## SA-SB TITRATION PROBLEMS KEY

1. In the beakers below:
A. Draw 2 moles HCl . SA solution (SA completely ionizes)
B. Draw what happens when 1 mole NaOH is added. Excess SA (moles $\mathrm{SA}>$ moles SB )
C. Draw what happens when 2 moles NaOH are added. Eq pt (moles $\mathrm{SA}=$ moles SB ); For SA-SB have neutral salt solution so $\mathrm{pH}=7$
D. Draw what happens when 3 moles NaOH are added. Excess SB (moles SB > moles SB )


Note: for titration problems, you will need to calculate moles or mmoles of acid and base. $\mathrm{M}=\frac{\mathrm{mol}}{\mathrm{L}}=\frac{\mathrm{mmol}}{\mathrm{mL}} \Rightarrow$ thus, moles $=\mathrm{L} \times \mathrm{M}$ or mmoles $=\mathrm{mL} \times \mathrm{M}$

## General steps for SA-SB titration:

1. Write $A-B$ neutralization reaction.
2. Calculate mmol of acid and base present.
3. Subtract smaller amount (LR) to find mmol of excess acid or base remaining.
4. Divide mmol excess acid by total $\mathrm{V}\left(\mathrm{mL}\right.$ ) to calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$(or mmol excess base by the total mL to find $\left[\mathrm{OH}^{-}\right]$)
5. $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$(or find pOH if $\left[\mathrm{OH}^{-}\right]$is present and convert to pH )
6. Consider titrating 20.00 mL of 0.200 M HCl with 0.100 M NaOH . SA SB
What volume of NaOH must be added to reach the equivalence point?
neutralization reaction: $\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}$
at EQ pt: moles acid = moles of base
mmoles $\mathrm{HCL}=20.00 \mathrm{~mL} \times\left(\frac{0.200 \mathrm{mmol} \mathrm{HCl}}{\mathrm{mL}}\right)=4.00 \mathrm{mmol} \mathrm{HCl}=4.00 \mathrm{mmol} \mathrm{NaOH}$
$\mathrm{mL} \mathrm{NaOH}=4.00 \mathrm{mmol}\left(\frac{\mathrm{mL}}{0.100 \mathrm{mmol}}\right)=\mathbf{4 0 . 0} \mathrm{mL} \mathrm{NaOH}=\mathrm{V} \mathrm{NaOH}$ at eq pt
Calculate the pH of the solution after the following volumes of NaOH have been added:
a) 0 ml of NaOH added - only SA is present initially:

Since SA completely ionizes: $[\mathrm{HCl}]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.200 \mathrm{M} \mathrm{HCl}(3 \mathrm{sf})$
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad \mathrm{pH}=-\log (0.200) \quad \mathrm{pH}=0.700$ Vlow pH for SA
b) 5.00 mL NaOH - When SB is added to SA , a neutralization reaction occurs:
neutralization reaction: $\mathbf{H C l}+\mathbf{N a O H} \rightarrow \mathbf{N a C l}+\mathbf{H}_{2} \mathbf{O}$
$\mathrm{mmol} \mathrm{HCl}=20.00 \mathrm{~mL} \times 0.200 \mathrm{M}=4.00 \mathrm{mmol} \mathrm{HCl}$
$\mathrm{mmol} \mathrm{NaOH}=5.00 \mathrm{~mL} \times 0.100 \mathrm{M}=0.500 \mathrm{mmol} \mathrm{NaOH}$ (Limiting Reactant!)
mmol excess acid $=4.00 \mathrm{mmol}-0.500 \mathrm{mmol}=3.50 \mathrm{mmol} \mathrm{HCl}$
For SA: $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=[\mathrm{HCl}]$

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\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{3.50 \mathrm{mmoles}}{25.00 \mathrm{~mL}}=0.140 \mathrm{M}
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad \mathrm{pH}=-\log 0.140 \quad \mathrm{pH}=0.854 \checkmark \text { excess } S A, \mathrm{pH}<7
$$

c) $40.00 \mathrm{~mL} \mathrm{NaOH} \quad \mathrm{mmol} \mathrm{NaOH}=40.00 \mathrm{~mL} \times 0.100 \mathrm{M}=4.00 \mathrm{mmol} \mathrm{NaOH}$ from part b: $\mathrm{mmol} \mathrm{HCl}=4.00 \mathrm{mmol} \mathrm{HCl}$

## moles acid $=$ moles base $\Rightarrow \mathrm{pH}=7$ at Eq pt for SA-SB titration!

## $\checkmark$ All the acid and base has been neutralized and all that remains is $\mathbf{N a}^{+}, \mathrm{Cl}^{-}$and

 water. All neutral substances!d) $50.00 \mathrm{~mL} \mathrm{NaOH} \quad \mathrm{mmol} \mathrm{NaOH}=50.00 \mathrm{~mL} \times 0.100 \mathrm{M}=5.00 \mathrm{mmol} \mathrm{NaOH}$ from part b: mmol $\mathrm{HCl}=4.00 \mathrm{mmol} \mathrm{HCl}$ (Limiting Reactant!) mmol excess base $=5.00 \mathrm{mmol}-4.00 \mathrm{mmol}=1.00 \mathrm{mmol} \mathrm{NaOH}$

