

## Nomenclature

$A$	= constant in Eq.(4)	[°K]
$B$	= constant in Eq.(4)	[—]
$C$	= coefficient in Eq.(8)	[—]
$F$	= parameter in Eq.(8)	[—]
$K$	= vapor-liquid equilibrium ratio	[—]
$P_{i0}$	= vapor pressure of pure component $i$	[mmHg]
$T$	= temperature	[°K]
$x$	= mole fraction of liquid phase	[—]
$y$	= mole fraction of vapor phase	[—]
$\gamma$	= activity coefficient	[—]
〈Subscripts〉		
$i$ and $j$	= component $i$ and $j$	
1,2,3 and 4	= EtOH, iPrOH, AcOEt and AcOiPr respectively for reaction (5) MeOH, EtOH, AcOMe and AcOEt respectively for reaction (6)	
〈Abbreviations〉		
AcOH	= acetic acid	
AcOMe	= methyl acetate	
AcOEt	= ethyl acetate	

AcOiPr	= isopropyl acetate
EtOH	= ethanol
iPrOH	= isopropanol
MeOH	= methanol

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# VAPOR-LIQUID EQUILIBRIA OF BINARY AND TERNARY SYSTEMS CONTAINING HYDROGEN AND LIGHT HYDROCARBONS\*

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The vapor-liquid equilibrium relations of the hydrogen-methane, the hydrogen-ethylene, the hydrogen-ethane, the hydrogen-methane-ethylene and the hydrogen-ethylene-ethane systems were determined by a static method at several temperatures from  $-25^{\circ}\text{C}$  to  $-170^{\circ}\text{C}$  and at pressures up to 100 atm. From the data obtained, features of the phase equilibria of hydrogen-light hydrocarbon mixtures are discussed.

The Benedict-Webb-Rubin equation was successfully applied to predict the vapor-liquid equilibria of the present systems above the normal boiling point of the heaviest hydrocarbon.

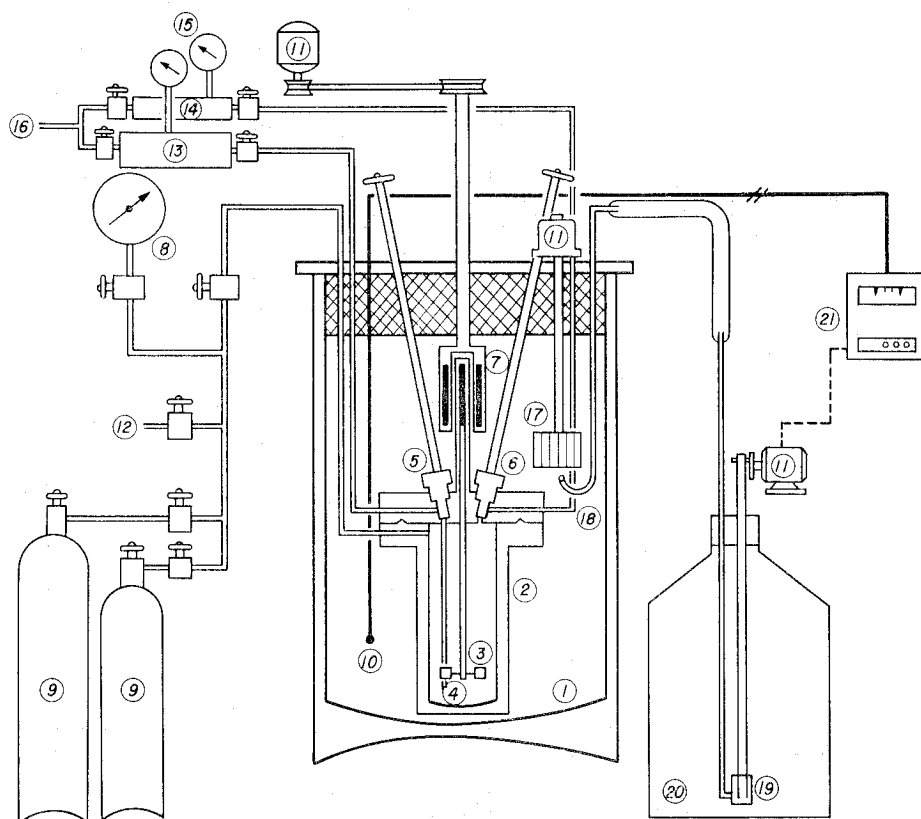
## Introduction

The vapor-liquid equilibria of systems containing hydrogen and light hydrocarbons have been of much interest to the petroleum industry, especially in regard to the recovery of hydrogen. Reliable vapor-liquid equilibrium data in the low temperature ranges are required in the design of fractionation facilities for efficient separation of hydrogen from cracker effluent. So several hydrogen-light hydrocarbon systems have been studied experimentally. Benham *et al.*<sup>3)</sup> showed the data sources of vapor-liquid equi-

libria already published for hydrogen-hydrocarbon systems. However, the data of an interesting system are occasionally limited in temperature and pressure ranges and the data points are scarce, so that reasonable interpolation or extrapolation can hardly be expected. Therefore, the present work was aimed to obtain more extensive vapor-liquid equilibrium data and to provide comprehensive sets for the hydrogen-light hydrocarbon mixtures. The hydrogen-methane, hydrogen-ethylene, hydrogen-ethane, hydrogen-methane-ethylene and hydrogen-ethylene-ethane systems were measured by a static method.<sup>8,12)</sup> The data of the hydrogen-ethylene-ethane system will be found for the first time in the present paper. Experimental temperatures covered are from  $-25^{\circ}\text{C}$  to  $-170^{\circ}\text{C}$ . From the data obtained, features of the

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- |                                  |                                       |
|----------------------------------|---------------------------------------|
| ① Vacuum cryostat                | ⑫ to Vacuum pump                      |
| ② Equilibrium cell               | ⑬ Liquid sampler                      |
| ③ Magnetic stirrer               | ⑭ Vapor sampler                       |
| ④ Capillary tube                 | ⑮ Compound gauge                      |
| ⑤ Liquid sample valve            | ⑯ to Gas chromatograph                |
| ⑥ Vapor sample valve             | ⑰ Fan                                 |
| ⑦ External magnet                | ⑱ Liquid nitrogen spray nozzle        |
| ⑧ Pressure gauge                 | ⑲ Plunger pump                        |
| ⑨ Sample gas bomb                | ⑳ Liquid nitrogen container           |
| ⑩ Copper-constantan thermocouple | ㉑ Temperature controller and recorder |
| ⑪ Motor                          |                                       |

Fig. 1 Schematic diagram of the experimental apparatus

phase equilibria of the hydrogen-light hydrocarbon systems are discussed. The critical temperature of hydrogen, as is well known, is very low, so that the hydrogen molecule in a solution behaves as a supercritical component. A theoretical study from statistical thermodynamics of the characteristics of the hydrogen molecule in a hydrocarbon solution is of interest. The present data may be useful for comparison with the theory proposed.

