Vapor-Liquid Phase Behavior of the Hydrogen-Propane and Hydrogen-Carbon Monoxide-Propane Systems

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Vapor-liquid equilibria data for the hydrogen-propane binary system and the hydrogen-carbon monoxide-propane system were taken at temperatures of —185° to +75°C. and under pressures as high as 3000 psi. Vapor-liquid data for the hydrogen-carbon monoxide-propane system are reported at —50°, 0°, and +50°C. at pressures of 500, 1000, and 2000 lb./sq.in. abs. for each of the three temperatures. The Krichevsky-Kasarnovsky equation adequately correlated the solubility data of hydrogen in the liquid phase of the hydrogen-propane system. Hydrogen-propane data are compared with the data of two previous studies.

Experimental data were collected in order to test empirical and semiempirical methods for the prediction of phase behavior and to confirm and to fill in gaps existing in previous data. Although the theoretical approach to this problem is not sufficiently developed for the conditions of this study, the data should be useful in the development and testing of future theories.

Additional data* on the hydrogen-propane binary system and the hydrogen-carbon monoxide-propane ternary system are provided because low temperature phase behavior data are necessary for the evaluation of cryogenic purification processes for hydrogen. Phase data for the hydrogen-carbon monoxide-propane ternary system are based on those of Stein, Claitor, and Geist (*1*). Their data are limited to a single temperature of −187.5°C. under a maximum pressure of 475 lb./sq. in. abs. The hydrogen-propane system has been studied by Burriss et al. (*2*) and by Williams and Katz (*3*). The former study was carried out under 8000 lb./sq. in. abs. between 4.4° and 87.8°C. In the latter study the maximum pressure was 8000 lb./sq. in. abs., and the temperature range, from −184° to +23.9°C.

EXPERIMENTAL METHOD

The apparatus and method have been described by Sinor et al. (*4*) and by Trust (*5*). Vapor and liquid samples were extracted from a magnetically stirred, static equilibrium cell having an internal volume of 100 cc. The isothermal bath in which the cell was contained could be maintained at a constant temperature over the range of −196° to +85°C. by balancing the cooling effect of liquid nitrogen coolant with a controlled electrical heat input. The temperature levels of the equilibrium cell were controlled and measured to within ±0.05°C.

A platinum resistance thermometer, the sensing element, was calibrated against a laboratory standard platinum resistance thermometer which, in turn, had been calibrated by the National Bureau of Standards. Pressures were measured with Heise bourdon tube gages, which were calibrated with a Ruska pressure balance. The accuracy of the pressure measurements is believed to be within ±3 lb/sq.in. of reported values.

Samples withdrawn from the equilibrium cell were passed directly to a F & M Model 720 chromatograph for analysis. Chromatographic responses for the unknown samples were compared to responses of known samples that had been prepared by mixing pure component gases at measured pressures into five mixing vessels. During sampling the pressure drop was reduced by minimizing the "dead volume" in the sampling system and by removing for analyses three duplicates each of small liquid and vapor samples. The pressure drop within the cell was only 5 to 10 lb./sq.in. below the initial pressure, depending on the temperature and pressure level within the cell.

The purities of the mixtures, as determined by gas chromatography, were hydrogen, 99.93 mole %; carbon monoxide, 99.79 mole %; and propane, 99.91 mole %.

EXPERIMENTAL DATA

Hydrogen-Propane System

Experimental data covering temperatures of −175° to +75°C. under pressures up to 3000 lb./sq. in. abs. are tabulated in Table I. Vapor phase data were not measured below −100°C. as the propane content in the vapor phase

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was too small for precise chromatographic measurement.

Over small ranges of temperature, the solubility of hydrogen in the liquid phase increases with increasing temperature for pressures substantially above the vapor pressure of propane. At pressures below the critical pressure of propane, however, the percent solubility of hydrogen passes through a maximum and decreases to zero at the temperature corresponding to the vapor pressure (Figure 1). Retrograde phenomena were observed in the hydrogen-propane system at temperatures as low as −100°C.

Analytical functions in power series of pressure were fitted to the experimental vapor and liquid isothermal data. The average standard deviation between the smoothed curves and the experimental data was 0.10 mole % for the liquid phase and 0.37 mole % for the vapor phase.

