



Modelling and experimental measurement of the closed equilibrium system of H₂O–SrS

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Abstract. This study investigates the H₂O–SrS (strontium sulphide) equilibrium system at [SrS] between 0.125 and 88.064 mM (mmol·L⁻¹) in a closed oxygen-free test system at 25 °C (the measured system's pH being in the range of 10.0–13.1). The distribution of ions and molecules in this system is described in a structural scheme. A proton transfer model was developed to calculate the pH, concentrations of formed ions and molecules in the system by using an iteration method. In the formation of the basic equilibrium system of H₂O–SrS, the dissociation of SrS in aqueous media causes the release of the S²⁻ ions that will accept a certain quantity of protons ($\Delta[\text{H}^+]_{\text{S}^{2-}}$), originating from the reversible dissociation of water ($\Delta[\text{H}^+]_{\text{H}_2\text{O}}$). In the final closed system of H₂O–SrS, after adding larger amounts ($\geq 10 \text{ g}\cdot\text{L}^{-1}$) of salt into MilliQ water, strontium hydroxide was formed as a precipitate. Proton transfer parameters, pH, and equilibrium concentrations of ions and molecules in the liquid phase were calculated and experimentally validated.

Key words: solubility product of SrS ($K_{\text{SP,SrS}}$), dissociation constants of H₂S, proton-centric model of the H₂O–SrS equilibrium system

1. INTRODUCTION

Strontium sulphide (SrS) and other strontium compounds are formed in several industrial processes, including metallurgy and energy production. For example, besides CaS and FeS, traces of strontium (up to 371 mg·kg⁻¹) [1] and its compounds (including SrS) have been detected in the ash of oil shale processed by the circulating fluidized-bed (CFB) combustion technology. That type of oil shale was first discovered at Kukruse Stage (and named as 'kukersite') in Estonia [1,2]. Moreover, this alkaline residue is used as a fast-acting neutralizer of acidic soils and for the production of building materials. The interaction of the residue with water generates highly alkaline leachate, which contains (in addition to CaCO₃, Ca(OH)₂, CaO, MgO, etc.) a significant amount of sulphurous compounds (including SrSO₄ and SrS) due to complex chemical reactions [1–9].

As SrS is slightly water-soluble, it dissociates to form Sr²⁺, S²⁻, HS⁻ and H₂S_(w) in aqueous media. In addition, OH⁻ and H⁺ ions originate from the dissociation of water. The equilibrium concentrations of particles formed in the oxygen-free SrS aqueous solution are mainly dependent on the system's temperature and pH, the value of the latter is influenced by the amount of salt added [10–13]. Terres and Brückner have discovered that when the concentration of SrS in the oxygen-free aqueous solution increases to the point where it exceeds the corresponding solubility product of strontium hydroxide ($K_{\text{SP,Sr(OH)}_2}$), the latter will crystallize out of the solution in the form of strontium octahydrate (Sr(OH)₂·8H₂O) [14]. What is more, hydrogen sulphide, which forms a weak acid in the aqueous solution, impacts significantly the solubility of SrS [14,15].

There is also a large discrepancy in the published values of the second acid dissociation constant of H₂S ($K_{\text{a}2}$), ranging from 10⁻¹² to 10⁻¹⁹ mol·L⁻¹ (at temperatures 20–30 °C) [16–21]. A possible explanation for the wide

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variation of K_{a2} in the published values could lie in the measurement techniques and the accuracy of the methods (e.g. UV-Vis spectrophotometry, potentiometry and ion-selective potentiometry, Raman spectroscopy, etc.) used for determining the concentration ratio of S^{2-} and HS^- ions, exerting an influence on the obtained results [12]. It has been suggested [16] that the use of K_{a2} in calculating the concentrations of sulphur species (e.g. S^{2-} , HS^- , H_2S) in aqueous solutions and predicting the solubility of metal sulphides should be avoided because of the uncertainty of the available data in the relevant literature. Moreover, the forming HS^- ions in ambient (sulphur-containing) aqueous solutions could oxidize rapidly into sulphates (SO_4^{2-}), sulphites (SO_3^{2-}), thiosulphates ($S_2O_3^{2-}$), and polysulphides (S_n^{2-}) [22,23]. Therefore, in order to avoid this, all measurements should be carried out in the deoxygenated medium by using an inert gas headspace. Recent studies [3,12,24,25] indicate that in the closed equilibrium system of H_2O – SrS mainly HS^- ions are present in the pH range between 9 and 11 ($\geq 99\%$ of the total sulphur species). The equilibrium system is formed after the dissociation of SrS in the aqueous solution.

In the present study, the model of the closed system of H_2O – SrS was upgraded on the basis of proton transfer principles. Previous experiments have shown that upon adding solid SrS into oxygen-free MilliQ water, the $[Sr^{2+}]$ and $[S^{2-}]$ ions will be released by the reversible dissociation of salt in the aqueous solution [12]. At the first step of the reaction, S^{2-} ions will react with a certain amount of protons ($[H^+]_{H_2O}$) which originate from the dissociation of water, and as a result, HS^- ions will be formed. After that also OH^- ions will be released and they become a dominant species, as the value of K_w must remain unchanged, which in its turn causes a rapid increase in the pH value of this equilibrium system [3,12]. The formation of dihydrogen sulphide in the aqueous solution ($(H_2S)_w$) after SrS dissolution could additionally increase its solubility, but since its amounts are minor (as the volume of the gaseous phase was $\leq 5\%$ of the total volume of the closed reaction cell) in experimental measurements, it could be omitted from theoretical calculations. Thus, protons have a central role in the evolution of the SrS – H_2O equilibrium.

