#### Acid and base titration

One of the common questions seen in many forms on the AP Chemistry exam related to acid and base titration relates to the pH at the equivalence point for a titration of a strong acid with a strong base, or a weak acid with a strong base.

#### Question:

The pH at the equivalence point for a strong acid and a strong base is equal to 7. Explain.

### Answer:

At the equivalence point what is equivalent are the moles of acid and moles of base. When we look at a sample problem we can see this in an ICE table. Consider the titration of a 25.0 mL sample of 0.150 M NaOH with 0.250 M HCl.

According to stoichiometry we can calculate the volume of 0.250 M HCl required to reach the equivalence point in the titration.

The reaction that is taking place is;

Initial Change Equilibrium

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

So we can setup an ICE table using this reaction.

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

In this problem we have enough information, given the volume and molarity of NaOH to calculate the initial moles of NaOH;

 $25.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.150 \text{ mol NaOH}}{1 \text{ L}}\right) = 0.00375 \text{ mol NaOH}$  $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$ Initial 0.00375 mol Change Equilibrium

An equivalence point means two important characteristics: 1) moles of acid must equal moles of base; and 2) all of the original acid or base to be titrated must completely react.

So if all of the base reacts, than the Change amount of base must equal the Initial amount of base.

 $\begin{array}{rll} & \operatorname{HCl}_{(aq)} & + & \operatorname{NaOH}_{(aq)} \rightarrow \operatorname{NaCl}_{(aq)} + \operatorname{H_2O}_{(l)} \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ &$ 

Since the stoichiometry coefficient indicate a one-to-one ratio than the amount of acid reacting in moles must equal the amount of base reacting.

 $\begin{array}{rl} \operatorname{HCl}_{(aq)} &+ & \operatorname{NaOH}_{(aq)} \rightarrow \operatorname{NaCl}_{(aq)} + \operatorname{H_2O}_{(l)} \\ \text{Initial} & & 0.00375 \text{ mol} \\ \text{Change} & -0.00375 \text{ mol} & -0.00375 \text{ mol} \\ \text{Equilibrium} \end{array}$ 

Since at the equivalence point the moles of acid reacting must equal the moles of base reacting the ICE table become,

	$HCl_{(aq)}$ +	NaOH <sub>(aq)</sub>	$\rightarrow \operatorname{NaCl}(aq) + \operatorname{H}_2\operatorname{O}(l)$
Initial		0.00375 mol	
Change	-0.00375 mol	-0.00375 mol	
Equilibrium	0	0	

To have 0 moles of acid after the reaction must mean we have the same amount acid Initially as has reacted,

	$HCl_{(aq)}$	+ $NaOH_{(aq)}$ -	$\rightarrow$ NaCl <sub>(aq)</sub>	+ $H_2O_{(l)}$
Initial	0.00375 mol	0.00375 mol	0	0
Change	-0.00375 mol	-0.00375 mol	0.00375 mol	0.00375 mol
Equilibrium	0	0	0.00375 mol	0.00375 mol

So now we can calculate the volume of 0.250 M HCl required to completely react with 25.0 mL of 0.150 M NaOH.

0.00375 mol HCl  $\left(\frac{1 \text{ L}}{0.250 \text{ mol HCl}}\right) \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 15.0 \text{ mL HCl}$ 

So the volume of 15.0 mL 0.250 M HCl is required to reach the equivalence point of a titration of 25.0 mL of 0.150 M NaOH.

Basically, we arrived at this volume of HCl through a series of conversions using the stoichiometry of the balanced neutralization reaction.

$$25.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) \left(\frac{0.150 \text{ mol NaOH}}{1 \text{ L}}\right) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}}\right) \left(\frac{1 \text{ L}}{0.250 \text{ mol HCl}}\right) \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 15.0 \text{ mL}$$

#### WATCH OUT!!

Students will try to use  $M_1V_1 = M_2V_2$  to calculate the volume of 0.0250 M HCl required to neutralize 25.0 mLs of 0.150 M NaOH. This relationship should ONLY be used for dilutions, even if students make the equation to look different,  $M_{acid}V_{acid} = M_{base}V_{base}$ . The calculation looks surprising,

Solving for Vacid

$$V_{acid} = \left(\frac{M_{base}V_{base}}{M_{acid}}\right)$$
$$V_{acid} = \left(\frac{25.0 \text{ mL} \cdot 0.150 \text{ M NaOH}}{0.250 \text{ M HCl}}\right) = 15.0 \text{ mL HCl}$$

But the problem is that there is no conversion from moles of NaOH to moles of HCl in this setup. The student has not used the stoichiometry of the balanced chemical equation.

