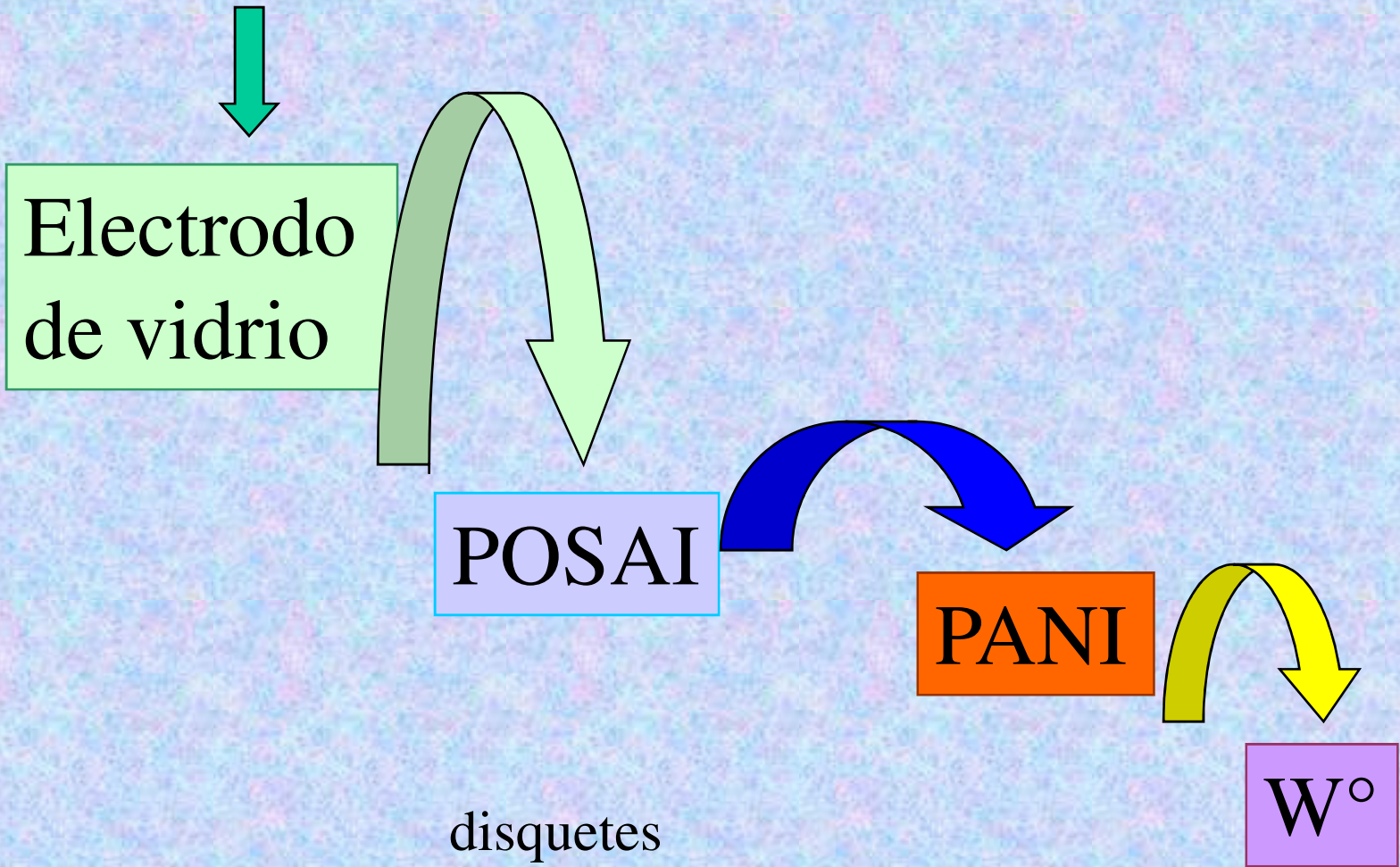


ELECTRODOS SELECTIVOS A H⁺



