Chapter 15 Tutorial

Due: 11:00pm on Wednesday, November 28, 2012

Note: To understand how points are awarded, read your instructor's Grading Policy.

---

pH of a Buffer Solution

Solutions that contain a weak acid, HA, and its conjugate base, $\mathrm{A^-}$, are called *buffer solutions* because they resist drastic changes in pH. The principal reaction is

$$\mathrm{HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)}$$

Unbuffered, a weak acid would ionize and the net reaction would proceed forward to reach equilibrium. However, when a significant amount of conjugate base is already present, the extent of the net reaction forward is diminished. Thus, equilibrium concentrations of HA and $\mathrm{A^-}$ are approximately equal to their initial concentrations.

Part A

Calculate the pH of the solution made by adding 0.50mol of propanoic acid, ($\mathrm{C_2H_5COOH}$ or $\mathrm{HC_3H_5O_2}$) and 0.30 mol of sodium propanoate ($\mathrm{C_2H_5COONa}$ or $\mathrm{NaC_3H_5CO_2}$) to 1.00 L of water. The value of K_a for $\mathrm{C_2H_5COOH}$ is 1.3×10^{-5}.

Express your answer numerically using two decimal places.

Hint 1. How to approach the problem

The principal reaction and the equilibrium equation for this buffer solution are

$$\mathrm{C_2H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_5COO^-(aq)}$$

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{C_2H_5COO^-}]}{[\mathrm{C_2H_5COOH}]}$$

where all concentrations are equilibrium concentrations. But since this is a buffer, the equilibrium concentrations of acid and conjugate base are approximately equal to their initial concentrations.

Substitute the approximate equilibrium concentration values into the K_a expression and solve for $[\mathrm{H_3O^+}]$. Then use $[\mathrm{H_3O^+}]$ to calculate the pH.

Hint 2. Calculate the concentration of hydronium ion

Calculate the concentration of $\mathrm{H_3O^+}$ in the solution.

Express the molar concentration numerically using two significant figures.

Hint 1. Express K_a in terms of the molar concentration of the hydronium ion

If the change in initial concentration of $\mathrm{C_2H_5COOH}$ is assigned the value "x," the following table expresses the equilibrium concentrations in terms of this variable:

	$\mathrm{C_2H_5COOH}$	+	$\mathrm{H_2O}$	$\rightleftharpoons$	$\mathrm{H_3O^+}$	+	$\mathrm{C_2H_5COO^-}$
Initial (M)	0.50				0		0.30
Change (M)	$-x$				$+x$		$+x$
Final (M)	$0.50-x$				x		$0.30+x$

In terms of equilibrium concentrations,

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{C_2H_5COO^-}]}{[\mathrm{C_2H_5COOH}]}$$

How would you express K_a in terms of x?

Express K_a in terms of x.

ANSWER:

K_a = $\frac{x(0.30+x)}{0.50-x}$

ANSWER:

$[H_3O^+]$ = 2.2×10^{-5} M

ANSWER:

pH = 4.66

Correct

When the concentrations of acid and base in a buffer solution are equal, $[H_3O^+] = K_a$ and $pH = pK_a$. When there is more acid than base, $[H_3O^+] > K_a$ and $pH < pK_a$. The pK_a for C_2H_5COOH is 4.89. As expected, the calculated pH is less than pK_a.

An alternate method to calculate the pH of this solution would be to employ the Henderson-Hasselbalch equation which is shown below,

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

where base represents the propanoate ion ($C_2H_5COO^-$) and acid the propanoic acid (C_2H_5COOH).

pH Changes in Buffers

A solution of a weak acid (HA) and its conjugate base (A^-),

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

is called a buffer and will resist a change in pH. If acid is added, the reaction shifts to consume the added H^+, forming more HA. When base is added, the base will react with H^+, reducing its concentration. The reaction then shifts to replace H^+ through the dissociation of HA into H^+ and A^-. In both instances, $[H^+]$ tends to remain constant.

The pH of a buffer is calculated by using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Part A

What is the pH of a buffer prepared by adding 0.708mol of the weak acid HA to 0.608mol of NaA in 2.00 L of solution? The dissociation constant K_a of HA is 5.66×10^{-7}.

Express the pH numerically to two decimal places.

