

Elektromotorna sila zbog razlike koncentracije reaktanata

Predavanje 9, 20.03.2020.

Udžbenik: S. Mentus, Elektrohemija, 2008, strane 114-120

Sta do sada znamo?

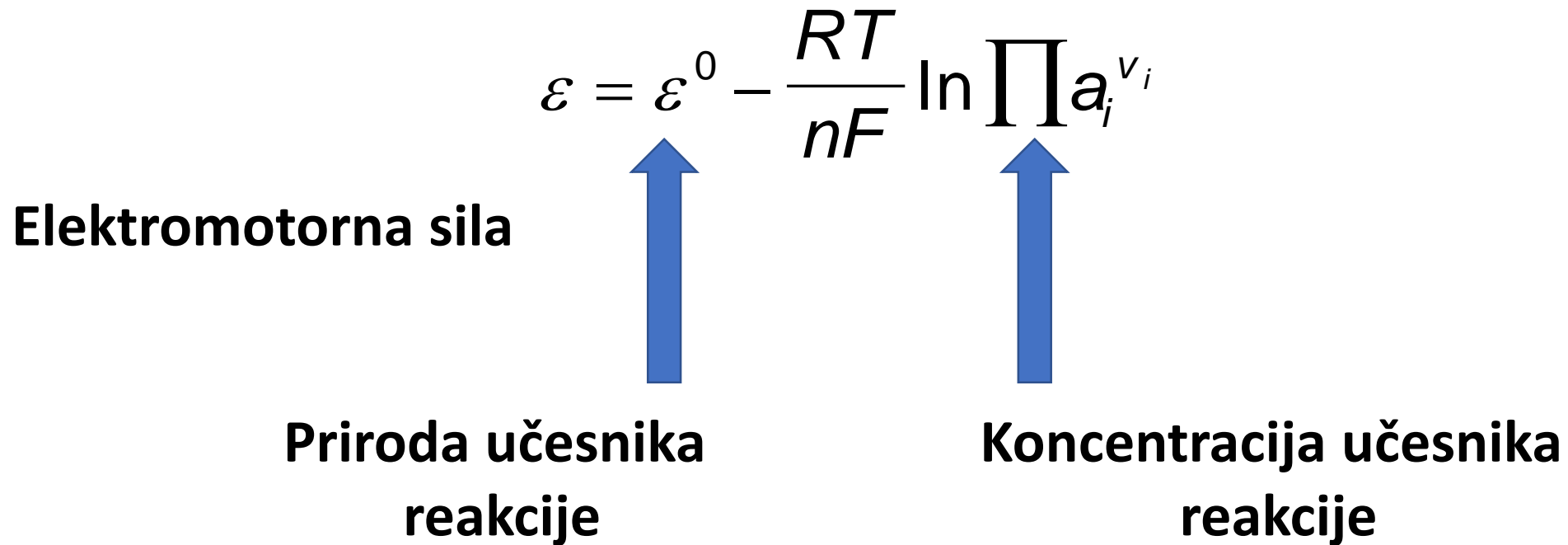
$$\Delta G = -nF\varepsilon$$

$$\varepsilon = \varepsilon^0 - \frac{RT}{nF} \ln \prod a_i^{v_i}$$

$$\varepsilon^0 = \frac{-\Delta G^0}{nF}$$

Standardna elektromotorna sila

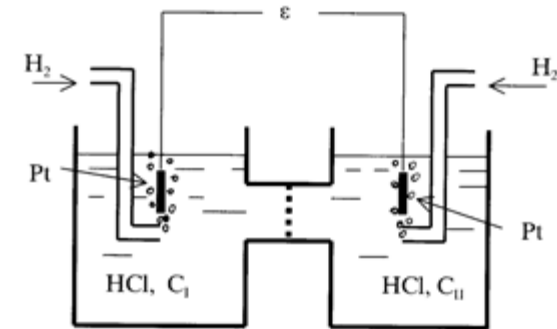
Sta do sada znamo?