2. DERIVATION OF THE THEORETICAL MODEL OF THE CLOSED EQUILIBRIUM SYSTEM OF H_2O – SrS

The developed theoretical model of H_2O – SrS is based on the proton transfer concept [26–28]. For modelling the self-regulating complex system, it should be taken into account that chemical reactions in aqueous solutions proceed relatively fast compared to other liquids. For

example, the dissociation reaction of water into H^+ and OH^- ions is the fastest reaction rate known in the aqueous solutions with the rate constant $k = 1.4 \times 10^{11} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ [29]. The structural scheme of the closed equilibrium system of H_2O – SrS is presented in Fig. 1.

According to Fig. 1, Sr^{2+} and S^{2-} ions will be released by the reversible dissolution of SrS when a surplus amount of SrS is added. At the next step of the reaction, the S^{2-} ions will accept a certain amount of protons ($\Delta[H^+]_{S^{2-}}$) which originate from the reversible dissociation reactions of water ($\Delta[H^+]_{H_2O}$) [28]. The K_{SP} value of $Sr(OH)_2$ will be exceeded when $[SrS] \geq 83.552 \text{ mM}$ ($\text{mmol} \cdot \text{L}^{-1}$) is added into the initial closed equilibrium system of H_2O – SrS . The ions and molecules in the equilibrium system of H_2O – SrS are quantitatively distributed in accordance with their equilibrium constants [3,12,26–28]. Their values in the investigated equilibrium system can be presented as follows (1–5):

$$K_{a1} = \frac{[H^+] \times [HS^-]}{[H_2S]_w} \cong 1.047 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} \quad [30], \quad (1)$$

$$K_{a2} = \frac{[H^+] \times [S^{2-}]}{[HS^-]} \cong 1.202 \times 10^{-15} \text{ mol} \cdot \text{L}^{-1} \quad [31], \quad (2)$$

$$K_w = [H^+] \times [OH^-] \cong 1.01 \times 10^{-14} (\text{mol} \cdot \text{L}^{-1})^2 \quad [32], \quad (3)$$

$$K_{SP, SrS} = [Sr^{2+}] \times [S^{2-}] = 2.143 \times 10^{-6} (\text{mol} \cdot \text{L}^{-1})^2 \quad [12], \quad (4)$$

$$K_{SP, Sr(OH)_2} = [Sr^{2+}] \times [OH^-]^2 = 3.2 \times 10^{-4} (\text{mol} \cdot \text{L}^{-1})^3 \quad [32]. \quad (5)$$

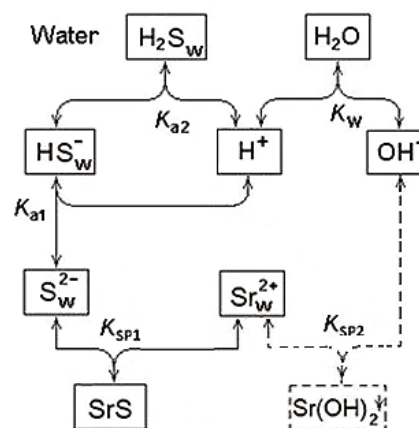


Fig. 1. Structural scheme demonstrating the distribution of ions and molecules in the closed equilibrium system of H_2O – SrS , where K_{a1} is the first acid dissociation constant of H_2S , K_{a2} the second acid dissociation constant of H_2S , K_w the ion-product constant of water, K_{SP1} the solubility product constant of SrS , and K_{SP2} the solubility product constant of $Sr(OH)_2$.

For calculating the concentrations of unknown variables, the base-dissociation or ionization constants (K_{b1} and K_{b2}) are expressed as follows Eqs (6–7):

$$K_{b1} = \frac{[\text{H}_2\text{S}]_w \times [\text{OH}^-]}{[\text{HS}^-]} = \frac{K_w}{K_{a1}} \cong 9.65 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}, \quad (6)$$

$$K_{b2} = \frac{[\text{HS}^-][\text{OH}^-]}{[\text{S}^{2-}]} = \frac{K_w}{K_{a2}} \cong 8.40 \text{ mol} \cdot \text{L}^{-1}. \quad (7)$$

In order to simplify the developed model of the closed equilibrium system of H₂O–SrS, the charge balance equation in the liquid phase is presented as:

$$2[\text{Sr}^{2+}] + [\text{H}^+] = 2[\text{S}^{2-}] + [\text{HS}^-] + [\text{OH}^-], \quad (8)$$

and the molar balance equation for calculating the mass of sulphur species as:

$$[\text{Sr}^{2+}] = [\text{S}^{2-}] + [\text{HS}^-] + [\text{H}_2\text{S}]_w. \quad (9)$$

The concentrations of the unknown variables ($[\text{S}^{2-}]$, $[\text{H}_2\text{S}]_w$, $[\text{H}^+]$) in charge (Eq. 8) and molar balance (Eq. 9) equations were eliminated by replacing their concentrations from Eqs 1–5 with the known values of $[\text{HS}^-]$ and $[\text{OH}^-]$ as follows (Eqs 10–12):

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}, \quad (10)$$

$$[\text{S}^{2-}] = \frac{[\text{HS}^-] \times [\text{OH}^-]}{K_{b2}}, \quad (11)$$

$$[\text{H}_2\text{S}]_w = \frac{K_{b1} \times [\text{HS}^-]}{[\text{OH}^-]}. \quad (12)$$

As a result of replacing the variables, the system is characterized by two equations with two unknown concentrations ($[\text{S}^{2-}]$ and $[\text{H}_2\text{S}]_w$). The equilibrium distribution of sulphide forms and the corresponding value of ion concentration in the liquid phase should simultaneously satisfy the conditions of the balance of moles and charges in the closed system of H₂O–SrS. In order to calculate their values by an iterative method, the charge ($[\text{HS}^-]_z$) and molar ($[\text{HS}^-]_M$) balance equations were converted to the following forms (Eqs 13, 14):

$$[\text{HS}^-] = [\text{HS}^-]_z = \frac{2[\text{Sr}^{2+}] + \frac{K_w}{[\text{OH}^-]} - [\text{OH}^-]}{\frac{2[\text{OH}^-]}{K_{b2}} + 1}, \quad (13)$$

$$[\text{HS}^-] = [\text{HS}^-]_M = \frac{[\text{Sr}^{2+}] - \Delta[\text{H}_2\text{S}]_w}{\frac{[\text{OH}^-]}{K_{b2}} + 1 + \frac{K_{b1}}{[\text{OH}^-]}}. \quad (14)$$

