CHAPTER 14
ELECTRODES AND POTENTIOMETRY

14-1. (a) $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$

$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$

(b) $E = E_+ - E_- = 0.241 - 0.197 = 0.044$ V

14-2. (a) 0.326 V (b) 0.086 V (c) 0.019 V (d) –0.021 V (e) 0.021 V

14-3. $E = E_+ - E_-$

$$E = \left\{0.771 - 0.059\,16 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}\right\} - (0.241) = 0.684 \text{ V}$$

14-4. $E = E^\circ - 0.059\,16 \log \mathcal{A}_{Cl^-}$

$0.280 = 0.268 - 0.059\,16 \log \mathcal{A}_{Cl^-} \Rightarrow \mathcal{A}_{Cl^-} = 0.627$

14-5. For the saturated Ag-AgCl electrode, we can write: $E = E^\circ - 0.059\,16 \log \mathcal{A}_{Cl^-}$. Putting in $E = 0.197$ and $E^\circ = 0.222$ V gives $\mathcal{A}_{Cl^-} = 2.6_5$. For the S.C.E., we can write: $E = E^\circ - 0.059\,16 \log \mathcal{A}_{Cl^-} = 0.268 \text{ V} - 0.059\,16 \log 2.6_5$ $= 0.243$ V.

14-6. (a) $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ $\qquad E^\circ = 0.339$ V

(b) $$E_+ = 0.339 - \frac{0.059\,16}{2} \log \frac{1}{[Cu^{2+}]} = 0.309 \text{ V}$$

(c) $E = E_+ - E_- = 0.309 - 0.241 = 0.068$ V

14-7. A silver electrode serves as an indicator for Ag^+ by virtue of the equilibrium $Ag^+ + e^- \rightleftharpoons Ag(s)$ that occurs at its surface. If the solution is saturated with silver halide, then $[Ag^+]$ is affected by changes in halide concentration. Therefore, the electrode is also an indicator for halide.

14-8. $V_e = 20.0$ mL. $Ag^+ + e^- \rightleftharpoons Ag(s) \Rightarrow E_+ = 0.799 - 0.059\,16 \log \dfrac{1}{[Ag^+]}$

0.1 mL: $$[Ag^+] = \underbrace{\left(\frac{19.9}{20.0}\right)}_{\substack{\text{Fraction} \\ \text{remaining}}} \underbrace{(0.050\,0 \text{ M})}_{\substack{\text{Original} \\ \text{concentration}}} \underbrace{\left(\frac{10.0}{10.1}\right)}_{\substack{\text{Dilution} \\ \text{factor}}} = 0.049\,3 \text{ M}$$

$$E = E_+ - E_- = \left\{0.799 - 0.059\,16 \log \frac{1}{0.049\,3}\right\} - 0.241 = 0.481 \text{ V}$$

30.0 mL: This is 10.0 mL past V_e $\Rightarrow$ $[Br^-] = \left(\frac{10.0}{40.0}\right)(0.025\,0\text{ M}) = 0.006\,25\text{ M}$

$$[Ag^+] = K_{sp}/[Br^-] = (5.0 \times 10^{-13})/0.006\,25 = 8.0 \times 10^{-11}\text{ M}$$

$$E = E_+ - E_- = \left\{0.799 - 0.059\,16 \log \frac{1}{8.0 \times 10^{-11}}\right\} - 0.241 = -0.039\text{ V}.$$

14-9. The reaction in the right half-cell is $Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$

$$E = E_+ - E_-$$

$$-0.027 = 0.852 - \frac{0.059\,16}{2} \log \frac{1}{[Hg^{2+}]} - (0.241)$$

$$\Rightarrow [Hg^{2+}] = 2.7 \times 10^{-22}\text{ M}.$$

The cell contains 5.00 mmol EDTA (in all forms) and 1.00 mmol Hg(II) in 100 mL. 1.00 mmol EDTA reacts with 1.00 mmol Hg(II), leaving 4.00 mmol EDTA.

$$K_f = \frac{[HgY^{2-}]}{[Hg^{2+}][Y^{4-}]} = \frac{[HgY^{2-}]}{[Hg^{2+}]\alpha_{Y4-}[EDTA]}$$

$$K_f = \frac{(1.00\text{ mmol}/100\text{ mL})}{(2.7 \times 10^{-22})(0.30)(4.00\text{ mmol}/100\text{ mL})} = 3.1 \times 10^{21}$$

14-10. (a) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\qquad E^\circ = 0.771\text{ V}$

(b) $E = E_+ - E_-$

$$-0.126 = 0.771 - 0.059\,16 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.241 \Rightarrow \frac{[Fe^{2+}]}{[Fe^{3+}]} = 1.2 \times 10^{11}$$

