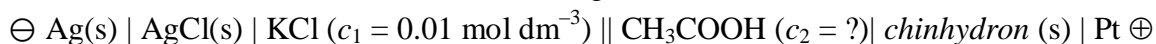


Problem 11-06 Concentration of the electrolyte from dissociation constant and cell potential

Determine the concentration of the acetic acid in the galvanic cell



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, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$). Standard reduction potentials are

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

Assume that the activities can be replaced by relative concentrations.

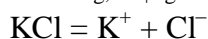
$$[c_2 = 0.0157 \text{ mol dm}^{-3}]$$

Solution:

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

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

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



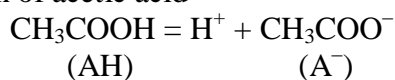
$$\gamma_{\pm} = 1 \Rightarrow a_{\text{Cl}^-} \approx c_{\text{Cl}^-} / c^{\text{st}} = c_{\text{KCl}} = 0.01 \text{ mol dm}^{-3} \quad (c^{\text{st}} = 1 \text{ mol dm}^{-3})$$

Right \oplus : $\text{C}_6\text{H}_4\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- = \text{C}_6\text{H}_4(\text{OH})_2$
(Ch) (H)

$$E_{\text{right, red}} = E_{\text{Ch}|\text{H}}^\ominus - \frac{RT}{2F} \ln \frac{1}{a_{\text{H}^+}^2} = E_{\text{Ch}|\text{H}}^\ominus + \frac{RT}{F} \ln a_{\text{H}^+}$$

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

Dissociation of acetic acid



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

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

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

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

Calculation of the conversion x from the cell potential:

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

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

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

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

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

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