

CHEMISTRY 31
Fall, 2017 - Dixon
Homework Set 3.2 Solutions

Ch. 8: 19, 21, 23, 29a

19. Write a charge balance for a solution of H_2SO_4 in water if the H_2SO_4 ionizes to HSO_4^- and SO_4^{2-} .

Charge balance: $[\text{H}^+] = [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] + [\text{OH}^-]$

21. a) Write the charge and mass balances for a solution made by dissolving MgBr_2 to give Mg^{2+} , Br^- , MgBr^+ , and MgOH^+ .

Charge balance: $2[\text{Mg}^{2+}] + [\text{H}^+] + [\text{MgOH}^+] + [\text{MgBr}^+] = [\text{Br}^-] + [\text{OH}^-]$

Mass balance: $[\text{Mg}^{2+}]_{\text{total}}/[\text{Br}^-]_{\text{total}} = 1/2$ or $2[\text{Mg}^{2+}]_{\text{total}} = [\text{Br}^-]_{\text{total}}$

$2([\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{MgBr}^+]) = [\text{Br}^-] + [\text{MgBr}^+]$

b) Modify the mass balance if the solution was made by dissolving 0.2 mol MgBr_2 in 1 L.

$[\text{Mg}^{2+}]_{\text{total}} = 0.20 \text{ M} = [\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{MgBr}^+]$

$[\text{Br}^-]_{\text{total}} = 0.40 \text{ M} = [\text{Br}^-] + [\text{MgBr}^+]$

23. For a 0.1 M aqueous solution of sodium acetate, $\text{Na}^+\text{CH}_3\text{CO}_2^-$, one mass balance is simply $[\text{Na}^+] = 0.1 \text{ M}$. Write a mass balance involving acetate.

If the acetate doesn't react further, $[\text{CH}_3\text{CO}_2^-] = 0.1 \text{ M}$.

However, 1 mole of CH_3CO_2^- reacts with water to form 1 mole of $\text{CH}_3\text{CO}_2\text{H}$.

So, mass balance equation is: $[\text{CH}_3\text{CO}_2\text{H}] + [\text{CH}_3\text{CO}_2^-] = 0.1 \text{ M}$.

29. a) Following the example of $\text{Mg}(\text{OH})_2$ in section 7-5, write the equations needed to find the solubility of $\text{Ca}(\text{OH})_2$. Include activity coefficients where appropriate. Equilibrium constants are in Appendixes F and I.

Using the systematic method, we can determine the solubility of $\text{Ca}(\text{OH})_2$.

Step 1) Reactions:

(1) $\text{Ca}(\text{OH})_2(\text{s}) \leftrightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad K_{\text{sp}} = 6.5 \times 10^{-6}$

(2) $\text{Ca}^{2+} + \text{OH}^- \leftrightarrow \text{CaOH}^+ \quad K = 10^{1.30} = 19.95$

(3) $\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}^+ + \text{OH}^- \quad K_{\text{w}} = 1.0 \times 10^{-14}$

Step 2) Charge Balance Reaction:

$2[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{H}^+] = [\text{OH}^-]$

Step 3) Mass Balance Reactions:

This is particularly difficult and not needed (you can realize it is not needed by skipping ahead to steps 4 and 5). However, it can be done in the following manner.

$[\text{Ca}]_{\text{source}}/[\text{OH}]_{\text{source}} = 1/2 = \{[\text{Ca}^{2+}] + [\text{CaOH}^+]\}/\{[\text{OH}^-] + [\text{CaOH}^+] - [\text{H}^+]\}$

The first two terms in the numerator and denominator are from the existing Ca and OH containing terms, respectively. However, the third term in the denominator arises from reaction 3. When reaction 3 occurs, one of the OH^- is lost in the formation of water. Since we can not add the production of water ($[\text{H}_2\text{O}]$ stays the same within measurement), we can account for this by a co-loss of $[\text{H}^+]$.

