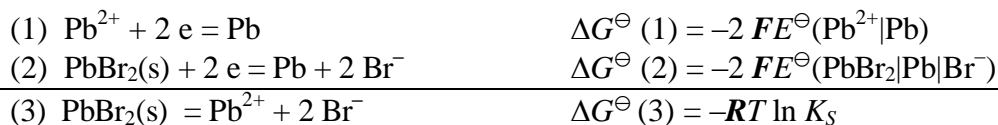


Problem 11-15 Standard potential from solubility

The solubility of lead bromide in water at 25 °C is 3.82 g in 1 dm³ of solution ($M = 367 \text{ g mol}^{-1}$). The standard reduction potential of the lead electrode is $E^\ominus(\text{Pb}^{2+}|\text{Pb}) = -0.126 \text{ V}$. If you can take all the activity coefficients as equal to one, calculate from these data the standard reduction potential of the second-kind electrode $\text{PbBr}_2|\text{Pb}|\text{Br}^-$.

$$[E^\ominus(\text{PbBr}_2|\text{Pb}|\text{Br}^-) = -0.284 \text{ V}]$$

Solution:



$$\begin{aligned} \Delta G^\ominus(3) &= \Delta G^\ominus(2) - \Delta G^\ominus(1) \\ -RT \ln K_S &= -FE^\ominus(\text{PbBr}_2|\text{Pb}|\text{Br}^-) - (-FE^\ominus(\text{Pb}^{2+}|\text{Pb})) \\ \ln K_S &= 2 \frac{F}{RT} [E^\ominus(\text{PbBr}_2|\text{Pb}|\text{Br}^-) - E^\ominus(\text{Pb}^{2+}|\text{Pb})] \end{aligned}$$

$$E^\ominus(\text{PbBr}_2|\text{Pb}|\text{Br}^-) = E^\ominus(\text{Pb}^{2+}|\text{Pb}) + \frac{RT}{2F} \cdot \ln K_S$$

Calculation of K_S from the experimental value of solubility (c_{PbBr_2})

$$c_{\text{Pb}^{2+}} = c_{\text{PbBr}_2} \quad , \quad c_{\text{Br}^-} = 2 c_{\text{PbBr}_2}$$

$$K_S = a_{\text{Pb}^{2+}} \cdot a_{\text{Br}^-}^2 = \gamma_+ \cdot \frac{c_{\text{Pb}^{2+}}}{c^{\text{st}}} \cdot \gamma_-^2 \cdot \left(\frac{c_{\text{Br}^-}}{c^{\text{st}}} \right)^2 = \gamma_\pm^3 \cdot c_{\text{PbBr}_2} \cdot (2c_{\text{PbBr}_2})^2 \quad , \quad c^{\text{st}} = 1 \text{ mol dm}^{-3}$$

$$\gamma_\pm = 1$$

$$K_S = 4 (c_{\text{PbBr}_2})^3$$

$$c_{\text{PbBr}_2} = 3.82 \text{ g dm}^{-3} = \frac{3.82}{367} = 1.040872 \cdot 10^{-2} \text{ mol dm}^{-3}$$

$$K_S = 4 (1.040872 \cdot 10^{-2})^3 = 4.5108 \cdot 10^{-6}$$

$$E^\ominus(\text{PbBr}_2|\text{Pb}|\text{Br}^-) = -0.126 + \frac{8.314 \cdot 298.15}{2 \cdot 96485.3} \cdot \ln 4.5108 \cdot 10^{-6} = -0.126 - 0.158$$

$$E^\ominus(\text{PbBr}_2|\text{Pb}|\text{Br}^-) = -0.284 \text{ V}$$