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

pH of the solution containing 0.001 mol dm^{-3} of acetic acid (HA) together with other monobasic acid (HB) in concentration 0.001 mol dm^{-3} was determined to be 3.78. The dissociation constant of the acetic acid (standard state of infinite dilution, c^{st} = 1 mol dm^{-3}) is $K_{HA} = 1.75 \cdot 10^{-5}$. 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

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

Solution:

(1) $HA = A^- + H^+$ $\quad x_1 = \xi_1/V$ $\quad K_1 = K_{HA} = \dfrac{a_{H^+} \cdot a_{A^-}}{a_{HA}} = 1.75 \cdot 10^{-5}$

(2) $HB = B^- + H^+$ $\quad x_2 = \xi_2/V$ $\quad K_2 = K_{HB} = \dfrac{a_{H^+} \cdot a_{B^-}}{a_{HB}} = ?$

(3) $H_2O = H^+ + OH^-$ $\quad x_3 = \xi_3/V$ $\quad K_3 = K_w = a_{H^+} \cdot a_{OH^-} = 1.008 \cdot 10^{-14}$

Balance:

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

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

$c_{HA} = c_0 - x_1$

$c_{A^-} = x_1$

$c_{HB} = c_0 - x_2$

$c_{B^-} = x_2$

$c_{H^+} = x_1 + x_2 + x_3$ $\quad$ pH = 3.76 $\Rightarrow$ $a_{H^+} \approx c_{H^+} = 10^{-3.78} = 1.6596 \cdot 10^{-4}$ mol dm^{-3}

$c_{OH^-} = x_3$ $\quad K_w = 1.008 \cdot 10^{-14} = a_{H^+} \cdot a_{OH^-} \approx c_{H^+} \cdot c_{OH^-}$ ($c^{st} = 1$ mol dm^{-3}, $\gamma_i = 1$)

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

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

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

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

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

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

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