Vapor-Liquid Equilibria of Light Hydrocarbons at Low Temperatures and Elevated Pressures in Hydrocarbon Solvents

Methane-Propane–*n*-Heptane, Methane-Ethane–*n*-Heptane, and Methane-Propane-Toluene Systems

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This paper presents an experimental study of the phase behavior of methane, ethane, and propane in *n*-heptane and toluene solvents. Temperatures of interest range from 0° to −100° F. Pressures are from 100 to as high as 1600 p.s.i.a. Vapor-liquid equilibrium constants in these systems were calculated using gas chromatographic retention data. Improvements in the existing chromatographic techniques were made to allow accurate determination of methane phase behavior. The results of the experimental work compared favorably with comparable literature data and showed good internal consistency.

THE PHASE BEHAVIOR of hydrocarbon systems has been widely studied experimentally and theoretically. The higher temperature work has been adequately referenced by Katz and Rzasa (*9*), Muckleroy (*16*), and the American Petroleum Institute (*6*). Low temperature vapor-liquid equilibria has been generally referenced by Flynn (*7*), while specific references to paraffinic systems have been made by Price and Kobayashi (*17*) and later by Chang, Hurt, and Kobayashi (*4*).

Primary objectives of this work were to explore the behavior of more complex systems containing light and heavy hydrocarbons at lower temperatures; to study systems containing both paraffin and aromatic hydrocarbons; to analyze the results of the experimental studies; and to advance the chromatographic equipment and techniques to accomplish the experimental objectives. The results of the correlational effort are reported elsewhere (*27, 28*).

Gas-liquid partition chromatography (GLPC) was chosen as the means of obtaining phase equilibrium data. The advantages of GLPC techniques are principally its simplicity, speed, and sensitivity. Previous work in this laboratory (*12, 13, 24*) has firmly established the validity and applicability of the technique to binary and ternary systems composed of light hydrocarbons in a heavier molecular weight hydrocarbon solvent. Further development of the technique was required to meet the primary objectives of this work. It was necessary, for example, to improve and validate the technique to measure *K*-values ($K_i = y_i/x_i$) for methane.

The systems and conditions chosen for this study were: (1) methane-propane-*n*-heptane at temperatures between 0° and −100° F. and at pressures to 1000 p.s.i.a.; (2) methane-ethane-*n*-heptane at temperatures between 0° and −60° F. and at pressures to 1000 p.s.i.a.; (3) methane-propane-toluene at −40° F. and at pressures to 1000 p.s.i.a.

K-values were obtained for each of the two light components in these systems for various concentrations of the intermediate component in the gas phase. In addition, the *K*-value was measured for ethane at vanishingly small concentrations (infinite dilution) in systems 1 and 3.

Koonce and Kobayashi (*15*) surveyed chromatographic work of the type done here.

PREVIOUS WORK

Hurt (*8*) studied the methane-propane-*n*-heptane system in 1963, but later results of Koonce and Kobayashi (*15*) and Kohn (*10*) showed his results to be of dubious validity. Current low temperature studies by Chang, Hurt, and Kobayashi (*4*) in this laboratory, using classical vapor-recycle techniques, have resulted in methane-*n*-heptane binary data, with methane solubilities in essential agreement with those of Kohn (*10*). In addition, the vapor phase concentrations of *n*-heptane were obtained over the entire range of the studies. Chang (*3*) has also obtained methane-toluene data at −40° F. Methane-propane (*1, 17, 21*) and methane-ethane (*2, 17*) binary data and methane-ethane-propane ternary data (*17*) have been obtained down to −200° F. and pressures up to the criticals for the mixtures.

Additional related references of particular interest which have appeared recently are given below:

System	Temperature	Reference
Methane-*n*-butane	−80° to 280° F.	(*19*)
Methane-*n*-hexane	−110° to 150° C.	(*22*)
Methane-*n*-octane	−110° to 150° C.	(*11*)
Methane-*n*-nonane	−25° to 75° C.	(*23*)
Methane-*n*-decane	−20° to 40° C.	(*14*)

Stalkup and Deans (*25*) and Stalkup and Kobayashi (*26*) evaluated ethane, propane, and *n*-butane *K*-values at essentially infinite dilution in the methane-*n*-decane and methane-*n*-hexadecane systems at temperatures between −20° and 160° F. and pressures to 2000 p.s.i.a. Koonce (*12*) and Koonce and Kobayashi (*15*) evaluated *K*-values for propane at finite concentrations in the methane-propane-*n*-decane system for temperatures between −20° and 70° F. and pressures to 1000 p.s.i.a. They also studied the methane-propane-*n*-heptane system at −20° and −40° F. for pressures to 1000 p.s.i.a.

THEORY

Stalkup and Kobayashi (*26*) derived the basic equation used in this work to obtain *K*-values from chromatographic elution data, and discussed its application to radioactively tagged solute samples. The relation has also been discussed by Stalkup and Deans (*25*) and is:

$$K_i = \frac{Z_m RTW}{P(V_{R_i} - V_G)} \cdot \frac{1}{(1 - y_1/K_1 - \ldots - y_N/K_N)} \qquad (1)$$

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This equation relates the K-value of component i to retention data in an N-component carrier gas which is soluble in the stationary liquid phase. The V_R in the equation applies to the retention volume of a tagged solute sample. Only at infinitely dilute concentrations does the equation hold for an untagged solute sample. This follows from the requirement of Equation 1 that the solute sample molecules be completely distinguishable from other molecules in the system.

Equation 1 was used exclusively to relate retention data of solute samples to K-values. The solute samples were tritium-tagged isotopes of methane, ethane, and propane. Within the experimental accuracy of the measurements, K-values determined from isotope retention data were the same as those obtained under the same conditions from untagged sample retention data.

Gas chromatographic techniques have previously been unsuccessful in measuring methane K-values satisfactorily. Koonce and Kobayashi (*15*) and Stalkup and Kobayashi (*26*) both attributed this to per cent errors in (V_{R_1} – V_G). For a highly volatile component like methane, (V_{R_1} – V_G) is very small and small errors in V_{R_1} and V_G are greatly magnified in the per cent error in (V_{R_1} – V_G). Koonce and Kobayashi (*15*) determined V_{R_1} and V_G from separate runs. V_G was always determined from elution data of tagged methane in a pure methane elution gas. Hence, for runs with mixture elution gases, V_R and V_G were determined from runs with two different elution gases, one with mixture elution gas and one with methane.

Ideally, (V_{R_1} – V_G) could be determined from the difference in retention between a completely unretained peak (a measure of V_G) and the methane peak obtained from a single injection of a mixture of the two. However, no such unretained component exists in a vapor-liquid system, especially at conditions near the system critical where the retention of all components tend to become the same. To measure methane K-values, tritium was used as a relatively unretained component.

Equation 1 can be rewritten as:

$$V_{R_1} - V_G = \frac{Z_M RTW}{PK_i(1 - y_1/K_1 - \ldots - y_N/K_N)} \tag{2}$$

This equation applies to any tagged solute pulse. Equation 2 can be written for both the tritium and methane peaks obtained by injecting a solute sample containing both. For example, the equation for the methane K-value in the methane-solvent binary system is:

$$K_1 = \frac{RT_aWZ_a}{f_a\,(t_{R_1^*} - t_{R_T^*})}\left(1 - \frac{K_1}{K_T}\right) \tag{3}$$

The ratio K_1/K_T was always less than about 0.1 and was as low as 0.02 for the lowest temperature. K_T was estimated from the Chao and Seader correlation (*5*). Errors in the estimation are probably large, but the corresponding effect on the methane K-value calculation would be small for the range of this study. The success of the method is shown in Table I, a comparison between K-values obtained by GLPC for methane in the methane–n-heptane system with the same data obtained from static measurements by Chang, Hurt, and Kobayashi (*4*). Large columns were used for the methane runs to raise ($t_{R_1^*}$ – $t_{R_T^*}$) as large as possible.

