Chemistry 102 **ANSWER KEY**

REVIEW QUESTIONS
Chapter 16

1. For each reaction below, identify the Brønsted-Lowry acid and base and their conjugates:

A) $NH_4^+ (aq) + CN^- (aq) \rightleftharpoons HCN (aq) + NH_3 (aq)$

acid **base** **conj acid** **conj base**

B) $(CH_3)_3N (aq) + H_2O (l) \rightleftharpoons (CH_3)_3NH^+ (aq) + OH^- (aq)$

base **acid** **conj acid** **conj base**

C) $HCHO_2 (aq) + PO_4^{3-} (aq) \rightleftharpoons CH_2O^- (aq) + HPO_4^{2-} (aq)$

acid **base** **conj base** **conj acid**

2. Identify the Lewis acid and base in each of the following reactions:

A) $Fe(ClO_4)_3 (s) + 6\ H_2O (l) \rightleftharpoons Fe(H_2O)_6^{3+} (aq) + 3\ ClO_4^- (aq)$

Acid **Base**

B) $(CH_3)_3N (g) + BF_3 (g) \rightleftharpoons (CH_3)_3NBF_3 (s)$

Base **Acid**

C) $HIO (lq) + NH_2^- (lq) \rightleftharpoons NH_3 (l) + IO^- (lq)$

(lq denotes liquid ammonia as solvent)

Acid **Base**

3. For each of the following descriptive statements, provide an interpretation in terms of the Bronsted-Lowry, the Lewis theory, or both, as appropriate.

a) Hydrogen bromide, HBr, dissolves in water to form an acidic solution.

$$HBr + H_2O \longrightarrow H_3O^+ + Br^-$$

	HBr	H_2O
Bronsted-Lowry	**acid**	**base**
Lewis	**acid**	**base**

b) Sodium hydride, NaH, reacts with water to form a basic solution.

$$NaH + H_2O \longrightarrow NaOH + H_2$$

	NaH	H_2O
Lewis	**base**	**acid**

c) Sulfur dioxide, SO_2, dissolves in water to form an acidic solution.

$$SO_2\ (g) + H_2O\ (l) \rightleftharpoons H_2SO_3\ (aq)$$

	SO_2	H_2O
Lewis	**acid**	**base**

4. Complete the table below by calculating the missing entries and indicating whether each solution is acidic or basic:

$[H^+]$	**$[OH^-]$**	**pH**	**pOH**	**acidic or basic?**
$2.5\text{x}10^{-4}$ M	**$4.0\text{x}10^{-11}$ M**	**3.60**	**10.40**	**acidic**
$1.4\text{x}10^{-7}$ M	$6.9\text{x}10^{-8}$ M	**6.84**	**7.16**	**acidic**
$6.3\text{x}10^{-4}$ M	**$1.6\text{x}10^{-11}$ M**	3.20	**10.80**	**acidic**
$5.6\text{x}10^{-9}$ M	**$1.8\text{x}10^{-6}$ M**	**8.25**	5.75	**basic**

5. For each pair shown below, choose the stronger base:

   a) **F^-** or Cl^-

      HF is a weaker acid than HCl. Therefore, its conjugate base (F^-) is a stronger base than Cl^-.

   b) Cl^- or **H_2O**

      The conjugate acid of water (H_3O^+) is a weaker acid than HCl. Therefore, water is a stronger base than Cl^-.

   c) ClO_4^- or **ClO_2^-**

      $HClO_2$ is weaker acid than $HClO_4$. Therefore, its conjugate base (ClO_2^-) is a stronger base than ClO_4^-.

6. Calculate the $[H^+]$ and $[OH^-]$ for each of the following strong acid or base solution:

   a) 1.8×10^{-4} M HBr

      $[H^+] = [HBr] = 1.8 \times 10^{-4}$ M $\qquad [OH^-] = \frac{K_w}{[H^+]} = \frac{1.0\times10^{-14}}{1.8\times10^{-4}} = 5.6\times10^{-11}$ M

   b) 0.0895 M $HClO_4$

      $[H^+] = [HClO_4] = 0.0895$ M $\qquad [OH^-] = \frac{K_w}{[H^+]} = \frac{1.0\times10^{-14}}{0.0895} =$ M

   c) 3.2×10^{-3} M KOH

      $[OH^-] = [KOH] = 3.2 \times 10^{-3}$ M $\qquad [H^+] = \frac{K_w}{[OH^-]} = \frac{1.0\times10^{-14}}{3.2\times10^{-3}} = 3.1\times10^{-12}$ M

   d) 0.0075 M $Ca(OH)_2$

      $[OH^-] = 2 \times [Ca(OH)_2] = 1.5 \times 10^{-2}$ $\qquad [H^+] = \frac{K_w}{[OH^-]} = \frac{1.0\times10^{-14}}{1.5\times10^{-2}} = 6.7\times10^{-13}$ M

