Chapter 23 Problems (2, 4, 7, 13, 14)

2. The source of the alkaline error in pH measurements with the glass electrode comes from exchange of Na^+ ions in the membrane surface with H^+ from the water. Essentially, the electrode starts to respond to Na^+ as its activity would be very high compared to H^+ at pH ≥ 13.

4. A thin region of the membrane becomes hydrated with water and exchanges H^+ with the external solution. The equilibrium constant for this process is very large

$$H^+_{soln} + Na^+Gl^-_{glass} \rightleftharpoons Na^+_{soln} + H^+Gl^-_{glass}$$

This must occur for the membrane/electrode to respond to H^+

7. a. asymmetry potential → difference in membrane potential when identical solutions are placed on both sides of the membrane. Likely due to physical differences in properties on both sides of membrane

b. a boundary potential → the potential difference that arises from differences in H^+ ion activity on either side of the membrane

$$E_{mis} = E_b + E_{asy}$$ very small

c. a junction potential → arises from unequal distribution of cations and anions across a boundary/membrane due to differences in the rates at which these species diffuse. Occurs at salt bridge that connects analyte solution from outer reference electrode.

d. potential of a crystalline membrane used to measure F^- → arises from the degree of dissociation of a LaF_3 membrane with F^- solutions on either side

$$LaF_3 \rightleftharpoons LaF_2^+ + F^-$$

equilibrium on inner and outer side of membrane!

13. anode = SCE ref. Electrode

$$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^- \quad E^\circ = 0.268V$$

a.

cathode = $E = 0.771 + \frac{0.0592}{1} \log \frac{0.0250}{0.0450} = 0.784V$

$$Fe^{+3} + e^- \rightleftharpoons Fe^{+2} \quad E^\circ = 0.771V$$

$E_{cell} = E_c - E_a = 0.784 - 0.268 = \underline{\underline{0.498V}}$

Pt is an inert indicator electrode that responds to both Fe^{+3} & Fe^{+2}

b. anode = SCE ref. Electrode

$$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^- \quad E^\circ = 0.268V$$

cathode = $Zn^{+2} + 2e^- \rightleftharpoons Zn \quad E^\circ = -0.763V$

$E = -0.763V + \frac{0.0592}{2} \log \frac{(2.28\times10^{-3})}{1} = -0.841V$

$E_{cell} = E_c - E_a = -0.841V - 0.268V = \underline{\underline{-1.11V}}$

c. anode Sat'd Ag/AgCl ref

$AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^- \quad E^\circ$ (satd KCl) $\Rightarrow$ 4 M KCl

$E = 0.222 + \frac{0.0592}{1} \log \frac{1}{[4]} = \underline{0.186V}$

cathode = $Ti^{+3} + e^- \rightleftharpoons Ti^{+2} \quad E^\circ = -0.369V$

$E = -0.369 + \frac{0.0592}{1} \log \frac{(0.0250)}{(0.0450)} = -0.384V$

$E_{cell} = -0.384V - 0.186V = \underline{\underline{-0.570V}}$

Pt is inert indicator electrode that responds to both Ti^{+3} and Ti^{+2}

d. anode $\Rightarrow$ Ag/AgCl ref.

$E^\circ_{satd} = -0.186V$

cathode $\Rightarrow$ $\quad E^\circ = 0.536V$

$$I_3^- + 2e^- \rightleftharpoons 3I^-$$

$$E = 0.536\,V + \frac{0.0592}{2} \log \frac{I_3^-}{[I^-]^3} = 0.536\,V + \frac{0.0592}{2} \log \frac{(0.00667)}{(0.00433)^3}$$

$$= 0.681\,V$$

$$E_{cell} = 0.681 - 0.186 = \underline{\underline{0.495\,V}}$$

(14)

a. shorthand notation for the cell would be:

$SCE\,//\,CuBr_{(sat'd)},\, Br^-_{(aq)}\,(xM)\,/\,Cu$

b. $Cu^{\cancel{+2}} + \cancel{e}^- \rightleftharpoons Cu_{(s)} \quad E^\circ = 0.521\,V$

$CuBr \rightleftharpoons Cu^+ + Br^- \qquad K_{sp} = [Cu^+][Br^-] = 5.2\times10^{-9}$

$$E = 0.521 + \frac{0.0592}{1} \log \frac{[Cu^+]}{1} \qquad [Cu^+] = \frac{K_{sp}}{[Br^-]}$$

$$E = 0.521 + \frac{0.0592}{1} \log \frac{K_{sp}}{[Br^-]}$$

when $[Br^-] = 1M$ then $E = E^\circ_{CuBr}$

$$E^\circ_{CuBr} = 0.521 + \frac{0.0592}{1} \log \frac{K_{sp}}{[Br^-]} = 0.521 + \frac{0.0592}{1} \log \frac{5.2\times10^{-9}}{1}$$

$$E^\circ_{CuBr} = \underline{\underline{0.031\,V}}$$

c. $E_{cell} = E_c - E_a = E_{right} - E_{left}$

$$E_{right} = E_c = E_{CuBr} + \frac{0.0592}{1} \log \frac{1}{[Br^-]}$$

$$= E^\circ_{CuBr} - 0.0592 \log [Br^-]$$

$pBr = -\log [Br^-]$

$E_c = E^0_{CuBr} + 0.0592\, pBr$

SCE E^0 value

$E_{cell} = E_c - E_A = (E^0_{CuBr} + 0.0592\, pBr) - 0.244$

rearrange the equation and solve for pBr

$E_{cell} - E^0_{CuBr} + 0.244 = 0.0592\, pBr$

$E_{cell} - 0.031 + 0.244 = 0.0592\, pBr$

$$\frac{E_{cell} + 0.213}{0.0592} = pBr$$

d. $E_{cell} = -0.095V$

$$\frac{E_{cell} + 0.213}{0.0592} = pBr = \frac{-0.095 + 0.213}{0.0592} = pBr$$

$pBr = 1.99$

$[Br^-] = 10^{-pBr} = 1.02 \times 10^{-2} M$