

## NOMENCLATURE

$A, B, C, D$  = constants  
 $d$  = density, grams per ml.  
 $p$  = vapor pressure, mm. or pounds per square inch absolute  
 $p^0$  = vapor pressure of pure components at boiling point of solution  
 $P$  = total still pressure  
 $P_a$  = isothermal vapor pressure of azeotrope  
 $P_r$  = isothermal vapor pressure of reference substance  
 $R$  = ideal gas constant  
 $T$  = absolute temperature  
 $x$  = mole fraction in liquid phase  
 $y$  = mole fraction in vapor phase  
 $z_i$  = multiplication factor  
 $\phi_i$  = molar volume of pure liquid at solution boiling point  
 $\beta_i$  = second virial coefficient of vapor  
 $\gamma^D$  = activity coefficient  
 $\gamma_i$  = activity coefficient, corrected

## Subscripts

1 refers to more volatile component, 2-propanol  
 2 refers to less volatile component, water

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Detailed operating instructions for the high pressure still are available upon request from Edward L. Simons.

# Phase Behavior in the Hydrogen Sulfide-Water System

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**B**OTH hydrogen sulfide and water are encountered in many petroleum reservoirs. A knowledge of the phase behavior of mixtures of these two components forms a part of the background of information requisite for an understanding of effective means of producing petroleum. The early investigations of the hydrogen sulfide-water system were directed primarily to a study of hydrates and to the development of generalizations of phase behavior for binary systems. De Forcrand and coworkers (2, 3, 5) studied the hydrogen sulfide-water system in some detail, placing primary emphasis on the properties of the hydrates. Villard reviewed the history and made studies of this and other systems forming hydrates (22). Scheffer studied this system in some detail, determined the three-phase pressures with accuracy (15), and followed this experimental investigation with an overall review (17) at states involving solid phases. At a much later date Scheffer and Korvezee established with some certainty the composition of the hydrate (9) and confirmed the earlier finding of de Forcrand (4) that the hydrate contains 6 molecules of water per molecule of hydrogen sulfide. The higher values obtained earlier (2, 6) appear to have resulted from the occlusion of water in the hydrate.

Only limited data concerning the solubility of hydrogen sulfide in water have been obtained (7). The quadruple point was well established (15-17) by Scheffer. Schreinemakers (20) discussed the significance of the quadruple point and the triple point curves in this system, and Wright and Maass (24) determined the pressures and temperatures for equilibrium of the hydrate, the aqueous liquid, and the gas phase at temperatures near the freezing point of water.

The volumetric and phase behavior of water has been investigated in detail and was summarized by Keenan and Keyes (8). These data have been employed in the present study and no reference to the basic investigations is made. Hydrogen sulfide has been studied less extensively. Murphy (11) determined the volumetric behavior and measured the vapor pressure of this compound, and West (23) summarized its thermodynamic properties. Additional data concerning the volumetric behavior and vapor pressure recently became available (12).

The present study relates to measurements of the three-phase pressures and temperatures which are associated with the quadruple point found by Scheffer (15) at a temperature of 85.1° F. and a pressure of 325 pounds per square inch. The composition of the coexisting phases in a two-phase equilibrium involving an aqueous liquid and a gas phase for temperatures between 100° and 340° F. was determined. The measurements were made at pressures as high as 5200 pounds per square inch. The composition of the hydrogen sulfide-rich liquid was also measured at temperatures below the critical temperature of that compound.

## METHODS AND APPARATUS

The equipment employed was similar to that utilized in an earlier study (19) of nitrogen dioxide, with the exception that a somewhat smaller spherical pressure vessel, for brevity called a bomb, was used in the present investigation. The details of the construction of the bomb are shown in Figure 1. An unsupported-area seal was provided to close the threaded joint. The design of the seal is depicted in an enlarged insert in this figure. Lead sealing rings were employed in the present investigation, al-

though it has been found that carefully annealed gold rings may be used effectively for measurements at temperatures higher than the melting point of lead. No difficulty was experienced with the lead seals from corrosion or mechanical failure at temperatures up to 340° F. The bomb was constructed of Type 310 steel which contained 25 weight % chromium and 20 weight % nickel. This metal stock was found to be relatively resistant to corrosion by mixtures of water and hydrogen sulfide. The interior surface of the bomb was plated with chromium to a thickness of 0.003 inch.

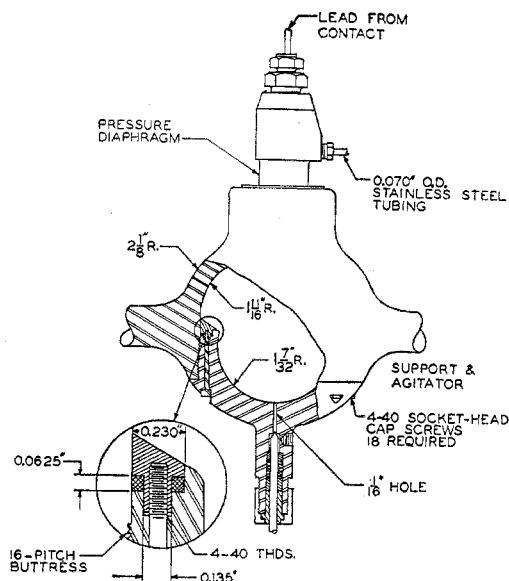


Figure 1. Details of Construction of Spherical Pressure Vessel

The pressure within the bomb was determined with the aid of an aneroid-type diaphragm shown in Figure 2. It was found that the plane diaphragm used earlier (19) gave measurable variations of calibration with time. The aneroid type of diaphragm used in the present studies was prepared from Type 302 steel which was rolled in a direction parallel to the plane of the diaphragm. It was machined to a thickness of 0.010 inch as a part of the cup, *A*, shown in Figure 2. The convolutions were prepared by grinding the plane diaphragm to the form illustrated in this figure. The dimensions are not critical, but those shown yielded a diaphragm with the sensitivity of approximately 0.2 pound per square inch per 0.001 inch movement of the center. As indicated in this figure, the diaphragm was supported on both sides and successfully withstood pressure differentials as great as 2000 pounds per square inch. A lead ring was employed at *B* of Figure 2 to seal the bomb and to retain the liquid used to back the diaphragm. No other changes were made in the constant volume equipment used earlier (19).

