S5-1. (a) $y(\pm 0.4_{08}) = -0.75_0(\pm 0.14_4)x + 3.9_{17}(\pm 0.4_{93})$

(b) Uncertainty in $x = \frac{0.408}{0.75}\left[1 + (3.89)^2\left(\frac{3}{24}\right) + \frac{35}{24} - 2\,(3.89)\,\frac{9}{24}\right]^{1/2} = 0.65$

S5-2. (a) Subtract 0.002 from each area, and plot (μg/mL) vs area:

$\Rightarrow$ slope = 0.008 73 and intercept = 0.002 6

(b) Corrected area = 0.156 = 0.008 72 [Ag] + 0.002 6

$\Rightarrow$ [Ag] = 17.6 μg/mL.

S5-3. First, note that s_y = 0.003 2.

0.156 (±0.003 2) = 0.008 73 (±0.000 13) [Ag] + 0.002 6 (±0.002 5)

Putting the uncertainties into the equation for uncertainty in x gives

[Ag] = 17.6 (±0.4) μg/mL.

S5-4. (a) $[\text{dopamine}]_f = [\text{dopamine}]_i \left(\frac{90.0}{100.0}\right)$

(b) $[S]_f = (0.015\,6 \text{ M})\left(\frac{2.00 \text{ mL}}{100.0 \text{ mL}}\right) = 0.312 \text{ mM}$

(c) $\frac{[\text{dopamine}]_i}{0.312 \text{ mM} + 0.900[\text{dopamine}]_i} = \frac{34.6 \text{ nA}}{58.4 \text{ nA}} \Rightarrow [\text{dopamine}]_i = 0.396 \text{ mM}$

S5-5. $\frac{A_A}{[A]} = F\left(\frac{A_B}{[B]}\right)$

$\Rightarrow \frac{0.71}{[80.0 \text{ nM}]} = F\left(\frac{1}{[64.0 \text{ nM}]}\right)$

$\Rightarrow$ F = 0.568

$\frac{A_A}{[A]} = F\left(\frac{A_B}{[B]}\right)$

$\Rightarrow \frac{1.21}{[A]} = 0.568\left(\frac{1}{[930 \text{ nM}]}\right)$

$\Rightarrow [A] = 1.98 \times 10^3 \text{ nM} = 1.98\ \mu\text{M}$

S5-6. (a)-(b) Corrected signal (mV) = $94._4$ (±3.7) [C_2H_2, vol%] + 10.05 (±0.7_3)

The x-intercept is 0.1065 and Equation 5-17 gives an uncertainty of 0.0113.

[C_2H_2, vol%] = 0.106 (±0.011) vol%

S5-7. $$\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}} \Rightarrow [X]_i I_{S+X} = [S]_f I_X + [X]_f I_X$$

$$I_{S+X} = \underbrace{\left(\frac{I_X}{[X]_i}\right)}_{\text{slope}} [S]_f + \underbrace{\frac{[X]_f}{[X]_i} I_X}_{\text{intercept}}$$

Setting $I_{S+X} = 0$ gives $\frac{I_X}{[X]_i} [S]_f = -\frac{[X]_f}{[X]_i} I_X$, which is true when $[S]_f = -[X]_f$

S5-8. (a) $y(\pm 0.17) = -0.159\,_{75}(\pm 0.019\,_{15})x + 308._{95}(\pm 38._{00})$

(b) y(at 2 010) = (–0.159 75)(2 010) + 308.95 = –12.15

temperature = $10^y = 7 \times 10^{-13}$ K.

Extrapolation of experimental progress is nonsense.

There is no way to predict future progress.

S6-1. (a) $K = [Cl^-]\,[OCl^-] / [OH^-]^2\, P_{Cl_2}$ (b) $K = 1/P_{I_2}$

S6-2. Remain unchanged.

