

# Ion selektivne elektrode i mjerenje pH

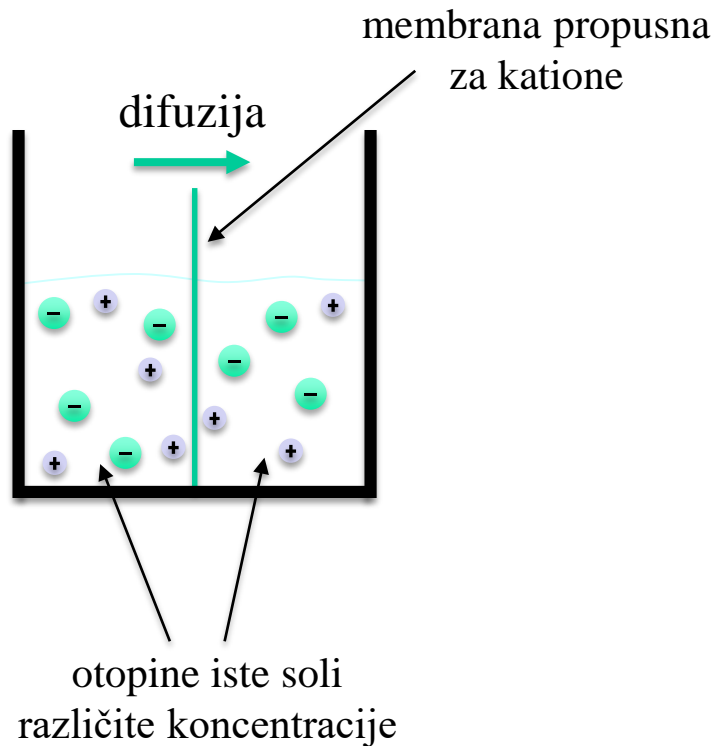
# Ion selektivne elektrode

- Elektrode čiji je potencijal (primarno) ovisan o jednoj ionskoj vrsti
- Razlika potencijala koja se uspostavlja na međupovršini membrana/ispitivana otopina jedini je promijenjivi doprinos ukupnom potencijalu indikatorske elektrode odnosno razlici potencijala indikatorska elektroda/referentna elektroda
- Koriste se membrane od različitih materijala ovisno o analitu (ionu na koji je elektroda selektivna) i ostalim željenim svojstvima
- Sadrže inertnu referentnu elektrodu (najčešće Ag/AgCl)

# Vrste ion selektivnih elektroda

- staklene elektrode – selektivne za  $H^+$  i druge monovalentne katione ( $Na^+$ ,  $Ag^+$ ,  $K^+$ ,  $Li^+$   $NH_4^+$ )
- ion selektivne elektrode s čvrstom membranom
- selektivne elektrode s heterogenom čvrstom membranom
- selektivne elektrode s tekućom membranom
- elektrode za plinove
- enzimске elektrode

