

Chapter 16

Acid-Base Equilibrium

Chapter 16 suggested problems

10th Ed. - 16.x: 13, 15, 17, 27, 29, 31, 37, 41, 43, 45, 53, 59, 61, 70, 71, 75, 77, 81, 91, 93, 99, 101, 116

11th Ed. - 16.x: 15, 17, 19, 29, 31, 33, 39, 43, 45, 47, 53, 59, 61, 70, 71, 75, 77, 81, 91, 93, 99, 101, 120

Chapter Objectives

After completing this chapter, you should, *at a minimum*, be able to do the following. This information can be found in my lecture notes for this and other chapters and also in your text.

1. Correctly answer all of the questions suggested above and in the quiz for this chapter.
 2. Define basic terms such as Arrhenius acid, Arrhenius base, Brønsted-Lowry acid, Brønsted-Lowry base, Lewis acid, Lewis base, hydronium ion, strong acid, weak acid, strong base, weak base, conjugate acid-base pair, conjugate acid, conjugate base, autoionization of water, ion-product constant, ionization constant, amphoteric, neutral solution, acidic solution, basic solution, pH, pOH, acid dissociation constant, diprotic acid, triprotic acid, polyprotic acid, base dissociation constant, oxyacid.
 3. List the common strong acids and bases and the common weak acids and bases. Define what strong and weak always mean in aqueous chemistry.
 4. Explain why K_w is temperature dependant.
 5. Explain the relationship between K_w and whether a solution is neutral, acidic, or basic.
 6. Be able to calculate the pH and pOH of solutions of strong acids and bases.
 7. Be able to calculate the acid dissociation constant for a weak acid.
 8. Use the acid dissociation constant to calculate the pH of a weak acid solution, and the concentrations of other species in the equilibrium solution.
 9. Use acid dissociation constants to calculate the pH and the concentrations of other species in the equilibrium solution of a weak diprotic acid.
 10. Write the equations that describe the generic aqueous behavior of a weak acid, the conjugate base of a weak acid, a weak base, and the conjugate acid of a weak base.
 11. Describe the relationship between the autoionization constant of water and the acid and base dissociation constants of a weak acid-base pair.
 12. Be able to account for the acid-base properties of salt solutions.
 13. Describe the factors that affect acid strength on a molecular level.
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Class Notes

I. Basic acid-base theories and concepts

A. General

1. Acid: from Latin "acidus" meaning sour
2. Bases: slippery, sour, from Old English "to bring low;" when bases are added to acids they lower the acid concentration

B. Arrhenius concept

1. Acid: substance that donates a hydrogen ion in aqueous solution
2. Base: substance that donates a hydroxide ion in aqueous solution
3. Bare ions do not exist in solution, but rather as ion-solvent clusters, so H^+ is represented as H_3O^+ even though in reality there are probably clusters of 3-7 water molecules around each hydrogen ion
4. H_3O^+ and OH^- are important because of their relevance to the equilibrium

$$2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$$

C. Brønsted-Lowry concept

1. Acid: substance that can transfer a proton to another substance
2. Base: substance that can accept a proton from another substance
3. Not necessarily in aqueous solution
4. This is an expansion on the Arrhenius theory because there are numerous substances besides hydroxide ion that can accept protons e.g. ammonia, amines and heterocyclic compounds such as pyridine, oxyanions (conjugate bases), alkoxides, etc.
 - a. Amphiprotic (amphoteric): substances that can act either as acids or bases e.g. hydrogen sulfate, hydrogen carbonate, hydrogen sulfide, etc.