or $2[\text{Ca}^{2+}] + 2[\text{CaOH}^+] = [\text{OH}^-] + [\text{CaOH}^+] - [\text{H}^+]$

If we rearrange this equation, we get $2[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{H}^+] = [\text{OH}^-]$, which is the charge balance equation

Step 4)

$$(1) K_{sp} = 6.5 \times 10^{-6} = \gamma_{Ca}[Ca^{2+}]\gamma_{OH}^2[OH^-]^2$$

$$(2) K = 19.95 = \gamma_{CaOH}[CaOH^+]/\gamma_{Ca}[Ca^{2+}]\gamma_{OH}[OH^-]$$

$$(3) K_w = 1.0 \times 10^{-14} = \gamma_H[H^+]\gamma_{OH}[OH^-]$$

Step 5) Unknown species: $[Ca^{2+}]$, $[CaOH^+]$, $[H^+]$ and $[OH^-]$

Equations: 1 charge balance/mass balance (the mass balance equation is redundant) and 3 equilibrium equation

Step 6) It is not actually asked that you solve this equation.

Ch. 9: 3, 6, 8, 11, 19, 21, 26, 34, 35, 40 added – I forgot to give buffer problem examples

3. Calculate the pH of 5.0×10^{-8} M $HClO_4$. What fraction of total H^+ in this solution is derived from dissociation of water?

Because the concentration of $HClO_4$, a strong acid, is so low, it appears that water can be a significant source of H^+ and we should use the systematic approach to solving this problem.

Step 1) Reactions: 1) $HClO_4 \rightarrow H^+ + ClO_4^-$ and 2) $H_2O(l) \leftrightarrow H^+ + OH^-$

Step 2) Charge balance: $[H^+] = [OH^-] + [ClO_4^-]$

Step 3) Mass balance $[ClO_4^-] = [HClO_4]_o = 5.0 \times 10^{-8}$ M (and also the charge balance equation)

Step 4) Equilibrium Equations: $K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$ (neglecting activity)

Step 5) 3 unknowns ($[H^+]$, $[ClO_4^-]$, and $[OH^-]$); 3 equations (charge balance, mass balance and equilibrium)

Step 6) Solving the problem:

$$[ClO_4^-] = 5.0 \times 10^{-8} \text{ M}$$

$$\text{Charge balance becomes } [H^+] = [OH^-] + 5.0 \times 10^{-8} \text{ M or } [OH^-] = [H^+] - 5.0 \times 10^{-8} \text{ M}$$

$$1.0 \times 10^{-14} = [H^+][OH^-] = [H^+]([H^+] - 5.0 \times 10^{-8} \text{ M}) = [H^+]^2 - 5.0 \times 10^{-8} \text{ M}[H^+]$$

$$[H^+]^2 - 5.0 \times 10^{-8} \text{ M}[H^+] - 1.0 \times 10^{-14} = 0$$

$$[H^+] = \{ 5.0 \times 10^{-8} \text{ M} + [(-5.0 \times 10^{-8} \text{ M})^2 + 4.0 \times 10^{-14}]^{0.5} \} / 2 = 1.28 \times 10^{-7} \text{ M}$$

$$\text{pH} = 6.89$$

$$\text{fraction} = [H^+]_{H_2O} / [H^+]_{total} = [OH^-] / [H^+] = (1.0 \times 10^{-14} / 1.28 \times 10^{-7}) / 1.28 \times 10^{-7}$$

$$\text{fraction} = 0.61$$

6. Find the pH and fraction of dissociation (α) of a 0.100 M solution of the weak acid HA with $K_a = 1.00 \times 10^{-5}$.

Since the K_a value is not low and the concentration is high, it should be possible to use the ICE method (as opposed to needing to use the systematic method).

