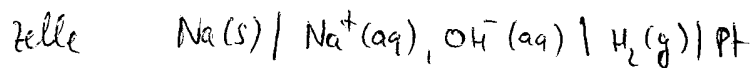
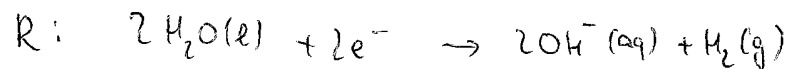
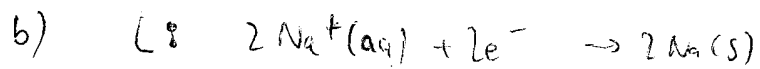
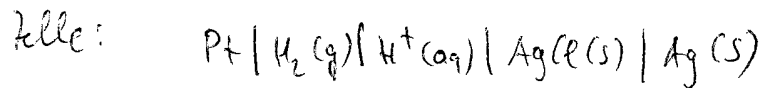
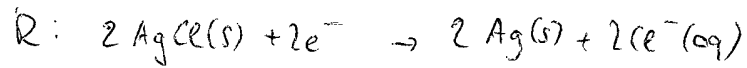
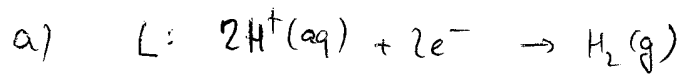
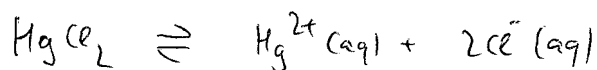


Übungsblatt 13 – Lösungen

A 13.1:



A 13.2:



$$K_L = a_{\text{Hg}^{2+}} \cdot a_{\text{Ce}^{-}}^2 \approx \frac{m_{\text{Hg}^{2+}}}{m^{\ominus}} \cdot \frac{m_{\text{Ce}^{-}}^2}{(m^{\ominus})^2}$$

$$m_{\text{Hg}^{2+}} \stackrel{!}{=} 2$$

$$m_{\text{Ce}^{-}} = 2 m_{\text{Hg}^{2+}} = 2e$$

$$\Rightarrow K_L = \frac{2 \cdot (2e)^2}{(m^{\ominus})^3} = \frac{4e^3}{(m^{\ominus})^3}$$

$$\Rightarrow e = \left( \frac{K_L}{4} \right)^{1/3} m^{\ominus} \quad m^{\ominus} = 1 \text{ mol kg}^{-1}$$

$$\Delta G_R^{\ominus} = -RT \ln K_L$$

$$\Delta G_R^{\ominus} = \sum_{\text{Prod}} \nu \Delta G_B^{\ominus} - \sum_{\text{Ed}} \nu \Delta G_B^{\ominus} =$$

$$= \Delta G_B^{\ominus}(\text{Hg}^{2+}, \text{aq}) + 2\Delta G_B^{\ominus}(\text{Ce}^{-}, \text{aq}) - \Delta G_B^{\ominus}(\text{HgCe}_2, \text{s}) =$$

$$= (164.4 + 2 \cdot (-131.23) - (-178.6)) \text{ kJ mol}^{-1} =$$

$$= +80.54 \text{ kJ mol}^{-1}$$

$$\ln K_L = - \frac{\Delta G_R^{\ominus}}{RT} = \frac{-80.54 \cdot 10^3 \text{ J mol}^{-1}}{8.314 \cdot 298 \text{ J K}^{-1} \text{ mol}^{-1} \cdot \text{K}} = -32.51$$

$$\Rightarrow K_L = 7.62 \cdot 10^{-15} \quad \Rightarrow e = 1.24 \cdot 10^{-5} \text{ mol kg}^{-1}$$

