# Heterogeneous Phase Equilibria of the Hydrogen Sulfide–Carbon Dioxide System

**D. P. SOBOCINSKI and FRED KURATA**

**University of Kansas, Lawrence, Kansas**

**An experimental study on the system hydrogen sulfide-carbon dioxide was performed from the critical region to the solid-liquid-vapor region. For seven mixtures individual phase diagrams were determined by the establishment of dew, volume percentage liquid, bubble, critical, and triple points. A splendid study of this system had been reported earlier by Bierlein and Kay (*1*) for temperatures above 32°F. However from a temperature point of view this earlier work represents about one half of the phase diagram from the critical locus to the locus of triple points. Hence in this study particular attention was devoted to the lower temperature regions.**

**Equilibrium constants were determined from 100 to 1,200 lb./sq. in. abs. Vapor and liquid equilibrium compositions from this investigation were compared with those obtained by Bierlein and Kay (*1*) at 20, 40, 60, and 80 atm.**

**Solid-liquid-vapor loci were found to meet at a minimum temperature, lower than either of the individual pure component triple points, due to the formation of a eutectic mixture consisting of 12.5 mole % carbon dioxide. Vapor and liquid compositions in equilibrium with solid were established along the vapor-liquid-solid carbon dioxide and vapor-liquid-solid hydrogen sulfide loci.**

Hydrogen sulfide and carbon dioxide are two acidic components frequently found with the hydrocarbons of petroleum reservoirs.

After crude oil is refined, these constituents, the hydrogen sulfide and carbon dioxide, tend to concentrate in the light fractions, and physical separation schemes require knowledge of the phase behavior of such systems.

Moreover the behavior of hydrogen sulfide and carbon dioxide is becoming increasingly important in connection with the removal of these components from natural gases. Various concentrations of these gases can be effectively removed by different scrubbing and sorption schemes. However for the large-scale removal of these impurities considerable interest has centered on low temperature processes, where these components can be removed by distillation, as immiscible liquids, or as solids.

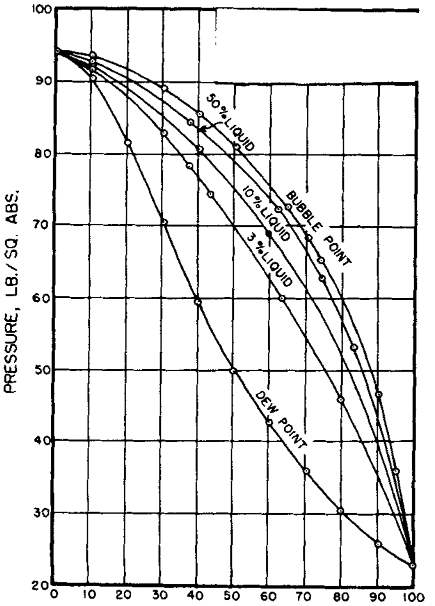

**Fig. 1. Pressure-composition diagram at −60°F. for hydrogen sulfide–carbon dioxide system.**

The phase behavior, vapor-liquid equilibrium compositions, triple-point loci, and triple point liquid compositions were reported for the methane–carbon dioxide system by Donnelly and Katz (*2*). Their data extended from the critical point of carbon dioxide to −110°F; triple-point studies for this system were extended to −260°F. by Kohn and Kurata (*3*).

Reamer, Sage, and Lacey (*4*) have studied the phase and volumetric behavior of the methane-hydrogen sulfide system from 40° to 340°F. and at pressures from 200 to 10,000 lb./sq. in. abs. Kohn and Kurata (*5*) verified much of the work of Reamer *et al.* and extended the study of this system to −160°F., encountering a locus of "type *K*—singular points" (*6*), where one of two phases is in critical identity with a third phase. These phases were shown to consist of a methane rich vapor phase, a methane rich liquid phase, and a hydrogen sulfide rich liquid phase.

The hydrogen sulfide-carbon dioxide binary has been studied by Bierlein and Kay (*1*) from 0°C. to the critical temperature of hydrogen sulfide. Earlier Steckel (*7*) had reported isothermal dew and bubble-point pressures for this system at 0°, −26.8°, and −52°C. His results at 0°C., though qualitatively similar, differed somewhat quantitatively from those of Bierlein and Kay.

The only known published work concerning the methane–carbon dioxide-hydrogen sulfide ternary is that of Robinson and Bailey (*18*). These investigators reported equilibrium constants for each component as a function of pressure and the ratio of other components at 100°F. and 600, 1,200 and 1,800 lb./sq. in. abs.

## APPARATUS

Equipment for this study was built and reported by Kohn and Kurata (*8*) and was a modification of earlier equipment used by Davis (*9*).

Basically this equipment consists of two major units. One unit serves as a reservoir which maintains the gas to be studied at a constant temperature above its cricondentherm temperature.

A second unit houses a calibrated glass equilibrium cell, heating unit, liquid nitrogen cooling coil and expansion section, a means for agitation, and a resistance thermometer. All these are immersed in a bath of appropriate fluid maintained at constant temperature or varied by proper use of the cooling system or heating element.

When the temperature and pressure conditions of the gas mixture confined in the equilibrium cell are controlled, the various phase changes may be visually observed. Where necessary a special sampling device permits various phases in the cell to be obtained for analytical purposes. Volumetric data can also be obtained concurrently by metering the gas to be studied into the equilibrium cell.

## PROCEDURE

The experimental method involved obtaining dew- and bubble-point pressures

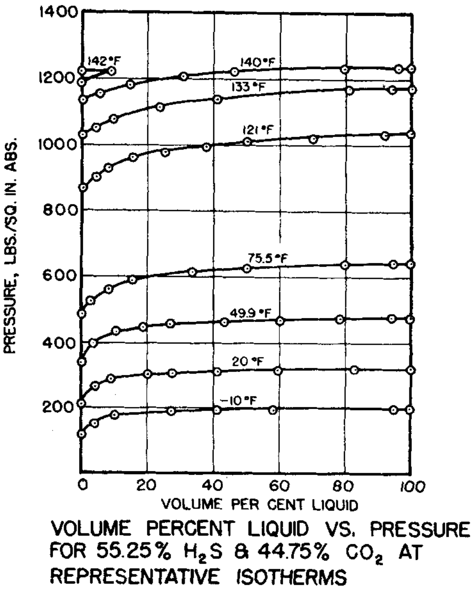

**Fig. 2. Volume percentage liquid vs. pressure for 55.25% hydrogen sulfide and 44.75% carbon dioxide at representative isotherms.**

at various isotherms for a number of gas mixtures. Volume percentage liquid at intermediate pressures for each mixture at each isotherm was also obtained in proceeding from dew to bubble points by reading the calibrations on the equilibrium cell.