T-X plots at constant pressure show that these data agree closely with the liquid phase data of Williams and Katz (3), but are above the data of Burriss et al. (2) on the 1000 and 2000 lb./sq. in. abs. isobars. Figure 2 shows that the greatest differences exist at 2000 lb./sq. in. abs. The average standard deviation of the Williams and Katz data from our data was 0.118 mole % hydrogen for the liquid phase and 1.73 mole % propane for the vapor phase. A comparison of interpolated experimental data from Burriss et al. gives an average standard deviation of 0.698 mole % hydrogen for the liquid phase and 1.66 mole % for the vapor phase. It should be emphasized that these comparisons were made over the temperature range of −185° to +25°C. for Williams and Katz and over the range of 0°C. to +75°C. for Burriss et al.

K-factor plots for both hydrogen and propane are shown in Figures 3 and 4. An equation was fitted to the K-factors for hydrogen in the hydrogen-propane system from −185° to +50°C. with pressures up to 3000 lb./sq. in. abs. This equation predicts the K-factors of hydrogen within 5% for all values tested. The form of the equation is

$$\log_{10} K = A_1(T) + A_2(T)\log_{10}(P/100) \qquad (1)$$

where $A_1(T), A_2(T)$ are functions of temperature. $A_1(T)$ and $A_2(T)$ are given by

$$A_1(T) = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5/T + C_6/T^2 \qquad (2)$$

and

$$A_2(T) = B_1 + B_2T + B_3T^2 + B_4T^3 + B_5T^4 \qquad (3)$$

TABLE 1. VAPOR-LIQUID DATA FOR THE HYDROGEN-PROPANE SYSTEM[*]

Pressure, lb./sq. in. abs.	Liquid, mole % H_2	Vapor, mole % C_3	Liquid, mole % H_2	Vapor, mole % C_3
	−175°C.		−50°C.	
200	—	—	0.777	4.3800
250	0.21	—	—	—
500	—	—	2.047	2.5780
750	—	—	2.952	1.8730
1,000	0.56	—	3.960	1.4150
1,500	0.74	—	5.761	—
2,000	—	—	7.418	1.1080
2,250	1.08	—	—	—
2,500	—	—	8.869	0.9310
3,000	1.34	—	10,750	1.0360
	−160°C.		−25°C.	
250	—	—	1.065	16.670
300	0.27	—	—	—
500	—	—	2.427	8.141
1,000	0.93	—	4.751	3.830
1,500	—	—	—	2.860
1,700	1.47	—	—	—
2,000	—	—	9.034	2.500
2,500	—	—	—	1.280
2,600	2.14	—	—	—
3,000	—	—	13.400	2.140
	−150°C.		0.0°C.	
250	0.31	—	—	—
300	—	—	1.342	27.550
500	—	—	2.373	19.370
1,000	1.10	—	5.220	10.300
1,500	—	—	7.724	8.088
2,000	2.07	—	10.920	7.160
2,500	2.42	—	13.400	6.808
3,000	2.81	—	15.860	6.656
	−125°C.		+25°C.	
150	0.25	—	—	—
250	—	—	0.884	—
300	0.52	—	—	—
400	—	—	—	42.400
	−125°C.		+25°C.	
500	—	—	2.486	—
600	1.06	—	—	—
900	1.54	—	—	—
1,000	—	—	6.020	19.980
1,300	2.18	—	—	—
1,500	—	—	9.712	15.450
1,700	2.74	—	—	—
2,000	—	—	12.390	14.270
2,100	3.29	—	—	—
2,500	—	—	16.490	12.070
2,800	4.43	—	—	—
3,000	4.73	—	19.450	11.320
	−100°C.		+50°C.	
250	0.61	0.217	—	—
300	0.77	0.188	—	—
500	1.21	0.135	2.284	61.16
1,000	2.41	0.101	6.794	39.87
1,500	—	—	11.140	30.24
2,000	4.41	0.099	15.470	26.59
2,500	5.45	—	20.100	23.98
2,600	—	0.112	—	—
2,900	6.18	0.116	—	—
3,000	6.45	0.120	24.460	22.50
	−75°C.		+75°C.	
250	—	1.2880	—	—
270	0.908	—	—	—
500	1.659	0.7000	—	—
750	—	—	3.819	74.13
1,000	3.159	0.4700	6.804	61.60
1,250	—	—	9.755	57.00
1,500	—	0.4190	13.050	51.08
2,000	—	0.3980	—	—
2,250	—	—	23.650	47.77
2,500	7.220	0.4080	—	—
2,700	—	—	—	47.69
3,000	8.468	0.4300	35.260	—

[*] Composition data should be rounded to three significant digits.

