

Phase Equilibrium in the System Water–Hydrogen Sulphide: Modelling the Phase Behavior with an Equation of State

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In the light of the information presented by Carroll and Mather (1989), a new interpretation is presented for the often-quoted, smoothed data of Selleck, Carmichael and Sage (1952) for the phase equilibrium in the system water–hydrogen sulphide. The data of Carroll and Mather show that the liquid–liquid–vapour locus extends to higher temperatures than believed by Selleck et al. Experimental data from several sources are correlated using the Stryjek–Vera (1986a) modification of the Peng–Robinson (1976) equation of state. It is demonstrated that the fit of the raw data via the equation of state is as good as the smoothing of Selleck et al.

À la lumière des données publiées par Carroll et Mather (1989), on présente une nouvelle interprétation des données ajustées souvent citées de Selleck, Carmichael et Sage (1952) pour l'équilibre de phase dans le système eau–hydrogène sulfuré. Les données de Carroll et Mather montrent que le point triple liquide–liquide–vapeur est valide à des températures plus élevées que ne le pensaient Selleck et al. Les données expérimentales issues de plusieurs sources sont corrélées à l'aide de la modification de Stryjek–Vera (1986a) de l'équation d'état de Peng–Robinson (1976). On démontre que le calage des données brutes par l'équation d'état est aussi valable que le lissage de Selleck et al.

Keywords: H₂O–H₂S phase equilibrium, V–L equilibrium, L–L equilibrium, L–L–V equilibrium.

Recent observations by Carroll and Mather (1989) for the liquid–liquid–vapour locus for hydrogen sulphide–water raised some questions about the fluid phase behavior for this system in general. This study re-evaluates the data in the literature and presents a new correlation for the fluid phase equilibria for this system. A new model is presented for the vapour–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE) and liquid–liquid–vapour equilibrium (LLVE) based on an equation of state.

Previous experimental studies

There have been many previous experimental investigations of the system hydrogen sulphide–water. The study of Selleck et al. (1951, 1952) is the benchmark study for this system. It was a comprehensive study which established some of the phase boundaries on the pressure–temperature diagram. Data in the 1952 paper were smoothed and extrapolated from the raw data which were presented in the 1951 supplementary publication. In their investigation of the vapour–liquid region, Selleck et al. examined the two phases separately. A variable volume cell was used to determine bubble points. A mixture of known composition and lean in H₂S was injected into the cell and compressed isothermally. A discontinuity in the derivative of volume with respect to pressure indicated a phase transition. A constant volume cell was used for direct measurement of the composition of a gas in equilibrium with an aqueous phase of unknown composition. Visual observation of the cell's contents was not possible with either of their autoclaves. Kozintseva (1965) measured phase equilibria from 160° to 330°C; partial pressures of H₂S were less than 210 kPa. In a study of the solubility of sour gas mixtures in water and brine, Vogel (1971) made some bubble-point measurements for H₂S in water at 104.4°C. Vogel obtained his break points in a manner similar to Selleck et al. Some of these points, however, were not bubble points but the transition from the vapour–liquid region to the liquid–liquid through the three-phase point. Lee and Mather (1972) measured the solubility of H₂S in water for eleven isotherms from 10° to 180°C. The pressures for these measurements were up to approximately 7 MPa or until a third phase was encountered depending on the temperature.

Gillespie et al. (1984) measured some vapour–liquid and liquid–liquid equilibria for this system as well. Their data were in the temperature range 37.8° to 315.6°C and at pressures up to 21 MPa. Carroll and Mather (1989) investigated the LLVE for this system from the quadruple point (29.4°C and 2.23 MPa) to the three-phase critical end point (106.2°C and 9.39 MPa).

There have also been several studies at low pressure. Wright and Maass (1932) determined the solubility of H₂S in water from 5° to 60°C at pressures up to 500 kPa. Clarke and Glew (1971) measured the solubilities of H₂S and D₂S in water and heavy water for temperatures from 0° to 50°C and pressures below 100 kPa.