The pressure within the system was determined by means of a pressure balance (14) which was calibrated against the vapor pressure of carbon dioxide at the ice point (1). The balance has changed in calibration by less than 0.04% during the past decade, and even with the added uncertainties of calibration introduced by the presence of the diaphragm it is believed that the pressures were known within 0.1% or 1 pound per square inch, whichever was larger. The diaphragm was calibrated as a function of temperature at low pressures by the use of a mercury-in-glass manometer to determine the difference in pressure required to move the diaphragm enough to actuate a signal light. Its behavior at high pressures was ascertained by the use of a mercury-in-steel U-tube (14) to determine, with the aid of a balance, the actual pressure within the bomb. These data indicate a systematic

change in the additive correction for the diaphragm of approximately 1.10 pounds per square inch as a result of a change in temperature from 100° to 340° F. No measurable influence of the effect of pressure upon the calibration of the diaphragm was noted.

The isochoric vessel was not well suited to measurements of bubble point pressures of this system. For this purpose the apparatus shown schematically in Figure 3 was employed.

A displacement plunger, *A*, of conventional design (14) was used to introduce or withdraw working fluid from the vessel, *B*. This vessel was immersed in an oil bath, *C*, which was maintained at a constant temperature by means of a mercury-and-glass regulator used in conjunction with an electronic thyrotron control circuit. The sample of hydrogen sulfide and water was confined within a glass piston-cylinder combination, *D*. The piston and cylinder were constructed from a hypodermic syringe of relatively thin-walled glass and were carefully ground and lapped to give a substantially fluid-tight joint, *E*. The glass piston-cylinder combination was attached to the closure of the pressure vessel by means of a tapered spring-loaded joint, *F*. A valve, *G*, constructed of Carpenter 20 steel was used in introducing and withdrawing the samples from the piston-cylinder combination. It was found that, if the working liquid in *H* was relatively immiscible with the system under investigation, the transfer of material from the interior of the cylinder was less than 0.1% of the sample in a period of approximately one week. A polymerized tetrafluoromethane with a viscosity of approximately 150 centipoises at 100° F. was employed as the confining liquid. This compound was found to be completely inert and relatively immiscible with either the hydrogen sulfide or water. Agitation of the sample was obtained by oscillation of the vessel, *B*.

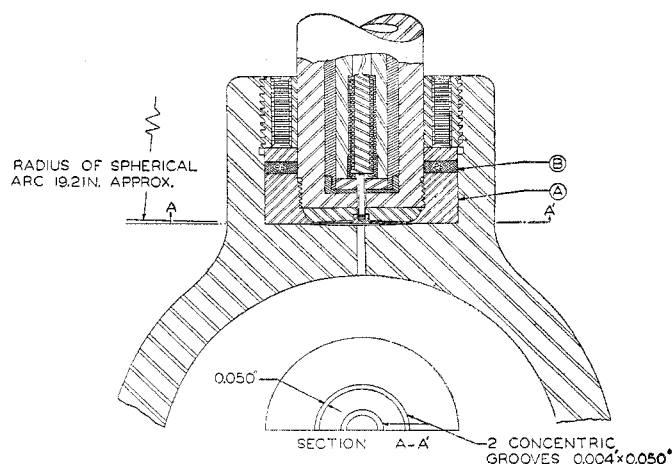


Figure 2. Assembly of Diaphragm Used for Pressure Measurements

The temperature of the working section for both the steel spherical bomb and the glass piston-cylinder combination was determined by means of platinum-in-glass, strain-free resistance thermometers. These working instruments were compared with a similar device which has been calibrated by the National Bureau of Standards. Mueller-type bridges were employed for the measurement of the resistance of the thermometer. The temperature of the spherical bomb was known within 0.03° F. of the international platinum scale while the temperature of the glass piston-cylinder combination was determined within 0.1° F. of that scale.

In the case of the volumetric measurements the quantity of water and hydrogen sulfide introduced into the spherical bomb vessel was established gravimetrically by the use of weighing bombs (13). The quantities of water and hydrogen sulfide were determined with an uncertainty of not more than 0.15%. However, the uncertainties as to the total volume of the spherical vessel as a function of pressure and temperature increased the probable error in the determination of the specific volume to 0.25%.



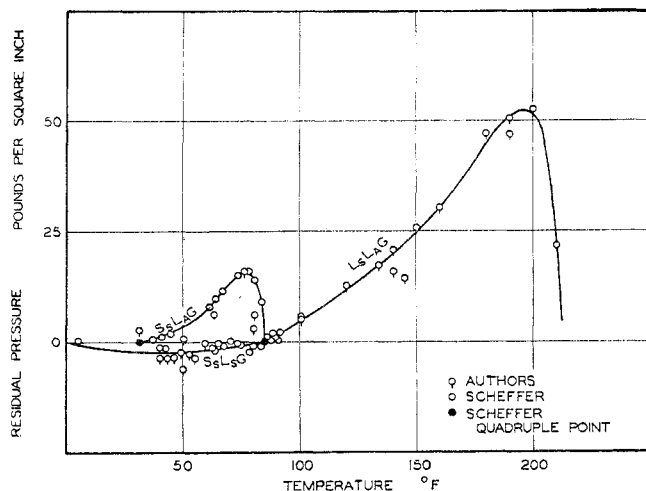


Figure 6. Residual Pressure-Temperature Diagram for Three Three-Phase Equilibria in Hydrogen Sulfide-Water System

#### MATERIALS

The distilled water employed in this investigation was obtained from the laboratory supply and was deaerated by refluxing for an extended period at low pressure. The hydrogen sulfide was prepared by the hydrolysis of aluminum sulfide. The evolved gas was dried over anhydrous calcium sulfate and fractionated in a glass column packed with single turns of glass helices at a reflux ratio of approximately 40 to 1. The initial and final 10% portions of the overhead from each fractionation were discarded and the center portion of the second fractionation was collected at liquid air temperature and at a pressure below 0.001 pound per square inch. The hydrogen sulfide was stored in stainless steel weighing bombs (13). The compound prepared by these methods showed less than 0.2 pound per square inch decrease in vapor pressure upon change in the fraction in the gas phase from 0.2 to 0.9.