D. Lewis concept

1. Acid: substance that can accept an electron pair from another substance
2. Base: substance that can donate an electron pair to another substance
3. Not necessarily in aqueous solution
4. Coordinate covalent bond formation
5. Examples: ammonia - ammonium, transition metal complexes and ligands,

e.g. $\text{Al}(\text{H}_2\text{O})_6^{3+}$

E. Strong and weak acids and bases

1. Strong acids - completely dissociate in aqueous solution: HCl, HBr, HI, HNO_3 , H_2SO_4 , HClO_4
2. Weak acids - incomplete dissociation in aqueous solution: HF, H_3PO_4 , H_2CO_3 , H_2S , organic acids
3. Strong bases - completely dissociate in aqueous solution: Group I hydroxides, Group II hydroxides (except beryllium and magnesium), ammonium hydroxides
4. Weak bases - incomplete dissociation in aqueous solution: ammonia, amines
5. Note that "strong" and "weak" seldom give an accurate sense of how corrosive the substance might be

II. Conjugate acid-base pairs

A. The anion of an acid is its conjugate base

1. $\text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{HB}^+$
2. HA is a stronger acid than HB^+
3. Reaction proceeds toward formation of the weaker acid
4. $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$

B. The cation of a base is its conjugate acid

1. $\text{B} + \text{HA} \rightleftharpoons \text{HB}^+ + \text{A}^-$
2. B is a stronger base than A^-
3. Reaction proceeds toward formation of the weaker base
4. $\text{HB}^+ + \text{H}_2\text{O} \rightleftharpoons \text{B} + \text{H}_3\text{O}^+$

C. Relative strengths

1. The stronger the acid, the weaker its conjugate base
2. The stronger the base, the weaker its conjugate acid
3. "In every acid-base reaction the position of the equilibrium favors transfer of the proton to the stronger base." (BLB 10th: p. 675)

III. The autoionization of water

- A. Water is amphoteric
- B. $2 \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- C. $K_c = [\text{H}_3\text{O}^+][\text{OH}^-] / [\text{H}_2\text{O}]^2$
- D. $K_c[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$
- E. K_w is called the ion-product constant for water (ionization constant)
- F. As is the case with all equilibrium constants, K_w is temperature dependent and at 24°C $K_w = 1.0 \times 10^{-14}$
- G. Implication: since $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and since $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, then $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$
- H. When $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ the solution is said to be neutral
- I. The variation of $\text{p}K_w$ and $\text{p}K_c$ for deuterium oxide with temperature (CRC: D-167,168)

$\text{p}K_w$	temperature $^\circ\text{C}$	$\text{p}K_c$ for D_2O
14.9435	0	
14.7338	5	
14.5346	10	15.439
14.3463	15	
14.1669	20	15.049
14.0000	24	
13.9965	25	14.869
13.8330	30	14.699
13.6801	35	
13.5348	40	14.385
13.3960	45	
13.2617	50	14.103
13.1369	55	
13.0171	60	

IV. The pH scale

- A. The "p function:" $\text{p}(x) = -\log(x)$
- Used to make various numbers more "friendly" - $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, K_a , K_b
- B. $\text{pH} = -\log [\text{H}_3\text{O}^+]$
- C. Meaning

1. $\text{pH} = 7$: $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, neutral solution
2. $\text{pH} < 7$: $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, acidic solution
3. $\text{pH} > 7$: $[\text{H}_3\text{O}^+] < [\text{OH}^-]$, basic solution

D. Measurement of pH is done with indicators, litmus papers, and instruments

E. Calculating pH

1. For 1.0 M HNO_3 , $[\text{H}_3\text{O}^+] = 1.0 \text{ M}$, $\text{pH} = ?$
2. For 6.0 M HClO_4 , $[\text{H}_3\text{O}^+] = 6.0 \text{ M}$, $\text{pH} = ?$
3. For 0.25 M HCl , $[\text{H}_3\text{O}^+] = 0.25 \text{ M}$, $\text{pH} = ?$
4. For 9.0 M H_2SO_4 , $[\text{H}_3\text{O}^+] = 18.0 \text{ M}$, $\text{pH} = ?$

F. Calculating pOH

1. Just as $\text{pH} = -\log [\text{H}_3\text{O}^+]$, $\text{pOH} = -\log [\text{OH}^-]$
2. $\text{pH} + \text{pOH} = 14$
3. Examples
 - a. If the pH of an acid solution is 2.45, what is the $[\text{OH}^-]$?
 - b. If the pOH of a solution of base is 3.76, what is the pH of the solution? the $[\text{H}_3\text{O}^+]$?