The Peng–Robinson–Stryjek–Vera Equation

An equation of state which has been widely applied to petroleum systems (hydrocarbons and a few associated non-hydrocarbons such as CO₂, H₂S and N₂) was proposed by Peng and Robinson (1976). Unfortunately, this equation does not work well for water and other polar substances. Accurate prediction of the pure component vapour pressure is a prerequisite for accurate multicomponent VLE calculations. The original Peng–Robinson equation does not accurately predict the saturation pressure of water. Stryjek and Vera (1986a) modified the Peng–Robinson equation to make it more widely applicable. The Peng–Robinson–Stryjek–Vera (PRSV) equation is:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \quad (1)$$

$$a(T) = a(T_c) \cdot \alpha \quad (2)$$

$$a(T_c) = 0.45724 R^2 T_c^2 / P_c \quad (3)$$

$$\alpha = [1 + \kappa (1 - T_R^{1/2})]^2 \quad (4)$$

$$\kappa = \kappa_0 + \kappa_1 (1 + T_R^{1/2}) (0.7 - T_R) \quad (5)$$

TABLE 1
Parameters for the PRSV Equation of State

Comp	T_c (K)	P_c (kPa)	ω	κ_1	$\Sigma \Delta P/P /NP$	NP	Range
H ₂ O	647.3	22090.	0.344	-0.06635	0.21 %	36	0.44 < T_R < 0.98
H ₂ S	373.4	8960.	0.100	0.15981	0.56 %	16	0.56 < T_R < 0.97

$$\kappa = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.019654\omega^3 \dots \dots \dots (6)$$

$$b = 0.07780 RT_c/P_c \dots \dots \dots (7)$$

and κ_1 is an empirical parameter obtained by fitting the pure component vapour pressure. It was found to be uncorrelated with any pure component property, even for hydrocarbons. Hydrogen sulphide was not included in the list of substances given by Stryjek and Vera. The κ_1 for H₂S was found by fitting the vapour pressures given by Goodwin (1983). Table 1 summarizes the constants used in this study. The critical constants for water were taken from Keenan et al. (1978) and for H₂S from Goodwin. The last three columns of Table 1 indicate how well the PRSV equation predicts the vapour pressure of the pure components. The sixth column is the average absolute relative error of the predicted vapour pressure for NP points over the indicated temperature range. For water, the predicted vapour pressure was compared with the values of Keenan et al.

To apply an equation of state to a mixture a set of mixing rules is required. For a cubic equation like the PRSV equation the following rules are usually employed:

$$a = \frac{\Sigma \Sigma x_i x_j (a_i a_j)^{1/2} (1 - \delta_{ij})}{i j} \dots \dots \dots (8)$$

$$b = \Sigma x_i b_i \dots \dots \dots (9)$$

where δ_{ij} is a binary interaction parameter that is obtained from experimental vapour-liquid equilibrium data. These mixing rules have been successfully applied to petroleum systems.

Optimum interaction parameters were obtained for the system H₂S-H₂O by minimizing the error in the predicted bubble-point pressure. These interaction parameters are plotted on Figure 1. A weighted least squares regression was performed to obtain the following correlation:

$$\delta_{ij} = -0.4860 + 2.092 \times 10^{-3}T - 1.87 \times 10^{-6}T^2 \dots \dots \dots (10)$$

The weighting factor used was the number of experimental points for a given temperature. Unlike petroleum systems where the interaction parameter is nearly a constant for a given system, the interaction parameter for this system shows a strong temperature dependence. A more subtle effect is the composition dependence. Below 60°C there is a definite trend — the parameter from the Lee and Mather data is greater than that from Wright and Maass which in turn is greater than Clarke and Glew. This is the order of increasing H₂S concentration in the aqueous phase. Above 60°C, the scatter about the regression line is random and could probably be explained in terms of experimental error. Thus a more advanced mixing rule is required.

