Chapter 14 Electrodes and Potentiometry

14-1, 14-3, 14-6, 14-8, 14-9, 14-14, 14-15, 14-18, 14-26, 14-33, 14-34, 14-35, 14-36, 14-38, 14-40

14-1

a)

Silver-silver chloride electrode

$$AgCl_{(s)} + e^- \leftrightarrow Ag_{(s)} + Cl^-$$

Calomel electrode

$$1/2Hg_2Cl_{2(s)} + e^- \leftrightarrow Hg_{(l)} + Cl^-$$

b)

$$Ecell = E_+ - E_- = E^0_+ - E^0_- - 0.05916/n(\log\{[Cl^-]/[Cl^-]\})$$
$$= 0.241 - 0.197 = 0.044\ V$$

The concentration of $[Cl^-]$ in both cells is controlled by KCl saturation. Thus, $[Cl^-]_{SCE} = [Cl^-]_{Ag\text{-}AgCl}$ and the log term goes to zero.

14-3

$$Ecell(Ag/AgCl) = \{0.771 - 0.05916 \log[Fe^{+2}]/[Fe^{+3}])\} - 0.197$$

$$Ecell(SCE) = \{0.771 - 0.05916 \log[Fe^{+2}]/[Fe^{+3}])\} - 0.241$$
$$= \{0.771 - 0.05916 \log(2.5*10^{-3})\} - 0.241$$
$$= 0.684\ V$$

14.5

$E_{(Ag/AgCl\ ref)} = E^0_{(Ag/AgCl)} - 0.05916 \log [\mathscr{A}_{Cl-}]_{sat}$

$0.197 = 0.222 - 0.05916 \log [\mathscr{A}_{Cl-}]_{sat}$

$[\mathscr{A}_{Cl-}]_{sat} = 10^{(-(.197-.222)/.05916)} = 2.65\ M$

$E_{(Hg/Hg2Cl2\ ref)} = E^0_{(Hg/Hg2Cl2)} - 0.05916 \log [\mathscr{A}_{Cl-}]_{sat}$

$E_{(Hg/Hg2Cl2\ ref)} = 0.268 - 0.05916 \log (2.65) = 0.243\ V$

14.6

$Cu^{+2} + 2e- \leftrightarrow Cu(s)$ reduction

$E_+ = E^0_+ - (0.05916/2)\log(1/[Cu^{+2}])$

$E = E_+ - E_- = \{E^0_+ - (0.05916/2)\log(1/[Cu^{+2}])\} - 0.241\ V$

$= \{0.339 - (0.05916/2)\log(1/0.10)\} - 0.241\ V$

$= 0.068\ V$

14.8

reduction

$Ag^+ + e- \leftrightarrow Ag(s)$ $E^0 = 0.7993\ V$

$Ecell = \{0.7993 – 0.05916 \log(1/[Ag^+])\} – 0.241\ V$

As NaBr is added, the Br^- will form a precipitate with Ag^+, changing the $[Ag^+]$ and thus changing the cell voltage.

$Ksp(AgBr) = 5.0 \cdot 10^{-13} = [Ag^+][Br^-]$

At 0.1 mL added:

(0.1 mL)(0.025M) = 0.0015 mmol Ag^+ consumed

$[Ag^+]$ = {(10.0 mL)(0.0500) – (0.10 mL)(.025)}/(10.1 mL)
= $4.93*10^{-2}$ M

Ecell = {0.7993 – 0.05916 log(1/0.0493)} – 0.241 V
= 0.481 V

At 10.0 mL added:

$[Ag^+]$ = {(10.0 mL)(0.0500) – (10.0 mL)(.025)}/(20.0 mL)
= $1.25*10^{-2}$ M

Ecell = {0.7993 – 0.05916 log(1/0.0125)} – 0.241 V
= 0.446 V

At 20.0 mL added:

We have reached the equivalence point

(20 mL)(0.025M) = 0.5 mmol Ag^+ consumed

Ksp(AgBr) = $5.0*10^{-13} = [Ag^+][Br^-] = [Ag^+]^2$

$[Ag^+] = 7.1*10^{-7}$ M

Ecell = {0.7993 – 0.05916 log(1/($7.1*10^{-7}$))} – 0.241 V = 0.194 V

At 30.0 mL added:

We have excess Br^-

(10 mL)(0.025M) = 0.25 mmol excess Br^- consumed

[Br-] = (0.25 mmol)/(40 mL) = $6.25*10^{-3}$ M

Ksp(AgBr) = $5.0*10^{-13} = [Ag^+][Br^-] = [Ag^+](6.25*10^{-3})$

$[Ag^+] = 8.0*10^{-11}$ M

Ecell = {0.7993 – 0.05916 log(1/($8.0*10^{-11}$))} – 0.241 V
= -0.039 V

15-9 (from 7^{th} Ed.)