(c) $$\frac{K_f(FeEDTA^-)}{K_f(FeEDTA^{2-})} = \frac{[FeEDTA^-]}{[Fe^{3+}][EDTA^{4-}]} \div \frac{[FeEDTA^{2-}]}{[Fe^{2+}][EDTA^{4-}]}$$

$$= \frac{[FeEDTA^-]}{[FeEDTA^{2-}]} \cdot \frac{[Fe^{2+}]}{[Fe^{3+}]} = \left(\frac{1.00 \times 10^{-3}}{2.00 \times 10^{-3}}\right)(1.2 \times 10^{11}) = 6 \times 10^{10}$$

14-11. $$E = E_+ - E_- = -0.429 - 0.059\,16 \log \frac{[CN^-]^2}{[Cu(CN)_2^-]} - 0.197$$

Putting in $E = -0.440$ V and $[Cu(CN)_2^-] = 1.00$ mM gives $[CN^-] = 0.847$ mM.

$$pH = pK_a(HCN) + \log \frac{[CN^-]}{[HCN]} = 9.21 + \log \frac{8.47 \times 10^{-4}}{1.00 \times 10^{-3} - 8.47 \times 10^{-4}} = 9.95_4$$

Now we use the pH to see how much HA reacted with KOH:

	HA	+	OH^-	$\rightarrow$	A^-	+	H_2O
initial mmol	10.0		x		—		
final mmol	$10.0 - x$		—		x		

$$\text{pH} = \text{p}K_a(\text{HA}) + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$9.95_4 = 9.50 + \log \frac{x}{10.0 - x} \Rightarrow x = 7.4_0 \text{ mmol of } \text{OH}^-$$

$$[\text{KOH}] = \frac{7.4_0 \text{ mmol}}{25.0 \text{ mL}} = 0.29_6 \text{ M}$$

14-12. Junction potential arises because different ions diffuse at different rates across a liquid junction, leading to a separation of charge. The resulting electric field retards fast-moving ions and accelerates the slow-moving ions until a steady-state junction potential is reached. This limits the accuracy of a potentiometric measurement, because we do not know what part of a measured cell voltage is due to the process of interest and what is due to the junction potential. The cell in Figure 13-4 has no junction potential because there are no liquid junctions.

14-13. H^+ has greater mobility than K^+. The HCl side of the HCl | KCl junction will be negative because H^+ diffuses into the KCl region faster than K^+ diffuses into the HCl region. K^+ has a greater mobility than Na^+, so this junction has the opposite sign. The HCl | KCl voltage is larger, because the difference in mobility between H^+ and K^+ is greater than the difference in mobility between K^+ and Na^+.

14-14. Relative mobilities:

$K^+ \rightarrow 7.62$ $\qquad$ $NO_3^- \rightarrow 7.40$

$5.19 \leftarrow Na^+$ $\qquad$ $7.91 \leftarrow Cl^-$

Both the cation and anion diffusion cause negative charge to build up on the left.

14-15. Velocity = mobility × field = $(36.30 \times 10^{-8}\ \text{m}^2/(\text{s}\cdot\text{V})) \times (7\,800\ \text{V/m}) = 2.83 \times 10^{-3}\ \text{m s}^{-1}$ for H^+ and $(7.40 \times 10^{-8})(7\,800) = 5.77 \times 10^{-4}\ \text{m s}^{-1}$ for NO_3^-. To cover 0.120 m will require $(0.120\ \text{m})/(2.83 \times 10^{-3}\ \text{m s}^{-1}) = 42.4$ s for H^+ and $(0.120)/(5.77 \times 10^{-4}) = 208$ s for NO_3^-.

14-16. (a) $E^\circ = 0.799\ \text{V} \Rightarrow K = 10^{0.799/0.059\,16} = 3.20 \times 10^{13}$

(b) $K' = 10^{0.801/0.059\,16} = 3.46 \times 10^{13}$. $K'/K = 1.08$. The increase is 8%.

(c) $K = 10^{0.100/0.059\,16} = 49.0$. $\qquad K' = 10^{0.102/0.059\,16} = 53.0$

$K'/K = 1.08$. The change is still 8%.