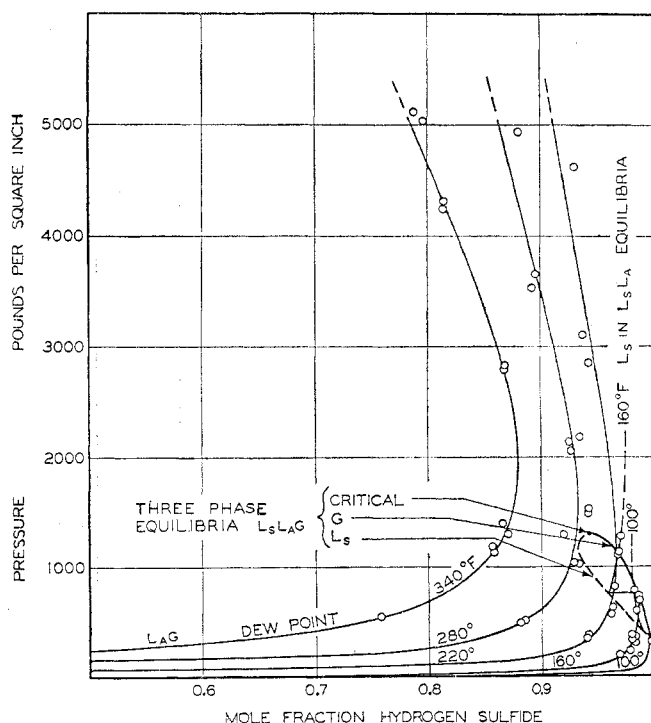


Figure 7. Mole Fraction Hydrogen Sulfide in Gas and Hydrogen Sulfide-Rich Liquid Phases for Heterogeneous Mixtures of Hydrogen Sulfide and Water

#### EXPERIMENTAL RESULTS

The measurements which were made upon the hydrogen sulfide-water system may be divided into three classes. The first relates to the determination of the equilibrium pressure as a function of temperature for homogeneous or heterogeneous mixtures under substantially isochoric conditions. Such information establishes the locus of three-phase states as well as volumetric data for the one-, two-, and three-phase regions. The second class involves measurements of the pressure as a function of specific volume for several predetermined temperatures. The latter studies have been limited to gas-aqueous liquid equilibria for compositions rich in water. The primary objective of the second type of investigation was the determination of bubble point pressure as a function of temperature and composition. The third class relates to the direct measurement of the composition of individual phases when forming a part of a heterogeneous equilibrium. The experimental results will be discussed in terms of these three classes of measurements.

A total of 11 different mixtures of water and hydrogen sulfide were investigated in the stainless steel bomb. A portion of the results of these measurements is shown in Figure 5. The detailed experimental data upon which this figure was based are available (21). Good agreement with the data of Scheffer (15, 17) was found for the three-phase equilibria. Throughout this discussion the following symbols for the several phases which have been identified are employed: solid hydrate,  $S_s$ , hydrogen sulfide-rich liquid,  $L_s$ , aqueous liquid,  $L_a$ , and gas,  $G$ . Discontinuities at the smaller specific volumes were found in the isochoric pressure-temperature coefficients at the three-phase equilibria. The data of Wright and Maass (24) were included in Figure 5 and indicate slightly lower three-phase pressures than were obtained from the present measurements. However, the three-phase equilibrium,  $S_sL_aG$ , is in accord with the earlier studies of Scheffer (15). In order to illustrate the agreement of the several sets of data along the  $S_sL_sG$ ,  $L_sL_aG$ , and the  $S_sL_aG$  three-phase equilibrium loci, the data from several investigators have been presented on a residual basis in Figure 6. In this diagram the reference pressures were defined by the following three expressions which apply to the  $L_sL_aG$ ,  $S_sL_aG$ , and the  $S_sL_sG$  equilibria, respectively:

$$\log P_R = 5.70443 - \frac{1739.45}{T} \quad (1)$$

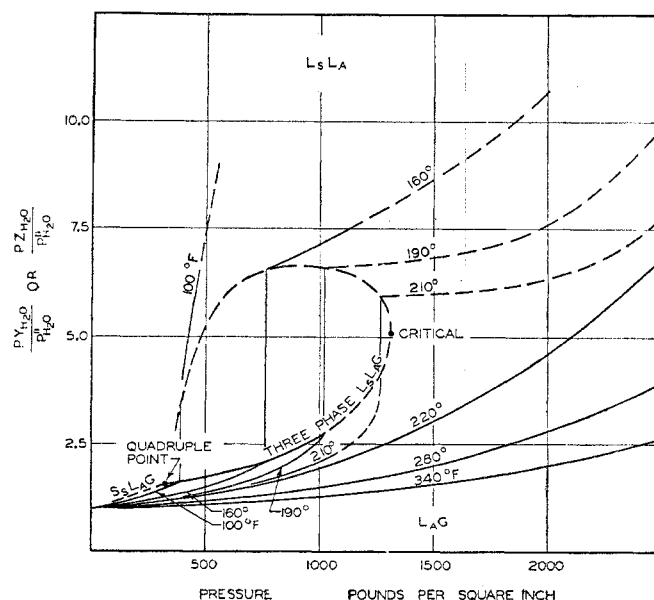


Figure 8. Effect of Pressure upon Mole Fraction Water in Gas Phase or Hydrogen Sulfide-Rich Liquid Phase

$$\log P_R = 15.11835 - \frac{6867.98}{T} \quad (2)$$

$$\log P_R = 5.57440 - \frac{1668.63}{T} \quad (3)$$

The deviation of the experimental data from the reference quantities is sufficiently small to permit a rather clear picture of the precision with which these quantities were measured. The residual pressure decreases to substantially zero at the quadruple point temperature which has been taken as 85.1° F.

Table I presents the pressures and temperatures corresponding to the several three-phase equilibria of Figures 4 and 5. This table represents critically chosen values based upon the measurements of Scheffer (15) and upon the present investigation. The quadruple point recorded in Table I is based primarily upon the work of Scheffer (16, 17) and the value chosen is in good agreement with present measurements. No direct determinations were made of the composition of the hydrate. The work of Korvezee and Scheffer (9) indicates a composition corresponding to six molecules of water per molecule of hydrogen sulfide. In their opinion a small quantity of water was usually occluded during the formation of hydrate. This occlusion may have accounted for the irregular values found by Scheffer (17) by the direct analysis of the hydrate phase. Scheffer and Meijer (18) applied the Clapeyron equation to the evaluation of the composition of the hydrate at the  $S_2S_2L_2G$  quadruple point. For temperatures above the quadruple point at 85.1° F., hydrate is found only at progressively higher pressures along the  $S_2L_2L_a$  equilibrium curve. In this higher temperature region the composition of the gas phase was determined along the three-phase equilibrium,  $L_2L_aG$ , and the two-phase equilibrium,  $L_2G$ . The results of these analyses are available (21). Figure 7 presents the mole fraction hydrogen sulfide in the gas phase as a function of pressure for the several temperatures investigated. The experimental points have been included. The behavior of the hydrogen sulfide-rich liquid is not known with certainty except near the three-phase locus shown in the figure. The isothermal effect of

