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:

$$\ominus\ \mathrm{Me(s)}\ |\ \mathrm{MeCl_2(s)}\ |\ \mathrm{MeCl_2}\ (\textit{saturated solution})\ |\ \mathrm{Cl_2}\ (p = 130\ \mathrm{kPa})\ |\ \mathrm{Pt}\ \oplus\ .$$

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:

$$E^{\ominus}(\mathrm{Me^{2+}|Me}) = +0.562\ \mathrm{V}\ ,\ E^{\ominus}(\mathrm{Cl_2|Cl^-}) = 1.358\ \mathrm{V}$$

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

$[K_{\mathrm{MeCl_2}} = 1.58\cdot10^{-13}]$

Solution:

$t = 22℃\ ,\ \ T = 295.15\ \mathrm{K}$
$E = 1.174\ \mathrm{V}$
$E^{\ominus}(\mathrm{Me^{2+}|Me}) = +0.562\ \mathrm{V}$
$E^{\ominus}(\mathrm{Cl_2|Cl^-}) = 1.358\ \mathrm{V}$

(1)	$\mathrm{Me^{2+}} + 2\ \mathrm{e} = 2\ \mathrm{Me}$	$\Delta G_1^{\ominus} = -2\,\boldsymbol{F}E^{\ominus}(\mathrm{Me^{2+}|Me})$
(2)	$\mathrm{MeCl_2(s)} + 2\ \mathrm{e} = \mathrm{Me} + 2\ \mathrm{Cl^-}$	$\Delta G_2^{\ominus} = -2\,\boldsymbol{F}E^{\ominus}(\mathrm{MeCl_2|Me|Cl^-})$
(3)	$\mathrm{MeCl_2(s)} = \mathrm{Me^{2+}} + 2\ \mathrm{Cl^-}$	$\Delta G_3^{\ominus} = -\boldsymbol{R}T\ln K_S$

$$\Delta G_3^{\ominus} = \Delta G_2^{\ominus} - \Delta G_1^{\ominus}$$
$$-\boldsymbol{R}T\ln K_S = -2\,\boldsymbol{F}E^{\ominus}(\mathrm{MeCl_2|Me|Cl^-}) - (-2\,\boldsymbol{F}E^{\ominus}(\mathrm{Me^{2+}|Me}))$$
$$\ln K_S = \frac{2\boldsymbol{F}}{\boldsymbol{R}T}\left[E^{\ominus}(\mathrm{MeCl_2|Me|Cl^-}) - \boldsymbol{F}E^{\ominus}(\mathrm{Me^{2+}|Me})\right]$$

Calculation of $E^{\ominus}(\mathrm{MeCl_2|Me|Cl^-})$ at 22 °C from E of the cell:

Left ⊖: $\mathrm{Me} + 2\ \mathrm{Cl^-} \rightarrow \mathrm{MeCl_2(s)} + 2\ \mathrm{e}$

$$E_{\mathrm{left}} = E^{\ominus}(\mathrm{Me|Cl^-|MeCl_2}) - \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ln\frac{1}{a_{\mathrm{Cl^-}}} =$$
$$= -E^{\ominus}(\mathrm{MeCl_2|Me|Cl^-}) - \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ln\frac{1}{a_{\mathrm{Cl^-}}}$$

Right ⊕: $\mathrm{Cl_2} + 2\ \mathrm{e} \rightarrow 2\ \mathrm{Cl^-}$

$$E_{\mathrm{right}} = E^{\ominus}(\mathrm{Cl_2|Cl^-}) - \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ln\frac{a_{\mathrm{Cl^-}}^2}{a_{\mathrm{Cl_2}}}$$

$$E = E_{\mathrm{left}} + E_{\mathrm{right}} = -E^{\ominus}(\mathrm{MeCl_2|Me|Cl^-}) + E^{\ominus}(\mathrm{Cl_2|Cl^-}) - \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ln\frac{1}{a_{\mathrm{Cl^-}}} - \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ln\frac{a_{\mathrm{Cl^-}}^2}{a_{\mathrm{Cl_2}}}$$

$$a_{\mathrm{Cl_2}} \cong \frac{p_{\mathrm{Cl_2}}}{p^{\mathrm{st}}}\ °(\text{ideal gas})$$

$$E^{\ominus}(\mathrm{MeCl_2|Me|Cl^-}) = E^{\ominus}(\mathrm{Cl_2|Cl^-}) - \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ln\left(\frac{1}{\cancel{a_{\mathrm{Cl^-}}^2}}\cdot\frac{\cancel{a_{\mathrm{Cl^-}}^2}}{a_{\mathrm{Cl_2}}}\right) - E =$$
$$= 1.358 + \frac{8.314\cdot295.15}{2\cdot96485.3}\cdot\ln\left(\frac{130}{101.325}\right) - 1.174$$

$E^{\ominus}_{\mathrm{Ag|Cl^-|AgCl}} = 0.18717\ \mathrm{V}$

$$\ln K_S = \frac{2\cdot96485,3}{8,314\cdot295,15}\cdot(0.18717 - 0.562) = -29.47637$$

$K_S = 1.58\cdot10^{-13}$