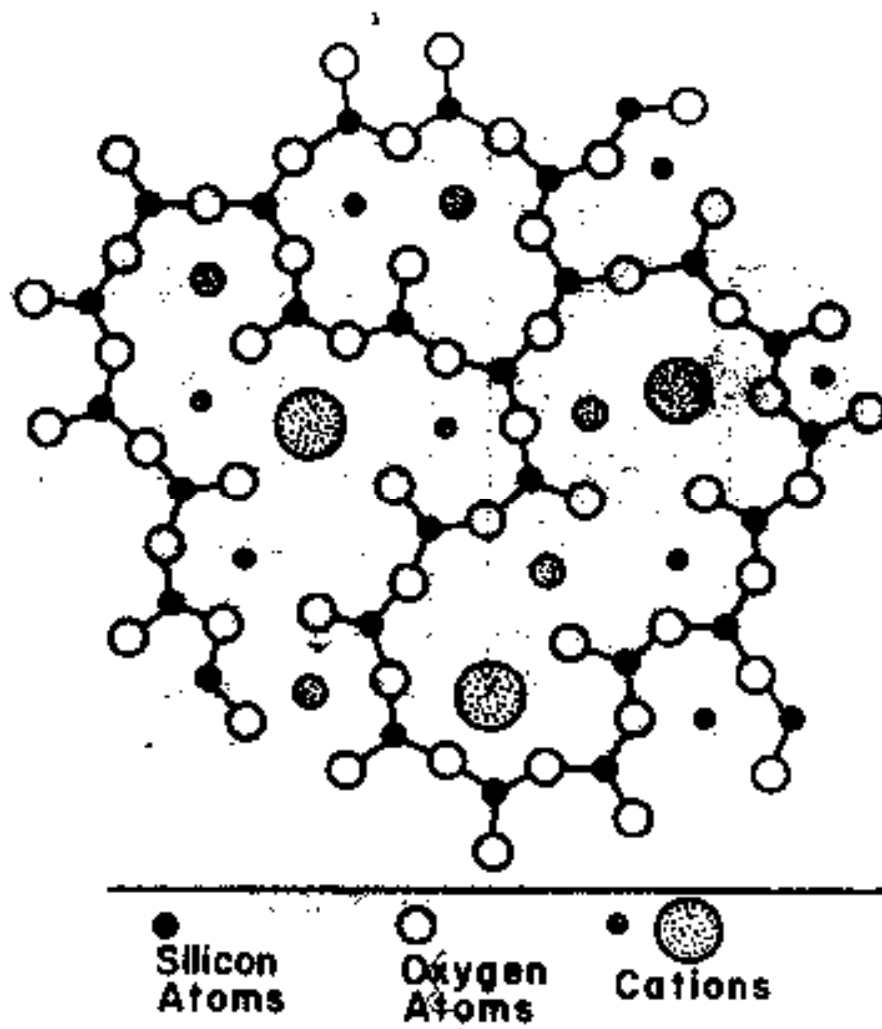
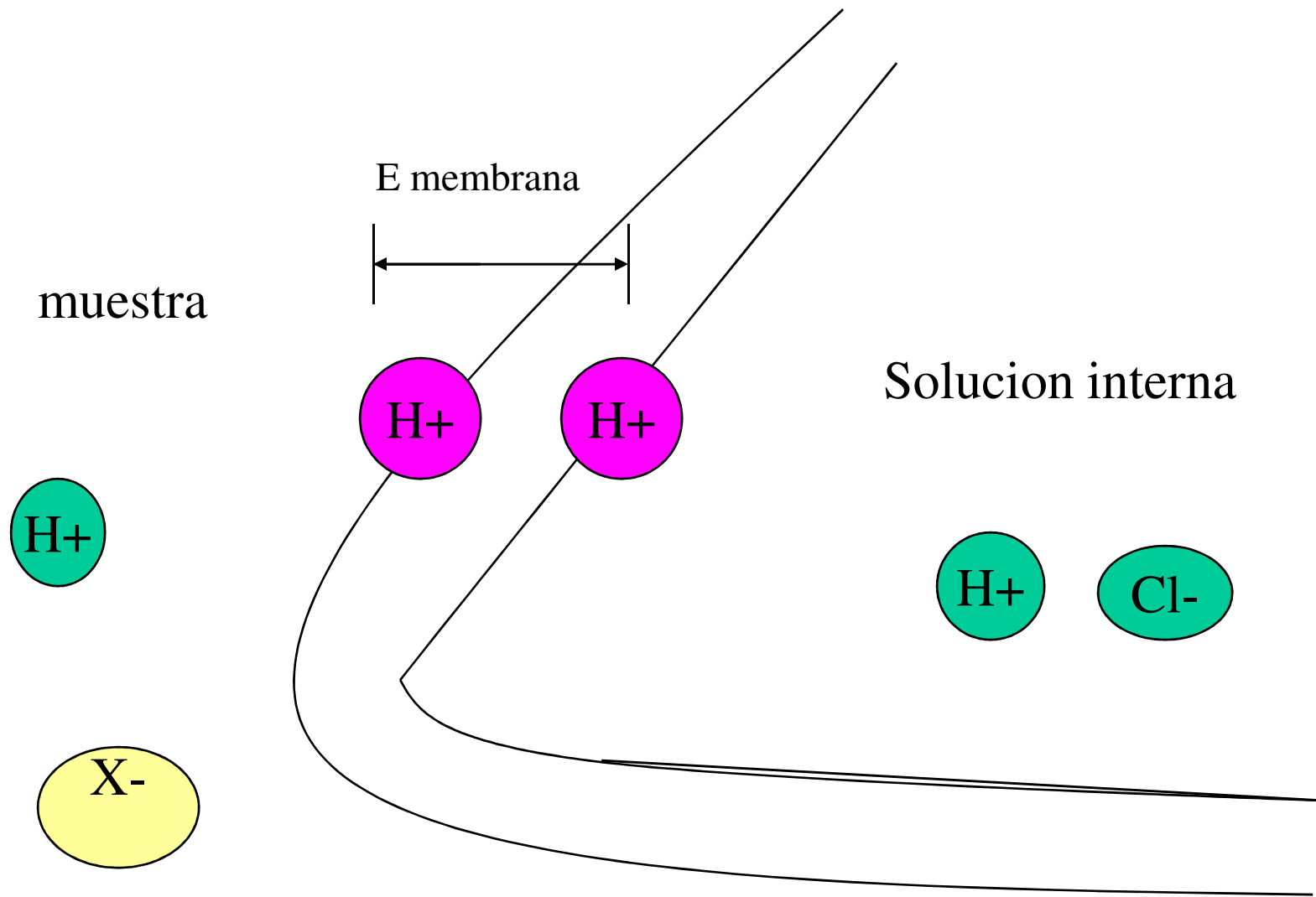


