Problem 10-11 Conductivity, molar conductivity, dissociation constant

What amount of acetic acid (in moles) must be dissoved in 1.5 dm^3 of solution in order that its conductivity was $7.13 \cdot 10^{-3}$ S m^{-1} (conductivity of water has the value of $1.6 \cdot 10^{-4}$ S m^{-1})? Dissociation constant of the acetic acid is $1.75 \cdot 10^{-5}$ (standard state infinite dilution, c^{st} = 1 mol dm^{-3}, activity coefficients of all species can be taken as equal to one). Limiting molar conductivities:

$$\lambda^\infty (H^+) = 0.03497 \text{ S m}^2 \text{ mol}^{-1} \;,\; \lambda^\infty (A^-) = 0.00409 \text{ S m}^2 \text{ mol}^{-1}$$

[n = 0.003 mol (c_0 = 0.002 mol dm^{-3})]

Solution:

$CH_3COOH = H^+ + CH_3COO^-$
$CH_3COOH \equiv HA \;,\; CH_3COO^- \equiv A^-$

$$K_{HA} = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} = \frac{\gamma_+ \cdot c_{H^+} \cdot \gamma_- \cdot c_{A^-}}{\gamma_{HA} \cdot c_{HA}} \cdot \frac{1}{c^{st}} = \frac{\gamma_\pm^2 \cdot c_0 \cdot \alpha^2}{1-\alpha} \ldots., \quad c^{st} = 1 \text{ mol dm}^{-3} \;, \gamma_{HA} = 1 \,, \quad \gamma_\pm = 1$$

Conversion degree from conductivity:

$$\alpha = \frac{\lambda}{\lambda^\infty}$$

$$\lambda = \frac{\kappa_{HA}}{c_0 \cdot 10^3}$$ (c_0- concentration of HA in mol dm^{-3}, $c_0 \cdot 10^3$ – concentration of HA in mol m^{-3})

$\kappa_{solution} = 7.13 \cdot 10^{-3}$ S m^{-1},
$\kappa_{water} = 1.6 \cdot 10^{-4}$ S m^{-1}
$\kappa_{HA} = \kappa_{solution} - \kappa_{water} = 7.14 \cdot 10^{-3} - 1.6 \cdot 10^{-4} = 6.98 \cdot 10^{-3}$ S m^{-1}

Limiting molar conductivity of HA:

$$\lambda^\infty_{HA} = \lambda^\infty_{H^+} + \lambda^\infty_{A^-} = 0.03497 + 0.00409 = 0.03906 \text{ S m}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{6.98 \cdot 10^{-3}}{0.03906 \cdot c_0 \cdot 10^3} = \frac{1.787 \cdot 10^{-4}}{c_0}$$

$$K_{HA} = 1.75 \cdot 10^{-5} = c_0 \cdot \frac{\left(\frac{1.787 \cdot 10^{-4}}{c_0}\right)^2}{1 - \frac{1.787 \cdot 10^{-4}}{c_0}} = \frac{(1.787 \cdot 10^{-4})^2}{c_0 - 1.787 \cdot 10^{-4}}$$

$$c_0 = 1.787 \cdot 10^{-4} + \frac{(1.787 \cdot 10^{-4})^2}{1.75 \cdot 10^{-5}} = 1.787 \cdot 10^{-4} + 1.82478 \cdot 10^{-3}$$

c_0 = 0.002 mol dm^{-3}

The amount of moles of acetic acid dissolved in the volume V = 1.5 dm^3:

$n = c_0 \cdot V = 0.002 \cdot 1.5 = 0.003$ mol