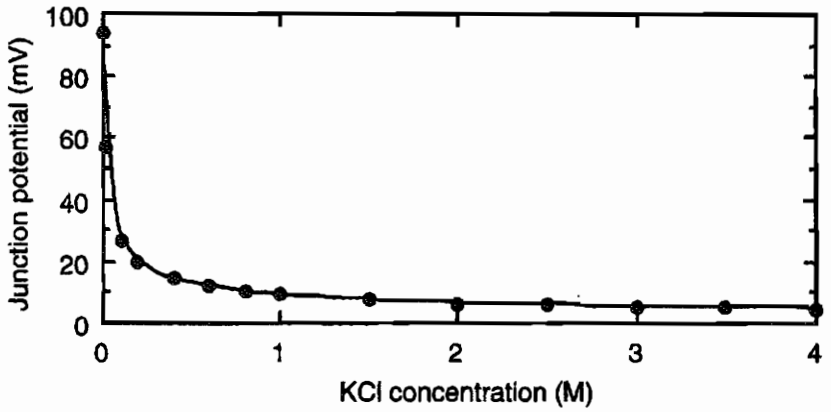
14-17. Both half-cell reactions are the same ($AgCl + e^- \rightleftharpoons Ag + Cl^-$) and the concentration of Cl^- is the same on both sides. In principle, the voltage of the cell would be 0 if there were no junction potential. The measured voltage can be attributed to the junction potential. In practice, if both sides contained 0.1 M HCl (or 0.1 M KCl), the two electrodes would probably produce a small voltage because no two real cells are identical. This voltage can be measured and subtracted from the voltage measured with the HCl | KCl junction.

14-18. (a) In phase α, we have 0.1 M H^+ ($u = 36.3 \times 10^{-8}$ m^2 s^{-1} V^{-1}) and 0.1 M Cl^- ($u = 7.91 \times 10^{-8}$ m^2 s^{-1} V^{-1}). In phase β, we have 0.1 M K^+ ($u = 7.62 \times 10^{-8}$ m^2 s^{-1} V^{-1}) and 0.1 M Cl^- ($u = 7.91 \times 10^{-8}$ m^2 s^{-1} V^{-1}). Substituting into the Henderson equation gives

$$E_j = \frac{(36.3 \times 10^{-8})[0 - 0.1] + (7.62 \times 10^{-8})[0.1 - 0] - (7.91 \times 10^{-8})[0.1 - 0.1]}{(36.3 \times 10^{-8})[0 - 0.1] + (7.62 \times 10^{-8})[0.1 - 0] + (7.91 \times 10^{-8})[0.1 - 0.1]} \times$$

$$0.059\,16 \log \frac{(36.3 \times 10^{-8})(0.1) + (7.91 \times 10^{-8})(0.1)}{(7.62 \times 10^{-8})(0.1) + (7.91 \times 10^{-8})(0.1)} = 26.9 \text{ mV}$$

(b)



(c)

[HCl]	y M HCl | 1mM KCl	y M HCl | 4 M KCl
10^{-4} M	9.1 mV	4.6 mV
10^{-3} M	26.9 mV	3.6 mV
10^{-2} M	57.3 mV	3.0 mV
10^{-1} M	93.6 mV	4.7 mV

14-19. Ideally, the electrode should be calibrated at 37° using two buffers bracketing the pH of the blood. It would be reasonable to use the MOPSO and HEPES buffers in Table 14-3 that are recommended for use with physiologic fluids. The pH of these standards at 37°C is 6.695 and 7.370. The standards should be

thermostatted to 37° during calibration, and the blood should also be at 37° during the measurement.

14-20. Uncertainty in pH of standard buffers, junction potential, junction potential drift, sodium or acid errors at extreme pH values, equilibration time, hydration of glass, temperature of measurement and calibration, and cleaning of electrode

14-21. The error measured in the graph is –0.33 pH units. The electrode will indicate $11.00 - 0.33 = 10.67$.

14-22. Saturated potassium hydrogen tartrate and 0.05 *m* potassium hydrogen phthalate

14-23. If the alkaline solution has a high concentration of Na^+ (as in NaOH), the Na^+ cation competes with H^+ for cation exchange sites on the glass surface. The glass responds as if H^+ were present, and the apparent pH is lower than the actual pH.

14-24. The junction potential changes from –6.4 mV to –0.2 mV. A change of $6.4 - 0.2 = +6.2$ mV appears to be a pH change of $+6.2/59.16 = +0.10$ pH units.

14-25. (a) $(4.63)(59.16\text{ mV}) = 274$ mV. The factor 59.16 mV is the value of $(RT \ln 10)/F$ at 298.15 K.

(b) At 310.15 K (37°C), $(RT \ln 10)/F$

$= (8.314\,5\text{ J mol}^{-1}\text{ K}^{-1})(310.15\text{ K})(\ln 10)/(96\,485\text{ C mol}^{-1}) = 61.54$ mV

$(4.63)(61.54\text{ mV}) = 285$ mV.

