Aqueous Acids and Bases

Relationships between [H+] and [OH-]

Calculation of pH and pOH

ionization of water

$$2H_2O \rightleftharpoons H^+ + OH^-$$

$$2H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$
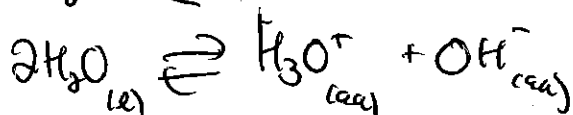
$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \quad \leftarrow constant$$

$$K_w = K[H_2O]^2$$

$$\boxed{K_w = [H_3O^+][OH^-]}$$

$$\boxed{K_w = 1\times10^{-14}} \quad @25°C$$

if neutral $[H_3O^+] = [OH^-]$

$$K_w = [H_3O^+]^2 \quad or \quad K_w = [OH^-]^2$$

$$[H_3O^+] = \boxed{1\times10^{-7}} = \sqrt{K_w}$$

$$= \sqrt{1\times10^{-14}}$$

$$pH = -\log[H^+] \quad or \quad -\log[H_3O^+]$$

$$pOH = -\log[OH^-]$$

$$[H^+] = 10^{-pH} \qquad [OH^-] = 10^{-pOH}$$

$$pH + pOH = 14 \qquad K_a \times K_b = 1\times10^{-14}$$

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STRONG ACIDS AND STRONG BASES

There are very few strong acids. For our purposes, we need consider only the six species listed

Common Strong Acids

STRONG ACID	MOLECULAR FORMULA	MOLECULAR STRUCTURE
Hydrochloric acid	HCl	H—Cl
Hydrobromic acid	HBr	H—Br
Hydriodic acid	HI	H—I
Nitric acid	HNO_3	H—O—N—O (with ∥ O below)
Sulfuric acid	H_2SO_4	H—O—S—O—H (with O above and O below)
Perchloric acid	$HClO_4$	H—O—Cl—O (with O above and O below)

HCl, HNO_3 and H_2SO_4 rank among the most important industrial chemicals

Strong acids are strongly dissociat[ed]

Exercises

(1) Calculate $[H^+]$ and the pH of a 0.250 M solution of nitric acid, HNO_3.

$$pH = -\log [H^+]$$

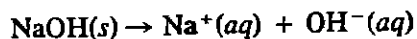$$[HNO_3] = [H^+] = .250 \, M$$

$$pH = -\log [H^+] = -\log(.250)$$

$$pH = .602$$

(2) What is the molarity of a solution of hydrobromic acid with a pH of 1.78?

$$[H^+] = 10^{-pH}$$

$$[H^+] = 10^{-pH} = 10^{-1.78} = .0166 \, M = [HBr]$$

Strong Bases

A strong base dissociates completely in water to release OH^- ions. Sodium hydroxide, NaOH, is the most common strong base. It dissolves readily in water to give a solution containing Na^+ and OH^- ions:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

As with all strong bases, this reaction goes to completion. In a 0.10 M NaOH solution, prepared by dissolving 0.10 mol NaOH in enough water to give one liter of solution, the concentration of *undissociated* NaOH is virtually zero. In this solution, the concentrations of Na^+ and OH^- are 0.10 M. The pH is 13.00.

Strong bases are limited to

These are the only strong bases

1. **The hydroxides of the Group 1 metals** (LiOH, NaOH, KOH, RbOH, CsOH).
2. **The hydroxides of the heavier Group 2 metals,** $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$. With these compounds, two moles of OH^- are produced for every mole of solid that dissociates:

$$Ca(OH)_2(s) \rightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$$
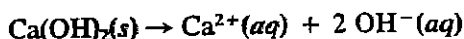
Exercises

(1) Calculate the pH of a solution prepared by dissolving 2.08 g of KOH in enough water to make 500.0 mL of solution.

$$2.08g\left(\frac{1\,mole}{56.1g}\right) = \frac{.0371\,mol\,KOH}{.5\,L} = .0742\,M\,KOH =$$

$$.0742\,M = [OH^-]$$

$$pOH = -\log[OH^-] = -\log(.0742) = 1.13 \quad pH = 12.87$$

(2) A student is to dissolve 8.75 g of $Sr(OH)_2$ in enough water to get a final volume of 0.65 L. What should the pH of the solution be?

$$8.75g\,Sr(OH)_2\left(\frac{1\,mole}{121.6}\right) = \frac{.0720\,mol}{.65\,L} = .111\,M\,Sr(OH)_2\left(\frac{2\,mol}{1\,mol\,Sr(OH)_2}\right)$$

$$[OH^-] = .221\,M$$

$$pOH = -\log[OH^-] = -\log[.221M]$$

$$pOH = .656 \quad pH = 13.34$$

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14. Acids and Bases

Questions and Problems: pp. 504 - 507

[H⁺], [OH⁻], pH, and pOH

1. Calculate [OH⁻] in solutions that have the following values for [H⁺]:
   a. $4.0 \times 10^{-3} M$ b. $3.0 M$

a) $pH = -\log(4.0 \times 10^{-3})$

   $pH = 2.40$

   $pOH = 11.6$

   $[OH^-] = 10^{-pOH} = 2.51 \times 10^{-12} M$

b) $pH = -\log(3.0)$

   $pH = -.477$

   $pOH = 14.477$

   $[OH^-] = 10^{-14.477} = \underline{3.33 \times 10^{-15} M}$

2. Calculate [H⁺] in solutions in which [OH⁻] is
   a. $0.0010 M$ b. $3.4 \times 10^{-4} M$

a) $pOH = -\log(.001)$

   $pOH = 3$

   $pH = 11$

   $[H^+] = 10^{-11} = \boxed{1 \times 10^{-11} M}$

b) $pOH = -\log(3.4 \times 10^{-4})$

   $pOH = 3.47$

   $pH = 10.53$

   $[H^+] = 10^{-10.53} = \boxed{2.95 \times 10^{-11} M}$

3. Find the pH of solutions with the following [H⁺]. Classify each as acidic or basic.
   a. $1 \times 10^{-2} M$
   b. $6.2 \times 10^{-10} M$

a) $pH = -\log(1 \times 10^{-2}) = 2.00$

   Acidic

b) $pH = -\log(6.2 \times 10^{-10}) = 9.21$

   Basic

Calculate [H$^+$] and [OH$^-$] in solutions with the follow-
ing pH:
  a. 4.0   b. 8.52

a) $pH = 4$
   $pOH - 10$

$[H^+] = 10^{-4}$ $[OH^-] = 10^{-10}$

b) $pH = 8.52$
   $pOH = 5.48$

$[H^+] = 10^{-8.52} = 3.02 \times 10^{-9} M$

$[OH^-] = 10^{-5.48}$

$[OH^-] = 3.31 \times 10^{-6} M$

6. Find [H$^+$] and [OH$^-$] in solutions having the following
pOH:
  a. 9.0   b. 3.20

$pOH = 9$ $[OH^-] = 10^{-9}$

$pH = 5$ $[H^+] = 10^{-5}$

$pOH = 3.2$ $10^{-3.2} = 6.31 \times 10^{-4} M = [OH^-]$

$pH = 10.8$ $10^{-10.8} = 1.58 \times 10^{-11} M = [H^+]$

Find [H$^+$], and the pH of the following solutions:
  a. 0.30 M HBr
  b. A solution made by diluting 10.0 mL of 6.00 M HCl
     to 0.300 L with water.

a) $[H^+] = [HBr] = .3M$ $pH = -\log(.3) = .523M$

b) $(10 mL)(6M) = (300 mL)(M_2)$
   $M_2 = .200M = [HCl] = [H^+]$

$pH = -\log(.200) = \boxed{.699 M}$

17 Find [OH$^-$], and the pOH of the following
solutions:
  a. 0.50 M KOH
  b. A solution made by dissolving 100.0 g NaOH in enough
     water to make 500.0 mL of solution.

a) $[OH^-] = [KOH] = .50M$ $pOH = -\log[OH^-] = -\log(.5) = \boxed{.301}$

b) $100 g NaOH \left(\frac{1 mole}{40 g}\right) = \frac{2.5 \, moles \, NaOH}{.5L} = 5M \, NaOH = [OH^-]$

$pOH = -\log(5M) = \boxed{-.699}$ 5
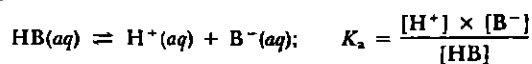
Weak acids

General description

Definition:

A weak acid is one that only partially dissociates in water to give H^+ and the anion.