The Benedict-Webb-Rubin equation was applied to predict the vapor-liquid equilibria of the present systems, and its applicability and limitation are shown.

#### Apparatus and Experimental Procedure

Fig. 1 shows a schematic diagram of the equilibrium cell and sampling manifold. Gases from bombs are introduced into the cell, (2), and after two-phase equilibrium has been established, liquid and vapor samples are drawn off for composition analysis through valves (5) and (6), respectively. The cell and sample

lines are made of stainless steel. The internal volume of the cell is approximately 500 cc.

Temperature inside the vacuum cryostat was controlled by adjusting the evaporation rate of liquid nitrogen, which was injected from (20). It was measured with a copper-constantan thermocouple which had been calibrated to the normal boiling point of nitrogen, the melting point of mercury and the ice point. The thermocouple was further checked by measuring the vapor pressure of methane and ethane in the experimental temperature ranges. The accuracy of calibrated temperatures was believed to be within  $\pm 0.1^\circ\text{C}$ . The temperature fluctuation inside the cryostat were less than  $\pm 0.1^\circ\text{C}$ .

Pressure was measured with a Bourdon gauge which had been calibrated against a dead-weight gauge. All presented values of pressure are believed to be accurate to within  $\pm 0.1$  atm.

Samples were analyzed by a gas chromatograph with a thermal conductivity detector. Activated charcoal was used as the column packing material

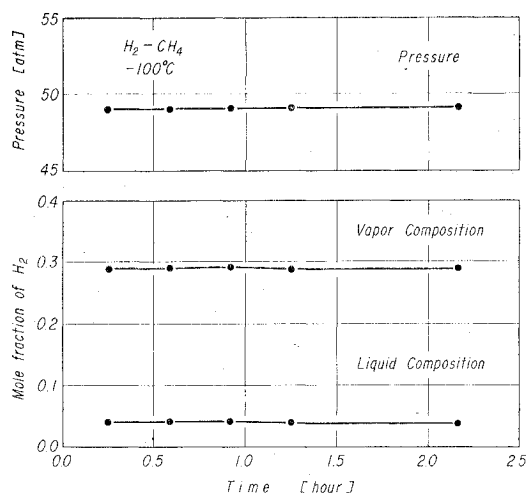


Fig. 2 Changes of compositions and pressures with time for the hydrogen-methane system

and argon was used as the carrier gas. Calibration charts of moles against peak areas were prepared for all components and the compositions determined were believed to be accurate to within 1 per cent, though the error will be larger in the extremely dilute range.

To begin a run, the cell was evacuated and the cryostat was brought to the desired temperature. Enough hydrocarbons were introduced to fill the cell approximately half full of liquid. The amount of hydrocarbons charged was measured roughly by directly weighing a bomb. The system was then pressurized with hydrogen while the cell content was agitated with a stirrer, (3). The agitation was performed by using an external magnet which was rotated by a motor, (11). As hydrogen dissolves in the liquid phase during agitation, the system pressure drops and more hydrogen must be added to maintain constant pressure. Equilibrium was indicated when the system pressure reached a constant value. The changes of compositions and pressure with time are shown in Fig. 2. It is found from this figure that the compositions of both phases and pressure seldom change after 15 min., because of the high efficiency of the agitation. Whenever samples are drawn off, the stirring motor must be stopped to prevent entrainment. In the present work, samples were introduced into the gas chromatograph after one hour, which seemed to be sufficient time to achieve complete equilibrium. When samples of liquid and vapor were to be taken, they were withdrawn through the stainless tubes and then flushed in the chambers, (13) and (14) respectively. The chambers were attached to prevent the separation of the sample into gas and liquid in the sample lines. After flushing, the gas samples expanded were then introduced individually into the gas chromatograph. The first sample taken was disposed of without analysis because it probably contained non-equilibrium portions in the dead spaces. Pressure change during a run could be neglected for

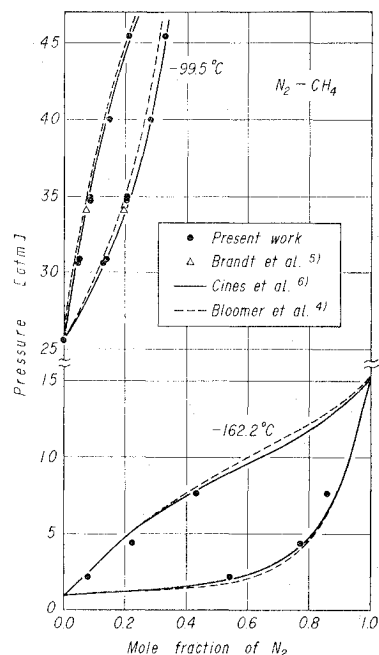


Fig. 3 Comparison of the present results with the literature values in the vapor-liquid equilibria of the nitrogen-methane system

the large content in the cell.

The hydrogen used in this study was furnished by the Nippon Sanso Co., Ltd. and the hydrocarbons by the Takachiho Chemical Industry Co., Ltd. Purities were 99.99 mole % for hydrogen, 99.9 mole % for methane, 99.7 mole % for ethane and 99.5 mole % for ethylene, and the gases were used without further purification.

The present experimental procedure was checked by measuring the vapor-liquid equilibria of the nitrogen-methane system, because the temperature range of the vapor-liquid coexisting region was similar to the present experimental temperature range. The vapor-liquid equilibrium data of the above system have been reported by several workers using various techniques. Brandt *et al.*<sup>5)</sup>, Bloomer *et al.*<sup>4)</sup> and Cines *et al.*<sup>6)</sup> have determined the vapor-liquid equilibria of the nitrogen-methane system by dynamic flow, dew-bubble point and circulation methods respectively. The good agreement between present and previous work is shown in Fig. 3.

