

Accurate Thermodynamic Model for the Calculation of H₂S Solubility in Pure Water and Brines

Zhenhao Duan,^{*,†} Rui Sun,[†] Rong Liu,[‡] and Chen Zhu[§]

State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China, Faculty of Earth Sciences, China University of Geosciences, Wuhan, 430074, China, and Department of Geological Sciences, Indiana University, Bloomington, Indiana 47401

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A thermodynamic model calculating the solubility of hydrogen sulfide (H₂S) in pure water and in aqueous NaCl solutions (0–6 M, 273–500 K, 0–200 bar) is presented. The model is based on a specific particle interaction theory for the liquid phase and a highly accurate equation of state for the vapor phase. With this specific interaction approach, this model is able to predict H₂S solubility in other systems, such as H₂S–H₂O–Na₂SO₄, H₂S–H₂O–CaCl₂, H₂S–H₂O–KCl, and H₂S–seawater, without fitting experimental data from these systems. Comparison of the model predictions with experimental data indicates that the model is within or close to experimental uncertainty, which is about 7% in H₂S solubility. The model is programmed and can be downloaded from the website: www.geochem-model.org/programs.htm. Online calculation is also made available on the website: www.geochem-model.org/models.htm. The H₂S solubility model can be used together with numerical speciation-solubility modeling codes such as PHREEQC to calculate sulfide mineral solubility in H₂S saturated brines. An example calculation for galena solubility is given.

1. Introduction

H₂S is one of the most important gases in nature and has been found in natural gases^{1,2} and fluid inclusions.^{3,4} It is also one of the important components in flue gas generated from power plants or the coal gasification process.^{5,6} Sequestration of the gases into geological brine formation is one of the promising options for the reduction of greenhouse gases.⁷ Co-injection of both CO₂ and H₂S from flue gas may reduce the cost of gas sequestration. Therefore, accurate prediction of H₂S solubility in pure water or in aqueous NaCl solutions over a wide range of temperatures, pressures, and ionic strengths, especially where data do not exist or where the data are scattered, is important for the prediction of the capacity and fate of the injected gases, as well as for geochemical applications.

There have been many experimental studies on the solubility of H₂S in pure water and in aqueous NaCl solutions. Because the H₂S solutions are very corrosive, experimental measurements are generally limited to a relatively small range of temperatures, pressures, and/or ionic strengths, and the data are in general very scattered and difficult to use. In order to provide useful model that can best represent experimental data and reduce

experimental “noise”, theorists have tried different approaches to model the H₂S solubility in aqueous solutions. There have been quite a few models published.^{8–10,12–14} Among these, the model developed by Carroll and Mather⁸ is the most accurate to calculate the solubility of H₂S in pure water at low pressures ($P < 10$ bar). Carroll and Mather⁹ tried to predict the solubility of H₂S in pure water in a larger temperature range (from 313 to 513 K) and up to higher pressures from the Peng–Robinson–Stryjek–Vera equation of state (PRSV EOS). However, this model can only agree well with some of experimental data. It underestimates H₂S solubility at low pressure ($P < 10$ bar) and overestimates H₂S solubility at high temperatures ($T > 450$ K). Barta and Bradley¹⁰ published a semi-empirical model to predict H₂S solubility in aqueous NaCl solution from the Pitzer interaction model.¹¹ This model can only represent data at low partial pressures of H₂S ($P_{\text{H}_2\text{S}} < 30$ bar). Based on the equation of state developed by Carroll and Mather⁹ for an H₂S–H₂O system and the Pitzer theory, Suleimenov and Krupp¹² presented a model to predict the solubility of H₂S in NaCl solutions up to 593 K and 2.5 M NaCl, but it is not accurate in general. The geochemical code PHREEQC¹³ can calculate H₂S solubility at 1 atm, but it overestimates H₂S solubility at high pressure (> 10 bar) because it assumes that H₂S behaves as an idea gas. Another geochemical code SUPCRT92¹⁴ cannot calculate H₂S solubility

* Corresponding author. E-mail: duanzhenhao@yahoo.com.

[†] Chinese Academy of Sciences.

[‡] China University of Geosciences.

[§] Indiana University.

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directly but can calculate the equilibrium constant for H₂S solubility. However, the equilibrium constant predicted by SUPCRT92 will underestimate H₂S solubility at temperatures greater than 423 K.

In this article, we present a model for this system covering a large T – P – m range with high accuracy. The chemical potential of hydrogen sulfide in the vapor phase is calculated using the accurate equation of state (EOS) proposed by Duan et al.,¹⁵ and the chemical potential of H₂S in the liquid phase is modeled with a specific interaction approach.¹¹ The equations of the model will be discussed in the next section. To evaluate the experimental measurements, the available data are reviewed in section 3. We found that most of the major data sets are consistent. The parameters are evaluated from as many experimental data sets as possible. The model is compared with experimental data in section 4. In section 5, we try to predict H₂S solubility in non-NaCl solutions and in seawater. Finally, some conclusions are drawn.

2. Phenomenological Description of Gas Solubility

H₂S solubility in aqueous solutions is determined from the balance between its chemical potential in the liquid phase, $\mu_{\text{H}_2\text{S}}^{\text{l}}$, and that in the gas phase, $\mu_{\text{H}_2\text{S}}^{\text{v}}$. The potential can be written in terms of fugacity in the vapor phase and activity in the liquid phase as

$$\mu_{\text{H}_2\text{S}}^{\text{l}}(T, P, m) = \mu_{\text{H}_2\text{S}}^{\text{l}(0)}(T, P) + RT \ln a_{\text{H}_2\text{S}}(T, P, m) = \mu_{\text{H}_2\text{S}}^{\text{l}(0)}(T, P) + RT \ln m_{\text{H}_2\text{S}} + RT \ln \gamma_{\text{H}_2\text{S}}(T, P, m) \quad (1)$$

$$\mu_{\text{H}_2\text{S}}^{\text{v}}(T, P, y) = \mu_{\text{H}_2\text{S}}^{\text{v}(0)}(T) + RT \ln f_{\text{H}_2\text{S}}(T, P, y) = \mu_{\text{H}_2\text{S}}^{\text{v}(0)}(T) + RT \ln y_{\text{H}_2\text{S}} P + RT \ln \varphi_{\text{H}_2\text{S}}(T, P, y) \quad (2)$$

At equilibrium, $\mu_{\text{H}_2\text{S}}^{\text{l}} = \mu_{\text{H}_2\text{S}}^{\text{v}}$, and we obtain

$$\ln \frac{y_{\text{H}_2\text{S}} P}{m_{\text{H}_2\text{S}}} = \frac{\mu_{\text{H}_2\text{S}}^{\text{l}(0)}(T, P) - \mu_{\text{H}_2\text{S}}^{\text{v}(0)}(T)}{RT} - \ln \phi_{\text{H}_2\text{S}}(T, P, y) + \ln \gamma_{\text{H}_2\text{S}}(T, P, m) \quad (3)$$