T is the temperature in degrees Kelvin. Values for the constants are:

$$
\begin{aligned}
C_1 &= +0.1044506 \times 10^{2}\\
C_2 &= -0.4918058 \times 10^{-1}\\
C_3 &= +0.1463825 \times 10^{-3}\\
C_4 &= -0.1832662 \times 10^{-6}\\
C_5 &= -0.6299007 \times 10^{3}\\
C_6 &= +0.2480422 \times 10^{5}\\
B_1 &= -0.9919057\\
B_2 &= +0.6428202 \times 10^{-2}\\
B_3 &= -0.7115923 \times 10^{-4}\\
B_4 &= +0.2627935 \times 10^{-6}\\
B_5 &= -0.3204383 \times 10^{-9}
\end{aligned}
$$

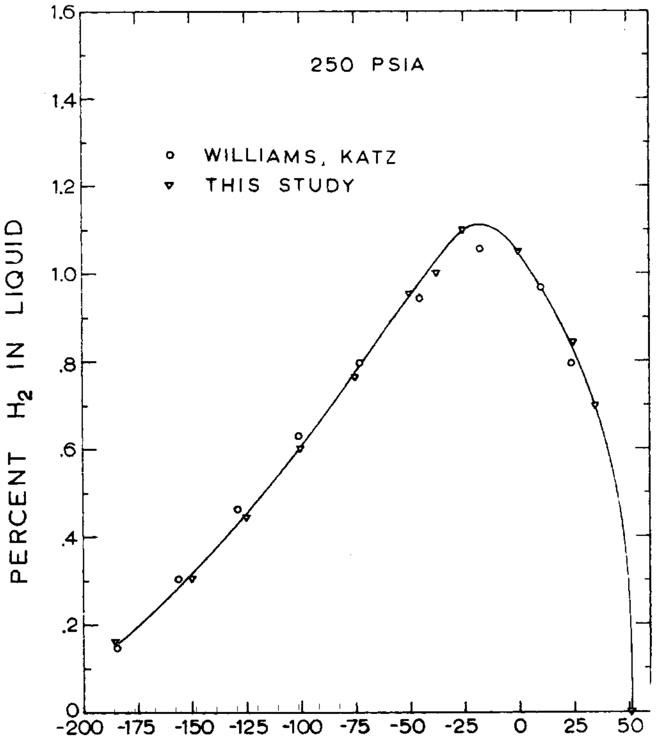

Fig. 1. Temperature-composition diagram for the liquid phase of the hydrogen-propane system at 250 lb./sq.in.abs.

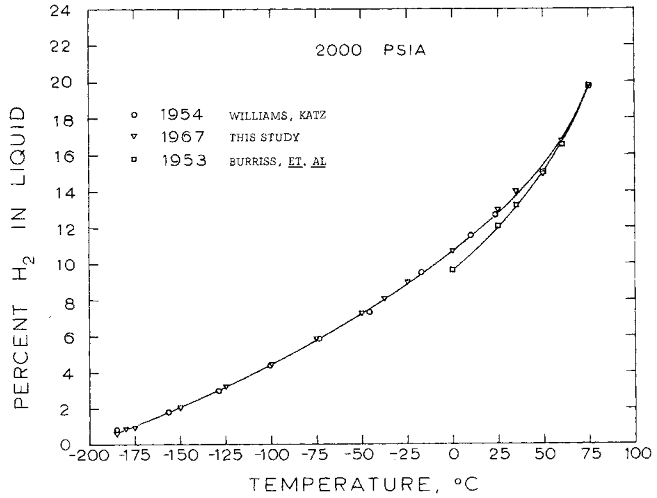

Fig. 2. Temperature-composition diagram for the liquid phase of the hydrogen-propane system at 2,000 lb./sq.in.abs.

