases were used for determination of the column void volume V_G at each temperature and pressure condition. Each sample was injected twice and the retention time was taken as the average value for the two successive injections.

EXPERIMENTAL RESULTS

Solute *K* values for carbon dioxide at infinite dilution in the methane-decane system at temperatures of 40°, 70°, 100°, 125°, and 150°F. and pressures from 100 to 1,750 lb./sq.in.abs. were determined from chromatographic elution data via Equations (3) and (4). Solubility and volumetric data on the system methane–*n*-decane were taken from the literature (*18, 19*), as were the volumetric properties of methane gas (*18, 20*).

Figure 3 and Table 1 give the experimentally determined *K* values of carbon dioxide at infinite dilution in the methane–*n*-decane system as a function of pressure for six isotherms. In Figure 4 the same *K* values are plotted isobarically. These data appear to be self-consistent.

The apparatus and procedure employed in this study were checked by comparing *K* values of propane in methane-decane determined in the course of this work with similar data of Stalkup (*9*) and Koonce (*10*). Figure 5 shows the comparisons. Our results are in good agreement with the more recent data of Koonce with an average deviation of 2.2% and a maximum difference of 4%.

ACTIVITY COEFFICIENTS IN LIQUID SOLUTIONS

The literature contains numerous equations for activity coefficients in liquid solutions. A useful one is that of Scatchard-Hildebrand for regular solutions (*21*), which was used by Chao and Seader (*22*) in their general correlation of vapor-liquid equilibria for hydrocarbon systems.

According to regular solution theory, the activity coefficient γ_k of component k is given by

$$\ln \gamma_k = \frac{V_k}{RT}\left[a_{kk} - 2\sum_j \phi_j a_{kj} + \sum_i \sum_j \phi_i \phi_j a_{ij}\right] \quad (5)$$

where a_{ij} is the cohesive energy density of interaction between i and j, ϕ_i is the volume fraction of i, and V_k is the molar volume of k.

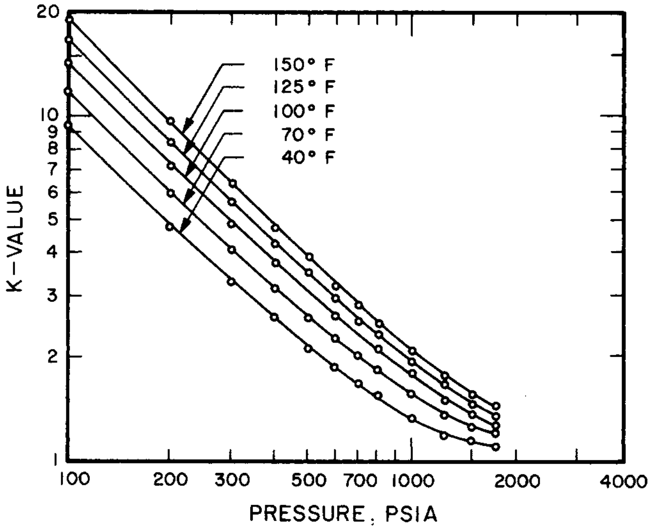

Fig. 3. *K* values for carbon dioxide at infinite dilution in the methane–*n*-decane system.

