K-Values at Essentially Infinite Dilution for Carbon Dioxide and Hydrogen Sulfide in the Methane–*n*-Octane System at Low Temperatures and Elevated Pressures

KOICHI ASANO[1], TOMOKO NAKAHARA, and RIKI KOBAYASHI
William Marsh Rice University, Houston, Texas 77001

Gas-liquid partition chromatography with the hypothetical perfect gas perturbation method was used to determine the infinite dilution *K*-values for carbon dioxide and hydrogen sulfide in the methane-*n*-octane system at 20°, 0°, –20°, and –40° C and at nine pressures from 20 to 1500 psia. Carbon dioxide and hydrogen sulfide showed positive deviation from Raoult's law.

Vapor-liquid equilibrium data are needed for absorber calculations on natural gas systems to follow the distribution of naturally occurring nonhydrocarbon components. Infinite dilution data are useful not only for design calculations but also for the theoretical development of correlations. The data presented here are for the nonhydrocarbons carbon dioxide and hydrogen sulfide, each in the methane-*n*-octane system at low temperature and high pressure.

EXPERIMENTAL

Method. Gas-liquid partition chromatography (GLPC) has proven satisfactory for vapor-liquid equilibrium measurements. Figure 1 gives a schematic flow diagram of the experimental system. The experimental method has been described by Van Horn and Kobayashi (*10*), Masukawa and Kobayashi (*6*), and Koonce and Kobayashi (*5*).

The GLPC columns were 50- and 90-cm lengths of ¼-in. copper tubing. The longer columns were used for methane determinations. The packing used was 30- to 50-mesh acid-washed fire brick (Curtin ChromoPak Pink, No. 8-837K), which was dried at least 3 hr at 200° C and soaked in research grade *n*-octane to give a fixed liquid content. An analytical balance was used for weighing the dry fire brick sample, wet fire brick sample, empty column, and wet-packed column. Fresh columns were prepared for each isotherm and each system, and the weights were checked several times during the measurements on each isotherm with the saturator used to maintain the desired fixed liquid content.

Conditions. The temperature was held constant at 20°, 0°, –20°, and –40° C to ± 0.1° C. The temperature was measured by a 10 junction thermopile against an ice reference. The pressures were 20 to 1500 psia as measured by manometers and Heise gages with an accuracy of 0.2% as certified by the manufacturer. All gages used in this laboratory are periodically returned to the manufacturer for any necessary recalibration and are occasionally checked in the laboratory against precision Ruska dead-weight gages. The methane purity was given as 99.99% and the *n*-octane as 99.88% by the suppliers. Each perturbing gas purity was better than 99.6%.

Calculation. The calculation method has been extensively discussed (*5, 8, 9, 10*). Only the summary equations are repeated here.

The *K*-value for the *i*th component is given by

$$K_i = Z_m RTW/\left[P(V_{R_i} - V_G)\left(1 - \frac{y_1}{K_1} - \frac{y_2}{K_2} - \ldots - \frac{y_n}{K_n}\right)\right] \quad (1)$$

In terms of the elution gas, methane, for this experiment, we have

$$K_M = Z_M RTW/[P(V_{R_M} - V_G)(1 - 1/K_M)] \quad (2)$$

The hypothetical perfect gas perturbation method (*6*) may be used to determine V_G, the free gas volume. In this method V_G is obtained from retention volume measurements on spherical gases, such as He, Ne, Ar, and CH_4, by extrapolation to perfect gas conditions with respect to a parameter such as polarizability. Two basic problems in the determination of V_G are the accurate determination of the retention volumes, especially for He, Ne, and Ar; and the choice of the parameter to be used for the extrapolation. These uncertainties in V_G lead to uncertainties in the *K*-value from Equation 1. Koonce and Kobayashi (*5*) observed that an error of 0.5% in the value of V_G introduces an error of approximately 5.0% in the *K*-value for methane calculated from Equation 2.

