

The solubility of hydrogen sulphide in water from 0 to 90°C and pressures to 1 MPa

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Abstract—There exists some controversy about the solubility of hydrogen sulphide in water—notably the effect of pressure on the solubility. This paper reviews the experimental data for this system for temperatures between 0 and 90°C and for pressures up to 1 MPa. A simple model is used to correlate all of the data, including data that had previously been rejected as inaccurate. It is demonstrated that observed deviations from the strict Henry's law can be explained by the non-ideality of the vapour phase. Also, non-idealities in the liquid phase are negligible for the stated range of temperature and pressure.

INTRODUCTION

SOME CONTROVERSY exists about the solubility of hydrogen sulphide in water and the effect of pressure on the solubility. This paper examines the available data for this system and presents a model which can be applied to all of the data for pressures up to 1 MPa.

Many of the early low pressure solubility experiments assumed that the strict Henry's law could be applied. That is, at constant temperature, the solubility is proportional to the pressure. Data were collected at near atmospheric pressure and were thus corrected to 101.3 kPa (1 atm). WRIGHT and MAASS (1932a,b) observed that the strict Henry's law does not apply to hydrogen sulphide in water, even at relatively low pressures. In this paper, it is shown that the observed deviations can be explained by the non-idealities of the vapour phase for pressures up to 1 MPa. Also, up to about 125 kPa the strict Henry's law does apply to within an error of about 1%. Therefore, the data of the earlier investigators should be re-examined.

PREVIOUS EXPERIMENTAL WORK

The following investigators report the solubility of hydrogen sulphide in water at 101.3 kPa: WINKLER (1906) from 0 to 90°C; KENDALL and ANDREWS (1921) at 25°C; KISS *et al.* (1937) at 0.05, 12.5 and 25°C. All of these studies measured the solubility at near atmospheric pressure and the reported values were corrected to atmospheric pressure.

HARKNESS and KELMAN (1967) measured the solubility at 30°C. GERRARD (1972) obtained the solubility at 0, 10 and 20°C. DOUABUL and RILEY (1979) measured it from 0 to 30°C. These values were obtained at 101.3 kPa and were not adjusted.

The following studies report the solubility as a function of both temperature and pressure. WRIGHT and MAASS (1932a,b) made measurements from 5 to 60°C at pressures up to about 500 kPa. CLARKE and GLEW (1971) obtained vapour-liquid equilibrium data from 0 to 50°C at pressures to 100 kPa. LEE and MATHER (1977) measured the solubility from 10 to 180°C and pressures up to 7 MPa or until a third phase was encountered. Much of their data is at pressures below 1 MPa.

Two other important studies of this system were made by SELLECK *et al.* (1951, 1952) and GILLESPIE *et al.* (1984). Un-

fortunately, most of these data are at pressures outside the area of interest in this study. DRUMMOND (1981) obtained some mass temperature pressure measurements for this system; temperatures ranged from 30 to 355°C and pressures up to 20 MPa. KOZINTSEVA (1964) measured the solubility of H₂S at 160 to 330°C and partial pressures of H₂S were less than 210 kPa. Most of the data from these two studies are outside the range of temperature and pressure of this work.

THE MODEL

The condition for phase equilibrium in a closed system is that each component must have the same chemical potential in all phases. Equivalently, by definition, the fugacities of each component must also be the same in all phases. From this starting point, one approach to vapour-liquid equilibrium is the so-called two-fluid model, because different standard states are used for the vapour and liquid phases. The equality of the fugacities may be expressed in terms of activity and fugacity coefficients:

$$\gamma_i x_i f_i^0 = y_i P \hat{\phi}_i \quad [i = 1, 2] \quad (1)$$

where γ_i is the activity coefficient, x_i is the mole fraction of component i in the liquid, f_i^0 is the liquid phase reference fugacity, y_i is the mole fraction of i in the vapour, P is the total pressure, and $\hat{\phi}_i$ is the vapour phase fugacity coefficient. For a gas in a solvent, it is convenient to use the modified Henry's law for the solute (reference fugacity based on Henry's constant) and the modified Raoult's law for the solvent (reference fugacity based on the pure component vapour pressure). Thus for the solvent, Eqn. (1) becomes:

$$\gamma_1 x_1 P_1^0 \exp(v_1 [P - P_1^0]/RT) = y_1 P \hat{\phi}_1 \quad (2)$$

where P_1^0 is the vapour pressure of the pure solvent and the exponential term is the Poynting factor; v_1 is the molar volume of the solvent. R is the universal gas constant and T is the absolute temperature. The Poynting term is the effect of pressure on the reference fugacity. For the solute:

$$\gamma_2 x_2 H_{21} \exp(\bar{v}_2^\infty [P - P_1^0]/RT) = y_2 P \hat{\phi}_2 \quad (3)$$

where H_{21} is the Henry's constant and \bar{v}_2^∞ is the partial molar volume of the solute at infinite dilution. Here again, the exponential term is the Poynting factor. In the derivation of

Table 1 Henry's Constants for Hydrogen Sulphide in Water (MPa/mol frac)

Temp (°C)	Optimum Values	Correlations		
		Equation (6)	CLARKE and GLEW	LEE and MATHER
0	26.517	26.706	26.668	29.130
5	31.433	31.385	31.467	33.438
10	36.878	36.546	36.694	38.102
15	42.278	42.319	42.319	43.113
20	48.478	48.243	48.309	48.461
25	54.745	54.708	54.622	54.129
30	60.000	61.510	61.212	60.097
40	75.574	75.859	75.020	72.834
50	90.398	90.565	89.312	86.443
60	104.972	104.771	103.668	100.651
71	119.338	118.708	119.070*	116.616
90	134.911	135.327	143.514*	143.834

* - extrapolated

Eqns. (2) and (3) it is assumed that v_1 and \bar{v}_2^g are independent of pressure. This method for vapour-liquid equilibrium uses the unsymmetric convention for activity coefficients. Thus, in the limit as x_1 approaches unity (pure solvent), both γ_1 and γ_2 approach one.

An analysis of the data for hydrogen sulphide in water over a wide range of temperature and pressure shows that, for pressures less than 1 MPa and temperatures between 0 and 90°C, the activity coefficients and Poynting factors are unity (or at least the product of the two is unity). Thus Eqns. (2) and (3) reduce to:

$$x_1 P_1^0 = y_1 P \hat{\phi}_1 \quad (4)$$

$$x_2 H_{21} = y_2 P \hat{\phi}_2 \quad (5)$$

If it is further assumed that $\hat{\phi}_1 = 1$ then Eqn. (4) reduces to the strict Raoult's law and Eqn. (5) to the strict Henry's law.

In this work, Eqns. (4) and (5) were used along with the following parameters. The vapour pressure of water is taken from KEENAN *et al.* (1978). Fugacity coefficients of the vapour phase are calculated using the REDLICH and KWONG (1949) equation of state. The mixing rules used are those proposed by REDLICH and KWONG (1949) and do not include interaction parameters. Critical constants, required for the equa-

tion of state, were taken from KEENAN *et al.* (1978) for water and from GOODWIN (1983) for hydrogen sulphide. New values for the Henry's constants were obtained by minimizing the deviations of the predicted solubilities from the experimental values. A single Henry's constant was calculated at each temperature by using the combined data of WRIGHT and MAASS (1932a,b); CLARKE and GLEW (1971); and LEE and MATHER (1977). These Henry's constants, called the optimum values, are listed in Table 1 and are shown graphically on Fig. 1. A least-squares regression yields the following correlation:

$$\ln H_{21} = -3.3747 + 0.072437T - 1.10765$$

$$\times 10^{-4} T^2 - 1549.159/T + 0.144237 \ln T \quad (6)$$

where T is in K and H_{21} is in MPa/mol frac. The correlation fits the optimum values to an average error of 0.43% and a maximum error of 1.03%. The form of the correlation used is based on the assumption that the heat capacity is a quadratic function of temperature. It is an extended form of the expression used by CLARKE and GLEW (1971). For comparison purposes, Henry's constants calculated from the correlations of CLARKE and GLEW (1971) and LEE and MATHER (1977) are also given in Table 1. In the results presented later in this paper, the calculations were performed using the optimum values and not the correlation except where noted. This prevents an error due to the correlation from entering the calculation. Equation (6) is provided for interpolation purposes.