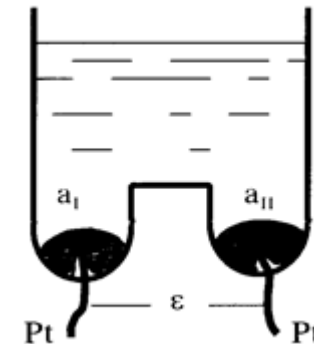
Koncentracioni galvanski elementi

EMS je rezultat različitih aktivnosti (istih) učesnika anodne i katodne reakcije

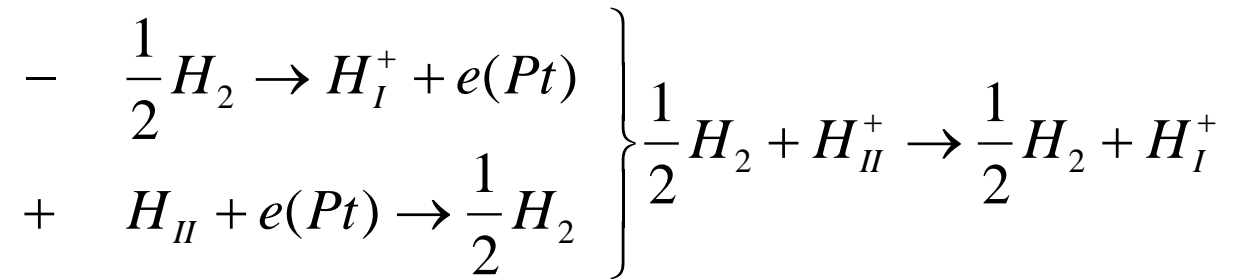
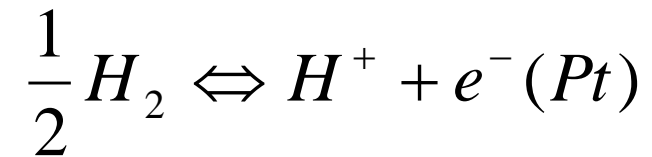
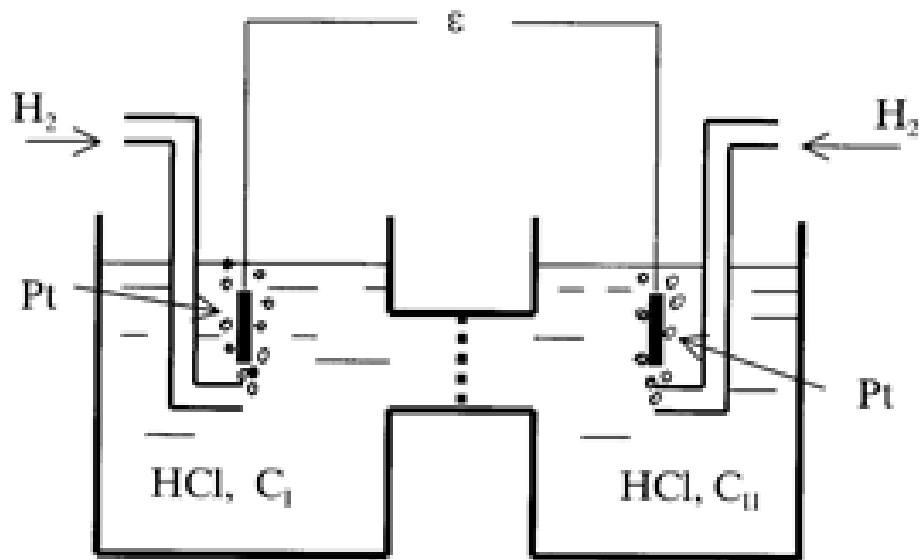
1. Koncentracioni elementi sa različitim koncentracijama elektrolita



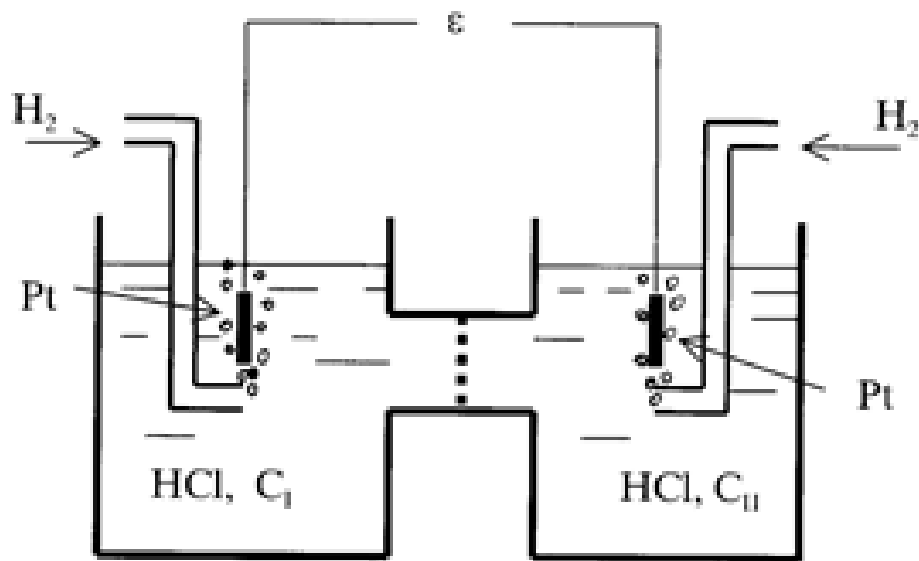
2. Koncentracioni elementi sa različitim koncentracijama metalnih faza



