The Equilibrium Phase Properties of the Ethane–Hydrogen Sulfide System at Subambient Temperatures

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Vapor and liquid equilibrium phase compositions were determined for the ethane-hydrogen sulfide system at 50.0, −0.1, −49.4, and −99.8 °F over the complete concentration range at pressures between the vapor pressure of hydrogen sulfide and the pressure of the minimum boiling azeotrope. The equilibrium ratios were calculated for each component in the binary system. An equal area integral test showed good thermodynamic consistency of the data. The capability of the Peng-Robinson equation of state for predicting the behavior of this system is illustrated.

A knowledge of the behavior of hydrocarbon systems containing hydrogen sulfide is important in the production and processing of natural gases and condensate fluids. The behavior of the individual hydrocarbon–non-hydrocarbon binary pairs making up these complex systems is important because interaction parameters which are calculated from the binary data are required whenever equations of state or generalized correlations are used to predict the behavior of multicomponent systems. Ethane is universally found in reservoir fluids and hydrogen sulfide is frequently found in concentrations ranging from a few parts per million to 60% or more. For these reasons a knowledge of the equilibrium phase properties of the ethane–hydrogen sulfide binary system is of considerable importance in engineering work.

Kay and Brice (*3*) studied the liquid–vapor equilibrium relations in this system over a temperature range from about 40 to 180 °F. Since many industrial processes now operate at temperatures below this level, it was considered desirable to obtain phase behavior data at lower temperatures extending down to about −100 °F. In view of the formation of an ethane-rich azeotrope in this system and the influence this has on the ability to separate hydrogen sulfide from ethane it was considered important to identify the azeotropic composition over the entire temperature range of interest.

Experimental Method

The experiments were carried out in a constant volume vapor–liquid equilibrium cell which has been described in detail in an earlier publication (*2*). The cell had an internal capacity of approximately 250 ml and was fabricated from type 316 stainless steel. It was equipped with bull's eye type observation ports and specially designed integrally mounted sampling valves for both liquid and vapor phases. Equilibrium was attained with a Teflon coated magnetic stirrer driven by an externally mounted magnetic pile. The entire cell assembly was mounted inside an ethane refrigerated and liquid nitrogen cooled cryostat.

The temperature of the cell contents was measured with a calibrated copper–constantan thermocouple and is believed known to ±0.1 °F. The pressure was measured using a series of calibrated Heise gauges having ranges of 0–100, 0-250, and 0-2000 psi. Pressures are believed known to within 0.1% of full scale. Subatmospheric pressures were obtained by using a differential pressure transducer to measure the difference between the system and atmospheric pressures.

The hydrogen sulfide used in this work was obtained from Matheson, Inc., and had a stated liquid phase purity of at least 99.8 mole %. This material was distilled once and the condensed liquid phase was used. This was judged to have a purity of at least 99.9 mole % with the major impurities being carbon dioxide and propane. The ethane was Phillips Petroleum research grade with a minimum purity of 99.99 mole %. This was used without further treatment.

The composition of the equilibrium phases was determined using a Model 5750 Hewlett Packard gas chromatograph with a thermal conductivity cell detector. The column was made from ⅛ in. diameter stainless steel tubing 6 ft long packed with Porapak QS. The oven temperature was held at 140 °F. The areas of peaks were monitored by a direct connection to an IBM 1800 data acquisition and control computer. The chromatographic program gave corrected peak areas and converted them to mole fraction compositions. These values were checked periodically using a Hewlett-Packard Model 7100B recorder equipped with a disk integrator.

The chromatograph was calibrated using pure components and the response was linear with a 0.5-ml sample loop at pressures up to 2.2 psia. The response factor for converting area fraction to mole fraction was 1.096 for hydrogen sulfide relative to 1.000 for ethane.

Experimental Results

Experimental measurements on the equilibrium phase compositions were made at 50.0, −0.1, −49.4, and −99.8 °F. At each temperature, the phase compositions were determined at 10–12 pressures ranging from the vapor pressure of hydrogen sulfide at the given temperature to the pressure of the azeotrope. The results of these measurements together with the calculated equilibrium ratios are given in Table I. The pressure–equilibrium phase composition relationships are shown in Figures 1 and 2. Representative examples of the equilibrium ratios are shown for temperatures of −49.4 and −99.8 °F in Figure 3.

