Phase Equilibria of the Propane-Hydrogen Sulfide System from the Cricondontherm to the Solid-Liquid-Vapor Region

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The phase-equilibria data of the propane-hydrogen sulfide system has been previously investigated from 32°F. to the critical locus. Since this represents about one-half of the phase data, the primary purposes of the present study were to complete the data to the solid-liquid-vapor region which starts about —125°F. and to verify the results of other investigators at the higher temperatures.

Five mixtures of propane-hydrogen sulfide were studied, ranging from 8.6 to 78.3% propane, with the dew- and bubble-point method. A temperature-composition diagram for six isobars from 400 to 20 lb./sq. in. abs. presents most of the essential data. Vaporization equilibrium constants are tabulated together with the x-y data for these isobars. The data of Kay and Rambosek (3) and Steckel (4) were verified to within 2% except near the vicinity of the azeotrope.

A new method was used to fix the temperature of the azeotrope for two of the five mixtures and a sixth mixture. The determination of the azeotropic temperatures was made by a graphical method in which the differences between the dew- and the bubble-point pressures for each mixture were plotted against the temperature. The minimum value of the curve corresponds to the temperature of the azeotrope. The application of this method to the data of Kay and Rambosek (3) gave results which were in agreement with this study, while the original results by these authors as determined by an indirect method were in poor agreement.

A measure of the reliability of the composition, temperature, and pressure data of the solid-liquid-vapor region was indicated when checks within 5% were found with Dalton's law of partial pressures.

Hydrogen sulfide is frequently found in petroleum hydrocarbon mixtures, such as natural gas or light refinery gases. Because it is corrosive, highly toxic, and has an objectionable odor it must be removed before the gas can be used. Hydrogen sulfide is usually removed by scrubbing with organic amines. If phase data of such systems are available at low temperatures, physical means of separation can be evaluated.

The separation of the light hydrocarbons by low-temperature distillation is now widely practiced. For example ethane and ethylene are being separated from other light gases by low-temperature processes. This type of separation is less expensive than other separation processes under certain conditions. Before the feasibility of low-temperature separation processes can be evaluated the low-temperature phase and volumetric relations of these mixtures must be established.

Studies of the propane-hydrogen sulfide system have been made by Kay and Rambosek (3), Steckel (4), and Gilliland and Scheeline (5). However little of these data extend below 32°F. This study was initiated to investigate the phase equilibria of the propane-hydrogen sulfide system from the cricondontherm down to the solid-liquid-vapor region and to verify the work of other investigators at the higher temperatures. The data presented here will permit the evaluation and design of the separation of hydrogen sulfide from propane by low-temperature distillation.

EXPERIMENTAL APPARATUS AND PROCEDURE

The complete description of the experimental apparatus and procedure is given by Kohn and Kurata (*1*, *2*) and Davis (*6*).

Briefly the experimental method used was the dew-and bubble-point method. The experimental runs were made on a gas sample contained in a cell of constant volume immersed in a constant-temperature bath. The cell was made of heavy walled glass tubing, and its contents were stirred with a steel ball which was raised and lowered by means of a manually operated magnet. Gas was admitted to the cell in measured increments from a high-pressure source, so that as the pressure was raised the system passed successively and isothermally through the states of superheated vapor, saturated vapor, mixed vapor and liquid, and finally saturated liquid.

The technique for determining the phase behavior of the solid-liquid-vapor region as well as the solid-liquid region has been described by Donnelly and Katz (*7*).

MATERIALS

The first step in the preparation of gas mixtures of hydrogen sulfide and propane was the purification of the individual constituents. A pure grade of hydrogen sulfide was obtained. The dew- and bubble-point difference of this material at a temperature near 32°F. was in excess of 80 lb./sq. in. indicating unsatisfactory purity.

The crude hydrogen sulfide was purified by a series of batch distillation (about ten) near the dry-ice temperature by discarding about 5% of the bottoms in each case. The light constituents in the hydrogen sulfide gas were next removed. This was done at the dry-ice temperature by purging the light constituents from its stainless steel container by means of the hydrogen sulfide gas itself. As much as ten times the volume of the vapor space was purged in this manner, and calculations showed that the concentration of any light components would thus be reduced to a negligible value.

After these treatments the dew and the bubble points of the purified hydrogen sulfide showed only a difference of 2 lb./sq. in. near 32°F. Furthermore in a quality range of 10% to 100% liquid the pressure differential was 1 lb./sq. in.

