Chapter 21

Potentiometry

1

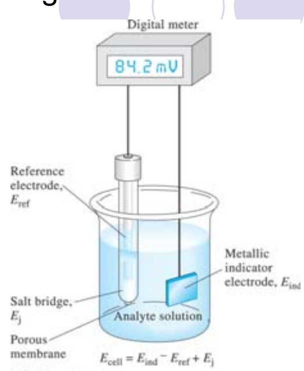
Definition

- Potentiometric methods are based upon measurements of the **potential** of electrochemical cells in the **absence** of appreciable currents.
  - → an equilibrium measurement
  - → the Nernst equation is applicable.

2

Instrumental Configuration

- All equipment is simple: an **indicator** electrode, a **reference** electrode and a **potential measuring device**.



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REF ELECTRODE

Reference electrode |salt bridge | analyte solution | indicator electrode

E_{ref} E_j E_{ind}

$$E_{cell} = (E_{ind} - E_{ref}) + E_j \qquad (E_j \sim mV)$$

4

Applications of Potentiometry

- Billions of these measurements are made annually. Importance in environmental and medical applications.

  For example,

  pH, conductivity, ion selective electrodes (ISEs, Cl^-, Ca^{2+},HCN, SO_2, NH_3), blood gas analysis (O_2, CO_2).

5

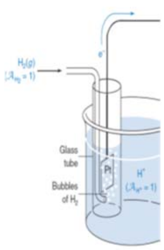
Reference Electrodes

- Purpose: provide stable potential against which other potentials can be reliably measured
- Criteria:
  - stable (time, temperature)
  - reproducible (you, me)
  - potential shouldn't be altered by passage of small current
  - easily constructed
  - convenient for use

6

SHE (NHE)

Pt, H_2 (1.0 atm)|H^+ (a_{H+} = 1.00 M)



Advantages

- International standard E^0 ≡ 0 V at ALL temperature.
- One of most reproducible potentials, ±1 mV

Disadvantages

- Inconvenience
  - Pt black easily poisoned by organics, sulfide, cyanide, etc.
  - Hydrogen explosive
  - Sulfuric and hydrochloric strong acids

7

Practical Reference Electrodes (Secondary Ref. Electrodes)

Aqueous

- SCE (Saturated Calomel Electrode)
- Ag/AgCl (KCl, x M)
- Ferrocene methanol--Fc-CH_2OH—water soluble,

→ added directly to the analyte solution.

Non-aqueous

- Ag/Ag^+ (x M $AgNO_3$)
- Pseudo (Quasi) references
  - Pt, Ag wires
- Ferrocene—Internal standard potential ref.

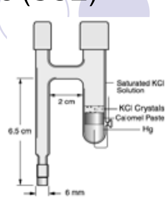
→ added directly to the analyte solution.

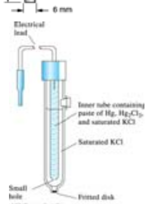
8

Saturated Calomel Electrodes (SCE)

- Hg(l)|Hg_2Cl_2|KCl(Sat'd)||
- E^0 = 0.241 V vs. SHE @ 25°C

Hg_2Cl_2: calomel, mercury (I) chloride, or mercurous chloride





Advantages

- Most polarographic data ref'd to SCE

Disadvantages

- Hg toxic
- solubility of KCl temperature dependent dE/dT = -0.67 mV/K (must quote temperature)

9

Calomel Electrodes

$Hg_2Cl_2(s) + 2e = 2Hg(l) + 2Cl^-$ $E^0_{Hg_2Cl_2/Cl^-} = 0.268$ V vs SHE

$$E_{Hg_2Cl_2/Cl^-} = E^0_{Hg_2Cl_2/Cl^-} + \frac{RT}{2F}\ln\frac{1}{(a_{Cl^-})^2} = 0.268 - 0.0592\log a_{Cl^-}$$

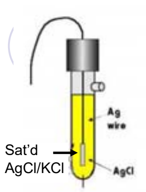
$a_{Cl^-} \nearrow, E_{Hg_2Cl_2/Cl^-} \searrow$.   (Satured KCl, $[Cl^-]$~4.5 M)

Electrode (298K)	Acronym	Potential vs. SHE
$Hg(l)/Hg_2Cl_2(s)/KCl$ (0.1 M)		0.3356
$Hg/Hg_2Cl_2(s)/KCl$ (1 M)	NCE	0.2801
$Hg(l)/Hg_2Cl_2(s)/KCl$ (sat'd)	SCE	0.2444
$Hg(l)/Hg_2Cl_2(s)/$ NaCl (sat'd)	SSCE	0.2360