14-26. pH of 0.025 *m* KH_2PO_4/0.025 *m* Na_2HPO_4 at 20°C = 6.881

pH of 0.05 *m* potassium hydrogen phthalate at 20°C = 4.002

$$\frac{E_{\text{unknown}} - E_{S1}}{\text{pH}_{\text{unknown}} - \text{pH}_{S1}} = \frac{E_{S2} - E_{S1}}{\text{pH}_{S2} - \text{pH}_{S1}}$$

$$\frac{E_{\text{unknown}} - (-18.3\text{ mV})}{\text{pH}_{\text{unknown}} - 6.881} = \frac{(+146.3\text{ mV}) - (-18.3\text{ mV})}{4.002 - 6.881} = -57.17_3\text{ mV/pH unit}$$

$$\text{pH}_{\text{unknown}} = \frac{E_{\text{unknown}} - (-18.3\text{ mV})}{-57.17_3\text{ mV/pH unit}} + 6.881 = 5.686$$

Observed slope = -57.17_3 mV/pH unit

$$\text{Theoretical slope} = -\frac{RT \ln 10}{F}$$

$$= -\frac{[8.314\,47\text{ V·C/(mol·K)}][293.15\text{ K}] \ln 10}{9.648\,53 \times 10^4\text{ C/mol}} = -0.058\,17\text{ V}$$

$$\beta = \frac{\text{observed slope}}{\text{theoretical slope}} = \frac{-57.17_3 \text{ mV}}{-58.17 \text{ mV}} = 0.983$$

14-27. (a) There is negligible change in the concentrations of the buffer species when we mix the acid $H_2PO_4^-$ with its conjugate base, HPO_4^{2-}. The ionic strength of 0.025 0 *m* KH_2PO_4 (a 1:1 electrolyte) is 0.025 0 *m*. The ionic strength of 0.025 0 *m* Na_2HPO_4 (a 2:1 electrolyte) is 0.075 0 *m*. The total ionic strength is 0.100 *m*.

(b) $$K_2 = \frac{[H^+]\gamma_{H^+}[HPO_4^{2-}]\gamma_{HPO_4^{2-}}}{[H_2PO_4^-]\gamma_{H_2PO_4^-}}$$

But $K_2 = 10^{-7.198}$ and $[H^+]\gamma_{H^+} = 10^{-pH} = 10^{-6.865}$

Therefore, $$\frac{\gamma_{HPO_4^{2-}}}{\gamma_{H_2PO_4^-}} = \frac{K_2[H_2PO_4^-]}{[H^+]\gamma_{H^+}[HPO_4^{2-}]} = \frac{10^{-7.198}[0.025\,0]}{10^{-6.865}[0.025\,0]} = 0.464_5$$

(We can use molality or any other units for concentrations because they cancel in the numerator and denominator.)

(c) To get a pH of 7.000, we need to increase the concentration of base (HPO_4^{2-}) and decrease the concentration of acid ($H_2PO_4^-$). To maintain a constant ionic strength, we must decrease KH_2PO_4 three times as much as we increase Na_2HPO_4, because Na_2HPO_4 contributes three times as much as KH_2PO_4 to the ionic strength. So let's increase Na_2HPO_4 by x and decrease KH_2PO_4 by $3x$.

$$K_2 = \frac{[H^+]\gamma_{H^+}[HPO_4^{2-}]\gamma_{HPO_4^{2-}}}{[H_2PO_4^-]\gamma_{H_2PO_4^-}}$$

$$\Rightarrow 10^{-7.198} = \frac{10^{-7.000}[0.025\,0 + x]}{[0.025\,0 - 3x]}(0.464_5) \Rightarrow x = 0.001\,8 \text{ } m.$$

The new concentrations should be Na_2HPO_4 = 0.026 8 *m* and KH_2PO_4 = 0.019 6 *m*.

14-28. Analyte ions equilibrate with ion-exchange sites at the outer surface of the ion-selective membrane. Diffusion of analyte ions out of the membrane creates a slight charge imbalance (an electric potential difference) across the interface between the membrane and the analyte solution. Changes in analyte ion concentration in the solution change the potential difference across the outer boundary of the ion-selective membrane.

A compound electrode contains a second chemically active membrane outside the ion-selective membrane. The second membrane may be semipermeable and only allow the species of interest to pass through. Alternatively, the second membrane may contain a substance (such as an enzyme) that reacts with analyte to generate the species to which the ion-selective membrane responds.

14-29. The selectivity coefficient $K_{A,X}^{Pot}$ tells us the relative response of an ion-selective electrode to the ion of interest (A) and an interfering ion (X). The smaller $K_{A,X}^{Pot}$, the more selective is the electrode (smaller response to the interfering ion).

14-30. A mobile molecule dissolved in the membrane liquid phase binds tightly to the ion of interest and weakly to interfering ions.

14-31. A metal ion buffer maintains the desired (small) concentration of metal ion from a large reservoir of metal complex (ML) and free ligand (L). If you just tried to dissolve 10^{-8} M metal ion in most solutions or containers, the metal would probably bind to the container wall or to an impurity in the solution and be lost.

14-32. Electrodes respond to *activity*. If the ionic strength is constant, the activity coefficient of analyte will be constant in all standards and unknowns. In this case, the calibration curve can be written directly in terms of concentration.