Hint 1. How to approach the problem

The pH of the buffer can be calculated by using the following equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

Calculate the $\mathrm{p}K_\mathrm{a}$ by taking the negative log of the dissociation constant K_a. Calculate the approximate $[\mathrm{A}^-]$ and $[\mathrm{HA}]$ by using the volume of the buffer and the number of moles of NaA and HA used in preparing the buffer.

Hint 2. Determine the value of the p*K* a

What is the $\mathrm{p}K_\mathrm{a}$ value for this acid?

Express your answer numerically to two decimal places.

Hint 1. How to calculate the p*K* a

Recall that $\mathrm{p}K_\mathrm{a} = -\log K_\mathrm{a}$.

ANSWER:

$\mathrm{p}K_\mathrm{a}$ = 6.25

Hint 3. Determine the concentration of HA

Based on the initial amount of HA and the volume of the buffer, what is the molar concentration of HA in the buffer?

Express the molar concentration numerically.

Hint 1. How to determine the concentration

In a buffer, the concentration of the weak acid can be approximated very closely by using the initial concentration of the acid:

$$M = \frac{\text{moles of acid}}{\text{liters of solution}}$$

ANSWER:

$[\mathrm{HA}]$ = 0.354 M

Hint 4. Determine the concentration of A⁻

Based on the initial amount of NaA and the volume of the buffer, what is the molar concentration of A^- in the buffer?

Express the molar concentration numerically.

Hint 1. How to determine the concentration

The salt NaA dissociates completely as shown by the equation

$$\mathrm{NaA(s)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{A^-(aq)}$$

Therefore, the concentration of the anion can be closely approximated by the initial concentration of the salt:

$$M = \frac{\text{moles of salt}}{\text{liters of solution}}$$

ANSWER:

$[\mathrm{A^-}]$ = 0.304 M

ANSWER:

pH = 6.18

Correct

Since both the acid and base exist in the same volume, we can skip the concentration calculations and use the number of moles in the Henderson-Hasselbalch equation to calculate the pH. The answer will be the same.

Part B

What is the pH after 0.150mol of HCl is added to the buffer from Part A? Assume no volume change on the addition of the acid.

Express the pH numerically to two decimal places.

Hint 1. How to approach the problem

The addition of an acid to the reaction, by Le Châtelier's principle, will cause the equilibrium to shift to the left:

$$\mathrm{HA(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{A^-(aq)}$$

The shift will increase the amount HA and decrease the amount of $\mathrm{A^-}$. The amount of change is equal to the number of moles of acid added because of the 1:1 stoichiometry; that is, HA will increase by the number of moles of acid added and $\mathrm{A^-}$ will decrease by the number of moles of acid added. The pH of the buffer can be calculated by using the following equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

Calculate the $\mathrm{p}K_\mathrm{a}$ by taking the negative log of K_a. Calculate the approximate $[\mathrm{A^-}]$ and $[\mathrm{HA}]$ by using the volume of the buffer and the number of moles of NaA and HA after the shift.

Hint 2. Determine the concentration of HA

Based on the initial amount of HA, the amount of HCl added, and the volume of the buffer, what is the molar concentration of HA in the buffer after the addition of the acid?

Express the molar concentration numerically.

Hint 1. How to determine the concentration of the weak acid

After the addition of the acid, the equilibrium for the reaction shifts to the left. Because of the 1:1 stoichiometry of HCl, $\mathrm{H^+}$, $\mathrm{A^-}$, and HA, a good approximation for the amount of HA formed is the amount of HCl added. Thus, the weak acid concentration can then be calculated as follows:

Initial moles HA	0.708mol
Change	$+0.150\mathrm{mol}$
Equilibrium moles HA	$0.708\mathrm{mol} + 0.150\mathrm{mol}$

Then

$$M = \frac{\text{equilibrium moles of acid}}{\text{liters of solution}}$$

ANSWER:

$[\mathrm{HA}]$ = 0.429 M

Hint 3. Determine the concentration of A⁻

Based on the initial amount of $\mathrm{A^-}$, the amount of HCl added, and the volume of the buffer, what is the molar concentration of $\mathrm{A^-}$ in the buffer after the addition of the acid?

Express the molar concentration numerically.