Ksp(AgCl) = $1.8*10^{-10}$
Ksp(AgI) = $8.3*10^{-17}$
AgCl is much more soluble than AgI. Therefore, the AgI will precipitate first followed by the precipitation of the AgCl. See titration curve below problem. Another way of stating this is that until we get past the first equivalence point the product [Ag^+] and [Cl^-] are too low to precipitate any AgCl.

As a result, the Ag^+ concentration will depend upon the solubility of AgI from 0 to 50 ml.

a)
At 25 mL added:

[I^-] = (mmol I^- initial – mmol Ag^+ added)/total volume
= (25.0*0.200-25*0.1)/75.0 = 0.0333 M

[Ag^+] = Ksp_I/(0.0333)

b)
From 50-125 ml [Ag^+] can be calculated using the Ksp for AgCl or AgI, but using Ksp(AgCl) is advantageous because we calculate the [Cl^-] fairly easily.

At 75.0 ml added

[Cl^-] = (mmol Cl^- initial – mmol Ag^+ added after 1^{st} eq. pt.)/total volume
= (25.0*0.200-25.0*0.10)/125.0 = 0.0200 M

[Ag^+] = Ksp_{Cl}/(0.0200)

c)

$$Ecell = \{0.7993 – 0.05916 \log(1/[Ag^+])\} – 0.241\ V$$

d)

$$Ecell = \{0.7993 – 0.05916 \log([Cl^-]/Ksp_{Cl}\} – 0.241\ V$$
$$= \{0.7993 – 0.05916 \log([I^-]/Ksp_I\} – 0.241\ V$$

halfway to the first eq. Pt.:

$$Ecell_{1/2\ 1st\ eq} = \{0.7993 – 0.05916 \log(0.0333/Ksp_I\} – 0.241\ V$$

halfway to the 2nd eq. Pt.:

$$Ecell_{1/2\ 2cd\ eq} = \{0.7993 – 0.05916 \log(0.0200/Ksp_{Cl}\} – 0.241\ V$$

You should be able to convince yourself that as the titration proceeds, the Ecell becomes more and more positive, because $[I^-]/Ksp$ becomes smaller and smaller as the I^- is titrated. Therefore,

$$\Delta E = 0.388\ V = Ecell_{1/2\ 2cd\ eq} - Ecell_{1/2\ 1st\ eq}$$
$$= 0.05916 \log(0.0333/Ksp_I\} - 0.05916 \log(0.0200/Ksp_{Cl}\}$$
$$= 0.05916 \log(0.0333Ksp_{Cl}/0.0200Ksp_I)$$

$$10^{(0.338)/(0.05916)} = 1.67Ksp_{Cl}/Ksp_I$$

$$Ksp_{Cl}/Ksp_I = (1/1.67)(10^{(0.338)/(0.05916)})$$
$$= 2.2*10^6$$

14.13

Table 15-1 (ion mobilities)

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

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 $28.68*10^{-8}$, and the difference in ion mobility between Na^+ and K^+ is $–2.43*10^{-8}$.

14.14

The difference in ion mobility between Cl^- and NO_3^- is $0.51*10^{-8}$, and the difference in ion mobility between Na^+ and K^+ is $–2.43*10^{-8}$. 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.

