2.3.2 Types of Liquid Junctions

- The magnitude of the force exerted by the field is $|z_i| e\mathcal{E}$.
  - e: the electronic charge.

- The frictional drag can be approximated from the Stokes law as 6πηrv,
  - η: the viscosity of the medium
  - r: the radius of the ion
  - v: the velocity.

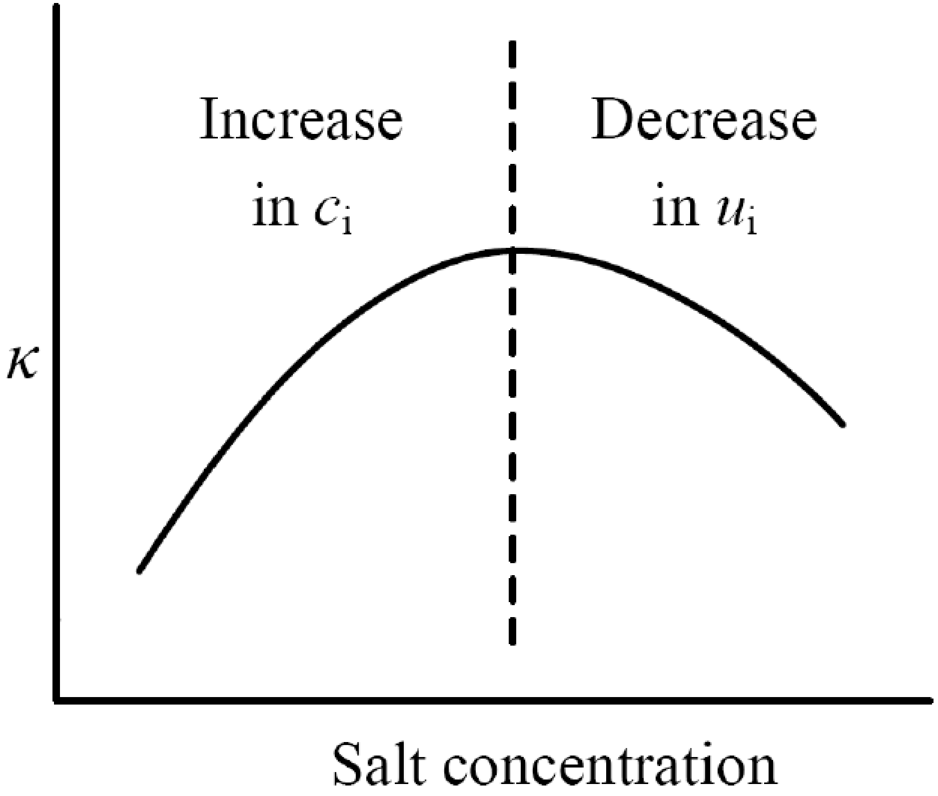
- When the terminal velocity is reached,

→ the mobility is:

$$u_i = \frac{v}{\mathcal{E}} = \frac{|z_i|e}{6\pi\eta r}$$

2.3.2 Types of Liquid Junctions

$$\boxed{\kappa = F \sum_{i} |z_i| u_i C_i}$$



2.3.2 Types of Liquid Junctions

- The transference number for species i

→ is merely the contribution to conductivity made by that species divided by the total conductivity:

$$\boxed{t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j}} \qquad \kappa = F \sum_i |z_i| u_i C_i$$

2.3.2 Types of Liquid Junctions

- For solutions of simple, pure electrolytes (i.e., one positive and one negative ionic species), such as KCl, $CaCl_2$, and HNO_3,

→ conductance is often quantified in terms of the equivalent conductivity, Λ, which is defined by

$$\boxed{\Lambda = \frac{\kappa}{C_{eq}}}$$

→ where C_{eq} is the concentration of positive (or negative) charges (Clzl = C_{eq}).

→ Thus, Λ expresses the conductivity per unit concentration of charge.

- Since Clzl = C_{eq} for either ionic species in these systems, one finds that

$$\left.\begin{aligned} \kappa &= F\sum_i |z_i| u_i C_i \\ \Lambda &= \frac{\kappa}{C_{eq}} \end{aligned}\right\} \quad \Lambda = F(u_+ + u_-)$$

→ where u_+ refers to the cation and u_- to the anion.

2.3.2 Types of Liquid Junctions

$$\Lambda = F(u_+ + u_-)$$

- This relation suggests that Λ could be regarded as the sum of individual equivalent ionic conductivities,

$$\Lambda = \lambda_+ + \lambda_- \qquad \lambda_i = Fu_i$$

- In these simple solutions,
  → then, the transference number t_i is given by

$$t_i = \frac{\lambda_i}{\Lambda} \qquad t_i = \frac{u_i}{u_+ + u_-}$$

2.3.2 Types of Liquid Junctions

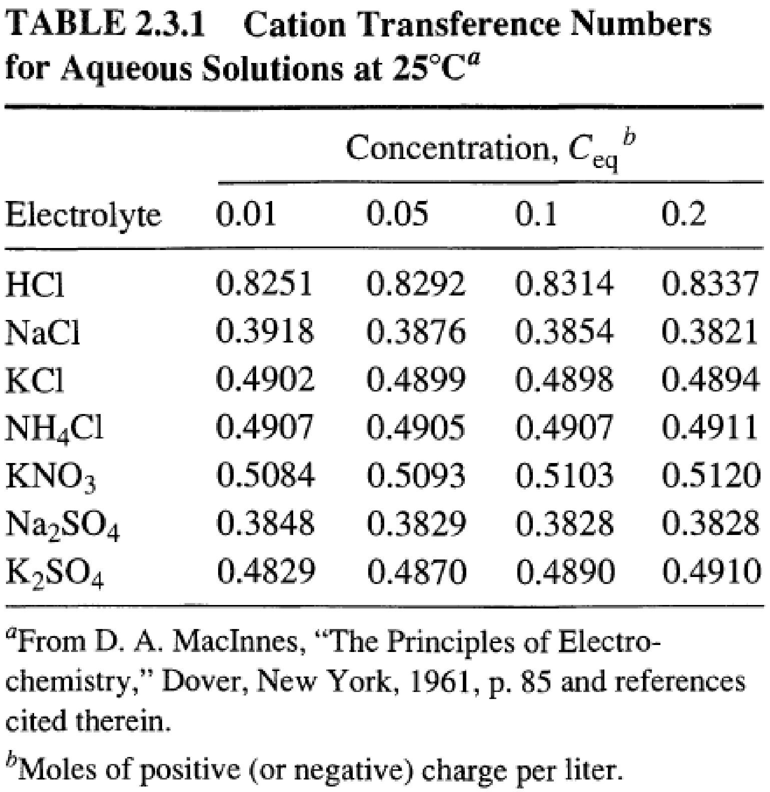


TABLE 2.3.1 Cation Transference Numbers for Aqueous Solutions at 25°C[a]

	Concentration, C_{eq}[b]			
Electrolyte	0.01	0.05	0.1	0.2
HCl	0.8251	0.8292	0.8314	0.8337
NaCl	0.3918	0.3876	0.3854	0.3821
KCl	0.4902	0.4899	0.4898	0.4894
NH_4Cl	0.4907	0.4905	0.4907	0.4911
KNO_3	0.5084	0.5093	0.5103	0.5120
Na_2SO_4	0.3848	0.3829	0.3828	0.3828
K_2SO_4	0.4829	0.4870	0.4890	0.4910

[a] From D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 85 and references cited therein.

[b] Moles of positive (or negative) charge per liter.