Discussion

Considerable difficulty was encountered in obtaining reliable data on this binary system, particularly at the lowest temperature. It will be noticed from Figure 2 that the rate of change of pressure with composition along the bubble point locus is exceedingly small such that over a wide part of the composition range, a change in pressure of about 0.5 psi can cause a change in composition of up to 30 mole %. For this reason phase samples were not taken for analysis until the system pressure had remained constant for at least an hour.

The composition of the minimum boiling point azeotrope was obtained from large graphical representations of the pressure–composition data at each temperature. The values are given in Table II. These are compared to the values presented graphically by Kay and Brice (*3*), and it will be noted that the change in azeotrope composition with temperature obtained in this work is less than that shown in the extrapolated region by these authors. A carefully drawn cross plot of Kay and Brice's data to give a pressure–composition diagram at 80 °F showed an azeotrope composition of about 88 mole % ethane which is in good agreement with the trend obtained in this work at lower temperatures.

Table I. Equilibrium Phase Properties for the Ethane-Hydrogen Sulfide System

Pressure (psia) p	Ethane concen Liquid x	Ethane concen Vapor y	Equilibrium constant Ethane K_{C_2}	Equilibrium constant Hydrogen sulfide K_{H_2S}	Pressure (psia) p	Ethane concen Liquid x	Ethane concen Vapor y	Equilibrium constant Ethane K_{C_2}	Equilibrium constant Hydrogen sulfide K_{H_2S}
		50.0 °F					−0.1 °F		
228.5	0.0241	0.1174	4.871	0.904	93.2	0.0095[a]	0.0888	9.347	0.920
250.5	0.0498	0.2013	4.042	0.841	112.3	0.0375	0.2509	6.691	0.778
278.0	0.0849	0.2848	3.355	0.782	147.3	0.1169	0.4442	3.800	0.629
300.7	0.1314	0.3716	2.828	0.724	175.6	0.2330	0.5597	2.402	0.574
340.5	0.2264	0.4791	2.116	0.673	187.4	0.3316	0.6360	1.918	0.545
366.5	0.3126	0.5334	1.706	0.679	199.8	0.4524	0.6674	1.475	0.607
383.5	0.3938	0.5784	1.469	0.696	212.4	0.6385	0.7408	1.160	0.717
404.7	0.5143	0.6388	1.242	0.744	217.0	0.7080	0.7729	1.092	0.778
422.5	0.5847	0.6845	1.171	0.760	221.7	0.8683	0.8724	1.005	0.969
433.2	0.6731	0.7220	1.073	0.850	221.6	0.9392	0.9322	0.993	1.115
439.5	0.7639	0.7920	1.037	0.881	220.1	0.9736	0.9703	0.997	1.125
442.3	0.8451	0.8580	1.015	0.917					
442.7	0.9026	0.9031	1.001	0.995					
441.6	0.9510	0.9436	0.992	1.151					
		−49.4 °F					−99.8 °F		
37.2	0.0175[a]	0.2203	12.59	0.794	9.45	0.0085[a]	0.2602	30.61	0.746
52.0	0.0600	0.4592	7.65	0.575	14.3	0.0291	0.5272	18.12	0.487
63.7	0.1119	0.5830	5.21	0.470	19.7	0.0627	0.6614	10.55	0.361
75.7	0.2114	0.6619	3.13	0.429	24.3	0.1313	0.7441	5.67	0.295
85.2	0.4065	0.7203	1.77	0.471	27.3	0.2189	0.7774	3.55	0.285
91.2	0.6219	0.7691	1.24	0.611	29.5	0.4158	0.8024	1.93	0.338
94.7	0.8000	0.8338	1.04	0.831	31.0	0.7298	0.8463	1.16	0.569
95.4	0.8453	0.8625	1.02	0.889	31.6	0.8448	0.8848	1.05	0.742
95.7	0.9356	0.9277	0.992	1.123	31.6	0.9160	0.8988	0.981	1.205
95.1	0.9741	0.9670	0.993	1.274	31.5	0.9583	0.9453	0.986	1.312

[a] Smoothed value.

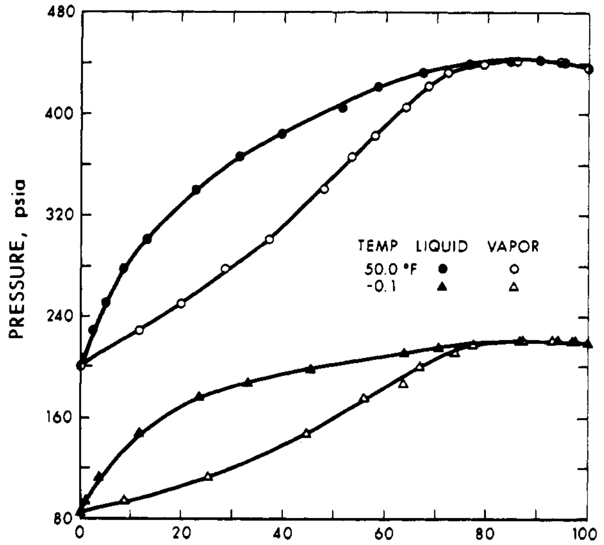

Figure 1. Pressure-equilibrium phase composition diagram for the ethane-hydrogen sulfide system at 50 and −0.1 °F.

