

## RESEARCH NOTES

## Equilibrium Expressions Related to the Solubility of the Sour Corrosion Product Mackinawite

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A major problem in the oil and gas industry is corrosion in sour (or H<sub>2</sub>S-containing) environments. Low concentrations of H<sub>2</sub>S act to inhibit corrosion, because of the formation of a protective iron sulfide film/scale on steel surfaces; large concentrations can lead to pitting, severe localized corrosion, and catastrophic failure. Therefore, the solubility and hydrothermal stability of iron sulfides is particularly relevant to corrosion. To understand the mechanisms that are associated with the hydrothermal formation of iron sulfides, it is important to reliably estimate equilibrium constants for all the reactions involved, including those for the dissolution and dissociation of H<sub>2</sub>S. In this study, equations for determining the equilibrium constants that are related to the solubility of mackinawite are evaluated, and the most appropriate expressions are described. Also, the most relevant expressions for the solubility of H<sub>2</sub>S and for the first dissociation constant of H<sub>2</sub>S are reviewed. It is recommended that the second dissociation constant be avoided in calculations, because of the large uncertainty involved in previously reported values.

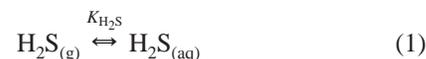
### 1. Introduction

Thermodynamic studies of systems that contain hydrogen sulfide and iron sulfide are of particular relevance to various research areas,<sup>1–9</sup> including geochemistry, oceanography, sedimentology, chalcogenide synthesis, and, because of the production of oil and gas in sour environments, corrosion. Although small concentrations of H<sub>2</sub>S seem to act to inhibit corrosion, because of the formation of a protective iron sulfide film/scale on steel surfaces, large concentrations can lead to pitting, severe localized corrosion, and catastrophic failure.

To understand the mechanisms associated with the hydrothermal formation and stability of iron sulfides, it is important to be able to reliably estimate equilibrium constants for all the reactions involved. To this end, several thermodynamic studies have been dedicated to the investigation of pertinent sulfide systems. However, significant discrepancies do exist between the reported solubility and dissociation constants for hydrogen sulfide (H<sub>2</sub>S), as well as the solubility product constants and, hence, the solubility limits, for iron sulfides. Note that many types of iron sulfides occur,<sup>1,4–9</sup> such as amorphous iron sulfide (FeS), mackinawite (Fe<sub>1+x</sub>S), cubic iron sulfide (FeS), troilite (FeS), pyrrhotite (Fe<sub>1–x</sub>S/FeS<sub>1+x</sub>), smythite (Fe<sub>3+x</sub>S<sub>4</sub>), greigite (Fe<sub>3</sub>S<sub>4</sub>), and pyrite (FeS<sub>2</sub>). Mackinawite, which has the chemical formula Fe<sub>1+x</sub>S (where  $x = 0.057–0.064$ ),<sup>5</sup> is a prevalent type of iron sulfide and usually forms as a precursor to other types of sulfides; therefore, it is evaluated here.<sup>9</sup>

As part of a larger project related to the CO<sub>2</sub>/H<sub>2</sub>S corrosion of mild steel oil and gas pipelines, the objective of the present research was to evaluate the equations that can be used for the determination of equilibrium constants related to the solubility of mackinawite. However, the work pertaining to the prediction of the solubility product ( $K_{sp}$ ) of mackinawite cannot be examined separately from the previous studies, in regard to discussing (i) the solubility constant of gaseous H<sub>2</sub>S ( $K_{H_2S}$ ), the first acid dissociation constant of H<sub>2</sub>S ( $K_{a,1}$ ), and the second acid dissociation constant of H<sub>2</sub>S ( $K_{a,2}$ ), for the reasons explained below.

