Table II. Carbon Dioxide + 1-Methylnaphthalene Vapor-Liquid Equilibrium Data

p, atm	x_{CD}	y_{CD}	K_{CD}	K_M
		189.9 °C		
20.47	0.0499	0.9836	19.71	0.0173
29.73	0.0730	0.9877	13.53	0.0133
39.9	0.0967	0.9898	10.24	0.0113
50.2	0.1198	0.9903	8.266	0.0110
		270.3 °C		
20.95	0.0422	0.9024	21.38	0.1019
30.04	0.0622	0.9239	14.85	0.0811
39.8	0.0821	0.9376	11.42	0.0680
50.8	0.1061	0.9461	8.917	0.0603
		350.4 °C		
20.56	0.0336	0.6423	19.12	0.3701
30.03	0.0533	0.7288	13.67	0.2865
39.6	0.0745	0.7790	10.46	0.2388
48.9	0.0942	0.8065	8.562	0.2136
		430.4 °C		
30.19	0.0338	0.3112	9.207	0.7129
39.4	0.0584	0.4236	7.253	0.6121
48.3	0.0831	0.4936	5.940	0.5523

Glossary

K	vaporization equilibrium ratio, $K = y/x$
p	pressure, atm
t	temperature, °C
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Subscript

CD	carbon dioxide
D	diphenylmethane
M	1-methylnaphthalene

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Vapor–Liquid Phase Equilibria in the Ternary System Hydrogen + Methane + Tetralin

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Vapor–liquid phase equilibrium of ternary mixtures of H_2 + CH_4 + tetralin was studied at two temperatures, 462 and 663 K, and at pressures from 50 to 250 atm. Relative concentrations of hydrogen to methane were varied, and three observations were made at each condition of temperature and pressure. The response of the *K* values to changing compositions was determined.

Introduction

This work is part of a continuing study of phase equilibrium in mixtures of light gases and heavy liquids at elevated temperatures and pressures. Reports from this laboratory have so far been almost exclusively concerned with binary mixtures of one light gas plus one heavy liquid, the only exceptions being two ternary mixtures of hydrogen in mixed solvents (*5*). In this work we report ternary mixtures of two light gases plus one solvent. The relative concentrations of hydrogen to methane were systematically varied, and three observations were made at each temperature and pressure in order to reveal the response of the *K* values to the changing compositions.

No phase equilibria data on this ternary system have appeared in the literature, but the constituent binaries hydrogen + tetralin (*8*) and methane + tetralin (*7*) have been reported. Previous studies of ternary mixtures of hydrogen and methane were all related to light solvents at much lower temperatures (*1–4*, *6*).

Experimental Section

The apparatus used in this study was for the most part the same as described by Simnick et al. (*8*). However, changes were made in the gas feed system and in the sampling and analysis systems.

A Matheson gas mixer (Dyna-Blender Model SP-1601) has been installed to provide a mixed gas stream at a set composition from individual cylinders of hydrogen and methane. Composition of the mixed gas was found to stay constant within ±0.5 mol %.

Downstream from the blender two vessels of about 1 L each were placed in series in front of the compressor in order to reduce pressure fluctuations and to promote mixing.

Effluents from the equilibrium cell were reduced in pressure and cooled in the same way as previously described (*8*) to produce a liquid stream and a gas stream. The quantity of the gas stream was measured volumetrically and the liquid gravimetrically. For determination of the gas composition, the separated gas streams were sampled in a sample valve, and the samples were picked up by a stream of helium gas. A Carle 111-H gas chromatograph received the helium-carried stream

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Table I. Hydrogen + Methane + Tetralin Vapor-Liquid Equilibrium Data