# Elektrokemijska ravnoteža polupropusne membrane

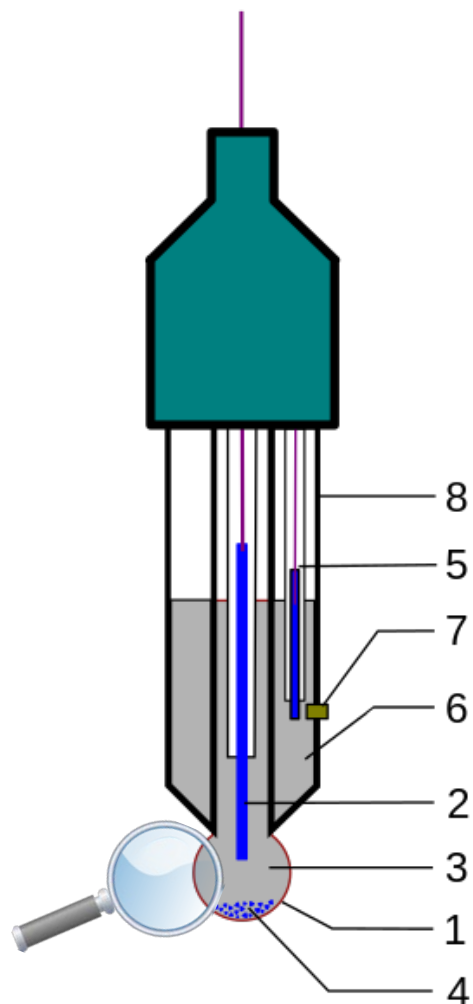


$$\mu_{el,+}^{\alpha} = \mu_{el,+}^{\beta}$$

$$\mu_{+}^{\alpha} + zF\phi^{\alpha} = \mu_{+}^{\beta} + zF\phi^{\beta}$$

$$\phi^{\beta} - \phi^{\alpha} = \Delta\phi = -\frac{RT}{zF} \ln \frac{a_{+}^{\beta}}{a_{+}^{\alpha}}$$

# Kombinirana staklena elektroda

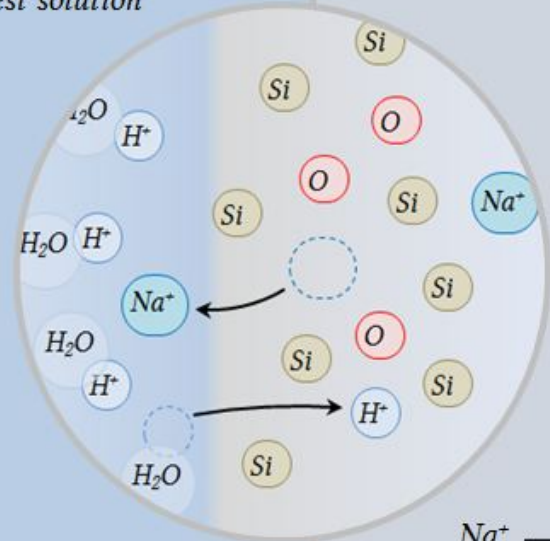


1. Staklena membrana
2. Interna referentna elektroda (npr. Ag/AgCl)
3. Otopina koja sadrži potencijal odredbene ione interne ref. el. i staklene membrane (npr. HCl,  $c = 0,1 \text{ mol dm}^{-3}$ )
4. Suvišak teško topljive soli (npr. AgCl)
5. „vanjska” referentna elektroda
6. otopina koja sadrži potencijal odredbene ione ref. el. (npr. KCl, sat.)
7. kontakt (sinter staklo, polupropusna keramika...)
8. tijelo elektrode (cijevčica od „običnog” stakla)

External solution → Hydrated gel (~10nm) ← Glass membrane (0.1mm) → Hydrated gel (~10nm) ← Internal solution

Unknown hydrogen activity: unknown pH of a test solution

Fixed hydrogen activity: known pH of a reference buffer solution (HCl)



$Na^+$  ions migrate through the glass to whichever side has the lowest  $H^+$  concentration



← Potential difference between the internal gel-solution interface and the external gel-solution interface:  $E_B$ , the boundary potential →

# Elektromotivnost kombinirane staklene elektrode

- primjer elektrode selektivne za  $H^+$

$Ag | AgCl | HCl || \textit{staklena membrana} || \textit{analit} || AgCl | Ag$

$$E = \phi_D(\textit{terminal vanjske ref. el.}) - \phi_L(\textit{terminal interne ref. el.}) =$$

$$\begin{aligned} &= \Delta\phi_{\frac{Ag}{AgCl}} + \Delta\phi_{\frac{AgCl}{HCl(aq)}} + \Delta\phi(\textit{kontakt}) \\ &+ \Delta\phi_{HCl(aq)/gel} + \Delta\phi_{gel/staklo} + \Delta\phi_{staklo/gel} + \\ &+ \Delta\phi_{gel/analit} + \Delta\phi_{analit/AgCl} + \Delta\phi_{AgCl/Ag} \end{aligned}$$

$$E = \textit{konst.} + \Delta\phi_{gel/analit} = E^\circ + \frac{RT}{F} \ln(a_{H^+})$$