S6-3.

$$Cu^+ + N_3^- \rightleftharpoons CuN_3(s) \qquad K_1 = \frac{1}{4.9 \times 10^{-9}}$$

$$HN_3 \rightleftharpoons H^+ + N_3^- \qquad K_2 = 2.2 \times 10^{-5}$$

$$Cu^+ + HN_3 \rightleftharpoons CuN_3(s) + H^+ \qquad K_3 = K_1K_2 = 4.5 \times 10^3$$

S6-4. $Q = [H^+][OH^-] = 6.0 \times 10^{-12} > K \Rightarrow$ reaction goes to the left.

S6-5. $K_3 = e^{-\Delta G_3^\circ/RT} = K_1 \cdot K_2 = e^{-\Delta G_1^\circ/RT}\, e^{-\Delta G_2^\circ/RT}$

$e^{-\Delta G_3^\circ/RT} = e^{-(\Delta G_1^\circ + \Delta G_2^\circ)/RT}$ $\quad \therefore\ \Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

S6-6. $K = e^{-\Delta G^\circ/RT} \Rightarrow \ln K = -\Delta G^\circ/RT \Rightarrow \Delta G^\circ = -RT \ln K$

(a) $\Delta G^\circ = -\left(8.314\,5\ \frac{\text{J}}{\text{mol·K}}\right)(298.15\ \text{K}) \ln(6.5 \times 10^{-5}) = 23.9$ kJ/mol

(b) $\Delta G^\circ = 63.6$ kJ/mol

S6-7. (a) Positive.

(b) $\Delta G^\circ = (+) = \Delta H^\circ - T\Delta S^\circ$. Since $-T\Delta S^\circ$ is negative, ΔH° must be positive. The reaction is endothermic.

S6-8. (a)

$$\underset{\text{FM } 331.73}{Ag_2CrO_4(s)} \overset{K_{sp}}{\rightleftharpoons} \underset{2x}{2Ag^+} + \underset{x}{CrO_4^{2-}}$$

$(2x)^2(x) = 1.2 \times 10^{-12} \Rightarrow x = 6.6_9 \times 10^{-5}$ M

(b) $6.6_9 \times 10^{-5}$ M $= 0.022_2$ g/L $= 0.002\,2_2$ g/100 mL

(c) $[Ag^+] = 13._4 \times 10^{-5}$ M $= 0.014\,4$ g/L $= 0.014\,4$ mg/mL $= 14.4$ µg/mL $= 14.4$ ppm

S6-9.

$$Cu(s) + Cu^{2+} \rightleftharpoons 2\,Cu^+ \qquad K_1 = 9.6 \times 10^{-7}$$

$$2\,Cu^+ + 2\,Cl^- \rightleftharpoons 2\,CuCl(s) \qquad K_2 = 1/K_{sp}^2 = 1/(1.9 \times 10^{-7})^2$$

$$Cu(s) + Cu^{2+} + 2\,Cl^- \rightleftharpoons 2\,CuCl(s) \qquad K = K_1K_2 = 2.7 \times 10^7$$

S6-10. (a) $PbI_2(s) \underset{}{\overset{K_{sp}}{\rightleftharpoons}} Pb^{2+} + 2I^-$
FM 461.0 $\quad x \quad 2x$

$x(2x)^2 = 7.9 \times 10^{-9} \Rightarrow x = 1.2_5 \times 10^{-3}$ M $= 0.57_8$ g/L

(b) $[Pb^{2+}](0.063\,4)^2 = 7.9 \times 10^{-9} \Rightarrow x = 1.9_7 \times 10^{-6}$ M $= 9.0_6 \times 10^{-4}$ g/L

S6-11. $Ca(C_2O_4)(s) \overset{K_{sp} = 1.3 \times 10^{-8}}{\rightleftharpoons} Ca^{2+} + C_2O_4^{2-}$

We want to reduce $[C_2O_4^{2-}]$ to 1.0×10^{-4} M :

$[Ca^{2+}][1.0 \times 10^{-4}] = 1.3 \times 10^{-8} \Rightarrow [Ca^{2+}] = 1.3 \times 10^{-4}$ M

S6-12. $Ca(OH)_2$: $K_{sp} = 6.5 \times 10^{-6}$ $Mg(OH)_2$: $K_{sp} = 7.1 \times 10^{-12}$

We want to reduce $[Mg^{2+}]$ to 2.0×10^{-5} M

$[Mg^{2+}][OH^-]^2 = [2.0 \times 10^{-5}][OH^-]^2 = 7.1 \times 10^{-12} \Rightarrow [OH^-] = 5.9_6 \times 10^{-4}$ M

Will this precipitate 0.10 M Ca^{2+}?

