Termoøving 13

Kjapp teori

1) I en galvanisk celle produseres strøm ved en elektrokjemisk reaksjon, imens i en elektrolysecelle brukes strøm for å sette i gang en elektrokjemisk reaksjon

2) Det er potensialet i en elektrokjemiske celle hvor den ene halvdelen er en standard hydrogencelle.

3) $\Delta G = -z \cdot F \cdot E$

4) Nernst likning kan brukes til å bestemme E i cellen når konsentrasjoner eller temperatur endres.

Oppgave 1

1) Anode: $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$

Katode: $2AgCl(s) + 2e^- \rightleftharpoons 2Ag(s) + 2Cl^-(aq)$

Totalrx: $Zn(s) + 2AgCl(s) \rightleftharpoons ZnCl_2(aq) + 2Ag(s)$

2) $\Delta_r G^\circ = -z \cdot F \cdot E^\circ = -2 \cdot 96500 \cdot 0{,}9853 \cdot (10^{-3}\ \frac{kJ}{J})$

$\underline{\underline{\Delta_r G^\circ = -190{,}2\ kJ/mol}}$

3) Nernst likning: $E = E^\circ - \frac{RT}{zF} \ln Q$, $E^\circ = 0{,}9853\ V$, $E = 1{,}1566\ V$, $T = 298\ K$, $z = 2$

$$Q = \frac{a_{Zn^{2+}} \cdot a_{Cl^-}^2 \cdot a_{Ag(s)}^2}{a_{Zn(s)}^1 \cdot a_{AgCl(s)}^2} = a_{Zn^{2+}} \cdot a_{Cl^-}^2$$

$$= \gamma_\pm^3 \cdot m_{Zn^{2+}} \cdot m_{Cl^-}^2, \quad m_{Zn^{2+}} = \frac{1}{2} m_{Cl^-} = m$$

$$\Rightarrow E = E^\circ - \frac{RT}{zF} \ln(\gamma_\pm^3 \cdot m_{Zn^{2+}} \cdot m_{Cl^-}^2)$$

$$\gamma_\pm = \exp\left[\frac{zF}{3RT}(E^\circ - E) - \frac{1}{3}\ln(4m^3)\right]$$

$\underline{\underline{\gamma_\pm = 0{,}724}}$

Oppgave 2

1) Anode: $Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e^-$

Katode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$

Totalt: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightleftharpoons 2\,PbSO_4(s) + 2H_2O(l)$

$$\Delta_r G = -zFE = -2 \cdot 96485\,(1{,}9174 + 56\cdot10^{-6}\cdot25 + 108\cdot10^{-8}\cdot25^2)\ J/mol$$

$$= -370{,}5\ kJ/mol$$

$$\Delta_r S = -\left(\frac{\partial \Delta_r G}{\partial T}\right)_p = zF\left(\frac{\partial E}{\partial T}\right)_p = zF\,(56\cdot10^{-6} + 2\cdot108\cdot10^{-8}\,T)$$

$$= 2\cdot96485\cdot(56\cdot10^{-6} + 2\cdot108\cdot10^{-8}\cdot25)\ J/K\cdot mol$$

$$= 21{,}23\ J/K\cdot mol$$

$$\Delta_r H = \Delta_r G + T\Delta_r S = -364{,}1\ kJ/mol$$

2) $E^\circ = -E^\circ_{SO_4^{2-}|PbSO_4|Pb} + E^\circ_{SO_4^{2-}|PbSO_4|PbO_2} = 0{,}355 + 1{,}685$

$$E^\circ = 2{,}040\ V$$

$$E = 1{,}9174 + 56\cdot10^{-6}\cdot25 + 108\cdot10^{-8}\cdot25^2$$

$$E = 1{,}9195\ V$$

Antar: $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \Rightarrow C_{H^+} = 2C_{H_2SO_4} = 2C_{SO_4^{2-}}$

Nernst: $E = E^\circ - \frac{RT}{zF}\ln Q \qquad Q = \frac{a^2_{H_2O}}{a^2_{H_2SO_4}} = \frac{1^2}{\gamma_\pm^6 \cdot C_{H^+}^4 \cdot C_{SO_4^{2-}}^2}$

$$\gamma_\pm = \sqrt[6]{\exp\left(\frac{zF}{RT}\left[E^\circ - E\right]\right)\cdot\frac{1}{16\cdot C_{H_2SO_4}}}$$

$$\gamma_\pm = 0{,}132$$

Oppgave 3

La $m_1 = 0{,}001$ mol/kg , $m_2 = 0{,}01$ mol/kg

- Celle I: (Dobbeltcelle)

  - Venstre

    Anode: $\frac{1}{2} H_2(g) \rightleftharpoons H^+(m_1) + e^-$

    Katode: $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(m_1)$

    Totalt: $\frac{1}{2} H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + HCl(m_1)$

