## $\mathrm{S}_{\mathrm{F}}$ <br> ANSWER KEY 2

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## REVIEW QUESTIONS ABOUT ACIDS AND BASES

1. A Brønsted-Lowry acid is defined as a proton $\left(\mathrm{H}^{+}\right)$donor.

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

Reaction of a weak acid and water: $\mathrm{HX}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{X}^{-}$
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: $\mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}, \mathrm{HNO}_{3}, \mathrm{H}_{2} \mathrm{SO}_{4}$, and $\mathrm{HClO}_{4}$. The other acids are classified as weak acids.
10. The inventory of 1 M HCl is $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 \mathrm{M}$ and $\left[\mathrm{Cl}^{-}\right]=1 \mathrm{M}$.

The inventory of a 1 M solution of any strong acid, HX , is $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 \mathrm{M}$ and $\left[\mathrm{X}^{-}\right]=1 \mathrm{M}$.
The inventory of a 1 M solution of any weak acid, HY , is $[\mathrm{HY}]=1 \mathrm{M}$.
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 $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{Cl}^{-}$. Thus, the solution contains many ions to support conductivity.
12. Although HCl and $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ both react as acids with water and the initial amount of HCl and $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ were the same, the resulting solutions are very different. As mentioned above, HCl reacts with water to a large extent to form $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{Cl}^{-}$ions and thus the resulting solution contains many ions to support conductivity. On the other hand, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ reacts with water to form $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$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 $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ 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 $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right.$and $\left.\mathrm{Z}^{-}\right)$than the acid HY reacted to produce ions $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right.$and $\left.\mathrm{Y}^{-}\right)$. 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 $\mathrm{OH}^{-}$and the conjugate acid to a large extent. A weak base is then defined as any base that reacts with water to form $\mathrm{OH}^{-}$and the conjugate acid to a small extent.
15. Reaction of a strong base and water: $\mathrm{B}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{HB}^{+}+\mathrm{OH}^{+}$

Reaction of a weak acid and water: $\mathrm{B}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{HB}^{+}+\mathrm{OH}$
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: $\mathrm{N}^{-3}, \mathrm{P}^{-3}, \mathrm{As}^{-3}, \mathrm{O}^{-2}, \mathrm{~S}^{-2}, \mathrm{Se}^{-2}, \mathrm{Te}^{-2}, \mathrm{H}^{-}, \mathrm{NH}_{2}^{-}$, and $\mathrm{NH}^{-2}$. The other bases are classified as weak bases.
17. The inventory of $1 \mathrm{M} \mathrm{Na}_{2} \mathrm{O}$ is $\left[\mathrm{Na}^{+}\right]=2 \mathrm{M}$ and $\left[\mathrm{OH}^{-}\right]=2 \mathrm{M}$.

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

The inventory of a 1 M solution of any strong base, B , is $\left[\mathrm{HB}^{+}\right]=1 \mathrm{M}$ and $\left[\mathrm{OH}^{-}\right]=1 \mathrm{M}$.
The inventory of a 1 M solution of any weak base, B , is $[\mathrm{B}]=1 \mathrm{M}$.
18. Liquid $\mathrm{NH}_{3}$ does not conduct because $\mathrm{NH}_{3}$ is a molecule and therefore without being involved in some kind of ionization process (like an acid/base reaction) the liquid $\mathrm{NH}_{3}$ contains no ions to support conductivity.

When the $\mathrm{NH}_{3}$ was added to the water to form the $1 \mathrm{M} \mathrm{NH}_{3}$ solution a chemical reaction occurred to a small extent to form $\mathrm{NH}_{4}^{+}$and $\mathrm{OH}^{-}$. 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 $\left(\mathrm{HZ}^{+}\right.$and $\left.\mathrm{OH}^{-}\right)$than the base Y reacted to produce ions $\left(\mathrm{HY}^{+}\right.$and $\left.\mathrm{OH}^{-}\right)$. Thus, base Z must be a stronger base than Y .
21. A. Reaction (i): $\mathrm{HR}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{R}^{-}$Small Extent

Reaction (ii): $\mathrm{HR}+\mathrm{G}^{-} \longrightarrow \mathrm{HG}+\mathrm{R}^{-} \quad$ Large Extent
Reaction (iii): $\mathrm{HY}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Y}^{-}$Large Extent
B. Reaction (i): $\mathrm{H}_{3} \mathrm{O}^{+}>\mathrm{HR}$

Reaction (ii): HR > HG
Reaction (iii): $\mathrm{HY}>\mathrm{H}_{3} \mathrm{O}^{+}$
C. Reaction (i): $\mathrm{R}^{-}>\mathrm{H}_{2} \mathrm{O}$

Reaction (ii): $\mathrm{G}^{-}>\mathrm{R}^{-}$
Reaction (iii): $\mathrm{H}_{2} \mathrm{O}>\mathrm{Y}^{-}$
D.

E. The reaction involved is:

Reaction (iv): $\mathrm{HB}+\mathrm{R}^{-} \longrightarrow \mathrm{HR}+\mathrm{B}^{-}$Small Extent
Since the solution is deep red then there must be a lot of $\mathrm{R}^{-}$present and therefore the reaction only went to a small extent. Thus, $\mathrm{B}^{-}>\mathrm{R}^{-}$as bases and $\mathrm{HR}>\mathrm{HB}$ 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 $\mathrm{B}^{-}$and $\mathrm{G}^{-}$as bases) ONE of the two following reactions must be performed and the extent of reaction determined.

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

## QUESTIONS ON EQUATION WRITING

22. a. Inventory of $0.1 \mathrm{M} \mathrm{HCl}: \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{Cl}^{-}\right]=0.1 \mathrm{M}$.

Inventory of $0.1 \mathrm{M} \mathrm{KOH}:\left[\mathrm{K}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{OH}^{-}\right]=0.1 \mathrm{M}$.
Reaction: $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\ell)$
Large Extent
b. Inventory of $0.1 \mathrm{M} \mathrm{HNO}_{3}: \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{NO}_{3}{ }^{-}\right]=0.1 \mathrm{M}$.

Inventory of $0.1 \mathrm{M} \mathrm{NH}_{3}:\left[\mathrm{NH}_{3}\right]=0.1 \mathrm{M}$.
Reaction: $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{NH}_{3}(\mathrm{aq}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell)+\mathrm{NH}_{4}^{+}(\mathrm{aq})$
Large Extent
c. Inventory of $0.1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}:\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{HSO}_{4}^{-}\right]=0.1 \mathrm{M}$.

Inventory of $0.1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}:\left[\mathrm{Na}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}\right]=0.1 \mathrm{M}$.
Reaction: $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(\mathrm{aq}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell)+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq}) \quad$ Large Extent
d. Inventory of $0.1 \mathrm{M} \mathrm{NaHSO}_{4}$ : $\left[\mathrm{Na}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{HSO}_{4}{ }^{-}\right]=0.1 \mathrm{M}$.

Inventory of $0.1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}:\left[\mathrm{Na}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}\right]=0.1 \mathrm{M}$.
Reaction: $\mathrm{HSO}_{4}{ }^{-}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}(\mathrm{aq}) \longrightarrow \mathrm{SO}_{4}{ }^{-2}(\mathrm{aq})+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq}) \quad$ Large Extent
e. Inventory of $0.1 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}:\left[\mathrm{NH}_{4}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{Cl}^{-}\right]=0.1 \mathrm{M}$.

Inventory of $0.1 \mathrm{M} \mathrm{NaOH}:\left[\mathrm{Na}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{OH}^{-}\right]=0.1 \mathrm{M}$.
Reaction: $\mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell)+\mathrm{NH}_{3}(\mathrm{aq})$
Large Extent
f. Inventory of $0.1 \mathrm{M} \mathrm{NaHCO}_{3}:\left[\mathrm{Na}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{HCO}_{3}^{-}\right]=0.1 \mathrm{M}$.

Inventory of $0.1 \mathrm{M} \mathrm{KOH}:\left[\mathrm{Li}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{OH}^{-}\right]=0.1 \mathrm{M}$.
Reaction: $\mathrm{HCO}_{3}^{-}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell)+\mathrm{CO}_{3}{ }^{-2}(\mathrm{aq})$
Large Extent
g. Inventory of $0.1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}:\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]=0.1 \mathrm{M}$.

Inventory of $0.1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}:\left[\mathrm{Na}^{+}\right]=0.1 \mathrm{M},\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]=0.1 \mathrm{M}$.
Reaction: $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(\mathrm{aq}) \longrightarrow \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}(\mathrm{aq})+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})$
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 $0.1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}:\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]=0.1 \mathrm{M}$.