10

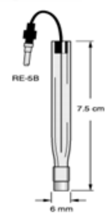
Ag/AgCl

- Ag wire coated with AgCl(s), immersed in NaCl or KCl solution
- E^0 = 0.222 V vs. SHE @ 25˚C



Advantages
- chemical processing industry has standardized on this electrode
- convenient
- rugged/durable

Disadvantages
- solubility of KCl/NaCl temperature dependent dE/dT = -0.73 mV/K (must quote temperature)

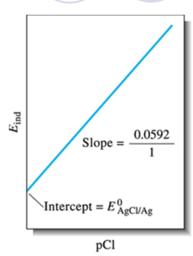


11

$AgCl + e = Ag + Cl^-$

$$E_{Ag/AgCl} = E^0 + 0.0592\log\frac{1}{a_{Cl^-}}$$
$$= E^0 - 0.0592\log a_{Cl^-}$$
$$= E^0 + 0.0592\text{pCl}$$

$a_{Cl^-} \nearrow, E_{Ag/AgCl} \searrow$.

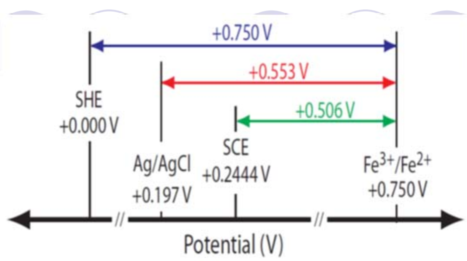


12

TABLE 23-1 Potentials of Reference Electrodes in Aqueous Solutions

	Electrode Potential vs. SHE, V				
Temperature, °C	0.1 M[c] Calomel[a]	3.5 M[c] Calomel[b]	Saturated[c] Calomel[a]	3.5 M[b,c] Ag-AgCl	Saturated[b,c] Ag-AgCl
10	—	0.256	—	0.215	0.214
12	0.3362	—	0.2528	—	—
15	0.3362	0.254	0.2511	0.212	0.209
20	0.3359	0.252	0.2479	0.208	0.204
25	0.3356	0.250	0.2444	0.205	0.199
30	0.3351	0.248	0.2411	0.201	0.194
35	0.3344	0.246	0.2376	0.197	0.189
38	0.3338	—	0.2355	—	0.184
40	—	0.244	—	0.193	—

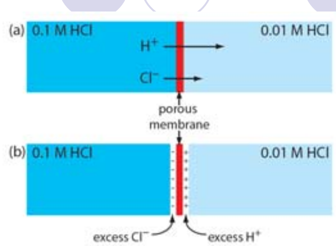
13

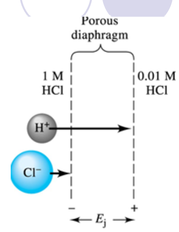


Relationship between the potential of an Fe^{3+}/Fe^{2+} half-cell relative to the reference electrodes. The potential vs. S.H.E. is shown in blue, the potential vs. Ag/Ag is shown in red, and the potential vs. SCE is shown in green.

14

Liquid Junction Potentials





Differences in ion mobility give rise to junction potentials (Unequal distribution). Solution: salt bridge containing a high concentration of KCl or $NaNO_3$.

15

Indicator Electrodes

- Electrode used with reference electrode to measure potential of unknown solution.
- For a good indicator electrode (working electrode)

→ potential proportional to the analyte ion activity;

→ specific (one ion) or selective (several ions).

$$E_{cell} = E_{indicator} - E_{ref} = f(a_Y)$$

16

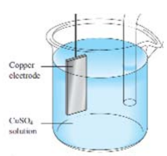
Two General Types of Indicator Electrodes

- Metallic Indicator Electrodes;
  → the electrode *normally* consists of a metal, and the electrode potential is directly correlated to the concentration (activity) of the analyte.
- Membrane Indicator Electrodes [Ion Selective Electrodes (ISE)].
  → a key component of the electrode is a membrane (cystalline or non-cystalline membrane)

17

Electrode of the First Kind

- Metal in contact with its cations or non-metal (via a noble metal) in contact with its anions
- EXAMPLES:
  - Cu/Cu^{2+}
  - Zn/Zn^{2+}
  - SHE (Pt, $H_2|H^+$)
  - Pt, $Cl_2(g)/Cl^-$
  - Ag /Ag^+ (nonaqueous reference electrode)