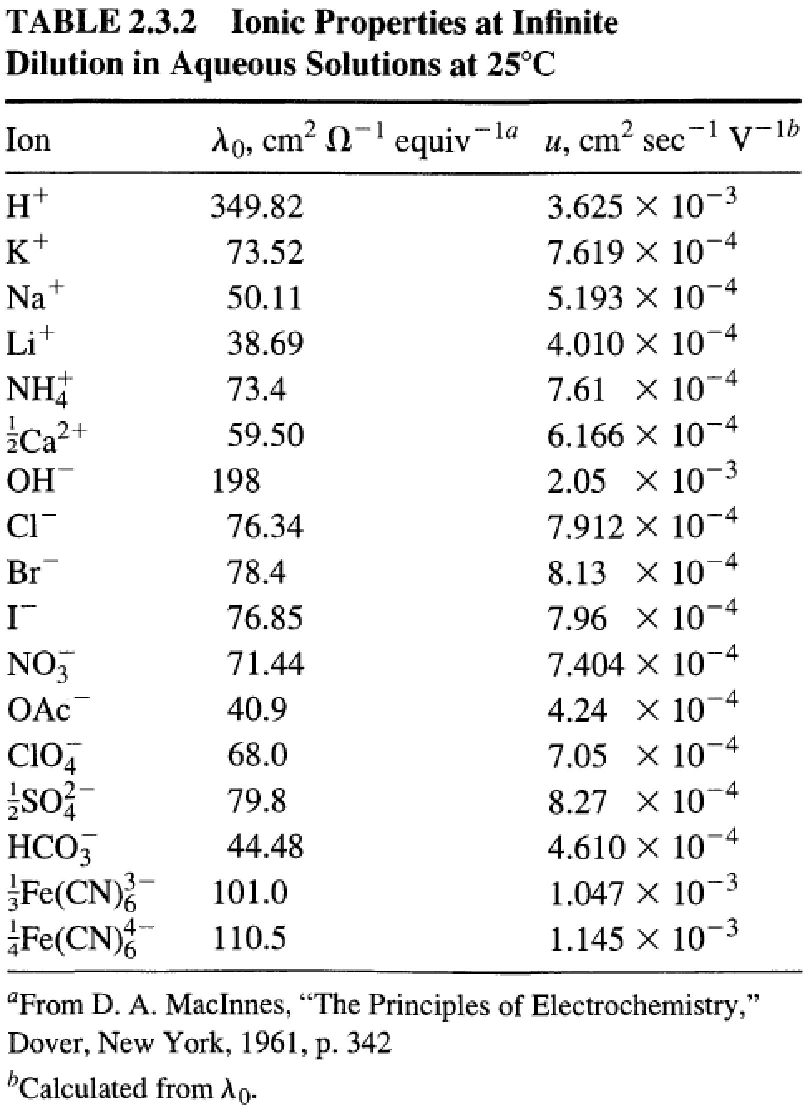


TABLE 2.3.2 Ionic Properties at Infinite Dilution in Aqueous Solutions at 25°C

Ion	λ_0, cm^2 Ω^{-1} equiv^{-1}[a]	u, cm^2 sec^{-1} V^{-1}[b]
H^+	349.82	3.625×10^{-3}
K^+	73.52	7.619×10^{-4}
Na^+	50.11	5.193×10^{-4}
Li^+	38.69	4.010×10^{-4}
NH_4^+	73.4	7.61×10^{-4}
$\frac{1}{2}Ca^{2+}$	59.50	6.166×10^{-4}
OH^-	198	2.05×10^{-3}
Cl^-	76.34	7.912×10^{-4}
Br^-	78.4	8.13×10^{-4}
I^-	76.85	7.96×10^{-4}
NO_3^-	71.44	7.404×10^{-4}
OAc^-	40.9	4.24×10^{-4}
ClO_4^-	68.0	7.05×10^{-4}
$\frac{1}{2}SO_4^{2-}$	79.8	8.27×10^{-4}
HCO_3^-	44.48	4.610×10^{-4}
$\frac{1}{3}Fe(CN)_6^{3-}$	101.0	1.047×10^{-3}
$\frac{1}{4}Fe(CN)_6^{4-}$	110.5	1.145×10^{-3}

[a] From D. A. MacInnes, "The Principles of Electrochemistry," Dover, New York, 1961, p. 342

[b] Calculated from λ_0.

λ_{0i}: obtained by extrapolation to infinite dilution

2.3.2 Types of Liquid Junctions

- It is convenient to use these λ_{0i} values to estimate t_i for mixed electrolytes by the following equation:

$$t_i = \frac{|z_i| u_i C_i}{\sum_j |z_j| u_j C_j}$$

$$\lambda_i = F u_i$$

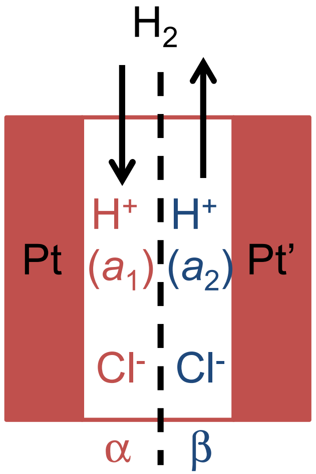
$$\boxed{t_i = \frac{|z_i| C_i \lambda_i}{\sum_j |z_j| C_j \lambda_j}}$$

Mid-term Exam

April 26, 2018
(9:30-11:00)

Scope: Ch. 1, 2

2.3.4 Calculation of Liquid Junction Potentials



- Consider the cell:

$$\ominus \text{Pt/H}_2\text{(1 atm)/}\overset{\alpha}{\underset{(a_1)}{\text{H}^+,\text{Cl}^-}}\text{/}\overset{\beta}{\underset{(a_2)}{\text{H}^+,\text{Cl}^-}}\text{/H}_2\text{(1 atm)/Pt}'\oplus$$

- At equilibrium under the null-current condition,

→ chemical transformations at the metal-solution interfaces are:

$$\tfrac{1}{2}\text{H}_2 \rightleftharpoons \text{H}^+(\alpha) + e(\text{Pt})$$
$$\text{H}^+(\beta) + e(\text{Pt}') \rightleftharpoons \tfrac{1}{2}\text{H}_2$$

- The electrochemical free energy change for each of them individually is zero.
- Of course, this is also true for their sum:

$$\text{H}^+(\beta) + e(\text{Pt}') \rightleftharpoons \text{H}^+(\alpha) + e(\text{Pt}),$$

2.3.4 Calculation of Liquid Junction Potentials

- Since the electrochemical free energy change is zero,

$$\mathrm{H}^+\,(\beta) + e(\mathrm{Pt}') \rightleftharpoons \mathrm{H}^+\,(\alpha) + e(\mathrm{Pt}),$$

$$\bar{\mu}^{\beta}_{H^+} + \bar{\mu}^{\mathrm{Pt}'}_{\mathrm{e}} = \bar{\mu}^{\alpha}_{\mathrm{H}^+} + \bar{\mu}^{\mathrm{Pt}}_{\mathrm{e}}$$

$$FE = F(\phi^{\mathrm{Pt}'} - \phi^{\mathrm{Pt}}) = \bar{\mu}^{\beta}_{\mathrm{H}^+} - \bar{\mu}^{\alpha}_{\mathrm{H}^+}$$

$$E = \frac{RT}{F} \ln \frac{a_2}{a_1} + (\phi^{\beta} - \phi^{\alpha})$$

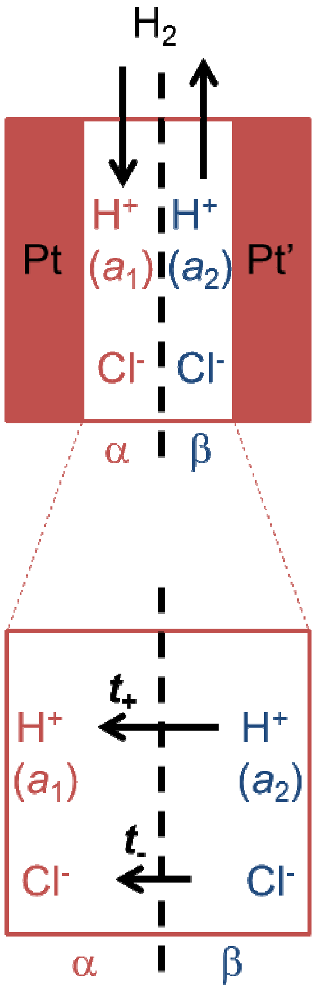
→ The first component of E

: the Nernst relation for the reversible chemical change

→ $\phi^{\beta} - \phi^{\alpha}$: liquid junction potential.