TABLE I. PRESSURES AND TEMPERATURES FOR THREE-PHASE EQUILIBRIA IN THE HYDROGEN SULFIDE-WATER SYSTEM

| Temp.,<br>° F.  | Pressure,<br>Lb./Sq. Inch<br>Absolute | Pressure,<br>Lb./Sq. Inch<br>Absolute | Temp.,<br>° F.    |
|---|---------------------------------------|---------------------------------------|-------------------|
| Hydrate-Aqueous Liquid-Gas ( $S_2L_2G$ ) <sup>a</sup>               |                                       |                                       |                   |
| 31.3 <sup>b</sup>   | 13.5                                  | 13.5 <sup>b</sup>                     | 31.3 <sup>b</sup> |
| 40.0  | 22.8                                  | 50.0                                  | 53.6              |
| 50.0  | 40.6                                  | 100.0                                 | 65.6              |
| 60.0  | 72.4                                  | 150.0                                 | 72.6              |
| 70.0  | 129.1                                 | 200.0                                 | 77.6              |
| 80.0  | 231.5                                 | 250.0                                 | 81.2              |
| 85.1 <sup>b</sup>   | 324.7                                 | 300.0                                 | 84.0              |
|   |                                       | 324.7 <sup>b</sup>                    | 85.1              |
| Hydrate-Ice-Gas ( $S_2S_2G$ ) <sup>c</sup>                          |                                       |                                       |                   |
| 0.0   | 6.4                                   | 5.0                                   | -8.8              |
| 5.0   | 7.3                                   | 10                                    | 17.9              |
| 10.0  | 8.2                                   |                                       |                   |
| 15.0  | 9.3                                   |                                       |                   |
| 20.0  | 10.5                                  |                                       |                   |
| 25.0  | 11.8                                  |                                       |                   |
| 30.0  | 13.1                                  |                                       |                   |
| 31.3 <sup>b</sup>   | 13.5                                  |                                       |                   |
| Hydrate-Hydrogen Sulfide-Rich Liquid-Gas ( $S_2L_2G$ )              |                                       |                                       |                   |
| 10.0  | 106.0                                 | 100.0                                 | 6.8               |
| 20.0  | 126.2                                 | 150.0                                 | 30.4              |
| 30.0  | 149.0                                 | 200.0                                 | 49.2              |
| 40.0  | 174.3                                 | 250.0                                 | 65.2              |
| 50.0  | 202.1                                 | 300.0                                 | 78.9              |
| 60.0  | 232.8                                 | 324.7 <sup>b</sup>                    | 85.1              |
| 70.0  | 266.7                                 |                                       |                   |
| 80.0  | 304.2                                 |                                       |                   |
| 85.1 <sup>b</sup>   | 324.7                                 |                                       |                   |
| Aqueous Liquid-Hydrogen Sulfide-Rich Liquid-Gas ( $L_2L_2G$ )       |                                       |                                       |                   |
| 85.1 <sup>b</sup>   | 324.7                                 | 324.7 <sup>b</sup>                    | 85.1              |
| 90.0  | 345.2                                 | 400.0                                 | 102.0             |
| 100.0   | 390.1                                 | 500.0                                 | 121.1             |
| 110.0   | 439.5                                 | 600.0                                 | 137.3             |
| 120.0   | 493.6                                 | 700.0                                 | 152.1             |
| 130.0   | 552.6                                 | 800.0                                 | 165.4             |
| 140.0   | 616.6                                 | 900.0                                 | 177.5             |
| 150.0   | 685.6                                 | 1000.0                                | 188.6             |
| 160.0   | 759.4                                 | 1100.0                                | 198.4             |
| 170.0   | 837.8                                 | 1200.0                                | 206.4             |
| 180.0   | 921.2                                 | 1300.0                                | 212.0             |
| 190.0   | 1013.2                                |                                       |                   |
| 200.0   | 1116.4                                |                                       |                   |
| 210.0   | 1257.7                                |                                       |                   |
| Hydrate-Aqueous Liquid-Hydrogen Sulfide-Rich Liquid ( $S_2L_2L_2$ ) |                                       |                                       |                   |
| 85.1 <sup>b</sup>   | 324.7                                 | 324.7 <sup>b</sup>                    | 85.1              |
| 86.0  | 1135.0                                | 500.0                                 | 85.3              |
| 87.0  | 2058.0                                | 1000.0                                | 85.8              |
| 88.0  | 3039.0                                | 1500.0                                | 86.4              |
| 89.0  | 4038.0                                | 2000.0                                | 86.9              |
| 90.0  | 5086.0                                | 2500.0                                | 87.5              |
|   |                                       | 3000.0                                | 88.0              |
|   |                                       | 3500.0                                | 88.5              |
|   |                                       | 4000.0                                | 89.0              |
|   |                                       | 4500.0                                | 89.5              |
|   |                                       | 5000.0                                | 89.9 <sup>d</sup> |

<sup>a</sup> Authors and Scheffer (15).

<sup>b</sup> Quadruple point.

<sup>c</sup> Scheffer (15).

<sup>d</sup> Extrapolated.

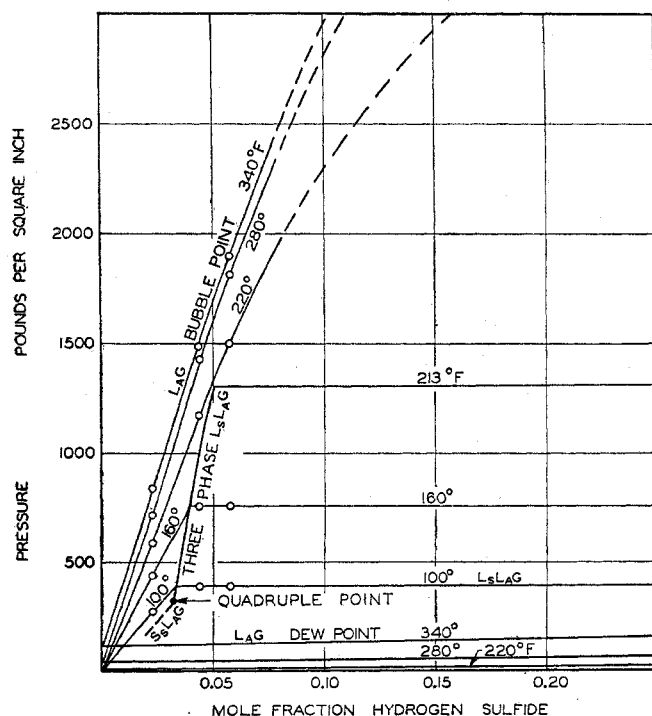


Figure 9. Composition of Aqueous Bubble Point Liquid in Hydrogen Sulfide-Water System

pressure upon the composition of this liquid phase appears from present indications to be rather complex.