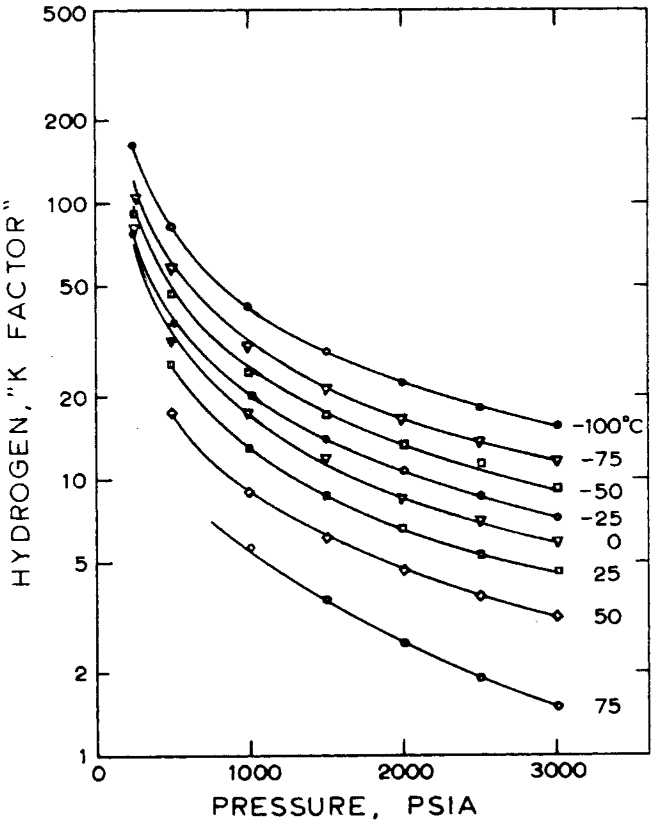

Fig. 3. Hydrogen "K-factor" for the hydrogen-propane system.

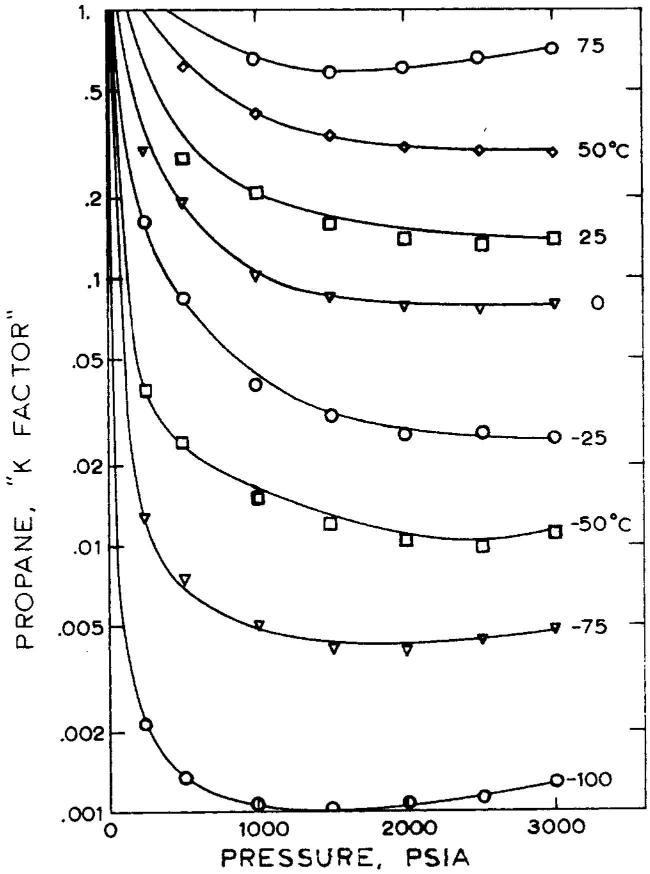

Fig. 4. Propane "K-factor" for the hydrogen-propane system.

No general equation for the propane K-factors was determined.

Hydrogen-Carbon Monoxide-Propane System

Vapor-liquid equilibrium data for the hydrogen-carbon monoxide-propane ternary system were determined at −50°, 0°, and +50°C. at pressures of 500, 1000, and 2000 lb./sq. in. abs. (Table 2). The liquid-composition locus for a given temperature and pressure is almost linear between the carbon monoxide-propane and hydrogen-propane liquid compositions. This straight-line relationship is not apparent for the vapor phase data, which showed much more scatter than the liquid phase data; it was not possible to establish the true curvature of the vapor phase loci.

DATA CORRELATION

Hydrogen-Propane System

Liquid-phase data for the hydrogen-propane system were correlated by the Krichevsky-Kasarnovsky equation (*6*). Orentlicher and Prausnitz (*7*) have reviewed the thermodynamics of hydrogen solubility in cryogenic liquids and have discussed the application of the Krichevsky-Kasarnovsky and Krichevsky-Ilinskaya equations to these systems.

