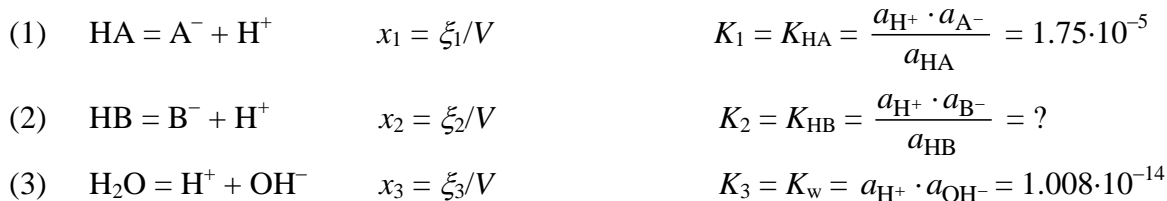


Problem 8-04 Solution of two weak acids – dissociation constant

pH of the solution containing $0.001 \text{ mol dm}^{-3}$ of acetic acid (HA) together with other monobasic acid (HB) in concentration $0.001 \text{ mol dm}^{-3}$ was determined to be 3.78. The dissociation constant of the acetic acid (standard state of infinite dilution, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$) is $K_{\text{HA}} = 1.75 \cdot 10^{-5}$. Find the value of the dissociation constant of acid HB. Ionic product of water K_w at these conditions has the value of $1.008 \cdot 10^{-14}$. Assume that all activity coefficients are equal to one

$$[K_{\text{HB}} = 1.26 \cdot 10^{-5}]$$

Solution:



Balance:

$$c^{\text{st}} = 1 \text{ mol dm}^{-3}$$

$$(c_{\text{HA}})_0 = (c_{\text{HB}})_0 = c_0 = 0.001 \text{ mol dm}^{-3}.$$

$$c_{\text{HA}} = c_0 - x_1$$

$$c_{\text{A}^-} = x_1$$

$$c_{\text{HB}} = c_0 - x_2$$

$$c_{\text{B}^-} = x_2$$

$$c_{\text{H}^+} = x_1 + x_2 + x_3$$

$$c_{\text{OH}^-} = x_3$$

$$\text{pH} = 3.78 \Rightarrow a_{\text{H}^+} \approx c_{\text{H}^+} = 10^{-3.78} = 1.6596 \cdot 10^{-4} \text{ mol dm}^{-3}$$

$$K_w = 1.008 \cdot 10^{-14} = a_{\text{H}^+} \cdot a_{\text{OH}^-} \approx c_{\text{H}^+} \cdot c_{\text{OH}^-} \quad (c^{\text{st}} = 1 \text{ mol dm}^{-3}, \gamma_i = 1)$$

$$c_{\text{OH}^-} = x_3 = \frac{K_w}{c_{\text{H}^+}} = \frac{1.008 \cdot 10^{-14}}{1.6596 \cdot 10^{-4}} = 6.0738 \cdot 10^{-11} \text{ mol dm}^{-3}$$

$$a_i \approx c_i / c^{\text{st}} \quad (\gamma_i = 1) \quad , \quad c^{\text{st}} = 1 \text{ mol dm}^{-3}$$

$$K_1 = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} \approx \frac{\frac{c_{\text{H}^+}}{c^{\text{st}}} \cdot \frac{c_{\text{A}^-}}{c^{\text{st}}}}{\frac{c_{\text{HA}}}{c^{\text{st}}}} = \frac{(x_1 + x_2 + x_3) \cdot x_1}{c_0 - x_1} = \frac{1.6596 \cdot 10^{-4} \cdot x_1}{0.001 - x_1}$$

$$1.6596 \cdot 10^{-4} \cdot x_1 = 1.75 \cdot 10^{-5} \cdot 0.001 - 1.75 \cdot 10^{-5} \cdot x_1$$

$$x_1 = \frac{1.75 \cdot 10^{-8}}{(1.6596 \cdot 10^{-4} + 1.75 \cdot 10^{-5})} = 9.5389 \cdot 10^{-5} \text{ mol dm}^{-3}$$

$$x_2 = c_{\text{H}^+} - x_1 - x_3 = 1.6596 \cdot 10^{-4} - 9.5389 \cdot 10^{-5} - 6.0738 \cdot 10^{-11} = 7.0571 \cdot 10^{-5} \text{ mol dm}^{-3}$$

$$K_2 = \frac{a_{\text{H}^+} \cdot a_{\text{B}^-}}{a_{\text{HB}}} \approx \frac{\frac{c_{\text{H}^+}}{c^{\text{st}}} \cdot \frac{c_{\text{B}^-}}{c^{\text{st}}}}{\frac{c_{\text{HB}}}{c^{\text{st}}}} = \frac{(x_1 + x_2 + x_3) \cdot x_2}{c_0 - x_2} = \frac{1.6596 \cdot 10^{-4} \cdot 7.0571 \cdot 10^{-5}}{0.001 - 7.0571 \cdot 10^{-5}} = 1.26 \cdot 10^{-5}$$