Similar techniques were used to obtain infinite dilution K-values of ethane and propane. The sample pulse for these runs was composed of tagged ethane and/or tagged propane and tagged methane. The carrier gas was pure methane. The equation for the K-value of a component i at infinite dilution in the binary system is:

$$K_i = \frac{RT_aW}{[f_a\,(t_{R_i^*} - t_{R_1^*})/Z_a + RT_aW/(K_1 - 1)]\,(1 - 1/K_1)} \tag{4}$$

The methane K-value, K_1, is the K-value in the binary system, as determined classically by Chang (*3, 4*). K_1 can also be determined chromatographically, using Equation 3.

The ternary systems were formed by flowing a mixture elution gas of known composition through the column. The liquid equilibrated to the flowing vapor by absorbing the soluble components from the flowing elution gas. Hence, the three necessary phase rule variables required to define the ternary system were temperature, pressure, and vapor composition. Once equilibrium was established, K-values obtained were those of the components in the ternary system at the fixed temperature, pressure, and composition.

As pointed out by Koonce and Kobayashi (*15*), it is possible to determine the K-value of each component of the elution gas by GLPC using tagged solute samples. The equations describing the elution of tagged molecules of each component (Equation 1) are solved simultaneously for the K-values. Different columns were used, a large one to determine the methane elution data, and a smaller one for the elution data of the other components. The result for a binary elution gas of component 1 (methane) and component k (ethane or propane) with i at infinite dilution is:

$$K_k = \frac{\alpha_k + y_k[1 + (\alpha_k - y_1)/(\alpha_1 + y_1)]}{1 + [(\alpha_k - y_1)/(\alpha_1 + y_1)]\,[1 + \alpha_1/K_T]} \tag{5}$$

$$K_1 = \frac{\alpha_1 + y_1}{1 - y_k/K_k + \alpha_1/K_T} \tag{6}$$

$$K_i = \frac{\alpha_i}{1 - y_1/K_1 - y_k/K_k + \alpha_i/K_1} \tag{7}$$

$$\alpha_1 = \left\{\frac{RT_aW}{f_a(t_{R_1^*} - t_{R_T^*})/Z_a}\right\}_1$$

$$\alpha_i = \left\{\frac{RT_aW}{f_a(t_{R_i^*} - t_{R_1^*})/Z_a}\right\}_k$$

$$\alpha_k = \left\{\frac{RT_aW}{f_a(t_{R_k^*} - t_{R_1^*})/Z_a}\right\}_k$$

where subscript 1 denotes a run through the long methane column, and subscript k a run through the smaller column. As before, the pulse injected into column k consists of methane, component i (the infinite dilution component), and component k, all tagged, which separates into methane, i, and k peaks. The $t_{R_1^*}$, $t_{R_i^*}$, and $t_{R_k^*}$ contained in α_i and α_k refer to the retention times of these three peaks, respectively.

Equation 3 was used to calculate the methane K-value in the methane-heptane and methane-toluene binaries. Equation 4 was used for infinite dilution ethane and propane K-values in the two methane binaries. Finally, Equations 5, 6, and 7 were employed to calculate methane, ethane, and propane K-values in the ternaries of methane-ethane–n-heptane, methane-propane–n-heptane, and methane-propane-toluene systems. The elution time data and type of sample required were as follows:

1. Methane K-values in binary. Sample consisted of tritium and tagged methane, which separated into two peaks, a tritium peak and a methane peak. Retention times recorded were for the tritium peak $t_{R_T^*}$, and methane peak $t_{R_1^*}$.

2. Propane and ethane at infinite dilution. Sample consisted of tagged methane and propane or tagged methane and ethane. Retention times were recorded for the methane peak $t_{R_1^*}$, and the ethane $t_{R_2^*}$, or propane peak $t_{R_3^*}$, on a single run.

3. Methane in the ternary. Sample consisted of tritium and tagged methane, as in the binary.

4. Propane and ethane in the ternary. Sample consisted of tagged methane, ethane, and propane, all in the same pulse. Retention times were recorded for the methane peak $t_{R_1^*}$, ethane peak $t_{R_2^*}$, and propane peak $t_{R_3^*}$. No propane retention data were obtained in the methane-ethane-n-heptane ternary.

EXPERIMENTAL

The equipment and procedures used were similar to those described by Koonce and Kobayashi (*15*). The principal difference in technique was the use of multiple solute samples in one injection with the resulting improvement in the K-value calculation. The main changes in equipment were use of a presaturator for binary system runs and a smaller ionization chamber for radioactivity detection, eliminating the need for an ionization chamber purge gas. A schematic of the equipment is shown in Figure 1.

The fixed liquids used were research grade n-heptane and toluene. Solute samples were all tagged components

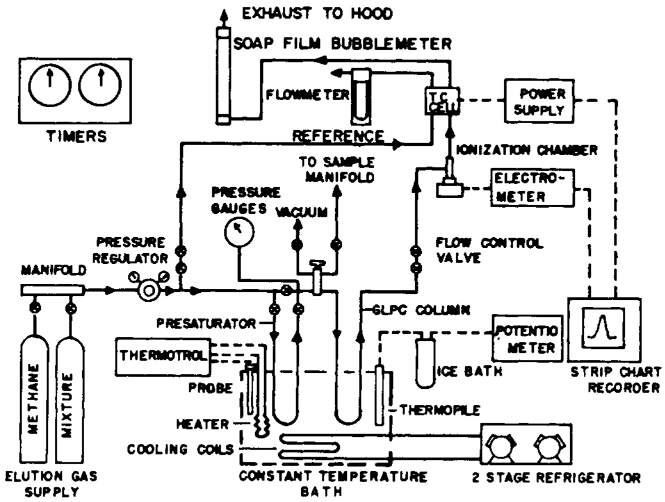

Figure 1. Schematic diagram of apparatus

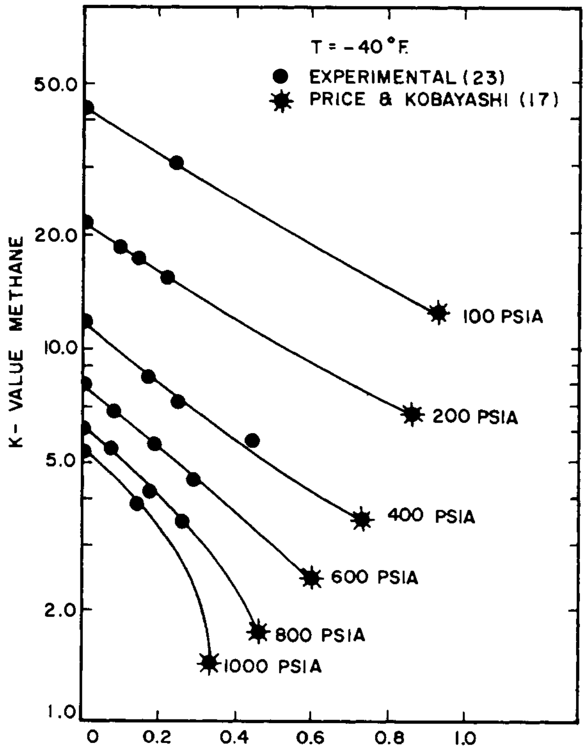

Figure 2. Methane K-value in the C_1-C_3-toluene system, T = −40° F.

