Problem 11-02 Determination of $\gamma_\pm$ 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

$$\ominus\ \mathrm{Fe(s)}\ |\ \mathrm{FeCl_3}\ (c = 0.01\ \mathrm{mol\ dm^{-3}})\ |\ \mathrm{Cl_2}\ (p = 101.325\ \mathrm{kPa})\ |\ \mathrm{Pt}\ \oplus$$

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

$$E^\ominus(\mathrm{Fe^{3+}|Fe}) = -0.036\ \mathrm{V} \quad \text{and} \quad E^\ominus(\mathrm{Cl_2|Cl^-}) = 1.36\ \mathrm{V}.$$

[$\gamma_\pm$ = 0.4685]

Solution:

1. $\ominus$ Fe (g) = Fe^{3+} (aq) + 3 e

$$E_1 = E^\ominus(\mathrm{Fe|Fe^{3+}}) - \frac{\boldsymbol{R}T}{3\boldsymbol{F}} \ln a_{\mathrm{Fe^{3+}}}$$

$$E^\ominus(\mathrm{Fe|Fe^{3+}}) = -E^\ominus(\mathrm{Fe^{3+}|Fe}) = -(-0.036)\ \mathrm{V}$$

2. $\oplus$ Cl_2 (g) + 2 e = 2 Cl^- (aq)

$$E_2 = E^\ominus(\mathrm{Cl_2|Cl^-}) - \frac{\boldsymbol{R}T}{2\boldsymbol{F}} \ln \frac{a^2_{\mathrm{Cl^-}}}{a_{\mathrm{Cl_2}}}$$

$$E^\ominus(\mathrm{Cl_2|Cl^-}) = 1.36\ \mathrm{V} \quad , \ a_{\mathrm{Cl_2}} \approx \frac{p_{\mathrm{Cl_2}}}{p^{\mathrm{st}}} = \frac{101.325}{101.325} = 1$$

$$E = E_1 + E_2 = -E^\ominus(\mathrm{Fe^{3+}|Fe}) + E^\ominus(\mathrm{Cl_2|Cl^-}) - \frac{\boldsymbol{R}T}{3\boldsymbol{F}} \ln a_{\mathrm{Fe^{3+}}} - \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln a_{\mathrm{Cl^-}}$$

$$= -E^\ominus(\mathrm{Fe^{3+}|Fe}) + E^\ominus(\mathrm{Cl_2|Cl^-}) - \underbrace{\frac{\boldsymbol{R}T}{3\boldsymbol{F}} (\ln a_{\mathrm{Fe^{3+}}} + \ln a^3_{\mathrm{Cl^-}})}_{\frac{\boldsymbol{R}T}{3\boldsymbol{F}} \ln (a_{\mathrm{Fe^{3+}}} \cdot a^3_{\mathrm{Cl^-}})}$$

Activities:

$FeCl_3 = Fe^{3+} + 3\ Cl^-$

$c_{\mathrm{Fe^{3+}}} = c$, $c_{\mathrm{Cl^-}} = 3\,c$, $z_C = 3$, $z_A = 1$

$$a_{\mathrm{Fe^{3+}}} \cdot a^3_{\mathrm{Cl^-}} = \gamma_{\mathrm{Fe^{3+}}} \cdot \frac{c_{\mathrm{Fe^{3+}}}}{c^{\mathrm{st}}} \cdot \gamma^3_{\mathrm{Cl^-}} \cdot \frac{c^3_{\mathrm{Cl^-}}}{(c^{\mathrm{st}})^3} = \gamma^4_\pm \cdot c \cdot (3\,c)^3 = \gamma^4_\pm \cdot 27 \cdot c^4$$

$$c^{\mathrm{st}} = 1\ \mathrm{mol\ dm^{-3}},\ c = 0.01\ \mathrm{mol\ dm^{-3}}$$

$$E = -E^\ominus(\mathrm{Fe^{3+}|Fe}) + E^\ominus(\mathrm{Cl_2|Cl^-}) - \frac{\boldsymbol{R}T}{3\boldsymbol{F}} \cdot \underbrace{\ln (\gamma^4_\pm \cdot 27 \cdot c^4)}_{4 \ln(\gamma_\pm) + \ln(27 \cdot c^4)}$$

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

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

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

$$\gamma_\pm = 0.46847$$