Figure 8 shows the product of the pressure and of the mole fraction water in the gas phase or hydrogen sulfide-rich liquid phase divided by the vapor pressure of water. The experimental

TABLE II. COMPOSITIONS OF THE COEXISTING GAS, HYDROGEN SULFIDE-RICH LIQUID, AND AQUEOUS LIQUID PHASES

| Pressure,<br>Lb./Sq. Inch<br>Absolute | Temp.,<br>° F.     | Mole Fraction Hydrogen<br>Sulfide |                    |                     | Equilibrium Ratio<br>for Hydrogen<br>Sulfide |       |
|---------------------------------------|--------------------|-----------------------------------|--------------------|---------------------|--|-------|
|                                       |                    | G                                 | L <sub>s</sub>     | L <sub>a</sub>      | Y/Z  | Y/X   |
| 324.7 <sup>a</sup>                    | 85.1 <sup>a</sup>  | 0.9971 <sup>b</sup>               | 0.997 <sup>b</sup> | 0.0323 <sup>b</sup> | 1.000  | 30.87 |
| 400.0                                 | 102.0              | 0.9958                            | 0.991 <sup>b</sup> | 0.0335              | 1.005  | 29.73 |
| 600.0                                 | 137.3              | 0.9916                            | 0.9727             | 0.0369              | 1.019  | 26.87 |
| 800.0                                 | 165.4              | 0.9854                            | 0.9554             | 0.0402              | 1.031  | 24.51 |
| 1000.0                                | 188.6              | 0.9758                            | 0.9402             | 0.0435              | 1.038  | 22.43 |
| 1250.0                                | 209.7              | 0.9552                            | 0.9325             | 0.0479              | 1.021  | 19.94 |
| 1306.0 <sup>c</sup>                   | 212.3 <sup>c</sup> | 0.9423                            | 0.9423             | 0.0488              | 1.000  | 19.31 |

<sup>a</sup> Quadruple point.

<sup>b</sup> Extrapolated data.

<sup>c</sup> Critical state for gas and hydrogen sulfide-rich liquid.

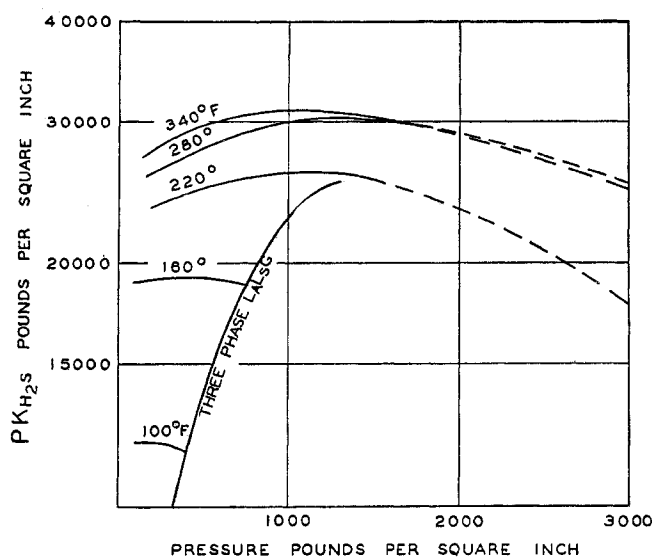


Figure 10. Pressure-Equilibrium Ratio Product for Hydrogen Sulfide between Gas and Aqueous Liquid Phases

results have been smoothed with respect to pressure, temperature, and composition and are recorded in Table II for the  $L_sL_aG$  three-phase equilibrium and in Table III for the  $L_aG$  two-phase equilibrium.

Figure 9 shows the relation of the composition of bubble point aqueous liquid to pressure for a series of temperatures. The points correspond to experimentally determined discontinuities in the isothermal volume-pressure derivative at bubble point. These measurements were made with the glass piston-cylinder combination which has been described.

The composition data submitted in Table III permit the calculation of the gas-liquid equilibrium ratios for water and hydrogen sulfide. These ratios for the two-phase equilibrium be-