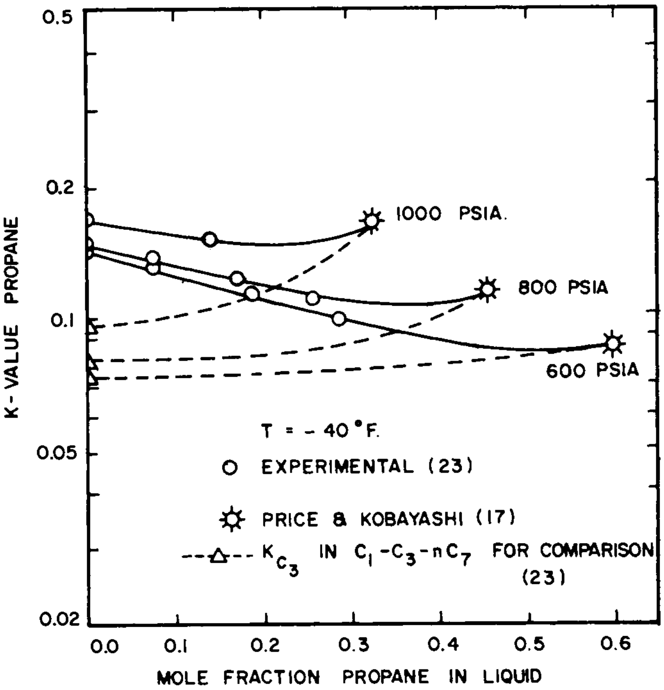

Figure 3. Propane K-value in the C_1-C_3-toluene system, T = −40° F.

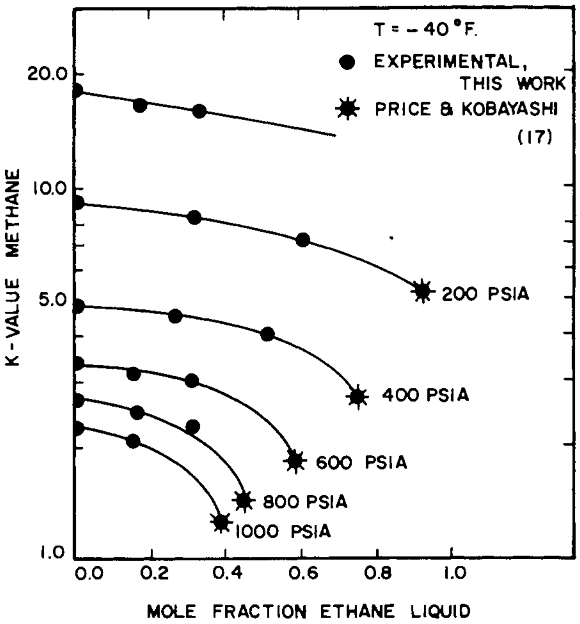

Figure 4. Methane K-value in the C_1-C_2-nC_7 system, T = −40° F.

diluted with methane. Flow rates ranged from 50 to 130 cc. per minute at room temperature and atmospheric pressure, as measured by the flowmeter.

Gas mixtures were prepared from pure components and analyzed chromatographically and by mass spectrometry. Reproducibility of five analyses of each mixture was within 1 to 1.5% of the stated ethane or propane compositions. The methane and methane-propane mixtures contained about 0.2% carbon dioxide and nitrogen. Impurities in the methane-ethane mixtures were less than 0.05%, consisting mostly of nitrogen. Propylene and heavier components were less than 10 p.p.m. Heptane and toluene gas compositions were much less than 1% for most runs. The small quantity of these solvents present in the gas was estimated from *K*-values given by Chang (*3*, *4*) and Hurt (*8*).

First, the methane-propane-*n*-heptane system was studied. Data were obtained isothermally for methane and propane at -20°, -40°, -60°, -80°, and -100° F. Only infinite dilution data were taken at 0° F. Elution data for ethane were obtained in all mixtures at -20°, -40°, and -60° F., by including tagged ethane in the sample pulse.

At least four fresh columns were used for each isotherm of the methane-propane-heptane system, two large columns (methane columns) and two small columns (propane columns). Data were taken for calculation of methane *K*-values in one series of runs, then data for propane and ethane *K*-values in another series.

The methane-ethane-*n*-heptane system was run at -20°, -40°, and -60° F. in a similar manner to the methane-propane-heptane system. Each data point required separate runs for methane and ethane elution data, as before. Also, four columns were normally used on each isotherm. The ethane columns were longer than the propane columns, and contained more heptane, to make $(t_{R_2^*} - t_{R_1^*})$ as large as possible. No propane elution data were obtained, since retention times were too long through the larger columns.

The methane-propane-toluene system was run only at -40° F. Procedures were the same as those for the methane-propane-heptane system, except that more mixture points were obtained. The marked composition effect required that as many mixture data points as possible be taken.

n-Heptane and toluene are slightly volatile components, so *W*, the moles of heavy component in the column, decreased slightly during the course of several runs. This was normally accounted for by periodic weighing of the

Table I. Methane *K*-values in the Methane–*n*-Heptane and Methane-Toluene Systems

Comparisons of GLPC data with classical results of Chang, Hurt, and Kobayashi (*4*)

T, ° F.	*P*, P.S.I.A.	K_{C_1} (GLPC)	K_{C_1} (*4*)	Dev., %[a]
		A. Methane–*n*-Heptane		
-20	100	19.93	20.38	-2.2
	200	10.31	10.10	+2.1
	400	5.42	5.31	+2.1
	600	3.80	3.74	+1.6
	800	2.96	2.93	+1.0
-40	100	18.33	18.00	+1.8
	200	9.24	9.08	+1.8
	400	4.87	4.80	+1.5
	600	3.39	3.34	+1.5
	800	2.70	2.68	+0.7
-60	100	15.58	15.92	-2.1
	200	8.08	8.10	-0.2
	400	4.16	4.31	-3.5
	600	3.01	3.07	-2.0
-80	100	13.16	13.77	-4.4
	200	7.05	7.10	-0.7
	400	3.65	3.80	-3.9
	600	2.57	2.64	-2.6
	800	2.02	2.09	-3.3
-100	100	11.43	11.81	-3.1
	200	6.00	6.12	-2.0
	400	3.06	3.21	-4.7
	600	2.11	2.17	-2.8
		B. Methane-Toluene		
-40	100	43.91	43.36	+1.3
	200	21.48	21.61	-0.6
	400	11.37	11.78	-2.6

[a] $[(K_{C_1}\ (\text{GLPC}) - K_{C_1}\ (4)]/K_{C_1}\ (4)$.

