10. Junction potential

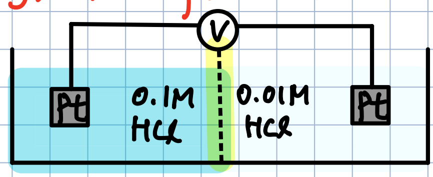
1 Review

→ mobility & conductivity ($u_i = \dfrac{|z_i| e}{6\pi\eta r}$, $\kappa = F\sum_i |z_i| u_i c_i$)

→ transference number ($t_i = \dfrac{|z_i| u_i c_i}{\sum_j |z_j| u_j c_j}$)

2 Liquid Junction potential

→



⇒ " $2H^+ + 2e^- \rightarrow H_2$ "

① In 0.1M HCl : $E_{eq} = E^\circ + \dfrac{RT}{2F}\ln\dfrac{(a^s_{H^+})^2}{f_{H_2}} = E^\circ + \dfrac{RT}{2F}\ln\dfrac{(0.01)^2}{1}$

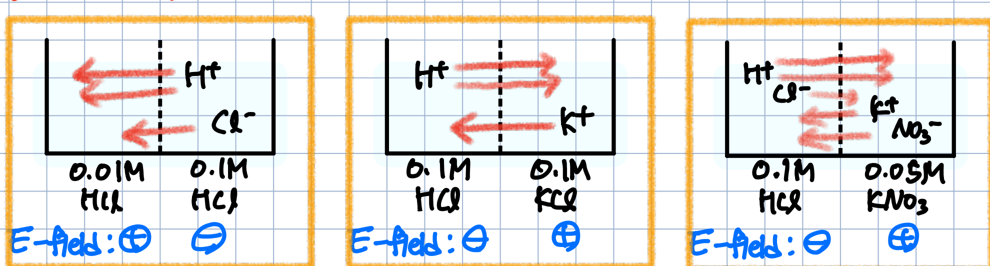
② In 0.01M HCl : $E_{eq} = E^\circ + \dfrac{RT}{2F}\ln\dfrac{(a^s_{H^+})^2}{f_{H_2}} = E^\circ + \dfrac{RT}{2F}\ln\dfrac{(0.1)^2}{1}$

∴ E_{cell} = ② − ① = $\cancel{59.2\,mV}$

↳ $E_{cell} = E_{Nernst} + E_j$ (∵ Ion transfer)

3 Liquid junction potential case ① ~ ③

→



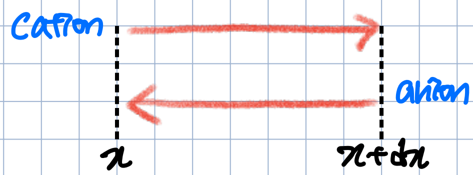
① concentration gradient ($u_i = \dfrac{|z_i| F D_i}{RT}$, H^+ ↑)

② potential difference

③ Ion passage → equal rate

④ Steady state potential → " liquid junction potential "

→ calculation :



$\begin{cases} \left|\frac{t_i}{z_i}\right| \text{ mole 이동} \\ \text{electrochemical potential} : \bar{\mu}_i \ \& \ \bar{\mu}_i + d\bar{\mu}_i \end{cases}$

↳ differential in free E : $dG = \sum_i \frac{t_i}{z_i} d\bar{\mu}_i$

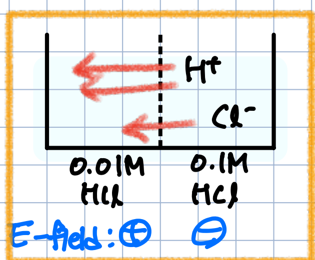
↳ steady state : $\int_\alpha^\beta dG = \sum_i \int_\alpha^\beta \frac{t_i}{z_i} d\bar{\mu}_i = 0$

↳ ⓐ aqueous condition , $\mu^{o\alpha} = \mu^{o\beta}$

$$\therefore \sum_i \int_\alpha^\beta \frac{t_i}{z_i} d\bar{\mu}_i = \sum_i \int_\alpha^\beta \frac{t_i}{z_i} d(\cancel{\mu_i^o} + RT\ln a_i + zF\phi) = \sum_i \int_\alpha^\beta \frac{t_i}{z_i} RT\, d\ln a_i + F\int_\alpha^\beta d\phi = 0$$

$$\therefore E_j = \phi^\beta - \phi^\alpha = -\frac{RT}{F} \sum_i \int_\alpha^\beta \frac{t_i}{z_i} d\ln a_i$$

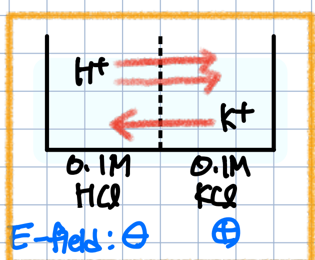
→

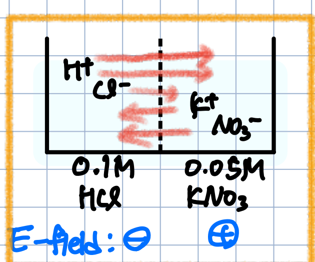


$\begin{cases} t_{+,\alpha} = t_{+,\beta} \\ t_{-,\alpha} = t_{-,\beta} \end{cases}$ $(t_\alpha = t_\beta)$

$\Rightarrow E_j = \phi^\beta - \phi^\alpha = (t_+ - t_-) \frac{RT}{F} \ln \frac{a_1}{a_2}$ → 동일한 농도 조건에서도 t의 조절에 따라 E_j 최소화 가능

$(a_1 = a^\alpha_{H^+} = a^\alpha_{Cl^-}$, $a_2 = a^\beta_{H^+} = a^\beta_{Cl^-}$, mean activity)





① activity = concentration

② concentration : linear

for ②&③

$$E_j = \phi^\beta - \phi^\alpha = \frac{\sum \frac{|z_i| u_i}{z_i} [c_i(\beta) - c_i(\alpha)]}{\sum |z_i| u_i [c_i(\beta) - c_i(\alpha)]} \cdot \frac{RT}{F} \ln \frac{\sum |z_i| u_i c_i(\alpha)}{\sum |z_i| u_i c_i(\beta)}$$

↳ Henderson equation

for ②

$E_j = \pm \frac{RT}{F} \ln \frac{\Lambda_\beta}{\Lambda_\alpha}$ (±: 공통이온의 전하)

↳ Lewis-Sargent relation