These equations (13, 14) contain only one unknown ($[\text{OH}^-]$), which will be derived from the corresponding pH of the closed equilibrium system of H₂O–SrS by using its different values [28]. In addition, most iterative methods are based on the termination criterion, which allows to eliminate the unknown concentration of formed ions and molecules present in this system while their corresponding values are relatively small, with the aim of simplifying the mathematical calculations performed by means of the specially developed Turbo Pascal (version 5.5 for MS–DOS) program “iterSrSa.bas” [26–28,33].

3. MATERIALS AND METHODS

The solubility of SrS salt was determined potentiometrically by using a pH-meter, after which the ratios of the measured and theoretical concentrations of dissolved ions and molecules (Sr^{2+} , OH^- , H^+ , HS^- , H_2S , and S^{2-}) were compared in the SrS–H₂O equilibrium system. For experimental measurements, only analytical grade reagents were used (provided by Alfa Aesar, Germany) and the determinations of ions from SrS aqueous solutions were performed after reaching the equilibrium state, which could be seen by the stabilization of the measured pH value. Each determination was made in at least three replicates in order to achieve a sufficient confidence level.

Solid strontium sulphide (99.9%, Alfa Aesar, Germany) was weighed with analytical balance (Scaltec SBC 31, Germany; measuring accuracy of ± 0.001 g). The MilliQ purified water (1000 mL) was purged with argon (99.999% Ar) for about half an hour to remove oxygen (O_2) and carbon dioxide (CO_2) to avoid the oxidation of sulphide (mainly HS^-) ions and the sedimentation of strontium carbonate. The efficiency of oxygen removal was controlled by the measurements of dissolved oxygen (DO) in water (oxygen-meter Marvet Junior MJ2000, Elke Sensor, Estonia).

The experiments were carried out at normal pressure (101325 Pa) in air-tightly closed glass bottles (with the volume of 1200 mL), which were filled with purged MilliQ ultrapure water and inserted into a thermostated water bath (Assistant 3180, Germany) with a magnetic stirrer (Stuart Scientific magnetic stirrer SM5) in order to keep a constant temperature of 25 ± 0.2 °C and a stirring speed of about 150–200 rpm during measurements.

The pH of the mixture was measured with the pH-meter (JENWAY 3520, UK), which was connected to a special pH-electrode (JENWAY Model No. 924-076, standard error of ± 0.003) intended for highly alkaline solutions. It was calibrated before each measurement at pH values of 7.00, 10.00, and 13.00 in buffer solutions with a standard error of ± 0.002 . The pH electrode was inserted tightly into the cover of the reaction cell, which

was connected with a computer and a program for measurement (Dataway version 1.1; JENWAY, UK), registering the pH values of SrS aqueous solutions.

The total amount of sulphur-containing species (the sum of dissolved H_2S , HS^- and S^{2-}) was determined iodometrically, where the excess of added iodine was titrated back with sodium thiosulphate [34,35]. Typically, a sample of 5–20 mL was collected for analysis. For comparison with titration, the concentration of bisulphide was measured by UV-Vis spectrometry, where the received calibration curve was linear within the studied range ($[\text{HS}^-] = 1\text{--}9 \text{ mg}\cdot\text{L}^{-1}$) [3,12,36–38]. A scanning UV-Vis spectrophotometer (Perkin Elmer, Lambda 35, UK) with a 10-mm quartz cell was used for absorbance measurements of the concentration of HS^- ions in the SrS aqueous solution against MilliQ water as a blank. The concentration of strontium ions was determined by direct titration with ethylene-diamine tetraacetate (EDTA) [3,34].

The $[\text{HS}^-]$ ions in the sample were determined by the calibration curve, prepared through preliminary measurements by using sodium bisulphide (99.9%, Alfa Aesar, Germany). The time for the analysis after the dissolution process was considered to be critical because of a possible oxidation of samples which could get in contact with air [38,39]. To avoid this, all analyses were carried out immediately after reaching the equilibrium state in the SrS aqueous solution and the collected samples were kept in closed cuvettes under inert gas (argon) [3,12].

4. RESULTS AND DISCUSSION

An experimental study was conducted with the purpose of controlling the validity of the developed theoretical model of $\text{H}_2\text{O}\text{--}\text{SrS}$. The results of the experimental measurements of this closed equilibrium system indicate that the concentration values of ions (e.g. $[\text{Sr}^{2+}]$, $[\text{OH}^-]$) were close to the theoretically calculated ones, as seen in Tables 1 and 2. The calculations of the final equilibrium concentrations of $[\text{Sr}^{2+}]$, $[\text{S}^{2-}]$, $[\text{H}_2\text{S}]_w$, and pH were performed on the basis of the calculated equilibrium concentrations of $[\text{HS}^-]$ and $[\text{OH}^-]$ or $[\text{H}^+]$ ions. Furthermore, the amount of protons bound by S^{2-} ions and their quantity released from the dissociation of water ($[\text{H}^+_{\text{H}_2\text{O}}]$) were also taken into account [26–28]. In order to calculate the closed equilibrium system's pH, concentrations of formed ions and molecules, different previously published values [12,16] of K_{a2} were used and compared with the experimentally obtained results in the $[\text{SrS}]$ range of 0.125–83.552 mM. As a result, the closest correlation between the calculated and the measured values of parameters of the investigated system was at $K_{a2} = 1.202\cdot 10^{-15}$ [31].

