Problem 11-07 Concentration of dissociation constant from cell potential

The following galvanic cell was assembled to the determination of the dissociation constant of the dichloroacetic acid:

$$\ominus\ \text{Pt} \mid \text{H}_2\,(p = 119.4\ \text{kPa}) \mid \text{CHCl}_2\text{COOH}\ (c_1 = 0.015\ \text{mol dm}^{-3}) \parallel$$
$$\parallel \text{KCl}\ (c_2 = 0.1\ \text{mol dm}^{-3}) \mid \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Hg}(\ell)\ \oplus\ .$$

At the temperature of 25 °C the cell potential was $E = 0.449$ V. What is the value of the dissociation constant of the dichloroacetic acid for the standard state infinite dilution, $c^{\text{st}} = 1$ mol dm^{-3} under assumption that activity coefficients are equal to one. The reduction potential of the right half-cell is $E_{\text{red,calom}} = 0.3338$ V. At given pressure hydrogen exhibits ideal behaviour. Standard state for hydrogen: ideal gas at 25 °C and $p^{\text{st}} = 101.325$ kPa.

[$K_{\text{dis}} = 0.0547$]

Solution:

Left $\ominus$: ½ H_2 (g) = H^+ + e (oxidation)

$$E_{\text{left}} = 0 - \frac{RT}{F}\ln\frac{a_{\text{H}^+}}{a_{\text{H}_2}^{1/2}} \quad , \quad a_{\text{H}_2} \approx \frac{p_{\text{H}_2}}{p^{\text{st}}}$$

$$= \frac{8.314\cdot 298.15}{96485.3}\cdot\left(\ln\left(\frac{119.4}{101.325}\right)^{1/2} - \ln a_{\text{H}^+}\right)$$

$$= 2.10855\cdot 10^{-3} - 2.569116\cdot 10^{-2}\cdot \ln a_{\text{H}^+}$$

Right $\oplus$: ½ Hg_2Cl_2 + e $\rightarrow$ Hg + Cl^- (reduction)

$E_{\text{right}} = 0.3338$ V ($t = 25$ °C)

$E = E_{\text{left, ox}} + E_{\text{right, red}}$

$0.449 = 2.10855\cdot 10^{-3} - 2.569116\cdot 10^{-2}\cdot \ln a_{\text{H}^+} + 0.3338$

$$\ln a_{\text{H}^+} = -\frac{0.449 - 0.3338 - 2.10855\cdot 10^{-3}}{2.569116\cdot 10^{-2}} = -4.40196$$

$a_{\text{H}^+} \approx c_{\text{H}^+}/c^{\text{st}} = 0.01225_{33}$ mol dm^{-3}

Dissociation:

$$\underset{\text{(AH)}}{\text{CHCl}_2\text{COOH}} = \text{H}^+ + \underset{(\text{A}^-)}{\text{CHCl}_2\text{COO}^-}$$

Balance: $c_{\text{AH}} = c_1 - x = 0.015 - 0.01225_{33} = 2.7467\cdot 10^{-3}$ mol dm^{-3}

(c_1 – analytical concentration of AH, $x = c_{\text{H}^+} = 0.01225_{33}$ mol dm^{-3})

$c_{\text{H}^+} = c_{\text{A}^-} = 0.01225_{33}$ mol dm^{-3}

$\gamma_i = 1 \Rightarrow a_{\text{H}^+} \approx c_{\text{H}^+}/c^{\text{st}}$ ($c^{\text{st}} = 1$ mol dm^{-3})

$$K_{\text{AH}} = \frac{a_{\text{H}^+}\cdot a_{\text{A}^-}}{a_{\text{AH}}} = \frac{c_{\text{H}^+}\cdot c_{\text{A}^-}}{c_{\text{AH}}}\cdot\frac{1}{c^{\text{st}}} = \frac{0.0122533^2}{2.7467\cdot 10^{-3}} = 5.466\cdot 10^{-2}$$