

The results of the experimental solubility data are tabulated in Table II. In Figure 3 the methane K-values are presented. Figure 4 shows the extrapolation of the solubility data to the vapor pressure of *n*-decane. A temperature crossplot of the K-values for methane obtained from the solubility data in this work along with those obtained by Sage and Lacey (6) at higher temperatures is presented in Figure 5. The agreement of results from the experiments outlined herein with those of more complex static equilibrium studies is quite favorable.

#### ADVANTAGE OF THE SOLUBILITY TECHNIQUE

The validity of the volumetric, static experiments described herein for determining the solubility of a highly volatile material in another which is quite non-volatile is established by the consistency of the results with those of other investigators. The technique has the distinct advantage of furnishing vapor-liquid equilibria information from *P-V-T* measurements, with no need for sampling or analysis of either phase when the assumption that the vapor contains essentially none of the nonvolatile components is valid.

#### ACKNOWLEDGMENT

The authors wish to acknowledge the Petroleum Research Fund of the American Chemical Society for support of this work, Tennessee Gas Transmission Co. and Associated Oil and Gas Co. for their donation of methane gas, and the Phillips Petroleum Co. for their donation of *n*-decane.

#### NOMENCLATURE

- $C_D$  = volume of capillary tubing from equilibrium system to the high pressure mercury manometer.  
 $C_M$  = volume per unit length of the right leg of the high pressure manometer.  
 $g$  = local acceleration of gravity.  
 $g_c$  = standard acceleration of gravity.  
 $h_G$  = height of the base of the piston above the reference plane.  
 $h_L$  = height of left leg of high pressure mercury manometer above reference plane.  
 $h_R$  = height of right leg of high pressure mercury manometer above reference plane.  
 $n_{10}$  = moles of *n*-decane admitted to equilibrium cell.  
 $N_A$  = moles of methane dissolved in or absorbed by *n*-decane.  
 $N_i$  = moles of methane in cell before admission of *n*-decane.  
 $N_F$  = moles of methane in vapor phase after admission of *n*-decane.  
 $P$  = system pressure as measured with dead weight piston gauge.

- $P_0$  = initial pressure in known volume before expansion into equilibrium cell to determine cell volume.  
 $P_i$  = initial pressure in equilibrium cell before admission of *n*-decane to the cell.  
 $P_F$  = final pressure in equilibrium cell after expansion from known volume or after admission of *n*-decane.  
 $P_G$  = uncorrected pressure indicated by weights placed on dead weight piston gauge.  
 $P_B$  = barometric pressure in piston gauge pressure measurement  
 $T$  = system temperature (absolute)  
 $T_a$  = ambient temperature (absolute)  
 $v_i$  = molal volume of component *i*.  
 $V$  = volume of equilibrium system  
 $V_{10}$  = total volume of *n*-decane admitted to the equilibrium cell  
 $V_F$  = gas volume of equilibrium system after admission of *n*-decane  
 $V_0$  = calibrated known volume used  
 $V_D$  = dead volume of capillary tubing and manometer used to transmit pressure from equilibrium system to piston gauges  
 $V_{D_0}$  = value of  $V_D$  before expansion from  $V_0$  into  $V$   
 $V_{D_i}$  = initial value of  $V_D$  before admission of *n*-decane into  $V$   
 $V_{D_F}$  = value of  $V_D$  corresponding to  $V_F$   
 $x_1$  = mole fraction methane in the liquid phase at equilibrium  
 $Z_0$  = compressibility factor corresponding to  $P_0, T$   
 $Z_i$  = compressibility factor corresponding to  $P_i, T$   
 $Z_F$  = compressibility factor corresponding to  $P_F, T$   
 $Z_{D_0}$  = compressibility factor corresponding to  $P_0, T_a$   
 $Z_{D_i}$  = compressibility factor corresponding to  $P_i, T_a$   
 $Z_{D_F}$  = compressibility factor corresponding to  $P_F, T_a$   
 $\rho_{10}$  = density of *n*-decane  
 $\rho_0$  = density of piston gauge oil  
 $\rho_{Hg}$  = density of mercury

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RECEIVED for review December 11, 1963. Accepted March 26, 1964.

## Vapor-Liquid Equilibrium Coefficients Determined by Gas-Liquid Partition Chromatography

### The Systems Methane-Propane-*n*-Decane and Methane-Propane-*n*-Heptane

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THE VALIDITY of using gas-liquid partition chromatography (GLPC) to determine vapor-liquid equilibrium data has been established by a number of workers. Porter, Deal, and Stross (15), and Anderson and Napier (1) found

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agreement between partition coefficients determined by GLPC near atmospheric pressures and those obtained by classical static methods. Stalcup and Kobayashi (20) reported agreement between K-values or vapor-liquid equilibrium coefficients determined chromatographically at pressures up to 2000 p.s.i.a. and those reported by the

NGAA (14). Several authors (11, 21, 22) have reported agreement between activity coefficients measured by GLPC and those measured by conventional techniques. Of the previous investigators only Stalkup and Kobayashi used an elution gas or carrier gas which was appreciably soluble in the fixed liquid phase. These authors introduced the use of a binary elution gas, although their work with the 2-component carrier was not extensive.

