

Problems, Chapter 16 (with solutions) NOTE: Unless otherwise stated, assume T = 25.°C in all problems)

1) What is the Arrhenius definition of an acid? Of a base?

An Arrhenius acid is a substance that produces H<sup>+</sup> ions when added to water. An Arrhenius base is a substance that produces OH<sup>-</sup> ions when added to water.

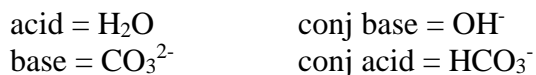
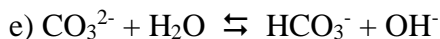
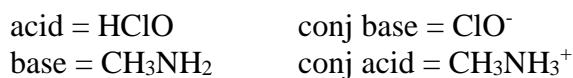
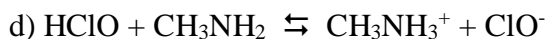
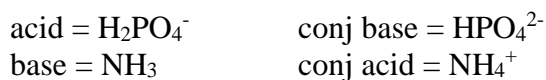
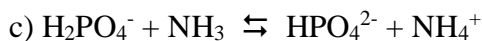
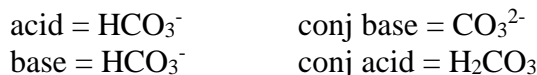
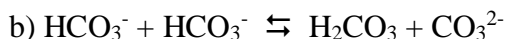
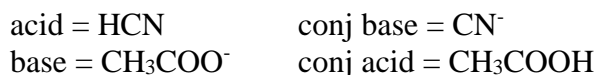
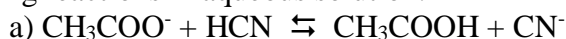
2) What is the Bronsted-Lowry definition of an acid? Of a base?

A Bronsted acid is a proton donor, and forms a conjugate base after donating a proton. A Bronsted base is a proton acceptor, and forms a conjugate acid after accepting a proton.

3) What is the Lewis definition of an acid? Of a base?

A Lewis acid is an electron pair acceptor. A Lewis base is an electron pair donor.

4) (16.2) Identify the acid-conjugate base and base-conjugate acid pairs in each of the following reactions in aqueous solution.

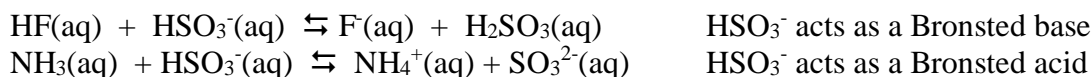


5) Identify each of the following species as a strong acid, weak acid, strong soluble base, insoluble base, or weak base.

- a) HCN (weak acid)
- b) Cu(OH)<sub>2</sub> (insoluble base)
- c) HNO<sub>2</sub> (weak acid)
- d) NaOH (strong soluble base)
- e) HClO<sub>3</sub> (strong acid)
- f) HClO (weak acid)
- g) NH<sub>3</sub> (weak base)

6) What is meant by the term amphoteric. Show by giving an appropriate set of reactions how the HSO<sub>3</sub><sup>-</sup> anion exhibits amphoteric properties.

A substance is amphoteric if it can behave as either a Bronsted acid or a Bronsted base, depending on the particular reaction taking place. For example, for HSO<sub>3</sub><sup>-</sup>



7) Complete the table (all solutions are at 25. °C)

[H <sub>3</sub> O <sup>+</sup> ]	[OH <sup>-</sup> ]	pH	Acid or base
3.5 x 10 <sup>-3</sup>	<u>2.9 x 10<sup>-12</sup></u>	<u>2.46</u>	<u>acid</u>
<u>2.6 x 10<sup>-8</sup></u>	3.8 x 10 <sup>-7</sup>	<u>7.58</u>	<u>base</u>
1.8 x 10 <sup>-9</sup>	<u>5.6 x 10<sup>-6</sup></u>	<u>8.74</u>	<u>base</u>
<u>7.1 x 10<sup>-8</sup></u>	<u>1.4 x 10<sup>-7</sup></u>	7.15	base

8) The value for the autoionization constant for water at T = 40.0 °C is K<sub>w</sub> = 2.92 x 10<sup>-14</sup>. What are the values for [H<sub>3</sub>O<sup>+</sup>], [OH<sup>-</sup>], and pH for a neutral aqueous solution at this temperature?