Koncentracijski elementi sa različitim koncentracijama elektrolita



Koncentracioni elementi sa različitim koncentracijama elektrolita

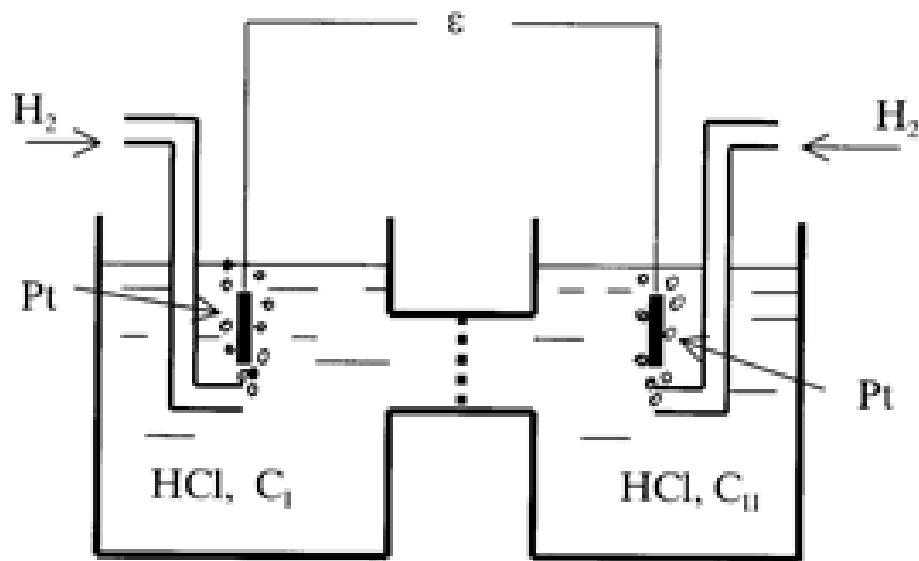


$$\Delta G = \frac{1}{2} \mu_{H_2} + \mu_{H^+} - \frac{1}{2} \mu_{H_2} - \mu_{H^+} = \mu_{H^+} - \mu_{H^+}$$

$$\Delta G = \left(\mu_{H^+,I}^0 - \mu_{H^+,II}^0 \right) + RT \ln \frac{a_{H^+,I}}{a_{H^+,II}}$$

Kolika je standardna EMS koncentracionog galvanskog elementa?

Koncentracioni elementi sa različitim koncentracijama elektrolita



$$\varepsilon = \frac{RT}{F} \ln \frac{a_{\pm, I}}{a_{\pm, II}} = \frac{RT}{F} \ln \frac{a_{\pm, konc}}{a_{\pm, razb}}$$

$$U = \varepsilon \pm E_d$$

$$U = \frac{RT}{F} \ln \frac{a_{\pm, konc}}{a_{\pm, razb}} - (t_- - t_+) \frac{RT}{F} \ln \frac{a_{\pm, razb}}{a_{\pm, konc}}$$

Koncentracioni elementi sa različitim koncentracijama elektrolita

Primer izračunavanja EMS u prisustvu difuzionog potencijala

Galvanski element je sačinjen od dve vodonične elektrode s rastvorima HCl kao elektrolitima, od kojih koncentrovaniji ima srednju jonsku aktivnost 0,1 a razblaženiji 0,01 mol dm⁻³. Naći napon između elektroda na 25 °C ako difuzioni potencijal nije uklonjen.