- In general, for a chemically reversible system under null current conditions,

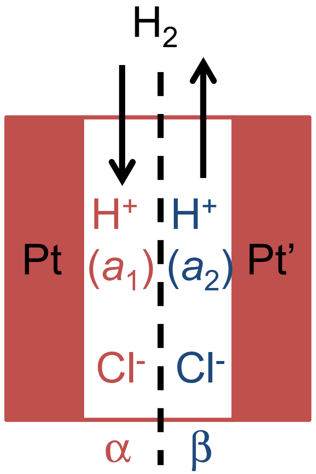
$$E_{\mathrm{cell}} = E_{\mathrm{Nernst}} + E_{\mathrm{j}}$$



2.3.4 Calculation of Liquid Junction Potentials

- Consider the cell:

$$\ominus \text{Pt}/\text{H}_2(1\ \text{atm})/\overset{\alpha}{\underset{(a_1)}{\text{H}^+}}, \text{Cl}^-/\overset{\beta}{\underset{(a_2)}{\text{H}^+}}, \text{Cl}^-/\text{H}_2(1\ \text{atm})/\text{Pt}'\oplus$$



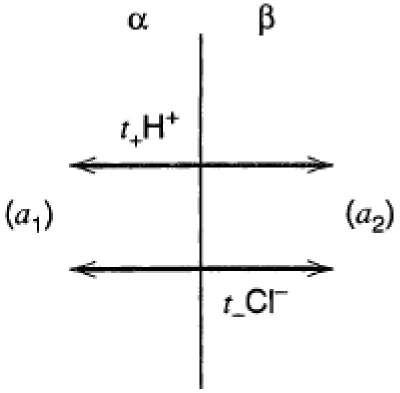
- At equilibrium under the null-current condition,

→ chemical transformations at the metal-solution interfaces are:

$$\tfrac{1}{2}\text{H}_2 \rightleftharpoons \text{H}^+\ (\alpha) + e(\text{Pt})$$
$$\text{H}^+\ (\beta) + e(\text{Pt}') \rightleftharpoons \tfrac{1}{2}\text{H}_2$$

- The electrochemical free energy change for each of them individually is zero.

2.3.4 Calculation of Liquid Junction Potentials



- To evaluate E_j, consider the charge transport at the liquid junction

→ At equilibrium under the null-current condition,

$$t_+H^+(\alpha) + t_-Cl^-(\beta) \rightleftharpoons t_+\, H^+\, (\beta) + t_-\, Cl^-\, (\alpha)$$

→ The electrochemical free energy change for charge transport across the junction = 0

$$t_+(\overline{\mu}^{\alpha}_{\mathrm{H}^+} - \overline{\mu}^{\beta}_{\mathrm{H}^+}) + t_-(\overline{\mu}^{\beta}_{Cl^-} - \overline{\mu}^{\alpha}_{Cl^-}) = 0$$

$$t_+\left[RT\ln\frac{a^{\alpha}_{\mathrm{H}^+}}{a^{\beta}_{\mathrm{H}^+}} + F(\phi^{\alpha} - \phi^{\beta})\right] + t_-\left[RT\ln\frac{a^{\beta}_{\mathrm{Cl}^-}}{a^{\alpha}_{\mathrm{Cl}^-}} - F(\phi^{\beta} - \phi^{\alpha})\right] = 0$$

- Activity coefficients for single ions cannot be measured with thermodynamic rigor

  → hence they are usually equated to a measurable mean ionic activity coefficient.

- Under this procedure

$$a^{\alpha}_{\mathrm{H}^+} = a^{\alpha}_{\mathrm{Cl}^-} = a_1 \qquad a^{\beta}_{\mathrm{H}^+} = a^{\beta}_{\mathrm{Cl}^-} = a_2.$$

2.3.4 Calculation of Liquid Junction Potentials

- Since $t_+ + t_- = 1$, for a type 1 junction involving 1:1 electrolytes

$$t_+\left[RT \ln \frac{a_{\mathrm{H}^+}^{\alpha}}{a_{\mathrm{H}^+}^{\beta}} + F(\phi^{\alpha} - \phi^{\beta})\right] + t_-\left[RT \ln \frac{a_{\mathrm{Cl}^-}^{\beta}}{a_{\mathrm{Cl}^-}^{\alpha}} - F(\phi^{\beta} - \phi^{\alpha})\right] = 0$$

$$\boxed{E_{\mathrm{j}} = (\phi^{\beta} - \phi^{\alpha}) = (t_+ - t_-)\frac{RT}{F}\ln\frac{a_1}{a_2}}$$

- For example, HCl solutions with a_1 = 0.01 and a_2 = 0.1.

→ From Table 2.3.1 that t_+ = 0.83 and t_- = 0.17

→ hence at 25°C

$$E_{\mathrm{j}} = (0.83 - 0.17)(59.1)\log\left(\frac{0.01}{0.1}\right) = -39.1\ \mathrm{mV}$$

2.3.4 Calculation of Liquid Junction Potentials

- For the total cell with a_1 = 0.01 and a_2 = 0.1,

  → the measured cell potential is:

$$E = \frac{RT}{F} \ln \frac{a_2}{a_1} + (\phi^{\beta} - \phi^{\alpha})$$

$$E = 59.1 \log \frac{a_2}{a_1} + E_{\mathrm{j}} = 59.1 - 39.1 = 20.0 \text{ mV}$$

➔ the junction potential is a substantial component of the measured cell potential

➔ How can we decrease the junction potential?

$$\boxed{E_{\mathrm{j}} = (\phi^{\beta} - \phi^{\alpha}) = (t_{+} - t_{-}) \frac{RT}{F} \ln \frac{a_1}{a_2}}$$

For KCl, t_+ = 0.49

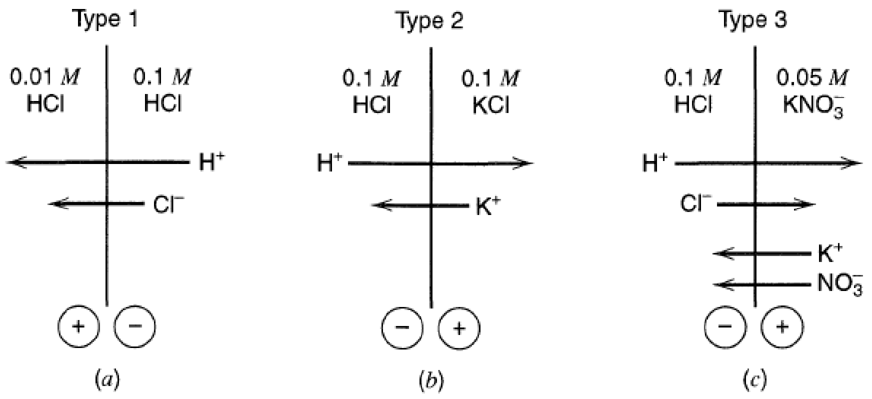
If a_1/a_2 = 0.1, E_j = 1.2 mV

2.3.4 Calculation of Liquid Junction Potentials

- In the derivation above,

we made the implicit assumption that the transference numbers were constant throughout the system.

➔ A good approximation for junctions of type 1.



- For type 2 and type 3 systems, it clearly cannot be true.

  ➔ transference numbers are not constant throughout the system.

  ➔ need to use the differential equation

2.3.4 Calculation of Liquid Junction Potentials

- Let us imagine the junction region to be sectioned into an infinite number of volume elements having compositions that range smoothly from the pure α-phase composition to that of pure β.