7. People often take milk of magnesia to reduce the discomfort associated with acid stomach or heartburn. The recommended dose is 1 teaspoon, which contains 400 mg of $Mg(OH)_2$. What volume of HCl solution with a pH of 1.3 can be neutralized by one dose of milk of magnesia? (Calculate answer to 2 sig figs).

$$\mathbf{2\ HCl + Mg(OH)_2 \rightarrow MgCl_2 + 2\ H_2O}$$

$$\mathbf{[HCl] = [H_3O^+] = 10^{-1.3} = 0.050\ M}$$

$$\mathbf{400\ mg\ Mg(OH)_2 \times \frac{1\ g}{10^3\ mg} \times \frac{1\ mol}{58.32\ g} \times \frac{2\ mol\ HCl}{1\ mol\ Mg(OH)_2} \times \frac{1\ L}{0.050\ mol\ HCl} \times \frac{10^3\ mL}{1\ L} = 270\ mL\ HCl}$$

8. Calculate the $[H_3O^+]$ and $[OH^-]$ for solutions with the following pH values:

a) 2.63

$$\mathbf{[H_3O^+] = 10^{-2.63} = 2.3x10^{-3}\ M}$$

$$\mathbf{[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0x10^{-14}}{2.3x10^{-3}} = 4.3x10^{-12}\ M}$$

b) 14.25

$$\mathbf{[H_3O^+] = 10^{-14.25} = 5.6x10^{-15}\ M}$$

$$\mathbf{[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0x10^{-14}}{5.6x10^{-15}} = 1.8\ M}$$

9. Using values of K_a in your textbook, arrange the following acids in order of **(a)** increasing acid strength, and **(b)** decreasing percent ionization:

	C_6H_5OH	HNO_2	CH_3CO_2H	HOCl
K_a	**$1.3x10^{-10}$**	**$4.6x10^{-4}$**	**$1.8x10^{-5}$**	**$2.9x10^{-8}$**

a) The larger K_a value, the stronger the acid. Therefore,

$$\mathbf{C_6H_5OH < HOCl < CH_3CH_2OH < HNO_2}$$

b) The larger K_a value, the greater the ionization. Therefore,

$$\mathbf{HNO_2 > CH_3CH_2OH > HOCl > C_6H_5OH}$$

10. A 0.10 M solution of lactic acid ($HC_3H_5O_3$) has a pH of 2.44. Calculate K_a for lactic acid.

$$[H^+] = 10^{-2.44} = 3.6x10^{-3}\ M$$
$$[C_3H_5O_3^-]=[H^+]= 3.6x10^{-3}\ M$$
$$[HC_3H_5O_3]= 0.10 - (3.6x10^{-3}) \approx 0.10$$
$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = \frac{(3.6x10^{-3})^2}{0.10} = 1.3x10^{-4}$$

11. A 0.200 M solution of a weak acid HX is 9.4% ionized. Calculate the pH and K_a for this acid.

$$[H^+] = [A^-] = 0.200 \text{ x } 0.094 = 0.019\ M$$
$$pH = -\log(0.019) = 1.72$$
$$[HA]= 0.200 - 0.019 = 0.181$$
$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(0.019)^2}{0.181} = 2.0x10^{-3}$$

12. Calculate the pH of a 0.050 M solution of ethylamine ($C_2H_5NH_2$, K_b= 6.4 $x10^{-4}$).

$$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$$

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{x^2}{0.050 - \cancel{x}} = 6.4x10^{-4}$$
$$x = [OH^-] = \sqrt{(0.050)(6.4x10^{-4})} = 5.7x10^{-3}\ M$$
$$pOH = -\log(5.7x10^{-3}) = 2.24$$
$$pH = 14.00 - 2.24 = 11.76$$

13. The K_a for hydrocyanic acid, HCN, is 5.0 $x10^{-10}$. What is the K_b for CN^-?

$$K_b = \frac{K_w}{K_a} = \frac{1.0x10^{-14}}{5.0x10^{-10}} = 2.0x10^{-5}$$

14. Hydrosulfuric acid is a polyprotic acid with the following equilibria:

$$H_2S\,(aq) \rightleftharpoons H^+\,(aq) + HS^-\,(aq) \qquad Ka_1 = 1.1 \times 10^{-7}$$
$$HS^-\,(aq) \rightleftharpoons H^+\,(aq) + S^{2-}\,(aq) \qquad Ka_2 = 1.2 \times 10^{-13}$$

a) Calculate the pH of a 0.100 M H_2S solution.