18

- Electrode response given by Nernst equation (Nernstian):

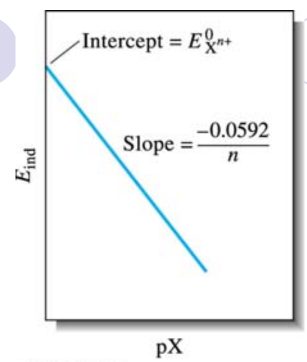
$$M^{n+} + ne = M(s)$$

$$E = E^0 + \frac{RT}{nF} \ln a_{M^{n+}}$$

$$E = E^0 + \frac{0.0592}{n} \log a_{M^{n+}} \quad (at\ 298K)$$

$$= E^0 - \frac{0.0592}{n} \text{pM}$$

19

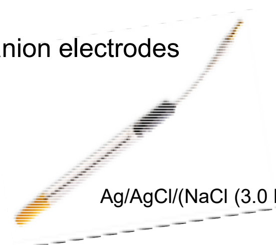


Potential response for an electrode of the first kind

20

Electrode of the Second Kind

- Metal in contact with sparingly soluble salt of the metal
- Common name: anion electrodes
- EXAMPLES:
  - Ag/AgCl(s)
  - $Hg/Hg_2Cl_2(s)/Cl^-$

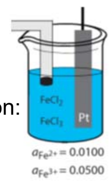


Ag/AgCl/(NaCl (3.0 M)

21

Metallic Redox Indicator Electrodes

- Electrodes that merely serve as sources or sinks for electrons
- Common names: redox, inert, unattackable
- EXAMPLES:
  Pt, Au, GC (Glassy Carbon)
- Response:
  For Pt in contact with Fe^{2+}, Fe^{3+} in solution:
  $E = E^0 + 0.0592\log([Fe^{3+}]/[Fe^{2+}])$



22

Membrane (or Ion Selective) Electrodes

Properties of Membrane:

- Low solubility - solids, semi-solids and polymers
- Some electrical conductivity - often by doping
- Selectivity - part of membrane binds/reacts with analyte

23

Two general types - Crystalline and Non-crystalline membranes

- Crystalline membranes
  Single crystal - LaF_3 for F^-
  Polycrystalline or mixed crystal – Ag_2S for S^{2-} and Ag^+
- Non-crystalline membranes
  Glass - silicate glasses for H^+, Na^+
  Liquid - liquid ion exchanger for Ca^{2+}
  Immobilized liquid - liquid/PVC matrix for Ca^{2+} and NO_3^-

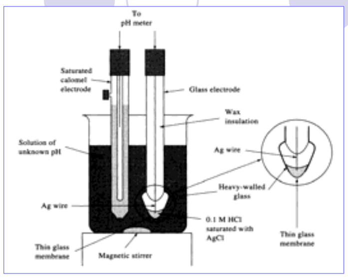
24

How does a pH probe work?

- https://www.youtube.com/watch?v=P1wRXTI2L3I

25

Glass Membrane Electrode

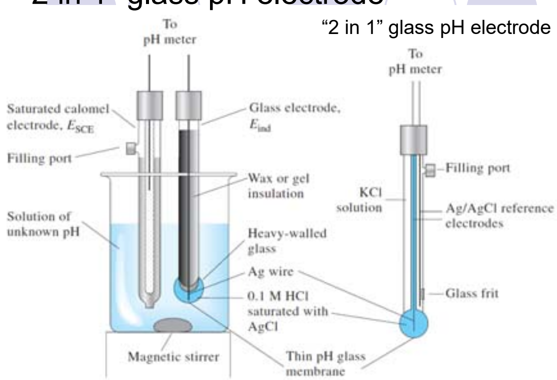


- Contains Two ref. electrodes.
- Internal Ag/AgCl electrode is part of glass membrane electrode.
- The thin glass membrane is pH sensitive, NOT the Ag/AgCl

$$\overbrace{\text{SCE}}^{\text{Ref 1}}\,||\,\overbrace{H_3O^+(a=a_1)}^{\text{Analyte}}|\overbrace{\text{Membrane}|H_3O^+(a=a_2),\underbrace{Cl^-(a=1\text{ M}),AgCl(\text{sat'd})|Ag}_{\text{Ref 2}}}^{\text{Glass Electrode}}$$