T, K	p, atm	x_H	x_M	x_T	y_H	y_M	y_T
					0.8847[a]	0.1153[a]	
462.3	49.7	0.0256	0.00834	0.9661	0.8825	0.1033	0.01417
462.2	101.0	0.0508	0.01513	0.9341	0.8892	0.1031	0.00769
462.2	150.3	0.0742	0.0204	0.9054	0.8934	0.1014	0.00519
462.4	249.4	0.1194	0.0309	0.8497	0.8929	0.1031	0.00398
					0.7817[a]	0.2183[a]	
462.2	49.9	0.0232	0.01525	0.9616	0.7780	0.2068	0.01518
462.2	100.5	0.0459	0.0289	0.9252	0.7899	0.2009	0.00920
462.2	150.1	0.0695	0.0403	0.8902	0.7921	0.2007	0.00714
462.3	252.8	0.1105	0.0556	0.8338	0.8154	0.1785	0.00621
					0.5334[a]	0.4666[a]	
462.3	50.0	0.0171	0.0339	0.9490	0.5489	0.4344	0.01677
462.2	100.4	0.0333	0.0639	0.9029	0.5514	0.4377	0.01090
462.2	150.5	0.0506	0.0922	0.8573	0.5501	0.4403	0.00961
462.3	249.1	0.0863	0.1301	0.7836	0.5830	0.4076	0.00938
					0.9087[a]	0.0913[a]	
663.4	50.0	0.0435	0.0065	0.9491	0.4608	0.0428	0.4965
663.3	101.5	0.1080	0.0156	0.8762	0.6471	0.0609	0.2920
663.3	151.3	0.1666	0.0211	0.8119	0.7182	0.0595	0.2223
663.5	250.2	0.2762	0.0315	0.6920	0.7631	0.0601	0.1768
					0.8007[a]	0.1993[a]	
663.4	50.0	0.0393	0.0124	0.9483	0.4135	0.0854	0.5012
663.3	99.9	0.0981	0.0303	0.8717	0.5741	0.1179	0.3080
663.4	146.3	0.1387	0.0450	0.8163	0.6105	0.1356	0.2539
663.4	252.1	0.2604	0.0732	0.6664	0.6754	0.1368	0.1879
					0.5265[a]	0.4375[a]	
663.3	50.1	0.0284	0.0308	0.9408	0.2865	0.2081	0.5054
663.2	100.9	0.0722	0.0764	0.8514	0.3931	0.2819	0.3250
663.3	150.5	0.1129	0.1114	0.7745	0.4227	0.3055	0.2718

[a] Feed gas.

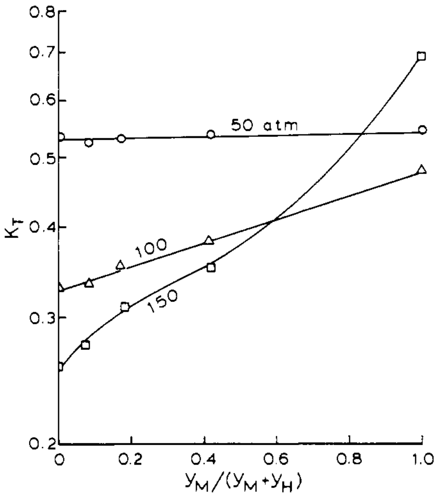

Figure 1. K values of tetralin at 663 K.

and separated the hydrogen from it by permeation through a heated palladium tube. The permeated hydrogen was picked up by a stream of nitrogen on the other side of the palladium tube and detected in a thermal conductivity detector. The remaining helium-carried stream flowed through a packed column and then a thermal conductivity detector.

The chromatograph was calibrated with Matheson primary standard mixtures of hydrogen and methane. Five mixtures at hydrogen compositions of 1, 25, 50, 75, and 99% were used for the calibration. The responses from the chromatograph were integrated by using a Columbia Scientific integrator (Model CAS 208E). The calibration was checked daily during this work.

The purities of the materials used in this study were 99.95% for hydrogen and 99+% for both the methane and tetralin which were the same as in our previous work (*7*, *8*).