(a) Nernst:  $E = E_0 - \frac{RT}{zF} \ln Q$   $z=2$

$$\Rightarrow E = E_0 - \frac{RT}{2F} \ln (a_{H^+}^2 \cdot a_{e^-}^2)$$

$$Q = \frac{a_{Ag(s)}^2 \cdot a_{H^+}^2 \cdot a_{e^-}^2}{a_{AgCl(s)}^2 \cdot a_{H_2(g)}}$$

$$a_{Ag(s)} = a_{AgCl(s)} = a_{H_2(g)} = 1$$

$$a_+^2 \cdot a_-^2 = \gamma_{\pm}^4 \left(\frac{m_+}{m^\ominus}\right)^2 \left(\frac{m_-}{m^\ominus}\right)^2 = \gamma_{\pm}^4 \left(\frac{m}{m^\ominus}\right)^4$$

$$m_+ = m_- = m = 0.01 \text{ mol kg}^{-1}$$

$$\Rightarrow E = E_0 - \frac{RT}{2F} \ln (\gamma_{\pm} m)^4 = E_0 - \frac{2RT}{F} \ln (\gamma_{\pm} m)$$

b)  $\Delta G_R = -zFE = -2 \cdot 96485 \text{ C mol}^{-1} \cdot 0.4658 \text{ V} =$   
 $= -89.89 \text{ kJ mol}^{-1}$

c)  $E_0 = E + \frac{2RT}{F} \ln (\gamma_{\pm} m) =$

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2}$$

$$\frac{m}{m^\ominus} = 0.01$$

$$z_+ = z_{H^+} = 1 \quad z_- = z_{e^-} = 1$$

$$I = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2) =$$

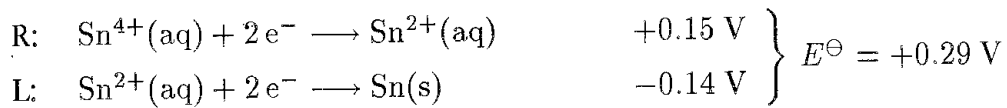
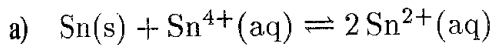
$$= \frac{1}{2} (2m) = m$$

$$\log \gamma_{\pm} = -0.509 \cdot (0.01)^{1/2} = -0.0509 \Rightarrow \gamma_{\pm} = 0.889$$

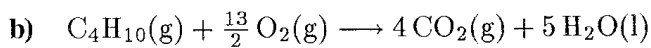
$$E_0 = 0.4658 \text{ V} + \frac{0.0514}{2 \cdot 8.314 \cdot 298} \frac{\text{J K}^{-1} \text{ mol}^{-1} \cdot \text{K}}{96485 \text{ C mol}^{-1}} \cdot \ln(0.889 \cdot 0.01) = \underline{\underline{0.223 \text{ V}}}$$

**A 13.4:**

Nach Gl. 10–15 ist jeweils  $\ln K = \frac{\nu F E^\ominus}{RT}$

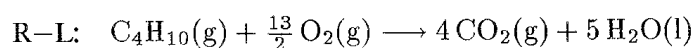
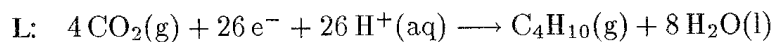
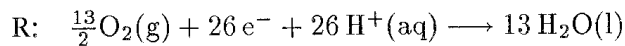


$$\ln K = \frac{(2) \cdot (0.29 \text{ V})}{25.693 \text{ mV}} = 22.6 \quad K = \boxed{6.5 \times 10^9}$$

**A 13.5:**

$$\begin{aligned} \Delta_{\text{R}} G^\ominus &= 4 \Delta_{\text{B}} G^\ominus(\text{CO}_2, \text{g}) + 5 \Delta_{\text{B}} G^\ominus(\text{H}_2\text{O}, \text{l}) - \Delta_{\text{B}} G^\ominus(\text{C}_4\text{H}_{10}, \text{g}) \\ &= [(4) \cdot (-394.36) + (5) \cdot (-237.13) - (-17.03)] \text{ kJ mol}^{-1} \quad (\text{Tabellen 2.11 und 2.12}) \\ &= -2746.06 \text{ kJ mol}^{-1} \end{aligned}$$

Bei dieser Reaktion ist die Anzahl  $\nu$  der übertragenen Elektronen nicht so direkt erkennbar wie im Teil a). Um  $\nu$  zu ermitteln, teilen wir die Zellenreaktion in zwei Halbreaktionen auf:



Also ist  $\nu = 26$ , und es folgt

$$E = \frac{-\Delta G^\ominus}{\nu F} = \frac{+2746.06 \text{ kJ mol}^{-1}}{(26) \cdot (96.485 \text{ kC mol}^{-1})} = \boxed{+1.09 \text{ V}}$$