## Titration Calculations

## Strong Acid/Strong Base Calculations

(1) Use balanced equation to do stoichiometric calculation.
(2) Determine pH from amount of strong acid/base that is in excess.

Note: At stoichiometry point of equal acid and base, $\mathrm{pH}=7$.

## Example:

What is pH after $0.0 \mathrm{~mL}, 10.0 \mathrm{~mL}$, at equivalence point, and 50.0 mL of base has been added during a titration to 25.0 mL of a 0.12 M HCl solution with 0.15 M NaOH solution?

For strong acid/base titration, perform stoichiometry calculation first; then calculation resulting concentration with total volume; finally, calculate pH directly.
(A) 0.0 mL base: Solution is $0.12 \mathrm{M} \mathrm{HCl} \mathrm{pH}=-\log [\mathrm{H}+]=-\log (0.12)=0.92$
(B) 10.0 mL added base:

| $\mathrm{HCl}(\mathrm{aq})$ | + | $\mathrm{NaOH}(\mathrm{aq})$ | -> | $\mathrm{H}_{2} \mathrm{O}(1)$ | $+$ | $\mathrm{NaCl}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $(0.0250 \mathrm{~L})(0.12 \mathrm{M})$ |  | $(0.0100 \mathrm{~L})(0.15 \mathrm{M})$ |  |  |  |  |
| 0.0030 mol |  | 0.0015 mol |  |  |  | 0 |
| - 0.0015 mol |  | - 0.0015 mol |  |  |  | $+0.0015 \mathrm{~mol}$ |
| 0.0015 mol |  | 0 |  |  |  | 0.0015 mol |

$[\mathrm{HCl}]=0.0015 \mathrm{~mol} / 0.0350 \mathrm{~L}=0.043 \mathrm{M}$
Therefore since strong acid: $\left[\mathrm{H}^{+}\right]=0.043 \mathrm{M}$ so $\quad \mathrm{pH}=-\log (0.043)=1.37$
(C) At Equivalence Point:

Volume of base added $=(0.0030 \mathrm{~mol} \mathrm{HCl})(1 \mathrm{~mol} \mathrm{NaOH} / 1 \mathrm{~mol} \mathrm{HCl})(1 \mathrm{~L} / 0.15 \mathrm{~mol} \mathrm{NaOH})$

$$
=0.020 \mathrm{~L}=20 . \mathrm{mL} \text { added base }
$$

Since NaCl does not hydrolyze water, pH is neutral 7.00.
(D) 50.0 mL added base:

| $\mathrm{HCl}(\mathrm{aq})$ | + | $\mathrm{NaOH}(\mathrm{aq})$ | -> | $\mathrm{H}_{2} \mathrm{O}(1)$ | + | $\mathrm{NaCl}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $(0.0250 \mathrm{~L})(0.12 \mathrm{M})$ |  | (0.0500L)(0.15M) |  |  |  |  |
| 0.0030 mol |  | 0.0075 mol |  |  |  | 0 |
| $\underline{-0.0030 ~ \mathrm{~mol}}$ |  | $\underline{-0.0030 ~ \mathrm{~mol}}$ |  |  |  | $\underline{+0.0030 ~ \mathrm{~mol}}$ |
| 0 mol |  | 0.0045 mol |  |  |  | 0.0030 mol |

$[\mathrm{NaOH}]=0.0045 \mathrm{~mol} / 0.0750 \mathrm{~L}=0.060 \mathrm{M}$
Therefore since strong base left: $\left[\mathrm{OH}^{-}\right]=0.060 \mathrm{M} \quad$ so $\mathrm{pOH}=-\log (0.060)=1.22$
$\mathrm{pH}=12.78$

What is pH after $0.0 \mathrm{~mL}, 10.0 \mathrm{~mL}$, at equivalence point, and 50.0 mL of base has been added during a titration to 25.0 mL of a 0.12 M HF solution with 0.15 M NaOH solution? $\mathrm{K}_{\mathrm{a}}=6.8 \times 10^{-4}$
(1) Use balanced equation to do stoichiometric calculation.
(2) Determine new concentrations by dividing by total volume.
(3) Use appropriate equilibrium reaction and ICE chart to determine pH .

