

Problem 11-16 Solubility product from the cell potential

The measurement of solubility of slightly soluble chloride MeCl_2 can be realized in this cell:



At the temperature of 22°C the cell potential was found to be 1.174 V . Determine the solubility product of MeCl_2 if you know the values of the standard potentials:

$$E^\ominus(\text{Me}^{2+} \mid \text{Me}) = +0.562 \text{ V} , E^\ominus(\text{Cl}_2 \mid \text{Cl}^-) = 1.358 \text{ V}$$

You can assume the ideal behaviour of chlorine (standard state ideal gas at actual temperature and $p^{\text{st}} = 101.325 \text{ kPa}$).

$$[K_{\text{MeCl}_2} = 1.58 \cdot 10^{-13}]$$

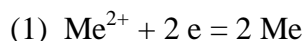
Solution:

$$t = 22^\circ\text{C} , T = 295.15 \text{ K}$$

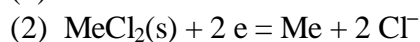
$$E = 1.174 \text{ V}$$

$$E^\ominus(\text{Me}^{2+} \mid \text{Me}) = +0.562 \text{ V}$$

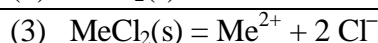
$$E^\ominus(\text{Cl}_2 \mid \text{Cl}^-) = 1.358 \text{ V}$$



$$\Delta G_1^\ominus = -2 F E^\ominus(\text{Me}^{2+} \mid \text{Me})$$



$$\Delta G_2^\ominus = -2 F E^\ominus(\text{MeCl}_2 \mid \text{Me} \mid \text{Cl}^-)$$



$$\Delta G_3^\ominus = -RT \ln K_S$$

$$\begin{aligned} \Delta G_3^\ominus &= \Delta G_2^\ominus - \Delta G_1^\ominus \\ -RT \ln K_S &= -2 F E^\ominus(\text{MeCl}_2 \mid \text{Me} \mid \text{Cl}^-) - (-2 F E^\ominus(\text{Me}^{2+} \mid \text{Me})) \\ \ln K_S &= \frac{2F}{RT} [E^\ominus(\text{MeCl}_2 \mid \text{Me} \mid \text{Cl}^-) - E^\ominus(\text{Me}^{2+} \mid \text{Me})] \end{aligned}$$

Calculation of $E^\ominus(\text{MeCl}_2 \mid \text{Me} \mid \text{Cl}^-)$ at 22°C from E of the cell:

$$\begin{aligned} \text{Left } \ominus: \text{Me} + 2 \text{Cl}^- &\rightarrow \text{MeCl}_2(\text{s}) + 2 \text{e} & E_{\text{left}} &= E^\ominus(\text{Me} \mid \text{Cl}^- \mid \text{MeCl}_2) - \frac{RT}{2F} \ln \frac{1}{a_{\text{Cl}^-}} = \\ & & &= -E^\ominus(\text{MeCl}_2 \mid \text{Me} \mid \text{Cl}^-) - \frac{RT}{2F} \ln \frac{1}{a_{\text{Cl}^-}} \end{aligned}$$

$$\text{Right } \oplus: \text{Cl}_2 + 2 \text{e} \rightarrow 2 \text{Cl}^- \quad E_{\text{right}} = E^\ominus(\text{Cl}_2 \mid \text{Cl}^-) - \frac{RT}{2F} \ln \frac{a_{\text{Cl}^-}^2}{a_{\text{Cl}_2}}$$

$$E = E_{\text{left}} + E_{\text{right}} = -E^\ominus(\text{MeCl}_2 \mid \text{Me} \mid \text{Cl}^-) + E^\ominus(\text{Cl}_2 \mid \text{Cl}^-) - \frac{RT}{2F} \ln \frac{1}{a_{\text{Cl}^-}} - \frac{RT}{2F} \ln \frac{a_{\text{Cl}^-}^2}{a_{\text{Cl}_2}}$$

$$a_{\text{Cl}_2} \cong \frac{p_{\text{Cl}_2}}{p^{\text{st}}} \circ (\text{ideal gas})$$

$$\begin{aligned} E^\ominus(\text{MeCl}_2 \mid \text{Me} \mid \text{Cl}^-) &= E^\ominus(\text{Cl}_2 \mid \text{Cl}^-) - \frac{RT}{2F} \ln \left(\frac{1}{\cancel{a_{\text{Cl}^-}^2}} \cdot \frac{\cancel{a_{\text{Cl}^-}^2}}{a_{\text{Cl}_2}} \right) - E = \\ &= 1.358 + \frac{8.314 \cdot 295.15}{2 \cdot 96485.3} \cdot \ln \left(\frac{130}{101.325} \right) - 1.174 \end{aligned}$$

$$E_{\text{Ag}|\text{Cl}^-|\text{AgCl}}^\ominus = 0.18717 \text{ V}$$

$$\ln K_S = \frac{2 \cdot 96485.3}{8.314 \cdot 295.15} \cdot (0.18717 - 0.562) = -29.47637$$

$$K_S = 1.58 \cdot 10^{-13}$$