V. Strong acids and bases

- A. In pure water $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$
- B. When substances are added to pure water that dissociate and form either H_3O^+ or OH^- , the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ of the solution change but the product of the concentrations is still equal to K_w , i.e., $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ remains true

C. Strong acids dissociate completely

1. What is the $[\text{H}_3\text{O}^+]$ of an aqueous solution of a strong acid? Since dissociation = 100%, $[\text{H}_3\text{O}^+] = [\text{acid}]_i$
 - a. For 1.0 M HNO_3 , $[\text{H}_3\text{O}^+] = 1.0 \text{ M}$
 - b. For 6.0 M HClO_4 , $[\text{H}_3\text{O}^+] = 6.0 \text{ M}$
 - c. For 0.25 M HCl , $[\text{H}_3\text{O}^+] = 0.25 \text{ M}$

- d. For 9.0 M H_2SO_4 , $[\text{H}_3\text{O}^+] = 18.0 \text{ M}$
2. The contribution of water ($2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$) to the $[\text{H}_3\text{O}^+]$ of the solution can be safely ignored unless the hydrogen ion concentration is around 1×10^{-4} or less
3. What is the $[\text{OH}^-]$ of an aqueous solution of a strong acid?
- Since $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+]$
 - Given a 0.25 M HCl solution, what is $[\text{OH}^-]$? ($4 \times 10^{-14} \text{ M}$)
 - Given a 0.040 M H_2SO_4 solution, what is $[\text{OH}^-]$? ($1.25 \times 10^{-13} \text{ M}$)
- D. Weak acids do not dissociate completely and will be examined later
- E. Strong bases dissociate completely
- What is the $[\text{OH}^-]$ of an aqueous solution of a strong base? Since dissociation = 100%, $[\text{OH}^-] = [\text{base}]_i$
 - The contribution of water ($2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$) to the $[\text{OH}^-]$ of the solution can be safely ignored unless the hydroxide ion concentration is around 1×10^{-4} or less
 - For 1.0 M NaOH, $[\text{OH}^-] = 1.0 \text{ M}$
 - For 6.0 M NH_4OH , $[\text{OH}^-] = 6.0 \text{ M}$
 - For 0.25 M KOH, $[\text{OH}^-] = 0.25 \text{ M}$
 - For 9.0 M $\text{Ba}(\text{OH})_2$, $[\text{OH}^-] = 18.0 \text{ M}$
 - What is the $[\text{H}_3\text{O}^+]$ of an aqueous solution of a strong base?
 - Since $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-]$
 - Given a 0.25 M NaOH solution, what is $[\text{H}_3\text{O}^+]$? ($4 \times 10^{-14} \text{ M}$)
 - Given a 0.040 M $\text{Sr}(\text{OH})_2$ solution, what is $[\text{H}_3\text{O}^+]$? ($1.25 \times 10^{-13} \text{ M}$)
- F. Weak bases do not dissociate completely and will be examined later

VI. Weak acids

- A. Strong acids dissociate ~100%, e.g. 1 M HCl yields 1 M H^+
- B. Weak acids dissociate much less than 100%, e.g. 1 M $\text{HC}_2\text{H}_3\text{O}_2$ does not yield 1

M H⁺

C. Can the equilibrium concentration of [H⁺] for a weak acid be calculated?

D. Given $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$

- $K = [\text{H}_3\text{O}^+] \cdot [\text{A}^-] / [\text{HA}] \cdot [\text{H}_2\text{O}]$
- Since [H₂O] is constant, $K \cdot [\text{H}_2\text{O}] = [\text{H}_3\text{O}^+] \cdot [\text{A}^-] / [\text{HA}] = K_a$
- K_a is called the acid dissociation (ionization) constant
- Each weak acid has its own unique acid dissociation constant
- K_a for any acid is determined experimentally (BLB 10: 685, Table 16.2 provides a list of values)
- The smaller the value of K_a , the weaker the acid

