

Buffers

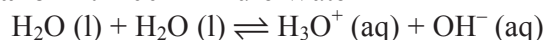
How can a solution neutralize both acids and bases?

Why?

Buffer solutions are a mixture of substances that have a fairly constant pH regardless of addition of acid or base. They are used in medicine, industry and manufacturing to keep the pH of a solution stable regardless of other reactions that might be occurring. You have buffers in your blood, for example, because the proper function of enzymes is dependent on the pH of your blood staying in a narrow range. Eating, breathing and exercising can all alter the acidity or basicity of your blood, but the buffers in your blood help control the pH and keep all of your enzymes working properly.

Model 1 – Comparing Solutions:

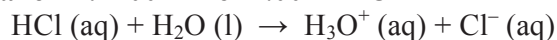
Beaker A: 100 mL Pure Water



WB WA CA CB

		⇌	H ₃ O ⁺	OH ⁻
I	—		0	0
C	—		+1.0×10 ⁻⁷	+1.0×10 ⁻⁷
E	—		1.0×10 ⁻⁷	1.0×10 ⁻⁷

Beaker B: 100 mL of 1.00 M HCl

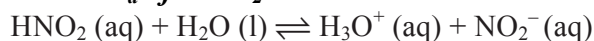


SA WB CA CB

		→	H ₃ O ⁺	Cl ⁻
I	1.00		0	0
C	-1.00		+1.00	+1.00
F	0		1.00	1.00

Beaker C: 100 mL of 1.00 M HNO₂

$$K_a \text{ of } \text{HNO}_2 = 4.6 \times 10^{-4}$$



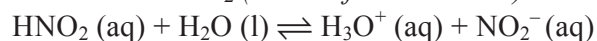
WA WB CA CB

		⇌	H ₃ O ⁺	NO ₂ ⁻
I	1.00		0	0
C	-x		+x	+x
E	1.00 - x		x	x
	0.98		2.1×10 ⁻²	2.1×10 ⁻²

$$K_a = 4.6 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x \cdot x}{1.00 - x}$$

$$4.6 \times 10^{-4} \approx \frac{x^2}{1.00} \text{ and } x = 2.1 \times 10^{-2}$$

Beaker D: 100 mL of 1.00 M HNO₂ mixed with 100 mL of 1.00 M NaNO₂ (*Be careful-dilution!!!*)



WA WB CA CB

		⇌	H ₃ O ⁺	NO ₂ ⁻
I	0.500		0	0.500
C	-x		+x	+x
E	0.500 - x		x	0.500 + x
	0.500		4.6×10 ⁻⁴	0.500

$$K_a = 4.6 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x(0.500 + x)}{(0.500 - x)}$$

$$4.6 \times 10^{-4} \approx \frac{x(0.500)}{0.500} \text{ and } x = 4.6 \times 10^{-4}$$

- For each beaker in Model 1, *underneath each reaction equation*, write SA (strong acid), SB (strong base), WA (weak acid), or WB (weak base) for the reactants; and write CA (conjugate acid) or CB (conjugate base) for the products.
- For Beaker A and B, fill in the ICE/ICF charts to determine all equilibrium/final concentrations of the molecules or ions. ICF (“final”) is used for reactions that go to completion, such as reactions with strong acids or bases. For these the change will stoichiometrically consume the limiting reactant.
- For Beaker C and D, fill in the ICE charts, using “x” values as needed. Then, underneath each ICE chart, write the K_a expression and show calculations to determine the value of “x.” Then, go back and modify values in the Equilibrium row so that each concentration is a numerical value. (*Substitute in all “x” values.*)

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4. Imagine that 1.00 M sodium hydroxide was added dropwise to each of the beakers in Model 1. List the species in each beaker that would react with this added base and neutralize significant quantities (at least 0.05 mole) of it. If neutralization is not likely to occur, write “none.”

Beaker A Pure Water	Beaker B HCl (aq)	Beaker C HNO ₂ (aq)	Beaker D HNO ₂ with NaNO ₂
none	H ₃ O ⁺	HNO ₂	HNO ₂

5. Imagine that 1.00 M hydrochloric acid was added dropwise to each of the beakers in Model 1. List the species in each beaker that could react with this added acid and neutralize significant quantities (at least 0.05 mole) of it. If neutralization is not likely to occur, write “none.”

