## CH 302 Spring 2008 Worksheet 6 Key

1. You have a 750 mL solution of 0.1 M methylamine. You can't find the $\mathrm{K}_{\mathrm{b}}$ for methylamine but notice that the $\mathrm{K}_{\mathrm{a}}$ for its conjugate acid is $1 \times 10^{-9}$. What is the pH of the methylamine solution?

Answer: $\quad \mathrm{K}_{\mathrm{w}}=\mathrm{K}_{\mathrm{a}} \mathrm{K}_{\mathrm{b}}=1 \times 10^{-14}$ so $\mathrm{K}_{\mathrm{b}}=1 \times 10^{-5}$

$$
\left[\mathrm{OH}^{-}\right]=\left(\mathrm{K}_{\mathrm{b}} \mathrm{C}_{\mathrm{b}}\right)^{1 / 2}=\left[(0.1)\left(10^{-5}\right)\right]^{1 / 2}=10^{-3}
$$

$$
\mathrm{pOH}=3 \quad \mathrm{pH}=14-\mathrm{pOH}=\underline{\mathbf{1 1}}
$$

2. You decide to titrate it against 1 M hydrochloric acid. When you've added 25 mL of the HCl to the solution, what is the pH ?

Answer: $\quad$ You have 0.075 mol ammonia and 0.025 mol HCl . Neutralize:
You end up with 0.05 mol ammonia and 0.025 mol ammonium ion $\left(\mathrm{NH}_{4}{ }^{+}\right)$. This is a buffer.

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right]=\mathrm{K}_{\mathrm{b}}\left(\mathrm{C}_{\mathrm{b}} / \mathrm{C}_{\mathrm{a}}\right)=10^{-5}(0.05 / 0.025)=2 \times 10^{-5}} \\
& \mathrm{pOH}=-\log \left(2 \times 10^{-5}\right)=4.7 \quad \mathrm{pH}=14-4.7=\underline{\mathbf{9 . 3}}
\end{aligned}
$$

3. You continue the titration. What is the pH when you've added 75 mL HCl total? What is this point called?

Answer: You have 0.075 mol of each. Neutralize: You end up with 0.075 mol of ammonium ion. This is a weak acid.

$$
\left[\mathrm{H}^{+}\right]=\left(\mathrm{K}_{\mathrm{a}} \mathrm{C}_{\mathrm{a}}\right)^{1 / 2}
$$

Remember $\mathrm{Ka}=\mathrm{Kw} / \mathrm{Kb}=10^{-14} / 10^{-5}=10^{-9}$
Also remember that the total volume is $75 \mathrm{~mL}+750 \mathrm{~mL}=775 \mathrm{~mL}$

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]=\left[\left(10^{-9}\right)(0.075 \mathrm{~mol} / 0.775 \mathrm{~L})\right]^{1 / 2}=9.8 \times 10^{-6} \mathrm{M}} \\
& \mathrm{pH}=-\log \left(9.8 \times 10^{-6}\right)=\underline{\mathbf{5 . 0}}
\end{aligned}
$$

4. You keep going until you've added 100 mL HCl . What is this final pH ?

Answer: $\quad$ You have 0.075 mol ammonia and 0.1 mol HCl . Neutralize: You end up with 0.025 mol $\mathrm{H}+$ and 0.075 mol ammonium ion. The ammonium ions are weak; ignore them. This is a strong acid solution.

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]=\mathrm{C}_{\mathrm{a}}=0.025 \mathrm{~mol} /(0.850 \mathrm{~L})=0.029 \mathrm{M}} \\
& \mathrm{pH}=-\log (0.029 \mathrm{M})=\underline{\mathbf{1 . 5}}
\end{aligned}
$$

5. AgCl has a $\mathrm{K}_{\mathrm{sp}}$ of $1.77 \times 10^{-10}$. What is the molar solubility of AgCl ?

Answer: $\quad \mathrm{K}_{\mathrm{sp}}=\mathrm{x}^{2}$

$$
\mathrm{x}=\left(\mathrm{K}_{\mathrm{sp}}\right)^{1 / 2}=\left(1.77 \times 10^{-10}\right)^{1 / 2}=\underline{\mathbf{1 . 3 3} \times 10^{-5}}
$$

6. $\mathrm{Mg}_{3}\left(\mathrm{PO}_{4}\right)_{2}$ has a $\mathrm{K}_{\text {sp }}$ of $9.86 \times 10^{-25}$. What is the molar solubility of $\mathrm{Mg}_{3}\left(\mathrm{PO}_{4}\right)_{2}$ ?