In Tables 1 and 2, the experimental results generally correspond to the theoretical model, as the calculated concentrations of formed ions, molecules and pH in this equilibrium system (at $[\text{SrS}]$ 0.125–83.552 mM) were close to the measured values, especially at lower amounts of salt added ($[\text{SrS}] \leq 1.671 \text{ mM}$).

According to Table 2, the main species of sulphur in the SrS aqueous solutions in the pH range of 10.0–13.1 was bisulphide, as $[\text{HS}^-]$ was about 81–99% of its total amount of sulphurous compounds (S_{total}). In addition, the measured values of $[\text{Sr}^{2+}]$ (determined by direct titration with EDTA titration) and $[\text{OH}^-]$ ions remained almost unchanged at $\text{pH} \leq 13.1$ because the solubility product (K_{SP}) value for $\text{Sr}(\text{OH})_2$ was exceeded at $[\text{SrS}] \geq 83.552 \text{ mM}$ ($\geq 10\,000 \text{ mg}\cdot\text{L}^{-1}$) and precipitation (in the form of strontium octahydrate, $\text{Sr}(\text{OH})_2\cdot 8\text{H}_2\text{O}$) occurred (Fig. 2) [14,32,39–41].

The difference between the measured lower concentration of Sr^{2+} ions and the calculated values was also confirmed by the formation of a precipitate in the closed equilibrium system of $\text{H}_2\text{O}\text{--}\text{SrS}$, when $[\text{SrS}] \geq 1.671 \text{ mM}$, as presented in Fig. 3 [12].

The experimental data indicate that the first equilibrium state was detected at the $\text{H}_2\text{O}\text{--}\text{SrS}$ system's pH value 11.18 ± 0.02 , where the corresponding $[\text{SrS}] = 1.671 \text{ mM}$ ($K_{\text{SP},\text{SrS}}$) [12]. Moreover, the measured $[\text{Sr}^{2+}]$ ions in the SrS aqueous solutions were almost equal to the calculated values at $[\text{SrS}] \leq 1.67 \text{ mM}$, when the solid phase was not present and the added salt was completely dissociated in this closed equilibrium system (Fig. 3) [3,12]. The determined values of $[\text{Sr}^{2+}]$, $[\text{HS}^-]$ and $[\text{OH}^-]$ ions show that the concentration of hydroxide ions was significantly higher when $[\text{SrS}] \geq 1.671 \text{ mM}$ in

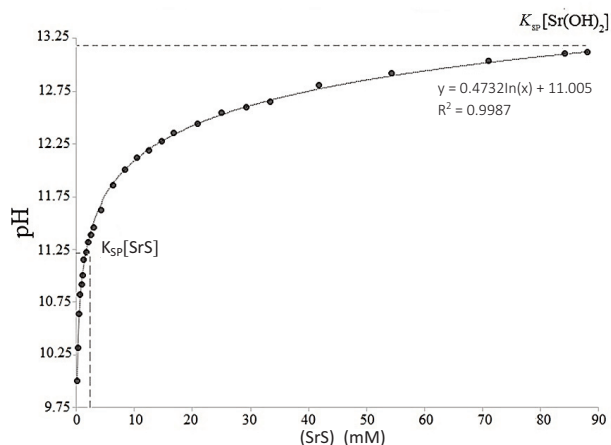


Fig. 2. Measured and calculated pH values of SrS aqueous solutions (in the $[\text{SrS}]$ range of 0.125–88.064 mM), where the vertical dashed lines refer to the solubility points which correspond to the measured values of $K_{\text{SP},\text{SrS}}$ and $K_{\text{SP},\text{Sr}(\text{OH})_2}$ [12,32].

Table 1. Calculated concentration of formed ions, molecules and pH in the equilibrium system of H₂O–SrS (0.125–83.552 mM), where $K_{a1} = 1.041 \cdot 10^{-8} \text{ mol} \cdot \text{L}^{-1}$; $K_{a2} = 1.202 \cdot 10^{-15}$ [31] $\text{mol} \cdot \text{L}^{-1}$ and $K_W = 1.01 \cdot 10^{-14} (\text{mol} \cdot \text{L}^{-1})^2$ at 25 °C

[SrS] $\text{mg} \cdot \text{L}^{-1}$	[Sr ²⁺] $\text{mmol} \cdot \text{L}^{-1}$	[S ²⁻] $\text{mmol} \cdot \text{L}^{-1}$, %	[HS ⁻] $\text{mmol} \cdot \text{L}^{-1}$	[H ₂ S] _w $\text{mmol} \cdot \text{L}^{-1}$	[OH ⁻] $\text{mmol} \cdot \text{L}^{-1}$	pH (calc.)
15	0.125	4×10^{-6} (0.003%)	0.1249 (99.920%)	9.68×10^{-5} (0.077%)	0.123	10.09
50	0.418	4.1×10^{-5} (0.010%)	0.4179 (99.967%)	9.70×10^{-5} (0.023%)	0.418	10.62
100	0.836	1.62×10^{-4} (0.019%)	0.8357 (99.969%)	9.70×10^{-5} (0.012%)	0.836	10.92
150	1.253	3.64×10^{-4} (0.029%)	1.2525 (99.963%)	9.70×10^{-5} (0.0077%)	1.253	11.09
200	1.671	6.48×10^{-4} (0.039%)	1.6703 (99.955%)	9.70×10^{-5} (0.0058%)	1.670	11.22
250	2.089	1.012×10^{-3} (0.048%)	2.0879 (99.947%)	9.70×10^{-5} (0.0046%)	2.089	11.32
300	2.507	1.457×10^{-3} (0.058%)	2.5054 (99.938%)	9.70×10^{-5} (0.0039%)	2.506	11.39
500	4.178	4.043×10^{-3} (0.097%)	4.1739 (99.901%)	9.70×10^{-5} (0.0023%)	4.174	11.62
1000	8.355	0.01614 (0.193%)	8.3388 (99.806%)	9.70×10^{-5} (0.0012%)	8.339	11.92
2000	16.711	0.06431 (0.385%)	16.6466 (99.6146%)	9.70×10^{-5} (5.8×10^{-4} %)	16.647	12.21
3000	25.066	0.1441 (0.575%)	24.9218 (99.425%)	9.70×10^{-4} (3.87×10^{-3} %)	24.922	12.39
4000	33.421	0.2553 (0.764%)	33.1656 (99.236%)	9.70×10^{-4} (2.90×10^{-3} %)	33.166	12.52
5000	41.776	0.3974 (0.951%)	41.3786 (99.049%)	9.70×10^{-4} (2.32×10^{-3} %)	41.379	12.61
6500	54.309	0.5686 (1.047%)	53.7394 (98.951%)	9.70×10^{-4} (1.79×10^{-3} %)	53.739	12.73
8500	71.019	1.0141 (1.428%)	70.0048 (98.572%)	9.70×10^{-4} (1.37×10^{-3} %)	70.005	12.85
10000	83.552	1.4279 (1.709%)	82.1241 (98.291%)	9.70×10^{-4} (1.16×10^{-3} %)	82.124	12.92