The standard chemical potential of H₂S in liquid phase, $\mu_{\text{H}_2\text{S}}^{\text{l}(0)}$ is the chemical potential in hypothetically ideal solution of unit molality.¹⁶ The vapor phase standard chemical potential, $\mu_{\text{H}_2\text{S}}^{\text{v}(0)}$, is the hypothetically ideal gas chemical potential when the pressure is equal to 1 bar. In the parametrization, $\mu_{\text{H}_2\text{S}}^{\text{v}(0)}$, as a reference number, can be set to any number because only the difference between $\mu_{\text{H}_2\text{S}}^{\text{l}(0)}$ and $\mu_{\text{H}_2\text{S}}^{\text{v}(0)}$ is important. Here, we set it to zero for convenience. According to the equation of state of Duan et al.,¹⁵ the fugacity coefficient of H₂S in the vapor phase of H₂S–H₂O mixtures differs little from that of pure H₂S at temperatures between 273 and 500 K. Therefore, $\ln \phi_{\text{H}_2\text{S}}$ can be calculated from the EOS for pure H₂S (see Appendix A).¹⁵ Because there are few vapor composition measurements for the H₂S–H₂O–NaCl system in the temperature range of this study, we have to assume that the partial pressure of water in vapor mixture is the same as the saturation pressure of water. Consequently, $y_{\text{H}_2\text{S}}$ can be approximately calculated from

$$y_{\text{H}_2\text{S}} = (P - P_{\text{H}_2\text{O}})/P \quad (4)$$

where $P_{\text{H}_2\text{O}}$ is the saturation pressure of water, which is calculated from the empirical equation of Shibue.¹⁷ The above assumption may lead to errors (up to about 5%) for $\mu_{\text{H}_2\text{S}}^{\text{l}(0)}/RT$ and $\ln \gamma_{\text{H}_2\text{S}}$. However, these errors approximately cancel each other in our parametrization and the effect on the calculation of H₂S solubility is negligible. A virial expansion of excess Gibbs energy¹¹ is used to obtain $\ln \gamma_{\text{H}_2\text{S}}$,

$$\ln \gamma_{\text{H}_2\text{S}} = \sum_c 2\lambda_{\text{H}_2\text{S}-c} m_c + \sum_a 2\lambda_{\text{H}_2\text{S}-a} m_a + \sum_c \sum_a \zeta_{\text{H}_2\text{S}-a-c} m_c m_a \quad (5)$$

where λ and ζ are second-order and third-order interaction parameters, respectively, and c and a represent cations and anions, respectively. Substituting eq 5 in eq 3, we have

$$\ln \frac{y_{\text{H}_2\text{S}} P}{m_{\text{H}_2\text{S}}} = \frac{\mu_{\text{H}_2\text{S}}^{\text{l}(0)}}{RT} - \ln \phi_{\text{H}_2\text{S}} + \sum_c 2\lambda_{\text{H}_2\text{S}-c} m_c + \sum_a 2\lambda_{\text{H}_2\text{S}-a} m_a + \sum_c \sum_a \zeta_{\text{H}_2\text{S}-a-c} m_c m_a \quad (6)$$

In the above equation, λ , ζ , and the dimensionless standard chemical potential, $\mu_{\text{H}_2\text{S}}^{\text{l}(0)}/RT$, are dependent upon temperature and total pressure. Following Pitzer et al.,¹⁸ we select the following equation for the parameters:

$$\text{Par}(T, P) = c_1 + c_2 T + c_3/T + c_4 T^2 + c_5/(680 - T) + c_6 P + c_7 P/(680 - T) + c_8 P^2/T \quad (7)$$

Equations 6 and 7 form the basis of our parametrization for the model.

3. Review of Solubility Data of H₂S

H₂S solubility in pure water and in aqueous NaCl solutions has been measured for various temperatures, pressures, and ionic strengths (Table 1).^{12,19–32} The data of Winkler,¹⁹ Wright and

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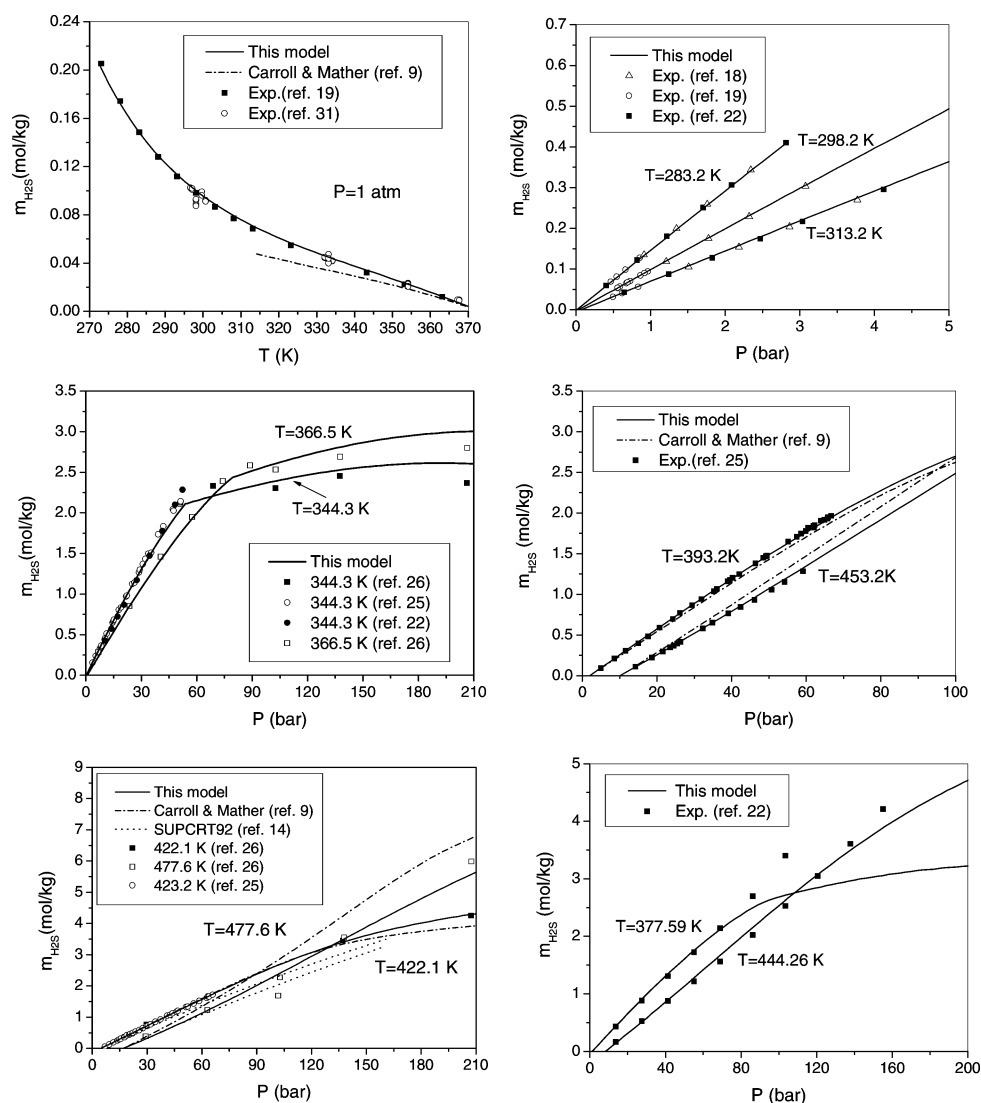


Figure 1. H_2S solubility in pure water (the prediction of this model vs experimental data and other models).