TABLE   Dissociation Constants of Weak Acids* at 25°C

	ACID	K_a
Sulfurous acid	H_2SO_3	1.7×10^{-2}
Hydrogen sulfate ion	HSO_4^-	1.0×10^{-2}
Chlorous acid	$HClO_2$	1.0×10^{-2}
Hydrofluoric acid	HF	6.9×10^{-4}
Nitrous acid	HNO_2	6.0×10^{-4}
Formic acid	$HCHO_2$	1.9×10^{-4}
Benzoic acid	$HC_7H_5O_2$	6.6×10^{-5}
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}
Propionic acid	$HC_3H_5O_2$	1.4×10^{-5}
Carbonic acid	H_2CO_3	4.4×10^{-7}
Hydrogen sulfide	H_2S	1.0×10^{-7}
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}
Hydrogen sulfite ion	HSO_3^-	6.0×10^{-8}
Hypochlorous acid	$HClO$	2.8×10^{-8}
Hypobromous acid	$HBrO$	2.6×10^{-9}
Hydrocyanic acid	HCN	5.8×10^{-10}
Ammonium ion	NH_4^+	5.6×10^{-10}
Hydrogen carbonate ion	HCO_3^-	4.7×10^{-11}
Hydrogen phosphate ion	HPO_4^{2-}	4.5×10^{-13}
Hydrogen sulfide ion	HS^-	1×10^{-13}

decreasing acid strength

*In each case the dissociation reaction is of the type:

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq); \qquad K_a = \frac{[H^+] \times [B^-]}{[HB]}$$

Qualitative interpretation of K_a.

1. The smaller the dissociation constant is, the weaker the acid is.
2. When comparing two weak acids with the same concentration, the acid with the smaller dissociation constant
   a. is weaker.
   b. has a smaller $[H^+]$.
   c. has a higher pH.
   d. has a larger $[HB]$.

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Exercises

A solution of $HClO_2$ is prepared by dissolving 1.369 g of $HClO_2$ in enough water to make 100.0 cm^3 of solution. The pH of the resulting solution is 1.36.

(1) Write the reaction for the dissociation of $HClO_2$.
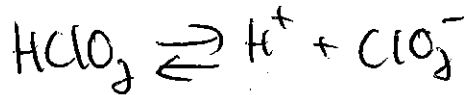
$$HClO_2 \rightleftharpoons H^+ + ClO_2^-$$

(2) Write the expression for K_a.

$$K_a = \frac{[H^+][ClO_2^-]}{[HClO_2]}$$

$$[H^+] = 10^{-pH} = 10^{-1.36} = .0437 \text{ M}$$

$$[HClO_2] = \frac{1.369 g}{100 mL}\left(\frac{1000 mL}{1 L}\right)\left(\frac{1 mole}{68.5 g}\right)$$

$$[HClO_2] = .200 \text{ M}$$

(3) Calculate K_a.

$$K_a = \frac{[.0437][.0437]}{[.200]\;.1563}\;\boxed{.0122}$$

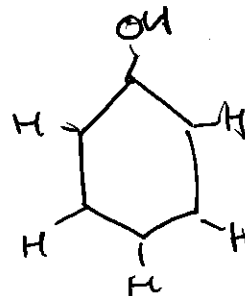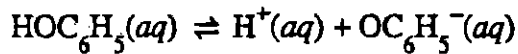| SPECIES	ORIG CONC	CHANGE		EC	
$HClO_2$	.200	$-x$ .0437		.200 $-x$ .1563	
H^+	0	$+x$ .0437	x	.0437	
ClO_2^-	0	$+x$ .0437	x	.0437	

· Applications of K_a

Exercises

a. Phenol (HOC_6H_5) has dissociation constant 1.6×10^{-10}

K_a

Determine $[H^+]$ in a solution prepared by dissolving 0.500 mol of phenol to form 5.00 L of solution.

The equation for the dissociation of phenol is

$$HOC_6H_5(aq) \rightleftharpoons H^+(aq) + OC_6H_5^-(aq)$$

$$K_a = \frac{[H^+][OC_6H_5^-]}{[HOC_6H_5]}$$

$$[HOC_6H_5] = \frac{.5 \, mol}{5L} = .1$$

SPECIES	I OC	C CHANGE	E EC
HOC_6H_5	.1 M	$-x$	$.1-x$
H^+	0	$+x$	x
$OC_6H_5^-$	0	$+x$	x

$$1.6 \times 10^{-10} = \frac{x^2}{(.1-x)}$$

$$1.6 \times 10^{-11} - 1.6 \times 10^{-10} x = x^2$$

$$x^2 + 1.6 \times 10^{-10} x - 1.6 \times 10^{-11} = 0$$
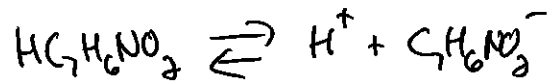
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-1.6 \times 10^{-10} \pm \sqrt{(1.6 \times 10^{-10})^2 - 4(1)(-1.6 \times 10^{-11})}}{2(1)}$$

$$x = 4 \times 10^{-6} = [H^+] \qquad pH = 5.40$$

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Equilibrium Calculations, Weak Acids

29. Para-aminobenzoic acid (PABA), $HC_7H_6NO_2$, is used in some sunscreen agents. A solution is made by dissolving 0.030 mol PABA to form a liter of solution. The solution has $[H^+] = 8.1 \times 10^{-4}$ M. Calculate K_a for para-amino-benzoic acid.

$$HC_7H_6NO_2 \rightleftharpoons H^+ + C_7H_6NO_2^-$$

$$K_a = \frac{[H^+][C_7H_6NO_2^-]}{[HC_7H_6NO_2]}$$

	I	C	E
PABA	.03	−x	.03−x → .03−8.1×10⁻⁴ = .02919
H⁺	0	+x	x → 8.1×10⁻⁴
PABA⁻	0	+x	x → 8.1×10⁻⁴

$x = 8.1 \times 10^{-4}$

$$K_a = \frac{(8.1 \times 10^{-4})^2}{.02919}$$

$$\boxed{K_a = 2.25 \times 10^{-5}}$$

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31. Benzoic acid, $HC_7H_5O_2$, is present in many berries. A benzoic acid solution prepared by dissolving 1.00 g of benzoic acid in 350.0 mL of solution has a pH of 2.91. What is the K_a for benzoic acid?
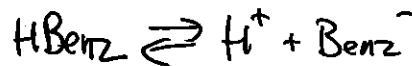
$$HBenz \rightleftharpoons H^+ + Benz^-$$

$$K_a = \frac{[H^+][Benz^-]}{[HBenz]}$$

	I	C	E
HBenz	.0234 M	−x	.0234−x → .02217
H⁺	0	+x	x → .00123
Benz⁻	0	+x	x → .00123

$$\frac{1g \, HBenz}{.35 \, L} \left(\frac{1 \, mole}{122 \, g} \right) = .0234 \, M$$

