SF INSTRUCTOR: EMAIL ADDRESS:

CHM 2046 ANSWER KEY 2



OFFICE: K-223 PHONE: 395-5303

REVIEW QUESTIONS ABOUT ACIDS AND BASES

DON SWIETER

don.swieter@sfcollege.edu

- A Brønsted-Lowry acid is defined as a proton (H⁺) donor. A Brønsted-Lowry base is defined as a proton (H⁺) acceptor.
- 2. In order to function as a proton (H^+) donor the species must have at least one H in the formula.
- 3. In order to function as a proton (H⁺) acceptor the species must have at least one unshared pair of electrons to bond to the incoming proton (H⁺).
- 4. The products are the conjugate acid (of the reactant base) and the conjugate base (of the reactant acid). The conjugate acid is defined as the acid created when a reactant base accepts one H⁺. The conjugate base is defined as the base created when a reactant acid donates one H⁺.
- 5. a. H_3O^+ b. H_2O c. NH_4^+ d. HX e. H_2X^+ 6. a. OH^- b. O^{-2} c. NH_2^- d. X^- e. H_2O
- 7. In terms of their reaction with water, a strong acid is defined as any acid that reacts with water to form H_3O^+ and the conjugate base to a **large extent**. A weak acid is then defined as any acid that reacts with water to form H_3O^+ and the conjugate base to a **small extent**.
- 8. Reaction of a strong acid and water: $HX + H_2O \longrightarrow H_3O^+ + X^-$ Reaction of a weak acid and water: $HX + H_2O \longrightarrow H_3O^+ + X^-$

There is no difference between the **equation** for a strong acid reacting with water and the **equation** for a weak acid reacting with water. The only difference between a strong and a weak acid is the extent of reaction (see problem 7).

- 9. The six common strong acids are: HCl, HBr, HI, HNO₃, H₂SO₄, and HClO₄. The other acids are classified as weak acids.
- 10. The inventory of 1 M HCl is $[H_3O^+] = 1$ M and $[Cl^-] = 1$ M.

The inventory of a 1 M solution of any strong acid, HX, is $[H_3O^+] = 1$ M and $[X^-] = 1$ M.

The inventory of a 1 M solution of any weak acid, HY, is [HY] = 1 M.

11. Liquid HCl does not conduct because HCl is a molecule and therefore without being involved in some kind of ionization process (like an acid/base reaction) the liquid HCl contains no ions to support conductivity. When the HCl was added to the water to form the 1 M HCl solution a chemical reaction occurred to a large extent to form H_3O^+ and Cl^- . Thus, the solution contains many ions to support conductivity.

- 12. Although HCl and $HC_2H_3O_2$ both react as acids with water and the initial amount of HCl and $HC_2H_3O_2$ were the same, the resulting solutions are very different. As mentioned above, HCl reacts with water to a large extent to form H_3O^+ and Cl^- ions and thus the resulting solution contains many ions to support conductivity. On the other hand, $HC_2H_3O_2$ reacts with water to form H_3O^+ and $C_2H_3O_2^-$ ions to only a small extent and therefore the resulting solution contains only a relatively small number of ions to support conductivity. Therefore, 1 M HCl is a good conductor of electricity and 1 M $HC_2H_3O_2$ is a poor conductor of electricity.
- 13. As mobile ions are necessary for a solution to conduct electricity, it follows that more ions will enable a solution to conduct electricity better. Thus, if the solution of HZ conducts better than the solution of HY, it follows that the HZ solution contains more ions than the HY solution. Therefore the acid HZ must have reacted more with the water to produce ions (H_3O^+ and Z^-) than the acid HY reacted to produce ions (H_3O^+ and Y^-). Thus, acid HZ must be a **stronger** acid than HY.
- 14. In terms of their reaction with water, a strong base is defined as any base that reacts with water to form OH⁻ and the conjugate acid to a **large extent**. A weak base is then defined as any base that reacts with water to form OH⁻ and the conjugate acid to a **small extent**.
- 15. Reaction of a strong base and water: $B + H_2O \longrightarrow HB^+ + OH^-$ Reaction of a weak acid and water: $B + H_2O \longrightarrow HB^+ + OH^-$

There is no difference between the **equation** for a strong base reacting with water and the **equation** for a weak base reacting with water. The only difference between a strong and a weak base is the extent of reaction.

- 16. The ten common strong bases are: N^{-3} , P^{-3} , As^{-3} , O^{-2} , S^{-2} , Se^{-2} , Te^{-2} , H^{-} , NH_{2}^{-} , and NH^{-2} . The other bases are classified as weak bases.
- 17. The inventory of 1 M Na₂O is $[Na^+] = 2$ M and $[OH^-] = 2$ M.

Recall that the O^{-2} ion is a strong base and therefore reacts with water to form its conjugate acid (OH^{-}) and the conjugate base of water $(OH^{-})!$

The inventory of a 1 M solution of any strong base, B, is $[HB^+] = 1M$ and $[OH^-] = 1 M$.

The inventory of a 1 M solution of any weak base, B, is [B] = 1 M.

18. Liquid NH₃ does not conduct because NH₃ is a molecule and therefore without being involved in some kind of ionization process (like an acid/base reaction) the liquid NH₃ contains no ions to support conductivity.

When the NH_3 was added to the water to form the 1 M NH_3 solution a chemical reaction occurred to a small extent to form NH_4^+ and OH^- . Thus, the solution contains a few ions to support some conductivity.

19. The conductivity of solutions of molecular acids and molecular bases is due to these materials reacting with the water solvent to create ions. The stronger the acid (or base), the more conductive the resulting solution will be. Therefore the degree of conductivity gives a measure of the strength of the acid (or base). However, for **ionic** acids (or bases) the solutions will always be highly conductive since the solutions will **always** contain many ions regardless of strength (after all, the solutes are ionic). Therefore, conductivity is **useless** in assessing the acid (or base) strengths of ionic acids (or bases).

- 20. As discussed in problem 13 above, mobile ions are necessary for a solution to conduct electricity. More ions will enable a solution to conduct electricity better. Thus, if the solution of Z conducts better than the solution of Y, it follows that the Z solution contains more ions than the Y solution. Therefore the base Z must have reacted more with the water to produce ions (HZ⁺ and OH⁻) than the base Y reacted to produce ions (HY⁺ and OH⁻). Thus, base Z must be a **stronger** base than Y.
- 21. A. Reaction (i): $HR + H_2O \longrightarrow H_3O^+ + R^-$ Small Extent Reaction (ii): $HR + G^- \longrightarrow HG + R^-$ Large Extent Reaction (iii): $HY + H_2O \longrightarrow H_3O^+ + Y^-$ Large Extent B. Reaction (i): $H_3O^+ > HR$ Reaction (ii): HR > HGReaction (ii): $HY > H_3O^+$ C. Reaction (i): $R^- > H_2O$ Reaction (i): $G^- > R^-$ Reaction (ii): $H_2O > Y^-$ D. <u>Acids</u> <u>Bases</u> Stronger $\frac{Acids}{LHY} = \frac{Bases}{Y^-}$ Weaker

Stronger
$$\begin{vmatrix} ACIdS & Bases \\ HY & Y^- \\ H_3O^+ & H_2O \\ HR & R^- \\ HG & G^- \\ \end{vmatrix}$$
 Weaker $HG & G^- \\ \downarrow$ Stronger

E. The reaction involved is:

Reaction (iv): HB + $R^- \longrightarrow HR + B^-$ Small Extent

Since the solution is deep red then there must be a lot of R^- present and therefore the reaction only went to a small extent. Thus, $B^- > R^-$ as bases and HR > HB as acids. This arrangement places HB below HR on the table. It is unclear whether it is stronger or weaker than HG. To decide on the relative strength of HB and HG as acids (also B^- and G^- as bases) ONE of the two following reactions must be performed and the extent of reaction determined.

Reaction (va): HB + $G^- \longrightarrow HG + B^-$ Extent ? OR Reaction (vb): HG + $B^- \longrightarrow HB + G^-$ Extent ?

