

Chapter 15  
Electrodes and Potentiometry

Ag/AgCl reference electrode

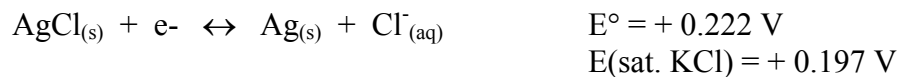


Figure 15.3

Standard Calomel Electrode (SCE)

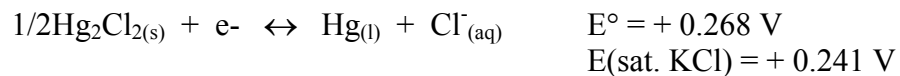


Fig. 15-5

Indicator electrodes

Ag, Cu, Zn, Cd, Hg

Most metals are unsuitable (irreversible reduction on metal surface)

Cu indicator electrode

Anode - Ag/AgCl reference electrode

Cathode -  $\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu}_{(s)}$

$$E = E_+ - E_- = \{0.339 - 0.05916/2 \log(1/[Cu^{2+}])\} - \{0.241\}$$

$$E = 0.098 + 0.02958 \log [Cu^{2+}] \text{ or}$$

$$E \text{ (in mV)} = 98 + 29.58 \log[Cu^{2+}]$$

Measure E for a series of standard  $CuNO_3$  solutions and plot E vs.  $\log[Cu^{2+}]$

Slope = 29.58 mV

Intercept = 98 mV

### Junction potential

Any time two dissimilar electrolytes are in contact a potential difference arises at their interface (usually in the 1-5 mV range).

Ion mobility (diffusion in water) - Table 15.1 and 15.2

The junction potential places a fundamental limit on the accuracy of a potentiometric measurement

### 15.14

Table 15-1 (ion mobilities)

$Na^+$	$5.19 \cdot 10^{-8}$
$H^+$	$36.30 \cdot 10^{-8}$
$K^+$	$7.62 \cdot 10^{-8}$

The junction potential develops as a result of differences in ion mobility, and it is proportional to the magnitude and sign of the difference. The difference in ion mobility between  $H^+$  and  $K^+$  is  $28.68 \cdot 10^{-8}$ , and the difference in ion mobility between  $Na^+$  and  $K^+$  is  $-2.43 \cdot 10^{-8}$ .

### 15.15

The difference in ion mobility between  $Cl^-$  and  $NO_3^-$  is  $0.51 \cdot 10^{-8}$ , and the difference in ion mobility between  $Na^+$  and  $K^+$  is  $-2.43 \cdot 10^{-8}$ . Since  $Na^+/K^+$  has the largest difference, it should be used to determine which side of the junction potential is negative.  $K^+$  has the larger ion mobility, and, therefore, the  $KNO_3$  side of the junction will be negatively charged. However, it should be noted that the  $Cl^-/NO_3^-$  mobilities also cause a build up of negative charge on the  $KNO_3$  side of the junction.

## Ion-Selective Electrodes

(Let the junction potential work for you!!!!)

An analyte sensitive membrane between two reference electrodes

Fig 15-8

Entropy of dilution – species will naturally diffuse from region of high concentration to lower concentration

Free energy change from concentration gradient =  $-RT\ln(\mathcal{A}_m/\mathcal{A}_{sol})$

Free Energy of solvation =  $\Delta G_{solv}$

However, with a charged analyte and a selective membrane, an imbalance in the charges will develop.

Free Energy change from the separation of charge =  $-nFE$

These are opposing forces, and at equilibrium they balance.

$$\Delta G_{solv} - RT\ln(\mathcal{A}_m/\mathcal{A}_{sol}) = -nFE_{j.p.}$$

$$E_{j.p.} = \Delta G_{solv}/nF - RT/nF \ln(\mathcal{A}_m/\mathcal{A}_{sol})$$

$$E_{j.p.} = \Delta G_{solv}/nF - RT/nF \ln(\mathcal{A}_m) + RT/nF \ln(\mathcal{A}_{sol})$$

$$E_{j.p.} = \text{constant1} + RT/nF \ln(\mathcal{A}_{sol})$$

$$E_{cell} = E_+ - E_- + \text{constant1} + RT/nF \ln(\mathcal{A}_{sol}) - \{\text{constant2} + RT/nF \ln(\mathcal{A}_{inner})\} + j.p.2$$