$pH = 2.91$

$[H^+] = 10^{-2.91} = .00123$

$$\boxed{K_a = 6.82 \times 10^{-5}}$$

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35. Lactic acid ($K_a = 1.4 \times 10^{-4}$) is present in sore muscles after vigorous exercise. For a 1.3 M solution of lactic acid, calculate

a. $[H^+]$ b. $[OH^-]$ c. pH   d. % dissociation

$$HLac \rightleftharpoons H^+ + Lac^-$$

	I	C	E
HLac	1.3	−x	1.3−x
H⁺	0	+x	x
Lac⁻	0	+x	x

$$K_a = \frac{(x)^2}{1.3-x}$$

$$1.4 \times 10^{-4} = \frac{x^2}{1.3-x}$$

$\%diss = \frac{.0134}{1.3} \times 100$

1.03%

$$x^2 + 1.4 \times 10^{-4}x - 1.82 \times 10^{-4} = 0$$

$$x = \frac{-1.4 \times 10^{-4} \pm \sqrt{(1.4 \times 10^{-9})^2 - 4(1)(-1.82 \times 10^{-4})}}{2(1)}$$

$\boxed{x = .0134 = [H^+]}$

$[OH^-] = \frac{1 \times 10^{-14}}{.0134} = 7.46 \times 10^{-13}$

c) $pH = 1.87$

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Weak Bases

Species that act as weak bases

1. Molecules
   a. ammonia—NH_3
   b. amines, which can be represented generally as R_3N, where R can be H, CH_3, etc.

2. Anions

   Any anion that is the conjugate base of a weak acid.

TABLE   Dissociation Constants of Some Weak Bases* at 25°C

BASE	FORMULA	K_b	
Hydrogen sulfite ion	HSO_3^-	5.9×10^{-13}	
Dihydrogen phosphate ion	$H_2PO_4^-$	1.4×10^{-11}	
Fluoride ion	F^-	1.4×10^{-11}	
Nitrite ion	NO_2^-	1.7×10^{-11}	
Formate ion	CHO_2^-	5.3×10^{-11}	
Benzoate ion	$C_7H_5O_2^-$	1.5×10^{-10}	
Aniline	$C_6H_5NH_2$	3.8×10^{-10}	increasing basic strength
Acetate ion	$C_2H_3O_2^-$	5.6×10^{-10}	
Propionate ion	$C_3H_5O_2^-$	7.1×10^{-10}	
Hydrogen carbonate ion	HCO_3^-	2.3×10^{-8}	
Hydrogen sulfide ion	HS^-	1.0×10^{-7}	
Hydrogen phosphate ion	HPO_4^{2-}	1.6×10^{-7}	
Sulfite ion	SO_3^{2-}	1.7×10^{-7}	
Hypochlorite ion	ClO^-	3.6×10^{-7}	
Hypobromite ion	BrO^-	3.8×10^{-6}	
Cyanide ion	CN^-	1.7×10^{-5}	
Ammonia	NH_3	1.8×10^{-5}	
Carbonate ion	CO_3^{2-}	2.1×10^{-4}	
Methyl amine	CH_3NH_2	4.2×10^{-4}	
Phosphate ion	PO_4^{3-}	2.2×10^{-2}	
Sulfide ion	S^{2-}	1×10^{-1}	

*In each case the dissociation reaction is of the type:

$$B^-(aq) + H_2O \rightleftharpoons OH^-(aq) + HB(aq); \quad K_b = \frac{[OH^-] \times [HB]}{[B^-]}$$
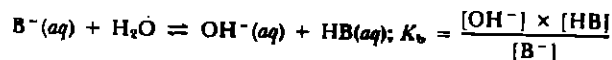
PLEASE NOTE CAREFULLY:

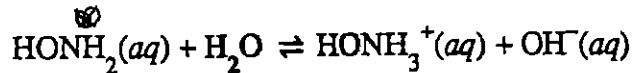The mathematical relationship between K_a and K_b is as follows:

$$(K_a)(K_b) = K_w$$

where

$$K_w = 1 \times 10^{-14}$$

Determination of [OH$^-$]

Exercises

Hydroxylamine (HONH$_2$) reacts with water according to the equation

$$HONH_2(aq) + H_2O \rightleftharpoons HONH_3^+(aq) + OH^-(aq)$$

The equilibrium constant for this equation is called K$_b$. It is 9.1×10^{-9}. Calculate [OH$^-$] and the pH of a one-liter solution of hydroxylamine containing 6.6 g of hydroxylamine.

$$K_b = \frac{[OH^-][HONH_3^+]}{[HONH_2]}$$

$$\frac{6.6g \, HONH_2}{1L}\left(\frac{1 \, mole}{33g}\right) = .2M$$

$$9.1 \times 10^{-9} = \frac{(x)(x)}{.2-x}$$

$$1.82 \times 10^{-9} - 9.1 \times 10^{-9}x = x^2$$

$$x^2 + 9.1 \times 10^{-9}x - 1.82 \times 10^{-9} = 0$$

SPECIES	OC	CHANGE	EC
HONH$_2$	.2M	$-x$	.2-x
HONH$_3^+$	0	$+x$	x
OH$^-$	0	$+x$	x

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-9.1 \times 10^{-9} + \overbrace{\sqrt{(9.1 \times 10^{-9})^2 - 4(1)(1.82 \times 10^{-9})}}^{8.53 \times 10^{-5}}}{2(1)}$$

$$x = 4.27 \times 10^{-5} = [OH^-]$$

$$[OH^-] = 4.27 \times 10^{-5} M$$

$$[H^+] = 2.34 \times 10^{-10} M$$

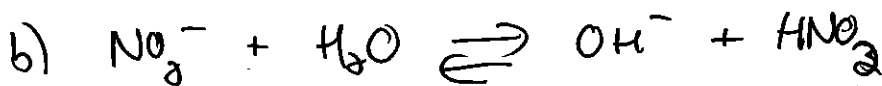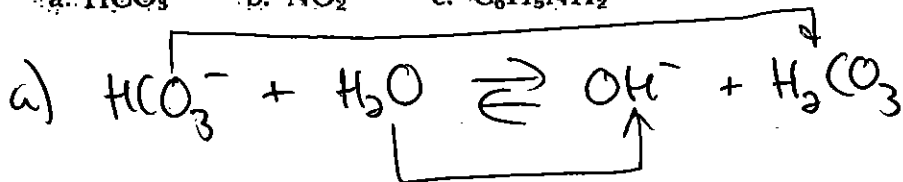$$pH = -\log[H^+] = 9.63$$

or

$$pOH = -\log[OH^-] = 4.37$$

$$pH = 14 - pOH = 9.63$$

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Dissociation Expressions, Weak Bases

49. Write an equation for the dissociation in water of each of the following weak bases: $B^- + H_2O \rightleftharpoons OH^- + HB$

a. HCO_3^- b. NO_2^- c. $C_6H_5NH_2$

a) $HCO_3^- + H_2O \rightleftharpoons OH^- + H_2CO_3$

b) $NO_2^- + H_2O \rightleftharpoons OH^- + HNO_2$

c) $C_6H_5NH_2 + H_2O \rightleftharpoons OH^- + C_6H_5NH_3^+$
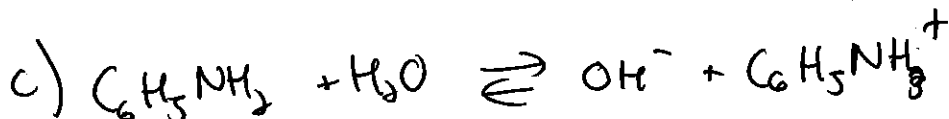
Equilibrium Calculations, Weak Bases

