Problem 11-04 Gas pressure at the electrode from E; activity coefficients

The potential of the galvanic cell

$$\ominus\ \mathrm{Ni(s)}\ |\ \mathrm{NiCl_2}\ (c = 0.01\ \mathrm{mol\ dm^{-3}})\ |\ \mathrm{Cl_2}\ (p = ?\ \mathrm{kPa})\ |\ \mathrm{Pt}\ \oplus$$

at the temperature of 25 °C is E = 1.793 V. Under assumption of ideal behaviour of chlorine, calculate its pressure on the right electrode (standard state p^{st} = 101.325 kPa). The mean activity coefficient of the cell electrolyte calculate using Debye-Hückel law (A = 1.172 $\mathrm{dm^{3/2}\ mol^{-1/2}}$) – according to the ionic strength choose an appropriate form of this law.

$$E^{\ominus}(\mathrm{Ni^{2+}|Ni}) = -0.250\ \mathrm{V} \quad \text{and} \quad E^{\ominus}(\mathrm{Cl_2|Cl^-}) = 1.36\ \mathrm{V}.$$

[$p_{\mathrm{Cl_2}}$ = 238.65 kPa ($\gamma_{\pm}$ = 0.7075 (extended Debye-Hückel law)]

Solution:

$\ominus$ Ni = Ni^{2+} + 2 e

$$E_- = E^{\ominus}_{\mathrm{Ni|Ni^{2+}}} - \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln a_{\mathrm{Ni^{2+}}} \quad , \quad E^{\ominus}_{\mathrm{Ni|Ni^{2+}}} = -E^{\ominus}_{\mathrm{Ni^{2+}|Ni}} = -0.250\ \mathrm{V}$$

$\oplus$ Cl_2 + 2 e = 2 Cl^-

$$E_+ = E^{\ominus}_{\mathrm{Cl_2|Cl^-}} - \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln \frac{a^2_{\mathrm{Cl^-}}}{a_{\mathrm{Cl_2}}} \quad , \quad E^{\ominus}_{\mathrm{Cl_2|Cl^-}} = 1.36\ \mathrm{V}$$

$$E = E_- + E_+ = -E^{\ominus}_{\mathrm{Ni^{2+}|Ni}} - \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln a_{\mathrm{Ni^{2+}}} + E^{\ominus}_{\mathrm{Cl_2|Cl^-}} - \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln \frac{a^2_{\mathrm{Cl^-}}}{a_{\mathrm{Cl_2}}} =$$

$$= -E^{\ominus}_{\mathrm{Ni^{2+}|Ni}} + E^{\ominus}_{\mathrm{Cl_2|Cl^-}} - \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln \frac{a_{\mathrm{Ni^{2+}}} \cdot a^2_{\mathrm{Cl^-}}}{a_{\mathrm{Cl_2}}}$$

$$a_{\mathrm{Cl_2}} \approx \frac{p_{\mathrm{Cl_2}}}{p^{st}}$$

$NiCl_2 = Ni^+ + 2\ Cl^-$

$$a_{\mathrm{Ni^{2+}}} \cdot a^2_{\mathrm{Cl^-}} = (\gamma_{\mathrm{Ni^{2+}}} \cdot \frac{c_{\mathrm{Ni^{2+}}}}{c^{st}}) \cdot (\gamma_{\mathrm{Cl^-}} \cdot \frac{c_{\mathrm{Cl^-}}}{c^{st}})^2$$

$$c^{st} = 1\ \mathrm{mol\ dm^{-3}} \quad , \quad c_{\mathrm{Ni^{2+}}} = c\ , \quad c_{\mathrm{Cl^-}} = 2\,c \quad (c = c_{\mathrm{NiCl_2}})$$

$$a_{\mathrm{Ni^{2+}}} \cdot a^2_{\mathrm{Cl^-}} = \gamma^3_{\pm} \cdot 4\,c^3$$

$$I = \tfrac{1}{2}\left(c_{\mathrm{Ni^+}} \cdot 1^2 + c_{\mathrm{Cl^-}} \cdot 2^2\right) = \tfrac{1}{2}\left(c \cdot 2^2 + 2c \cdot 1^2\right) = 3c = 0.03\ \mathrm{mol\ dm^{-3}}$$

$0.001 < I < 0.1$ – we use the extended form

$$\ln \gamma_{\pm} = -\frac{A \cdot z_C \cdot z_A \cdot \sqrt{I}}{1+\sqrt{I}} \quad , \quad z_C = 2\ , \ z_A = 1 \quad , \quad A = 1.172\ \mathrm{dm^{3/2}\ mol^{-1/2}}$$

$$\ln \gamma_{\pm} = -\frac{1.172 \cdot 2 \cdot 1 \cdot \sqrt{0.03}}{1+\sqrt{0.03}} = -0.34605$$

$\gamma_{\pm}$ = 0.70747

$$\ln \frac{p_{\mathrm{Cl_2}}}{p^{st}} = \frac{2\boldsymbol{F}}{\boldsymbol{RT}}\left(E + E^{\ominus}_{\mathrm{Ni^{2+}|Ni}} - E^{\ominus}_{\mathrm{Cl_2|Cl^-}}\right) + \ln(\gamma^3_{\pm} \cdot 4\,c^3)$$

$$\ln \frac{p_{\mathrm{Cl_2}}}{101.325} = \frac{2 \cdot 96485.3}{8.314 \cdot 298.15} \cdot (1.793 - 0.250 - 1.36) + \ln(0.70747^3 \cdot 4 \cdot 0.01^3) =$$

$$= 14.324 - 13.4674 = 0.8566$$

$p_{\mathrm{Cl_2}}$ = 2.353314 · 101.325 = 238.65 kPa