

# Stoichiometry and stability of Fe(II) hydrosulphide complexes at 22–100°C

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Most of our current knowledge on the stability of the hydrosulphide complexes of the transition and precious metals has come from solubility studies. This is a consequence of the very low solubilities of their sulphides which do not allow metal concentrations sufficiently high enough for the application of other methods such as spectroscopy. With the development of increasingly sensitive analytical techniques, the solubility method continues to provide a useful approach to the determination of metal complex stoichiometry and stability. The hydrosulphide complexes of Fe(II) are one speciation scheme which is not, as yet, adequately determined. The presence of these complexes has important implications to transport of iron and the mechanisms of iron sulphide formation in anoxic seawater, during diagenesis, as well as in hydrothermal ore-depositing environments. In addition, the availability of iron as a nutrient to microbial organisms in anoxic waters may be partly controlled by the presence of these complexes (Balistrieri *et al.*, 1994). In the present study, the solubility of FeS in solutions containing reduced sulphur is being investigated with the aim of determining the speciation of Fe(II) as hydrosulphide complexes.

## Theory

The base solubility of FeS can be expressed as:

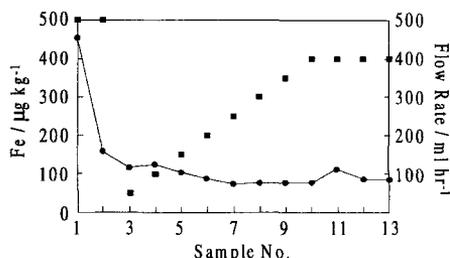
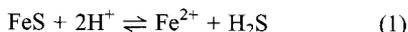
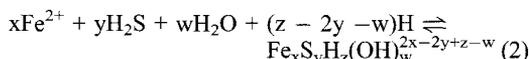


FIG. 1. The solubility of troilite (circles) at pH = 6.8 and ΣS = 0.1 mol kg<sup>-1</sup> at differing flow rates (squares).

and the general complexation reaction of Fe<sup>2+</sup> as hydrosulphide, hydroxide, and mixed complexes is best represented by



If reactions (1) and (2) are combined and summed over all complexes, the total solubility of FeS (mol kg<sup>-1</sup>) can be formulated, that is,

$$m_{\text{Fe}} = \sum_x \sum_y \sum_z \sum_w K_{\text{sp}}^x \beta_{\text{xyzw}} \alpha_{\text{H}_2\text{S}}^{y-x} \alpha_{\text{H}^+}^{z-2y-2x} \gamma_{\text{Fe}_x\text{S}_y\text{H}_z(\text{OH})_w}^{2x-2y+z-w} \quad (3)$$

where  $K_{\text{sp}}$  is the solubility product of FeS and  $\beta_{\text{xyzw}}$  is the cumulative stability constant of the complex. By taking the logarithm of this expression and differentiating with respect to pH, the pH dependence of each complex can be determined, i.e.

$$\frac{\partial \log m_{\text{Fe}}}{\partial \log m_{\text{H}_2\text{S}}} = 2y - z + w - 2x \quad (4)$$

and dependence on total sulphur concentration can be similarly derived by differentiation with respect to the logarithm of the molality of total sulphur,

$$\frac{\partial \log m_{\text{Fe}}}{\partial \log m_{\text{H}_2\text{S}}} = y - x \quad (5)$$

Using these expressions, it is possible to determine the Fe(II) speciation from solubility measurements made at differing pH and total sulphur.

## Method

FeS was prepared by sealing elemental Fe and S in large volume glass ampoule. These were evacuated, filled with N<sub>2</sub>, and then placed in a high temperature oven at 800°C for 6 hours, after which, the tubes were removed and allow to slowly cool. X-ray diffraction analysis showed the characteristic peaks of troilite. FeS solubility measurements were undertaken using a flow-through column contained in a heated oven. This approach provides distinct advantages over static

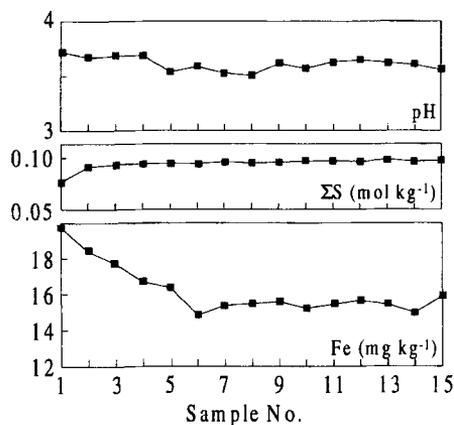


FIG. 2. The solubility of troilite at a constant flow rate of  $200 \text{ ml hr}^{-1}$ ,  $\text{pH} \sim 3.60$  and  $\Sigma\text{S} \sim 0.1 \text{ mol kg}^{-1}$ . The median values for each of these parameters from each flow-through experiment are used in Fig. 3.

experiments in that: experiments are fairly rapid therefore avoiding the problem of  $\text{H}_2\text{S}$  loss and oxidation; equilibrium is reached rapidly because of a low instantaneous fluid/mineral ratio; many replicate samples are possible; and large sample volumes are possible. Full details of the apparatus can be found in Mountain and Seward (1998).