14.17

Both half cells consist of the standard Ag/AgCl reference cell.

$$E_+ = E_+{}^0{}_{(Ag+)} - 0.05916 \log\{1/[Ag^+]\}$$
$$E_+ = E_+{}^0{}_{(Ag+)} - 0.05916 \log\{[Cl^-]/Ksp_{AgCl}\}$$

$$E_- = E_-{}^0{}_{(Ag+)} - 0.05916 \log\{1/[Ag^+]\}$$
$$E_- = E_-{}^0{}_{(Ag+)} - 0.05916 \log\{[Cl^-]/Ksp\}$$

$$Ecell = \Delta E^0 - 0.05916 \log\{[Cl^-]_+/[Cl^-]_-\} + \text{junction potential}$$

Because the $[Cl^-]$ is controlled by the Ksp of AgCl for both cells, $[Cl^-]_+ = [Cl^-]_-$, and the equation above reduces to

Ecell = junction potential

14.25

a)

ΔpH = 4.63

assume

$\beta = 0.98$

The formula, ΔpH*59.16 = cell voltage (in mV), is given in the book. Here is the derivation of this formula with the inclusion of the β factor. Let n = pH on the inside of the membrane.

$$E_{cell} = \text{constant} + 0.05916\beta\log(10^{-n}/10^{-(n+4.63)})$$
$$E_{cell} = \text{constant} + 0.05916\beta\log(10^{-n+(n+4.63)})$$
$$E_{cell} = \text{constant} + 0.05916\beta\log(10^{4.63})$$
$$E_{cell} = \text{constant} + (0.05916)(4.63)\beta\log(10)$$

Therefore,

The voltage generated by pH gradient = (0.05916)(4.63)β

If $\beta = 1.00$, then voltage = 274 mV

b)

RT/F = 0.05916 at 298 K

RT/F = 0.06154 at 312 K

voltage generated by pH gradient = (0.06154) β (4.63)

If $\beta = 1.00$, then voltage = 285 mV

14.29

The selectivity coefficient gives the sensitivity of our analyte relative to a potential interference. The lower the selectivity coefficient, the higher the selectivity for our analyte, which means that are sample can contain a higher relative concentration of the other ionic species without interfering with the analysis of our analyte.

14.31

A metal ion buffer is a high resistance to changes in the metal ion concentration (similar to an acid base buffer; high concentrations of a weak acid and its conjugate base maintains a constant $[H^+]$). Just as a dilute solution of strong acid is not very resistant to pH change, a dilute solution of a metal ion is not very resistant to changes in pM^+.

14.33

a)

$-0.230 = C - 0.05916\log[CN^-]$

$C = -0.230 + 0.05916\log(10^{-3}) = -0.407\ V$

b)

$-0.300 = -0.407 – 0.05916\log[CN-]$

$[CN^-] = 10^{-(-0.300+0.407)/0.05916} = 0.016\ M$

c)

$E = C - 0.05916\log[CN^-]$

We can write two separate equations that contain two unknowns. Solve the equations simultaneously. I chose to subtract them to remove C.

$-0.230 = C - 0.05916\log(10^{-3})$

$- \quad -0.300 = C - 0.05916\log[CN^-]$

$(-0.230 + 0.300) = \{-0.05916\log(10^{-3}) + 0.05916\log[CN^-] \}$

$0.070 = 0.05916 \{\log[CN^-] + 3\log(10)\}$

$0.070/0.05916 = \log[CN^-] + 3$

$[CN^-] = 10^{(0.070/0.05916) - 3}$

$= 0.015\ M$

14.34

$$E = C + \beta(0.05916/2)\log[Mg^{2+}]$$

We can write two separate equations that contain two unknowns. Solve the equations simultaneously. I chose to subtract them to remove C.

$$E_1 = C + \beta(0.05916/2)\log(1.00*10^{-4})$$
$$E_2 = C + \beta(0.05916/2)\log(1.00*10^{-3})$$

$$\Delta E = \beta(0.05916/2)\log(1.00*10^{-4}/1.00*10^{-3})$$
$$= \beta(0.05916/2)\log(10)$$

assuming $\beta = 1.00$

$$= 0.05916/2 \text{ or } 29.6\ mV$$

14.35

We can write two separate equations that contain two unknowns. Solve the equations simultaneously. I chose to subtract them to remove C.