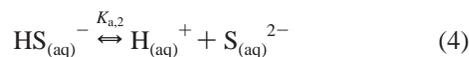
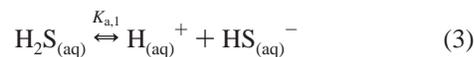
When H<sub>2</sub>S dissolves in water, the vapor–liquid equilibrium of H<sub>2</sub>S is described as



$K_{H_2S}$  represents the solubility constant of H<sub>2</sub>S, in units of mol/(L bar):

$$K_{H_2S} = \frac{[H_2S_{(aq)}]}{[H_2S_{(g)}]} \quad (2)$$

The dissociation equilibria for H<sub>2</sub>S and HS<sup>−</sup> can then be written as



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**Table 1. Equilibrium Constants of  $K_{H_2S}$  in Hydrogen Sulfide Systems**

| equation for $K_{H_2S}$   | reference  |
|---|--|
| $K_{H_2S} = \exp\left[-41.0563 + 66.4005\left(\frac{100}{T_K}\right) + 15.1060 \ln\left(\frac{T_K}{100}\right)\right]$                  | Weiss <sup>10</sup>  |
| $K_{H_2S} = 10^{-(3898.56/T_K) - (12.4914 \ln T_K) + 0.00831109T_K + 82.7622}$  | Roberts <sup>12</sup>  |
| $K_{H_2S} = \frac{10}{\exp\left[-3.3747 + 0.072437T_K - 1.10765 \times 10^{-4}T_K^2 - \frac{1549.159}{T_K} + 0.144237 \ln(T_K)\right]}$ | Carroll and Mather <sup>13</sup>                               |
| $K_{H_2S} = 10^{-[634.27 + 0.2709T_K - (0.11132 \times 10^{-3}T_K^2) - (16719/T_K) - (261.9 \log T_K)]}$                                | Suleimenov and Krupp <sup>14</sup>                             |
| $K_{H_2S} = 10^{-0.71742672 - (0.012145427T_K) + (5.6659982 \times 10^{-5})T_K^2 - (8.1902716 \times 10^{-8})T_K^3}$                    | Nordsveen et al. <sup>15</sup> (based on IUPAC <sup>16</sup> ) |

$K_{a,1}$  is the first acid dissociation constant of  $H_2S$ , in units of mol/L;  $K_{a,2}$  is the second acid dissociation constant of  $H_2S$ , in

$$K_{a,1} = \frac{[H_{(aq)}^+][HS_{(aq)}^-]}{[H_2S_{(aq)}]} \quad (5)$$

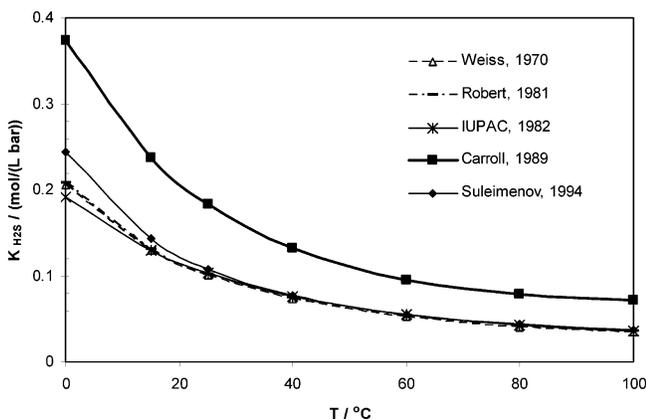
units of mol/L:

$$K_{a,2} = \frac{[H_{(aq)}^+][S_{(aq)}^{2-}]}{[HS_{(aq)}^-]} \quad (6)$$

Therefore, the discussion of the most suitable expressions for  $K_{sp}$  will start by reviewing the pertinent expressions for  $K_{H_2S}$ ,  $K_{a,1}$ , and  $K_{a,2}$ . To calculate the concentrations of sulfide species, several research groups have investigated the thermodynamics of the hydrogen sulfide system by conducting experiments or using theoretical thermodynamic models. These are briefly reviewed below. The attempt was not to conduct an in-depth review of the studies related to  $K_{H_2S}$ ,  $K_{a,1}$ , and  $K_{a,2}$ , but rather to evaluate the resulting mathematical expressions, with the ultimate goal being the prediction of  $K_{sp}$  for mackinawite.