51. Write the net ionic equation for the reaction that makes solutions of sodium benzoate, $NaC_7H_5O_2$, basic. K_a for benzoic acid is 6.6×10^{-5}. Find

a. K_b for the reaction.
b. the pH of a 0.23 M solution of sodium benzoate.

$$\underset{Benz^-}{C_7H_5O_2^-} + H_2O \rightleftharpoons \underset{H\,Benz}{HC_7H_5O_2} + OH^-$$
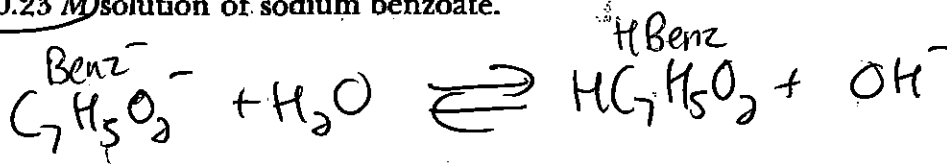
a) $K_b = ? = \dfrac{K_w}{K_a} = \dfrac{1 \times 10^{-14}}{6.6 \times 10^{-5}} = 1.52 \times 10^{-10}$

$$K_b = \frac{[HBenz][OH^-]}{[Benz^-]}$$

	I	C	E
Benz⁻	.23 M	−x	.23−x
OH⁻	0	+x	x
HBenz	0	+x	x

$1.52 \times 10^{-10} = \dfrac{x^2}{(.23-x)}$

$x^2 + 1.52 \times 10^{-10}\,x - 3.48 \times 10^{-11} = 0$

$x = \dfrac{-1.52 \times 10^{-10} \pm \sqrt{(1.52 \times 10^{-10})^2 - 4(1)(-3.48 \times 10^{-11})}}{2(1)}$
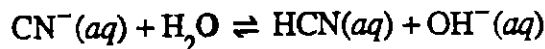
$x = 5.91 \times 10^{-6} = [OH^-]$

$pOH = 5.23$

$pH = 8.77$

Determining the pH of a salt solution.

Exercises

Determine the pH of a 0.100 M aqueous solution of NaCN.
The K_a for HCN is 5.8×10^{-10}.

$$CN^-(aq) + H_2O \rightleftharpoons HCN(aq) + OH^-(aq) \qquad K_b = 1.72 \times 10^{-5}$$

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

$$1.72 \times 10^{-5} = \frac{(x)(x)}{(.1-x)}$$

SPECIES	OC	CHANGE	EC
CN^-	.100	$-x$	$.1-x$
OH^-	0	$+x$	x
HCN	0	$+x$	x

$$1.72 \times 10^{-6} - 1.72 \times 10^{-5}x = x^2$$

$$x^2 + 1.72 \times 10^{-5}x - 1.72 \times 10^{-6} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} , \quad \frac{-1.72 \times 10^{-5} \pm \sqrt{(1.72 \times 10^{-5})^2 - 4(1)(-1.72 \times 10^{-6})}}{2(1)}$$

$$x = 1.32 \times 10^{-3} = [OH^-]$$

$$[H^+] = \frac{1 \times 10^{-14}}{1.32 \times 10^{-3}} = 7.58 \times 10^{-12}$$

$$\boxed{pH = 11.1}$$

ACID-BASE PROPERTIES OF SALT SOLUTIONS

At this point, you should be able to predict correctly that an aqueous solution of HI or H_2SO_4 is acidic while a solution of NaOH or NH_3 is basic. Solutions of $NaNO_2$ or NH_4I might be more difficult for you to classify. These two compounds, and many others, such as NaCl, $Zn(NO_3)_2$, and $CuSO_4$, are salts. A salt is an ionic compound containing a cation other than H^+ and an anion other than OH^- or O^{2-}.

NEUTRAL IONS (NONBASIC AND NONACIDIC)

A neutral ion does not react with water to produce H^+ or OH^- ions. Hence, it does not affect the pH. There are relatively few neutral ions. We see from Table ⋅ that

— the neutral anions are those derived from strong acids.

— the neutral cations are those derived from strong bases.

BASIC ANIONS

Recall from Section 14.3 that any anion derived from a weak acid acts as a weak base in water solution. There is a small army of such anions. Those listed in Table 14.7 are typical examples. In contrast, there are no common basic cations.
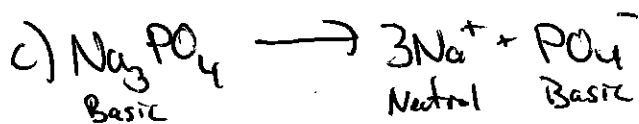
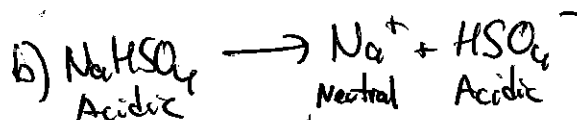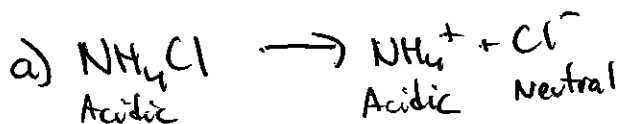## ACIDIC IONS

Acidic ions include

— all cations except those of the alkali metals and the heavier alkaline earths.

— the HSO_4^- and $H_2PO_4^-$ anions.

TABLE   Acid-Base Properties of Some Common Ions in Water Solution

	NEUTRAL		BASIC		ACIDIC
Anion	Cl^- Br^- I^-	NO_3^- ClO_4^- SO_4^{2-}	$C_2H_3O_2^-$ F^- CO_3^{2-} S^{2-} PO_4^{3-}	CN^- NO_2^- HCO_3^- HS^- HPO_4^{2-}	HSO_4^- $H_2PO_4^-$
Cation	Li^+ Na^+ K^+	Ca^{2+} Ba^{2+}	none		Mg^{2+} Al^{3+} NH_4^+ transition metal ions

, Write net ionic equations to explain the acidity or basicity of the various salts listed

a. NH_4Cl b. $NaHSO_4$
c. Na_3PO_4 d. KNO_3
e. $KHCO_3$ f. NaCN

a) $NH_4Cl \longrightarrow NH_4^+ + Cl^-$
  Acidic   Acidic Neutral

b) $NaHSO_4 \longrightarrow Na^+ + HSO_4^-$
  Acidic   Neutral Acidic

c) $Na_3PO_4 \longrightarrow 3Na^+ + PO_4^-$
  Basic   Neutral Basic

d) $KNO_3 \longrightarrow K^+ + NO_3^-$
  Neutral   neutral Neutra

e) $KHCO_3 \longrightarrow K^+ + HCO_3^-$
  Basic   neutral Basic

f) $NaCN \longrightarrow Na^+ + CN^-$
  B   N   B

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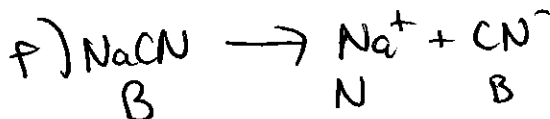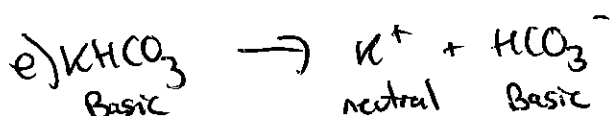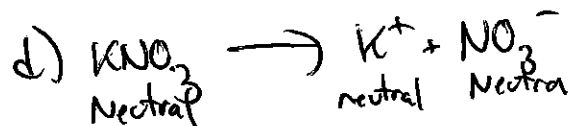
Salt Solutions