The molecular weight of the purified hydrogen sulfide determined by gas-density measurements was found to be 34.02, just 0.2% below the accepted value of 34.08. The vapor pressure of the purified hydrogen sulfide agreed to within 2 lb./sq. in. with Sage and Lacey (*8*) at the 50% condensed value. From a knowledge of the possible impurities, methyl mercaptan, carbon disulfide, and methylene chloride, it is believed that the purity of the distilled hydrogen sulfide was 99.9% or better.

A research-grade purity of propane was obtained. The difference between the dew and the bubble points near 32°F. was found to be 6 lb./sq. in. After purging the expected impurity, ethane, from the vapor space by means of the propane itself, one could reduce the pressure differential between the dew and the bubble points to only 1 lb./sq. in.

For the purified propane the experimental molecular weight was calculated to be 44.09, checking identically with the accepted value. Its vapor pressure at the 50% condensed value agreed within 1 lb./sq. in. of that given by Sage and Lacey (*9*). Therefore it is believed that the purity of the propane after purging was about 99.9%.

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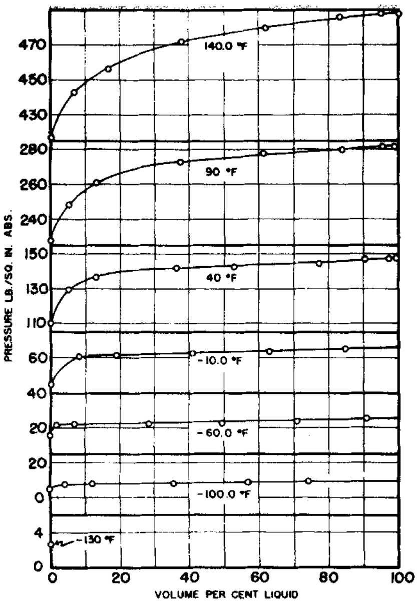

Fig. 1. Phase behavior of mixture 4.

PREPARATION OF GAS MIXTURES

In preparation of the first gas mixture of hydrogen sulfide and propane the first step was to evacuate one of the stainless steel cylinders contained in the reservoir housing. A weighed amount of purified hydrogen sulfide was then allowed to condense in this cylinder after it had been packed with dry ice. From the knowledge of the amount of hydrogen sulfide condensed a weighed amount of purified propane was permitted to condense into the hydrogen sulfide cylinder, approximating the composition of the desired mixture. Subsequent mixtures, successively richer in propane, were prepared by weighing in additional quantities of propane into the gas reservoir. The precise determination of the composition of the gas mixture was made by gas-density measurements.

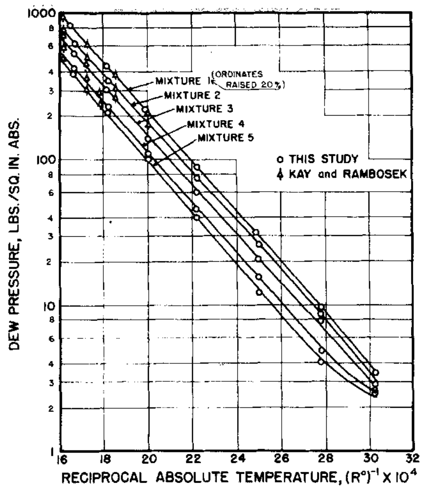

Fig. 3. Semilog pressure-temperature plots of experimental mixtures.

GAS ANALYSIS

Compositions of the mixtures were determined by the gas-density method. By the use of accurate compressibility factors for the two gases at room temperature and pressure (8, 9) it is possible to accurately determine the molecular weight of the mixture from the density measurement. The composition of the mixture is then computed from the molecular weight.

ERRORS

The average deviation of the apparent molecular weights from which compositions were calculated was 0.09%. The accuracy to be expected in the composition from a relative error in the molecular weight of 0.1% is 0.3 to 0.4%, depending upon the composition. The magnification of error is due to the small difference in the molecular weights of hydrogen sulfide and propane. The error in compositions can be shown to be inversely proportional to the difference of the molecular weights of the individual components.