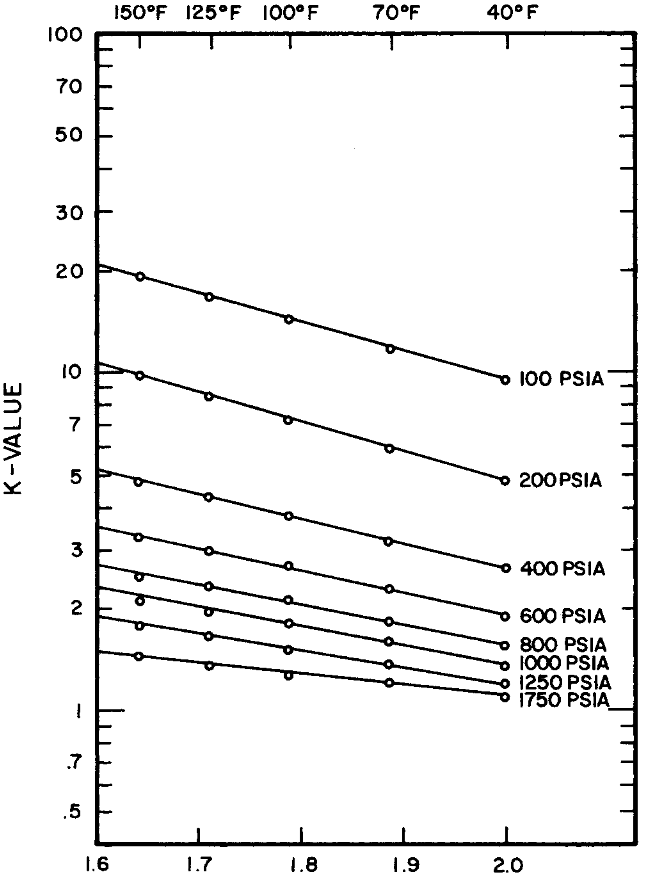

Fig. 4. *K* values for carbon dioxide at infinite dilution in the methane–*n*-decane system.

Equation (5) expresses the activity coefficient in the symmetric convention, that is

$$\gamma_k \rightarrow 1 \quad \text{as} \quad x_k \rightarrow 1 \quad (6)$$

where x_k is the mole fraction of k. The activity coefficient may be expressed in the unsymmetric convention (normalized to the state of infinite dilution) by the following relation:

$$\ln \gamma_k^* = \ln \gamma_k - \lim_{x_s \rightarrow 1} \ln \gamma_k \quad (7)$$

where s denotes the least volatile component in solution. The asterisk in Equation (7) is used to emphasize the fact that the activity coefficient is in the unsymmetric conven-

TABLE 1. *K*-VALUES OF CARBON DIOXIDE AT INFINITE DILUTION IN THE METHANE-*n*-DECANE SYSTEM

Pressure (lb./sq.in.abs.)	40°F.	70°F.	100°F.	125°F.	150°F.
100	9.563	11.92	14.51	16.95	19.21
200	4.819	6.064	7.271	8.539	9.841
300	3.322	4.123	4.933	5.725	6.431
400	2.648	3.210	3.837	4.308	4.791
500	2.157	2.645	——	3.556	3.985
600	1.906	2.318	2.691	3.035	3.257
700	1.717	2.052	——	2.651	2.885
800	1.581	1.874	2.146	2.352	2.525
1,000	1.351	1.601	1.835	1.975	2.123
1,250	1.204	1.385	1.522	1.687	1.801
1,500	1.162	1.274	1.379	1.481	1.584
1,750	1.123	1.218	1.289	1.373	1.475

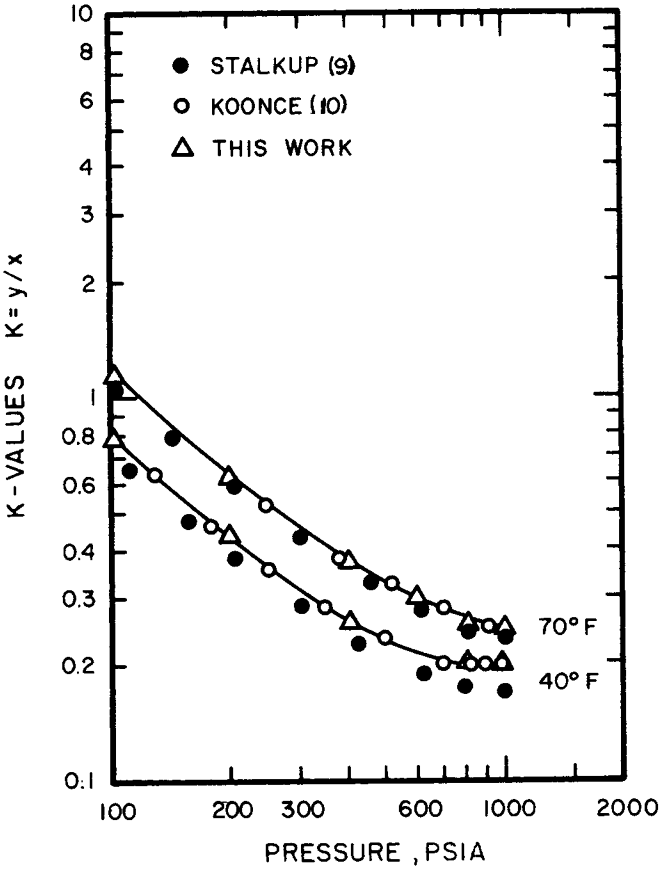

Fig. 5. Comparison of *K* values for propane at infinite dilution in the methane–*n*-decane system.

tion. Thus Equation (5) yields

$$\ln(\gamma_k^*)_{SH} = \frac{V_k}{RT}\left[-2\sum_j \phi_j a_{kj} + \sum_i\sum_j \phi_i \phi_j a_{ij} + 2a_{ks} - a_{ss}\right] \tag{8}$$

The subscript SH denotes Scatchard-Hildebrand theory.