Figure 1-6. Structure of a glass membrane as elucidated from X-ray diffraction studies. [Courtesy of the late George A. Perley and Leeds & Northrup Co., *Anal. Chem.*, 21:395 (1949).]



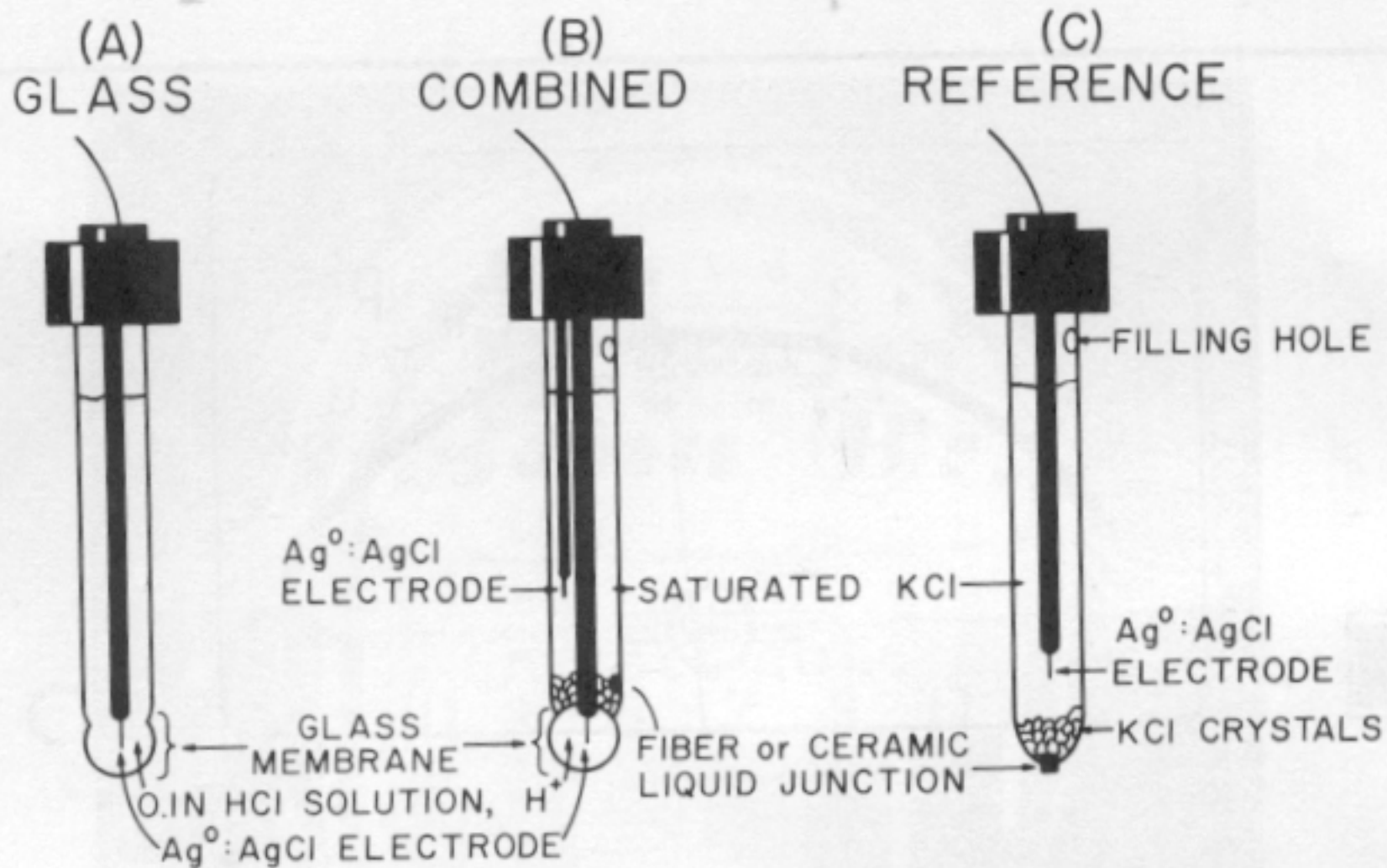