$$\mathbf{K_{a1} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.100 - \cancel{x}} = 1.1x10^{-7}}$$

$$\mathbf{x = [H^+]=[HS^-] = \sqrt{(0.100)(1.1x10^{-7})} = 1.0x10^{-4}\ M}$$

$$\mathbf{pH = -log\,(1.0x10^{-4}) = 4.00}$$

b) Calculate the $[S^{2-}]$ for the solution above.

$$\mathbf{K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.0x10^{-4} + \cancel{y})(y)}{(1.0x10^{-4}) - \cancel{y}} = 1.2x10^{-13}}$$

$$\mathbf{y = [S^{2-}] = 1.2x10^{-13}\ M}$$

15. Sodium benzoate, $C_6H_5CO_2Na$, is the salt of the weak acid, benzoic acid ($C_6H_5CO_2H$). A 0.10 M solution of sodium benzoate has a pH of 8.60 at room temperature.

a) Calculate the K_b value for benzoate ion ($C_6H_5CO_2^-$).

$$\mathbf{C_6H_5CO_2^- + H_2O \rightleftharpoons C_6H_5CO_2H + OH^-}$$

$$\mathbf{pOH = 14.00 - 8.60 = 5.40}$$

$$\mathbf{[OH^-] = [C_6H_5CO_2^-] = 10^{-5.40} = 4.0x10^{-6}}$$

$$\mathbf{[C_6H_5CO_2H] = 0.10 - (4.0x10^{-6}) \approx 0.10}$$

$$\mathbf{K_b = \frac{[C_6H_5CO_2H][OH^-]}{[C_6H_5CO_2^-]} = \frac{(4.0x10^{-6})^2}{0.10} = 1.6x10^{-10}}$$

b) Calculate the K_a value for benzoic acid.

$$\mathbf{K_a = \frac{K_w}{K_b} = \frac{1.0x10^{-14}}{1.6x10^{-10}} = 6.3x10^{-5}}$$

16. Potassium sorbate ($KC_6H_7O_2$) is the salt of the weak acid, sorbic acid ($HC_6H_7O_2$) with Ka = 1.7×10^{-5}), and is commonly added to cheese to prevent mold. What is the pH of a solution containing 4.93 g of potassium sorbate in 500 mL of solution?

$$\mathbf{4.93\ \cancel{g}\ x\ \frac{1\ mol}{150.1\ \cancel{g}}\ x\ \frac{1}{0.500\ L} = 0.0657\ M}$$

$$\mathbf{C_6H_7O_2^- + H_2O \rightleftharpoons HC_6H_7O_2 + OH^-}$$

$$\mathbf{K_b = \frac{K_w}{K_a} = \frac{1.0x10^{-14}}{1.7x10^{-5}} = 5.9x10^{-10}}$$

$$\mathbf{K_b = \frac{[HC_6H_7O_2][OH^-]}{[C_6H_7O_2^-]} = \frac{x^2}{0.0657 - x} = 5.9x10^{-10}}$$

$$\mathbf{x = [OH^-] = \sqrt{(0.0657)(5.9x10^{-10})} = 6.2x10^{-6}\ M}$$

$$\mathbf{pOH = -log(6.2x10^{-6}) = 5.21 \qquad pH = 14.00 - 5.21 = 8.79}$$

17. Calculate the pH of solutions prepared by:

a) Diluting 75 mL of 0.10 M $HClO_4$ to a volume of 350 mL.

$$\mathbf{[H^+]=[HClO_4] = \frac{(0.10\ M)(75\ mL)}{350\ mL} = 2.\underline{1}4x10^{-2} M}$$

$$\mathbf{pH = -log\ (2.\underline{1}4x10^{-2}) = 1.67}$$

b) Dissolving 4.8 g of $Ca(OH)_2$ in 250 mL of solution.

$$\mathbf{[OH^-]= 2x[Ca(OH)_2]= 2(\frac{4.8\ g}{74.10 g/mol}\ x\ \frac{1}{0.250\ L}) = 0.5\underline{1}8\ M}$$

$$\mathbf{pOH = -log\ 0.5\underline{1}8 = 0.29}$$

$$\mathbf{pH = 14.00 - 0.29 = 13.71}$$

c) Dissolving 3.25 g of NH_4Cl in 125 mL of solution.