the SrS aqueous solutions, because an additional amount of protons ($\Delta[\text{H}^+]_{\text{H}_2\text{O}}$) were bound by sulphide ions after the dissociation of salt. Additionally, the measured ratio of $[\text{S}_{\text{total}}]/[\text{OH}^-]$ in the supersaturated SrS aqueous solutions ($[\text{SrS}] \geq 1.671 \text{ mM}$) was significantly lower (p -value < 0.05), as compared with $[\text{SrS}] \leq 1.671 \text{ mM}$. The determined amounts of total sulphide species $[\text{S}_{\text{total}}]$ in this system (including $[\text{HS}^-]$), as well as $[\text{Sr}^{2+}]$, decreased along with the increase in $[\text{SrS}]$ (Fig. 4 and Table 2).

As seen in Fig. 4 and Table 2, the experimentally determined values of the concentration of Sr^{2+} ions in the $[\text{SrS}]$ range of 0.125–1.671 mM are in accordance with the developed theoretical model (Table 1), but at higher

amounts of added salt ($[\text{SrS}] \geq 1.671 \text{ mM}$) the measured values are significantly lower due to supersaturation. Therefore, the latter should also be taken into account in developing the given theoretical model. Nevertheless, the experimentally measured final stabilized pH values of the closed equilibrium system of H₂O–SrS, which corresponds to its equilibrium state, were generally close to the theoretical ones and the small differences in the obtained values at higher $[\text{SrS}]$ might be due to the accuracy of determination techniques and the equipment used. In fact, the obtained results generally support the validity of the developed theoretical model of H₂O–SrS and the same approach can also be applied to other complex systems (e.g. phosphoric acid equilibrium).

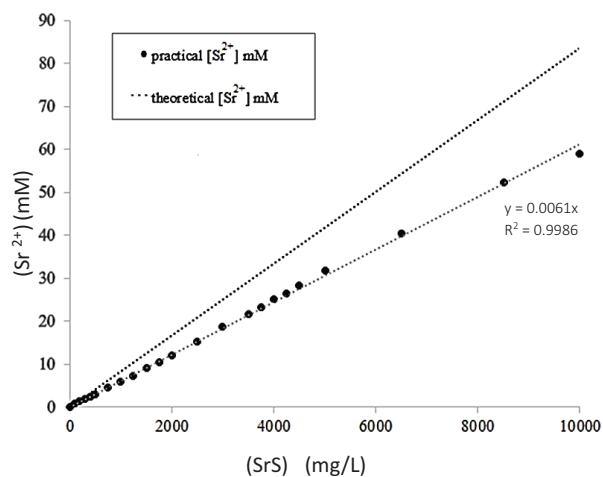


Fig. 3. Calculated and measured (EDTA titration) values of $[\text{Sr}^{2+}]$ ions in SrS aqueous solutions in the range of $[\text{SrS}]$ 15–10 000 $\text{mg}\cdot\text{L}^{-1}$ (0.125–83.552 mM).

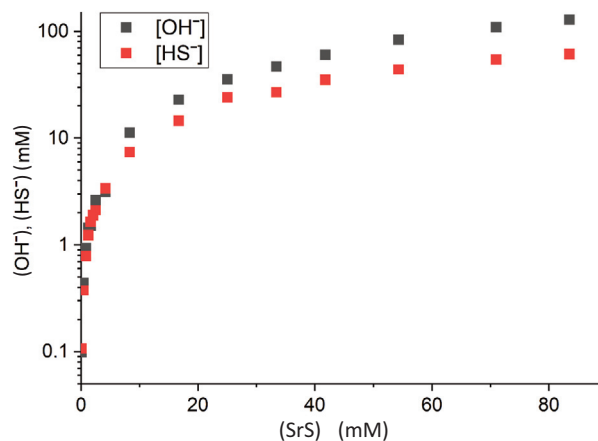


Fig. 4. Correlation between the experimentally measured $[\text{HS}^-]$ and $[\text{OH}^-]$ ions in the $[\text{SrS}]$ range of 15–10 540 $\text{mg}\cdot\text{L}^{-1}$ (0.125–83.552 mM) in logarithmic scale.

