

# Phase Equilibrium in the System Water-Hydrogen Sulphide: Experimental Determination of the LLV Locus

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Experimental data are presented for the liquid-liquid-vapour (LLV) equilibrium for the system water-hydrogen sulphide. Conditions ranged from the hydrate-liquid-liquid-vapour quadruple point (29.4°C and 2.23 MPa) to beyond the critical temperature of hydrogen sulphide (100.3°C). The maximum temperature at which three phases can exist is 106.2°C at 9.39 MPa. This is 6°C higher than previously believed.

Des données expérimentales sont présentées pour l'équilibre liquide-liquide-vapeur (LLV) pour le système de sulfure d'hydrogène-eau. Des conditions vont du point quadruple hydrate-liquide-liquide-vapeur (29,4°C et 2,23 MPa) au-delà de la température critique du sulfure d'hydrogène (100,3°C). La température maximale à laquelle les trois phases peuvent exister est 106,2°C à 9,39 MPa, soit 6°C de plus que ce que l'on pensait précédemment.

Keywords: phase equilibria, H<sub>2</sub>O-H<sub>2</sub>S; liquid-liquid-vapour equilibrium; three-phase critical point.

The system hydrogen sulphide-water is an important one in industrial practice. For example, the dual temperature process for producing heavy water utilizes these two components. The process involves the transfer of deuterium atoms between the hydrogen sulphide and the water. Since the transfer rates are quite low, this process is carried out in tall tray towers. Therefore accurate phase and chemical equilibrium data are required for the optimum design and operation of these plants. Also, water and H<sub>2</sub>S are present in many natural hydrocarbon reservoirs, especially in Alberta. Hydrogen sulphide is highly toxic and, at low concentrations, has an offensive odour. Thus, H<sub>2</sub>S must be separated from the natural gas before the hydrocarbon can be delivered to the consumer. The process for stripping the H<sub>2</sub>S usually employs an aqueous-based solvent. Finally, the combination of H<sub>2</sub>S and water is highly corrosive. Catastrophic failure may result if the correct precautions are not taken when handling fluids containing H<sub>2</sub>S and water.

The system H<sub>2</sub>S-H<sub>2</sub>O is also of geochemical interest. Many mineral deposits are formed from the precipitation of solids from hot aqueous (hydrothermal) solutions. If these solutions are in contact with H<sub>2</sub>S, the process may result in the formation of sulphide minerals. Thus an understanding of the phase behavior in the system H<sub>2</sub>S-H<sub>2</sub>O is important for the accurate analysis of these mineral forming processes. Also, these hydrothermal reservoirs are becoming important sources of energy. The presence of H<sub>2</sub>S in these hot fluids poses a problem similar to that in the natural gas industry.

The system H<sub>2</sub>S-H<sub>2</sub>O displays many interesting features including the formation of a hydrate. The H<sub>2</sub>S-H<sub>2</sub>O hydrate persists to temperatures as high as 30°C. Unlike many simpler systems, this system has an interrupted critical locus. In the Scott and van Konynenburg (1970) classification of fluid phase behavior the system H<sub>2</sub>O-H<sub>2</sub>S is Type III. A discrepancy between the smoothed data of Selleck et al. (1952) and the observations of Vogel (1971) led to this investigation of the liquid-liquid-vapour (LLV) equilibrium. Measurements were made of the pressure and temperature along the LLV locus and the critical end point was established. Also, a few compositions for the co-existing phases were measured.

