Ion-selective electrode (Ch 15-4 to 15-6)

- To describe the principle of the I.S.E. and its advantages and limitations (Do Ex. 15-32 & 15-37)
- To describe the four types of I.S.E. (Do Ex. 15-27)
- To describe the working principle of the glass electrode and perform related calculations (Do Ex. 15-26)
- To describe the sources of errors in pH measurements (Do Ex. 15-21 & 15-24)
- To describe the working principle of the solid state electrode and perform related calculations (Do Ex. 15-34 & 15-48)
- To calculate and use selectivity coefficients (Do Ex. 15-28, 15-35 & 15-39)
- To perform calculations regarding the uses of I.S.E. (Do Ex. 15-37 & 15-40)

Principle of ion-selective electrode (I.S.E.)

An ideal I.S.E. consists of a thin membrane across which only the intended ion can be transported.

The transport of ions from a high conc. to a low one through a selective binding with some sites within the membrane creates a potential difference.

See Fig. 15-8 for the development of a potential difference across a calcium-ion selective membrane

Principle of I.S.E.

When a neutral species diffuses from a region of activity, A_1, to a region of activity, A_2, there is a free energy change (decrease),

$$\Delta G = -RT \ln\left(\frac{A_1}{A_2}\right)$$

For a charged species, this decrease should equal the electrical work done to the surroundings.

$$-RT \ln\left(\frac{A_1}{A_2}\right) = -nFE \qquad or \qquad -RT \ln\left(\frac{A_1}{A_2}\right) = -nF(-E)$$

for a positive species *for a negative species*

$$\therefore E = \frac{RT}{zF}\ln\left(\frac{A_1}{A_2}\right) = \frac{0.05916}{z}\ln\left(\frac{A_1}{A_2}\right) \quad at \quad 25^\circ C$$

where z is the charge of the species, including the sign

So 59.16 mV is developed for every 10-fold difference in activity of H^+ (or every pH unit). Note that it is 29.58 mV for Ca^{2+}.

Types of I.S.E.

1. Glass membrane (i.e. H^+ electrode)
2. Solid-state electrode (e.g. F^- electrode uses a Eu^{2+}-doped LaF_3 crystal)
3. Liquid-based electrode (e.g. Ca^{2+} electrode uses a liquid chelator)
4. Compound electrode (e.g. CO_2 gas sensing electrode) see Fig 15-21

Advantages and limitations of I.S.E.

Advantages:
1. Linear response: over 4 to 6 orders of magnitude of A.
2. Non-destructive: no consumption of analyte.
3. Non-contaminating.
4. Short response time: in sec. or min. useful in indust. applications.
5. Unaffected by color or turbidity.

Limitations:
1. Precision is rarely better than 1%.
2. Electrodes can be fouled by proteins or other organic solutes.
3. Interference by other ions.
4. Electrodes are fragile and have limited shelf life.
5. Electrodes respond to the activity of uncomplexed ion. So ligands must be absent or masked. μ must be kept constant.

The glass electrode

$$\underbrace{Ag(s)\,|\,AgCl(s)\,|\,Cl^-(aq)}_{outer\ \ reference\ \ electrode}\,\|\,H^+\underbrace{(aq, outside)}_{analyte\ \ solution}\underset{\overset{\uparrow}{\text{Glass membrane}}}{\vdots}H^+\underbrace{(aq, inside)}_{inner\ \ H^+\ \ solution}, \underbrace{Cl^-(aq)\,|\,AgCl(s)\,|\,Ag(s)}_{inner\ \ reference\ \ electrode}$$

$$E = E_{asym} + 0.05916\log\left(\frac{A_{H^+,outside}}{A_{H^+,inside}}\right)$$

A typical pH combination electrode, incorporating the glass indicator electrode and reference electrode in one body, see Fig 15-9.

The glass electrode

Most of the metal cations (e.g. Na^+) in the hydrated gel layer diffuse out of the glass membrane and into the solution, see Fig 15-12.

Concomitantly, H^+ from solution diffuse into the membrane.

Response of glass electrode (at 25 °C):

$$E = E_{asym} + 0.05916 \log\left(\frac{A_{H^+,outside}}{A_{H^+,inside}}\right)$$

During two-point calibration, the y-intercept can be corrected by the "calibrate" knob.

The slope is corrected by the "slope" or "temperature" knob during pH meter calibration.

Errors in pH measurements

1. pH of buffer standards: only accurate to ±0.01 pH unit.

2. Junction potential: exists if μ of the analyte is different from that of the pH standards. To minimize this, use pH standards with the same μ.

3. Junction potential drift: exists when there is formation of AgCl (precipitation) or Ag (reduction) at the porous plug. To minimize this, recalibrate the electrode every 2 h.