$$E_{Fox} = C - \beta(0.05916)\log([F^-]_{Fox})$$
$$E_{Prov} = C - \beta(0.05916)\log([F^-]_{Prov})$$

$$\Delta E = \{-\beta(0.05916)\log([F^-]_{Fox})\} - \{-\beta(0.05916)\log([F^-]_{Prov})\}$$
$$0.0400 = \beta(0.05916)\log([F^-]_{Prov}) - \beta(0.05916)\log([F^-]_{Fox})$$
$$0.0400 = \beta(0.05916)\log([F^-]_{Prov}/[F^-]_{Fox})$$

assuming $\beta = 1.00$:

$$10^{(0.0400)/(0.05916)} = (1.00\ mg/L)/[F^-]_{Fox}$$

$$[F^-]_{Fox} = 10^{-(0.0400)/(0.05916)} = 0.211\ mg/L$$

14.36

Of the Group 1 metals K^+ causes the most interference

Of the Group 2 metals Sr^{2+} and Ba^{2+} cause the most interference

The $\log(K_{K+/Li+}) = -2$. The $[K^+]$ would have to be 100 times the $[Li^+]$ to give equal responses.

14.38

I did not worry about using activity. The methods we used to calculate the activity coefficient do not work well at an ionic strength of 2.0 M, anyway.

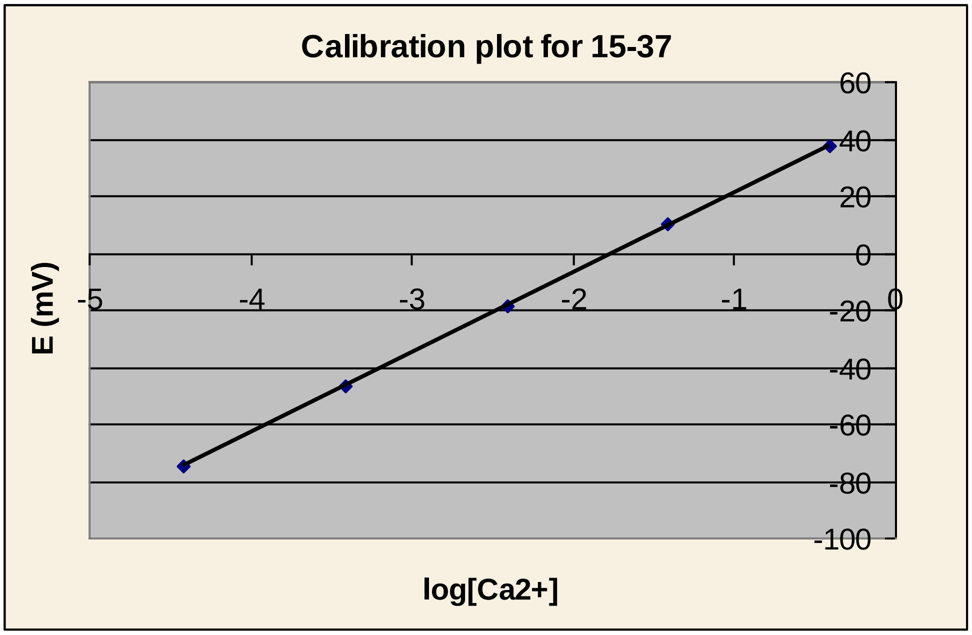
$E = C + (59.16/2)\beta\log[Ca^{+2}]$

plot $\log[Ca^{+2}]$ vs E

Using "Inset, Function, log" you can have excel calculate $\log[Ca^{+2}]$.

Using "Insert, Function, slope", you can chose the x column and the y column and excel will calculate the slope of the plot.

Using "Insert, Function, intercept", you can chose the x column and the y column and excel will calculate the slope of the plot.



b)
We would expect slope to be $(59.16/2)\beta = (29.58\text{ mV})\beta$. The slope of our plot (from Excel) = 28.06 mV.
So, $\beta = 0.949$

The intercept = C = 50.81 mV

c)

$$E = 50.81 + 28.06 \log[Ca^{+2}]$$

$$-22.5 = 50.81 + 28.06 \log[Ca^{+2}]$$

$$[Ca^{+2}] = 10^{((-22.5-50.81)/28.06)} = 2.44*10^{-3}\text{ M}$$

14.39

$$E = C + 59.16 \log([Li^{+2}] + k_{Li/H+}[H^{+}])$$

(Where E is in units of mV)
At pH 7.2

$E = -0.333\text{ V} = -333\text{ mV}$

$[Li^{+}] = 3.44*10^{-4}\text{ M}$

$[H^+] = 6.31*10^{-8}$ M
$E_{7.2} = C + 59.16\log\{3.44*10^{-4} + (4*10^{-4})(6.3*10^{-8})\}$
The contribution from H^+ is negligible at this pH
$-333 = C + 59.16\log(3.44*10^{-4})$
C = -128 mV

