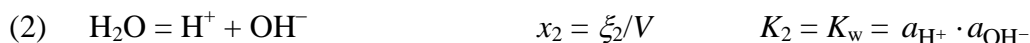
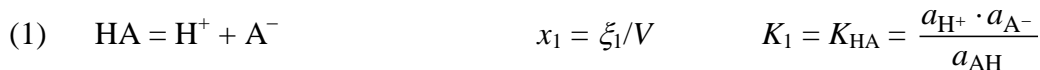


Problem 8-02 Solution of weak acid – dissociation constant

pH of aqueous solution of weak acid HA, prepared at 18°C in concentration $2.5 \cdot 10^{-5} \text{ mol dm}^{-3}$, was determined to be 6.8. Calculate the value of the dissociation constant for the standard state of infinite dilution, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$ (assume that all activity coefficients are equal to one). Ionic product of water K_w at these conditions has the value of $5.826 \cdot 10^{-15}$.

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

Solution:



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

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

$$\begin{aligned} c_{\text{H}^+} &= x_1 + x_2 & \text{pH} = 6.8 &\Rightarrow a_{\text{H}^+} \approx c_{\text{H}^+} = 10^{-6.8} = 1.584893 \cdot 10^{-7} \text{ mol dm}^{-3} \\ c_{\text{OH}^-} &= x_2 & K_w &= 5.826 \cdot 10^{-15} = a_{\text{H}^+} \cdot a_{\text{OH}^-} \approx c_{\text{H}^+} \cdot c_{\text{OH}^-} \\ & & & (c^{\text{st}} = 1 \text{ mol dm}^{-3}, \gamma_i = 1) \end{aligned}$$

$$x_2 = c_{\text{OH}^-} = \frac{K_w}{c_{\text{H}^+}} = \frac{5.826 \cdot 10^{-15}}{1.584893 \cdot 10^{-7}} = 3.6759575 \cdot 10^{-8} \text{ mol dm}^{-3}$$

$$c_{\text{A}^-} = x_1 = c_{\text{H}^+} - x_2 = 1.584893 \cdot 10^{-7} - 3.6759575 \cdot 10^{-8} = 1.21728 \cdot 10^{-7} \text{ mol dm}^{-3}$$

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

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

$$K_{\text{HA}} = \frac{c_{\text{H}^+} \cdot x_1}{c_0 - x_1} = \frac{1.584893 \cdot 10^{-7} \cdot 1.21728 \cdot 10^{-7}}{2.5 \cdot 10^{-5} - 1.21728 \cdot 10^{-7}}$$

$$K_{\text{HA}} = 7.75479 \cdot 10^{-10}$$