Table 1. Measurements of H_2S Solubility

authors	system	T ($^{\circ}\text{C}$)	P (bar)	N^a
Winkler ¹⁹	pure water	0–90	1.013	14
Wright and Maass ²⁰	pure water	5–60	0–5	34
Wright and Maass ²¹	pure water	5–60	0–5	34
Selleck et al. ²²	pure water	37–170	6–210	50
Kozintseva ²³	pure water	160–330	7–140	14
Clarke and Glew ²⁴	pure water	0–50	0–1	36
Lee and Mather ²⁵	pure water	10–180	1–70	355
Gillespie et al. ²⁶	pure water	38–204	10–210	44
Kapustinsky & Anvaer ²⁷	NaCl , KCl	25	1.013	2
Kozintseva ²⁸	NaCl , Na_2SO_4 , CaCl_2	202–262	16–60	13
Douabul and Riley ²⁹	seawater	0–30	1.013	7
Drummond ³⁰	NaCl (0–6 M)	30–380	6–200	474
Barrett et al. ³¹	NaCl (0–5 M)	25–95	1.013	172
Suleimenov & Krupp ¹²	NaCl (0–2.5 M)	20–320	0–140	72
Xia et al. ³²	NaCl (4–6 M)	40–120	10–100	71
Xia et al. ³²	Na_2SO_4 (0–1 M)	40–120	10–100	81
Xia et al. ³²	$(\text{NH}_4)_2\text{SO}_4$ (1.9–4 M)	40–120	10–100	73

^a Number of measurements.

Maass,^{20,21} Clarke and Glew,²⁴ and Barrett et al.³¹ for H_2S solubility in pure water were measured at relatively low pressures ($P < 5$ bar). These data sets agree well with each other. Lee and Mather²⁵ reported H_2S solubility in pure water

Table 2. Interaction Parameters

T – P coefficient	$\mu_{\text{H}_2\text{S}}^{(0)}/RT$	$\lambda_{\text{H}_2\text{S}-\text{Na}}$	$\zeta_{\text{H}_2\text{S}-\text{Na}-\text{Cl}}$
c_1	42.564957	8.5004999E–2	–1.0832589E–2
c_2	–8.6260377E–2	3.5330378E–5	
c_3	–6084.3775	–1.5882605	
c_4	6.8714437E–5		
c_5	–102.76849		
c_6	8.4482895E–4	1.1894926E–5	
c_7	–1.0590768		
c_8	3.5665902E–3		

at moderate pressures up to 70 bar. Selleck et al.²² and Gillespie et al.²⁶ reported H_2S solubility in pure water at pressures up to 200 bar. However, there is a large discrepancy between the two data sets at these pressures. The data of Selleck et al.²² above 121 bar are not measured but extrapolated from the data from lower pressures. This data set shows a trend that H_2S solubility rapidly increases with the increasing pressure at pressures more than 100 bar, whereas the data set of Gillespie et al.²⁶ indicates an opposite trend. The solubility of gases (such as CO_2 and CH_4) is in general increased with pressure, but the slope gradually decreases. Thus, the data of Selleck et al.²² at high pressures are in question. Carroll and Mather⁹ also analyzed the data set of Selleck et al.²² and concluded that the data of Selleck et al.²² at high pressures ($P > 100$ bar) are not reliable. Therefore, the data of Selleck et al.²² at high pressure (> 100

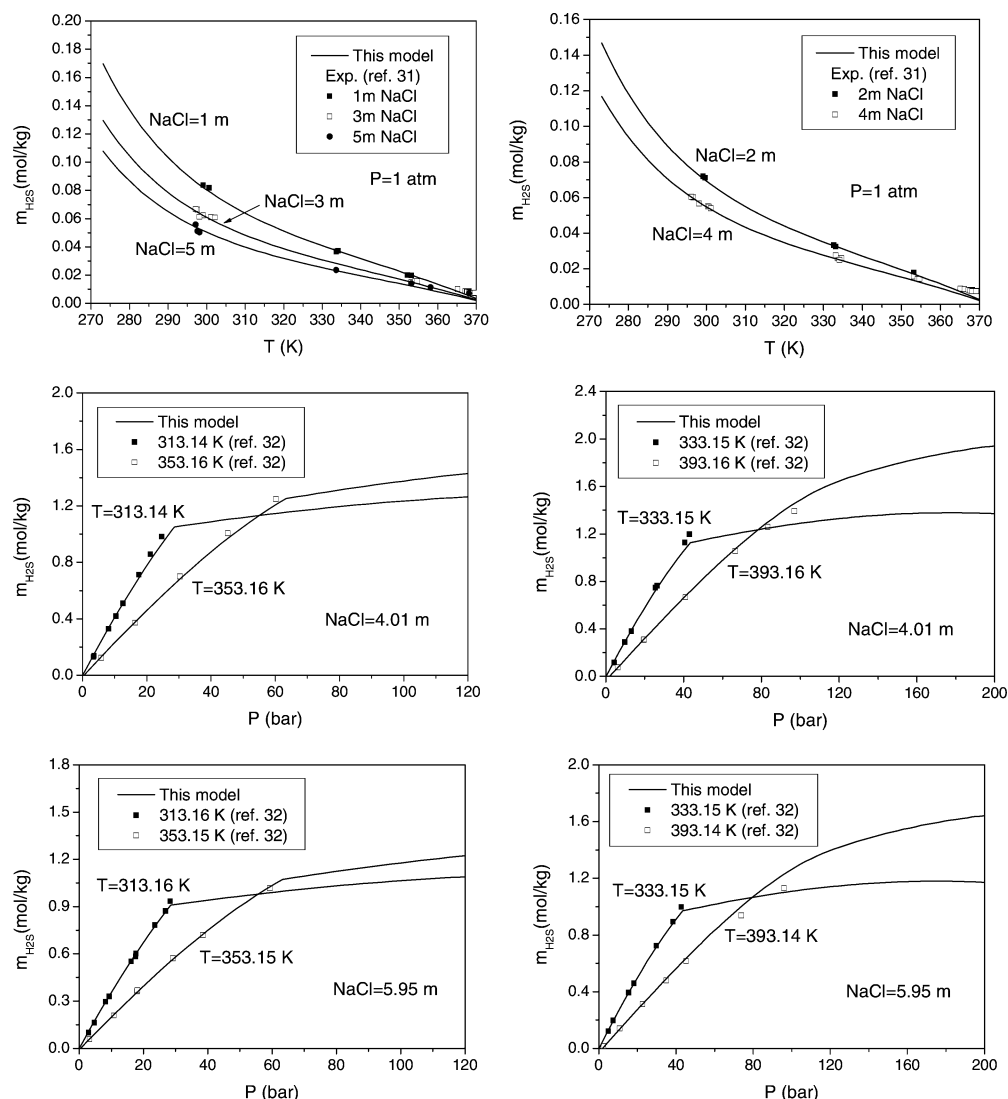


Figure 2. H_2S solubility in aqueous NaCl solutions (the prediction of this model vs experimental data).

bar) are used in the parametrization with low weight. The data set of Drummond³⁰ covers a large temperature range (from 293 to 623 K). A small portion of Drummond's data points between 310 and 350 K deviate from the general data set by more than 10%. The data of Suleimenov and Krupp¹² are consistent with that of Drummond³⁰ with an average deviation of about 7%. Generally, most of the H_2S solubility data are consistent within errors of about 7%, although there are some data points with large discrepancies. As the temperature increases, the corrosive behavior of H_2S solutions intensifies, making measurements more and more difficult and the data less and less certain. Therefore, this study only tries to model H_2S solubility at temperatures below 500 K.