The procedure used to determine the critical values for the mixtures involved taking finite decrements in temperature (starting above the cricondentherm) along with discrete increases in pressure to obtain the upper dew points. The point where the locus of dew points became the locus of bubble points (or vice versa depending upon critical location) was the critical point.

The locus of the solid-liquid-vapor boundary and crystal points were obtained by noticing where the formation of solids occurred at the terminal ends of the dew and bubble points.

With binary systems no samples need to be taken in the divariant vapor-liquid region to establish equilibrium compositions. This generally is not true for the vapor-liquid-solid region. However for a binary on a triple-point locus the system remains univariant. Thus by maintaining constant temperature one can sample any phase without upsetting equilibrium; however sampling must be accomplished slowly to prevent pressure or temperature disturbances in the system.

## MATERIALS

### Hydrogen Sulfide

Hydrogen sulfide used in this investigation was stated to be 99.9 mole % pure. However the change in pressure from the dew to bubble point at 45°F. was found to be in excess of 40 lb./sq. in. The pressure slope (pressure vs. volume percentage liquid) indicated that some heavy ends were present but that light ends were predominant. A number of packed adsorption schemes were devised with activated alumina, activated charcoals, and molecular sieves and were used at different temperatures to remove many of the heavy ends. It was hoped that slow weathering of the cylinder hydrogen sulfide would remove the light ends (felt to be mainly hydrogen). Re-evaluation of the conditioned gas still showed a 10 to 12 lb./sq. in. pressure change between the dew and bubble points.

To improve purity the hydrogen sulfide was batch distilled 6 to 8 times at from −50° to 0°F. The upper 5 to 10% was discarded. The middle 80% was condensed with dry ice and bottoms were discarded. A dew- and bubble-point pressure check of the hydrogen sulfide so purified frequently showed less than a 2 lb./sq. in. differential at 45°F., with 90% of the hydrogen sulfide condensing within a 1 lb./sq. in. differential.

When the batch distilled hydrogen sulfide was lowered to dry-ice temperature and below, and 1% of the system was withdrawn as vapor and discarded, a recheck of the dew- and bubble-point differential at 45°F. showed that it was

TABLE 1. EQUILIBRIUM VAPORIZATION CONSTANTS FOR THE HYDROGEN SULFIDE—CARBON DIOXIDE SYSTEM

| Temperature, °F. | Mole fraction $H_2S$, vapor phase | Mole fraction $H_2S$, liquid phase | Equilibrium constants, | |
|---|---|---|---|---|
| | | | $H_2S$ | $CO_2$ |
| | Pressure = 100 lb./sq. in. abs. | | | |
| 0 | 0.840 | 0.984 | 0.854 | 10.00 |
| −10 | 0.700 | 0.956 | 0.732 | 6.82 |
| −20 | 0.572 | 0.915 | 0.625 | 5.04 |
| −30 | 0.450 | 0.850 | 0.529 | 3.67 |
| −40 | 0.329 | 0.714 | 0.461 | 2.35 |
| −50 | 0.204 | 0.501 | 0.407 | 1.60 |
| −55 | 0.102 | 0.282 | 0.362 | 1.25 |
| | Pressure = 200 lb./sq. in. abs. | | | |
| 45 | 0.922 | 0.983 | 0.938 | 4.59 |
| 40 | 0.855 | 0.967 | 0.884 | 4.39 |
| 30 | 0.723 | 0.931 | 0.777 | 4.01 |
| 20 | 0.590 | 0.887 | 0.665 | 3.63 |
| 10 | 0.475 | 0.822 | 0.578 | 2.95 |
| 0 | 0.369 | 0.720 | 0.513 | 2.25 |
| −10 | 0.259 | 0.547 | 0.473 | 1.64 |
| −20 | 0.120 | 0.235 | 0.511 | 1.15 |
| −22 | 0.075 | 0.141 | 0.531 | 1.08 |
| | Pressure = 300 lb./sq. in. abs. | | | |
| 70 | 0.894 | 0.978 | 0.914 | 4.82 |
| 60 | 0.770 | 0.948 | 0.812 | 4.42 |
| 50 | 0.651 | 0.907 | 0.718 | 3.75 |
| 40 | 0.540 | 0.850 | 0.635 | 3.07 |
| 30 | 0.436 | 0.752 | 0.580 | 2.27 |
| 20 | 0.340 | 0.630 | 0.540 | 1.78 |
| 10 | 0.241 | 0.449 | 0.537 | 1.38 |
| 5 | 0.175 | 0.301 | 0.581 | 1.18 |
| 2 | 0.119 | 0.195 | 0.610 | 1.09 |
| | Pressure = 400 lb./sq. in. abs. | | | |
| 90 | 0.871 | 0.971 | 0.897 | 4.45 |
| 80 | 0.750 | 0.933 | 0.804 | 3.73 |
| 70 | 0.637 | 0.884 | 0.721 | 3.13 |
| 60 | 0.540 | 0.815 | 0.663 | 2.49 |
| 50 | 0.449 | 0.725 | 0.619 | 2.00 |
| 40 | 0.355 | 0.605 | 0.587 | 1.63 |
| 30 | 0.251 | 0.430 | 0.584 | 1.31 |
| 25 | 0.185 | 0.317 | 0.583 | 1.19 |
| 20 | 0.095 | 0.164 | 0.579 | 1.08 |
| | Pressure = 500 lb./sq. in. abs. | | | |
| 110 | 0.899 | 0.975 | 0.922 | 4.04 |
| 100 | 0.784 | 0.935 | 0.839 | 3.32 |
| 90 | 0.680 | 0.885 | 0.768 | 2.78 |
| 80 | 0.583 | 0.826 | 0.706 | 2.40 |
| 70 | 0.489 | 0.750 | 0.652 | 2.04 |
| 60 | 0.395 | 0.640 | 0.617 | 1.68 |
| 50 | 0.303 | 0.497 | 0.610 | 1.39 |
| 40 | 0.185 | 0.290 | 0.638 | 1.15 |
| 35 | 0.100 | 0.154 | 0.649 | 1.06 |
| | Pressure = 600 lb./sq. in. abs. | | | |
| 130 | 0.957 | 0.989 | 0.968 | 3.91 |
| 120 | 0.835 | 0.947 | 0.881 | 3.11 |
| 110 | 0.731 | 0.901 | 0.811 | 2.72 |
| 100 | 0.638 | 0.848 | 0.752 | 2.38 |
| 90 | 0.548 | 0.780 | 0.703 | 2.05 |
| 80 | 0.460 | 0.700 | 0.657 | 1.80 |
| 70 | 0.369 | 0.577 | 0.640 | 1.49 |
| 60 | 0.272 | 0.419 | 0.649 | 1.25 |
| 50 | 0.140 | 0.209 | 0.670 | 1.09 |
| 47 | 0.088 | 0.130 | 0.677 | 1.05 |
| | Pressure = 800 lb./sq. in. abs. | | | |
| 150 | 0.891 | 0.959 | 0.929 | 2.66 |
| 140 | 0.790 | 0.914 | 0.864 | 2.44 |
| 130 | 0.695 | 0.860 | 0.808 | 2.17 |
| 120 | 0.604 | 0.800 | 0.755 | 1.98 |
| 110 | 0.522 | 0.720 | 0.725 | 1.71 |
| 100 | 0.440 | 0.626 | 0.703 | 1.50 |
| 90 | 0.352 | 0.505 | 0.697 | 1.31 |
| 80 | 0.245 | 0.356 | 0.688 | 1.17 |
| 70 | 0.112 | 0.150 | 0.747 | 1.04 |
| 68 | 0.075 | 0.100 | 0.750 | 1.03 |

