

PHASE EQUILIBRIA IN HYDROCARBON-WATER SYSTEMS

IV-Vapor-Liquid Equilibrium Constants in the Methane-Water and Ethane-Water Systems

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INTRODUCTION

The equilibrium constants for methane and for water, and for ethane and water have been calculated from experimental data for the two binary systems.^{2,3,11,12} These constants are for the two-phase systems for the temperature range of 100° to 340°F and the pressure range of 200 to 10,000 psia.

The constants for ethane are greater than those for methane. Equilibrium constants for a natural gas from a natural gas-water system⁶ are about the same as those for methane. Equilibrium constants for water in all three systems are very nearly the same over the greater part of the range of temperatures and pressures studied.

In ideal solutions, the vapor-liquid equilibrium constants for a component should be the same in all such solutions at a given temperature and pressure.⁵ Few solutions are ideal, and consequently the use of generalized constants often leads to error in situations where they do not actually apply. In decidedly non-ideal systems, it is desirable to have equilibrium constant data for the specific system.

Vaporization equilibrium constants may be calculated either by thermodynamic methods or from experimental vapor-liquid equilibrium data. In the thermodynamic calculation, the equilibrium constant K may be shown to be¹⁰

$$K = f_{v_i}/f_p \dots \dots \dots (1)$$

where f_{v_i} is the fugacity of the pure component i at the given temperature and at the vapor pressure of the pure component, and f_p is the fugacity of pure i in the gaseous state at the temperature and total pressure of the system. At best the thermodynamic calculation results in a K applicable to ideal solutions. Equilibrium constants calculated from Equation (1) have been found to have only limited agreement with experimental values, even though the solutions for which they were calculated approached ideality.^{8,9} If the more volatile component is at a temperature above its critical, the accuracy of the equilibrium constant for the component is made more doubtful by the use of the vapor pressure term under such conditions. In order to make the thermodynamic calculation on a component above its critical temperature, one must resort to one of the empirical methods of extrapolation of the vapor pressure to conditions above its critical point.¹³ Application of the thermodynamic equilibrium constant then to the methane-water or the ethane-water systems would be risky since the systems are non-ideal, and the methane and ethane are above their critical in most petroleum operations.

ETHANE-WATER SYSTEM

In the temperature range of from 100° to 340°F and for pressures up to 10,000 psia, the vapor-liquid equilibrium data

²References given at end of paper.
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Table I—Vaporization Equilibrium Constants for Ethane in the Ethane-Water System

Pressure psia	100°F	160°F	220°F	280°F	340°F
200	3,034	5,639	6,335	4,962	3,678
400	1,868	2,837	3,194	2,557	1,882
600	1,496	2,074	2,159	1,729	1,280
800	1,333	1,746	1,747	1,339	1,001
1,000	1,260	1,583	1,515	1,146	838
1,250	1,215	1,457	1,326	993	723
1,500	1,177	1,366	1,198	898	652
2,000	1,125	1,265	1,035	789	554
2,500	1,092	1,200	971	726	489
3,000	1,071	1,142	924	679	445
3,500	1,042	1,093	885	645	416
4,000	1,018	1,049	854	620	396
4,500	990	1,012	833	599	384
5,000	968	984	813	579	374
6,000	925	941	772	550	354
7,000	899	909	736	528	337
8,000	888	874	704	511	322
9,000	885	841	679	494	308
10,000	882	813	663	479	295

Table II—Vaporization Equilibrium Constants for Water in the Ethane-Water System

Pressure psia	$K \times 10^3$				
	100°F	160°F	220°F	280°F	340°F
200	5.009	24.49	87.83	250.7	595.5
400	2.642	12.69	45.08	127.9	303.7
600	1.860	8.783	30.80	86.98	206.6
800	1.475	6.837	23.73	66.66	158.2
1,000	1.245	5.679	19.52	54.51	129.2
1,250	1.066	4.755	16.17	44.91	106.3
1,500	0.950	4.150	13.97	38.45	90.60
2,000	0.813	3.412	11.22	30.55	71.81
2,500	0.735	2,981	9.620	25.81	60.54
3,000	0.689	2.711	8.562	22.75	53.33
3,500	0.659	2.523	7.836	20.56	48.16
4,000	0.641	2.392	7.308	19.08	44.36
4,500	0.627	2,294	6.913	17.94	41.48
5,000	0.621	2.220	6.611	17.04	39.16
6,000	0.618	2.120	6.181	15.73	35.70
7,000	0.620	2.070	5.898	14.78	33.28
8,000	0.624	2.032	5.658	13.99	31.26
9,000	0.627	1.995	5.439	13.35	29.53
10,000	0.630	1.954	5.215	12.77	28.04