For SB: $\left[\mathrm{OH}^{-}\right]=[\mathrm{NaOH}]$

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\left[\mathrm{OH}^{-}\right]=\frac{1.00 \mathrm{mmoles}}{70.00 \mathrm{~mL}}=0.01429 \mathrm{M}
$$

$\mathrm{pOH}=-\log (0.01429)=1.845$
$\mathrm{pH}=12.155 \checkmark$ excess $\mathrm{SB}, \mathrm{pH}>7$

## WA-SB TITRATION PROBLEMS KEY

1. In the beakers below.
A. Draw 2 moles of acetic acid. WA (For 2 moles of WA - assume it has not ionized)
B. Draw what happens when 1 mole KOH is added. (Buffer: WA, conj base)
C. Draw what happens when 2 moles KOH are added. Eq pt (WB hydrolysis)
D. Draw what happens when 3 moles KOH are added. Excess SB remains

2. Consider the titration of 50.00 mL of $0.100 \mathrm{M} \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ with 0.150 M KOH . For acetic acid, $\mathrm{K}_{\mathrm{a}}=1.8 \times 10^{-5} \quad \mathrm{WA} \mathrm{SB}$
For WA-SB titration problems, you must consider what substances are present and write the appropriate hydrolysis or neutralization reaction!
What volume of NaOH must be added to reach the equivalence point?
neutralization: $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{NaOH} \rightarrow \mathrm{NaCH}_{3} \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$
at EQ pt: moles acid = moles of base
mmoles $=50.00 \mathrm{~mL} \times\left(\frac{0.100 \mathrm{mmol} \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}}{\mathrm{mL}}\right)=5.00 \mathrm{mmol} \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}=5.00 \mathrm{mmol} \mathrm{KOH}$
$\mathrm{mL} \mathrm{KOH}=5.00 \mathrm{mmol}\left(\frac{\mathrm{mL}}{0.150 \mathrm{mmol}}\right)=33.33 \mathrm{~mL} \mathrm{NaOH}=\mathrm{V} \mathrm{NaOH}$ at eq pt

Calculate the pH of the solution after the following volumes of NaOH have been added:
a) 0 mL KOH - we just have a WA solution!

Strategy: write WA hydrolysis, ICE \& $\mathrm{K}_{\mathrm{a}}, \mathbf{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

|  | $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O}(l)$ | $\leftrightarrows$ | $\mathrm{H}_{3} \mathrm{O}^{+}$ | $+\mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{I}(\mathrm{M})$ | 0.100 |  | 0 | 0 |
| $\mathrm{C}(\mathrm{M})$ | -x |  | +x | +x |
| $\mathrm{E}(\mathrm{M})$ | $0.100-\mathrm{x}$ |  | x | x |

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]} \text { Assume } \times \text { is small! } 1.8 \times 10^{-5}=\frac{x^{2}}{0.100} \\
& \left.\mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{\left(1.8 \times 10^{-5}\right) \times(0.100}\right)=1.34 \times 10^{-3} \mathrm{M}
\end{aligned}
$$

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\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad \mathrm{pH}=-\log 1.34 \times 10^{-3} \quad \mathrm{pH}=2.87 \checkmark \text { relatively low } \mathrm{pH} \text { for } \mathrm{WA}
$$

## Other regions of WA curve:

1. Write WA-SB neutralization reaction.
2. Calculate mmol of acid and base present.
3. Plug mol into change table to determine what remains after neutralization:
$\Rightarrow$ If moles HA > moles SB, both HA and $A^{-1}$ are present so it's a buffer problem.
$\Rightarrow$ If moles $\mathrm{HA}=$ moles SB , only $\mathrm{A}^{-}$is left so its WB problem (eq pt).
$\Rightarrow$ If moles $\mathrm{SB}>$ moles WA, excess $\mathrm{OH}^{-}$is left so its SB problem.
b) $10.00 \mathrm{~mL} \mathrm{KOH} \quad \mathrm{mmoles} \mathrm{KOH}=\mathrm{mmol} \mathrm{OH}^{-}=10.00 \mathrm{~mL} \times 0.150 \mathrm{M}=1.50 \mathrm{mmol} \mathrm{KOH}$ mmoles $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}=50.00 \mathrm{~mL} \times 0.100 \mathrm{M}=5.00 \mathrm{mmol} \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$
neutralization: $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}+\mathrm{H}_{2} \mathrm{O}$

| Neutralization rxn | $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}+\mathrm{H}_{2} \mathrm{O}(I)$ |  |  |  |
| :--- | :---: | :---: | :---: | :--- |
| initial (mmol) | 5.00 | 1.50 | 0 |  |
| Change $(\mathrm{mmol})$ | -1.50 | -1.50 | +1.50 |  |
| Final (mmol) | 3.50 | 0 | 1.50 |  |

$\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{WA})$ and $\mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}(\mathrm{WB})$ remain = buffer solution!
*Can use HH equation - have WA and Conjugate Base!

