

CHAPTER 16: ACID-BASE EQUILIBRIA

Part One: Pure Solutions of Weak Acids, Bases (water plus a single electrolyte solute)

A. Weak Monoprotic Acids. (Section 16.1)



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{H}_2\text{O}][\text{HAc}]}, \text{ but since } [\text{H}_2\text{O}] \text{ always} = 55.5 \text{ M}$$

$$K_c[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]}, \text{ set } K_c[\text{H}_2\text{O}] \equiv K_a$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]} \quad K_a = \text{acid ionization constant}$$

$$\text{p}K_a = -\log K_a$$

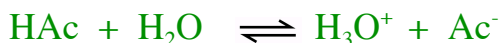
$$\text{p}K_a \uparrow \text{ strength } \downarrow$$

2. See Table 16.1 K_a of weak acids:

TABLE 16.1		Acid-Ionization Constants at 25°C*	
Substance	Formula	K_a	
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	1.7×10^{-5}	
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	6.3×10^{-5}	
Boric acid	H_3BO_3	5.9×10^{-10}	
Carbonic acid	H_2CO_3	4.3×10^{-7}	
	HCO_3^-	4.8×10^{-11}	
Cyanic acid	HOCN	3.5×10^{-4}	
Formic acid	HCHO_2	1.7×10^{-4}	
Hydrocyanic acid	HCN	4.9×10^{-10}	
Hydrofluoric acid	HF	6.8×10^{-4}	
Hydrogen sulfate ion	HSO_4^-	1.1×10^{-2}	
Hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	$1.2 \times 10^{-13\dagger}$	
Hypochlorous acid	HClO	3.5×10^{-8}	
Nitrous acid	HNO_2	4.5×10^{-4}	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	5.6×10^{-2}	
	HC_2O_4^-	5.1×10^{-5}	
Phosphoric acid	H_3PO_4	6.9×10^{-3}	
	H_2PO_4^-	6.2×10^{-8}	
	HPO_4^{2-}	4.8×10^{-13}	
Phosphorous acid	H_2PHO_3	1.6×10^{-2}	
	H_2PHO_3^-	7×10^{-7}	
Propionic acid	$\text{HC}_3\text{H}_5\text{O}_2$	1.3×10^{-5}	
Pyruvic acid	$\text{HC}_3\text{H}_3\text{O}_3$	1.4×10^{-4}	
Sulfurous acid	H_2SO_3	1.3×10^{-2}	
	HSO_3^-	6.3×10^{-8}	

3. Calculation of equilibrium concentrations from K_a :

What is the pH of a 2.0 M aqueous solution of acetic acid?



<i>initial</i>	2.0 M	$10^{-7} \approx 0$	0
<i>change</i>	-x	+x	+x
<i>at equilib</i>	2.0-x	x	x

$$K_a = \frac{x^2}{2.0 - x} = 1.8 \times 10^{-5}$$

Could solve the quadratic equation, but there is a simplifying approximation that is very accurate:

$$2.0 - x \approx 2.0, \text{ since } x \ll 2.0 \text{ M}$$

$$\frac{x^2}{2.0} \approx 1.8 \times 10^{-5} \text{ so } x^2 \approx 3.6 \times 10^{-5} \text{ so } x \approx \sqrt{3.6 \times 10^{-5}} = 0.0060 \text{ M}$$

$$[\text{H}_3\text{O}^+] = x = 0.0060 \text{ M}$$

$$\text{pH} = -\log(6.0 \times 10^{-3}) = 2.2$$

Check your approximation:

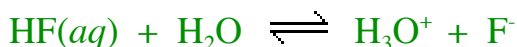
$$\begin{array}{l} \text{Is} \quad 2.0 - x \approx 2.0 \\ \quad \quad x \ll 2.0 \text{ and } 0.006 \ll 2.0 \text{ yes!!} \end{array}$$

4. General formula:

$$\text{pure solution of weak monoprotic acid} \quad [\text{H}_3\text{O}^+] = \sqrt{C_A K_a}$$

where C_A = formal concentration of the weak acid

5. Example: Calculate pH of 1.0 M HF(aq).



<i>initial</i>	1.0 M	0	0
<i>at equilib</i>	1.0 - x	x	x

$$K_a = \frac{x^2}{1.0 - x} = 7.2 \times 10^{-4}$$

Assume $x \ll 1.0$

$$\frac{x^2}{1.0} = 7.2 \times 10^{-4}$$

$$x = \sqrt{7.2 \times 10^{-4}} = 2.68 \times 10^{-2} = 0.0268 \text{ M}$$

Now, is $x \ll 1.0 \text{ M}$?

$0.0268 \ll 1.00$ borderline!

Could do a successive approximation:

$$\frac{x^2}{1.0 - 0.0268} = 7.2 \times 10^{-4}, \text{ where } 0.0268 \text{ is trial solution}$$

$$\frac{x^2}{0.9732} = 7.2 \times 10^{-4}$$

$$x^2 = 7.01 \times 10^{-4}$$

$$x = \sqrt{7.01 \times 10^{-4}} = 0.0265 \text{ M (not much change, really unnecessary)}$$

$$[F^-] = [H_3O^+] = x = 0.0265 \text{ M}$$

$$\text{pH} = 1.58$$

6. Percent ionization calculation of weak acid:

$$\% \text{ ionization} = \frac{[HAc]_{\text{ionized}}}{[HAc]_{\text{total}}} \times 100\%$$