In the present work  $K$ -values or  $y/x$  values have been obtained for methane and propane in both the methane-propane- $n$ -decane system and the methane-propane- $n$ -heptane system. In the  $n$ -decane system data have been taken for 70°, 40°, 0° and -20° F. over the pressure range 20-1000 p.s.i.a. and the propane vapor composition range 0-16.27 mole per cent yielding liquid composition with up to 62.3 mole per cent propane. For the  $n$ -heptane system data were obtained for -20° and -40° F. for the pressure range 100-1000 p.s.i.a. and the propane vapor composition range 0-4.31 per cent. The elution data have been used in the theoretical plate theory of chromatography outlined by Stalkup (18) and Koonce (8) as well as the rate theory approach to chromatography given by Stalkup and Deans (19). The first required that the sample molecules be distinguishable from all others in the system. Distinguishability of sample molecules was achieved by using radioactively tagged samples. The second, the rate theory, allows the use of indistinguishable sample molecules.

## EXPERIMENTAL

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

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

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

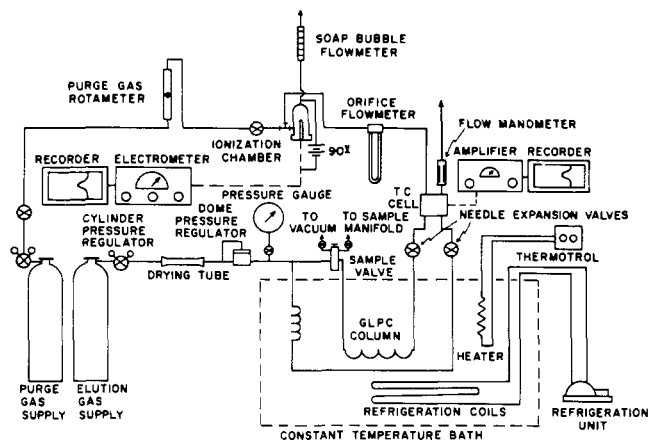


Figure 1. Schematic diagram of the high pressure GLPC apparatus

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

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

The columns used in this study were  $\frac{3}{16}$  inch stainless steel tubes from 6 inches to 18 inches in length. The columns were packed with firebrick on which  $n$ -decane or  $n$ -heptane had been impregnated by the procedure described by Keulemans (7). After several pressure points the column being used was removed, capped at its extremities, cleaned and dried, and then weighed on a large analytical balance to determine the loss of fixed liquid due to evaporation into the flowing gas stream.

Column pressure above 50 p.s.i.a. was measured with a Heise gauge subdivided into 2 p.s.i. increments. Below 50 p.s.i.a. a mercury manometer was used for pressure measurement. Temperature was controlled and measured to 0.1° F.

Briefly, the experimental procedure was to adjust the flow of elution gas, whether pure methane or a mixture of methane and propane, to approximately 70 cc./min. at STP after establishing the desired column temperature and pressure. After allowing sufficient time for the elution gas to achieve equilibrium with the fixed  $n$ -decane, a  $\frac{1}{4}$  cc. (STP) sample of gaseous solute was introduced into the column. The samples were mixtures of radioactive methane diluted with nonradioactive methane and radioactive propane diluted with a 50-50 mixture of nonradioactive methane and nonradioactive propane. The time required for the two peak concentrations to appear in the effluent stream was then measured for both detection schemes.

## MATERIALS

The dried methane gas was analyzed mass spectrographically and found to contain 99.7 per cent methane, 0.2 per cent nitrogen, and 0.1 per cent other components, mainly ethane.

The propane used for the mixtures and in some cases to dilute tracer material was Phillips Instrument Grade propane with a stated purity of 99.5 mole per cent. The radioactive gases used were  $C^{14}H_4$  and  $H_3C-C^{14}H_2-CH_3$  obtained from the New England Nuclear Corporation of Boston, Mass.

Both the *n*-decane and the *n*-heptane were Research Grade materials also obtained from the Phillips Petroleum Co. with stated purities of 99.35 and 99.90 per cent, respectively.

The solid support material was a screened 30–50 mesh, acid-washed C-3 firebrick purchased from the W.H. Curtin Co.

## DISCUSSION AND RESULTS

A familiar result of theoretical derivations presented by several authors (12, 23) relating the retention volume

of a solute to its equilibrium partition coefficient is the following:

$$V_{R_i} = V_R + V_L/H_k \quad (1)$$

Others (18, 20) have shown how this relation may be used to obtain an expression for the *K*-value for a binary elution gas soluble in the fixed liquid. The result is:

$$K_k = \frac{y_k}{x_k} = \frac{Z_M RTW}{P(V_{R_i}^* - V_R)(1 - y_{1/K_1} - y_{2/K_2})} \quad (2)$$

for *k* = 1,2; 1 corresponding to propane, 2 to methane.

Table I. *K*-values for Methane and Propane and Vapor Liquid Phase Compositions in the System Methane–Propane–*n*-Decane at 70° F.