$Q = [Ca^{2+}][OH^-]^2 = (0.10)(5.9_6 \times 10^{-4})^2 = 3.5_5 \times 10^{-8} < K_{sp}$

$\Rightarrow$ $Ca(OH)_2$ will not precipitate.

S6-13. $[Pb^{2+}] = K_{sp}/[I^-]^2 = (7.9 \times 10^{-9}) / (0.050)^2 = 3.1_6 \times 10^{-6}$ M

$[PbI^+] = K_1[Pb^{2+}][I^-] = 1.5_8 \times 10^{-5}$ M

$[PbI_2(aq)] = \beta_2[Pb^{2+}][I^-]^2 = 1.1_1 \times 10^{-5}$ M

$[PbI_3^-] = \beta_3[Pb^{2+}][I^-]^3 = 3.2_8 \times 10^{-6}$ M

$[PbI_4^{2-}] = \beta_4[Pb^{2+}][I^-]^4 = 5.9_2 \times 10^{-7}$ M

S6-14. $[Ag^+] = K_{sp}/[Cl^-]$ $[AgCl_3^{2-}] = K_3[AgCl_2^-][Cl^-]$

$[AgCl_2^-] = K_2[Cl^-]$ $\qquad [Ag]_{total} = [Ag^+] + [AgCl_2^-] + [AgCl_3^{2-}]$

	(a) 0.010 M Cl^-	(b) 0.20 M Cl^-	(c) 2.0 M Cl^-
$[Ag^+]$	$1.8_0 \times 10^{-8}$ M	$9.0_0 \times 10^{-10}$ M	$9.0_0 \times 10^{-11}$ M
$[AgCl_2^-]$	$1.5_0 \times 10^{-4}$ M	$0.003\,0_0$ M	0.030_0 M
$[AgCl_3^{2-}]$	$7.3_5 \times 10^{-7}$ M	$0.000\,29_4$ M	0.029_4 M
$[Ag]_{total}$	$1.5_0 \times 10^{-4}$ M	$0.003\,2_9$ M	0.059_4 M

S6-15. HSO_3^- , H_2O

S6-16.

<u>acid</u>	<u>base</u>
H_2O	OH^-
$H_3\overset{+}{N}CH_2CH_2NH_2$	$H_2NCH_2CH_2NH_2$

S6-17. (a) $[H^+] = 1.0 \times 10^{-3}$ M $\Rightarrow$ pH $= -\log [H^+] = 3.00$

(b) $[H^+] = 0.050$ M $\Rightarrow$ pH $= 1.30$

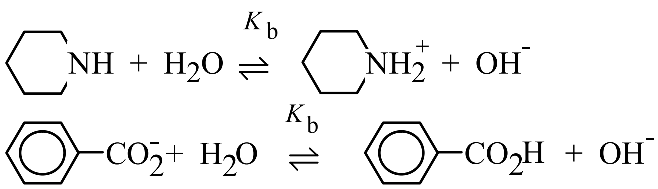
(c) $[OH^-] = 0.050$ M $\Rightarrow [H^+] = K_w / [OH^-] = 2.0 \times 10^{-13}$ M $\Rightarrow$ pH $= 12.70$

(d) $[OH^-] = 3.0$ M $\Rightarrow [H^+] = 3.3 \times 10^{-15}$ M $\Rightarrow$ pH $= 14.48$

(e) $[OH^-] = 0.005\,0$ M $\Rightarrow [H^+] = 2.0 \times 10^{-12}$ M $\Rightarrow$ pH $= 11.70$