QUESTIONS ON EQUATION WRITING

22. a. Inventory of 0.1 M HCl: $[H_3O^+] = 0.1 \text{ M}$, $[Cl^-] = 0.1 \text{ M}$. Inventory of 0.1 M KOH: $[K^+] = 0.1 \text{ M}$, $[OH^-] = 0.1 \text{ M}$. Reaction: H_3O^+ (aq) + OH⁻ (aq) \longrightarrow 2 $H_2O(\ell)$ Large Extent b. Inventory of 0.1 M HNO₃: $[H_3O^+] = 0.1 \text{ M}$, $[NO_3^-] = 0.1 \text{ M}$. Inventory of 0.1 M NH₃: $[NH_3] = 0.1 \text{ M}$. Reaction: H_3O^+ (aq) + NH₃ (aq) \longrightarrow $H_2O(\ell)$ + NH₄⁺ (aq) Large Extent

- c. Inventory of 0.1 M H₂SO₄ : $[H_3O^+] = 0.1$ M, $[HSO_4^-] = 0.1$ M. Inventory of 0.1 M NaC₂H₃O₂ : $[Na^+] = 0.1 \text{ M}, [C_2H_3O_2^-] = 0.1 \text{ M}.$ Reaction: $H_3O^+(aq) + C_2H_3O_2^-(aq) \longrightarrow H_2O(\ell) + HC_2H_3O_2(aq)$ Large Extent d. Inventory of 0.1 M NaHSO₄ : $[Na^+] = 0.1 \text{ M}$, $[HSO_4^-] = 0.1 \text{ M}$. Inventory of 0.1 M NaC₂H₃O₂ : $[Na^+] = 0.1 \text{ M}, [C_2H_3O_2^-] = 0.1 \text{ M}.$ Reaction: $HSO_4^-(aq) + C_2H_3O_2^-(aq) \longrightarrow SO_4^{-2}(aq) + HC_2H_3O_2(aq)$ Large Extent e. Inventory of 0.1 M NH₄Cl: $[NH_4^+] = 0.1 \text{ M}, [Cl^-] = 0.1 \text{ M}.$ Inventory of 0.1 M NaOH: $[Na^+] = 0.1 \text{ M}$, $[OH^-] = 0.1 \text{ M}$. Reaction: $NH_4^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) + NH_3(aq)$ Large Extent f. Inventory of 0.1 M NaHCO₃ : $[Na^+] = 0.1 \text{ M}$, $[HCO_3^-] = 0.1 \text{ M}$. Inventory of 0.1 M KOH: $[Li^+] = 0.1 \text{ M}$, $[OH^-] = 0.1 \text{ M}$. Reaction: $HCO_3^{-}(aq) + OH^{-}(aq) \longrightarrow H_2O(\ell) + CO_3^{-2}(aq)$ Large Extent g. Inventory of 0.1 M HC₂H₃O₂ : $[HC_2H_3O_2] = 0.1$ M. Inventory of 0.1 M NaC₂H₃O₂ : $[Na^+] = 0.1 \text{ M}$, $[C_2H_3O_2^-] = 0.1 \text{ M}$. Reaction: $HC_2H_3O_2(aq) + C_2H_3O_2(aq) \longrightarrow C_2H_3O_2(aq) + HC_2H_3O_2(aq)$
 - **NOTE:** This reaction is between the strongest acid and the strongest base present in appreciable amount but as the reactants and products are the same, the reaction goes nowhere!
- h. Inventory of 0.1 M HC₂H₃O₂ : $[HC_2H_3O_2] = 0.1$ M. Inventory of 0.1 M MgSO₄ : $[Mg(H_2O)_6^{+2}] = 0.1$ M, $[SO_4^{-2}] = 0.1$ M. Reaction: $HC_2H_3O_2$ (aq) + SO_4^{-2} (aq) $\longrightarrow C_2H_3O_2^{-1}$ (aq) + HSO_4^{-1} (aq) Small Extent
- i. Inventory of 0.1 M HC₂H₃O₂ : [HC₂H₃O₂] = 0.1 M. Reaction: HC₂H₃O₂ (aq) + H₂O (ℓ) \longrightarrow C₂H₃O₂⁻ (aq) + H₃O⁺ (aq) Small Extent

QUESTIONS ABOUT THE AUTO-IONIZATION OF WATER

23. $2 \text{ H}_2 \text{O} (\ell) \implies \text{H}_3 \text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq})$

This equilibrium is present in ANY solution that contains H_2O .

- 24. $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$
- 25. Using the equilibrium presented in problem 23 above, $2 H_2O(\ell) \equiv H_3O^+(aq) + OH^-(aq)$ and letting x represent the amount of H_3O^+ and OH^- generated by the equilibrium the equilibrium constant expression becomes,

 $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} = x^2$

Solving for x gives, $\mathbf{x} = [H_3O^+] = [OH^-] = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$

- 26. If an acid is added to water the $[H_3O^+]$ will increase. The equilibrium will shift towards the water side in order to reduce the $[H_3O^+]$. This shift will reduce the $[H_3O^+]$ but not to the original value so that the overall $[H_3O^+]$ will be greater than 1.0×10^{-7} M. However, the shift will also reduce the $[OH^-]$ and therefore it will become less than 1.0×10^{-7} M.
- 27. If a base is added to water the $[OH^-]$ will increase. The equilibrium will shift towards the water side in order to reduce the $[OH^-]$. This shift will reduce the $[OH^-]$ but not to the original value so that the overall $[OH^-]$ will be greater than 1.0×10^{-7} M. However, the shift will also reduce the $[H_3O^+]$ and therefore it will become less than 1.0×10^{-7} M.

28. a) HCl + H₂O \longrightarrow H₃O⁺ + Cl⁻

b) Yes, although the above reaction takes place measurably to 100 %, there is still the equilibrium which is present in any water containing system.

c)
$$2 H_2O(\ell) \equiv H_3O^+(aq) + OH^-(aq).$$

- d) The added HCl will cause the $[H_3O^+]$ to increase which will shift the equilibrium in part c) towards the left. Therefore the contribution of H_3O^+ from the water in this solution must be less than it is in pure water. Thus the H_3O^+ contributed by the equilibrium must be less than 1.0×10^{-7} M which in this case is negligible in comparison to the H_3O^+ contributed by the reaction of HCl with water which is 0.10 M.
- e) $[H_3O^+] = 0.10 \text{ M}$ (the only significant source is the HCl) $\therefore pH = 1.00$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} = (0.10) \times [OH^-]$$

Solving for [OH⁻] gives [OH⁻] = $\frac{1.0 \times 10^{-14}}{0.10}$ = 1.0×10^{-13}

29. a) NaOH \longrightarrow Na⁺ + OH⁻

- b) Yes, although the above reaction takes place measurably to 100 %, there is still the equilibrium which is present in any water containing system.
- c) $2 H_2O(\ell) \iff H_3O^+(aq) + OH^-(aq).$
- d) The added NaOH will cause the $[OH^-]$ to increase which will shift the equilibrium in part c) towards the left. Therefore the contribution of OH^- from the water in this solution must be less than it is in pure water. Thus the OH^- contributed by the equilibrium must be less than 1.0×10^{-7} M which in this case is negligible in comparison to the OH^- contributed by the dissolution of NaOH with water which is 0.10 M.
- e) $[OH^{-}] = 0.10 \text{ M}$ (the only significant source is the NaOH)

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} = [H_3O^+] \times (0.10)$$

Solving for $[H_3O^+]$ gives $[H_3O^+] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}$ \therefore pH = 13.00

- 30. a) HBr + $H_2O \longrightarrow H_3O^+ + Br^$
 - b) Yes, although the above reaction takes place measurably to 100 %, there is still the equilibrium which is present in any water containing system.

c)
$$2 H_2 O(\ell) \equiv H_3 O^+(aq) + OH^-(aq).$$

d) The added HBr will cause the $[H_3O^+]$ to increase which will shift the equilibrium in part c) towards the left. Therefore the contribution of H_3O^+ from the water in this solution must be less than it is in pure water. Thus the H_3O^+ contributed by the equilibrium must be less than 1.0×10^{-7} M which in this case is **NOT** negligible in comparison to the H_3O^+ contributed by the reaction of HBr with water which is 5.0×10^{-8} M.

e)
$$2 H_2O(\ell) \longrightarrow H_3O^+(aq) + OH^-(aq).$$

Start $5.0 \times 10^{-8} M = 0 M$
Change $x = x$
Equil. $5.0 \times 10^{-8} M + x = x$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} = (5.0 \times 10^{-8} + x) \cdot (x) = 5.0 \times 10^{-8}x + x^2$$

Rearranging gives

$$x^{2} + 5.0 \times 10^{-8}x - 1.0 \times 10^{-14} = 0$$

Solving for [OH⁻] gives

$$\begin{bmatrix} OH^{-} \end{bmatrix} = \mathbf{x} = \frac{-5.0 \times 10^{-8} + \sqrt{(5.0 \times 10^{-8})^2 + 4.0 \times 10^{-14}}}{2} = 7.8 \times 10^{-8}$$

$$\therefore \quad \begin{bmatrix} H_3O^{+} \end{bmatrix} = 5.0 \times 10^{-8} + 7.8 \times 10^{-8} = 12.8 \times 10^{-8} = 1.3 \times 10^{-7} \quad \therefore \quad pH = 6.89$$

