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Received for review January 12, 1976. Accepted March 16, 1977.

A Crude Oil–Natural Gas System Vapor–Liquid Equilibrium Ratios (Data at 250 °F and System Containing 20% C_{7+})

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Vapor–liquid equilibrium ratios (*K* values) have been determined experimentally on a Devonian crude oil–natural gas system containing 20% of the C_{7+} or heavy fraction. The data were obtained at 250 °F and five pressures.

Some of the new and improved oil recovery methods require use of vapor–liquid equilibrium ratios to estimate the total oil recovery. Woertz provided a recent correlation, and his paper cites sources of vapor–liquid equilibrium ratio data (*2*). The need for additional experimental data is clearly evident. This paper presents the vapor–liquid equilibrium constants (*K* values) between a crude oil and natural gas system.

A Devonian crude oil of 40° API gravity from New Mexico free of hydrogen sulfide, nitrogen, or carbon dioxide and forming no precipitates when mixed with gas at high pressures was used as the base crude. Hexane–*n*-pentane, *n*-butane, propane, ethane gas, and a Texas natural gas were added to form the desired mixture. The mixture was prepared so that it contained 20.06% C_{7+} in the total system. The C_{7+} fraction of each system was characterized by measurement of its specific gravity and molecular weight. Sufficient volume of the C_{7+} fraction was not available for ASTM distillation.

The basic apparatus consisted of a Ruska high pressure equilibrium cell in a constant temperature oil bath. Podbielniak low temperature fractional distillation apparatus with an external kettle was used for the analyses. A Hart pressure balance was used for pressure measurements. A high pressure storage cell was used to store the total mixture. See Figure 1. A Ruska mercury pump was used for fluid displacement. The benzene freezing point depression apparatus was equipped with a Beckmann thermometer.

The desired materials were charged into an evacuated rocking mixing cell using displacement with mercury into a fluid storage cell. This formed the total mixture. The mixed sample was displaced into the equilibrium cell located in the oil bath. The sample was expanded to a two-phase condition and rocked until constant pressure achieved. A constant pressure was maintained on the equilibrium sample during displacement of either a gas or liquid phase sample into the Podbielniak low temperature fractional distillation apparatus. An external kettle on the Podbielniak column was used to collect the heptanes–plus residue. The density was determined by weight and volume using a 2.0-mL pycnometer. The molecular weight of the C_{7+} was determined by the freezing point depression of benzene measured with a Beckmann thermometer.

Table I. Total Composition of Mixture and Equilibrium Values at 1795 psia, Temperature 250 °F

Component	Total composition mol fraction	1795 psia Gas frac	Liquid frac	*K*-Value Y_i/X_i
Methane	0.4747	0.7771	0.2885	2.6937
Ethane	0.0651	0.0737	0.0570	1.2938
Propane	0.0489	0.0446	0.0532	0.8386
n-Butane	0.0661	0.0385	0.0833	0.4623
n-Pentane	0.0687	0.0283	0.0919	0.3079
Hexane	0.0759	0.0211	0.1087	0.1940
Heptanes–plus	0.2006	0.0167	0.3174	0.0526
	1.0000	1.0000	1.0000	
Heptanes–plus:				
Mol wt	181.0	105.9	182.3	
Sp gr 60/60	0.8259	0.7314	0.8266	

The pressure is considered to within ±0.08% using the Hart pressure balance. The average mole fraction deviation in composition analysis on duplicate samples was 0.0036.

The total composition of the mixture is shown in Table I as well as equilibrium constants at 1795 psia. The equilibrium constant (*K* value) is the mole fraction of a component in the vapor divided by the mole fraction of the component in the liquid.

The bubble point of this mixture at 250 °F was found to be 3190 psia. Tables II and III show the equilibrium constants at pressures of 2095, 2295, 2545, and 2845 psia and a temperature of 250 °F.

Figure 2 shows a plot of the experimental *K*-value data as a function of pressure. The NGAA correlations for each component are shown as the solid lines (*1*). The NGAA *K* values for the C_{7+} shown plotted were assumed to be the average of heptane and octane *K* values. The NGAA method was used to calculate the convergence pressure. The critical temperature of the heptanes–plus fraction in the overall system was obtained from the plot of the critical temperatures of straight chain paraffin hydrocarbons against molecular weight.

A comparison of these experimental *K* values with the charts published by Woertz shows the experimental data for methane and ethane to be lower and the experimental data of the heavier components to be higher than the Woertz charts *K* values. The

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[†] Deceased.