14-33. (a) $-0.230 = \text{constant} - 0.059\,16 \log (1.00 \times 10^{-3}) \Rightarrow \text{constant} = -0.407\ \text{V}$

(b) $-0.300 = -0.407 - 0.059\,16 \log x \Rightarrow x = 1.5_5 \times 10^{-2}\ \text{M}$

(c) $-0.230 = \text{constant} - 0.059\,16 \log (1.00 \times 10^{-3})$

$-0.300 = \text{constant} - 0.059\,16 \log x$

subtract: $0.070 = -0.059\,16 \log \dfrac{1.00 \times 10^{-3}}{x} \Rightarrow x = 1.5_2 \times 10^{-2}\ \text{M}$

14-34. $E_1 = \text{constant} + \dfrac{0.059\,16}{2} \log [1.00 \times 10^{-4}]$

$E_2 = \text{constant} + \dfrac{0.059\,16}{2} \log [1.00 \times 10^{-3}]$

$\Delta E = E_2 - E_1 = \dfrac{0.059\,16}{2} \log \dfrac{1.00 \times 10^{-3}}{1.00 \times 10^{-4}} = +0.029\,6\ \text{V}$

14-35. $[F^-]_{\text{Providence}} = 1.00\ \text{mg F}^-/\text{L} = 5.26 \times 10^{-5}\ \text{M}$

$E_{\text{Providence}} = \text{constant} - 0.059\,16 \log [5.26 \times 10^{-5}]$

$E_{\text{Foxboro}} = \text{constant} - 0.059\,16 \log [F^-]_{\text{Foxboro}}$

$$\Delta E = E_{\text{Foxboro}} - E_{\text{Providence}} = 0.040\,0\text{ V}$$

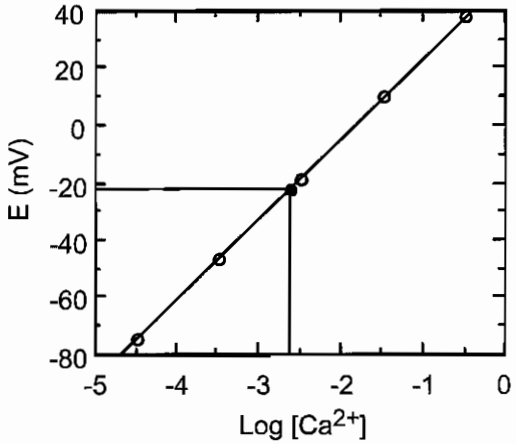
$$= -0.059\,16 \log \frac{[F^-]_{\text{Foxboro}}}{5.26 \times 10^{-5}} \Rightarrow [F^-]_{\text{Foxboro}} = 1.11 \times 10^{-5}\text{ M} = 0.211\text{ mg/L}$$

14-36. K^+ has the largest selectivity coefficient of Group 1 ions and therefore interferes the most. Sr^{2+} and Ba^{2+} are the worst of the Group 2 ions. Since $\log K^{\text{Pot}}_{Li^+,K^+} \approx -2$, there must be 100 times more K^+ than Li^+ to give equal response.

14-37. $$\frac{[ML]}{[M][L]} = 4.0 \times 10^8 = \frac{0.030\text{ M}}{[M](0.020\text{ M})} \Rightarrow [M] = 3.8 \times 10^{-9}\text{ M}$$

14-38. (a) The least squares parameters are

$$E = 51.10\ (\pm 0.24) + 28.14\ (\pm 0.08_5) \log [Ca^{2+}] \quad (s_y = 0.2_7)$$



(b) The slope is 0.028 14 V = β(0.059 16 V)/2 ⇒ β = 0.951.

(c) If we use Equation 4-27 in a spreadsheet, we find log $[Ca^{2+}]$ = $-2.615_3(\pm 0.007_2)$ using $s_y = 0.3$ and $k = 4$.

From Table 3-1, we can write that if $F = 10^x$, $e_F/F = (\ln 10)e_x$.

In this problem, $F = [Ca^{2+}] = 10^{-2.615_3(\pm 0.007_2)}$

$e_F/F = (\ln 10)(0.007_2) = 0.016_6$

$e_F = (0.016_6)F = 4.0 \times 10^{-5} \Rightarrow F = 2.43(\pm 0.04) \times 10^{-3}$ M.

14-39. At pH 7.2 the effect of H^+ will be negligible because $[H^+] << [Li^+]$:

$-0.333\text{ V} = \text{constant} + 0.059\,16 \log [3.44 \times 10^{-4}] \Rightarrow \text{constant} = -0.128\text{ V}$.