The beauty of this model is its simplicity. Non-idealities in the liquid phase are neglected. For the vapour phase, the non-idealities are modelled using a simple equation of state. The justification for these approximations is the excellent fit of experimental data from three independent sources. A summary of the equations used in this study is presented in the Appendix.

In this study, the ionization of H_2S in the aqueous phase has been neglected. The ionization constant for the first dissociation of H_2S is $3.9 \cdot 10^{-8}$ at 0°C and $3.0 \cdot 10^{-7}$ at 100°C and is an increasing function of temperature over the indi-

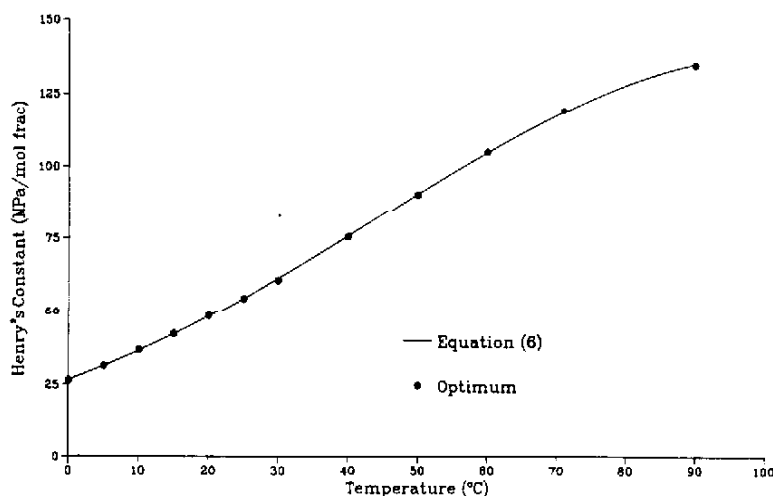


FIG. 1. Henry's constants for hydrogen sulphide in water.

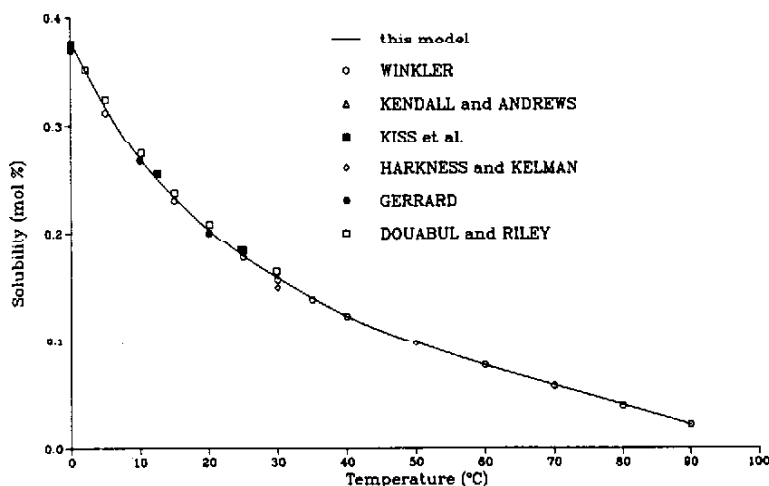


FIG. 2. The solubility of hydrogen sulphide in water at 0.1013 MPa (1 atm).

cated range (BARBERO *et al.*, 1982). MYERS (1986) reviewed the literature and concluded that $1 \cdot 10^{-19}$ is the "best" value for the second ionization constant at 25°C. There is, however, some controversy about its exact value; but, it is exceedingly small. Thus, the assumption that all of the H₂S in the aqueous phase is in the molecular form is a good one.

EQUILIBRIUM CALCULATIONS

The above model was used to calculate the vapour-liquid equilibrium for the system H₂O-H₂S from 0 to 90°C and pressures to 1 MPa. The calculation procedure used is summarized in the Appendix.

