

Elektrokemija

Seminar

13.5.2025.

1. Izračunajte prosječne koeficijente aktiviteta vodenih otopina NaCl sljedećih molaliteta prema Debye-Hückelovom zakonu i Debye-Hückelovom graničnom zakonu i usporedite ih s eksperimentalno određenim vrijednostima pri 25 °C:

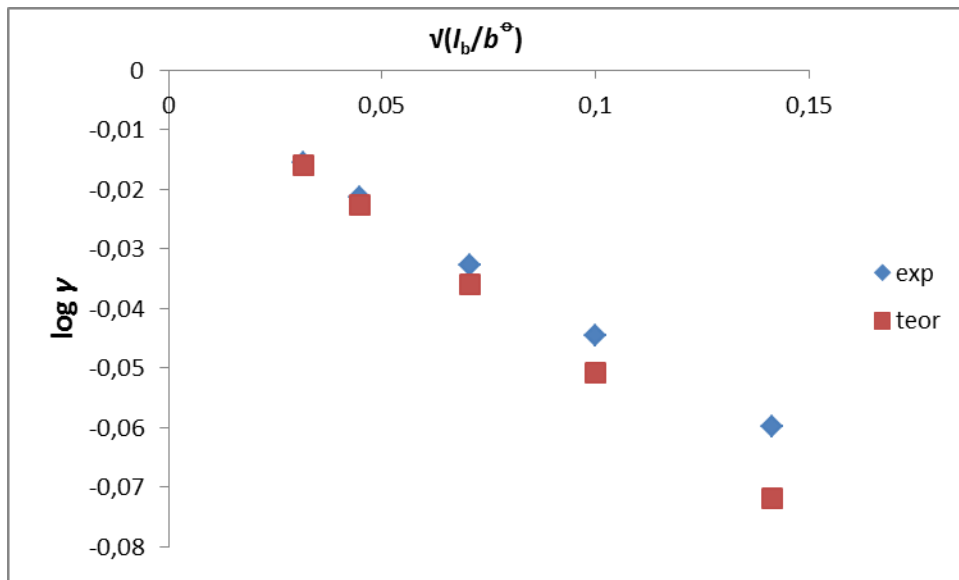
$\frac{b}{\text{mol kg}^{-1}}$	0,001	0,002	0,005	0,01	0,02
$(\bar{\gamma}_{\pm})_{\text{exp}}$	0,9649	0,9519	0,9275	0,9024	0,8712

DHL

$$-\log \gamma_{\pm} = \frac{|z_+ z_-| \cdot A_b \cdot \sqrt{I_b / b^{\ominus}}}{1 + \sqrt{I_b / b^{\ominus}}}$$