The most extensive studies of H_2S solubility in aqueous NaCl solutions are those of Drummond,³⁰ Barrett et al.,³¹ Suleimenov and Krupp,¹² and Xia et al.³² Barrett et al.³¹ measured H_2S solubility in aqueous NaCl solution at 1 atm. Some of the data of Barrett et al.³¹ deviate from others by about 10%. Xia et al.³² reported H_2S solubility in aqueous NaCl solution from 313 to 393 K, from 10 to 100 bar, and from 4 to 6 M. The measurements of Drummond³⁰ cover a large temperature–pressure–ionic strength (T – P – m) range (293–593 K, 0–140 bar, and 0–6 M). However, there is a large discrepancy between the data measured in the cooling and heating processes,³⁰ and the deviation between them is more than 20%. Because we have

no reliable criterion to determine which data are more accurate, we include all these inconsistent data in the parametrization with less weight in the fitting. We note that experimental measurements of H_2S solubility in NaCl solutions at high pressure ($P > 100$ bar) and high temperature ($T > 393$ K) range are absent.

H_2S solubility data in other salts than NaCl aqueous solutions at elevated pressures are very limited. Xia et al.³² published some experimental H_2S solubility data in aqueous Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ solutions from 313 to 393 K and from 10 to 100 bar with molality up to 6 M. Kapustinsky and Anvaer²⁷ reported one data point on H_2S solubility in aqueous KCl solution at 298 K. Kozintseva²⁸ measured H_2S solubility in aqueous CaCl_2 solution at 475 K and 17 bar, noticing that the partial pressure of H_2S is only about 1 bar.

4. Parameterization and Comparison with Experimental Data

To calculate the H_2S solubility as a function of temperature, pressure, and salt composition, we need to determine the parameters, λ and ζ , for Na^+ and Cl^- in liquid as well as the standard chemical potential, $\mu_{\text{H}_2\text{S}}^{(0)}$, in eq 6. Because measurements can only be made in electronically neutral solutions, one

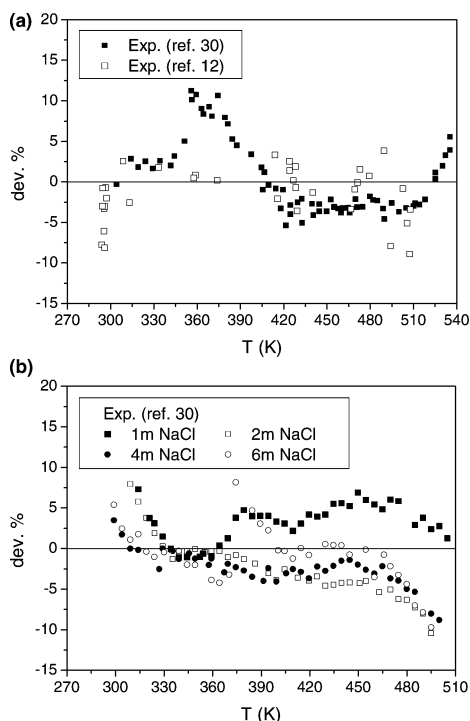


Figure 3. Deviation of this model from the experimental data of Drummond³⁰ and Suleimenov and Krupp¹²: (a) H₂S–H₂O system, (b) H₂S–H₂O–NaCl system. The deviation is defined as $100\% \times (m_{\text{H}_2\text{S}}^{\text{model}} - m_{\text{H}_2\text{S}}^{\text{exp}})/m_{\text{H}_2\text{S}}^{\text{exp}}$.

of the parameters must be assigned arbitrarily.³³ We set $\lambda_{\text{H}_2\text{S}-\text{Cl}}$ to zero and fit the remaining parameters. The term $\mu_{\text{H}_2\text{S}}^{(0)}/RT$ was first evaluated using the H₂S solubility data in pure water with a standard error of 4.6%. Then, $\lambda_{\text{H}_2\text{S}-\text{Na}}$ and $\zeta_{\text{H}_2\text{S}-\text{Na}-\text{Cl}}$ were evaluated simultaneously by least-square fitting of solubility data in aqueous NaCl solutions with a standard error of 5.2%. The third-order interaction parameter, $\zeta_{\text{H}_2\text{S}-\text{Na}-\text{Cl}}$, is smaller than the second-order interaction parameter, $\lambda_{\text{H}_2\text{S}-\text{Na}}$, by about 1 order of magnitude. The temperature and pressure-dependent coefficients are listed in Table 2.

By substituting the parameters into eq 6, the H₂S solubility in pure water and aqueous NaCl solutions can be calculated. Figures 1 and 2 compare the prediction of this model with the experimental data. Figure 3 shows the deviation of this model from the experimental data of Drummond³⁰ and the data of Suleimenov and Krupp.¹² It can be seen from these figures that most experimental data can be represented by this model adequately, within or close to experimental uncertainty (about 7%). For the solubility of H₂S in pure water at high pressures ($P > 100$ bar), this model agrees well with the experimental data of Gillespie et al.²⁶ Considering that the data of Selleck et al.²² at pressures more than 100 bar are questionable as discussed in Section 3, the large deviation of this model from them is not a surprise. The prediction of the model of Carroll and Mather⁹ is also shown in Figure 1. It is obvious that the model of Carroll and Mather⁹ can not accurately predict H₂S solubility in pure water at low pressures ($P < 5$ bar) and at high temperatures and high pressures ($T > 450$ K, $P > 50$ bar). SUPCRT92¹⁴ can accurately predict the gas H₂S solubility at temperatures below 423 K, but it underestimates H₂S solubility at temperatures above 423 K. For the solubility of H₂S in aqueous NaCl solution, there is a large discrepancy among the data of Drummond³⁰ as

Table 3. Calculated H₂S Solubility (moles per kilogram) in Pure Water

<i>P</i> (bar)	<i>T</i> (K)							
	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15
1	.0875	.0442	.0119	.0000	.0000	.0000	.0000	.0000
5	.4430	.2613	.1700	.0967	.0066	.0000	.0000	.0000
10	.8633	.5244	.3647	.2568	.1461	.0000	.0000	.0000
20	1.6182	1.0194	.7425	.5745	.4282	.2546	.0216	.0000
30	1.8415	1.4680	1.1019	.8869	.7128	.5183	.2634	.0000
40	1.8963	1.8630	1.4391	1.1914	.9982	.7892	.5180	.1527
50	1.9479	2.0275	1.7501	1.4855	1.2824	1.0661	.7846	.4015
60	1.9958	2.0870	2.0302	1.7664	1.5635	1.3473	1.0625	.6683
80		2.1952	2.4180	2.2772	2.1083	1.9171	1.6480	1.2548
100		2.2874	2.5573	2.6979	2.6162	2.4857	2.2655	1.9096
120		2.3618	2.6765	2.9914	3.0707	3.0399	2.9050	2.6278
140		2.4167	2.7750	3.1879	3.4578	3.5669	3.5553	3.4029
160		2.4507	2.8514	3.3440	3.7752	4.0554	4.2049	4.2269
180		2.4633	2.9045	3.4681	4.0346	4.4984	4.8432	5.0903
200		2.4539	2.9334	3.5586	4.2481	4.8940	5.4604	5.9828