The Flory-Huggins theory of solutions (*23, 24*) has been shown by Kohn (*25*) to be useful for correlating phase equilibrium data on methane in paraffin solvents. Cheung and Zander (*26*) found that solubilities of solid carbon dioxide and hydrogen sulfide in liquid hydrocarbons are well represented by a combination of the Scatchard-Hildebrand and Flory-Huggins theories, the latter to account for effects of molecular size differences. According to the Flory-Huggins theory

$$\ln(\gamma_k)_{FH} = \ln\left(\frac{V_k}{\sum_i x_i V_i}\right) + \sum_i \phi_i\left(1 - \frac{V_k}{V_i}\right) \tag{9}$$

or in the unsymmetric convention

$$\ln(\gamma_k^*)_{FH} = \ln\frac{V_s}{\sum_i x_i V_i} + \sum \phi_i\left(1 - \frac{V_k}{V_i}\right) - \left(1 - \frac{V_k}{V_s}\right) \tag{10}$$

Following Hildebrand and Scott (*21*), the Scatchard-Hildebrand and Flory-Huggins equations may be combined to give

$$\ln\gamma_k^* = \ln(\gamma_k^*)_{SH} + \ln(\gamma_k^*)_{FH} \tag{11}$$

or

$$\ln\gamma_k^* = \frac{V_k}{RT}\left[-2\sum_j \phi_j a_{kj} + \sum_i\sum_j \phi_i \phi_j a_{ij} + 2a_{ks} - a_{ss}\right] + \ln\left(\frac{V_s}{\sum_i x_i V_i}\right) + \sum_i \phi_i\left(1 - \frac{V_k}{V_i}\right) - \left(1 - \frac{V_k}{V_s}\right) \tag{12}$$

ACTIVITY COEFFICIENTS FROM EXPERIMENTAL DATA

The liquid-phase activity coefficients for carbon dioxide at infinite dilution in methane-decane solutions were evaluated from the GLC data of this work by the procedure described below.

The vapor liquid equilibrium K value may be written for a given component i as

$$K_i = \frac{\dfrac{f_i^L}{x_i P}}{\dfrac{f_i^V}{y_i P}} \tag{13}$$

Thus

$$\frac{f_i^L}{x_i} = K_i \psi_i^V P \tag{14}$$

Henry's law constant H_i is defined by

$$H_i = \lim_{x_s \to 1}\left(\frac{f_i^L}{x_i}\right) \tag{15}$$

so

$$H_i = \lim_{x_s \to 1}(K_i \psi_i^V P) \tag{16}$$

The unsymmetric coefficient is given by

$$\gamma_i^* = \frac{f_i^L}{x_i H_i} \tag{17}$$

or, using Equation (14)

$$\gamma_i^* = \frac{K_i \psi_i^V P}{H_i} \tag{18}$$

In the present experiment, the solute (component 2) was always at infinite dilution, so

$$\gamma_2^{*\infty} = \frac{K_2^{\infty} \psi_2^{V\infty} P}{H_2} \tag{19}$$

Equation (19) illustrates how the liquid-phase activity coefficient for an infinitely dilute component may be calculated from GLC data. Additional information is required on the vapor-phase fugacity coefficient and solvent vapor pressure (where $x_s = 1$).

For the system under study here, calculation of the vapor-phase fugacity coefficient of carbon dioxide required only information on carbon dioxide at infinite dilution in gaseous methane, since the concentration of decane in the vapor phase was negligibly small as shown by literature data on methane-decane (*18, 19*).

The partial volumetric behavior of carbon dioxide in gaseous methane has been measured by the present authors (*27*). The vapor-phase fugacity coefficient is related to the partial volume by

$$RT \ln \psi_2^{V\infty} = \int_0^P \left(\overline{V}_2^{V\infty} - \frac{RT}{P}\right) dP \tag{20}$$

For purposes of the present study, the $\psi_2^{V\infty}$ values for carbon dioxide were calculated from a modified form of the Benedict-Webb-Rubin equation of state. The modified equation, designed to fit the authors' partial volumetric data, is discussed elsewhere (*27*).