Solubility

The predicted solubilities at atmospheric pressure are plotted on Fig. 2 along with experimental data from several sources. Most of the data lie within 3% of the prediction. An exception is the point of HARKNESS and KELMAN (1967), which deviates by 5.7%. The value obtained by Harkness and Kelman is significantly different from the 30°C point of WINKLER (1906) as well. DOUABUL and RILEY (1979) compared their data with previously published values. They state that their solubilities agree to within 0.7%, but their values were consistently larger than the values of the other researchers. They did not do a detailed comparison with the data of WINKLER (1906) stating that Winkler's data were "mainly of historical interest." Deviations between the data of DOUABUL and RILEY (1979) and this model are about 1 to 4%. Also, this model predicts solubilities lower than reported by Douabul and Riley. It is important to note that none of the experimental points shown on Fig. 2 was used to calculate the optimum Henry's constants. Table 2 lists the solubilities at atmospheric pressure from several sources. The experimental values are compared with those calculated in this work.

Figure 3 shows the calculated aqueous phase compositions from 0 to 90°C for twelve isotherms. Included on this plot are the experimental data of WRIGHT and MAASS (1932a,b);

CLARKE and GLEW (1971); and LEE and MATHER (1977). The agreement among the three sets of data is very good. Also, the model presented is a good fit of the data. The broken line on this figure is the hydrate-aqueous liquid-vapour locus and is estimated from SELLECK *et al.* (1952).

Vapour phase composition

The literature contains few data for the vapour compositions for this system. CLARKE and GLEW (1971) report com-

Table 2 The Solubility of Hydrogen Sulphide in Water at Atmospheric Pressure From Various Sources

Temp (°C)	Solubility (mol %)							
	Calculation		Experimental Values					
	(A)	(B)	(1)	(2)	(3)	(4)	(5)	(6)
0.0	0.376	0.374	0.368	—	0.376	—	0.371	—
0.05	—	0.373	—	—	—	—	—	—
2.10	—	0.348	—	—	—	—	—	0.351
5.0	0.317	0.317	0.312	—	—	—	—	—
5.05	—	0.317	—	—	—	—	—	0.324
10.0	0.269	0.272	0.267	—	—	—	—	0.267
10.19	—	0.270	—	—	—	—	—	0.274
12.5	—	0.252	—	—	0.255	—	—	—
15.0	0.233	0.234	0.230	—	—	—	—	—
15.04	—	0.234	—	—	—	—	—	0.237
20.0	0.203	0.204	0.201	—	—	—	0.200	—
20.10	—	0.203	—	—	—	—	—	0.208
24.72	—	0.179	—	—	—	—	—	0.184
25.0	0.178	0.178	0.177	0.184	0.183	—	—	—
29.82	—	0.157	—	—	—	—	—	0.154
30.0	0.158	0.157	0.156	—	—	0.149	—	—
35.0	—	0.139	0.138	—	—	—	—	—
40.0	0.123	0.123	0.123	—	—	—	—	—
50.0	0.096	0.096	0.096	—	—	—	—	—
60.0	0.077	0.077	0.077	—	—	—	—	—
70.0	—	0.059	0.058	—	—	—	—	—
71.0	0.057	0.058	—	—	—	—	—	—
80.0	—	0.042	0.040	—	—	—	—	—
90.0	0.023	0.023	0.023	—	—	—	—	—

(A) Optimum Henry's Constants
(B) Henry's Constants From Equation (6)