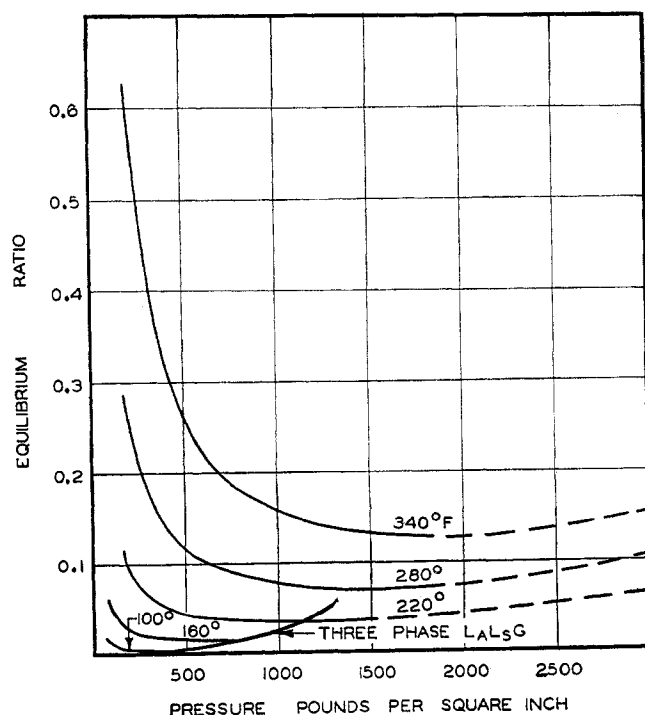


Figure 11. Equilibrium Ratios for Water between Gas and Aqueous Liquid Phases

TABLE III. COMPOSITIONS OF THE COEXISTING GAS AND AQUEOUS LIQUID PHASES

| Pressure,<br>Lb./Sq. Inch<br>Absolute | Mole Fraction<br>Hydrogen Sulfide |                      | Equilibrium Ratio   |                     |
|---------------------------------------|-----------------------------------|----------------------|---------------------|---------------------|
|                                       | <i>G</i>                          | <i>L<sub>a</sub></i> | Hydrogen<br>sulfide | Water               |
| 100° F.                               |                                   |                      |                     |                     |
| 100                                   | 0.9894                            | 0.0082               | 120.6               | 0.0107              |
| 150                                   | 0.9925                            | 0.0123               | 80.69               | 0.0076              |
| 200                                   | 0.9940                            | 0.0165               | 60.24               | 0.0061              |
| 250                                   | 0.9949                            | 0.0207               | 48.06               | 0.0052              |
| 300                                   | 0.9954                            | 0.0250               | 39.82               | 0.0047              |
| 390.1 <sup>a</sup>                    | 0.9960                            | 0.0333               | 26.62               |                     |
| 160° F.                               |                                   |                      |                     |                     |
| 100                                   | 0.9493                            | 0.0050               | 189.9               | 0.0510              |
| 150                                   | 0.9643                            | 0.0076               | 126.88              | 0.0360              |
| 200                                   | 0.9726                            | 0.0102               | 95.35               | 0.0277              |
| 250                                   | 0.9771                            | 0.0128               | 76.34               | 0.0232              |
| 300                                   | 0.9801                            | 0.0154               | 63.64               | 0.0202              |
| 400                                   | 0.9837                            | 0.0206               | 47.75               | 0.0166              |
| 500                                   | 0.9856                            | 0.0258               | 38.20               | 0.0150              |
| 600                                   | 0.9865                            | 0.0310               | 31.82               | 0.0139              |
| 700                                   | 0.9868                            | 0.0364               | 27.11               | 0.0136              |
| 759.4 <sup>a</sup>                    | 0.9869                            | 0.0395               | 24.95               |                     |
| 220° F.                               |                                   |                      |                     |                     |
| 200                                   | 0.9046                            | 0.0077               | 117.48              | 0.0961              |
| 400                                   | 0.9477                            | 0.0156               | 60.75               | 0.0531              |
| 600                                   | 0.9597                            | 0.0230               | 41.73               | 0.0412              |
| 800                                   | 0.9647                            | 0.0301               | 32.05               | 0.0364              |
| 1000                                  | 0.9664                            | 0.0371               | 25.97               | 0.0349              |
| 1250                                  | 0.9665                            | 0.0463               | 20.81               | 0.0351              |
| 1500                                  | 0.9651                            | 0.0577               | 16.73               | 0.0370              |
| 1750                                  | 0.9630                            | 0.0690 <sup>b</sup>  | 13.96 <sup>b</sup>  | 0.0399 <sup>b</sup> |
| 2000                                  | 0.9602                            | 0.0823               | 11.67               | 0.0434              |
| 2250                                  | 0.9568                            | 0.0973               | 9.83                | 0.0479              |
| 2500                                  | 0.9531                            | 0.1145               | 8.32                | 0.0530              |
| 2750                                  | 0.9491                            | 0.1346               | 7.05                | 0.0588              |
| 3000                                  | 0.9451                            | 0.1586               | 5.96                | 0.0652              |
| 3500                                  | 0.9371                            | .....                | .....               | .....               |
| 4000                                  | 0.9288                            | .....                | .....               | .....               |
| 4500                                  | 0.9203                            | .....                | .....               | .....               |
| 5000                                  | 0.9115                            | .....                | .....               | .....               |
| 280° F.                               |                                   |                      |                     |                     |
| 200                                   | 0.7375                            | 0.0057               | 129.4               | 0.2640              |
| 400                                   | 0.8589                            | 0.0127               | 67.63               | 0.1429              |
| 600                                   | 0.8984                            | 0.0191               | 47.04               | 0.1036              |
| 800                                   | 0.9155                            | 0.0250               | 36.63               | 0.0867              |
| 1000                                  | 0.9248                            | 0.0308               | 30.03               | 0.0776              |
| 1250                                  | 0.9307                            | 0.0382               | 24.36               | 0.0721              |
| 1500                                  | 0.9330                            | 0.0463               | 20.15               | 0.0703              |
| 1750                                  | 0.9327                            | 0.0550               | 16.96               | 0.0713              |
| 2000                                  | 0.9303                            | 0.0647 <sup>b</sup>  | 14.38 <sup>b</sup>  | 0.0746 <sup>b</sup> |
| 2250                                  | 0.9263                            | 0.0750               | 12.35               | 0.0798              |
| 2500                                  | 0.9213                            | 0.0860               | 10.71               | 0.0865              |
| 2750                                  | 0.9159                            | 0.0978               | 9.37                | 0.095               |
| 3000                                  | 0.9104                            | 0.1106               | 8.23                | 0.106               |
| 3500                                  | 0.8986                            | .....                | .....               | .....               |
| 4000                                  | 0.8870                            | .....                | .....               | .....               |
| 4500                                  | 0.8750                            | .....                | .....               | .....               |
| 5000                                  | 0.8630                            | .....                | .....               | .....               |
| 340° F.                               |                                   |                      |                     |                     |
| 200                                   | 0.3981                            | 0.0029               | 137.3               | 0.6037              |
| 400                                   | 0.6828                            | 0.0094               | 72.64               | 0.3202              |
| 600                                   | 0.7772                            | 0.0155               | 50.14               | 0.2263              |
| 800                                   | 0.8224                            | 0.0214               | 38.43               | 0.1815              |
| 1000                                  | 0.8466                            | 0.0273               | 31.01               | 0.1577              |
| 1250                                  | 0.8646                            | 0.0351               | 24.63               | 0.1403              |
| 1500                                  | 0.8742                            | 0.0435               | 20.10               | 0.1315              |
| 1750                                  | 0.8788                            | 0.0520               | 16.90               | 0.1278              |
| 2000                                  | 0.8797                            | 0.0610 <sup>b</sup>  | 14.42 <sup>b</sup>  | 0.1281 <sup>b</sup> |
| 2250                                  | 0.8779                            | 0.0705               | 12.45               | 0.1314              |
| 2500                                  | 0.8740                            | 0.0805               | 10.86               | 0.1370              |
| 2750                                  | 0.8681                            | 0.0910               | 9.54                | 0.145               |
| 3000                                  | 0.8606                            | 0.1024               | 8.40                | 0.155               |
| 3500                                  | 0.8486                            | .....                | .....               | .....               |
| 4000                                  | 0.8248                            | .....                | .....               | .....               |
| 4500                                  | 0.8061                            | .....                | .....               | .....               |
| 5000                                  | 0.7864                            | .....                | .....               | .....               |

<sup>a</sup> Three-phase equilibrium involving aqueous liquid, hydrogen sulfide-rich liquid, and gas.

<sup>b</sup> Composition of aqueous liquid at all higher pressures obtained by extrapolation.

tween gas and aqueous liquid have been included in a part of this table. It is probable that the average uncertainty in the composition of the gas phase is 0.002 mole fraction hydrogen sulfide. The equilibrium ratios for hydrogen sulfide and for water are shown as a function of pressure in Figures 10 and 11, respectively. As a result of the uncertainties in the compositions of the coexisting phases, the equilibrium ratios may involve errors of as much as 2%. The maximum two-phase pressure for the hydrogen sulfide-water system at temperatures above 220° F. is well in excess of 5000 pounds per square inch. Because the rate of

corrosion of the spherical bomb increased markedly at the higher pressures the measurements were not carried to pressures above 5200 pounds per square inch.