TABLE 1. (Continued)

| Temperature, °F. | Mole fraction $H_2S$, vapor phase | Mole fraction $H_2S$, liquid phase | Equilibrium constants, $H_2S$ | $CO_2$ |
|---|---|---|---|---|
| | Pressure = 1,000 lb./sq. in. abs. | | | |
| 175 | 0.937 | 0.966 | 0.970 | 1.85 |
| 170 | 0.894 | 0.941 | 0.950 | 1.80 |
| 160 | 0.805 | 0.891 | 0.903 | 1.79 |
| 150 | 0.715 | 0.840 | 0.851 | 1.78 |
| 140 | 0.630 | 0.781 | 0.807 | 1.70 |
| 130 | 0.540 | 0.701 | 0.770 | 1.54 |
| 120 | 0.451 | 0.599 | 0.753 | 1.37 |
| 110 | 0.364 | 0.487 | 0.747 | 1.24 |
| 100 | 0.270 | 0.360 | 0.750 | 1.14 |
| 90 | 0.155 | 0.195 | 0.795 | 1.05 |
| 85 | 0.072 | 0.090 | 0.800 | 1.02 |
| | Pressure = 1,200 lb./sq. in. abs. | | | |
| 195 | 0.939 | 0.962 | 0.976 | 1.61 |
| 190 | 0.901 | 0.938 | 0.961 | 1.60 |
| 180 | 0.830 | 0.888 | 0.935 | 1.52 |
| 170 | 0.760 | 0.835 | 0.910 | 1.45 |
| 160 | 0.684 | 0.774 | 0.884 | 1.40 |
| 150 | 0.610 | 0.696 | 0.876 | 1.28 |
| 140 | 0.545 | 0.595 | 0.916 | 1.12 |
| 135 | 0.515 | 0.535 | 0.963 | 1.04 |
| 132.2 | 0.500 | 0.500 | 1.000 | 1.000 |

less than 1 lb./sq. in., with 90% condensing within ½ lb./sq. in. Calculations based on the worst of probable impurities, (methyl mercaptan, methylene chloride, and carbon disulfide) indicated that the hydrogen sulfide was at least 99.94 mole % pure. Material of the above purity was used in this study.

### Carbon Dioxide

When carbon dioxide was passed through silica gel, a 2 to 2½ lb./sq. in. differential existed between dew and bubble points at 66°F., with 90% condensing within 1 lb./sq. in. Experimental vapor pressures agreed well with those reported in the literature (*10*). This carbon dioxide was estimated to have a minimum purity of 99.5 mole %, a probable purity of 99.9 mole %.

## TRIPLE POINTS OF THE PURE CONSTITUENTS

### Hydrogen Sulfide

The triple point of the hydrogen sulfide used in this work was consistently found to be −120.8° ± 0.1°F. This temperature does not agree with the triple-point temperature as commonly reported in the various data sources. The triple point for hydrogen sulfide appears to be based, among others, on the work of Maass and McIntosh (*11*) and Cardoso and Arni (*12*) whose triple-point temperatures appear to have been obtained incidentally in connection with their determinations of the vapor pressure of hydrogen sulfide. Although earlier workers found even lower values, the accepted value is reported to be −117.2°F. The freezing point of hydrogen sulfide under atmospheric pressure has been determined more recently by several investigators and is reported as