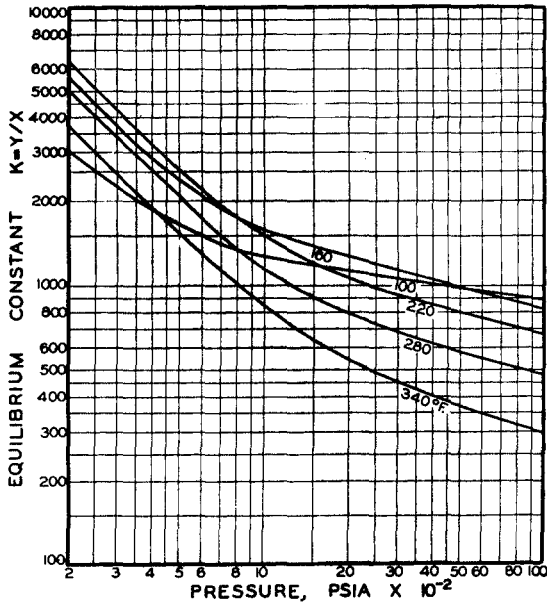


FIG. 1—EQUILIBRIUM CONSTANTS FOR ETHANE IN ETHANE-WATER SYSTEM (K-P).

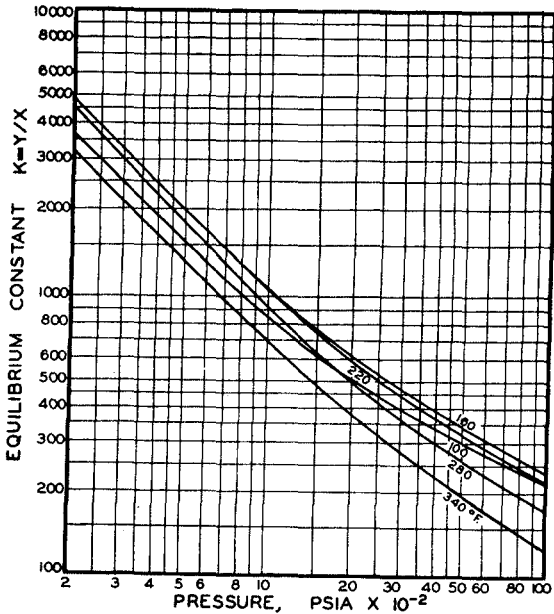


FIG. 4—EQUILIBRIUM CONSTANTS FOR METHANE IN METHANE-WATER SYSTEM (K-P).

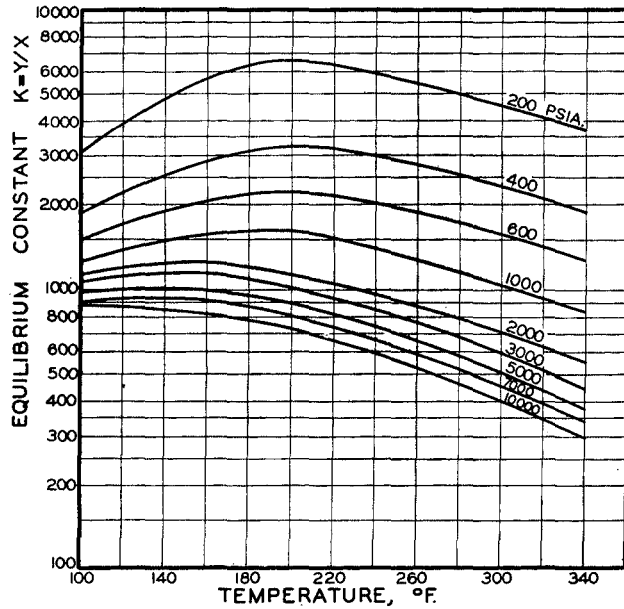


FIG. 2—EQUILIBRIUM CONSTANTS FOR ETHANE IN ETHANE-WATER SYSTEM (K-T).