Press., P.S.I.A.	Vapor Composition			Liquid Composition			Methane <i>K</i> -values			Propane <i>K</i> -values		
	<i>y</i> <sub>C<sub>1</sub></sub>	<i>y</i> <sub>C<sub>2</sub></sub>	<i>y</i> <sub>C<sub>10</sub></sub>	<i>x</i> <sub>C<sub>1</sub></sub>	<i>x</i> <sub>C<sub>2</sub></sub>	<i>x</i> <sub>C<sub>10</sub></sub>	<i>K</i> <sub>C<sub>1</sub></sub> <sup>a</sup>	<i>K</i> <sub>C<sub>2</sub></sub> <sup>b</sup>	% Dev.	<i>K</i> <sub>C<sub>1</sub></sub> <sup>a</sup>	<i>K</i> <sub>C<sub>2</sub></sub> <sup>c</sup>	% Dev.
31.0	1.0	~0	~0	0.0119	~0	0.9881	...	84.0	...	3.66	3.63	-0.8
51.5	1.0	0	0	0.0195	0	0.9805	...	51.3	...	2.28	2.27	-0.4
54.0	1.0	0	0	0.0203	0	0.9797	...	49.2	...	2.21	2.21	0
92.0	1.0	0	0	0.0339	0	0.9661	...	29.5	...	1.26	1.26	0
248	1.0	0	0	0.0862	0	0.9138	...	11.6	...	0.527	0.532	+0.9
382	1.0	0	0	0.130	0	0.870	...	7.70	...	0.377	0.378	+0.3
514	1.0	0	0	0.172	0	0.828	...	5.82	...	0.326	0.323	-0.9
698	1.0	0	0	0.217	0	0.783	...	4.60	...	0.280	0.278	-0.7
911	1.0	0	0	0.265	0	0.735	...	3.77	...	0.253	0.255	+0.8
41.0	0.9792	0.0208	~0	0.0153	0.0076	0.9771	71.5	64.0	+13.6	2.73	2.77	+1.5
70.3	0.9792	0.0208	0	0.0258	0.0130	0.9612	28.9	38.0	-22.8	1.60	1.63	+1.8
103.0	0.9792	0.0208	0	0.0370	0.0173	0.9457	23.6	26.5	-10.9	1.20	1.21	+1.3
201	0.9792	0.0208	0	0.0704	0.0319	0.8977	12.5	13.9	-9.4	0.653	0.658	+0.8
300	0.9792	0.0208	0	0.102	0.0441	0.854	8.93	9.60	-6.5	0.472	0.480	+1.5
398	0.9792	0.0208	0	0.132	0.0535	0.815	6.90	7.40	-6.7	0.389	0.391	+0.5
598	0.9792	0.0208	0	0.191	0.0658	0.743	5.37	5.12	+4.9	0.316	0.317	+0.3
800	0.9792	0.0208	0	0.243	0.0746	0.682	3.95	4.03	-1.9	0.279	0.282	+1.1
995	0.9792	0.0208	0	0.280	0.0806	0.639	3.22	3.50	-8.0	0.258	0.259	+0.3
42.0	0.9569	0.0431	~0	0.0153	0.0165	0.9682	32.4	62.5	-51.0	2.62	2.60	-0.8
70.5	0.9669	0.0430	0	0.0253	0.0263	0.9484	40.5	37.8	+4.9	1.64	1.65	+0.6
102	0.9569	0.0431	0	0.0360	0.0362	0.9278	27.9	26.6	+4.9	1.19	1.21	+1.7
201	0.9569	0.0431	0	0.0684	0.0664	0.8652	14.4	14.0	+2.8	0.649	0.655	+0.9
301	0.9569	0.0431	0	0.0999	0.0902	0.8099	7.87	9.58	-17.8	0.478	0.476	-0.4
420	0.9569	0.0431	0	0.137	0.113	0.750	6.36	7.00	-9.1	0.382	0.384	-0.5
599	0.9569	0.0431	0	0.191	0.136	0.673	5.60	5.02	+11.5	0.318	0.319	+0.3
775	0.9569	0.0431	0	0.236	0.150	0.614	3.79	4.06	-6.6	0.288	0.289	+0.3
978	0.9569	0.0431	0	0.275	0.157	0.568	3.29	3.48	-5.5	0.274	0.277	+1.1
44.0	0.9310	0.0690	~0	0.0155	0.0260	0.9585	114	60.0	+90.5	2.65	2.65	-0
74.0	0.9310	0.0690	0	0.0257	0.0426	0.9317	15.0	36.2	-58.6	1.62	1.60	-1.2
110	0.9310	0.0690	0	0.0378	0.0627	0.8995	30.3	24.6	+23.2	1.10	1.10	0
192	0.9310	0.0690	0	0.0638	0.101	0.835	14.4	14.6	-1.4	0.685	0.695	+1.4
292	0.9310	0.0690	0	0.0940	0.140	0.766	10.2	9.90	+3.0	0.493	0.499	+1.2
404	0.9310	0.0690	0	0.129	0.174	0.697	7.81	7.20	+8.5	0.396	0.400	+1.0
596	0.9310	0.0690	0	0.186	0.209	0.605	5.07	5.00	+1.4	0.330	...	...
794	0.9310	0.0690	0	0.234	0.233	0.533	4.18	3.98	+5.5	0.296	0.298	+0.7
991	0.9310	0.0690	0	0.274	0.242	0.484	3.68	3.40	+8.2	0.285	0.286	+0.3
52.5	0.9056	0.0944	~0	0.0179	0.0427	0.9394	54.0	50.5	+6.9	2.21	2.24	+1.4
108	0.9056	0.0944	0	0.0359	0.0874	0.8767	21.7	25.2	-13.9	1.08	1.10	+1.8
201	0.9056	0.0944	0	0.0647	0.143	0.792	12.9	14.0	-7.9	0.660	0.675	+2.3
300	0.9056	0.0944	0	0.0941	0.196	0.710	8.72	9.62	-9.3	0.481	0.483	+0.4
402	0.9056	0.0944	0	0.128	0.234	0.638	7.10	7.10	0	0.403	0.403	0
595	0.9056	0.0944	0	0.184	0.283	0.533	5.52	4.93	+12.0	0.333	0.327	-1.8
801	0.9056	0.0944	0	0.234	0.318	0.448	4.12	3.87	+6.5	0.297	0.291	-2.0
997	0.9056	0.0944	0	0.274	0.323	0.403	3.23	3.31	-2.4	0.292	0.290	-0.7
48.0	0.8691	0.1309	~0	0.0158	0.0545	0.9297	150.1	55.1	+173	2.40	2.47	+2.9
100	0.8691	0.1309	0	0.0320	0.109	0.859	38.3	27.2	+41.0	1.20	1.20	-0
195	0.8691	0.1309	0	0.0599	0.196	0.744	13.0	14.5	-11.0	0.669	0.679	+1.5
300	0.8691	0.1309	0	0.0905	0.269	0.641	9.97	9.60	+3.8	0.487	0.490	+0.6
396	0.8691	0.1309	0	0.124	0.317	0.559	8.08	7.00	+15.4	0.413	0.417	+1.0
593	0.8691	0.1309	0	0.179	0.376	0.445	5.57	4.85	+14.8	0.348	0.341	-2.0
803	0.8691	0.1309	0	0.231	0.408	0.361	4.03	3.77	+6.9	0.321	0.315	-1.8
994	0.8691	0.1309	0	0.268	0.422	0.310	3.28	3.24	+1.3	0.310	0.306	-1.3
60.0	0.8373	0.1627	~0	0.0189	0.0847	0.8969	...	...	...	1.92	1.95	+1.6
109	0.8373	0.1627	0	0.0334	0.148	0.819	33.9	25.1	+59.0	1.10	1.12	+1.5
200	0.8373	0.1627	0	0.0598	0.242	0.698	16.7	14.0	+19.3	0.673	0.674	+0.1
302	0.8373	0.1627	0	0.0881	0.329	0.583	9.00	9.50	-5.3	0.494	0.495	+0.2
407	0.8373	0.1627	0	0.122	0.390	0.488	7.18	6.85	+4.8	0.417	0.416	-0.2
607	0.8373	0.1627	0	0.182	0.462	0.356	5.17	4.60	+12.4	0.352	0.346	-1.7
793	0.8373	0.1627	0	0.225	0.496	0.279	3.96	3.72	+6.5	0.328	0.321	-2.1
998	0.8373	0.1627	0	0.268	0.507	0.225	3.21	3.13	+2.9	0.321	0.315	-1.8