55. State whether 1 M solutions of the following salts in water would be acidic, basic, or neutral.

  a. NH_4Cl b. NH_4CN (Tables 14.3, 14.6)
  c. Na_3PO_4 d. KNO_3
  e. $KHCO_3$ f. $NaCN$

a) Acidic (NH_4^+ is acidic, Cl^- is neutral)

b) ~~Acidic~~ Neutral (NH_4^+ is acidic, CN^- is basic)

c) Basic (Na^+ is neutral, PO_4^{-3} is basic)

d) Neutral (K^+ is neutral, NO_3^- is neutral)

e) Basic (K^+ is neutral, HCO_3^- is basic)

f) Basic (Na^+ is neutral, CN^- is basic)

Acid-Base Models

63. For each of the following reactions, indicate the Brönsted-Lowry acids and bases. What are the conjugate acid-base pairs?

  a. $H_3O^+ + HSO_3^-(aq) \rightleftharpoons H_2SO_3(aq) + H_2O$
  b. $HF(aq) + OH^-(aq) \rightleftharpoons F^-(aq) + H_2O$
  c. $NH_4^+(aq) + H_2O \rightleftharpoons NH_3(aq) + H_3O^+$

$$HB + A^- \rightleftharpoons HA + B^-$$

Acid is a proton donor
Base is a proton acceptor

a) HSO_3^- is accepting the hydrogen - Base
   H_3O^+ is donating the hydrogen - Acid
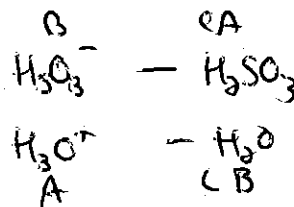
$$\begin{array}{cc} B & cA \\ HSO_3^- & - H_2SO_3 \\ H_3O^+ & - H_2O \\ A & cB \end{array}$$

b) HF is donating the hydrogen - Acid $A\,HF \rightarrow F^- - cB$
   OH^- is accepting the hydrogen - Base $B\,OH^- \rightarrow H_2O - cA$

c) NH_4^+ is donating - A $A\,NH_4^+ \rightarrow cB\;NH_3$

   H_2O is accepting   B $B\;H_2O \rightarrow cA\;H_2O$
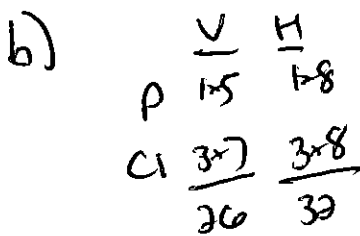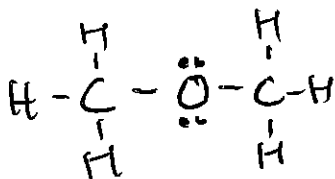
15
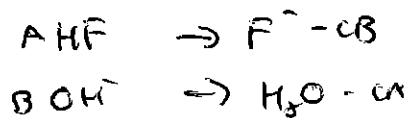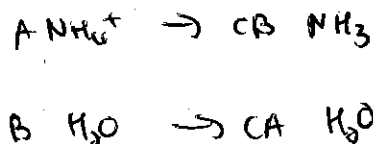
67. Classify each of the following species as either a Lewis acid or a Lewis base. Draw Lewis structures where necessary.
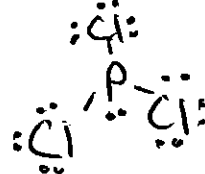
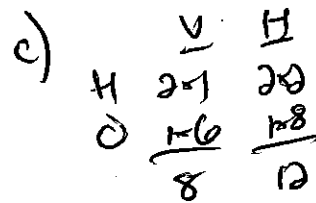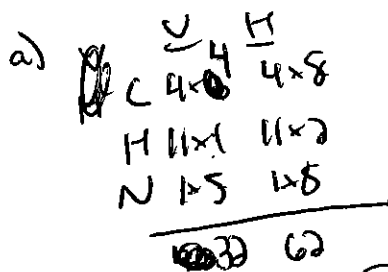a. CH_3OCH_3 b. PCl_3 c. H_2O

a)

	V	H
C	2-4 2×8	
H	6×1 6×2	
O	1×6 1×8	
	20	36

bonds = 8

$\frac{36-20}{2}$

e^- pair donor
Base

H-C-O-C-H structure with H atoms

b)

	V	H
P	1×5 1×8	
Cl	3×7 3×8	
	26	32

bonds = 3

Cl-P-Cl structure

Lewis Base
e^- donor

c)

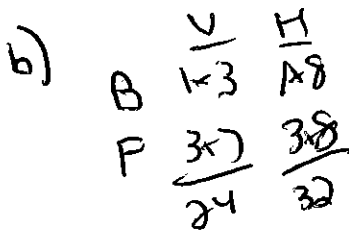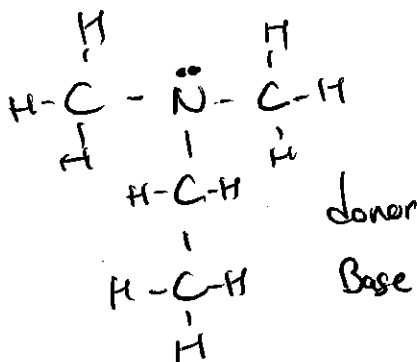|	V	H
H	2×1 2×2	
O	1×6 1×8	
	8	12
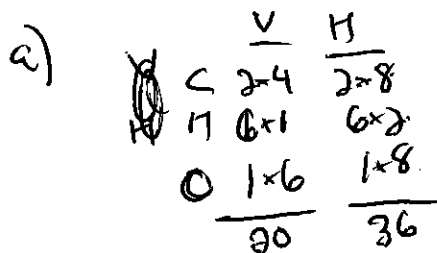
bonds = 2

H-O-H structure

Lewis Base
e^- donor

68. Classify each of the following species as either a Lewis acid or a Lewis base. Draw Lewis structures where necessary.
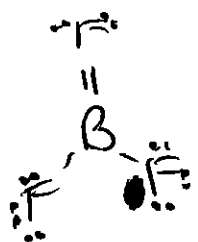
a. $H_3C-N-CH_3$ with C_2H_5 b. BF_3 c. $BeCl_2$

a)

	V	H
C	4×4 4×8	
H	11×1 11×2	
N	1×5 1×8	
	32	62

bonds = 15

H-C-N-C-H structure with H-C-H groups

donor
Base

b)

	V	H
B	1×3 1×8	
F	3×7 3×8	
	24	32

bonds = 4

F-B-F structure

acceptor
Acid

c)

	V	H
Be	1×2 1×8	
Cl	2×7 2×8	
	16	24

4 bonds

Cl=Be=Cl structure
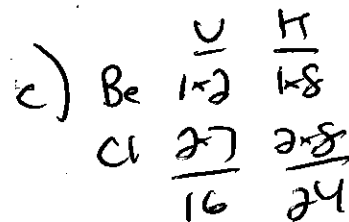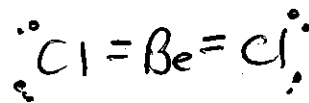
Acceptor
Acid

14
Equilibria in Acid-Base Solutions

I. Buffers
A. Definition: _a solution that resists pH change when OH⁻ or H⁺ are added_

B. Characteristics of a buffer
  1. It contains two species — one that can react with H⁺, and the other with OH⁻.
  2. $[HB]_{eq} \approx [HB]_0$
     $[B^-]_{eq} \approx [B^-]_0$
  3. The pH of a buffer is independent of volume. Thus

$$[H^+] = K_a \frac{[HB]}{[B^-]} = K_a \frac{(\text{moles HB})}{(\text{moles B}^-)}$$