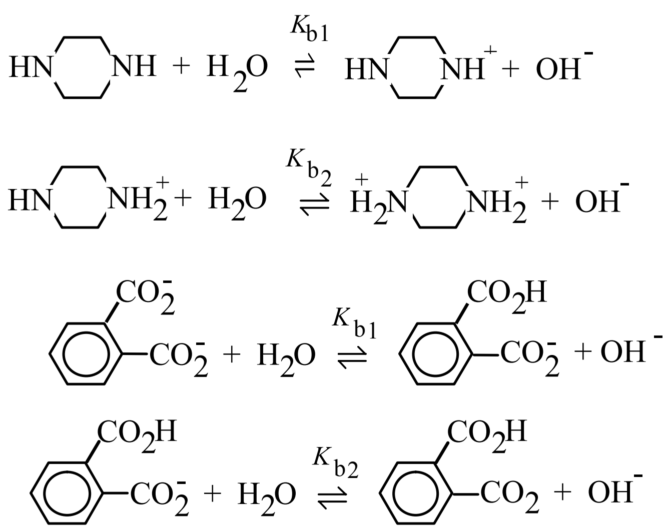
S6-18. $HCO_2H \overset{K}{\rightleftharpoons} HCO_2^- + H^+$ $\qquad$ $CH_3NH_3^+ \overset{K_a}{\rightleftharpoons} CH_3NH_2 + H^+$

S6-19.

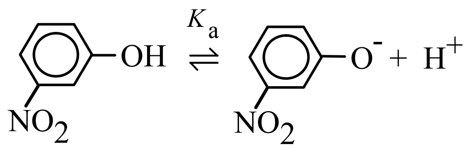


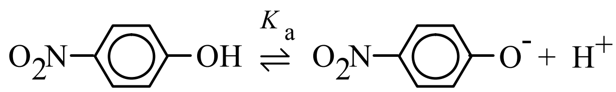
S6-20. $HPO_4^{2-} \overset{K_a}{\rightleftharpoons} H^+ + PO_4^{3-}$ $\qquad$ $HPO_4^{2-} + H_2O \overset{K_b}{\rightleftharpoons} H_2PO_4^- + OH^-$

S6-21.

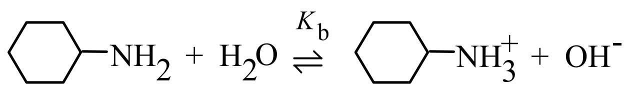


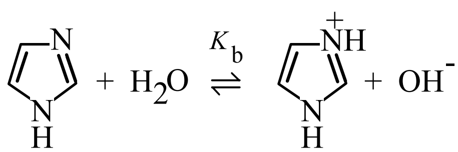
S6-22. 4-nitrophenol has the larger K_a.





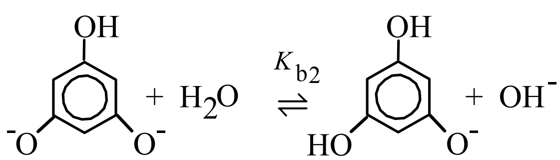
S6-23. Cyclohexylamine has the larger K_b.





S6-24. $OCl^- + H_2O \rightleftharpoons HOCl + OH^-$ $\qquad K_b = K_w/K_a = 3.3 \times 10^{-7}$

S6-25. $HSO \overset{K_{a2}}{\rightleftharpoons} H^+ + SO_4^{2-}$



S6-26. $K_{b1} = \dfrac{K_w}{K_{a3}} = 2.49 \times 10^{-8}$

$K_{b2} = \dfrac{K_w}{K_{a2}} = 5.78 \times 10^{-10}$

$K_{b3} = \dfrac{K_w}{K_{a1}} = 1.34 \times 10^{-11}$

CHAPTER 7: SUPPLEMENTARY SOLUTIONS
LET THE TITRATIONS BEGIN

S7-1. 1.00 mL of 0.027 3 M Ce^{4+} = 0.027 3 mmol of Ce^{4+}. This will react with half as many mol of oxalic acid = 0.013 65 mmol of $H_2C_2O_4 \cdot 2H_2O$ = 1.72 mg.