At pH 1.1
$[H^+] = 7.94*10^{-2}$ M
$E_{1.1} = -128 \text{ mV} + 59.16\log(3.44*10^{-4} + 4*10^{-4}*7.94*10^{-2})$
The contribution from H^+ is not negligible at pH = 1.1
$E_{1.1} = -331$ mV

14.44
$E = \text{intercept} + \text{slope} \log\{[Ca^{2+}] + k_{Ca2+,Mg2+}[Mg^{2+}]\}$

We can calculate the slope and intercept using the first two points, where $[Mg^{2+}] = 0$

$\text{Slope} = (-52.6-16.1)/(\log(1.00\cdot10^{-6})-\log(2.43\cdot10^{-4}) = 28.798$
Intercept = 120.2

Use the slope and intercept and the third point to determine $k_{Ca2+,Mg2+}$.

$10^{\{(-38.0-120)/28.798\}} = 1.00\cdot10^{-6} + k_{Ca2+,Mg2+}(3.68\cdot10^{-6})$
$k_{Ca2+,Mg2+} = (10^{\{(-38.0-120)/28.798\}} - 1.00\cdot10^{-6})/ 3.68\cdot10^{-6}$
$k_{Ca2+,Mg2+} = 6.015\cdot10^{-4}$

14.45

This is from Chapter 13, the one that we skipped.

Pb^{2+} + EDTA $\leftrightarrow$ PbY^{2-}
The equilibrium constant for this reaction is the conditional formation constant, $Kf`_{(Pb2+\ @\ pH=4.34)}$

$Kf`_{(Pb2+\ @\ pH=4.34)} = Kf_{(Pb2+)}\ \alpha_{Y4-} = (10^{18})(1.46\cdot10^{-8}) = 1.46\cdot10^{10}$

$Kf`_{(Pb2+\ @\ pH=4.34)} = 1.46\cdot10^{10} = [PbY^{2-}]/[Pb^{2+}][EDTA]$

$[Pb^{2+}]_0 = (1.0\ mL)(0.10)/(1.0 + 100\ mL) = 0.00099\ M$

$[EDTA]_0 = (100.0\ mL)(0.050)/(1.0 + 100\ mL) = 0.0495\ M$

$[Pb^{2+}]_{eq} = 0.0009900990099 - x$

$[EDTA]_{eq} = 0.0495 – x$

$[PbY^{2-}] = x$

$Kf`_{(Pb2+\ @\ pH=4.34)} = 1.46\cdot10^{10} = x/\{(9.900990099\cdot10^{-4}-x)(.0495-x)$
Solve for x
$x = 9.900990085\cdot10^{-4}\ M$

$[Pb^{2+}]_{eq} = 9.900990099\cdot10^{-4} - x$
$= 1.4\cdot10^{-12}\ M$

15.44 (7th Ed)

$K = 10^{6.54} = [Pb(C_2O_4)_2^{2-}]/[Pb^{2+}][C_2O_4^{2-}]^2$

$[Pb^{2+}]_0 = (0.100 \text{ mmol})/(10.00 \text{ mL}) = 0.0100 \text{ M}$

$[C_2O_4^{2-}]_0 = (2.00 \text{ mmol})/(10.00 \text{ mL}) = 0.200 \text{ M}$

$[Pb^{2+}]_{eq} = 0.0100 - x$

$[C_2O_4^{2-}]_{eq} = 0.200 – 2x$

$[PbY^{2-}] = x$

$K = 10^{6.54} = x/\{(0.0100-x)(0.200-2x)$
Solve for x
$x = 9.99911 \cdot 10^{-3}$ M

$[Pb^{2+}]_{eq} = 1.00 \cdot 10^{-2} - x$
$=8.9 \cdot 10^{-8}$ M

b)
To make a buffer at $1.00 \cdot 10^{-7}$ M

Let $x = [C_2O_4^{2-}]_0$

$K = 10^{6.54} = (0.0100-1.00 \cdot 10^{-7})/\{(1.00 \cdot 10^{-7})(x)^2\}$

X = 0.16982 M, which corresponds to adding 1.7 mmol of $C_2O_4^{2-}$.