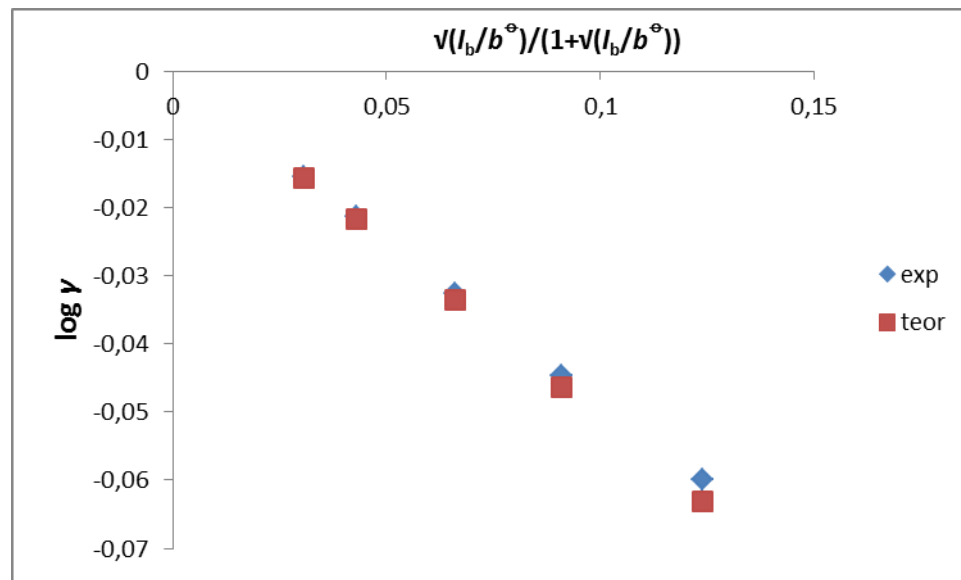
DHLL

$$-\log \gamma_{\pm} = |z_+ z_-| \cdot A_b \cdot \sqrt{I_b / b^{\ominus}}$$



DHLL

DHL



2. Izračunajte koncentracijsku konstantu ionizacije octene kiseline u vodenoj otopini koja sadrži veliki suvišak KCl koncentracije $c = 0,1 \text{ mol dm}^{-3}$ s obzirom na octenu kiselinu čija koncentracija iznosi $1 \cdot 10^{-4} \text{ mol dm}^{-3}$. Standardna konstanta ionizacije octene kiseline pri $25 \text{ }^{\circ}\text{C}$ iznosi $1,753 \cdot 10^{-5}$. U računu koristite Debye-Hückelov zakon (DHL) za određivanje prosječnih koeficijenata aktiviteta.

$$-\log \gamma_{\pm} = \frac{|z_+ z_-| \cdot A \cdot \sqrt{I_c / c^{\ominus}}}{1 + \sqrt{I_c / c^{\ominus}}}$$

$$\left. \begin{array}{l} A_c = 0,509 \\ A_b = 0,511 \end{array} \right\} A = 0,51 \text{ u zadatcima}$$

$$K^{\ominus} = \frac{a(\text{CH}_3\text{COO}^-) \cdot a(\text{H}^+)}{a(\text{CH}_3\text{COOH})}; a_i = \frac{c_i}{c^{\ominus}} \cdot \gamma_i$$

$$K^{\ominus} = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{H}^+]}{[\text{CH}_3\text{COOH}]} \cdot \frac{\gamma(\text{CH}_3\text{COO}^-) \cdot \gamma(\text{H}^+)}{c^{\ominus} \cdot \gamma(\text{CH}_3\text{COOH})}$$

$\gamma = 1$ za nenabijene vrste

$$K^{\ominus} = K_c \cdot \frac{\gamma(\text{CH}_3\text{COO}^-) \cdot \gamma(\text{H}^+)}{c^{\ominus}} = K_c \cdot \frac{\left(\overline{\gamma_{\pm}}\right)^2}{c^{\ominus}}$$

Geometrijski prosjek

$$I_c = \frac{1}{2} \left(c(K^+) + c(Cl^-) \right) = c(KCl) = 0,1 \text{ mol dm}^{-3}$$

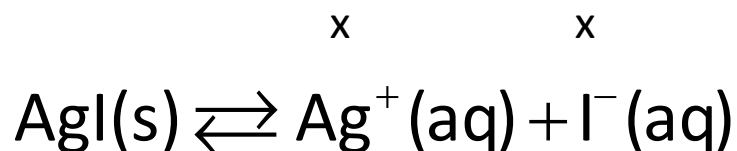
$c(KCl) \gg c(CH_3COOH)$
 Zanemariv doprinos octene
 kiseline ionskoj jakosti otopine

$$-\log \gamma_{\pm} = 0,1225$$

$$\gamma_{\pm} = 0,754$$

$$K_c = \frac{K^{\ominus} \cdot c^{\ominus}}{\left(\overline{\gamma_{\pm}} \right)^2} = 3,083 \cdot 10^{-5} \text{ mol dm}^{-3}$$

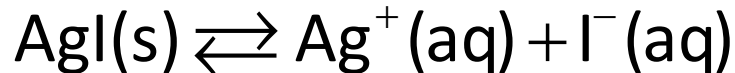
3. Standardna konstanta otapanja (produkt topljivosti) AgI u vodi pri 25 °C iznosi $8,568 \cdot 10^{-17}$. Primijenite Debye-Hückelov granični zakon (DHLL) i izračunajte topljivost AgI u vodenoj otopini AgNO_3 koncentracije 5 mol m^{-3} pri 25 °C i tlaku od 1 bar.



