Solutions -Chapter 9

1. In aqueous solutions the equilibrium $H_2O = H^+ + OH^-$ exists at all times, is described by

$$Kw = [H^+][OH^-].$$

Any species that can can produce protons or hydroxyl ions will affect the equilibrium position of the above. HBr of 10^{-4} molarity will make the hydroxyl ion concentration to an upper limit of 10^{-10} molar. The only source of hydroxyl here is the splitting of water, which, case splits to a lesser degree than pure water.

3. conc. of hydronium ion from the strong acid is in the order of that from autoprotolysis of water the systematic approach is required.

$$C_{ClO4} := 5.0\cdot 10^{-8}$$

charge balance: $C_H = C_{OH} + C_{ClO4}$

equilibria: $K_w = C_H \cdot C_{OH}$ $\qquad K_w := 1.0\cdot 10^{-14}$

algebra: $C_H = C_{OH} + C_{ClO4}$ has solution(s) $C_{OH} = C_H - C_{ClO4}$

$K_w = C_H \cdot C_{OH}$ by substitution, yields $K_w = C_H \cdot (C_H - C_{ClO4})$

has solution(s)

$$C_H := \begin{pmatrix} \frac{1}{2}\cdot C_{ClO4} - \frac{1}{2}\cdot\sqrt{C_{ClO4}{}^2 + 4\cdot K_w} \\ \frac{1}{2}\cdot C_{ClO4} + \frac{1}{2}\cdot\sqrt{C_{ClO4}{}^2 + 4\cdot K_w} \end{pmatrix}$$

$$C_H = \begin{pmatrix} -7.8078\times 10^{-8} \\ 1.2808\times 10^{-7} \end{pmatrix}$$

discard negative value.

$$C_H := 1.281\cdot 10^{-7}$$

fraction from water = $\dfrac{C_H - C_{ClO4}}{C_H} = 0.6097$

4. (a)

$pH := 1.092 \qquad C_H := 0.100$

$pH = -\log(\gamma \cdot C_H)$ has solution(s) $\gamma := \dfrac{\exp(-pH\cdot \ln(10))}{C_H}$

$\gamma = 0.8091$ table value = 0.83

(b) using the same procedure as in (a)

$pH := 2.102 \qquad C_H := 0.0100$

$pH = -\log(\gamma \cdot C_H)$ has solution(s) $\gamma := \dfrac{\exp(-pH \cdot \ln(10))}{C_H}$

$\gamma = 0.7907$

7. Ionization of BH^+; $BH^+ = B + H^+$

a - x x x at equilibrium (APPROXIMATION)

a = formal concentration

x = analytical concentration of (B and H)

$a := 0.100 \qquad K_b := 1.0 \cdot 10^{-4} \qquad K_a := \dfrac{K_w}{K_b}$

$K_a = \dfrac{C_B \cdot C_H}{C_{BH}}$

$K_a = \dfrac{x \cdot x}{a - x}$ has solution(s) $x := \begin{pmatrix} \dfrac{-1}{2} \cdot K_a - \dfrac{1}{2} \cdot \sqrt{K_a{}^2 + 4 \cdot K_a \cdot a} \\ \dfrac{-1}{2} \cdot K_a + \dfrac{1}{2} \cdot \sqrt{K_a{}^2 + 4 \cdot K_a \cdot a} \end{pmatrix}$

$x = \begin{pmatrix} -3.1623 \times 10^{-6} \\ 3.1622 \times 10^{-6} \end{pmatrix} \quad x := 3.162 \cdot 10^{-6}$

$pH := -\log(x)$

$pH = 5.5$

12. HA = H+ + A-

F-x x x (APPROXIMATION) at equilibrium

$F := 0.045 \qquad \alpha := \dfrac{.60}{100}$

$\alpha = \dfrac{x}{F}$ has solution(s) $x := \alpha \cdot F$

$K_a := \dfrac{x \cdot x}{F - x} \qquad K_a = 1.6298 \times 10^{-6}$

$pK_a := -\log(K_a) \qquad pK_a = 5.7879$

13 (a). HA = H+ + A-

F-x x x (APPROXIMATION) at equilibrium

$F := 10^{-2.00}$ QUITE A HIGH CONC.

