Spannung der Sauerstoff-Elektrode

a) $2\,H_2O \rightleftharpoons O_2 + 4\,H^+ + 4\,e^-$ (sauer)

$$U_{O_2} = U^0_{O_2} + \frac{R \cdot T}{z \cdot F} \cdot ln \frac{p_{O_2} \cdot a^4_{H^+}}{a^2_{H_2O}}$$

$$U^0_{O_2} = \frac{\Delta G^0_{B,ox} - \Delta G^0_{B,red}}{z \cdot F} = \frac{4(\Delta G^0_{B,H^+}) + \Delta G^0_{B,O_2} - 2(\Delta G^0_{B,H_2O})}{4 \cdot F} = \frac{(0 + 113{,}38)\,kcal \cdot mol \cdot V}{4 \cdot 23{,}05\,kcal \cdot mol}$$

$$U^0_{O_2} = 1{,}2297\,V \sim 1{,}23\,V_H \qquad \left(\Delta G^0_{sauer} = 113{,}38\,\frac{kcal}{mol}\right)$$

$$U_{O_2} = 1{,}23\,V + \frac{0{,}059V}{4} \cdot log \frac{p_{O_2} \cdot a^4_{H^+}}{a^2_{H_2O}} \qquad / \; a_{H_2O} = 1$$

$$U_{O_2} = 1{,}23\,V + \left(\frac{0{,}059V}{4} \cdot log\, p_{O_2}\right) + \left(\frac{0{,}059V}{4} \cdot log\, a^4_{H^+}\right)$$

mit $p_{O_2} = 1bar$ und $pH = -log\, a_{H^+}$ folgt

$$\boxed{U_{O_2} \approx 1{,}23\,V - 0{,}059V \cdot pH} = \text{EMK}$$

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b) $4\,OH^- \rightleftharpoons O_2 + 2\,H_2O + 4\,e^-$ (basisch)

$$U_{O_2} = U^0_{O_2} + \frac{R \cdot T}{z \cdot F} \cdot ln \frac{p_{O_2} \cdot a^2_{H_2O}}{4 a_{OH^-}}$$

$$U^0_{O_2} = \frac{\Delta G^0_{B,ox} - \Delta G^0_{B,red}}{z \cdot F} = \frac{\Delta G^0_{B,O_2} + 2(\Delta G^0_{B,H_2O}) - 4(\Delta G^0_{B,OH^-})}{4 \cdot F} = \frac{(0 - 113{,}38 + 150{,}38)\,kcal \cdot mol \cdot V}{4 \cdot 23{,}05\,kcal \cdot mol}$$

$$U^0_{O_2} = 0{,}401\,V_H \qquad \left(\Delta G^0_{bas.} = 37\,\frac{kcal}{mol}\right)$$

$$U_{O_2} = 0{,}401\,V + \frac{0{,}059V}{4} \cdot log \frac{p_{O_2} \cdot a^2_{H_20}}{a^4_{OH^-}} \qquad / \; a_{H_2O} = 1,\; p_{O_2} = 1bar$$

$$U_{O_2} = 0{,}401\,V + \frac{0{,}059V}{4} \cdot log\, a^{-4}_{OH^-} = 0{,}401\,V + \frac{0{,}059V \cdot (-4)}{4} \cdot log\, a_{OH^-} \qquad / \; log\, a_{OH^-} = -14 + pH$$

$$U_{O_2} = 0{,}401\,V - 0{,}059V \; log\, a_{OH^-} = 0{,}401\,V - 0{,}059V \cdot (-14 + pH)$$

$$U_{O_2} = 0{,}401\,V + 0{,}826V - 0{,}059V \cdot pH = 1{,}227 - 0{,}059\,V \cdot pH$$

$$\boxed{U_{O_2} \approx 1{,}23\,V - 0{,}059V \cdot pH} = \text{EMK}$$

ΔG^0_B-Werte in kcal/mol: $\Delta G^0_{B,H^+} = \Delta G^0_{B,O_2} = 0$, $\Delta G^0_{B,OH^-} = -37{,}595$, $\Delta G^0_{B,H_20} = -56{,}69$