## Previous studies

The work of Selleck et al. (1951, 1952) is considered to be the benchmark for the system H<sub>2</sub>S-H<sub>2</sub>O. Selleck et al. (1952) present tables of smoothed values for the pressures and temperatures along several three-phase loci which were based on experimental measurements. They concluded that the LLV locus ends at the critical point of H<sub>2</sub>S. Note, that Reamer et al. (1950), from the same laboratory as Selleck et al., reported the critical point of hydrogen sulphide as 100.4°C and 9.00 MPa. Selleck et al. concluded that the LLV locus ended at 100.3°C and 9.00 MPa. Scheffer (1913) measured three-phase equilibrium for the system H<sub>2</sub>S-H<sub>2</sub>O in the region near the quadruple point at 29.5°C. He measured the LLV locus up to 33.2°C. In a study of the solubility of sour gas mixtures in water and brine, Vogel (1971) made some bubble point measurements for H<sub>2</sub>S in water. He observed the formation of a third phase at 104.4°C. Vogel coupled his observations with the smoothed data of Selleck et al. and incorrectly concluded that the system H<sub>2</sub>S-H<sub>2</sub>O violated the Gibbs phase rule. Vogel believed that a three-phase region existed on the pressure-temperature projection. The phase rule indicates that for a two-component mixture and three phases, there is only one degree of freedom. This corresponds to a curve on the P-T plane. A reinterpretation of the work of Vogel indicates that the three-phase point that he observed was at 104.4°C and 8.90 ± 0.17 MPa.

## Experimental work

Experiments were conducted in a flow-type cell as depicted in Figure 1. The cell is a high pressure liquid level gauge, designed for clear viewing of its contents. The volume of the cell is about 75 cm<sup>3</sup>. To ensure sufficient mass within the system, a vapour reservoir of about 250 cm<sup>3</sup> is attached to the top of the cell. To encourage equilibrium, vapour is drawn off the reservoir and circulated through the condensed phases. The recirculation pump is a magnetic piston pump, similar to the one devised by Ruska et al. (1970). The void volume of the pump is about 100 cm<sup>3</sup>. All parts in contact with the wet H<sub>2</sub>S are constructed from 316 stainless steel with the exception of the piston in the recirculation pump.

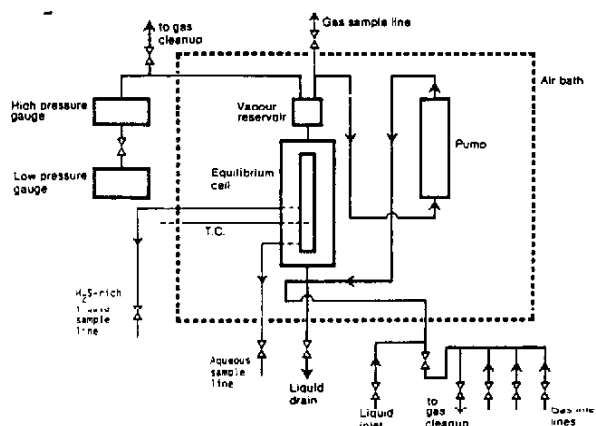


Figure 1 — Schematic diagram of apparatus.

Since it had to be ferromagnetic, the piston was made from Carpenter 450. The cell, reservoir and pump are housed in a constant temperature air bath. Pressure was measured using two Heise bourdon tube gauges (one 6.9 MPa [1000 psi] and the other 20.7 MPa [3000 psi]) and temperature was measured with an iron/constantan (Type J) thermocouple. The pressure gauges were accurate to 0.1% of full scale and were calibrated using a dead weight gauge. The thermocouple was calibrated against a platinum resistance thermometer. Output from the thermocouple was measured using a Hewlett-Packard Model #3450A digital voltmeter. The temperature of the air bath was controlled using a Hallikainen Thermostat controller. Since the pressure gauges were at ambient temperature, the lines leading to the gauges were wrapped with heating tape to prevent hydrate formation.

To perform a run, approximately 20 cm<sup>3</sup> of water was placed in the cell. Hydrogen sulphide was bubbled through the liquid for about half an hour to ensure that all of the air was flushed out of the system. Using only the pressure in the H<sub>2</sub>S bottle, pressures of about 1.7 MPa could be attained in the system. A spindle press was used to increase the amount of H<sub>2</sub>S in the system. The outside of the barrel of the press was packed with ice. Hydrogen sulphide was condensed into the barrel of the press. Thus liquid H<sub>2</sub>S would be pumped into the cell. Injection continued until there was a sufficient amount of H<sub>2</sub>S-rich liquid. To construct the pressure-temperature locus, the controller was set and the system was allowed about 24 h to attain equilibrium. As the critical point at the end of the three-phase locus was approached, longer times were allowed (to a maximum of 48 h). As the temperature changed the pressure tracked the LLV locus in much the same way a pure component would track its vapour pressure. Once equilibrium was reached, the pressure and temperature were recorded. The controller settings were then changed to obtain another point.