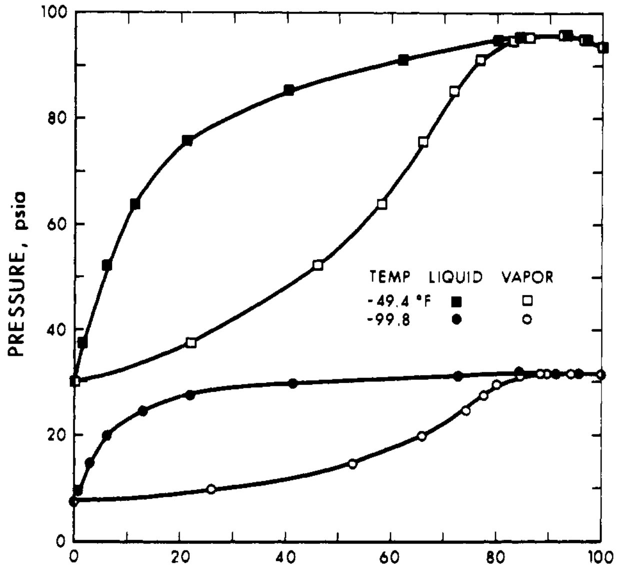

Figure 2. Pressure-equilibrium phase composition diagram for the ethane-hydrogen sulfide system at −49.4 and −99.8 °F.

Checks on the reliability of the experimental data were carried out in two ways. The first was to use the integral equal area test based on the Gibbs-Duhem equation and the second was to predict the data at each of the four temperatures using the Peng-Robinson equation of state (*4*).

The activity coefficients for the equal area test were calculated using the procedures and the pure component and mixture parameters given by Prausnitz and Chueh (*5*). The symmetric convention of normalization was used for the activity coefficients of each component.

The results of this thermodynamic consistency test are given in Table III and are seen to range from +0.1 to −5.8 %. In this test the percent inconsistency was defined by

Percent inconsistency =

$$\frac{-\int_0^1 \ln \frac{\gamma_2}{\gamma_1}\, dx_2}{\left|\int_0^1 \ln \gamma_1\, dx_1\right| + \left|\int_0^1 \ln \gamma_2\, dx_2\right|}(100)$$

which is the same as that used by Fredenslund and Mollerup (*1*) for their work on the ethane-carbon dioxide system. In this

Table II. Azeotrope Compositions in the Ethane–Hydrogen Sulfide Binary System

Temp (°F)	Azeotrope composition, mole fraction ethane This work	 Kay and Brice (*3*)
50	0.885	0.86
0	0.895	0.92
−50	0.897	—
−100	0.892	—

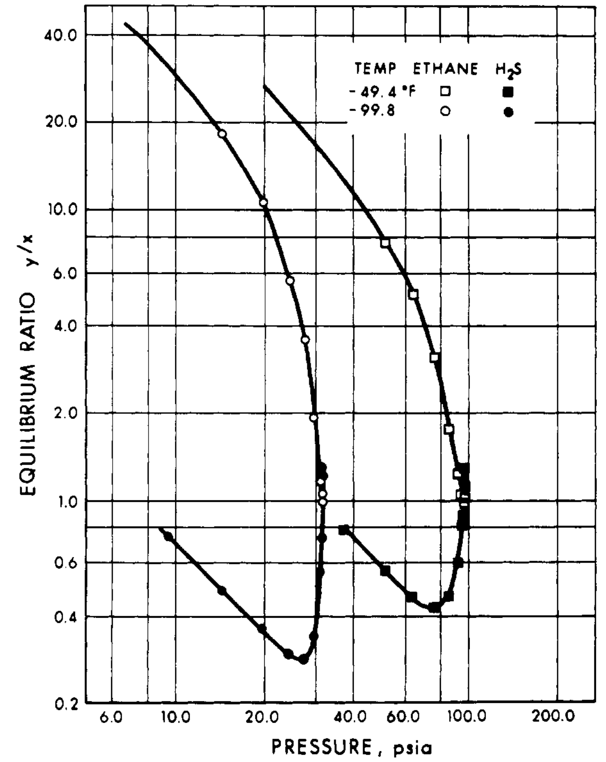

Figure 3. Equilibrium ratios for ethane and hydrogen sulfide in the ethane–hydrogen sulfide binary system at −49.4 and −99.8 °F.