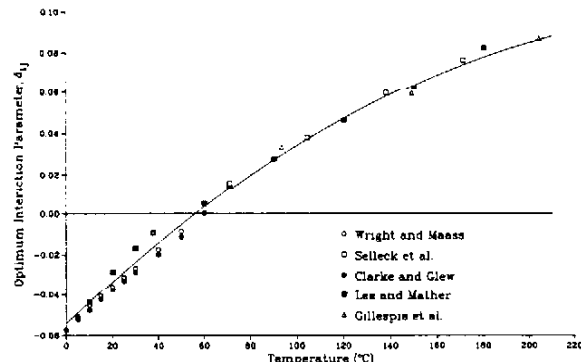


Figure 1 Optimum interaction parameters for the PRSV Equation with the original mixing rule.

A mixing rule was proposed by Stryjek and Vera (1986b) which incorporates a composition effect.

$$a = \frac{\Sigma \Sigma x_i x_j (a_i a_j)^{1/2} [1 - k_{ij} k_{ji} / (x_i k_{ij} + x_j k_{ji})]}{i j} \dots (11)$$

By analogy to the activity coefficient model, they called this a van Laar-type rule. Optimum interaction parameters were obtained from the raw data of Selleck et al. and Gillespie et al. and they are presented in Table 2, where component 1 is water. In this case both VLE and LLE data were considered. The optimization was conducted by minimizing the error for both the H₂S-rich and aqueous phases. A least squares regression yields

$$k_{12} = 0.819 - 0.00159T \dots \dots \dots (12)$$

$$k_{21} = -0.190 + 0.000605T \dots \dots \dots (13)$$

Unfortunately the parameters are a function of temperature. Also, the form of Equation (11) requires that k_{12} and k_{21} have the same sign. Thus Equations (12) and (13) are limited to the range 315 < T < 513 K (42° < t < 240°C).

Phase Behavior

The PRSV equation was used to correlate VLE, LLE and LLVE for this system. There have been other attempts to correlate the phase behavior of the system H₂O-H₂S using an equation of state. Two noteworthy examples are Evelein et al. (1976) and Peng and Robinson (1980). Both of these studies were impaired by their reliance on the smoothed data of Selleck et al. This work is not dependent on the interpretation of Selleck et al. and this model incorporates data from other sources as well.

First consider the 104.4°C isotherm. Figure 2 shows the pressure-composition diagram at this temperature. Included on this plot are the raw data of Selleck et al., the data of Vogel, the smoothed values of Selleck et al. and the prediction based on the PRSV equation with the van Laar-type

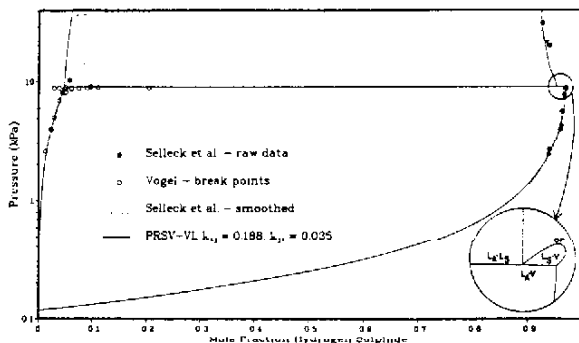


Figure 2 — Pressure composition diagram at 104.4°C.