E. Using K_a to find [H⁺] and using [H⁺] to find K_a

1. A 0.10 M solution of lactic acid (CH₃CHOHCOOH) has a pH of 2.43. What is the K_a for lactic acid?

- $\text{HLac} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Lac}^-$
- If pH = 2.43 then $[\text{H}^+] = 3.7 \times 10^{-3} \text{ M}$
- $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Lac}^-] / [\text{HLac}]$
-

	[HLac]	[H ₃ O ⁺]	[Lac ⁻]
initial	0.10	0	0
x	-x	+x	+x
eqb	0.10 - x	x	x

- Since we know the pH, we know that $x = [\text{H}_3\text{O}^+]_{\text{eqb}} = 3.7 \times 10^{-3} \text{ M}$
 - $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Lac}^-] / [\text{HLac}] = x^2 / (0.10 - x) = (3.7 \times 10^{-3})^2 / (0.10 - 3.7 \times 10^{-3}) = 1.4 \times 10^{-4}$
 - How much lactic acid ionizes? $(3.7 \times 10^{-3} / 0.10) \times 100 = 3.7\%$
2. Calculate the pH of a 0.020 M solution of benzoic acid ($K_a = 6.3 \times 10^{-5}$).
- $\text{HBen} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Ben}^-$
 - $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Ben}^-] / [\text{HBen}]$

c.

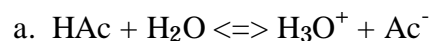
	[HBen]	[H ₃ O ⁺]	[Ben ⁻]
initial	0.020	0	0
x	-x	+x	+x
eqb	0.020 - x	x	x

d. $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Ben}^-] / [\text{HBen}] = x^2 / 0.020 - x$

e. Using the quadratic equation $x = 1.09 \times 10^{-3}$

f. If $[\text{H}_3\text{O}^+] = 1.09 \times 10^{-3}$ M, then pH = 2.96

3. Given a 0.10 M solution of acetic acid ($K_a = 1.8 \times 10^{-5}$), find the equilibrium concentrations of all species and find the pH of the solution.



b. $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Ac}^-] / [\text{HAc}]$

c.

	[HAc]	[H ₃ O ⁺]	[Ac ⁻]
initial	0.10	0	0
x	-x	+x	+x
eqb	0.10 - x	x	x

d. $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Ac}^-] / [\text{HAc}] = x^2 / 0.10 - x$

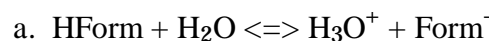
e. Using the quadratic equation $x = 1.33 \times 10^{-3}$

f. If $x = 1.33 \times 10^{-3}$ then $[\text{H}_3\text{O}^+] = [\text{Ac}^-] = 1.33 \times 10^{-3}$ M and $[\text{HAc}] = 0.10 - 1.33 \times 10^{-3} = 0.09867$ M

g. If $[\text{H}_3\text{O}^+] = 1.33 \times 10^{-3}$ M, then pH = 2.88

h. Note: if $[\text{HA}]_i$ is at least 100 times greater than K_a then the assumption ($[\text{HA}]_i - x = [\text{HA}]_{\text{eqb}}$) can be used and the problem can be solved without the quadratic equation

4. Given a 0.0010 M solution of formic acid ($K_a = 1.8 \times 10^{-4}$) find the pH of the solution.



b. $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Form}^-] / [\text{HForm}]$

c.

	[HForm]	[H ₃ O ⁺]	[Form ⁻]
initial	0.0010	0	0
x	-x	+x	+x
eqb	0.0010 - x	x	x

d. Note that K_a is not 100x greater than $[\text{HForm}]_i$

e. $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Form}^-] / [\text{HForm}] = x^2 / 0.0010 - x$

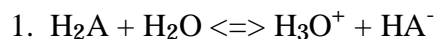
f. Using the quadratic equation $x = 3.44 \times 10^{-4}$

g. If $x = 3.44 \times 10^{-4}$ then $[\text{H}_3\text{O}^+] = 3.44 \times 10^{-4} \text{ M}$ and $\text{pH} = 3.46$