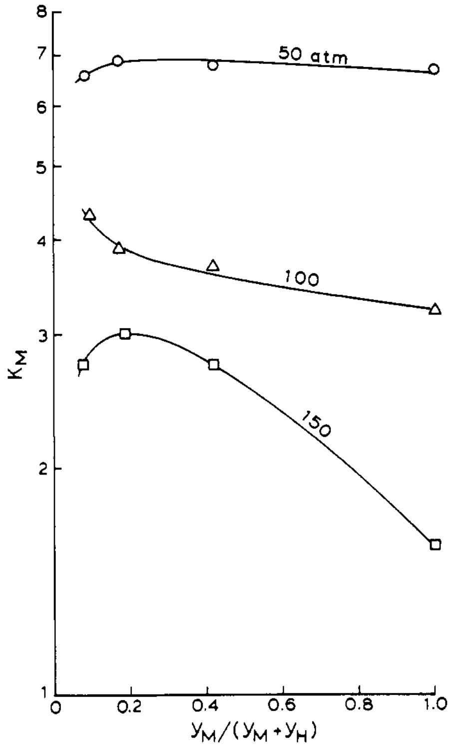

Figure 2. K values of methane at 663 K.

Results and Discussion

Compositions of both the saturated vapor and liquid phases were determined at 462 and 663 K and at four pressures from 50 to 250 atm at each temperature. Observations were made with three gas feeds of approximately 90, 80, and 50 mol %

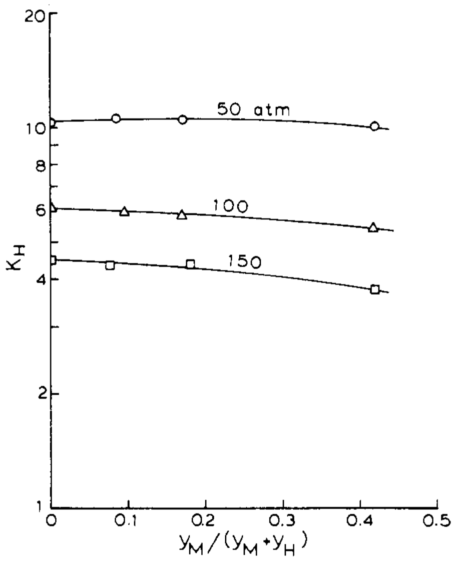

Figure 3. *K* values of hydrogen at 663 K.

in hydrogen at each temperature and pressure. Table I presents the results.

All flow rates were kept constant during one experiment at a fixed T, p, and feed gas. The constancy of flow rates is a required condition for equilibrium to exist between the cell effluents for systems of more than two components. The liquid feed was set by means of a positive displacement pump which was kept at a constant setting. The flow rate of the cell overhead effluent was controlled by a metering valve. At the start of each experiment, this valve was adjusted for adequate flow. Once the adjustment was made, the valve was not varied in the course of the experiment. The gas stream from the cell overhead effluent was measured with a wet test meter at all times and was observed to be at a constant rate to within 1% in the course of any one experiment.

At least two samples were taken from each cell effluent stream during one experiment. The volumetric measurements of the multiple samples agreed to within 1%. The GC composition analyses of the gases from the multiple samples agreed to within 2%. The averages of the multiple samples are shown in Table I. Also shown in Table I are the feed gas compositions which were kept constant for a series of pressures at (approximately) the same temperature.

Figures 1–3 show the variation of *K* values with the tetralin-free mole fraction of methane in the equilibrium gas at 663 K. A substantial variation of the *K* values with the gas composition is observed at the higher pressures. Tetralin is most sensitive and hydrogen the least sensitive. At 462 K the sensitivity is increased for tetralin but decreased for hydrogen and methane.

The terminal points in Figure 1 correspond to binary mixtures of hydrogen + tetralin and methane + tetralin. In Figure 2 only one end of the curves can be shown, and this corresponds to methane + tetralin. In Figure 3 only one end is shown corresponding to hydrogen + tetralin. The binary mixture data from our previous investigations (*7*, *8*) were interpolated to give the terminal points here. The new ternary mixture data are smoothly joined to the previously reported binary data in all cases.

Acknowledgment

Dr. G. D. Nageshwar assisted in the measurements.

Glossary

p	pressure, atm
T	temperature, K
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

H	hydrogen
M	methane
T	tetralin

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