S7-2. Let x = mg $FeCl_2$ and $(27.73 - x)$ = mg KCl

mmol Ag^+ = 2 mmol $FeCl_2$ + mmol KCl

$$(18.49\text{ mL})(0.022\,37\text{ M}) = \frac{2\,x\text{ mg}}{126.75\text{ mg/mmol}} + \frac{(27.73 - x)\text{ mg}}{74.55\text{ mg/mmol}}$$

$$\Rightarrow x = 17.61\text{ mg FeCl}_2 = 7.76\text{ mg Fe} = \frac{7.76\text{ mg}}{27.73\text{ mg}} \times 100 = 28.0\text{ wt \% Fe.}$$

S7-3. (a) $\text{mol Hg}^{2+} = \frac{1}{2}\text{ mol Cl}^- = \frac{1}{2}\,\frac{0.147\,6\text{ g}}{58.442\text{ g/mol}} = 1.263 \times 10^{-3}\text{ mol}$

$$[\text{Hg}^{2+}] = \frac{1.263 \times 10^{-3}\text{ mol}}{0.028\,06\text{ L}} = 0.045\,00\text{ M}$$

(b) $(0.022\,83\text{ L Hg(NO}_3)_2)\,(0.045\,00\text{ mol/L}) = 1.027\text{ mmol Hg}^{2+}$

$= 2.055\text{ mmol Cl}^- = 72.85\text{ mg Cl}^-\text{ in }2.000\text{ mL} = 36.42\text{ mg Cl}^-/\text{mL}$

S7-4. $Br^- + Ag^+ \rightarrow AgBr(s)$

$$\text{Equivalence point} = \frac{(20.00\text{ mL})(0.053\,20\text{ M})}{(0.051\,10\text{ M})} = 20.82\text{ mL}$$

(a) $$[\text{Br}^-] = \underbrace{\left(\frac{20.82 - 20.00}{20.82}\right)}_{\text{Fraction remaining}}\underbrace{(0.053\,20\text{ M})}_{\text{Initial concentration}}\underbrace{\left(\frac{20.00}{40.82}\right)}_{\text{Dilution factor}} = 1.027 \times 10^{-3}\text{ M}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Br}^-]} = \frac{5.0 \times 10^{-13}}{1.027 \times 10^{-3}} = 4.9 \times 10^{-10}\text{ M}$$

$\text{pAg}^+ = -\log(4.9 \times 10^{-10}) = 9.31$

(b) At the equivalence point, $[\text{Ag}^+] = [\text{Br}^-] = \sqrt{K_{sp}} = 7.07 \times 10^{-7}\text{ M}$.

$\text{pAg}^+ = -\log[\text{Ag}^+] = 6.15$

(c) $$[\text{Ag}^+] = \underbrace{(0.051\,1\text{ M})}_{\text{Initial concentration}}\underbrace{\left(\frac{22.60 - 20.82}{42.60}\right)}_{\text{Dilution factor}} = 2.14 \times 10^{-3}\text{ M} \Rightarrow \text{pAg}^+ = 2.67$$

S7-5. $Hg^{2+} + 2SCN^- \rightarrow Hg(SCN)_2(s)$ $\quad K_{sp} = 2.8 \times 10^{-20}$

$$\text{Equivalence point} = 2\ \frac{(50.00\text{ mL})(0.0246\text{ M})}{(0.104\text{ M})} = 23.65\text{ mL}$$

$$0.25\ V_e = 5.91\text{ mL}: [Hg^{2+}] = \underbrace{\tfrac{3}{4}}_{\substack{\text{Fraction}\\\text{remaining}}}\ \underbrace{(0.0246\text{ M})}_{\substack{\text{Initial}\\\text{concentration}}}\ \underbrace{\left(\frac{50.00}{55.91}\right)}_{\substack{\text{Dilution}\\\text{factor}}} = 0.0165\text{ M}$$

$$pHg^{2+} = -\log[Hg^{2+}] = 1.78$$

$$0.50\ V_e = 11.83\text{ mL}: [Hg^{2+}] = \tfrac{1}{2}(0.0246\text{ M})\left(\frac{50.00}{61.83}\right) = 0.00995\text{ M} \qquad pHg^{2+} = 2.00$$