mentioned in section 3. The prediction of this model agrees well with the data of Drummond³⁰ measured in the heating process but deviates by more than 10% from the data points measured in the cooling process. Figures 1, 2, and 3 also suggest that our model covers a wide T – P – m range. Solubilities of H₂S in pure water and in 1, 2, 4, 6 M NaCl solutions (273–513 K, 0–200 bar) calculated from this model are compiled in Tables 3–7, respectively. Because H₂S hydrate can form at low temperatures ($T < 306$ K) and higher pressures in the H₂S–H₂O system, we fit an empirical equation to predict the dissociation pressure of H₂S hydrate at a given temperature (see Appendix B). One should be aware of the T – P range where the H₂S hydrate is thermodynamically stable, when the calculation is approaching the low-temperature range.

5. H₂S Solubility in Seawater: Extrapolation of the Model

The advantage of the specific interaction approach is that the model, though evaluated from binary and ternary data, can be applied to more complex systems.³⁴ Natural waters often contain NaCl, MgCl₂, CaCl₂, and sulfate and carbonate salts, although NaCl is often the major component. Because of data limitations, a model directly fitted to experimental measurements is possible only for the H₂S–NaCl–H₂O system. In order to treat more complex systems, we included K⁺, Ca²⁺, Mg²⁺, SO₄²⁻ in this model with an approximation proposed by Duan et al.³⁵ This approach was also successfully used for the prediction of N₂ solubility³⁶ and CO₂ solubility³⁷ in non-NaCl salt solutions.

As Duan et al.³⁵ proposed, the interaction parameters (λ and ζ) of the same charge ions have roughly the same value, and the CH₄–bivalent cation interaction parameters are about twice as large as CH₄–monovalent interaction parameters within the accuracy of the experiment, which is true at different temperatures and pressures. The CH₄–anion interaction parameters are relatively small and therefore contribute little to the calculations. Hence, Duan et al.³⁵ approximated all CH₄–monovalent cation and CH₄–bivalent cation interaction parameters as $\lambda_{\text{CH}_4-\text{Na}}$ and $2\lambda_{\text{CH}_4-\text{Na}}$, respectively. Here, we adopt this approach to deal with the solubility of H₂S in seawater-type brines. We approximate all H₂S–monovalent cation and H₂S–bivalent cation

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Table 4. Calculated H₂S Solubility (moles per kilogram) in 1 M Aqueous NaCl Solution

P (bar)	T (K)								
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15
1	.1679	.0740	.0375	.0108	.0000	.0000	.0000	.0000	.0000
5		.3738	.2201	.1434	.0828	.0095	.0000	.0000	.0000
10		.7282	.4412	.3066	.2166	.1259	.0070	.0000	.0000
20		1.3645	.8572	.6232	.4821	.3610	.2194	.0315	.0000
30		1.5524	1.2340	.9241	.7430	.5981	.4387	.2323	.0000
40		1.5982	1.5656	1.2064	.9972	.8357	.6638	.4436	.1498
50		1.6413	1.7033	1.4665	1.2426	1.0723	.8938	.6648	.3563
60		1.6812	1.7529	1.7007	1.4768	1.3061	1.1272	.8952	.5776
80			1.8428	2.0244	1.9024	1.7590	1.5999	1.3802	1.0636
100			1.9193	2.1398	2.2523	2.1805	2.0710	1.8912	1.6054
120			1.9807	2.2384	2.4958	2.5574	2.5297	2.4198	2.1990
140			2.0257	2.3196	2.6583	2.8778	2.9653	2.9567	2.8389
160			2.0533	2.3823	2.7869	3.1399	3.3685	3.4925	3.5184
180			2.0628	2.4255	2.8889	3.3536	3.7337	4.0182	4.2295
200			2.0540	2.4484	2.9626	3.5291	4.0592	4.5260	4.9638

Table 5. Calculated H₂S Solubility (moles per kilogram) in 2 M Aqueous NaCl Solution

P (bar)	T (K)								
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15
1	.1453	.0639	.0325	.0100	.0000	.0000	.0000	.0000	.0000
5		.3223	.1894	.1236	.0724	.0116	.0000	.0000	.0000
10		.6277	.3794	.2634	.1868	.1107	.0126	.0000	.0000
20		1.1758	.7366	.5345	.4135	.3110	.1931	.0384	.0000
30		1.3373	1.0600	.7920	.6362	.5129	.3794	.2088	.0000
40		1.3764	1.3444	1.0335	.8530	.7151	.5707	.3881	.1470
50		1.4132	1.4623	1.2559	1.0622	.9163	.7658	.5756	.3221
60		1.4473	1.5045	1.4559	1.2617	1.1151	.9639	.7708	.5097
80			1.5808	1.7320	1.6241	1.4997	1.3645	1.1814	.9212
100			1.6456	1.8298	1.9215	1.8573	1.7634	1.6135	1.3794
120			1.6975	1.9131	2.1280	2.1766	2.1514	2.0600	1.8808
140			1.7352	1.9815	2.2652	2.4475	2.5193	2.5131	2.4206
160			1.7580	2.0340	2.3735	2.6688	2.8594	2.9646	2.9931
180			1.7653	2.0698	2.4591	2.8487	3.1670	3.4071	3.5917
200			1.7569	2.0884	2.5206	2.9960	3.4406	3.8340	4.2090

Table 6. Calculated H₂S Solubility (moles per kilogram) in 4 M Aqueous NaCl Solution

P (bar)	T (K)								
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15
1	.1160	.0508	.0261	.0090	.0000	.0000	.0000	.0000	.0000
5		.2557	.1497	.0980	.0590	.0143	.0000	.0000	.0000
10		.4977	.2993	.2074	.1481	.0912	.0197	.0000	.0000
20		.9317	.5804	.4195	.3245	.2462	.1590	.0471	.0000
30		1.0591	.8347	.6209	.4976	.4024	.3025	.1781	.0174
40		1.0895	1.0580	.8093	.6660	.5586	.4497	.3157	.1425
50		1.1181	1.1501	.9828	.8282	.7139	.5997	.4596	.2770
60		1.1445	1.1827	1.1386	.9829	.8672	.7518	.6091	.4208
80			1.2415	1.3529	1.2631	1.1633	1.0589	.9231	.7356
100			1.2911	1.4277	1.4924	1.4380	1.3641	1.2528	1.0851
120			1.3305	1.4912	1.6508	1.6825	1.6602	1.5927	1.4667
140			1.3587	1.5429	1.7553	1.8892	1.9404	1.9368	1.8766
160			1.3752	1.5823	1.8372	2.0574	2.1986	2.2790	2.3103
180			1.3796	1.6085	1.9014	2.1935	2.4314	2.6136	2.7628
200			1.3717	1.6214	1.9470	2.3042	2.6378	2.9355	3.2283

interaction parameters as $\lambda_{\text{H}_2\text{S}-\text{Na}}$ and $2\lambda_{\text{H}_2\text{S}-\text{Na}}$, respectively, and approximate all ternary parameters as $\zeta_{\text{H}_2\text{S}-\text{Na}-\text{Cl}}$. With these approximations, the following equation is obtained.