Figure 6 shows the $(f_2^{L\infty}/x_2)$ values for carbon dioxide calculated from the experimental GLC data via Equation (14). Values of H_2 were determined from such figures, according to Equation (16), and are shown in Figure 7; activity coefficients were then evaluated from Equation (19).

The Henry constant for carbon dioxide determined in this manner should be the same as that in a methane-free system of carbon dioxide in *n*-decane, since an extrapolation to the vapor pressure of *n*-decane was made. The phase equilibrium of the binary system carbon dioxide to *n*-decane was measured by Reamer and Sage (*29*), from which we have determined Henry constant for carbon dioxide in the temperature range of our work. The results are shown in Figure 7 for comparison with our data. The agreement is good with deviations in the order of 1 to 2%.

APPLICATION OF EQUATIONS TO EXPERIMENTAL DATA

The experimental activity coefficients calculated as described above are at the varying total pressure of the system. On the other hand, the Scatchard-Hildebrand and Flory-Huggins equations apply at a constant P_0. For purposes of comparison, the equation values were converted to system conditions by the relation

$$\ln(\gamma_k^{*\infty}) = \ln(\gamma_k^{*\infty})_{P_0} + \frac{1}{RT}\int_{P_0}^{P} \overline{V}_k^{L\infty}\, dP \tag{21}$$

where P_0 is the solvent vapor pressure. Equation (12) was applied at P_0 to account for temperature and composition effects, and the resultant γ values converted to system pressure P by use of Equation (21).

In order to apply Equations (12) and (21) to carbon dioxide at infinite dilution in methane-decane solutions, the following substitutions were made:

$$a_{11} = \delta_1^2 \text{ (methane)}$$

$$a_{22} = \delta_2^2 \text{ (carbon dioxide)}$$

$$a_{33} = \delta_3^2 \text{ (decane)}$$

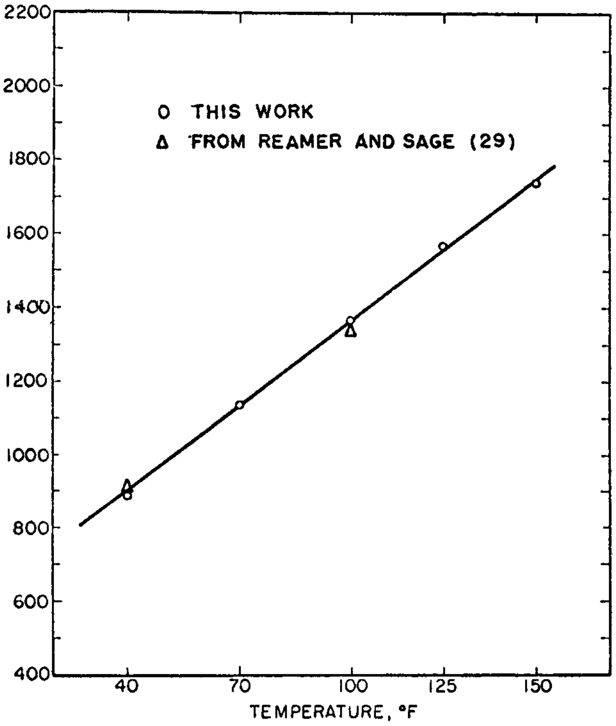

Fig. 6. Liquid-phase fugacity of carbon dioxide at infinite dilution in the methane–n-decane system.