Hint 1. How to determine the concentration of the acid anion

After the addition of the acid, the reaction equilibrium shifts in the reverse direction. Because of the 1:1 stoichiometry of HCl, $\mathrm{H^+}$, $\mathrm{A^-}$, and HA, a good approximation of the amount of $\mathrm{A^-}$ lost is closely approximated by the amount of HCl added. Therefore

Initial moles $\mathrm{A^-}$	0.608mol
Change	$-0.150\mathrm{mol}$
Equilibrium moles $\mathrm{A^-}$	$0.608\mathrm{mol}-0.150\mathrm{mol}$

and then the concentration is given by

$$M=\frac{\text{equilibrium moles of anion}}{\text{liters of solution}}$$

ANSWER:

$[\mathrm{A^-}]$ = 0.229 M

ANSWER:

pH = 5.98

Correct

Even though a significant amount of a strong acid was added, the pH of the buffer changed very little. If this amount of acid was added to 2.00 L of pure water, the pH would change from 7.00 to 1.12.

Part C

What is the pH after 0.195mol of NaOH is added to the buffer from Part A? Assume no volume change on the addition of the base.

Express the pH numerically to two decimal places.

Hint 1. How to approach the problem

By Le Châtelier's principle, the addition of a base will cause the equilibrium to shift in the forward direction because the $\mathrm{OH^-}$ from the NaOH reacts with $\mathrm{H^+}$ to produce water. This reduces the concentration of $\mathrm{H^+}$ and causes the shift to the right:

$$\mathrm{HA(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{A^-(aq)}$$

The shift will decrease the amount of HA and increase the amount of $\mathrm{A^-}$. The amount of change is equal to the number of moles of acid added because of the 1:1 stoichiometry; that is, HA will decrease by the number of moles of base added and A^- will increase by the number of moles of base added. The pH of the buffer can be calculated using the following equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

Calculate the approximate $[\mathrm{A}^-]$ and $[\mathrm{HA}]$ by using the volume of the buffer and the final number of moles of NaA and HA.

Hint 2. Determine the concentration of HA

Based on the initial amount of HA, the amount of NaOH added, and the volume of the buffer, what is the molar concentration of HA in the buffer after the addition of the base?

Express the molar concentration numerically.

Hint 1. How to determine the concentration of the weak acid

After the addition of the base, NaOH, the equilibrium for the reaction shifts in the forward direction. Because of the 1:1 stoichiometry of NaOH, H^+, A^-, and HA, a good approximation for the amount of HA lost is closely approximated by the amount of NaOH added. The weak acid concentration can than be calculated as follows:

Initial moles HA	0.708 mol
Change	$-0.195 \mathrm{mol}$
Equilibrium moles HA	$0.708 \mathrm{mol} - 0.195 \mathrm{mol}$

Then

$$M = \frac{\text{equilibrium moles of acid}}{\text{liters of solution}}$$

ANSWER:

$[\mathrm{HA}]$ = 0.257 M

Hint 3. Determine the concentration of A⁻

Based on the initial amount of A^-, the amount of NaOH added, and the volume of the buffer, what is the molar concentration of A^- in the buffer after the addition of the base?

Express the molar concentration numerically to two decimal places.

Hint 1. How to determine the concentration of the acid anion

After the addition of the base, the equilibrium for the reaction shifts in the forward direction. Because of the 1:1 stoichiometry of NaOH, H^+, A^-, and HA, a good approximation of the amount of A^- formed is closely approximated by the amount of NaOH added. Therefore

Initial moles A^-	0.608 mol
Change	$+0.195 \mathrm{mol}$
Equilibrium moles A^-	$0.608 \mathrm{mol} + 0.195 \mathrm{mol}$

and the concentration is given by

$$M = \frac{\text{equilibrium moles of anion}}{\text{liters of solution}}$$

ANSWER:

$[A^-]$ = 0.402 M

ANSWER:

pH = 6.44

Correct

Even though a significant amount of strong base was added, the pH of the buffer changed very little. If this amount of base was added to 2.00 L of pure water, the pH would change from 7.00 to 12.98.

Base/Acid Ratios in Buffers

Just as pH is the negative logarithm of $[\mathrm{H_3O^+}]$, $\mathrm{p}K_\mathrm{a}$ is the negative logarithm of K_a,

$$\mathrm{p}K_\mathrm{a} = -\log K_\mathrm{a}$$

The Henderson-Hasselbalch equation is used to calculate the pH of buffer solutions:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

Notice that the pH of a buffer has a value close to the $\mathrm{p}K_\mathrm{a}$ of the acid, differing only by the logarithm of the concentration ratio $[\mathrm{base}]/[\mathrm{acid}]$.