U čistoj vodi ili prisustvu elektrolita koji ne utječe na navedenu ravnotežu: topljivost je jednaka koncentraciji jedne ili druge ionske vrste, odnosno x

$$c(\text{AgNO}_3) \quad x$$

$$x + c(\text{AgNO}_3) \gg x$$



U prisustvu elektrolita koji sadrži zajednički kation ili anion, odnosno dolazi do pomaka ravnoteže ulijevo: topljivost je jednaka koncentraciji vrste koje ima manje u otopini

$$K_s^\ominus = \frac{a(\text{Ag}^+) \cdot a(\text{I}^-)}{\underbrace{a(\text{AgI})}} = \frac{c(\text{Ag}^+) \cdot c(\text{I}^-)}{(c^\ominus)^2} \cdot \underbrace{\left(\overline{\gamma_\pm}\right)^2} = \frac{c(\text{AgNO}_3) \cdot c(\text{I}^-)}{(c^\ominus)^2} \cdot \left(\overline{\gamma_\pm}\right)^2$$

Po definiciji jednako 1

Geometrijski prosjek
koeficijenata aktiviteta
ionskih vrsta u ravnoteži
(sudionika reakcije)

$$\text{Topljivost} = x = c(I^-)$$

$$X = \frac{K_s^{\ominus} \cdot (c^{\ominus})^2}{c(\text{AgNO}_3) \cdot (\gamma_{\pm})^2}$$

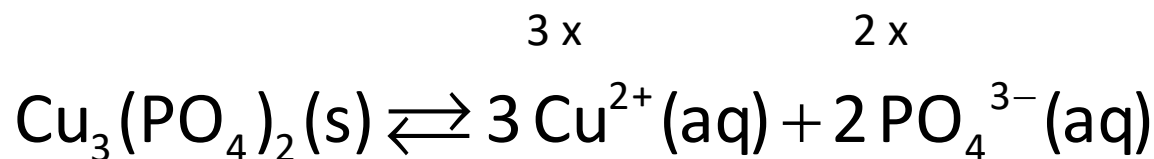
$$-\log \overline{\gamma_{\pm}} = \left| z_+ z_- \right| \cdot A \cdot \sqrt{I_c / c^{\ominus}}$$

$\uparrow$
AgI
 $\uparrow$
AgNO₃

$$x = 2,02 \cdot 10^{-14} \text{ mol dm}^{-3}$$

$$\overline{\gamma_{\pm}} = 0,920$$

4. Standardna konstanta otapanja $\text{Cu}_3(\text{PO}_4)_2$ u vodi pri 25 °C iznosi $1,37 \cdot 10^{-37}$. Izračunajte topljivost $\text{Cu}_3(\text{PO}_4)_2$.



$$K_s^\ominus = \frac{a^3(\text{Cu}^{2+}) \cdot a^2(\text{PO}_4^{3-})}{a(\text{Cu}_3(\text{PO}_4)_2)} = \frac{c^3(\text{Cu}^{2+})}{(c^\ominus)^3} \cdot \gamma^3(\text{Cu}^{2+}) \cdot \frac{c^2(\text{PO}_4^{3-})}{(c^\ominus)^2} \cdot \gamma^2(\text{PO}_4^{3-})$$

$$\left(\overline{\gamma_\pm}\right)^5 = \gamma^3(\text{Cu}^{2+}) \cdot \gamma^2(\text{PO}_4^{3-})$$

$$I_c \rightarrow 0; \gamma = 1$$

$$K_s^{\ominus} = \frac{(3x)^3 \cdot (2x)^2}{(c^{\ominus})^5} = \frac{108 \cdot x^5}{(c^{\ominus})^5}$$

$$x = \sqrt[5]{\frac{K_s^{\ominus} \cdot (c^{\ominus})^5}{108}} = 1,66 \cdot 10^{-8} \text{ mol dm}^{-3}$$

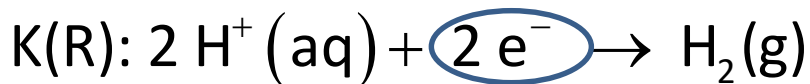
5. Izračunajte elektromotivnost članka

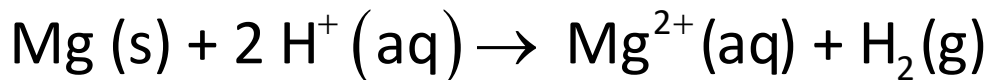
$\text{Mg(s)} \mid \text{Mg}^{2+}(\text{aq}, a = 1 \cdot 10^{-3}) \parallel \text{H}^{+}(\text{aq}, a = 1) \mid \text{H}_2(\text{g}, p = 1 \text{ bar}) \mid \text{Pt(s)}$ pri 25 °C.