Table II. *K*-Value Propane in C_1-nC_7 System

	T = -20° F.		*T* = -40° F.	
Pressure, P.S.I.A.	Koonce	This work	Koonce	This work
100	0.299	0.296	0.206	0.196
200	0.173	0.170	0.116	0.112
400	0.115	0.112	0.0820	0.0772
600	0.105	0.100	0.0783	0.0783
800	0.107	0.102	0.0886	0.0798
1000	0.119	0.113	0.118	0.0995

Table III. *K*-values of Propane at Infinite Dilution in the Methane–*n*-Heptane System

Pressure, P.S.I.A.	Temperature, ° F. 0	-20	-40	-60	-80	-100
100	0.427	0.296	0.196	0.123	0.0713	0.0405
200	0.241	0.170	0.112	0.0707	0.0430	0.0252
400	0.155	0.112	0.0772	0.0512	0.0316	0.0211
600	0.134	0.100	0.0738	0.0517	0.0367	0.0284
800	0.130	0.102	0.0798	0.0616	0.0531	0.0652
1000	0.137	0.113	0.0955	0.0843	0.0957	
1200	0.154	0.132	0.122	0.129		
1400	0.174	0.164	0.163			
1600	0.195					

Table IV. *K*-values of Ethane at Infinite Dilution in the Methane–*n*-Heptane System

Pressure, P.S.I.A.	Temperature, ° F. 0	-20	-40	-60
100	2.092	1.600	1.204	0.878
200	1.131	0.877	0.675	0.486
400	0.657	0.527	0.414	0.309
600	0.508	0.423	0.340	0.263
800	0.466	0.392	0.316	0.264
1000	0.448	0.379	0.325	0.298
1200	0.447	0.397	0.369	0.367
1400		0.427	0.410	
1576		0.464		

Table V. *K*-values of Ethane and Propane at Infinite Dilution in the Methane-Toluene System

T = -40° F.

Pressure, P.S.I.A.	*K*, Ethane	*K*, Propane
100	2.836	0.428
200	1.406	0.242
400	0.831	0.160
600	0.667	0.143
800	0.603	0.148
1000	0.604	0.169

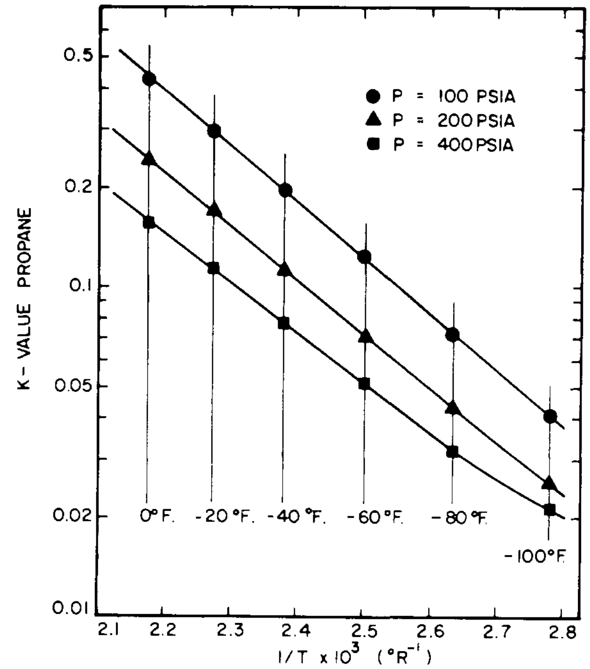

Figure 5. *K*-Value for propane at infinite dilution in the C_1-nC_7 system as function of reciprocal temperature—low pressure

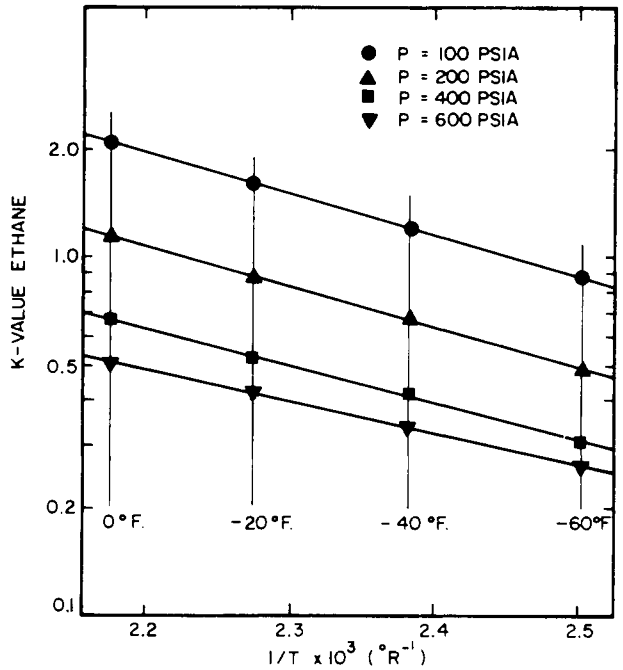

Figure 7. *K*-Value for ethane at infinite dilution in the C_1-nC_7 system as function of reciprocal temperature—low pressure

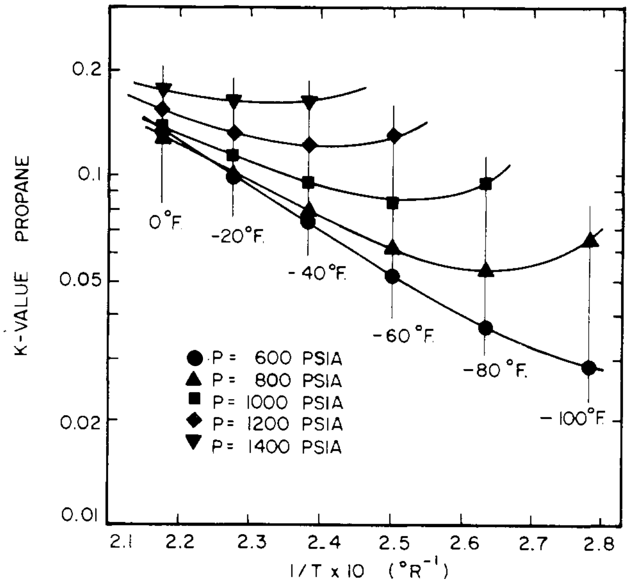

Figure 6. *K*-Value for propane at infinite dilution in the C_1-nC_7 system as function of reciprocal temperature—high pressure

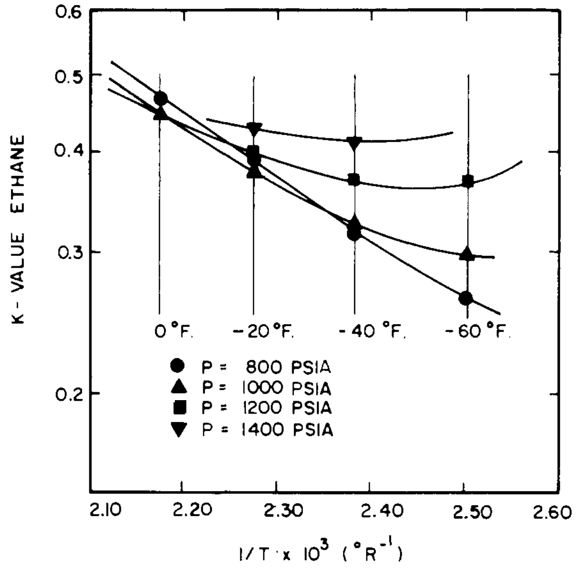

Figure 8. *K*-Value for ethane at infinite dilution in the C_1-nC_7 system as function of reciprocal temperature—high pressure

column with the difference in successive weighings being the loss in liquid. The technique is described by Koonce and Kobayashi (*15*).