**Selektivnost** prema određenom ionu postiže se promjenom sastava stakla

H<sup>+</sup>

SiO<sub>2</sub>(72)-CaO(8)-Na<sub>2</sub>O(20)

SiO<sub>2</sub>(72,2)-CaO(6,4)-Na<sub>2</sub>O(21,4) - Corning

Na<sup>+</sup>

SiO<sub>2</sub>(71)-Al<sub>2</sub>O<sub>3</sub>(18)-Na<sub>2</sub>O(11)

ostali kationi (K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, NH<sub>4</sub><sup>+</sup>)

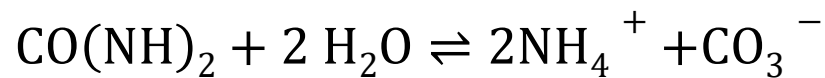
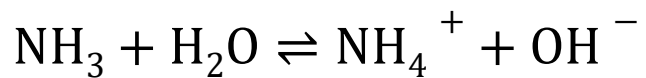
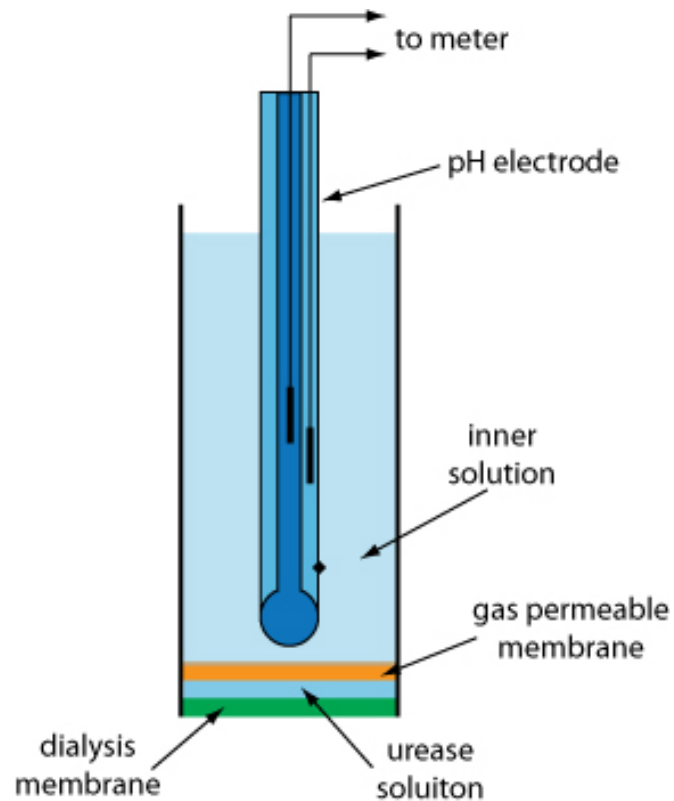
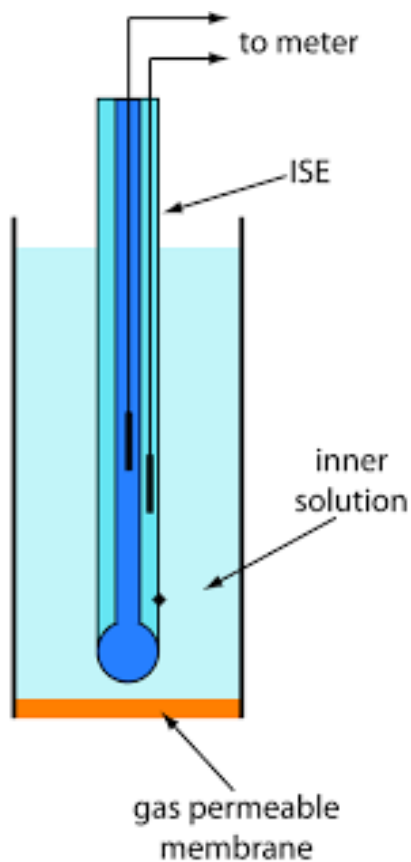
SiO<sub>2</sub>(69)-Al<sub>2</sub>O<sub>3</sub>(4)-Na<sub>2</sub>O(27)