  - Høyre

    Anode: $Ag(s) + Cl^-(m_2) \rightleftharpoons AgCl(s) + e^-$

    Katode: $H^+(m_2) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$

    Totalt: $Ag(s) + HCl(m_2) \rightleftharpoons \frac{1}{2} H_2(g) + AgCl(s)$

  - Totalt

    $HCl(m_2) \rightleftharpoons HCl(m_1)$

- Celle 2

  Anode: $\frac{1}{2} H_2(g) \rightleftharpoons H^+(m_1) + e^-$

  Transport: $t_+ H^+(m_1) \rightleftharpoons t_+ H^+(m_2)$

  Transport: $t_- Cl^-(m_2) \rightleftharpoons t_- Cl^-(m_1)$

  Katode: $H^+(m_2) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$

  Totalt: $t_+ H^+(m_1) + t_- Cl^-(m_2) + H^+(m_2) \rightleftharpoons H^+(m_1) + t_+ H^+(m_2) + t_- Cl^-(m_1)$

  $\Rightarrow t_- Cl^-(m_2) + \underbrace{(1 - t_+)}_{= t_-} H^+(m_2) \rightleftharpoons t_- Cl^-(m_1) + \underbrace{(1 - t_+)}_{= t_-} H^+(m_1)$

  $\Rightarrow t_- HCl(m_2) \rightleftharpoons t_- HCl(m_1)$

1) $E_1 = 0 - \frac{RT}{F} \ln \frac{a_{HCl}(m_1)}{a_{HCl}(m_2)} = -\frac{RT}{F} \ln \frac{\gamma_\pm^2(m_1)\, m_{H^+}(m_1)\, m_{Cl^-}(m_1)}{\gamma_\pm^2(m_2)\, m_{H^+}(m_2)\, m_{Cl^-}(m_2)}$

Hvis $\gamma_\pm(m_1) = \gamma_\pm(m_2)$

$$E_1 = -\frac{RT}{F} \ln\left(\frac{m_1^2}{m_2^2}\right) = -\frac{8{,}3145 \cdot 298{,}2}{96485} \ln\left(\frac{0{,}001^2}{0{,}01^2}\right)$$

$$\underline{\underline{E_1 = 0{,}118\,V}}$$

2) $E_1 = E^\circ - \frac{RT}{F} \ln\left(\frac{a_{HCl}(m_1)}{a_{HCl}(m_2)}\right) = -\frac{RT}{F} \ln Q_1$

$E_2 = E^\circ - \frac{RT}{F} \ln\left(\frac{a_{HCl}(m_1)}{a_{HCl}(m_2)}\right)^{t_-} = -t_- \frac{RT}{F} \ln Q_2$, ser at $Q_1 = Q_2$

$$\underline{\underline{\frac{E_2}{E_1} = t_- = \frac{0{,}02}{0{,}115} = 0{,}174}}, \quad t_+ = 1 - t_- = 0{,}826$$

3) Siden $\gamma_\pm(1) = \gamma_\pm(2)$

$$E_1(T) = -\frac{R \cdot T}{F} \ln Q = T \cdot k$$

$$\Rightarrow E_1 = kT_1 \Rightarrow k = \frac{E_1}{T_1}$$
$$E_2 = kT_2 \Rightarrow k = \frac{E_2}{T_2}$$
$$\Rightarrow k = k \Rightarrow \frac{E_1}{T_1} = \frac{E_2}{T_2}$$
$$E_2 = \frac{T_2}{T_1} E_1$$

$$E_2(0°C) = \frac{273{,}2}{298{,}2} \cdot 0{,}118$$

$$\underline{E_2(0°C) = 0{,}108\ V}$$

4) Bruker uttrykket fra 1)

- Ved $m_1 = 0{,}001$ og $m_2 = 0{,}01$

$$E_1 = -\frac{RT}{F} \ln\left(\frac{\gamma_\pm^2(m_1) m_1^2}{\gamma_\pm^2(m_2) m_2^2}\right) = -\frac{8{,}3145 \cdot 298{,}2}{96485} \ln\left(\frac{0{,}965^2 \cdot 0{,}001^2}{0{,}904^2 \cdot 0{,}01^2}\right)$$

$$\underline{E_1 = 0{,}115\ V}$$

- 10 ganger høyere $\Rightarrow m_1 = 0{,}01$, $m_2 = 0{,}1$ $\Rightarrow \gamma_\pm(m_1) = 0{,}904$, $\gamma_\pm(m_2) = 0{,}796$

$$\underline{E_1 = 0{,}112\ V}$$

$\Rightarrow$ $\underline{E_1$ blir mindre hvis konsentrasjonene er 10 ganger høyere.}