## 2. Solubility of Mackinawite

**2.1. Solubility and Dissociation of Hydrogen Sulfide.** The  $H_2S$  equilibrium constant equations for  $K_{H_2S}$  that have been provided by various researchers are shown in Table 1. Weiss<sup>10</sup> proposed an equation to predict  $K_{H_2S}$  that fits the extensive measurements that were conducted by Douabul and Riley.<sup>11</sup> Several groups of authors later proposed alternative equations to predict  $K_{H_2S}$  as a function of temperature, as listed in Table 1. These different equations have been used to calculate the solubility constant of  $H_2S$ , as shown in Figure 1. This shows that predictions made by these equations are in good agreement,



**Figure 1.** Comparison of hydrogen sulfide solubility ( $K_{H_2S}$ ) predictions, using different models described by Weiss,<sup>10</sup> Robert,<sup>12</sup> Hogfeldt (IUPAC),<sup>16</sup> Carroll and Mather,<sup>13</sup> and Suleimenov and Krupp.<sup>14</sup>

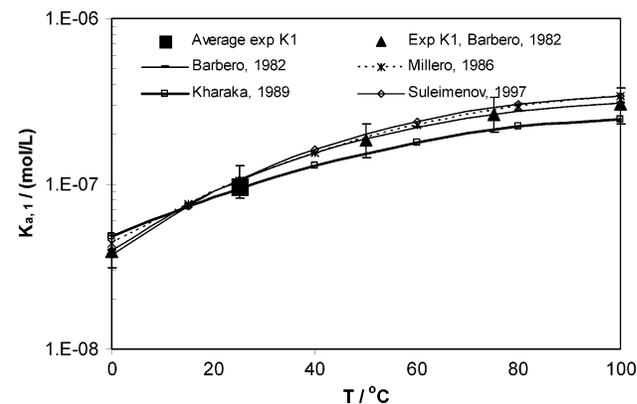
**Table 2. Values of the First Dissociation Constant ( $K_{a,1}$ ) of  $H_2S$  in Water at 25 °C**

| $K_{a,1}$              | reference(s)  |
|------------------------|---|
| $1.000 \times 10^{-8}$ | Flaschka et al. <sup>17</sup>   |
| $5.754 \times 10^{-8}$ | Day and Underwood <sup>18</sup>   |
| $8.511 \times 10^{-8}$ | Tumanova et al. <sup>19</sup>   |
| $8.711 \times 10^{-8}$ | Loy and Himmelblau <sup>20</sup>  |
| $8.913 \times 10^{-8}$ | Ringborn, <sup>21</sup> Kubli, <sup>22</sup> Su et al. <sup>23</sup>  |
| $9.124 \times 10^{-8}$ | Bruner and Zawadzki, <sup>24</sup> Thiel and Gessner, <sup>25</sup> Swift and Butler, <sup>26</sup> Weast <sup>27</sup> |
| $9.551 \times 10^{-8}$ | Ellis and Golding, <sup>28</sup> Harris <sup>29</sup>   |
| $1.000 \times 10^{-7}$ | Pecsok et al., <sup>31</sup> Kolthoff, <sup>32</sup> Ellis and Giggenbach, <sup>33</sup> Skoog and West <sup>34</sup>   |
| $1.023 \times 10^{-7}$ | Kubli, <sup>22</sup> Konopik and Leberl, <sup>35</sup> Pohl, <sup>36</sup> Blackburn <sup>37</sup>                      |
| $1.047 \times 10^{-7}$ | Khodakovskii et al., <sup>38</sup> Berner, <sup>1</sup> Goldhaber and Kaplan <sup>39</sup>                              |
| $1.071 \times 10^{-7}$ | Wright and Maass, <sup>40</sup> Kapustinskii <sup>41</sup>  |
| $1.096 \times 10^{-7}$ | Latimer <sup>42</sup>   |
| $9.632 \times 10^{-8}$ | average   |

except for the values calculated with the Carroll equation.<sup>13</sup> Therefore, it is suggested that any of the equations, with the exception of the Carroll equation,<sup>13</sup> should be used to calculate the solubility constant of  $H_2S$  and subsequently predict the solubility of mackinawite.