  4. Henderson-Hasselbalch equation

$$\boxed{pH = pK_a + \log \frac{[B^-]}{[HB]}}$$

C. Determination of H⁺ (pH)

Exercises

  1. Calculate the pH of a solution with a volume of 1.000 L that contains 2.70 g of HCN and 2.45 g of NaCN. K_a for HCN is 5.8 × 10⁻¹⁰.

$$[H^+] = K_a \times \frac{[HCN]}{[CN^-]}$$

$$= 5.8 \times 10^{-10} \times \frac{(\text{mol HCN})}{(\text{mol CN}^-)}$$

$$\text{moles HCN} = 2.70\,g \times \frac{1\,mol}{27.03\,g} = 0.100$$

$$2.70\,g\,HCN \left(\frac{1\,mole}{27\,g} \right) = .100 \text{ mdg Hav}$$

$$\text{moles } CN^- = 2.45\,g\,NaCN \left(\frac{1\,mol}{49\,g} \right)$$

$$.05 \text{ moles } CN^-$$

$$\text{moles } CN^- = \text{moles NaCN} = 2.45\,g \times \frac{1\,mol}{49.0\,g} = 0.0500$$

We now substitute into the ionization constant equation and calculate [H⁺].

$$[H^+] = 5.8 \times 10^{-10} \times \frac{0.100\,\text{mol HCN}}{0.0500\,\text{mol CN}^-} = 1.2 \times 10^{-9}\,M$$

The pH of the buffer is 8.94.

$$[H^+] = K_a \frac{\text{moles HB}}{\text{moles B}} = K_a \frac{\text{moles Hav}}{\text{moles av}}$$

$$[H^+] = K_a \left(\frac{.01}{.05} \right)$$

$$[H^+] = 1.16 \times 10^{-9}$$

$$pH = -\log[H^+]$$
$$= 8.94$$

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$$[H^+] = K_a \frac{[HB]}{[B^-]} \qquad \text{or} \qquad pH = pK_a + \log\left(\frac{[B^-]}{[HB]}\right)$$

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

2. Calculate the pH of a buffer prepared by adding 6.56 grams of sodium acetate, $NaC_2H_3O_2$, to 1.00 L of 0.100 M acetic acid, $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$). (E1)

$$6.56g\, NaC_2H_3O_2 \left(\frac{1\, mole\, NaC_2H_3O_2}{82g}\right) = .08\, moles\; NaC_2H_3O_2$$

$$\boxed{.08\, moles\; C_2H_3O_2^-}$$

$$K_a = \frac{[C_2H_3O_2^-][H^+]}{[H_2C_2H_3O_2]}$$

$$.1\, M\; HC_2H_3O_2 \times 1\, L =$$

$$\boxed{.1\, moles\; HC_2H_3O_2}$$

$$[H^+] = K_a \left(\frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]}\right)$$

$$[H^+] = 1.8 \times 10^{-5} \left(\frac{.1\, mole\, HAc}{.08\, mol\, Ac^-}\right) = \boxed{2.25 \times 10^{-5}}$$

$$pH = -\log\left(2.25 \times 10^{-5}\right)$$

$$\boxed{pH = 4.65}$$

D. Choosing a buffer system

1. When required to prepare a buffer solution with a particular pH, you are really being asked to determine the ratio of the concentration of the weak acid [HB] to the concentration of its conjugate base [B⁻]. Follow the steps outlined below to help you in this process.

   a. Calculate [H⁺] from the given pH.

   b. Rearrange the ionization constant expression for the weak acid to get the weak acid–conjugate base ratio expression. Substitute pertinent information and calculate to get a numerical ratio.

   c. Assume the moles of conjugate base to be 1.00, and determine the mass of the salt of that conjugate base accordingly.

   d. The number of moles of weak acid is the numerical ratio obtained in (b). Determine the mass of weak acid corresponding to that number. You now have the "recipe" for the buffer.

2. *Exercises*

   a. Suppose that you want to prepare an $H_2PO_4^-$ – HPO_4^{2-} buffer with a pH of 7.00. Taking the K_a of $H_2PO_4^-$ ($H_2PO_4^- \rightleftharpoons H^+$ (aq) + HPO_4^{2-} (aq)) to be 6.2×10^{-8}, how many grams of NaH_2PO_4 and Na_2HPO_4 should you add to water to make this buffer?

   Solution We follow the steps outlined above.

   (1) $[H^+]$ = inv log(−7.00) = 1.0×10^{-7} M

   (2) We use the ionization constant expression of the weak acid to calculate the weak acid – conjugate base ratio.

$$K_a = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

Rearranging and substituting, we get

$$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{[H^+]}{K_a} = \frac{1.0 \times 10^{-7}}{6.2 \times 10^{-8}} = 1.6$$

This means that for every mole of weak base (HPO_4^{2-}), we need 1.6 moles of weak acid ($H_2PO_4^-$).

   (3) We now calculate the mass of (Na_2HPO_4). Since we need one mole of HPO_4^{2-}, we also need one mole of Na_2HPO_4. Thus

$$\text{mass } Na_2HPO_4 = 1.0 \text{ mol} \times \frac{142\,g}{1\,mol} = 1.4 \times 10^2 \text{ g}$$

   (4) Using the same argument as used in (3), we calculate the mass of NaH_2PO_4 required. We see that we need 1.6 moles of weak acid $H_2PO_4^-$, so we also need 1.6 mol of NaH_2PO_4. The mass needed is therefore

$$\text{mass } NaH_2PO_4 = 1.6 \text{ mol} \times \frac{120\,g}{1\,mol} = 1.9 \times 10^2 \text{ g}$$

Therefore, to get a buffer of pH 7.0, dissolve 1.4×10^2 g of Na_2HPO_4 and 1.9×10^2 g of NaH_2PO_4. It doesn't matter how much water you use because the pH of a buffer is not affected by the volume of the solution.

(handwritten annotations):

WA → CB

$H_2PO_4^- \longrightarrow H^+ + HPO_4^{2-}$

$[H^+] = 10^{-7}$

$$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{[H^+]}{K_a} = \frac{1 \times 10^{-7}}{6.2 \times 10^{-8}}$$

$$\frac{1.6 \text{ moles } H_2PO_4^-}{1 \text{ mole } HPO_4^{2-}}$$

b. How many grams of sodium formate, $NaCHO_2$, must be added to 1.00 L of 0.250 M formic acid, $HCHO_2$, to obtain a buffer with pH 4.00? (E2)

