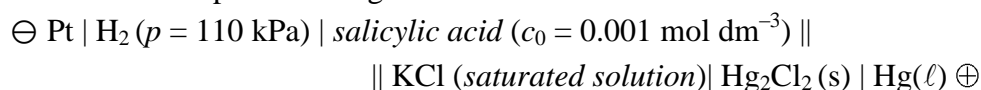


### Problem 11-05 Cell potential and dissociation constant

What is the value of the potential of galvanic cell



at the temperature of 25 °C. The dissociation constant of salicylic acid for the standard state infinite dilution,  $c^{\text{st}} = 1 \text{ mol dm}^{-3}$ , is  $1.05 \cdot 10^{-3}$ . Reduction potential of the saturated calomel electrode is  $E_{\text{red, calom}} = 0.2438 \text{ V}$ . 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  $p^{\text{st}} = 101.325 \text{ kPa}$ .

$$[E = 0.4343 \text{ V}]$$

**Solution:**

HS  $\equiv$  salicylic acid



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

$$c_{\text{HS}} = c_0 - x$$

$$c_{\text{H}^+} = c_{\text{S}^-} = x$$

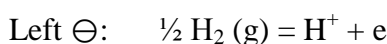
$$K = \frac{a_{\text{H}^+} \cdot a_{\text{S}^-}}{a_{\text{HS}}} = \frac{\gamma_+ \cdot c_{\text{H}^+} \cdot \gamma_- \cdot c_{\text{S}^-}}{c_{\text{HS}} \cdot c^{\text{st}}} = \gamma_{\pm}^2 \cdot \frac{x^2}{c_0 - x} \quad , \quad \gamma_{\pm} = 1 \quad , \quad a_i \approx \frac{c_i}{c^{\text{st}}} \quad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

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

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

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

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



$$E_{\text{left}} = 0 - \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{a_{\text{H}_2}^{1/2}} \quad , \quad a_{\text{H}^+} \approx \frac{c_{\text{H}^+}}{c^{\text{st}}} \quad , \quad a_{\text{H}_2} \approx \frac{p_{\text{H}_2}}{p^{\text{st}}} \\ c^{\text{st}} = 1 \text{ mol dm}^{-3} \quad , \quad \gamma_i = 1 \quad , \quad p^{\text{st}} = 101.325 \text{ kPa},$$



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

$$E = E_{\text{left}} + E_{\text{right}} = - \frac{RT}{F} \ln \frac{c_{\text{H}^+}}{(p_{\text{H}_2} / p^{\text{st}})^{1/2}} + 0.2438 = \\ = - \frac{8.314 \cdot 298.15}{96485.3} \cdot \ln \frac{6.26357 \cdot 10^{-4}}{(110/101.325)^{1/2}} + 0.2438 = 0.19054 + 0.2438 \\ E = 0.4343 \text{ V}$$