Table II. Equilibrium Values at 2095 and 2295 psia, Temperature 250 °F

	2095 psia			2295 psia		
Component	Gas fraction	Liquid fraction	K-Value Y_i/X_i	Gas fraction	Liquid fraction	K-Value Y_i/X_i
Methane	0.7704	0.3287	2.3438	0.7717	0.3643	2.1184
Ethane	0.0706	0.0595	1.1851	0.0711	0.0595	1.1944
Propane	0.0435	0.0525	0.8287	0.0433	0.0521	0.8313
n-Butane	0.0390	0.0807	0.4828	0.0395	0.0782	0.5050
n-Pentane	0.0325	0.0854	0.3809	0.0308	0.0848	0.3637
Hexane	0.0247	0.1054	0.2344	0.0220	0.0965	0.2277
Heptanes-plus	0.0193	0.2878	0.0672	0.0216	0.2646	0.0815
	1.0000	1.0000		1.0000	1.0000	
Heptanes-plus:						
Mol wt	110.0	187.0		108.5	186.6	
Sp gr 60/60	0.7486	0.8295		0.7416	0.8287	

Table III. Equilibrium Values at 2545 and 2845 psia, Temperature 250 °F

	2545 psia			2845 psia		
Component	Gas fraction	Liquid fraction	K-Value Y_i/X_i	Gas fraction	Liquid fraction	K-Value Y_i/X_i
Methane	0.7639	0.3902	1.9577	0.7514	0.4257	1.7649
Ethane	0.0689	0.0612	1.1256	0.0685	0.0646	1.0605
Propane	0.0439	0.0531	0.8270	0.0428	0.0510	0.8392
n-Butane	0.0403	0.0742	0.5427	0.0419	0.0682	0.6152
n-Pentane	0.0340	0.0764	0.4448	0.0354	0.0727	0.4876
Hexane	0.0213	0.0911	0.2338	0.0287	0.0880	0.3260
Heptanes-plus	0.0277	0.2538	0.1091	0.0313	0.2298	0.1360
	1.0000	1.0000		1.0000	1.0000	
Heptanes-plus						
Mol wt	115.3	184.5		126.0	181.5	
Sp gr 60/60	0.7506	0.8306		0.7639	0.8271	

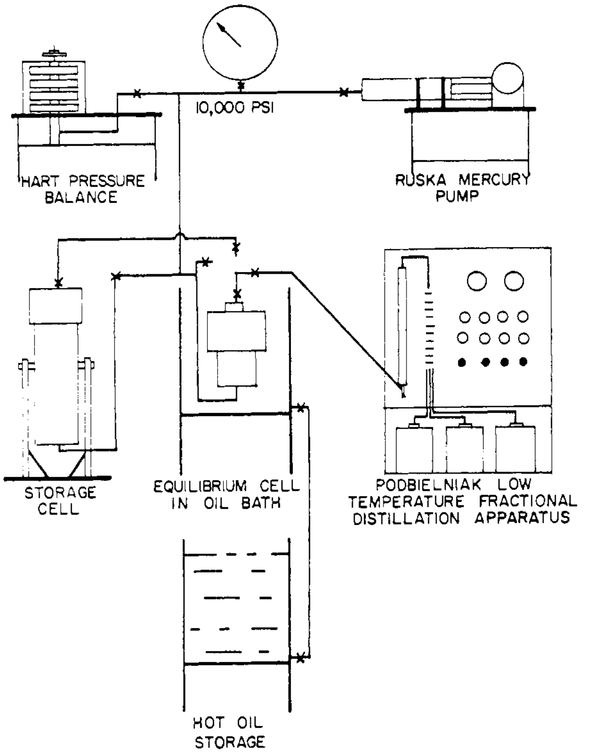

Figure 1. Equipment for the experimental determination of K values.

same deviation trend is observed in Woertz comparison in his paper of experimental data from Atlantic Richfield Company which is in the same pressure and temperature range as the data presented in this paper. No changes were observed in K values published in the 1972 edition of the Gas Processors Suppliers Association Engineering Data Book from the earlier edition of the book in the pressure and temperature range investigated.

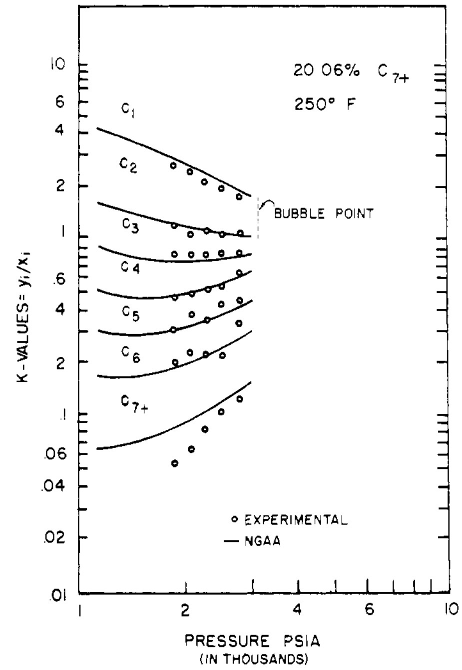

Figure 2. Comparison of experimental and NGAA K values.

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Received for review April 26, 1976. Accepted March 11, 1977.