<sup>a</sup> Calculated from radioactive retention data. <sup>b</sup> Estimated from an empirical correlation (3).

<sup>c</sup> Calculated from thermal conductivity retention data.

Equation 2 has been solved (8) explicitly for  $K_1$  and  $K_2$  to give:

$$K_1 = \frac{Z_M RTW}{P(V_{R_1}^* - V_g)} + y_1 + \left( \frac{V_{R_2}^* - V_g}{V_{R_1}^* - V_g} \right) y_2 \quad (3)$$

$$K_2 = \frac{Z_M RTW}{P(V_{R_2}^* - V_g)} + \left( \frac{V_{R_1}^* - V_g}{V_{R_2}^* - V_g} \right) y_1 + y_2 \quad (4)$$

The assumptions made in the derivation of Equation 2 and thus Equations 3 and 4 are instantaneous equilibrium, negligibly small sample volume, constant partition coefficient at all points along the length of the column, and distinguishability of sample molecules.

The first and third assumptions have been validated theoretically by Stalkup and Deans (19), and the second assumption by Stalkup and Kobayashi (20) and in this present work. As mentioned previously, distinguishability

Table II. K-values for Methane and Propane and Vapor and Liquid Phase Compositions in the System Methane-Propane-n-Decane at 40° F.

Press., P.S.I.A.	Vapor Compositions			Liquid Composition			Methane K-values			Propane K-values		
	$y_{c_1}$	$y_{c_2}$	$y_{c_{10}}$	$x_{c_1}$	$x_{c_2}$	$x_{c_{10}}$	$K_{c_1}^a$	$K_{c_1}^b$	%, Dev.	$K_{c_2}^a$	$K_{c_2}^c$	%, Dev.
22.3	1.0	0	~0	0.0091	~0	0.9909	...	110.0	...	3.39	3.54	+4.0
29.5	1.0	0	0	0.0118	0	0.9882	...	85.1	...	2.49	2.55	+2.5
49.8	1.0	0	0	0.0203	0	0.9797	...	49.3	...	1.56	1.56	+0.1
82.0	1.0	0	0	0.0331	0	0.9669	...	30.2	...	0.949	0.954	+0.7
128.0	1.0	0	0	0.0508	0	0.9492	...	19.7	...	0.634	0.631	-0.5
180	1.0	0	0	0.0699	0	0.9301	...	14.3	...	0.463	0.466	+0.7
180	1.0	0	0	0.0962	0	0.9038	...	10.4	...	0.358	0.360	+0.6
350	1.0	0	0	0.129	0	0.871	...	7.73	...	0.284	0.285	+0.3
499	1.0	0	0	0.178	0	0.822	...	5.62	...	0.235	0.235	-0
697	1.0	0	0	0.237	0	0.763	...	4.22	...	0.202	0.203	+0.5
814	1.0	0	0	0.265	0	0.735	...	3.78	...	0.199	0.199	0
887	1.0	0	0	0.282	0	0.718	...	3.55	...	0.200	0.199	-0.5
985	1.0	0	0	0.303	0	0.697	...	3.30	...	0.200	0.198	-1.0
50.0	0.9792	0.0208	~0	0.0200	0.0137	0.9663	124	49.0	+153	1.52	1.50	-1.3
103	0.9792	0.0208	0	0.0406	0.0276	0.9318	23.7	24.1	-1.7	0.754	0.757	+0.4
201	0.9792	0.0208	0	0.0759	0.0484	0.8757	13.0	12.9	+0.6	0.430	0.430	-0
298	0.9792	0.0208	0	0.110	0.0646	0.825	9.25	8.90	-2.8	0.322	0.319	-0.9
396	0.9792	0.0208	0	0.144	0.0773	0.779	6.90	6.82	+1.2	0.269	0.268	-0.4
599	0.9792	0.0208	0	0.206	0.0929	0.701	5.18	4.75	+9.1	0.224	0.221	-1.3
789	0.9792	0.0208	0	0.265	0.0981	0.637	3.94	3.70	+6.5	0.212	0.211	-0.5
1023	0.9792	0.0208	0	0.322	0.100	0.578	2.95	3.04	-3.0	0.207	0.209	+1.0
46.0	0.9569	0.0431	~0	0.0180	0.0268	0.9552	106.7	53.2	+101	1.61	1.61	0
102	0.9569	0.0431	0	0.0391	0.0555	0.9054	26.4	24.5	+7.7	0.776	0.770	-0.8
