

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⁺ ions when added to water. An Arrhenius base is a substance that produces OH⁻ ions when added to water.

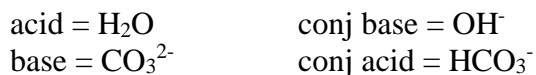
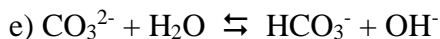
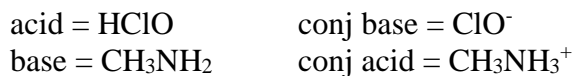
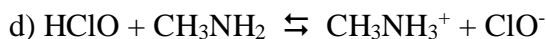
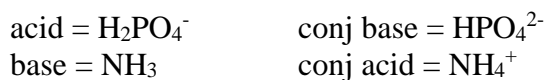
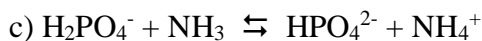
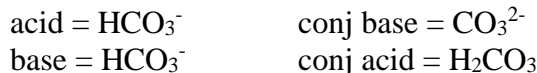
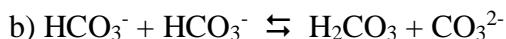
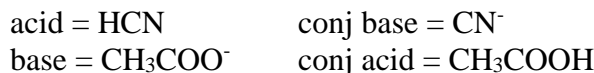
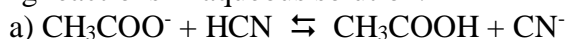
2) What is the Bronsted-Lowry definition of an acid? Of a base?

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.

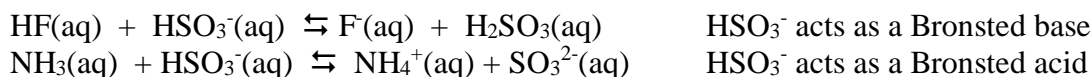


5) Identify each of the following species as a strong acid, weak acid, strong soluble base, insoluble base, or weak base.

- a) HCN (weak acid)
- b) Cu(OH)₂ (insoluble base)
- c) HNO₂ (weak acid)
- d) NaOH (strong soluble base)
- e) HClO₃ (strong acid)
- f) HClO (weak acid)
- g) NH₃ (weak base)

6) What is meant by the term amphoteric. Show by giving an appropriate set of reactions how the HSO₃⁻ 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 HSO₃⁻



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

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

8) The value for the autoionization constant for water at T = 40.0 °C is K_w = 2.92 x 10⁻¹⁴. What are the values for [H₃O⁺], [OH⁻], and pH for a neutral aqueous solution at this temperature?

The autoionization reaction is



	Initial	Change	Equilibrium
H ₃ O ⁺	0	x	x
OH ⁻	0	x	x

So $(x)(x) = x^2 = 2.92 \times 10^{-14}$ $x = (2.92 \times 10^{-14})^{1/2} = 1.71 \times 10^{-7}$

So for a neutral solution [H₃O⁺] = [OH⁻] = 1.71 x 10⁻⁷ M

$$\text{pH} = -\log_{10}(1.71 \times 10^{-7}) = 6.77$$

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

a) 2.8×10^{-4} M Ba(OH)₂.

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

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

b) 5.2×10^{-4} M HNO₃.

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

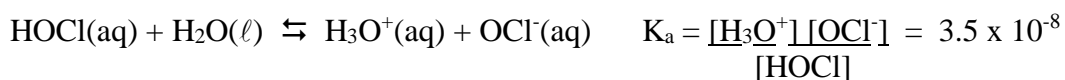
10) How many grams of NaOH would be needed to prepare 500.0 mL of a solution with pH = 12.50?

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

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

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

11) What are the pH and the percent dissociation for a 0.0800 M aqueous solution of hypochlorous acid (HOCl), a weak acid, at T = 25. °C. At this temperature the acid equilibrium constant is $K_a = 3.5 \times 10^{-8}$.



	Initial	Change	Equilibrium
H ₃ O ⁺	0	x	x
OCl ⁻	0	x	x
HOCl	0.0800	- x	0.0800 - x

So $\frac{(x)(x)}{(0.0800 - x)} = 3.5 \times 10^{-8}$ Assume $x \ll 0.0800$, then

$$\frac{x^2}{(0.0800)} = 3.5 \times 10^{-8}$$

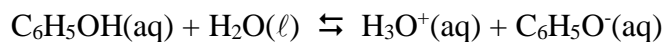
$$x^2 = (0.0800)(3.5 \times 10^{-8}) = 2.8 \times 10^{-9}$$

$$x = (2.8 \times 10^{-9})^{1/2} = 5.3 \times 10^{-5} \quad \text{pH} = -\log_{10}(5.3 \times 10^{-5}) = 4.28$$

The percent dissociation is

$$\% \text{ dissociation} = \frac{[\text{OCl}^-]_{\text{eq}}}{[\text{HOCl}]_{\text{initial}}} \times 100 \% = \frac{5.3 \times 10^{-5}}{0.0800} \times 100 \% = 0.07 \%$$