At pH 1.1 ($[H^+] = 0.079$ M), we must include interference by H^+:

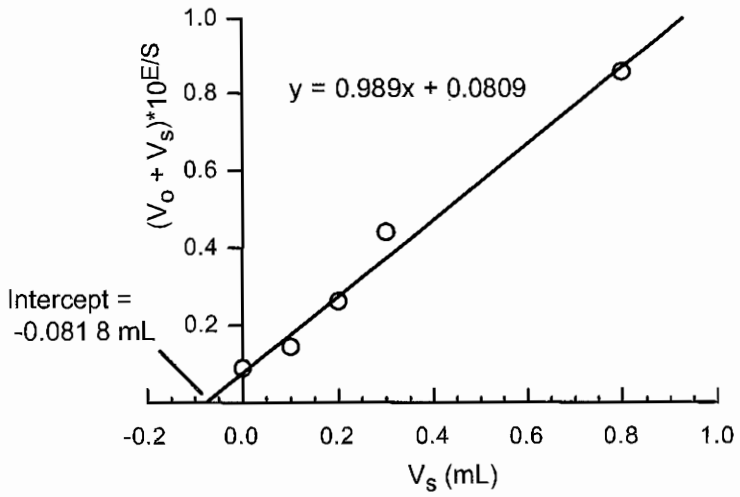
$E = -0.128 + 0.059\,16 \log [3.44 \times 10^{-4} + (4 \times 10^{-4})(0.079)] = -0.331$ V.

14-40. The function to plot on the y-axis is $(V_o + V_s)\,10^{E/S}$, where $S = -(\beta RT \ln 10)/nF$. (The minus sign comes from the equation for the response of the electrode, which has a minus sign in front of the log term.) Putting in $\beta = 0.933$, $R = 8.314\ 5$ J/(mol·K), $F = 96\ 485$ C/mol, $T = 303.15$ K, and $n = 2$ gives $S = -0.028\ 06$ J/C = 0.028 06 V. (You can get the relation of J/C = V from the equation $\Delta G = -nFE$, in which the units are J = (mol)(C/mol)(V).)

V_s (mL)	E (V)	y
0	0.079 0	0.084 1
0.100	0.072 4	0.144 9
0.200	0.065 3	0.259 9
0.300	0.058 8	0.443 8
0.800	0.050 9	0.856 5

The graph has a slope of $m = 0.989$ and an intercept of $b = 0.080\ 9$, giving an x-intercept of $-b/m = -0.081\ 8$ mL. The concentration of original unknown is

$$c_X = -\frac{(x\text{-intercept})\,c_S}{V_o} = -\frac{(-0.081\ 8\text{ mL})(0.020\ 0\text{ M})}{55.0\text{ mL}} = 3.0 \times 10^{-5}\text{ M}.$$

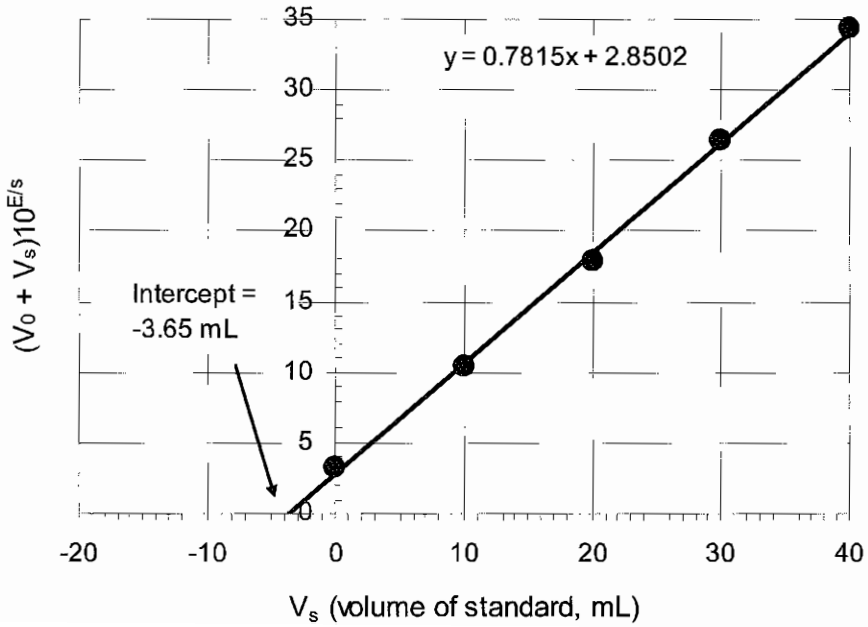


14 41. (a) The following spreadsheet and graph are shown. The x-intercept is at –3.65 mL with a standard deviation in cell B26 of $s = 0.484$ mL. The intercept gives us the concentration of ammonia nitrogen in the volume $V_0 = 101.0$ mL:

$$x\text{-intercept} = -3.65\text{ mL} = -\frac{V_0 c_X}{c_S}$$

$$\Rightarrow c_X = \frac{(x\text{-intercept})c_S}{V_0} = \frac{(3.65\text{ mL})(10.0\text{ ppm})}{101.0\text{ mL}} = 0.361_4\text{ ppm}$$