Figure 1-5. The structural features of glass, combined, and reference electrodes.

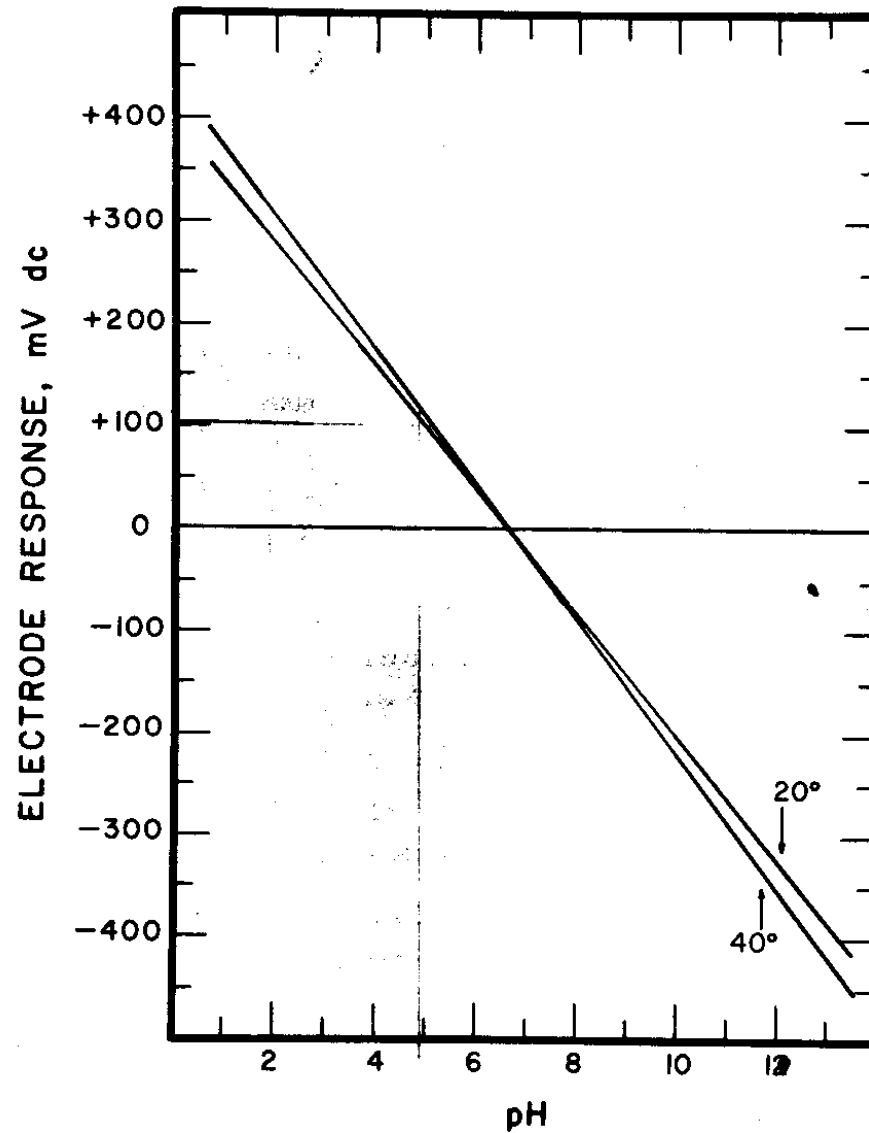


Figure 1-9. Effect of varying pH on the output potential of a glass electrode at 20 and 40°C. (Courtesy of Radiometer A/S, Copenhagen.)