$$\% \text{ ionization} = \frac{[Ac^-]}{[HAc] + [Ac^-]} \times 100\%$$

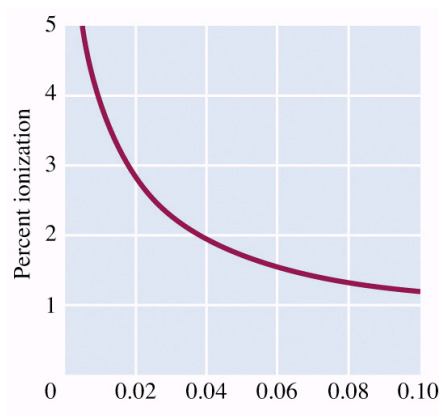
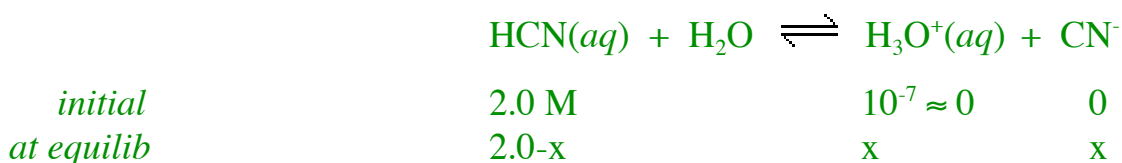


Figure 16.3

7. Example: Calculate % ionization in a 2.0 M solution of $\text{HCN}(aq)$.



$$\frac{x^2}{2.0 - x} = 4.0 \times 10^{-10}$$

$$\frac{x^2}{2.0} \approx 4.0 \times 10^{-10}$$

$$x^2 = 8.0 \times 10^{-10}$$

$$x = 2.8 \times 10^{-5} = [\text{H}_3\text{O}^+] = [\text{CN}^-]$$

$$\begin{aligned} \% \text{ ioniz} &= \frac{2.8 \times 10^{-5} M}{2.0 M} \times 100\% \\ &= 1.4 \times 10^{-3}\% = 0.0014\% \text{ (very small percent)} \end{aligned}$$

$$\text{pH} = -\log(2.8 \times 10^{-5}) = 4.55$$

B. Polyprotic Acids. (Section 16.2)

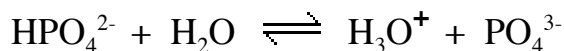
1. Consider H_3PO_4 : Have three simultaneous equilibria!!



$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3}$$



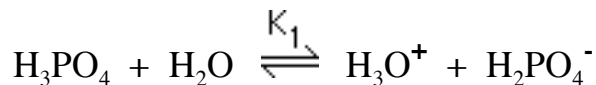
$$K_2 = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.2 \times 10^{-8}$$



$$K_3 = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 3.6 \times 10^{-13}$$

2. Simplifying factor: $[\text{H}_3\text{O}^+]$ present at equilibrium will be almost totally due to first step of ionization.
3. Calculate the conc. of all species present in 2.00 M H_3PO_4 .

a. First ionization:



at equilib. 2.00 - x x x

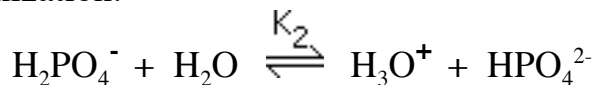
$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{x^2}{2.00 - x}$$

$$x \approx \sqrt{2.00K_1} = \sqrt{2.00 \times 7.5 \times 10^{-3}} = 0.122 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{H}_2\text{PO}_4^-] = 0.122 \text{ M}$$

$$\text{pH} = -\log(.122) = 0.912$$

b. Second ionization:



0.122 - y 0.122 + y y

$$K_2 = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{(0.122 + y)y}{0.122 - y}$$

Assume $y \ll 0.122 \text{ M}$

$$K_2 = 6.2 \times 10^{-8} \approx \frac{0.122}{0.122} y$$

$$y = 6.2 \times 10^{-8} = K_2$$

OR:

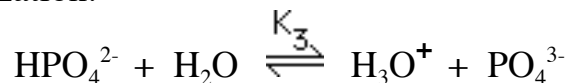
$$[\text{HPO}_4^{2-}] = K_2 = 6.2 \times 10^{-8}$$

General rule: anion produced by second ionization = K_2

Second ionization produces additional $6.2 \times 10^{-8} M$ of H_3O^+ , which is negligible.

Still $[H_3O^+] = 0.122 M$ (from first ionization)

c. Third ionization:



$$6.2 \times 10^{-8} M - z \qquad 0.122 + z \qquad z$$

$$K_3 = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.122 + z)z}{6.2 \times 10^{-8} - z}$$

Assume $z \ll 6.2 \times 10^{-8} M$

$$K_3 = 3.6 \times 10^{-13} = \frac{0.122z}{6.2 \times 10^{-8}}$$

$$z = 1.83 \times 10^{-19} M$$

$$[PO_4^{3-}] = 1.83 \times 10^{-19} M$$

$$\text{General rule: } [PO_4^{3-}] = K_3 K_2 / [H_3O^+] = K_3 K_2 / \sqrt{C_A K_1}$$

(where C_A is formal conc. of polyprotic acid $2.00 M$)

4. Summary - for pure solution of:

a. Weak monoprotic acid:

$$[H^+] \approx \sqrt{C_A K_a}$$

b. Weak diprotic acid (weak at both stages):

$$[H^+] = \sqrt{C_A K_1}$$

$$[HA^-] = \text{same}$$

$$[A^{2-}] = K_2$$

c. Weak triprotic acid:

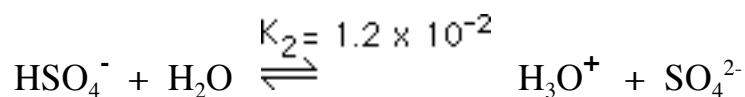
$$[\text{H}^+] = \sqrt{C_A K_1}$$

$$[\text{H}_2\text{A}^-] = \text{same}$$

$$[\text{HA}^{2-}] = K_2$$

$$[\text{A}^{3-}] = K_3 K_2 / [\text{H}^+]$$

5. Strong polyprotic acid H_2SO_4 :



Suppose we have 2.00 M H_2SO_4 .

a. First ionization goes completely:

$$[\text{H}_2\text{SO}_4] = 0$$

$$[\text{HSO}_4^-] = 2.00 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 2.00 \text{ M}$$

b. Second ionization is weak:



$$2.00 - x \qquad \qquad 2.00 + x \quad x$$

$$K_2 = 1.2 \times 10^{-2} = \frac{(2.00 + x)x}{2.00 - x}$$

Try $x \ll 2.00$ approx.

$$1.2 \times 10^{-2} \approx \frac{2.00x}{2.00}$$

$$x = 1.2 \times 10^{-2} = 0.012 \text{ M}$$

$$[\text{SO}_4^{2-}] = 0.012 \text{ M} = K_2$$

$$[\text{H}_3\text{O}^+] = 2.00 \text{ M} + 0.012 \text{ M} \approx 2.012 \text{ M}$$

$$[\text{HSO}_4^-] = 2.00 - 0.012 \approx 1.99 \text{ M}$$

C. Weak Monoprotic Bases. (Section 16.3)

1. Calculate conc. of species present and pH of 0.10 M aqueous NH_3 .



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.10 - x} = 1.8 \times 10^{-5}$$

$$x^2 = 1.8 \times 10^{-6}$$

$$[\text{NH}_4^+] = [\text{OH}^-] = x = 1.34 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.34 \times 10^{-3}}$$

$$[\text{H}_3\text{O}^+] = 7.45 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log(7.45 \times 10^{-12}) = 11.1$$

2. General formula:

$$\text{pure aqueous of weak base} \quad [\text{OH}^-] = \sqrt{C_B K_b}$$

where C_B = formal concentration of the base

TABLE 16.2		Base-Ionization Constants at 25°C	
Substance	Formula	K_b	
Ammonia	NH_3	1.8×10^{-5}	
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	4.2×10^{-10}	
Dimethylamine	$(\text{CH}_3)_2\text{NH}$	5.1×10^{-4}	
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	4.7×10^{-4}	
Hydrazine	N_2H_4	1.7×10^{-6}	
Hydroxylamine	NH_2OH	1.1×10^{-8}	
Methylamine	CH_3NH_2	4.4×10^{-4}	
Pyridine	$\text{C}_5\text{H}_5\text{N}$	1.4×10^{-9}	
Urea	NH_2CONH_2	1.5×10^{-14}	

Part Two: Acidity and Basicity of Salts in Aqueous Solution

A. Salts from Neutralizing Strong Base with Strong Acid. (Section 16.4)

1. Cations from strong soluble bases:

e.g., Na^+ , K^+ , Ca^{2+} , Sr^{2+} ... (these ions have no effect on pH)

2. Anions from strong acids:

e.g., Cl^- , Br^- , I^- , ClO_4^- ... (no effect on pH)

3. These salts produce neutral solutions.

a. The anion is the conjugate base of a strong acid so are very weak bases.

B. Salts from Neutralizing Strong Bases with Weak Acids. (Section 16.4)

1. Again, cations are Na^+ , K^+ ...

2. Anions from weak acids:

e.g., Ac^- , NO_2^- , CN^- , OCl^- ...

3. These conjugate bases of weak acids WILL affect pH by following reactions called hydrolysis (or solvolysis) reactions:



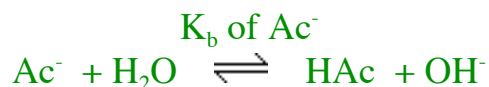
4. These salts produce basic solutions. If Ac^- is a base, what is its K_b ?

$$K_b = \frac{K_w}{K_a(\text{of HAc})}$$

OR:

$$K_w = K_a K_b \quad \text{a,b are conj acid/base pair}$$

5. Problem: What is pH of 1.0 NaAc solution?



$$K_b = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]} = \frac{K_w}{K_a(\text{of HAc})}$$

$$\frac{x^2}{1.0 - x} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

$$x \approx \sqrt{1.0 \times 5.55 \times 10^{-10}}; \quad x = 2.36 \times 10^{-5} M$$

$$[\text{OH}^-] = 2.36 \times 10^{-5} M$$

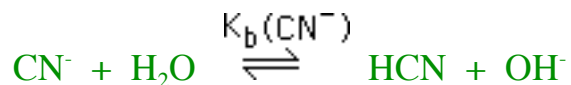
$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.36 \times 10^{-5}} = 4.24 \times 10^{-10} M$$

pH = 9.37 (basic); Therefore, Ac^- acts as weak base.

6. Problem: What is pH of 0.20 M NaCN? K_a for HCN is 4.0×10^{-10} ?

NaCN is salt containing conj base CN^- of weak acid HCN.

$$K_b(\text{CN}^-) = \frac{K_w}{K_a(\text{of HCN})} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 0.25 \times 10^{-4}$$



$$0.20 - x \qquad \qquad \qquad x \qquad \qquad x$$

$$K_b(\text{CN}^-) = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$0.25 \times 10^{-4} = \frac{x^2}{0.20 - x}$$

$$x \approx \sqrt{0.20 \times 0.25 \times 10^{-4}}$$

$$x = 2.24 \times 10^{-3} M = [\text{OH}^-] = [\text{HCN}]$$

$$\text{pOH} = 2.65; \text{pH} = 11.3 \quad \text{quite alkaline!!}$$

Since HCN is such a weak acid, CN^- makes a good base, though still a weak base.