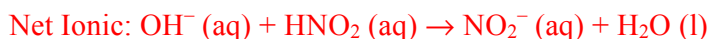
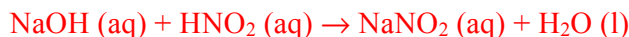
Beaker A Pure Water	Beaker B HCl (aq)	Beaker C HNO ₂ (aq)	Beaker D HNO ₂ with NaNO ₂
none	none	none	NO ₂ ⁻

6. Which beaker in Model 1 was able to neutralize significant quantities of both acid and base? D

Read This!

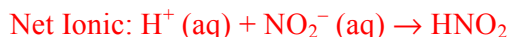
A buffer solution is one that can neutralize both small quantities of acid and small quantities of base. This is possible because the solution contains significant quantities of both a weak acid and a weak base (*the weak base is usually the conjugate base of the weak acid*). Thus, a buffer can neutralize a significant amount of any strong acid or any strong base that is added, allowing the solution to keep a fairly constant pH.

7. Which beaker in Model 1 contains a buffer? D For this buffer...
- What species is the weak acid? HNO₂ What species is the weak base? NO₂⁻
 - Write the neutralization reaction that would take place if 1.0 M NaOH was added to this buffer. (*Hint—what species in the buffer will react with the added OH⁻?*) Also, explain why the pH of the solution would stay fairly constant after the addition of some NaOH.



The pH stays fairly constant because the weak acid (HNO₂) in the buffer consumes all of the added strong base OH⁻ and forms the weak base NO₂⁻ and water. Thus, all strong base has been removed and for small amounts of OH⁻, the relative amounts of HNO₂ and NO₂⁻ remain fairly constant. Thus, the [H⁺], as calculated for beaker D above, remains fairly constant.

- Write the neutralization reaction that would take place if 1.0 M HCl was added to this buffer. (*Hint—what species in the buffer will react with the added H₃O⁺?*) Also, explain why the pH of the solution would stay fairly constant after the addition of some HCl.



As above, the pH stays fairly constant because the weak base (NO₂⁻) in the buffer consumes all the added strong acid H⁺ and forms the weak acid HNO₂ and water. Thus, all strong acid has been removed and for small amounts of H⁺, the relative amounts of HNO₂ and NO₂⁻ remain fairly constant. Thus, the [H⁺], as calculated for beaker D above, remains close to the K_a.

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- d) Now suppose one keeps adding 1.0 M HCl to this buffer until a total of 101 mL of 1.0M HCl have been added. At this point, the pH of the solution will be very acidic. Why is this the case?

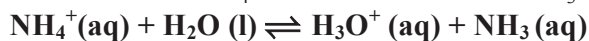
At this point, 0.101 mol of HCl will have been added to 0.100 mol of NO_2^- , completely using it up and leaving behind an excess of 0.001 mol of H^+ in 301 mL, for a concentration of 0.0033 M and a pH of 2.479.

8. Fill in the chart below to determine which of the following solutions are buffer solutions. To do so, first, determine the three most predominant species in the solution. Second, underneath each predominant species, label each with either strong acid (SA), strong base (SB), weak acid (WA), weak base (WB) or neutral ion (N) (*A neutral ion could be the conjugate base of a strong acid and so would be too weak to be a base in H_2O , or it could be the conjugate acid of a strong base and so would be too weak to be an acid in H_2O*). Lastly, state whether the solution is a buffer solution.

Substances mixed in equal volumes	List the three most predominant species in the solution. Underneath each species, label with either SA, SB, WA, WB or N			Is the solution a buffer?
a) 1.0 M HCl and 1.0 M NaCl	<u>H_3O^+</u> SA	<u>Cl^-</u> N	<u>Na^+</u> N	No
b) 1.0 M HNO_2 and 1.0 M HNO_3	<u>HNO_2</u> WA	<u>H_3O^+</u> SA	<u>NO_3^-</u> N	No
c) 1.0 M NH_4Cl and 1.0 M NH_3	<u>NH_4^+</u> WA	<u>Cl^-</u> N	<u>NH_3</u> WB	Yes
d) 1.0 M CH_3COOH and 1.0 M NaCl	<u>CH_3COOH</u> WA	<u>Na^+</u> N	<u>Cl^-</u> N	No
e) 1.0 M HF and 1.0 M NaF	<u>HF</u> WA	<u>Na^+</u> N	<u>F^-</u> WB	Yes
f) 1.0 M H_2SO_4 and 1.0 M Na_2SO_4	<u>Na^+</u> N	<u>HSO_4^-</u> WA	<u>—</u>	No
g) 1.0M KOH and 1.0M KCl	<u>K^+</u> N	<u>Cl^-</u> N	<u>OH^-</u> SB	No
h) 1.0M $\text{Ca}(\text{OH})_2$ and 1.0M HCl	<u>Ca^{2+}</u> N	<u>Cl^-</u> N	<u>OH^-</u> SB	No