Table 2. Experimentally measured values of pH, concentrations of ions ($[\text{Sr}^{2+}]$, $[\text{OH}^-]$) and all sulphur forms (S_{total} , including $[\text{HS}^-]$) in 0.125–88.064 mM $[\text{SrS}]$ aqueous solutions [12]

$[\text{SrS}]$ (mM)	pH	$[\text{OH}^-]$ (mM)	$[\text{Sr}^{2+}]$ (mM)	$[S_{\text{total}}]$ (mM) ^a	$[\text{HS}^-]$ (mM) ^b
0.125 ± 0.01	10.00 ± 0.02	0.100	0.117 ± 0.04	0.122 ± 0.05	0.107 ± 0.06
0.418 ± 0.01	10.64 ± 0.02	0.437	0.345 ± 0.06	0.411 ± 0.04	0.374 ± 0.03
0.836 ± 0.01	10.97 ± 0.02	0.933	0.659 ± 0.06	0.821 ± 0.05	0.782 ± 0.03
1.253 ± 0.01	11.16 ± 0.02	1.445	0.975 ± 0.08	1.232 ± 0.06	1.229 ± 0.04
1.671 ± 0.01	11.18 ± 0.02	1.514	1.356 ± 0.08	1.647 ± 0.05	1.643 ± 0.03
2.089 ± 0.01	11.28 ± 0.02	1.905	1.625 ± 0.08	2.054 ± 0.10	1.892 ± 0.06
2.507 ± 0.01	11.42 ± 0.02	2.630	2.014 ± 0.10	2.429 ± 0.15	2.106 ± 0.06
4.178 ± 0.02	11.60 ± 0.02	3.981	3.286 ± 0.12	3.472 ± 0.27	3.368 ± 0.18
8.355 ± 0.02	12.05 ± 0.02	11.220	6.512 ± 0.14	7.991 ± 0.35	7.356 ± 0.30
16.711 ± 0.03	12.36 ± 0.02	22.909	12.56 ± 0.16	16.54 ± 0.65	14.54 ± 0.48
25.066 ± 0.03	12.55 ± 0.02	35.481	18.25 ± 0.20	24.83 ± 0.76	24.02 ± 0.66
33.421 ± 0.03	12.67 ± 0.02	46.774	24.82 ± 0.26	32.03 ± 0.98	26.86 ± 0.84
41.776 ± 0.04	12.78 ± 0.02	60.256	31.78 ± 0.38	38.67 ± 1.25	35.11 ± 0.98
54.309 ± 0.04	12.92 ± 0.02	83.176	40.49 ± 0.44	49.58 ± 1.46	43.88 ± 1.20
71.019 ± 0.05	13.04 ± 0.02	109.648	52.32 ± 0.48	63.56 ± 2.08	54.34 ± 1.92
83.552 ± 0.06	13.11 ± 0.02	128.825	59.04 ± 0.56	73.72 ± 2.54	61.22 ± 2.18
88.064 ± 0.06	13.12 ± 0.02	131.826	59.38 ± 0.64	NA	NA

^a Measured iodometrically.

^b Measured spectrophotometrically.

NA – not applicable.

5. CONCLUSIONS

A model of the closed system of H₂O–SrS was developed in the course of the present study and it was upgraded on the basis of proton transfer principles, where H⁺ ions play the central role. The developed model also takes into account the system's pH, equilibrium concentrations of the formed ions and molecules in the liquid phase. These essential parameters of the closed system of H₂O–SrS were calculated as well as experimentally validated.

The concentrations of different sulphide forms were determined spectrophotometrically, potentiometrically and by iodometric titration. The current study indicates that after adding larger amounts of salt ([SrS] ≥ 10 g·L⁻¹) into MilliQ water, strontium hydroxide (in the form of Sr(OH)₂·8H₂O) was formed as a precipitate because $K_{SP,Sr(OH)_2}$ was exceeded.

The present study suggests that further investigations are needed for describing strontium sulphide solubilisation in water. The developed model of equilibrium in the closed system of H₂O–SrS can be used to determine concentrations of all components in the water phase over a wide range of natural and industrial

conditions, based on the known concentrations of dissolved sulfur compounds in the water phase. The model allows one to assess the impact of anthropogenic processes in the environment and could be applied in environmental technology as well as in healthcare (e.g. for modelling hazardous H₂S behaviour in the environment). Moreover, as sulphur compounds (including HS⁻, H₂S and S²⁻) tend to oxidize and decompose quickly in the air, their analysing methods also need improvement to prevent it from happening. Thus, further studies are necessary to determine the concentration of different sulphur species in aqueous solutions and to calculate the exact value of the second acid dissociation constant (K_{a2}) of H₂S.

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APPENDIX

```

10 SCREEN 0
20 WIDTH 80
30 CLS
40 PRINT "22.05 - 03.06.2019"                program 'iterSrSa.bas' Copyright ( C ) 2019 by Alexey Mashirin. All rights reserved.
42 PRINT
44 PRINT "for iteration determination [OH-] by dissociation SrS in H2O"
46 PRINT " by nonsaturation and known transfer D[H2S] in gase phase"
48 PRINT
50 PRINT " FORMULS: [HS-]z = [HS-]m  "
52 PRINT
54 PRINT " [HS-]m = { [Sr++]-D[H2S]w } / { [OH]/Kb2 + 1 + Kb1/[OH-] } "
56 PRINT
58 PRINT " [HS-]z = { 2*[Sr++] + Kw/[OH-] - [OH-] } / { 1 + 2*[OH-]/Kb2 } "
60 PRINT
62 PRINT " [Sr++] = Dm(Ca++) / Vw;          D[H2S]w = Dm(H2S)w / Vw "
64 PRINT " Dm(Sr++),mol = Dm(SrS),g / M(SrS); Dm(H2S)w,mol = Dm(H2S)w,g / M(H2S) "
66 PRINT " M(SrS) = 119.686 g/mol;          M(H2S) = 34.0818 g/mol "
68 PRINT
70 PRINT " by t=25 grad C: Kb1=9.65e-8; Kb2=8.403; Kw=1.01e-14 "
rem 72 PRINT "          Va=0.6 litre; Vw=0.4 litre; kH=0.401 "
72 PRINT "          Ksp,SrS=3.98e-4; Ksp,Sr(OH)2=3.2e-4 "
74 PRINT
76 PRINT " [S-] = [HS-]*[OH-]/Kb2 "
78 PRINT " [H2S]w = Kb1*[HS-]/[OH-];          [H2S]a = kH*[H2S]w "
80 PRINT " m(Sx)w = Vw*{ [S-]+[HS-]+[H2S]w }; m(H2S)a = Va*[H2S]a "
82 PRINT " [H+] = Kw/[OH-];          pH = -0.43429 * ln[H+] "
84 PRINT

rem 90 KB1=9.65E-8:KB2=8.403:KW=1.01E-14:KSPSRS=3.98e-4:KSPSROH=3.2e-4

92 MSRS=119.686:MH2S=34.0818
rem 92 KH=0.401:VW=0.4:VA=0.6

100 INPUT " Calculation of [HS-]z,[HS-]m (Y/N) ";C1$