$$\ln m_{\text{H}_2\text{S}} = \ln y_{\text{H}_2\text{S}} \phi_{\text{H}_2\text{S}} P - \mu_{\text{H}_2\text{S}}^{(0)}/RT - 2\lambda_{\text{H}_2\text{S}-\text{Na}}(m_{\text{Na}} + 0.42m_{\text{NH}_4} + 2m_{\text{Ca}} + 2m_{\text{Mg}}) - \zeta_{\text{H}_2\text{S}-\text{Na}-\text{Cl}}m_{\text{Cl}}(m_{\text{Na}} + m_{\text{NH}_4} + m_{\text{Mg}} + m_{\text{Ca}}) - 0.18m_{\text{SO}_4} \quad (8)$$

In order to test this approximation, we compared eq 8 with experimental data of H₂S solubility in aqueous Na₂SO₄ and (NH₄)₂SO₄ solutions,³² aqueous KCl solution,²⁷ aqueous CaCl₂

solutions,²⁸ and seawater,²⁹ respectively. Figures 4–6 show that this approximate approach can predict H₂S solubility data in aqueous Na₂SO₄ and (NH₄)₂SO₄ solutions and in seawater (the chemical composition of seawater is from Holland³⁸) with an absolute average deviation of less than 5%, which is within the experimental uncertainty. Table 8 indicates that eq 8 can predict the solubility of H₂S in aqueous KCl solution, but for the H₂S solubility in aqueous CaCl₂ solution, the deviation of this model is more than 15%. We doubt the reliability of the three data

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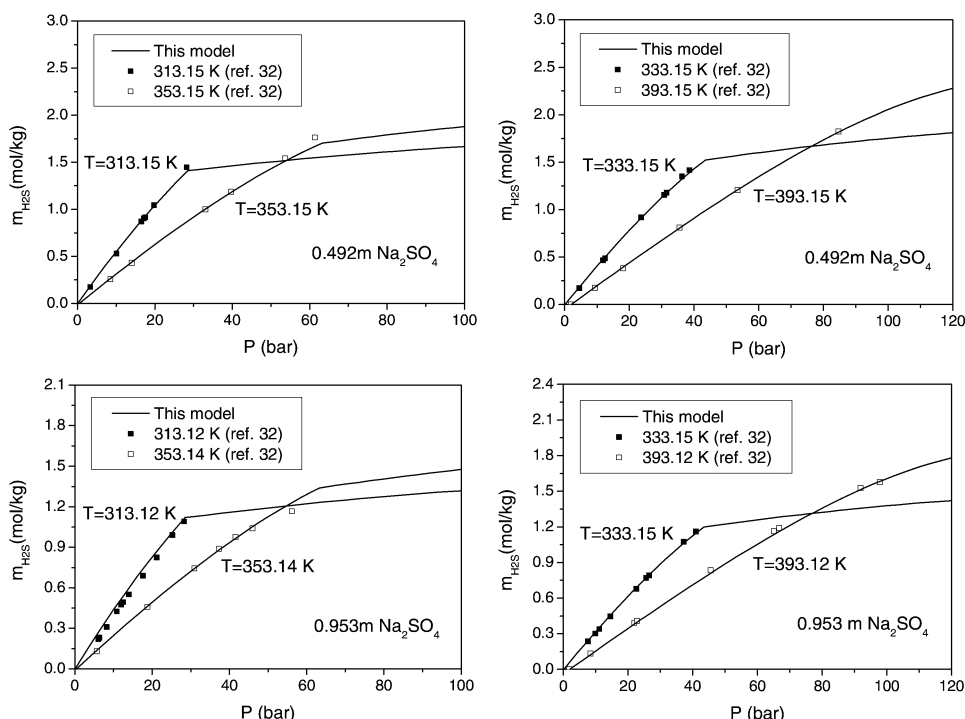


Figure 4. H₂S solubility in aqueous Na₂SO₄ solutions (the prediction of this model vs experimental data).

Table 7. Calculated H₂S Solubility (moles per kilogram) in 6 M Aqueous NaCl Solution

P (bar)	T (K)								
	273.15	303.15	333.15	363.15	393.15	423.15	453.15	483.15	513.15
1	.1010	.0440	.0227	.0085	.0000	.0000	.0000	.0000	.0000
5		.2212	.1290	.0845	.0519	.0158	.0000	.0000	.0000
10		.4303	.2574	.1780	.1275	.0807	.0234	.0000	.0000
20		.8050	.4987	.3589	.2772	.2116	.1405	.0513	.0000
30		.9147	.7167	.5305	.4240	.3433	.2610	.1610	.0342
40		.9405	.9079	.6910	.5666	.4750	.3845	.2762	.1389
50		.9647	.9865	.8385	.7038	.6057	.5102	.3964	.2513
60		.9870	1.0138	.9709	.8345	.7346	.6376	.5212	.3712
80			1.0632	1.1523	1.0709	.9831	.8944	.7829	.6334
100			1.1046	1.2148	1.2638	1.2132	1.1490	1.0571	.9239
120			1.1372	1.2675	1.3963	1.4174	1.3954	1.3392	1.2402
140			1.1602	1.3101	1.4830	1.5895	1.6280	1.6242	1.5792
160			1.1731	1.3422	1.5506	1.7289	1.8418	1.9069	1.9372
180			1.1757	1.3632	1.6031	1.8411	2.0340	2.1827	2.3098
200			1.1679	1.3727	1.6398	1.9319	2.2037	2.4474	2.6924

Table 8. Solubility of H₂S in Aqueous KCl or CaCl₂ Solution: Comparison of the Prediction of Equation 9 with the Experimental Data

T (K)	P (bar)	salt	m _{H2S} (exp)	m _{H2S} (model)
298.2	1.045	1.03M KCl	.0907 ^a	.0865
475.2	18.727	.27M CaCl ₂	.0279 ^b	.0232
475.2	18.717	.66M CaCl ₂	.0233 ^b	.0199
475.2	18.647	.63M CaCl ₂	.0220 ^b	.0188

^a Kapustinsky and Anvaer.²⁷ ^b Kozintseva.²⁸

points because the partial pressure of H₂S is too small as compared to the total pressure.

6. Calculation of Galena Solubility in NaCl Brines

The H₂S solubility model described in the preceding pages can be linked to speciation and solubility models to calculate sulfide mineral solubility in H₂S saturated aqueous solutions. Below, we give an example of calculations of galena (PbS) solubility in NaCl brines. In this study, we used the computer code PHREEQC 2.12,¹³ which has an option for Pitzer's specific

ion-interaction model¹¹ to calculate activity coefficients using parameters from a database for Pitzer model parameters. This option of Pitzer's approach was adopted from the program PHRQPITZ with ion-interaction parameters from Plummer et al.³⁹ The Pitzer equations in the program PHRQPITZ are based on the formulation of Harvie and Weare⁴⁰ and Harvie et al.³³

In order to calculate galena solubility in H₂S-saturation aqueous solutions with different NaCl concentrations, we should know the equilibrium constants for Pb–chloride complexes and relevant ion-interaction parameters. The specific ion-interaction parameters between dissolved H₂S and NaCl determined by this study were used. Following the approximation proposed in section 5, we set $\lambda_{\text{H}_2\text{S}-\text{Pb}}$ to be twice $\lambda_{\text{H}_2\text{S}-\text{Na}}$ and set $\zeta_{\text{H}_2\text{S}-\text{Pb}-\text{Cl}}$ to be equal to $\zeta_{\text{H}_2\text{S}-\text{Na}-\text{Cl}}$. The log K values for galena dissolution were taken from Barrett and Anderson.⁴¹ The equilibrium

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(40) Harvie, C. E.; Weare, J. H. *Geochim. Cosmochim. Acta* **1980**, *44*, 981.