4. Equilibration time: It takes time for an electrode to equilibrate with the analyte solution, esp. in a poorly buffered solution (pH varies greatly).

5. Dehydration of glass membrane: If the membrane has dried out, recondition it in water for several hours before use.

6. Temperature: A pH meter should be calibrated at the temperature at which pH measurements will be made.

7 Na or alkaline error: when A_{H+} is very low & A_{Na+} is high, the pH electrode responds to Na^+ as if it were H^+. So the apparent A_{H+} is higher, or apparent pH is lower.

8. Acid error: In strong acid, perhaps the glass surface is saturated with H^+, so the apparent A_{H+} is lower & the apparent pH is higher, see Fig 15-15.

Solid-state electrode

This is based on an inorganic crystal doped with a small amount of ions of a different valency to create vacant sites.

For instance, in a F^- ion electrode, a LaF_3 crystal is doped with EuF_2 so that there are anion vacancies for the migration of F^- through the LaF_3 crystal, see Fig. 15-17.

Response of F^- ion electrode (see Fig 15-16):

E = constant - (0.05916) log ($A_{F-, outside}$)
  = constant - (0.05916) log γ_{F-} - (0.05916) log [F^-]

At high pH, there is interference by OH^- (Note $k_{F-, OH-} = 0.1$)

At low pH, F^- is converted to HF ($pK_a = 3.17$) to which the electrode is insensitive.

Solid-state electrode

The analyte solution is usually diluted in a high μ buffer to keep the pH (at 5.5) and μ constant.

$\therefore$ E = constant´ - (0.05916) log [F^-]

Therefore, a plot of E versus log [F^-] should yield a straight line with a negative slope, see Fig. 15-18.

Liquid-based electrode

An ISE consists of a liquid ion exchanger (e.g. di-(n-decyl)phosphate) incorporated in a PVC membrane, see Fig 15-20.

In contrast to F- ISE, a plot of E versus log [Ca^{2+}] should yield a straight line with a positive slope.

Selectivity coefficients

An electrode used to measure ion A selectively may also slightly responds to ion X. For instance, a pH electrode responds to Na^+ when [H^+] 10^{-12} M and [Na^+] 10^{-2} M.

The smaller the selectivity coefficient is, the less is the interference by X.

The response of an I.S.E. is thus represented by

$$E = constant \pm \frac{0.05916}{n} \log\left[A_A + \sum_X (k_{A,X} A_X{}^{z_A/z_X}) \right]$$

If A and X have the same charges, we have:

$$E = constant \pm \frac{0.05916}{n} \log\left[A_A + \sum_X (k_{A,X} A_X) \right]$$

If the I.S.E. is the cathode (or the positive terminal), the sign before the log term is positive if A is a cation (e.g. Ca^{2+}), and negative if A is an anion (e.g. F^-).

Selectivity coefficients

Eg. in Sec 15-5: What will be the difference in electrode potentials of 1.0×10^{-4} M F^- at pH 5.5 and pH 10.5 (k_{F^-, OH^-} = 0.1).

$$\begin{aligned} &At \quad pH\,5.5 \quad E = constant - 0.05916\log(1.0\times10^{-4} + 0.1\times10^{(-14+5.5)}) \\ &\qquad\qquad\qquad = constant + 236.6\,mV \end{aligned}$$

$$\begin{aligned} &At \quad pH\,10.5 \quad E = constant - 0.05916\log(1.0\times10^{-4} + 0.1\times10^{(-14+10.5)}) \\ &\qquad\qquad\qquad = constant + 229.5\,mV \end{aligned}$$

The difference is 7.1 mV.

The value at pH 10.5 is 7.1 mV lower, which you might have mistakenly concluded that [F^-] was 32% higher.

Uses of I.S.E.

E.g. in Sec 15-5: (External calibration curve of I.S.E.) The following potentials (versus S.C.E.) were observed for a F^- I.S.E. immersed in standard solution of F^- (maintained at a constant m of 0.1 M with $NaNO_3$). What is [F^-] if the potential is 0.0 mV?

[F^-] / M:	1.00×10^{-5}	1.00×10^{-4}	1.00×10^{-3}
E / mV:	100.0	41.5	-17.0

E.g. in Sec 15-6: (Single point standard addition of I.S.E.) A perchlorate I.S.E. immersed in 50.0 mL of unknown perchlorate solution gave a potential of 358.7 mV versus S.C.E. When 1.00 mL of 0.050 M $NaClO_4$ was added, the potential changed to 346.1 mV. Assuming that the electrode has a Nernst response, find [ClO_4^-] in the unknown.