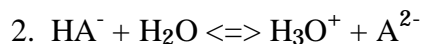
h. If the assumption is used then $x = 4.24 \times 10^{-4}$ and $\text{pH} = 3.37$

VII. Diprotic and polyprotic acids

A. Two step dissociations



a. $K_{a1} = [\text{H}_3\text{O}^+] \cdot [\text{HA}^-] / [\text{H}_2\text{A}]$



a. $K_{a2} = [\text{H}_3\text{O}^+] \cdot [\text{A}^{2-}] / [\text{HA}^-]$

B. General rules if $K_{a1} / K_{a2} > 1000$

1. Nearly all $[\text{H}_3\text{O}^+]$ will come from the first dissociation, and $[\text{HA}^-]$ will be roughly equal to $[\text{H}_3\text{O}^+]$

2. $[\text{H}_3\text{O}^+]$ produced in the second dissociation will be insignificant

3. $[\text{A}^{2-}] = K_{a2}$

C. An example: find the pH of a solution of 0.45 M sulfurous acid (H_2SO_3 ; $K_{a1} = 1.2 \times 10^{-2}$, $K_{a2} = 6.2 \times 10^{-8}$)

1. Start with the first dissociation: $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_3^-$

2.

	[H ₂ SO ₃]	[H ₃ O ⁺]	[HSO ₃ ⁻]
initial	0.45	0	0
x	-x	+x	+x
eqb	0.45 - x	x	x

3. $K_{a1} = [\text{H}_3\text{O}^+]\cdot[\text{HSO}_3^-] / [\text{H}_2\text{SO}_3] = x^2 / 0.45 - x$
4. Based on the quadratic equation: $x = 0.068$
5. $[\text{HSO}_3^-] = 0.068 \text{ M}$ (this is preliminary and based on the results of the second dissociation), $[\text{H}_2\text{SO}_3] = 0.45 - 0.068 = 0.382 \text{ M}$
6. Now consider the second dissociation: $\text{HSO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_3^{2-}$
- 7.

	$[\text{HSO}_3^-]$	$[\text{H}_3\text{O}^+]$	$[\text{SO}_3^{2-}]$
initial	0.068	0.068	0
x	-x	+x	+x
eqb	$0.068 - x$	$0.068 + x$	x

8. $K_{a2} = [\text{H}_3\text{O}^+]\cdot[\text{SO}_3^{2-}] / [\text{HSO}_3^-] = (x)(0.068 + x) / 0.068 - x$
9. $0 = x^2 + x(0.068 + K_{a2}) - 0.068K_{a2}$
10. Since $0.068 \gg K_{a2}$, $[x(0.068 + K_{a2}) = 0.068x]$ and based on the simplified quadratic equation: $x = 6.2 \times 10^{-8}$
11. At equilibrium:
 - a. $[\text{H}_3\text{O}^+] = 0.068 + 6.2 \times 10^{-8} = 0.068 \text{ M}$; $\text{pH} = 1.17$
 - b. $[\text{HSO}_3^-] = 0.068 - 6.2 \times 10^{-8} = 0.068 \text{ M}$
 - c. $[\text{SO}_3^{2-}] = 6.2 \times 10^{-8} = K_{a2}$

VIII. Weak bases

A. Generic behavior for weak bases

1. $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{HB}^+ + \text{OH}^-$
2. $K_c = [\text{HB}^+]\cdot[\text{OH}^-] / [\text{B}]\cdot[\text{H}_2\text{O}]$
3. Base dissociation constant: $K_b = K_c\cdot[\text{H}_2\text{O}] = [\text{HB}^+]\cdot[\text{OH}^-] / [\text{B}]$
4. K_b is determined experimentally (Ebbing: 693, Table 16.2 provides a list of values)
5. The smaller the value of K_b , the weaker the base

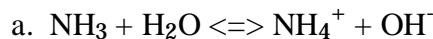
B. There is a relationship between the K_a and K_b of any conjugate acid-base pair

