OTHER ANALYTE SELECTIVE ELECTRODES

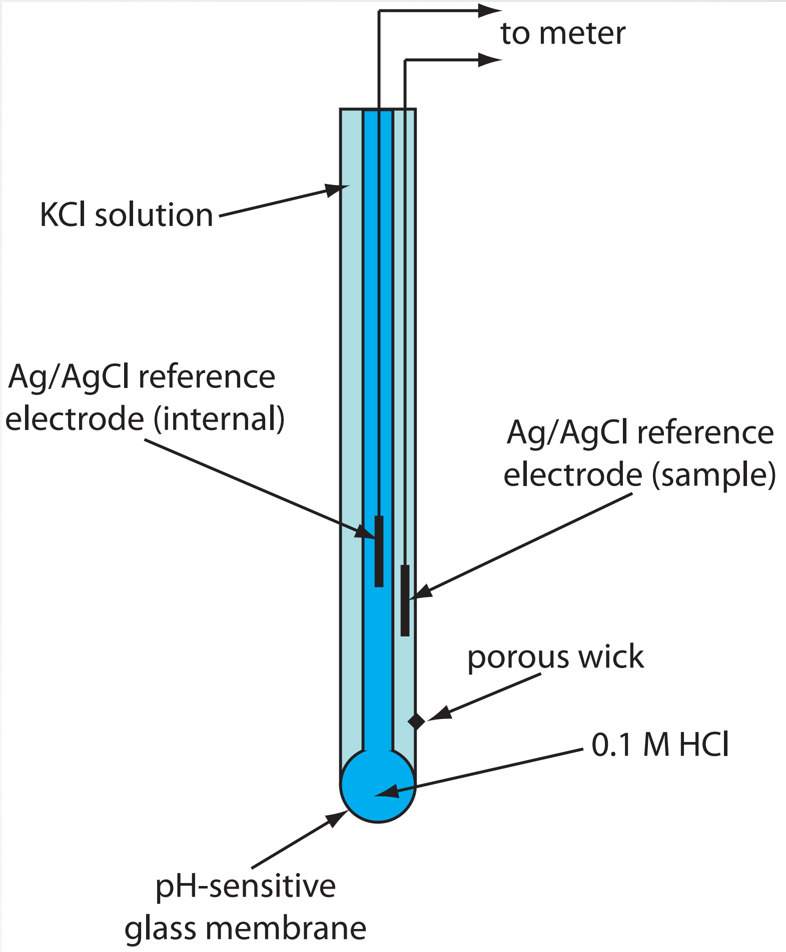
SDSU CHEM 251

GLASS ION SELECTIVE ELECTRODES

- Glass ion selective electrodes are formed from specialized very thin (~50 μm) glass membranes.
- The hydration of the membrane leads to the deprotonation of the silanols resulting in anionic charged groups ($-SiO^-$).
- The binding of cations to the charged sites on either side of the membrane produces the potential across the membrane.

pH GLASS ELECTRODE

- The first commercial pH electrode was developed by Corning with a membrane composed of 22% Na_2O, 6% CaO, 72% SiO_2.
- It was effective from pH 0.5 to 9 - at more basic pH values sodium could outcompete hydrogen for the binding sites.
- Changes in the glass (Li_2O for Na_2O and BaO for CaO) yield electrodes with greater range (up to pH 12).



OTHER GLASS ELECTRODES

Table 11.1 Representative Examples of Glass Membrane Ion-Selective Electrodes for Analytes Other than H^+

analyte	membrane composition	selectivity coefficients[a]
Na^+	11% Na_2O, 18% Al_2O_3, 71% SiO_2	$K_{Na^+/H^+} = 1000$ $K_{Na^+/K^+} = 0.001$ $K_{Na^+/Li^+} = 0.001$
Li^+	15% Li_2O, 25% Al_2O_3, 60% SiO_2	$K_{Li^+/Na^+} = 0.3$ $K_{Li^+/K^+} = 0.001$
K^+	27% Na_2O, 5% Al_2O_3, 68% SiO_2	$K_{K^+/Na^+} = 0.05$