The Krichevsky-Kasarnovsky equation is

$$\log_{10}\frac{f_1}{x_1} = \log_{10} H + \frac{\overline{V}_1{}^{\infty}(P - P_2{}^s)}{2.303\, RT} \tag{4}$$

where H is a function of temperature only

$$H = \operatorname*{limit}_{x_1 \to 0} \frac{f_1}{x_1}$$

Assumptions for the Krichevsky-Kasarnovsky equation are that the liquid phase is dilute, and deviations from Henry's law due to composition effects are negligible, and that the partial molal volume of hydrogen in the liquid phase is independent of pressure and is equal to the partial molal volume at infinite dilution.

A further assumption is that the Lewis and Randall fugacity rule is valid for hydrogen in the vapor phase; that is, that the vapor phase fugacity of hydrogen is

$$f_1 = y_1 f_1{}^0 \tag{5}$$

where $f_1{}^0$ is evaluated at the temperature and total pressure of the system. Hydrogen fugacities were obtained from Benham et al. (*8*).

Somewhat more complex than the Krichevsky-Kasarnovsky equation is the Krichevsky-Ilinskaya equation. It takes into account deviations from Henry's law due to the effect of composition in addition to the effect of total pressure. If x_1 (mole fraction of hydrogen in liquid) is small, as is generally the case at low temperatures, the activity coefficient for the dissolved hydrogen gas in liquid propane can be approximated by

$$\log_{10} \gamma_1 = \frac{C}{RT}(x_2{}^2 - 1) \tag{6}$$

When this effect of composition is considered, Equation (4) becomes the Krichevsky-Ilinskaya equation:

$$\log_{10}\frac{f_1}{x_1} = \log_{10} H + \frac{C}{RT}(x_2{}^2 - 1) + \frac{\overline{V}_1{}^{\infty}(P - P_2{}^s)}{2.303\, RT} \tag{7}$$

The use of this more complex equation did not seem warranted because the Krichevsky-Kasarnovsky equation appeared to be adequate.

Plots of the Krichevsky-Kasarnovsky equation are shown in Figures 5 and 6 for temperatures of −185° up to 0°C. The intercept with the ordinate is log H, and the slope of the line is $\overline{V}_1{}^{\infty}/2.303\, RT$. Values of H and $\overline{V}_1{}^{\infty}$ were calculated from Figures 5 and 6 and plotted in Figures 7 and 8, respectively. As expected, the calculated values for $\overline{V}_1{}^{\infty}$ scatter considerably, for a 2% error in the liquid-phase composition for hydrogen causes roughly a 25% error in $\overline{V}_1{}^{\infty}$.

TABLE 2. VAPOR-LIQUID DATA FOR THE HYDROGEN-CARBON MONOXIDE-PROPANE SYSTEM

Liquid		Vapor	
% H_2	% CO	% H_2	% CO
−50°C., 500 lb./sq.in.abs.			
0.51	7.24	19.33	78.30
0.92	5.33	37.52	60.95
1.64	1.91	76.07	22.53
1.80	1.15	84.74	14.14
−50°C., 1000 lb./sq.in.abs.			
0.51	16.83	7.02	89.87
1.07	14.21	16.42	80.87
1.80	10.52	36.28	61.32
3.00	5.40	66.25	31.76
−50°C., 2000 lb./sq.in.abs.			
0.80	33.84	4.22	90.83
0.81	33.16	4.36	90.77
3.25	21.86	30.00	66.74
5.25	10.72	58.77	39.27
6.72	4.11	83.78	14.77
0°C., 500 lb./sq.in.abs.			
0.43	6.70	10.01	67.97
1.34	4.05	37.01	42.58
1.78	2.76	51.57	29.19
2.22	1.65	61.88	18.78
0°C., 1000 lb./sq.in.abs.			
2.26	10.08	29.16	57.02
2.97	7.74	42.95	44.55
4.34	5.09	66.10	22.80
0°C., 2000 lb./sq.in.abs.			
5.30	19.76	32.04	57.54
5.46	18.62	32.79	55.48
6.34	16.32	42.46	49.20
6.70	15.95	46.08	47.09
8.64	9.52	63.66	30.04
9.18	9.52	63.72	29.20
50°C., 500 lb./sq.in.abs.			
0.47	3.66	3.39	33.63
0.85	2.66	15.95	26.09
0.94	2.59	16.52	23.89
1.61	1.00	31.52	10.63
50°C., 1000 lb./sq.in.abs.			
1.10	12.25	6.85	50.72
2.60	8.67	22.98	41.11
4.30	4.93	40.53	23.89
50°C., 2000 lb./sq.in.abs.			
6.97	24.91	15.89	42.03
10.69	12.08	38.07	26.55

Experimental K-factors from Williams and Katz (3) were compared to K-factors calculated from Equation (4), using the parameters in Figures 7 and 8. Conclusions concerning the range of validity of the Krichevsky-Kasarnovsky equation were as follows:

(1) For temperatures below −100°C., the Krichevsky-Kasarnovsky equation is valid for pressures up to at least 9000 lb./sq. in.