Answer: $\quad \mathrm{K}_{\text {sp }}=(3 \mathrm{x})^{3}(2 \mathrm{x})^{2}=10 \mathrm{x}^{5}$

$$
\mathrm{x}=\left(\mathrm{K}_{\text {sp }} / 108\right)^{1 / 5}=\left(9.86 \times 10^{-25} / 108\right)^{1 / 5}=\underline{\mathbf{6 . 2 0} \times 10^{-6}}
$$

7. Given the following compounds and $\mathrm{K}_{\mathrm{sp}}$ values, rank the compounds from most to least soluble.

| Compound | $\mathbf{K}_{\text {sp }}$ |  | Molar solubility |
| :---: | :---: | :---: | :---: |$\quad$ Rank


| $\mathrm{Fe}(\mathrm{OH})_{3}$ | $6.3 \times 10^{-38}$ | $2.9 \times 10-10$ | 1 |
| :---: | :--- | :--- | :--- |
| $\mathrm{Fe}_{2} \mathrm{~S}_{3}$ | $1.4 \times 10^{-88}$ | $1.1 \times 10-18$ | 4 |

8. You drop 0.1 g of solid NaOH in an Olympic-sized swimming pool full of pure water (volume $=2.5 \mathrm{x}$ $10^{6} \mathrm{~L}$. What is the pH of the pool?

Answer: $\quad$ Calculate Cb

$$
\mathrm{C}_{\mathrm{b}}=(0.1 \mathrm{~g} /(40 \mathrm{~g} / \mathrm{mol})) /\left(2.5 \times 10^{6} \mathrm{~L}\right)=10^{-9} \mathrm{M}
$$

If we use our approximation,

$$
\left[\mathrm{OH}^{-}\right]=\mathrm{C}_{\mathrm{b}}=10^{-9}
$$

But water contributes 100 times this much, so we can't ignore it.

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right]=10^{-9}+10^{-7}=1.01 \times 10^{-7}} \\
& \mathrm{pOH}=-\log \left(1.01 \times 10^{-7}\right)=6.996 \quad \mathrm{pH}=\mathbf{7 . 0 0 4}
\end{aligned}
$$

(Or, $\mathbf{p H} \approx 7$ )
9. What if you'd dropped 10 kg of NaOH into the pool?

Answer: You drop in 100,000 times as much $\mathrm{NaOH}, \mathrm{C}_{\mathrm{b}}$ is 100,000 times larger.

$$
\mathrm{C}_{\mathrm{b}}=10^{-4} \mathrm{M}
$$

Now our approximation holds.

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right]=10^{-4} \mathrm{M}} \\
& \mathrm{pOH}=4 \quad \mathrm{pH}=\mathbf{1 0}
\end{aligned}
$$

10. List the assumptions that must be true for us to obtain reasonably accurate answers when using equations like $\left[\mathrm{H}^{+}\right]=\mathrm{C}_{\mathrm{a}}$ or $\left[\mathrm{OH}^{-}\right]=\left(\mathrm{K}_{\mathrm{b}} \mathrm{C}_{\mathrm{b}}\right)^{0.5}$.

Answer: $\quad \mathrm{Ks}$ are far apart—with respect to $\mathrm{K}_{\mathrm{w}}$ it means the $\mathrm{K}_{\mathrm{a}}$ or $\mathrm{K}_{\mathrm{b}}$ is $1 \times 10^{-10}$ or larger C is large enough-with respect to water they are values greater than $10^{-5}$
11. Briefly explain the major reason that any of the above assumptions being false would invalidate our approximations.

Answer: In either case, it means that the contribution of $\mathrm{H}+$ or OH - from other species in solution is non-negligible. With respect to water it means that $10^{-7} \mathrm{M} \mathrm{H}^{+}$or $\mathrm{OH}^{-}$is at least $1 \%$ of the contribution to total.
12. You have a neutralization reaction, $\mathrm{OH}^{-}+\mathrm{HA} \leftrightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{A}^{-}$. Given the following starting concentrations of $\mathrm{OH}^{-}$and HA , give the end concentrations of $\mathrm{OH}^{-}, \mathrm{HA}$, and $\mathrm{A}^{-}$.
a. Initial: $\left[\mathrm{OH}^{-}\right]=0.1 \mathrm{M}$
[HA] $=1 \mathrm{M}$
Final: $\left[\mathrm{OH}^{-}\right]=0 \mathrm{M}$
$[\mathrm{HA}]=0.9 \mathrm{M}$
$\left[\mathrm{A}^{-}\right]=0.1 \mathrm{M}$
b. Initial: $\left[\mathrm{OH}^{-}\right]=1 \mathrm{M}$
$[\mathrm{HA}]=1 \mathrm{M}$
Final: $\left[\mathrm{OH}^{-}\right]=0 \mathrm{M}$
$[\mathrm{HA}]=0 \mathrm{M}$
$\left[\mathrm{A}^{-}\right]=1 \mathrm{M}$
c. Initial: $\left[\mathrm{OH}^{-}\right]=1 \mathrm{M}$
$[\mathrm{HA}]=0.1 \mathrm{M}$
$[\mathrm{HA}]=0 \mathrm{M}$
$\left[\mathrm{A}^{-}\right]=0.1 \mathrm{M}$
Answer: Simple limiting reagent stuff. In a, OH - is the limiting reagent, in b , there is no limiting reagent (or both are, however you want to look at it), and in c, HA is the limiting reagent.

