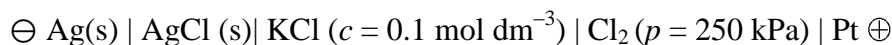


### Problem 11-17 Cell potential from thermodynamic quantities

The mean value of entropy change in the temperature interval 25 – 40 °C associated with the formation of one mole of the solid silver chloride from the elements in their standard states is  $\Delta_f S^\ominus(\text{AgCl, s}) = 57.9 \text{ J mol}^{-1} \text{ K}^{-1}$ . Calculate the standard cell potential and the cell potential at 25 and 40 °C of the cell



Chlorine exhibits ideal behaviour (standard state an ideal gas at actual temperature and pressure  $p^{\text{st}} = 101.325 \text{ kPa}$ ). From the following data pick up those which you need to your calculation:

$$E^\ominus(\text{AgCl} | \text{Ag} | \text{Cl}^-) = 0.222 \text{ V},$$

$$E^\ominus(\text{K}^+ | \text{K}) = -2.925 \text{ V}$$

$$E^\ominus(\text{Ag}^+ | \text{Ag}) = +0.799 \text{ V}$$

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

$$[E^\ominus(25) = 1.138 \text{ V}, E(25) = 1.1496 \text{ V}; E^\ominus(40) = 1.147 \text{ V}, E(40) = 1.1586 \text{ V}]$$

**Solution:**

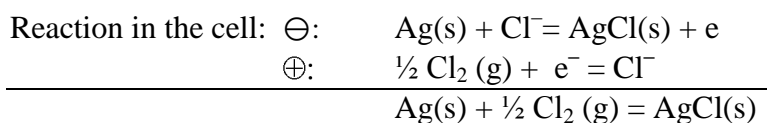
$$\begin{aligned} \text{Left } \ominus: \quad \text{Ag(s)} + \text{Cl}^- &= \text{AgCl(s)} + e^- & E_{\text{left}} &= E_{\text{Ag, Cl}^- | \text{AgCl}}^\ominus - \frac{RT}{F} \ln \frac{1}{a_{\text{Cl}^-}} \\ & & \text{At } 25^\circ\text{C} & E_{\text{Ag, Cl}^- | \text{AgCl}}^\ominus = -E_{\text{AgCl} | \text{Ag, Cl}^-}^\ominus = -0.222 \text{ V} \\ \text{Right } \oplus: \quad \frac{1}{2} \text{Cl}_2 + e^- &\rightarrow \text{Cl}^- & E_{\text{right}} &= E_{\text{Cl}_2 | \text{Cl}^-}^\ominus - \frac{RT}{F} \ln \frac{a_{\text{Cl}^-}}{(a_{\text{Cl}_2})^{1/2}} \\ & & \text{At } 25^\circ\text{C} & E_{\text{Cl}_2 | \text{Cl}^-}^\ominus = 1.36 \text{ V} \end{aligned}$$

$$E = E_{\text{left}} + E_{\text{right}} = E_{\text{Ag, Cl}^- | \text{AgCl}}^\ominus - \frac{RT}{F} \ln \frac{1}{a_{\text{Cl}^-}} + E_{\text{Cl}_2 | \text{Cl}^-}^\ominus - \frac{RT}{F} \ln \frac{a_{\text{Cl}^-}}{(a_{\text{Cl}_2})^{1/2}}, \quad a_{\text{Cl}_2} \approx \frac{p_{\text{Cl}_2}}{p^{\text{st}}}$$

$$E = E^\ominus + \frac{RT}{F} \cdot \ln \frac{p_{\text{Cl}_2}}{p^{\text{st}}}$$

$$E^\ominus(25^\circ\text{C}) = E_{\text{Cl}_2 | \text{Cl}^-}^\ominus + E_{\text{Ag, Cl}^- | \text{AgCl}}^\ominus = 1.36 + (-0.222) = 1.138 \text{ V}$$

$$E(25^\circ\text{C}) = 1.138 + \frac{8,314 \cdot 298,15}{96485,3} \cdot \ln \left( \frac{250}{101,325} \right)^{1/2} = 1.138 + 0.0116 = 1.1496 \text{ V}$$



$$\Delta G^\ominus = \Delta_f G^\ominus(\text{AgCl}) = -z F E^\ominus, \quad \Delta S^\ominus = \Delta_f S^\ominus(\text{AgCl}) = -F \left( \frac{dE^\ominus}{dT} \right) = 57.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S^\ominus = \Delta_f S^\ominus(\text{AgCl}) = -F \left( \frac{dE^\ominus}{dT} \right) = 57.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\frac{dE^\ominus}{dT} \doteq \frac{dE}{dT} = -\frac{\Delta_f S^\ominus}{F} = -\frac{57.9}{96485.3} = 6 \cdot 10^{-4} \text{ V K}^{-1} \quad \left[ \frac{\text{C} \cdot \text{V}}{\text{J K}^{-1} \text{ mol}^{-1}} \right] \left[ \frac{\text{J K}^{-1} \text{ mol}^{-1}}{\text{C mol}^{-1}} \right]$$

Temperature dependences:

$$E^\ominus(t) = E^\ominus(25) + 6 \cdot 10^{-4} \cdot (t - 25)$$

$$E^\ominus(40) = E^\ominus(25) + 6 \cdot 10^{-4} \cdot (40 - 25) = 1.138 + 0.009 = 1.147 \text{ V}$$

$$E(t) = E(25) + 6 \cdot 10^{-4} \cdot (t - 25)$$

$$E(40) = E(25) + 6 \cdot 10^{-4} \cdot (40 - 25) = 1.1496 + 0.009 = 1.1586 \text{ V}$$