C. Salts from Neutralizing Weak Base with Strong Acid. (Section 16.4)

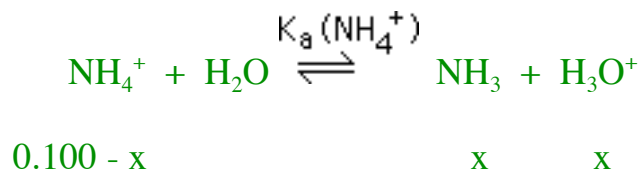
1. Cations are conj acids of that weak base: e.g., NH_4^+
2. Anions: e.g., Cl^- , Br^- , $\text{I}^- \dots$
3. These salts will produce acid solutions.
4. If NH_4^+ is an acid, what is its K_a ?

$$K_a(\text{NH}_4^+) = \frac{K_w}{K_b(\text{NH}_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

5. What is the pH of 0.100 M NH_4Cl solution?



Then:



$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$5.55 \times 10^{-10} = \frac{x^2}{0.100 - x}$$

$$x \approx \sqrt{0.100 \times 5.55 \times 10^{-10}}$$

$$x = 7.45 \times 10^{-6} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 7.45 \times 10^{-6} \text{ M}$$

$$\text{pH} = 5.13 \quad \text{slightly acidic}$$

D. Salts from Neutralizing Weak Acid and Weak Base. (Section 16.4)

1. Cation is slightly acidic:



2. Anion is slightly basic:



3. Produces \approx neutral solutions if:

$$K_a(\text{parent acid}) \approx K_b(\text{parent base})$$

4. Example: NH_4Ac (ammonium acetate)

$$K_a(\text{NH}_4^+) = \frac{K_w}{K_a(\text{NH}_3)} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

parent base is NH_3

$$K_b(\text{Ac}^-) = \frac{K_w}{K_a(\text{HAc})} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

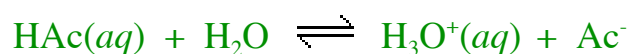
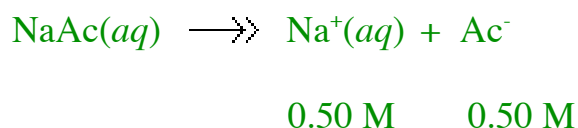
parent acid is HAc

Neutral solution!

Part Three: Solutions With More Than One Electrolyte

A. The Common Ion Effect. (Section 16.5)

1. Common-ion effect: the shift in an ionic equilibrium caused by the addition of another solute that provides an ion that takes part in the equilibrium.
2. Example: Solution of weak acid plus soluble salt containing its conjugate base.
3. Problem: A solution is prepared which is 1.0 M HAc and 0.50 M NaAc. What is its pH?



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]}$$

$$1.8 \times 10^{-5} = \frac{x(0.50 + x)}{1.0 - x}$$

Make assumption that $1.0 - x \approx 1.0$ and $0.50 + x \approx 0.5$

$$1.8 \times 10^{-5} = \frac{x(0.50)}{1.0}$$

$$x = 3.6 \times 10^{-5} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 3.6 \times 10^{-5} \text{ M}$$

$$[\text{Ac}^-] = 0.50 + x \approx 0.50 \text{ M}$$

$$[\text{HAc}] = 1.0 - x \approx 1.00 \text{ M}$$

$$\text{pH} = -\log (3.6 \times 10^{-5}) = 4.44$$

4. What would the pH of pure 1.0 M HAc have been?

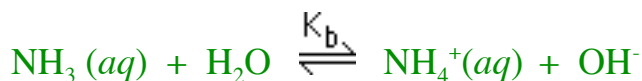
$$[\text{H}_3\text{O}^+] = \sqrt{1.0 \times 1.8 \times 10^{-5}} = 4.24 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.37 \text{ (more acidic!)}$$

5. Adding the conjugate base Ac^- in the form of the salt NaAc raised pH by 2 points, making solution less acidic.
6. Common ion effect means effect of having Ac^- ions from two different sources:
- HAc
 - NaAc
- (two electrolytes have Ac^- in common)
7. Solution of weak base plus soluble salt containing its conjugate acid.
8. Example: A solution which is 0.20 M $\text{NH}_3(\text{aq})$ and 0.30 M $\text{NH}_4\text{Cl}(\text{aq})$. What is its pH?



$$0.30 \text{ M}$$



<i>initial</i>	0.20 M	0.30 M	$\approx 0 \text{ M}$
<i>at equilib</i>	0.20-x	0.30+x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

$$\frac{x(0.30 + x)}{0.20 - x} = 1.8 \times 10^{-5}$$

$$\frac{0.30x}{0.20} \approx 1.8 \times 10^{-5}$$

$$x = 1.2 \times 10^{-5} \text{ M}$$

$$[\text{OH}^-] = 1.2 \times 10^{-5} \text{ M}$$

$$[\text{NH}_4^+] \approx 0.30 \text{ M}$$

$$[\text{NH}_3] \approx 0.20 \text{ M}$$

$$\text{pH} = ?? \quad [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-5}} = 8.33 \times 10^{-10} \text{ M}$$

$$\text{pH} = 9.08$$

B. Buffer Solutions. (Section 16.6)

1. The two previous examples were, in reality, buffer solutions.
2. Buffer solutions are those which **resist changes in pH when other acids or bases are added**.
3. Prepare by mixing solution of:
 - a. weak acid and its salt in comparable amounts.