(Ka = 1.6 X10⁻⁴)

$$HCHO_2 \longrightarrow H^+ + CHO_2^-$$
Acid   CB (B⁻)
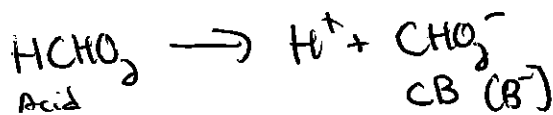
$$\frac{[HCHO_2]}{[CHO_2^-]} = \frac{[H^+]}{Ka} = \frac{1\times10^{-4}}{1.6\times10^{-4}}$$

$$Ka = \frac{[H^+][CHO_2^-]}{[HCHO_2]}$$
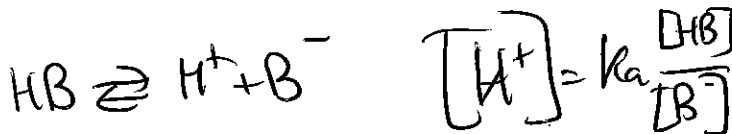
$$\frac{[HCHO_2]}{[CHO_2^-]} = \frac{.625}{1}$$

$$[H^+] = 10^{-pH} = 1\times10^{-4}$$

moles $HCHO_2$ = .25M×1L = .250 moles

$$\frac{.250 \text{ moles}}{x} = .625$$

x = moles formate ion = .400 moles CHO_2^-

= .400 moles $NaCHO_2 \left(\dfrac{68 g}{1 \text{ mole}}\right) = \boxed{27.2g\ NaCHO_2}$

$$HB \rightleftharpoons H^+ + B^- \qquad [H^+] = Ka\frac{[HB]}{[B^-]}$$

E. Adding H⁺ or OH⁻ to a buffer

1. Adding H⁺

a. Recall that a buffer has one species that can react with H⁺ ions. This species is the conjugate base B⁻. Thus when H⁺ is added to a buffer. the following reaction occurs.

$$H^+ (aq) + B^- (aq) \rightleftharpoons HB (aq)$$
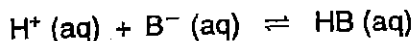
b. Addition of H⁺ does two things to the buffer:

(1) It makes more acid. The concentration of the weak acid in the buffer system after the addition of H⁺ is

total moles HB = (moles HB)₀ + moles H⁺ added

(2) It uses up conjugate base. The reaction above shows that for every mole of H⁺ added, an equal amount of weak base reacts. Therefore, the concentration of weak base (or conjugate base) after H⁺ addition is

total moles B⁻ = (moles B⁻)₀ − moles H⁺ added

2. Adding OH⁻

a. A buffer also has a species that can react with OH⁻ ions. This species is the weak acid. The reaction is

$$HB \text{ (aq)} + OH^- \text{ (aq)} \rightleftharpoons B^- \text{ (aq)} + H_2O$$
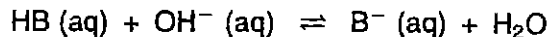
b. Addition of OH⁻ ion does two things to a buffer:

(1) It makes more base. Each mole of OH⁻ added makes an equivalent amount of weak base B⁻. Thus

$$\text{total moles } B^- = (\text{moles } B^-)_0 + \text{moles } OH^- \text{ added}$$

(2) It uses up weak acid. Each mole of OH⁻ added uses up an equivalent amount of weak acid.

$$\text{total moles } HB = (\text{moles } HB)_0 - \text{moles } OH^- \text{ added}$$

F. Buffer limitations

1. The buffer can "absorb" the large pH changes that adding strong acid or strong base imposes on a system as long as it has enough of the species to react with H⁺ or OH⁻. A buffer that has 0.100 mol HB and 0.100 mol B⁻, for example, can only take up to 0.100 mol H⁺ or OH⁻. After that, if say 0.200 mol H⁺ is added, then 0.100 mol H⁺ is unreacted and the pH of the resulting solution is reflected in the concentration of the H⁺ in the system that now has 0.100 mol H⁺.

b. A buffer is prepared by mixing 500.0 mL of 1.250 M ammonia and 25.00 g of ammonium chloride.

(1) Calculate the pH of the buffer. **(E3)**

(For NH_4^{+1}: $K_a = 5.6 \times 10^{-10}$)

$$\overset{HB}{NH_4^+} \rightleftharpoons \overset{H}{H^+} + \overset{B^-}{NH_3}$$
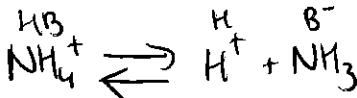
$$K_a = \frac{[H^+][NH_3]}{[NH_4^+]}$$

$$\left(1.25 \frac{mol\ NH_3}{L}\right) \times .5L = .625\ moles\ NH_3$$

$$25g\ NH_4Cl \left(\frac{1\ mole}{53.5g}\right) = .467\ moles\ NH_4Cl = .467\ moles\ NH_4^+$$

$$[H^+] = \frac{K_a[NH_4^+]}{[NH_3]} = \frac{(5.6 \times 10^{-10})(.467)}{(.625)}$$

$$[H^+] = 4.19 \times 10^{-10} \quad \boxed{pH = 9.38}$$

$$K_a = 5.6 \times 10^{-10} \qquad [NH_3] = .625 \text{ moles}$$
$$NH_4^+ = .467 \text{ moles}$$

(2) Calculate the pH of the buffer after 0.0125 mole of H⁺ is added to the buffer. **(E4)**

moles $NH_4^+ = .467 + .0125 = .4795$ moles NH_4^+

moles $NH_3 = .625 - .0125 = .6125$ moles NH_3

$$[H^+] = K_a \left(\frac{[NH_4^+]}{[NH_3]} \right) = 5.6 \times 10^{-10} \left(\frac{.4795}{.6125} \right) \qquad \boxed{pH = 9.36}$$

$$[H^+] = 4.38 \times 10^{-10}$$

(3) Calculate the pH of the buffer after 0.120 mol of OH⁻ is added to the buffer. **(E5)**

moles $NH_4^+ \quad .467 - .120 = .347$ moles NH_4^+

moles $NH_3 \quad .625 + .120 = .745$ moles NH_3

$$[H^+] = 5.6 \times 10^{-10} \left(\frac{.347}{.745} \right) = 2.61 \times 10^{-10}$$
$$\boxed{pH = 9.58}$$

(4) Calculate the pH of the buffer after 0.750 mol of OH⁻ is added to the buffer. **(E6)**

moles $NH_4^+ = .467 - .750$

moles $NH_3 = .625 + .750$

LIMITATIONS

Not enough acid to react w/ all OH⁻

$.75 - .467 = .283$ moles OH⁻ unreacted

$[H^+] = \dfrac{1 \times 10^{-14}}{.283}$

pOH = .548

$\boxed{pH = 13.45}$

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II. Acid-Base Indicators

A. Nature of an indicator

1. What does it do? *marks the endpoint of a titration by changing color. It also shows pH change w/ a color change*

2. What is it derived from? *complex organic dyes which are weak acid (HIn)*

$$HIn \rightleftharpoons H^+ + In^-$$

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

3. Color

   a. When $[HIn]/[In^-] > 10$:

   (1) the principal species is *HIn (acid)*

   (2) the color observed is that of *Acid*

$$\frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_a}$$

   b. When $[HIn]/[In^-] < 0.10$:

   (1) the principal species is *In⁻ (Base)*

   (2) the color observed is that of *Base*

   c. When $[HIn] \approx [In^-]$:
   the color observed is that of *intermediate color (neutral)*