So teachers..... do not let your students use this relationship!!! Do the calculation using stoichiometry.

So at the equivalence point the moles of acid added are equal to the moles of base present. As seen in the ICE table that means that after the reaction is complete, there is no HCl or NaOH remaining, only moles of NaCl remain. Since NaCl is a salt of a strong acid and a strong base the pH of the solution is equal to 7.

## Question:

The pH at the equivalence point for a weak acid and a strong base is greater than 7. Explain.

## Answer:

At the equivalence point what is equivalent are the moles of acid and moles of base. When we look at a sample problem we can see this in an ICE table. Consider the titration of a 25.0 mL sample of 0.150 M NaOH with 0.250 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>.

According to stoichiometry we can calculate the volume of  $0.250 \text{ M HC}_2\text{H}_3\text{O}_2$  required to reach the equivalence point in the titration. (only this time will use a short cut.)

The reaction that is taking place is;

$$\mathrm{HC}_{2}\mathrm{H}_{3}\mathrm{O}_{2(aq)} + \mathrm{NaOH}_{(aq)} \rightarrow \mathrm{NaC}_{2}\mathrm{H}_{3}\mathrm{O}_{2(aq)} + \mathrm{H}_{2}\mathrm{O}_{(l)}$$

So to calculate the volume of  $0.250 \text{ M HC}_2\text{H}_3\text{O}_2$  to reach the equivalence point,

$$25.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) \left(\frac{0.150 \text{ mol NaOH}}{1 \text{ L}}\right) \left(\frac{1 \text{ mol HC}_2\text{H}_3\text{O}_2}{1 \text{ mol NaOH}}\right) \left(\frac{1 \text{ L}}{0.250 \text{ mol HC}_2\text{H}_3\text{O}_2}\right) \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 15.0 \text{ mL}$$

(NOTICE!! The volume of 0.250 M  $HC_2H_3O_2$  required to neutralize 25.0 mLs of 0.150 M NaOH is the same as the volume of 0.250 M HCl!!

So now we can setup an ICE table to determine what species are present at the equivalenc point of the titration between  $HC_2H_3O_2$  and NaOH.

 $\begin{array}{c} \mathrm{HC_2H_3O_2(\mathit{aq})} + \mathrm{NaOH}(\mathit{aq}) \to \mathrm{NaC_2H_3O_2(\mathit{aq})} + \mathrm{H_2O}(\mathit{l})\\ \\ \mathrm{Initial}\\ \mathrm{Change}\\ \mathrm{Equilibrium} \end{array}$ 

In this problem we have enough information, given the volume and molarity of NaOH to calculate the initial moles of NaOH;

25.0 mL 
$$\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) \left(\frac{0.150 \text{ mol NaOH}}{1 \text{ L}}\right) = 0.00375 \text{ mol NaOH}$$
  
HC<sub>2</sub>H<sub>3</sub>O<sub>2(*aq*)</sub> + NaOH<sub>(*aq*)</sub>  $\rightarrow$  NaC<sub>2</sub>H<sub>3</sub>O<sub>2(*aq*)</sub> + H<sub>2</sub>O<sub>(*l*)</sub>  
Initial 0.00375 mol  
Change  
Equilibrium

An equivalence point means two important characteristics: 1) moles of acid must equal moles of base; and 2) all of the original acid or base to be titrated must completely react.

So if all of the base reacts, than the Change amount of base must equal the Initial amount of base.

 $\begin{array}{c} \mathrm{HC_2H_3O_2(aq)} + \mathrm{NaOH}_{(aq)} \rightarrow \mathrm{NaC_2H_3O_2(aq)} + \mathrm{H_2O}_{(l)}\\ \mathrm{Initial} & 0.00375 \ \mathrm{mol}\\ \mathrm{Change} & -0.00375 \ \mathrm{mol}\\ \mathrm{Equilibrium} \end{array}$ 

Since the stoichiometry coefficient indicate a one-to-one ratio than the amount of acid reacting in moles must equal the amount of base reacting.

