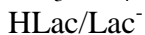
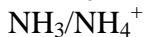
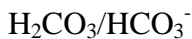


# Buffers

Buffer solutions are made up of either a weak acid and its conjugate base or a weak base and its conjugate acid.

Examples of buffers:



## Henderson – Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

The first thing you need to do when reading a buffer problem is determine which compound is the weak acid (or weak base) and which component is the conjugate base (or acid). For example, HF is a weak acid whose conjugate base is  $\text{F}^-$ . The  $\text{F}^-$  is added in the form of a salt NaF. In water 100% of the NaF separates into  $\text{Na}^+$  and  $\text{F}^-$  ions. The  $\text{Na}^+$  ions are spectator ions and are not included in the equation.

If you are given a  $\text{K}_a$  then it is the easiest (but not required) to set up an equation with acid on the left side (see example i-a) If you write the equation with base on the left you will need to use the  $\text{K}_b$  (see example i-b). In many cases a buffer problem can be easily solved using Henderson – Hasselbalch Equation (see example i-c).

### Example:

- i Calculate the pH of the buffer solution that is 0.15 M HF and 0.15 M  $\text{F}^-$ .  $\text{K}_a$  for HF is  $6.8 \times 10^{-4}$ .

*We can solve this problem in 3 different ways*

- a Using  $\text{K}_a$

Conc. (M)	HF	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{F}^-$
Initial [ ]	0.15				0		0.15
Change [ ]	- x				+ x		+ x
Equilibrium [ ]	0.15 - x				x		0.15 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4} = \frac{x(0.15+x)}{0.15-x}$$

Solve the equation for  $x$  assuming that  $x$  is negligible compared to 0.15. (If you have forgotten the rule for ignoring  $x$  see Chemical Equilibrium handout)

$$\frac{0.15x}{0.15} = 6.8 \times 10^{-4} \Rightarrow x = 6.8 \times 10^{-4} \Rightarrow [\text{H}_3\text{O}^+] = 6.8 \times 10^{-4}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.8 \times 10^{-4})$$

$$\text{pH} = 3.17$$

or

b Using  $K_b$

Conc. (M)	F <sup>-</sup>	+	H <sub>2</sub> O	⇌	HF	+	OH <sup>-</sup>
Initial [ ]	0.15				0.15		0
Change [ ]	- x				+ x		+ x
Equilibrium [ ]	0.15 - x				0.15 + x		x

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = 1.5 \times 10^{-11} = \frac{(0.15+x)x}{0.15-x}$$

Solve the equation for  $x$  assuming that  $x$  is negligible compared to 0.15

$$\frac{0.15x}{0.15} = 1.5 \times 10^{-11} \Rightarrow x = 1.5 \times 10^{-11} \Rightarrow [\text{OH}^-] = 1.5 \times 10^{-11}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.5 \times 10^{-11}) = 10.83$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 10.83$$

$$\text{pH} = 3.17$$

or

c Using the Henderson – Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = -\log K_a + \log \frac{[\text{F}^-]}{[\text{HF}]}$$

$$\text{pH} = -\log(6.8 \times 10^{-4}) + \log \frac{0.15}{0.15} = 3.17 + \log 1 = 3.17 + 0$$

$$\text{pH} = 3.17$$

### Adding strong acid or strong base to the buffer solution

By adding a small amount of HCl (strong acid) to the buffer, the HCl will react with the base part of the buffer. At the end of this irreversible reaction no HCl will be left. The base will then convert to a weak acid, which then dissociates only slightly into  $\text{H}_3\text{O}^+$ . Therefore, the pH drops only a little.

By adding a small amount of NaOH (strong base) to the buffer, the NaOH will react with the acid part of the buffer. At the end of this irreversible reaction no NaOH will be left. The acid will then convert to a weak base, which then dissociates only slightly into  $\text{OH}^-$ . Therefore, the pH goes up only a little.

Steps for calculating the pH of a buffer solution after acid or base has been added to it:

1. Write an equation for irreversible reaction of the strong acid with the base component of the buffer or the irreversible reaction of the strong base and the acid component of the buffer. Note that the ion associated with the strong acid/base becomes a spectator ion and is NOT involved in the reaction.
2. Calculate the moles of the conjugate acid/base pair of the buffer and the moles of strong acid or base added to the buffer.
3. Under the irreversible equation write a chart showing moles of all the reaction components before the reaction starts, the change into moles of the reactants and products and the moles of all components after the reaction is over. This is called the BCA chart (*see example below*).
4. Find the limiting reagent.
5. Calculate the moles of all substances after the reaction is over.
6. At this point if the strong acid/base added to the buffer was the limiting reagent we still have a buffer solution. Calculate the concentration of the buffer solution by taking into consideration any volume changes in the solution.
7. Calculate the pH of the buffer solution in any of the 3 ways shown above.