$$0.75\ V_e = 17.74\text{ mL}: [Hg^{2+}] = \tfrac{1}{4}(0.0246\text{ M})\left(\frac{50.00}{67.74}\right) = 0.00454\text{ M} \qquad pHg^{2+} = 2.34$$

$$V_e = [Hg^{2+}][SCN^-]^2 = (x)(2x)^2 = K_{sp} \Rightarrow x = [Hg^{2+}] = 1.9 \times 10^{-7}\text{ M} \quad pHg^{2+} = 6.72$$

$$1.05\ V_e = 24.84\text{ mL}: [SCN^-] = \underbrace{(0.104\text{ M})}_{\substack{\text{Initial}\\\text{concentration}}}\underbrace{\left(\frac{24.84 - 23.65}{74.84}\right)}_{\substack{\text{Dilution}\\\text{factor}}} = 0.00165\text{ M}$$

$$[Hg^{2+}] = \frac{K_{sp}}{[SCN^-]^2} = \frac{2.8 \times 10^{-20}}{(0.00165)^2} = 1.02 \times 10^{-14}\text{ M} \Rightarrow pHg^{2+} = 13.99$$

$$1.25\ V_e = 29.57\text{ mL}: [SCN^-] = (0.104\text{ M})\left(\frac{29.57 - 23.65}{79.57}\right) = 0.00774\text{ M}$$

$$[Hg^{2+}] = \frac{K_{sp}}{[SCN^-]^2} = 4.68 \times 10^{-16}\text{ M} \Rightarrow pHg^{2+} = 15.33$$

S7-6. First reaction: $SO_4^{2-} + Ra^{2+} \rightarrow RaSO_4(s)$ $\quad K_{sp} = 4.3 \times 10^{-11}$

$$V_{e1} = (100\text{ mL})\left(\frac{0.0500\text{ M}}{0.250\text{ M}}\right) = 20.00\text{ mL}$$

Second reaction: $SO_4^{2-} + Sr^{2+} \rightarrow SrSO_4(s)$ $\quad K_{sp} = 3.2 \times 10^{-7}$

$$V_{e2} = 20.00 + 20.00 = 40.00\text{ mL}$$

(a) 10.00 mL: Half of the Ra^{2+} has reacted.

$$[Ra^{2+}] = \underbrace{\tfrac{1}{2}}_{\substack{\text{Fraction}\\\text{remaining}}} \underbrace{(0.050\,0\text{ M})}_{\substack{\text{Initial}\\\text{concentration}}} \underbrace{\left(\frac{100.00}{110.00}\right)}_{\substack{\text{Dilution}\\\text{factor}}} = 0.022\,7\text{ M}$$

$$[SO_4^{2-}] = \frac{K_{sp}(RaSO_4)}{[Ra^{2+}]} = 1.89 \times 10^{-9}\text{ M} \Rightarrow pSO_4^{2-} = 8.72$$

(b) 19.00 mL: 19/20 of the Ra^{2+} has reacted.

$$[Ra^{2+}] = \left(\frac{1.00}{20.00}\right)(0.050\,0\text{ M})\left(\frac{100.00}{119.00}\right) = 0.002\,10\text{ M}$$

$$[SO_4^{2-}] = \frac{K_{sp}(RaSO_4)}{[Ra^{2+}]} = 2.05 \times 10^{-8}\text{ M} \Rightarrow pSO_4^{2-} = 7.69$$

(c) 21.00 mL: 1/20 of the Sr^{2+} has reacted.

$$[Sr^{2+}] = \left(\frac{19.00}{20.00}\right)(0.050\,0\text{ M})\left(\frac{100.00}{121.00}\right) = 0.039\,3\text{ M}$$

$$[SO_4^{2-}] = \frac{K_{sp}(SrSO_4)}{[Sr^{2+}]} = 8.14 \times 10^{-6}\text{ M} \Rightarrow pSO_4^{2-} = 5.09$$

(d) 30.00 mL: Half of the Sr^{2+} has reacted.

$$[Sr^{2+}] = \tfrac{1}{2}(0.050\,0\text{ M})\left(\frac{100.00}{130.00}\right) = 0.019\,2\text{ M}$$

$$[SO_4^{2-}] = \frac{K_{sp}(SrSO_4)}{[Sr^{2+}]} = 1.67 \times 10^{-5}\text{ M} \Rightarrow pSO_4^{2-} = 4.78$$

(e) 40.00 mL: Second equivalence point.