TABLE 1. EQUILIBRIUM VAPORIZATION CONSTANTS OF THE PROPANE—HYDROGEN SULFIDE SYSTEM

			Equilibrium constants	
Temp., °F.	Mole fraction propane (vapor)	Mole fraction propane (liquid)	Propane	Hydrogen sulfide
Pressure = 400 lb./sq. in. abs.				
160	0.960	0.979	0.981	1.90
150	0.847	0.917	0.924	1.84
140	0.734	0.847	0.866	1.74
130	0.621	0.766	0.811	1.62
120	0.502	0.666	0.754	1.49
110	0.374	0.515	0.726	1.29
100	0.184	0.230	0.800	1.06
99	0.081	0.081	1.00	1.00
Pressure = 300 lb./sq. in. abs.				
130	0.919	0.964	0.954	2.25
120	0.794	0.903	0.878	2.12
110	0.666	0.829	0.805	1.95
100	0.525	0.735	0.715	1.79
90	0.383	0.602	0.636	1.55
80	0.236	0.376	0.627	1.22
76	0.91	0.901	1.00	1.00
Pressure = 200 lb./sq. in. abs.				
95	0.870	0.946	0.919	2.41
90	0.800	0.917	0.872	2.41
80	0.656	0.852	0.770	2.32
70	0.513	0.771	0.665	2.13
60	0.370	0.633	0.585	1.72
50	0.226	0.402	0.562	1.29
50	0.060 V′	0.027 L′	2.22	0.966
45	0.153	0.220	0.695	1.09
44	0.142	0.142	1.00	1.00
Pressure = 100 lb./sq. in. abs.				
50	0.919	0.973	0.945	3.00
40	0.774	0.920	0.841	2.83
30	0.626	0.857	0.730	2.62
20	0.479	0.770	0.622	2.27
10	0.33	0.580	0.569	1.60
6	0.26	0.405	0.642	1.24
6	0.10 V′	0.070 L′	1.43	0.968
5	0.190	0.190	1.00	1.00
Pressure = 50 lb./sq. in. abs.				
10	0.926	0.985	0.940	4.93
0	0.766	0.944	0.811	4.18
—10	0.602	0.887	0.679	3.52
—20	0.444	0.783	0.567	2.56
—28	0.037 V′	0.024 L′	1.54	0.987
—28	0.316	0.560	0.564	1.55
—30	0.275	0.410	0.671	1.23
—30	0.105 V′	0.065 L′	1.62	0.957
—30.8	0.240	0.240	1.00	1.00
Pressure = 20 lb./sq. in. abs.				
—40	0.820	0.960	0.854	4.50
—50	0.640	0.900	0.711	3.60
—60	0.455	0.830	0.548	3.21
—66	0.365	0.745	0.490	2.49
—66	0.026 V′	0.015 L′	1.73	0.989
—68	0.330	0.680	0.485	2.09
—68	0.080 V′	0.054 L′	1.48	0.973
—69.2	0.300	0.300	1.00	1.00

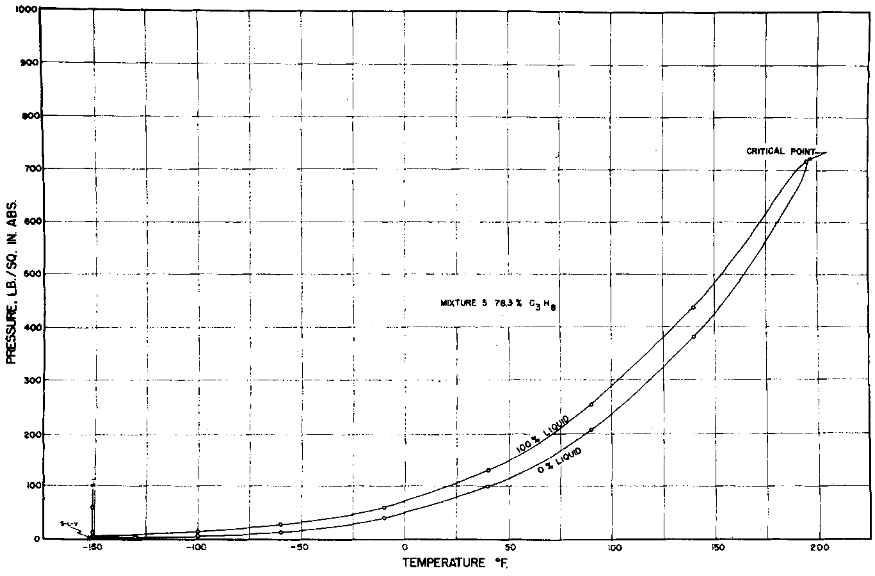

Fig. 2. P-T diagram for mixture 5.