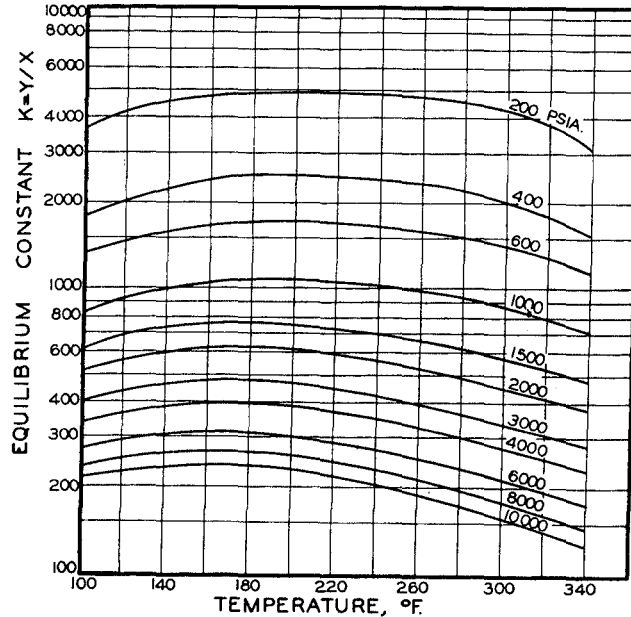


FIG. 5—EQUILIBRIUM CONSTANTS FOR METHANE IN METHANE-WATER SYSTEM (K-T).

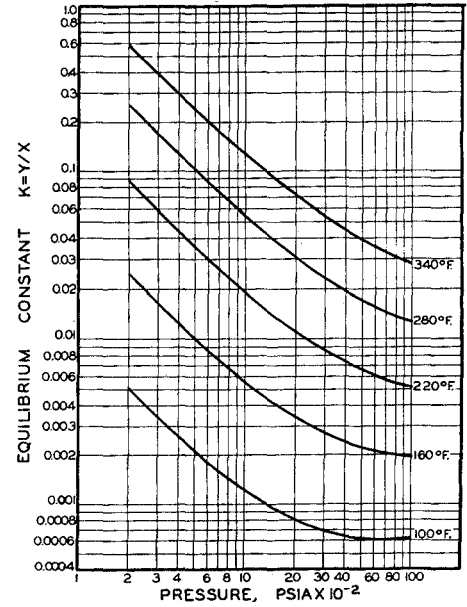


FIG. 3—EQUILIBRIUM CONSTANTS FOR WATER IN ETHANE-WATER SYSTEM (K-P).

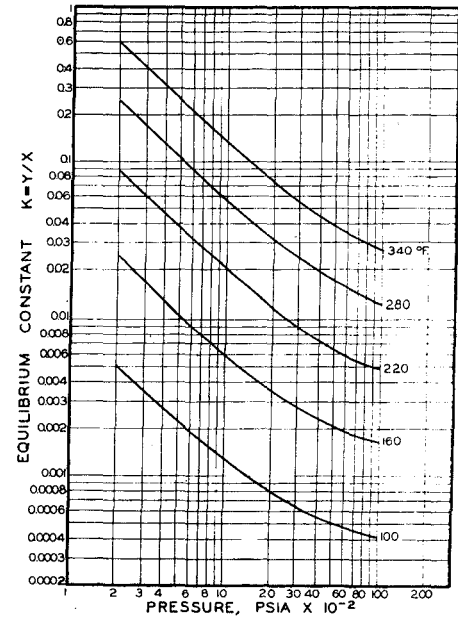


FIG. 6—EQUILIBRIUM CONSTANTS FOR WATER IN METHANE-WATER SYSTEM (K-P).

Table III — Experimental Determinations of Vapor Phase Composition in the Ethane-Water System at 100°F

Pressure psia	Mole Fraction H ₂ O x 10 ³		Experimental % Deviation
	Experimental	Literature Smoothed ¹²	
608	2.090	1.830	+ 14.2
629	1.836	1.790	+ 2.57
655	1.638	1.733	- 5.48
718	1.726	1.605	+ 7.54
728	1.195	1.570	- 23.9
1,745	0.919	0.910	+ 1.00
Average Deviation			9.11%

Table IV — Vaporization Equilibrium Constants for Methane in Methane-Water System

Pressure psia	100°F	160°F	220°F	280°F	340°F
200	3,644	4,804	4,847	4,537	3,080
400	1,889	2,425	2,491	2,244	1,620
600	1,313	1,654	1,693	1,501	1,130
800	1,013	1,273	1,297	1,149	873
1,000	833	1,052	1,054	929	705
1,250	701	878	856	750	568
1,500	617	761	736	631	478
2,000	512	620	595	489	377
2,500	445	536	505	413	318
3,000	399	476	444	365	280
3,500	365	432	400	328	252
4,000	337	397	368	299	230
5,000	297	346	321	258	198
6,000	270	310	288	231	176
7,000	251	284	265	210	159
8,000	236	264	247	195	145
9,000	224	249	232	181	134
10,000	214	237	219	171	125