➔ the passage of positive charge from x toward x+dx might be depicted as in the following figure:

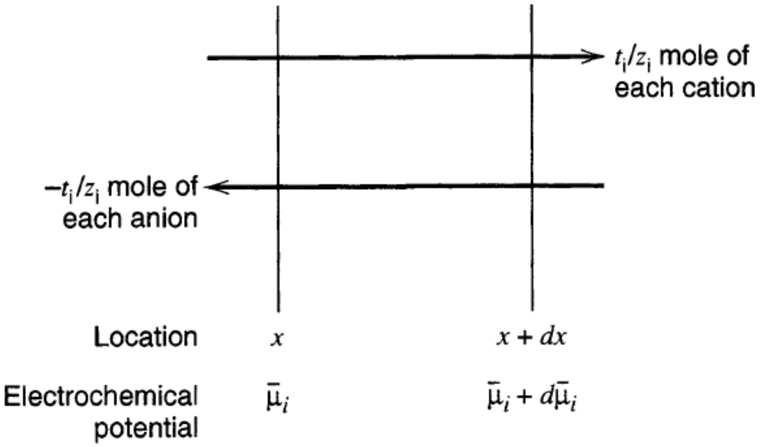


Figure 2.3.7 Transfer of net positive charge from left to right through an infinitesimal segment of a junction region. Each species must contribute t_i moles of charge per mole of overall charge transported; hence $t_i|z_i|$ moles of that species must migrate.

➔ For each mole of charge passed from x to x+dx,

$\frac{t_i}{|z_i|}$ moles of species i must move

2.3.4 Calculation of Liquid Junction Potentials

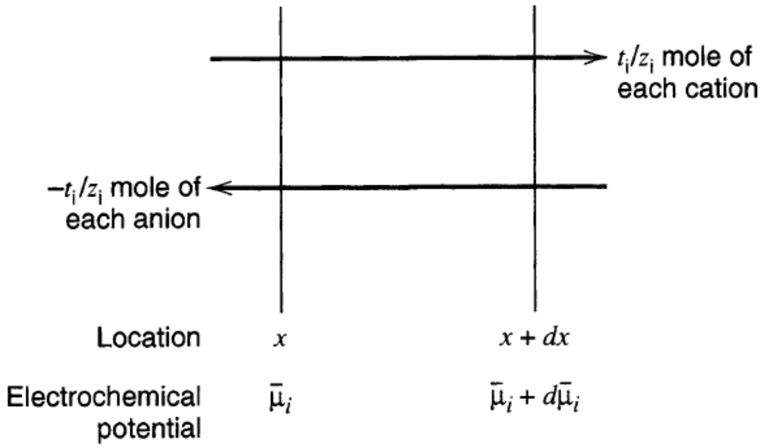


Figure 2.3.7 Transfer of net positive charge from left to right through an infinitesimal segment of a junction region. Each species must contribute t_i moles of charge per mole of overall charge transported; hence $t_i|z_i|$ moles of that species must migrate.

- So, the change in electrochemical free energy upon moving any species =

$$\frac{t_i}{z_i} d\bar{\mu}_i$$

- The differential in free energy is:

$$d\bar{G} = \sum_i \frac{t_i}{z_i} d\bar{\mu}_i$$

2.3.4 Calculation of Liquid Junction Potentials

- Integrating from the α phase to the β phase at equilibrium,

$$\int_{\alpha}^{\beta} d\overline{G} = 0 = \sum_{i} \int_{\alpha}^{\beta} \frac{t_i}{z_i}\, d\overline{\mu}_i$$

- If both phase are same solutions such as aqueous solutions,

➔ we can assume that μ_i^0 for the α phase is the same as that for the β phase

$$\sum_{i} \int_{\alpha}^{\beta} \frac{t_i}{z_i} RT\, d\ln a_i + \left(\sum_{i} t_i\right) F \int_{\alpha}^{\beta} d\phi = 0$$

Since $\Sigma t_i = 1$,

$$\boxed{E_j = \phi^{\beta} - \phi^{\alpha} = \frac{-RT}{F} \sum_{i} \int_{\alpha}^{\beta} \frac{t_i}{z_i}\, d\ln a_i}$$

➔ the general expression for the junction potential

2.3.4 Calculation of Liquid Junction Potentials

$$\boxed{E_{\mathrm{j}} = \phi^{\beta} - \phi^{\alpha} = \frac{-RT}{F}\sum_{\mathrm{i}}\int_{\alpha}^{\beta}\frac{t_{\mathrm{i}}}{z_{\mathrm{i}}}\,d\ln a_{\mathrm{i}}}$$

$$t_{\mathrm{i}} = \frac{|z_{\mathrm{i}}|u_{\mathrm{i}}C_{\mathrm{i}}}{\sum_{\mathrm{j}}|z_{\mathrm{j}}|u_{\mathrm{j}}C_{\mathrm{j}}}$$

- By assuming

(a) that concentrations of ions everywhere in the junction are equivalent to activities

(b) that the concentration of each ion follows a linear transition between the two phases

➔ Approximate values for *E_j* can be obtained in the form of

$$\boxed{E_{\mathrm{j}} = \frac{\sum_{\mathrm{i}}\frac{|z_{\mathrm{i}}|u_{\mathrm{i}}}{z_{\mathrm{i}}}[C_{\mathrm{i}}(\beta) - C_{\mathrm{i}}(\alpha)]}{\sum_{\mathrm{i}}|z_{\mathrm{i}}|u_{\mathrm{i}}[C_{\mathrm{i}}(\beta) - C_{\mathrm{i}}(\alpha)]}\frac{RT}{F}\ln\frac{\sum_{\mathrm{i}}|z_{\mathrm{i}}|u_{\mathrm{i}}C_{\mathrm{i}}(\alpha)}{\sum_{\mathrm{i}}|z_{\mathrm{i}}|u_{\mathrm{i}}C_{\mathrm{i}}(\beta)}}$$

: the Henderson equation

2.4.1 Selective Interfaces

- Suppose a selectively permeable membrane having an interface between two electrolyte phases across which only a single ion could penetrate.

$$\int_{\alpha}^{\beta} d\overline{G} = 0 = \sum_{i} \int_{\alpha}^{\beta} \frac{t_i}{z_i} d\overline{\mu}_i \qquad \sum_{i} \int_{\alpha}^{\beta} \frac{t_i}{z_i} RT\, d \ln a_i + \left(\sum_{i} t_i\right) F \int_{\alpha}^{\beta} d\phi = 0$$

- but it could be simplified by recognizing that the transference number for the permeating ion is unity, while that for every other ion is zero.

- If both electrolytes are in a common solvent, one obtains by integration

$$\frac{RT}{z_i} \ln \frac{a_i^{\beta}}{a_i^{\alpha}} + F(\phi^{\beta} - \phi^{\alpha}) = 0$$

: where ion i is the permeating species.