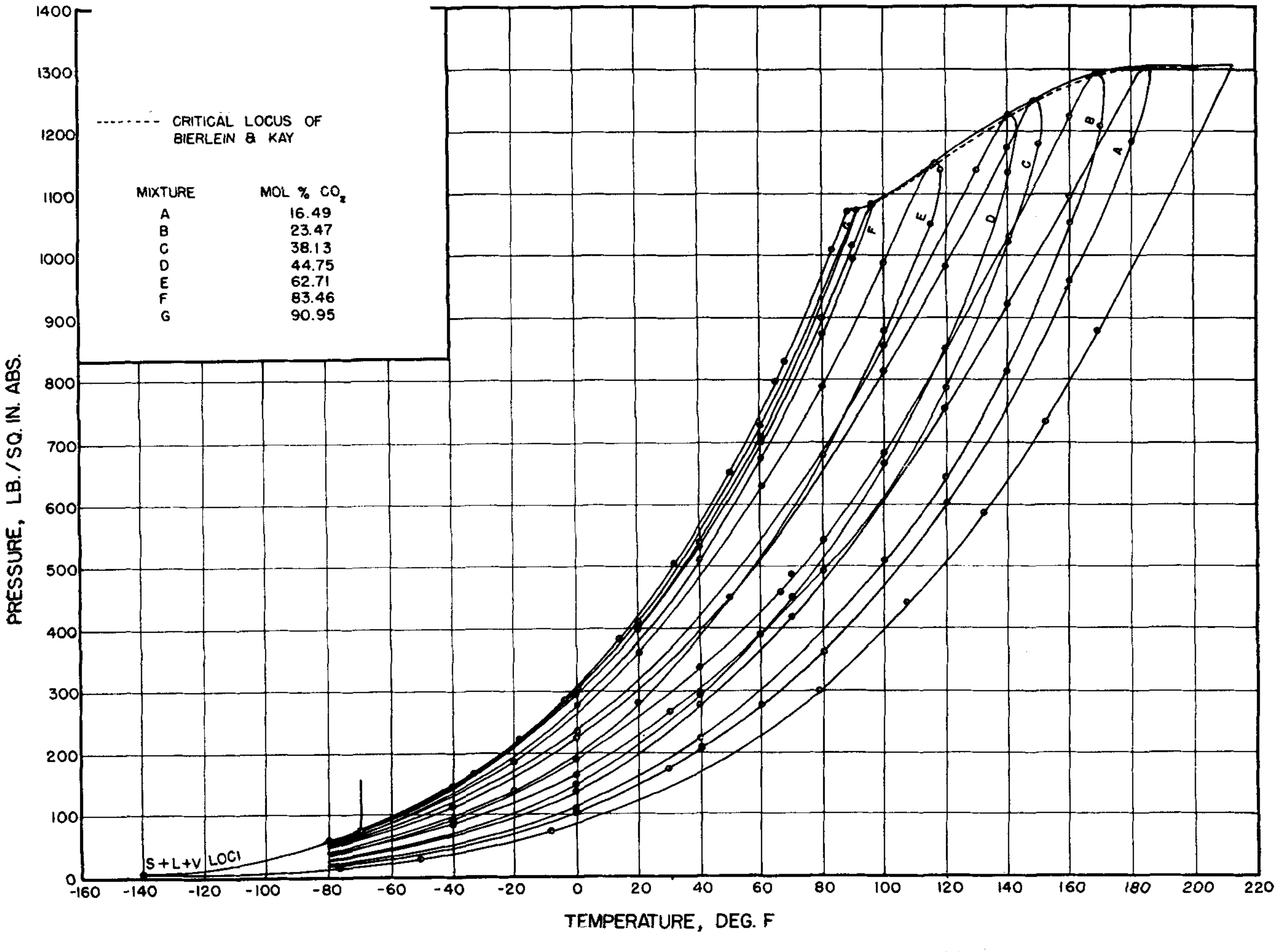

**Fig. 3. Pressure-temperature diagram for the hydrogen sulfide-carbon dioxide system.**

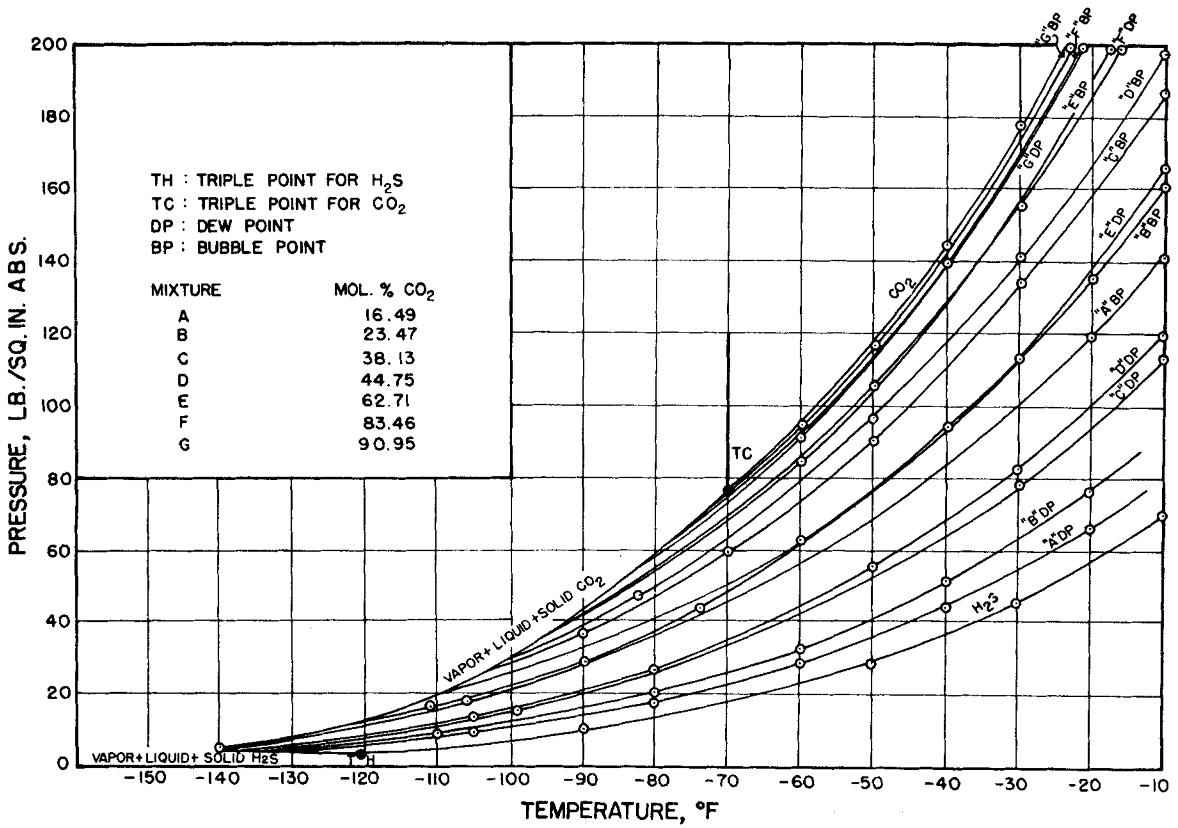

Fig. 4. Low temperature-pressure diagram for the hydrogen sulfide–carbon dioxide system describing $S + L + V$ loci.