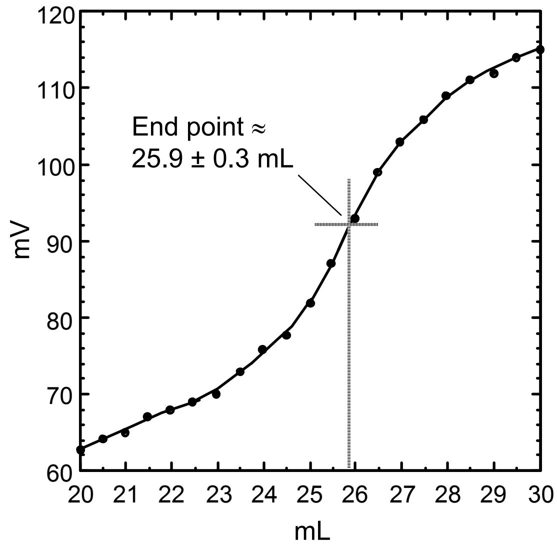
$$[Sr^{2+}][SO_4^{2-}] = x^2 = 3.2 \times 10^{-7} \Rightarrow [SO_4^{2-}] = 5.7 \times 10^{-4}$$

$$\Rightarrow pSO_4^{2-} = 3.25$$

(f) 50.00 mL: There is 10.00 mL of excess SO_4^{2-}.

$$[SO_4^{2-}] = (0.250\text{ M})\left(\frac{10.00}{150.00}\right) = 0.016\,7\text{ M} \Rightarrow pSO_4^{2-} = 1.78$$

S7-7. (a) I estimate that the end point is near 25.9 mL. It is not very sharp and my guess could easily be off by ±0.3 mL (maybe even a little worse). Based on this end point, mol Ag^+ delivered at the end point = (0.004 123 mM)(0.025 9 mL) = 0.106$_8$ mmol. This equals mol Cl^- in 100.0 mL of stream water, so $[Cl^-]$ = 0.106$_8$ mmol/100.0 mL = 1.06$_8$ mM = 37.9 mg Cl^-/L = 37.9 µg Cl^-/mL



(b) 25.9 ± 0.3 mL = 25.9 ± $1._{16}$%. An uncertainty of $1._{16}$% in the resulting molarity will be (0.011 6)(1.06_8 mM) = 0.012 mM. A reasonable expression of the molarity is $1.06_8 \pm 0.01_2$ mM or 1.07 ± 0.01 mM.

(c) The average difference between the two methods is (1.5 + 0.6 – 1.5 + 0.5 + 1.1 + 0.5 + 0.4)/7 = +0.443. The standard deviation of the differences is

$$s_d = \sqrt{\frac{\sum(d_i - \bar{d})^2}{n-1}} = 0.945$$

$$t_{\text{calculated}} = \frac{\bar{d}}{s_d}\sqrt{n} = \frac{0.443}{0.945}\sqrt{7} = 1.24 < t_{\text{table}} = 2.447$$

$t_{\text{calculated}} < t_{\text{table}}$ for 6 degrees of freedom at 95% confidence

The results are <u>not different</u> from each other.