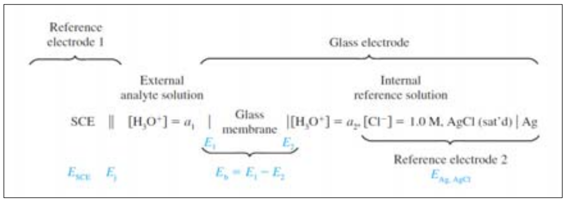
26

"2 in 1" glass pH electrode



27

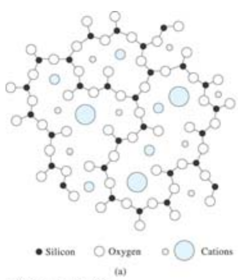
•Contains Two ref. electrodes.
•Internal Ag/AgCl electrode is part of glass membrane electrode.
•The thin glass membrane is pH sensitive, NOT the Ag/AgCl



28

Glass Membrane Structure

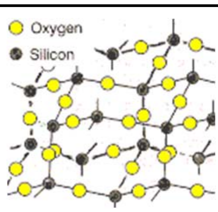
SiO_4^{4-} framework with charge balancing cations
- SiO_2 72 %, Na_2O 22 %, CaO 6 %

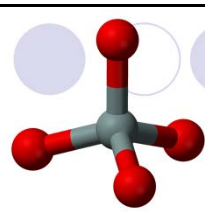


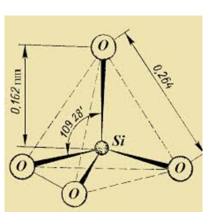
Cross-section view of a silicate glass structure. In addition to the 3 Si-O bonds shown, each Si is bonded to an additional O atom, either above or below the plane of the paper.

(b)

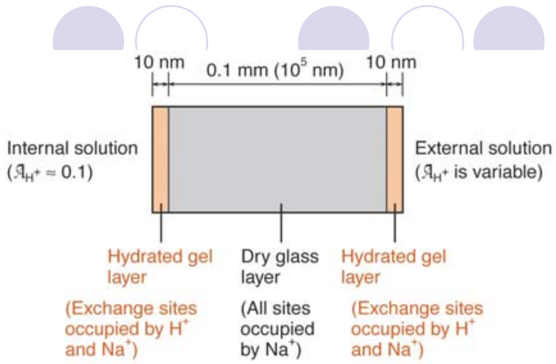
29







30



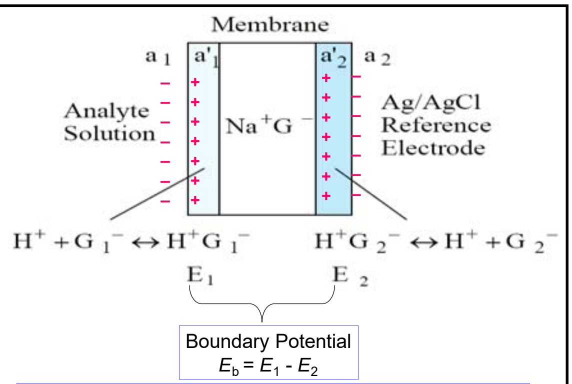
31

In aqueous solutions, ion exchange reactions occur at surface

$$\underset{\text{soln}}{H^+} + \underset{\text{glass}}{Na^+Glass^-} \rightleftharpoons \underset{\text{soln}}{Na^+} + \underset{\text{glass}}{H^+Glass^-}$$

- H^+ carries current near surface
- Na^+ carries current in interior
- Ca^{2+} carries no current (immobile)

32



For glass electrode: $E_{glass} = E_b + E_{internal\ ref}$

33

Boundary Potential

$$E_b = E_1 - E_2 = 0.0592\log\frac{a_1}{a_2}$$

as a_2 is the hydrogen ion activity of the internal solution (constant)

$$E_b = L' + 0.0592\log a_1 = L' - 0.0592\text{pH}$$

where

$$L'\ (\text{constant}) = -0.0592\log a_2$$

34

The pH Meter Potential

$$E_{\text{cell}} = E_{\text{glass electrode}} - E_{\text{external ref}}$$
$$= (E_b + E_{\text{internal ref}}) - E_{\text{external ref}}$$
$$= [(L' - 0.0592\text{pH}) + E_{\text{internal ref}}] - E_{\text{external ref}}$$
$$= (L' + E_{\text{internal ref}} - E_{\text{external ref}}) - 0.0592\text{pH}$$
$$E_{\text{cell}} = K - 0.0592\text{pH}$$