A limited number of measurements was made of the composition of the hydrogen sulfide-rich liquid and these are presented in Table IV. In this instance the liquids  $L_s$  and  $L_a$  were in equilibrium and no gas phase was present. These measurements were made at temperatures of 100° and 160° F. and indicate a relatively small mole fraction of water in the hydrogen sulfide-rich liquid. The composition of this phase in the  $L_sL_aG$  equilibrium is recorded in Table II which includes the corresponding equilibrium ratios for hydrogen sulfide. A number of values of molal volume of bubble point aqueous liquid are recorded in Table V. The volumetric data may involve uncertainties as large as 3%. The detailed data are available (21).

#### DISCUSSION OF BEHAVIOR

The data which have been submitted relate primarily to the experimental results obtained and have not been directed to the portrayal of the over-all behavior of the system. By combining the measurements of Scheffer (15, 17) and those of the present investigation the several fields can be defined, although some of the details can be established only semiquantitatively.

Figure 12 presents the effect of pressure upon the composition of the coexisting phases at 40° F. The composition scale near each of the pure components has been enlarged to show the details of the behavior to better advantage. The breaks in the horizontal lines and in the several curves indicate where this change in scale takes place. At pressures below 21 pounds per square inch, which correspond to the  $S_sL_aG$  equilibrium at 40° F., the system is predominantly aqueous liquid plus gas. The dew point curve shown as  $L_aG$  was obtained from a consideration of ideal solutions (10) and is open to uncertainty. The bubble point curve shown along the left side of the diagram was estimated from the behavior found at higher temperatures as is presented in Figure 9. At pressures above the  $S_sL_aG$  equilibrium line the hydrate exists and the solubility of the hydrogen sulfide and water in the hydrate has been indicated by the two nearly vertical lines near the hydrate composition of approximately

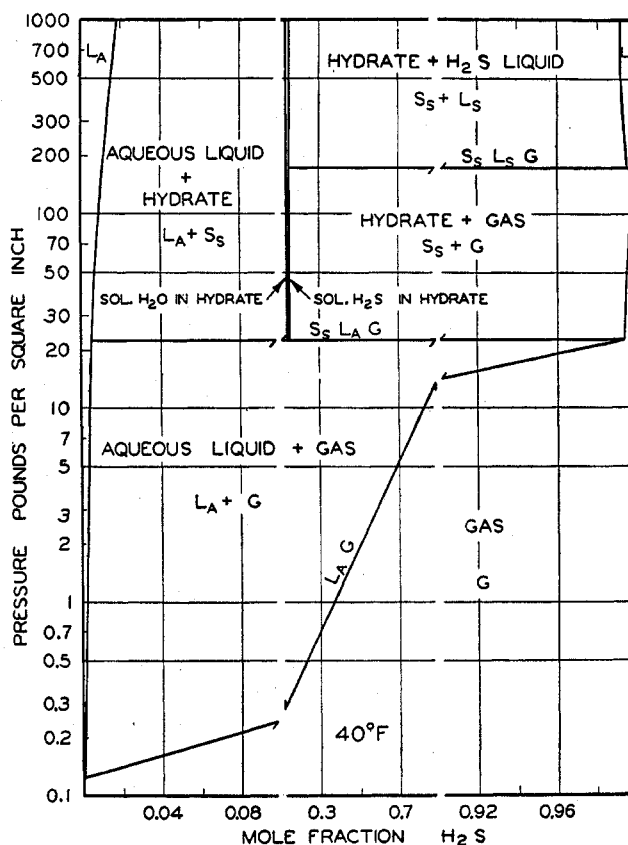


Figure 12. Pressure-Composition Diagram for Hydrogen Sulfide-Water System at 40° F.

0.143 mole fraction hydrogen sulfide. The aqueous liquid-hydrate field becomes progressively smaller at higher pressures because of the increased mole fraction of hydrogen sulfide in the aqueous liquid. At compositions richer in hydrogen sulfide than that corresponding to the hydrates, gas and hydrate coexist as would be expected from a consideration of Figure 5. For pressures above 180 pounds per square inch the  $S_sG$  field gives way to the  $S_sL_s$  field. A small range of compositions near pure hydrogen sulfide involves single-phase gas and single-phase liquid regions. This condition corresponds to compositions richer in hydrogen sulfide than that of dew point and bubble point, respectively. The compositions corresponding to these phase boundaries were estimated from experimental data obtained at higher temperatures.

A pressure-composition diagram for six temperatures is shown in Figure 13. An enlarged scale for compositions near that of the pure components has been employed. For temperatures below the  $S_sL_aL_sG$  quadruple point the composition of the gas phase and of the aqueous liquid phase along the  $S_sL_aG$  equilibrium has been indicated and the behavior at 40° F. portrayed. The four-phase state involving aqueous solid,  $S_s$ , hydrate,  $S_s$ , aqueous liquid,  $L_a$ , and gas,  $G$ , has been indicated at a temperature of 31.3° F. which was taken from Scheffer (9). The dew point curves at compositions near pure hydrogen sulfide have been included as a dashed line. At temperatures above the  $S_sL_aL_sG$  quadruple point, the behavior of the system along the  $L_aL_sG$  three-phase equilibrium has been portrayed. The change in composition at bubble point with pressure in the two-phase  $L_aG$  equilibrium is presented for two temperatures and the composition of the aqueous liquid along the three-phase  $L_aL_sG$  equilibrium is shown. The composition of the gas phase in the latter

TABLE IV. APPROXIMATE COMPOSITION OF THE HYDROGEN SULFIDE-RICH LIQUID IN EQUILIBRIUM WITH AN AQUEOUS LIQUID

| Pressure, Lb./Sq. Inch Absolute | Mole Fraction Hydrogen Sulfide, $L_s$ | Pressure, Lb./Sq. Inch Absolute | Mole Fraction Hydrogen Sulfide, $L_s$ |
|---------------------------------|---------------------------------------|---------------------------------|---------------------------------------|
| 100° F.                         |                                       | 160° F.                         |                                       |
| 390.1 <sup>a</sup>              | 0.9920                                | 759.4 <sup>a</sup>              | 0.9591                                |
| 400.0                           | 0.9908                                | 800.0                           | 0.9605                                |
| 600.0                           | 0.9841                                | 1000.0                          | 0.9660                                |
| 800.0                           | 0.9824 <sup>b</sup>                   | 1250.0                          | 0.9701                                |
| 1000.0                          | 0.980                                 | 1500.0                          | 0.9726                                |
|                                 |                                       | 1750.0                          | 0.9740 <sup>b</sup>                   |
|                                 |                                       | 2000.0                          | 0.975                                 |
|                                 |                                       | 2250.0                          | 0.974                                 |
|                                 |                                       | 2500.0                          | 0.973                                 |
|                                 |                                       | 2750.0                          | 0.972                                 |
|                                 |                                       | 3000.0                          | 0.971                                 |
|                                 |                                       | 3500.0                          | 0.967                                 |

<sup>a</sup> Three-phase equilibrium involving hydrogen sulfide-rich liquid, aqueous liquid, and gas.