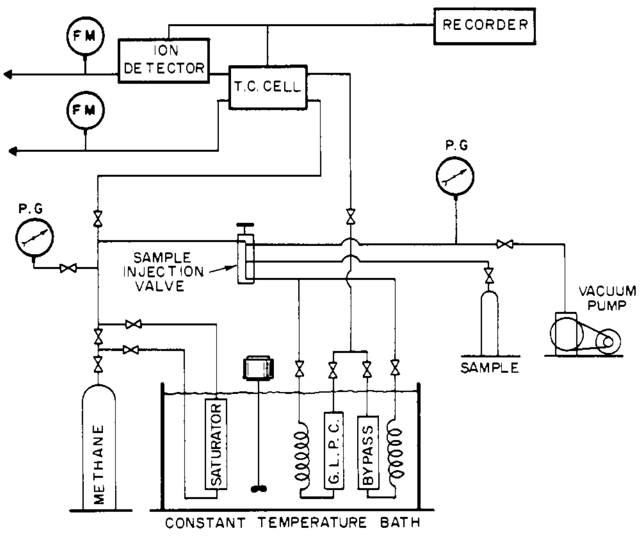

Figure 1. Schematic diagram of apparatus

---

[1] Present address, Tokyo Institute of Technology, Tokyo, Japan.

Table I. *K*-Values for Carbon Dioxide at Infinite Dilution in Methane–*n*-Octane

Pressure, psia	Temperature							
	20° C		0° C		–20° C		–40° C	
	Exptl	Smoothed	Exptl	Smoothed	Exptl	Smoothed	Exptl	Smoothed
20	57.7	51.0	37.2	37.2	28.1	25.4	16.5	16.5
100	12.3	11.9	8.45	8.60	6.17	5.87	3.78	3.80
200	6.19	6.50	4.46	4.71	3.11	3.24	2.06	2.11
400	3.35	3.32	2.41	2.47	1.77	1.75	1.16	1.20
600	2.34	2.35	1.80	1.80	1.33	1.30	0.882	0.880
800	1.88	1.88	1.46	1.46	1.11	1.11	0.793	0.800
1000	1.62	1.64	1.31	1.30	0.985	1.00	0.737	0.740
1250	1.51	1.51	1.19	1.22	0.947	0.950	0.725	0.711
1500	1.41	1.41	1.13	1.15	0.950	0.950	0.813	0.800

Table II. *K*-Values for Hydrogen Sulfide at Infinite Dilution in Methane–*n*-Octane

Pressure, psia	Temperature							
	20° C		0° C		–20° C		–40° C	
	Exptl	Smoothed	Exptl	Smoothed	Exptl	Smoothed	Exptl	Smoothed
20	12.5	10.5	9.37	6.70	5.81	4.00	2.77	2.20
100	3.17	2.99	2.05	1.90	1.26	1.16	0.649	0.650
200	1.67	1.70	1.10	1.10	0.670	0.670	0.364	0.390
400	0.954	0.970	0.626	0.650	0.407	0.400	0.230	0.230
600	0.714	0.714	0.488	0.488	0.306	0.310	0.184	0.184
800	0.589	0.589	0.421	0.421	0.290	0.284	0.181	0.181
1000	0.517	0.540	0.399	0.400	0.275	0.280	0.186	0.186
1250	0.525	0.520	0.378	0.390	0.298	0.298	0.217	0.217
1500	0.518	0.518	0.392	0.392	0.318	0.318	0.275	0.265

Another possibility for obtaining V_G exists from an indirect calculation based on methane. Rearrangement of Equation 2 gives

$$V_G = V_{R_M} - Z_M RTW/[P(K_M - 1)] \qquad (3)$$

The use of this equation requires independent experimental K_M data for the same experimental system, which in this case for methane–*n*-octane are available from Kohn and Bradish (*4*). The reliability of their data has been examined by two methods: Comparison of similar data of the same laboratory (*3*) with other investigations (*1*, *2*) for the methane–*n*-heptane system was well within the experimental error with an average deviation in the *K*-values of 1.74%. A regular systematic behavior of the methane *K*-values in the paraffin systems from *n*-heptane through *n*-decane was observed for the pressure-temperature range investigated. The *n*-nonane values were determined by the same investigators (*7*), but the *n*-decane values were obtained in this laboratory (*5*). Based on this two-directional analysis, the authors have concluded that the experimental data by Kohn and Bradish for methane-*n*-octane should be valid.