Inventory of $0.1 \mathrm{M} \mathrm{MgSO}_{4}:\left[\mathrm{Mg}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{+2}\right]=0.1 \mathrm{M},\left[\mathrm{SO}_{4}^{-2}\right]=0.1 \mathrm{M}$.
Reaction: $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{SO}_{4}^{-2}(\mathrm{aq}) \longrightarrow \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}(\mathrm{aq})+\mathrm{HSO}_{4}{ }^{-}(\mathrm{aq}) \quad$ Small Extent
i. Inventory of $0.1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}:\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]=0.1 \mathrm{M}$.

Reaction: $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\ell) \longrightarrow \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
Small Extent

## QUESTIONS ABOUT THE AUTO-IONIZATION OF WATER

23. $2 \mathrm{H}_{2} \mathrm{O}(\ell) \leftleftarrows=\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

This equilibrium is present in ANY solution that contains $\mathrm{H}_{2} \mathrm{O}$.
24. $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$
25. Using the equilibrium presented in problem 23 above, $2 \mathrm{H}_{2} \mathrm{O}(\ell) \rightleftharpoons \Longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$ and letting $x$ represent the amount of $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$generated by the equilibrium the equilibrium constant expression becomes,

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}=\mathrm{x}^{2}
$$

Solving for x gives, $\mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]=\sqrt{\mathrm{K}_{\mathrm{w}}}=\sqrt{1.0 \times 10^{-14}}=1.0 \times 10^{-7}$
26. If an acid is added to water the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$will increase. The equilibrium will shift towards the water side in order to reduce the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. This shift will reduce the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$but not to the original value so that the overall $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$will be greater than $1.0 \times 10^{-7} \mathrm{M}$. However, the shift will also reduce the $\left[\mathrm{OH}^{-}\right]$and therefore it will become less than $1.0 \times 10^{-7} \mathrm{M}$.
27. If a base is added to water the $\left[\mathrm{OH}^{-}\right]$will increase. The equilibrium will shift towards the water side in order to reduce the $\left[\mathrm{OH}^{-}\right]$. This shift will reduce the $\left[\mathrm{OH}^{-}\right]$but not to the original value so that the overall $\left[\mathrm{OH}^{-}\right]$will be greater than $1.0 \times 10^{-7} \mathrm{M}$. However, the shift will also reduce the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ and therefore it will become less than $1.0 \times 10^{-7} \mathrm{M}$.
28. a) $\mathrm{HCl}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Cl}^{-}$
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) $\quad 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftleftarrows=二 \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$.
d) The added HCl will cause the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$to increase which will shift the equilibrium in part c) towards the left. Therefore the contribution of $\mathrm{H}_{3} \mathrm{O}^{+}$from the water in this solution must be less than it is in pure water. Thus the $\mathrm{H}_{3} \mathrm{O}^{+}$contributed by the equilibrium must be less than $1.0 \times 10^{-7} \mathrm{M}$ which in this case is negligible in comparison to the $\mathrm{H}_{3} \mathrm{O}^{+}$contributed by the reaction of HCl with water which is 0.10 M .
e) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.10 \mathrm{M}$ (the only significant source is the HCl )
$\therefore \mathrm{pH}=1.00$

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}=(0.10) \times\left[\mathrm{OH}^{-}\right]
$$

Solving for $\left[\mathrm{OH}^{-}\right]$gives $\left[\mathrm{OH}^{-}\right]=\frac{1.0 \times 10^{-14}}{0.10}=1.0 \times 10^{-13}$
29. a) $\mathrm{NaOH} \longrightarrow \mathrm{Na}^{+}+\mathrm{OH}^{-}$
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) $2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons=\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$.
d) The added NaOH will cause the $\left[\mathrm{OH}^{-}\right]$to increase which will shift the equilibrium in part c ) towards the left. Therefore the contribution of $\mathrm{OH}^{-}$from the water in this solution must be less than it is in pure water. Thus the $\mathrm{OH}^{-}$contributed by the equilibrium must be less than $1.0 \times 10^{-7} \mathrm{M}$ which in this case is negligible in comparison to the $\mathrm{OH}^{-}$contributed by the dissolution of NaOH with water which is 0.10 M .
e) $\left[\mathrm{OH}^{-}\right]=0.10 \mathrm{M}$ (the only significant source is the NaOH )

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \times(0.10)
$$

Solving for $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$gives $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{1.0 \times 10^{-14}}{0.10}=1.0 \times 10^{-13} \quad \therefore \mathrm{pH}=13.00$
30. a) $\mathrm{HBr}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Br}^{-}$
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) $\quad 2 \mathrm{H}_{2} \mathrm{O}(\ell) \rightleftharpoons=\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$.
d) The added HBr will cause the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$to increase which will shift the equilibrium in part c ) towards the left. Therefore the contribution of $\mathrm{H}_{3} \mathrm{O}^{+}$from the water in this solution must be less than it is in pure water. Thus the $\mathrm{H}_{3} \mathrm{O}^{+}$contributed by the equilibrium must be less than $1.0 \times 10^{-7} \mathrm{M}$ which in this case is NOT negligible in comparison to the $\mathrm{H}_{3} \mathrm{O}^{+}$contributed by the reaction of HBr with water which is $5.0 \times 10^{-8} \mathrm{M}$.
e) $\quad 2 \mathrm{H}_{2} \mathrm{O}(\ell) \rightleftharpoons \Longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \quad+\mathrm{OH}^{-}(\mathrm{aq})$.
Start $\quad 5.0 \times 10^{-8} \mathrm{M} \quad 0 \mathrm{M}$

| Change | x | x |
| :--- | :---: | :---: |
| Equil. | $5.0 \times 10^{-8} \mathrm{M}+\mathrm{x}$ | x |

$$
\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}=\left(5.0 \times 10^{-8}+\mathrm{x}\right) \cdot(\mathrm{x})=5.0 \times 10^{-8} \mathrm{x}+\mathrm{x}^{2}
$$

Rearranging gives

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

Solving for $\left[\mathrm{OH}^{-}\right]$gives
$\left[\mathrm{OH}^{-}\right]=\mathrm{x}=\frac{-5.0 \times 10^{-8}+\sqrt{\left(5.0 \times 10^{-8}\right)^{2}+4.0 \times 10^{-14}}}{2}=7.8 \times 10^{-8}$
$\therefore \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.0 \times 10^{-8}+7.8 \times 10^{-8}=12.8 \times 10^{-8}=1.3 \times 10^{-7} \quad \therefore \mathrm{pH}=6.89$
32. a) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$from water is negligible so the final $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is equal to 1.0 M
b) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$from water is negligible so the final $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is equal to $2.0 \times 10^{-4} \mathrm{M}$
c) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$from water is NOT negligible so the quadratic must be solved which yields a final $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ equal to $1.1_{6} \times 10^{-7} \mathrm{M}$
d) $\left[\mathrm{OH}^{-}\right]$from water is negligible so the final $\left[\mathrm{OH}^{-}\right]$is equal to 1.0 M and $\therefore\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.0 \times 10^{-14} \mathrm{M}$
e) $\left[\mathrm{OH}^{-}\right]$from water is negligible so the final $\left[\mathrm{OH}^{-}\right]$is equal to $2.0 \times 10^{-4} \mathrm{M}$ !!
$\therefore\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.0 \times 10^{-11} \mathrm{M}$
f) $\left[\mathrm{OH}^{-}\right]$from water is NOT negligible so the quadratic must be solved which yields a final $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$equal to $8.6_{1} \times 10^{-8} \mathrm{M}$
32. a) $\mathrm{pH}=0.00$
b) $\mathrm{pH}=3.70$
c) $\mathrm{pH}=6.94$
d) $\mathrm{pH}=14.00$
e) $\mathrm{pH}=10.30$
f) $\mathrm{pH}=7.06$
33. $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$therefore $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\operatorname{alog}(-\mathrm{pH})=10^{-\mathrm{pH}}$
a) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{0.50}=3.1{ }_{6} \mathrm{M}$
$\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} / 3.1_{6}=3.2 \times 10^{-15} \mathrm{M}$
b) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-1.0}=0.1 \mathrm{M}$
$\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} / 0.1=1 \times 10^{-13} \mathrm{M}$
c) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-4.30}=5.0 \times 10^{-5} \mathrm{M}$ $\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} / 5.0 \times 10^{-5}=2.0 \times 10^{-10} \mathrm{M}$
d) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-9.7}=2 \times 10^{-10} \mathrm{M}$
$\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} / 2 \times 10^{-10}=5 \times 10^{-5} \mathrm{M}$
e) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-14.60}=2.5 \times 10^{-15} \mathrm{M}\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} / 2.5 \times 10^{-15}=4.0 \mathrm{M}$
34. a) $\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \leftleftarrows=\Longrightarrow \mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
b) $\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}\right]}=4.9 \times 10^{-5}$
c) Yes, $\quad 2 \mathrm{H}_{2} \mathrm{O}(\ell) \rightleftarrows=\Longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
d) There are two assumptions that can be made.