2.3.4 Calculation of Liquid Junction Potentials

- Rearrangement gives

$$E_m = -\frac{RT}{z_i F} \ln \frac{a_i^\beta}{a_i^\alpha}$$

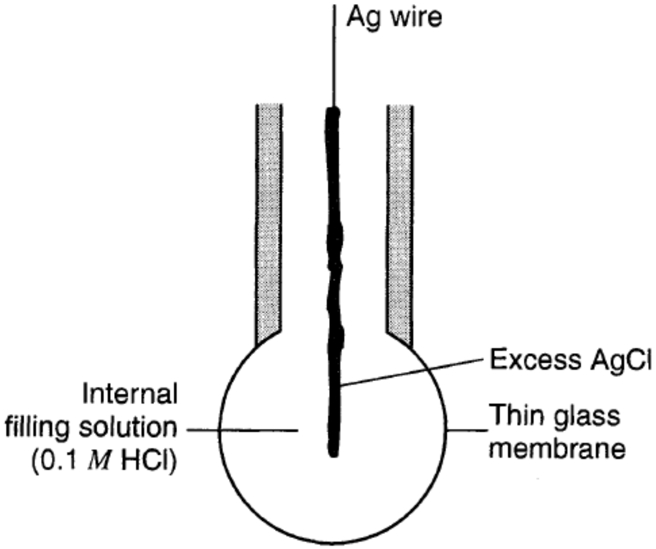
→ often called the membrane potential, E_m

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

2.4.2 Glass Electrodes

- Glass electrodes have the ion-selective properties of glass/electrolyte interfaces

  ➔ have been used for measurements of pH and the activities of alkali ions



Dry glass membrane

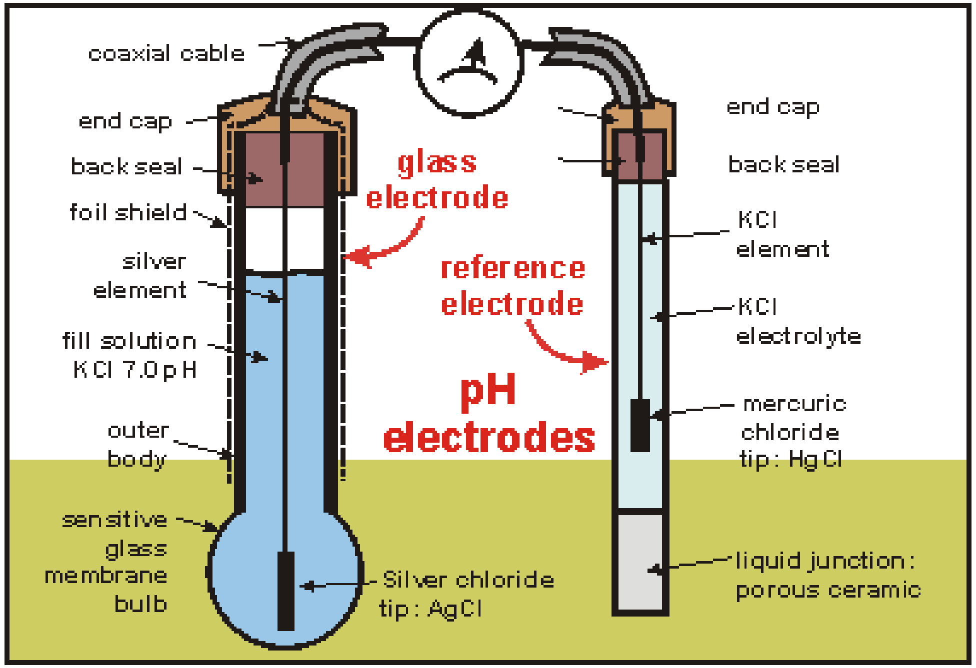
: about 50 μm thick,

: charge transport occurs exclusively by the mobile cations present in the glass.

→ Usually, these are alkali ions, such as Na^+ or Li^+.

: Hydrogen ion from solution does not contribute to conduction in this region.

2.4.2 Glass Electrodes



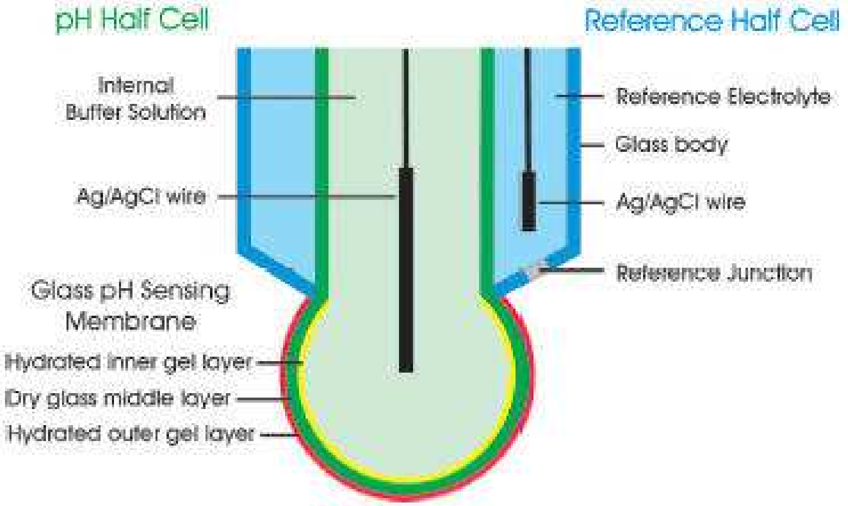


Figure 1 Typical combination pH electrode.

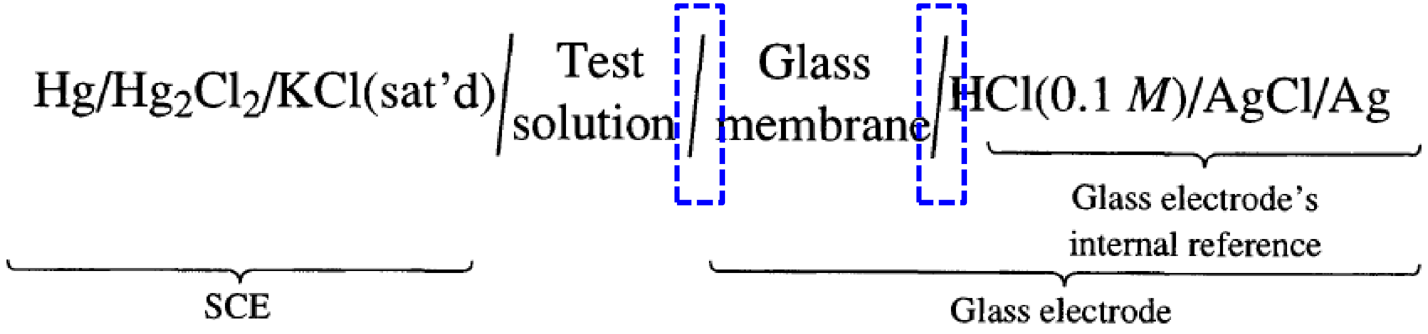
- To make measurements,

→ the thin membrane is fully immersed in the test solution

→ the potential of the electrode is registered with respect to a reference electrode such as an SCE.

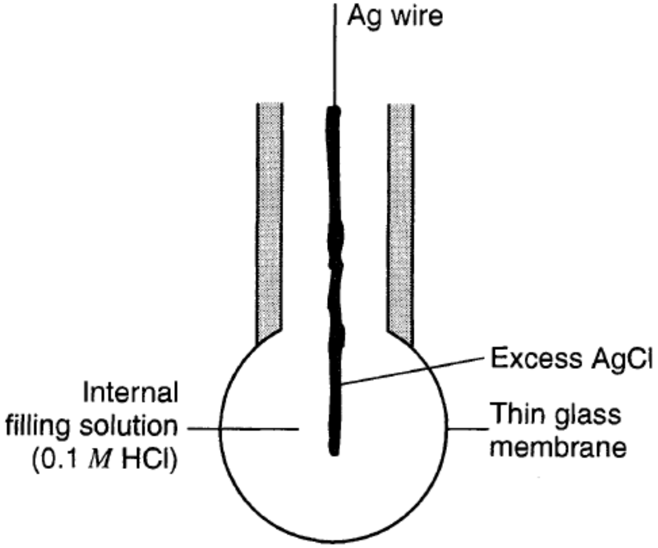
2.4.2 Glass Electrodes

- Thus, the cell becomes



- The overall potential difference of the cell at two points includes:
  - i) the interfacial potential difference at the Hg and Ag electrodes (constant)
  - ii) the liquid junction between the SCE and the test solution (assume that it is small and constant)
  - ii) the junction between test solution and glass membrane & the junction between internal filling solution and glass membrane