From Equations 1 and 3, the *K*-value at infinite dilution for CO_2 and H_2S may be obtained relative to methane at equilibrium in *n*-octane by

$$1 - K_M/K_i = (K_M - 1)(V_{R_M} - V_R)P/(Z_M RTW) \qquad (4)$$

The methane compressibility factors were obtained from the equation of state by Vennix (*11*, *12*).

The use of this indirect method, Equation 4, obviates the necessity for a precise determination of V_G. The methane retention volume appears only in a difference term with the retention volume of the other gas. The V_R for H_2S was 2 to 3 times as large as the V_R for methane, and the V_R for CO_2 was 1.2 to 2.4 times as large as the V_R for methane.

When an attempt was made to utilize the direct hypothetical perfect gas perturbation method to determine V_G, the resulting *K*-values for methane from Equation 2 differed from the Kohn and Bradish data by as much as 13%, with an average relative error of 6.5%.

Table III. Interpolated *K*-Values for Methane in Methane–*n*-Octane from Kohn and Bradish (*4*) Experimental Data

Pressure, atm	Temperature			
	20° C	0° C	–20° C	–40° C
1.36	142.0	128.0	111.3	96.0
6.81	29.8	26.6	23.3	19.4
13.61	15.2	13.4	11.8	10.0
27.22	7.80	7.00	6.10	5.20
40.83	5.35	4.82	4.28	3.67
54.43	4.15	3.75	3.35	2.85
68.05	3.47	3.10	2.82	2.40
85.06	2.97	2.65	2.41	2.04
102.07	2.65	2.32	2.13	1.81

RESULTS AND DISCUSSION

Tables I and II present *K*-values calculated by Equation 4 for CO_2 and H_2S at infinite dilution in the methane–*n*-octane system. Table III gives the *K*-values of methane used in the calculation of the values in Tables I and II, as obtained by interpolation of data of Kohn and Bradish.

The pressures of the three tables correspond, but atmosphere units are used in Table III since this was the unit used by Kohn and Bradish. Since the vapor phase is essentially pure methane (*4*), the liquid composition may be obtained from Table III and

$$x_M = 1.0/K_M \qquad (5)$$

The *K*-values of CO_2 in the methane–*n*-octane system were compared with those found by Yudovitch (*13*) in the methane–*n*-decane system and were almost identical, as expected. The *K*-values for both H_2S and CO_2 show positive deviation from Raoult's law.

The experimental *K*-values were plotted *vs.* reciprocal absolute temperature and smoothed. The resulting values were plotted *vs.* pressure and the final "best" values, consistent with both temperature and pressure, are presented

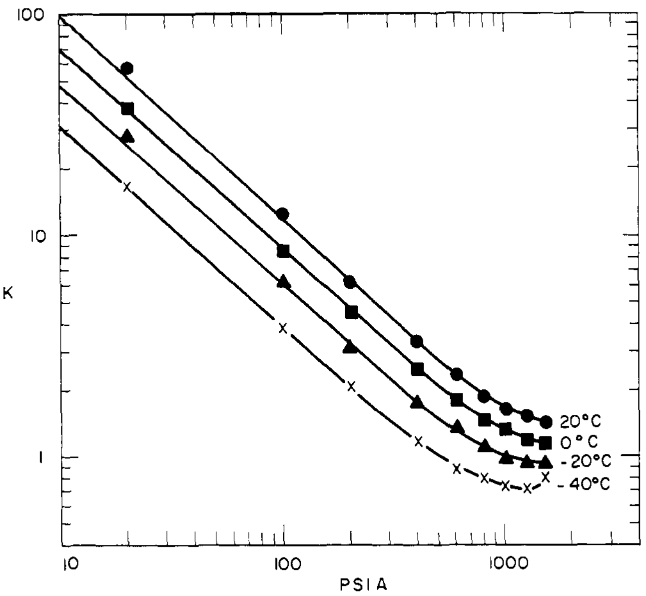

Figure 2. Recommended smoothed *K*-values for CO_2 at infinite dilution in methane–n-octane system

