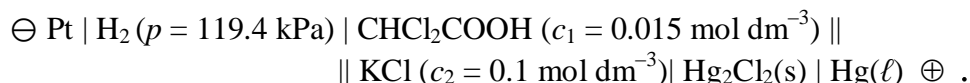


### Problem 11-07 Concentration of dissociation constant from cell potential

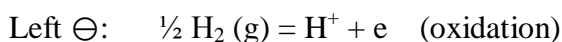
The following galvanic cell was assembled to the determination of the dissociation constant of the dichloroacetic acid:



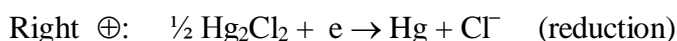
At the temperature of 25 °C the cell potential was  $E = 0.449 \text{ V}$ . What is the value of the dissociation constant of the dichloroacetic acid for the standard state infinite dilution,  $c^{\text{st}} = 1 \text{ mol dm}^{-3}$  under assumption that activity coefficients are equal to one. The reduction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

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

Solution:



$$\begin{aligned} E_{\text{left}} &= 0 - \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{a_{\text{H}_2}^{1/2}}, \quad a_{\text{H}_2} \approx \frac{p_{\text{H}_2}}{p^{\text{st}}} \\ &= \frac{8.314 \cdot 298.15}{96485.3} \cdot \left( \ln \left( \frac{119.4}{101.325} \right)^{1/2} - \ln a_{\text{H}^+} \right) \\ &= 2.10855 \cdot 10^{-3} - 2.569116 \cdot 10^{-2} \cdot \ln a_{\text{H}^+} \end{aligned}$$



$$E_{\text{right}} = 0.3338 \text{ V} \quad (t = 25^\circ\text{C})$$

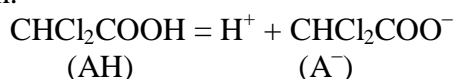
$$E = E_{\text{left, ox}} + E_{\text{right, red}}$$

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

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

$$a_{\text{H}^+} \approx c_{\text{H}^+}/c^{\text{st}} = 0.0122533 \text{ mol dm}^{-3}$$

Dissociation:



$$\text{Balance: } c_{\text{AH}} = c_1 - x = 0.015 - 0.0122533 = 2.7467 \cdot 10^{-3} \text{ mol dm}^{-3}$$

$$(c_1 - \text{analytical concentration of AH, } x = c_{\text{H}^+} = 0.0122533 \text{ mol dm}^{-3})$$

$$c_{\text{H}^+} = c_{\text{A}^-} = 0.0122533 \text{ mol dm}^{-3}$$

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

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