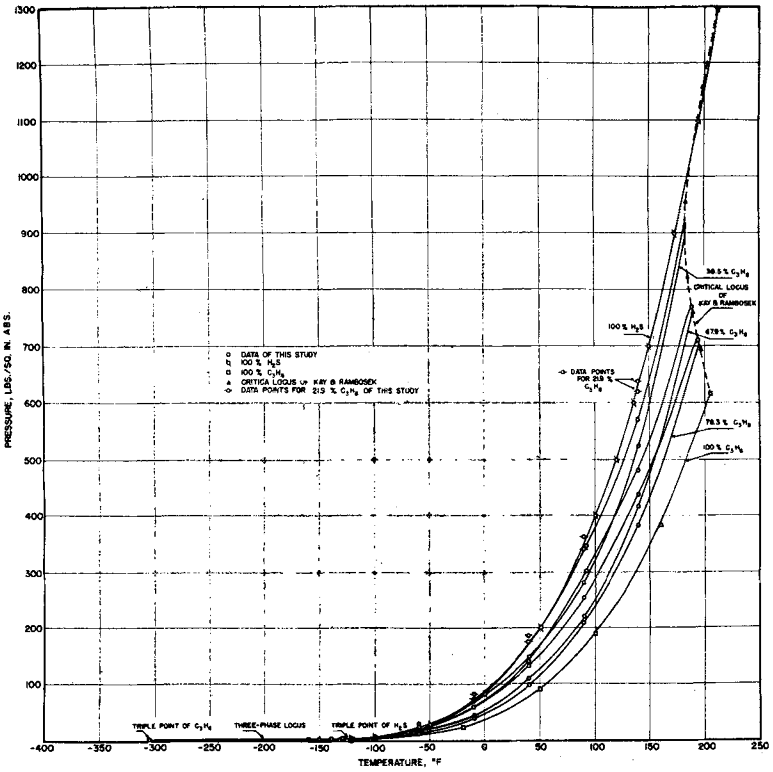

Fig. 4. Phase border curves of propane-hydrogen sulfide system.

TABLE 2. COMPARISON OF AZEOTROPE LOCI IN THE PROPANE—HYDROGEN SULFIDE SYSTEM

	Mole fraction propane		
Temp., °F.	This study	Kay and Rambosek	Steckel
120		0.14	
100	0.08	0.155	
80	0.102	0.17	
60	0.123	0.188	0.095
40	0.146	0.208	0.118
20	0.17		0.146
0	0.20		0.175
—20	0.229		0.207
—40	0.26		
—60	0.29		
—80	0.32		
—96	0.34		

TABLE 3. THREE-PHASE VAPOR AND LIQUID COMPOSITIONS

Mixture	Mixture comp. % propane	Mole per cent propane Vapor comp.	Liquid comp.	Temp., °F.
1	8.6	16.2	9.5	—134.2
2	21.9	24.8	24.7	—138.3
3	38.5	28.9	29.8	—140.2
4	67.9	34.5	36.7	—147.8
5	78.3	33.5	34.3	—156.1

All temperature measurements of the low-temperature bath were made with a platinum resistance thermometer and are believed to be accurate within 0.1°F. Temperature changes of 0.05°F. could easily be detected.

Pressures as read from a bourdon pressure gauge were probably accurate to 1 to 2 lb./sq. in. Subatmospheric pressures were measured with a mercury manometer and were probably accurate to 2 mm. of mercury.

RESULTS

Some of the original experimental data are presented in phase-behavior curves of the vapor-liquid region in which the pressure is plotted against the volume per cent liquid for various isotherms. The isotherms were taken close to the following temperatures: 140°, 90°, 40°, —10°, —60°, and —100°F. The dew-point pressure at —130°F. was also indicated. A series of five mixtures containing 8.6, 21.9, 38.5, 67.9, and 78.3% propane were studied. Typical curves for a mixture containing 67.9% propane are shown in Figure 1.

A typical pressure-temperature diagram is shown in Figure 2. This diagram is for mixture 5 containing 78.3% propane. The critical point for this mixture was 718 lb./sq. in. abs. and 195°F. Of the mixtures studied this mixture showed the greatest difference between the dew and bubble pressures. The solid-liquid-vapor and solid-liquid border curves are indicated on the diagram. Solid hydrogen sulfide forms at a temperature of —150.9°F., under a pressure of 1.1 lb./sq. in. abs.