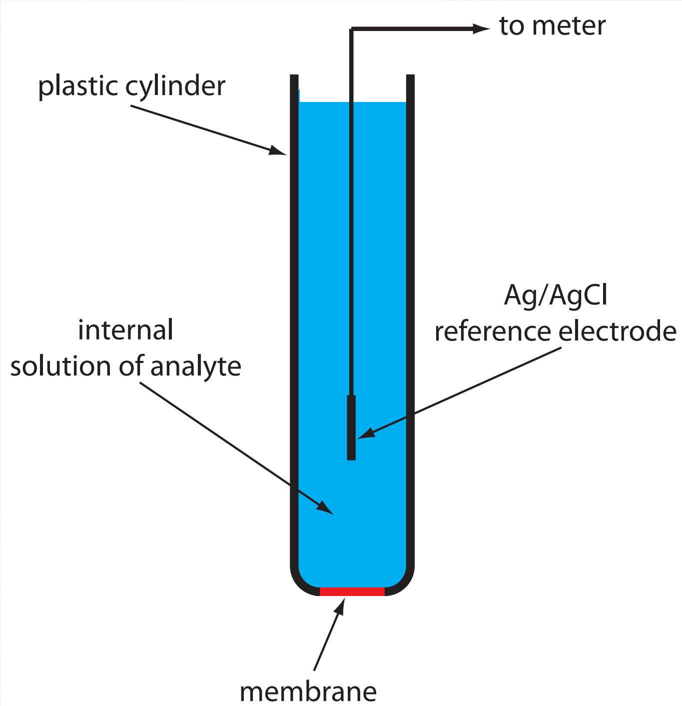
A range of other glass membrane electrodes can be made with varied selectivities for common cations.

SOLID-STATE ISE

- Solid-state ion selective membranes come in two varieties - polycrystalline inorganic salts or sing crystal inorganic salt.

- For polycrystalline ISEs the membrane (1-2 mm thick) is composed of a pellet of inorganic salt, either a pure salt or a mixture (e.g. Ag_2S alone or with other sulfides or silver salts).

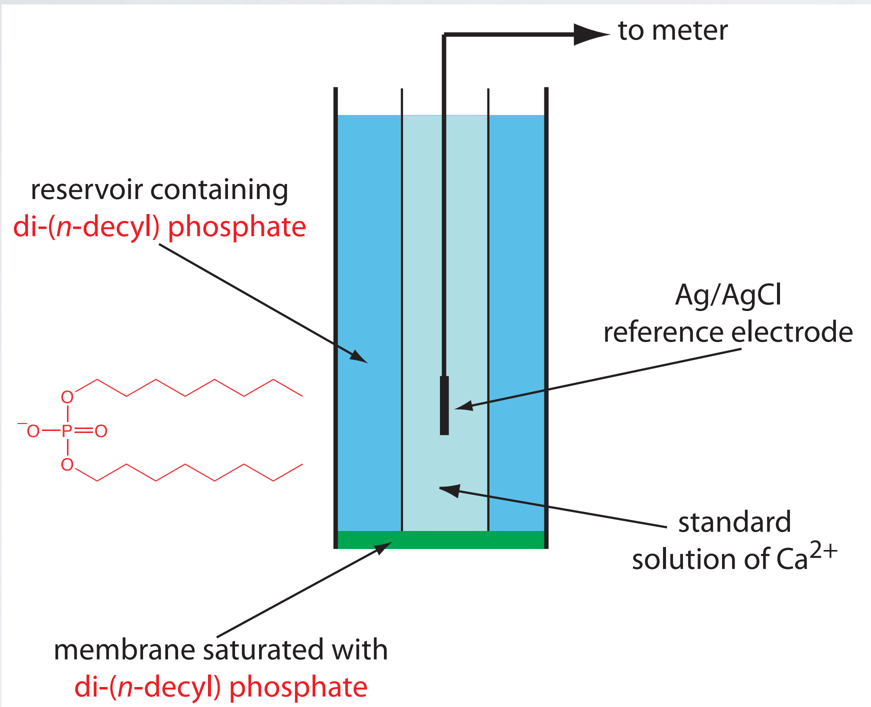
- The potential arises from the dissolution of the membrane to various extents on either side of the membrane.