2.4.2 Glass Electrodes



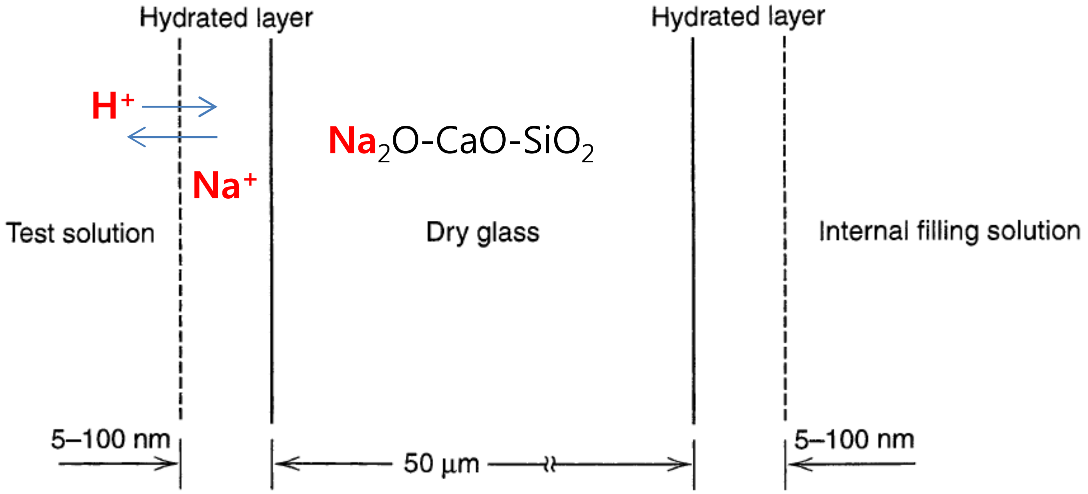


Figure 2.4.2 Schematic profile through a glass membrane.

- The faces of the membrane in contact with solution differ from the bulk,

  → in that the silicate structure of the glass is hydrated.

- The hydrated layers are thin. (H^+ can be permeable in the hydrated layer)
- The silicate network has an affinity for certain cations, which are adsorbed (probably at fixed anionic sites) within the structure.

  → This action creates a charge separation that alters the interfacial potential difference.

2.4.2 Glass Electrodes

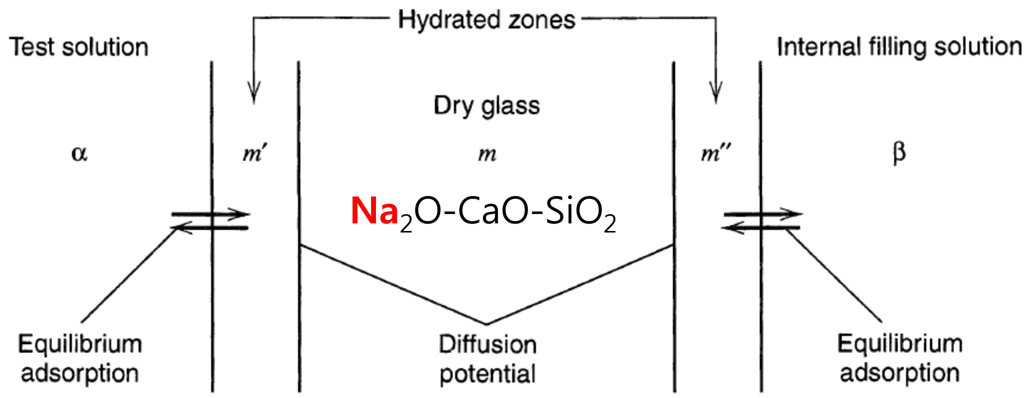


Figure 2.4.3 Model for treating the membrane potential across a glass barrier.

- Let us consider a model for the glass membrane like that shown in the Figure.
- The glass will be considered as comprising three regions.

1) In the interfacial zones, m′ and m"

→ equilibrium with constituents in solution through adsorption and desorption of only cations (only cations are permeable through hydrated zones)

2) The bulk of the glass, m

→ conduction takes place by a single species, which is taken as Na$^+$ in this example

2.4.2 Glass Electrodes

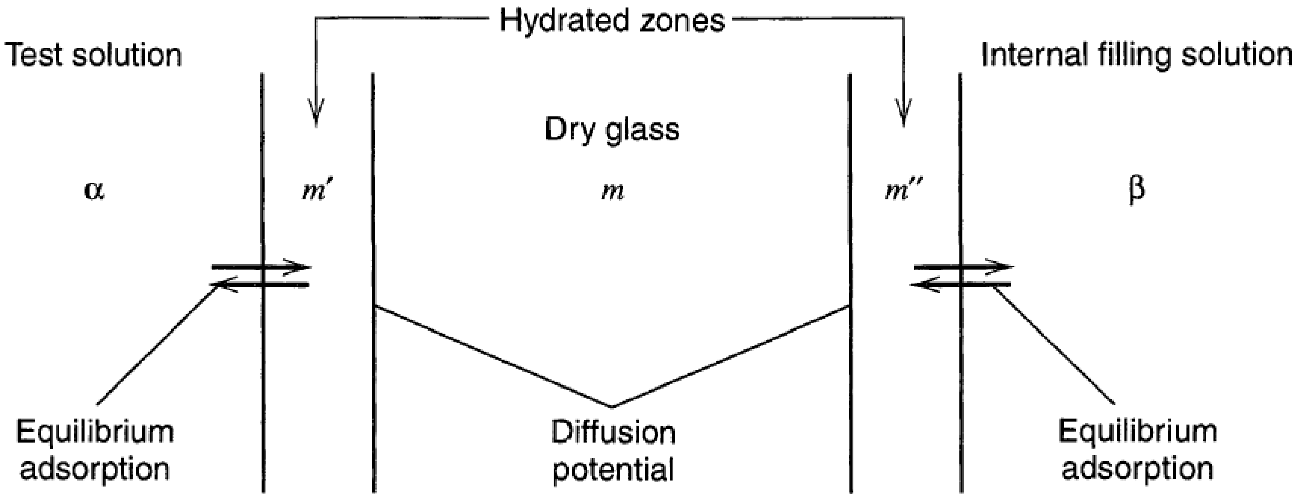


Figure 2.4.3 Model for treating the membrane potential across a glass barrier.

- The whole system therefore comprises five phases

➔ the overall difference in potential across the membrane

= the sum of four contributions from the junctions between the various zones:

$$E_m = (\phi^{\beta} - \phi^{m''}) + (\phi^{m''} - \phi^{m}) + (\phi^{m} - \phi^{m'}) + (\phi^{m'} - \phi^{\alpha})$$

2.4.2 Glass Electrodes

$$E_m = (\underline{\phi^{\beta} - \phi^{m''}}) + (\phi^{m''} - \phi^{m}) + (\phi^{m} - \phi^{m'}) + (\underline{\phi^{m'} - \phi^{\alpha}})$$

- The first and last terms

: interfacial potential differences arising from an equilibrium balance of selective charge exchange across an interface

→ occurs near selectively permeable membrane (m)

: cations are only permeable in this example

→ This condition is known as Donnan equilibrium

- The magnitude of the resulting potential difference can be evaluated from electrochemical potentials.

→ Suppose we have Na^+ and H^+ as interfacially active ions.