	A	B	C	D	E	F	G	H
1	Standard Addition: Ammonia in Seawater							
2								
3	V_0 =	101	mL					
4	c_S =	10	ppm					
5	s =	0.0566	V					
6								
7	x			y				
8	Added standard	E = cell	$V_0 + V_s$	$(V_0 + V_s)10^{E/s}$				
9	(mL)	voltage (V)	(mL)	(mL)				
10	0.00	-0.0844	101.0	3.26				
11	10.00	-0.0581	111.0	10.44				
12	20.00	-0.0469	121.0	17.95				
13	30.00	-0.0394	131.0	26.37				
14	40.00	-0.0347	141.0	34.37				
15								
16		LINEST output:			Highlight cells B17:D19			
17	m	0.7815	2.8502	b	Type '=LINEST(D10:D14,A10:A14,TRUE,TRUE)			
18	s_m	0.0137	0.3364	s_b	Press CTRL+SHIFT+ENTER (on PC)			
19	R^2	0.9991	0.4343	s_y	Press COMMAND+RETURN (on Mac)			
20								
21	x-intercept = -b/m =	-3.647	mL			To find 95% confidence interval		
22	n =	5	B22 = COUNT(A10:A14)			we need Student's t for		
23	Mean y =	18.479	B23 = AVERAGE(D10:D14)			3 degrees of freedom		
24	$\Sigma(x_i - \text{mean } x)^2$ =	1000	B24 = DEVSQ(A10:A14)			TINV(0.05,3) =	3.182446	
25	Std deviation of					t*s =	1.541109	
26	x-intercept =	0.484	mL					
27	B26 = (C19/ABS(B17))*SQRT((1/B22) + B23^2/(B17^2*B24))							



The concentration of ammonia nitrogen in the original 100.0 mL of seawater, which had been diluted from 100.0 to 101.0 mL, is $\frac{101.0\text{ mL}}{100.0\text{ mL}}(0.3614\text{ ppm}) = 0.365\text{ ppm}$. The 95% confidence interval is equal to Student's t times the standard deviation:

$$95\%\text{ confidence interval} = \pm t \cdot s = \pm(3.18)(0.484\text{ mL}) = \pm 1.54\text{ mL}$$

where t is for 95% confidence and $5 - 2 = 3$ degrees of freedom because there are 5 data points on the standard addition curve. You can find t in the table of Student's t or you can compute it with the statement "=TINV(0.05,3)" in cell G24 in the spreadsheet. The confidence interval of ±1.54 mL corresponds to a relative uncertainty of $100 \times \frac{1.54\text{ mL}}{3.65\text{ mL}} = 42\%$.

The absolute uncertainty is (0.042)(0.365 ppm) = 0.15 ppm. The concentration of ammonia nitrogen in the seawater can be expressed as 0.36 ± 0.15 ppm.

(b) Added standards should increase analytical signal by a factor of 1.5 to 3. In this experiment, analytical signal is $(V_0 + V_S)10^{E/S} = 3.26$ mL for unknown and 34.37 mL for final standard. The final signal is 10 times as great as the initial signal, which is ~3 times more than the recommended limit.

14-42. For the first line of data, with $A = Na^+$ and $X = Mg^{2+}$

$$\log K_{A,X}^{Pot} = \frac{z_A F(E_X - E_A)}{RT\ln 10} + \log\left(\frac{\mathcal{A}_A}{\mathcal{A}_X^{z_A/z_X}}\right)$$

$$= \frac{(+1)(96\,485\text{ C/mol})(-0.385\text{ V})}{(8.3145\text{ V·C/[mol·K]})(294.65\text{ K})\ln 10} + \log\left(\frac{10^{-3}}{(10^{-3})^{1/2}}\right) = -8.09.$$

For the second line of data, $\log K_{A,X}^{Pot} = -8.15$.

The first and second lines should give the same selectivity coefficient. The difference is experimental error.

For the third line of data, with $A = Na^+$ and $X = K^+$:

$$\log K_{A,X}^{Pot} = \frac{(+1)(96\,485\text{ C/mol})(-0.285\text{ V})}{(8.3145\text{ V·C/[mol·K]})(294.65\text{ K})\ln 10} + \log\left(\frac{10^{-3}}{(10^{-3})^{1/1}}\right) = -4.87.$$

For the fourth line of data, $\log K_{A,X}^{Pot} = -4.87$.