35

Alkaline Error/Acid Error

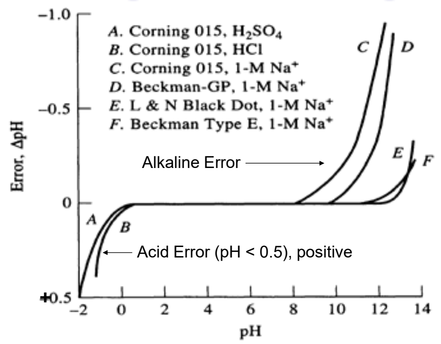
- At high pH, glass electrode indicates pH less than true value (negative error)

$$H^+(\text{soln}) + \text{Glass}^- \rightleftharpoons H^+\text{-Glass}^-(\text{membrane})$$

$$Na^+(\text{soln}) + \text{Glass}^- \rightleftharpoons Na^+\text{-Glass}^-(\text{membrane})$$

- Low pH → high [H^+] → glass electrode indicates pH higher than true value (positive error) (Reason not well understood, one reason: saturation effect)

36



Most accurate region: pH 0.5→ 10

37

Selectivity Coefficients

$$E_b = K' + 0.05921\log(a_1 + k_{H,B}b_1)$$

(For all membrane Electrodes)

Where $k_{H,B}$ is the *selectivity coefficient* for the electrode

b_1 is the activity of the alkali metal

Range between 0 (no interference) to 1 (as sensitive to alkali and hydrogen ions) to >1 (large interference)

38

For a Corning 015 glass membrane, the selectivity coefficient K_{H^+/Na^+} is $\approx 10^{-11}$. What is the expected error if we measure the pH of a solution in which the activity of H^+ is 2×10^{-13} and the activity of Na^+ is 0.05?

SOLUTION

A solution in which the actual activity of H^+, $(a_{H^+})_{act}$, is 2×10^{-13} has a pH of 12.7. Because the electrode responds to both H^+ and Na^+, the apparent activity of H^+, $(a_{H^+})_{app}$, is

$$(a_{H^+})_{app} = (a_{H^+})_{act} + (K_{H^+/Na^+} \times a_{Na^+}) =$$
$$2 \times 10^{-13} + (10^{-11} \times 0.05) = 7 \times 10^{-13}$$

The apparent activity of H^+ is equivalent to a pH of 12.2, an error of –0.5 pH units.

39

Precaution in use of pH electrode/meter

- Place the new/dry electrode into a distilled water for ~24 h before use.
- Always keep the electrode in distilled water after use.
- Fill electrolyte solution for external ref. if necessary.
- Use suitable buffer solutions (2 buffers, fresh) to calibrate the electrode/meter first.
- Avoid using the electrode in strong basic/acid solution (pH 0.5-10,12)
- Errors in low ionic strength solutions (e.g., lake sample)

40

Operational Definition of pH

- $\because E_{cell} = K - 0.0592\text{pH}$

  $$\text{pH} = \frac{K - E_{cell}}{0.0592}$$

  $\therefore$ In a standard buffer

  $$\text{pH}_s = \frac{K - E_s}{0.0592} \qquad K = 0.0592\text{pH}_s + E_s$$

  In a unknown solution

  $$\text{pH}_u = \frac{K - E_u}{0.0592} = \frac{(0.0592\text{pH}_s + E_s) - E_u}{0.0592}$$

  $$\text{pH}_u = \text{pH}_s + \frac{E_s - E_u}{0.0592} = \text{pH}_s - \frac{(E_u - E_s)}{0.0592}$$

41

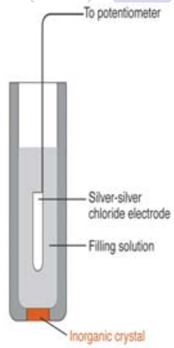
Glass Electrodes for Other Cations

- Maximize $k_{H,B}$ for other ions by modifying glass surface (usually adding Al_2O_3 or B_2O_3)
- Possible to make glass membrane electrodes for Na^+, K^+, NH_4^+, Cs^+, Rb^+, Li^+, Ag^+ ...