First, one can assume that since $\mathrm{K}_{\mathrm{a}}$ is much greater than $\mathrm{K}_{\mathrm{w}}$ then the contribution to the total $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$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., $\mathrm{x} \ll 1.0$ and therefore $1.0-\mathrm{x}=1.0$ )
e) $\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
$1.0-\mathrm{x}$
x
x

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(1.0-\mathrm{x})}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(1.0)}=4.9 \times 10^{-5}
$$

Rearranging gives $x=\sqrt{4.9 \times 10^{-5}}=7.0 \times 10^{-3} \quad$ Therefore, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=7.0 \times 10^{-3} \mathrm{M}$

Using the relationship $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$
Solving for $\left[\mathrm{OH}^{-}\right]$gives $\left[\mathrm{OH}^{-}\right]=\frac{1.0 \times 10^{-14}}{7.0 \times 10^{-3}}=1.4 \times 10^{-12}$
Since, $\left[\mathrm{OH}^{-}\right]$is equal to the contribution of water to the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$then our first approximation is valid.
Likewise, since $1.0 \mathrm{M}-7.0 \times 10^{-3} \mathrm{M}=1.0 \mathrm{M}$, to the number of Sig Figs present in our problem then our second approximation is valid.
35. a) $\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows=\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
b) $\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}\right]}=4.9 \times 10^{-5}$
c) Yes, $2 \mathrm{H}_{2} \mathrm{O}(\ell) \rightleftarrows=\Longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
d) There are two assumptions that can be made.

First, one can assume that since $\mathrm{K}_{\mathrm{a}}$ is much greater than $\mathrm{K}_{\mathrm{w}}$ then the contribution to the total $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$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., $\mathrm{x} \ll 1.0$ and therefore $1.0-\mathrm{x}=1.0$ )
e) $\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
$0.00010-\mathrm{x} \quad \mathrm{x} \quad \mathrm{x}$

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(0.00010-\mathrm{x})}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(0.00010)}=4.9 \times 10^{-5}
$$

Rearranging gives $\quad x=\sqrt{4.9 \times 10^{-9}}=7.0 \times 10^{-5}$ Therefore, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=7.0 \times 10^{-5} \mathrm{M}$

Using the relationship $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$
Solving for $\left[\mathrm{OH}^{-}\right]$gives $\left[\mathrm{OH}^{-}\right]=\frac{1.0 \times 10^{-14}}{7.0 \times 10^{-5}}=1.4 \times 10^{-10}$
Since, $\left[\mathrm{OH}^{-}\right]$is equal to the contribution of water to the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$then our first approximation is valid.
BUT, since $0.00010 \mathrm{M}-7.0 \times 10^{-5} \mathrm{M}=0.00003 \mathrm{M}$, 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 $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{C}_{8} \mathrm{H}_{7} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{8} \mathrm{H}_{7} \mathrm{O}_{2}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(0.00010-\mathrm{x})}=4.9 \times 10^{-5}
$$

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

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

Now, solving for $\left[\mathrm{OH}^{-}\right]$gives $\left[\mathrm{OH}^{-}\right]=\frac{1.0 \times 10^{-14}}{5.0 \times 10^{-5}}=2.0 \times 10^{-10}$
36. a) Assume that the water equilibrium contributes a negligible amount of $\mathrm{H}_{3} \mathrm{O}^{+}$. Thus the only important equilibrium is :

$$
\begin{array}{cc} 
& \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \\
\text { Equil. } & 0.50-\mathrm{x}
\end{array} \mathrm{H}_{2} \mathrm{O} \rightleftharpoons \underset{\mathrm{C}}{2} \rightleftharpoons \underset{3}{\rightleftharpoons} \mathrm{C}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

Assume that $\mathrm{x} \ll 0.50$ therefore $0.50-\mathrm{x}=0.50$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]}{\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{0.50}=1.8 \times 10^{-5}
$$

Rearranging gives $\quad x=\sqrt{9.0 \times 10^{-6}}=3.0 \times 10^{-3} \quad$ Therefore, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=3.0 \times 10^{-3} \mathrm{M}$
Since $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is much larger than $1.0 \times 10^{-7}$ 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 $\left[\mathrm{OH}^{-}\right]=\mathrm{K}_{\mathrm{w}} /\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.0 \times 10^{-14} / 3.0 \times 10^{-3}=3.3 \times 10^{-12}$.

Therefore the $\mathrm{pH}=-\log \left(3.0 \times 10^{-3}\right)=2.52$
b) Assume that the water equilibrium contributes a negligible amount of $\mathrm{H}_{3} \mathrm{O}^{+}$. Thus the only important equilibrium is :

$$
\mathrm{HOCl}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{OCl}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

Equil. $0.0035-\mathrm{x} \quad \mathrm{x}$ x
Assume that $\mathrm{x} \ll 0.0035$ therefore $0.0035-\mathrm{x}=0.0035$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OCl}^{-}\right]}{[\mathrm{HOCl}]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{0.0035}=2.9 \times 10^{-8}
$$

Rearranging gives $\quad \mathrm{x}=\sqrt{1.0_{15} \times 10^{-10}}=1.0 \times 10^{-5} \quad$ Therefore, $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.0 \times 10^{-5} \mathrm{M}$
Since $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is much larger than $1.0 \times 10^{-7}$ 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 $\left[\mathrm{OH}^{-}\right]=\mathrm{K}_{\mathrm{w}} /\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.0 \times 10^{-14} / 1.0 \times 10^{-5}=1.0 \times 10^{-9}$.

Therefore the $\mathrm{pH}=-\log \left(1.0 \times 10^{-5}\right)=5.00$
c) Assume that the water equilibrium contributes a negligible amount of $\mathrm{H}_{3} \mathrm{O}^{+}$. Thus the only important equilibrium is :

Equil. $0.30-\mathrm{x} \quad \mathrm{x} \quad \mathrm{x}$
Assume that $\mathrm{x} \ll 0.30$ therefore $0.30-\mathrm{x}=0.30$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{SO}_{4}^{-2}\right]}{\left[\mathrm{HSO}_{4}^{-}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{0.30}=1.2 \times 10^{-2}
$$

Rearranging gives $x=\sqrt{3.6 \times 10^{-3}}=6.0 \times 10^{-2}$ Therefore, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=6.0 \times 10^{-2} \mathrm{M}$
Since $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is much larger than $1.0 \times 10^{-7}$ 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 $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{SO}_{4}^{-2}\right]}{\left[\mathrm{HSO}_{4}^{-}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(0.30-\mathrm{x})}=1.2 \times 10^{-2}
$$

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

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{x}=\frac{-1.2 \times 10^{-2}+\sqrt{\left(1.2 \times 10^{-2}\right)^{2}+1.44 \times 10^{-2}}}{2}=5.4 \times 10^{-2}
$$

Now, solving for $\left[\mathrm{OH}^{-}\right]$gives $\left[\mathrm{OH}^{-}\right]=\frac{1.0 \times 10^{-14}}{5.4 \times 10^{-2}}=1.8 \times 10^{-13}$
Therefore the $\mathrm{pH}=-\log \left(5.4 \times 10^{-2}\right)=1.27$
d) Assume that the water equilibrium contributes a negligible amount of $\mathrm{H}_{3} \mathrm{O}^{+}$. Thus the only important equilibrium is :

Equil. $0.010-\mathrm{x}$

$$
\mathrm{HIO}_{3}
$$

$$
\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=
$$

$$
\mathrm{IO}_{3}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

$$
\mathrm{x}
$$

$$
\mathrm{x}
$$

Assume that $\mathrm{x} \ll 0.010$ therefore $0.010-\mathrm{x}=0.010$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{IO}_{3}^{-}\right]}{\left[\mathrm{HIO}_{3}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{0.010}=1.6 \times 10^{-1}
$$

Rearranging gives $\quad x=\sqrt{1.6 \times 10^{-3}}=4.0 \times 10^{-2} \quad$ Therefore, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=4.0 \times 10^{-2} \mathrm{M}$
Since $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is much larger than $1.0 \times 10^{-7}$ 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 $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$.