Stoichiometric Reaction:

$$
\mathrm{HF}(\mathrm{aq}) \quad+\mathrm{NaOH}(\mathrm{aq}) \quad->\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad+\mathrm{NaF}(\mathrm{aq})
$$

Equilibrium Reaction:

$$
\mathrm{HF}(\mathrm{aq}) \quad+\quad \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad->\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \quad+\quad \mathrm{F}^{-}(\mathrm{aq})
$$

(A) Addition of 0.0 mL of base:

Only weak acid present.

|  | $\mathrm{HF}(\mathrm{aq})$ | + | $\mathrm{H}_{2} \mathrm{O}$ | $\Leftrightarrow$ | $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ | + |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I | 0.12 M |  |  |  | 0 | $\mathrm{~F}^{-}(\mathrm{aq})$ |
| C | -x |  |  |  | +x | 0 |
| E | $0.12-\mathrm{x}$ |  |  |  | x | +x |

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{F}^{-}\right]}{[\mathrm{HF}]} \\
& \mathrm{x}=8.7 \times 10^{-3} \mathrm{M} \quad \mathrm{pH}=-\log \left(8.7 \times 10^{-4}=\frac{\mathrm{x}^{2}}{(0.12-\mathrm{x})}\right. \\
&
\end{aligned}
$$

(B) What is pH after 10.0 mL of 0.15 M NaOH solution has been added to 25.0 mL of 0.12 M HF solution? $\quad \mathrm{K}_{\mathrm{a}}=6.8 \times 10^{-4}$
(1) Use balanced equation to do stoichiometric calculation.
(2) Determine new concentrations by dividing by total volume.
(3) Use appropriate equilibrium reaction and ICE chart to determine pH .
(1) Stoichiometric Reaction:

| $\mathrm{HF}(\mathrm{aq})$ | + | $\mathrm{NaOH}(\mathrm{aq}) \quad->$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | + | $\mathrm{NaF}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (0.0250L)(0.12M) |  | (0.0100L)(0.15M) |  |  |  |
| 0.0030 mol |  | 0.0015 mol |  |  | 0 |
| $\underline{-0.0015 ~ \mathrm{~mol}}$ |  | $\underline{-0.0015 \mathrm{~mol}}$ |  |  | $\pm+0.0015 \mathrm{~mol}$ |
| 0.0015 mol |  | 0 mol |  |  | 0.0015 mol |

(2) New concentrations:
$[\mathrm{HF}]=0.0015 \mathrm{~mol} / 0.0350 \mathrm{~L}=0.043 \mathrm{M}$
$\left[\mathrm{F}^{-}\right]=0.0015 \mathrm{~mol} / 0.0350 \mathrm{~L}=0.043 \mathrm{M}$
(3) Equilibrium Reaction:

|  | $\mathrm{HF}(\mathrm{aq})$ | + | $\mathrm{H}_{2} \mathrm{O}$ | $\Leftrightarrow$ | $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ | + |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I | 0.043 M |  |  |  | 0 | $\mathrm{~F}^{-}(\mathrm{aq})$ |
| C | -x |  |  |  | +x | 0.043 M |
| E | $0.043-\mathrm{x}$ |  |  |  | x | +x |

$$
\begin{aligned}
\mathrm{K}_{\mathrm{a}} & =\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{F}^{-}\right]}{[\mathrm{HF}]} \\
\mathrm{x} & =6.8 \times 10^{-4}=\frac{(\mathrm{x}(0.43+\mathrm{x}))}{(0.43-\mathrm{x})} \\
& 10^{-4} \mathrm{M}
\end{aligned} \mathrm{pH}=-\log \left(6.8 \times 10^{-4}\right)=3.17
$$

Note: Could also use Henderson-Hasselbalch equation since this is buffer region of titration curve.
(C) What is pH at equivalence point?

First need to determine volume at equivalence point.
$(0.0250 \mathrm{~L})\left(\frac{0.12 \mathrm{~mol} \mathrm{HF}}{1 \mathrm{~L}}\right)\left(\frac{1 \mathrm{~mol} \mathrm{NaOH}}{1 \mathrm{~mol} \mathrm{HF}}\right)\left(\frac{1 \mathrm{~L}}{0.15 \mathrm{~mol} \mathrm{NaOH}}\right)=0.0200 \mathrm{~L}$ or 20.0 mL
(1) Use balanced equation to do stoichiometric calculation.
(2) Determine new concentrations by dividing by total volume.
(3) Use appropriate equilibrium reaction and ICE chart to determine pH .
(1) Stoichiometric Reaction:

| $\mathrm{HF}(\mathrm{aq})$ | + | $\mathrm{NaOH}(\mathrm{aq})$ | -> | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | + | $\mathrm{NaF}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (0.0250L)(0.12M) |  | (0.0200L)(0. |  |  |  |  |
| 0.0030 mol |  | 0.0030 mol |  |  |  | 0 |
| - 0.0030 mol |  | - 0.0030 mol |  |  |  | 0.0030 mol |
| 0 |  | 0 |  |  |  | 0.0030 mol |

(2) New concentrations:
$[\mathrm{HF}]=0 \mathrm{~mol} / 0.0450 \mathrm{~L}=0 \mathrm{M}$
$\left[\mathrm{F}^{-}\right]=0.0030 \mathrm{~mol} / 0.0450 \mathrm{~L}=0.067 \mathrm{M}$

$$
\mathrm{K}_{\mathrm{b}}=\frac{1 \times 10^{-14}}{6.8 \times 10^{-4}}=1.5 \times 10^{-11}
$$