32. a) $[H_3O^+]$ from water is negligible so the final $[H_3O^+]$ is equal to 1.0 M

- b) $[H_3O^+]$ from water is negligible so the final $[H_3O^+]$ is equal to 2.0×10^{-4} M
- c) $[H_3O^+]$ from water is **NOT** negligible so the quadratic must be solved which yields a final $[H_3O^+]$ equal to $1.1_6 \times 10^{-7}$ M
- d) $[OH^{-}]$ from water is negligible so the final $[OH^{-}]$ is equal to 1.0 M and $\therefore [H_{3}O^{+}] = 1.0 \times 10^{-14} M$
- e) $[OH^{-}]$ from water is negligible so the final $[OH^{-}]$ is equal to $2.0 \times 10^{-4} \text{ M} !!$ $\therefore [H_3O^{+}] = 5.0 \times 10^{-11} \text{M}$
- f) [OH⁻] from water is **NOT** negligible so the quadratic must be solved which yields a final $[H_3O^+]$ equal to $8.6_1 \times 10^{-8}$ M

32. a) $pH = 0.00$	b)	pH =	3.	70)
--------------------	----	------	----	----	---

- c) pH = 6.94 d) pH = 14.00
- e) pH = 10.30 f) pH = 7.06

33.
$$pH = -log[H_3O^+]$$
 therefore $[H_3O^+] = alog(-pH) = 10^{-pH}$
a) $[H_3O^+] = 10^{-pH} = 10^{0.50} = 3.1_6 M$ $[OH^-] = 1.0 \times 10^{-14} / 3.1_6 = 3.2 \times 10^{-15} M$
b) $[H_3O^+] = 10^{-pH} = 10^{-1.0} = 0.1 M$ $[OH^-] = 1.0 \times 10^{-14} / 0.1 = 1 \times 10^{-13} M$
c) $[H_3O^+] = 10^{-pH} = 10^{-4.30} = 5.0 \times 10^{-5} M$ $[OH^-] = 1.0 \times 10^{-14} / 5.0 \times 10^{-5} = 2.0 \times 10^{-10} M$
d) $[H_3O^+] = 10^{-pH} = 10^{-9.7} = 2 \times 10^{-10} M$ $[OH^-] = 1.0 \times 10^{-14} / 2 \times 10^{-10} = 5 \times 10^{-5} M$
e) $[H_3O^+] = 10^{-pH} = 10^{-14.60} = 2.5 \times 10^{-15} M$ $[OH^-] = 1.0 \times 10^{-14} / 2.5 \times 10^{-15} = 4.0 M$
34. a) $HC_8H_7O_2 + H_2O$ \rightleftharpoons $C_8H_7O_2^- + H_3O^+$
b) $K_a = \frac{[H_3O^+][C_8H_7O_2^-]}{[HC_8H_7O_2]} = 4.9 \times 10^{-5}$
c) Yes, $2H_2O$ (ℓ) \longleftarrow H_3O^+ (aq) + OH^- (aq)

d) There are two assumptions that can be made.

First, one can assume that since K_a is much greater than K_w then the contribution to the total $[H_3O^+]$ coming from the water equilibrium is negligible in comparison to the amount coming from the phenylacetic acid.

Second, one can assume that the loss of phenylacetic acid is negligible in comparison to the total concentration of phenylacetic. (I.e., $x \ll 1.0$ and therefore 1.0 - x = 1.0)

e)
$$HC_8H_7O_2 + H_2O \implies C_8H_7O_2^- + H_3O^+$$

1.0 - x x x

$$K_{a} = \frac{[H_{3}O^{+}][C_{8}H_{7}O_{2}^{-}]}{[HC_{8}H_{7}O_{2}]} = \frac{(x)\bullet(x)}{(1.0-x)} = \frac{(x)\bullet(x)}{(1.0)} = 4.9 \times 10^{-5}$$

Rearranging gives $x = \sqrt{4.9 \times 10^{-5}} = 7.0 \times 10^{-3}$ Therefore, $[H_3O^+] = 7.0 \times 10^{-3}M$

Using the relationship $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Solving for [OH⁻] gives [OH⁻] =
$$\frac{1.0 \times 10^{-14}}{7.0 \times 10^{-3}}$$
 = 1.4 × 10⁻¹²

Since, $[OH^{-}]$ is equal to the contribution of water to the $[H_3O^{+}]$ then our first approximation is valid.

Likewise, since 1.0 M – 7.0×10^{-3} M = 1.0 M, to the number of Sig Figs present in our problem then our second approximation is valid.

35. a) $HC_8H_7O_2 + H_2O \iff C_8H_7O_2^- + H_3O^+$

b)
$$K_a = \frac{[H_3O^+][C_8H_7O_2^-]}{[HC_8H_7O_2]} = 4.9 \times 10^{-5}$$

c) Yes,
$$2 H_2 O(\ell) \equiv H_3 O^+(aq) + OH^-(aq)$$

d) There are two assumptions that can be made.

First, one can assume that since K_a is much greater than K_w then the contribution to the total $[H_3O^+]$ coming from the water equilibrium is negligible in comparison to the amount coming from the phenylacetic acid.

Second, one can assume that the loss of phenylacetic acid is negligible in comparison to the total concentration of phenylacetic. (I.e., $x \ll 1.0$ and therefore 1.0 - x = 1.0)

e) $HC_8H_7O_2 + H_2O \iff C_8H_7O_2^- + H_3O^+$ 0.00010 - x x x

$$K_{a} = \frac{[H_{3}O^{+}][C_{8}H_{7}O_{2}^{-}]}{[HC_{8}H_{7}O_{2}]} = \frac{(x)\bullet(x)}{(0.00010 - x)} = \frac{(x)\bullet(x)}{(0.00010)} = 4.9 \times 10^{-5}$$

Rearranging gives $x = \sqrt{4.9 \times 10^{-9}} = 7.0 \times 10^{-5}$ Therefore, $[H_3O^+] = 7.0 \times 10^{-5}M$

Using the relationship $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Solving for [OH⁻] gives [OH⁻] =
$$\frac{1.0 \times 10^{-14}}{7.0 \times 10^{-5}}$$
 = 1.4 × 10⁻¹⁰

Since, $[OH^{-}]$ is equal to the contribution of water to the $[H_3O^{+}]$ then our first approximation is valid.

BUT, since 0.00010 M – 7.0×10^{-5} M = 0.00003 M, to the number of Sig Figs present in our problem then our second approximation is **NOT** valid. Therefore we use the quadratic equation to solve the problem and find the correct values for the [H₃O⁺] and [OH⁻].

$$K_{a} = \frac{[H_{3}O^{+}][C_{8}H_{7}O_{2}^{-}]}{[HC_{8}H_{7}O_{2}]} = \frac{(x)\bullet(x)}{(0.00010 - x)} = 4.9 \times 10^{-5}$$

Rearranging gives: $x^2 + 4.9 \times 10^{-5} x - 4.9 \times 10^{-9} = 0$

$$[H_{3}O^{+}] = x = \frac{-4.9 \times 10^{-5} + \sqrt{(4.9 \times 10^{-5})^{2} + 1.96 \times 10^{-8}}}{2} = 5.0 \times 10^{-5}$$

Now, solving for [OH⁻] gives [OH⁻] = $\frac{1.0 \times 10^{-14}}{5.0 \times 10^{-5}}$ = 2.0 × 10⁻¹⁰

- 36. a) Assume that the water equilibrium contributes a negligible amount of H_3O^+ . Thus the only important equilibrium is :

Assume that $x \ll 0.50$ therefore 0.50 - x = 0.50.

$$K_{a} = \frac{[H_{3}O^{+}][C_{2}H_{3}O_{2}^{-}]}{[HC_{2}H_{3}O_{2}]} = \frac{(x)\cdot(x)}{0.50} = 1.8 \times 10^{-5}$$

Rearranging gives $x = \sqrt{9.0 \times 10^{-6}} = 3.0 \times 10^{-3}$ Therefore, $[H_3O^+] = 3.0 \times 10^{-3}M$

Since $[H_3O^+]$ is much larger than 1.0×10^{-7} then our first approximation is valid. And, since $0.50 - 3.0 \times 10^{-3} = 0.50$ to the number of Sig Figs used in our problem then our second approximation is valid. The $[OH^-] = K_w/[H_3O^+] = 1.0 \times 10^{-14} / 3.0 \times 10^{-3} = 3.3 \times 10^{-12}$.