## Examples:

- i Calculate the pH of the solution formed when 7.0 ml of 0.10 M NaOH is added to 100 ml of the 0.15 M HF/F<sup>-</sup> buffer solution (*this is the buffer solution that we used to calculate the pH in the example above*). The K<sub>a</sub> for HF is 6.8 x 10<sup>-4</sup>.

$$\text{mol HF} = 0.15 \frac{\text{mol HF}}{\text{L}} \times 0.100\text{L} = 0.015 \text{ mol HF}$$

$$\text{mol F}^- = 0.15 \frac{\text{mol F}^-}{\text{L}} \times 0.100\text{L} = 0.015 \text{ mol F}^-$$

$$\text{mol OH}^- = 0.10 \frac{\text{mol OH}^-}{\text{L}} \times 0.0070\text{L} = 0.00070 \text{ mol OH}^-$$

*Irreversible Reaction. (Note: Chart done in moles NOT molarity)*

mol	HF	+	OH <sup>-</sup>	→	F <sup>-</sup>	+	H <sub>2</sub> O
<b>Before</b>	0.015		0.00070		0.015		
<b>Change</b>	- 0.00070		-0.00070		+ 0.00070		
<b>After</b>	0.014		0		0.016		

Final volume = 107 ml

*Now find the new molarities*

$$[\text{HF}] = \frac{0.014 \text{ mol}}{0.107\text{L}} = 0.13 \text{ M}$$

$$[\text{F}^-] = \frac{0.016 \text{ mol}}{0.107\text{L}} = 0.15 \text{ M}$$

*Reversible reaction. (Note: Chart usually done in molarity so it can be directly used in K<sub>a</sub> equation)*

Conc. (M)	HF	+	H <sub>2</sub> O	⇌	H <sub>3</sub> O <sup>+</sup>	+	F <sup>-</sup>
<b>Initial [ ]</b>	0.13				0		0.15
<b>Change [ ]</b>	- x				+ x		+ x
<b>Equilibrium [ ]</b>	0.13 - x				x		0.15 + x

*Now we can calculate the pH in any of the 3 ways (this example is done only in 2 ways)*

Using  $K_a$  since HF is a weak acid and on the left side of the equation

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4} = \frac{x(0.15+x)}{0.13-x}$$

*Solve the equation for x assuming that x is negligible compared to 0.15 and 0.13*

$$\frac{0.15x}{0.13} = 6.8 \times 10^{-4} \Rightarrow 1.2x = 6.8 \times 10^{-4} \Rightarrow x = 5.7 \times 10^{-4} \Rightarrow [\text{H}_3\text{O}^+] = 5.7 \times 10^{-4}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.7 \times 10^{-4})$$

**pH = 3.24** (the pH went up when strong base was added)

or

Using Henderson – Hasselbalch Equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = -\log K_a + \log \frac{[\text{F}^-]}{[\text{HF}]}$$

$$\text{pH} = -\log(6.8 \times 10^{-4}) + \log \frac{0.15}{0.13} = 3.17 + \log 1.2 = 3.17 + 0.079$$

**pH = 3.25** (the answers may differ a little because of the significant figure rule and rounding of the numbers)

- ii Calculate the pH of the solution when 5.0 ml of 0.10 M HCl is added to 100 ml of the original 0.15M HF/F<sup>-</sup> buffer solution.

$$\text{mol HF} = 0.15 \frac{\text{mol HF}}{\text{L}} \times 0.100\text{L} = 0.015 \text{ mol HF}$$

$$\text{mol F}^- = 0.15 \frac{\text{mol F}^-}{\text{L}} \times 0.100\text{L} = 0.015 \text{ mol F}^-$$

mol HCl =  $0.10 \frac{\text{mol HCl}}{\text{L}} \times 0.0050\text{L} = 0.00050 \text{ mol HCl}$  (in  $\text{H}_2\text{O}$ , HCl becomes  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$ .  $\text{Cl}^-$  is a spectator ion and not involved in the reaction.)

*Irreversible Reaction*

mol	$\text{F}^-$	+	$\text{H}_3\text{O}^+$	$\rightarrow$	HF	+	$\text{H}_2\text{O}$
<b>Before</b>	0.015		0.00050		0.015		
<b>Change</b>	- 0.00050		-0.00050		+ 0.00050		
<b>After</b>	0.015		0		0.016		

Final volume = 105 ml

$$[\text{HF}] = \frac{0.016 \text{ mol}}{0.105 \text{ L}} = 0.15 \text{ M}$$

$$[\text{F}^-] = \frac{0.015 \text{ mol}}{0.105 \text{ L}} = 0.14 \text{ M}$$

*Reversible Reaction*

Conc. (M)	HF	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{F}^-$
<b>Initial [ ]</b>	0.15				0		0.14
<b>Change [ ]</b>	- x				+ x		+ x
<b>Equilibrium [ ]</b>	$0.15 - x$				x		$0.14 + x$