example - HF and NaF (acidic buffer)

OR:

- b. weak base and its salt in comparable amounts.

example - NH_3 and NH_4Cl (basic buffer)

4. Calculating the pH of an acidic buffer:

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a$$

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

$$[\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

$$-\log[\text{H}^+] = -\log K_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

$$\text{pH} = \text{p}K_a - \log \left(\frac{[\text{acid}]}{[\text{salt}]} \right)$$

Henderson-Hasselbach Equation:

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{salt}]}{[\text{acid}]}\right)$$

5. Use it: A buffer solution is 1.0 M HF and 0.5 M NaF. What is pH? K_a of HF is 7.2×10^{-4} .

$$[\text{acid}] = 1.0 \text{ M} \quad [\text{salt}] = 0.5 \text{ M}$$

$$\begin{aligned}\text{pH} &= \text{pK}_a + \log\left(\frac{[\text{salt}]}{[\text{acid}]}\right) \\ &= -\log(7.2 \times 10^{-4}) + \log(0.5/1.0) \\ &= 3.143 + (-.301)\end{aligned}$$

$$\text{pH} = 2.842$$

6. Special important case: When $[\text{acid}] = [\text{salt}]$.

$$\text{pH} = \text{pK}_a + \log(1)$$

$$\text{pH} = \text{pK}_a$$

Therefore, the pK_a of an acid tells us approximately the pH of its buffer solution.

7. For basic buffers:

$$\text{pOH} = \text{pK}_b + \log\left(\frac{[\text{salt}]}{[\text{base}]}\right)$$

C. Buffering Action.

1. Now let's demonstrate the buffering action:

- a. Prepare 500 mL of buffer solution which is 1.00 M acetic acid and 1.00 M sodium acetate. Calculate pH.