#### Experimental Results and Discussions

The vapor-liquid equilibrium data of four binary and two ternary systems are listed in Tables 1~6. The methane-ethylene binary system was measured as the basic data for studying a ternary system containing methane and ethylene. The typical  $P-x$  (pressure-composition),  $T-x$  (temperature-composition) diagrams and  $K$ -value diagram are presented in Figs. 4~6. Fig. 4 shows the good agreement between the present data and those of Katz *et al.*<sup>2)</sup> and of Yorizane *et al.*<sup>13)</sup> for the hydrogen-methane system. As shown

**Table 1** Experimental results for the hydrogen-methane system

Temp. [°C]	Press. [atm]	$x_{H_2}$	$x_{CH_4}$	$y_{H_2}$	$y_{CH_4}$
-170.0	19.7	0.0142	0.986	0.953	0.0473
	40.8	0.0337	0.966	0.967	0.0332
	60.4	0.0569	0.943	0.969	0.0314
	80.9	0.0708	0.929	0.970	0.0300
	90.0	0.0819	0.918	0.969	0.0308
-150.0	10.1	0.00730	0.993	0.683	0.317
	20.0	0.0192	0.981	0.818	0.182
	39.8	0.0385	0.961	0.886	0.114
	59.8	0.0616	0.938	0.904	0.0957
	80.7	0.0816	0.918	0.911	0.0887
	100.5	0.101	0.899	0.908	0.0917
-130.1	10.6	0.00310	0.997	0.214	0.786
	19.9	0.0168	0.983	0.541	0.459
	40.2	0.0477	0.952	0.721	0.279
	59.1	0.0684	0.932	0.779	0.221
	78.7	0.0992	0.901	0.802	0.198
	100.2	0.127	0.873	0.810	0.190
-101.1	86.4	0.136	0.864	0.435	0.565
	102.2	0.201	0.799	0.429	0.571
-99.5	35.2	0.0168	0.983	0.148	0.852
	40.1	0.0257	0.974	0.206	0.794
	59.9	0.0709	0.929	0.362	0.638
	70.1	0.0938	0.906	0.406	0.594
	80.6	0.124	0.876	0.424	0.576
	82.7	0.131	0.869	0.424	0.576
	99.2	0.190	0.810	0.420	0.580
	102.0	0.205	0.795	0.411	0.589
	106.9	0.225	0.775	0.401	0.599

**Table 2** Experimental results for the hydrogen-ethylene system

Temp. [°C]	Press. [atm]	$x_{H_2}$	$x_{C_2H_4}$	$y_{H_2}$	$y_{C_2H_4}$
-150.0	20.0	0.00531	0.995	0.996	0.00434
	40.0	0.00932	0.991	0.997	0.00291
	60.0	0.0127	0.987	0.998	0.00238
	80.0	0.0146	0.985	0.998	0.00212
-125.0	20.0	0.00743	0.993	0.979	0.0212
	40.0	0.0131	0.987	0.985	0.0147
	60.0	0.0185	0.982	0.988	0.0120
	80.0	0.0266	0.973	0.990	0.0105
-100.0	20.0	0.00865	0.991	0.921	0.0793
	40.0	0.0164	0.984	0.954	0.0465
	60.0	0.0281	0.972	0.964	0.0358
	80.0	0.0361	0.964	0.968	0.0317
-75.0	20.0	0.0100	0.990	0.747	0.253
	40.0	0.0207	0.979	0.863	0.137
	60.0	0.0370	0.963	0.890	0.110
	80.0	0.0489	0.951	0.909	0.0906
-50.0	20.0	0.00843	0.992	0.438	0.562
	40.0	0.0265	0.974	0.673	0.327
	60.0	0.0448	0.955	0.760	0.240
	80.0	0.0603	0.940	0.797	0.203
-25.0	30.0	0.00988	0.990	0.209	0.791
	40.0	0.0212	0.979	0.331	0.669

**Table 3** Experimental results for the hydrogen-ethane system

Temp. [°C]	Press. [atm]	$x_{H_2}$	$x_{C_2H_6}$	$y_{H_2}$	$y_{C_2H_6}$
-125.0	20.0	0.00618	0.994	0.986	0.0139
	40.0	0.0122	0.988	0.991	0.00907
	60.0	0.0156	0.984	0.994	0.00604
	80.0	0.0221	0.978	0.995	0.00507
-100.0	20.0	0.00888	0.991	0.964	0.0358
	40.0	0.0168	0.983	0.977	0.0226
	60.0	0.0240	0.976	0.983	0.0171
	80.0	0.0336	0.966	0.985	0.0150
-75.0	20.0	0.0108	0.989	0.881	0.119
	40.0	0.0210	0.979	0.930	0.0700
	60.0	0.0319	0.968	0.947	0.0535
	80.0	0.0448	0.955	0.951	0.0488
-50.0	20.0	0.0118	0.988	0.688	0.312
	40.0	0.0257	0.974	0.812	0.188
	60.0	0.0412	0.959	0.862	0.138
	80.0	0.0557	0.944	0.884	0.116

**Table 4** Experimental results for the methane-ethylene system

Temp. [°C]	Press. [atm]	$x_{CH_4}$	$x_{C_2H_4}$	$y_{CH_4}$	$y_{C_2H_4}$
-75.0	10.1	0.107	0.893	0.623	0.377
	20.0	0.311	0.689	0.789	0.211
	20.0	0.312	0.688	0.799	0.201
	39.9	0.738	0.262	0.912	0.0877
-50.0	20.0	0.123	0.877	0.443	0.557
	40.0	0.398	0.602	0.708	0.292
	55.0	0.616	0.384	0.764	0.236
-25.0	30.0	0.0809	0.919	0.242	0.758
	40.0	0.172	0.828	0.385	0.615
	45.0	0.242	0.758	0.453	0.547
	50.0	0.284	0.716	0.478	0.522
	60.0	0.395	0.605	0.513	0.487

in Fig. 4, the  $P$ - $x$  diagram shows that the solubility of hydrogen in liquid methane increases with temperature at higher pressure. This reverse-order solubility<sup>3)</sup> is a noticeable feature in the system consisting of a very light (low critical temperature) component, such as helium or hydrogen. Hydrogen concentrations in vapor phase are plotted against temperatures in Fig. 7. This figure shows that the purity of hydrogen in the recovery gas can be increased rapidly by lowering the temperature, and that operation under higher pressure is advantageous. However, no effect of temperature and pressure is found below about  $-150^\circ\text{C}$ , and the upper limit of hydrogen purity is approximately 98 per cent. For further purification, the selective removal of methane by adsorption or absorption may be required.<sup>9)</sup>

To test the validity of the present results for ternary systems, an empirical method was adopted. As shown in Fig. 8, the straight-line relationship holds well. This relationship has been shown to hold for the hydrogen-carbon monoxide-carbon dioxide<sup>8)</sup> and