Therefore the pH = $-\log(3.0 \times 10^{-3}) = 2.52$

b) Assume that the water equilibrium contributes a negligible amount of H_3O^+ . Thus the only important equilibrium is :

Assume that $x \ll 0.0035$ therefore 0.0035 - x = 0.0035.

$$K_{a} = \frac{[H_{3}O^{+}][OC1^{-}]}{[HOC1]} = \frac{(x) \cdot (x)}{0.0035} = 2.9 \times 10^{-8}$$

Rearranging gives $x = \sqrt{1.0_{15} \times 10^{-10}} = 1.0 \times 10^{-5}$ Therefore, $[H_{3}O^{+}] = 1.0 \times 10^{-5}M$

Since $[H_3O^+]$ is much larger than 1.0×10^{-7} then our first approximation is valid. And, since $0.0035 - 1.0 \times 10^{-5} = 0.0035$ to the number of Sig Figs used in our problem then our second approximation is valid. The $[OH^-] = K_w/[H_3O^+] = 1.0 \times 10^{-14} / 1.0 \times 10^{-5} = 1.0 \times 10^{-9}$.

Therefore the pH = $-\log(1.0 \times 10^{-5}) = 5.00$

c) Assume that the water equilibrium contributes a negligible amount of H_3O^+ . Thus the only important equilibrium is :

Assume that $x \ll 0.30$ therefore 0.30 - x = 0.30.

$$K_{a} = \frac{[H_{3}O^{+}][SO_{4}^{-2}]}{[HSO_{4}^{-}]} = \frac{(x)\cdot(x)}{0.30} = 1.2 \times 10^{-2}$$

Rearranging gives $x = \sqrt{3.6 \times 10^{-3}} = 6.0 \times 10^{-2}$ Therefore, $[H_3O^+] = 6.0 \times 10^{-2}M$

Since $[H_3O^+]$ is much larger than 1.0×10^{-7} then our first approximation is valid. But, since $0.30 - 6.0 \times 10^{-2} = 0.24$ to the number of Sig Figs used in our problem then our second approximation is NOT valid. Therefore we use the quadratic equation to solve the problem and find the correct values for the $[H_3O^+]$ and $[OH^-]$.

$$K_{a} = \frac{[H_{3}O^{+}][SO_{4}^{-2}]}{[HSO_{4}^{-}]} = \frac{(x)^{\bullet}(x)}{(0.30 - x)} = 1.2 \times 10^{-2}$$

Rearranging gives: $x^2 + 1.2 \times 10^{-2} x - 3.6 \times 10^{-3} = 0$

$$[H_{3}O^{+}] = x = \frac{-1.2 \times 10^{-2} + \sqrt{(1.2 \times 10^{-2})^{2} + 1.44 \times 10^{-2}}}{2} = 5.4 \times 10^{-2}$$

Now, solving for [OH⁻] gives [OH⁻] = $\frac{1.0 \times 10^{-14}}{5.4 \times 10^{-2}}$ = 1.8 × 10⁻¹³

Therefore the pH = $-\log(5.4 \times 10^{-2}) = 1.27$

d) Assume that the water equilibrium contributes a negligible amount of H_3O^+ . Thus the only important equilibrium is :

Assume that $x \ll 0.010$ therefore 0.010 - x = 0.010.

$$K_{a} = \frac{[H_{3}O^{+}][IO_{3}]}{[HIO_{3}]} = \frac{(x) \cdot (x)}{0.010} = 1.6 \times 10^{-1}$$

Rearranging gives
$$x = \sqrt{1.6 \times 10^{-3}} = 4.0 \times 10^{-2}$$
 Therefore, $[H_3O^+] = 4.0 \times 10^{-2}M$

Since $[H_3O^+]$ is much larger than 1.0×10^{-7} then our first approximation is valid. But, since $0.010 - 4.0 \times 10^{-2} = -0.030$!!! to the number of Sig Figs used in our problem then our second approximation is NOT valid. Therefore we use the quadratic equation to solve the problem and find the correct values for the $[H_3O^+]$ and $[OH^-]$.

$$K_{a} = \frac{[H_{3}O^{+}][IO_{3}]}{[HIO_{3}]} = \frac{(x) \cdot (x)}{(0.010 - x)} = 1.6 \times 10^{-1}$$

Rearranging gives: $x^2 + 1.6 \times 10^{-1} x - 1.6 \times 10^{-3} = 0$

$$[H_{3}O^{+}] = x = \frac{-1.6 \times 10^{-1} + \sqrt{(1.6 \times 10^{-1})^{2} + 6.4 \times 10^{-3}}}{2} = 9.4_{43} \times 10^{-3}$$

Now, solving for [OH⁻] gives [OH⁻] = $\frac{1.0 \times 10^{-14}}{9.4_{43} \times 10^{-3}} = 1.1 \times 10^{-12}$

Therefore the pH = $-\log(9.4_{43} \times 10^{-3}) = 2.02$

37. a)
$$K_b = K_w / K_{a(CA)} = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

b) $K_b = K_w / K_{a(CA)} = 1.0 \times 10^{-14} / 1.2 \times 10^{-2} = 8.3 \times 10^{-13}$

c)
$$K_b = K_w / K_{a(CA)} = 1.0 \times 10^{-14} / 5.6 \times 10^{-11} = 1.8 \times 10^{-4}$$

38. a) $C_2H_3O_2^- + H_2O \iff HC_2H_3O_2 + OH^-$

b)
$$K_{b} = \frac{[OH^{-}][HC_{2}H_{3}O_{2}]}{[C_{2}H_{3}O_{2}]} = 5.6 \times 10^{-10}$$

c) Yes,
$$2 H_2 O(\ell) \rightleftharpoons H_3 O^+(aq) + OH^-(aq)$$

d) There are two assumptions that can be made.

First, one can assume that since K_b is much greater than K_w then the contribution to the total $[OH^-]$ coming from the water equilibrium is negligible in comparison to the amount coming from the acetate ion.

Second, one can assume that the loss of acetate ion is negligible in comparison to the total concentration of acetate ion. (I.e., $x \ll 1.0$ and therefore 1.0 - x = 1.0)

e)
$$C_{2}H_{3}O_{2}^{-} + H_{2}O \iff HC_{2}H_{3}O_{2} + OH^{-}$$

 $1.0 - x \qquad x \qquad x$
 $K_{b} = \frac{[OH^{-}][HC_{2}H_{3}O_{2}]}{[C_{2}H_{2}O_{2}^{-}]} = \frac{(x)\bullet(x)}{(1.0 - x)} = \frac{(x)\bullet(x)}{(1.0)} = 5.5_{6} \times 10^{-10}$

Rearranging gives $x = \sqrt{5.5_6 \times 10^{-10}} = 2.3_6 \times 10^{-5}$ Therefore, [OH⁻] = $2.3_6 \times 10^{-5}$ M

Using the relationship $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Solving for [H₃O⁺] gives [H₃O⁺] = $\frac{1.0 \times 10^{-14}}{2.3_6 \times 10^{-5}}$ = 4.2₄×10⁻¹⁰

Since, $[OH^{-}]$ is equal to the contribution of water to the $[H_3O^{+}]$ then our first approximation is valid.

Likewise, since $1 \text{ M} - 2.3_6 \times 10^{-5} \text{ M} = 1 \text{ M}$, to the number of Sig Figs present in our problem then our second approximation is valid.

Therefore the pH = $-\log(4.2_4 \times 10^{-10}) = 9.37$

39. a) $OCl^- + H_2O \implies HOCl + OH^-$

b)
$$K_{b} = \frac{[OH^{-}][HOC1]}{[OC1^{-}]} = \frac{K_{w}}{K_{a(HOC1)}} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.4_{5} \times 10^{-7}$$

c) Yes,
$$2 H_2 O(\ell) \implies H_3 O^+(aq) + OH^-(aq)$$

d) There are two assumptions that can be made.

First, one can assume that since K_b is much greater than K_w then the contribution to the total $[OH^-]$ coming from the water equilibrium is negligible in comparison to the amount coming from the hypochlorite ion.