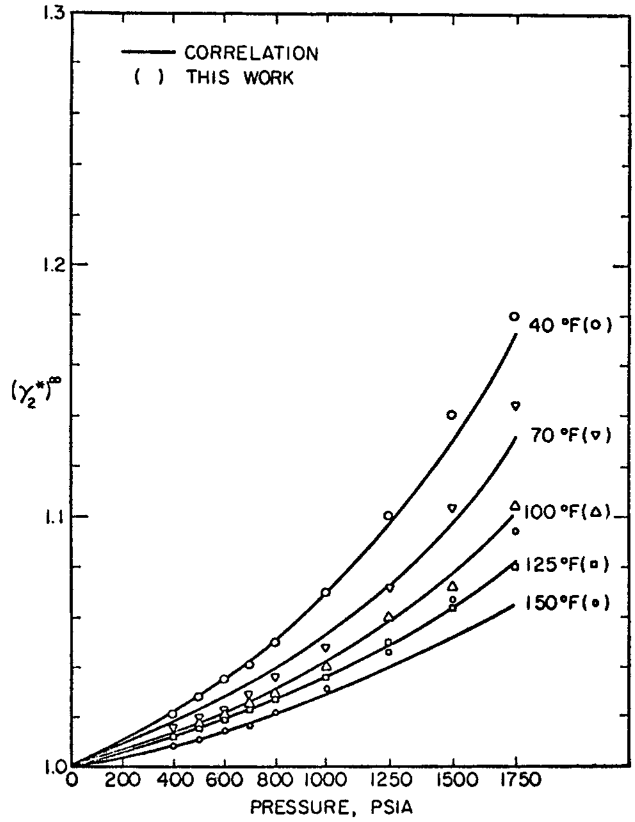

Fig. 7. Henry's law constant for carbon dioxide in the methane–n-decane system.

where δ_i is the solubility parameter of component i, and is presumed known. Considerable simplification is obtained upon setting $\phi_2 = 0$

$$\ln\left(\frac{K_2{}^\infty\ \psi_2{}^{V\infty}\ P}{H_2}\right) = \frac{2V_2}{RT}\phi_1\ (a_{23} - a_{12})$$

$$+ \frac{V_2}{RT}\left[\phi_1{}^2\ \delta_1{}^2 + (\phi_3{}^2 - 1)\ \delta_3{}^2 + 2\ \phi_1\ \phi_3\ a_{13}\right] + \ln\frac{V_3}{V_m}$$

$$- \phi_1\left(\frac{V_2}{V_1} - \frac{V_2}{V_3}\right) + \frac{1}{RT}\int_0^P \overline{V}_2{}^{L\infty}\ dP \qquad (22)$$

The solubility parameters, molar volumes, and volume fractions were taken from the literature (*18*, *19*, *21*, *22*). The liquid partial molar volumes of carbon dioxide are not experimentally available and were estimated by the method of Chueh and Prausnitz (*28*).

The interaction parameters in Equation (22) can, in principle, be estimated from phase equilibrium data on binary systems according to

$$\ln\left(\frac{K_2\ \psi_2\ P}{H_2}\right) = \frac{V_2}{RT}(\phi_1{}^2 - 1)\ (\delta_1{}^2 + \delta_2{}^2 - 2\ a_{12})$$

$$+ \ln\frac{V_1}{V_m} - \phi_2\left(1 - \frac{V_2}{V_1}\right) + \frac{1}{RT}\int_0^P \overline{V}_2{}^L\ dP \qquad (23)$$

from which the value of a_{12} to best fit the experimental data can be determined. Similar procedures give a_{13} and a_{23}.

The methane-decane interaction constant a_{13} was evaluated by fitting Equation (23) to phase equilibrium data on the methane-decane binary system (*18*, *19*) to yield a least squares fit to the activity coefficient.

For prediction of carbon dioxide activity coefficients, Equation (22) shows that a_{13} and $(a_{23} - a_{12})$ need be evaluated. Thus, with a_{13} known $(a_{23} - a_{12})$ can be found by direct fit to the ternary data, or a_{12} and a_{23} may be determined separately from data on the carbon dioxide-methane and carbon dioxide-decane binary systems. Both procedures were investigated in this work. For the binary system studied, the phase equilibrium data and carbon dioxide partial volumes for the carbon dioxide-decane system were taken from the work of Reamer et al. (*29*). For carbon dioxide-methane, the phase equilibrium data of Donnelly et al. (*30*) were used; liquid partial volumes were estimated by the method of Chueh and Prausnitz (*28*).

Vapor fugacity coefficients were evaluated from the Redlich-Kwong equation as modified by Chueh and Prausnitz (*31*). Interaction parameters k_{ij} for this equation of state were evaluated from volumetric gas-phase data on methane-decane (*18*) and carbon dioxide-decane (*29*), with the resultant values being $k_{13} = 0.105$ and $k_{23} = 0.152$. The above information permitted evaluation of a_{13} and a_{23}, based on K values of the light component in the binary system, according to Equation (23).