	HA	\leftrightarrow	H ⁺	+	A ⁻
Initial	0.100				
Change	-x		+x		+x
Equilibrium	0.100 - x		x		x

$$1.00 \times 10^{-5} = [H^+][A^-] / [HA] = x^2 / (0.100 - x)$$

If we assume $x \ll 0.100$, this becomes $x^2 = 1.00 \times 10^{-6}$ or $x = 1.00 \times 10^{-3}$ M. This is a factor of 100 less than 0.100 M so our assumption should be not bad. Then, **pH = 3.000**. If we used the complete quadratic equation, we would get $x = 9.95 \times 10^{-4}$ M or pH = 3.002 (which is barely significantly different).

$$\alpha = [A^-] / [HA]_o = 0.00100 / 0.100 = \mathbf{0.0100} \text{ (or using the quadratic equation, } \alpha = 0.00995)$$

8. Find the pH and concentrations of $(\text{CH}_3)_3\text{N}$ and $(\text{CH}_3)_3\text{NH}^+$ in a 0.060 M solution of trimethylammonium chloride.

$$K_a((\text{CH}_3)_3\text{NH}^+) = 1.58 \times 10^{-10}$$

$$K_a = [(\text{CH}_3)_3\text{N}][\text{H}^+]/[(\text{CH}_3)_3\text{NH}^+]$$

$$[(\text{CH}_3)_3\text{NH}^+]_o = 0.060 \text{ M}$$

$$[\text{H}^+] = [(\text{CH}_3)_3\text{N}] = x \quad (\text{assuming } x \gg 10^{-7})$$

$$[(\text{CH}_3)_3\text{NH}^+] = 0.060 \text{ M} \quad (\text{assuming } 0.060 \text{ M} \gg x)$$

$$x^2 = K_a \cdot 0.060 \quad x = (1.58 \times 10^{-10} \cdot 0.060)^{0.5}$$

$$[\text{H}^+] = [(\text{CH}_3)_3\text{N}] = 3.1 \times 10^{-6} \text{ M}$$

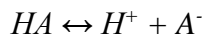
both assumptions are true ($x = 30 \cdot 10^{-7}$)

$$\text{pH} = 5.51$$

$$[(\text{CH}_3)_3\text{NH}^+] = 0.060 \text{ M}$$

11. A 0.0450 M solution of benzoic acid has a pH of 2.78. Calculate the pK_a for this acid.

If we call benzoic acid, HA, we know that HA reacts as:



$$[\text{H}^+] = 10^{-\text{pH}} = 0.00166 \text{ M} \quad (\text{only significant to two sig figs})$$

Since $\text{H}^+ > \text{H}^+$ from water, we know that $[\text{H}^+] = [\text{A}^-]$ and from our mass balance equation, we know that $[\text{HA}]_o = 0.0450 \text{ M} = [\text{HA}] + [\text{A}^-]$

$$\text{or } [\text{HA}] = [\text{HA}]_o - [\text{A}^-] = 0.0450 - 0.00166 = 0.0433 \text{ M}$$

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}] = (0.00166)^2/0.0433 = 6.35 \times 10^{-5} \text{ or } \text{pK}_a = 4.20$$

19. Find the pH and fraction of association (α) of a 0.100 M solution of the weak base B with $K_b = 1.00 \times 10^{-5}$.

Since the K_b value is not low and the concentration is high, it should be possible to use the ICE method (as opposed to needing to use the systematic method).

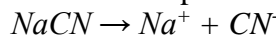
	B	+	H ₂ O	\leftrightarrow	BH ⁺	+	OH ⁻
Initial	0.100						
Change	-x				+x		+x
Equilibrium	0.100 - x				x		x

$$1.00 \times 10^{-5} = [\text{BH}^+][\text{OH}^-]/[\text{B}] = x^2/(0.100 - x)$$

If we assume $x \ll 0.100$, this becomes $x^2 = 1.00 \times 10^{-6}$ or $x = 1.00 \times 10^{-3} \text{ M}$. This is a factor of 100 less than 0.100 M so our assumption should be not bad. Then, $\text{pH} = 14 - \text{pOH} = 11.000$. If we used the complete quadratic equation, we would get $x = 9.95 \times 10^{-4} \text{ M}$ or $\text{pH} = 10.998$ (which is barely significantly different).