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\begin{array}{ll}
\mathrm{pH}=-\log \mathrm{K}_{\mathrm{a}}+\log \left(\frac{\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}\right) & \mathrm{pH}=-\log 1.8 \times 10^{-5}+\log (1.50 / 3.50) \\
\mathrm{pH}=4.74+-.368 & \mathrm{pH}=4.380
\end{array}
$$

$\mathrm{pH} \uparrow$ after SB added; now have buffer soln containing acetic acid and acetate ions.
c) the equivalence point volume of $\mathrm{KOH}=33.33 \mathrm{~mL}$ WA-SB eq pt is WB problem!
from part b, mmoles $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}=5.00 \mathrm{mmol} \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$
mmoles $\mathrm{KOH}=\mathrm{mmol} \mathrm{OH}^{-}=33.33 \mathrm{~mL} \times 0.150 \mathrm{M}=5.00 \mathrm{mmol} \mathrm{KOH}$
neutralization: $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}+\mathrm{H}_{2} \mathrm{O}$
Neutralization rxn $\quad \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}+\mathrm{H}_{2} \mathrm{O}(I)$

| initial (mmol) | 5.00 | 5.00 | 0 |  |
| :--- | :---: | :---: | :---: | :---: |
| Change (mmol) | -5.00 | -5.00 | +5.00 |  |
| Final (mmol) | 0 | 0 | 5.00 |  |

At eq pt: all WA \& SB have reacted, only $\mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}$(WB) remains!
$\Rightarrow$ Set up WB hydrolysis rxn, solve $\mathrm{K}_{\mathrm{b}}$ for $\mathrm{x}=\left[\mathrm{OH}^{-}\right]$
Convert mmol (or mol) acetate to Molarity - must use $M$ in $K_{b}$ expression!
$\mathrm{M}=\frac{\mathrm{mmol}}{\mathrm{mL} \text { acid }+\mathrm{mL} \text { base }} \quad\left[\mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}\right]=\frac{5.00 \mathrm{mmol}}{50.00+33.33 \mathrm{~mL}}=0.0600 \mathrm{M}$
WB hydrolysis: $\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightarrows \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-}$

|  | $\mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}+\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-}$ |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{I}(\mathrm{M})$ | 0.0600 |  | 0 |  |
| $\mathrm{C}(\mathrm{M})$ | -x |  | +x |  |
| $\mathrm{E}(\mathrm{M})$ | $0.0600-\mathrm{x}$ |  | x |  |

Need $\mathrm{K}_{\mathrm{b}}$ instead of $\mathrm{K}_{\mathrm{a}}$ for WB: $\mathrm{K}_{\mathrm{b}}$ for $\mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}=\frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}=5.56 \times 10^{-10}$
$\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{CO}_{2}^{-}\right]} \quad 5.56 \times 10^{-10}=\frac{x^{2}}{0.0600}$
$\mathrm{x}=\left[\mathrm{OH}^{-}\right]=\sqrt{0.0600\left(5.56 \times 10^{-10}\right)}=5.78 \times 10^{-6} \mathrm{M}$
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=-\log 5.78 \times 10^{-6}=5.24 \quad \mathrm{pH}=14-5.24=\underline{8.76}$
$\Rightarrow \checkmark$ At the equivalence point for a WA/SB titration, the $\mathrm{pH}>7$ due to the $\mathrm{OH}^{-}$produced by the conjugate base hydrolysis reaction.
d) 50.00 mL of KOH
from part b, mmoles $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}=5.00 \mathrm{mmol} \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$
mmoles $\mathrm{KOH}=\mathrm{mmol} \mathrm{OH}^{-}=50.00 \mathrm{~mL} \times 0.150 \mathrm{M}=7.50 \mathrm{mmol} \mathrm{OH}^{-}$
neutralization: $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}+\mathrm{H}_{2} \mathrm{O}$

| Neutralization rxn | $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ |  |  |  |
| :--- | :---: | :---: | :---: | ---: |
| initial (mmol) | 5.00 | 7.50 | 0 |  |
| Change (mmol) | -5.00 | -5.00 | +5.00 |  |
| Final (mmol) | 0 | 2.50 | 5.00 |  |

moles excess SB remaining $\mathbf{=} \mathbf{2 . 5 0}$ mmoles KOH
$\mathrm{M} \mathrm{OH}^{-}=\mathrm{M} \mathrm{KOH}=\frac{2.50 \mathrm{mmol}}{100 \mathrm{~mL}}=0.0250 \mathrm{M} \mathrm{OH}^{-}$
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=-\log 0.0250=1.602 \quad \mathrm{pH}=14-1.602=\underline{12.398}$
$\checkmark$ high pH since SB not all neutralized
*Excess NaOH remains - this is the primary source of $\mathrm{OH}^{-}$. We can neglect the hydrolysis of the conjugate base because this contributes a relatively small amount of $\mathrm{OH}^{-}$ compared to the amount that comes directly from the excess NaOH .