Second, one can assume that the loss of hypochlorite ion is negligible in comparison to the total concentration of hypochlorite ion. (I.e., $x \ll 0.75$ and therefore 0.75 - x = 0.75)

e)
$$OCl^- + H_2O \iff HOCl + OH^-$$

0.75 - x x x

$$K_{b} = \frac{[OH^{-}][HOC1]}{[OC1^{-}]} = \frac{(x) \cdot (x)}{(0.75 - x)} = \frac{(x) \cdot (x)}{(0.75)} = 3.4_{5} \times 10^{-7}$$

Rearranging gives $x = \sqrt{3.4_5 \times 10^{-7} \times 0.75} = 5.0_9 \times 10^{-4}$ Therefore, [OH⁻] = $5.0_9 \times 10^{-4}$ M

Using the relationship $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Solving for
$$[H_3O^+]$$
 gives $[H_3O^+] = \frac{1.0 \times 10^{-14}}{5.0_9 \times 10^{-4}} = 1.9_7 \times 10^{-11}$

Since, $[OH^{-}]$ is equal to the contribution of water to the $[H_3O^{+}]$ then our first approximation is valid.

Likewise, since $0.75 \text{ M} - 5.0_9 \times 10^4 \text{ M} = 0.75 \text{ M}$, to the number of Sig Figs present in our problem then our second approximation is valid.

Therefore the pH = $-\log(1.9_7 \times 10^{-11}) = 10.71$

40. The principal acid/base equilibrium always involves the strongest acid present in appreciable amounts reacting with the strongest base present in appreciable amounts.

The principal pH determining equilibrium always involves EITHER the strongest acid present in appreciable amounts reacting with water OR the strongest base present in appreciable amounts reacting with water. The choice depends on the K_a of the acid and the K_b of the base with the species which has the HIGHER constant will determine the pH of the solution.

- 41. a) The principal acid/base equilibrium: $HC_2H_3O_2 + H_2O \rightleftharpoons C_2H_3O_2^- + H_3O^+$ The principal pH determining equilibrium: $HC_2H_3O_2 + H_2O \rightleftharpoons C_2H_3O_2^- + H_3O^+$
 - b) The principal acid/base equilibrium: $HC_2H_3O_2 + C_2H_3O_2^- \iff C_2H_3O_2^- + HC_2H_3O_2$ The principal pH determining equilibrium: $HC_2H_3O_2 + H_2O \iff C_2H_3O_2^- + H_3O^+$
 - c) The principal acid/base equilibrium: $NH_4^+ + SO_4^{-2} \rightleftharpoons HSO_4^- + NH_3$ The principal pH determining equilibrium: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
 - d) The principal acid/base equilibrium: $HCO_3^- + HCO_3^- \iff H_2CO_3 + CO_3^{-2}$ The principal pH determining equilibrium: $HCO_3^- + H_2O \iff H_2CO_3 + OH^-$
- 42. B, C, D as these are the only solutions that contain both a weak acid and weak base in appreciable amounts.
- 43. a) 1 M HC₂H₃O₂

As stated in problem 41 a, the principal acid/base equilibrium AND the principal pH determining equilibrium are:

$$\begin{array}{rcl} \text{HC}_{2}\text{H}_{3}\text{O}_{2} &+ &\text{H}_{2}\text{O} &\rightleftharpoons &\text{C}_{2}\text{H}_{3}\text{O}_{2}^{-} &+ &\text{H}_{3}\text{O}^{+} \\ \hline & & X & X \\ \hline & & X & X \\ \text{Weightain the equation of the equati$$

b) 1 M $HC_2H_3O_2$ and 1 M $NaC_2H_3O_2$

As stated in problem 41 b, the principal acid/base equilibrium is:

$$HC_2H_3O_2 + C_2H_3O_2 = \longrightarrow C_2H_3O_2 + HC_2H_3O_2$$

Which goes nowhere and can therefore be ignored.

The principal pH determining equilibrium is:

$$HC_{2}H_{3}O_{2} + H_{2}O \rightleftharpoons C_{2}H_{3}O_{2}^{-} + H_{3}O^{+}$$
(a) eq 1 - X 1 + X X

$$K_{a} = \frac{(X) \times (1 + X)}{1 - X} = 1.8 \times 10^{-5}$$
after assuming 1 ± X = 1 this reduces

$$K_{a} = X = 1.8 \times 10^{-5}$$

$$\therefore pH = 4.7_{4}$$

c) $1 M (NH_4)_2 SO_4$

As stated in problem 41 c, the principal acid/base equilibrium is:

 $NH_4^{+}+SO_4^{-2} \quad \overleftarrow{====} HSO_4^{-}+NH_3$

Before we can solving the equilibrium problem for this system we must first determine the value of K_{eq} for this equilibrium.

$$K_{eq} = \frac{[NH_3][HSO_4^-]}{[NH_4^+][SO_4^{-2}]} = \frac{[NH_3][HSO_4^-]}{[NH_4^+][SO_4^{-2}]} \cdot \frac{[H_3O^+]}{[H_3O^+]} = \frac{[H_3O^+][NH_3]}{[NH_4^+]} \cdot \frac{[HSO_4^-]}{[H_3O^+][SO_4^{-2}]}$$

Thus we can see:

$$K_{eq} = \frac{[NH_3][HSO_4^-]}{[NH_4^+][SO_4^{-2}]} = K_{a(NH_4^+)} \cdot \frac{1}{K_{a(HSO_4^-)}} = 5.5_6 \times 10^{-10} \cdot \frac{1}{1.0 \times 10^{-2}} = 5.5_6 \times 10^{-8}$$

Returning to the equilibrium,

after assuming 1 - X = 1 this reduces to

$$K_{eq} = \frac{[NH_3][HSO_4]}{[NH_4^+][SO_4^{-2}]} = \frac{X^2}{(2)} = 5.5_6 \times 10^{-8} \text{ or } X = \sqrt{2 \cdot 5.5_6 \times 10^{-8}} = 3_3 \times 10^{-4}$$

: $[NH_3] = [HSO_4-] = X = 3_3 \times 10^{-4} \text{ M} \& [NH_4^+] = 2 - X = 2 \text{ M} \& [SO_4^{-2}] = 1 - X = 1 \text{ M}$ Now to solve the principle pH determining equilibrium (ignoring the contribution from water):

$$K_{a} = \frac{(Y) \times (3_{\cdot 3} \times 10^{-4} + Y)}{2 - Y} = 5_{\cdot 6} \times 10^{-10}$$

after assuming $3_{.3} \times 10^{-4} + Y = 3_{.3} \times 10^{-4}$ this reduces to

$$K_{a} = \frac{(Y) \times (3_{\cdot_{3}} \times 10^{-4})}{2} = 5_{\cdot_{6}} \times 10^{-10} \text{ and } \therefore Y = \frac{(2) \cdot (5_{\cdot_{6}} \times 10^{-10})}{(3_{\cdot_{3}} \times 10^{-4})} = 3_{\cdot_{4}} \times 10^{-6}$$
$$\therefore [NH_{3}] = 3_{\cdot_{3}} \times 10^{-4} \text{ M } \& [NH_{4}^{+}] = 2 - Y = 2 \text{ M } \& [H_{3}O^{+}] = 3_{\cdot_{4}} \times 10^{-6} \text{ M}$$

(the assumption that $3_{.3} \times 10^{-4} + Y = 3_{.3} \times 10^{-4}$ valid)

To check on our assumption that the contribution from water is negligible,

$$2 \text{ H}_{2}\text{O} (\ell) \iff \text{H}_{3}\text{O}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq})$$
(a) eq $3_{.4} \times 10^{-6} + Z$ Z
 $\mathbf{K}_{\mathbf{w}} = (\mathbf{Z}) \times (\mathbf{3}_{.4} \times 10^{-6} + \mathbf{Z}) = 1.0 \times 10^{-14}$
assuming that $3_{.4} \times 10^{-6} + \mathbf{Z} = 3_{.4} \times 10^{-6}$ this reduces to
 $\mathbf{K}_{\mathbf{w}} = (\mathbf{Z}) \times (\mathbf{3}_{.4} \times 10^{-6}) = 1.0 \times 10^{-14}$ or $\mathbf{Z} = \frac{1.0 \times 10^{-14}}{\mathbf{3}_{.4} \times 10^{-6}} = \mathbf{3}_{.0} \times 10^{-9}$
Yes, the assumption, $3_{.4} \times 10^{-6} + \mathbf{Z} = 3_{.4} \times 10^{-6}$ is valid. Thus, $[\text{H}_{3}\text{O}^{+}] = 3_{.4} \times 10^{-6}$ M and

$$pH = 5.4_8$$

d) 1 M NaHCO₃

As stated in problem 41 d, the principal acid/base equilibrium is:

 HCO_3^- + $\text{HCO}_3^ \rightleftarrows$ H_2CO_3 + CO_3^{-2}

Before we can solving the equilibrium problem for this system we must first determine the value of K_{eq} for this equilibrium.