→ Then at the α/m' interface,

$$\bar{\mu}^{\alpha}_{H^+} = \bar{\mu}^{m'}_{H^+}$$
$$\bar{\mu}^{\alpha}_{Na^+} = \bar{\mu}^{m'}_{Na^+}$$

2.4.2 Glass Electrodes

$$\overline{\mu}_{\mathrm{H}^+}^{\alpha} = \overline{\mu}_{\mathrm{H}^+}^{\mathrm{m}'}$$

$$\mu_{\mathrm{H}^+}^{0\alpha} + RT \ln a_{\mathrm{H}^+}^{\alpha} + F\phi^{\alpha} = \mu_{\mathrm{H}^+}^{0\mathrm{m}'} + RT \ln a_{\mathrm{H}^+}^{\mathrm{m}'} + F\phi^{\mathrm{m}'}$$

$$(\phi^{\mathrm{m}'} - \phi^{\alpha}) = \frac{\mu_{\mathrm{H}^+}^{0\alpha} - \mu_{\mathrm{H}^+}^{0\mathrm{m}'}}{F} + \frac{RT}{F} \ln \frac{a_{\mathrm{H}^+}^{\alpha}}{a_{\mathrm{H}^+}^{\mathrm{m}'}}$$

- An equivalent treatment of the interface between β and m" gives:

$$(\phi^{\beta} - \phi^{\mathrm{m}''}) = \frac{\mu_{\mathrm{H}^+}^{0\mathrm{m}''} - \mu_{\mathrm{H}^+}^{0\beta}}{F} + \frac{RT}{F} \ln \frac{a_{\mathrm{H}^+}^{\mathrm{m}''}}{a_{\mathrm{H}^+}^{\beta}}$$

$\mu_{\mathrm{H}^+}^{0\alpha} = \mu_{\mathrm{H}^+}^{0\beta}$ because both α and β are aqueous solutions.

$$\mu_{\mathrm{H}^+}^{0\mathrm{m}'} = \mu_{\mathrm{H}^+}^{0\mathrm{m}''}$$

2.4.2 Glass Electrodes

$$E_{\mathrm{m}} = (\phi^{\beta} - \phi^{\mathrm{m}''}) + \underline{(\phi^{\mathrm{m}''} - \phi^{\mathrm{m}})} + \underline{(\phi^{\mathrm{m}} - \phi^{\mathrm{m}'})} + (\phi^{\mathrm{m}'} - \phi^{\alpha})$$

- The second and third components:

  : junction potentials within the glass membrane.

  : use the Henderson equation

$$\boxed{E_{\mathrm{j}} = \frac{\sum_{\mathrm{i}} \frac{|z_{\mathrm{i}}|u_{\mathrm{i}}}{z_{\mathrm{i}}}[C_{\mathrm{i}}(\beta) - C_{\mathrm{i}}(\alpha)]}{\sum_{\mathrm{i}} |z_{\mathrm{i}}|u_{\mathrm{i}}[C_{\mathrm{i}}(\beta) - C_{\mathrm{i}}(\alpha)]} \frac{RT}{F} \ln \frac{\sum_{\mathrm{i}} |z_{\mathrm{i}}|u_{\mathrm{i}}C_{\mathrm{i}}(\alpha)}{\sum_{\mathrm{i}} |z_{\mathrm{i}}|u_{\mathrm{i}}C_{\mathrm{i}}(\beta)}}$$

- Univalent positive charge carriers in this example

  ➔ hence we can specialize the Henderson equation for the interface between m and m′ as

$$(\phi^{\mathrm{m}} - \phi^{\mathrm{m}'}) = \frac{RT}{F} \ln \frac{u_{\mathrm{H}^+} a^{\mathrm{m}'}_{\mathrm{H}^+} + u_{\mathrm{Na}^+} a^{\mathrm{m}'}_{\mathrm{Na}^+}}{u_{\mathrm{Na}^+} a^{\mathrm{m}}_{\mathrm{Na}^+}}$$

: where the concentrations have been replaced by activities

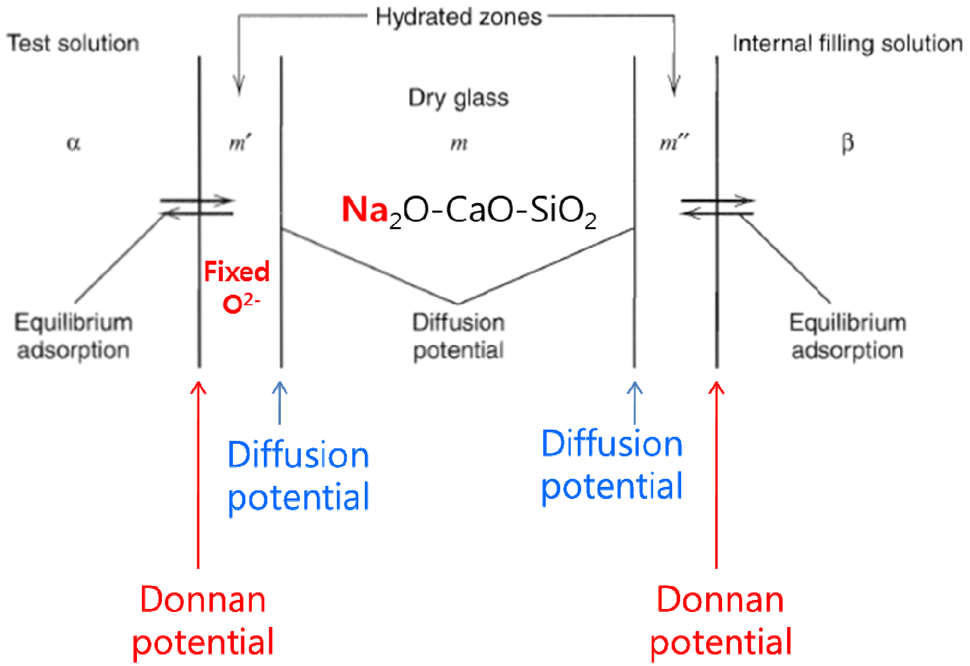
2.4.2 Glass Electrodes

- Similarly, for the interface between m and m″

$$(\phi^{m''} - \phi^{m}) = \frac{RT}{F} \ln \frac{u_{Na^+}\, a_{Na^+}^{m}}{u_{H^+}\, a_{H^+}^{m''} + u_{Na^+}\, a_{Na^+}^{m''}}$$

2.4.2 Glass Electrodes

$$E_m = (\phi^{\beta} - \phi^{m''}) + (\phi^{m''} - \phi^{m}) + (\phi^{m} - \phi^{m'}) + (\phi^{m'} - \phi^{\alpha})$$



Na_2O-CaO-SiO_2

Fixed O^{2-}

Diffusion potential

Diffusion potential

Donnan potential

Donnan potential

$$(\phi^{\beta} - \phi^{m''}) = \cancel{\frac{\mu^{0m''}_{H^+} - \mu^{0\beta}_{H^+}}{F}} + \frac{RT}{F}\ln\frac{a^{m''}_{H^+}}{a^{\beta}_{H^+}}$$

✚

$$(\phi^{m'} - \phi^{\alpha}) = \cancel{\frac{\mu^{0\alpha}_{H^+} - \mu^{0m'}_{H^+}}{F}} + \frac{RT}{F}\ln\frac{a^{\alpha}_{H^+}}{a^{m'}_{H^+}}$$

✚

$$(\phi^{m''} - \phi^{m}) = \frac{RT}{F}\ln\frac{\cancel{u_{Na^+}a^{m}_{Na^+}}}{u_{H^+}a^{m''}_{H^+} + u_{Na^+}a^{m''}_{Na^+}}$$

✚

$$(\phi^{m} - \phi^{m'}) = \frac{RT}{F}\ln\frac{u_{H^+}a^{m'}_{H^+} + u_{Na^+}a^{m'}_{Na^+}}{\cancel{u_{Na^+}a^{m}_{Na^+}}}$$

2.4.2 Glass Electrodes

- When we add all component potential differences to obtain the whole potential difference across the membrane,

$$E_{\mathrm{m}} = \frac{RT}{F} \ln \frac{a_{\mathrm{H}^+}^{\alpha}\, a_{\mathrm{H}^+}^{\mathrm{m}''}}{a_{\mathrm{H}^+}^{\beta} a_{\mathrm{H}^+}^{\mathrm{m}'}} \qquad \text{(Donnan Term)}$$

$$+ \frac{RT}{F} \ln \frac{(u_{\mathrm{Na}^+}/u_{\mathrm{H}^+}) a_{\mathrm{Na}^+}^{\mathrm{m}'} + a_{\mathrm{H}^+}^{\mathrm{m}'}}{(u_{\mathrm{Na}^+}/u_{\mathrm{H}^+}) a_{\mathrm{Na}^+}^{\mathrm{m}''} + a_{\mathrm{H}^+}^{\mathrm{m}''}} \qquad \text{(Diffusion term)}$$