Solutions were prepared from triply-distilled water, deoxygenated by boiling under a high purity nitrogen stream. Solution pH was modified by addition of either 50% NaOH or 70%  $\text{HClO}_4$ . Reduced sulphur was added by bubbling the solution with  $\text{N}_2\text{-H}_2\text{S}$  gas mixtures, the composition of which was determined by the concentration of reduced sulphur desired. After the solution was forced through the column and collected in the effluent syringe, its  $\Sigma\text{S}$  concentration and pH were measured. This was followed by acidification and bubbling with nitrogen (in order to remove the  $\text{H}_2\text{S}$ ) and analysis for total Fe by flame atomic absorption.

## Results

In order to establish that equilibrium is reached during flow-through experiments, it is necessary to vary solution flow rate and observe the response of iron concentration. Figure 1 shows the results from an experiment at  $22^\circ\text{C}$  in which the flow rate was varied between 50 and 500 ml/hr. Iron concentrations decrease to a relatively constant value of about  $70\text{--}80 \mu\text{g kg}^{-1}$  and are not dependent on flow rate. This is good evidence that equilibrium is attained rapidly in the column allowing further experiments to be carried out

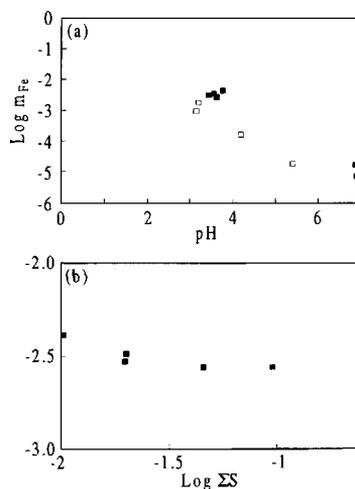


FIG. 3. Median solubilities for (a) 10 flow through experiments. Open squares are experiments at  $\Sigma\text{S} \sim 0.1 \text{ mol kg}^{-1}$ . (b) Median solubilities for 5 flow through experiments at  $\text{pH} = 3.4\text{--}3.8$ .

at relatively fast flow rates ( $>200 \text{ ml hr}^{-1}$ ).

Figure 2 shows an example of a typical flow through experiment at  $\text{pH} \sim 3.6$  and  $\Sigma\text{S} \sim 0.1 \text{ mol kg}^{-1}$  in which a concentration plateau of about  $15.5 \text{ mg kg}^{-1}$  was obtained. These data are reduced to a single point by taking the median value of  $\Sigma\text{Fe}$ ,  $\Sigma\text{S}$  and  $\text{pH}$ . These median values for all experiments are summarized in Fig. 3a where a clear  $-1$  dependence of Fe concentration on pH is evident between pH 3–6 for points at  $\Sigma\text{S} \sim 0.1 \text{ mol kg}^{-1}$ . If mononuclear complexes are assumed (i.e.  $x = 1$ ) and hydroxide complexing is not present (i.e.  $w = 0$ ) because of the low pH (Baes and Mesmer, 1976) then, according to equation (4), complexes with the relationship  $2y - z = 1$  satisfy the solubility data. Further constraints on the value of  $y$  and  $z$  can be obtained by determining the dependence of iron concentration on total sulphur. In Fig. 3b, median values for five experiments at approximately constant pH ( $\sim 3.5$ ) but differing sulphur concentration show a near zero slope and, according to equation (5), this means that  $y - x = 0$ . The only integer values which satisfy these two simple equations are  $y = 1$  and  $z = 1$  and, therefore, the complex must be  $\text{FeHS}^+$ . The slightly higher solubilities of Fe in the low sulphur region of Fig. 3b can be attributed to an increasing contribution of  $\text{Fe}^{2+}$  ( $x = 1, y = z = w = 0$ ) which has a  $-1$  sulphur dependence. Therefore, early results suggest that in the acid region the speciation of iron as hydro-sulphide complexes is dominated by  $\text{Fe}^{2+}$  and  $\text{FeHS}^+$ .