Problem 11-06 Concentration of the electrolyte from dissociation constant and cell potential

Determine the concentration of the acetic acid in the galvanic cell

$\ominus$ Ag(s) | AgCl(s) | KCl (c_1 = 0.01 mol dm^{-3}) || CH_3COOH (c_2 = ?)| *chinhydron* (s) | Pt $\oplus$

the potential of which is 0.1642 V at 25 °C. Dissociation constant of acetic acid at this temperature has the value of $1.75{\cdot}10^{-5}$ (standard state infinite dilution, c^{st} = 1 mol dm^{-3}). Standard reduction potentials are

$$E^{\ominus}\text{(Chinon|Hydrochinon)} = 0.699\text{ V} \quad \text{and} \quad E^{\ominus}(\text{AgCl|Ag|Cl}^-) = 0.222\text{ V}$$

Assume that the activities can be replaced by relative concentrations.

[c_2 = 0.0157 mol dm^{-3}]

Solution:

Left $\ominus$: $\quad Ag(s) + Cl^- = AgCl(s) + e$ (oxidation)

$$E_{\text{left, ox}} = E^{\ominus}_{Ag,Cl^-|AgCl} - \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{1}{a_{Cl^-}} = E^{\ominus}_{Ag,Cl^-|AgCl} + \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln a_{Cl^-}$$

$$E^{\ominus}_{Ag,Cl^-|AgCl} = -E^{\ominus}_{AgCl|Ag,Cl^-} = -0.222\text{ V}$$

$$KCl = K^+ + Cl^-$$

$\gamma_{\pm} = 1 \;\Rightarrow\; a_{Cl^-} \approx c_{Cl^-}/c^{st} = c_{KCl} = 0.01$ mol dm^{-3} $\quad$ (c^{st} = 1 mol dm^{-3})

Right $\oplus$: $\quad C_6H_4O_2 + 2\,H^+ + 2\,e = C_6H_4(OH)_2$

(Ch) (H)

$$E_{\text{right. red}} = E^{\ominus}_{Ch|H} - \frac{\boldsymbol{RT}}{2\boldsymbol{F}}\ln\frac{1}{a^2_{H^+}} = E^{\ominus}_{Ch|H} + \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln a_{H^+}$$

$$E^{\ominus}_{Ch|H} = +0.699\text{ V}$$

Dissociation of acetic acid

$$CH_3COOH = H^+ + CH_3COO^-$$

(AH) (A^-)

Balance: $c_{AH} = c_2 - x$ $\quad$ (c_2 – analytical concentration of acetic acid)

$c_{H^+} = c_{A^-} = x$

For $\gamma = 1 \;\Rightarrow\; a_{H^+} \approx c_{H^+}/c^{st}$ $\quad$ (c^{st} = 1 mol dm^{-3})

$$K_{AH} = \frac{a_{H^+}\cdot a_{A^-}}{a_{AH}} = \frac{c_{H^+}\cdot c_{A^-}}{c_{AH}}\cdot\frac{1}{c^{st}} = \frac{x^2}{c_2 - x}$$

Calculation of the conversion x from the cell potential:

$$E = E_{\text{left}} + E_{\text{right}} = E^{\ominus}_{Ag,Cl^-|AgCl} + \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln a_{Cl^-} + E^{\ominus}_{Ch|H} - \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln a_{H^+}$$

$$\ln a_{H^+} = \frac{\boldsymbol{F}}{\boldsymbol{RT}}\cdot(E - E^{\ominus}_{Ag,Cl^-|AgCl} - E^{\ominus}_{Ch|H}) - \ln a_{Cl^-} =$$

$$= \frac{96485.3}{8.314\cdot 298.15}\cdot(0.1642 - (-0.222) - 0.699) - \ln 0.01 = -7.570225$$

$$a_{H^+} = 5.15576\cdot 10^{-4} = x$$

$$c_2 = x + \frac{x^2}{K_{AH}} = 5.15576\cdot 10^{-4} + \frac{(5.15576\cdot 10^{-4})^2}{1.75\cdot 10^{-5}}$$

$$c_2 = 0.0157\text{ mol dm}^{-3}$$