(1) WINKLER (2) KENDALL and ANDREWS (3) KISS *et al.*
(4) HARKNESS and KELMAN (5) GERRARD (6) DOUABUL and RILEY

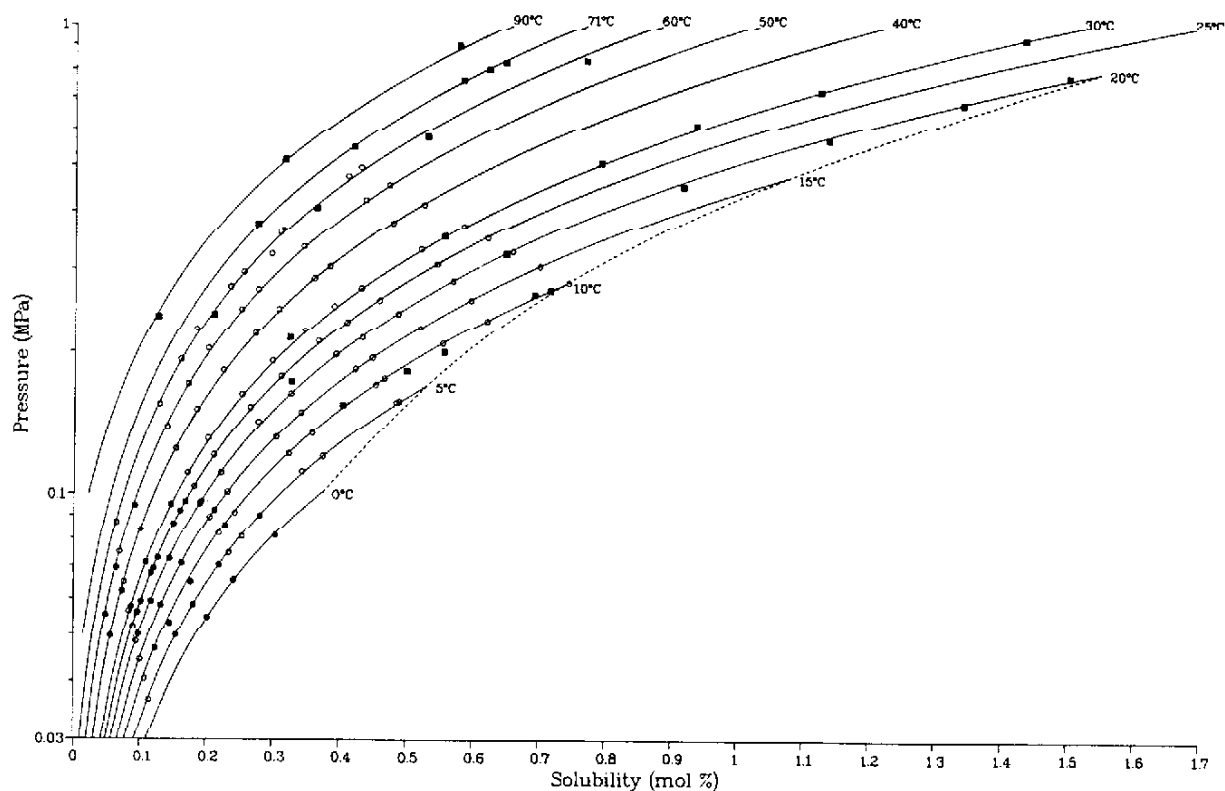


FIG. 3. The effect of temperature and pressure on the solubility of hydrogen sulphide in water: ○ WRIGHT and MAASS (1932a,b), ● CLARKE and GLEW (1971) and ■ LEE and MATHER (1977).

positions up to 100 kPa. SELLECK *et al.* (1951, 1952) and GILLESPIE *et al.* (1984) also report a few compositions, but most of these are at pressures above 1 MPa. WRIGHT and MAASS (1932a,b) give vapour phase compositions, but these were obtained by assuming that the partial pressure of water equals its vapour pressure.

Figure 4 shows the water content of the vapour at pressures below 100 kPa. The points on this plot are the data of CLARKE and GLEW (1971). Note, at these low pressures, the partial pressure of water is very nearly equal to its vapour pressure, since the fugacity coefficients are near unity at these pressures. Figure 5 shows the vapour compositions at higher pressures

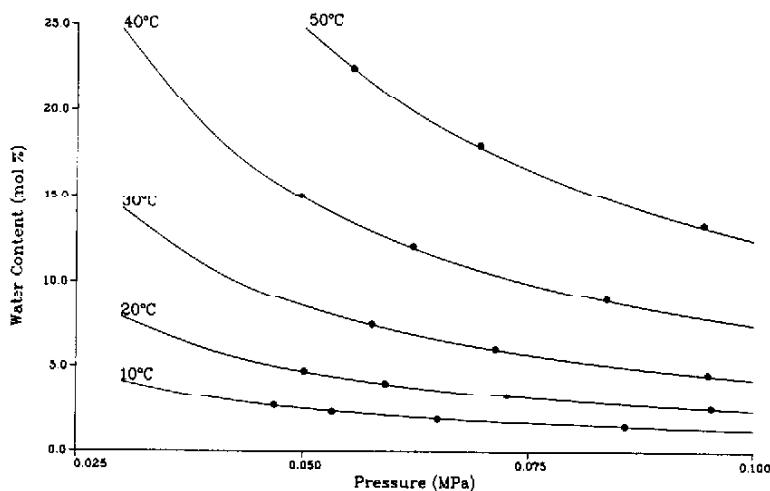


FIG. 4. Water content of the vapour at pressures below 0.1 MPa. Data from CLARKE and GLEW (1971).