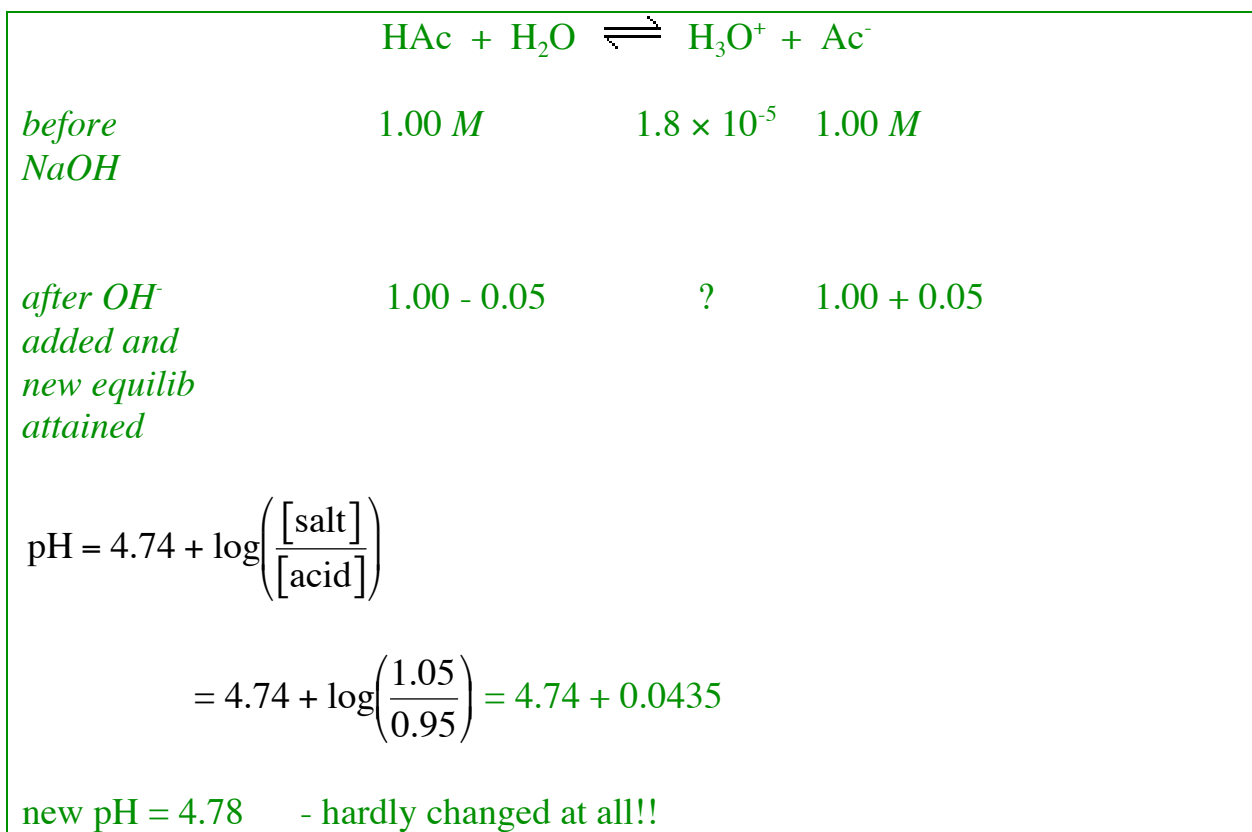


$$[\text{acid}] = [\text{salt}], \text{ so:}$$

$$\text{pH} = \text{pK}_a = -\log(1.8 \times 10^{-5}) = 4.74$$

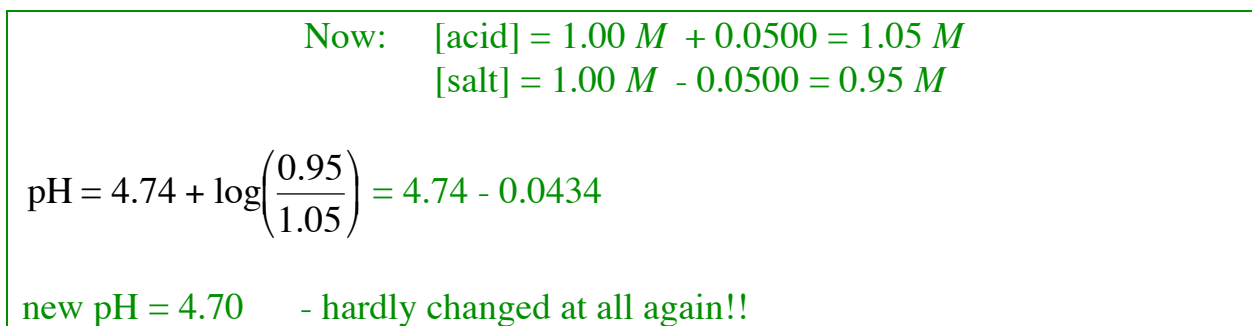
- b. Add 1.00 gram of NaOH to this buffer solution. What is new pH?

$$\frac{1.00 \text{ g}}{40.0 \text{ g/mol}} = 0.025 \text{ mol}; \quad \frac{0.025 \text{ mol}}{0.500 \text{ L}} = 0.050 \text{ M}$$



- c. Instead suppose we had added 2.50g HClO₄. What is new pH?

$$\frac{2.50 \text{ g}}{100.4 \text{ g/mol}} = 0.0250 \text{ mol}; \quad \frac{0.0250 \text{ mol}}{0.500 \text{ L}} = 0.0500 \text{ M}$$



2. For comparison, what if we added 2.50 g HClO_4 to 500 mL of simply 1.00 M HAc ? (not a buffer solution)



<i>before</i> <i>HClO_4</i>	1.00 M	1.8×10^{-5}	1.8×10^{-5}
<i>after</i> <i>HClO_4</i>	1.00	0.0500 M	\uparrow <i>no conjugate base to react with</i>

$$[\text{H}^+] = .0500 \text{ M}; \text{ pH} = 1.30$$

Almost all $[\text{H}^+]$ new comes from the strong acid, not weak.

3. Try a basic buffer:

- a. Prepare 1.000 L of 0.500 M NH_3 and 0.400 M NH_4Cl . What is pH? K_b of NH_3 is 1.8×10^{-5} .

$$\text{pOH} = \text{p}K_b + \log\left(\frac{[\text{salt}]}{[\text{base}]}\right)$$

$$= 4.74 + \log\left(\frac{0.400}{0.500}\right) = 4.74 - 0.0969$$

$$\text{pOH} = 4.64 \text{ so } \text{pH} = 14 - \text{pOH} = 9.36$$

- b. Now add 2.0 g NaOH . What is new pH?

$$\frac{2.0\text{g}}{40.0 \text{ g/mol}} = 0.050 \text{ mol in 1 L} = 0.050 \text{ M}$$



<i>before</i> <i>NaOH</i>	0.500 M	1.8×10^{-5}	0.400 M
		\uparrow <i>OH^- reacts with strongest acid present & neutralizes part</i>	
<i>after</i> <i>NaOH</i>	0.500 + .050 M		0.400 - .050 M

$$\text{pOH} = \text{pK}_b + \log\left(\frac{0.350}{0.550}\right)$$

$$\text{pOH} = 4.54$$

$$\text{pH} = 14 - 4.54 = 9.45 \quad - \text{ little change}$$

Part Four: Titration Curves

A. Strong Acid/Strong Base Curve. (Section 16.7)

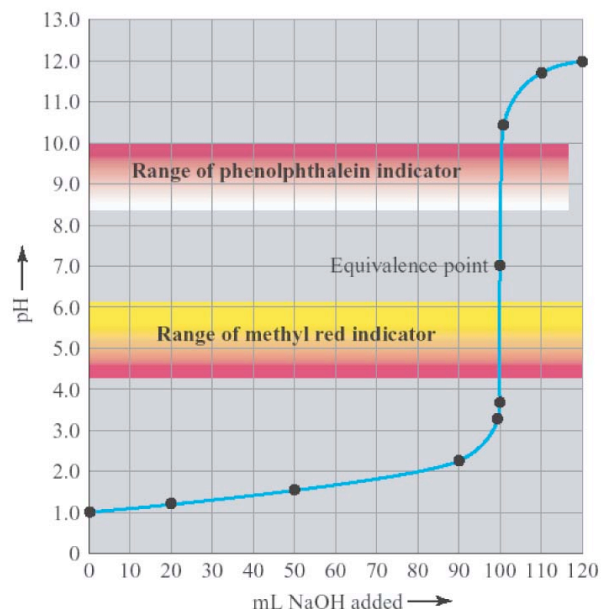
1. Titration curve is plot of pH versus volume of acid or base added.
2. Example: Start with 100.0 mL of 0.100 M HCl. Begin adding 0.100 M NaOH and plot pH.

Titration Data for 100.0 mL of 0.100 M HCl Versus NaOH

mL of 0.100 M NaOH Added	mmol NaOH Added	mmol Excess Acid or Base	pH
0.0	0.00	10.0 H ₃ O ⁺	1.00
20.0	2.00	8.0	1.18
50.0	5.00	5.0	1.48
90.0	9.00	1.0	2.28
99.0	9.90	0.10	3.30
99.5	9.95	0.05	3.60
100.0	10.00	0.00 (eq. pt.)	7.00
100.5	10.05	0.05 OH ⁻	10.40
110.0	11.00	1.00	11.68
120.0	12.00	2.00	11.96

© 2004 Thomson/Brooks Cole

3. Plot:



- Note: Curve is so vertical at equivalence point that mere drops of NaOH cause pH to change several units.
- One desires entire indicator color change to be in this vertical region.
- Thus, just a drop or two will produce complete color transition.
- Look at the following table. What other indicators would work here?