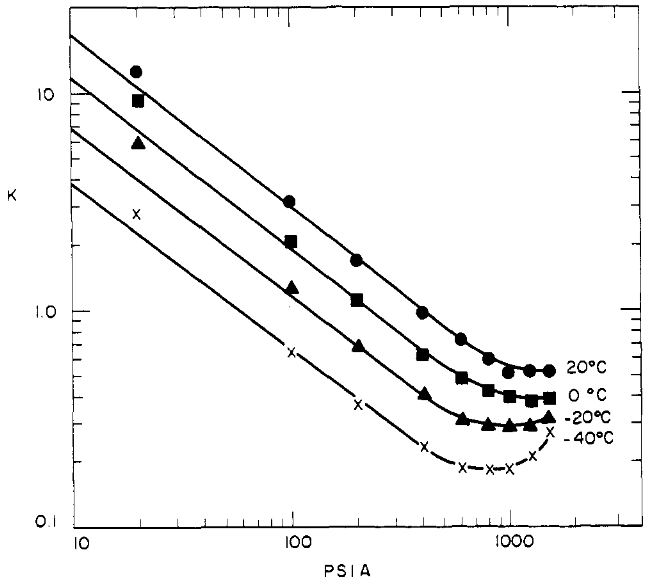

Figure 3. Recommended smoothed *K*-values for H_2S at infinite dilution in methane–*n*-octane system

in Figures 2 and 3 and also are tabulated in Tables I and II.

NOMENCLATURE

K = mole fraction vapor per mole fraction liquid
P = absolute pressure, atm or psia
R = gas constant, 0.08206 l. atm/gmole °K
T = absolute temperature, °K
V_G = free gas volume in column, l.
V_R = retention volume, l.
W = fixed liquid on packing, gmole
x = mole fraction
Z = compressibility factor

Subscripts

i = other component
M = methane
m = mixture
n = number of components

Superscript

∞ = infinite dilution

LITERATURE CITED

(1) Chang, H.L., Ph.D. Thesis, Rice University, Houston, Texas, December 1966. (Available from University Microfilms, 300 N. Zeeb Rd., Ann Arbor, Mich. 48106).
(2) Hurt, L.J., Ph.D. Thesis, Rice University, Houston, Texas, July 1962. (Available from University Microfilms, 300 N. Zeeb Rd., Ann Arbor, Mich. 48106).
(3) Kohn, J.P., *AIChE J.* **7**, 514 (1961).
(4) Kohn, J.P., Bradish, W.F., J. CHEM. ENG. DATA **9**, 5 (1964).
(5) Koonce, K.T., Kobayashi, Riki, *Ibid.*, **9**, 494 (1964).
(6) Masukawa, S., Kobayashi, Riki, *J. Gas Chromatogr.* **6**, 257 (1968).
(7) Shipman, L.M., Kohn, J.P., J. CHEM. ENG. DATA **11**, 176 (1966).
(8) Stalkup, F.I., Deans, H.A., *AIChE J.* **9**, 118 (1963).
(9) Stalkup, F.I., Kobayashi, Riki, *Ibid.*, **9**, 121 (1963).
(10) Van Horn, L.D., Kobayashi, Riki, J. CHEM. ENG. DATA **12**, 294 (1967).
(11) Vennix, A.J., Ph.D. Thesis, Rice University, Houston, Texas, April 1966. (Available from University Microfilms, 300 N. Zeeb Rd., Ann Arbor, Mich. 48106).
(12) Vennix, A.J., Kobayashi, Riki, *AIChE J.* **15**, 926 (1969).
(13) Yudovich, A., Ph.D. Thesis, Oklahoma State University, Stillwater, Oklahoma, May 1969.

RECEIVED for review March 19, 1970. Accepted August 12, 1970. Presented at AIChE Meeting, New Orleans, March 16-20, 1969. The Natural Gas Processors Association provided financial support for this project. *n*-Octane was donated by the Phillips Petroleum Co.