$$E^{\circ}(\text{Mg}^{2+} \mid \text{Mg}) = -2,363 \text{ V}$$

$$E^{\circ}(\text{H}^{+} \mid \text{H}_2) = 0 \text{ V}$$

Dogovorno se svi standardni redukcijski potencijali definiraju u odnosu na standardni redukcijski potencijal vodika





$z = 2 \rightarrow$ broj izmijenjenih elektrona po jediničnoj pretvorbi (gledamo ukupnu reakciju)

Elektromotivnost članka (ukupna reakcija):
razlika elektromotivnosti katode i anode

$$E = (E_K^\ominus - E_A^\ominus) - \frac{RT}{zF} \ln \frac{a(\text{Mg}^{2+}) \cdot a(\text{H}_2)}{a(\text{Mg}) \cdot a^2(\text{H}^+)}$$

$p(\text{H}_2)/p^\ominus = 1$

Po definiciji 1

Zadano: $a = 1$

$$E = +2,363 \text{ V} - \frac{RT}{zF} \ln(1 \cdot 10^{-3})$$

$$F = 96\,485 \text{ C mol}^{-1}$$

$$E = 2,452 \text{ V}$$

6. Izračunajte elektromotivnost članka:



pri 25 °C. Molalitet otopine KBr iznosi 0,05 mol kg⁻¹, a molalitet otopine Cd(NO₃)₂ iznosi 0,01 mol kg⁻¹. Koristite Debye-Hückelov zakon za određivanje ionskih koeficijenata aktiviteta.

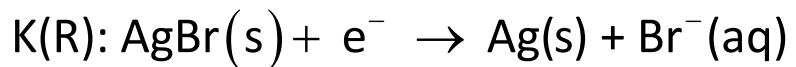
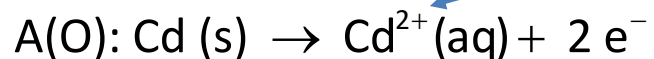
$$E^\ominus (\text{Cd}^{2+} \mid \text{Cd}) = -0,40 \text{ V}$$

$$E^\ominus (\text{AgBr, Br}^- \mid \text{Ag}) = 0,07 \text{ V}$$

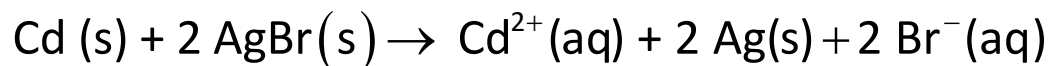
Kod elektrokemijskih članaka koristit ćemo ionske koeficijente aktiviteta redoks aktivnih vrsta!

$$-\log \gamma_i = \frac{z_i^2 \cdot A \cdot \sqrt{I_c / c^\ominus}}{1 + \sqrt{I_c / c^\ominus}}$$

Iz topljive soli



pomnožiti s 2 i zbrojiti s gornjom
jednadžbom; $z = 2$



Reakciju pišemo s redoks
aktivnom vrstom u nedisociranom
obliku (slabo topljiva sol)

$$E = (E_K^{\ominus} - E_A^{\ominus}) - \frac{RT}{zF} \ln \frac{a(\text{Cd}^{2+}) \cdot a^2(\text{Ag}) \cdot a(\text{Br}^{-})}{a(\text{Cd}) \cdot a^2(\text{AgBr})}$$

$$E = (E_K^\ominus - E_A^\ominus) - \frac{RT}{zF} \ln \left[\frac{b(\text{Cd}^{2+})}{b^\ominus} \cdot \gamma(\text{Cd}^{2+}) \cdot \frac{b^2(\text{Br}^-)}{(b^\ominus)^2} \cdot \gamma^2(\text{Br}^-) \right]$$

Ionske jakosti korištene za izračun pojedinih koeficijenata aktiviteta – paziti na sastav elektrolita za svaki polučlanak!

