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 $\Delta_f S^{\ominus}(\mathrm{AgCl,\ s}) = 57.9\ \mathrm{J\ mol^{-1}\ K^{-1}}$. Calculate the standard cell potential and the cell potential at 25 and 40 °C of the cell

$$\ominus\ \mathrm{Ag(s)\ |\ AgCl\ (s)|\ KCl}\ (c = 0.1\ \mathrm{mol\ dm^{-3}})\ |\ \mathrm{Cl_2}\ (p = 250\ \mathrm{kPa})\ |\ \mathrm{Pt}\ \oplus$$

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

$E^{\ominus}(\mathrm{AgCl|Ag|Cl^-}) = 0.222$ V, $\quad E^{\ominus}(\mathrm{Ag^+|Ag}) = +0.799$ V

$E^{\ominus}(\mathrm{K^+|K}) = -2.925$ V $\quad E^{\ominus}(\mathrm{Cl_2|Cl^-}) = +1.36$ V

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

Solution:

Left $\ominus$: $\mathrm{Ag(s) + Cl^- = AgCl(s) + e}$ $\qquad E_{\mathrm{left}} = E^{\ominus}_{\mathrm{Ag,Cl^-|AgCl}} - \dfrac{RT}{F}\ln\dfrac{1}{a_{\mathrm{Cl^-}}}$

At 25 °C $\qquad E^{\ominus}_{\mathrm{Ag,Cl^-|AgCl}} = -E^{\ominus}_{\mathrm{AgCl|Ag,Cl^-}} = -0.222$ V

Right $\oplus$: $\mathrm{\tfrac{1}{2}\ Cl_2 + e^- \rightarrow Cl^-}$ $\qquad E_{\mathrm{right}} = E^{\ominus}_{\mathrm{Cl_2|Cl^-}} - \dfrac{RT}{F}\ln\dfrac{a_{\mathrm{Cl^-}}}{(a_{\mathrm{Cl_2}})^{1/2}}$

At 25 °C $\qquad E^{\ominus}_{\mathrm{Cl_2|Cl^-}} = 1.36$ V

$$E = E_{\mathrm{left}} + E_{\mathrm{right}} = E^{\ominus}_{\mathrm{Ag,Cl^-|AgCl}} - \frac{RT}{F}\ln\frac{1}{a_{\mathrm{Cl^-}}} + E^{\ominus}_{\mathrm{Cl_2|Cl^-}} - \frac{RT}{F}\ln\frac{a_{\mathrm{Cl^-}}}{(a_{\mathrm{Cl_2}})^{1/2}} \quad , \quad a_{\mathrm{Cl_2}} \approx \frac{p_{\mathrm{Cl_2}}}{p^{\mathrm{st}}}$$

$$E = E^{\ominus} + \frac{RT}{F}\cdot\ln\frac{p_{\mathrm{Cl_2}}}{p^{\mathrm{st}}}$$

$E^{\ominus}(25\ ^{\circ}\mathrm{C}) = E^{\ominus}_{\mathrm{Cl_2|Cl^-}} + E^{\ominus}_{\mathrm{Ag,Cl^-|AgCl}} = 1.36 + (-0.222) = 1.138$ V

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

Reaction in the cell: $\ominus$: $\mathrm{Ag(s) + Cl^- = AgCl(s) + e}$

$\oplus$: $\mathrm{\tfrac{1}{2}\ Cl_2\ (g) + e^- = Cl^-}$

$\mathrm{Ag(s) + \tfrac{1}{2}\ Cl_2\ (g) = AgCl(s)}$

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

$$\Delta S^{\ominus} = \Delta_f S^{\ominus}(\mathrm{AgCl}) = -F\left(\frac{\mathrm{d}E^{\ominus}}{\mathrm{d}T}\right) = 57.9\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$\frac{\mathrm{d}E^{\ominus}}{\mathrm{d}T} \doteq \frac{\mathrm{d}E}{\mathrm{d}T} = -\frac{\Delta_f S^{\ominus}}{F} = -\frac{57.9}{96485.3} = 6\cdot 10^{-4}\ \mathrm{V\ K^{-1}} \qquad \left[\frac{\mathrm{C\cdot V}}{\mathrm{J\ K^{-1}\ mol^{-1}}\ /\ \mathrm{C\ mol^{-1}}}\right]$$

Temperature dependences:

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

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

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

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