Table V — Vaporization Equilibrium Constants for Water in Methane-Water System

Pressure psia	K x 10 ³				
	100°F	160°F	220°F	280°F	340°F
200	5.089	24.85	88.79	251.47	596.61
400	2.709	13.02	45.95	129.33	306.96
600	1.914	9.010	31.64	88.70	210.39
800	1.515	7.082	24.49	68.33	161.68
1,000	1.277	5.894	20.20	56.25	132.57
1,250	7.086	4.948	16.78	46.43	109.40
1,500	0.956	4.308	14.47	39.82	93.72
2,000	0.796	3.510	11.60	31.58	74.05
2,500	0.700	3.038	9.891	26.65	62.25
3,000	0.637	2.719	8.739	23.38	54.47
3,500	0.592	2.494	7.926	21.04	48.87
4,000	0.558	2.324	7.303	19.29	44.77
5,000	0.512	2.088	6.444	16.90	38.87
6,000	0.481	1.933	5.880	15.32	34.89
7,000	0.457	1.823	5.491	14.17	31.96
8,000	0.439	1.748	5.211	13.29	29.76
9,000	0.424	1.689	5.003	12.61	28.03
10,000	0.414	1.648	4.834	12.07	26.61

have been determined by Reamer, Olds, Sage, and Lacey¹² for the vapor phase, and by Culberson, Horn, and McKetta⁴ and Culberson and McKetta² for the liquid phase. Throughout this region of pressures and temperatures, only two phases were present at any time. The critical temperature of ethane is 90°F; therefore, an ethane-rich liquid phase was not present. Likewise, the conditions of temperature and pressure in the hydrate region⁷ are not considered here.

With the vapor-liquid equilibrium data available, it was possible to calculate the equilibrium constants since by definition

$$K = y_i/x_i \dots \dots \dots (2)$$

In Equation (2), y_i is the mole fraction of component i in the vapor phase, and x_i is the mole fraction of the same component in the liquid phase.

Vaporization constants calculated by Equation (2) have been tabulated for ethane in Table I and plotted in Figs. 1 and 2. In Table II are tabulated the vaporization equilibrium constants for water in the ethane-water system. These constants for water are plotted in Fig. 3. In Fig. 3, it may be noted that at 100°F the equilibrium constant passes through a minimum and would probably continue to increase as the pressure increased to the convergence pressure.

METHANE-WATER SYSTEM

In the temperature range of 100° to 340°F and for pressures up to 10,000 psia, the vapor phase data were determined by Olds, Sage, and Lacey¹¹ and the liquid phase data by Culberson and McKetta.³ As was the case in the ethane-water system, only the hydrocarbon-rich vapor phase and the water-rich liquid phase were present. The hydrate region is not covered, and the methane was above its critical temperature.

Equilibrium constants were calculated by Equation (2) and these values are tabulated in Table IV for methane and in Table V for water. Figs. 4 and 5 are plots of the equilibrium constants for methane. Equilibrium constants for water are shown in Figs. 6 and 7.

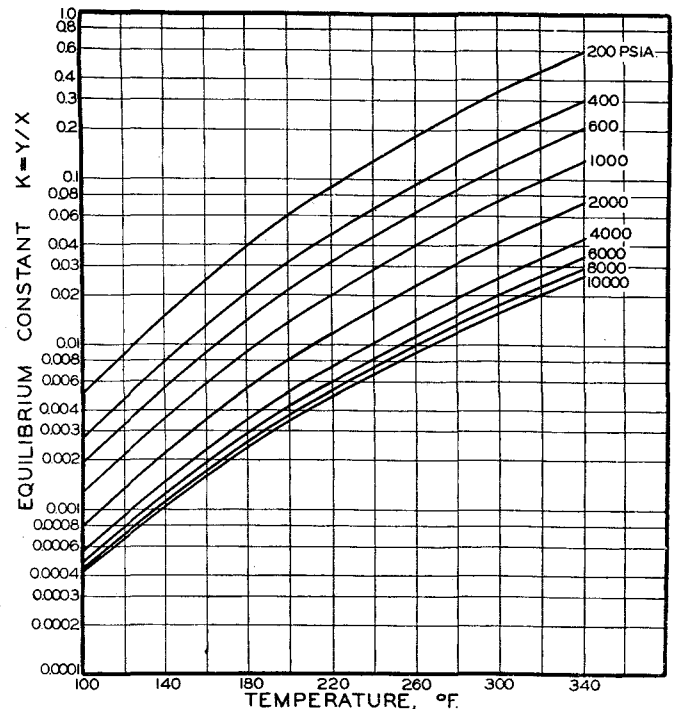


FIG. 7 — EQUILIBRIUM CONSTANTS FOR WATER IN METHANE-WATER SYSTEM (K-T).