Range and Color Changes of Some Common Acid–Base Indicators													
Indicators	pH Scale												
	1	2	3	4	5	6	7	8	9	10	11	12	13
methyl orange	red			yellow									
methyl red	red				yellow								
bromthymol blue	yellow						blue						
neutral red	red						yellow						
phenolphthalein	colorless								bright pink		colorless beyond 13.0		

- Problem: strong acid/strong base titration.

Titrate 200.0 mL of 0.500 M HBr with 0.400 M KOH.

- What is pH at the start of the titration?

pH of 0.500 M HBr

$[H^+] = 0.500 \text{ M}$

$pH = -\log(0.500) = 0.301$

- What is pH after 50.0 mL of base added?

Start: 200.0 mL * 0.500 M HBr = 100.0 mmol acid

Add: 50.0 mL of 0.400 M KOH = 20.0 mmol base

OH^- will neutralize an equivalent amount of acid, so will have left only 80.0 mmol acid.

$[H^+] = 80.0 \text{ mmol acid} / 250.0 \text{ mL tot vol} = 0.32 \text{ M}$

$pH = -\log(0.32) = 0.49$

B. Weak Acid/Strong Base Titration Curve. (Section 16.7)

1. Start with 100 mL solution of the acid 0.100 M HAc. Add 0.100 M solution dropwise.
2. Titration data:

Titration Data for 100.0 mL of 0.100 M CH₃COOH with 0.100 M NaOH

mL 0.100 M NaOH Added	mmol Base Added	mmol Excess Acid or Base	pH
0.0 mL	0	10.0 CH ₃ COOH	2.89
20.0 mL	2.00	8.00	4.14
50.0 mL	5.00	5.00	4.74
75.0 mL	7.50	2.50	5.22
90.0 mL	9.00	1.00	5.70
95.0 mL	9.50	0.50	6.02
99.0 mL	9.90	0.10	6.74
100.0 mL	10.0	0 (equivalence point)	8.72
101.0 mL	10.1	0.10 OH ⁻	10.70
110.0 mL	11.0	1.0	11.68
120.0 mL	12.0	2.0	11.96

3. Let's calculate one of these points for practice. Calculate pH after adding 20.0 mL of NaOH solution.

Start: 100.0 mL of 0.100 M HAc = 0.0100 moles HAc

Add: 20.0 mL of 0.100 M NaOH = 0.0020 moles NaOH

$$\text{Then: } [\text{HAc}] = \frac{0.0080 \text{ moles}}{120 \text{ mL}} = 0.0666 \text{ M}$$

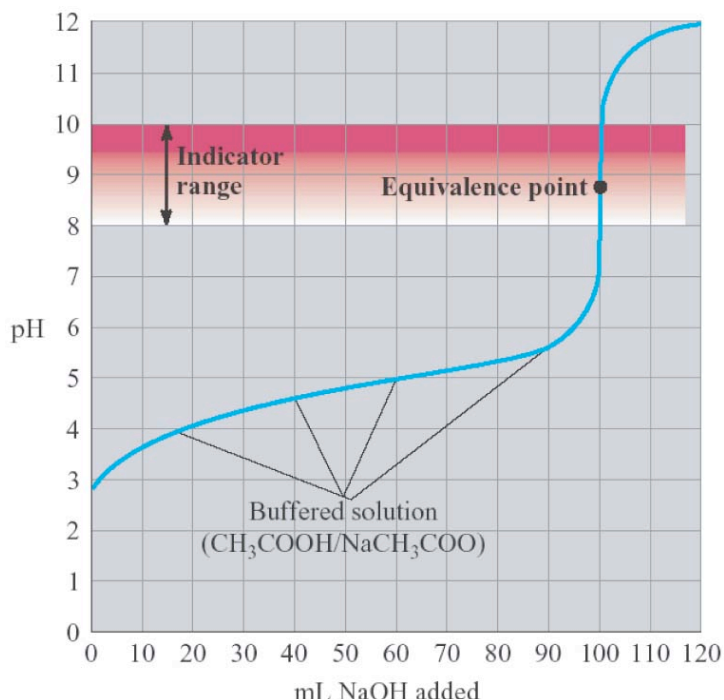
$$[\text{Ac}^-] = \frac{0.0020 \text{ moles}}{120 \text{ mL}} = 1.66 \times 10^{-2} \text{ M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Ac}^-]}{[\text{HAc}]}$$

$$1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+] 1.66 \times 10^{-2}}{0.0666}$$

$$[\text{H}_3\text{O}^+] = 7.20 \times 10^{-5} \text{ M} \quad \text{so} \quad \text{pH} = 4.14$$

4. Plot:



5. Problem: Titrate 200.0 mL of 0.500 M KHP (weak acid, $K_a = 1.0 \times 10^{-4}$) with 0.500 M NaOH.

a. What is the pH at the start of the titration?

KHP is simply a weak acid, so treat as a pure solution of a weak monoprotic acid.

$$[H^+] \approx \sqrt{C_A K_a} \approx \sqrt{0.500 * 1.0 \times 10^{-4}}$$

$$[H^+] = 0.00707 \text{ M}$$

$$\text{pH} = 2.15$$

b. What is the pH after 50.0 mL of base has been added?