Another method was used to control loss of liquid in the methane-solvent binaries. When pure methane was the elution gas, the stream was presaturated with the fixed liquid vapors in the presaturating column upstream of the sample injection valve. Much less liquid loss was observed and pressures nearer the critical were obtainable. Since liquid losses became slight, more runs were made between column weighings, and *W* was known with a higher degree of confidence.

The pressure limits of the GLPC technique in this work were determined by the rate of liquid loss. At pressures where critical phenomena (*20*) played a large part, losses in *W* were too great to prorate over successive runs with accuracy, especially for runs requiring long equilibration periods between mixture elution gases and the liquid.

DISCUSSION OF RESULTS

Phase Behavior. Methane *K*-values in a series of binary systems with normal paraffins show an unusual behavior. For a fixed pressure and temperature, the methane *K*-value increases with the carbon number of the solvent up to a point, reaches a maximum, then apparently decreases slightly. This behavior was also reported by Sage and Lacey (*21*) for solutions at higher temperature. The phenomenon is a revelation of the nonideal behavior of mixtures containing nonpolar components of widely different molecular size. Mixtures of this type show negative deviations from Raoult's law ($\gamma_1 < 1.0$).

K-values of methane in the C_1-toluene binary and of ethane and propane at infinite dilutions in the C_1-toluene binary show strong positive deviations from Raoult's law, because the liquid phase is almost entirely aromatic. At concentrations of propane well into the C_1-C_3-toluene ternary, positive deviations become smaller, because an appreciable amount of propane is dissolved in the liquid, making the liquid more paraffinic. The same tie point, that of the C_1-C_3 binary, is approached as in the C_1-C_3-nC_7 system. Therefore, liquid solution behavior ranges from that of a paraffin solute in an essentially pure aromatic solvent, to that of a paraffin solute in a paraffinic solvent. The result is a very large dependence of the paraffin *K*-values on the composition of the intermediate, propane. The results are shown in Figures 2 and 3, which are plots of methane and propane *K*-values as functions of mole fraction propane in the liquid.

Comparison with Results of Other Investigations. Few comparable systems exist for this work. Comparison for propane in the C_1-C_3-nC_7 system can be made to the −20° and −40° F. isotherms run by Koonce and Kobayashi (*15*). The methane *K*-values obtained by GLPC in the C_1-nC_7 system and in the C_1-toluene system are compared with Chang's (*3, 4*) results in Table I. It is also possible to test consistency of these data with the C_1-C_3 and C_1-C_2 data of Price and Kobayashi (*17*).

The data reported by Koonce and Kobayashi (*15*) for propane at infinite dilution in the C_1-nC_7 system are compared with these data in Table II. Koonce (*12*) used the methane *K*-values determined by Hurt (*8*) for the C_1-nC_7 system. These differed considerably from the results of Chang (*3*), which were used here, at the lower pressures.

Koonce's original data for propane was corrected using Equation 4 to reflect the change in methane *K*-values. The results are listed in Table II. Reasonably good agreement was obtained at low pressures for the propane infinite dilution *K*-values. However, deviations increase with pressure. The −40° F. isotherm shows the poorest agreement. Koonce's −40° F. results are approximately 5% above those of this work at low pressure, and reach a maximum of 19% above at 1000 p.s.i.a. His −20° F. isotherm is from 1% high at low pressure to 6% high at 1000 p.s.i.a. The high values of Koonce at −40° F. are not consistent with the lower temperature data of this work. They also indicate convergence to the critical at a lower pressure than that determined by Chang, Hurt, and Kobayashi (*4*). Koonce (*12*) determined the free gas volume of his GLPC columns at low pressure for the methane-propane-*n*-heptane system and corrected for the additional methane liquid present in the columns at the high pressures by using partial molal methane volumes extrapolated from Reamer, Sage, and Lacey (*18*). In this work, the free gas volume was effectively determined for each pressure. The error in the V_G calculation used by Koonce could account for the deviation shown between −20° F. points, and for part of the error at −40° F.

The comparison between GLPC results and Chang's (*4*) classically obtained results for methane *K*-values in C_1-nC_7 is shown in Table I. The average absolute deviation for

Table VI. Phase Compositions for the Methane-Propane–*n*-Heptane System with Ethane at Infinite Dilution ($Y_{C_2} = 0$, $X_{C_2} = 0$) and *K*-values for Methane, Ethane, and Propane

Pressure, P.S.I.A.	Vapor Composition		Liquid Composition			*K*-values		
	Y_{C_1}	Y_{C_3}	X_{C_1}	X_{C_3}	X_{C_7}	K_{C_1}	K_{C_2}	K_{C_3}
				$T = -20°$ F.				
100[a]	1.000	0.000	0.0490	0.000	0.9510	20.38	1.600	0.296
100	0.9595	0.0405	0.048	0.132	0.820	19.9[c]	1.634	0.306
100	0.9233	0.0767	0.050	0.255	0.695	18.54	1.603	0.301
100	0.8691	0.1309	0.047	0.428	0.525	18.5[c]	1.621	0.305
100[b]	0.706	0.294	0.050	0.950	0.000	14.3	1.50	0.310
200[a]	1.000	0.000	0.0989	0.000	0.9011	10.10	0.877	0.170
200	0.9784	0.0216	0.100	0.127	0.773	9.78		0.170
200	0.9595	0.0405	0.098	0.236	0.666	9.74	0.877	0.172
200	0.9233	0.0767	0.102	0.450	0.448	9.07	0.867	0.170
200[b]	0.847	0.153	0.117	0.883	0.000	7.25	0.822	0.173
400[a]	1.000	0.000	0.1883	0.000	0.8117	5.307	0.527	0.112
400	0.9800	0.0200	0.190	0.178	0.632	5.16	0.516	0.112
400	0.9595	0.0405	0.197	0.362	0.441	4.88	0.517	0.112
400[b]	0.901	0.099	0.236	0.764	0.000	3.81	0.486	0.130
600[a]	1.000	0.000	0.2668	0.000	0.7331	3.744	0.423	0.100
600	0.9800	0.0200	0.264	0.199	0.537	3.71	0.408	0.100
600	0.9784	0.0216	0.268	0.198	0.534	3.66	0.410	0.101
600	0.9595	0.0405	0.273	0.404	0.323	3.51	0.404	0.100
600[b]	0.925	0.075	0.350	0.650	0.000	2.63	0.430	0.116
800[a]	1.000	0.000	0.3412	0.000	0.6588	2.927	0.392	0.102
800	0.9784	0.0216	0.361	0.193	0.446	2.71	0.397	0.112
800	0.9595	0.0405	0.405	0.353	0.242	2.37[c]	0.395	0.115
800[b]	0.934	0.066	0.535	0.465	0.000	1.75	0.450	0.143
1000[a]	1.000	0.000	0.4078	0.000	0.5922	2.449	0.379	0.114
1000	0.9784	0.0216	0.426	0.172	0.402	2.30	0.388	0.126
1000[b]	0.906	0.094	0.565	0.435	0.000	1.60	0.506	0.216
				$T = -40°$ F.				
100[a]	1.000	0.000	0.0555	0.000	0.9445	18.00	1.204	0.196
100	0.9800	0.0200	0.056	0.101	0.843	17.55[c]	1.186	0.197
100	0.9595	0.0405	0.057	0.205	0.738	16.70	1.199	0.198
100	0.9233	0.0767	0.056	0.397	0.547	16.39	1.132	0.193
100[b]	0.810	0.190	0.065	0.935	0.000	12.5	1.110	0.203
200[a]	1.000	0.000	0.1101	0.000	0.8899	9.08	0.675	0.112
200	0.9800	0.0200	0.112	0.180	0.708	8.75	0.647	0.111