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{IO}_{3}^{-}\right]}{\left[\mathrm{HIO}_{3}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(0.010-\mathrm{x})}=1.6 \times 10^{-1}
$$

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

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=x=\frac{-1.6 \times 10^{-1}+\sqrt{\left(1.6 \times 10^{-1}\right)^{2}+6.4 \times 10^{-3}}}{2}=9.443 \times 10^{-3}
$$

Now, solving for $\left[\mathrm{OH}^{-}\right]$gives $\left[\mathrm{OH}^{-}\right]=\frac{1.0 \times 10^{-14}}{9.4_{43} \times 10^{-3}}=1.1 \times 10^{-12}$
Therefore the $\mathrm{pH}=-\log \left(9.4_{43} \times 10^{-3}\right)=2.02$
37. a) $\mathrm{K}_{\mathrm{b}}=\mathrm{K}_{\mathrm{w}} / \mathrm{K}_{\mathrm{a}(\text { CA })}=1.0 \times 10^{-14} / 1.8 \times 10^{-5}=5.6 \times 10^{-10}$
b) $\mathrm{K}_{\mathrm{b}}=\mathrm{K}_{\mathrm{w}} / \mathrm{K}_{\mathrm{a}(\mathrm{CA})}=1.0 \times 10^{-14} / 1.2 \times 10^{-2}=8.3 \times 10^{-13}$
c) $\mathrm{K}_{\mathrm{b}}=\mathrm{K}_{\mathrm{w}} / \mathrm{K}_{\mathrm{a}(\mathrm{CA})}=1.0 \times 10^{-14} / 5.6 \times 10^{-11}=1.8 \times 10^{-4}$
38. a) $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \Longrightarrow \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}^{-}$
b) $\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]}=5.6 \times 10^{-10}$
c) Yes, $2 \mathrm{H}_{2} \mathrm{O}(\ell) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
d) There are two assumptions that can be made.

First, one can assume that since $\mathrm{K}_{\mathrm{b}}$ is much greater than $\mathrm{K}_{\mathrm{w}}$ then the contribution to the total $\left[\mathrm{OH}^{-}\right]$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., $\mathrm{x} \ll 1.0$ and therefore $1.0-\mathrm{x}=1.0$ )
e) $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{OH}^{-}$
$1.0-\mathrm{x} \quad \mathrm{x} \quad \mathrm{x}$

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{O}_{2}^{-}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(1.0-\mathrm{x})}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(1.0)}=5.5_{6} \times 10^{-10}
$$

Rearranging gives $\mathrm{x}=\sqrt{5.5_{6} \times 10^{-10}}=2.3_{6} \times 10^{-5}$ Therefore, $\left[\mathrm{OH}^{-}\right]=2.3_{6} \times 10^{-5} \mathrm{M}$

Using the relationship $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$
Solving for $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$gives $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{1.0 \times 10^{-14}}{2.3_{6} \times 10^{-5}}=4.2_{4} \times 10^{-10}$
Since, $\left[\mathrm{OH}^{-}\right]$is equal to the contribution of water to the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$then our first approximation is valid.
Likewise, since $1 \mathrm{M}-2.3_{6} \times 10^{-5} \mathrm{M}=1 \mathrm{M}$, to the number of Sig Figs present in our problem then our second approximation is valid.

Therefore the $\mathrm{pH}=-\log \left(4.2_{4} \times 10^{-10}\right)=9.37$
39. a) $\mathrm{OCl}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{HOCl}+\mathrm{OH}$
b) $\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}\right][\mathrm{HOCl}]}{\left[\mathrm{OCl}^{-}\right]}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{K}_{\mathrm{a}(\mathrm{HOCl})}}=\frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}}=3.4_{5} \times 10^{-7}$
c) Yes, $2 \mathrm{H}_{2} \mathrm{O}(\ell) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
d) There are two assumptions that can be made.

First, one can assume that since $\mathrm{K}_{\mathrm{b}}$ is much greater than $\mathrm{K}_{\mathrm{w}}$ then the contribution to the total $\left[\mathrm{OH}^{-}\right]$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 $0.75-\mathrm{x}=0.75$ )
e) $\mathrm{OCl}^{-}+\mathrm{H}_{2} \mathrm{O} \leftleftarrows=\mathrm{HOCl}+\mathrm{OH}^{-}$
$0.75-\mathrm{x} \quad \mathrm{x}$

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}\right][\mathrm{HOCl}]}{\left[\mathrm{OCl}^{-}\right]}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(0.75-\mathrm{x})}=\frac{(\mathrm{x}) \cdot(\mathrm{x})}{(0.75)}=3.4_{5} \times 10^{-7}
$$

Rearranging gives $\quad x=\sqrt{3.4_{5} \times 10^{-7} \times 0.75}=5.0_{9} \times 10^{-4}$ Therefore, $\left[\mathrm{OH}^{-}\right]=5.0_{9} \times 10^{-4} \mathrm{M}$

Using the relationship $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$
Solving for $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$gives $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{1.0 \times 10^{-14}}{5.0_{9} \times 10^{-4}}=1.9_{7} \times 10^{-11}$
Since, $\left[\mathrm{OH}^{-}\right]$is equal to the contribution of water to the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$then our first approximation is valid.
Likewise, since $0.75 \mathrm{M}-5.0_{9} \times 10^{-4} \mathrm{M}=0.75 \mathrm{M}$, to the number of Sig Figs present in our problem then our second approximation is valid.

Therefore the $\mathrm{pH}=-\log \left(1.9_{7} \times 10^{-11}\right)=10.71$
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 $\mathrm{K}_{\mathrm{a}}$ of the acid and the $\mathrm{K}_{\mathrm{b}}$ 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: $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons==\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$

The principal pH determining equilibrium: $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \Longrightarrow \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
b) The principal acid/base equilibrium: $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-} \rightleftharpoons=\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ The principal pH determining equilibrium: $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows=\Longrightarrow \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}$
c) The principal acid/base equilibrium: $\mathrm{NH}_{4}^{+}+\mathrm{SO}_{4}^{-2} \leftleftarrows=二 \mathrm{HSO}_{4}^{-}+\mathrm{NH}_{3}$ The principal pH determining equilibrium: $\mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows=\Longrightarrow \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}$
d) The principal acid/base equilibrium: $\mathrm{HCO}_{3}{ }^{-}+\mathrm{HCO}_{3}{ }^{-} \leftleftarrows=\Longrightarrow \mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{CO}_{3}{ }^{-2}$ The principal pH determining equilibrium: $\mathrm{HCO}_{3}{ }^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \Longrightarrow \mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{OH}^{-}$
42. B, C, D as these are the only solutions that contain both a weak acid and weak base in appreciable amounts.
43. a) $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$

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

$$
\begin{aligned}
& \text { @ eq } \\
& \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \\
& 1-\mathrm{X}
\end{aligned}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \underset{2}{\rightleftarrows} \underset{\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}}{ }+\underset{\mathrm{X}}{\mathrm{H}_{3} \mathrm{O}^{+}}
$$

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{\mathrm{X}^{2}}{1-\mathrm{X}}=1.8 \times 10^{-5} \quad \text { after assuming } 1-\mathrm{X}=1 \text { this reduces to } \\
& \mathrm{K}_{\mathrm{a}}=\mathrm{X}^{2}=1.8 \times 10^{-5} \text { or } \mathrm{X}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\mathrm{K}_{\mathrm{a}}}=\sqrt{1.8 \times 10^{-5}}=4.24 \times 10^{-3} \\
& \therefore \mathrm{pH}=2.3_{7}
\end{aligned}
$$

b) $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and $1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$

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

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-} \rightleftharpoons==\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}
$$

Which goes nowhere and can therefore be ignored.
The principal pH determining equilibrium is:

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{(\mathrm{X}) \times(1+\mathrm{X})}{1-\mathrm{X}}=1.8 \times 10^{-5} \\
& K_{a}=X=1.8 \times 10^{-5} \\
& \therefore \mathrm{pH}=4.7_{4}
\end{aligned}
$$

c) $1 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$

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

$$
\mathrm{NH}_{4}^{+}+\mathrm{SO}_{4}^{-2} \rightleftarrows=\mathrm{HSO}_{4}^{-}+\mathrm{NH}_{3}
$$

Before we can solving the equilibrium problem for this system we must first determine the value of $\mathrm{K}_{\mathrm{eq}}$ for this equilibrium.