Values of the first dissociation constant ( $K_{a,1}$ ) at room temperature, as measured by different authors, are shown in Table 2. The average  $K_{a,1}$  is  $9.632 \times 10^{-8}$  mol/L, with a standard deviation of  $1.955 \times 10^{-8}$  mol/L. Several equations were developed to calculate  $K_{a,1}$  at different temperatures, which are shown in Table 3. A comparison of the calculated and experimental values for  $K_{a,1}$  at different temperatures is shown in Figure 2. It is observed that all the calculated values for  $K_{a,1}$  agree well with the experimental results and can be used in predictions of the solubility of mackinawite.

The values of the second dissociation constant ( $K_{a,2}$ ), determined at room temperature, are shown in Table 4. Note



**Figure 2.** Comparison of experimental results and predictions of the first dissociation constants ( $K_{a,1}$ ), using different models described by Barbero et al.,<sup>43</sup> Millero,<sup>44</sup> Kharaka et al.,<sup>45</sup> and Suleimenov and Seward.<sup>46</sup>

Table 3. First Dissociation Constant ( $K_{a,1}$ ) of Hydrogen Sulfide at Different Temperatures

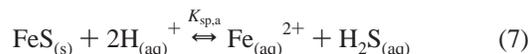
| equation for $K_{a,1}$  | reference                           |
|---|-------------------------------------|
| $K_{a,1} = 10^{\{(32216.8/T_K) + (97.7734 \ln T_K) - 0.097611T_K - (2.17087 \times 10^6)/T_K^2\} - 586.682}$      | Barbero et al. <sup>43</sup>        |
| $K_{a,1} = 10^{-[32.55 + (1519.44/T_K) - (15.672 \log T_K) - 0.02722T_K]}$  | Millero <sup>44</sup>               |
| $K_{a,1} = 10^{-[15.345 - 0.045676T_K + (5.9666 \times 10^{-5})T_K^2]}$   | Kharaka et al. <sup>45</sup>        |
| $K_{a,1} = 10^{782.43945 + 0.361261T_K - (1.6722 \times 10^{-4})T_K^2 - (20565.7315/T_K) - (142.741722 \ln T_K)}$ | Suleimenvo and Seward <sup>46</sup> |

Table 4. Values of the Second Dissociation Constant ( $K_{a,2}$ ) at Room Temperature (20–30 °C)

| $K_{a,2}$               | reference(s)   |
|-------------------------|--|
| $1.000 \times 10^{-19}$ | Myers <sup>47</sup>  |
| $6.310 \times 10^{-18}$ | Yagil <sup>48</sup>  |
| $1.000 \times 10^{-17}$ | Ellis and Giggenbach <sup>33</sup>   |
| $1.000 \times 10^{-16}$ | Licht et al. <sup>49</sup>   |
| $1.000 \times 10^{-15}$ | Skoog and West <sup>34</sup>   |
| $1.202 \times 10^{-15}$ | Knox, <sup>50</sup> Swift and Butler, <sup>26</sup><br>Day and Underwood <sup>18</sup>             |
| $7.079 \times 10^{-15}$ | Widmer and Schwarzenbach <sup>51</sup>   |
| $1.000 \times 10^{-14}$ | Ellis and Golding, <sup>28</sup> Ellis and Milestone, <sup>52</sup><br>Pecsok et al. <sup>31</sup> |
| $1.202 \times 10^{-14}$ | Flaschka et al. <sup>17</sup>  |
| $1.259 \times 10^{-14}$ | Harris <sup>29</sup>   |
| $1.413 \times 10^{-14}$ | Muhammad and Sundarahn <sup>53</sup>   |
| $1.660 \times 10^{-14}$ | Maronny <sup>54</sup>  |
| $7.943 \times 10^{-14}$ | Konopik and Leberl <sup>35</sup>   |
| $1.202 \times 10^{-13}$ | Kolthoff <sup>52</sup>   |
| $1.288 \times 10^{-13}$ | Blackbarn <sup>37</sup>  |
| $3.631 \times 10^{-13}$ | Kubli <sup>22</sup>  |
| $1.000 \times 10^{-12}$ | Su et al. <sup>23</sup>  |
| $1.148 \times 10^{-12}$ | Weast <sup>27</sup>  |
| $1.335 \times 10^{-13}$ | average  |