Cd^{2+} u otopini $\text{Cd}(\text{NO}_3)_2$

$$\begin{aligned} I_b &= \frac{1}{2} (4 \cdot b(\text{Cd}^{2+}) + b(\text{NO}_3^-)) = \frac{1}{2} (4 \cdot b(\text{Cd}(\text{NO}_3)_2) + 2 b(\text{Cd}(\text{NO}_3)_2)) \\ &= 3 b \text{ Cd}(\text{NO}_3)_2 = 0,03 \text{ mol kg}^{-1} \end{aligned}$$

$$-\log \gamma(\text{Cd}^{2+}) = \frac{4 \cdot 0,51 \sqrt{0,03}}{1 + \sqrt{0,03}} = 0,301$$

$$\gamma(\text{Cd}^{2+}) = 0,500$$

Br^- u otopini KBr

$$I_b = b(\text{KBr}) = 0,05 \text{ mol kg}^{-1}$$

$$-\log \gamma(\text{Br}^-) = \frac{1 \cdot 0,51 \sqrt{0,05}}{1 + \sqrt{0,05}} = 0,093$$

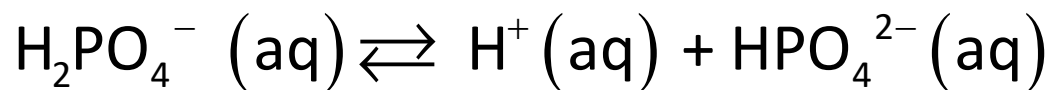
$$\gamma(\text{Br}^-) = 0,807$$

$$E = 0,62 \text{ V}$$

7. Izračunajte pH vodene otopine fosfatnog pufera pri 25 °C koji sadrži jednake koncentracije Na_2HPO_4 i NaH_2PO_4 ($c = 0,025 \text{ mol dm}^{-3}$). Koristite Debye-Hückelov zakon za određivanje ionskih koeficijenata aktiviteta.

$$K_{a,2} = 6,34 \cdot 10^{-8} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log a(\text{H}^+) = -\log \frac{c(\text{H}^+)}{c^\ominus} \cdot \gamma(\text{H}^+)$$



$$K_{a,2} = \frac{[\text{H}^+] \cdot [\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \rightarrow [\text{H}^+] = K_{a,2} \cdot \frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]} = K_{a,2}$$

$\swarrow \approx c(\text{NaH}_2\text{PO}_4)$
 $\nwarrow \approx c(\text{Na}_2\text{HPO}_4)$

$$-\log \gamma_i = \frac{z_i^2 \cdot A \cdot \sqrt{I_c / c^\ominus}}{1 + \sqrt{I_c / c^\ominus}}$$

$$\begin{aligned} I_c &= \frac{1}{2} \left(c(\text{Na}^+) + 4 \cdot c(\text{HPO}_4^{2-}) + c(\text{Na}^+) + c(\text{H}_2\text{PO}_4^-) \right) \\ &= \frac{1}{2} \left(2 c(\text{Na}_2\text{HPO}_4) + 4 \cdot c(\text{Na}_2\text{HPO}_4) + c(\text{NaH}_2\text{PO}_4) + c(\text{NaH}_2\text{PO}_4) \right) \\ &= 3 c(\text{Na}_2\text{HPO}_4) + c(\text{NaH}_2\text{PO}_4) = 0,1 \text{ mol dm}^{-3} \end{aligned}$$

$$-\log \gamma(\text{H}^+) = \frac{1 \cdot 0,51 \sqrt{0,1}}{1 + \sqrt{0,1}} = 0,1225$$

$$\gamma(\text{H}^+) = 0,754$$

$$\text{pH} = 7,32$$

8. Ukupna koncentracija fosfata u obliku H_2PO_4^- (aq) i HPO_4^{2-} (aq) u nekoj otopini iznosi $1 \cdot 10^{-3} \text{ mol dm}^{-3}$. Ako pH otopine iznosi 7,40, kolike su koncentracije pojedinih fosfatnih oblika u otopini? $\text{p}K_{a,2} = 7,21$. Pretpostavite idealno ponašanje otopine.

$$K_{a,2} = \frac{[\text{H}^+] \cdot [\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