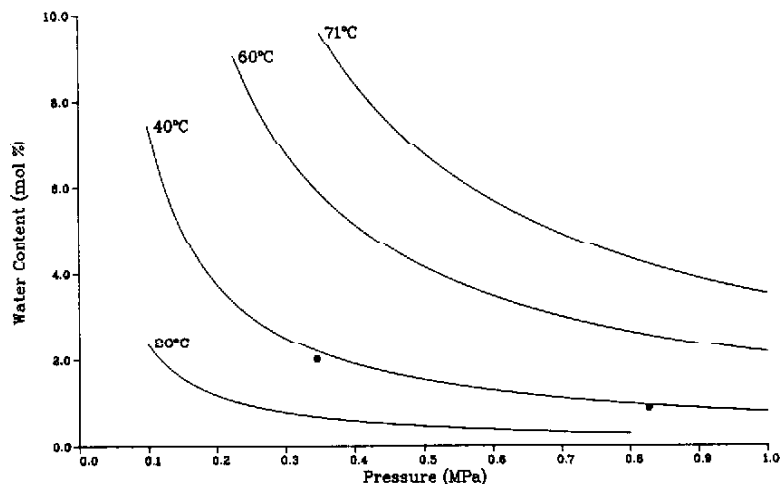


FIG. 5. Water content of the vapour at pressures below 1.0 MPa. Data from GILLESPIE *et al.* (1984) at 37.8°C.

as predicted by the model presented earlier. The points on this graph are from GILLESPIE *et al.* (1984) at 37.8°C.

Figure 6 compares the vapour compositions predicted by the model with the assumption of Raoult's law for three isotherms. At atmospheric pressure, the difference is only about 1%. At 0.5 MPa the deviations have increased to about 5% and at 1 MPa they are about 10%. This observation is true for all temperatures.

Figure 7 shows the fugacity coefficients for the hydrogen sulphide in the vapour as predicted by the REDLICH-KWONG (1949) equation. The compositions at which these fugacities were calculated are the equilibrium vapour compositions at the given temperature and pressure. Only above about 125 kPa do the fugacity coefficients become less than 0.99. Thus, at lower pressures the strict Henry's law is accurate to within 1%.

DISCUSSION

WILHELM *et al.* (1977) made a thorough review of the low pressure solubility of gases in water. In their review, they concluded that the data of WRIGHT and MAASS (1932a,b) and CLARKE and GLEW (1971) were the most reliable for hydrogen sulphide. Many other sets of data were rejected. Wright and Maass observed that the system water-hydrogen sulphide did not obey the strict Henry's law. However, this paper shows that at and below atmospheric pressure, this system does obey the strict Henry's law. Thus, the older data may indeed be of some value. For example, some of the data of WINKLER (1906) are at temperatures where no other data exist. Above about 125 kPa, the fugacity coefficients deviate significantly from unity. Their inclusion in the Henry's law model can adequately reproduce the solubility up to 1 MPa.

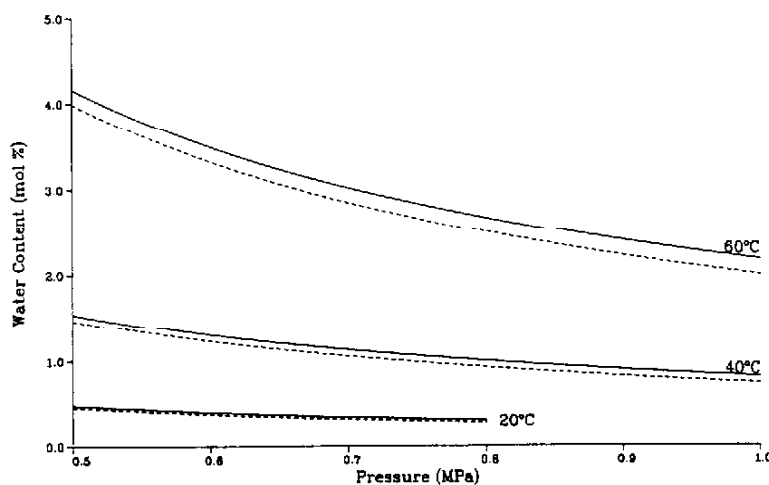


FIG. 6. A comparison between this model (solid line) and the simple Raoult's law (broken line) for the vapour compositions.