198	0.9569	0.0431	0	0.0730	0.0980	0.8290	11.4	13.1	-13.0	0.440	0.437	-0.7
300	0.9569	0.0431	0	0.108	0.133	0.759	8.53	8.82	-3.3	0.323	0.322	-0.3
397	0.9569	0.0431	0	0.143	0.156	0.701	6.42	6.70	-4.2	0.277	0.276	-0.4
589	0.9569	0.0431	~0	0.204	0.188	0.608	4.46	4.70	-5.1	0.229	0.226	-1.3
786	0.9569	0.0431	0	0.259	0.199	0.542	3.49	3.70	-5.7	0.217	0.213	-1.8
1002	0.9569	0.0431	0	0.309	0.200	0.491	3.01	3.10	-2.9	0.215	0.213	-1.4
49.5	0.9310	0.0690	~0	0.0188	0.0437	0.9375	99.9	49.5	+102	1.58	1.56	-1.3
113	0.9310	0.0690	0	0.0421	0.0965	0.8614	19.8	22.1	-10.4	0.715	0.720	+0.7
202	0.9310	0.0690	0	0.0727	0.156	0.771	12.8	12.8	0	0.441	0.438	-0.7
302	0.9310	0.0690	0	0.106	0.207	0.687	8.10	8.80	-8.0	0.333	0.328	-1.8
400	0.9310	0.0690	0	0.141	0.246	0.613	6.59	6.62	-0.5	0.280	0.278	-0.7
593	0.9310	0.0690	0	0.202	0.289	0.509	4.80	4.60	+4.3	0.239	0.234	-2.1
788	0.9310	0.0690	0	0.258	0.307	0.435	3.57	3.61	-1.1	0.225	0.221	-1.8
989	0.9310	0.0690	0	0.307	0.300	0.393	3.12	3.03	+2.9	0.230	...	...
42.0	0.9056	0.0944	~0	0.0156	0.0539	0.9305	68.6	58.0	+18.3	1.75	1.73	-1.0
96.1	0.9056	0.0944	0	0.0348	0.114	0.851	25.9	26.0	-0.4	0.829	0.837	+0.8
196	0.9056	0.0944	0	0.0686	0.208	0.723	12.2	13.2	-7.6	0.453	0.453	0
294	0.9056	0.0944	0	0.100	0.277	0.623	10.1	9.03	+12.0	0.341	0.338	-0.9
395	0.9056	0.0944	0	0.138	0.327	0.535	7.08	6.55	+8.1	0.289	0.285	-1.4
587	0.9056	0.0944	0	0.199	0.385	0.416	5.03	4.56	+10.3	0.245	0.240	-2.0
794	0.9056	0.0944	0	0.260	0.405	0.335	3.85	3.48	+10.3	0.233	...	...
898	0.9056	0.0944	0	0.287	0.410	0.303	...	3.15	...	0.230	...	...
1002	0.9056	0.0944	0	0.312	0.400	0.288	2.93	2.90	+1.0	0.236	...	...
44.0	0.8691	0.1309	~0	0.0156	0.0748	0.9096	175	55.7	+215	1.75	1.75	0
74.2	0.8691	0.1309	0	0.0261	0.121	0.853	63.8	33.3	+91.7	1.08	1.10	+1.8
104	0.8691	0.1309	0	0.0362	0.169	0.795	24.6	24.0	+23.4	0.773	0.781	+1.0
201	0.8691	0.1309	0	0.0674	0.286	0.647	12.3	12.9	-4.6	0.458	0.461	+0.7
297	0.8691	0.1309	0	0.0973	0.375	0.528	9.46	8.93	+5.9	0.349	0.339	-2.9
401	0.8691	0.1309	~0	0.136	0.442	0.422	7.64	6.40	+19.4	0.296	0.288	-2.7
597	0.8691	0.1309	0	0.204	0.513	0.283	4.81	4.26	+13.1	0.255	...	...
691	0.8691	0.1309	0	0.234	0.530	0.236	...	3.71	...	0.247	...	...
800	0.8691	0.1309	0	0.267	0.530	0.203	3.84	3.26	+17.8	0.247	...	...
901	0.8691	0.1309	0	0.293	0.528	0.180	...	2.97	...	0.248	...	...
999	0.8691	0.1309	0	0.312	0.498	0.190	3.12	2.79	+11.8	0.263	...	...
42.0	0.8373	0.1627	~0	0.0144	0.0830	0.9026	137	58.0	+136	1.96	1.95	-0.5
71.5	0.8373	0.1627	0	0.0242	0.148	0.828	35.4	34.6	+2.3	1.10	1.12	+1.8
102	0.8373	0.1627	0	0.0342	0.204	0.762	24.0	24.5	-2.0	0.798	0.812	+1.8
200	0.8373	0.1627	0	0.0644	0.355	0.581	11.8	13.0	-9.6	0.458	0.453	-1.1
300	0.8373	0.1627	0	0.0949	0.464	0.441	8.71	8.82	-5.4	0.351	0.342	-2.5
402	0.8373	0.1627	0	0.135	0.548	0.317	7.00	6.22	+12.5	0.297	0.291	-2.0
599	0.8373	0.1627	0	0.209	0.623	0.168	...	4.00	...	0.265	...	...