The autoionization reaction is



	Initial	Change	Equilibrium
H <sub>3</sub> O <sup>+</sup>	0	x	x
OH <sup>-</sup>	0	x	x

So (x)(x) = x<sup>2</sup> = 2.92 x 10<sup>-14</sup>                      x = (2.92 x 10<sup>-14</sup>)<sup>1/2</sup> = 1.71 x 10<sup>-7</sup>

So for a neutral solution [H<sub>3</sub>O<sup>+</sup>] = [OH<sup>-</sup>] = 1.71 x 10<sup>-7</sup> M

pH = -log<sub>10</sub>(1.71 x 10<sup>-7</sup>) = 6.77

9) (16.26) Find the pH of each of the following solutions:

a)  $2.8 \times 10^{-4}$  M  $\text{Ba}(\text{OH})_2$ .

$$[\text{OH}^-] = \frac{2.8 \times 10^{-4} \text{ mol Ba}(\text{OH})_2}{\text{L soln}} \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba}(\text{OH})_2} = 5.6 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log_{10}(5.6 \times 10^{-4}) = 3.25 ; \text{ so pH} = 14.00 - 3.25 = 10.75$$

b)  $5.2 \times 10^{-4}$  M  $\text{HNO}_3$ .

$$\text{A monoprotic strong acid, so pH} = -\log_{10}(5.2 \times 10^{-4}) = 3.28$$

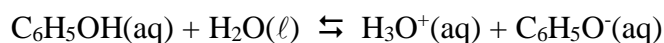
10) How many grams of NaOH would be needed to prepare 500.0 mL of a solution with pH = 12.50?

$$\text{pOH} = 14.00 - 12.50 = 1.50$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-1.50} = 0.0316 \text{ M} \quad \text{MW}(\text{NaOH}) = 40.00 \text{ g/mol}$$

$$\text{g NaOH} = 0.5000 \text{ L soln} \frac{0.0316 \text{ mol OH}^-}{\text{L soln}} \frac{1 \text{ mol NaOH}}{1 \text{ mol OH}^-} \frac{40.00 \text{ g NaOH}}{\text{mol NaOH}} = 0.632 \text{ g}$$

11) (16.52) Find the pH of an aqueous solution at 25. °C that is 0.34 M in phenol ( $\text{C}_6\text{H}_5\text{OH}$ ,  $K_a = 1.3 \times 10^{-10}$ ).



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} = 1.3 \times 10^{-10}$$

	Initial	Change	Equilibrium
$\text{H}_3\text{O}^+$	0	x	x
$\text{C}_6\text{H}_5\text{O}^-$	0	x	x
$\text{C}_6\text{H}_5\text{OH}$	0.34	-x	0.34 - x

$$\frac{(x)(x)}{(0.34 - x)} = 1.3 \times 10^{-10}$$

Assume  $x \ll 0.34$ . Then

$$\frac{x^2}{0.34} = 1.3 \times 10^{-10} \quad x^2 = (0.34)(1.3 \times 10^{-10}) = 4.42 \times 10^{-11}$$

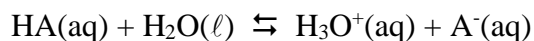
$$x = (4.42 \times 10^{-11})^{1/2} = 6.65 \times 10^{-6}$$

Since  $6.65 \times 10^{-6} \ll 0.34$ , our approximation was good. Therefore

$$[\text{H}_3\text{O}^+] = x = 6.65 \times 10^{-6} \text{ M} \quad \text{pH} = -\log_{10}(6.65 \times 10^{-6}) = 5.18$$

12) (16.58) The pH of an aqueous solution of an unknown monoprotic acid is  $\text{pH} = 6.20$  at  $T = 25.^\circ\text{C}$ . The concentration of the acid is  $0.010 \text{ M}$ . What is  $K_a$  for the acid?

Call the weak acid HA



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

Since  $\text{pH} = 6.20$ , then at equilibrium  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-6.20} = 6.31 \times 10^{-7} \text{ M}$

$$\text{But } [\text{A}^-] = [\text{H}_3\text{O}^+] = 6.31 \times 10^{-7} \text{ M}$$

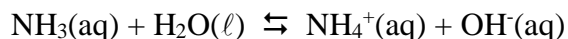
$$[\text{HA}] = 0.010 - 6.31 \times 10^{-7} = 0.010 \text{ M}$$

$$K_a = \frac{(6.31 \times 10^{-7})(6.31 \times 10^{-7})}{0.010} = 4.0 \times 10^{-11}$$

13) (16.70) Find the pH for each of the following solutions at  $T = 25.^\circ\text{C}$ .

