Solutions to Suggested Chapter 12 Problems

12-11. For 0.005 0 M $(CH_3CH_2CH_2)_4N^+Br^-$ plus 0.005 0 M $(CH_3)_4N^+Cl^-$, $\mu = 0.010$ M. The size of the ion $(CH_3CH_2CH_2)_4N^+$ is 800 pm.

At $\mu = 0.01$ M, $\gamma = 0.912$ for an ion of charge ±1 with $\alpha = 800$ pm.

$\mathcal{A} = (0.005\,0)(0.912) = 0.004\,6$

12-13. (a) $$\log\gamma = \frac{-0.51 \cdot 2^2 \cdot \sqrt{0.083}}{1 + (600\sqrt{0.083}/305)} = -0.375 \Rightarrow \gamma = 10^{-0.375} = 0.42_2$$

(b) $$\gamma = \left(\frac{0.083 - 0.05}{0.1 - 0.05}\right)(0.405 - 0.485) + 0.485 = 0.43_2$$

12-16. At an ionic strength of 0.050 M, $\gamma_{H^+} = 0.86$ and $\gamma_{OH^-} = 0.81$.

$[H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-} = (x)(0.86)(x)(0.81) = 1.0 \times 10^{-14}$

$\Rightarrow x = [H^+] = 1.2 \times 10^{-7}$ M

$pH = -\log([H^+]\gamma_{H^+}) = -\log((1.2 \times 10^{-7})(0.86)) = 6.99$

12-19. The ionic strength is 0.100 M from $(CH_3)_4N^+IO_3^-$, assuming that the concentration of ions derived from dissolution of $Ba(IO_3)_2$ is negligible.

$$Ba(IO_3)_2(s) \rightleftharpoons \underset{x}{Ba^{2+}} + \underset{\approx 0.100}{2IO_3^-} \qquad K_{sp} = 1.5 \times 10^{-9}$$

$$K_{sp} = 1.5 \times 10^{-9} = [Ba^{2+}]\,\gamma_{Ba^{2+}}\,[IO_3^-]^2\,\gamma_{IO_3^-}^2$$

$$= x(0.38)(2x + 0.100)^2\,(0.775)^2 \approx x(0.38)(0.100)^2\,(0.775)^2$$

$$\Rightarrow x = [Ba^{2+}] = 6.6 \times 10^{-7}\text{ M}$$

Our assumption is verified:

$[IO_3^-]$ from $Ba(IO_3)_2 = 2x = 1.32 \times 10^{-6}$ M $\ll 0.100$ M from $(CH_3)_4N^+IO_3^-$.

12-25. (a) $2[Mg^{2+}] + [H^+] = [Br^-] + [OH^-]$

(b) $2[Mg^{2+}] + [H^+] + [MgBr^+] = [Br^-] + [OH^-]$

12-29. (a) There is 3/2 as much calcium as phosphorus in the solution. So,

$$2[Ca^{2+}] = 3\{[PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]\}$$

(b) There is 3/2 as much sulfur as iron in the solution. So, $3\{[Fe^{3+}] + [Fe(OH)^{2+}] + [Fe(OH)_2^+] + [FeSO_4^+]\} = 2\{[SO_4^{2-}] + [HSO_4^-] + [FeSO_4^+]\}$

12-30. $Y_{total} = \frac{3}{2} X_{total}$

$$\underbrace{2[X_2Y_2^{2+}] + [X_2Y^{4+}] + 3[X_2Y_3] + [Y^{2-}]}_{Y_{total}} = \frac{3}{2}\underbrace{\{2[X_2Y_2^{2+}] + 2[X_2Y^{4+}] + 2[X_2Y_3]\}}_{X_{total}}$$

Canceling like terms on both sides allows us to simplify the mass balance to

$[Y^{2-}] = [X_2Y_2^{2+}] + 2[X_2Y^{4+}]$

12-37. (a) $\alpha_B = \dfrac{[B^+]}{[B] + [BH^+]} = \alpha_{A^-} = \dfrac{K_a}{[H^+] + K_a}$

$$= \frac{6.3 \times 10^{-6}}{10^{-4.00} + 6.3 \times 10^{-6}} = 0.059$$

$$\alpha_{BH^+} = \frac{[BH^+]}{[B] + [BH^+]} = \alpha_{HA} = \frac{[H^+]}{[H^+] + K_a}$$

$$= \frac{10^{-4.00}}{10^{-4.00} + 6.3 \times 10^{-6}} = 0.94$$

(b), (c)

	α_B	α_{BH^+}
pH = 5.00:	0.39	0.61
pH = 6.00:	0.86	0.14

12-38. (a) $K_a = K_w/K_b = 10^{-10.00}$

$$\alpha_B = \frac{K_a}{[H^+]+K_a} = \frac{10^{-10.00}}{10^{-9.00} + 10^{-10.00}} = 0.090_9$$

$$\alpha_{BH^+} = \frac{[H^+]}{[H^+]+K_a} = \frac{10^{-9.00}}{10^{-9.00} + 10^{-10.00}} = 0.90_9$$

(b), (c)

	α_B	α_{BH^+}
pH = 10.00:	0.50_0	0.50_0
pH = 10.30:	0.66_6	0.33_4

12-40.

	A	B	C	D	E	F	G
1	Fractional composition of diprotic acid						
2							
3	pK1 =	pH	[H+]	Denominator	Alpha(H2A)	Alpha(HA-)	Alpha(A2-)
4	3.02	1	1.00E-01	1.01E-02	9.91E-01	9.46E-03	3.13E-06
5	pK2 =	2	1.00E-02	1.10E-04	9.13E-01	8.71E-02	2.89E-04
6	4.48	3	1.00E-03	1.99E-06	5.03E-01	4.81E-01	1.59E-02
7	K1 =	4	1.00E-04	1.37E-07	7.29E-02	6.96E-01	2.31E-01
8	9.55E-04	5	1.00E-05	4.13E-08	2.42E-03	2.31E-01	7.66E-01
9	K2 =	6	1.00E-06	3.26E-08	3.07E-05	2.93E-02	9.71E-01
10	3.31E-05	7	1.00E-07	3.17E-08	3.15E-07	3.01E-03	9.97E-01
11		8	1.00E-08	3.16E-08	3.16E-09	3.02E-04	1.00E+00
12							
13	A8 = 10^-A4		D4= C4^2+$A$8*C4+$A$8*$A$10			F4 = $A$8*C4/D4	
14	C4 = 10^-B4		E4 = C4^2/D4			G4 = $A$8*$A$10/D4	