42

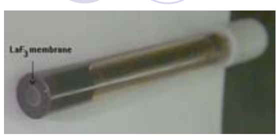
Crystalline Membrane Electrode

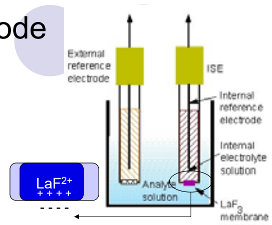
- Usually ionic compound
- Single crystal
- Crushed powder, melted and formed
- Sometimes doped (Li^+) to increase conductivity
- Operation similar to glass membrane



43

Fluoride ISE Electrode





Lanthanum Fluoride (LaF_3) single crystal membrane

$LaF_3(s) \rightleftarrows LaF_2^+(s) + F^-$ (aq) (Double layer formed)

$E_{cell} = K - 0.0592 \log a_{F^-} = K + 0.0592 pF$

Response down to 1 μM F^-

44

Universal Equation of Membrane Electrode

$$E_{cell} = K \pm \frac{0.0592}{n} \lg M^{n\pm}$$

$$= K \mp \frac{0.0592}{n} pM^{n\pm}$$

M^{n+} – *cation with n electrons invloved*

M^{n-} – *anion with n electrons invloved*

Example: Ca^{2+} membrane electrode

$$E_{cell} = K + \frac{0.0592}{2} \lg Ca^{2+} = K - \frac{0.0592}{2} pCa$$

45

Table 15-5 Properties of solid-state ion-selective electrodes

Ion	Concentration range (M)	Membrane material	pH range	Interfering species
F^-	10^{-6}–1	LaF_3	5–8	OH^- (0.1 M)
Cl^-	10^{-4}–1	AgCl	2–11	CN^-, S^{2-}, I^-, $S_2O_3^{2-}$, Br^-
Br^-	10^{-5}–1	AgBr	2–12	CN^-, S^{2-}, I^-
I^-	10^{-6}–1	AgI	3–12	S^{2-}
SCN^-	10^{-5}–1	AgSCN	2–12	S^{2-}, I^-, CN^-, Br^-, $S_2O_3^{2-}$
CN^-	10^{-6}–10^{-2}	AgI	11–13	S^{2-}, I^-
S^{2-}	10^{-5}–1	Ag_2S	13–14	

Table 15-6 Properties of liquid-based ion-selective electrodes

Ion	Concentration range (M)	Carrier	Solvent for carrier	pH range	Interfering species
Ca^{2+}	10^{-5}–1	Calcium didecylphosphate	Dioctylphenyl-phosphonate	6–10	Zn^{2+}, Pb^{2+}, Fe^{2+}, Cu^{2+}
K^+	10^{-6}–1	Valinomycin	Dioctylsebacate	4–9	Rb^+, Cs^+, NH_4^+
NO_3^-	10^{-5}–1	Tridodecylhexadecylammonium nitrate	Octyl-2-nitrophenyl ether	3–8	ClO_4^-, I^-, ClO_3^-, Br^-, HS^-, CN^-
ClO_4^-	10^{-5}–1	Tris(substituted 1,10-phenanthroline) iron(II) perchlorate	*p*-Nitrocymene	4–10	I^-, NO_3^-, Br^-
BF_4^-	10^{-5}–1	Tris(substituted 1,10-phenanthroline) nickel(II) tetrafluoroborate	*p*-Nitrocymene	2–12	NO_3^-

46

Molecular Selective Electrodes

- The electrochemical signal (potential) is related to certain types of *molecules*

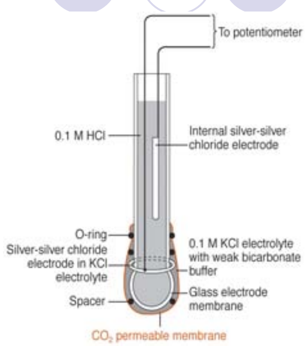
(1) → Gas-sensing probes
e.g., CO_2, NH_3, NO_2

(2) → Biocatalytic membrane electrodes
Immobilized enzyme bound to gas permeable membrane
e.g., Urea

47

CO_2 Gas-sensing Electrode

- **Work by the permeation of gas across a selective membrane**
- **The gas changes the pH inside the electrode (on the inside of the membrane) and this signal is proportional to the gas concentration.**



48

Chapter 21 Summary

- Cells for potentiometric determinations
- Measurement of cell potentials
- Determination of pH with the glass electrode
- Determination of ions with membrane electrodes
- Molecular sensing electrodes

49

Important Equations

$$E_{cell} = (E_{ind} - E_{ref}) + E_j \qquad (E_j \sim mV)$$

$$E_b = L' + 0.0592 \log a_1 = L' - 0.0592\text{pH}$$

$$E_{cell} = K \pm \frac{0.0592}{n} \lg \text{M}^{n\pm}$$

$$= K \mp \frac{0.0592}{n} \text{pM}^{n\pm}$$

$$\text{pH}_u = \text{pH}_s + \frac{E_s - E_u}{0.0592} = \text{pH}_s - \frac{(E_u - E_s)}{0.0592}$$

50