(*Continued on page 300*)

Table VI. Phase Compositions for the Methane-Propane–*n*-Heptane System with Ethane at Infinite Dilution (Y_{C_2} = 0, X_{C_2} = 0) and *K*-values for Methane, Ethane, and Propane (*Continued*)

Pressure, P.S.I.A.	Vapor Composition		Liquid Composition			*K*-values		
	Y_{C_1}	Y_{C_3}	X_{C_1}	X_{C_3}	X_{C_7}	K_{C_1}	K_{C_2}	K_{C_3}
				$T = -40°$ F.				
200	0.9595	0.0405	0.116	0.360	0.524	8.30	0.649	0.112
200[b]	0.900	0.100	0.135	0.865	0.000	6.70	0.611	0.116
400[a]	1.000	0.000	0.2081	0.000	0.7919	4.804	0.414	0.0772
400	0.9902	0.0098	0.211	0.128	0.661	4.70	0.395	0.0765
400	0.9800	0.0200	0.218	0.259	0.523	4.50[c]	0.396	0.0772
400	0.9713	0.0287	0.224	0.373	0.403	4.34		0.077[c]
400	0.9595	0.0405	0.233	0.524	0.243	4.11[c]	0.387	0.0772
400[b]	0.937	0.063	0.267	0.733	0.000	3.50	0.393	0.086
600[a]	1.000	0.000	0.2990	0.000	0.7010	3.343	0.340	0.0738
600	0.9894	0.0106	0.307	0.143	0.550	3.22[c]	0.337	0.0742
600	0.9713	0.0287	0.333	0.383	0.284	2.92	0.326	0.0750
600[b]	0.949	0.051	0.395	0.605	0.000	2.41	0.340	0.084
800[a]	1.000	0.000	0.3728	0.000	0.6272	2.681	0.316	0.0798
800	0.9894	0.0106	0.385	0.132	0.483	2.57	0.317	0.0806
800	0.9713	0.0287	0.414	0.332	0.254	2.35	0.311	0.0863
800[b]	0.948	0.052	0.546	0.0454	0.000	1.74	0.415	0.114
1000[a]	1.000	0.000	0.4481	0.000	0.5519	2.230	0.325	0.0955
1000	0.9894	0.0106	0.454	0.109	0.437	2.18	0.325	0.0976
1000	0.9784	0.0216	0.501	0.193	0.306	1.95	0.359	0.112
1000[b]	0.944	0.056	0.659	0.341	0.000	1.43	0.62	0.165
				$T = -60°$ F.				
100[a]	1.000	0.000	0.0628	0.000	0.9372	15.92	0.878	0.123
100	0.9902	0.0098	0.065	0.080	0.855	15.34		0.122[c]
100	0.9800	0.0200	0.065	0.158	0.776	14.9[c]	0.873	0.126
100	0.9713	0.0287	0.065	0.235	0.700	14.99		
100	0.9595	0.0405	0.067	0.331	0.602	14.3[c]	0.846	0.122
100	0.9233	0.0767	0.070	0.651	0.279	13.24	0.806	0.118
100[b]	0.885	0.115	0.085	0.915	0.000	10.8	0.779	0.126
200[a]	1.000	0.000	0.1235	0.000	0.8765	8.096	0.486	0.0707
200	0.9800	0.0200	0.131	0.275	0.594	7.52	0.476	0.0726
200	0.9713	0.0287	0.134	0.402	0.464	7.26	0.469	0.0714
200[b]	0.938	0.062	0.162	0.838	0.000	5.77	0.429	0.074
400[a]	1.000	0.000	0.2322	0.000	0.7678	4.306	0.309	0.0512
400	0.9902	0.0098	0.239	0.184	0.577	4.15[c]	0.307	0.0532
400	0.9894	0.0106	0.244	0.204	0.552	4.05		0.05[c]
400	0.9800	0.0200	0.242	0.388	0.370	4.05	0.296	0.0515
400[b]	0.961	0.039	0.320	0.680	0.000	2.99	0.270	0.058
600[a]	1.000	0.000	0.3255	0.000	0.6745	3.072	0.263	0.0517
600	0.9894	0.0106	0.353	0.195	0.452	2.81	0.252	0.0543
600	0.9800	0.0200	0.390	0.362	0.248	2.52	0.257	0.0552
600[b]	0.966	0.034	0.464	0.536	0.000	2.09	0.254	0.064
800[a]	1.000	0.000	0.4117	0.000	0.5883	2.428	0.264	0.0616
800	0.9894	0.0106	0.459	0.156	0.385	2.15	0.265	0.0676
800[b]	0.960	0.040	0.616	0.384	0.000	1.56	0.291	0.104
1000[a]	1.000	0.000	0.4921	0.000	0.5079	2.031	0.298	0.0843
1000[b]	0.943	0.057	0.842	0.158	0.000	1.12	0.469	0.36
				$T = -80°$ F.				
100[a]	1.000	0.000	0.0726	0.000	0.9274	13.77		0.0713
100	0.9902	0.0098	0.076	0.134	0.790	13.0[c]	0.604	0.0731
100	0.9800	0.0200	0.078	0.282	0.640	12.51		0.071[c]
100	0.9713	0.0287	0.079	0.411	0.510	12.30	0.576	0.0698
100[b]	0.929	0.071	0.100	0.900	0.000	9.28		0.078
200[a]	1.000	0.000	0.1409	0.000	0.8591	7.100		0.0430
200	0.9902	0.0098	0.145	0.224	0.631	6.83	0.332	0.0439
200	0.9800	0.0200	0.166	0.455	0.379	5.90	0.334	0.0440
200[b]	0.963	0.037	0.200	0.800	0.000	4.80		0.046
400[a]	1.000	0.000	0.2630	0.000	0.7370	3.802		0.0316
400	0.9902	0.0098	0.298	0.290	0.412	3.33	0.218	0.0338
400[b]	0.976	0.024	0.395	0.605	0.000	2.47		0.0405
600[a]	1.000	0.000	0.3780	0.000	0.6220	2.645		0.0367
600	0.9902	0.0098	0.432	0.241	0.327	2.29	0.193	0.0406
600[b]	0.977	0.023	0.546	0.454	0.000	1.79		0.051
800[a]	1.000	0.000	0.4765	0.000	0.5235	2.090		0.0531
				$T = -100°$ F.				
100[a]	1.000	0.000	0.0847	0.000	0.9153	11.81		0.0405
100	0.9902	0.0098	0.095	0.248	0.657	10.43		0.0395
100	0.9800	0.0200	0.104	0.498	0.398	9.39		0.0401
100[b]	0.959	0.041	0.125	0.875	0.000	7.67		0.047
200[a]	1.000	0.000	0.1635	0.000	0.8365	6.116		0.0252
200	0.9902	0.0098	0.197	0.386	0.417	5.03		0.0254
200[b]	0.979	0.021	0.221	0.779	0.000	4.41		0.027
400[a]	1.000	0.000	0.3110	0.000	0.6890	3.215		0.0211
400	0.9902	0.0098	0.396	0.398	0.206	2.50		0.0246
400[b]	0.986	0.014	0.476	0.524	0.000	2.03		0.0278

[a] Methane *K*-values and phase compositions for X_{C_3} = 0.000 are from Chang, Hurt, and Kobayashi (*4*). [b] *K*-values and phase compositons for X_{C_7} = 0.000 are from Price and Kobayashi (*17*). [c] Interpolated value.