$$\mathbf{NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3}$$

$$\mathbf{[NH_4^+]=[NH_4Cl]= 3.25\ g\ x\ \frac{1\ mol}{53.50\ g}\ x\ \frac{1}{0.125\ L} = 0.486\ M}$$

$$\mathbf{K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{0.486 - \cancel{x}} = 5.6x10^{-10}}$$

$$\mathbf{x = [H_3O^+] = \sqrt{(0.486)(5.6x10^{-10})} = 1.\underline{6}5x10^{-5}\ M}$$

$$\mathbf{pH = -log\ (1.\underline{6}5x10^{-5}) = 4.78}$$

18. For each pair, determine which is the stronger acid, and provide a brief explanation for your choice.

a) **H_2SO_4** and H_2SeO_4

H_2SO_4 since sulfur is more electronegative than selenium causing the O—H bond to become more polar.

b) CH_3CO_2H and **CCl_3CO_2H**

The more electronegative Cl atoms in CCl_3CO_2H cause the O—H bond to become more polar and trichloroacetic acid to have greater acidity.

c) HPO_4^{2-} and **$H_2PO_4^-$**

Acidic hydrogens are easier lost from a less negatively charged species, therefore $H_2PO_4^-$ is more acidic.

19. Arrange the solutions below in order of increasing basicity (assume concentrations to be the same):

CH_3NH_3Br KOH KBr KCN $C_5H_5NHNO_2$

CH_3NH_3Br < $C_5H_5NHNO_2$ < KBr < KCN < KOH
least basic **most basic**

CH_3NH_3Br (cation is weakly acidic; anion is pH neutral)

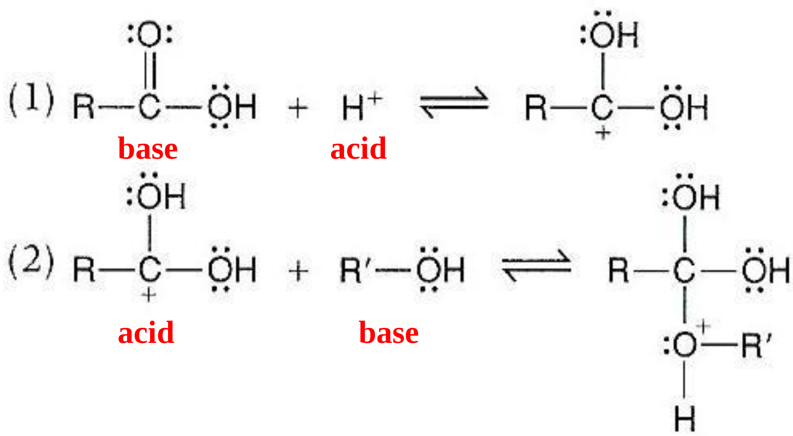
$C_5H_5NHNO_2$ (cation is weakly acidic; anion is weakly basic)

KBr (both cation and anion are pH neutral)

KCN (cation is pH neutral; anion is weakly basic)

KOH (strong base)

20. Esters, RCOOR’, are important organic compounds that are active ingredients in the odors of fruits, and have important uses in the food and cosmetics industries. Shown below are the first two steps in the mechanism for synthesis of these compounds. Identify the Lewis acids and bases in these two steps:



21. For each list below, rank in order of decreasing acid strength (highest to lowest):

a) $CCl_3CH_2O–H$ $CH_2ClCH_2O–H$ $CHCl_2CH_2O–H$

CCl_3CH_2OH > $CHCl_2CH_2OH$ > CH_2ClCH_2OH

(the increasing number of electronegative groups on the neighboring carbon atom makes the acidic bond more polar through inductive effect, and the acid stronger)

b) $CH_3CH_2CH_2COOH$ $CH_3CH_2\underset{|\atop Cl}{C}HCOOH$

$ClCH_2CH_2CH_2COOH$ $CH_3\underset{|\atop Cl}{C}HCH_2COOH$

$CH_3CH_2CHClCOOH$ > $CH_3CHClCH_2COOH$ > $ClCH_2CH_2CH_2COOH$ > $CH_3CH_2CH_2COOH$

(the closer the electronegative Cl atom to the acidic bond, the more polar the bond, and the stronger the acid)

c) CH_3CH_2OH $CH_3CH_2NH_2$ CH_3CH_2SH $CH_3CH_2CH_3$

CH_3CH_2OH > $CH_3CH_2NH_2$ > CH_3CH_2SH > $CH_3CH_2CH_3$

(the more electronegative the atom forming the acidic bond, the more polar the bond and the stronger the acid)

