Equivalence Point of the Polyprotic Acid H_2SO_3

This is the derivation that the pH at the equivalence point for most polyprotic weak acids = the average of pK_{a1} and pK_{a2}

At the first equivalence point, HSO_3^- is present in solution.

Equation for the HSO_3^- in water acting as an acid:

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = 6.3 \times 10^{-8}$$

Equation for the HSO_3^- in water acting as a base:

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq) \qquad K_{b1} = K_w/K_{a1} = 6.7 \times 10^{-13}$$

Add the two equations together:

$$2HSO_3^-(aq) + 2H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq) + SO_3^{2-}(aq) + H_3O^+(aq) \qquad K = K_{a2} \times (K_w/K_{a1})$$

But we see that the ionization of water is present in this equation so pull it out:

$$2HSO_3^-(aq) \rightleftharpoons H_2SO_3(aq) + SO_3^{2-}(aq) \qquad K = K_{a2}/K_{a1} = 4.2 \times 10^{-6}$$

$$2H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq) \qquad K_w = 1.0 \times 10^{-14}$$

The principal reaction is the one with the largest K value.

$K_{a1} = \dfrac{[H_30^+][HSO_3^-]}{[H_2SO_3]}$ and $K_{a2} = \dfrac{[H_3O+][SO_3^{2-}]}{[HSO_3^-]}$

Rearrange and set both equal to $[H_3O+]$ since we want pH:

$[H_3O^+] = \dfrac{K_{a1}[H_2SO_3]}{[HSO_3^-]}$ and $[H_3O^+] = \dfrac{K_{a2}[HSO_3^-]}{[SO_3^{2-}]}$

$\dfrac{K_{a1}[H_2SO_3]}{[HSO_3^-]} \times \dfrac{K_{a2}[HSO_3^-]}{[SO_3^{2-}]} = [H_3O^+]^2$ So $\dfrac{K_{a1}K_{a2}[H_2SO_3]}{[SO_3^{2-}]} = [H_3O^+]^2$

Since the principle reaction is $2HSO_3^-(aq) \rightleftharpoons H_2SO_3(aq) + SO_3^{2-}(aq)$

$[H_2SO_3] = [SO_3^{2-}]$ So $\dfrac{K_{a1}K_{a2}\cancel{[H_2SO_3]}}{\cancel{[SO_3^{2-}]}} = [H_3O^+]^2$ becomes $K_{a1}K_{a2} = [H_3O^+]^2$

Now since $pH = -\log [H_3O^+]$:

$\log K_{a1} + \log K_{a2} = 2 \log [H_3O^+]$ (divide both sides by 2)

$\dfrac{\log K_{a1} + \log K_{a2}}{2} = \log [H_3O^+]$ Now since $pH = -\log [H_3O^+]$:

$pH = \dfrac{-\log K_{a1} + -\log K_{a2}}{2} = -\log [H_3O^+]$

$pH = \dfrac{pK_{a1} + pK_{a2}}{2}$

So the pH for the first equivalence point of the polyprotic acid H_2SO_3 is $\dfrac{(-\log 1.5 \times 10^{-2}) + (-\log 6.3 \times 10^{-8})}{2} = 4.51$