<sup>a</sup> Calculated from radioactive retention data. <sup>b</sup> Estimated from an empirical correlation (3).

<sup>c</sup> Calculated from thermal conductivity retention data.



was accomplished by using radioactively tagged solute samples. The comparison of the K-values of this work with those obtained by classical means serves as a distinct verification of the validity of all four assumptions.

Essentially the same assumptions enter into the analytical solution of the differential equations describing the rate processes occurring in a chromatographic column as presented by Stalcup and Deans (19); with the exception of the last assumption. The result is:

$$V_{R_1} - V_g = \frac{Z_M RT W K_1 K_2}{P}$$

$$\left\{ \frac{(K_1 - 1) y_1 \left[ 1 - y_2 \frac{d \ln K_2}{y_2} \right] + (K_2 - 1) y_2 \left[ 1 - y_1 \frac{d \ln K_1}{d y_1} \right]}{[K_2 K_1 - K_1 + y_1 (K_1 - K_2)]^2} \right\} \quad (5)$$

Here  $V_R$  refers to the retention volume calculated from the observed retention time for a solute sample detected in the effluent by monitoring some physical property, such as thermal conductivity. Having independent knowledge of the compositional dependence of the K-values from the experiments using radioactive tracers and Equations 3 and 4 allows the evaluation of the term  $(d \ln K_1 / d y_1)$  at each point. Equation 5 may then be solved explicitly for  $K_1$  in the following manner:

$$K_1 = \frac{b + (b^2 - 4ac)^{1/2}}{2a} \quad (6)$$

where:

$$a = 1 + \frac{1}{K_2} \left[ \frac{1}{K_2} (1 - 2y_1 + y_1^2) - 2(1 - y_1) - A A_0 y_1 \right]$$

$$b = B A_0 \left( 1 - \frac{1}{K_2} - y_1 \right) + \frac{2y_1^2}{K_2} + A_0 \frac{y_1}{K_2} (B - A) + 2y_1 \left( 1 - \frac{1}{K_2} \right)$$

$$c = y_1^2$$

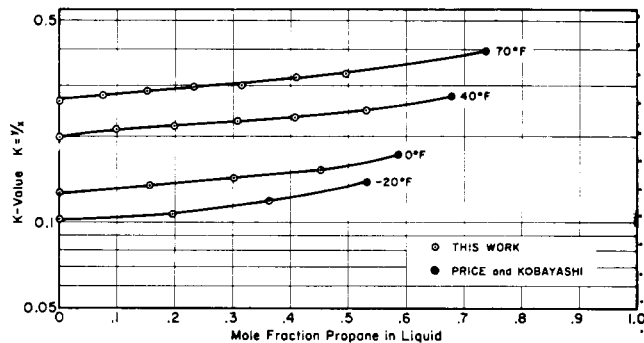


Figure 2. K-value for propane as a function of propane concentration in the liquid phase in the system methane-propane-*n*-decane at 800 p.s.i.a.

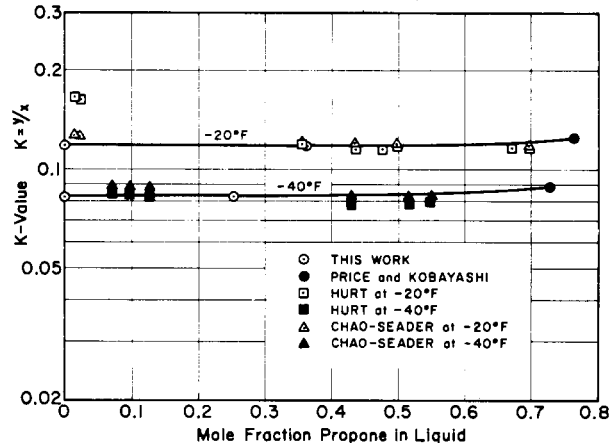


Figure 3. K-value for propane as a function of propane concentration in the liquid phase in the system methane-propane-*n*-heptane at 400 p.s.i.a.

Table V. K-values for Methane and Propane and Vapor and Liquid Phase Compositions in the System Methane-Propane-*n*-Heptane at -20° F.