Table VII. Phase Compositions for the Methane-Ethane–n-Heptane System and K-values for Methane and Ethane

Pressure, P.S.I.A.	Vapor Composition		Liquid Composition			K-values	
	Y_{C_1}	Y_{C_2}	X_{C_1}	X_{C_2}	X_{C_7}	K_{C_1}	K_{C_2}
			$T = -20°$ F.				
100[a]	1.000	0.000	0.0490	0.000	0.9510	20.38	1.600
100	0.786	0.214	0.042	0.132	0.826	18.7	1.616
100	0.595	0.405	0.032	0.252	0.716	18.5	1.604
100[b]	Below ethane vapor pressure						
200[a]	1.000	0.000	0.0989	0.000	0.9011	10.10	0.877
200	0.786	0.214	0.084	0.235	0.681	9.39	0.907
200	0.595	0.405	0.067	0.453	0.480	8.84	0.895
200[b]	0.176	0.824	0.030	0.970	0.000	5.90	0.850
400[a]	1.000	0.000	0.1883	0.000	0.8117	5.307	0.527
400	0.891	0.109	0.179	0.203	0.618	5.01	0.537
400	0.786	0.214	0.165	0.390	0.445	4.78	0.548
400[b]	0.552	0.448	0.181	0.819	0.000	3.03	0.547
600[a]	1.000	0.000	0.2668	0.000	0.7331	3.744	0.423
600	0.891	0.109	0.254	0.248	0.498	3.51	0.439
600	0.786	0.214	0.250	0.474	0.276	3.14	0.451
600[b]	0.669	0.331	0.325	0.675	0.000	2.02	0.490
800[a]	1.000	0.000	0.3412	0.000	0.6588	2.927	0.392
800	0.9456	0.0544	0.331	0.138	0.531	2.86	0.395
800	0.891	0.109	0.342	0.264	0.394	2.61	0.413
800[b]	0.715	0.285	0.470	0.530	0.000	1.52	0.538
1000[a]	1.000	0.000	0.4078	0.000	0.5922	2.449	0.379
1000	0.9456	0.0544	0.396	0.141	0.463	2.39	0.386
1000	0.891	0.109	0.393	0.268	0.339	2.27	0.406
1000[b]	0.698	0.302	0.521	0.479	0.000	1.34	0.632
			$T = -40°$ F.				
100[a]	1.000	0.000	0.0555	0.000	0.9445	18.00	1.204
100	0.786	0.214	0.047	0.172	0.781	16.61	1.243
100	0.595	0.405	0.037	0.328	0.635	16.00	1.233
100[b]	Below ethane vapor pressure				0.000		
200[a]	1.000	0.000	0.1101	0.000	0.8899	9.080	0.675
200	0.786	0.214	0.094	0.316	0.590	8.35	0.678
200	0.595	0.405	0.082	0.605	0.313	7.26	0.667
200[b]	0.370	0.630	0.071	0.929	0.000	5.25	0.680
400[a]	1.000	0.000	0.2081	0.000	0.7919	4.804	0.414
400	0.891	0.109	0.197	0.262	0.541	4.52	0.416
400	0.786	0.214	0.194	0.513	0.293	4.05	0.417
400[b]	0.675	0.325	0.249	0.751	0.000	2.73	0.433
600[a]	1.000	0.000	0.2990	0.000	0.7010	3.343	0.340
600	0.9456	0.0544	0.298	0.157	0.545	3.17	0.346
600	0.891	0.109	0.296	0.312	0.392	3.01	0.350
600[b]	0.770	0.230	0.416	0.584	0.000	1.84	0.395
800[a]	1.000	0.000	0.3728	0.000	0.6272	2.681	0.316
800	0.9456	0.0544	0.380	0.163	0.457	2.49	0.334
800	0.891	0.109	0.391	0.317	0.292	2.28	0.344
800[b]	0.796	0.204	0.556	0.444	0.000	1.43	0.460
1000[a]	1.000	0.000	0.4481	0.000	0.5519	2.230	0.325
1000	0.9456	0.0544	0.453	0.155	0.392	2.09	0.350
1000[b]	0.771	0.229	0.612	0.388	0.000	1.26	0.59
			$T = -60°$ F.				
100[a]	1.000	0.000	0.0628	0.000	0.9372	15.92	0.878
100	0.786	0.214	0.055	0.243	0.702	14.40	0.880
100	0.595	0.405	0.044	0.471	0.485	13.59	0.860
100[b]	0.219	0.781	0.023	0.977	0.000	9.30	0.800
200[a]	1.000	0.000	0.1235	0.000	0.8765	8.096	0.486
200	0.891	0.109	0.120	0.222	0.658	7.45	0.491
200	0.786	0.214	0.112	0.437	0.451	7.00	0.490
200[b]	0.572	0.428	0.125	0.875	0.000	4.60	0.490
400[a]	1.000	0.000	0.2322	0.000	0.7678	4.306	0.309
400	0.9456	0.0544	0.243	0.175	0.582	3.89	0.311
400	0.891	0.109	0.240	0.348	0.412	3.72	0.313
400[b]	0.776	0.224	0.324	0.676	0.000	2.40	0.332
600[a]	1.000	0.000	0.3255	0.000	0.6745	3.072	0.263
600	0.9456	0.0544	0.346	0.200	0.454	2.74	0.271
600	0.891	0.109	0.352	0.390	0.258	2.53	0.279
600[b]	0.846	0.154	0.511	0.489	0.000	1.65	0.316
800[a]	1.000	0.000	0.4117	0.000	0.5883	2.428	0.264
800	0.9456	0.0544	0.440	0.197	0.363	2.15	0.277
800[b]	0.875	0.125	0.678	0.322	0.000	1.29	0.389
1000[a]	1.000	0.000	0.4921	0.000	0.5079	2.031	0.298
1000[b]	0.928	0.072	0.892	0.108	0.000	1.04	0.670

[a] Methane K-values and phase compositions for $X_{C_2} = 0.000$ are from Chang, Hurt, and Kobayashi (*4*). [b] K-values and phase compositions for $X_{C_7} = 0.000$ are from Price and Kobayashi (*17*).

