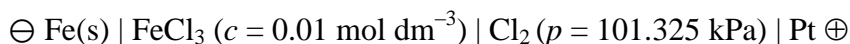


Problem 11-02 Determination of γ_{\pm} from the cell potential

Find the value of the mean activity coefficient of the ferric chloride in the FeCl_3 solution at 25°C . The potential of the cell



is $E = 1.5515 \text{ V}$. You can assume the ideal behaviour of chlorine (standard state ideal gas at actual temperature and $p^{\text{st}} = 101.325 \text{ kPa}$). As the standard state for electrolyte take infinite dilution, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$. Standard reduction potentials of the half-cells are

$$E^\ominus(\text{Fe}^{3+}|\text{Fe}) = -0.036 \text{ V} \quad \text{and} \quad E^\ominus(\text{Cl}_2|\text{Cl}^-) = 1.36 \text{ V}.$$

$$[\gamma_{\pm} = 0.4685]$$

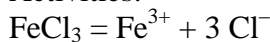
Solution:

$$\begin{aligned} 1. \ominus \text{Fe (g)} &= \text{Fe}^{3+} (\text{aq}) + 3 \text{ e} & E_1 &= E^\ominus(\text{Fe}|\text{Fe}^{3+}) - \frac{RT}{3F} \ln a_{\text{Fe}^{3+}} \\ & & E^\ominus(\text{Fe}|\text{Fe}^{3+}) &= -E^\ominus(\text{Fe}^{3+}|\text{Fe}) = -(-0.036) \text{ V} \\ 2. \oplus \text{Cl}_2 (\text{g}) &+ 2 \text{ e} = 2 \text{Cl}^- (\text{aq}) & E_2 &= E^\ominus(\text{Cl}_2|\text{Cl}^-) - \frac{RT}{2F} \ln \frac{a_{\text{Cl}^-}^2}{a_{\text{Cl}_2}} \end{aligned}$$

$$E^\ominus(\text{Cl}_2|\text{Cl}^-) = 1.36 \text{ V} \quad , \quad a_{\text{Cl}_2} \approx \frac{p_{\text{Cl}_2}}{p^{\text{st}}} = \frac{101.325}{101.325} = 1$$

$$\begin{aligned} E &= E_1 + E_2 = -E^\ominus(\text{Fe}^{3+}|\text{Fe}) + E^\ominus(\text{Cl}_2|\text{Cl}^-) - \frac{RT}{3F} \ln a_{\text{Fe}^{3+}} - \frac{RT}{F} \ln a_{\text{Cl}^-} \\ &= -E^\ominus(\text{Fe}^{3+}|\text{Fe}) + E^\ominus(\text{Cl}_2|\text{Cl}^-) - \frac{RT}{3F} (\ln a_{\text{Fe}^{3+}} + \ln a_{\text{Cl}^-}^3) \\ & \quad \underbrace{\hspace{10em}}_{\frac{RT}{3F} \ln (a_{\text{Fe}^{3+}} \cdot a_{\text{Cl}^-}^3)} \end{aligned}$$

Activities:



$$c_{\text{Fe}^{3+}} = c \quad , \quad c_{\text{Cl}^-} = 3c \quad , \quad z_K = 3 \quad , \quad z_A = 1$$

$$\begin{aligned} a_{\text{Fe}^{3+}} \cdot a_{\text{Cl}^-}^3 &= \gamma_{\text{Fe}^{3+}} \cdot \frac{c_{\text{Fe}^{3+}}}{c^{\text{st}}} \cdot \gamma_{\text{Cl}^-}^3 \cdot \frac{c_{\text{Cl}^-}^3}{(c^{\text{st}})^3} = \gamma_{\pm}^4 \cdot c \cdot (3c)^3 = \gamma_{\pm}^4 \cdot 27 \cdot c^4 \\ c^{\text{st}} &= 1 \text{ mol dm}^{-3}, c = 0.01 \text{ mol dm}^{-3} \end{aligned}$$

$$E = -E^\ominus(\text{Fe}^{3+}|\text{Fe}) + E^\ominus(\text{Cl}_2|\text{Cl}^-) - \frac{RT}{3F} \cdot \underbrace{\ln (\gamma_{\pm}^4 \cdot 27 \cdot c^4)}_{4 \ln (\gamma_{\pm}) + \ln (27 \cdot c^4)}$$

$$1.5515 = -(-0.036) + 1.36 - \frac{8.314 \cdot 298.15}{3 \cdot 96485.3} \cdot [4 \ln (\gamma_{\pm}) + \ln (27 \cdot c^4)]$$

$$4 \ln \gamma_{\pm} = \frac{1.5515 - 0.036 - 1.36}{8.56372 \cdot 10^{-3}} + \ln (27 \cdot 0.01^4) = 18.157998 - 15.124844 = -3.0331542$$

$$\ln \gamma_{\pm} = -0.75829$$

$$\gamma_{\pm} = 0.46847$$