SINGLE CRYSTAL ISE

- Single crystal ISEs also rely on the dissolution of the membrane to generate the potential.
- The fluoride ISE uses a LaF_3 crystal doped with some EuF_2 - the EuF_2 provides some vacancies to improve the diffusion F^- ions through the membrane.
- The differing extents of dissolution of the LaF_3 on either side of the membrane (sample vs. internal solution) yield the potential that can be measured.
- Fluoride ISE are highly selective, with only hydroxide interfering ($K_{F-/OH-} = 0.1$) necessitating lower pH solutions for accurate analyses.

LIQUID BASED ISE



These electrodes use very hydrophobic compounds to selectively allow the transport of desired analytes across the membrane.

Table 11.3 Representative Examples of Liquid-Based Ion-Selective Electrodes

analyte	membrane composition	selectivity coefficients[a]
Ca^{2+}	di-(*n*-decyl) phosphate in PVC	$K_{Ca^{2+}/Zn^{2+}} = 1–5$ $K_{Ca^{2+}/Al^{3+}} = 0.90$ $K_{Ca^{2+}/Mn^{2+}} = 0.38$ $K_{Ca^{2+}/Cu^{2+}} = 0.070$ $K_{Ca^{2+}/Mg^{2+}} = 0.032$
K^+	valinomycin in PVC	$K_{K^+/Rb^+} = 1.9$ $K_{K^+/Cs^+} = 0.38$ $K_{K^+/Li^+} = 10^{-4}$ $K_{K^+/Na^+} = 10^{-5}$
Li^+	ETH 149 in PVC	$K_{Li^+/H^+} = 1$ $K_{Li^+/Na^+} = 0.05$ $K_{Li^+/K^+} = 0.007$
NH_4^+	nonactin and monactin in PVC	$K_{NH_4^+/K^+} = 0.12$ $K_{NH_4^+/H^+} = 0.016$ $K_{NH_4^+/Li^+} = 0.0042$ $K_{NH_4^+/Na^+} = 0.002$
ClO_4^-	$Fe(o\text{-phen})_3^{3+}$ in *p*-nitrocymene with porous membrane	$K_{ClO_4^-/OH^-} = 1$ $K_{ClO_4^-/I^-} = 0.012$ $K_{ClO_4^-/NO_3^-} = 0.0015$ $K_{ClO_4^-/Br^-} = 5.6\times10^{-4}$ $K_{ClO_4^-/Cl^-} = 2.2\times10^{-4}$
NO_3^-	tetradodecyl ammonium nitrate in PVC	$K_{NO_3^-/Cl^-} = 0.006$ $K_{NO_3^-/F^-} = 9\times10^{-4}$