Part A

Acetic acid has a K_a of 1.8×10^{-5}. Three acetic acid/acetate buffer solutions, A, B, and C, were made using varying concentrations:

1. $[\mathrm{acetic\ acid}]$ ten times greater than $[\mathrm{acetate}]$,
2. $[\mathrm{acetate}]$ ten times greater than $[\mathrm{acetic\ acid}]$, and
3. $[\mathrm{acetate}] = [\mathrm{acetic\ acid}]$.

Match each buffer to the expected pH.

Drag each item to the appropriate bin.

Hint 1. How to approach the problem

Consider the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

- If the concentrations of acid and base are equal, then $[\mathrm{base}]/[\mathrm{acid}] = 1$.

  $\log(1) = 0$, so the equation becomes $\mathrm{pH} = \mathrm{p}K_\mathrm{a}$.
- If $[\mathrm{base}]$ is ten times greater than $[\mathrm{acid}]$, then $[\mathrm{base}]/[\mathrm{acid}] = 10$.

  $\log(10) = 1$, so the equation becomes $\mathrm{pH} = \mathrm{p}K_\mathrm{a} + 1$.
- If $[\mathrm{acid}]$ is ten times greater than $[\mathrm{base}]$, then $[\mathrm{base}][\mathrm{acid}] = 1/10$.

$\log(1/10) = -1$, so the equation becomes $\mathrm{pH} = \mathrm{p}K_\mathrm{a} - 1$.

Hint 2. Calculate p*K* a

Given $K_\mathrm{a} = 1.8 \times 10^{-5}$, calculate $\mathrm{p}K_\mathrm{a}$.

Express your answer numerically using two decimal places.

ANSWER:

$\mathrm{p}K_\mathrm{a}$ = 4.74

ANSWER:

Correct

Part B

How many grams of dry NH_4Cl need to be added to 1.70 L of a 0.700 M solution of ammonia, NH_3, to prepare a buffer solution that has a pH of 8.92? K_b for ammonia is 1.8×10^{-5}.

Express your answer numerically in grams to three significant figures.

Hint 1. How to approach the problem

NH_4^+ is the conjugate acid for NH_3. You will need to calculate $\mathrm{p}K_\mathrm{a}$ for NH_4^+. Then you can use the Henderson-Hasselbalch equation to find the concentration ratio $[\mathrm{base}]/[\mathrm{acid}]$. Once you know the ratio, you can determine the required molar concentration of the salt and then calculate the mass of the salt.

Hint 2. Calculate the p*K* a for NH4 $^+$

K_b for NH_3 is 1.8×10^{-5}. Calculate $\mathrm{p}K_\mathrm{a}$ for its conjugate, NH_4^+.

Express your answer numerically using two decimal places.

Hint 1. Calculate *K* a

K_b for NH_3 is 1.8×10^{-5}. Calculate K_a for its conjugate, NH_4^+.

Express your answer numerically using four significant figures.

Hint 1. How to approach the problem

For any conjugate acid-base pair,

$$K_a \times K_b = K_w = 1.0 \times 10^{-14}$$

ANSWER:

K_a = 5.555×10^{-10}

ANSWER:

pK_a = 9.26

Hint 3. Calculate the ratio of base to acid

What $[NH_3]/[NH_4^+]$ ratio is required for a buffer solution that has pH = 8.92? The pK_a for NH_4^+ is 9.26.

Express your answer numerically using three significant figures.

Hint 1. How to approach the problem

Use the Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

and solve it for the concentration ratio.

ANSWER:

$\frac{[NH_3]}{[NH_4^+]}$ = 0.457

Hint 4. Calculate the concentration of NH4 +

The $[NH_3]/[NH_4^+]$ ratio is equal to 0.457. The concentration of NH_3 in the buffer is 0.700 M . Calculate the concentration of NH_4Cl.

Express the molar concentration numerically using three significant figures.

Hint 1. How to approach the problem

Since NH_4Cl is fully dissociated in the solution, the salt concentration is equal to the NH_4^+ ion concentration. Find $[NH_4^+]$ from the given ratio.

ANSWER:

$[NH_4^+]$ = 1.53 M

Hint 5. Calculate the number of moles of NH_4Cl

Calculate the number of moles of NH_4Cl in 1.70 L of the solution if the concentration is 1.53 M .