Now we can calculate the pH in any of the 3 ways (this example is done only in 2 ways)

Using  $K_a$  since HF is a weak acid and on the left side of the equation

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.8 \times 10^{-4} = \frac{x(0.14+x)}{0.15-x}$$

Solve the equation for x assuming that x is negligible compared to 0.15 and 0.13

$$\frac{0.14x}{0.15} = 6.8 \times 10^{-4} \Rightarrow 0.93x = 6.8 \times 10^{-4} \Rightarrow x = 7.3 \times 10^{-4} \Rightarrow [\text{H}_3\text{O}^+] = 7.3 \times 10^{-4}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.3 \times 10^{-4})$$

**pH = 3.14** (*the pH went down when strong acid was added*)

**or**

Using Henderson – Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = -\log K_a + \log \frac{[\text{F}^-]}{[\text{HF}]}$$

$$\text{pH} = -\log(6.8 \times 10^{-4}) + \log \frac{0.14}{0.15} = 3.17 + \log 0.93 = 3.17 - 0.032$$

**pH = 3.14**

## Problems:

1. Calculate the pOH of the 0.250 M lactic acid, HLac, mixed with 0.150 M Lac<sup>-</sup>. The K<sub>a</sub> for HLac is 1.3 x 10<sup>-3</sup>. Solve this problem using the Henderson – Hasselbalch Equation.

**Solution**

2. Solution contains 10.0 g of pyridine, C<sub>5</sub>H<sub>5</sub>N and 15.0 g of HC<sub>5</sub>H<sub>5</sub>N per one liter of solution.

- i Calculate the pH of the solution if K<sub>b</sub> for C<sub>5</sub>H<sub>5</sub>N is 1.40 x 10<sup>-9</sup>. Solve this problem using the ICE chart.

**Solution**

- ii Calculate the pH of the solution when 10.00 ml of 2.00 M KOH is added to 1.00 L of the buffer solution. Solve this problem using the ICE chart.

**Solution**

- iii Calculate the pH of the solution when 20.00 ml of 2.00M HCl is added to 1.00 L of the buffer solution. Solve this problem using the Henderson – Hasselbalch Equation.

**Solution**

## Solutions:

1. Calculate the pOH of the 0.250 M lactic acid, HLac, mixed with 0.150 M Lac<sup>-</sup>. The K<sub>a</sub> for HLac is 1.30 x 10<sup>-3</sup>. Do this problem using the Henderson – Hasselbalch Equation.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = -\log K_a + \log \frac{[\text{Lac}^-]}{[\text{HLac}]}$$

$$\text{pH} = -\log(1.30 \times 10^{-3}) + \log \frac{0.150}{0.250} = 2.886 + \log 0.600 = 2.886 - 0.222 = 2.664$$

$$\text{pOH} = 14.000 - \text{pH}$$

$$\text{pOH} = 14.000 - 2.664$$

$$\text{pOH} = \mathbf{11.336}$$

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2. Solution contains 10.0 g of pyridine,  $C_5H_5N$  and 15.0 g of  $HC_5H_5N$  per one liter of solution.

- i Calculate the pH of the solution if  $K_b$  for  $C_5H_5N$  is  $1.40 \times 10^{-9}$ . Do this problem using the ICE chart.

*First convert grams to moles of  $C_5H_5N$  and  $HC_5H_5N$ , and then to molarity of the solution*

$$10.0 \text{ g } C_5H_5N \times \frac{1 \text{ mol } C_5H_5N}{79.1 \text{ g } C_5H_5N} = 0.126 \text{ mol } C_5H_5N$$

$$[C_5H_5N] = \frac{0.126 \text{ mol } C_5H_5N}{1L} = 0.126 \text{ M } C_5H_5N$$

$$15.0 \text{ g } HC_5H_5N \times \frac{1 \text{ mol } HC_5H_5N}{80.1 \text{ g } HC_5H_5N} = 0.187 \text{ mol } HC_5H_5N$$

$$[HC_5H_5N] = \frac{0.187 \text{ mol } HC_5H_5N}{1L} = 0.187 \text{ M}$$

*Now write the equation followed by an ICE chart*

Conc. (M)	$C_5H_5N$	+	$H_2O$	$\rightleftharpoons$	$HC_5H_5N^+$	+	$OH^-$
Initial [ ]	0.126				0.187		0
Change [ ]	- x				+ x		+ x
Equilibrium [ ]	$0.126 - x$				$0.187 + x$		x

