Problem 8-02 Solution of weak acid – dissociation constant

pH of aqueous solution of weak acid HA, prepared at 18 °C in concentration $2.5\cdot10^{-5}$ mol dm^{-3}, was determined to be 6.8. Calculate the value of the dissociation constant for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3} (assume that all activity coefficients are equal to one). Ionic product of water K_w at these conditions has the value of $5.826\cdot10^{-15}$.

[$K_{HA} = 7.755\cdot10^{-10}$]

Solution:

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

(2) $H_2O = H^+ + OH^-$ $\quad x_2 = \xi_2/V$ $\quad K_2 = K_w = a_{H^+}\cdot a_{OH^-}$

$c_{HA} = c_0 - x_1$

$c_{A^-} = x_1$

$c_{H^+} = x_1 + x_2$

$c_{OH^-} = x_2$

pH = 6.8 $\Rightarrow$ $a_{H^+} \approx c_{H^+} = 10^{-6,8} = 1.584893\cdot10^{-7}$ mol dm^{-3}

$K_v = 5.826\cdot10^{-15} = a_{H^+}\cdot a_{OH^-} \approx c_{H^+}\cdot c_{OH^-}$

(c^{st} = 1 mol dm^{-3}, γ_i = 1)

$$x_2 = c_{OH^-} = \frac{K_v}{c_{H^+}} = \frac{5.826\cdot10^{-15}}{1.584893\cdot10^{-7}} = 3.6759575\cdot10^{-8} \text{ mol dm}^{-3}$$

$c_{A^-} = x_1 = c_{H^+} - x_2 = 1.584893\cdot10^{-7} - 3.6759575\cdot10^{-8} = 1.21728\cdot10^{-7}$ mol dm^{-3}

$$K_{HA} = \frac{a_{H^+}\cdot a_{A^-}}{a_{AH}} = \frac{\gamma_+\cdot\dfrac{c_{H^+}}{c^{st}}\cdot\gamma_-\cdot\dfrac{c_{A^-}}{c^{st}}}{\gamma_{AH}\cdot\dfrac{c_{AH}}{c^{st}}} = \frac{\gamma_\pm^2\cdot c_{H^+}\cdot x_1}{c_0 - x_1}\cdot\frac{1}{c^{st}}$$

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

$$K_{HA} = \frac{c_{H^+}\cdot x_1}{c_0 - x_1} = \frac{1.584893\cdot10^{-7}\cdot1.21728\cdot10^{-7}}{2.5\cdot10^{-5} - 1.21728\cdot10^{-7}}$$

K_{HA} = $= 7.75479\cdot10^{-10}$