How to find the concentration of sulfuric acid (H_2SO_4), HSO_4^- and SO_4^{2-}

In some biological systems sulfate (SO_4^{2-}) play an important role as an electron acceptor for various microbial processes such as anaerobic respiration.

When sulfate is present some HSO_4^- is present as well and in very acidic solutions H_2SO_4 is present. How much can be found of each depend among others on pH.

To calculate individual concentrations of H_2SO_4, HSO_4^- and SO_4^{2-} we start by defining their ionization or dissociation constant for sulfuric acid and each of the ions HSO_4^- and SO_4^{2-}. In each case another derivation has been made that is to be used later on.

$$K_a^{HSO_4^-} = \frac{H^+ \cdot SO_4^{2-}}{HSO_4^-} \Rightarrow \frac{HSO_{4-}}{H^+ \cdot SO_4^{2-}} = \frac{1}{K_a^{HSO_4^-}}$$

$$K_a^{H_2SO_4} = \frac{H^+ \cdot HSO_4^-}{H_2SO_4} \Rightarrow \frac{H_2SO_4}{H^+ \cdot HSO_4^-} = \frac{1}{K_a^{H_2SO_4}}$$

$$K_a^{HSO_4^-} \cdot K_a^{H_2SO_4} = \frac{H^+ \cdot SO_4^{2-}}{HSO_4^-} \cdot \frac{H^+ \cdot HSO_4^-}{H_2SO_4} = \frac{H^+ \cdot H^+ \cdot SO_4^{2-}}{H_2SO_4}$$

When this is done we need to establish the relationship between total concentration of H_2SO_4, HSO_4^- and SO_4^{2-} and the dissociation constants and their derivations as derived above. Here, THSO is total sulfur on those three forms.

$$THSO = H_2SO_4 + HSO_4^- + SO_4^{2-} = HSO_4^- (1 + \frac{H_2SO_4}{HSO_4^-} + \frac{SO_4^{2-}}{HSO_4^-})$$

In this case HSO_4^- is isolated from sulfuric acid and sulfate.

$$HSO_4^- = \frac{THSO}{(1 + \frac{H_2SO_4}{HSO_4^-} + \frac{SO_4^{2-}}{HSO_4^-})} = \frac{THSO}{(1 + \frac{H^+ \cdot H_2SO_4}{H^+ \cdot HSO_4^-} + \frac{H^+ \cdot SO_4^{2-}}{H^+ \cdot HSO_4^-})} \Rightarrow$$

$$HSO_4^- = \frac{THSO}{(1 + \frac{H^+}{K_a^{H_2SO_4}} + \frac{K_a^{HSO_4^-}}{H^+})}$$

It's easy to do exactly the same and in this case just isolating sulfate:

$$THSO = H_2SO_4 + HSO_4^- + SO_4^{2-} = SO_4^{2-} (1 + \frac{H_2SO_4}{SO_4^{2-}} + \frac{HSO_4^{2-}}{SO_4^{2-}})$$

$$SO_4^{2-} = \frac{THSO}{(1 + \frac{H_2SO_4}{SO_4^{2-}} + \frac{HSO_4^{2-}}{SO_4^{2-}})} = \frac{THSO}{(1 + \frac{H^+ \cdot H_2SO_4}{H^+ \cdot SO_4^{2-}} + \frac{H^+ \cdot HSO_4^{2-}}{H^+ \cdot SO_4^{2-}})} \Rightarrow$$

$$SO_4^{2-} = \frac{THSO}{(1 + \frac{H^+}{K_a^{H_2SO_4}} + \frac{H^+}{K_a^{HSO_4^{2-}}})}$$

And the same for sulfuric acid:

$$THSO = H_2SO_4 + HSO_4^- + SO_4^{2-} = H_2SO_4(1 + \frac{HSO_4^-}{H_2SO_4} + \frac{SO_4^{2-}}{H_2SO_4})$$

$$H_2SO_4 = \frac{THSO}{(1 + \frac{HSO_4^-}{H_2SO_4} + \frac{SO_4^{2-}}{H_2SO_4})} = \frac{THSO}{(1 + \frac{H^+ \cdot HSO_4^-}{H^+ \cdot H_2SO_4} + \frac{H^+ \cdot SO_4^{2-}}{H^+ \cdot H_2SO_4})} =$$

$$THSO - HSO_4^- - SO_4^{2-} = H_2SO_4 = \frac{THSO}{(1 + \frac{K_a^{H_2SO_4}}{H^+} + H^+ \cdot H^+ \cdot K_a^{HSO_4^-} \cdot K_a^{H_2SO_4})}$$

If you are going to do some charge balance equation calculations using the Newton Raphson equation for solving the balance, its essential to know the differential equations of H_2SO_4, HSO_4^- and SO_4^{2-}, so here they are:

$$(SO_4^{2-})' = \frac{-THSO \cdot (\frac{1}{K_a^{H_2SO_4}} + \frac{1}{K_a^{HSO_4^-}})}{(\frac{H^+}{K_a^{H_2SO_4}} + \frac{H^+}{K_a^{HSO_4^-}} + 1)^2}$$

$$(HSO_4^-)' = \frac{-THSO \cdot (\frac{1}{K_a^{H_2SO_4}} - \frac{K_a^{HSO_4^-}}{(H^+)^2})}{(1 + \frac{K_a^{HSO_4^-}}{H^+} + \frac{H^+}{K_a^{H_2SO_4}})^2}$$