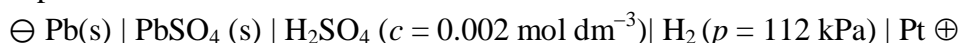


### Problem 11-03 Calculation of the cell potential, $\gamma_{\pm} \neq 1$

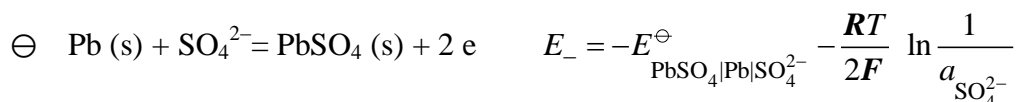
Calculate the potential of the electrochemical cell



at the temperature of 25 °C. Assume that the sulphuric acid is completely dissociated to the second degree. To the determination of the mean activity coefficient use the Debye-Hückel law ( $A = 1.172 \text{ dm}^{3/2} \text{ mol}^{-1/2}$ ). Standard state for electrolyte: infinite dilution,  $c^{\text{st}} = 1 \text{ mol dm}^{-3}$ . In these conditions, hydrogen exhibits ideal behaviour (standard state  $p^{\text{st}} = 101.325 \text{ kPa}$ ).

$$[E = 0.1295 \text{ V } (\gamma_{\pm} = 0.8449 - \text{extended D-H law})]$$

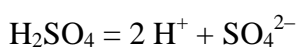
**Solution:**



$$E = E_- + E_+ = -E_{\text{PbSO}_4|\text{Pb}|\text{SO}_4^{2-}}^{\ominus} - \frac{RT}{2F} \ln \frac{1}{a_{\text{SO}_4^{2-}}} - \frac{RT}{2F} \ln \frac{a_{\text{H}_2}}{a_{\text{H}^+}^2} = -E_{\text{PbSO}_4|\text{Pb}|\text{SO}_4^{2-}}^{\ominus} - \frac{RT}{2F} \ln \frac{a_{\text{H}_2}}{a_{\text{H}^+}^2 \cdot a_{\text{SO}_4^{2-}}}$$

$$a_{\text{H}_2} \approx \frac{p_{\text{H}_2}}{p^{\text{st}}} = \frac{112}{101,325}$$

Activity of the electrolyte:



$$a_{\text{H}^+}^2 \cdot a_{\text{SO}_4^{2-}} = (\gamma_{\text{H}^+} \cdot \frac{c_{\text{H}^+}}{c^{\text{st}}})^2 \cdot (\gamma_{\text{SO}_4^{2-}} \cdot \frac{c_{\text{SO}_4^{2-}}}{c^{\text{st}}})$$

$$c^{\text{st}} = 1 \text{ mol dm}^{-3}, \quad c_{\text{H}^+} = 2c, \quad c_{\text{SO}_4^{2-}} = c \quad (c = c_{\text{H}_2\text{SO}_4})$$

$$a_{\text{H}^+}^2 \cdot a_{\text{SO}_4^{2-}} = \gamma_{\pm}^3 \cdot 4c^3$$

$$I = \frac{1}{2} (c_{\text{H}^+} \cdot 1^2 + c_{\text{SO}_4^{2-}} \cdot 2^2) = \frac{1}{2} (2c \cdot 1^2 + c \cdot 2^2) = 3c = 3 \cdot 0.002 = 0.006 \text{ mol dm}^{-3}$$

$0.001 < I < 0.1$  - extended Debye-Hückel law is advisable

$$\ln \gamma_{\pm} = -\frac{A \cdot z_{\text{C}} \cdot z_{\text{A}} \cdot \sqrt{I}}{1 + \sqrt{I}}, \quad z_{\text{C}} = 1, \quad z_{\text{A}} = 2, \quad A = 1.172 \text{ dm}^{3/2} \text{ mol}^{-1/2}$$

$$\ln \gamma_{\pm} = -\frac{1.172 \cdot 1 \cdot 2 \cdot \sqrt{0.006}}{1 + \sqrt{0.006}} = -0.16851$$

$$\gamma_{\pm} = 0.84492$$

$$\begin{aligned} E &= 0.359 + \frac{8.314 \cdot 298.15}{2 \cdot 96485.3} \cdot \left( \ln (\gamma_{\pm}^3 \cdot 4c^3) - \ln \frac{112}{101.325} \right) = \\ &= 0.359 + 0.0128456 \cdot \left( \ln (0.84492^3 \cdot 4 \cdot 0.002^3) - \ln \frac{112}{101.325} \right) \end{aligned}$$

$$E = 0.1295 \text{ V}$$