(2) The Krichevsky-Kasarnovsky equation is adequate to at least 4000 lb./sq. in. from −50° to −100°C.

(3) The data show that the Krichevsky-Kasarnovsky equation is valid for pressures at least up to 3000 lb./sq. in. in the range 0.0° to −50°C.

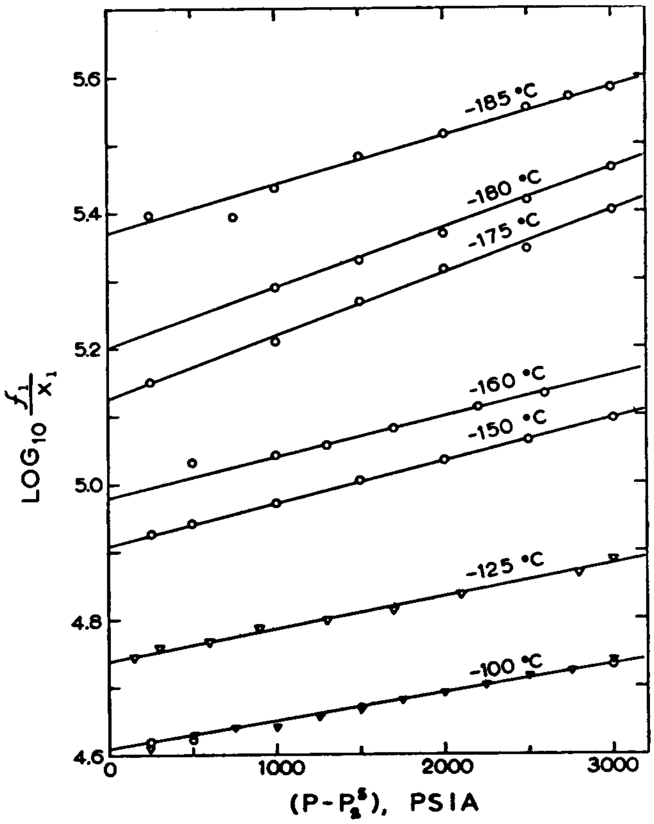

Fig. 5. Graphical analysis of the Krichevsky-Kasarnovsky equation for then hydrogen-propane system at —185° to —100°C.

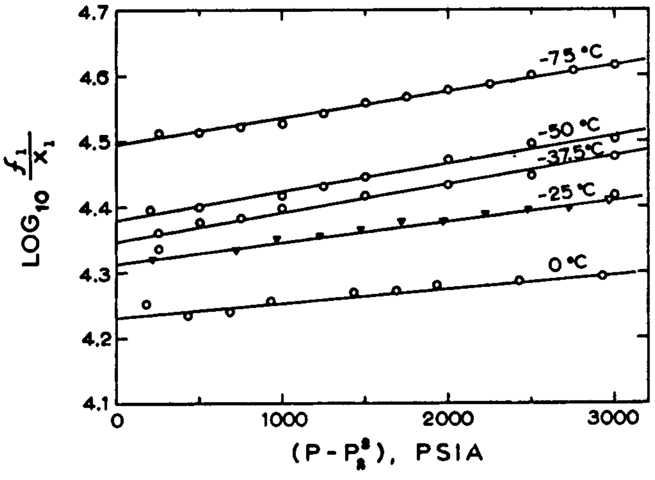

Fig. 6. Graphical analysis of the Krichevsky-Kasarnovsky equation for the hydrogen-propane system at —75° to 0°C.

