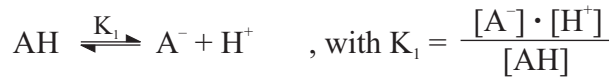


Derivation of the pK_a-equations for fitting of absorption data

1) Two species: AH and A⁻ ≅ one pK_a-value

Consider the following acid-base equilibrium:



Both species, AH and A⁻, show an UV absorption δ :

$$\delta_{\text{total}} \cdot ([\text{AH}] + [\text{A}^-]) = \delta_{\text{AH}} \cdot [\text{AH}] + \delta_{\text{A}^-} \cdot [\text{A}^-]$$

Taking both equations together gives the following expression:

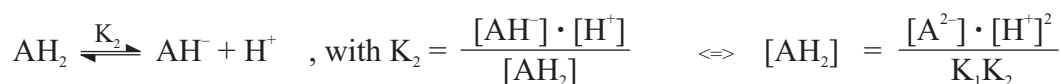
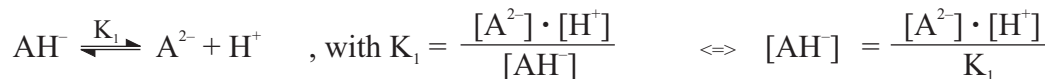
$$\delta_{\text{total}} \cdot \left(\frac{[\text{A}^-] \cdot [\text{H}^+]}{K_1} + [\text{A}^-] \right) = \delta_{\text{AH}} \cdot \frac{[\text{A}^-] \cdot [\text{H}^+]}{K_1} + \delta_{\text{A}^-} \cdot [\text{A}^-]$$

$$\Leftrightarrow \delta_{\text{total}} \cdot \left(\frac{10^{-\text{pH}}}{10^{-\text{pK}_1}} + 1 \right) = \delta_{\text{AH}} \cdot \frac{10^{-\text{pH}}}{10^{-\text{pK}_1}} + \delta_{\text{A}^-}$$

$$\Leftrightarrow \delta_{\text{total}} = \frac{\delta_{\text{A}^-} + \delta_{\text{AH}} \cdot 10^{\text{pK}_1 - \text{pH}}}{1 + 10^{\text{pK}_1 - \text{pH}}}$$

2) Three species: AH₂, AH⁻, and A²⁻ ≅ two pK_a-values

Consider the following acid-base equilibria:



All species, AH₂, AH⁻ and A²⁻, show an UV absorption δ :

$$\delta_{\text{total}} \cdot ([\text{AH}_2] + [\text{AH}^-] + [\text{A}^{2-}]) = \delta_{\text{AH}_2} \cdot [\text{AH}_2] + \delta_{\text{AH}^-} \cdot [\text{AH}^-] + \delta_{\text{A}^{2-}} \cdot [\text{A}^{2-}]$$

Taking all three equations together gives the following expression:

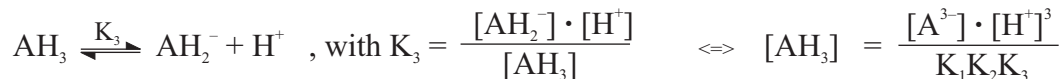
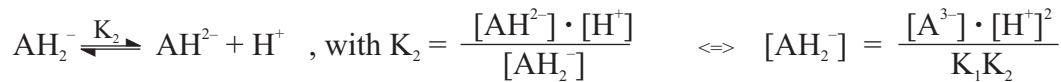
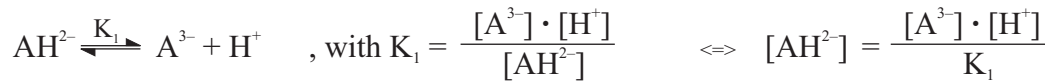
$$\delta_{\text{total}} \cdot \left(\frac{[\text{A}^{2-}] \cdot [\text{H}^+]^2}{K_1 K_2} + \frac{[\text{A}^{2-}] \cdot [\text{H}^+]}{K_1} + [\text{A}^{2-}] \right) = \delta_{\text{AH}_2} \cdot \frac{[\text{A}^{2-}] \cdot [\text{H}^+]^2}{K_1 K_2} + \delta_{\text{AH}^-} \cdot \frac{[\text{A}^{2-}] \cdot [\text{H}^+]}{K_1} + \delta_{\text{A}^{2-}} \cdot [\text{A}^{2-}]$$