Express your answer numerically in moles.

Hint 1. Molarity formula

Recall that

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in L}}$$

ANSWER:

number of moles of NH_4Cl = 2.60 mol

Hint 6. Calculate the molar mass of NH_4Cl

What is the molar mass of NH_4Cl? Recall that you can access a periodic table by clicking the "Tools" link in the upper right corner of the main question window.

Express your answer numerically in grams per mole to three significant figures.

ANSWER:

molar mass = 53.5 g/mol

ANSWER:

mass of NH_4Cl = 139 g

Correct

± Titration of Strong Acid with Strong Base

100. mL of 0.200 M HCl is titrated with 0.250 M $NaOH$.

Part A

What is the pH of the solution after 50.0 mL of base has been added?

Express the pH numerically.

Hint 1. How to approach the problem

Consider the reaction

$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{H_2O} + \mathrm{NaCl}$$

HCl and NaOH react in a 1:1 ratio. You should find the number of millimoles of each that you have, then determine whether any acid or base is left over after the two compounds react.

Hint 2. Calculate the amount of acid

How many millimoles of HCl are in 100. mL of 0.200 M HCl?

Express your answer numerically.

Hint 1. How to approach the problem

Molarity is defined as the number of moles per liter, or millimoles per milliliter. Thus one has the relation

$$\mathrm{molarity} \times \mathrm{milliliters} = \mathrm{millimoles}$$

Using millimoles (instead of moles) in titration calculations will often cut down on the amount of unit conversion.

ANSWER:

amount of HCl = 20.0 mmol

Hint 3. Calculate the amount of base

How many millimoles of NaOH are in 50.0 mL of 0.250 M NaOH?

Express your answer numerically.

Hint 1. How to approach the problem

Molarity is equal to moles per liter, or millimoles per milliliter. Thus you can use the relation

$$\mathrm{molarity} \times \mathrm{milliliters} = \mathrm{millimoles}$$

Using millimoles (instead of moles) in titration calculations will often cut down on the amount of unit conversion.

ANSWER:

amount of NaOH = 12.5 mmol

Hint 4. Determine the amount of leftover acid

How much HCl is leftover after the 20.0 mmol of HCl reacts with the 12.5 mmol of NaOH?

Express your answer in units of millimoles.

ANSWER:

amount of Hcl = 7.5 mmol

Hint 5. Find the concentration of leftover acid

The total volume of this solution is now 150. mL ($100.\ \mathrm{mL} + 50.0\ \mathrm{mL}$). What is the concentration of 7.5 mmol of HCl in a volume of 150. mL?

Express your answer in units of molarity.

Hint 1. How to approach the problem

Use the relation $M = \frac{\mathrm{mol}}{\mathrm{L}}$ or $M = \frac{\mathrm{mmol}}{\mathrm{mL}}$.

ANSWER:

$[\mathrm{HCl}]$ = 0.050 M

ANSWER:

pH = 1.30

Correct

Part B

What is the pH of the solution at the equivalence point?

Express the pH numerically.

Hint 1. The meaning of "equivalence point"

The equivalence point is the point at which equal amounts of acid and base have reacted.

ANSWER:

pH = 7.00

Correct

In a strong acid with strong base titration, the products are completely neutral. Therefore, when all the acid has reacted with the base, the solution must be neutral.

Mixing Strong Acids and Bases

Imagine that you are in chemistry lab and need to make 1.00L of a solution with a pH of 2.60.

You have in front of you

- 100 mL of 7.00×10^{-2} M HCl,
- 100 mL of 5.00×10^{-2} M NaOH, and
- plenty of distilled water.

You start to add HCl to a beaker of water when someone asks you a question. When you return to your dilution, you accidentally grab the wrong cylinder and add some NaOH. Once you realize your error, you assess the situation. You have 83.0mL of HCl and 87.0mL of NaOH left in their original containers.

Part A

Assuming the final solution will be diluted to 1.00L , how much more HCl should you add to achieve the desired pH?

Express your answer numerically in milliliters to three significant figures.