*Now write the equilibrium equation and substitute the information from the chart*

$$K_b = \frac{[HC_5H_5N^+][OH^-]}{[C_5H_5N]} = \frac{(0.187 + x)x}{(0.126 - x)} = 1.40 \times 10^{-9}$$

*Solve the equation for x assuming that x is negligible compared to 0.126 and 0.187*

$$\frac{0.187x}{0.126} = 1.40 \times 10^{-9} \Rightarrow 1.76 \times 10^{-10} = 0.187x \Rightarrow x = 9.43 \times 10^{-10}$$

$$[OH^-] = 9.43 \times 10^{-10} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (9.43 \times 10^{-10}) = 9.025$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 9.025$$

$$\text{pH} = 4.975$$

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- ii Calculate the pH of the solution when 10.00 ml of 2.00 M KOH is added to 1.00 L of the buffer solution. Do this problem using the ICE chart.

First write the BCA chart using the moles that you calculated in part i) for  $C_5H_5N$  and  $HC_5H_5N$  and find the moles of KOH.

$$\text{mol OH}^- = 2.00 \frac{\text{mol}}{\text{L}} \times 0.01000 \text{L} = 0.0200 \text{ mol OH}^-$$

mol	$HC_5H_5N^+$	+	$OH^-$	$\rightarrow$	$C_5H_5N$	+	$H_2O$
Before	0.187		0.0200		0.126		
Change	- 0.0200		-0.0200		+ 0.0200		
After	0.167		0		0.146		

Final volume = 1.010 L

$$[HC_5H_5N^+] = \frac{0.167 \text{ mol}}{1.010 \text{L}} = 0.165 \text{ M}$$

$$[C_5H_5N] = \frac{0.146 \text{ mol}}{1.010 \text{L}} = 0.145 \text{ M}$$

Now write the equation followed by an ICE chart

Conc. (M)	$C_5H_5N$	+	$H_2O$	$\rightleftharpoons$	$HC_5H_5N^+$	+	$OH^-$
Initial [ ]	0.145				0.167		0
Change [ ]	- x				+ x		+ x
Equilibrium [ ]	$0.145 - x$				$0.167 + x$		x

Now write the equilibrium equation and substitute the information from the chart

$$K_b = \frac{[HC_5H_5N^+][OH^-]}{[C_5H_5N]} = \frac{(0.167 + x)x}{(0.145 - x)} = 1.40 \times 10^{-9}$$

Solve the equation for x assuming that x is negligible compared to 0.145 and 0.167

$$\frac{0.167x}{0.145} = 1.40 \times 10^{-9} \Rightarrow 2.03 \times 10^{-10} = 0.167x \Rightarrow x = 1.00 \times 10^{-9}$$

$$[\text{OH}^-] = 1.00 \times 10^{-9} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.00 \times 10^{-9}) = 9.000$$

$$\text{pH} = 14.000 - \text{pOH} = 14.000 - 9.000$$

$$\text{pH} = \mathbf{5.000}$$
 (*pH raised when strong base added; was 4.975*)

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- iii Calculate the pH of the solution when 20.00 ml of 2.00M HCl is added to 1.00 L of the buffer solution. Do this problem using the Henderson – Hasselbalch Equation.

*First write the BCA chart using the moles that you calculated in part i) for C<sub>5</sub>H<sub>5</sub>N and HC<sub>5</sub>H<sub>5</sub>N and find the moles of HCl.*

$$\text{mol HCl} = 2.00 \frac{\text{mol}}{\text{L}} \times 0.02000 \text{L} = 0.0400 \text{ mol OH}^-$$

mol	C <sub>5</sub> H <sub>5</sub> N	+	HCl	→	HC <sub>5</sub> H <sub>5</sub> N <sup>+</sup>	+	Cl <sup>-</sup>
Before	0.126		0.0400		0.187		
Change	- 0.0400		-0.0400		+ 0.0400		
After	0.086		0		0.227		

Final volume = 1.020 L

$$[\text{HC}_5\text{H}_5\text{N}^+] = \frac{0.227 \text{ mol}}{1.020 \text{L}} = 0.223 \text{ M}$$

$$[\text{C}_5\text{H}_5\text{N}] = \frac{0.086 \text{ mol}}{1.020 \text{L}} = 0.084 \text{ M}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{K}_a = \frac{\text{K}_w}{\text{K}_b} = \frac{1 \times 10^{-14}}{1.40 \times 10^{-9}} = 7.14 \times 10^{-6}$$

$$\text{pH} = -\log \text{K}_a + \log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{HC}_5\text{H}_5\text{N}]}$$

$$\text{pH} = -\log(7.14 \times 10^{-6}) + \log \frac{0.084}{0.223} = 5.146 + \log 0.38 = 5.146 - 0.42$$

**pH = 4.73** (pH lowered when strong base added; was 4.975)

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