−121.9°F. The freezing point of the hydrogen sulfide used by he authors under local barometric pressure (about 735 mm Hg) was found to be −121.7°± 0.1°F.

Regardless of the purification upon the hydrogen sulfide the literature triple-point temperature could not be confirmed. Even by differentially removing as vapor 80% of the hydrogen sulfide confined in an equilibrium cell as liquid at incipient freezing, no perceptible change could be effected in the value for the triple point.

The triple point was redetermined with hydrogen sulfide generated in a Kipp apparatus. This hydrogen sulfide was purified in a manner similar to that reported above, that is by repeated batch distillations. Again the triple-point temperature value was found to be −120.8°F. Concentration of the Kipp generated hydrogen sulfide at incipient freezing to 20% of the initial liquid made no significant change in the value for the triple-point temperature.

The temperature in the triple-point determinations was measured with a platinum resistance thermometer calibrated against a National Bureau of Standards calibrated platinum resistance thermometer. The thermometer–Mueller bridge circuit used by the authors was compared to another independently calibrated platinum resistance thermometer-bridge circuit. Deviation between the two thermometer-bridge circuits at −120°F. was approximately 0.2°F.

The measured triple-point pressure of hydrogen sulfide was found to be 3.5 lb./sq. in. abs. ± 0.2 lb./sq. in. The value in the *International Critical Tables* is 3.33 lb./sq. in. abs.

### Carbon Dioxide

Equipment used in hydrogen sulfide triple-point determinations was similarly used for carbon dioxide. The triple point of the carbon dioxide used in the work was found to exist at −69.9°F. ± 0.05°F. and 76.9 lb./sq. in. abs. Triple-point values commonly reported for carbon dioxide (*10*) are −69.9°F. and 5.2 atm. (76.5 lb./sq. in. abs.).

## EXPERIMENTAL COMPOSITIONS AND ANALYSIS

Seven mixtures of hydrogen sulfide and carbon dioxide that were prepared for study contained the following amounts of carbon dioxide: 16.49, 23.47, 38.13, 44.75, 62.71, 83.46, and 90.95 mole %. These mixtures were prepared by condensing with dry ice hydrogen sulfide which was admitted under its own vapor pressure into an evacuated stainless steel cylinder in the reservoir unit. Subsequently the hydrogen sulfide was diluted with carbon dioxide. Initial and final weights of the hydrogen sulfide cylinder plus the known volumetric addition of carbon dioxide allowed approximate compositions to be calculated.

Gas analyses were made with density determinations obtained by direct weighings. This method required accurate compressibility factors for the pure components at atmospheric pressure and room temperatures. Low-pressure compressibility factors, determined under identical conditions for the purified hydrogen sulfide, were found to be greater than those reported by Reamer, Sage, and Lacey (*13*) by slightly more than 0.1% and had an average deviation of 0.055%. Unlike those interpolated from West (*14*) atmospheric pressure compressibility factors derivable from the work of Moles (*15*) agreed moderately well with those of Reamer, Sage, and Lacey (*13*).

Atmospheric pressure compressibility factors for carbon dioxide determined for analytical purposes in this work agreed to about 0.1% with those values reported by Bottomley *et al.* (*16*). These had an average deviation of 0.061%.

Since no correction was made for gas adsorption within the density bulbs, and since the analytical procedure may have possessed intrinsically a 0.1% deviation in the absolute values for compressibility factors (or molecular weights), the constants for the pure components, as determined in this work, were used in analytical calculations. In this way possible inaccuracies were cancelled in the relative molecular weight determinations. The mean average deviation of the samples for all mixtures analyzed in this manner was 0.14%.

Spot checks indicated a linear relationship for compressibility factors of mixtures. Hence a trial and error method with interpolation determined compressibility factors for mixtures.

## RESULTS

Most of the data for a mixture was obtained in the form of volume percentage liquid vs. pressure, with parameters of temperature. In addition to describing the system more extensively this method sometimes provided a further verification on dew- and bubble-point pressures by extrapolation of the volume percentage data to 0 and 100% liquid conditions. In this system, particularly at lower temperatures, there was a large pressure differential for a mixture at its dew point and that of the mixture containing only several percent liquid. Figure 1 presents a typical isotherm for the hydrogen sulfide–carbon dioxide system at −60°F., where generally about 50% of the pressure change between dew and bubble points occurs with less than 3% liquid in the system. With increasing temperatures isotherms show a lower slope in volume percentage liquid-pressure plots. Complete volume percentage-pressure data for the mixtures in this study can be found in the work of Sobocinski (*17*). Typical volume percentage liquid vs. pressure data at several isotherms are presented in Figure 2 for a 55.25% hydrogen sulfide and 44.75% carbon dioxide mixture.

### Pressure-Temperature Diagram

A generalized pressure-temperature plot for the hydrogen sulfide-carbon dioxide system appears as Figure 3. Dew- and bubble-point pressures for each of the seven mixtures are presented along with vapor-pressure curves for hydrogen sulfide and carbon dioxide. This plot is similar to that presented by Bierlein and Kay (*1*) but represents the results of a single study on the system in question from the critical locus to the solid-liquid-vapor region. The dashed line on Figure 3 represents the critical locus as found by Bierlein and Kay.

### Equilibrium Compositions

Large scale pressure-temperature diagrams were cross plotted to furnish isobaric compositions for the system as a function of temperature. Such isobars were prepared for 100, 200, 300, 400, 500, 600, 800, 1,000, and 1,200 lb./sq. in. abs. In Table 1 equilibrium vaporization constants determined from these graphs are presented along with the vapor and liquid equilibrium compositions for each of the isobars. It is difficult to assign some degree of error to the compositions obtained in this manner. However it is felt that the data presented are accurate to the second decimal place. Possibly greater error exists with the higher pressure data and with the data for carbon dioxide rich mixtures. A comparison of equilibrium compositions obtained from this study with those of Bierlein and Kay (*1*) was made at 20, 40, 60, and 80 atm. Table 2 shows an average composition deviation of 3.2% for vapor and 2.2% for liquid.*

### Solid Liquid-Vapor Loci

Figures 4, 5, 6, and 7 furnish information concerning the low-temperature regions of the system and describe behavior along solid-liquid-vapor loci.