Results of the above calculations are discussed in the following section.

DISCUSSION OF RESULTS

In discussing the results of equilibrium data correlations, comparisons are usually made between experimental and predicted K values. The present correlation may be expressed in terms of K values from Equation (22)

$$\ln K_2{}^\infty = \frac{2V_2}{RT}\phi_1\ (a_{23} - a_{12}) + \frac{V_2}{RT}\left[\phi_1{}^2\ \delta_1{}^2\right.$$

$$+ \delta_3^2 (\phi_3^2 - 1) + 2 \phi_1 \phi_3 a_{13}] + \ln \frac{V_3}{V_m}$$
$$- \phi_1 \left(\frac{V_2}{V_1} - \frac{V_2}{V_3} \right) + \frac{1}{RT} \int_0^P V_2^{L\infty} \, dP$$
$$- \ln \psi_2^{V\infty} - \ln P + \ln H_2 \qquad (24)$$

In order to apply Equation (24) to the general estimation of K values, one needs, in addition to the usual volumes, solubility parameters, and interaction coefficients, a knowledge of solute liquid partial volume and Henry's law constant. The partial volumes have been estimated in this work (*28*); however, information on Henry's law constants is still needed. We have chosen to use the experimental H_i values determined in this study and compare predicted and experimental activity coefficients, rather than K values. This permits conclusions to be drawn relative to the fitting of activity coefficients, independent of prediction of H_i. Furthermore, any errors in prediction of γ values may be viewed as contributing directly the same percentage error in K values, subject to additional error from H_i correlations if any are used.

As discussed in the previous section, the interaction energy parameters a_{ij} were evaluated by the fit of Equation (23) or (22) to binary or ternary data. The resultant parameters are listed below:

Components	Energy parameter, cal./cc.	Data source
Binary data:		
C_1-C_{10}, a_{13}	40.79	*18, 19*
CO_2-C_{10}, a_{23}	45.39	*23*
C_1-CO_2, a_{12}	49.51	*31*
Ternary data:		
$(a_{23}$-$a_{12})$	−4.86	This work

Figure 8 shows a comparison of the experimental activity coefficients and those predicted from Equation (22) using a_{13} from the methane-decane data and $(a_{23} - a_{12})$ from least squares fit of the activity coefficient data from this work. The absolute average deviation is 1.7%. Substantial deviations occur only on the 150°F. isotherm at pressures above 1,000 lb./sq.in.abs.

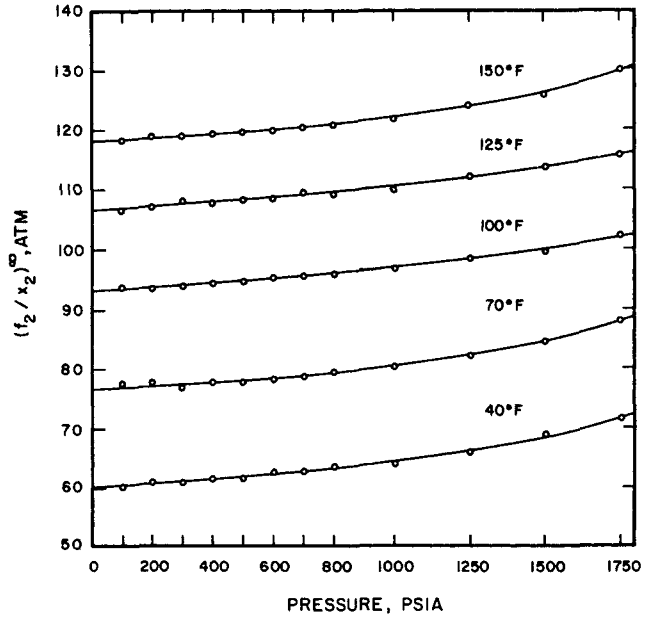

Fig. 8. Activity coefficient of carbon dioxide at infinite dilution in the methane–*n*-decane system.

A comparison of the accuracy of the correlation when the ternary data were used to establish $(a_{23} - a_{12})$ and when binary data were used to evaluate a_{12} and a_{23} separately is given below.