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{HSO}_{4}^{-}\right]}{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{SO}_{4}^{-2}\right]}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{HSO}_{4}^{-}\right]}{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{SO}_{4}^{-2}\right]} \cdot \frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NH}_{3}\right]}{\left[\mathrm{NH}_{4}^{+}\right]} \cdot \frac{\left[\mathrm{HSO}_{4}^{-}\right]}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{SO}_{4}^{-2}\right]}
$$

Thus we can see:

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{HSO}_{4}^{-}\right]}{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{SO}_{4}^{-2}\right]}=\mathrm{K}_{\mathrm{a}\left(\mathrm{NH}_{4}^{+}\right)} \cdot \frac{1}{\mathrm{~K}_{\mathrm{a}_{2}\left(\mathrm{HSO}_{4}^{-}\right)}}=5.5_{6} \times 10^{-10} \cdot \frac{1}{1.0 \times 10^{-2}}=5.5_{6} \times 10^{-8}
$$

Returning to the equilibrium,

$$
\begin{aligned}
& \mathrm{NH}_{4}^{+}+\mathrm{SO}_{4}^{-2} \rightleftharpoons \Longrightarrow \mathrm{HSO}_{4}{ }^{-}+\mathrm{NH}_{3} \\
& \text { @ eq } \begin{array}{lllll}
2-\mathrm{X} & 1-\mathrm{X} & \mathrm{X} & \mathrm{X}
\end{array} \\
& \mathrm{~K}_{\mathrm{eq}}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{HSO}_{4}^{-}\right]}{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{SO}_{4}^{-2}\right]}=\frac{(\mathrm{X})(\mathrm{X})}{(2-\mathrm{X})(1-\mathrm{X})}=5.5_{6} \times 10^{-8}
\end{aligned}
$$

after assuming $1-\mathrm{X}=1$ this reduces to

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{HSO}_{4}^{-}\right]}{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{SO}_{4}^{-2}\right]}=\frac{\mathrm{X}^{2}}{(2)}=5.5_{6} \times 10^{-8} \text { or } \mathrm{X}=\sqrt{2 \cdot 5.5_{6} \times 10^{-8}}=3_{3} \times 10^{-4}
$$

$\therefore\left[\mathrm{NH}_{3}\right]=\left[\mathrm{HSO}_{4}^{-}\right]=\mathrm{X}=3.3 \times 10^{-4} \mathrm{M} \&\left[\mathrm{NH}_{4}^{+}\right]=2-\mathrm{X}=2 \mathrm{M} \&\left[\mathrm{SO}_{4}^{-2}\right]=1-\mathrm{X}=1 \mathrm{M}$
Now to solve the principle pH determining equilibrium (ignoring the contribution from water):

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{(\mathrm{Y}) \times\left(3 .{ }_{3} \times 10^{-4}+\mathrm{Y}\right)}{2-\mathrm{Y}}=5.6 \times 10^{-10}
\end{aligned}
$$

after assuming $3.3 \times 10^{-4}+\mathrm{Y}=3 .{ }_{3} \times 10^{-4}$ this reduces to

$$
\begin{aligned}
\mathrm{K}_{\mathrm{a}} & =\frac{(\mathrm{Y}) \times\left(3.3^{\times} \times 10^{-4}\right)}{2}=5 . .^{\times 1} 0^{-10} \text { and } \therefore \quad \mathrm{Y}=\frac{(2) \cdot\left(5.6 \times 10^{-10}\right)}{\left(3 . ._{3} \times 10^{-4}\right)}=3.4 \times 10^{-6} \\
\therefore\left[\mathrm{NH}_{3}\right] & =3 ._{3} \times 10^{-4} \mathrm{M} \& \quad\left[\mathrm{NH}_{4}^{+}\right]=2-\mathrm{Y}=2 \mathrm{M} \quad \& \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=3.4 \times 10^{-6} \mathrm{M}
\end{aligned}
$$

(the assumption that $3.3 \times 10^{-4}+\mathrm{Y}=3.3 \times 10^{-4}$ valid)

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

$$
\mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(3 . ._{4} \times 10^{-6}+\mathrm{Z}\right)=1.0 \times 10^{-14}
$$

assuming that $3 ._{4} \times 10^{-6}+\mathrm{Z}=3.4 \times 10^{-6}$ this reduces to
$\mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(3.4 \times 10^{-6}\right)=1.0 \times 10^{-14}$ or $\mathrm{Z}=\frac{1.0 \times 10^{-14}}{3 . \mathrm{A}^{\times} \times 10^{-6}}=3 .{ }_{0} \times 10^{-9}$
Yes, the assumption, $3.4 \times 10^{-6}+\mathrm{Z}=3.4 \times 10^{-6}$ is valid. Thus, $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=3.4 \times 10^{-6} \mathrm{M}$ and

$$
\mathrm{pH}=5.4_{8}
$$

d) $1 \mathrm{M} \mathrm{NaHCO}_{3}$

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

$$
\mathrm{HCO}_{3}^{-}+\mathrm{HCO}_{3}^{-} \rightleftharpoons=\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{CO}_{3}^{-2}
$$

Before we can solving the equilibrium problem for this system we must first determine the value of $\mathrm{K}_{\mathrm{eq}}$ for this equilibrium.

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]} \cdot \frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]} \cdot \frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCO}_{3}^{-}\right]}
$$

Thus we can see:

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\mathrm{K}_{\mathrm{a}\left(\mathrm{HCO}_{3}^{-}\right)} \cdot \frac{1}{\mathrm{~K}_{\mathrm{a}\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)}}=5.6 \times 10^{-11} \cdot \frac{1}{4.3 \times 10^{-7}}=1.3_{0} \times 10^{-4}
$$

Returning to the equilibrium,

$$
\begin{array}{cl} 
& 2 \mathrm{HCO}_{3}^{-} \\
\text {@ eq } & 1-2 \mathrm{X} \\
\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{CO}_{3}^{-2} \\
\mathrm{~K}_{\mathrm{eq}} & =\frac{\mathrm{X}}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]} \\
& {\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}
\end{array}=\frac{(\mathrm{X})(\mathrm{X})}{(1-2 \mathrm{X})^{2}}=1.3_{0} \times 10^{-4} .
$$

after assuming $1-2 \mathrm{X}=1$ this reduces to
$\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\frac{\mathrm{X}^{2}}{(1)^{2}}=1.3_{0} \times 10^{-4}$ or $\mathrm{X}=\sqrt{1.3_{0} \times 10^{-4}}=1 .{ }_{1} \times 10^{-2}$
The assumption, $1-2 \mathrm{X}=1$ is valid. $\therefore\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=\left[\mathrm{CO}_{3}^{-2}\right]=\mathrm{X}=1 .{ }_{.1} \times 10^{-2} \mathrm{M}$
$\boldsymbol{\&}\left[\mathrm{HCO}_{3}^{-}\right]=1-2 \mathrm{X}=1 \mathrm{M}$

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

$$
\begin{aligned}
& \mathrm{HCO}_{3}{ }^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows=\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{OH} \\
& \text { @ eq } 1-\mathrm{Y} \quad 1 .{ }_{1} \times 10^{-2}+\mathrm{Y} \quad \mathrm{Y} \\
& \mathrm{~K}_{\mathrm{b}\left(\mathrm{HCO}_{3}^{-}\right)}=\frac{(\mathrm{Y}) \times\left(1.1 \times 10^{-2}+\mathrm{Y}\right)}{(1-\mathrm{Y})}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)}}=\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}}=2.3 \times 10^{-8}
\end{aligned}
$$

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

$$
\begin{aligned}
\mathrm{K}_{\mathrm{b}} & =\frac{(\mathrm{Y}) \times\left(1.1 \times 10^{-2}\right)}{1}=2.3 \times 10^{-8} \quad \text { and } \therefore \quad \mathrm{Y}=\frac{(1) \cdot\left(2.3 \times 10^{-8}\right)}{\left(1 . ._{1} \times 10^{-2}\right)}=2.1 \times 10^{-6} \\
\therefore\left[\mathrm{OH}^{-}\right] & =2 . ._{1} \times 10^{-6} \mathrm{M} \& \quad\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=1.1 \times 10^{-2} \mathrm{M} \&\left[\mathrm{HCO}_{3}^{-}\right]=1-\mathrm{Y}=1 \mathrm{M}
\end{aligned}
$$

To check on our assumption that the contribution from water is negligible and determine $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$,

$$
\begin{array}{cc} 
& 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \\
\mathrm{Z} & +\begin{array}{l}
\mathrm{OH}^{-}(\mathrm{aq}) \\
2.1_{1} \times 10^{-6}+\mathrm{Z}
\end{array}
\end{array}
$$