Hint 1. How to approach the problem

First calculate the number of moles of acid initially added to the beaker. Next, determine the number of moles of base that was accidentally added to this solution. Considering that the base will neutralize and equivalent number of moles of acid, determine the number of moles of H^+ actually present in the solution. Then, use the given pH of the desired solution to calculate the final $[H^+]$ needed and, using the final volume, convert to moles. Compare the actual number moles of H^+ to the desired number to find the number of moles of HCl that still need to be added. Finally, calculate the volume of 7.00×10^{-2} M HCl that would deliver that amount of H^+.

Hint 2. Determine the number of moles of acid present in the beaker

After the acid and base react, how many moles of acid are present in the beaker?

Express your answer numerically in moles.

Hint 1. Determine the number of moles of acid added

How many moles of acid were initially added to the beaker?

Enter your answer numerically in moles.

Hint 1. How to find the number of moles from molarity and volume

Recall that molarity is the number of moles per liter,

$$M = n/V$$
$$MV = n$$

where M is molarity, n is the number of moles, and V is the volume in *liters*.

Hint 2. Find the volume of acid added

How many *liters* of HCl were initially added to the beaker?

Enter your answer numerically in liters.

ANSWER:

1.70×10^{-2} L

ANSWER:

1.19×10^{-3} mol

Hint 2. Calculate the number of moles of base added

How many moles of base were added to the beaker?

Express your answer numerically in moles.

Hint 1. How to find the number of moles from molarity and volume

Recall that molarity is the number of moles per liter,

$$M = n/V$$
$$MV = n$$

where M is molarity, n is the number of moles, and V is the volume in *liters*.

Hint 2. Find the volume of base added

How many *liters* of $NaOH$ were added to the beaker?

ANSWER:

1.30×10^{-2}

ANSWER:

6.50×10^{-4} mol

ANSWER:

5.40×10^{-4} mol

Hint 3. Determine the desired number of moles of acid in the final solution

How many moles of $\mathrm{H^+}$ will the desired 1.00L solution at pH = 2.60 contain?

Express your answer numerically in moles to three significant figures.

Hint 1. Calculate the needed $[\mathrm{H^+}]$

If pH = 2.60, what is $[\mathrm{H^+}]$?

Express the molar concentration numerically to three significant figures.

Hint 1. How to calculate $[\mathrm{H^+}]$ from pH

Start with the equation

$$\mathrm{pH} = -\log[\mathrm{H^+}]$$

move the negative sign, then take the antilog of both sides to get

$$10^{-\mathrm{pH}} = [\mathrm{H^+}]$$

ANSWER:

$[\mathrm{H^+}]$ = 2.51×10^{-3} M

ANSWER:

2.51×10^{-3} mol

Hint 4. Determine the number of moles of acid that must be added

How many moles of additional HCl is needed to achieve the desired solution?

Express your answer numerically in moles.

ANSWER:

1.97×10^{-3} mol

ANSWER:

28.2 mL

Correct

Titrations

Learning Goal:

To learn about titration types and how to calculate pH at different points of titration.

In an acid-base titration, a *titrant* (solution of a base or acid) is added slowly to an *analyte* (solution of an acid or base). The titration is often monitored using a pH meter. A plot of pH as a function of the volume of titrant added is called a pH *titration curve*.

Prior to the titration, the pH is determined by the concentration of the analyte. When the titrant is added, it begins to neutralize the analyte. The decrease in the analyte concentration changes the pH. At the *equivalence point*, equivalent quantities of acid and base have been mixed together such that the acid-base reaction is complete, and the pH is determined by the product. In the case of a strong acid-strong base titration, the salt formed is neutral, and $\mathrm{pH} = 7$. In a weak acid-strong base titration, a basic salt is produced, and $\mathrm{pH} > 7$. In a weak base-strong acid titration, the salt is acidic, and $\mathrm{pH} < 7$. After the equivalence point, the pH is determined by the concentration of excess titrant.

Part A

Identify each type of titration curve. Note that the analyte is stated first, followed by the titrant.

Drag each graph to the appropriate bin.

Hint 1. How to approach the problem

The easiest curve to identify is the one with two equivalence points. The presence of two equivalence points means that the acid has two dissociable protons. After consuming one molar equivalent of $\mathrm{OH^-}$, all $\mathrm{H_2A}$ is converted to $\mathrm{HA^-}$ (the first equivalence point). At the second equivalence point, all $\mathrm{HA^-}$ is converted to $\mathrm{A^{2-}}$.

The other curves can be identified by the pH value at the equivalence point ($=7$, <7, or >7). Also consider that the analyte is always stated first in the name of the titration, and only one of the curves begins at a high pH.