$$K_{eq} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-3}][HCO_3^{-1}]} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-1}][HCO_3^{-1}]} \cdot \frac{[H_3O^{+}]}{[H_3O^{+}]} = \frac{[H_3O^{+}][CO_3^{-2}]}{[HCO_3^{-1}]} \cdot \frac{[H_2CO_3]}{[H_3O^{+}][HCO_3^{-1}]}$$

Thus we can see:

$$K_{eq} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-1}][HCO_3^{-1}]} = K_{a(HCO_3^{-1})} \cdot \frac{1}{K_{a(H_2CO_3)}} = 5.6 \times 10^{-11} \cdot \frac{1}{4.3 \times 10^{-7}} = 1.3_0 \times 10^{-4}$$

Returning to the equilibrium,

$$2 \text{ HCO}_{3}^{-} \xleftarrow{} \text{H}_{2}\text{CO}_{3} + \text{CO}_{3}^{-2}$$

$$(a) \text{ eq} \quad 1 - 2\text{X} \times \text{X}$$

$$\mathbf{K}_{eq} = \frac{[\text{H}_{2}\text{CO}_{3}][\text{CO}_{3}^{-2}]}{[\text{HCO}_{3}^{-}][\text{HCO}_{3}^{-}]} = \frac{(\text{X})(\text{X})}{(1 - 2\text{X})^{2}} = 1.3_{0} \times 10^{-4}$$

after assuming 1 - 2X = 1 this reduces to

$$K_{eq} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-1}][HCO_3^{-1}]} = \frac{X^2}{(1)^2} = 1.3_0 \times 10^{-4} \text{ or } X = \sqrt{1.3_0 \times 10^{-4}} = 1.1 \times 10^{-2}$$

The assumption, 1 - 2X = 1 is valid. \therefore [H₂CO₃] = [CO₃⁻²] = X = 1.₁ × 10⁻² M & [HCO₃⁻] = 1 - 2X = 1 M Now to solve the principle pH determining equilibrium (ignoring the contribution from water):

$$\begin{array}{rcrcrcr} HCO_3^- &+ & H_2O & \rightleftharpoons H_2CO_3 &+ & OH \\ @ eq & 1 - Y & & & 1_{\cdot_1} \times 10^{-2} + Y & & Y \end{array}$$

$$K_{b(HCO_{3})} = \frac{(Y) \times (1_{\cdot 1} \times 10^{-2} + Y)}{(1 - Y)} = \frac{K_{w}}{K_{a(H_{2}CO_{3})}} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2_{\cdot 3} \times 10^{-8}$$

after assuming $1.1\times 10^{-2}+Y=1.1\times 10^{-2}~$ this reduces to

$$K_{b} = \frac{(Y) \times (1_{\cdot 1} \times 10^{-2})}{1} = 2_{\cdot 3} \times 10^{-8} \text{ and } \therefore Y = \frac{(1) \cdot (2_{\cdot 3} \times 10^{-8})}{(1_{\cdot 1} \times 10^{-2})} = 2_{\cdot 1} \times 10^{-6}$$
$$\therefore [OH^{-}] = 2_{\cdot 1} \times 10^{-6} \text{ M \& } [H_{2}CO_{3}] = 1_{\cdot 1} \times 10^{-2} \text{ M \& } [HCO_{3}^{--}] = 1 - Y = 1 \text{ M}$$

To check on our assumption that the contribution from water is negligible and determine $[H_3O^+]$,

$$2 \text{ H}_{2}\text{O} (\ell) \iff \text{H}_{3}\text{O}^{+} (\text{aq}) + \text{OH}^{-} (\text{aq})$$
(a) eq Z $2.1_{1} \times 10^{-6} + Z$
 $K_{w} = (Z) \times (2._{1} \times 10^{-6} + Z) = 1.0 \times 10^{-14}$
assuming the contribution to $[\text{H}_{3}\text{O}^{+}]$ is negligible (that is the Z is small) this reduces to $K_{w} = (Z) \times (2._{1} \times 10^{-6}) = 1.0 \times 10^{-14}$ or $Z = \frac{1.0 \times 10^{-14}}{2._{1} \times 10^{-6}} = 4._{8} \times 10^{-9}$
Yes, Z is small compared to $2._{1} \times 10^{-6}$. Thus, $[\text{H}_{3}\text{O}^{+}] = Z = 4.8 \times 10^{-9}$ M and pH = 8.33

44. a) 1 M $HC_2H_3O_2$

When 0.10 moles of HCl are added to 1 M HC₂H₃O₂ the HCl will react with H₂O (the strongest base present in large amount) to form H₃O⁺ and Cl⁻ to 100%. Therefore after this reaction the $[H_3O^+] = [Cl^-] = 0.10 \text{ M}$

As before, the principal acid/base equilibrium AND the principal pH determining equilibrium is:

$$K_a = \frac{(X)(0.10+X)}{(1-X)} = 1.8 \times 10^{-5}$$

1 - X = 1 this reduces to

after assuming 0.10 + X = 0.1

$$K_a = (X)(0.10) = 1.8 \times 10^{-5} \text{ or } X = [C_2H_3O_2^-] = \frac{1.8 \times 10^{-5}}{0.10} = 1.8 \times 10^{-4}$$

:. the assumption is valid and $[H_3O^+] = 0.10 \text{ pH} = 10$ (the same pH that would be produced if 0.10 moles of HCl had been added to pure H₂O!!) This solution offered NO resistance to pH change. b) 1 M $HC_2H_3O_2$ and 1 M $NaC_2H_3O_2$

When 0.10 moles of HCl are added to a mixture of 1 M HC₂H₃O₂ and 1 M NaC₂H₃O₂, the HCl will react with C₂H₃O₂⁻, (the strongest base present in large amount) to form HC₂H₃O₂, and H₂O to 100%. Thus, after this reaction the [HC₂H₃O₂] = 1.1 M, [C₂H₃O₂⁻] = 0.9 M, & [Cl⁻] = 0.10 M

As stated in problem 43 b, the principal acid/base equilibrium is:

$$HC_2H_3O_2 + C_2H_3O_2 \rightarrow C_2H_3O_2 + HC_2H_3O_2$$

Which goes nowhere and can therefore be ignored.

The principal pH determining equilibrium is:

$$\begin{array}{rcl} HC_{2}H_{3}O_{2} &+ & H_{2}O &== & C_{2}H_{3}O_{2}^{-} &+ & H_{3}O^{+} \\ Init & 1.1 & & 0.9 \\ @ eq \ 1.1 - X & & 0.9 + X & X \\ K_{a} &= & \frac{(X) \times (0.9 + X)}{(1.1 - X)} &= 1.8 \times 10^{-5} & \text{after assuming } 0.9 + X = 0.9 \\ I.1 - X &= 1.1, \text{ this reduces to} \\ K_{a} &= & \frac{(X) \times (0.9)}{(1.1)} &= 1.8 \times 10^{-5} & \therefore & X = [H_{3}O^{+}] = \frac{(K_{a})(1.1)}{(0.9)} &= 2.2 \times 10^{-5} \end{array}$$

 \therefore pH = 4.66 (almost the same pH as before, the change in pH = 0.08!)

c)
$$1 \text{ M} (\text{NH}_4)_2 \text{SO}_4$$

When 0.10 moles of HCl are added to 1 M (NH₄)₂SO₄, the HCl will react with SO₄⁻², (the strongest base present in large amount) to form HSO₄⁻, and Cl⁻ to 100%. Thus, after this reaction the [HSO₄⁻] = 0.1 M, [SO₄⁻²] = 0.9 M, & [NH₄⁺] = 2.0 M & [Cl⁻] = 0.10 M

There is a NEW principal acid/base equilibrium now since the strongest acid (NOW) is HSO_4^- while the strongest base remains SO_4^{-2} :

$$\mathrm{HSO_4^{-}}$$
 + $\mathrm{SO_4^{-2}}$ \rightleftarrows $\mathrm{HSO_4^{-}}$ + $\mathrm{SO_4^{-2}}$

which goes nowhere and can therefore be ignored.