Compositions were measured by absorbing samples of each phase into a 1 mol/L NaOH solution. Samples of the H<sub>2</sub>S-rich phases were about 1 to 2 g and were absorbed in about 125 to 150 mL of caustic. A steel bomb was used to collect these samples. Aqueous phase samples were about 3 to 5 g and were absorbed in about 30 mL of caustic. The H<sub>2</sub>S content of the solution was determined by iodometric titrations (Kolthoff et al., 1969). The amount of water was obtained by measuring the mass of the sample and subtracting the amount of H<sub>2</sub>S. In order to keep the pressure drop to a minimum, the samples were withdrawn quite slowly. Thus, during sampling, the pressure never decreased by more than

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Experimental Data for the Three-Phase Locus for the System Water-Hydrogen Sulphide

Temperature (°C)	Three-Phase Pressure (MPa)	Vapour Pressure of H <sub>2</sub> S* (MPa)
29.4 (Q)	2.23	2.25
30.7	2.29	2.31
39.6	2.80	2.83
43.4	3.05	3.08
49.7	3.50	3.52
59.8	4.25	4.33
62.2	4.45	4.53
74.4	5.58	5.71
78.2	5.97	6.12
80.2	6.20	6.34
86.5	6.86	7.09
90.8	7.46	7.64
97.1	8.17	8.50
99.9	8.59	8.91
101.2	8.74	(-)
103.8	9.06	(-)
104.1	9.09	(-)
104.8	9.25	(-)
105.1	9.24	(-)
105.5	9.30	(-)
106.2 (K)	9.39	(-)

Q — quadruple point

K — three-phase critical end point

\* — Goodwin (1983) (above 100.3°C H<sub>2</sub>S is supercritical)

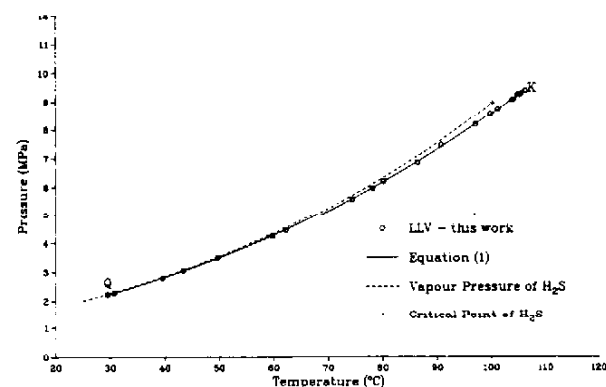


Figure 2 — The liquid-liquid-vapour locus for the system water-hydrogen sulphide (Q — hydrate-liquid-liquid-vapour quadruple point and K — three-phase critical end point).

0.07 MPa. Originally, compositions of the H<sub>2</sub>S-rich phases were to be measured using gas chromatography. This proved to be unreliable as reproducible results were not obtainable.

The hydrogen sulphide used was Matheson C.P. grade (purity of 99.6%). The H<sub>2</sub>S was used without further purification. Initially, the water was softened using an ion exchanger. It was then further purified in a laboratory still. The purity of the water was checked by measuring its electrical conductivity using an Industrial Instruments Inc. model 16B1 conductivity bridge and a Beckmann dip cell. The resistivity of the water was 4 MΩ · cm. Certified standard solutions of iodine and sodium thiosulphate, obtained from Fisher Scientific Co., were used for the iodometric titrations. The iodine was 0.1000 ± 0.0005 mol/L and the thiosulphate was 0.1000 ± 0.0002 mol/L.