► 2.4 SELECTIVE ELECTRODES (46–55)

2.4.1 Selective Interfaces

Suppose one could create an interface between two electrolyte phases across which only a single ion could penetrate. A selectively permeable membrane might be used as a separator to accomplish this end. Equation 2.3.34 would still apply; 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

$$\frac{RT}{z_i} \ln \frac{a_i^\beta}{a_i^\alpha} + F(\phi^\beta - \phi^\alpha) = 0 \quad (2.4.1)$$

where ion i is the permeating species. Rearrangement gives

$$E_m = -\frac{RT}{z_i F} \ln \frac{a_i^\beta}{a_i^\alpha} \quad (2.4.2)$$

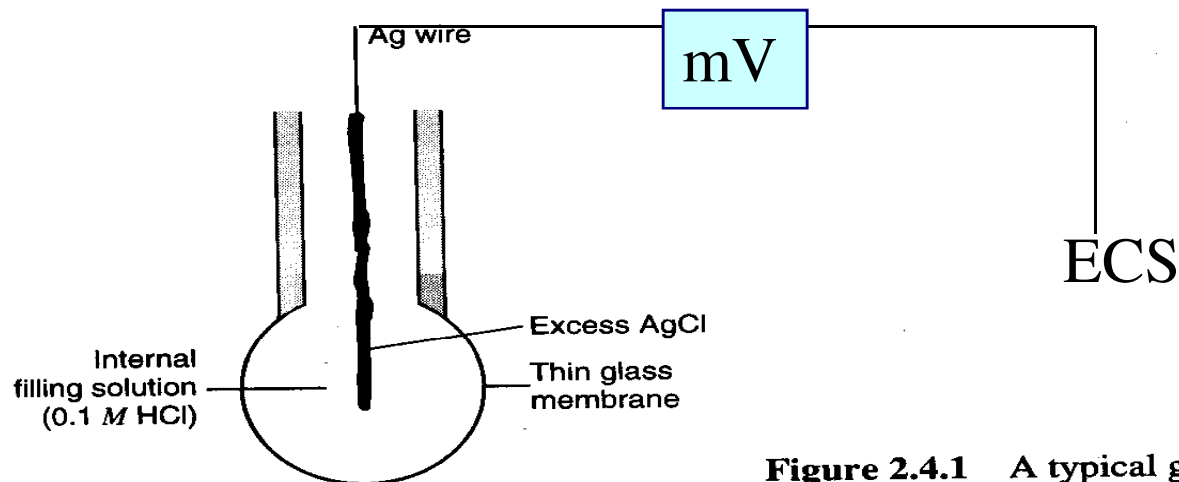
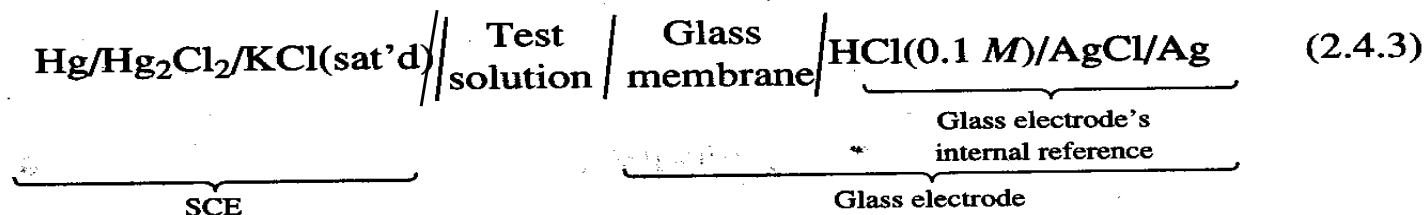


Figure 2.4.1 A typical glass electrode.

To make measurements, the thin membrane is fully immersed in the test solution, and the potential of the electrode is registered with respect to a reference electrode such as an SCE. Thus, the cell becomes,



The properties of the test solution influence the overall potential difference of the cell at two points. One of them is the liquid junction between the SCE and the test solution. From the considerations of Section 2.3.5, we can hope that the potential difference there is small and constant. The remaining contribution from the test solution comes from its effect on the potential difference across the glass membrane. Since all of the other interfaces in the cell feature phases of constant composition, changes in the cell potential can be wholly ascribed to the junction between the glass membrane and the test solution. If that interface is selective toward a single species i , the cell potential is