$\mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(2 .{ }^{1} \times 10^{-6}+\mathrm{Z}\right)=1.0 \times 10^{-14}$
assuming the contribution to $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is negligible (that is the Z is small) this reduces to
$\mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(2.1 \times 10^{-6}\right)=1.0 \times 10^{-14}$ or $\mathrm{Z}=\frac{1.0 \times 10^{-14}}{2 .{ }_{1} \times 10^{-6}}=4 .{ }_{8} \times 10^{-9}$
Yes, Z is small compared to $2 .{ }^{1} \times 10^{-6}$. Thus, $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{Z}=4.8 \times 10^{-9} \mathrm{M}$ and

$$
\mathrm{pH}=8.33
$$

44. a) $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$

When 0.10 moles of HCl are added to $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ the HCl will react with $\mathrm{H}_{2} \mathrm{O}$ (the strongest base present in large amount) to form $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{Cl}^{-}$to $100 \%$. Therefore after this reaction the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{Cl}^{-}\right]=0.10 \mathrm{M}$

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

$$
\begin{array}{lcc}
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows & \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-} & +\mathrm{H}_{3} \mathrm{O}^{+} \\
\text {Init. } 1 & 0 & 0.10 \\
\text { @ eq } 1-\mathrm{X} & & \mathrm{X}
\end{array} 0.10+\mathrm{X}
$$

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{(\mathrm{X})(0.10+\mathrm{X})}{(1-\mathrm{X})}=1.8 \times 10^{-5} \\
& 1-\mathrm{X}=1 \text { this reduces to after assu } \\
& \mathrm{K}_{\mathrm{a}}=(\mathrm{X})(0.10)=1.8 \times 10^{-5} \text { or } \mathrm{X}=\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]=\frac{1.8 \times 10^{-5}}{0.10}=1.8 \times 10^{-4}
\end{aligned}
$$

$\therefore \quad$ the assumption is valid and $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.10 \mathrm{pH}=10$
(the same pH that would be produced if 0.10 moles of HCl had been added to pure $\mathrm{H}_{2} \mathrm{O}$ !!) This solution offered NO resistance to pH change.
b) $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and $1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$

When 0.10 moles of HCl are added to a mixture of $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and $1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, the HCl will react with $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$, (the strongest base present in large amount) to form $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, and $\mathrm{H}_{2} \mathrm{O}$ to $100 \%$. Thus, after this reaction the $\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]=1.1 \mathrm{M},\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]=0.9 \mathrm{M}, \&$ $\left[\mathrm{Cl}^{-}\right]=0.10 \mathrm{M}$

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

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-} \rightleftharpoons=\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}
$$

Which goes nowhere and can therefore be ignored.
The principal pH determining equilibrium is:

$$
\begin{aligned}
& \quad \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \\
& \text { Init } \begin{array}{l}
1.1
\end{array} \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& \text {a eq } 1.1-\mathrm{X} \\
& 0.9+\mathrm{X} \quad \mathrm{X} \\
& \mathrm{~K}_{\mathrm{a}}=\frac{(\mathrm{X}) \times(0.9+\mathrm{X})}{(1.1-\mathrm{X})}=1.8 \times 10^{-5} \\
& \mathrm{~K}_{\mathrm{a}}=\frac{(\mathrm{X}) \times(0.9)}{(1.1)}=1.8 \times 10^{-5} \quad \therefore \quad \mathrm{X}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\left(\mathrm{K}_{\mathrm{a}}\right)(1.1)}{(0.9)}=2.2 \times 10^{-5} \\
& \therefore \mathrm{pH}=4.66 \text { (almost the same } \mathrm{pH} \text { as before, the change in } \mathrm{pH}=0.08!)
\end{aligned}
$$

c) $1 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$

When 0.10 moles of HCl are added to $1 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$, the HCl will react with $\mathrm{SO}_{4}{ }^{-2}$, (the strongest base present in large amount) to form $\mathrm{HSO}_{4}^{-}$, and $\mathrm{Cl}^{-}$to $100 \%$. Thus, after this reaction the $\left[\mathrm{HSO}_{4}^{-}\right]=0.1 \mathrm{M},\left[\mathrm{SO}_{4}^{-2}\right]=0.9 \mathrm{M}, \&\left[\mathrm{NH}_{4}^{+}\right]=2.0 \mathrm{M} \quad \& \quad\left[\mathrm{Cl}^{-}\right]=0.10 \mathrm{M}$

There is a NEW principal acid/base equilibrium now since the strongest acid (NOW) is $\mathrm{HSO}_{4}^{-}$while the strongest base remains $\mathrm{SO}_{4}^{-2}$ :

$$
\mathrm{HSO}_{4}^{-}+\mathrm{SO}_{4}^{-2} \rightleftarrows=\mathrm{HSO}_{4}^{-}+\mathrm{SO}_{4}^{-2}
$$

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 $\mathrm{HSO}_{4}^{-}$is the strongest acid present (it is stronger than $\mathrm{NH}_{4}^{+}$). (Ignoring the contribution from water):

$$
\begin{aligned}
& \mathrm{HSO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{SO}_{4}^{-2}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& \text {Init } 0.10 \quad 0.9 \\
& \text { @ eq } 0.10-\mathrm{X} \quad 0.9+\mathrm{X} \text { X } \\
& \mathrm{K}_{\mathrm{a}}=\frac{(\mathrm{X})(0.9+\mathrm{X})}{(0.10-\mathrm{X})}=1.0 \times 10^{-2}
\end{aligned}
$$

after assuming $0.10-\mathrm{X}=0.10$ and assuming $0.9-\mathrm{X}=0.9$, this reduces to

$$
\mathrm{K}_{\mathrm{a}}=\frac{(\mathrm{X})(0.90)}{(0.10)}=1.0 \times 10^{-2} \quad \text { and } \therefore \quad \mathrm{X}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{(0.10)\left(1.0 \times 10^{-2}\right)}{(0.9)}=1.1 \times 10^{-3}
$$

There is another equilibrium present that must be solved to check the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$.

$$
\begin{array}{lcc} 
& \mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons= & \mathrm{NH}_{3}
\end{array} \begin{gathered}
\mathrm{H}_{3} \mathrm{O}^{+} \\
\text {Init. } \\
2.0 \\
\text { @ eq } \\
2.0-\mathrm{Y}
\end{gathered} \mathrm{Y}_{1.1 \times 10^{-3}} \begin{aligned}
& \mathrm{Y}+1.1 \times 10^{-3} \\
& \mathrm{~K}_{\mathrm{a}}=\frac{(\mathrm{Y})\left(1.1 \times 10^{-3}+\mathrm{Y}\right)}{(2.0-\mathrm{Y})}=5.5_{6} \times 10^{-10} \\
&
\end{aligned}
$$

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

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

Yes, the contribution of $\mathrm{H}_{3} \mathrm{O}^{+}$from the reaction of $\mathrm{NH}_{4}^{+}$is negligible.
$\therefore\left[\mathrm{Cl}^{-}\right]=0.1 \mathrm{M} \mathrm{;}\left[\mathrm{HSO}_{4}^{-}\right]=0.1 \mathrm{M} ;\left[\mathrm{SO}_{4}^{-2}\right]=0.9 \mathrm{M} \mathrm{;}\left[\mathrm{NH}_{4}^{+}\right]=2.0 \mathrm{M}$ $\boldsymbol{\&}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.1 \times 10^{-3} \mathrm{M}$

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

$$
\begin{aligned}
& \quad 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \\
& \text { @ eq } \\
& \\
& 1.1 \times 10^{-3}+\mathrm{Z} \\
& \mathrm{H}_{3}(\mathrm{aq})+ \\
& \mathrm{OH}^{-}(\mathrm{aq}) \\
& \mathrm{Z}
\end{aligned}
$$

assuming the contribution to $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is negligible (that is the Z is small) this reduces to

$$
\mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(1.1 \times 10^{-3}\right)=1.0 \times 10^{-14} \text { or } \mathrm{Z}=\frac{1.0 \times 10^{-14}}{1.1 \times 10^{-3}}=9.1 \times 10^{-12}
$$

Yes, Z is small compared to $1.1 \times 10^{-3}$. Thus, $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.1 \times 10^{-3} \mathrm{M}$ and

$$
\mathrm{pH}=2.96 \text { (This is a change in } \mathrm{pH} \text { of } 2.88 \text {. It resisted the change somewhat but not }
$$ as much as part b.)

d) $1 \mathrm{M} \mathrm{NaHCO}_{3}$

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

$$
\mathrm{HCO}_{3}^{-}+\mathrm{HCO}_{3}^{-} \rightleftarrows \mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{CO}_{3}^{-2}
$$

Before we can solving the equilibrium problem for this system we must first determine the value of $\mathrm{K}_{\mathrm{eq}}$ for this equilibrium.
$\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]} \cdot \frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]} \cdot \frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCO}_{3}^{-}\right]}$