   d. Color is dependent on

   (1) pH of the solution

   (2) K_a of the indicator

$$pH = pK_a \qquad [H^+] = K_a$$

B. Distribution Curves

1. Sketch the general shape of the distribution curve of an indicator HIn.
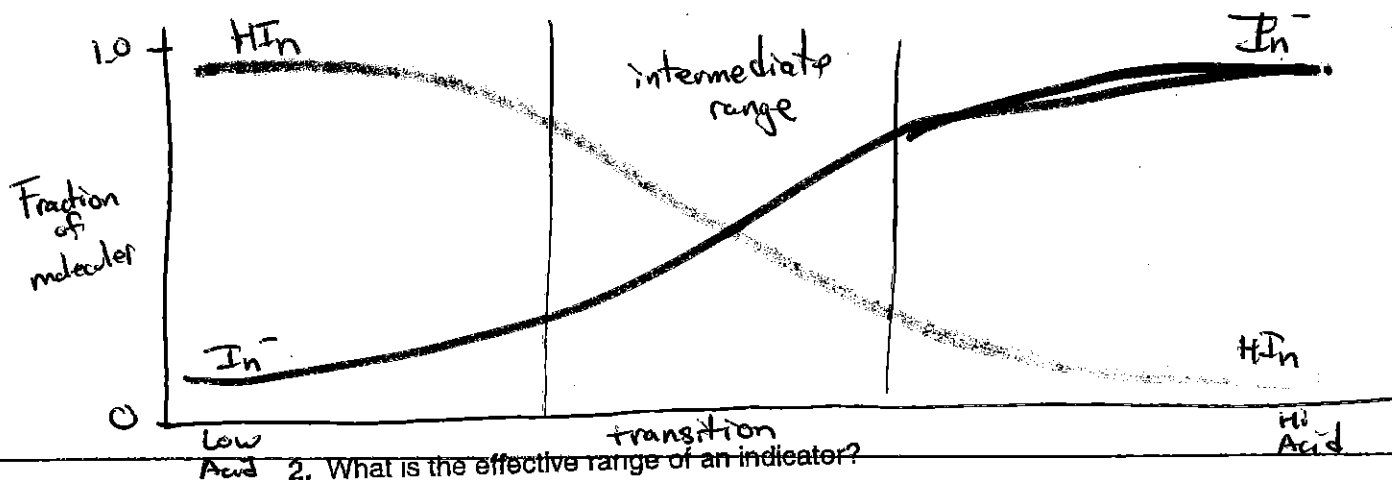
2. What is the effective range of an indicator?

Typical Acid-Base Indicators

INDICATOR	pH INTERVAL	ACID COLOR (LOWER pH)	BASE COLOR (HIGHER pH)
Methyl violet	0.0–1.6	yellow	violet
Methyl yellow	2.9–4.0	red	yellow
Methyl orange	3.1–4.4	red	yellow
Methyl red	4.8–6.2	red	yellow
Bromthymol blue	6.0–8.0	yellow	blue
Thymol blue	8.0–9.6	yellow	blue
Phenolphthalein	8.2–10.0	colorless	pink
Alizarin yellow	10.1–12.0	yellow	red

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III. Acid-Base Titrations

$HCl/NaOH$

A. Strong acid-strong base titration

1. Give an example and write the reaction that takes place.

$$H^+ + OH^- \longrightarrow H_2O$$
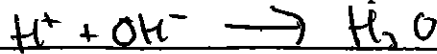
2. Draw the titration curve.
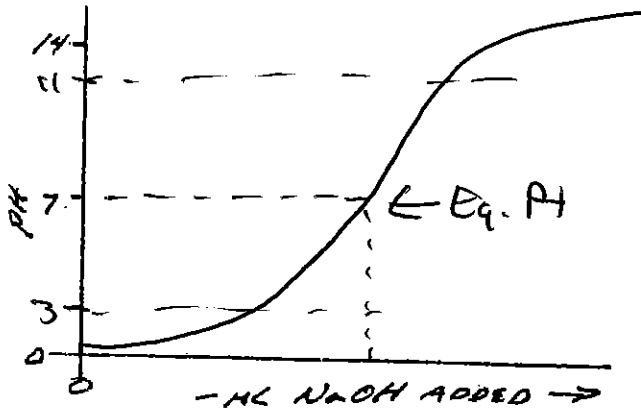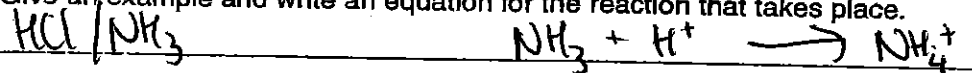

Label equivalence point

$pH = pKa$ @ Eq. Pt

3. pH at the equivalence point: _____

4. Species present in solution at the equivalence point: H_2O

5. Types of indicators that can be used for this titration: Bromthymol blue / phenolphthalein
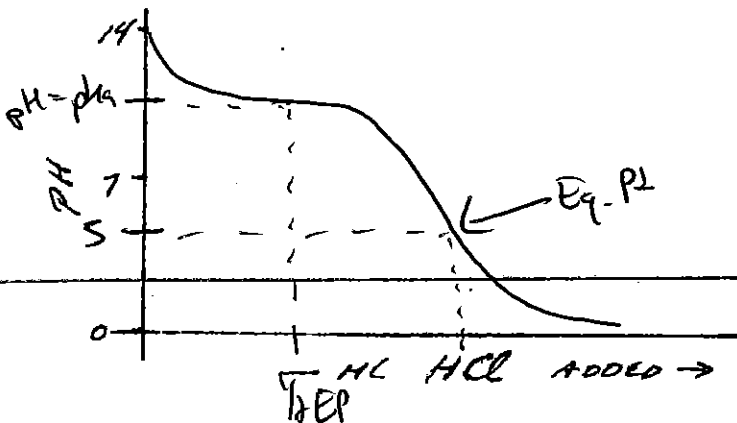Any indicator pH range 3-11 will work

B. Strong acid-weak base titration

1. Give an example and write an equation for the reaction that takes place.

HCl/NH_3 $\qquad$ $NH_3 + H^+ \longrightarrow NH_4^+$

Acidic Catia

2. Draw the titration curve.

Label equivalence point

Label buffer zone

@ ½ EP, $pH = pKa$

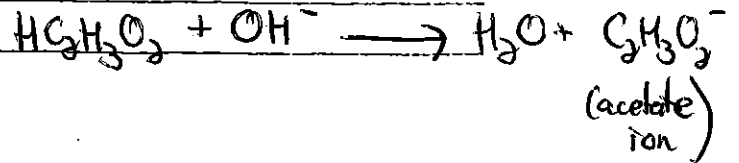3. What is the pH at the equivalence point and what are the species present in the resulting solution? $pH = 5$

NH_4^+

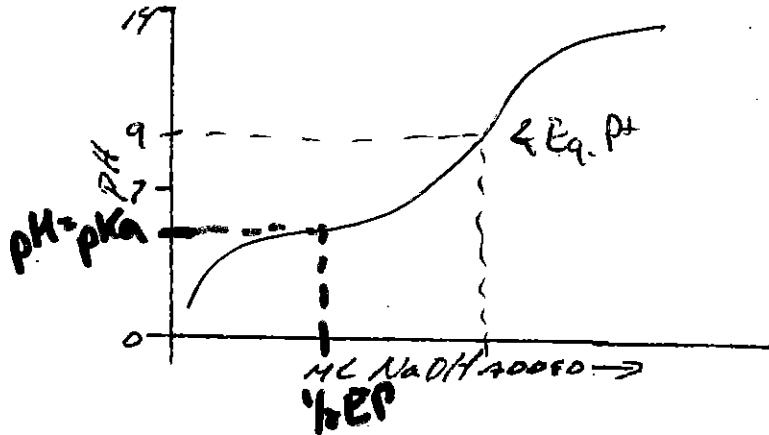4. What types of indicators can be used?

Methyl Red

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C. Weak acid-strong base titration

  1. Give an example and write an equation for the reaction that takes place.

  Acetic Acid $(HC_2H_3O_2)$/NaOH

  $$HC_2H_3O_2 + OH^- \longrightarrow H_2O + C_2H_3O_2^-$$
  (acetate ion)

  2. Draw the titration curve.

Label equivalence point

Label buffer zone

@ ½ EP: pH = pKa

  3. pH at the equivalence point: ≈ 9

  4. Species present in solution at the equivalence point: $H_2O + C_2H_3O_2^-$ (basic anion)

  5. Types of indicators that can be used for this titration: thymol blue
  ~~phthalein~~
  phenolphthalein