$K_a = \frac{x \cdot x}{F - x}$ $K_a := 9.8 \cdot 10^{-5}$

has solution(s)

$$x := \begin{pmatrix} \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot \sqrt{K_a^{\,2} + 4 \cdot K_a \cdot F} \\ \frac{-1}{2} \cdot K_a + \frac{1}{2} \cdot \sqrt{K_a^{\,2} + 4 \cdot K_a \cdot F} \end{pmatrix} \qquad x = \begin{pmatrix} -1.0402 \times 10^{-3} \\ 9.4216 \times 10^{-4} \end{pmatrix}$$

$pH := -\log\left(9.422 \cdot 10^{-4}\right)$ $pH = 3.0259$

$\alpha := \frac{x}{F}$ $\alpha = \begin{pmatrix} -0.104 \\ 0.0942 \end{pmatrix}$ $\alpha := 9.4$ %

(b)

$F := 10^{-10.00}$

$pH := 7$ because it is very dilute. $C_H := 10^{-pH}$

$\alpha = \frac{C_A}{C_A + C_{HA}}$ and $K_a = \frac{C_H \cdot C_A}{C_{HA}}$

has solution(s)

$C_A = \frac{C_{HA} \cdot K_a}{C_H}$

$\alpha = \frac{C_A}{C_A + C_{HA}}$ substitution, yields $\alpha = C_{HA} \cdot \frac{K_a}{\left[C_H \cdot \left(C_{HA} \cdot \frac{K_a}{C_H} + C_{HA}\right)\right]}$

simplifies to

$\alpha = \frac{K_a}{\left(K_a + C_H\right)}$

$$\alpha := \frac{K_a}{(K_a + C_H)} \qquad \alpha := 99.9\ \%$$

14. HA = H+ + A-
F-x x x (APPROXIMATION) at equilibrium

$$K_a := 1.05\cdot 10^{-10} \qquad F := 50\cdot 10^{-3} \qquad C_{Li} := 0.05 \quad C_{Br} := C_{Li}$$

$$pK_a := -\log(K_a) \qquad pK_a = 9.9788$$

$$\mu := \frac{1}{2}\cdot\left[C_{Li}\cdot 1^2 + C_{Br}\cdot(-1)^2\right]$$

Let ion = phenolate ion

$$\alpha_{ion} := 600 \qquad z_{ion} := -1$$

$$\log(\gamma_{ion}) = \frac{-0.51\cdot z_{ion}^{\ 2}\cdot\sqrt{\mu}}{1 + \frac{\alpha_{ion}\cdot\sqrt{\mu}}{305}}$$

has solution(s)

$$\gamma_{ion} := \exp\left[-6.375\cdot 10^{39}\cdot z_{ion}^{\ 2}\cdot\frac{\sqrt{\mu}}{\left(5.428\cdot 10^{39} + 1.779\cdot 10^{37}\cdot\alpha_{ion}\cdot\sqrt{\mu}\right)}\right]$$

$$\gamma_{ion} = 0.8333$$

$$\alpha_H := 800 \qquad z_H := 1$$

$$\log(\gamma_H) = \frac{-0.51\cdot z_H^{\ 2}\cdot\sqrt{\mu}}{1 + \frac{\alpha_H\cdot\sqrt{\mu}}{305}}$$

has solution(s)

$$\gamma_H := \exp\left[-6.375\cdot 10^{39}\cdot z_H^{\ 2}\cdot\frac{\sqrt{\mu}}{\left(5.428\cdot 10^{39} + 1.779\cdot 10^{37}\cdot\alpha_H\cdot\sqrt{\mu}\right)}\right]$$

$$\gamma_H = 0.8474$$

$$K_a = \frac{(\gamma_H \cdot x) \cdot (\gamma_{ion} \cdot x)}{(F - x)}$$ has solution(s)

$$x := \begin{bmatrix} \frac{-1}{[2 \cdot (\gamma_H \cdot \gamma_{ion})]} \cdot \left(K_a + \sqrt{K_a^{\,2} + 4 \cdot \gamma_H \cdot \gamma_{ion} \cdot K_a \cdot F}\right) \\ \frac{-1}{[2 \cdot (\gamma_H \cdot \gamma_{ion})]} \cdot \left(K_a - \sqrt{K_a^{\,2} + 4 \cdot \gamma_H \cdot \gamma_{ion} \cdot K_a \cdot F}\right) \end{bmatrix}$$

$$x = \begin{pmatrix} -2.7268 \times 10^{-6} \\ 2.7266 \times 10^{-6} \end{pmatrix} \qquad \alpha := \frac{x}{F} \qquad \alpha = \begin{pmatrix} -5.4536 \times 10^{-5} \\ 5.4533 \times 10^{-5} \end{pmatrix} \qquad \alpha := 0.0054$$ %