DETERMINATIONS OF VAPOR-PHASE
 COMPOSITIONS

The apparatus which was used to obtain the liquid phase data had never been used to determine the composition of a vapor phase. For that reason it was decided to make vapor phase determinations in the ethane-water and methane-water systems to study the applicability of the apparatus to such work. Only qualitative results were sought, and an elaborate analytical train was not set up. The train used consisted of drying tubes containing magnesium perchlorate, a saturator where the dehydrated hydrocarbon was resaturated with water, and a receiving flask where the resaturated hydrocarbon was collected over water which had in turn been previously saturated with the hydrocarbon. The amount of water in the sample was taken to be the gain in weight of the drying tubes. The amount of hydrocarbon was calculated from PVT conditions in the receiving flask where the hydrocarbon pressure was taken to be the total pressure less the vapor pressure of water at the temperature within the flask.

The results of such determinations are given in Table III for the ethane-water system and in Table VI for the methane-water system. In the ethane-water system, the average deviation of the experimental values from the smoothed curve is probably slightly greater than the average deviation of the data of Reamer, Olds, Sage, and Lacey.¹² The average deviation for the methane-water system shown in Table VI compares with that of Olds, Sage, and Lacey.¹¹

DISCUSSION

The equilibrium constants for methane and for ethane are compared with those for a natural gas in a natural gas-water system⁶ in Fig. 8. It is shown that the constant for the ethane is greater than those of the methane and natural gas. The natural gas was 88.51 per cent methane; therefore, it is not surprising that its equilibrium constants were approximately the same as those of pure methane. The water solvent evidences two major effects which are not indicated in the equilibrium constants normally accepted in hydrocarbon-solvent systems.¹ The equilibrium constants for the hydrocarbons in the hydrocarbon-water systems are much greater than for the hydrocarbons in water-free hydrocarbon systems. Also,

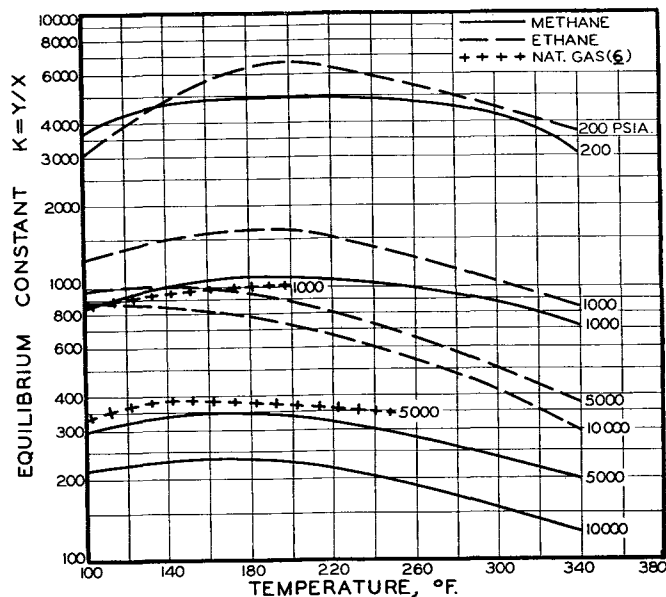


FIG. 8—COMPARISON OF EQUILIBRIUM CONSTANTS FOR LIGHT HYDROCARBONS IN WATER.

Table VI—Experimental Determinations of Vapor Phase Composition in the Methane-Water System at 100°F

Pressure psia	Mole Fraction $H_2O \times 10^3$		Experimental % Deviation
	Experimental	Literature Smoothed ¹¹	
758	1.770	1.580	+ 12.0
1,600	0.762	0.900	- 15.3
2,375	0.745	0.730	+ 2.06
3,615	0.483	0.580	- 16.7
5,185	0.502	0.515	- 2.52
Average Deviation			9.72%

in the water-solvent systems, the equilibrium constants for the hydrocarbons pass through a maximum not common to the hydrocarbon-solvent systems.

No graphical comparison was made of the equilibrium constants for water in the systems. In the methane-water and ethane-water systems, the constants for water are almost identical under all the conditions studied except for conditions of high pressure and low temperature. The greatest difference occurred at 100°F and 10,000 psi where the constants differed by about 50 per cent (based upon the methane).

In systems such as these where the composition of the liquid phase is of the order of 99+ mole per cent water, the equilibrium constants for the hydrocarbon will be controlled by the liquid phase. When the very small mole per cent of hydrocarbon is used in the denominator of Equation (2), it affects the value of K for the hydrocarbon tremendously. In the same manner, the composition of the vapor phase controls the value of the equilibrium constant for water since the denominator of Equation (2) is always approximately unity.

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