Press., P.S.I.A.	Vapor Composition			Liquid Composition			K-values	
	$y_{c_1}$	$y_{c_2}$	$y_{c_3}$	$x_{c_1}$	$x_{c_2}$	$x_{c_3}^a$	$K_{c_1}^a$	$K_{c_2}^c$
96.0	1.0	~0	~0	0.0568	~0	0.9432	17.6	0.313
212	1.0	0	0	0.114	0	0.886	8.75	0.168
400	1.0	0	0	0.196	0	0.804	5.10	0.116
608	1.0	0	0	0.280	0	0.720	3.57	0.107
807	1.0	0	0	0.353	0	0.647	2.83	0.109
990	1.0	0	0	0.412	0	0.588	2.43	0.120
107	0.9569	0.0431	~0	0.0560	0.147	0.797	17.1	0.294
240	0.9469	0.0431	0	0.111	0.275	0.614	8.60	0.157
422	0.9569	0.0431	0	0.195	0.375	0.430	4.90	0.115
603	0.9569	0.0431	0	0.304	0.378	0.318	3.15	0.114
795	0.9569	0.0431	0	0.414	0.339	0.247	2.31	0.127
993	0.9569	0.0431	0	0.517	0.275	0.208	1.85	0.157

<sup>a</sup>  $x_{c_3} = 1 - y_{c_1} - y_{c_2}$ . <sup>b</sup> Hurt (6). <sup>c</sup> Calculated from radioactive retention data.

Table VI. K-values for Methane and Propane and Vapor and Liquid Phase Compositions in the System Methane-Propane-*n*-Heptane at -40 F.

Press., P.S.I.A.	Vapor Composition			Liquid Composition			K-values	
	$y_{c_1}$	$y_{c_2}$	$y_{c_3}$	$x_{c_1}$	$x_{c_2}$	$x_{c_3}$	$K_{c_1}$	$K_{c_2}$
100	1.0	~0	~0	0.0667	~0	0.9333	15.0	0.200
200	1.0	0	0	0.120	0	0.880	8.30	0.118
396	1.0	0	0	0.216	0	0.784	4.62	0.0827
605	1.0	0	0	0.311	0	0.689	3.22	0.0786
805	1.0	0	0	0.389	0	0.611	2.57	0.0859
1008	1.0	0	0	0.455	0	0.545	2.20	0.110
97	0.9792	0.0208	0	0.0662	0.0959	0.8379	14.8	0.217
201	0.9792	0.0208	0	0.118	0.175	0.707	8.30	0.119
400	0.9792	0.0208	0	0.239	0.249	0.512	4.10	0.0835
605	0.9792	0.0208	0	0.338	0.261	0.401	2.90	0.0797
791	0.9792	0.0208	0	0.453	0.277	0.320	2.16	0.0917
991	0.9792	0.0208	0	0.560	0.176	0.264	1.75	0.118

<sup>a</sup>  $x_{c_3} = 1 - y_{c_1} - y_{c_2}$ . <sup>b</sup> Hurt (6). <sup>c</sup> Calculated from radioactive retention data.

$$A = 1 - y_2 \frac{d \ln K_2}{d y_2}$$

$$B = 1 - y_1 \frac{d \ln K_1}{d y_1}$$

$$A_0 = \frac{Z_M R T W}{P(V_{R_1} - V_g)}$$

Both Equations 2 and 6 require a knowledge of the total moles of nonvolatile, fixed liquid on the column packing, the compressibility factor of the elution gas, and the "free" gas volume of the elution network.

The "free" gas volume,  $V_g$ , was measured by eluting pure methane through the column and perturbing with radioactive methane. If Equation 2 is solved for  $V_g$  under these experimental conditions, continuing to represent methane by subscript 2, the result is:

$$V_g = V_{R_2} - \frac{Z_M R T W}{P(K_2 - 1)} \quad (7)$$

Precise values of the K-values for methane in the binary system are known (10), so that  $V_g$  may be obtained by this technique with an uncertainty of less than 1 per cent. The detailed error analysis of Equation 7 as well as those for Equation 3 and 4 is given in the original work (8) and also by Koonce and coworkers (9).

Partial molar volumes for methane and propane were extrapolated or estimated from the work of Sage and Lacey (17) and the increased volume of the liquid phase calculated for all conditions. The final value of  $V_g$  was then obtained by correcting the measured value for the swelling effect.

Pure methane compressibility factors were taken from the work of Mueller, Leland, and Kobayashi (13). Compressibility factors for the methane-propane mixtures were estimated from the generalized corresponding states charts given in Brown, Katz, Oberfell, and Alden (3).

The moles of fixed liquid (*n*-decane or *n*-heptane) on the column packing was determined initially by direct weighing. Any loss thereafter due to evaporation was also accounted for gravimetrically.

The K-values for methane determined from the use of elution data in Equation 4 were scattered randomly about a smooth curve. At high pressures this randomness which is of the order of 5-10 per cent can introduce as much as 2 per cent error in the calculated propane K-values. To improve the propane K-values the methane K-values,  $K_2$ , predicted by an empirical correlation (2) based on the phase behavior of many hydrocarbon systems available in the literature (6, 10, 16) were used in the following form of Equation 2:

$$K_1 = \frac{Z_M R T W}{P(V_{R_1} - V_g)} \left[ \frac{1}{1 - y_2 / K_2} \right] \quad (8)$$

The detailed error analyses referred to previously predicted a maximum expected error in the chromatographically determined methane K-value of up to 40 per cent. The observed fluctuation of the methane K-values of 5-10 per cent about the curve generated from the empirical correlation is indicative of the precision of  $V_{R_2}$ ,  $V_g$ , and  $W$ . The same error analysis predicted a maximum error of about 5 per cent in the propane K-value. From a study of the K-values obtained from this and other studies an uncertainty of 1.5 per cent for the propane K-values appears to be more reasonable.

The final K-values and vapor and liquid phase compositions resulting from this work as well as comparisons of the various techniques employed are presented in Tables I through VI. Figure 2 is a comparison of the infinite dilution K-values of this work with those of Stalkup and

Kobayashi (20). The discrepancy observed at high pressures is entirely attributable to the improved accuracy of  $V_g$ , the "free" gas volume, as measured by the technique outlined earlier in this paper. The uncertainty in this parameter as calculated by Stalkup and Kobayashi is about 10 per cent compared with an uncertainty of less than one per cent in this work.