Model 2 – pH of Buffer Solutions

Beaker 1

 100 mL 1.0 M NH₄Cl and 100 mL 1.0 M NH₃


$$K_a \text{ of } \text{NH}_4^+ = 5.6 \times 10^{-10} \quad \text{p}K_a \text{ of } \text{NH}_4^+ = \underline{9.25}$$

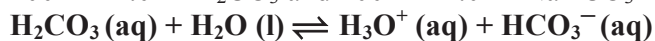
	NH ₄ ⁺	⇌	H ₃ O ⁺	NH ₃
I	0.500		0	0.500
C	-x		+x	+x
E	0.500 - x		X	0.500 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}; \quad [\text{H}_3\text{O}^+] = \frac{K_a[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$[\text{H}_3\text{O}^+] = \frac{(5.6 \times 10^{-10})(0.500 \cancel{-x})}{(0.500 \cancel{+x})} = 5.6 \times 10^{-10} \text{ M}$$

$$\text{pH} = -\log(5.6 \times 10^{-10}) = 9.25$$

Beaker 3

 100 mL 1.0 M H₂CO₃ and 100 mL 1.0 M NaHCO₃


$$K_a \text{ of } \text{H}_2\text{CO}_3 = 4.4 \times 10^{-7} \quad \text{p}K_a \text{ of } \text{H}_2\text{CO}_3 = \underline{6.36}$$

	H ₂ CO ₃	⇌	H ₃ O ⁺	HCO ₃ ⁻
I	0.500		0	0.500
C	-x		+x	+x
E	0.500 - x		X	0.500 + x

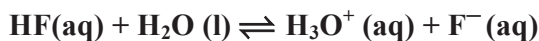
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}; \quad [\text{H}_3\text{O}^+] = \frac{K_a[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]}$$

$$[\text{H}_3\text{O}^+] = \frac{(4.4 \times 10^{-7})(0.500 \cancel{-x})}{(0.500 \cancel{+x})} = 4.4 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log(4.4 \times 10^{-7}) = 6.36$$

Beaker 2

100 mL 1.0 M HF and 100 mL 1.0 M NaF



$$K_a \text{ of } \text{HF} = 3.5 \times 10^{-4} \quad \text{p}K_a \text{ of } \text{HF} = \underline{3.46}$$

	HF	⇌	H ₃ O ⁺	F ⁻
I	0.500		0	0.500
C	-x		+x	+x
E	0.500 - x		X	0.500 + x

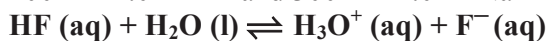
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}; \quad [\text{H}_3\text{O}^+] = \frac{K_a[\text{HF}]}{[\text{F}^-]}$$

$$[\text{H}_3\text{O}^+] = \frac{(3.5 \times 10^{-4})(0.500 \cancel{-x})}{(0.500 \cancel{+x})} = 3.5 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(3.5 \times 10^{-4}) = 3.46$$

Beaker 4

100 mL 1.0 M HF and 300 mL 1.0 M NaF



$$K_a \text{ of } \text{HF} = 3.5 \times 10^{-4} \quad \text{p}K_a \text{ of } \text{HF} = \underline{3.46}$$

	HF	⇌	H ₃ O ⁺	F ⁻
I	0.250		0	0.750
C	-x		+x	+x
E	0.250 - x		X	0.750 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}; \quad [\text{H}_3\text{O}^+] = \frac{K_a[\text{HF}]}{[\text{F}^-]}$$

$$[\text{H}_3\text{O}^+] = \frac{(3.5 \times 10^{-4})(0.250 \cancel{-x})}{(0.750 \cancel{+x})} = 1.2 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(1.2 \times 10^{-4}) = 3.93$$