```

```

102 PRINT
104 IF (C1$="y" OR C1$="Y") THEN 170 ELSE 4000

rem 110 INPUT " Vw,litre = ";VW
rem 112 IF VW=0 THEN 114 ELSE 116rem 114 VW=0.4
rem 116 PRINT "          inputed Vw = ";:PRINT USING "#.###";VW;
rem 118 PRINT " litre"

rem 120 INPUT " Va,litre = ";VA
rem 122 IF VA=0 THEN 124 ELSE 126
rem 124 VA=0.6
rem 126 PRINT "          inputed Va = ";:PRINT USING "#.###";VA;
rem 128 PRINT " litre"

rem 130 INPUT " Dm(SrS),g = ";DMSRSG
rem 132 IF DMSRSG=0 THEN 134 ELSE 136
rem 134 DMSRSG=0.4
rem 136 PRINT "          inputed Dm(SrS) = ";:PRINT USING "#.#####";DMSRSG;
rem 138 PRINT " g"

rem 140 DMSR=DMSRSG/MSRS:CSR=DMSR/VW
rem 142 PRINT " inputed: Dm(Sr++) = ";:PRINT USING "#.#####";DMSR;:PRINT " mol "
rem 144 PRINT "      [Sr++] = ";:PRINT USING "#.#####";CSR;:PRINT " mol/l "

rem 150 INPUT " Dm(H2S),g = ";DMH2SG
rem 152 IF DMH2SG=0 THEN 154 ELSE 156
rem 154 DMH2SG=0.01
rem 156 PRINT "          inputed Dm(H2S) = ";:PRINT USING "#.#####";DMH2SG;
rem 158 PRINT " g"

rem 160 DMH2S=DMH2SG/MH2S:DCH2S=DMH2S/VW
rem 162 PRINT " Dm(H2S) = ";:PRINT USING "#.#####";DMH2S;:PRINT " mol "
rem 164 PRINT " D[H2S] = ";:PRINT USING "#.#####";DCH2S;:PRINT " mol/l "
rem 166 PRINT

170 INPUT "[SrS],mmol/l = ";CSRSMML
172 CSR=CSRSMML/1000:CSRSMML=CSRSMML:CSRSMG=MSRS*CSRSMML
174 PRINT "          inputed [Sr++] = ";:PRINT USING "###.###";CSRSMML;
176 PRINT " mmol/l "
178 PRINT

180 INPUT "D[H2S],mmol/l = ";DCH2SMML
182 DCH2S=DCH2SMML/1000
184 PRINT "          inputed D[H2S] = ";:PRINT USING "###.###";DCH2SMML;
186 PRINT " mmol/l "
188 PRINT

rem 194 INPUT " input of EDTA-data [Sr++],mol/l = ";EDTACSR
rem 195 IF EDTACSR=0 THEN 197 ELSE 196
rem 196 CSR=EDTACSR
rem 197 PRINT "          inputed [Sr++] = ";:PRINT USING "#.#####";CSR;:PRINT " mol/l "
rem 198 PRINT

200 PRINT " iteration ...D[HS-] —> 0 "
202 PRINT

204 N=0
206 INPUT "  pH,in = ";PH
208 IF PH=0 THEN 210 ELSE 214
210 INPUT "          [OH-],in,mmol/l = ";COHMML
211 COH=COHMML/1000
212 GOTO 220
214 CH=10^(-PH):COH=KW/CH