Figure 4 is an extension of Figure 3 to low pressures and temperatures. Bubble-point and dew-point curves for each of the mixtures are shown to meet the solid region at triple points containing vapor, liquid, and either solid carbon dioxide or solid hydrogen sulfide.

The two triple-point loci found extend from the triple points of the pure components and meet at the eutectic temperature of −140.1°F. and 5 lb./sq. in. abs. This pressure and all pressures on the vapor-liquid-solid carbon dioxide representation are considered accurate to 1 lb./sq. in. Binary triple points with solid hydrogen sulfide are considered accurate to less than 1 lb./sq. in.

Compositions of the liquid and vapor in equilibrium with solid along the triple-point loci are presented on Figure 5 as a function of temperature. Liquid and vapor compositions become identical at the triple points for the pure components but pass through a maximum composition deviation at the eutectic temperature.

Thiel and Schulte (*19*) obtained vapor and liquid compositions for hydrogen sulfide and carbon dioxide in equilibrium with solid carbon dioxide at 14.5 lb./sq. in. abs. and −115.8°F. Their vapor composition was found to be 24.7% hydrogen sulfide and 75.3% carbon dioxide; liquid composition was found to be 74.6% hydrogen sulfide and 25.4% carbon dioxide. Composition results from this study at similar conditions indicated a vapor composition of 26.5% hydrogen sulfide and 73.5% carbon dioxide, and the liquid 78.0% hydrogen sulfide and 22.0% carbon dioxide.

Two methods were used to obtain the compositions along the three-phase loci. One method involved obtaining liquid and vapor samples at various known points along the curve at superatmospheric pressures. These were subsequently analyzed by gas-density measurements. Also for many of the seven mixtures, temperatures and pressures at which dew and bubble points first encountered solid were measured. The observed point of simultaneous incipient liquid and solid formation provided the composition of the vapor at this temperature-pressure point. This composition was the known mixture composition. Similarly the liquid in equilibrium with solid and vapor had a composition identical with that of the known mixture when, at its bubble point, solid was first encountered.

Not only were the previously mentioned mixtures used to determine triple-point compositions but several carbon dioxide lean mixtures were prepared to describe the composition, particularly of the liquid, along vapor, liquid, and solid (hydrogen sulfide or carbon dioxide) points.

The composition curves presented on Figure 5 represent the best plot for the differently obtained composition points. The liquid curve is in worst deviation from determined points by about 1.0 mole % composition. A composition deviation of 5 to 10 mole % might easily exist for the vapor composition plot and represents the most unrealiable portion of this work. The dashed portion of the vapor-composition plot estimates compositions where no dependable determinations were obtained.

On Figure 6 are plotted low-temperature isotherms for the hydrogen sulfide-carbon dioxide system as functions of pressure and composition. As indicated, dashed lines represent vapor and liquid compositions along triple-point loci. The

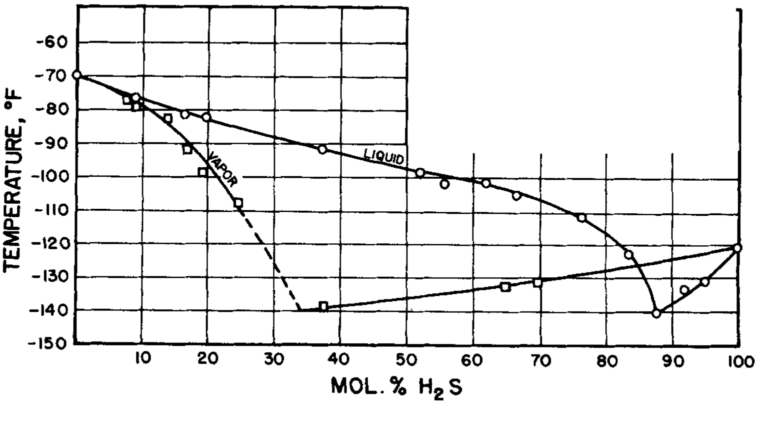

Fig. 5. Vapor and liquid composition along $V + L^+$ hydrogen sulfide solid and $V + L^+$ carbon dioxide solid loci for the hydrogen sulfide–carbon dioxide system.

---

*Tabular material has been deposited as document No. 6054 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

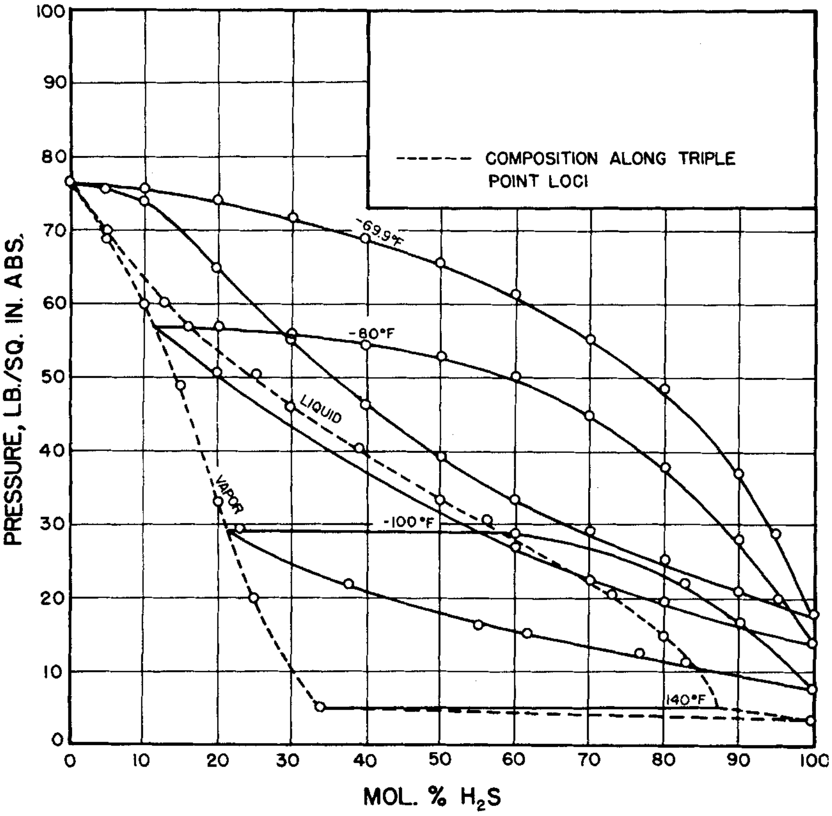

Fig. 6. Pressure-composition diagram for isotherms along the triple-point loci ($S + L + V$) for the system hydrogen sulfide–carbon dioxide.

line representing the −140.1°F. isotherm corresponds to the eutectic temperature.