A comparison of the dew-point data of this study with those of Kay and Rambosek (3) is shown in the semilogarithmic pressure-temperature plot of Figure 3. Except for the slight discrepancy in the case of mixture 4 the agreement in general is excellent. Furthermore consistency is indicated by the fact that a straight line can be drawn through most of the data points for each mixture down to a temperature near —100°F. At temperatures near —130°F. there were deviations from the straight lines. The ordinates of mixture 1 in this figure were raised 20% for clarity.

The phase border curves are presented in Figure 4. This is a composite diagram of the individual mixtures together with those of the pure constituents. The dew and bubble lines for mixtures 1 and 2 are not shown in this figure because they lie too close to the vapor-pressure curve of hydrogen sulfide; however their data points are shown. Good agreement is shown with the critical region of Kay and Rambosek (3). The three-phase region of the mixtures is terminated by the triple points of propane and hydrogen sulfide. Characteristic of a binary having an azeotrope (3) the mixtures illustrate the folding of the *P-T-X* space. For example some dew and bubble points lie above the vapor-pressure curve of pure hydrogen sulfide.

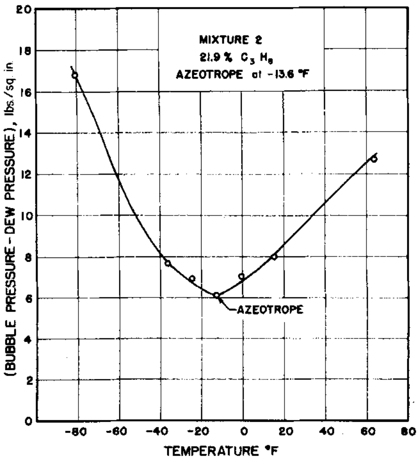

Fig. 5. Temperature determination of azeotrope of mixture 2.

With the pressure-temperature diagrams of the various mixtures now established, the temperature-composition diagrams can be determined by crossplotting the data at constant pressure. Preliminary crossplots of this kind indicated some uncertainty in the vicinity of the azeotropes due primarily to the small amounts of impurities in the propane and hydrogen sulfide. As noted by Kay and Rambosek (3) an adjustment of the curves near the azeotropes was therefore necessary to bring the dew and bubble points together.

Kay and Rambosek determined the azeotropes by plotting the composition

Table 4. Test of Three-Phase Data with Dalton's Law

Mixture	(1) Total press., mm. Hg	Temp., °F.	(3) Vapor press., solid H_2S mm. Hg	(4) Mole frac., propane in vapor	(5) (4) × (1) Partial press., of C_3H_8 mm. Hg	(6) (3) + (5) Sum of partial pressures mm. Hg
1	124.1	−134.2	105	0.162	20.1	125.1
2	108.5	−138.3	85	0.248	26.9	111.9
3	103.2	−140.2	77	0.289	29.8	106.8
4	79.9	−147.8	54.6	0.345	27.6	82.2
5	44.2	−156.1	35.3	0.335	14.8	50.1

of the vapor against the composition of the liquid. The intersections of a family of such curves at various pressures with the 45-deg. line gave the compositions of the azeotropes. The errors of such a procedure are considerable unless there is sufficient experimental data from a number of mixtures near the azeotrope to accurately establish the S-shaped curves.

In this study the azeotropes were determined by first preparing large semilogarithmic pressure-temperature plots of both the dew and bubble points. Over relatively large ranges straight lines could be drawn through the data, permitting accurate interpolations. From the original and interpolated values of the dew and bubble points plots were made of the difference between the dew- and bubble-point pressures as a function of temperature. In most cases fairly sharp minimum values were found indicating the composition and temperature of the azeotropes. In this way azeotropic compositions of 8.6, 21.9, and 14.5% propane were found to exist at 100°, −13.6°, and 35°F., respectively. An example of such a determination for mixture 2 is illustrated in Figure 5.

When the data of mixture 1 (10.16% propane) of Kay and Rambosek were analyzed with the method described above, the temperature and pressure of the azeotrope were found to be 100°F. and 402 lb./sq. in. abs. as compared with their values of 161°F. and 800 lb./sq. in. abs. It was not possible to subject their other mixtures to this test because of the lack of data below 32°F.