$$\alpha = [\text{BH}^+]/[\text{B}]_o = 0.00100/0.100 = 0.0100 \quad (\text{or using the quadratic equation, } \alpha = 0.00995)$$

21. Find the pH of 0.050 M NaCN.



Na^+ doesn't react further, but CN^- is the conjugate base of the weak acid HCN ($K_a = 6.2 \times 10^{-10}$)

It will react as a weak base in water:

	CN ⁻	+	H ₂ O	\leftrightarrow	HCN	+	OH ⁻
Initial	0.050						
Change	-x				+x		+x
Equilibrium	0.050 - x				x		x

$$K_b = K_w/K_a = 1.61 \times 10^{-5} = x^2/(0.050 - x)$$

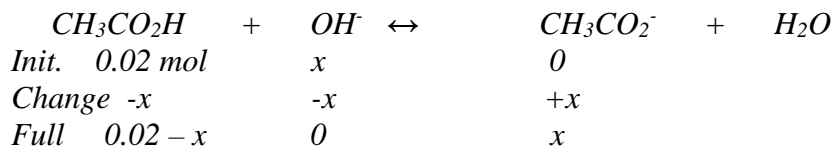
$$x^2 + 1.61 \times 10^{-5}x - 8.06 \times 10^{-7} = 0 \quad x = 8.9 \times 10^{-4} \text{ M} = [\text{OH}^-]$$

$$\text{pH} = 14 - \text{pOH} = \mathbf{10.95}$$

26. Describe how to prepare 100 mL of 0.200 M acetate buffer, pH 5.00 starting with pure liquid acetic acid and solutions containing ~3 M HCl and ~3 M NaOH.

1) Get a 100 mL volumetric flask and weigh 1.20 g (calculated from $0.1 \text{ L} \times 0.200 \text{ mol/L} \times 60 \text{ g/mol}$) of pure acetic acid into the volumetric flask

2) Calculate the moles of 3 M NaOH needed to get to a pH of 5.00. This is done by creating a mole table:



Now, we use the H-H equation: $\text{pH} = 5.00 = 4.756 + \log([\text{CH}_3\text{CO}_2^-]/[\text{CH}_3\text{CO}_2\text{H}])$ or

$$0.244 = \log[x/(0.02 - x)] \text{ or } 10^{0.244} = 1.754 = x/(0.02 - x) \text{ or } x = 0.0127 \text{ moles}$$

3) Determine the vol. of 3 M NaOH needed to get this number of moles

$$0.0127 = (3 \text{ M})V \text{ or } V = 4.25 \times 10^{-3} \text{ L or } 4.25 \text{ mL}$$

4) After adding the NaOH, dilute to the mark slowly.

34. Which of the following acids would be most suitable for preparing a buffer of pH 3.10?

i) hydrogen peroxide; ii) propanoic acid; iii) cyanoacetic acid; iv) 4-aminobenzenesulfonic acid.

This can be determined by first looking up pK_a values:

i) hydrogen peroxide – 11.65; ii) propanoic acid – 4.87; iii) cyanoacetic acid – 2.47; iv) 4-aminobenzenesulfonic acid – 3.232 (for conjugate base).

Either iii) or iv) could be used, but **4-aminobenzenesulfonic acid** has the pK_a closest to the desired pH.

35. A buffer was prepared by dissolving 0.100 mol of the weak acid HA ($K_a = 1.00 \times 10^{-5}$) plus 0.050 mol of its conjugate base Na^+A^- in 1.00 L. Find the pH.