(41) Barrett, T. J.; Anderson, G. M. *Geochim. Cosmochim. Acta* **1988**, *52*, 813.

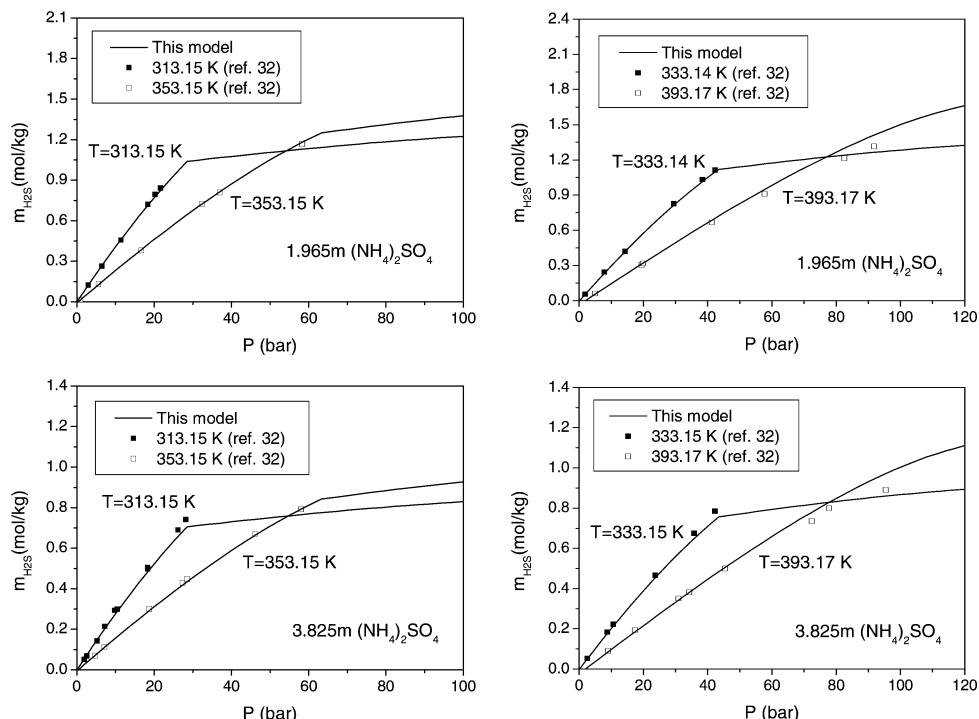


Figure 5. H_2S solubility in aqueous $(\text{NH}_4)_2\text{SO}_4$ solutions (the prediction of this model vs experimental data).

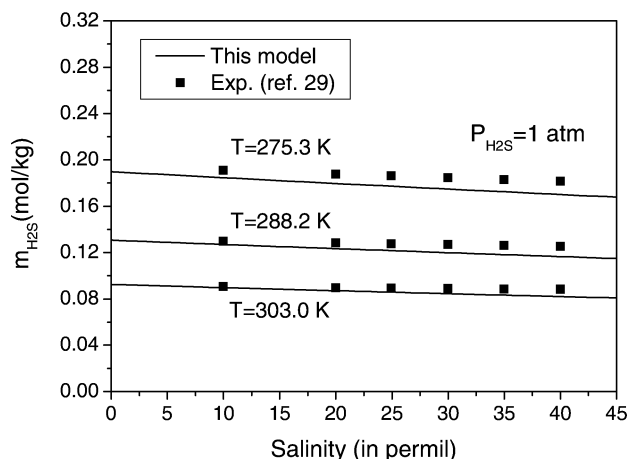


Figure 6. H_2S solubility in seawater (the prediction of this model vs experimental data).

constants for the first three Pb–chloride complexes and relevant ion–interaction parameters determined by Millero and Byrne⁴² were used. Felmy et al.⁴³ investigated PbCl_2 solubility in the NaCl – H_2O system at 25 °C and found it was necessary to include the aqueous complex PbCl_4^{2-} for the ion–interaction model to fit experimental data in the PbCl_2 – NaCl – H_2O system, especially in the concentrated NaCl brines. Thus, this study added the ion–interaction parameters relevant to PbCl_4^{2-} determined by Felmy et al.⁴³ in the calculation. The equilibrium constants for the aqueous complexes of Pb and ion–interaction parameters used in the modeling are given in Table 9.

Figure 7 shows the prediction of galena solubility at 25 °C and compares it to the experimental data of Barrett and Anderson⁴¹ in a NaCl concentration range of 1–5 M. The

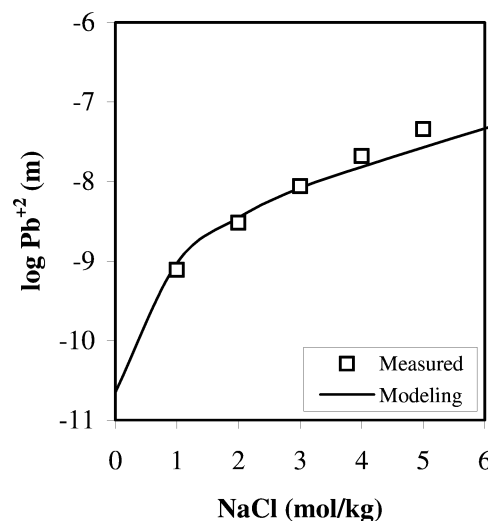


Figure 7. Galena solubility as a function of NaCl concentrations in H_2S saturation conditions at 25 °C. Symbols are experimental data from Barrett and Anderson,⁴¹ and the line is from speciation–solubility modeling.

prediction of this study agrees well with the experimental data. Similar calculations for other sulfide minerals are also possible but are limited by the availability of Pitzer parameters, particularly at high temperatures.

7. Conclusions

A H_2S solubility model has been developed based on the equation of state of Duan et al.¹⁵ and the theory of Pitzer.¹¹ Comparison with experimental data demonstrates that this model gives results within or close to experimental uncertainty (about 7%) in the temperature range from 273 to 500 K, with a possibility of extrapolating to 513 K, for pressures from 0 to 200 bar, and for ionic strengths from 0 to 6 M. Following the

(42) Millero, F. J.; Byrne, R. H. *Geochim. Cosmochim. Acta* **1984**, *48*, 1145.

(43) Felmy, A. R.; Onishi, L. M.; Foster, N. S.; Rustad, J. R.; Rai, D. T.; Mason, M. J. *Geochim. Cosmochim. Acta* **2000**, *64*, 3615.

