

Equivalence Point of the Polyprotic Acid H₂SO₃

**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, HSO₃⁻ is present in solution.

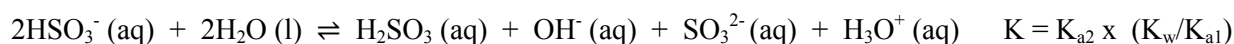
Equation for the HSO₃⁻ in water acting as an acid:



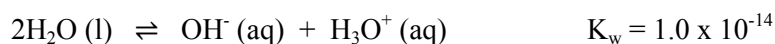
Equation for the HSO₃⁻ in water acting as a base:



Add the two equations together:



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



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

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} \quad \text{and} \quad K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]}$$

Rearrange and set both equal to [H₃O⁺] since we want pH:

$$[\text{H}_3\text{O}^+] = \frac{K_{a1}[\text{H}_2\text{SO}_3]}{[\text{HSO}_3^-]} \quad \text{and} \quad [\text{H}_3\text{O}^+] = \frac{K_{a2}[\text{HSO}_3^-]}{[\text{SO}_3^{2-}]}$$

$$\frac{K_{a1}[\text{H}_2\text{SO}_3]}{[\text{HSO}_3^-]} \times \frac{K_{a2}[\text{HSO}_3^-]}{[\text{SO}_3^{2-}]} = [\text{H}_3\text{O}^+]^2 \quad \text{So} \quad \frac{K_{a1}K_{a2}[\text{H}_2\text{SO}_3]}{[\text{SO}_3^{2-}]} = [\text{H}_3\text{O}^+]^2$$

Since the principle reaction is $2\text{HSO}_3^- (\text{aq}) \rightleftharpoons \text{H}_2\text{SO}_3 (\text{aq}) + \text{SO}_3^{2-} (\text{aq})$

$$[\text{H}_2\text{SO}_3] = [\text{SO}_3^{2-}] \quad \text{So} \quad \frac{K_{a1}K_{a2}[\cancel{\text{H}_2\text{SO}_3}]}{[\cancel{\text{SO}_3^{2-}}]} = [\text{H}_3\text{O}^+]^2 \quad \text{becomes} \quad K_{a1}K_{a2} = [\text{H}_3\text{O}^+]^2$$

Now since pH = -log [H₃O⁺]:

$$\log K_{a1} + \log K_{a2} = 2 \log [\text{H}_3\text{O}^+] \quad (\text{divide both sides by 2})$$

$$\frac{\log K_{a1} + \log K_{a2}}{2} = \log [\text{H}_3\text{O}^+] \quad \text{Now since pH} = -\log [\text{H}_3\text{O}^+] :$$

$$\text{pH} = \frac{-\log K_{a1} + -\log K_{a2}}{2} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2}$$

So the pH for the first equivalence point of the polyprotic acid H₂SO₃ is $\frac{(-\log 1.5 \times 10^{-2}) + (-\log 6.3 \times 10^{-8})}{2} = 4.51$