Table 5 Experimental results for the hydrogen-methane-ethylene system

$x_{H_2}$	$x_{CH_4}$	$x_{C_2H_4}$	$y_{H_2}$	$y_{CH_4}$	$y_{C_2H_4}$	$x_{H_2}$	$x_{CH_4}$	$x_{C_2H_4}$	$y_{H_2}$	$y_{CH_4}$	$y_{C_2H_4}$
-150.0°C 20.0atm						-100.0°C 40.0atm					
0.00698	0.189	0.804	0.934	0.0633	0.00243	0.0188	0.0902	0.891	0.857	0.0941	0.0488
0.00756	0.321	0.672	0.908	0.0898	0.00258	0.0197	0.251	0.729	0.711	0.243	0.0453
0.00930	0.476	0.515	0.877	0.122	0.00111	0.0237	0.389	0.587	0.607	0.346	0.0479
0.0118	0.625	0.363	0.856	0.143	0.00088	0.0271	0.602	0.371	0.449	0.514	0.0374
0.0177	0.826	0.157	0.842	0.157	0.00061	0.0278	0.712	0.260	0.386	0.585	0.0286
-150.0°C 40.0atm						-100.0°C 60.0atm					
0.0113	0.194	0.795	0.959	0.0386	0.00202	0.0314	0.0898	0.879	0.893	0.0696	0.0376
0.0131	0.309	0.678	0.944	0.0541	0.00207	0.0328	0.250	0.718	0.787	0.178	0.0352
0.0187	0.493	0.489	0.923	0.0756	0.00104	0.0391	0.376	0.585	0.699	0.263	0.0380
0.0254	0.631	0.344	0.914	0.0850	0.00056	0.0482	0.581	0.371	0.585	0.384	0.0314
0.0346	0.814	0.152	0.896	0.104	0.00051	0.0522	0.687	0.260	0.520	0.452	0.0279
-150.0°C 60.0atm						-100.0°C 80.0atm					
0.0171	0.193	0.790	0.965	0.0327	0.00193	0.0418	0.0938	0.864	0.910	0.0579	0.0325
0.0170	0.326	0.657	0.954	0.0450	0.00141	0.0465	0.243	0.710	0.820	0.147	0.0329
0.0263	0.501	0.473	0.937	0.0622	0.00051	0.0557	0.365	0.580	0.748	0.219	0.0334
0.0328	0.631	0.337	0.931	0.0687	0.00044	0.0693	0.566	0.365	0.639	0.330	0.0306
0.0504	0.803	0.147	0.911	0.0887	0.00060	0.0781	0.665	0.257	0.591	0.383	0.0269
-150.0°C 80.0atm						-75.0°C 20.0atm					
0.0251	0.193	0.782	0.970	0.0283	0.00183	0.00988	0.0327	0.957	0.644	0.101	0.254
0.0321	0.384	0.584	0.953	0.0457	0.00083	0.00843	0.0882	0.903	0.494	0.255	0.251
0.0388	0.491	0.470	0.943	0.0559	0.00083	0.00589	0.155	0.839	0.314	0.437	0.248
0.0527	0.617	0.331	0.937	0.0628	0.00032	0.00374	0.226	0.770	0.170	0.592	0.239
0.0678	0.782	0.150	0.922	0.0774	0.00030	0.00318	0.236	0.761	0.141	0.626	0.233
-125.0°C 20.0atm						-75.0°C 40.0atm					
0.00828	0.178	0.814	0.799	0.180	0.0217	0.0238	0.0912	0.885	0.700	0.160	0.140
0.00717	0.280	0.713	0.725	0.254	0.0212	0.0221	0.0916	0.886	0.705	0.147	0.149
0.00722	0.382	0.611	0.657	0.325	0.0176	0.0227	0.139	0.838	0.629	0.226	0.145
0.0107	0.518	0.471	0.570	0.415	0.0147	0.0198	0.312	0.669	0.400	0.468	0.132
0.0124	0.668	0.319	0.493	0.495	0.0123	0.0186	0.392	0.589	0.330	0.541	0.129
0.0149	0.856	0.129	0.400	0.594	0.00655	0.0116	0.576	0.413	0.145	0.741	0.114
-125.0°C 40.0atm						-75.0°C 60.0atm					
0.0165	0.174	0.809	0.883	0.102	0.0155	0.0375	0.116	0.846	0.743	0.144	0.114
0.0168	0.282	0.701	0.841	0.145	0.0148	0.0379	0.286	0.676	0.569	0.320	0.111
0.0212	0.373	0.606	0.801	0.185	0.0143	0.0393	0.384	0.577	0.492	0.409	0.0999
0.0249	0.511	0.464	0.747	0.241	0.0119	0.0383	0.561	0.401	0.328	0.577	0.0956
0.0304	0.653	0.317	0.708	0.283	0.00915	0.0380	0.686	0.276	0.216	0.698	0.0861
0.0386	0.835	0.126	0.651	0.344	0.00479	-75.0°C 80.0atm					
-125.0°C 60.0atm						0.0537	0.212	0.734	0.714	0.193	0.0932
0.0260	0.177	0.797	0.911	0.0767	0.0123	0.0564	0.284	0.660	0.642	0.263	0.0951
0.0278	0.280	0.692	0.877	0.113	0.0100	0.0651	0.509	0.426	0.445	0.462	0.0934
0.0333	0.368	0.599	0.847	0.142	0.0110	0.0743	0.666	0.260	0.296	0.617	0.0874
0.0369	0.508	0.456	0.810	0.181	0.00846	-50.0°C 20.0atm					
0.0436	0.649	0.307	0.772	0.221	0.00712	0.00632	0.0329	0.961	0.309	0.136	0.555
0.0641	0.815	0.121	0.729	0.268	0.00320	0.00497	0.0519	0.943	0.227	0.208	0.565
-125.0°C 80.0atm						0.00378	0.0745	0.922	0.153	0.282	0.565
0.0332	0.169	0.798	0.926	0.0647	0.00905	-50.0°C 40.0atm					
0.0376	0.274	0.688	0.894	0.0957	0.00985	0.0241	0.0914	0.885	0.482	0.190	0.328
0.0437	0.368	0.589	0.871	0.121	0.00863	0.0204	0.122	0.858	0.428	0.258	0.314
0.0502	0.498	0.452	0.842	0.151	0.00754	0.0172	0.192	0.791	0.302	0.386	0.311
0.0638	0.631	0.305	0.804	0.189	0.00688	0.0131	0.259	0.728	0.200	0.499	0.301
0.0924	0.789	0.118	0.746	0.232	0.00443	-25.0°C 30.0atm					
-100.0°C 20.0atm						0.00554	0.0332	0.961	0.115	0.106	0.780
0.00875	0.0886	0.903	0.752	0.168	0.0807	0.00392	0.0532	0.943	0.0708	0.166	0.763
0.00856	0.260	0.731	0.491	0.429	0.0800	0.00389	0.0498	0.946	0.0775	0.157	0.766
0.00808	0.400	0.592	0.329	0.600	0.0712	0.00179	0.0689	0.929	0.0333	0.219	0.748
0.00811	0.403	0.589	0.317	0.611	0.0724	-25.0°C 40.0atm					
0.00439	0.599	0.397	0.131	0.808	0.0609	0.0168	0.0498	0.933	0.233	0.123	0.644
						0.0135	0.0806	0.906	0.174	0.191	0.635
						0.00600	0.143	0.851	0.0629	0.315	0.623