13-19. State whether the given mixture forms a buffer (hint: you may have to neutralize first). Whether it does or not, calculate the $\mathrm{pH} . \mathrm{K}_{\mathrm{a}}$ for $\mathrm{HCOOH}=10^{-5}$.
13. $1 \mathrm{M} \mathrm{HCOOH}^{2}$ and $1 \mathrm{M} \mathrm{COOH}^{-}$

Answer: $\quad$ This is the definition of a buffer.

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]=\mathrm{K}_{\mathrm{a}}\left(\mathrm{C}_{\mathrm{a}} / \mathrm{C}_{\mathrm{b}}\right)=10^{-5}(1 / 1)=10^{-5}} \\
& \mathbf{p H}=\mathbf{H}
\end{aligned}
$$

14. 1 M HCOOH and 1 M NaOH

Answer: $\quad$ Neutralize. You end up with $1 \mathrm{M} \mathrm{COOH}^{-}$. This is not a buffer. It's a weak base.

$$
\begin{aligned}
{\left[\mathrm{OH}^{-}\right] } & =\left(\mathrm{K}_{\mathrm{b}} \mathrm{C}_{\mathrm{b}}\right)^{1 / 2}=\left[\left(10^{-14} / 10^{-5}\right)(1)\right]^{1 / 2} \\
& =\left[10^{-9}\right]^{1 / 2}=10^{-4.5} \\
\mathrm{pOH} & =4.5 \quad \mathrm{pH}
\end{aligned}
$$

15. 1 M HCOOH and 0.5 M NaOH

Answer: $\quad$ Neutralize. You end up with 0.5 M HCOOH and $0.5 \mathrm{M} \mathrm{COOH}^{-}$. This is a buffer. Notice that $\mathrm{C}_{\mathrm{a}} / \mathrm{C}_{\mathrm{b}}$ is the same as in $\# 13$; so $\mathbf{p H}=\mathbf{5}$.
16. 1 M HCl and 1 M HCOOH

Answer: This is a strong and a weak acid. This isn't a buffer. The weak acid doesn't matter.

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]=\mathrm{C}_{\mathrm{a}}=1 \mathrm{M}} \\
& \mathbf{p H}=\mathbf{0}
\end{aligned}
$$

17. 1 M HCl and $1 \mathrm{M} \mathrm{COOH}^{-}$

Answer: Neutralize. You end up with 1 M HCOOH . This isn't a buffer, it's a weak acid.
$\left[\mathrm{H}^{+}\right]=\left(\mathrm{K}_{\mathrm{a}} \mathrm{C}_{\mathrm{a}}\right)^{1 / 2}=\left[\left(10^{-5}\right)(1)\right]^{1 / 2}=10^{-2.5}$ $\mathrm{pH}=2.5$
18. $1 \mathrm{M} \mathrm{HCl}^{\text {and }} 5 \mathrm{M} \mathrm{COOH}^{-}$

Answer: Neutralize. You end up with $4 \mathrm{M} \mathrm{COOH}-$ and 1 M HCOOH . This is a buffer.

$$
\left[\mathrm{H}^{+}\right]=\mathrm{K}_{\mathrm{a}}\left(\mathrm{C}_{\mathrm{a}} / \mathrm{C}_{\mathrm{b}}\right)=10^{-5}(1 / 4)=2.5 \times 10^{-6}
$$

$$
\mathrm{pH}=-\log \left(2.5 \times 10^{-6}\right)=\underline{\mathbf{5 . 6}}
$$

19. 1 M HCl and $0.5 \mathrm{M} \mathrm{COOH}^{-}$

Answer: $\quad$ Neutralize. You end up with 0.5 M HCl and 0.5 M HCOOH . This is a strong acid/weak acid, not a buffer.

$$
\begin{aligned}
& {[\mathrm{H}+]=\mathrm{Ca}=0.5 \mathrm{M}} \\
& \mathrm{pH}=-\log (0.5)=\underline{\mathbf{0 . 3}}
\end{aligned}
$$

20. Write down the five types of neutralization reactions form MEMORY

Answer:

$$
\begin{array}{lr}
\mathrm{H}^{+}+\mathrm{OH}^{-} \leftrightarrow \mathrm{H}_{2} \mathrm{O} & \\
\mathrm{HA}+\mathrm{OH}^{-} \leftrightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{A}^{-} & \\
\mathrm{HB}^{+}+\mathrm{OH}^{-} \leftrightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{B} & \\
\mathrm{~B}+\mathrm{H}^{+} \leftrightarrow \mathrm{BH}^{+} & \left(\text {or } \mathrm{B}+\mathrm{H}_{3} \mathrm{O}^{+} \leftrightarrow \mathrm{BH}^{+}+\mathrm{H}_{2} \mathrm{O}\right) \\
\mathrm{A}^{-}+\mathrm{H}+\leftrightarrow \mathrm{HA} & \left(\text { or } \mathrm{A}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \leftrightarrow \mathrm{HA}+\mathrm{H}_{2} \mathrm{O}\right)
\end{array}
$$