Table VIII. Phase Compositions for the Methane-Propane-Toluene System with Ethane at Infinite Dilution ($Y_{C_2} = 0$, $X_{C_2} = 0$) and K-values for Methane, Ethane, and Propane

Pressure, P.S.I.A.	Vapor Composition		Liquid Composition			K-values		
	Y_{C_1}	Y_{C_3}	X_{C_1}	X_{C_3}	X_{tol}	K_{C_1}	K_{C_2}	K_{C_3}
				$T = -40°$ F.				
100[a]	1.000	0.000	0.0230	0.000	0.9770	43.36	2.836	0.428
100	0.9233	0.0767	0.030	0.245	0.725	30.75	1.964	0.313
100	0.869	0.131	0.044	0.558	0.398	19.7[c]	1.535	0.235
100[b]	0.810	0.190	0.065	0.935	0.000	12.5	1.110	0.203
200[a]	1.000	0.000	0.0462	0.000	0.9538	21.61	1.406	0.242
200	0.9784	0.0216	0.052	0.101	0.847	18.69	1.247	0.214
200	0.9713	0.0287	0.056	0.142	0.802	17.39	1.181	0.202
200	0.9595	0.0405	0.062	0.222	0.716	15.39	1.085	0.183
200	0.9233	0.0767	0.109	0.661	0.230	8.45[c]	0.711	0.116
200[b]	0.900	0.100	0.135	0.865	0.000	6.70	0.611	0.116
400[a]	1.000	0.000	0.0847	0.000	0.9153	11.78	0.831	0.160
400	0.9784	0.0216	0.117	0.167	0.716	8.37	0.676	0.130
400	0.9713	0.0287	0.135	0.247	0.618	7.21	0.612	0.116
400	0.9595	0.0405	0.168	0.444	0.388	5.70	0.485	0.0911
400[b]	0.937	0.063	0.267	0.733	0.000	3.50	0.393	0.086
600[a]	1.000	0.000	0.1246	0.000	0.8754	8.026	0.668	0.143
600	0.9894	0.0106	0.145	0.080	0.775	6.80	0.604	0.132
600	0.9784	0.0216	0.175	0.191	0.634	5.60	0.521	0.113
600	0.9713	0.0287	0.216	0.290	0.494	4.49	0.445	0.0989
600[b]	0.949	0.051	0.395	0.605	0.000	2.41	0.370	0.084
800[a]	1.000	0.000	0.1629	0.000	0.8371	6.139	0.603	0.148
800	0.9894	0.0106	0.182	0.076	0.742	5.42	0.543	0.139
800	0.9784	0.0216	0.234	0.176	0.590	4.19	0.462	0.123
800	0.9713	0.0287	0.278	0.260	0.462	3.49	0.431	0.110
800[b]	0.948	0.052	0.546	0.454	0.000	1.74	0.415	0.114
1000[a]	1.000	0.000	0.1860	0.000	0.8140	5.376	0.604	0.169
1000	0.9784	0.0216	0.250	0.143	0.607	3.90	0.488	0.151
1000[b]	0.944	0.056	0.659	0.341	0.000	1.43	0.62	0.165

[a] Methane K-values and phase compositions for X_{C_3} = 0.000 are from Chang, Hurt, and Kobayashi (*4*). [b] K-values and phase compositions for X_{C_7} = 0.000 are from Price and Kobayashi (*17*). [c] Interpolated values.

the points compared was 2.3% with a maximum of 4.7%. The GLPC results show a trend to negative deviations at temperatures below −40° F. and to positive deviations for −40° F. and above. This cannot be attributed to an isotope effect; rather, it is attributed to inaccuracies in the estimate of K_T, the K-value of tritium at infinite dilution in the system.

Figures 2 through 4 show the consistency of these data with those of Price and Kobayashi (*17*). The methane and propane K-values obtained in the C_1-C_3-nC_7 and C_1-C_3-toluene systems tend toward the respective C_1-C_3 binary K-values as a limit. The K-values of ethane at infinite dilution in these two ternary systems approach those for ethane at infinite dilution in the C_1-C_3 binary calculated from the correlation of Price and Kobayashi (*17*). Methane and ethane K-values in the C_1-C_2-nC_7 ternary are consistent with those in the C_1-C_2 binary system.

Error Analysis. The estimated certainties in the measurement of experimental variables are listed below:

Variable	Uncertainty
W	±1.5%
T	±0.05° K.
P	±1 p.s.i.a., $P \leq$ 1000 p.s.i.a. ±2 p.s.i.a., $P >$ 1000 p.s.i.a.
$f_a(t_{R_i} - t_{R_r})$	±0.5%
T_a	±0.1° K.

Several determinations were made of ethane and propane infinite dilution K-values for a given set of conditions. They reproduced within ±1.0% for propane and ±1.5% for ethane. Figures 5 to 8 also show consistency of the infinite dilution K-values between isotherms to be within these limits.

The best test of K-values obtained for methane in the binaries is given in Table I, a comparison of GLPC results with those of Chang, Hurt, and Kobayashi (*4*). The average absolute deviation was 2.3% with a maximum of 4.7%. It is estimated that mixture methane K-values were accurate within ±4%.

The average reliability of ethane K-values in the mixtures is estimated to be ±2.5% and that for propane to be ±2.0%. Somewhat better accuracy is to be expected at lower pressures, and slightly worse errors (up to ±4%) are possible at the highest pressures. These error estimates were substantiated by the reproducibility of the data, by cross plots of the data (as in Figures 5 to 8), and by the consistency of results at different compositions along an isobar for a given temperature.

The results of this study are presented in Tables III–VIII.

NOMENCLATURE

f_a = volumetric flow rate at P_a, T_a, cc. per minute
K = vapor-liquid equilibrium constant, y/x
P = total system pressure
P_a = atmospheric pressure
R = gas constant
T = absolute temperature
T_a = room temperature
t_R = retention time of a solute peak
V_G = void volume of GLPC column
V_L = total volume of liquid in GLPC column
V_R = retention volume of a solute peak, measured at column conditions

W = total moles of fixed liquid in the GLPC column
y = mole fraction in the vapor phase
Z = compressibility factor of methane
Z_a = compressibility factor of elution gas corresponding to P_a, T_a
Z_M = compressibility of elution gas

Superscripts

$*$ = property of tracer component

Subscripts

i, j, k = component identification
$1, 2$ = methane and solvent, respectively, in methane binaries
$1, 2, 3, T$ = methane, ethane, propane, and tritium, respectively

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Solubility Isotherms in the System Sodium Oxide–Boric Oxide–Water

Revised Solubility-Temperature Curves of Boric Acid, Borax, Sodium Pentaborate, and Sodium Metaborate

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Isotherms at 0°, 5°, 10°, 20°, 30°, 40°, 50°, 60°, 75°, and 94° C. have been determined in the system Na_2O–B_2O_3–H_2O in the range of Na_2O/B_2O_3 mole ratio from 0 to 1.2. The compounds found were those with Na_2O–B_2O_3–H_2O molar proportions 0:1:3, 1:1:1, 1:1:4, 1:1:8, 1:2:4, 1:2:5, 1:2:10, 1:5:2, 1:5:4, 1:5:10, 2:5:5, 2:5.1:7, and 2:9:11. Revised solubility-temperature curves are given for boric acid, borax, sodium pentaborate, and sodium metaborate.

EARLY WORK on the solubility isotherms in the system Na_2O-B_2O_3-H_2O, by Dukelski (*7*) at 30°, and by Sborgi *et al.* (*16*) at 0°, 20°, 35°, 45°, 60°, and 90° C., gives the approximate locations of the isotherms, but is limited and partly inaccurate. Isotherms at 35° and 50° in the region of Na_2O/B_2O_3 mole ratio from 0 to 0.5 were determined by Suhr (*17*), and agree well with the present work. Recently, Bouaziz and Milman have published diagrams showing the 100° isotherm (*5*) and portions of the 46°, 56°, and 80° isotherms (*11*). Their results differ from the present work in some respects.

In the present investigation, the 0°, 5°, 10°, 20°, 30°, 40°, 50°, 60°, 75°, and 94° C. isotherms were determined, including curves for several compounds which were unknown to the early investigators. Except for a few determinations at 40°, 60°, and 98.6° C., this work was limited to the region having Na_2/B_2O_3 mole ratios less than 1.2, which is of more practical interest than the very alkaline