1. $K_a K_b = K_w$

2. If, for ammonia, $K_b = 1.8 \times 10^{-5}$, find the value of K_a for the ammonium ion ($K_a = 5.6 \times 10^{-10}$)
3. If the K_a of formic acid is 1.8×10^{-4} find the value of K_b for formate ion. ($K_b = 5.6 \times 10^{-11}$)

C. K_b is calculated in the same way as values of K_a , by measuring the initial base concentration and pH (pOH) and solving for the equilibrium concentrations

1. A 0.15 M solution of ammonia has a pH of 11.20. What is the K_b of ammonia?



b. $K_b = [\text{NH}_4^+] \cdot [\text{OH}^-] / [\text{NH}_3]$

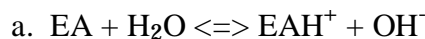
c.

	$[\text{NH}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$
initial	0.15	0	0
x	-x	+x	+x
eqb	0.15 - x	x	x

d. Given that the solution pH = 11.20, pOH = 14 - pH = 2.80; $[\text{OH}^-] = 1.585 \times 10^{-3}$

e. $K_b = [\text{NH}_4^+] \cdot [\text{OH}^-] / [\text{NH}_3] = x^2 / 0.15 - x = 1.69 \times 10^{-5}$ (reported value = 1.8×10^{-5})

2. Calculate the $[\text{OH}^-]$ of a 0.0750 M solution of ethylamine ($K_b = 6.4 \times 10^{-4}$) and the solution pH.



b. $K_b = [\text{EAH}^+] \cdot [\text{OH}^-] / [\text{EA}]$

c.

	$[\text{EA}]$	$[\text{EAH}^+]$	$[\text{OH}^-]$
initial	0.0750	0	0
x	-x	+x	+x
eqb	0.0750 - x	x	x

d. $K_b = [\text{EAH}^+] \cdot [\text{OH}^-] / [\text{EA}] = x^2 / 0.0750 - x$

e. Using the quadratic equation $x = 6.616 \times 10^{-3}$

f. If $x = 6.616 \times 10^{-3}$ then $[\text{OH}^-] = 6.616 \times 10^{-3}$ M and pOH = 2.18, so

$$\text{pH} = 11.82$$

IX. Acid-base properties of salt solutions

A. Many ions react with water to form either hydronium ion or hydroxide ion

1. Hydrolysis reactions - reactions in which water molecules are split into hydrogen and hydroxide ions

B. Anions with ionizable protons are *amphoteric*, capable of acting either as an acid or a base, depending on conditions

1. Examples: HSO_4^- , HCO_3^- , H_2PO_4^- , HPO_4^{2-} , etc.

C. Conjugate acid-base behavior

1. The conjugate bases of strong acids do not cause hydrolysis

a. Given the relationship between K_a and K_b ($K_a K_b = K_w$), of necessity when K_a is very large, K_b is very small

2. The conjugate bases of weak acids do cause hydrolysis

a. Generic hydrolysis reaction of conjugate bases: $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$

b. $K_b = K_w / K_a$

c. What is the pH of a 0.20 M solution of acetate ion?

i. For acetic acid $K_a = 1.8 \times 10^{-5}$, so for acetate ion $K_b = K_w / K_a = 5.56 \times 10^{-10}$

ii. $\text{Ac}^- + \text{H}_2\text{O} \rightleftharpoons \text{HAc} + \text{OH}^-$

iii. $K_b = [\text{HAc}] \cdot [\text{OH}^-] / [\text{Ac}^-]$

iv.

	$[\text{Ac}^-]$	$[\text{HAc}]$	$[\text{OH}^-]$
initial	0.20	0	0
x	-x	+x	+x
eqb	$0.20 - x$	x	x

v. $K_b = [\text{HAc}] \cdot [\text{OH}^-] / [\text{Ac}^-] = (x)(x) / 0.20 - x = x^2 / 0.20 - x$

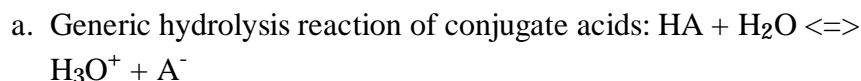
vi. Using the quadratic equation $x = 1.05 \times 10^{-4}$

vii. Since $[\text{OH}^-] = 1.05 \times 10^{-4}$ M, then $\text{pOH} = 4.98$ and $\text{pH} = 9.02$