Thus we can see:

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\mathrm{K}_{\mathrm{a}\left(\mathrm{HCO}_{3}^{-}\right)} \cdot \frac{1}{\mathrm{~K}_{\mathrm{a}\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)}}=5.6 \times 10^{-11} \cdot \frac{1}{4.3 \times 10^{-7}}=1.3 \times 10^{-4}
$$

Returning to the equilibrium,

$$
\begin{array}{r}
2 \mathrm{HCO}_{3}^{-} \rightleftharpoons \Longrightarrow \mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{CO}_{3}^{-2} \\
\mathrm{~K}_{\mathrm{eq}}=\frac{\left[\mathrm{eq}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\frac{(\mathrm{X})(\mathrm{X})}{(1.0-2 \mathrm{X})^{2}}=1.3_{0} \times 10^{-4}
\end{array}
$$

after assuming $1-2 \mathrm{X}=1$ this reduces to

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\frac{\mathrm{X}^{2}}{(1.0)^{2}}=1.3_{0} \times 10^{-4} \text { or } \mathrm{X}=\sqrt{1.3_{0} \times 10^{-4}}=1.1 \times 10^{-2}
$$

$\therefore\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=\left[\mathrm{CO}_{3}^{-2}\right]=\mathrm{X}=1.1 \times 10^{-2} \mathrm{M}$ \& $\left[\mathrm{HCO}_{3}^{-}\right]=1-2 \mathrm{X}=1 \mathrm{M}$
Now to solve the principle pH determining equilibrium (ignoring the contribution from water):

$$
\begin{aligned}
& \quad \mathrm{HCO}_{3}^{-}+\mathrm{H}_{2} \mathrm{O} \underset{1.1 \times 10^{-2}+\mathrm{Y}}{\stackrel{\mathrm{H}_{2} \mathrm{CO}_{3}}{\rightleftharpoons}+\mathrm{Y}} \mathrm{OH}^{-} \\
& \text {@ eq } 1-\mathrm{Y} \\
& \mathrm{~K}_{\mathrm{b}\left(\mathrm{HCO}_{3}^{-}\right)}=\frac{(\mathrm{Y}) \times\left(1.1 \times 10^{-2}+\mathrm{Y}\right)}{1.0-\mathrm{Y}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)}}=\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}}=2.3 \times 10^{-8}
\end{aligned}
$$

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

$$
\begin{aligned}
\mathrm{K}_{\mathrm{b}} & =\frac{(\mathrm{Y}) \times\left(1.1 \times 10^{-2}\right)}{1.0}=2.3_{3} \times 10^{-8} \quad \text { and } \therefore \quad \mathrm{Y}=\frac{(1.0) \cdot\left(2.3_{3} \times 10^{-8}\right)}{\left(1.1 \times 10^{-2}\right)}=2.1_{1} \times 10^{-6} \\
\therefore\left[\mathrm{OH}^{-}\right] & =2.1_{1} \times 10^{-6} \mathrm{M} \& \quad\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=1.1 \times 10^{-2} \mathrm{M} \&\left[\mathrm{HCO}_{3}^{-}\right]=1-\mathrm{Y}=1 \mathrm{M}
\end{aligned}
$$

To check on our assumption that the contribution from water is negligible and determine $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$,

$$
\begin{aligned}
& 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+ \\
& \mathrm{Z} \\
& \text { @ eq } \\
& \mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(2.1_{1} \times 10^{-6}+\mathrm{Z}\right)=1.0 \times 10^{-14} \\
& 2.1_{1} \times 10^{-6}+\mathrm{Zq}
\end{aligned}
$$

assuming the contribution to $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is negligible (that is the Z is small) this reduces to

$$
\mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(2.1_{1} \times 10^{-6}\right)=1.0 \times 10^{-14} \text { or } \mathrm{Z}=\frac{1.0 \times 10^{-14}}{2.1_{1} \times 10^{-6}}=4.7 \times 10^{-9}
$$

Yes, Z is small compared to $2.1_{1} \times 10^{-6}$. Thus, $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{Z}=4.7 \times 10^{-9} \mathrm{M}$ and $\mathrm{pH}=8.33$
45. a) $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$

When 0.10 moles of NaOH are added to $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ the NaOH will react with $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ (the strongest acid present in large amount) to form $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$to $100 \%$. Therefore after this reaction the $\left[\mathrm{Na}^{+}\right]=\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]=0.10 \mathrm{M}$ and $\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]=0.9$

As before, the principal acid/base equilibrium AND the principal pH determining equilibrium is:
$\therefore \quad$ the assumptions are valid and $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 .{ }_{6} \times 10^{-4} \mathrm{pH}=3.8_{0}$ This solution offered some resistance to pH change.
b) $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and $1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$

When 0.10 moles of NaOH are added to a mixture of $1 \mathrm{M} \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ and $1 \mathrm{M} \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, the NaOH will react with $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$, (the strongest acid present in large amount) to form $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$, and $\mathrm{H}_{2} \mathrm{O}$ to $100 \%$.
Thus, after this reaction, $\left[\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right]=0.9 \mathrm{M},\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]=1.1 \mathrm{M}, \&\left[\mathrm{Na}^{+}\right]=0.10 \mathrm{M}$
As stated in problem 43 b , the principal acid/base equilibrium is:

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-} \rightleftharpoons=\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}
$$

Which goes nowhere and can therefore be ignored.
The principal pH determining equilibrium is:

$$
\begin{aligned}
& \quad \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& \text {Init } 0.9 \\
& \\
& \text { @ eq } 0.9-\mathrm{X}
\end{aligned}
$$

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{(\mathrm{X}) \times(1.1+\mathrm{X})}{(0.9-\mathrm{X})}=1.8 \times 10^{-5} \\
& \text { es to } \mathrm{K}_{\mathrm{a}}=\frac{(\mathrm{X}) \times(1.1)}{(1.9)}=1.8 \times 10^{-5} \quad \therefore \quad \mathrm{X}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{\left(\mathrm{K}_{\mathrm{a}}\right)(0.9)}{(1.1)}=1.4_{7} \times 10^{-5}
\end{aligned}
$$

$\therefore \mathrm{pH}=4.83$ (almost the same pH as before, the change in $\mathrm{pH}=0.09$ !)
c) $1 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$

When 0.10 moles of NaOH are added to $1 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$, the NaOH will react with $\mathrm{NH}_{4}^{+}$, (the strongest acid present in large amount) to form $\mathrm{NH}_{3}$, and $\mathrm{H}_{2} \mathrm{O}$ to $100 \%$. Thus, after this reaction the $\left[\mathrm{NH}_{3}\right]=0.1 \mathrm{M},\left[\mathrm{SO}_{4}^{-2}\right]=1 \mathrm{M}, \&\left[\mathrm{NH}_{4}^{+}\right]=1.9 \mathrm{M} \quad \&\left[\mathrm{Na}^{+}\right]=0.10 \mathrm{M}$

There is a NEW principal acid/base equilibrium now since the strongest base (NOW) is $\mathrm{NH}_{3}$ while the strongest acid remains $\mathrm{NH}_{4}^{+}: \mathrm{NH}_{4}^{+}+\mathrm{NH}_{3} \rightleftarrows=\Longrightarrow \mathrm{NH}_{4}^{+}+\mathrm{NH}_{3}$ which goes nowhere and can therefore be ignored.

$$
\begin{aligned}
& \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \\
& \text {Init. } 0.9 \quad 0.10 \quad 0 \\
& \text { @ eq 0.9-X } \\
& 0.10+\mathrm{X} \quad \mathrm{X} \\
& \begin{array}{l}
\mathrm{K}_{\mathrm{a}}=\frac{(\mathrm{X})(0.10+\mathrm{X})}{(0.9-\mathrm{X})}=1.8 \times 10^{-5} \quad 0.9-\mathrm{X}=0.9, \text { this reduces to } \quad \text { after assuming } 0 \\
\mathrm{~K}_{\mathrm{a}}=\frac{(\mathrm{X})(0.10)}{(0.9)}=1.8 \times 10^{-5} \text { or } \mathrm{X}=\left[\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}\right]=\frac{\left(1.8 \times 10^{-5}\right)(0.9)}{0.10}=1 .{ }_{6} \times 10^{-4}
\end{array}
\end{aligned}
$$