In Figure 2 the consistency of the propane K-values in the *n*-decane system calculated from retention data with the binary methane-propane K-value measured statically by Price and Kobayashi (16) is demonstrated. Similarly, Figure 3 shows the substantial agreement of the propane K-values in the *n*-heptane system with those measured by Hurt (6) and calculated (5) from the Chao-Seader relationship (4). The propane K-values were also found to be in close agreement with the values predicted by NGAA (14).

The theoretical aspects of the problem and the error analyses of the equations involved have been explained elsewhere (8, 9).

#### ACKNOWLEDGMENT

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

#### NOMENCLATURE

- $H$  = equilibrium partition coefficient, moles per unit vol. in mobile phase/moles per unit vol. in liquid phase
- $K_k$  = vapor-liquid equilibrium coefficient defined as the ratio of mole fraction in the vapor phase to that in the liquid phase for a given component at equilibrium
- $P$  = total column pressure
- $R$  = gas constant
- $T$  = system temperature
- $V_{R_1}$  = correct retention volume measured by thermal conductivity detection for component  $k$ , i.e., the product of the time required for a solute peak to appear in the effluent and the gas flow rate at column conditions
- $V_{R_1}^*$  = correct retention volume measured by ionization produced by a radioactive solute sample of component  $k$
- $V_g$  = total system free gas volume
- $W$  = total moles of nonvolatile fixed liquids in the GLPC column
- $x_k$  = mole fraction of component  $k$  in the liquid
- $y_k$  = mole fraction of component  $k$  in the vapor
- $Z_M$  = compressibility factor of elution gas

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RECEIVED for review December 16, 1963. Accepted April 2, 1964.

## Viscosities of Saturated Alcohol Vapors at Room Temperature

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IN CONNECTION with a study of the reactions of sodium with alcohols, the coefficients of viscosity of several low molecular weight alcohols were needed at room temperature and at or below their equilibrium vapor pressures. Since no data could be found for the butanols, and the values of the coefficients for the other alcohols had to be extrapolated from higher pressures and from temperatures above the boiling points, it was decided to determine their values under the conditions described above.

### EXPERIMENTAL

Isopropyl alcohol was reagent grade from Baker and Adamson Co. The isobutyl alcohol was an Eastman Kodak product. *n*-Butyl alcohol was from Merck, and *n*-propyl, *sec*-butyl and *tert*-butyl alcohol were all from Matheson, Coleman and Bell. The alcohols were all distilled four times in vacuo, taking the middle third each time and discarding the rest. The infrared spectra showed no impurities. They were analyzed on a model 20 Barber-Coleman vapor phase chromatograph using a 12 ft., 1/8 in. o.d. column packed with 20% Armeen D (octadecenyl amine) from Armour Co., on chromosorb. The usual sample size was 0.5  $\mu$ l. The accuracy of the analysis is estimated to be 0.2%. The minimum purities of the alcohols were found to be: *n*-propyl alcohol, 99.4%; isobutyl alcohol, 99%; and all others, 99.8%.

Carbon dioxide was obtained from a tank and purified by four bulb-to-bulb distillations, retaining only the middle third each time. No further analysis was performed.

The capillary used was of glass attached to a conventional vacuum system and was calibrated by allowing carbon dioxide, the coefficient of viscosity of which was known (2), to flow through it for a measured length of time, collecting it in a liquid nitrogen cooled, tared bulb and weighing it. By using the Poiseuille expression, the capillary constant was determined. The Poiseuille equation was used to calculate the coefficient of viscosity by similarly allowing the alcohol vapor to flow through the capillary for a known

length of time, at a given temperature, and weighing the amount of alcohol taken. Flow conditions were such that no correction was needed for nonstreamline flow, nor for end effects.

### RESULTS AND DISCUSSION

The range of experimental temperatures was 296° to 302° K. and the coefficients were corrected to 298° K. by assuming a half-power dependence on the temperature. Five runs were made in each determination and column two of Table I gives the results along with the average deviation. Original data may be found elsewhere (3).

The viscosities of the vapors of methyl, ethyl, and the propyl alcohols were determined by Titani (3) and fitted by the Sutherland expression. For comparison, column three of Table I gives values of the viscosity extrapolated to 298° K. from the data of Titani using the expression given by him. These data are considered applicable only above the boiling points and, for *n*-propyl alcohol, it can be seen that the value determined at 298° K. in this work is over 3% lower than the value extrapolated from the high temperature data (above 390° K.). For isopropyl alcohol, the present value is less than 2% lower than the extrapolated value which is within experimental uncertainty. Because of

Table I. Coefficients of Viscosity of Alcohols at 298° K. (Micropoise) and Collision Diameters (Angstroms)

Alcohol	This Work	Titani (4)	$\sigma_2$ , Angstroms
methyl	...	95.49	(5.27)
ethyl	...	85.77	(6.09)
<i>n</i> -propyl	72.9 $\pm$ 1.0	75.31	7.06
isopropyl	75.7 $\pm$ 1.9	76.88	6.93
<i>n</i> -butyl	64.3 $\pm$ 1.6	...	7.92
isobutyl	67.4 $\pm$ 1.0	...	7.73
<i>sec</i> -butyl	68.7 $\pm$ 1.8	...	7.66
<i>tert</i> -butyl	73.7 $\pm$ 1.3	...	7.40

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