

Problem 11-09 Potential of redox electrode

5.4 g of ferric chloride and 2 g of ferrous chloride were dissolved in 2 dm³ of the distilled water. Thin platinum wire was then immersed into this solution. Assuming that all activity coefficients are equal to one calculate the reduction potential of this half-cell at the temperature of 25 °C. For the standard state of the electrolyte choose the state of infinite dilution, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$. Additional data:

$$M_{\text{Fe}} = 55.847 \text{ g mol}^{-1}, M_{\text{Cl}} = 35.453 \text{ g mol}^{-1}, E^{\ominus}(\text{Fe}^{3+}|\text{Fe}^{2+}) = 0.771 \text{ V}.$$

$$[E_{\text{Fe}^{3+}|\text{Fe}^{2+}} = 0.7391 \text{ V}]$$

Solution:

Concentration of the electrolyte:

$$V = 2 \text{ dm}^3$$

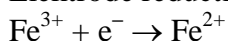
$$m_{\text{FeCl}_2} = 5.4 \text{ g}, M_{\text{FeCl}_2} = 55.847 + 2 \cdot 35.453 = 126.753 \text{ g mol}^{-1}$$

$$c_{\text{FeCl}_2} = \frac{m_{\text{FeCl}_2}}{M_{\text{FeCl}_2} \cdot V} = \frac{5.4}{126.753 \cdot 2} = 2.13 \cdot 10^{-2} \text{ mol dm}^{-3}$$

$$m_{\text{FeCl}_3} = 2 \text{ g}, M_{\text{FeCl}_3} = 55.847 + 3 \cdot 35.453 = 162.206 \text{ g mol}^{-1}$$

$$c_{\text{FeCl}_3} = \frac{m_{\text{FeCl}_3}}{M_{\text{FeCl}_3} \cdot V} = \frac{2}{162.206 \cdot 2} = 6.165 \cdot 10^{-3} \text{ mol dm}^{-3}$$

Elektrode reduction reaction:



$$E^{\ominus}(\text{Fe}^{3+}|\text{Fe}^{2+}) = 0.771 \text{ V}$$

$$E(\text{Fe}^{3+}|\text{Fe}^{2+}) = E^{\ominus}(\text{Fe}^{3+}|\text{Fe}^{2+}) - \frac{RT}{F} \cdot \ln \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}}$$

$\text{FeCl}_2 = \text{Fe}^{2+} + 2 \text{ Cl}^{-}$	$\text{FeCl}_3 = \text{Fe}^{3+} + 3 \text{ Cl}^{-}$
$a_{\text{Fe}^{2+}} = \gamma_{+} \cdot \frac{c_{\text{Fe}^{2+}}}{c^{\text{st}}} \approx c_{\text{FeCl}_2} \quad (c^{\text{st}} = 1 \text{ mol dm}^{-3})$	$a_{\text{Fe}^{3+}} = \gamma_{+} \cdot \frac{c_{\text{Fe}^{3+}}}{c^{\text{st}}} \approx c_{\text{FeCl}_3} \quad (c^{\text{st}} = 1 \text{ mol dm}^{-3})$

$$E(\text{Fe}^{3+}|\text{Fe}^{2+}) = 0.771 - \frac{8.314 \cdot 298.15}{96485.3} \cdot \ln \frac{2.13 \cdot 10^{-2}}{6.165 \cdot 10^{-3}} = 0.771 - 0.03185$$

$$E(\text{Fe}^{3+}|\text{Fe}^{2+}) = 0.7391 \text{ V}$$