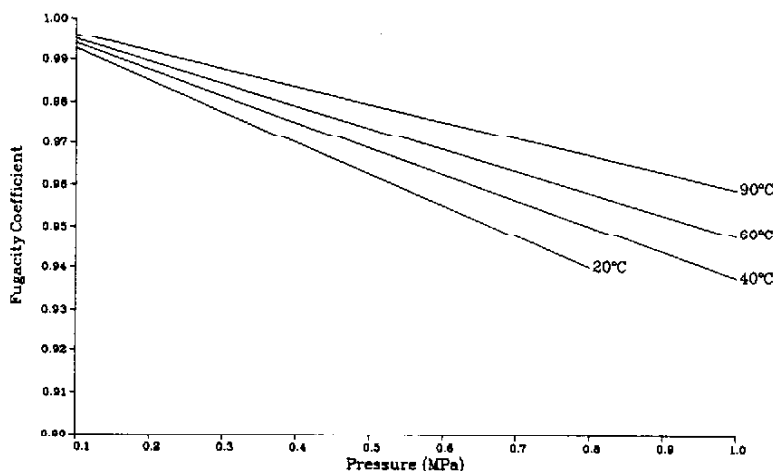


FIG. 7. Fugacity coefficients of hydrogen sulphide as predicted by the REDLICH-KWONG equation of state.

Thus, the deviations observed by WRIGHT and MAASS (1932a,b) can be accounted for by the vapour phase non-idealities.

It is ironic that Wright and Maass observed deviations from Henry's law, but assumed Raoult's law for the vapour. Deviations from both of these limiting laws can be explained by the same effect—non-ideality of the vapour phase.

At pressures above 1 MPa, the activity coefficients and the Poynting terms deviate significantly from unity. The Poynting factor is an increasing function of pressure and for this system the activity coefficients are a decreasing function. This compensating effect is the reason the Poynting term and the activity coefficients tend to cancel at lower pressures. Thus, to extend the model to higher pressures, some model for the effect of composition on the activity coefficients must be included as well as the Poynting correction.

New values for the Henry's constants are presented. These values were obtained from an optimum fit of the solubility data from three independent sources and adequately model solubilities from additional sources.

ADDENDUM

While this paper was in the review process, the work of BARRETT *et al.* (1988) was published. They measured the solubility of H_2S in water and NaCl solutions at about 25, 60, 80 and 95°C at 101.3 kPa. Figure 8 shows their data along with the prediction from the new model. The agreement between the experimental data and the prediction is quite good. Also shown on this plot is the correlation of BARRETT *et al.* (1988); although they did not collect data at 10°C, they extrapolated their correlation to that temperature. From Fig. 8 it is clear that this extrapolation is in error.

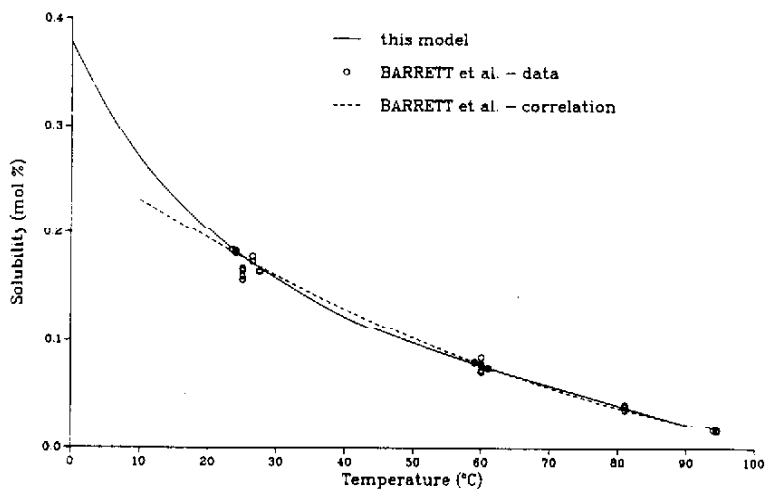


FIG. 8. A comparison between this model (solid line) and the work of BARRETT *et al.* (1988).