 $\begin{array}{c} \mathrm{HC_{2}H_{3}O_{2}(aq)} + \mathrm{NaOH}_{(aq)} \rightarrow \mathrm{NaC_{2}H_{3}O_{2}(aq)} + \mathrm{H_{2}O}_{(l)}\\ \mathrm{Initial} & 0.00375 \ \mathrm{mol}\\ \mathrm{Change} & -0.00375 \ \mathrm{mol} & -0.00375 \ \mathrm{mol}\\ \mathrm{Equilibrium} \end{array}$ 

Since at the equivalence point the moles of acid reacting must equal the moles of base reacting the ICE table become,

	$HC_2H_3O_{2(ac)}$	(aq) + NaOH $(aq)$	$\rightarrow$ NaC <sub>2</sub> H <sub>3</sub> O <sub>2(aq)</sub> + H <sub>2</sub> O <sub>(l)</sub>
Initial		0.00375 mol	-
Change	-0.00375 mol	-0.00375 mol	
Equilibrium	0	0	

To have 0 moles of acid after the reaction must mean we have the same amount acid Initially as has reacted,

	$HC_2H_3O_2(a)$	(aq) + NaOH $(aq)$	$\rightarrow NaC_2H_3O_2($	$aq) + H_2O(l)$
Initial	0.00375 mol	0.00375 mol	0	0
Change	-0.00375 mol	-0.00375 mol	0.00375 mol	0.00375 mol
Equilibrium	0	0	0.00375 mol	0.00375 mol

So at the equivalence point the moles of acid added are equal to the moles of base present. As seen in the ICE table. That means that after the reaction is complete, there is no  $HC_2H_3O_2$  or NaOH remaining, only moles of  $NaC_2H_3O_2$  remain.

Since  $NaC_2H_3O_2$  is a salt of a weak acid and a strong base, the solution is basic (pH greater than 7. This can be seen if we look carefully at the salt,  $NaC_2H_3O_2$ .

In water  $NaC_2H_3O_2$  will complete dissociate into  $Na^+$  and  $C_2H_3O_2^-$  ions.  $Na^+$  does change the pH of when dissolved in water, however  $C_2H_3O_2^-$  ions do effect the pH when dissolved in water. See the chemical equation below,

$$C_2H_3O_2^{-}(aq) + H_2O_{(l)} \rightarrow HC_2H_3O_2(aq) + OH^{-}(aq)$$

The magnitude of the equilibrium constant for this reaction is

$$K_b = \left(\frac{K_w}{K_a}\right) = \left(\frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}\right) = 5.5 \times 10^{-10}$$

In this particular case, from the ICE table above, at the equivalence point there are 0.00375 mol  $C_2H_3O_2^-$  in 40.0 mLs of solution (25.0 mL sample of 0.150 M NaOH and 15.0 mL of 0.250 M  $HC_2H_3O_2$ ), so

$$[C_2H_3O_2^{-}] = \left(\frac{0.00375 \text{ mol } C_2H_3O_2^{-}}{0.0400 \text{ L}}\right) = 0.0938 \text{ M}$$

The Initial amounts in the ICE table would then be,

 $\begin{array}{c} C_2H_3O_2^{-}(aq) + H_2O_{(l)} \rightarrow HC_2H_3O_2(aq) + OH^{-}(aq)\\ \text{Initial} & 0.0938 \text{ M} & - & 0 & 0\\ \text{Change} \end{array}$ 

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# Equilibrium

The Change amounts in the ICE table would then be,

	$C_2H_3O_2^{-}(a)$	$(aq) + H_2O_{(l)} \rightarrow$	$\rightarrow$ HC <sub>2</sub> H <sub>3</sub> O <sub>2(aq)</sub>	+ $OH^{-}(aq)$
Initial	0.0938 M	-	0	0
Change	-X	-	+X	+X
Equilibrium				

The Equilibrium amounts in the ICE table would then be,

	$C_2H_3O_2^{-}$	$(aq) + H_2O_{(l)} \rightarrow$	$HC_2H_3O_2(aq)$	$+ OH^{-}(aq)$
Initial	0.0938 M	-	0	0
Change	-X	-	+X	+X
Equilibrium	0.0938 - x	-	+X	+X

Substituting into the equilibrium expression,

$$K_{b} = \left(\frac{[HC_{2}H_{3}O_{2}][OH^{-}]}{[C_{2}H_{3}O_{2}^{-}]}\right) = 5.5 \text{ x } 10^{-10}$$
$$5.5 \text{ x } 10^{-10} = \left(\frac{x^{2}}{0.0938 \text{ - x}}\right)$$

and  $x = [OH^-]$  will be 2.66 x 10<sup>-5</sup> M. So the pOH = 4.57 and the pH = 9.42...and the solution is basic at the equivalence point.