TABLE 2
Optimum Interaction Parameters

Temp. (°C)	Original Rule δ_{12}	van Laar-type k_{12}	van Laar-type k_{21}	REF
71.1	0.0159	0.301	0.017	(1)
71.1	—	0.300	0.017	(2)
93.3	0.0333	0.226	0.032	(2)
98.9	—	0.206	0.035	(?)
100.4	—	0.211	0.037	(2)
104.4	0.0379	0.188	0.035	(1)
137.8	0.0598	0.155	0.035	(1)
148.9	0.0596	0.153	0.059	(2)
171.1	0.0767	0.102	0.074	(1)
204.4	0.0872	0.082	0.099	(2)

- (1) Selleck et al. (1951).
(2) Gillespie et al. (1984).

mixing rule using the optimum interaction parameters listed in Table 2. The insert on Figure 2 shows schematically the equilibria in the region of the binary critical point. The insert is not drawn to scale. The smoothing of Selleck et al. indicates they did not believe that this three-phase point existed. Vogel observed the formation of three phases at this temperature, but misinterpreted his results. The work of Carroll and Mather confirms the existence of the LLV point at this temperature. The fit of the raw data of Selleck et al. for this temperature using the PRSV equation is quite good with the exception of one point. Selleck et al. indicated that there was a bubble point at 5.723 mol% H_2S and 10.34 MPa which is inconsistent with the observations of Carroll and Mather. Figure 3 shows the pressure-volume data (converted to S.I.) from which Selleck et al. concluded there was a bubble point. From this figure it is clear that the actual phase transition point is at 9.23 MPa; numerical approximations of the derivative of volume with respect to pressure substantiate this conclusion. This transition is not a bubble point as Selleck et al. believed, but the change from the vapour-liquid region to the liquid-liquid region. An expected plateau for the LLVE point is probably too narrow to be observed on the scale of their experiments. From Carroll and Mather, the three-phase pressure at 104.4°C is estimated to be 9.16 MPa. This is in reasonable agreement with the value obtained from Figure 3. Thus, all of the raw data of Selleck et al. at 104.4°C fit the interpretation presented here. The major consequence of this observation is that the extrapolated aqueous phase compositions of Selleck et al. are too rich in H_2S by perhaps a factor of three.

Figures 4 and 5 show the 71.1°, 137.8° and 171.1°C isotherms. These are the pressure-composition diagrams for these temperatures, but they have been separated for clarity.

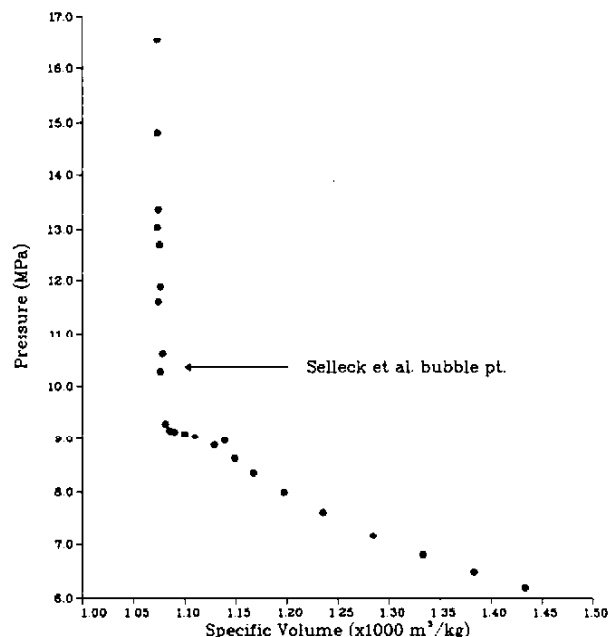


Figure 3 — Pressure-volume measurements of Selleck et al. for 5.723 mol% hydrogen sulphide at 104.4°C.

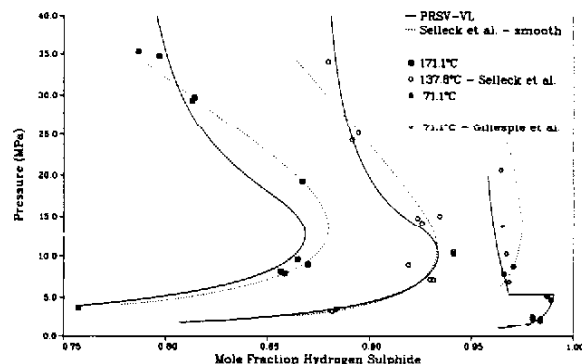


Figure 4 — Hydrogen sulphide-rich phase compositions at 71.1°, 137.8° and 171.1°C.