- Model 2 describes four buffer solutions, each consisting of a weak acid and its conjugate base. Using the given K_a of each acid, calculate the $\text{p}K_a$ of each acid and fill in values above each ICE chart.
- Fill in the ICE charts using “x’s” where needed. (*Be careful--watch out for dilution effects when determining initial concentrations.*) Then, underneath each ICE chart, write the K_a expression. Then, rearrange the K_a expression to solve for $[\text{H}_3\text{O}^+]$ (*no numbers yet!*). Then, plug in values from the ICE chart and obtain the numerical value of $[\text{H}_3\text{O}^+]$. In addition, determine the **pH** of each solution.
- Do all buffers solutions have a neutral pH? No. Justify your answer with data from Model 2.
The buffer systems have pH values from acidic (HF) to basic (NH₄⁺).
- When a buffer system consists of equal concentrations of a weak acid and its conjugate base, how does the $\text{p}K_a$ value of the weak acid compare to the pH of the solution? The pH = pK_a

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13. When a buffer consists of unequal concentrations of a weak acid and its conjugate base (as in beaker 4), is the pH significantly different from the pK_a of the weak acid? Yes Support your answer with data from Model 2.

Beaker 4 contains the same buffer system as beaker 2, but with more of the conjugate base. The pH of beaker 4 is nearly 0.5 pH units higher than that of beaker 2.

14. The buffers in Beaker 2 and 4 both consist of HF as the weak acid and F^- as the weak base. However, each buffer has a different ability to neutralize added HCl (They each have a different buffer capacity.) Which buffer solution (Beaker 2 or Beaker 4) would neutralize more moles of added HCl per liter of buffer solution? 4 Explain why.

Beaker 4 contains 0.300 mol of F^- while beaker 2 contains only 0.100 mol of F^- . Thus, beaker 4 can neutralize 3× the amount of added HCl (or other strong acid) as beaker 2.

15. Suppose 100 mL of 0.50 M HCl is added to the buffer in Beaker 4. Answer the following questions to determine the pH of the resulting solution.

- a) At right, complete the net ionic equation for the neutralization reaction that occurs. Then, fill in the ICF chart. *Watch out for dilution effects! Also-- HCl is a strong acid, so make the assumption that the reaction goes 100% to completion (not to equilibrium).*

	H_3O^+	+	<u>F^-</u>	\rightarrow	<u>HF</u>	+	<u>H_2O</u>
I	0.100 M		0.600 M		0.200 M		–
C	–0.100		–0.100		+0.100		–
F	0		0.500		0.300		–

- b) Now, let the solution come to equilibrium. Fill in the ICE chart below, by transferring the "Final" values from the previous ICF chart and putting them in as the "Initial" concentrations in the ICE chart below. Fill in the rest of the ICE chart using "x's" where needed. Write out the K_a expression and show calculations needed to determine the $[H_3O^+]$ and pH of the resulting solution.

	HF	+	H_2O	\rightleftharpoons	H_3O^+	+	F^-
I	0.300				0		0.500
C	–x				+x		+x
E	0.300 – x				x		0.500 + x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}; [H_3O^+] = \frac{K_a[HF]}{[F^-]}$$

$$[H_3O^+] = \frac{(3.5 \times 10^{-4})(0.300/x)}{(0.500+x)} = 2.1 \times 10^{-4} \text{ M}$$

$$pH = -\log(2.1 \times 10^{-4}) = 3.68$$

- c) What was the pH of the buffer before the addition of the HCl? 3.93 pH after the addition of HCl? 3.68
 d) Was the buffer effective at keeping the pH of the solution fairly constant? Yes

16. An industrial process requires a constant pH of 3.00. The weak acids available in the warehouse are the following:

benzoic acid ($HC_7H_3O_2$), $K_a = 6.3 \times 10^{-5}$	phosphorous acid (H_3PO_3), $K_a = 3.7 \times 10^{-2}$
nitrous acid (HNO_2), $K_a = 7.2 \times 10^{-4}$	hydrocyanic acid (HCN), $K_a = 6.2 \times 10^{-10}$

- a. Which of the four acids would be best to make a buffer for the industrial process? HNO_2
 Explain. (Hint: The best buffer has equal concentrations of the weak acid and its conjugate base.)
 HNO_2 is used because its pK_a is closest to 3.00.
- b. In addition to the weak acid, what other chemical is needed to prepare the buffer? NO_2^-
In order to make the buffer, the conjugate weak base must also be present.