Now to solve the principle pH determining equilibrium. Once again there is a new pH determining equilibrium present as HSO_4^- is the strongest acid present (it is stronger than NH_4^+). (Ignoring the contribution from water):

$$HSO_{4}^{-} + H_{2}O \iff SO_{4}^{-2} + H_{3}O^{+}$$
Init 0.10 0.9
@ eq 0.10 - X 0.9 + X X

$$K_{a} = \frac{(X)(0.9 + X)}{(0.10 - X)} = 1.0 \times 10^{-2}$$
after assuming 0.10 - X = 0.10 and assuming 0.9 - X = 0.9, this reduces to

$$K_{a} = \frac{(X)(0.90)}{(0.10)} = 1.0 \times 10^{-2} \text{ and } \therefore \quad X = [H_{3}O^{+}] = \frac{(0.10)(1.0 \times 10^{-2})}{(0.9)} = 1.1 \times 10^{-3}$$

There is another equilibrium present that must be solved to check the $[H_3O^+]$.

$$NH_{4}^{+} + H_{2}O \iff NH_{3} + H_{3}O^{+}$$
Init. 2.0
(a) eq 2.0 - Y

$$Y + 1.1 \times 10^{-3}$$

$$K_{a} = \frac{(Y)(1.1 \times 10^{-3} + Y)}{(2.0 - Y)} = 5.5_{6} \times 10^{-10}$$
after assuming 1.1 × 10⁻³ + Y = 1.1 × 10⁻³ and 2.0 = Y = 2.0 this reduce

after assuming $1.1 \times 10^{-3} + Y = 1.1 \times 10^{-3}$ and 2.0 - Y = 2.0, this reduces to

$$K_{a} = \frac{(Y) \times (1.1 \times 10^{-3})}{2.0} = 5.5_{6} \times 10^{-10} \text{ and } \therefore Y = \frac{(2.0) \cdot (5.5_{6} \times 10^{-10})}{(1.1 \times 10^{-3})} = 2.5_{3} \times 10^{-6}$$

Yes, the contribution of H_3O^+ from the reaction of NH_4^+ is negligible.

:. $[C1^{-}] = 0.1 \text{ M}$; $[HSO_{4}^{-}] = 0.1 \text{ M}$; $[SO_{4}^{-2}] = 0.9 \text{ M}$; $[NH_{4}^{+}] = 2.0 \text{ M}$ & $[H_{3}O^{+}] = 1.1 \times 10^{-3} \text{ M}$

To verify our assumption that the contribution from water is negligible,

$$2 H_2O \quad (\ell) \xrightarrow{} H_3O^+ (aq) + OH^- (aq)$$

$$@ eq \qquad 1.1 \times 10^{-3} + Z \qquad Z$$

$$K_{w} = (Z)(1.1 \times 10^{-3} + Z) = 1.0 \times 10^{-14}$$

assuming the contribution to $[H_3O^+]$ is negligible (that is the Z is small) this reduces to

$$K_w = (Z) \times (1.1 \times 10^{-3}) = 1.0 \times 10^{-14}$$
 or $Z = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-3}} = 9.1 \times 10^{-12}$

Yes, Z is small compared to 1.1×10^{-3} . Thus, $[H_3O^+] = 1.1 \times 10^{-3}$ M and

pH = 2.96 (This is a change in pH of 2.88. It resisted the change somewhat but **not** as much as part b.)

d) 1 M NaHCO₃

As stated in problem 41 d, the principal acid/base equilibrium is:

 $HCO_3^- + HCO_3^- \iff H_2CO_3 + CO_3^{-2}$

Before we can solving the equilibrium problem for this system we must first determine the value of K_{eq} for this equilibrium.

$$K_{eq} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-1}][HCO_3^{-1}]} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-1}][HCO_3^{-2}]} \cdot \frac{[H_3O^{+}]}{[H_3O^{+}]} = \frac{[H_3O^{+}][CO_3^{-2}]}{[HCO_3^{-1}]} \cdot \frac{[H_2CO_3]}{[H_3O^{+}][HCO_3^{-1}]}$$

Thus we can see:

$$K_{eq} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-1}][HCO_3^{-1}]} = K_{a(HCO_3^{-1})} \cdot \frac{1}{K_{a(H_2CO_3)}} = 5.6 \times 10^{-11} \cdot \frac{1}{4.3 \times 10^{-7}} = 1.3_0 \times 10^{-4}$$

Returning to the equilibrium,

after assuming 1 - 2X = 1 this reduces to

$$K_{eq} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-1}][HCO_3^{-1}]} = \frac{X^2}{(1.0)^2} = 1.3_0 \times 10^{-4} \text{ or } X = \sqrt{1.3_0 \times 10^{-4}} = 1.1 \times 10^{-2}$$

 $\therefore [H_2CO_3] = [CO_3^{-2}] = X = 1.1 \times 10^{-2} \text{ M} \quad \& \quad [HCO_3^{-1}] = 1 - 2X = 1 \text{ M}$ Now to solve the principle pH determining equilibrium (ignoring the contribution from water):

$$\begin{array}{rcl} HCO_{3}^{-} & + & H_{2}O & = & H_{2}CO_{3} & + & OH^{-} \\ \hline @ eq & 1 - Y & & 1.1 \times 10^{-2} + Y & Y \\ \hline K_{b(HCO_{3}^{-})} &= & \frac{(Y) \times (1.1 \times 10^{-2} + Y)}{1.0 - Y} &= & \frac{K_{w}}{K_{a(H_{2}CO_{3})}} &= & \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} &= & 2.3_{3} \times 10^{-8} \end{array}$$

after assuming $1.1 \times 10^{-2} + Y = 1.1 \times 10^{-2}\,$ and 1 - Y = 1, this reduces to

$$K_{b} = \frac{(Y) \times (1.1 \times 10^{-2})}{1.0} = 2.3_{3} \times 10^{-8} \text{ and } \therefore Y = \frac{(1.0) \cdot (2.3_{3} \times 10^{-8})}{(1.1 \times 10^{-2})} = 2.1_{1} \times 10^{-6}$$
$$\therefore [OH^{-}] = 2.1_{1} \times 10^{-6} \text{ M \& } [H_{2}CO_{3}] = 1.1 \times 10^{-2} \text{ M \& } [HCO_{3}^{-}] = 1 - Y = 1 \text{ M}$$

To check on our assumption that the contribution from water is negligible and determine [H₃O⁺],

$$\begin{array}{rcl} 2 \ \mathrm{H_2O} & (\ell) & \longrightarrow & \mathrm{H_3O^+} \, (\mathrm{aq}) & + & \mathrm{OH^-} \, (\mathrm{aq}) \\ @ \ eq & Z & & 2.1_1 \times 10^{-6} + Z \\ \mathbf{K_w} &= (\mathbf{Z}) \times (2.1_1 \times 10^{-6} + \mathbf{Z}) &= 1.0 \times 10^{-14} \\ \text{assuming the contribution to } [\mathrm{H_3O^+}] \text{ is negligible (that is the } . \end{array}$$

assuming the contribution to
$$[H_3O^+]$$
 is negligible (that is the Z is small) this reduces to
 $K_w = (Z) \times (2.1_1 \times 10^{-6}) = 1.0 \times 10^{-14}$ or $Z = \frac{1.0 \times 10^{-14}}{2.1_1 \times 10^{-6}} = 4.7 \times 10^{-9}$

Yes, Z is small compared to $2.1_1 \times 10^{-6}$. Thus, $[H_3O^+] = Z = 4.7 \times 10^{-9}$ M and pH = 8.33

45. a) 1 M $HC_2H_3O_2$

When 0.10 moles of NaOH are added to 1 M HC₂H₃O₂ the NaOH will react with HC₂H₃O₂ (the strongest acid present in large amount) to form H₂O and C2H₃O₂⁻ to 100%. Therefore after this reaction the $[Na^+] = [C2H_3O_2^{--}] = 0.10$ M and $[HC_2H_3O_2] = 0.9$

As before, the principal acid/base equilibrium AND the principal pH determining equilibrium is:

 $\begin{array}{rcl} HC_{2}H_{3}O_{2} &+ & H_{2}O & \rightleftharpoons & C_{2}H_{3}O_{2}^{-} &+ & H_{3}O^{+} \\ Init. & 0.9 & & 0.10 & 0 \\ @ eq & 0.9 - X & & 0.10 + X & X \\ K_{a} &= \frac{(X)(0.10 + X)}{(0.9 - X)} &= 1.8 \times 10^{-5} \\ & 0.9 - X &= 0.9, \text{ this reduces to} \end{array}$ after assuming 0.10 + X = 0

$$K_a = \frac{(X)(0.10)}{(0.9)} = 1.8 \times 10^{-5} \text{ or } X = [C_2H_3O_2^-] = \frac{(1.8 \times 10^{-5})(0.9)}{0.10} = 1.6 \times 10^{-4}$$

:. the assumptions are valid and $[H_3O^+] = 1._6 \times 10^{-4} \text{ pH} = 3.8_0$ This solution offered some resistance to pH change.

b) 1 M $HC_2H_3O_2$ and 1 M $NaC_2H_3O_2$

When 0.10 moles of NaOH are added to a mixture of 1 M $HC_2H_3O_2$ and 1 M $NaC_2H_3O_2$, the NaOH will react with $HC_2H_3O_2$, (the strongest acid present in large amount) to form $C_2H_3O_2^-$, and H_2O to 100%.