that there is a 7-orders-of-magnitude variation in the reported values, ranging from  $10^{-12}$  mol/L to  $10^{-19}$  mol/L. This is thought to be due to the difficulty of accurately measuring the  $HS^-$  and  $S^{2-}$  concentrations in solution. Table 5 shows the three equations for  $K_{a,2}$ , with the calculations at different temperatures shown in Figure 3, which mirror the large scatter in the measured values. Hence, it is suggested that using  $K_{a,2}$  to calculate the concentration of sulfide species and predict the solubility of mackinawite should be avoided, because of the uncertainty in the available data.

**2.2. Solubility Limit of Mackinawite: Various Expressions.** Many research groups have studied the solubility of mackinawite at room temperature. However, only a few studies have been conducted on the solubility of mackinawite as a function of temperature (e.g., Benning et al.<sup>58</sup>). Based on the experimental data, they proposed reaction 7 for the dissolution of mackinawite and eq 8 as a means to calculate the solubility limit of mackinawite in an acidic solution as a function of temperature:



$$K_{sp,a} = 10^{(2848.779/T_K) - 6.347} \quad (8)$$

where  $T_K$  is the temperature (in Kelvin) and  $K_{sp,a}$  is the solubility limit of mackinawite in an acidic solution for reaction 7, as expressed by

$$K_{sp,a} = \frac{[Fe^{2+}][H_2S]}{[H^+]^2} \quad (9)$$

Table 5. Second Dissociation Constant ( $K_{a,2}$ ) of  $H_2S$  at Different Temperatures

| equation for $K_{a,2}$   | reference                                  |
|--|--|
| $K_{a,2} = 10^{\{(31286/T_K) + (94.9734 \ln T_K) - 0.097611T_K - (2.17087 \times 10^6)/T_K^2\} - 607.722}$ | derived from Giggenbach <sup>55</sup>      |
| $K_{a,2} = 10^{-[23.93 - 0.030446T_K + (2.4831 \times 10^{-5})T_K^2]}$                                     | Kharaka et al. <sup>45</sup>               |
| $K_{a,2} = 10^{(0.1333T_K) - 43.4}$  | derived from Migdisov et al. <sup>56</sup> |

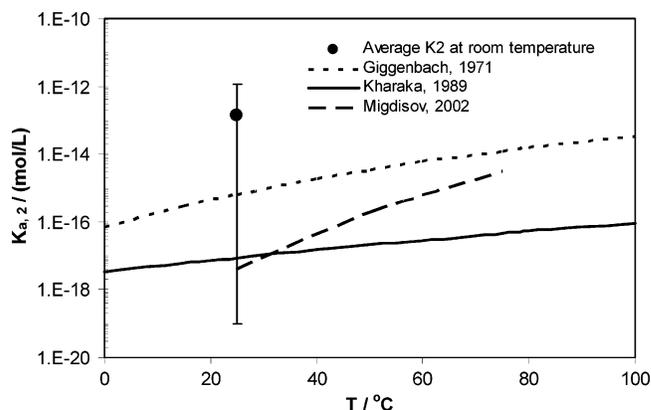
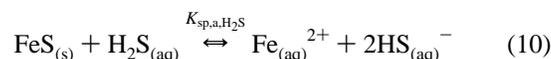


Figure 3. Comparison of predictions of the second dissociation constant ( $K_{a,2}$ ), using different models described by Giggenbach,<sup>55</sup> Kharaka et al.,<sup>45</sup> and Migdisov et al.<sup>56</sup>

Here, this is called the “[ $H^+$ ,  $H_2S$ ] based expression”. Various other expression types have been used to describe the mackinawite solubility limit, such as the “[ $H_2S$ ] based expression”, the “[ $H^+$ ,  $HS^-$ ] based expression”, the “[ $S^{2-}$ ] based expression”, and the “[ $H_2O$ ] based expression”, as discussed below.