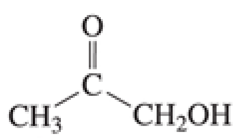
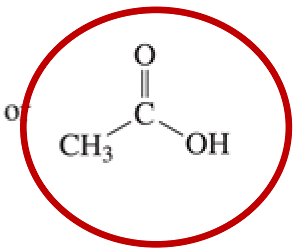
22. In each pair shown below, determine which is the stronger base:

a) **CH_3O^-** or CH_3S^-
(the larger S atom stabilizes the anion, making it a weaker base)

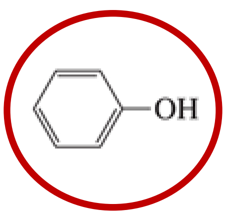
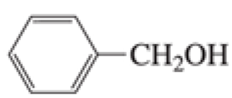
b) **Br^-** or I^- –
(the larger I atom stabilizes the anion, making it a weaker base)

c) **$ClCH_2CH_2O^-$** or $Cl_2CHCH_2O^-$
(the extra Cl atom stabilizes the anion by inductive effect, making it a weaker base)

23. For each pair shown below, determine which is the stronger acid:

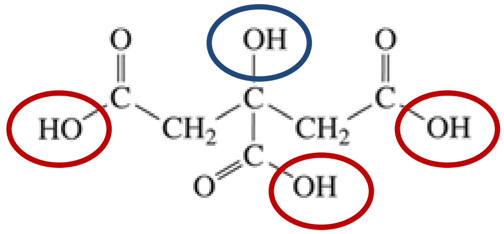
a)  or 

The anion of acetic acid ($CH_3CO_2^-$) is stabilized through resonance with the neighboring C=O group, making it a stronger acid.

b)  or 

The anion of phenol is stabilized through resonance with the neighboring pi bonds in the ring, making it a stronger acid.

24. Citrus fruits are rich in citric acid, a compound with four acidic hydrogens:



a) Identify the acidic hydrogen in this molecule. Which is the weakest? Why?

The acidic hydrogens are circled in the structure above.

The H indicated by the blue circle is the weakest acid since its anion is not stabilized by any resonance structures, contrary to the other 3 hydrogens indicated by the red circles.

b) Explain why the pK_a for the COOH group in the center of the molecule is lower than the pK_a of acetic acid.

The p*K*a of the COOH group in the center of the molecule is lower than the p*K*a of acetic acid because of a neighboring oxygen-containing group that withdraws electrons inductively and thereby stabilizes the conjugate base.

25. Using the information given, determine if reactants or products are favored in each equilibrium below:

a) $CH_3CO_2H + NH_3 \rightleftharpoons CH_3O^- + NH_4^+$

$pK_a = 4.8$ $\qquad\qquad\qquad$ $pK_a = 9.4$

Products are favored. The lower pKa for the acid on the reactant side indicates that it is a stronger acid. Reactions favor the weaker acid and base.

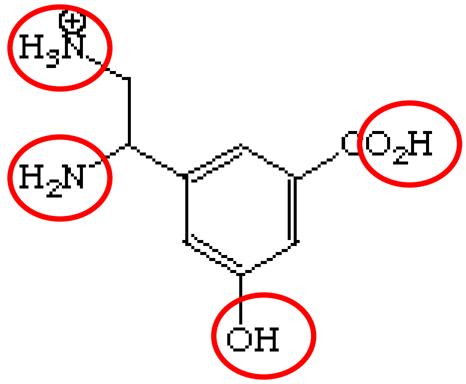
b) $CH_3CH_2OH + CH_3NH_2 \rightleftharpoons CH_3O^- + CH_3NH_3^+$

$pK_a = 15.9$ $\qquad\qquad\qquad$ $pK_a = 10.7$

Reactants are favored. The lower pKa for the acid on the product side indicates that it is a stronger acid. Reactions favor the weaker acid and base.

26. Identify the highest and lowest pK_a values for the hydrogens circled below:

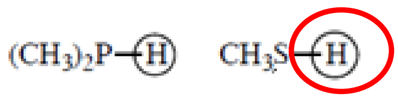
highest pK_a (most basic)



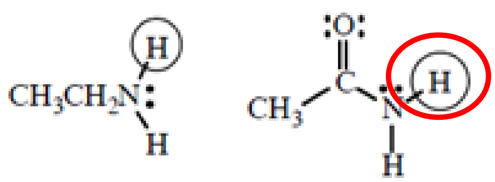
lowest pK_a (strongest acid)

27. Identify the more acidic hydrogen in each pair shown below:

(a)



(b)



(c)