(3) Equilibrium Reaction:

Only conjugate base now left. So must use equilibrium reaction for conjugate base and calculate $\mathrm{K}_{\mathrm{b}}$.

|  | $\mathrm{F}^{-}(\mathrm{aq})$ | + | $\mathrm{H}_{2} \mathrm{O}$ | $\Leftrightarrow$ | $\mathrm{OH}^{-}(\mathrm{aq})$ | + | $\mathrm{HF}(\mathrm{aq})$ |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I | 0.067 M |  |  |  | 0 | 0 |  |
| C | -x |  |  |  | +x |  | +x |
| E | $0.067-\mathrm{x}$ |  |  |  | x | x |  |

$$
\begin{aligned}
\mathrm{K}_{\mathrm{b}} & =\frac{\left[\mathrm{OH}^{-}\right][\mathrm{HF}]}{\left[\mathrm{F}^{-}\right]} \\
\mathrm{x} & =1.0 \times 10^{-6} \mathrm{M}
\end{aligned} \quad \mathrm{pOH}=-\log \left(1.0 \times 10^{-11}=\frac{\mathrm{x}^{2}}{(0.067-\mathrm{x})} \mathrm{m}=6.00 \text { so } \mathrm{pH}=8.00\right.
$$

(D) What is pH after 50.0 mL of 0.15 M NaOH solution has been added to 25.0 mL of 0.12 M HF solution? $\mathrm{K}_{\mathrm{a}}=6.8 \times 10^{-4}$
(1) Use balanced equation to do stoichiometric calculation.
(2) Determine new concentrations by dividing by total volume.
(3) Use appropriate equilibrium reaction and ICE chart to determine pH .
(1) Stoichiometric Reaction:

$$
\begin{array}{ccccc}
\mathrm{HF}(\mathrm{aq}) \\
(0.0250 \mathrm{~L})(0.12 \mathrm{M}) & + & \mathrm{NaOH}(\mathrm{aq}) & -> & \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \\
0.0030 \mathrm{~mol} & 0.0500 \mathrm{~L})(0.15 \mathrm{M}) & & \mathrm{NaF}(\mathrm{aq}) \\
\frac{-0.0030 \mathrm{~mol}}{0} & \frac{-0.0030 \mathrm{~mol}}{0.0045 \mathrm{~mol}} & & 0 \\
\hline 0 & & +0.0030 \mathrm{~mol} \\
\hline 0.0030 \mathrm{~mol}
\end{array}
$$

(2) New concentrations:

$$
\left[\mathrm{OH}^{-}\right]=0.0045 \mathrm{~mol} / 0.0750 \mathrm{~L}=0.060 \mathrm{M}
$$

$$
\left[\mathrm{F}^{-}\right]=0.0030 \mathrm{~mol} / 0.0750 \mathrm{~L}=0.040 \mathrm{M}
$$

$$
\mathrm{K}_{\mathrm{b}}=\frac{1 \times 10^{-14}}{6.8 \times 10^{-4}}=1.5 \times 10^{-11}
$$

(3) Equilibrium Reaction:

|  | $\mathrm{F}^{-}(\mathrm{aq})$ | + | $\mathrm{H}_{2} \mathrm{O}$ | $\Leftrightarrow$ | $\mathrm{OH}^{-}(\mathrm{aq})$ | + |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I | 0.040 M |  |  |  | 0.060 M | $\mathrm{HF}(\mathrm{aq})$ |
| C | -x |  |  |  | +x | 0 |
| E | $0.040-\mathrm{x}$ |  |  |  | $0.060+\mathrm{x}$ | +x |

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}\right][\mathrm{HF}]}{\left[\mathrm{F}^{-}\right]} \quad 1.5 \times 10^{-11}=\frac{(\mathrm{x}(0.060+\mathrm{x}))}{(0.040-\mathrm{x})}
$$

$\mathrm{x}=1.0 \times 10^{-11} \mathrm{M} \quad \mathrm{pOH}=-\log \left(1.0 \times 10^{-11}\right)=11.00$ so $\mathrm{pH}=3.00 ? ? ?$
NOTE: " $x$ " is NOT the OH - concentration. The OH - concentration is $0.060 \mathrm{M}+\mathrm{x}$. Since there is excess strong base in this last addition, the pH is determined by the strong base concentration. The weak conjugate base F- adds an insignificant amount.

$$
\left[\mathrm{OH}^{-}\right]=0.060+\mathrm{x}=0.060 \mathrm{M}+1.0 \times 10^{-11} \mathrm{M}=0.060 \mathrm{M}
$$

$$
\mathrm{pOH}=-\log (0.060)=1.22 \text { so } \mathrm{pH}=12.78
$$

