Problem 11-15 Standard potential from solubility

The solubility of lead bromide in water at 25 °C is 3.82 g in 1 dm^3 of solution (M = 367 g mol^{-1}). The standard reduction potential of the lead electrode is $E^\ominus(Pb^{2+}|Pb) = -0.126$ 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 $PbBr_2|Pb|Br^-$.

$[E^\ominus(PbBr_2|Pb|Br^-) = -0.284 \text{ V}]$

Solution:

(1) $Pb^{2+} + 2\,e = Pb$	$\Delta G^\ominus(1) = -2\,\boldsymbol{F}E^\ominus(Pb^{2+}\|Pb)$
(2) $PbBr_2(s) + 2\,e = Pb + 2\,Br^-$	$\Delta G^\ominus(2) = -2\,\boldsymbol{F}E^\ominus(PbBr_2\|Pb\|Br^-)$
(3) $PbBr_2(s) = Pb^{2+} + 2\,Br^-$	$\Delta G^\ominus(3) = -\boldsymbol{R}T \ln K_S$

$$\Delta G^\ominus(3) = \Delta G^\ominus(2) - \Delta G^\ominus(1)$$

$$-\boldsymbol{R}T \ln K_S = -\boldsymbol{F}E^\ominus(PbBr_2|Pb|Br^-) - (-\boldsymbol{F}E^\ominus(Pb^{2+}|Pb))$$

$$\ln K_S = 2\frac{\boldsymbol{F}}{\boldsymbol{R}T}\left[E^\ominus(PbBr_2|Pb|Br^-) - E^\ominus(Pb^{2+}|Pb)\right]$$

$$E^\ominus(PbBr_2|Pb|Br^-) = E^\ominus(Pb^{2+}|Pb) + \frac{\boldsymbol{R}T}{2\boldsymbol{F}} \cdot \ln K_S$$

Calculation of K_S from the experimental value of solubility (c_{PbPr2})

$$c_{Pb^{2+}} = c_{PbBr_2} \quad , \quad c_{Br^-} = 2\,c_{PbBr_2}$$

$$K_S = a_{Pb^{2+}} \cdot a^2_{Br^-} = \gamma_+ \cdot \frac{c_{Pb^{2+}}}{c^{st}} \cdot \gamma_-^2 \cdot \left(\frac{c_{Br^-}}{c^{st}}\right)^2 = \gamma_\pm^3 \cdot c_{PbBr_2} \cdot (2c_{PbBr_2})^2 \quad , \quad c^{st} = 1 \text{ mol dm}^{-3}$$

$$\gamma_\pm = 1$$

$$K_S = 4\,(c_{PbPr2})^3$$

$$c_{PbBr_2} = 3.82 \text{ g dm}^{-3} = \frac{3.82}{367} = 1.040872 \cdot 10^{-2} \text{ mol dm}^{-3}$$

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

$$E^\ominus(PbBr_2|Pb|Br^-) = -0.126 + \frac{8.314 \cdot 298.15}{2 \cdot 96485.3} \cdot \ln 4.5108 \cdot 10^{-6} = -0.126 - 0.158$$

$$E^\ominus(PbBr_2|Pb|Br^-) = -0.284 \text{ V}$$