equation, γ_1 and γ_2 are the liquid phase activity coefficients for each of the components relative to the pure liquid reference state fugacity, and x_1 and x_2 are the corresponding liquid phase mole fraction concentrations. An example representation of the activity coefficients calculated for the data at −99.8 °F is given in Figure 4.

The Peng–Robinson equation of state (*4*) has the form:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)}$$

where

$$a(T) = a(T_c) \cdot \alpha(T_R, \omega)$$

$$a(T_c) = 0.457\,24\,\frac{R^2 T_c^2}{P_c}$$

$$\alpha^{1/2}(T_R, \omega) = 1 + k(1 - T_R^{1/2})$$

$$k = 0.374\,64 + 1.542\,26\omega - 0.269\,92\omega^2$$

$$b = 0.077\,80\,\frac{RT_c}{P_c}$$

For mixtures, the constants are obtained from

$$b_m = \sum_i x_i b_i$$

$$a_m(T) = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2}$$

Table III. Results of Thermodynamic Consistency Test

Temp (°F)	% inconsistency
50.0	−3.0
−0.1	−5.8
−49.4	−5.3
−99.8	+0.1

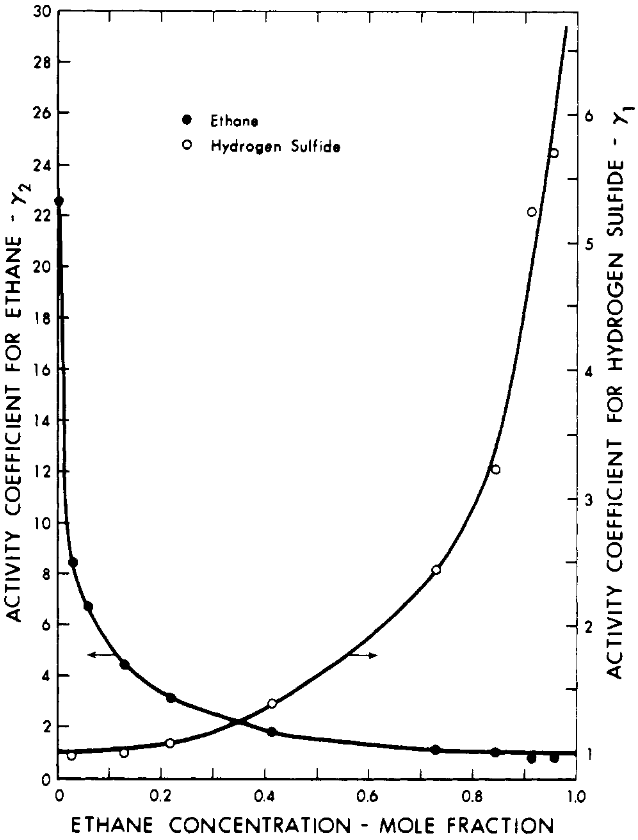

Figure 4. Liquid phase activity coefficients for ethane and hydrogen sulfide in the binary system at −99.8 °F.

In making the predictions of the equilibrium liquid phase and vapor phase compositions using this equation, the critical properties and acentric factors for the pure components were taken from Reid and Sherwood (*6*), and a value of 0.08 was used for the interaction parameter δ_{ij}. This value was obtained using only the high temperature data of Kay and Brice (*3*).

For the 45 experimentally measured liquid phase compositions, 44 of the predicted bubble point pressures differed from the experimental pressures by less than 3% and only 1 differed by more than 3%. In comparing the predicted and experimental vapor phase compositions from the same measured liquid compositions, it was found that 29 points differed by less than 3% and only 6 points differed by more than 5%. This confirms the ability of the Peng-Robinson equation to predict the behavior of difficult systems such as this with a minimum of experimental data.