```



```

220 N=N+1
222 CHSM=(CSR-DCH2S)/(COH/KB2+1+KB1/COH)
224 CHSZ=(2*CSR+KW/COH-COH)/(2*COH/KB2+1)226 DCHS=CHSM-CHSZ
226 DCHS=CHSM-CHSZ
228 CH=KW/COH:PH=-0.43429*LOG(CH)

230 PRINT " [OH-] = ";PRINT USING "#.#####^";COH;
232 PRINT " N = ";PRINT USING "#####";N
234 PRINT " [HS-]z = ";PRINT USING "#.#####^";CHSZ;
236 PRINT " [HS-]m = ";PRINT USING "#.#####^";CHSM
238 PRINT " D[HS-] = ";PRINT USING "#.#####^";DCHS;
240 PRINT " pH = ";PRINT USING "#####";PH
242 PRINT

250 INPUT " new iteration ('Enter') <-> no ('n') ";C2$
252 PRINT
254 IF (C2$="n" OR C2$="N") THEN 270 ELSE 256
256 PRINT
258 COH=COH-0.5*DCHS
260 GOTO 220

270 INPUT "Input new calculation (Y/N) ";C3$
272 PRINT
274 IF (C3$="y" OR C3$="Y") THEN 210 ELSE 300

300 INPUT " Calculation of [S—],[HS-],[H2S] and pH (Y/N) ";C5$
302 PRINT
304 IF (C5$="y" OR C5$="Y") THEN 310 ELSE 4000

310 CHS=(2*CSR+KW/COH-COH)/(2*COH/KB2+1):PRCHS=100*CHS/CSR:CHSMML=CHS*1000
312 CS=CHS*COH/KB2:PRCS=100*CS/CSR:CSMML=CS*1000
314 CH2SW=KB1*CHS/COH:PRCH2SW=100*CH2SW/CSR:CH2SWMML=CH2SW*1000:CH2SWMG=CH2SWMML*MH2S
316 PRDCH2S=100*DCH2S/CSR:DCH2SMML=DCH2S*1000
rem 318 CH2SA=KH*CH2SW
320 CH=KW/COH:PH=-0.43429*LOG(CH)

322 KSPFSROH=CSR*((COH)^2):KSPFSRS=CSR*CS
rem 322 MSXW=VW*(CS+CHS+CH2SW):MH2SA=VA*CH2SA
rem 324 PRSXW=100*MSXW/DMCA:PRSXA=100*MH2SA/DMCA:PRDMH2SW=100*DMH2SW/DMCA

330 PRINT " [Sr++],mmol/l = ";PRINT USING "#.#####^";CSRMMML;
331 PRINT " ([SrS],mg/l = ";PRINT USING "#.#####^";CSRSMG;:PRINT " )"

332 PRINT
333 PRINT " [S—],mmol/l = ";PRINT USING "#.#####^";CSMML;
334 PRINT " ";PRINT USING "#####";PRCS;:PRINT " %"
335 PRINT " [HS-],mmol/l = ";PRINT USING "#.#####^";CHSMML;
336 PRINT " ";PRINT USING "#####";PRCHS;:PRINT " %"
337 PRINT " [H2S]w,mmol/l = ";PRINT USING "#.#####^";CH2SWMML;
338 PRINT " ";PRINT USING "#####";PRCH2SW;:PRINT " %"
339 PRINT " [H2S]w,mg/l = ";PRINT USING "#.#####^";CH2SWMG
340 PRINT

REM 339 PRINT " [H2S]a = ";PRINT USING "#.#####^";CH2SA
REM 340 PRINT " m(Sx)w = ";PRINT USING "#.#####^";MSXW;
REM 342 PRINT " ";PRINT USING "#####";PRSXW;:PRINT " %"
REM 344 PRINT " m(H2S)a = ";PRINT USING "#.#####^";MH2SA;
REM 346 PRINT " ";PRINT USING "#####";PRSXA;:PRINT " %"
REM 348 PRINT " Dm(H2S)w = ";PRINT USING "#.#####^";DMH2SW;
REM 350 PRINT " ";PRINT USING "#####";PRDMH2SW;:PRINT " %"
REM 352 PRINT

354 PRINT " [H+],mol/l = ";PRINT USING "#.#####^";CH;

```

```

356 PRINT " [OH-],mmol/l = ";PRINT USING "#.#####^";COH*1000
358 PRINT " pH = ";PRINT USING "###.#####";PH
362 PRINT " [Sr++]*[OH-]^2 = ";PRINT USING "#.#####^";KSPFSROH;
364 PRINT " ref.: Ksp,Sr(OH)2=3.2e-4,(mol/l)^3"
366 PRINT " [Sr++]*[S—] = ";PRINT USING "#.#####^";KSPFSRS;
368 PRINT " ref.: Ksp,SrS=3.98e-4,(mol/l)^3"
370 PRINT

rem 311 PCNA=-0.43429*LOG(CNA)
rem 312 PCCO3=-0.43429*LOG(CCO3)
rem 313 PCHCO3=-0.43429*LOG(CHCO3)
rem 314 PCCO2W=-0.43429*LOG(CCO2W):PCCO2A=-0.43429*LOG(CCO2A)
rem 315 PDCCO2W=-0.43429*LOG(DCCO2W):PPMCO2A=-0.43429*LOG(PPMCO2A)
rem 316 PCCO2A=-0.43429*LOG(CCO2A)
rem 317 PSCCO2=-0.43429*LOG(SCCO2):PSCCO2W=-0.43429*LOG(SCCO2W):KV=VA/VW
rem 318 PKV=-0.43429*LOG(KV)

400 INPUT "Input new calculation (Y/N) ";C6$
402 PRINT
404 IF (C6$="y" OR C6$="Y") THEN 100 ELSE 4000

4000 PRINT "[Enter] or [Esc] to Quit!"
4010 END

```

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Tasakaalulise suletud süsteemi H₂O–SrS modelleerimine ja eksperimentaalne mõõtmine

Kalev Uiga, Ergo Rikmann, Ivar Zekker, Alexey Mashirin ja Toomas Tenno

Tasakaalulist süsteemi H₂O–SrS uuriti [SrS] vahemikus 0,125–88,064 mM (mmol·L⁻¹) hapnikuvabas suletud katsesüsteemis konstantsel temperatuuril 25 °C (eksperimentaalselt mõõdetud SrS vesilahuste pH väärtused olid vahemikus 10,0–13,1). Selles heterogeenses tasakaalulises süsteemis moodustuvate ionide ja molekulide jaotus on kirjeldatud struktuurskeemina. Käesoleva uurimistöö käigus töötati välja suletud tasakaalulise süsteemi H₂O–SrS mudel, mida täiendati prootonite ülekande põhimõtete alusel, kus vee dissotsiatsioonil tekkivatel H⁺ ioonidel on oluline tähtsus. Lisaks kasutati antud tasakaalulist süsteemi iseloomustavate oluliste parameetrite (näiteks pH, tekkivate ionide ja molekulide sisaldus jm) leidmiseks ja modelleerimiseks uudet prootoni ülekandel põhinevat arvutusmudelit, mis baseerub matemaatilisel iteratsioonil. Antud mudelit saab kasutada nii inimtegevusest tulenevate mõjude hindamiseks looduslikele veekogudele kui ka tööstuslike protsesside modelleerimiseks.