14-43. For Na^+: error in $\mathcal{A}_{H^+}(\%) = \frac{(10^{-8.6})^{1/1}(10^{-2.0})}{(10^{-8.0})^{1/1}} \times 100 = 0.25\%$

For Ca^{2+}: error in $\mathcal{A}_{H^+}(\%) = \frac{(10^{-7.8})^{2/1}(10^{-2.0})}{(10^{-8.0})^{2/1}} \times 100 = 2.5\%$

14-44. $E = \underset{A}{\text{constant}} + \underset{B}{\frac{\beta(0.059\,16)}{2}} \log([Ca^{2+}] + K^{Pot}_{Ca^{2+},Mg^{2+}}[Mg^{2+}])$

For the first two solutions we can write

$-52.6\text{ mV} = A + B \log(1.00 \times 10^{-6}) = A - 6B$

$+16.1\text{ mV} = A + B \log(2.43 \times 10^{-4}) = A - 3.614B.$

Subtraction gives $68.7\text{ mV} = 2.386\,B \Rightarrow B = 28.80\text{ mV}$.

Putting this value of B back into the first equation gives $A = 120.2\text{ mV}$.

The third set of data now gives the selectivity coefficient:

$-38.0\text{ mV} = 120.2 + 28.80 \log[10^{-6} + K^{Pot}_{Ca^{2+},Mg^{2+}}(3.68 \times 10^{-3})]$

$\Rightarrow K^{Pot}_{Ca^{2+},Mg^{2+}} = 6.0 \times 10^{-4}$

$E = 120.2 + 28.80 \log([Ca^{2+}] + 6.0 \times 10^{-4}[Mg^{2+}])$.

14-45. There is a large excess of EDTA in the buffer. We expect essentially all lead to be in the form PbY^{2-} (where Y = EDTA).

$[PbY^{2-}] = \frac{1.0}{101.0}(0.10\text{ M}) = 9.9 \times 10^{-4}\text{ M}$

$\text{Total EDTA} = \frac{100.0}{101.0}(0.050\text{ M}) = 0.049_5\text{ M}$

$\text{Free EDTA} = 0.049_5\text{ M} - \underset{\text{EDTA bound to } Pb^{2+}}{9.9 \times 10^{-4}\text{ M}} = 0.048_5\text{ M}$

$Pb^{2+} + Y^{4-} \rightleftharpoons PbY^{2-} \quad K_f' = \alpha_{Y^{4-}} K_f = (1.46 \times 10^{-8})(10^{18.0}) = 1.4_6 \times 10^{10}$

$K_f' = \frac{[PbY^{2-}]}{[Pb^{2+}][EDTA]}$

$\Rightarrow [Pb^{2+}] = \frac{[PbY^{2-}]}{K_f'[EDTA]} = \frac{9.9 \times 10^{-4}}{(1.4_6 \times 10^{10})(0.048_5)} = 1.4 \times 10^{-12}\text{ M}$

14-46. $[Hg^{2+}]$ in the buffers is computed from equilibrium constants for the solubility of HgX_2 and formation of complex ions such as HgX_3^-. Since the data for $HgCl_2$ are not in line with the data for $Hg(NO_3)_2$ and $HgBr_2$, equilibrium constants used for the $HgCl_2$ system could be in error. Whenever we make a buffer by mixing *calculated* quantities of reagents, we are at the mercy of the quality of tabulated equilibrium constants.

14-47. (a) $\text{slope} = 29.58\ \text{mV} = \dfrac{E_2 - E_1}{\log \mathcal{A}_2 - \log \mathcal{A}_1} = \dfrac{(-25.90) - 2.06}{\log \mathcal{A}_2 - (-3.000)}$

$$\Rightarrow \mathcal{A}_2 = 1.13 \times 10^{-4}$$

(b)

$$\underset{5.00 \times 10^{-4} - x}{Ca^{2+}} + \underset{(0.998)[(5.00 \times 10^{-4}) - x]}{A^{3-}} \rightleftharpoons \underset{x}{CaA^-}$$

But $\mathcal{A}_{Ca^{2+}} = 1.13 \times 10^{-4} = (5.00 \times 10^{-4} - x)\,(0.405)$

↑ γ from Table 7-1

$$\Rightarrow x = 2.2 \times 10^{-4}\ \text{M}$$

$$K_f = \frac{[CaA^-]\gamma_{CaA^-}}{[Ca^{2+}]\gamma_{Ca^{2+}}[A^{3-}]\gamma_{A^{3-}}}$$

$$K_f = \frac{(2.20 \times 10^{-4})(0.79)}{(1.13 \times 10^{-4})[(0.998)(5 \times 10^{-4} - 2.20 \times 10^{-4})](0.115)}$$

$$K_f = 4.8 \times 10^4$$

14-48. Analyte adsorbed on the surface of the gate changes the electric potential of the gate. This, in turn, changes the current between the source and drain. The potential that must be applied by the external circuit to restore the current to its initial value is a measure of the change in gate potential. Following the Nernst equation, there is close to a 59 mV change in gate potential for each factor-of-10 change in activity of univalent analyte at 25°C. The key to ion-specific response is to have a chemical on the gate that selectively binds one analyte.