Idealno ponašanje – koef. aktiviteta jednak 1

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{K_{a,2}}{[\text{H}^+]}$$

$$\text{pH} = -\log \frac{c(\text{H}^+)}{c^\ominus}$$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{K_{a,2}}{[\text{H}^+]} = \frac{10^{-\text{p}K_{a,2}} \cdot c^\ominus}{10^{-\text{pH}} \cdot c^\ominus} = 10^{\text{pH} - \text{p}K_{a,2}} = 1,5488$$

$$\left[\text{HPO}_4^{2-}\right] = 1,5488 \cdot \left[\text{H}_2\text{PO}_4^{-}\right]$$

$$\left[\text{HPO}_4^{2-}\right] + \left[\text{H}_2\text{PO}_4^{-}\right] = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$$

$$\left[\text{H}_2\text{PO}_4^{-}\right] = 3,92 \cdot 10^{-4} \text{ mol dm}^{-3}$$

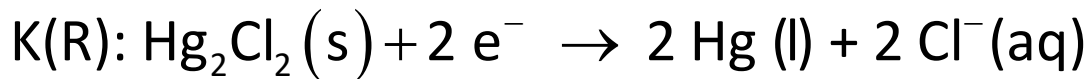
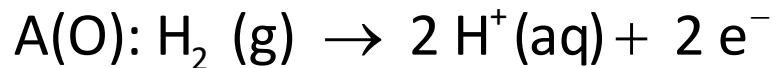
$$\left[\text{HPO}_4^{2-}\right] = 6,08 \cdot 10^{-4} \text{ mol dm}^{-3}$$

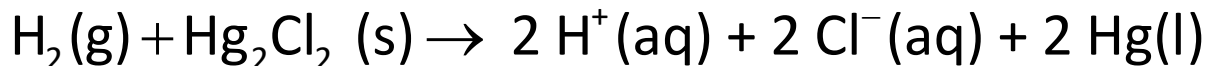
9. Izračunajte standardnu reakcijsku entalpiju i entropiju te Gibbsovu energiju pri 293 K za reakciju u elektrokemijskom članku: $\text{Pt(s)} \mid \text{H}_2(\text{g}) \mid \text{HCl(aq)} \mid \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Hg(l)}$.

Standardna elektromotivnost članka pri 293 K iznosi 0,2699 V, a pri 303 K iznosi 0,2669 V.

(pretpostavite da su u zadanom temperaturnom području standardna reakcijska entalpija i entropija konstantne).

Kolika je elektromotivnost navedenog članka pri 293 K ako je tlak vodika 1 bar, a pH vodene otopine HCl jednak 2?





Ovisnost standardne elektromotivnosti članka o temperaturi

$$\Delta_r G^\ominus = -zFE^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$E^\ominus = -\frac{\Delta_r H^\ominus}{zF} + \frac{\Delta_r S^\ominus}{zF} \cdot T$$

odsječak
na y-osi

nagib

U slučaju više podataka
 $E^\ominus(T)$ crtati graf

$$T_1 = 293 \text{ K}; E_1^\ominus = 0,2699 \text{ V}$$

$$T_2 = 303 \text{ K}; E_2^\ominus = 0,2669 \text{ V}$$

odsječak
na y-osi

$$-\frac{\Delta_r H^\ominus}{zF} = 0,3578 \text{ V}$$

Ako izračunamo jednadžbu pravca
kroz 2 točke:

$$\begin{aligned}\Delta_r H^\ominus &= -2 \cdot 96485 \text{ C mol}^{-1} \cdot 0,3578 \text{ V} = -69045 \text{ J mol}^{-1} \\ &= -69,04 \text{ kJ mol}^{-1}\end{aligned}$$

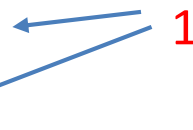
$$E^\ominus = (-3 \cdot 10^{-4} \text{ V K}^{-1}) \cdot T + 0,3578 \text{ V}$$