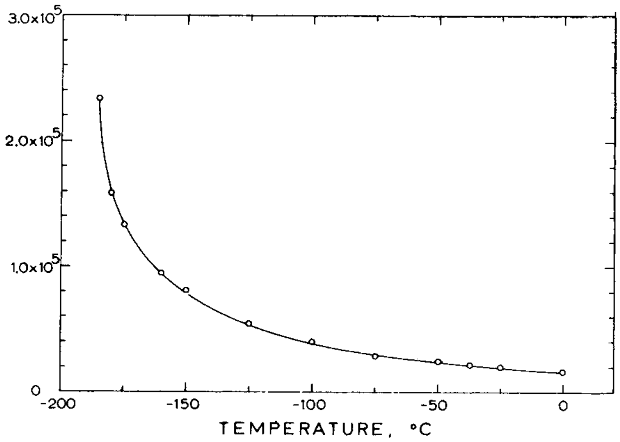

Fig. 7. Henry's law constants from the Krichevsky-Kasarnovsky equation for the hydrogen-propane system.

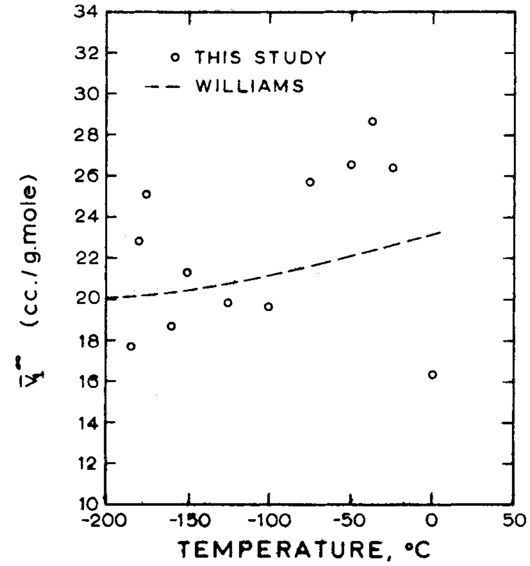

Fig. 8. Partial molal volume at infinite dilution for hydrogen in liquid propane.

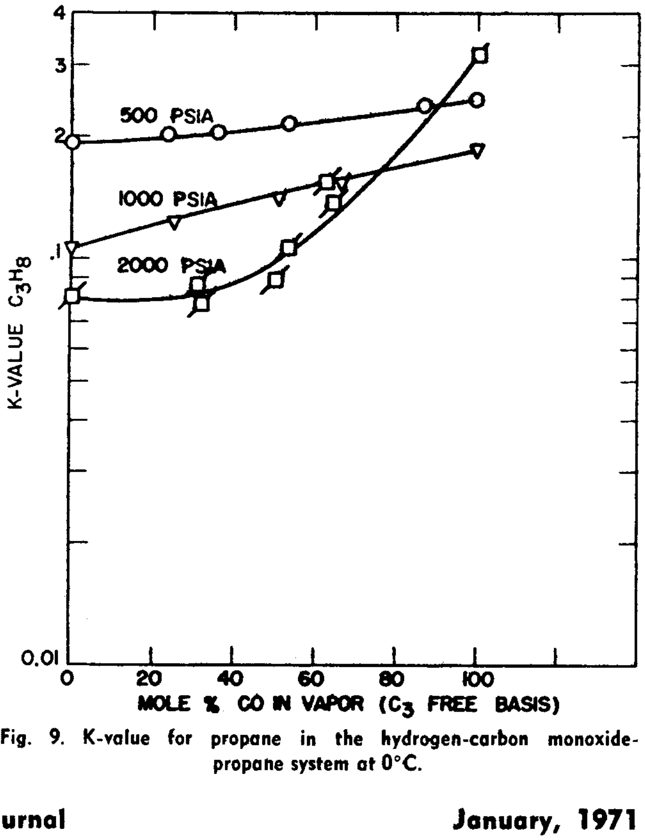

Fig. 9. K-value for propane in the hydrogen-carbon monoxide-propane system at 0°C.