12) (16.52) Find the pH of an aqueous solution at 25. °C that is 0.34 M in phenol (C₆H₅OH, K_a = 1.3 × 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
H ₃ O	0	x	x
C ₆ H ₅ O ⁻	0	x	x
C ₆ H ₅ OH	0.34	-x	0.34 - x

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

Assume x << 0.34. Then

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

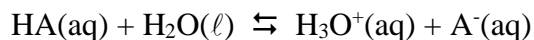
$$x = (4.42 \times 10^{-11})^{1/2} = 6.65 \times 10^{-6}$$

Since 6.65 × 10⁻⁶ << 0.34, our approximation was good. Therefore

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

13) The pH of an aqueous solution of an unknown monoprotic acid is pH = 5.20 at T = 25. °C. The concentration of the acid is 0.010 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 pH = 5.20, then at equilibrium [H₃O⁺] = 10^{-pH} = 10^{-5.20} = 6.31 × 10⁻⁶ M

$$\text{But } [A^-] = [H_3O^+] = 6.31 \times 10^{-6} \text{ M}$$

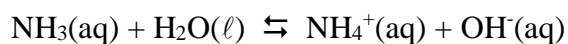
$$[HA] = 0.010 - 6.31 \times 10^{-6} = 0.010 \text{ M}$$

$$K_a = \frac{(6.31 \times 10^{-6})(6.31 \times 10^{-6})}{0.010} = 4.0 \times 10^{-9}$$

14) (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 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
NH_4^+	0	x	x
OH^-	0	x	x
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

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

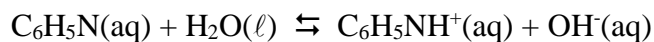
$$x = (1.8 \times 10^{-6})^{1/2} = 1.34 \times 10^{-3}$$

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
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

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

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

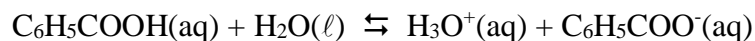
Since $9.22 \times 10^{-6} \ll 0.050$, our approximation was good.

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

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

15) 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
H_3O^+	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

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

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).

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

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

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

16) The acid dissociation constant for acetic acid (CH_3COOH) 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, CH_3COO^- ?
- Which of the following acids is a stronger acid than acetic acid: HNO_2 , $\text{C}_6\text{H}_5\text{COOH}$, HCN ?
- Which of the following anions is a stronger base than the acetate anion: NO_2^- , $\text{C}_6\text{H}_5\text{COO}^-$, 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.

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

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

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

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

Based on the values for K_a , HNO_2 and $\text{C}_6\text{H}_5\text{COOH}$ are stronger acids than CH_3COOH , and HCN is a weaker acid than CH_3COOH .

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 CN^- is a stronger base than CH_3COO^- , and NO_2^- and $\text{C}_6\text{H}_5\text{COO}^-$ are weaker bases than CH_3COO^- .

17) (16.10) Predict the relative acid strength of the following compounds: H₂O, H₂S, H₂Se.

For binary acids in the same column acid strength increases from top to bottom, so H₂Se > H₂S > H₂O.

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

a) H₂Te, HI, H₂S

H₂Te > H₂S (same group)

HI > H₂Te (same row)

So HI > H₂Te > H₂S

b) HClO, HClO₂, HBrO

HClO > HBrO (same group, same number of O)

HClO₂ > HClO (same third nonmetal, more O in HClO₂)

So HClO₂ > HClO > HBrO

19) Determine whether each salt will form a solution that is acidic, basic, or neutral.

a) C₂H₅NH₃NO₃ strong acid + weak base salt, so acidic

b) K₂CO₃ weak acid + strong base salt, so basic

c) RbI strong acid + strong base salt, so neutral

d) NH₄ClO weak acid + weak base salt, so approximately neutral (might be slightly acidic or basic)

20) (16.96) Find the pH of a 0.082 M solution of NaF (K_a for HF is 7.1 x 10⁻⁴).

NaF(s) → Na⁺(aq) + F⁻(aq)

Initial F⁻ concentration is 0.082 M

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

F⁻(aq) + H₂O(ℓ) ⇌ HF(aq) + OH⁻(aq)

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

K_a K_b = 1.0 x 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

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

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

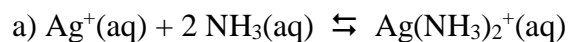
Since $1.08 \times 10^{-6} \ll 0.082$, our approximation was good.

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

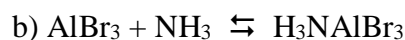
$$\text{pH} = 14.00 - 5.97 = 8.03$$

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

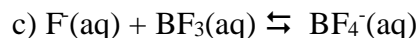
A Lewis acid is an electron pair acceptor, and a Lewis base is an electron pair donor.



Ag^+ is a Lewis acid, NH_3 is a Lewis base (Ag^+ is accepting electron pairs from the N atom in NH_3).



AlBr_3 is a Lewis acid, and NH_3 is a Lewis base (Al is accepting an electron pair from the N atom in NH_3).



BF_3 is a Lewis acid, and F^- is a Lewis base (B is accepting an electron pair from the F anion).