Error in Predicted Carbon Dioxide Activity Coefficient

$(a_{23}$-$a_{12})$ from ternary data			a_{12}, a_{23} from binary data		
Ave. abs. % error	Max. % error	Ave. % error	Ave. abs. % error	Max. % error	Ave. % error
1.7	8.8	−0.04	1.8	10.3	0.8

The above comparison shows that the use of binary data only to establish the energy parameters yields predictions essentially as accurate as the use of the ternary data. This is a consequence of the good agreement between the values of $(a_{23} - a_{12})$ calculated from binary data, −4.12, and from the ternary data, −4.86.

The Scatchard-Hildebrand equations are frequently utilized with the approximation

$$a_{ij} = (a_i \; a_j)^{1/2} \qquad (25)$$

which permits mixture behavior to be estimated solely from pure component information. Recently, Cheung and Zander (*26*) accounted for deviations from the above rule through the use of a correction factor l_{12} defined by

$$a_{ij} = (a_i \; a_j)^{1/2} \, (1 - l_{ij}) \qquad (26)$$

where l_{ij} is evaluated from suitable data on binary mixtures. Cheung and Zander determined l_{12} for methane-carbon dioxide from low temperature data on the solubility of solid carbon dioxide in liquid methane. A comparison of l_{12} values from the present work and that of Cheung and Zander is given below

	This work	Cheung-Zander (*26*)
l_{12} (for $C_1 - CO_2$)	0.029	0.028 to 0.031

This agreement, based on data at diverse conditions, is excellent.

A further test of the present equations was conducted to evaluate the improvement, if any, furnished by addition of the Flory-Huggins term to the Scatchard-Hildebrand equation. To make such calculations, procedures identical to those described above were employed, except that the Flory-Huggins terms were deleted from Equations (22) and (23). The results are

Components	Energy parameter, cal./cc.	Data source
Binary data:		
C_1-C_{10}, a_{13}	32.17	*18, 19*
CO_2-C_{10}, a_{23}	71.53	*29*
C_1-CO_2, a_{12}	26.28	*31*
Ternary data:		
$(a_{23}$-$a_{12})$	18.04	

When the Scatchard-Hildebrand model was used with $(a_{23} - a_{12})$ established from the ternary data, the accuracy was essentially identical to the results when the Flory-

Huggins term was included. However, the above table shows that $(a_{23} - a_{12})$ from binary systems is 45.25 versus 18.04 from the ternary data. Thus deletion of the Flory-Huggins term results in failure to predict the carbon dioxide behavior in ternary solutions based solely on binary data. These results justify the use of the combined Scatchard-Hildebrand and Flory-Huggins equations.

CONCLUSIONS

The following conclusions have been drawn from this work:

1. Experimental K values of carbon dioxide at infinite dilution in the ternary system carbon dioxide-methane-decane were determined. Their reliability is supported by comparisons of K values of other components which were determined simultaneously and found to agree well with literature data.
2. Combination of the present data with results of a previous study of the partial volume of carbon dioxide in gaseous methane permitted evaluation of the activity coefficient of carbon dioxide in the liquid phase of high-pressure methane-decane mixtures.
3. Combined Scatchard-Hildebrand and Flory-Huggins equations for liquid-phase activity coefficients furnished accurate representation of the experimental data. The combined equations were found to be preferred to the use of the Scatchard-Hildebrand equation only.
4. Interaction energy parameters in the equations determined from data on binary systems were found to be useful for predicting behavior of carbon dioxide in the ternary system.

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NOTATION

A = exchange energy density
a = cohesive energy density
F = carrier gas flow rate
f = fugacity
H = Henry's law constant or enthalpy
K = vapor-liquid equilibrium constant
P = pressure
S = entropy
T = temperature
t_R = retention time
V = liquid molar volume
V_G = void volume in GLC column
V_L = volume of stationary liquid phase in the GLC column
V_R = retention volume
W_L = moles of stationary liquid phase in the GLC column
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z_G = compressibility factor of the carrier gas

Greek Letters

α = polarizability
γ = activity coefficient in liquid solution
δ = solubility parameter
ρ = molar density
ϕ = volume fraction
ψ = fugacity coefficient in vapor phase

Subscripts

1 = methane or solvent in a binary solution
2 = solute
3 = n-decane
a = ambient conditions
i, j, k = component in system
m = mixture
FH = Flory-Huggins
0 = pressure independent
SH = Scatchard-Hildebrand
S = solvent, heaviest component in system

Superscripts

L = liquid phase
0 = pure state
V = vapor phase
$*$ = unsymmetric convention
∞ = infinite dilution state

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