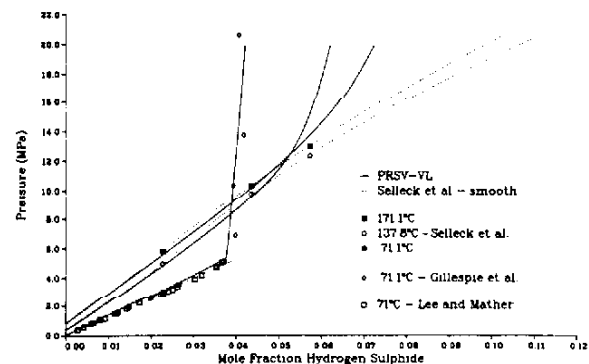


Figure 5 — Aqueous phase compositions at 71.1°, 137.8° and 171.1°C.

Aqueous phase compositions are on Figure 5 and H_2S -rich on Figure 4. Although presented separately, these curves were generated simultaneously. Predictions using the PRSV equation were performed using the optimum interaction parameters listed in Table 2 and not the correlations. Included on these figures are the LLE data of Gillespie et al. for the 71.1°C isotherm and the solubility data of Lee and Mather

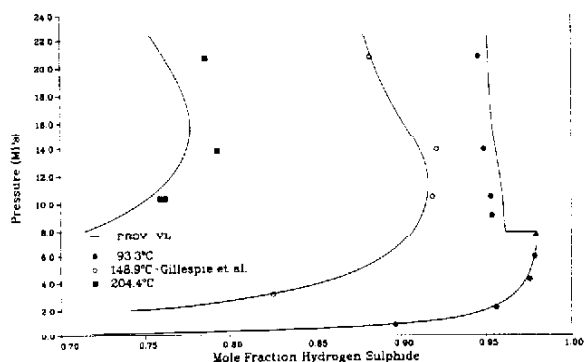


Figure 6 — Hydrogen sulphide-rich phase compositions at 93.3°, 148.9° and 204.4°C.

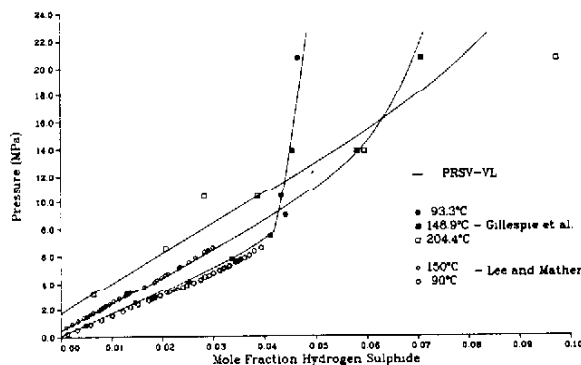


Figure 7 — Aqueous phase compositions at 93.3°, 148.9° and 204.4°C.

at 71°C. At 71.1°C Selleck et al. measured only a single bubble point. In general, the equation of state fits the raw data as well as the smoothing of Selleck et al., but the extrapolations of the aqueous phase compositions to higher pressures deviate significantly. One final note about Figure 4. Selleck et al. state that their composition measurements are accurate to ± 0.2 mol%. The diameter of the points on Figure 4 is about 0.25 mol%. Clearly their measurements are not as accurate as they claim.