$$\Leftrightarrow \delta_{\text{total}} \cdot \left(\frac{10^{-2\text{pH}}}{10^{-(\text{pK}_1 + \text{pK}_2)}} + \frac{10^{-\text{pH}}}{10^{-\text{pK}_1}} + 1 \right) = \delta_{\text{AH}_2} \cdot \frac{10^{-2\text{pH}}}{10^{-(\text{pK}_1 + \text{pK}_2)}} + \delta_{\text{AH}^-} \cdot \frac{10^{-\text{pH}}}{10^{-\text{pK}_1}} + \delta_{\text{A}^{2-}}$$

$$\Leftrightarrow \delta_{\text{total}} = \frac{\delta_{\text{A}^{2-}} + \delta_{\text{AH}^-} \cdot 10^{\text{pK}_1 - \text{pH}} + \delta_{\text{AH}_2} \cdot 10^{\text{pK}_1 + \text{pK}_2 - 2\text{pH}}}{1 + 10^{\text{pK}_1 - \text{pH}} + 10^{\text{pK}_1 + \text{pK}_2 - 2\text{pH}}}$$

3) Four species: AH_3 , AH_2^- , AH^- , and $A^{3-} \triangleq$ three pK_a -values

Consider the following acid-base equilibria:



All species, AH_3 , AH_2^- , AH^- and A^{3-} , show an UV absorption δ :

$$\delta_{\text{total}} \cdot ([AH_3] + [AH_2^-] + [AH^-] + [A^{3-}]) = \delta_{AH_3} \cdot [AH_3] + \delta_{AH_2^-} \cdot [AH_2^-] + \delta_{AH^-} \cdot [AH^-] + \delta_A \cdot [A^{3-}]$$

Taking all three equations together gives the following expression:

$$\begin{aligned} \delta_{\text{total}} \cdot \left(\frac{[A^{3-}] \cdot [H^+]^3}{K_1 K_2 K_3} + \frac{[A^{3-}] \cdot [H^+]^2}{K_1 K_2} + \frac{[A^{3-}] \cdot [H^+]}{K_1} + [A^{3-}] \right) \\ = \delta_{AH_3} \cdot \frac{[A^{3-}] \cdot [H^+]^3}{K_1 K_2 K_3} + \delta_{AH_2^-} \cdot \frac{[A^{3-}] \cdot [H^+]^2}{K_1 K_2} + \delta_{AH^-} \cdot \frac{[A^{3-}] \cdot [H^+]}{K_1} + \delta_A \cdot [A^{3-}] \\ \Leftrightarrow \delta_{\text{total}} \cdot \left(\frac{10^{-3pH}}{10^{-(pK_1+pK_2+pK_3)}} + \frac{10^{-2pH}}{10^{-(pK_1+pK_2)}} + \frac{10^{-pH}}{10^{-pK_1}} + 1 \right) = \delta_{AH_3} \cdot \frac{10^{-3pH}}{10^{-(pK_1+pK_2+pK_3)}} + \delta_{AH_2^-} \cdot \frac{10^{-2pH}}{10^{-(pK_1+pK_2)}} + \delta_{AH^-} \cdot \frac{10^{-pH}}{10^{-pK_1}} + \delta_A \end{aligned}$$

$$\Leftrightarrow \delta_{\text{total}} = \frac{\delta_A + \delta_{AH^-} \cdot 10^{pK_1 - pH} + \delta_{AH_2^-} \cdot 10^{pK_1+pK_2-2pH} + \delta_{AH_3} \cdot 10^{pK_1+pK_2+pK_3-3pH}}{1 + 10^{pK_1 - pH} + 10^{pK_1+pK_2-2pH} + 10^{pK_1+pK_2+pK_3-3pH}}$$

4) Assume two pK_a -values are (nearly) equal, e.g. pK_1 and pK_2

$$\Rightarrow \delta_{\text{total}} = \frac{\delta_A + \delta_{AH^-} \cdot 10^{pK_1 - pH} + \delta_{AH_2^-} \cdot 10^{2pK_1 - 2pH} + \delta_{AH_3} \cdot 10^{2pK_1+pK_3-3pH}}{1 + 10^{pK_1 - pH} + 10^{2pK_1 - 2pH} + 10^{2pK_1+pK_3-3pH}}$$

5) And so on...