Rešenje:

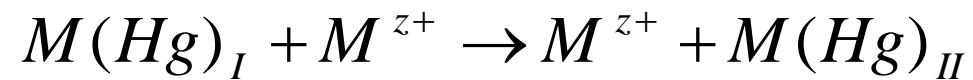
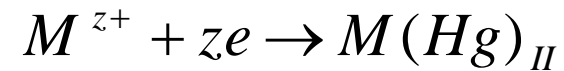
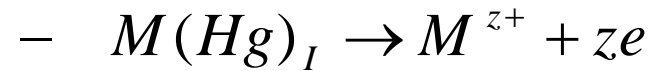
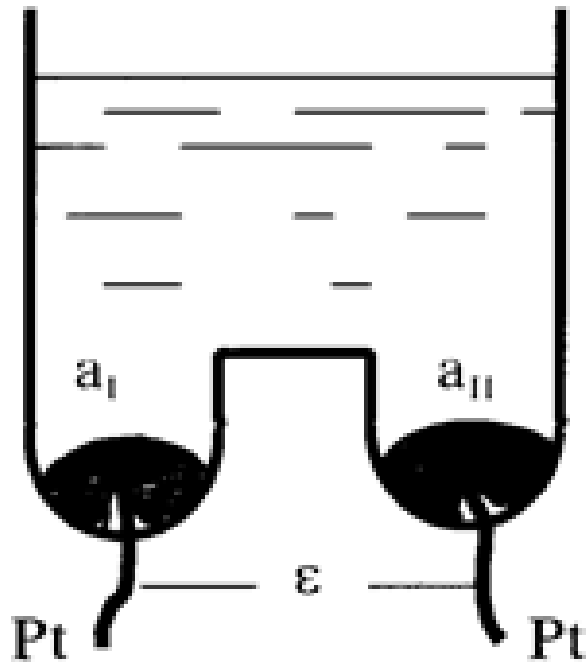
Prema jednačini (II.124) prilagođenoj za sobnu temperaturu i tabeli prenosnih brojeva II.6, difuzioni potencijal iznosi:

$$E_d = (0,17 - 0,83) \cdot 0,0591 \cdot \log \frac{0,01}{0,1} = 0,0391V$$

dok je napon na krajevima galvanskog elementa prema jednačini (III.17):

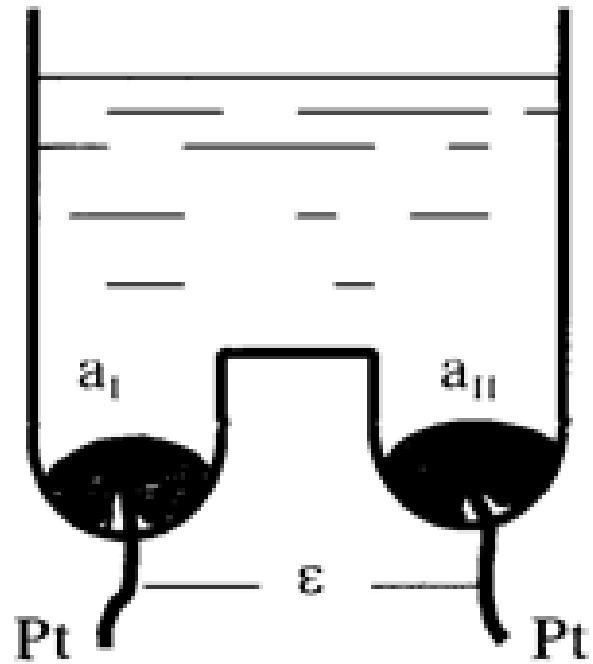
$$U = 0,0591 \cdot \log \frac{0,01}{0,1} - 0,0391 = 0,0591 - 0,0391 = 0,020V$$