3. The conjugate acids of strong bases do not cause hydrolysis

- a. Given the relationship between K_a and K_b ($K_a K_b = K_w$), of necessity when K_b is very large, K_a is very small

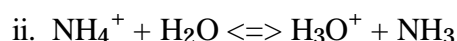
4. The conjugate acids of weak bases do cause hydrolysis



b. $K_a = K_w / K_b$

- c. What is the pH of a 0.50 M solution of ammonium ion?

i. For ammonia $K_b = 1.8 \times 10^{-5}$, so for ammonium ion $K_a = K_w / K_b = 5.56 \times 10^{-10}$



iii.

	$[NH_4^+]$	$[H_3O^+]$	$[NH_3]$
initial	0.20	0	0
x	-x	+x	+x
eqb	0.20 - x	x	x

iv. $K_a = [H_3O^+][NH_3] / [NH_4^+] = (x)(x) / 0.50 - x = x^2 / 0.50 - x$

v. Using the quadratic equation $x = 1.67 \times 10^{-5}$

vi. Since $[H_3O^+] = 1.67 \times 10^{-5}$ M, then $pH = 4.78$

5. Metal cations are acidic in aqueous solution because they are Lewis acids while water is a Lewis base; the strong electron accepting nature of metal ions polarizes O-H bonds and makes ionization easier

- D. Salt behavior depends on whether the cations and anions are the conjugate acids or bases of strong or weak acids

X. Factors that affect acid strength

A. Acid strength depends on how easily HA ionizes

B. The more easily broken the H-A bond, the more easily HA ionizes, i.e. acid strength is related to H-A bond strength

C. Two structural factors affect acid strength

1. The larger the atom bonding to H^+ the weaker the bond

- a. Ebbing: 663 - "As you go down the column of elements. . . the radius increases markedly. For this reason the size of atom X is the

dominant factor in determining acid strength. In going down a column of elements of the periodic table, the size of atom X increases, the H-X bond strength decreases, and the strength of the binary acid increases."

i. Bond strength: $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{HI}$

ii. Acid strength: $\text{H-F} < \text{H-Cl} < \text{H-Br} < \text{HI}$

2. The more polar the H-A bond, the greater the partial positive charge on the hydrogen atom and the more acidic it behaves, i.e. the more polarized the bond the easier it is to donate the hydrogen ion

a. Ebbing: 663 - "As you go across a row of elements of the periodic table, the atomic radius decreases slowly. For this reason, the relative strengths of the binary acids of these elements are less dependent on the size of atom X. Now the polarity of the H-X bond becomes the dominant factor in determining acid strength. Going across a row of elements in the periodic table, the electronegativity increases, the H-X bond polarity increases, and the acid strength increases."

i. EN: $\text{F} > \text{O} > \text{N} > \text{C}$

ii. Acidity: $\text{H-F} > \text{H-O} > \text{H-N} > \text{H-C}$

D. Oxyacids: e.g., HNO_3 , H_2SO_4 , HClO_4

1. A central atom "Y" is bonded to one or more O atoms, and the acidic hydrogen(s) are bonded to O atoms, not to "Y"
2. The electronegativity of Y affects the polarity - and therefore the strength - of the O-H bond
 - a. For oxyacids with the same number of oxygen atoms but different central atoms, as the EN of Y increases, acid strength increases
 - b. Acidity: $\text{H-O-Cl} > \text{H-O-Br} > \text{H-O-I}$
3. As the number of oxygen atoms bonded to the central atom increases, acid strength increases
 - a. $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$
 - b. $\text{EN}_\text{O} = 3.5$, $\text{EN}_\text{Cl} = 3.0$; this makes the O-Cl bond polar which introduces a partial positive charge on the Cl atom which in turn affects the charge distribution of the O-H bond; the more O-Cl bonds the greater the effect

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