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APPENDIX: SUMMARY OF EQUATIONS

The equations used to perform the calculations are briefly outlined here.

(1) Equality of fugacities:

$$x_1 P_1^0 = y_1 P \phi_1 \quad (4)$$

$$x_2 H_{21} = y_2 P \phi_2 \quad (5)$$

(2) Mass balance:

$$x_1 + x_2 = 1 \quad (A.1)$$

$$y_1 + y_2 = 1 \quad (A.2)$$

(3) Vapour pressure of water (from KEENAN et al., 1978):

$$P_1^0/P_c = \exp[\tau 10^{-5}(t_c - t) \sum_{i=1}^8 F_i (0.65 - 0.01t)^{(i-1)}] \quad (A.3)$$

where:

$$\begin{aligned} t &= \text{temperature, } ^\circ\text{C} \\ P_1^0 &= \text{vapour pressure, MPa} \\ P_c &= 22.088 \text{ MPa} \\ t_c &= 374.136 ^\circ\text{C} \\ \tau &= 1000/T, T \text{ in K} \\ F_1 &= -741.9242 \\ F_2 &= -29.72100 \\ F_3 &= -11.55286 \\ F_4 &= -0.8685635 \\ F_5 &= 0.1094098 \\ F_6 &= 0.439993 \\ F_7 &= 0.2520658 \\ F_8 &= 0.05218684 \end{aligned}$$

(4) Henry's constants (from Table 1) or:

$$\ln H_{21} = -3.3747 + 0.072437T - 1.10765 \times 10^{-4}T^2 - 1549.159/T + 0.144237 \ln T \quad (6)$$

(5) Vapour phase fugacity coefficients (the REDLICH-KWONG equation of state):

$$P = \frac{RT}{v-b} - \frac{a}{\sqrt{T}v(v-b)} \quad (A.4)$$

in cubic form:

$$v^3 - (RT/P)v^2 - (b_m^2 + b_m RT/P - a_m/P\sqrt{T})v - b_m a_m/P\sqrt{T} = 0 \quad (A.5)$$

pure component:

$$a_i = 0.42748R^2 T_{ci}^{5/2} / P_{ci} \quad (A.6)$$

$$b_i = 0.08664RT_{ci} / P_{ci} \quad (A.7)$$

mixtures:

$$a_m = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2} \quad (A.8)$$

$$b_m = \sum_i y_i b_i \quad (A.9)$$

fugacity coefficient:

$$\ln \hat{\phi}_i = (b_i/b_m)(Pv/RT - 1) - \ln [P(v - b_m)/RT] \\ - (a/bRT^{3/2})[2(a_i/a_m)^{1/2} - b_i/b_m] \ln (1 + v/b_m) \quad (\text{A.10})$$

To solve these equations for the solubility of H₂S at a given temperature and pressure, an iterative technique is used. From the temperature, one obtains the Henry's constant from Table 1 or from Eqn. (6) and the vapour pressure of water from Eqn. (A.3). For the initial pass, the fugacity coefficients are set equal to unity. Equations (4), (5), (A.1) and (A.2) are solved simultaneously to obtain the compositions of the two phases. The calculated vapour compositions are

then used to calculate the fugacity coefficients from the REDLICH-KWONG equation of state (see the next paragraph). These fugacity coefficients are then used to update the compositions by substituting them into Eqns. (4) and (5). The iterations continue until the compositions calculated on successive iterations do not differ significantly (here, the program stops if the difference is less than 10⁻⁶).

To solve the REDLICH-KWONG equation for the specific volume given the temperature, pressure and composition, it is more convenient to use the cubic form (Eqn. (A.5)). The Newton-Raphson method is employed to solve for v given T , P and y_i . For the first iteration, the ideal gas law is assumed. Once v has been calculated, the fugacity coefficients are obtained from Eqn. (A.10).