$$E = \text{constant} + \frac{RT}{zF} \ln a_i^{\text{soln}} \quad (2.4.4)$$

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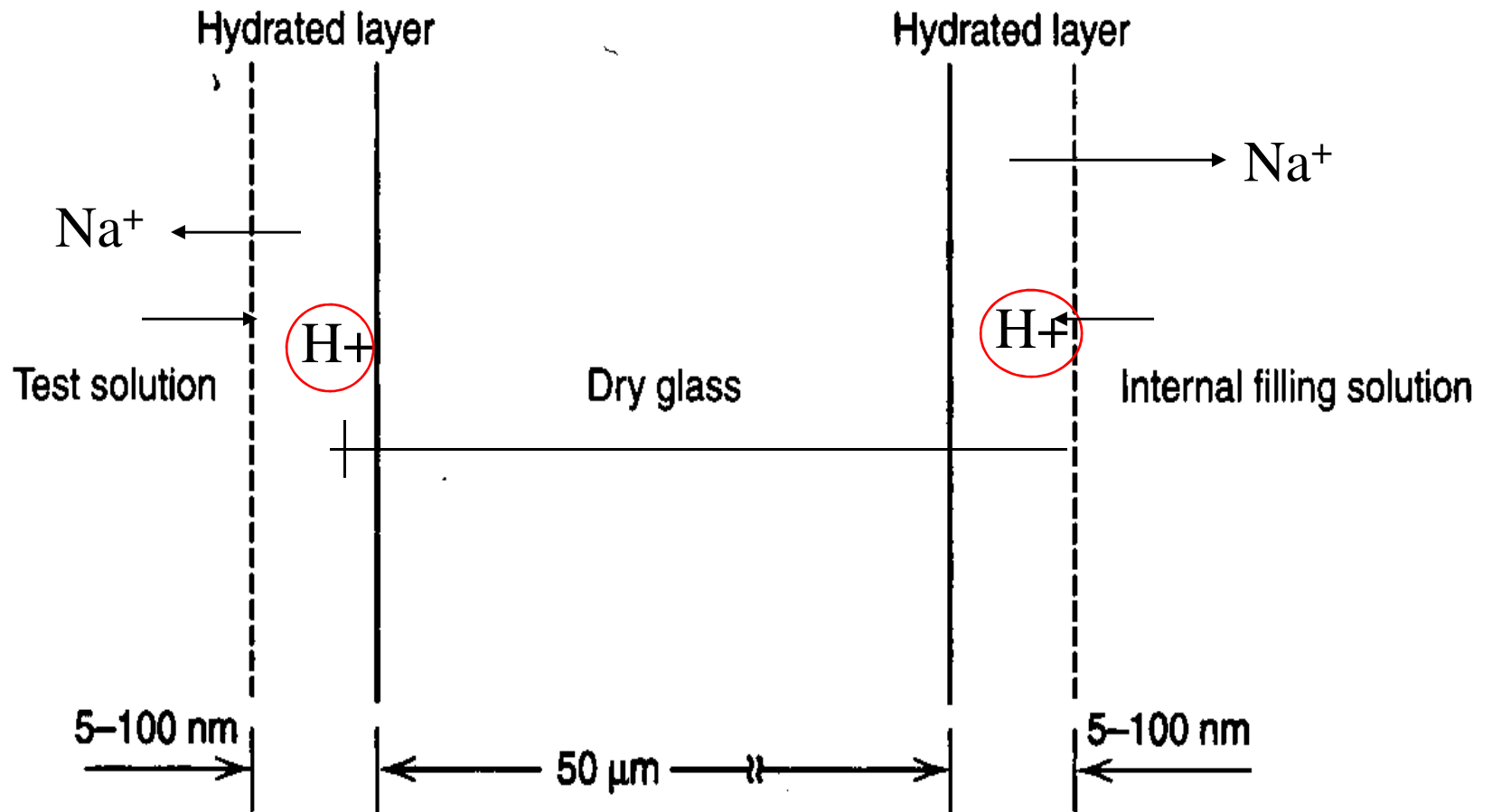


Figure 2.4.2 Schematic profile through a glass membrane.

BETWEEN THE VARIOUS ZONES.

$$E_m = (\phi^\beta - \phi^{m''}) + (\phi^{m''} - \phi^m) + (\phi^m - \phi^{m'}) + (\phi^{m'} - \phi^\alpha) \quad (2.4.5)$$