From the large semilogarithmic pressure-temperature diagrams of the various mixtures crossplots were constructed at pressures of 400, 300, 200, 100, 50, and 20 lb./sq. in. abs. These isobars are plotted in the temperature-composition diagram of Figure 6. On the same graph are shown the experimental and interpolated data of Kay and Rambosek (*3*) and Steckel (*4*), illustrating good agreement over most of the data; the only major disagreement is in the region of azeotropes. The region of the azeotropes found in this study is compared with those of Kay and Rambosek (*3*) and Steckel (*4*). It is seen that the azeotrope locus as determined by this study lies between those of the other investigators. A comparison of the azeotropic compositions as determined by this study, Kay and Rambosek, and Steckel are given in Table 2. It is shown that the azeotrope data of this study agree more nearly with Steckel, but the deviation ranges from 10 to 30%.

The vaporization equilibrium constants were determined from an enlarged plot of Figure 6. These are presented in Table 1 for pressures of 400, 300, 200, 100, 50, and 20 lb./sq. in. abs. Those data which were indicated by V′ and L′ in Table 1 are those taken from the vapor and liquid curves to the left of the azeotrope in Figure 6; other data are taken from the vapor and liquid curves to the right of the azeotrope. It is estimated that the data in the vapor-liquid region agreed with those of the other investigators within 2% over most of the range.

The vapor and liquid compositions along the solid-liquid-vapor region were analyzed from their gas densities after these phases were sampled by means of the special apparatus described by Kohn and Kurata (*1*, *2*). These, along with the mixture compositions, are given in Table 3.

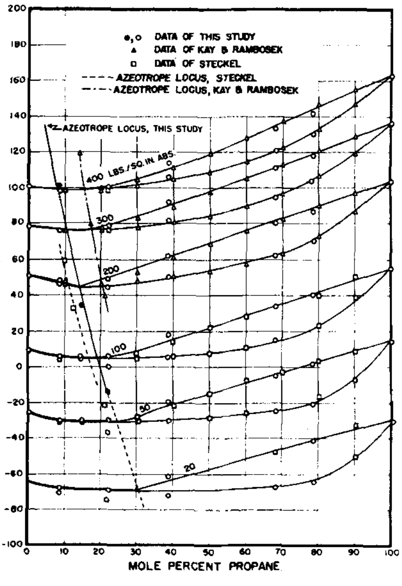

Fig. 6. Temperature-composition diagram of propane-hydrogen sulfide system.

A simple check can be made on the reliability of some of the experimental work in the three-phase region through use of Dalton's law of partial pressures. The total pressure in the equilibrium cell should be nearly equal to the sum of the partial pressures of propane and hydrogen sulfide. The partial pressure of hydrogen sulfide may be taken equal to the vapor pressure of solid hydrogen sulfide as the prevailing temperature as determined by Giauque (*10*). The partial pressure of propane is equal to the product of the total pressure multiplied by the mole fraction of propane in the vapor. The mole fraction of propane in the vapor is obtained from Table 3 which gives the vapor compositions along the solid-liquid-vapor region. The summary of this check is presented in Table 4.

A comparison of columns (1) and (6) in Table 4 shows good agreement with Dalton's law of partial pressures. The pressures agree to within 6 mm. of mercury, or within an average relative error of 5%. Since the pressures are low in the three-phase region, a reasonably good check with Dalton's law can be expected.

The complete data of this study has been presented by Brewer (*11*).

ACKNOWLEDGMENT

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LITERATURE CITED

1. Kohn, J. P., and Fred Kurata, *A.I.Ch.E. Journal*, **4**, 211 (1958).
2. ———, *Petrol. Proc.*, **11**, No. 12, 57 (1956).
3. Kay, W. B., and G. M. Rambosek, *Ind. Eng. Chem.*, **45**, 221 (1953).
4. Steckel, F., *Svensk. Kem. Tid.*, **57**, 209 (1945).
5. Gilliland, E. R., and H. W. Scheeline, *Ind. Eng. Chem.*, **32**, 48 (1940).
6. Davis, P. C., Ph.D. thesis, Univ. Kan., Lawrence (1951).
7. Donnelly, H. G., and D. L. Katz, *Ind. Eng. Chem.*, **46**, 511 (1954).
8. Sage, B. H., and W. N. Lacey, "Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide, and Carbon Dioxide," p. 36. Am. Petrol. Inst. (1955).
9. ———, "Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen," p. 36, Am. Petrol. Inst. (1950).
10. Giauque, W. F., *Am. Chem. Soc.*, **58**, 836 (1936).
11. Brewer, Jerome, Ph.D. thesis, Univ. Kan., Lawrence (1959).

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