## Results

The measured three-phase locus for the system  $H_2O-H_2S$  is presented in Table 1. The temperatures listed are accurate to about  $\pm 0.2^\circ C$  and the pressures to  $\pm 0.02$  MPa. The vapour pressure of  $H_2S$  is also listed because of its proximity to the three-phase locus for this system. The vapour pressure was obtained from the correlation of Goodwin (1983). This information is plotted on Figure 2. A critical locus extends from point K, the three-phase critical end point, to the critical point of  $H_2S$ , but that was not examined in this work. Point Q is the hydrate aqueous liquid  $H_2S$ -rich liquid-vapour quadruple point. Below this point LLV equilibrium does not exist (except for unstable supercooling). The data obtained in this laboratory were correlated with a Clausius-Clapeyron-type equation to obtain the following:

$$\ln P = 7.928 - 2156.9/T \dots\dots\dots (1)$$

where P is in MPa and T is in K. This equation fits the data with an average residual of 0.02 MPa and a maximum residual of 0.06 MPa. The maximum residual occurs at  $90.8^\circ C$ . The average absolute error was 0.28% and the maximum absolute error was 0.80% which also occurred at  $90.8^\circ C$ . Only the data obtained in this study were used to formulate Equation (1).

Equation (1) predicts the values obtained by Scheffer with a maximum error of 0.01 MPa. Between the quadruple point and about  $45^\circ C$ , there is essentially no difference between the smoothed values of Selleck et al. and Equation (1). For temperatures from  $45^\circ$  to about  $93^\circ C$ , the agreement is still quite good — an average error of 0.04 MPa and a maximum of 0.06 MPa. However, the smoothed values of Selleck et al. are at lower pressures than those predicted by Equation (1). Above  $90^\circ C$ , the deviations are as large as 0.42 MPa.

The compositions of the co-existing phases are listed in Table 2. The errors are estimated to be  $\pm 1$  mol% for the  $H_2S$ -rich phases and  $\pm 0.1$  mol% for the aqueous phase. Temperatures listed in this table are to the nearest degree Celsius. At the lowest two temperatures, the determination of the water content of the vapour is inaccurate. Hence the results are given as 99+ %  $H_2S$ .

At the lower temperatures, the aqueous phase is colourless to pale yellow in colour and the  $H_2S$ -rich phases are colourless. At approximately  $106.2^\circ C$  both the  $H_2S$ -rich liquid and the vapour phases become red-brown. This is the critical opalescence and indicative of the end point of the three-phase locus. At higher temperatures the  $H_2S$ -rich phase again becomes colourless. (Note, above the critical point there is only one  $H_2S$ -rich phase.) If one passes through the critical point rapidly (e.g. cooling the system by opening the door to the air bath) the  $H_2S$ -rich phases become opaque. This observation fixes the end point of the three-phase locus at  $106.2 \pm 0.2^\circ C$  and  $9.39 \pm 0.02$  MPa. This is approximately  $6^\circ C$  higher than reported by Selleck et al. (1951, 1952).

A few points were obtained along the hydrate- $H_2S$ -rich liquid-vapour and the hydrate-aqueous liquid-vapour loci. These points were measured in order to verify the location of the quadruple point. From this work, the quadruple point is estimated to be  $29.4 \pm 0.2^\circ C$  and  $2.23 \pm 0.02$  MPa which is in excellent agreement with the values of  $29.5^\circ C$  and 2.24 MPa found by Scheffer (1913). This apparatus was not suited for examining solid phases. Mixing was difficult as the solids plugged the recirculation pump and the lines connecting the

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Compositions of Co-existing Phases Along the LLV Locus

Temp. ( $^\circ C$ )	Aqueous Liquid	Mole Fraction $H_2S$	
		$H_2S$ -Rich Liquid	Vapour
40	0.0335	0.987	0.99+
60	0.0341	0.973	0.99+
80	0.0385	0.965	0.987
100	0.0440	0.951	0.975
105	0.0451	0.955	0.973

pump to the cell. Also, temperature control at near ambient conditions is very difficult and almost impossible at temperatures below about  $25^\circ C$ . In spite of the difficulties, the few values obtained were in good agreement with those found by Scheffer.

## Conclusions

New data are presented for the LLV equilibrium for the system  $H_2S-H_2O$ . The LLV locus is at slightly lower pressures than the vapour pressure of  $H_2S$ . It extends from the hydrate-aqueous liquid- $H_2S$ -rich liquid-vapour quadruple point ( $29.4^\circ C$  and 2.23 MPa) to a critical end point at  $106.2^\circ C$  and 9.39 MPa. The LLV curve extends to higher temperatures and pressures than given by Selleck et al.

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