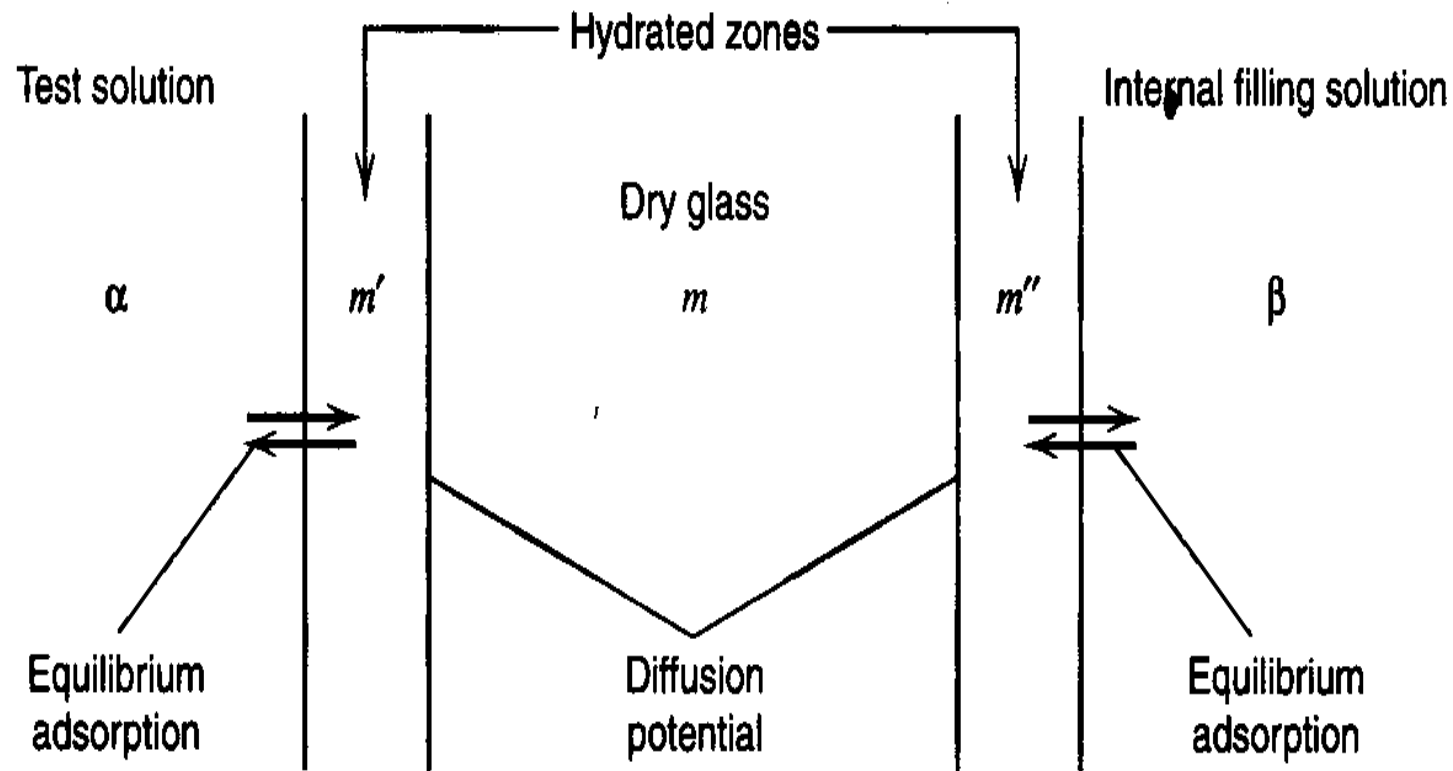


Figure 2.4.3 Model for treating the membrane potential across a glass barrier.

active ions. Then at the α/m' interface,

$$\bar{\mu}_{\text{H}^+}^{\alpha} = \bar{\mu}_{\text{H}^+}^{m'} \quad (2.4.6)$$

$$\bar{\mu}_{\text{Na}^+}^{\alpha} = \bar{\mu}_{\text{Na}^+}^{m'} \quad (2.4.7)$$

Expanding (2.4.6), we have

$$\mu_{\text{H}^+}^{0\alpha} + RT \ln a_{\text{H}^+}^{\alpha} + F\phi^{\alpha} = \mu_{\text{H}^+}^{0m'} + RT \ln a_{\text{H}^+}^{m'} + F\phi^{m'} \quad (2.4.8)$$

and rearrangement gives

$$(\phi^{m'} - \phi^{\alpha}) = \frac{\overbrace{\mu_{\text{H}^+}^{0\alpha} - \mu_{\text{H}^+}^{0m'}}^{\Delta\phi^0}}{F} + \frac{RT}{F} \ln \frac{a_{\text{H}^+}^{\alpha}}{a_{\text{H}^+}^{m'}} \quad (2.4.9)$$

