Problem 11-05 Cell potential and dissociation constant

What is the value of the potential of galvanic cell

$$\ominus\ \text{Pt} \mid H_2\,(p = 110\ \text{kPa}) \mid \textit{salicylic acid}\ (c_0 = 0.001\ \text{mol dm}^{-3}) \parallel$$
$$\parallel \text{KCl}\ (\textit{saturated solution}) \mid Hg_2Cl_2\,(\text{s}) \mid \text{Hg}(\ell)\ \oplus$$

at the temperature of 25 °C. The dissociation constant of salicylic acid for the standard state infinite dilution, c^{st} = 1 mol dm^{-3}, is $1.05{\cdot}10^{-3}$. Reduction potential of the saturated calomel electrode is $E_{\text{red,calom}}$ = 0.2438 V. All activity coefficients can be taken as equal to one. Under given conditions hydrogen exhibits ideal behaviour. For standard state for hydrogen take the ideal gas at actual temperature and pressure p^{st} = 101.325 kPa.

[E = 0.4343 V]

Solution:

HS ≡ salicylic acid

$HS = H^+ + S^-$

$c_0 = 0.001\ \text{mol dm}^{-3}$

$c_{HS} = c_0 - x$

$c_{H+} = c_{S-} = x$

$$K = \frac{a_{H^+}\cdot a_{S^-}}{a_{HS}} = \frac{\gamma_+\cdot c_{H^+}\cdot\gamma_-\cdot c_{S^-}}{c_{HS}\cdot c^{st}} = \gamma_\pm^2\cdot\frac{x^2}{c_0 - x} \quad , \quad \gamma_\pm = 1\ ,\ a_i \approx \frac{c_i}{c^{st}}\ ,\ c^{st} = 1\ \text{mol dm}^{-3}$$

$$1.05{\cdot}10^{-3} = \frac{x^2}{0.001 - x}$$

$$1.05{\cdot}10^{-6} - 1.05{\cdot}10^{-3}{\cdot}\ x = x^2$$

$$x = c_{H+} = -5.25{\cdot}10^{-4} \pm (2.75625{\cdot}10^{-7} + 1.05{\cdot}10^{-6})^{1/2} = -5.25{\cdot}10^{-4} \pm 1.151357{\cdot}10^{-3}$$

$$c_{H+} = 6.26357{\cdot}10^{-4}\ \text{mol dm}^{-3}$$

Left ⊖: $\tfrac{1}{2} H_2\,(g) = H^+ + e$

$$E_{\text{left}} = 0 - \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{a_{H^+}}{a_{H_2}^{1/2}} \quad , \quad a_{H^+} \approx \frac{c_{H^+}}{c^{st}} \quad , \quad a_{H_2} \approx \frac{p_{H_2}}{p^{st}}$$

$$c^{st} = 1\ \text{mol dm}^{-3}\ ,\ \gamma_i = 1 \quad , \quad p^{st} = 101.325\ \text{kPa},$$

Right ⊕: $\tfrac{1}{2} Hg_2Cl_2 + e \rightarrow Hg + Cl^-$

$$E_{\text{right}} = E_{\text{red, calom}} = 0.2438\ \text{V}$$

$$E = E_{\text{left}} + E_{\text{right}} = -\frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{c_{H^+}}{(p_{H_2}/p^{st})^{1/2}} + 0.2438 =$$

$$= -\frac{8.314\cdot 298.15}{96485.3}\cdot\ln\frac{6.26357\cdot 10^{-4}}{(110/101.325)^{1/2}} + 0.2438 = 0.19054 + 0.2438$$

E = 0.4343 V