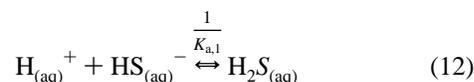
Benning et al.<sup>58</sup> reported a “[ $H_2S$ ] based expression” ( $K_{sp,H_2S}$ ) for the mackinawite solubility limit that was based on reaction 10:



where

$$K_{sp,H_2S} = \frac{[Fe^{2+}][HS^-]^2}{[H_2S]} \quad (11)$$

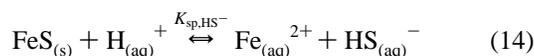
Given that one can write the reverse reaction for the first dissociation step for  $H_2S$  as



By combining reactions 10 and 12, the relationship between the two solubility constants is described as follows:

$$K_{sp,H_2S} = K_{sp,a}(K_{a,1})^2 \quad (13)$$

An “[ $H^+$ ,  $HS^-$ ] based expression” ( $K_{sp,HS^-}$ ) can also be used to describe the solubility limit of mackinawite.<sup>57</sup> It is based on the following reaction:

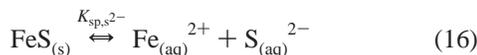


By combining reactions 14 and 12, reaction 7 is recovered.

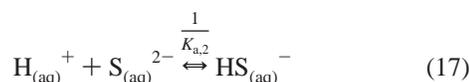
Hence, the solubility limit of mackinawite using the “[H<sup>+</sup>, HS<sup>-</sup>] based expression” is related to the others as follows:

$$K_{\text{sp,HS}^-} = K_{\text{sp,a}}K_{\text{a,1}} \quad (15)$$

The “[S<sup>2-</sup>] based expression” ( $K_{\text{sp,S}^{2-}}$ ) previously used to describe the mackinawite solubility limit involves the second dissociation constant for H<sub>2</sub>S. The initial reaction corresponds to the solubility of mackinawite:



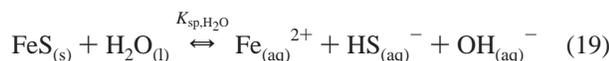
The reverse reaction for HS<sup>-</sup> dissociation corresponds to



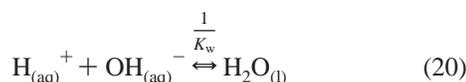
When this reaction is applied in conjunction with the reverse reaction for H<sub>2</sub>S dissociation (reaction 12) to obtain reaction 7, the solubility limit of mackinawite, based on the “[S<sup>2-</sup>] based expression”, can be written as

$$K_{\text{sp,S}^{2-}} = K_{\text{sp,a}}K_{\text{a,1}}K_{\text{a,2}} \quad (18)$$

Yet another way to describe this system can be done using a “[H<sub>2</sub>O] based expression” ( $K_{\text{sp,H}_2\text{O}}$ ). The starting point is the following reaction:



By accounting for water dissociation, one gets



where  $K_{\text{w}}$  is the water dissociation constant, which is a function of temperature.<sup>45</sup>

$$K_{\text{w}} = 10^{-[29.3868 - (0.0737549T_{\text{K}}) + (7.47881 \times 10^{-5}T_{\text{K}}^2)]} \quad (21)$$

By combining reactions 22, 23, and 12, reaction 7 is again obtained. Therefore, the solubility limit of mackinawite based on the “[H<sub>2</sub>O] based expression” can be written as

$$K_{\text{sp,H}_2\text{O}} = K_{\text{sp,a}}K_{\text{a,1}}K_{\text{w}} \quad (22)$$