Table 6 Experimental results for the hydrogen-ethylene-ethane system

$x_{H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$	$y_{H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$	$x_{H_2}$	$x_{C_2H_4}$	$x_{C_2H_6}$	$y_{H_2}$	$y_{C_2H_4}$	$y_{C_2H_6}$
-125.0°C 20.0atm						-75.0°C 20.0atm					
0.00621	0.220	0.774	0.983	0.00640	0.0104	0.0106	0.161	0.829	0.852	0.0480	0.100
0.00675	0.423	0.570	0.981	0.0112	0.00802	0.0102	0.265	0.725	0.843	0.0717	0.0852
0.00597	0.432	0.562	0.980	0.0126	0.00782	0.00970	0.494	0.497	0.816	0.124	0.0604
0.00587	0.636	0.358	0.977	0.0174	0.00576	0.0104	0.501	0.482	0.805	0.132	0.0631
0.00736	0.704	0.288	0.975	0.0195	0.00510	0.0104	0.615	0.375	0.787	0.161	0.0517
0.00642	0.704	0.290	0.977	0.0191	0.00396	0.0100	0.703	0.287	0.764	0.191	0.0453
-125.0°C 40.0atm						-75.0°C 40.0atm					
0.0123	0.220	0.768	0.990	0.00393	0.00651	0.0221	0.160	0.818	0.913	0.0274	0.0592
0.0123	0.222	0.766	0.990	0.00394	0.00625	0.0214	0.261	0.718	0.902	0.0428	0.0557
0.0121	0.439	0.549	0.988	0.00752	0.00455	0.0205	0.501	0.478	0.888	0.0734	0.0388
0.0129	0.424	0.564	0.987	0.00785	0.00472	0.0217	0.501	0.477	0.888	0.0742	0.0376
0.0132	0.637	0.350	0.986	0.0107	0.00332	0.0210	0.608	0.371	0.879	0.0910	0.0303
0.0116	0.693	0.296	0.985	0.0115	0.00318	0.0215	0.691	0.288	0.872	0.103	0.0256
-125.0°C 60.0atm						-75.0°C 60.0atm					
0.0162	0.219	0.765	0.993	0.00310	0.00425	0.0320	0.158	0.810	0.935	0.0201	0.0453
0.0160	0.434	0.550	0.990	0.00606	0.00408	0.0320	0.264	0.704	0.930	0.0302	0.0395
0.0163	0.639	0.345	0.990	0.00819	0.00232	0.0349	0.487	0.479	0.914	0.0559	0.0303
0.0162	0.693	0.291	0.989	0.00848	0.00227	0.0318	0.488	0.480	0.917	0.0544	0.0286
-125.0°C 80.0atm						-75.0°C 80.0atm					
0.0229	0.218	0.759	0.994	0.00266	0.00355	0.0351	0.603	0.362	0.908	0.0677	0.0240
0.0269	0.426	0.547	0.993	0.00445	0.00266	0.0332	0.683	0.284	0.898	0.0811	0.0210
0.0205	0.630	0.350	0.990	0.00778	0.00252	0.0449	0.160	0.795	0.944	0.0164	0.0397
0.0256	0.686	0.288	0.991	0.00785	0.00159	0.0437	0.260	0.697	0.940	0.0250	0.0347
-100.0°C 20.0atm						-75.0°C 80.0atm					
0.00816	0.224	0.768	0.954	0.0218	0.0240	0.0449	0.479	0.476	0.928	0.0469	0.0251
0.00922	0.455	0.536	0.943	0.0394	0.0179	0.0467	0.479	0.474	0.932	0.0455	0.0226
0.00919	0.608	0.383	0.933	0.0526	0.0143	0.0488	0.592	0.359	0.922	0.0573	0.0208
0.00896	0.710	0.281	0.932	0.0577	0.0108	0.0472	0.671	0.282	0.917	0.0648	0.0179
0.00800	0.764	0.229	0.931	0.0604	0.00904	-50.0°C 20.0atm					
-100.0°C 40.0atm						0.0105	0.223	0.767	0.575	0.150	0.275
0.0148	0.219	0.767	0.972	0.0120	0.0159	0.0103	0.328	0.662	0.542	0.221	0.238
0.0163	0.457	0.526	0.965	0.0230	0.0117	0.00947	0.524	0.466	0.520	0.315	0.165
0.0158	0.606	0.378	0.960	0.0310	0.00950	0.00879	0.713	0.278	0.428	0.456	0.116
0.0155	0.705	0.280	0.962	0.0315	0.00676	-50.0°C 40.0atm					
0.0154	0.753	0.231	0.960	0.0344	0.00579	0.0258	0.223	0.752	0.762	0.0818	0.156
-100.0°C 60.0atm						0.0256	0.327	0.647	0.737	0.125	0.138
0.0256	0.215	0.759	0.978	0.00934	0.0123	0.0255	0.522	0.453	0.706	0.193	0.101
0.0241	0.454	0.522	0.972	0.0180	0.00969	0.0273	0.685	0.288	0.656	0.272	0.0730
0.0265	0.600	0.374	0.970	0.0231	0.00695	-50.0°C 60.0atm					
0.0253	0.702	0.273	0.969	0.0257	0.00525	0.0411	0.221	0.738	0.807	0.0651	0.128
0.0281	0.741	0.231	0.968	0.0272	0.00519	0.0427	0.317	0.640	0.806	0.0920	0.101
-100.0°C 80.0atm						0.0421	0.507	0.451	0.780	0.143	0.0767
0.0330	0.217	0.750	0.980	0.00806	0.0116	0.0423	0.670	0.288	0.737	0.208	0.0549
0.0352	0.449	0.516	0.975	0.0161	0.00848	-50.0°C 80.0atm					
0.0341	0.597	0.369	0.974	0.0200	0.00624	0.0558	0.216	0.728	0.850	0.0508	0.0991
0.0334	0.694	0.273	0.973	0.0222	0.00467	0.0573	0.316	0.627	0.837	0.0746	0.0880
0.0350	0.732	0.233	0.973	0.0231	0.00398	0.0587	0.502	0.439	0.813	0.121	0.0657
						0.0585	0.661	0.280	0.778	0.173	0.0487