Table 9. Modeling Parameters for the H₂S–PbS–NaCl–H₂O System

reactions	log ₁₀ <i>K</i> (25 °C)	refs
Pb ²⁺ + Cl [−] = PbCl ⁺	1.48	Millero and Byrne ⁴²
Pb ²⁺ + 2Cl [−] = PbCl ₂	2.03	Millero and Byrne ⁴²
Pb ²⁺ + 3Cl [−] = PbCl ₃ [−]	1.88	Millero and Byrne ⁴²
Pb ²⁺ + 4Cl [−] = PbCl ₄ ^{2−}	0.14	Felmy et al. ⁴³
H ₂ S(g) = H ₂ S(aq)	−0.988	Johnson et al. ¹⁴
PbS (galena) + 2H ⁺ = Pb ²⁺ + H ₂ S(aq)	−7.90	Barrett and Anderson ⁴¹

Binary Parameters					
species	β ⁽⁰⁾	β ⁽¹⁾	β ⁽²⁾	C ^φ	refs
Pb ²⁺ –Cl [−]	0.26	1.64		0.088	Millero and Byrne ⁴²
PbCl ⁺ –Cl [−]	0.15				Millero and Byrne ⁴²
H ⁺ –PbCl ₃ [−]	0.27	0.63 ^a			Felmy et al. ⁴³
H ⁺ –PbCl ₄ ^{2−}	0.7				Felmy et al. ⁴³
Na ⁺ –PbCl ₃ [−]	0.092	0.65 ^a			Felmy et al. ⁴³
Na ⁺ –PbCl ₄ ^{2−}				0.424 ^a	Felmy et al. ⁴³

Ternary Parameters		
λ (Cl [−] –PbCl ₂ (aq))	0.11 ^a	Millero and Byrne ⁴²
λ (Na ⁺ –PbCl ₂ (aq))	0.11 ^a	Felmy et al. ⁴³
λ (Na ⁺ –H ₂ S(aq))	0.091	this study
λ (Pb ²⁺ –H ₂ S(aq))	0.181	this study
θ (Na ⁺ –Pb ²⁺)	0.10	Felmy et al. ⁴³
θ (Na ⁺ –PbCl ⁺)	0.097 ^a	Felmy et al. ⁴³
ζ (Na ⁺ –Cl [−] –H ₂ S(aq))	−0.0108	this study
ζ (Pb ²⁺ –Cl [−] –H ₂ S(aq))	−0.0108	this study

^a These numbers were corrected to the positive values.

approach adopted by Duan et al.,³⁵ this model is extended to predict H₂S solubility in more complex brines such as seawater with remarkable accuracy. This model can be used together with codes such as PHREEQC to calculate the solubility of sulfide minerals. The program to calculate H₂S solubility in pure water and in aqueous NaCl solution can be download from our website: <http://www.geochem-model.org/programs.htm>.

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Appendix A: Equation of State for H₂S

The equation of state for H₂S has the following form:

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{a_1 + a_2/T_r^2 + a_3/T_r^3}{V_r} + \frac{a_4 + a_5/T_r^2 + a_6/T_r^3}{V_r^2} + \frac{a_7 + a_8/T_r^2 + a_9/T_r^3}{V_r^4} + \frac{a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3}{V_r^5} + \frac{a_{13}}{T_r^3 V_r^2} \left(a_{14} + \frac{a_{15}}{V_r^2} \right) \exp \left(-\frac{a_{15}}{V_r^2} \right) \quad (\text{A1})$$

where P_r , T_r , and V_r are reduced pressure, reduced temperature, and reduced volume, respectively. They are defined as follows:

$$P_r = \frac{P}{P_c} \quad (\text{A2})$$

$$T_r = \frac{T}{T_c} \quad (\text{A3})$$

$$V_r = \frac{V}{V_c} \quad (\text{A4})$$

where P_c and T_c are the critical pressure and critical temperature, respectively. $T_c = 373.6$ K, and $P_c = 90.08$ bar. V_c is not the critical volume but is defined as follows:

$$V_c = \frac{RT_c}{P_c} \quad (\text{A5})$$

where R is the universal gas constant, $R = 8.314467$ Pa·m³·K^{−1}·mol^{−1}. The parameters of eq A1, a_1 – a_{15} , are evaluated from PVT and saturation pressure data of H₂S. Their values are listed in Table A1. The mole volume V of H₂S at a

Table A1. Parameters for Equation A1

parameter	value
a_1	5.2386075E−2
a_2	−2.7463906E−1
a_3	−9.6760173E−2
a_4	1.3618104E−2
a_5	−8.8681753E−2
a_6	4.1176908E−2
a_7	3.6354018E−4
a_8	2.2719194E−3
a_9	−7.6962514E−4
a_{10}	−2.1948579E−5
a_{11}	−1.1707631E−4
a_{12}	4.0756926E−5
a_{13}	5.7582260E−2
a_{14}	1.00
a_{15}	0.06

given T (K) and P (bar) is calculated as follows. First, V_r is calculated by substituting eqs A2 and A3 into eq A1 for a given T (K) and P ; V_r will be obtained by solving eq A1. Then, V is calculated from eq A4. The formula to calculate the fugacity coefficient of H₂S, which was deduced from eq A1, has the following form:

$$\ln \phi(T, P) = Z - 1 - \ln Z + \frac{a_1 + a_2/T_r^2 + a_3/T_r^3}{V_r} + \frac{a_4 + a_5/T_r^2 + a_6/T_r^3}{2V_r^2} + \frac{a_7 + a_8/T_r^2 + a_9/T_r^3}{4V_r^4} + \frac{a_{10} + a_{11}/T_r^2 + a_{12}/T_r^3}{5V_r^5} + \frac{a_{13}}{2T_r^3 a_{15}} \left[a_{14} + 1 - \left(a_{14} + 1 + \frac{a_{15}}{V_r^2} \right) \exp \left(-\frac{a_{15}}{V_r^2} \right) \right] \quad (\text{A6})$$

Appendix B: Empirical Model for the Equilibrium Pressure of H₂S Hydrate

H₂S hydrate is thermodynamically stable at low temperatures and high pressures. We use the following empirical equation to calculate the equilibrium pressure of H₂S hydrate at temperatures below 302.7 K:

$$\ln P = -54.05881 + 0.1492942T + 3624.257/T \quad (\text{B1})$$

When 302.7 K < T < 306 K, eq B2 is used

$$P = 400391.1 - 2754.777T + 4.731154T^2 \quad (\text{B2})$$

The units of T and P in eqs B1 and B2 are kelvin and bar, respectively. The parameters of eqs B1 and B2 are fitted to the experimental data compiled by Sloan.⁴⁴

List of Symbols

Notation

T = absolute temperature in kelvin

P = total pressure; = $P_{H_2S} + P_{H_2O}$ in bar

y = mole fraction of H_2S in the vapor phase

R = universal gas constant; = $0.08314467 \text{ bar}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

m = molality of H_2S or salts in the liquid phase

ϕ = fugacity coefficient

(44) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

γ = activity coefficient

μ = chemical potential

λ_{H_2S-ion} = the second-order interaction parameter

$\zeta_{H_2S-cation-anion}$ = the third-order interaction parameter

Par = parameter

Subscripts

a = anion

c = cation

Superscripts

v = vapor

l = liquid

(0) = standard state

aq = aqueous solution

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