In both cases it is easiest to first find pOH, and then convert to pH

a)  $0.10 \text{ M NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ )



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

	Initial	Change	Equilibrium
$\text{NH}_4^+$	0	x	x
$\text{OH}^-$	0	x	x
$\text{NH}_3$	0.10	- x	0.10 - x

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

Assume  $x \ll 0.10$  Then

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5} \quad x^2 = (1.8 \times 10^{-5})(0.10) = 1.8 \times 10^{-6}$$

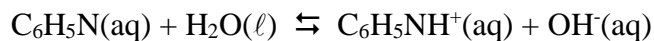
$$x = (1.8 \times 10^{-6})^{1/2} = 1.34 \times 10^{-3}$$

Since  $1.34 \times 10^{-3} \ll 0.10$ , our approximation was good.

$$\text{So } [\text{OH}^-] = x = 1.34 \times 10^{-3} \quad \text{pOH} = -\log_{10}(1.34 \times 10^{-3}) = 2.87$$

$$\text{pH} = 14.00 - 2.87 = 11.13$$

b) 0.050 M pyradine ( $\text{C}_5\text{H}_5\text{N}$ ,  $K_b = 1.7 \times 10^{-9}$ )



$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{N}]} = 1.7 \times 10^{-9}$$

	Initial	Change	Equilibrium
$\text{C}_6\text{H}_5\text{NH}^+$	0	x	x
$\text{OH}^-$	0	x	x
$\text{C}_6\text{H}_5\text{N}$	0.050	- x	0.050 - x

$$\frac{(x)(x)}{(0.050 - x)} = 1.7 \times 10^{-9}$$

Assume  $x \ll 0.050$  Then

$$\frac{x^2}{0.050} = 1.7 \times 10^{-9} \quad x^2 = (1.7 \times 10^{-9})(0.050) = 8.5 \times 10^{-11}$$

$$x = (8.5 \times 10^{-11})^{1/2} = 9.22 \times 10^{-6}$$

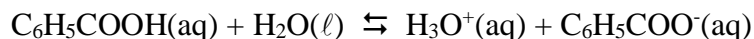
Since  $9.22 \times 10^{-6} \ll 0.050$ , our approximation was good.

$$\text{So } [\text{OH}^-] = x = 9.22 \times 10^{-6} \quad \text{pOH} = -\log_{10}(9.22 \times 10^{-6}) = 5.04$$

$$\text{pH} = 14.00 - 5.04 = 8.96$$

14) Determine the pH and percent ionization of a 0.220 M solution of benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ,  $K_a = 6.5 \times 10^{-5}$ ).

Benzoic acid is  $\text{C}_6\text{H}_5\text{COOH}$ ,  $K_a = 6.5 \times 10^{-5}$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = 6.5 \times 10^{-5}$$

	Initial	Change	Equilibrium
$\text{H}_3\text{O}^+$	0	x	x
$\text{C}_6\text{H}_5\text{COO}^-$	0	x	x
$\text{C}_6\text{H}_5\text{COOH}$	0.220	- x	0.220 - x

$$\frac{(x)(x)}{(0.220 - x)} = 1.8 \times 10^{-4}$$

Assume  $x \ll 0.220$ . Then

$$\frac{x^2}{0.220} = 6.5 \times 10^{-5} ; \quad x^2 = (0.220)(6.5 \times 10^{-5}) = 1.43 \times 10^{-5}$$

$$x = (1.43 \times 10^{-5})^{1/2} = 3.78 \times 10^{-3}$$

Is  $3.78 \times 10^{-3} \ll 0.225$  ? YES. (We say small if at least 10 times smaller).

$$\text{So pH} = -\log_{10}(3.78 \times 10^{-3}) = 2.42$$

$$\text{Now, percent ionization} = \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\%$$

$$\text{So \% ionization} = \frac{3.78 \times 10^{-3}}{0.220} \cdot 100\% = 1.7\%$$

15) The acid dissociation constant for acetic acid ( $\text{CH}_3\text{COOH}$ ) is  $K_a = 1.8 \times 10^{-5}$  at  $T = 25.^\circ\text{C}$ .

- What is  $\text{p}K_a$  for acetic acid?
- What is  $K_b$  for the acetate ion,  $\text{CH}_3\text{COO}^-$ ?
- Which of the following acids is a stronger acid than acetic acid:  $\text{HNO}_2$ ,  $\text{C}_6\text{H}_5\text{COOH}$ ,  $\text{HCN}$ ?
- Which of the following anions is a stronger base than the acetate anion:  $\text{NO}_2^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $\text{CN}^-$ ?