Thus, after this reaction, $[HC_2H_3O_2] = 0.9 \text{ M}$, $[C_2H_3O_2^-] = 1.1 \text{ M}$, & $[Na^+] = 0.10 \text{ M}$

As stated in problem 43 b, the principal acid/base equilibrium is:

$$HC_2H_3O_2 + C_2H_3O_2 = C_2H_3O_2 + HC_2H_3O_2$$

Which goes nowhere and can therefore be ignored.

The principal pH determining equilibrium is:

$$K_{a} = \frac{(X) \times (1.1 + X)}{(0.9 - X)} = 1.8 \times 10^{-5}$$
 after assuming 0.9 - X = (
(X) \times (1, 1) (X) = (X, 1, 1) (X,

this reduces to $K_a = \frac{(X) \times (1.1)}{(1.9)} = 1.8 \times 10^{-5}$ \therefore $X = [H_3O^+] = \frac{(K_a)(0.9)}{(1.1)} = 1.4_7 \times 10^{-5}$

 \therefore pH = 4.83 (almost the same pH as before, the change in pH = 0.09!)

c) $1 M (NH_4)_2 SO_4$

When 0.10 moles of NaOH are added to 1 M $(NH_4)_2SO_4$, the NaOH will react with NH_4^+ , (the strongest acid present in large amount) to form NH_3 , and H_2O to 100%. Thus, after this reaction the $[NH_3] = 0.1$ M, $[SO_4^{-2}] = 1$ M, & $[NH_4^+] = 1.9$ M & $[Na^+] = 0.10$ M

There is a NEW principal acid/base equilibrium now since the strongest base (NOW) is NH_3 while the strongest acid remains NH_4^+ : NH_4^+ + $NH_3 \iff NH_4^+$ + NH_3 which goes nowhere and can therefore be ignored. Now to solve the principle pH determining equilibrium which is different than before as NH_3 is present AND is a stronger base than SO_4^{-2} AND is a better base than NH_4 + is as an acid. (Ignoring the contribution from water):

$$K_{b} = \frac{(X)(1.9 + X)}{(0.10 - X)} = 5.5_{6} \times 10^{-8}$$
 after assuming 0.10 - X = 0.10

this reduces to

$$K_{b} = \frac{(X)(1.9)}{(0.10)} = 1.8 \times 10^{-5} \text{ and } \therefore X = [OH-] = \frac{(0.10)(1.8 \times 10^{-5})}{(1.9)} = 9.4_{7} \times 10^{-7}$$

The water equilibrium present that must be solved to check the $[H_3O^+]$.

$$K_w = (Y)(9.4_7 \times 10^{-7} + Y) = 1.0 \times 10^{-14}$$

after assuming $9.4_7 \times 10^{-7} + Y = 9.4_7 \times 10^{-7}$ this reduces to

$$K_w = (Y) \times (9.4_7 \times 10^{-7}) = 1.0 \times 10^{-14}$$
 and $\therefore Y = \frac{1.0 \times 10^{-14}}{9.4_7 \times 10^{-7}} = 1.0_8 \times 10^{-8}$

Yes, the contribution of OH^- from the reaction of H_2O is negligible.

: $[Na^+] = 0.1 \text{ M}$; $[SO_4^{-2}] = 1 \text{ M}$; $[NH_3] = 0.1 \text{ M}$; $[NH_4^+] = 1.9 \text{ M}$ & $[H_3O^+] = 1.0_8 \times 10^{-8} \text{ M}$

 $pH = 7.9_7$ (This is a change in pH of 2.4₉. It resisted the change somewhat but **not** as much as part b.)

d) 1 M NaHCO₃

When 0.10 moles of NaOH are added to 1 M NaHCO₃, the NaOH will react with HCO₃⁻, (the strongest acid present in large amount) to form CO_3^{-2} , and H₂O to 100%. Thus, after this reaction the $[CO_3^{-2}] = 0.1$ M, $[HCO_3^{-}] = 0.9$ M, & $[Na^+] = 1.10$ M

As stated in problem 41 d, the principal acid/base equilibrium is:

$$HCO_{3}^{-} + HCO_{3}^{-} \implies H_{2}CO_{3} + CO_{3}^{-2}$$

 $K_{eq} = \frac{[H_{2}CO_{3}][CO_{3}^{-2}]}{[HCO_{3}^{-}][HCO_{3}^{-}]} = 1.3_{0} \times 10^{-4}$

Returning to the equilibrium,

$$\begin{array}{rcl} & 2 \ \text{HCO}_3^{-} & \longleftrightarrow & \text{H}_2\text{CO}_3 & + & \text{CO}_3^{-2} \\ & \text{init} & 0.9 & & 0.1 \\ & @ \ \text{eq} & 0.9 - 2\text{X} & \text{X} & 0.1 + \text{X} \\ \end{array}$$
$$\begin{aligned} & \textbf{K}_{\text{eq}} &= \frac{[\text{H}_2\text{CO}_3][\text{CO}_3^{-2}]}{[\text{HCO}_3^{-}][\text{HCO}_3^{-}]} &= \frac{(\text{X})(0.1 + \text{X})}{(0.9 - 2\text{X})^2} &= 1.3_0 \times 10^{-4} \end{aligned}$$

after assuming 0.9 - 2X = 0.9 and 0.1 + X = 0.1 this reduces to

$$K_{eq} = \frac{[H_2CO_3][CO_3^{-2}]}{[HCO_3^{-1}][HCO_3^{-1}]} = \frac{0.1 \times X}{(0.9)^2} = 1.3_0 \times 10^{-4} \text{ or } X = \frac{1.3_0 \times 10^{-4} \times (0.9)^2}{(0.1)} = 1.0_5 \times 10^{-3}$$

:
$$[H_2CO_3] = X = 1.0_5 \times 10^{-3} \text{ M}$$
, $[CO_3^{-2}] = 0.1 \& [HCO_3^{-1}] = 0.9 - 2X = 0.9 \text{ M}$

Now to solve the NEW principle pH determining equilibrium (ignoring the contribution from water):

$$\begin{array}{rcl} & \text{CO}_{3}^{-2} & + & \text{H}_{2}\text{O} & = = \Rightarrow & \text{HCO}_{3}^{-} & + & \text{OH}^{-} \\ & \text{init} & 0.1 & & 0.9 \\ & @ \text{eq} & 0.1 - \text{Y} & & 0.9 + \text{Y} & \text{Y} \end{array}$$
$$\begin{array}{rcl} & \textbf{K}_{\text{w}} & = & \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = & 1.7_{9} \times 10^{-4} \end{array}$$

after assuming 0.9 + Y = 0.9 and that 0.1 - Y = 0.1, this reduces to

$$K_{b} = \frac{(Y) \times (0.9)}{(0.1)} = 1.7_{9} \times 10^{-4} \text{ and } \therefore Y = \frac{(0.1) \cdot (1.7_{9} \times 10^{-4})}{(0.9)} = 2_{\cdot 0} \times 10^{-5}$$
$$\therefore [OH^{-}] = 2_{\cdot 0} \times 10^{-5} \text{ M \& } [H_{2}CO_{3}] = 1.1 \times 10^{-2} \text{ M \& } [HCO_{3}^{--}] = 1 - Y = 1 \text{ M}$$

To check on our assumption that the contribution from water is negligible and determine $[H_3O^+]$,

$$2 \operatorname{H}_{2}O(\ell) \xrightarrow{} \operatorname{H}_{3}O^{+}(\operatorname{aq}) + OH^{-}(\operatorname{aq})$$

@ eq Z $2 \cdot_{0} \times 10^{-5} + Z$
$$K_{w} = (Z) \times (2 \cdot_{0} \times 10^{-5} + Z) = 1.0 \times 10^{-14}$$

assuming the contribution to
$$[H_3O^+]$$
 is negligible (that is the Z is small) this reduces to $K_w = (Z) \times (2.0 \times 10^{-5}) = 1.0 \times 10^{-14}$ or $Z = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-5}} = 5.0 \times 10^{-10}$

Yes, Z is small compared to $2_{.0} \times 10^{-5}$. Thus, $[H_3O^+] = Z = 5_{.0} \times 10^{-10}$ M and $pH = 9.3_0$ (This is a change in pH of 0.9_7 . It resisted the change somewhat; **not** as much as part b. but better than part c.)