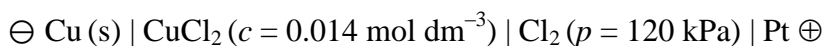


Problem 11-01 Calculation of the cell potential, $\gamma_{\pm} \neq 1$

Calculate the potential of the electrochemical cell



at 25 °C. Standard reduction potentials of the half-cells are

$$E^{\ominus}(\text{Cu}^{2+}|\text{Cu}) = 0.337 \text{ V}, E^{\ominus}(\text{Cl}_2|\text{Cl}^-) = 1.36 \text{ V}.$$

Standard states: $\text{Cl}_2(\text{g})$ the state of ideal gas at the actual temperature and at pressure of $p^{\text{st}} = 101.325 \text{ kPa}$; under actual conditions the chlorine can be taken as an ideal gas; electrolyte: infinite dilution, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$.

The mean activity coefficient calculate from the Debye-Hückel law ($A = 1.172 \text{ dm}^{3/2} \text{ mol}^{-1/2}$). Decide if you use the limiting or enhanced form.

$$[E = 1.1872 \text{ V } (\gamma_{\pm} = 0.67121 - \text{from extended D-H, because } 0.001 < I < 0.1)]$$

Solution:

$$1. \ominus \text{Cu (s)} = \text{Cu}^{2+} (\text{aq}) + 2 \text{ e} \quad E_1 = E^{\ominus}(\text{Cu}|\text{Cu}^{2+}) - \frac{RT}{2F} \ln a_{\text{Cu}^{2+}}$$

$$E^{\ominus}(\text{Cu}|\text{Cu}^{2+}) = -E^{\ominus}(\text{Cu}^{2+}|\text{Cu}) = -0.337 \text{ V}$$

$$2. \oplus \text{Cl}_2 (\text{g}) + 2 \text{ e} = 2 \text{ Cl}^- (\text{aq}) \quad E_2 = E^{\ominus}(\text{Cl}_2|\text{Cl}^-) - \frac{RT}{2F} \ln \frac{a_{\text{Cl}^-}^2}{a_{\text{Cl}_2}}$$

$$E^{\ominus}(\text{Cl}_2|\text{Cl}^-) = 1.36 \text{ V}$$

$$E = E_1 + E_2 = -E^{\ominus}(\text{Cu}^{2+}|\text{Cu}) + E^{\ominus}(\text{Cl}_2|\text{Cl}^-) - \frac{RT}{2F} \ln \frac{a_{\text{Cu}^{2+}} \cdot a_{\text{Cl}^-}^2}{a_{\text{Cl}_2}}$$

$$a_{\text{Cl}_2} \approx \frac{p_{\text{Cl}_2}}{p^{\text{st}}} \text{ (fugacity coefficient } \varphi = 1)$$



$$c_{\text{Cu}^{2+}} = c, \quad c_{\text{Cl}^-} = 2c, \quad z_{\text{K}} = 2, \quad z_{\text{A}} = 1$$

$$a_{\text{Cu}^{2+}} \cdot a_{\text{Cl}^-}^2 = \gamma_{\text{Cu}^{2+}} \cdot (c_{\text{Cu}^{2+}} / c^{\text{st}}) \cdot \gamma_{\text{Cl}^-}^2 \cdot (c_{\text{Cl}^-} / c^{\text{st}})^2 = \gamma_{\pm}^3 \cdot 4 (c / c^{\text{st}})^3, \quad c^{\text{st}} = 1 \text{ mol dm}^{-3}$$

Ionic strength:

$$I = 0.5 \cdot (c_{\text{Cu}^{2+}} \cdot 2^2 + c_{\text{Cl}^-} \cdot 1^2) = 0.5 \cdot (4c + 2c) = 3c = 3 \cdot 0.014 = 0.042 \text{ mol dm}^{-3}$$

For ionic strength $0.001 < I < 0.1$ the extended Debye-Hückel law (at 25 °C $A = 1.172 \text{ dm}^{3/2} \text{ mol}^{-1/2}$)

$$\ln \gamma_{\pm} = -\frac{z_{\text{K}} \cdot z_{\text{A}} \cdot A \cdot \sqrt{I}}{1 + \sqrt{I}} = -\frac{2 \cdot 1 \cdot 1.172 \cdot \sqrt{0.042}}{1 + \sqrt{0.042}} = -0.398673$$

$$\gamma_{\pm} = 0.67121$$

$$E = -E^{\ominus}(\text{Cu}^{2+}|\text{Cu}) + E^{\ominus}(\text{Cl}_2|\text{Cl}^-) - \frac{RT}{2F} \cdot \ln \frac{\gamma_{\pm}^3 \cdot 4 (c / c^{\text{st}})^3}{p_{\text{Cl}_2} / p^{\text{st}}}$$

$$E = -0.337 + 1.36 - \frac{8.314 \cdot 298.15}{2 \cdot 96485.3} \cdot \ln \frac{0.67121^3 \cdot 4 \cdot 0.014^3}{120 / 101.325} = -0.337 + 1.36 + 0.16423$$

$$E = 1.18723 \text{ V}$$