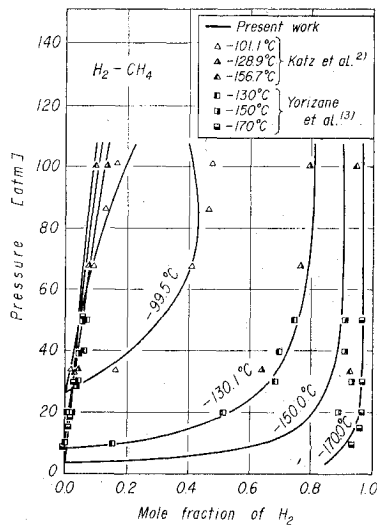


Fig. 4 P-x-y diagram for the hydrogen-methane system

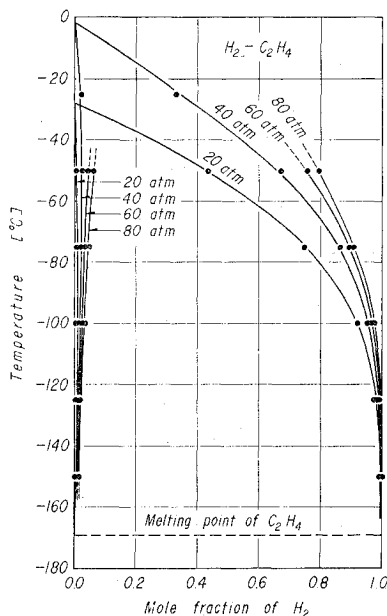


Fig. 5 T-x diagram for the hydrogen-ethylene system

the nitrogen-methane-carbon dioxide<sup>11)</sup> systems.

Typical examples of the changes of phase diagrams with temperature and pressure for the present ternary systems are illustrated in Figs. 9 and 10. With decreasing temperature, the concentration of hydrogen in the vapor phase becomes rich. By adding a heavier hydrocarbon than methane, the relative volatility of hydrogen to methane can be raised, as shown in Fig. 11, so that the purity of hydrogen in the recovery gas will be upgraded.

The Benedict-Webb-Rubin (BWR) equation<sup>1)</sup> was applied to predict the vapor-liquid equilibria of the present systems. A typical representation is

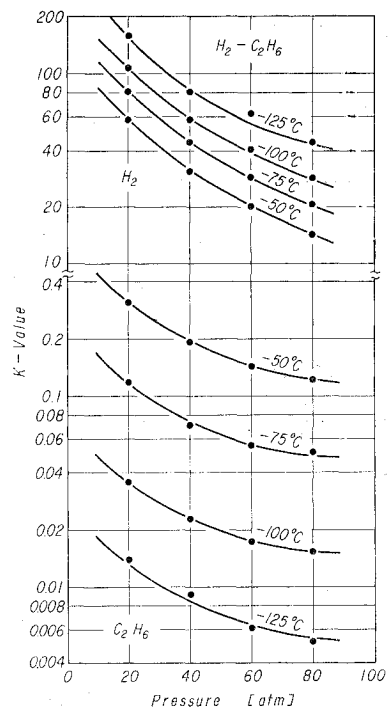


Fig. 6 K-value diagram for the hydrogen-ethane system

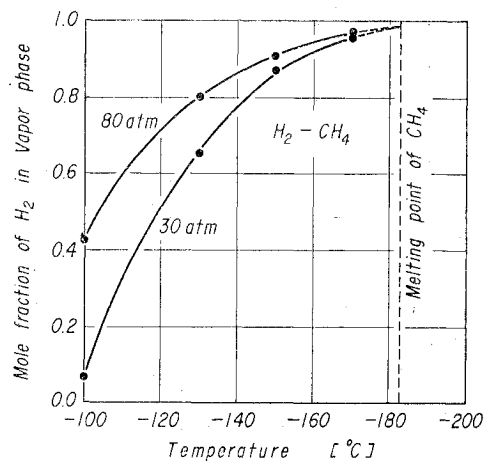


Fig. 7 Changes of hydrogen concentration in vapor phase with temperatures and pressures for the hydrogen-methane system

shown in Fig. 12 for the hydrogen-methane system. As shown in Fig. 12, the reverse-order solubility in a hydrogen-hydrocarbon system is well represented. Tables 7 and 8 compare the experimental results with those calculated by the BWR equation. The calculation procedure and the BWR constants adopted are the same as those in a previous paper.<sup>10)</sup> The equation is shown to give correct K-values when the system temperature is relatively high. However, in low temperature ranges, below the normal boiling point of the heaviest component, errors in predicted K-values cannot be neglected for heavy components.