<sup>b</sup> Compositions at all higher pressures extrapolated.

TABLE V. MOLAL VOLUMES OF BUBBLE POINT AQUEOUS LIQUID

| Temp., ° F. | Mole Fraction Hydrogen Sulfide  |                          |                                 |                          |                                 |                          |
|-------------|---------------------------------|--------------------------|---------------------------------|--------------------------|---------------------------------|--------------------------|
|             | 0.02267                         |                          | 0.04351                         |                          | 0.05723                         |                          |
|             | Pressure, lb./sq. inch absolute | Volume, cu. ft./lb. mole | Pressure, lb./sq. inch absolute | Volume, cu. ft./lb. mole | Pressure, lb./sq. inch absolute | Volume, cu. ft./lb. mole |
| 100         | 273                             | 0.2961                   | 390.1 <sup>a</sup>              | 0.3024                   | 390.1 <sup>a</sup>              | 0.3094                   |
| 160         | 443                             | 0.3040                   | 759.4 <sup>a</sup>              | 0.3097                   | 759.4 <sup>a</sup>              | 0.3179                   |
| 220         | 591                             | 0.3128                   | 1178.0                          | 0.3193                   | 1500.0                          | 0.3266                   |
| 280         | 720                             | 0.3240                   | 1419.0                          | 0.3329                   | 1796.0                          | 0.3386                   |
| 340         | 841                             | 0.3426                   | 1499.0                          | 0.3500                   | 1886.0                          | 0.3541                   |

<sup>a</sup> Three-phase pressure.

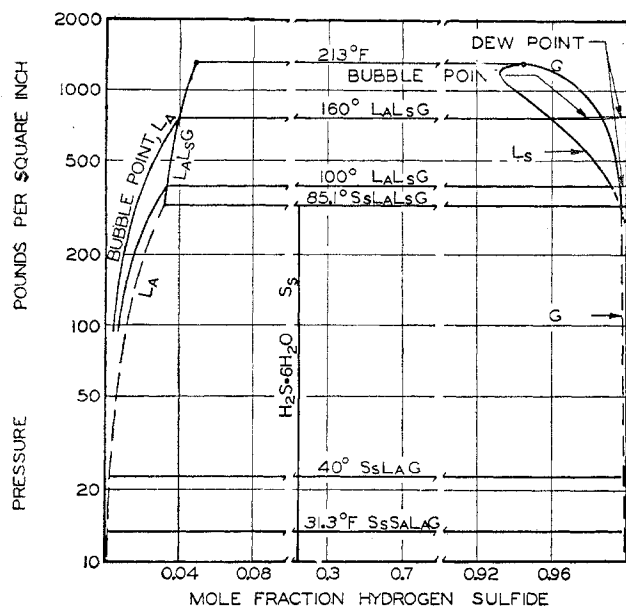


Figure 13. Pressure-Composition Diagram Including Three-Phase Equilibrium of Hydrate, Aqueous Liquid, and Gas

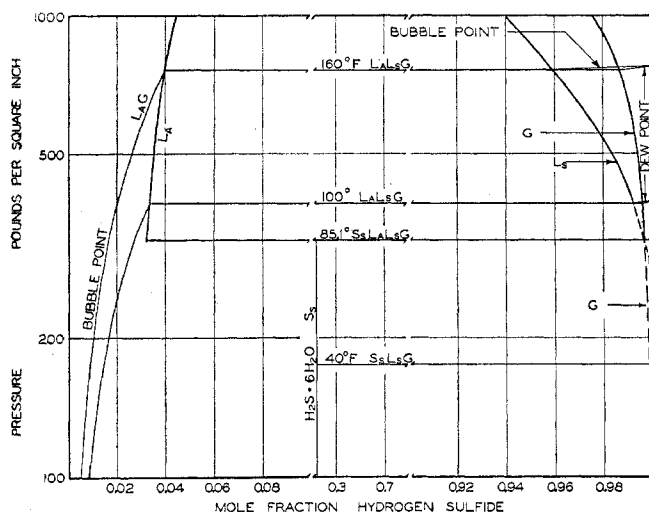


Figure 14. Pressure-Composition Diagram Including Three-Phase Equilibrium of Hydrate, Hydrogen Sulfide-Rich Liquid, and Gas

equilibrium and the behavior in the two-phase system at compositions near pure hydrogen sulfide are similar to those found for other binary systems at a three-phase state. At higher pressures the hydrogen sulfide-rich liquid and the gas phase reach a critical state at a pressure and temperature not greatly different from those for the critical state of pure hydrogen sulfide. It appears that the compositions of the hydrogen sulfide-rich liquid and the gas phase are nearly the same at the  $S_sL_aL_sG$  quadruple point.

Figure 14 presents still another pressure-composition diagram, similar to Figure 13 for temperatures above 85° F., describing the three-phase  $L_aL_sG$  equilibrium. However, below the  $S_sL_aL_sG$  quadruple point at 85.1° F., the diagram presents the behavior along the  $S_sL_sG$  curve. In this case the composition of the hydrogen sulfide-rich liquid has been approximated in the absence of direct experimental measurements. At present direct information concerning the composition of the gas phase associated with the  $S_sL_sG$  equilibrium is not available. The behavior at 40° F. has been indicated along with the expected behavior in the two-phase region adjacent to pure hydrogen sulfide.

Many more diagrams illustrating the behavior of this rather complex binary system can be prepared. However, it is believed that the data of Scheffer and those made available (21) from this work should satisfy most requirements concerning the phase behavior.

#### ACKNOWLEDGMENT

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#### NOMENCLATURE

- $G$  = gas
- $K$  = equilibrium ratio =  $Y/X$
- $L_a$  = aqueous liquid
- $L_s$  = hydrogen sulfide-rich liquid
- $P_R$  = reference pressure, pounds per square inch
- $S_a$  = aqueous solid
- $S_s$  = solid hydrate
- $T$  = temperature, ° R.
- $V$  = average specific volume, cubic feet per pound
- $X$  = mole fraction of a component in the aqueous liquid
- $Y$  = mole fraction of a component in the gas phase
- $Z$  = mole fraction of a component in the hydrogen sulfide-rich liquid

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#### Addenda

The following notice was omitted from the article "Gasification of Solid Fuels at Elevated Pressures" [Wilhelm Gumz, *IND. ENG. CHEM.*, **44**, 1071 (1952)]:

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