Figure 7 is an extension of Figure 6 to an enlarged low-pressure scale. Both graphs were obtained by cross plotting information contained on Figures 4 and 5.

### Errors

Subatmospheric pressures and some pressures to 2 atm. were measured with a mercury manometer. All other pressures were read on a calibrated Heise bourdon tube gauge. Dew-point pressures are estimated to be accurate to 1 lb./sq. in. at pressures below 500 lb./sq. in. and to 2 lb./sq. in. at pressures above 500 lb./sq. in. All bubble-point pressures are considered to be accurate to within less than 1 lb./sq. in.

Critical points are estimated as accurate to 1°F. and 5 lb./sq. in. for mixtures containing 60% and higher mole % hydrogen sulfide. Critical points for considered to be accurate to within 0.5°F. and 2 lb./sq. in.

All temperature measurements above −100°F. are considered to be accurate to 0.1°F.; below −100°F. to 0.2°F.

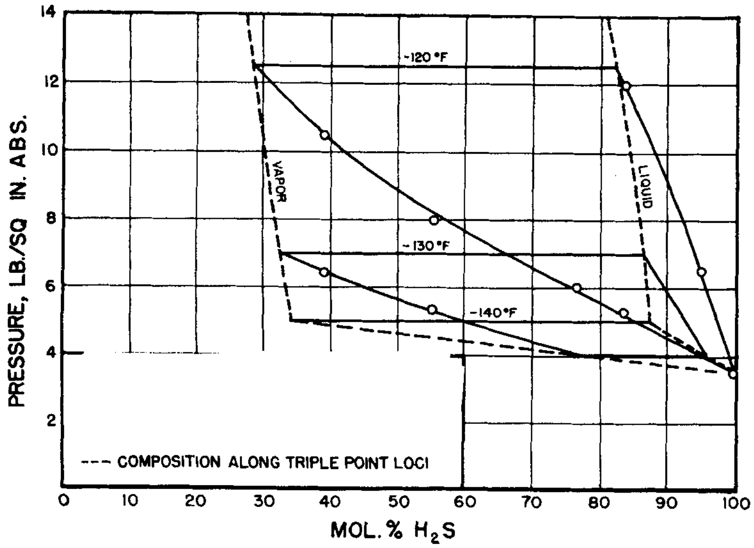

Fig. 7. Pressure-composition diagram for isotherms near eutectic temperature for the system hydrogen sulfide–carbon dioxide.

## DISCUSSION

For the most part the phase diagram for the hydrogen sulfide–carbon dioxide system exhibits no particularly unusual behavior. The critical locus exhibits neither a maximum nor a minimum but does approach the pure component critical points with a slope of almost zero. The tendency toward azeotropism at the carbon dioxide rich end is clearly suggested for any isotherm on Figure 3 by the flat profile of the bubble and dew points for mixtures containing 90.95 and 83.46 mole % carbon dioxide. This tendency increases with decreasing temperature (−69.9°F. isotherm on Figure 6), but as Steckel (7) had found to −52°C. the incipient minimum boiling mixture never quite forms, even below the triple point for carbon dioxide.

Two vapor-liquid-solid loci were specially interesting. Vapor, liquid and solid hydrogen sulfide and vapor, liquid and solid carbon dioxide ruled surfaces meet at −140.1°F. and 5 lb./sq. in. abs. At these conditions two other ruled surfaces representing S-S-L and S-S-V equilibria meet, thus establishing the quadruple point. Joint analyses of Figures 4 to 7 describe the behavior of mixtures in this region.

As an example it is assumed that a mixture containing 10 mole % carbon dioxide and 90 mole % hydrogen sulfide is maintained at its dew point by decreasing the pressure as the temperature is lowered. Reference to Figure 5 shows that this mixture will first encounter hydrogen sulfide solid on the vapor-liquid-solid hydrogen sulfide locus at −124°F. If the pressure of the system is now raised, solid hydrogen sulfide in equilibrium with liquid and vapor will be found to extend as low as −137.5°F. The pressures corresponding to these temperatures can be read from Figure 4 but can be found more accurately by referring to either Figure 6 or 7. From Figure 7 the range of triple-point pressures for the 90 mole % hydrogen sulfide mixture extends from 3.8 to 4.6 lb./sq. in abs. Figure 7 also furnishes corresponding dew- and bubble-point pressures for the mixture at −130 and −120°F.

As another example a system containing 60% hydrogen sulfide and 40% carbon dioxide is considered. Reference to Figures 5 to 7 shows that if the mixture is compressed isothermally from the vapor phase at some temperature above −133°F., for example −130°F., a dew point exists at 5 lb./sq. in. abs. (Fig. 7). Continued conpression increases the amount of liquid until at 7 lb./sq. in. abs. (Figure 7) vapor and liquid are in equili- mixtures with less hydrogen sulfide are brium with incipient solid carbon dioxide. Corresponding vapor and liquid compositions at −130°F. and 7 lb./sq. in. abs. are 32% hydrogen sulfide, 68% carbon dioxide and 85.5% hydrogen sulfide, 14.5% carbon dioxide respectively (Figure 5 or 7).