15. Cr^{+3} + H_2O = $Cr(OH)^{+2}$ + H^+

0.010 -x x x (APPROXIMATION) equilibrium concentrations

$$K_a = \frac{x \cdot x}{F - x} \qquad K_a := 10^{-3.80} \qquad F := 0.010$$

has solution(s)

$$x := \begin{pmatrix} \frac{-1}{2} \cdot K_a - \frac{1}{2} \cdot \sqrt{K_a} \cdot \sqrt{K_a + 4 \cdot F} \\ \frac{-1}{2} \cdot K_a + \frac{1}{2} \cdot \sqrt{K_a} \cdot \sqrt{K_a + 4 \cdot F} \end{pmatrix} \qquad x = \begin{pmatrix} -1.3407 \times 10^{-3} \\ 1.1822 \times 10^{-3} \end{pmatrix}$$

$$pH := -\log(0.0012) \qquad pH = 2.9208$$

Note:
H^+ is predominantly from the hydrolysis reaction.

$$\alpha := \frac{0.0012}{F} \qquad \alpha = 0.12$$

23. B + H_2O = BH + OH^-

0.10 -x x x (APPROXIMATION) equilibrium concentrations

$$pH := 9.28 \qquad pOH := 14 - pH \qquad pOH = 4.72 \qquad F := 0.10$$

$$x := 10^{-pOH}$$

Note:
OH^- is predominantly from the hydrolysis reaction.

$$K_b := \frac{x \cdot x}{F - x} \qquad K_b = 3.6315 \times 10^{-9}$$

24. B + H2O = BH + OH-

0.10 -x x x (APPROXIMATION) equilibrium concentrations

$\alpha := 0.020$ $F := 0.10$ $x := \alpha \cdot F$

$K_b := \frac{x \cdot x}{F - x}$ $K_b = 4.0816 \times 10^{-5}$

26. By implication an x molar buffer means the sum of concentrations of the conjugate pair is x molar. Weigh 1.201g (0.0200 moles) of acetic acid and place in a beaker and dissolve in about 60ml of water. Calibrate a pH meter with a pH electrode, immerse the pH electrode in he above solution. Add dropwise a strong solution (2-5 molar) NaOH solution with stirring and monitoring the pH until it reaches a pH of 5.00. Transfer the resulting soltion into a 100 mL volumetric flask fill it to the graduation mark.

34.

acid	pK_a	
hydrogen peroxide	11.65	
propanoic acid	4.874	
cyanoacetic acid	2.472	
4-aminobenzenesulfonic acid	3.232	most suitable because 3.10 lies in pK+-1.

35. $pK_a := 5.00$ $C_A := 0.050$ $C_{HA} := 0.100$

$pH := pK_a + \log\left(\frac{C_A}{C_{HA}}\right)$ $pH = 4.699$

38. $pK_b := 10.85$ $pK_a := 14.00 - pK_b$

$pH = pK_a + \log\left(\frac{1}{ratio}\right)$ $ratio = \frac{C_{HNO2}}{C_{NO2}}$

has solution(s)

$pH := 2$

$ratio := \frac{1}{10^{(pH - pK_a)}}$ $ratio = 14.1254$

$pH := 10.00$

$ratio := \frac{1}{10^{(pH - pK_a)}}$ $ratio = 1.4125 \times 10^{-7}$

39.

	HA	+	OH-	=	A^-	+	H2O
start (moles)	0.0210						
addition (moles)					x		
final	0.0210-x				x		

Added strong base produce an equal number of A^- ions, which is the major contributor of A^- in solution.

$$pH := 7.40 \qquad pK_a := 7.56$$

$$pH = pK_a + \log\left(\frac{x}{0.0210 - x}\right)$$

i.e. $$\frac{x}{0.0210 - x} = 10^{(pH - pK_a)}$$

has solution(s)

$$-21. \cdot \frac{10.^{(pH - 1. \cdot pK_a)}}{\left[-1000. - 1000. \cdot 10.^{(pH - 1. \cdot pK_a)}\right]} = 8.5874 \times 10^{-3}$$

$x := 0.0086$ moles

Volume of 0.626M KOH needed = $\frac{0.0086}{0.626} \cdot 1000 = 13.738$ ml.