GAS-SENSING ELECTRODES

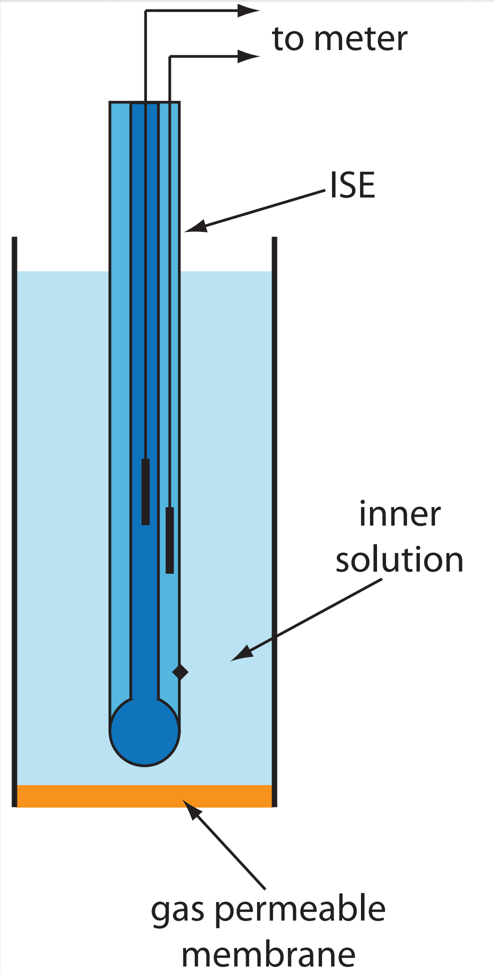
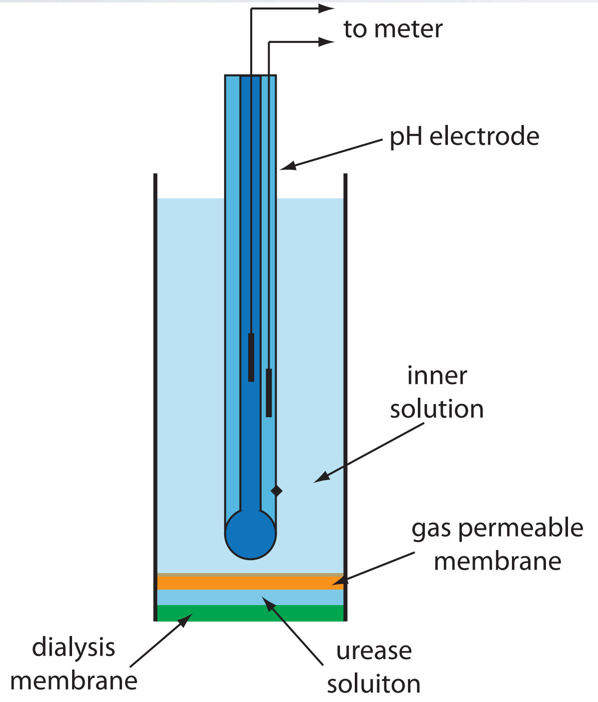


Table 11.4 Representative Examples of Gas-Sensing Electrodes

analyte	inner solution	reaction in inner solution	ion-selective electrode
CO_2	10 mM $NaHCO_3$ 10 mM NaCl	$CO_2(aq) + 2H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$	glass pH ISE
HCN	10 mM $KAg(CN)_2$	$HCN(aq) + H_2O(l) \rightleftharpoons CN^-(aq) + H_3O^+(aq)$	Ag_2S solid-state ISE
HF	1 M H_3O^+	$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$	F^- solid-state ISE
H_2S	pH 5 citrate buffer	$H_2S(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + H_3O^+(aq)$	Ag_2S solid-state ISE
NH_3	10 mM NH_4Cl 0.1 M KNO_3	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	glass pH ISE
NO_2	20 mM $NaNO_2$ 0.1 M KNO_3	$2NO_2(aq) + 3H_2O(l) \rightleftharpoons NO_3^-(aq) + NO_2^-(aq) + 2H_3O^+(aq)$	glass pH ISE
SO_2	1 mM $NaHSO_3$ pH 5	$SO_2(aq) + 2H_2O(l) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq)$	glass pH ISE

The gas permeable membrane allows the selective transport of gases from the sample solution into the electrode. In the electrode the gasses react to produce a secondary analyte that can be quantified with an ISE.

POTENTIOMETRIC BIOSENSORS



Biosensors most commonly utilize immobilized or trapped enzymes to act on the desired analyte as it diffuses into the electrode. The products of the enzymatic reaction can be monitored by an ISE.

Table 11.5 Representative Examples of Potentiometric Biosensors[a]

analyte	biologically active phase[b]	substance determined
5′-adenosinemonophosphate (5′-AMP)	AMP-deaminase (E)	NH_3
L-arginine	arginine and urease (E)	NH_3
asparagine	asparaginase (E)	NH_4^+
L-cysteine	*Proteus morganii* (B)	H_2S
L-glutamate	yellow squash (T)	CO_2
L-glutamine	*Sarcina flava* (B)	NH_3
oxalate	oxalate decarboxylas (E)	CO_2
penicillin	pencillinase (E)	H_3O^+
L-phenylalanine	L-amino acid oxidase/horseradish peroxidase (E)	I^-
sugars	bacteria from dental plaque (B)	H_3O^+
urea	urease (E)	NH_3 or H_3O^+

E = enzyme
B = bacteria
T = tissue