There is a table of acid ionization constants in Burge (Table 16.5) that may be of use in doing parts c and d of this problem.

a)  $pK_a = -\log_{10}(1.8 \times 10^{-5}) = 4.74$

b) For an acid/conjugate base pair,  $K_a K_b = 1.0 \times 10^{-14}$

$$K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

c)  $K_a(\text{HNO}_2) = 4.5 \times 10^{-4}$   
 $K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.5 \times 10^{-5}$   
 $K_a(\text{HCN}) = 4.9 \times 10^{-10}$

Based on the values for  $K_a$ ,  $\text{HNO}_2$  and  $\text{C}_6\text{H}_5\text{COOH}$  are stronger acids than  $\text{CH}_3\text{COOH}$ , and  $\text{HCN}$  is a weaker acid than  $\text{CH}_3\text{COOH}$ .

d) Since  $K_a K_b = 1.0 \times 10^{-14}$  for a weak acid/conjugate base pair, whichever weak acids that are stronger than acetic acid will have conjugate bases that are weaker bases than acetate ion. So  $\text{CN}^-$  is a stronger base than  $\text{CH}_3\text{COO}^-$ , and  $\text{NO}_2^-$  and  $\text{C}_6\text{H}_5\text{COO}^-$  are weaker bases than  $\text{CH}_3\text{COO}^-$ .

16) (16.10) Predict the relative acid strength of the following compounds:  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ .

For binary acids in the same column acid strength increases from top to bottom, so  $\text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$ .

17) Based on molecular structure arrange the binary compounds in order of increasing acid strength. Explain your reasoning.

a)  $\text{H}_2\text{Te}$ ,  $\text{HI}$ ,  $\text{H}_2\text{S}$

$\text{H}_2\text{Te} > \text{H}_2\text{S}$  (same group)

$\text{HI} > \text{H}_2\text{Te}$  (same row)

So  $\text{HI} > \text{H}_2\text{Te} > \text{H}_2\text{S}$

b)  $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HBrO}$

$\text{HClO} > \text{HBrO}$  (same group, same number of O)

$\text{HClO}_2 > \text{HClO}$  (same third nonmetal, more O in  $\text{HClO}_2$ )

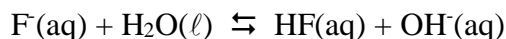
So  $\text{HClO}_2 > \text{HClO} > \text{HBrO}$

- 18) Determine whether each salt will form a solution that is acidic, basic, or neutral.
- a)  $C_2H_5NH_3NO_3$       strong acid + weak base salt, so acidic
  - b)  $K_2CO_3$               weak acid + strong base salt, so basic
  - c)  $RbI$                       strong acid + strong base salt, so neutral
  - d)  $NH_4ClO$               weak acid + weak base salt, so approximately neutral  
(might be slightly acidic or basic)

19 (16.96) Find the pH of a 0.082 M solution of NaF ( $K_a$  for HF is  $7.1 \times 10^{-4}$ ).



$F^-$  is the conjugate base of HF, a weak acid, so  $F^-$  is a weak base.  $Na^+$  has no acid/base properties.



$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

$K_a K_b = 1.0 \times 10^{-14}$  for an acid/conjugate base pair, so  $K_b$  for  $F^-$  is

$$K_b = \frac{1.0 \times 10^{-14}}{K_a} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-4}} = 1.41 \times 10^{-11}$$

	Initial	Change	Equilibrium
HF	0	x	x
$OH^-$	0	x	x
$F^-$	0.082	- x	0.082 - x

$$\frac{(x)(x)}{(0.082 - x)} = 1.41 \times 10^{-11}$$

Assume  $x \ll 0.082$  Then

$$\frac{x^2}{0.082} = 1.41 \times 10^{-11} \quad x^2 = (1.41 \times 10^{-11})(0.082) = 1.16 \times 10^{-12}$$

$$x = (1.16 \times 10^{-12})^{1/2} = 1.08 \times 10^{-6}$$

Since  $1.08 \times 10^{-6} \ll 0.082$ , our approximation was good.

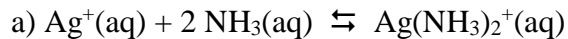
$$\text{So } [OH^-] = x = 1.08 \times 10^{-6} \quad pOH = -\log_{10}(1.08 \times 10^{-6}) = 5.97$$

$$pH = 14.00 - 5.97 = 8.03$$

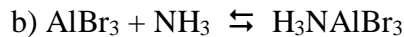


20) Identify the Lewis acid and Lewis base from among the reactants in each equation.

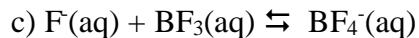
A Lewis acid is an electron pair acceptor, and a Lewis base is an electron pair donor.



$\text{Ag}^+$  is a Lewis acid,  $\text{NH}_3$  is a Lewis base ( $\text{Ag}^+$  is accepting electron pairs from the N atom in  $\text{NH}_3$ ).



$\text{AlBr}_3$  is a Lewis acid, and  $\text{NH}_3$  is a Lewis base (Al is accepting an electron pair from the N atom in  $\text{NH}_3$ ).



$\text{BF}_3$  is a Lewis acid, and  $\text{F}^-$  is a Lewis base (B is accepting an electron pair from the  $\text{F}^-$  anion).