ACTIVITY

S8-1. (a) 0.868 (b) 0.725 (c) 0.10 (d) 0.902

S8-2. The ionic strength is half way between 0.01 and 0.05 M $\Rightarrow \gamma = \frac{1}{2}(0.900 + 0.81) = 0.85_5$

S8-3. (a) $\log \gamma = \dfrac{-0.51 \cdot 1^2 \cdot \sqrt{0.038}}{1 + (350\sqrt{0.038}/305)} = -0.081\,2 \Rightarrow \gamma = 10^{-0.081\,2} = 0.82_9$

(b) $\gamma = \left(\dfrac{0.038 - 0.01}{0.05 - 0.01}\right)(0.81 - 0.900) + 0.900 = 0.83_7$

S8-4. $[Ag^+]^2 \gamma^2_{Ag^+} [CrO_4^{2-}]\gamma_{CrO_4^{2-}} = 1.2 \times 10^{-12}$

(a) For 0.05 M $KClO_4$, $\mu = 0.05$, $\gamma_{Ag^+} = 0.80$, $\gamma_{CrO_4^{2-}} = 0.445$

$(2x)^2 (0.80)^2 (x) (0.445) = 1.2 \times 10^{-12} \Rightarrow x = 1.0_2 \times 10^{-4}$ M

$[Ag^+] = 2x = 2.0_4 \times 10^{-4}$ M

(b) For 0.005 0 M $AgNO_3$, $\mu = 0.005$ M, $\gamma_{Ag^+} = 0.924$, $\gamma_{CrO_4^{2-}} = 0.740$

$[0.005\,0]^2 (0.924)^2 [CrO_4^{2-}] (0.740) = 1.2 \times 10^{-12} \Rightarrow [CrO_4^{2-}] = 7.6 \times 10^{-8}$ M

S8-5. Since we don't know the ionic strength, we begin by neglecting activity coefficients:

$[Tl^+][Br^-] = x^2 = K_{sp} = 3.6 \times 10^{-6} \Rightarrow x = 1.90 \times 10^{-3}$ M
$\Rightarrow \mu = 1.90 \times 10^{-3}$ M $\Rightarrow \gamma_{Tl^+} = 0.955$ and $\gamma_{Br^-} = 0.955$

For a second approximation, we add activity coefficients from the first calculation:

$[Tl^+]\gamma_{Tl^+} [Br^-]\gamma_{Br^-} = (x)(0.955)(x)(0.955) = K_{sp} \Rightarrow x = 1.99 \times 10^{-3}$ M
$\Rightarrow \mu = 1.99 \times 10^{-3}$ M $\Rightarrow \gamma_{Tl^+} = 0.954$ and $\gamma_{Br^-} = 0.954$

The third approximation is $(x)(0.954)(x)(0.954) = K_{sp} \Rightarrow x = 1.99 \times 10^{-3}$ M

S8-6. (a) $\mu = 0.050$ M $\Rightarrow \gamma_{H^+} = 0.86$

$\mathcal{A}_{H^+} = (0.050)(0.86) = 0.043$ pH $= -\log \mathcal{A}_{H^+} = 1.37$

(b) $\mu = 0.10$ M $\Rightarrow \gamma_{H^+} = 0.83$

$\mathcal{A}_{H^+} = (0.10)(0.83) = 0.083$ pH $= -\log \mathcal{A}_{H^+} = 1.08$

S8-7. (a) To find the activity coefficient for $\mu = 0.001$, we write

$$\log \gamma = \frac{-3.23\sqrt{0.001}}{1 + 2.57\sqrt{0.001}} + 0.198\,(0.001) = -0.094\,3. \quad \gamma = 10^{-0.094\,3} = 0.805$$

In a similar manner, we calculate the results below:

μ	0.001	0.01	0.1	0.5	1.0	1.5	2.0	3.0
γ	0.80_5	0.55_6	0.28_6	0.19_4	0.19_6	0.22_0	0.25_8	0.37_0
γ	0.870	0.675	0.405	($\leftarrow$ values from table)				

(b) $$\log \gamma = \frac{-3.23(\pm 0.32)\sqrt{0.1}}{1 + 2.57(\pm 0.32)\sqrt{0.1}} + 0.198\,(\pm 0.012) \cdot 0.1 = -0.543\,(\pm 0.065\,2)$$

$\gamma = 10^{-0.543(\pm 0.065\,2)} = 0.286 \pm e.$ Table 3-1 tells us that for $y = 10^x$,
$e_y = y \cdot 2.303 \cdot e_x = (0.286)(2.303)(0.065\,2) = 0.043.$ $\therefore$ $\gamma = 0.28_6 \pm 0.04_3$