Now to solve the principle pH determining equilibrium which is different than before as $\mathrm{NH}_{3}$ is present AND is a stronger base than $\mathrm{SO}_{4}^{-2}$ AND is a better base than $\mathrm{NH}_{4}+$ is as an acid. (Ignoring the contribution from water):

$$
\begin{array}{llrl} 
& \mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \underset{\mathrm{O}}{\rightleftarrows} \mathrm{NH}+{ }_{4}^{+} & + & \mathrm{OH}^{-} \\
\text {Init } & 0.10 & 1.9 & \\
\text { @ eq } & 0.10-\mathrm{X} & 1.9+\mathrm{X} & \mathrm{X} \\
& & \\
\mathrm{~K}_{\mathrm{b}}=\frac{(\mathrm{X})(1.9+\mathrm{X})}{(0.10-\mathrm{X})}=5.5_{6} \times 10^{-8} & \text { after assuming } 0.10-\mathrm{X}=0.10
\end{array}
$$

this reduces to

$$
\mathrm{K}_{\mathrm{b}}=\frac{(\mathrm{X})(1.9)}{(0.10)}=1.8 \times 10^{-5} \quad \text { and } \therefore \quad \mathrm{X}=[\mathrm{OH}-]=\frac{(0.10)\left(1.8 \times 10^{-5}\right)}{(1.9)}=9.44_{7} \times 10^{-7}
$$

The water equilibrium present that must be solved to check the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$.

|  | $2 \mathrm{H}_{2} \mathrm{O} \underset{\mathrm{O}}{\rightleftarrows} \mathrm{OH}^{-}$ |  |
| :--- | :---: | :---: |
| Init. | $9.4_{7} \times 10^{-7}$ | $\mathrm{H}_{3} \mathrm{O}^{+}$ |
| @ eq | $\mathrm{Y}+9.4_{7} \times 10^{-7}$ | Y |
|  |  |  |
| $\mathrm{K}_{\mathrm{w}}=$ | $(\mathrm{Y})\left(9.4_{7} \times 10^{-7}+\mathrm{Y}\right)=1.0 \times 10^{-14}$ |  |

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

$$
\mathrm{K}_{\mathrm{w}}=(\mathrm{Y}) \times\left(9.4_{7} \times 10^{-7}\right)=1.0 \times 10^{-14} \text { and } \therefore \quad \mathrm{Y}=\frac{1.0 \times 10^{-14}}{9.4_{7} \times 10^{-7}}=1.0_{8} \times 10^{-8}
$$

Yes, the contribution of $\mathrm{OH}^{-}$from the reaction of $\mathrm{H}_{2} \mathrm{O}$ is negligible.
$\therefore\left[\mathrm{Na}^{+}\right]=0.1 \mathrm{M} \mathrm{;}\left[\mathrm{SO}_{4}^{-2}\right]=1 \mathrm{M} \mathrm{;}\left[\mathrm{NH}_{3}\right]=0.1 \mathrm{M} \mathrm{;}\left[\mathrm{NH}_{4}^{+}\right]=1.9 \mathrm{M}$ $\boldsymbol{\&}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.0_{8} \times 10^{-8} \mathrm{M}$

$$
\begin{gathered}
\mathrm{pH}=7.9_{7} \text { (This is a change in } \mathrm{pH} \text { of } 2.4_{9} \text {. It resisted the change somewhat but not } \\
\text { as much as part b.) }
\end{gathered}
$$

d) $1 \mathrm{M} \mathrm{NaHCO}_{3}$

When 0.10 moles of NaOH are added to $1 \mathrm{M} \mathrm{NaHCO}_{3}$, the NaOH will react with $\mathrm{HCO}_{3}^{-}$, (the strongest acid present in large amount) to form $\mathrm{CO}_{3}{ }^{-2}$, and $\mathrm{H}_{2} \mathrm{O}$ to $100 \%$. Thus, after this reaction the $\left[\mathrm{CO}_{3}^{-2}\right]=0.1 \mathrm{M},\left[\mathrm{HCO}_{3}^{-}\right]=0.9 \mathrm{M}, \&\left[\mathrm{Na}^{+}\right]=1.10 \mathrm{M}$

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

$$
\mathrm{HCO}_{3}^{-}+\mathrm{HCO}_{3}^{-} \rightleftharpoons=\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{CO}_{3}^{-2}
$$

$$
\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=1.3_{0} \times 10^{-4}
$$

Returning to the equilibrium,

$$
\begin{aligned}
& 2 \mathrm{HCO}_{3}^{-} \rightleftharpoons=\mathrm{H}_{2} \mathrm{CO}_{3}+\mathrm{CO}_{3}^{-2} \\
& \text { init } 0.9 \quad 0.1 \\
& \text { @ eq } 0.9-2 \mathrm{X} \quad \mathrm{X} \quad 0.1+\mathrm{X} \\
& \mathrm{~K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\frac{(\mathrm{X})(0.1+\mathrm{X})}{(0.9-2 \mathrm{X})^{2}}=1.3_{0} \times 10^{-4}
\end{aligned}
$$

after assuming $0.9-2 \mathrm{X}=0.9$ and $0.1+\mathrm{X}=0.1$ this reduces to
$\mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]\left[\mathrm{CO}_{3}^{-2}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]\left[\mathrm{HCO}_{3}^{-}\right]}=\frac{0.1 \times \mathrm{X}}{(0.9)^{2}}=1.3_{0} \times 10^{-4}$ or $\mathrm{X}=\frac{1.3_{0} \times 10^{-4} \times(0.9)^{2}}{(0.1)}=1.0_{5} \times 10^{-3}$
$\therefore\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=\mathrm{X}=1.05 \times 10^{-3} \mathrm{M},\left[\mathrm{CO}_{3}^{-2}\right]=0.1 \boldsymbol{\&} \quad\left[\mathrm{HCO}_{3}^{-}\right]=0.9-2 \mathrm{X}=0.9 \mathrm{M}$
Now to solve the NEW principle pH determining equilibrium (ignoring the contribution from water):

$$
\begin{gathered}
\mathrm{CO}_{3}^{-2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons=\mathrm{HCO}_{3}^{-}+\mathrm{OH}^{-} \\
\text {init } 0.1 \\
\text { @ eq } 0.1-\mathrm{Y} \\
\\
\\
\mathrm{~K}_{\mathrm{b}\left(\mathrm{CO}_{3}^{-2}\right)}=\frac{0.9+\mathrm{Y}}{} \frac{(\mathrm{Y}) \times(0.9+\mathrm{Y})}{0.1-\mathrm{Y}}=\frac{\mathrm{K}_{\mathrm{w}}}{\mathrm{~K}_{\mathrm{a}\left(\mathrm{HCO}_{3}^{-}\right)}}=\frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}}=1.7_{9} \times 10^{-4}
\end{gathered}
$$

after assuming $0.9+\mathrm{Y}=0.9$ and that $0.1-\mathrm{Y}=0.1$, this reduces to

$$
\begin{aligned}
\mathrm{K}_{\mathrm{b}} & =\frac{(\mathrm{Y}) \times(0.9)}{(0.1)}=1.7_{9} \times 10^{-4} \text { and } \therefore \mathrm{Y}=\frac{(0.1) \cdot\left(1.7_{9} \times 10^{-4}\right)}{(0.9)}=2 ._{0} \times 10^{-5} \\
\therefore\left[\mathrm{OH}^{-}\right] & =2 .{ }_{0} \times 10^{-5} \mathrm{M} \&\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=1.1 \times 10^{-2} \mathrm{M} \&\left[\mathrm{HCO}_{3}^{-}\right]=1-\mathrm{Y}=1 \mathrm{M}
\end{aligned}
$$

To check on our assumption that the contribution from water is negligible and determine $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$,

$$
\begin{aligned}
& \quad 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\begin{array}{l}
\mathrm{OH}^{-}(\mathrm{aq}) \\
\mathrm{Z}
\end{array} \begin{array}{l}
2 .{ }_{0} \times 10^{-5}+\mathrm{Z} \\
\text { @ eq } \\
\mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(2.0 \times 10^{-5}+\mathrm{Z}\right)=1.0 \times 10^{-14}
\end{array}
\end{aligned}
$$

assuming the contribution to $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$is negligible (that is the Z is small) this reduces to

$$
\mathrm{K}_{\mathrm{w}}=(\mathrm{Z}) \times\left(2 .{ }_{0} \times 10^{-5}\right)=1.0 \times 10^{-14} \text { or } \mathrm{Z}=\frac{1.0 \times 10^{-14}}{2 .{ }_{0} \times 10^{-5}}=5 . ._{0} \times 10^{-10}
$$

Yes, Z is small compared to $2 .{ }_{0} \times 10^{-5}$. Thus, $\quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathrm{Z}=5 \cdot{ }_{0} \times 10^{-10} \mathrm{M}$ and $\mathrm{pH}=9.3_{0}$ (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 .)