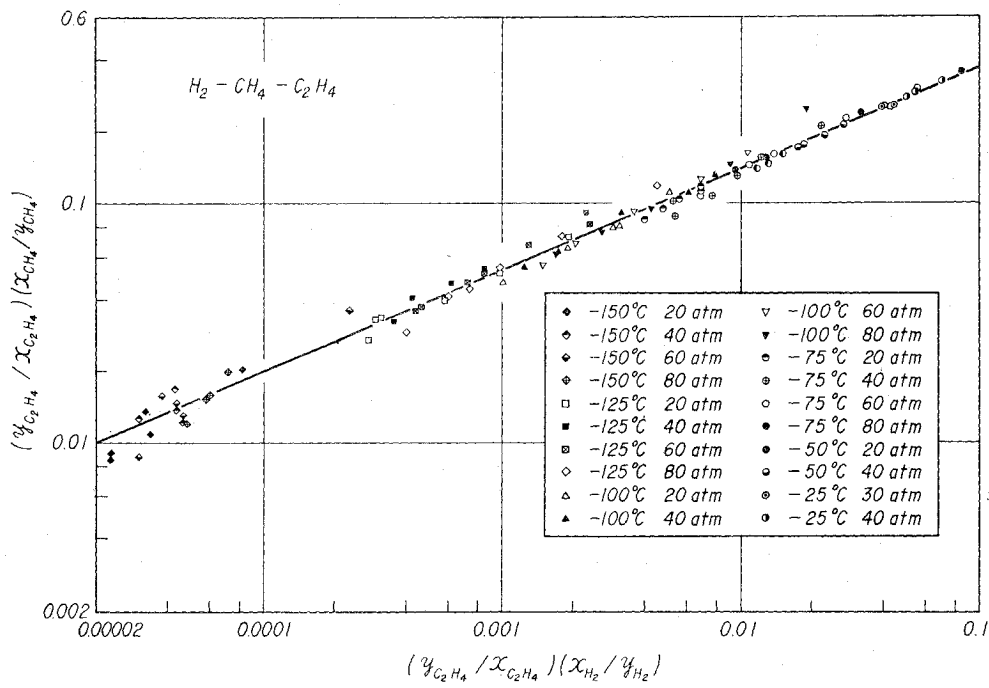


Fig. 8 Straight-line relationship for the hydrogen-methane-ethylene system

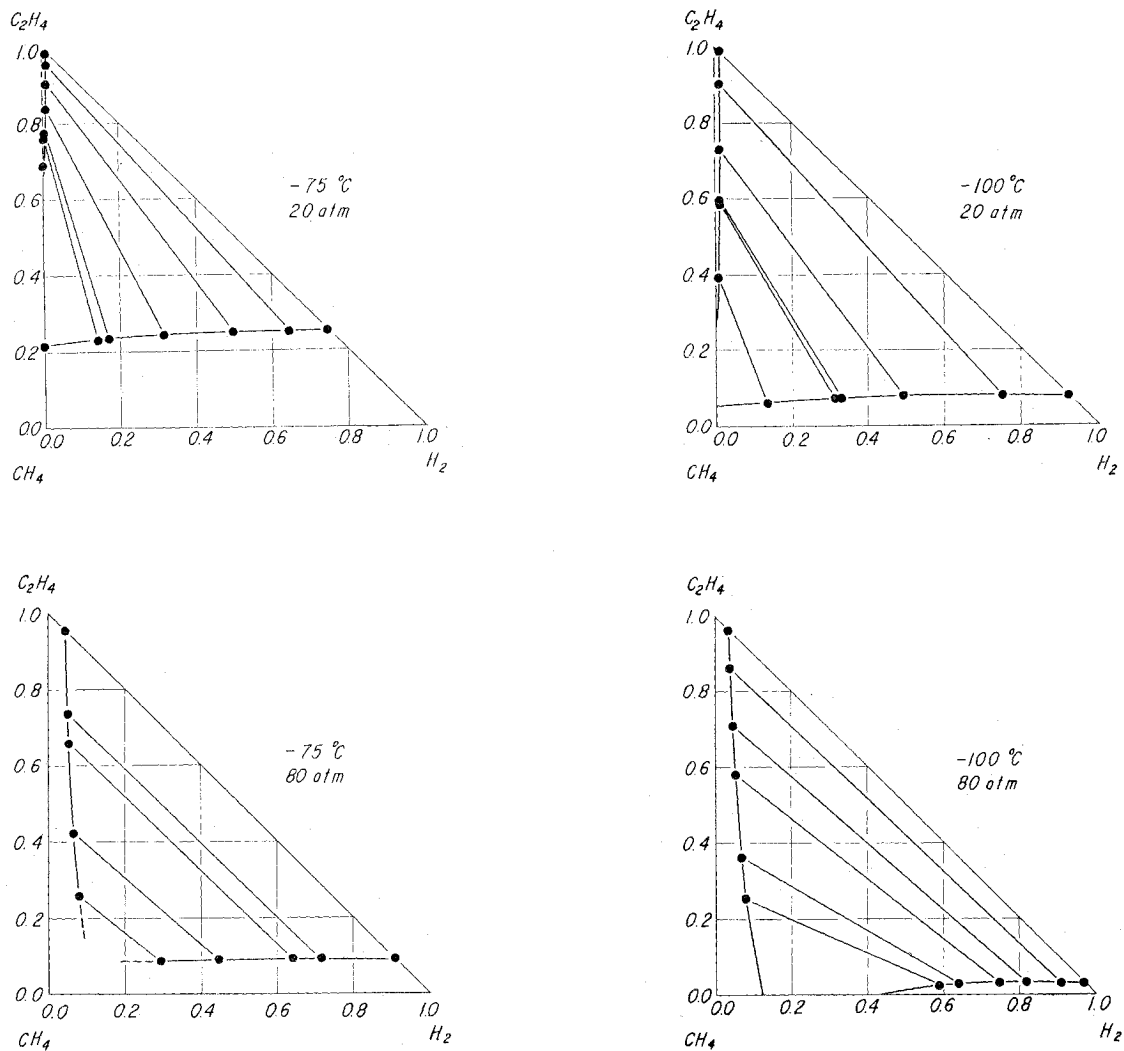


Fig. 9 Vapor-liquid equilibrium diagrams for the hydrogen-methane-ethylene system



