Problem 8-03 Solution of weak acid – concentration from pH

The dissociation constant of acrylic acid for the standard state of infinite dilution, $c^{st} = 1$ mol dm^{-3}, has the value of $5.5 \cdot 10^{-5}$. Assuming that all activity coefficients are equal to one and that you can neglect the water protolysis, calculate what amount of acrylic acid (in grams) you must dissolve in 100 cm^3 of water at 20 °C to obtain a solution with pH = 4.2. Ionic product of water K_w at these conditions has the value of $6.8 \cdot 10^{-15}$.

[$m_0 = 9.763 \cdot 10^{-4}$ g]

Solution:

pH = 4.2
m_0 = ?

(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 = 4.2 $\Rightarrow$ $a_{H+} \approx c_{H+} = 10^{-4,2} = 6.309573 \cdot 10^{-5}$ mol dm^{-3}

$K_w = 6.8 \cdot 10^{-15} = a_{H+} \cdot a_{OH-} \approx c_{H+} \cdot c_{OH-}$

($c^{st} = 1$ mol dm^{-3}, $\gamma_i = 1$, $a_{H2O} = 1$)

$$x_2 = c_{OH^-} = \frac{K_w}{c_{H^+}} = \frac{6.8 \cdot 10^{-15}}{6.309573 \cdot 10^{-5}} = 1.07773 \cdot 10^{-10} \text{ mol dm}^{-3}$$

$$c_{A-} = x_1 = c_{H+} - x_2 = 6.309573 \cdot 10^{-5} - 1.07773 \cdot 10^{-10} = 6.309552 \cdot 10^{-5} \text{ mol dm}^{-3}$$

(autoprotolysis of water is negligible)

$$K_{HA} = \frac{a_{H^+} \cdot a_{A^-}}{a_{AH}} = \frac{\gamma_+ \cdot \frac{c_{H^+}}{c^{st}} \cdot \gamma_- \cdot \frac{c_{A^-}}{c^{st}}}{\gamma_{AH} \cdot \frac{c_{AH}}{c^{st}}} = \frac{\gamma_\pm^2 \cdot (x_1 + x_2) \cdot x_1}{c_0 - x_1} \approx \frac{(x_1 + x_2) \cdot x_1}{c_0 - x_1} \quad , \; c^{st} = 1 \text{ mol dm}^{-3}$$

$$c_0 = x_1 + \frac{(x_1 + x_2) \cdot x_1}{K_{HA}} = 6.309552 \cdot 10^{-5} + \frac{(6.309552 \cdot 10^{-5} + 1.07773 \cdot 10^{-10}) \cdot 6.309552 \cdot 10^{-5}}{5.5 \cdot 10^{-5}}$$

$c_0 = 1.35478 \cdot 10^{-4}$ mol dm^{-3}

$M(CH_2{=}CHCOOH) = 3 \cdot 12.011 + 4 \cdot 1.008 + 2 \cdot 16 = 72.065$ g mol^{-1}
$V = 100$ cm^3 $= 0.1$ dm^3

$$c_0 = \frac{m_0}{M \cdot V} \quad \Rightarrow \quad m_0 = c_0 \cdot M \cdot V = 1.35478 \cdot 10^{-4} \cdot 72.065 \cdot 0.1 = 9.76324 \cdot 10^{-4} \text{ g}$$