j.p.2 is from the salt bridge

$$E_{cell} = \text{const} + RT/nF \ln(\mathcal{A}_{inner})$$

## Glass Electrode and the pH meter

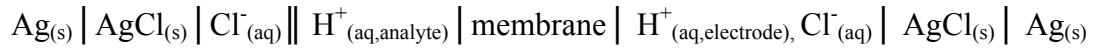


Fig 15-9

Fig 15-13

Charge imbalance on opposite sides of the glass electrode drives  $\text{Na}^+$  migration, creating a potential difference

$$E = \text{constant} + \beta 0.05916 \log(\mathcal{A}_{\text{H}^+(\text{analyte})})$$

### Errors in pH measurement (pg 329)

- 1 Accuracy of stds ( $\pm 0.01$ )
- 2 Junction potential at porous plug ( $\pm 0.01$ )
- 3 J.p. drift (recalibrate every 2 hrs)
- 4 Sodium error (high pH)
- 5 Acid error (membrane saturation)
- 6 Equilibration time (30 s with stirring) or many minutes
- 7 Hydration of glass (several hrs)
- 8 Temperature

Selectivity Coefficient –  $k_{A,X} = (\text{response to A})/(\text{response to X})$

An electrode that measures the activity of A also responds to X. The selectivity coefficient gives the relative response. The glass electrode is very selective,  $\text{Na}^+$  is the ion that interferes to the greatest extent, and  $k_{\text{H}^+,\text{Na}^+}$  is only about  $\approx 10^{-10}$ .

$$E = \text{constant} + \beta 0.05916 \log[\mathcal{A}_{\text{H}^+} + k_{\text{H}^+,\text{Na}^+} \mathcal{A}_{\text{Na}^+}]$$

$\text{Na}^+$  ion selective electrode (glass membrane)

$$K_{\text{Na}^+,\text{K}^+} = 3.6 \times 10^{-4}$$

$$K_{\text{Na}^+,\text{H}^+} = 36$$

$$E = \text{constant} + \beta 0.05916 \log[\mathcal{A}_{\text{Na}^+} + 36 \mathcal{A}_{\text{H}^+}]$$

$\text{K}^+$  ion selective electrode that uses valinomycin as a chelator

$$k_{\text{K}^+,\text{Na}^+} = 1 \times 10^{-5}$$

$$k_{\text{K}^+,\text{Cs}^+} = 0.44$$

$$k_{\text{K}^+,\text{Rb}^+} = 2.8$$

$$E = \text{constant} + \beta 0.05916 \log[\mathcal{A}_{\text{K}^+} + 0.44 \mathcal{A}_{\text{Cs}^+}]$$

Response of an ion-selective electrode

For positive ions,  $\text{X}^{n+}$

$$E = \text{constant} + \beta (59.16/n) \log[\mathcal{A}_{\text{X}^{n+}}]$$

For negative ions,  $\text{Y}^{n-}$

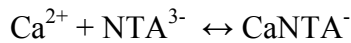
$$E = \text{constant} - \beta (59.16/n) \log[\mathcal{A}_{\text{Y}^{n-}}]$$

## Recent Breakthrough in sensitivity of liquid-based ion sensitive electrodes

Typical detection limits for ion-selective electrode are  $10^{-6}$  M ( $\mu$ M range)  
This limitation is due to leakage of the analyte ion from the internal filling solution across the membrane to the interface between the analyte and the membrane. If the filling solution contains a high concentration of analyte, this surface concentration is in the  $\mu$ M range.

However, using a dilute filling solution consisting of a metal ion buffer, dramatically reduces the surface concentration that derives from leakage. As a result, the detection limit decreases down to the pM range.

Metal ion buffer



$$K_f = [\text{CaNTA}^{-}] / [\text{Ca}^{2+}][\text{NTA}^{3-}] = 2.9 \times 10^6$$

Make a metal buffer solution that contains 0.100 M  $\text{CaNTA}^{-}$  and 0.100  $\text{NTA}^{3-}$ .

$$[\text{Ca}^{2+}] = [\text{CaNTA}^{-}] / [\text{NTA}^{3-}] K_f = 3.5 \times 10^{-7} \text{ M}$$

This metal ion buffer effectively maintains a constant  $[\text{Ca}^{2+}]$  of the filling solution.

Chapter 16  
Redox Titrations