Koncentracioni elementi sa različitim koncentracijama metalnih faza



$$\Delta G = \mu_{M^{z+}} + \mu_{M(Hg)_{II}} - \mu_{M(Hg)_I} - \mu_{M^{z+}}$$

Koncentracijski elementi sa različitim koncentracijama metalnih faza



$$\Delta G = \mu_{M(Hg)_{II}} - \mu_{M(Hg)_I}$$

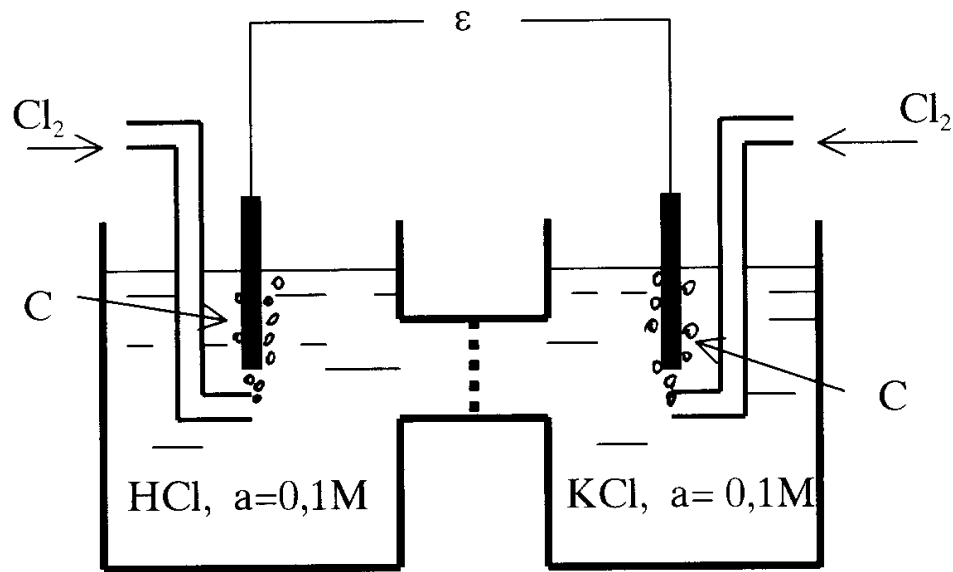
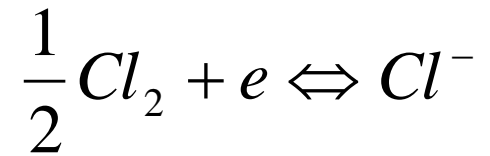
$$\Delta G = \mu_{M(Hg)_{II}}^0 - \mu_{M(Hg)_I}^0 + RT \ln a_{M(Hg)_{II}} - RT \ln a_{M(Hg)_I}$$

$$\Delta G = RT \ln \frac{a_{M(Hg)_{\text{razb}}}}{a_{M(Hg)_{\text{konc}}}} \quad \longrightarrow \quad \varepsilon = \frac{RT}{nF} \ln \frac{a_{M(Hg)_{\text{konc}}}}{a_{M(Hg)_{\text{razb}}}}$$

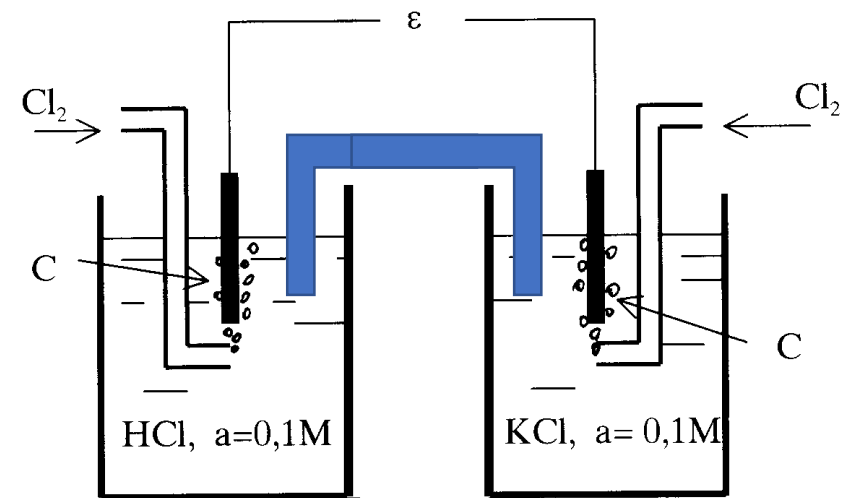
$$\varepsilon = -\frac{RT}{nF} \ln a_{M(Hg)}$$

Ako je jedna elektroda čist metal

Uklanjanje difuzionog potencijala



E_d oko 27 mV



C_{KCl} (M)	E_d (mV)
0,1	27
0,2	20
0,5	13
1,0	8,4
2,5	3,4
3,5	1,1
4,2 (zasićen)	< 1

Merenja prenosnih brojeva

$$U = \frac{RT}{F} \ln \frac{a_{\pm, konc}}{a_{\pm, razb}} - (t_- - t_+) \frac{RT}{F} \ln \frac{a_{\pm, razb}}{a_{\pm, kond}}$$

↑
 $1 - 2t_-$

1. Merenje – sa difuzionim potencijalom

2. Merenje – uklonjen difuzioni potencijal



RAZLIKA

$$(t_- - t_+) \frac{RT}{F} \ln \frac{a_{\pm, razb}}{a_{\pm, kond}}$$

Korisni linkovi (prođite kroz rešene primere u tekstovima)

- [https://chem.libretexts.org/Bookshelves/Analytical Chemistry/Supplemental Modules \(Analytical Chemistry\)/Electrochemistry/Voltaic Cells/Electrochemical Cells under Nonstandard Conditions/Concentration Cell](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Voltaic_Cells/Electrochemical_Cells_under_Nonstandard_Conditions/Concentration_Cell)
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