Glossary

$a(T)$	temperature dependent parameter in equation of state
b	parameter in equation of state
$1,2,i,j,m$	subscripts denoting pure components or a mixture
K_{C_2}	equilibrium ratio for ethane
K_{H_2S}	equilibrium ratio for hydrogen sulfide
P, P_c	pressure or critical pressure
R	gas constant

T, T_c, T_R	temperature, critical temperature, or reduced temperature
v	volume
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase
$\alpha(T_R,\omega)$	parameter used in determining equation of state constant
γ	liquid phase activity coefficient
δ_{ij}	parameter denoting *i–j* interaction
κ	parameter used in determining equation of state constant
ω	acentric factor

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Received for review May 27, 1976. Accepted September 20, 1976. The financial support provided for this work by the Gas Processors Association and the Alberta Research Council is sincerely appreciated.

Isothermal Vapor–Liquid Equilibria for the System 1,2-Dichloropropane–Propanal

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Vapor–liquid equilibrium data are determined for the system 1,2-dichloropropane–propanal at six temperatures. The system exhibits slight deviations from ideal behavior. The variation of g^E with composition suggests that the system may form an associated solution. The results are correlated with the Redlich–Kister and Wilson equations.

Binary systems containing propanal have not been studied intensively, and the literature is very poor on the subject (*1, 6, 8*). The main reason is the difficulty in obtaining accurate data for these systems because of the extreme instability of the aldehydes.

From a theoretical point of view, however, the equilibrium behavior of mixtures of polar molecules, such as the 1,2-dichloropropane–propanal system, is of interest; association between the aldehyde and the dichloropropane is expected. Furthermore, this system is very often applied in chemical processes (propylene oxide manufacture for instance).

Experimental Section

Purity of Material. The 1,2-dichloropropane purchased from Merck was employed without further purification, after gas chromatographic analysis failed to show any significant impurities. The propanal was an aqueous azeotrope, containing 1.8 wt % of water and having a normal boiling point of 47.87 °C. These values are somewhat different from those of Matsunaga and Katayama (*6*) (1.9 wt % and a normal boiling point of 47.8 °C). Before its use the aldehyde was distilled and dried over molecular sieves 3 Å in size (from Union Carbide). The physical properties of 1,2-dichloropropane and water-free propanal used for the measurement are summarized in Table I.

Apparatus and Procedure. The static isothermal ebulliometer is completely built of stainless steel (reservoir, valves, pipes). The complete description may be found in ref 3. Only slight modifications were made: the samples of the liquid phase for the analysis are withdrawn by applying vacuum and are immediately frozen in a liquid air trap. During the boiling the liquid phase is homogenized by a magnetic stirrer. The accuracy of the pressure measurements is better than 0.1 mmHg. The whole ebulliometer including the mercury manometer is maintained at a constant temperature (±0.02 °C) by a constant temperature bath. The temperature is measured by a Sneider thermometer with an accuracy of 0.02 °C. The analysis of the liquid phase is made with an Abbe refractometer. The calibration refractive index data appear in Table II. These data could be represented by three straight lines, with slopes, dn/dx, 0.0940 in the range of $0 \leqslant x_1 \leqslant 0.3$, 0.0766 in the range of $0.3 \leqslant x_1 \leqslant 0.6$, and 0.0630 in the range of $0.6 \leqslant x_1 \leqslant 1.0$. The accuracy of the composition within these ranges is equal to 0.002, 0.0026, and 0.0032, respectively. Because of the high volatility of the propanal, each refractive index determination was repeated several times and no appreciable deviation was observed in the measurements. Each composition was also confirmed by chromatographic analysis with a Perkin-Elmer 990 gas chromatograph.

Results

The total pressure measurements and the analysis of the liquid phase were made at six temperatures. The experimental results appear in Table III.

The vapor mole fraction and the liquid phase activity coefficients were calculated according to Barker's method (*2*). The fugacity coefficients in the vapor phase were obtained by using Löffler's equations (*5*) with three parameters (T/T_c, P/p_c, ω). For the binary vapor phase the mixing rule of Kay (*4*) was applied. The vapor pressures of the pure components are given by:

$$\log p_1{}^0 = 6.8271 - \frac{1216.60}{t + 212.57} \qquad (1)$$

for 1,2-dichloropropane and

$$\log p_2{}^0 = 7.825\,98 - \frac{1595.57}{t + 274.63} \qquad (2)$$

for propanal.

The Redlich–Kister and the Wilson equations were employed for the correlation of the activity coefficients.

The two-parameter Redlich–Kister equations are:

$$\ln \gamma_1 = (A + 3B)x_2{}^2 - 4Bx_2{}^3 \qquad (3)$$

$$\ln \gamma_2 = (A - 3B)x_1{}^2 + 4Bx_1{}^3 \qquad (4)$$