Figures 6 and 7 show the PRSV predictions for the 93.3°, 148.9° and 204.4°C isotherms along with the data of Gillespie et al. Once again, the aqueous and H₂S-rich phases are presented separately. Also shown on the aqueous phase plot are the 90° and 150°C isotherms of Lee and Mather. The fit of the lower two temperatures is excellent. Also, the agreement between the Lee and Mather data and the prediction is quite good considering that the interaction parameters were based solely on the Gillespie et al. data for these temperatures. The fit of the 204.4°C is not quite as good. This can partially be explained by the scatter in the experimental data. At 10.34 MPa Gillespie et al. report bubble points at both 3.87 and 2.83 mol% H₂S — a significant difference.

Predictions for the LLE are quantitatively not as good as the VLE, but they provide a good qualitative interpretation. The LLE predictions show a weak pressure dependence, unlike the smoothing of Selleck et al. This is true for the temperatures which are not shown on the previously mentioned figures.

Figure 8 shows predictions of the three-phase locus based on the PRSV equation. Two mixing rules are shown and the optimum interaction parameters were taken from the correlations [Equations (10), (12) and (13)]. A small critical locus would extend from the critical point of pure H₂S to the end

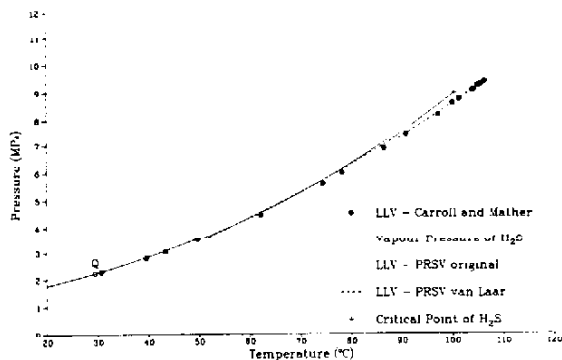


Figure 8 — Liquid-liquid-vapour locus for the system water-hydrogen sulphide (*Q* - hydrate-liquid-liquid-vapour quadruple point).

of the LLV locus. The point *Q* is the hydrate-liquid-liquid-vapour quadruple point at 29.4°C and 2.24 MPa. Using the original mixing rule, the predicted three-phase locus is at a lower pressure and extends to a higher temperature than the observed values. The agreement between the experiment and the van Laar-type rule is excellent, except that the prediction ends at about 104.5°C, slightly lower than the observed value of 106.2°C.

Conclusions

An equation of state (PRSV) was used to correlate fluid phase behavior in the system H₂S-H₂O. Data from many sources, including the raw data of Selleck et al. were examined. It was demonstrated that the smoothing and extrapolations of Selleck et al. are in error and in particular, the aqueous phase extrapolations are incorrect by up to a factor of three. Also, a new picture of the 104.4°C isotherm is presented which is consistent with the raw data of Selleck et al. The experimental data show a three-phase point at this temperature which their smoothing/extrapolations indicated did not exist.

Also, some of the advantages and limitations of the equation of state approach are demonstrated. The simple quadratic and linear mixing rules which have been successfully applied to hydrocarbon systems are not as useful for aqueous systems. Also, some of the more advanced mixing rules must be applied with caution.

Nomenclature

- a* = parameter in PRSV equation, MPa · m⁶/kmol²
- b* = parameter in PRSV equation, m³/kmol
- CP* = critical point
- k_{ij}* = interaction parameter in van Laar-type mixing rule
- L* = liquid phase
- NP* = number of points
- P* = pressure, MPa
- R* = gas constant, $R = 0.008\ 314$ MPa · m³/(kmol · K)
- T* = temperature, K
- V* = vapour phase
- v* = specific volume, m³/kmol
- x* = mole fraction

Greek:

- α = parameter in PRSV equation
- δ_{ij} = interaction parameter in original mixing rule

- κ = parameter in PRSV equation
 κ_0 = parameter in PRSV equation
 κ_1 = parameter in PRSV equation
 ω = acentric factor

Subscripts:

- A* = aqueous
c = critical
i = component *i*
j = component *j*
R = reduced
S = H₂S-rich

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