**Interferencija** drugih ionskih vrsta (monovalentnih kationa) relativno je slabo izražena u slučaju pH elektroda (uzrok alkalijske pogreške), ali je vrlo značajna kod ostalih ion selektivnih elektroda

$$E = E^{\circ'} + \frac{RT}{F} \ln(a_M + \sum k_i a_{Mi})$$

$k_i$ - koeficijeni selektivnosti





# Definicija i interpretacija pH

Sørensen 1909.

$$\text{pH} = -\lg \frac{[\text{H}^+]}{c^\circ}$$

$$\text{pH} = -\lg a(\text{H}^+) = -\lg \frac{[\text{H}^+] \gamma_{\text{H}}}{c^\circ}$$

# Definicija i interpretacija pH

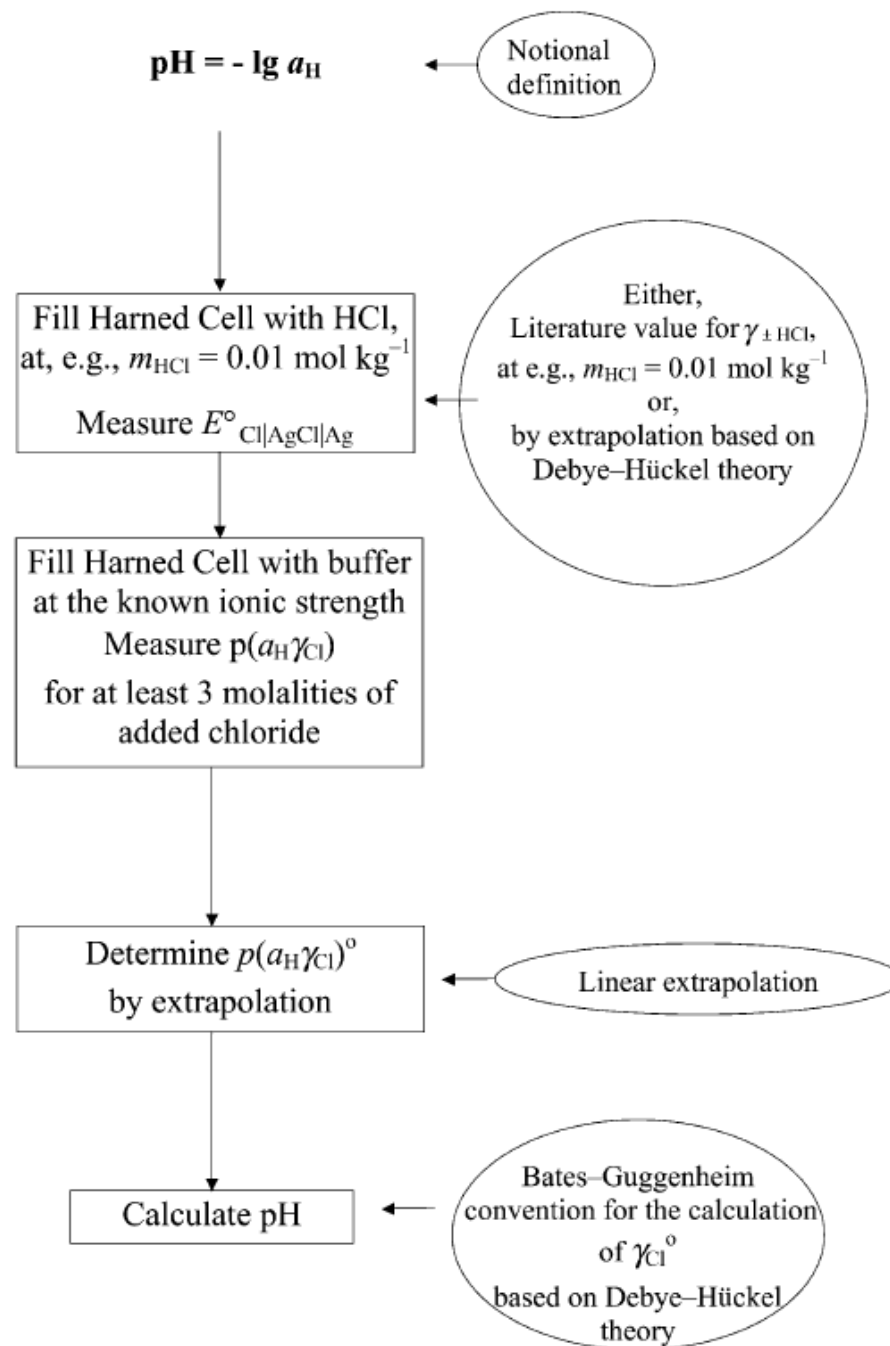
Harnedov članak - eliminiran difuzijski potencijal