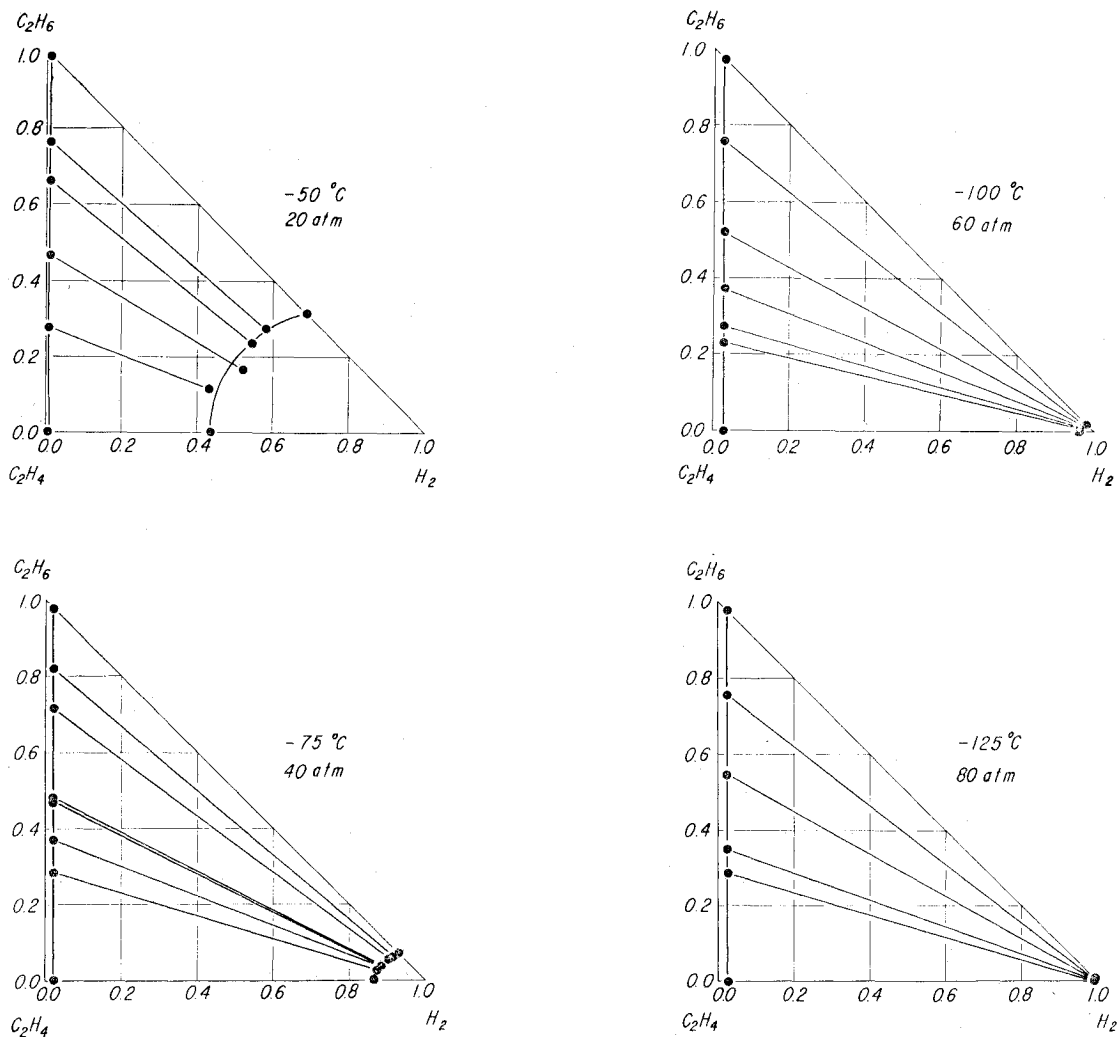


Fig. 10 Vapor-liquid equilibrium diagrams for the hydrogen-ethylene-ethane system

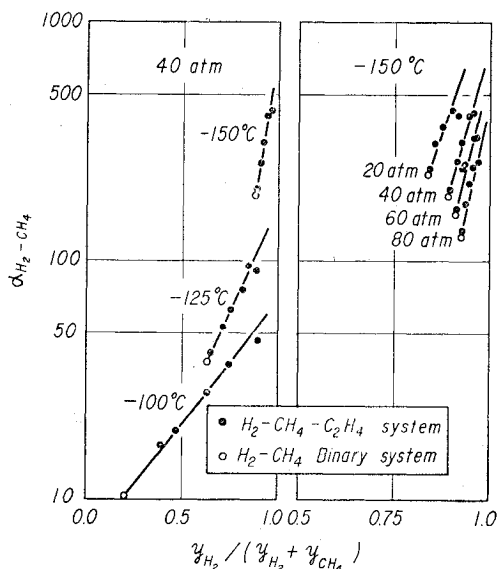


Fig. 11 Relative volatility of hydrogen to methane in the hydrogen-methane-ethylene system

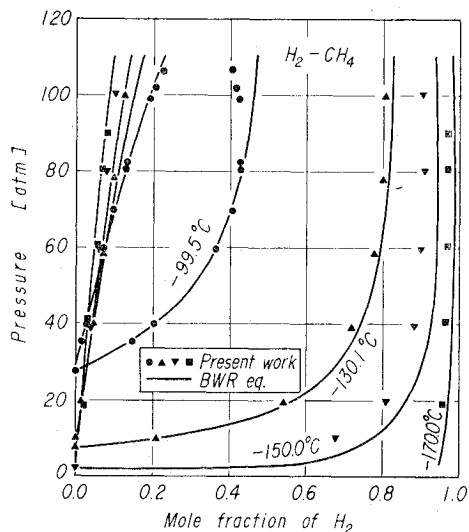


Fig. 12 Comparison of calculated and experimental P-x-y diagram for the hydrogen-methane system

Table 7 Comparison of experimental and calculated vapor-liquid equilibria for the hydrogen-methane-ethylene system

System	Temp. [°C]	Press. [atm]	No. of Data	Av. Dev.*		(Max. Dev.)[%]	
				Press.	H <sub>2</sub>	K-value	
						CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>
Hydrogen-	-150	20~80	20	18(41)	3(6)	30(39)	86(94)
Methane-	-125	20~80	24	18(33)	7(28)	18(27)	58(64)
Ethylene	-100	20~80	20	13(24)	6(21)	6(13)	20(31)
	-75	20~80	20	11(17)	3(12)	4(15)	3(16)
	-50	20~40	7	6(9)	9(15)	5(12)	9(14)
	-25	30~40	7	2(5)	12(20)	7(14)	4(6)

\*Dev. =  $\{|\text{Exp.} - \text{Calc.}|/\text{Exp.}\} \times 100$  [%]

Table 8 Comparison of experimental and calculated vapor-liquid equilibria for the hydrogen-ethylene-ethane system

System	Temp. [°C]	Press. [atm]	No. of Data	Av. Dev.		(Max. Dev.)[%]	
				Press.	H <sub>2</sub>	K-value	
						C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
Hydrogen-	-125	20~80	20	24(40)	0.9(2)	58(65)	82(86)
Ethylene-	-100	20~80	20	22(34)	0.7(7)	11(24)	28(41)
Ethane	-75	20~80	24	15(26)	0.8(2)	7(17)	9(22)
	-50	20~80	16	8(13)	4(14)	9(16)	7(18)

## Conclusion

The vapor-liquid equilibria of binary and ternary systems containing hydrogen and light hydrocarbons have been measured by a static method at various temperatures and pressures. The present experiment provides comprehensive sets of vapor-liquid equilibria of hydrogen and light hydrocarbons. All binary, ternary and quaternary vapor-liquid equilibria of the hydrogen-light hydrocarbons up to C<sub>2</sub> compounds can be obtained from the present data and the results of Cohen *et al.*<sup>7)</sup> for the hydrogen-methane-ethylene-ethane system. By using the data obtained, the features of phase equilibria were discussed. Further, the BWR equation was shown to be successful in predicting the vapor-liquid equilibria of the present binary and ternary systems except below the normal boiling point of the heaviest hydrocarbon.

## Nomenclature

$K$ = $K$ -value ( $=y/x$ )	[—]
$x$ = mole fraction in liquid phase	[—]
$y$ = mole fraction in vapor phase	[—]
$\alpha_{ij}$ = relative volatility ( $=K_i/K_j$ )	[—]

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