A series of the solubility product equations of mackinawite, as shown by eqs 13, 15, 18 and 22, can all be related to the original Benning et al.<sup>58</sup> study and can be used to predict the solubility limit of mackinawite. The aforementioned expressions for the solubility of mackinawite are generally suitable for temperatures of 0–100 °C and pH values in the range of 2–8. Among them, the “[H<sup>+</sup>, HS<sup>-</sup>] based expression” ( $K_{\text{sp,HS}^-}$ ) and the “[S<sup>2-</sup>] based expression” ( $K_{\text{sp,S}^{2-}}$ ) have been the most commonly accepted.<sup>1,6,57</sup> Considering the unacceptably large range of literature values for  $K_{\text{a,2}}$  (see previous discussion), the “[H<sup>+</sup>, HS<sup>-</sup>] based expression” here is suggested as being the more reliable method of the two. It is also noted that the mechanisms for different expressions are proposed by authors based on the possible theories for mackinawite formation. Further studies of the mechanisms of mackinawite formation are the subject of ongoing research.

**2.3. Solubility Limit of Mackinawite: Temperature Dependence.** An equation for the temperature dependency of the

solubility of mackinawite that utilizes the “[H<sup>+</sup>, HS<sup>-</sup>] based expression” ( $K_{\text{sp,HS}^-}$ ) is obtained via a combination of eqs 8 and 15:

$$K_{\text{sp,HS}^-} = 10^{(2848.779/T) - 6.347 + \log(K_{\text{a,1}})} \quad (23)$$

Benning et al.<sup>58</sup> used the solubility constant  $K_{\text{H}_2\text{S}}$  and the first dissociation constant of H<sub>2</sub>S ( $K_{\text{a,1}}$ ), as reported by Suleimenov.<sup>14,46</sup> To be consistent in the recommended approach, here, the equations from Suleimenov<sup>14,46</sup> are suggested for the prediction of  $K_{\text{H}_2\text{S}}$  and  $K_{\text{a,1}}$ , as a function of temperature:

$$K_{\text{H}_2\text{S}} = 10^{-[634.27 + 0.2709T_{\text{K}} - (0.11132 \times 10^{-3}T_{\text{K}}^2) - (16719/T_{\text{K}}) - 261.9 \log(T_{\text{K}})]} \quad (24)$$

$$K_{\text{a,1}} = 10^{782.43945 + 0.361261T_{\text{K}} - (1.6722 \times 10^{-4}T_{\text{K}}^2) - (20565.7315/T_{\text{K}}) - (142.741722 \ln(T_{\text{K}}))} \quad (25)$$

Berner<sup>1</sup> used the [S<sup>2-</sup>] based expression to determine a value for the  $K_{\text{sp,S}^{2-}}$  for mackinawite to be equal to  $2.83 \times 10^{-18}$  mol/L. Morse et al.<sup>57</sup> determined experimentally that  $K_{\text{sp,HS}^-} = 2.86 \times 10^{-4}$  mol/L at room temperature. However, using the “[H<sup>+</sup>, HS<sup>-</sup>] based expression” (eq 23), a value of  $K_{\text{sp,HS}^-} = 1.50 \times 10^{-4}$  mol/L is obtained. Not surprisingly, this is in good agreement with the experimental value reported by Morse et al.<sup>57</sup>

### 3. Conclusions

The selection of particular solubility and dissociation constant equations can have major consequences for prediction of the concentrations of species related to iron sulfide reactions. This study clarifies and compares the various equations used for the determination of equilibrium constants for solubility of hydrogen sulfide (H<sub>2</sub>S), H<sub>2</sub>S dissociation, and ultimately the solubility of mackinawite. A particular expression which is based on the concentrations of the H<sup>+</sup> and HS<sup>-</sup> ions ([H<sup>+</sup>] and [HS<sup>-</sup>], respectively) was determined to be the most reliable to predict the solubility of mackinawite, because of the fact the [S<sup>2-</sup>] cannot be predicted with any accuracy.

### Acknowledgment

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