- Na elektromotivnost utječe aktivitet kloridnih iona
- Nemoguće eliminirati utjecaj koeficijenta aktiviteta  $\text{Cl}^-$



$$E = E^\circ - \frac{RT \ln 10}{F} \log \frac{c(\text{Cl}^-) \gamma_{\text{Cl}^-}}{c^\circ} - \frac{RT \ln 10}{F} \text{pH}$$

# Hodogram određivanja pH standardnih pufera prema NIST



# Definicija i interpretacija pH

- Bates-Guggenheim konvencija:

$$-\lg \gamma_{\text{Cl,H}}^{\text{BG}} = \frac{A_c \sqrt{I_c / c^\circ}}{1 + B\sigma \sqrt{I_c / c^\circ}}$$

prema dogovoru:  $B \cdot \sigma = 1,5 \rightarrow r(\text{Cl}) = 4,6 \text{ \AA}$

# Definicija i interpretacija pH

$$\begin{aligned} E &= E^\circ - \frac{RT \ln 10}{\nu F} \lg \frac{[\text{Cl}^-] \gamma_{\text{Cl}}^{\text{BG}}}{c^\circ} + \frac{RT \ln 10}{\nu F} \lg \frac{[\text{H}^+] \gamma_{\text{H}}^{\text{BG}}}{c^\circ} \\ &= E^\circ - \frac{RT \ln 10}{\nu F} \lg \frac{[\text{Cl}^-] \gamma_{\text{Cl}}^{\text{BG}}}{c^\circ} + \frac{RT \ln 10}{\nu F} \text{pH} \end{aligned}$$

$$\text{pH}(X) = \text{pH}(S) + \frac{(E_X - E_S)F}{RT \ln 10}$$

**Table 2** Typical values of pH(PS) for primary standards at 0–50 °C (see Section 6.2).

Primary standards (PS)	Temp./°C										
	0	5	10	15	20	25	30	35	37	40	50
Sat. potassium hydrogen tartrate (at 25 °C)						3.557	3.552	3.549	3.548	3.547	3.549
0.05 mol kg <sup>-1</sup> potassium dihydrogen citrate	3.863	3.840	3.820	3.802	3.788	3.776	3.766	3.759	3.756	3.754	3.749
0.05 mol kg <sup>-1</sup> potassium hydrogen phthalate	4.000	3.998	3.997	3.998	4.000	4.005	4.011	4.018	4.022	4.027	4.050
0.025 mol kg <sup>-1</sup> disodium hydrogen phosphate + 0.025 mol kg <sup>-1</sup> potassium dihydrogen phosphate	6.984	6.951	6.923	6.900	6.881	6.865	6.853	6.844	6.841	6.838	6.833
0.03043 mol kg <sup>-1</sup> disodium hydrogen phosphate + 0.008695 mol kg <sup>-1</sup> potassium dihydrogen phosphate	7.534	7.500	7.472	7.448	7.429	7.413	7.400	7.389	7.386	7.380	7.367
0.01 mol kg <sup>-1</sup> disodium tetraborate	9.464	9.395	9.332	9.276	9.225	9.180	9.139	9.102	9.088	9.068	9.011
0.025 mol kg <sup>-1</sup> sodium hydrogen carbonate + 0.025 mol kg <sup>-1</sup> sodium carbonate	10.317	10.245	10.179	10.118	10.062	10.012	9.966	9.926	9.910	9.889	9.828