Isothermal compression of the 60% hydrogen sulfide mixture from the vapor phase at −133°F. shows that at 4.4 lb./sq. in. abs. the vapor is in equilibrium with incipient solid hydrogen sulfide and liquid. Continued compression causes the system to enter the vapor-liquid region until at 6.5 lb./sq. in. abs. solid carbon dioxide forms. At the latter condition vapor and liquid in equilibrium with solid carbon dioxide have compositions of 32.5% hydrogen sulfide, 67.5% carbon dioxide and 86% hydrogen sulfide, 14% carbon dioxide respectively.

If compression from the vapor phase for the 60% hydrogen sulfide mixture now occurs at −137°F., solid hydrogen sulfide forms. Upon further compression liquid forms at a vapor-liquid-solid hydrogen sulfide triple point at −137°F. and 4.7 lb./sq. in. abs. Vapor and liquid compositions at this point are 45% hydrogen sulfide, 55% carbon dioxide and 91% hydrogen sulfide, 9% carbon dioxide respectively. Vapor and liquid exist at pressures between 4.7 and 5.5 lb./sq. in. abs. at −137°F. At 5.5 lb./sq. in. abs. and −137°F. vapor, liquid, and solid carbon dioxide coexist where vapor composition is 33% hydrogen sulfide and liquid composition is 87% hydrogen sulfide.

Similar analyses can describe the behavior of any mixture in the low-temperature region. As directly indicated on Figures 5 to 7 systems containing between 12.5 and 66 mole % carbon dioxide have triple points at which vapor, liquid, and either solid hydrogen sulfide or solid carbon dioxide are in mutual equilibrium. Those mixtures with more than 66 mole % carbon dioxide can have vapor and liquid in equilibrium only with solid carbon dioxide; those with less than 12.5 mole % carbon dioxide have triple-point equilibria with solid hydrogen sulfide.

In view of the availability of the phase data at temperatures down to the solid-liquid-vapor loci of the three binary systems which comprise the methane-hydrogen sulfide–carbon dioxide ternary system, it is interesting to speculate about the behavior of the ternary.

It would be particularly interesting to know what influence carbon dioxide has upon the heterogeneous liquid-liquid-vapor behavior reported for the methane-hydrogen sulfide system (*5*).

## ACKNOWLEDGMENT

The authors wish to thank the Ethyl Corporation for their generous support of this work through their sponsoring of fellowships. Thanks are also due to Mr. Jerome Brewer for his considerable assistance in the laboratory program.

Phillips Petroleum Company donated the hydrocarbons used in the low-temperature bath.

## LITERATURE CITED

1. Bierlein, J. A., and W. B. Kay, *Ind. Eng. Chem.*, **45**, No. 3, 618 (1953).
2. Donnelly, H. G., and D. L. Katz, *ibid.*, **46**, 511 (1954).
3. Kohn, J. P., and Fred Kurata, Univ. Kansas, Lawrence (1955).
4. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **43**, 976 (1951).
5. Kohn, J. P., Ph.D. thesis, Univ. Kansas, Lawrence (1956).
6. Ricci, J. E., "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand, New York (1951).
7. Steckel, F., *Svensk Kem. Tidskr.*, **57**, 209 (1945); see (*1*).
8. Kohn, J. P., and Fred Kurata, *Pet. Proc.*, **11**, No. 12, 57 (1956).
9. Davis, P. C., Ph.D. thesis, Univ. Kansas, Lawrence (1951).
10. Lange, N. A., "Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio (1956).
11. Maass, O., and D. McIntosh, *Trans. Roy. Soc. Can.*, **3**, No. 8, 65 (1914).
12. Cardoso, E., and E. Armi, *J. Chem. Phys.*, **10**, 504 (1913).
13. Reamer, H. H., B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 140 (1950).
14. West, J. R., *Chem. Eng. Progr.*, **44**, No. 4, 287 (1948).
15. Moles, E., *Bull. soc. chim. France*, p. 1006 (Nov.-Dec. 1950).
16. Bottomley, G. A., D. S. Massie, and R. Whythlow-Gray, *Proc. Roy. Soc. (London)*, **A200**, 201 (1950).
17. Sobocinski, D. P., Ph.D. thesis, Univ. Kansas, Lawrence (in preparation).
18. Robinson, D. B., and J. A. Bailey, *Can. J. Chem. Eng.*, **35**, No. 4, 151 (December, 1957).
19. Thiel, A., and E. Schulte, *Z. physik. Chem.*, **96**, 328 (1920).

*Manuscript received December 8, 1958; revision received April 27, 1959; paper accepted April 27, 1959. Paper presented at A.I.Ch.E. Cincinnati meeting.*

---

# The Enthalpy of Water in the Liquid State

**ROBERT BYRNE and GEORGE THODOS**

**Northwestern University, Evanston, Illinois**

**The enthalpy of water in the liquid state has been calculated from 32°F. to temperatures approaching the critical and pressures ranging from saturated conditions to 160,000 lb./sq. in. abs. (approximately 11,000 atm). The results of this study are presented graphically and show that the influence of pressure on enthalpy is significant, particularly in the lower temperature region. At these conditions pressure is found to increase the enthalpy of liquid water by as much as 360 B.t.u./lb. above the corresponding enthalpy of the saturated liquid state.**

**A comprehensive literature search disclosed PVT data for water that permitted the construction of a density correlation. This correlation expressed in reduced coordinates extends from the normal freezing point of water to temperatures of 1,870°F. ($T_R = 2.0$) and pressures ranging up to 10,915 atm. ($P_R = 50$). The recent extensive PVT data of Kennedy reported in 1950 supplemented with the earlier data of Amagat and Bridgman allowed the calculation of enthalpies at these elevated temperatures and pressures. For these calculations basic thermodynamic relationships were adapted which utilized this reduced density correlation. This approach has made possible the extension of the thermodynamic properties of liquid water above the highest pressure reported by Keenan and Keys. Below this pressure of 6,000 lb./sq. in abs. good agreement was found to exist between the enthalpy values presented by Keenan and Keyes and those reported in this investigation.**

Considerable information is presented in the literature on the thermodynamic properties of nonpolar compounds. These substances are composed of electrically symmetrical molecules which tend to behave as perfect gases or ideal solutions. The hydrocarbons are characteristic of this class of compounds for which thermodynamic properties can be readily pre-