Nagib = „temperaturni koeficijent“

$$\Delta_r G^\ominus (293 \text{ K}) = -zFE^\ominus (293 \text{ K}) = -52,1 \text{ kJ mol}^{-1}$$

$$\frac{\Delta_r S^\ominus}{zF} = -3 \cdot 10^{-4} \text{ V K}^{-1}$$

$$\begin{aligned}\Delta_r S^\ominus &= -3 \cdot 10^{-4} \text{ V K}^{-1} \cdot 2 \cdot 96485 \text{ C mol}^{-1} \\ &= -57,9 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$E = (E_K^\ominus - E_A^\ominus) - \frac{RT}{zF} \ln \frac{a^2(\text{H}^+) \cdot a^2(\text{Cl}^-) \cdot a^2(\text{Hg})}{a(\text{H}_2) \cdot a(\text{Hg}_2\text{Cl}_2)}$$


$$\uparrow$$

$$p(\text{H}_2)/p^\ominus = 1$$

$$E = (E_K^\ominus - E_A^\ominus) - \frac{RT}{zF} \ln(a^2(\text{H}^+) \cdot a^2(\text{Cl}^-))$$



$$E^\ominus (293 \text{ K})$$

$$a(\text{H}^+) = a(\text{Cl}^-) = 10^{-\text{pH}} = 10^{-2}$$

$$E = 0,502 \text{ V}$$

10. Odredite standardnu Gibbsovu energiju i entalpiju stvaranja fumaratnog iona (F^{2-}) pri 298 K koristeći sljedeće podatke:

	$\Delta_f G^\ominus$ (298 K) / kJ mol ⁻¹	$\Delta_f H^\ominus$ (298 K) / kJ mol ⁻¹
sukcinat (S^{2-})	-690,44	-908,68
acetaldehid (A)	-139,08	-210,66
etanol (E)	-181,75	-287,02

Temperaturni koeficijent za proces $F^{2-} + E \rightarrow S^{2-} + A$ iznosi $-3,46 \cdot 10^{-5} \text{ V K}^{-1}$, a standardni elektrodni potencijali reakcija:

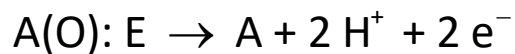
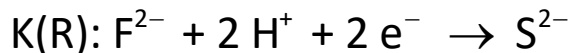


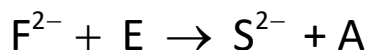
$$E^\ominus = 0,031 \text{ V}$$



$$E^\ominus = -0,197 \text{ V}$$

Obje reakcije napisane kao redukcija (tablice standardnih redukcijskih potencijala)!
 Katoda je uvijek ona elektroda s višim redukcijskim potencijalom, a kod druge elektrode (anode) se zapravo reakcija događa u suprotnom smjeru.





Oduzimanje tabličnih vrijednosti koje su navedene isključivo za reakciju redukcije; taj minus već uključuje obrnuti predznak potencijala za suprotnu reakciju na anodi

$$E^{\ominus}(298 \text{ K}) = E_K^{\ominus} - E_A^{\ominus} = 0,031 \text{ V} - (-0,197 \text{ V}) = 0,228 \text{ V}$$

$$E^{\ominus} = -\frac{\Delta_r H^{\ominus}}{zF} + \frac{\Delta_r S^{\ominus}}{zF} \cdot T$$

Nagib = „temperaturni koeficijent“

$$\frac{\Delta_r S^{\ominus}}{zF} = -3,46 \cdot 10^{-5} \text{ V K}^{-1}$$

$$\Delta_r H^\ominus = -zF \left(E^\ominus - \frac{\Delta_r S^\ominus}{zF} \cdot T \right) = -45987 \text{ J mol}^{-1}$$

$$= -45,987 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\ominus (298 \text{ K}) = -zFE^\ominus (298 \text{ K}) = -43,997 \text{ kJ mol}^{-1}$$

$$\Delta_r H^\ominus = \Delta_f H^\ominus (\text{S}^{2-}) + \Delta_f H^\ominus (\text{A}) - \Delta_f H^\ominus (\text{F}^{2-}) - \Delta_f H^\ominus (\text{E})$$

$$\Delta_f H^\ominus (\text{F}^{2-}) = -786,3 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\ominus = \Delta_f G^\ominus (\text{S}^{2-}) + \Delta_f G^\ominus (\text{A}) - \Delta_f G^\ominus (\text{F}^{2-}) - \Delta_f G^\ominus (\text{E})$$

$$\Delta_f G^\ominus (\text{F}^{2-}) = -603,8 \text{ kJ mol}^{-1}$$