The base converts some of the weak acid to its conjugate base (salt), so you have a buffer solution.

$$\text{Start: } 200 \text{ mL} * 0.500 \text{ M} = 100 \text{ mmol weak acid}$$

$$\text{Add: } 50 \text{ mL} * 0.500 \text{ M} = 25 \text{ mmol OH}^-$$

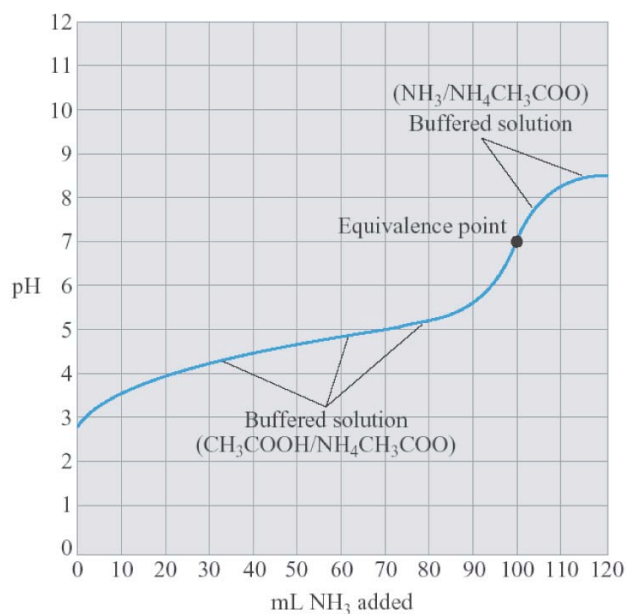
Use buffer equation:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log([\text{salt}]/[\text{acid}]) \\ &= -\log(1.0 \times 10^{-4}) + \log(25 \text{ mmol}/100 - 25 \text{ mmol}) \\ &= 4 - 0.477 = 3.52 \end{aligned}$$

C. Weak Acid with Weak Base Titration Curve.

1. Example: HAc with NH_3 .

2. Curve:



D. Titrate Weak Base with a Weak Acid:

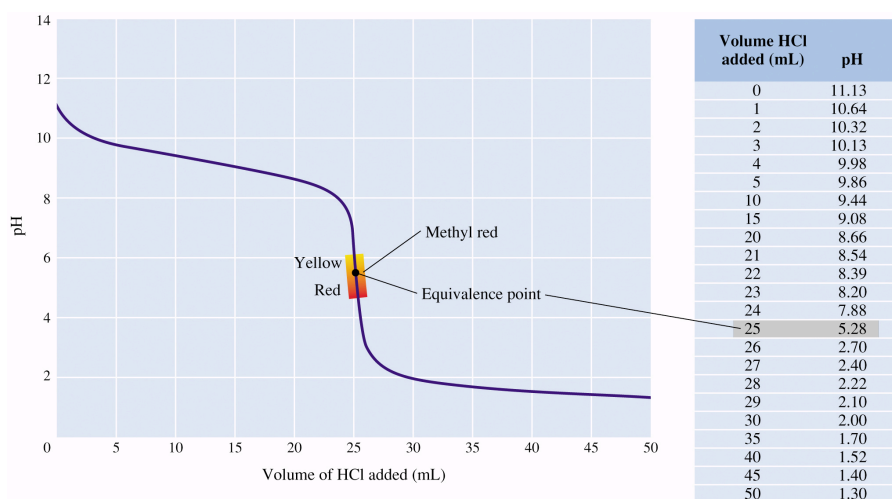
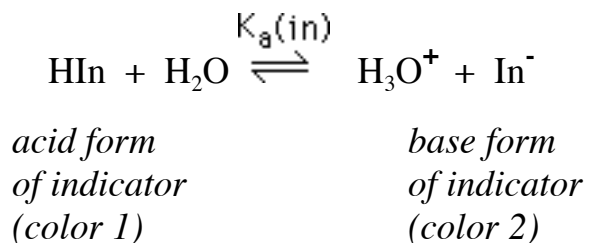


Figure 16.14

E. How Acid/Base Indicators Work. (optional)

1. Indicator is a weak acid itself. Symbolize it HIn:



pH where it changes $\approx \text{p}K_a$ of HIn.

2. Example: Bromothymol blue $K_a(\text{in}) = 7.9 \times 10^{-8}$; $\text{p}K_a = 7.1$



yellow

blue

Color depends on $\frac{[\text{In}^-]}{[\text{HIn}]}$ ratio:

if $\frac{[\text{In}^-]}{[\text{HIn}]} \geq 10$, then In^- color observed blue ($\text{pH} \geq 8$)

if $\frac{[\text{In}^-]}{[\text{HIn}]} \leq 1/10$, then HIn color observed yellow ($\text{pH} \leq 6$)

3. Since $\frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = K_a(\text{in})$

$$\text{Ratio } \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_a(\text{in})}{[\text{H}_3\text{O}^+]} = \text{depends on } [\text{H}_3\text{O}^+]$$

4. Add acid to solution, causes shift (\leftarrow), more HIn present.
5. Add base to solution, causes shift (\rightarrow), more In^- present.
6. Midpoint of change is when:

$$\frac{[\text{In}^-]}{[\text{HIn}]} = 1 = \frac{K_a(\text{in})}{[\text{H}_3\text{O}^+]}$$

Thus, when $[\text{H}_3\text{O}^+] = K_a(\text{in})$, or

$$\text{pH} = \text{p}K_a(\text{in})$$

(for Bromothymol blue $\text{p}K_a(\text{in}) = 7.1$, i.e. neutral is midpoint)

7. Tables of indicators and their $\text{p}K_a$ are available.