An equivalent treatment of the interface between β and m'' gives

$$(\phi^{\beta} - \phi^{m''}) = \frac{\mu_{\text{H}^+}^{0m''} - \mu_{\text{H}^+}^{0\beta}}{F} + \frac{RT}{F} \ln \frac{a_{\text{H}^+}^{m''}}{a_{\text{H}^+}^{\beta}} \quad (2.4.10)$$

$$(\phi^m - \phi^{m'}) = \frac{RT}{F} \ln \frac{u_{H^+} a_{H^+}^{m'} + u_{Na^+} a_{Na^+}^{m'}}{u_{Na^+} a_{Na^+}^m} \quad (2.4.11)$$

where the concentrations have been replaced by activities. Also, for the interface between m and m'' ,

$$(\phi^{m''} - \phi^m) = \frac{RT}{F} \ln \frac{u_{Na^+} a_{Na^+}^m}{u_{H^+} a_{H^+}^{m''} + u_{Na^+} a_{Na^+}^{m''}} \quad (2.4.12)$$

Now let us add the component potential differences, (2.4.9)–(2.4.12), as dictated by (2.4.5), to obtain the whole potential difference across the membrane:¹⁹

$$E_m = \frac{RT}{F} \ln \frac{a_{H^+}^\alpha a_{H^+}^{m''}}{a_{H^+}^\beta a_{H^+}^{m'}} \quad (\text{Donnan Term})$$

$$+ \frac{RT}{F} \ln \frac{(u_{Na^+}/u_{H^+}) a_{Na^+}^{m'} + a_{H^+}^{m'}}{(u_{Na^+}/u_{H^+}) a_{Na^+}^{m''} + a_{H^+}^{m''}} \quad (\text{Diffusion term}) \quad (2.4.13)$$

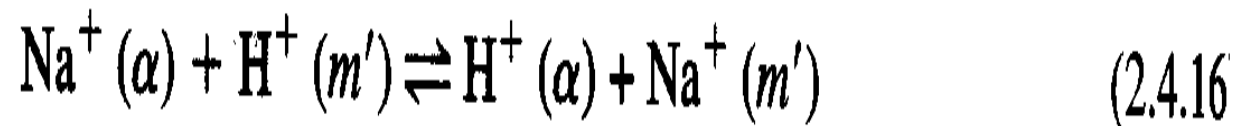
Some important simplifications can be made in this result. First, we combine the two terms in (2.4.13) and rearrange the parameters to give

$$E_m = \frac{RT}{F} \ln \frac{(u_{\text{Na}^+}/u_{\text{H}^+})(a_{\text{H}^+}^\alpha a_{\text{Na}^+}^{m'} / a_{\text{H}^+}^{m'}) + a_{\text{H}^+}^\alpha}{(u_{\text{Na}^+}/u_{\text{H}^+})(a_{\text{H}^+}^\beta a_{\text{Na}^+}^{m''} / a_{\text{H}^+}^{m''}) + a_{\text{H}^+}^\beta} \quad (2.4.14)$$

Now consider (2.4.6) and (2.4.7), which apply simultaneously. Their sum must also be true:

$$\bar{\mu}_{\text{Na}^+}^\alpha + \bar{\mu}_{\text{H}^+}^{m'} = \bar{\mu}_{\text{H}^+}^\beta + \bar{\mu}_{\text{Na}^+}^{m''} \quad (2.4.15)$$

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



$$K_{H^+,Na^+} = \frac{a_{H^+}^\alpha a_{Na^+}^{m'}}{a_{H^+}^{m'} a_{Na^+}^\alpha} \quad (2.4.17)$$

An equivalent expression, involving the same numeric value of K_{H^+,Na^+} , would apply to the interface between phases β and m' . These relations can be substituted into (2.4.14) to give

$$E_m = \frac{RT}{F} \ln \frac{(u_{Na^+}/u_{H^+})K_{H^+,Na^+} a_{Na^+}^\alpha + a_{H^+}^\alpha}{(u_{Na^+}/u_{H^+})K_{H^+,Na^+} a_{Na^+}^\beta + a_{H^+}^\beta} \quad (2.4.18)$$

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_{H^+,Na^+}^{pot} :

$$E_m = \frac{RT}{F} \ln \frac{a_{H^+}^\alpha + k_{H^+,Na^+}^{pot} a_{Na^+}^\alpha}{a_{H^+}^\beta + k_{H^+,Na^+}^{pot} a_{Na^+}^\beta} \quad (2.3.19)$$

If the β phase is the internal filling solution (of constant composition) and the α phase is the test solution, then the overall potential of the cell is

$$E = \text{constant} + \frac{RT}{F} \ln (a_{H^+}^\alpha + k_{H^+,Na^+}^{pot} a_{Na^+}^\alpha) \quad (2.4.20)$$

This expression tells us that

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ELECTROCHEMICAL METHODS

Fundamentals and
Applications

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