- When we combine the two terms and rearrange the parameters,

$$E_{\mathrm{m}} = \frac{RT}{F} \ln \frac{(u_{\mathrm{Na}^+}/u_{\mathrm{H}^+})(a_{\mathrm{H}^+}^{\alpha} a_{\mathrm{Na}^+}^{\mathrm{m}'}/a_{\mathrm{H}^+}^{\mathrm{m}'}) + a_{\mathrm{H}^+}^{\alpha}}{(u_{\mathrm{Na}^+}/u_{\mathrm{H}^+})(a_{\mathrm{H}^+}^{\beta} a_{\mathrm{Na}^+}^{\mathrm{m}''}/a_{\mathrm{H}^+}^{\mathrm{m}''}) + a_{\mathrm{H}^+}^{\beta}}$$

2.4.2 Glass Electrodes

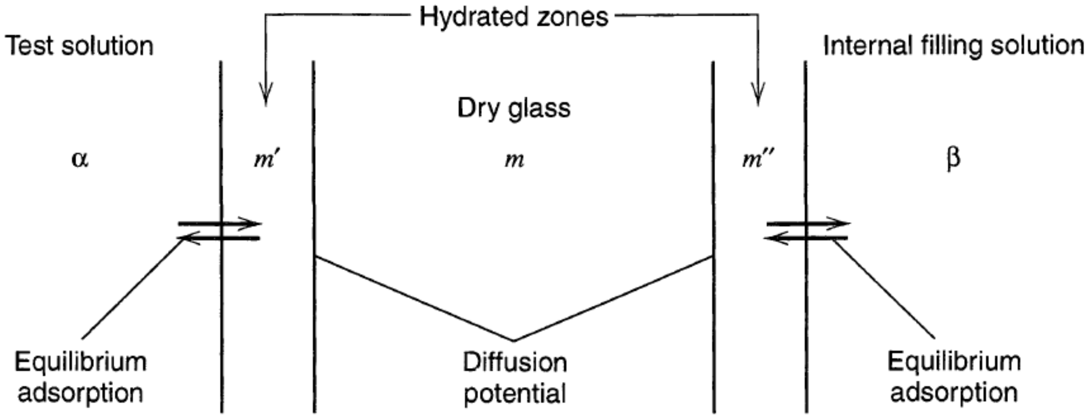


Figure 2.4.3 Model for treating the membrane potential across a glass barrier.

- At the α/m' interface:

$$\overline{\mu}^{\alpha}_{\mathrm{H}^+} = \overline{\mu}^{\mathrm{m}'}_{\mathrm{H}^+}$$
$$\overline{\mu}^{\alpha}_{\mathrm{Na}^+} = \overline{\mu}^{\mathrm{m}'}_{\mathrm{Na}^+}$$

- Their sum must also be true:

$$\overline{\mu}^{\alpha}_{\mathrm{Na}^+} + \overline{\mu}^{\mathrm{m}'}_{\mathrm{H}^+} = \overline{\mu}^{\alpha}_{\mathrm{H}^+} + \overline{\mu}^{\mathrm{m}'}_{\mathrm{Na}^+}$$

- This equation is a free energy balance for the ion-exchange reaction:

$$\mathrm{Na}^+\ (\alpha) + \mathrm{H}^+\ (m') \rightleftharpoons \mathrm{H}^+\ (\alpha) + \mathrm{Na}^+\ (m')$$

2.4.2 Glass Electrodes

- Since it does not involve net charge transfer,

→ it is not sensitive to the interfacial potential difference

→ it has an equilibrium constant given by

$$K_{\mathrm{H}^+,\mathrm{Na}^+} = \frac{a^{\alpha}_{\mathrm{H}^+} a^{\mathrm{m}'}_{\mathrm{Na}^+}}{a^{\mathrm{m}'}_{\mathrm{H}^+} a^{\alpha}_{\mathrm{Na}^+}}$$

$$K_{\mathrm{H}^+,\mathrm{Na}^+} = \frac{a^{\alpha}_{\mathrm{H}^+} a^{\mathrm{m}'}_{\mathrm{Na}^+}}{a^{\mathrm{m}'}_{\mathrm{H}^+} a^{\alpha}_{\mathrm{Na}^+}}$$

$$E_{\mathrm{m}} = \frac{RT}{F} \ln \frac{(u_{\mathrm{Na}^+}/u_{\mathrm{H}^+})(a^{\alpha}_{\mathrm{H}^+} a^{\mathrm{m}'}_{\mathrm{Na}^+}/a^{\mathrm{m}'}_{\mathrm{H}^+}) + a^{\alpha}_{\mathrm{H}^+}}{(u_{\mathrm{Na}^+}/u_{\mathrm{H}^+})(a^{\beta}_{\mathrm{H}^+} a^{\mathrm{m}''}_{\mathrm{Na}^+}/a^{\mathrm{m}''}_{\mathrm{H}^+}) + a^{\beta}_{\mathrm{H}^+}}$$

$$E_{\mathrm{m}} = \frac{RT}{F} \ln \frac{(u_{\mathrm{Na}^+}/u_{\mathrm{H}^+}) K_{\mathrm{H}^+,\mathrm{Na}^+} a^{\alpha}_{\mathrm{Na}^+} + a^{\alpha}_{\mathrm{H}^+}}{(u_{\mathrm{Na}^+}/u_{\mathrm{H}^+}) K_{\mathrm{H}^+,\mathrm{Na}^+} a^{\beta}_{\mathrm{Na}^+} + a^{\beta}_{\mathrm{H}^+}}$$

2.4.2 Glass Electrodes

$$E_m = \frac{RT}{F} \ln \frac{(u_{Na^+}/u_{H^+})K_{H^+,Na^+}a^{\alpha}_{Na^+} + a^{\alpha}_{H^+}}{(u_{Na^+}/u_{H^+})K_{H^+,Na^+}a^{\beta}_{Na^+} + a^{\beta}_{H^+}}$$

- Since $K_{H+,Na+}$ and u_{Na+}/u_{H+} are constants of the experiment,

→ it is convenient to define their product as the potentiometric selectivity coefficient, $k^{pot}_{H^+,Na^+}$

$$E_m = \frac{RT}{F} \ln \frac{a^{\alpha}_{H^+} + k^{pot}_{H^+,Na^+}a^{\alpha}_{Na^+}}{a^{\beta}_{H^+} + k^{pot}_{H^+,Na^+}a^{\beta}_{Na^+}}$$

- If the β phase is the internal filling solution (of constant composition) and the α phase is the test solution,

→ the overall potential of the cell is

$$\boxed{E = \text{constant} + \frac{RT}{F} \ln (a^{\alpha}_{H^+} + k^{pot}_{H^+,Na^+}a^{\alpha}_{Na^+})}$$

2.4.2 Glass Electrodes

$$\boxed{E = \text{constant} + \frac{RT}{F}\ln\left(a_{\mathrm{H}^+}^{\alpha} + k_{\mathrm{H}^+,\mathrm{Na}^+}^{\mathrm{pot}} a_{Na^+}^{\alpha}\right)}$$

- This expression tells us that

→ the cell potential is responsive to the activities of both Na⁺ and H⁺ in the test solution, and that the degree of selectivity between these species $k_{\mathrm{H}^+,\mathrm{Na}^+}^{\mathrm{pot}}$

$$\boxed{E = \text{constant} + \frac{RT}{F}\ln\left(a_{\mathrm{H}^+}^{\alpha} + \boxed{k_{\mathrm{H}^+,\mathrm{Na}^+}^{\mathrm{pot}} a_{Na^+}^{\alpha}}\right)}$$

➔ If this value is much less than a_{H+}^{α},

: then the membrane responds essentially exclusively to H^+