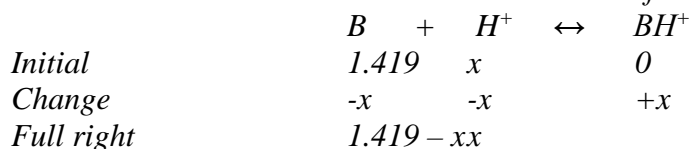
$$\text{pH} = \text{pK}_a + \log[\text{A}^-]/[\text{HA}] = 5.00 + \log(0.050/0.100) = \mathbf{4.70}$$

40. How many milliliters of 0.246 M HNO_3 should be added to 213 mL of 0.00666 M 2,2'-bipyridine to give a pH of 4.19?

$$\text{Let } 2,2'\text{-bipyridine} = \text{B} \text{ and moles of B} = (213 \text{ mL})(0.00666 \text{ mmol/mL}) = 1.419 \text{ mmol}$$

$$\text{pK}_a(\text{BH}^+) = 4.34$$

We need to make a mole table in the conversion of B to BH^+ by addition of HNO_3 :



$$\text{pH} = 4.19 = \text{pK}_a + \log[n(\text{B})/n(\text{BH}^+)] = 4.34 + \log(1.419 - x/x)$$

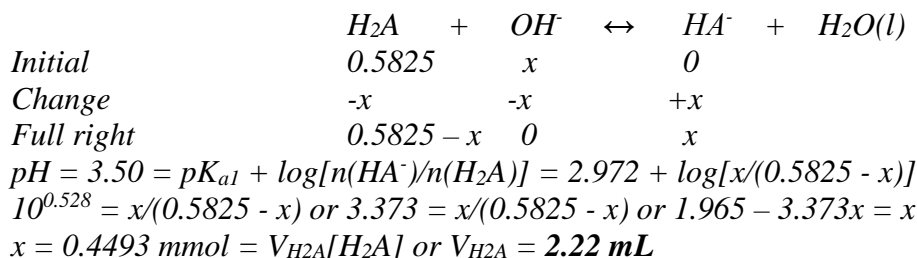
$$10^{4.19-4.34} = (1.419 - x)/x \text{ or } 0.708 = (1.419 - x)/x \text{ or } 0.708x = 1.419 - x$$

$$x = 0.831 \text{ mmol} = V_{\text{HNO}_3}[\text{HNO}_3] \text{ or } V_{\text{HNO}_3} = \mathbf{3.38 \text{ mL}}$$

Ch. 10: 3, 4, [not enough time] 13, 30

13. How many mL of 0.202 M NaOH should be added to 25.0 mL of 0.023 3 M salicylic acid (2-hydroxybenzoic acid) to adjust the pH to 3.50?

This is a buffer problem. The pK_a values of salicylic acid ($= H_2A$) are 2.972 and 13.7. Since the desired pH is close to the pK_{a1} , we need to add enough OH^- to convert some of H_2A to HA^- in a mole table:



30. Calculate $\alpha(H_2A)$, $\alpha(HA^-)$, and $\alpha(A^{2-})$ for cis-butenedioic acid at pH 1.00, 1.92, 6.00, 6.27, and 10.00. This is easiest using Excel with the equations for $\alpha(H_2A)$, $\alpha(HA^-)$, and $\alpha(A^{2-})$ given below:

$$\alpha(H_2A) = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

$$\alpha(HA^-) = \frac{[H^+]K_{a1}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

$$\alpha(A^{2-}) = \frac{K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}}$$

See spreadsheet:

	Cis-butenedioic acid				
	Ka1	Ka2			
	1.20E-02	5.37E-07			
pH	[H+]	alphaH2A	alphaHA-	alphaA2-	
1	0.1	0.89286	0.10714	5.75E-07	
1.9	0.012589	0.51197	0.48801	0.00002	
6	0.000001	0.00005	0.65058	0.34936	
6.27	5.37E-07	0.00002	0.50000	0.49997	
10	1E-10	1.55E-12	0.00019	0.99981	
	Cell	Equation			
	C9	=B9^2/(B9^2+B9*B\$6+B\$6*C\$6)			
	D9	=B9*B\$6/(B9^2+B9*B\$6+B\$6*C\$6)			
	E9	=1-(C9+D9)			

Ch. 11: 2, 6 [not enough time]