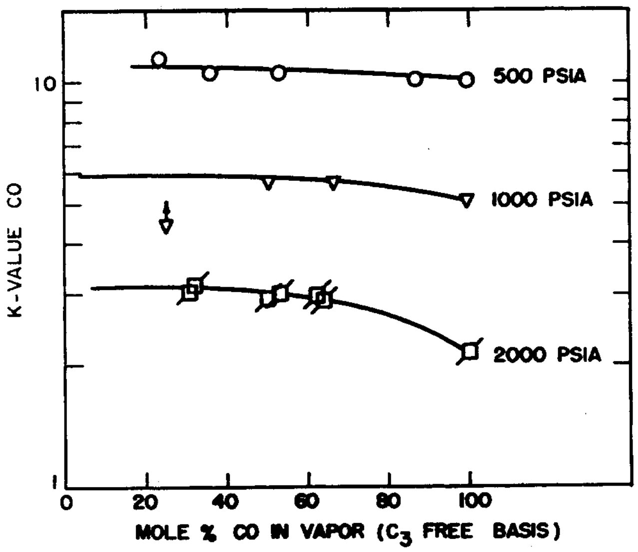

Fig. 10. K-value for carbon monoxide in the hydrogen-carbon monoxide-propane system at 0°C.

Hydrogen-Carbon Monoxide-Propane System

K-factors for each of the three components were calculated from the ternary composition data. As temperature and pressure alone are not sufficient to correlate these K-factors it was necessary to add a phase-rule parameter, that is, the carbon monoxide concentration in the vapor phase on a propane-free basis.

K-factors for propane, carbon monoxide, and hydrogen at 0°C are shown in Figures 9, 10, and 11, respectively. The carbon monoxide K-factors are shown to be only slightly temperature-dependent and relatively insensitive to the hydrogen/carbon monoxide ratio. Propane and hydrogen K-factors are, by contrast, strongly dependent on composition as well as temperature. For a given temperature and pressure, the K-factors for hydrogen decrease as the percent carbon monoxide in the vapor (on a propane-free basis) increases. Propane K-factors at constant temperature and pressure increase as the ratio of carbon monoxide to hydrogen in the vapor phase increases. Experimental K-factors for propane at −50°C exhibit large scatter due to the imprecision in vapor phase analyses at low propane concentrations.

ACKNOWLEDGMENT

Financial support of National Science Foundation Grant GK 705, which made this work possible, is gratefully acknowledged. Phillips Petroleum Company supplied the propane.

NOTATION

C = constant in the Krichevsky-Ilinskaya equation
f = fugacity, lb./sq. in. abs.
H = Henry's constant, lb./sq.in. abs.
K = equilibrium constant, y/x
P = absolute pressure, lb./sq. in.abs.
$P_2{}^s$ = vapor pressure of propane
R = gas law constant
T = temperature, °K.
$V_1{}^\infty$ = partial molal volume of hydrogen at infinite dilution, cc./g. mole

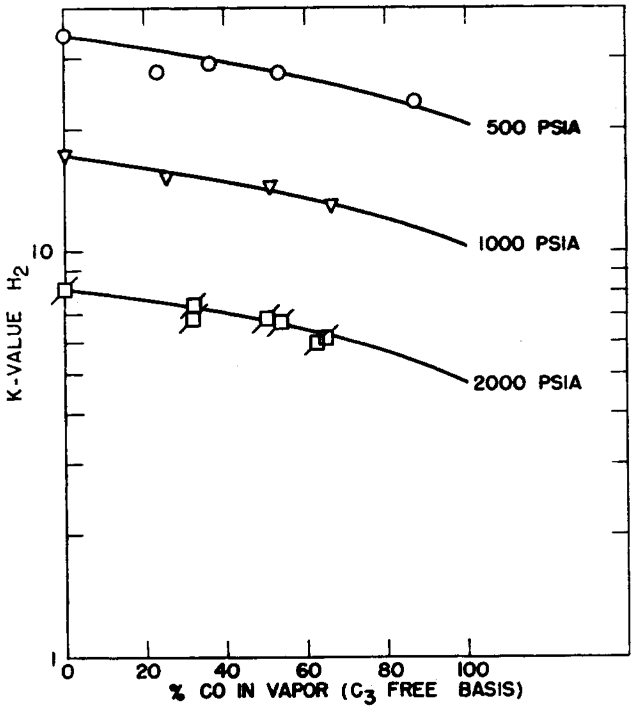

Fig. 11. K-value for hydrogen in the hydrogen-carbon monoxide-propane system at 0°C.

x = mole fraction in liquid phase
y = mole fraction in vapor phase
γ = liquid phase activity coefficient

Subscripts

1 = refers to hydrogen
2 = refers to propane

Superscripts

0 = pure component value at temperature and pressure of system
s = saturated vapor pressure
v = refers to vapor phase
L = refers to liquid phase

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Manuscript received June 4, 1968; revision received May 8, 1969; paper accepted May 9, 1969. Paper presented at AIChE Los Angeles meeting.