Hint 2. Identify what type of titration has the equivalence point at pH = 7

Which titration curve has the equivalence point at $\mathrm{pH} = 7$?

ANSWER:

● a strong acid-strong base titration curve
○ a weak acid-strong base titration curve
○ a weak base-strong acid titration curve

Hint 3. Identify what type of titration has the equivalence point at pH < 7

Which titration curve has the equivalence point at $\mathrm{pH} < 7$?

ANSWER:

○ a strong acid-strong base titration curve
○ a weak acid-strong base titration curve
● a weak base-strong acid titration curve

Hint 4. Identify what type of titration has the equivalence point at pH > 7

Which titration curve has the equivalence point at $\mathrm{pH} > 7$?

ANSWER:

○ a strong acid-strong base titration curve
● a weak acid-strong base titration curve
○ a weak base-strong acid titration curve

ANSWER:

Correct

Part B

A 50.0-mL volume of 0.15 $\mathrm{M\ HBr}$ is titrated with 0.25 $\mathrm{M\ KOH}$. Calculate the pH after the addition of 20.0mL of KOH.

Express your answer numerically.

Hint 1. How to approach the problem

First, calculate the molar amounts of the reactants. Next, consider that an acid and a base will react to completion until one of the reactants is used up:

$$\mathrm{HBr(aq) + KOH(aq) \rightarrow H_2O(l) + KBr(aq)}$$

Which reactant remains and at what concentration?

Hint 2. Calculate the amount of HBr in the initial solution

How much acid does a 50.0-mL volume of 0.15 M HBr contain?

Express your answer numerically in millimoles.

Hint 1. How to approach the problem

Recall that $M = \mathrm{mol/L} = \mathrm{mmol/mL}$.Thus, $M \times \mathrm{mL} = \mathrm{mmol}$.

ANSWER:

amount of HBr = 7.50 mmol

Hint 3. Calculate the amount of KOH added

How much base does 20.0mL of 0.25 M KOH contain?

Express your answer numerically in millimoles.

Hint 1. How to approach the problem

Recall that $M = \mathrm{mol/L} = \mathrm{mmol/mL}$. Thus, $M \times \mathrm{mL} = \mathrm{mmol}$.

ANSWER:

amount of KOH = 5.0 mmol

Hint 4. Calculate the amount of the reactant in excess

A solution containing 5.0mmol of KOH was mixed with a solution containing 7.5 mmol of HBr. How much acid is left after the reaction?

Express your answer numerically in millimoles.

ANSWER:

2.50 mmol

Hint 5. Calculate the final concentration of the acid

Knowing that the final solution contains 2.5mmol of HBr, calculate the final concentration of the acid. Note that $M = \mathrm{mmol/mL}$.

Express the molar concentration numerically.

ANSWER:

$[\mathrm{HBr}]$ = 3.57×10^{-2} M

ANSWER:

pH = 1.45

Correct

Part C

A 75.0-mL volume of 0.200 M $\mathrm{NH_3}$ ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.500 M $\mathrm{HNO_3}$. Calculate the pH after the addition of 23.0mL of $\mathrm{HNO_3}$.

Express your answer numerically.

Hint 1. How to approach the problem

First, calculate the molar amounts of the reactants. Next, consider that an acid and a base will react to completion until one of the reactants is used up:

$$\mathrm{NH_3(aq) + H_3O^+(aq) \rightarrow NH_4{}^+(aq) + H_2O(l)}$$

If there is leftover $\mathrm{NH_3}$, you will have an $\mathrm{NH_3/NH_4{}^+}$ buffer system. The pH of a buffer can be calculated using the Henderson-Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{NH_3}]}{[\mathrm{NH_4{}^+}]}$$

Since both species of the conjugate acid-base pair coexist in the same volume, we can use the ratio of the millimoles instead of the concentration ratio.

Hint 2. Calculate the amount of $\mathrm{NH_4{}^+}$ produced

How much $\mathrm{NH_3}$ was converted to $\mathrm{NH_4{}^+}$ when 75.0 mL of 0.200 M $\mathrm{NH_3}$ was mixed with 23.0mL of 0.500 M acid?

Express your answer numerically in millimoles.

Hint 1. Limiting reactant

If you calculate the number of millimoles of acid and base, you will see that the acid is limiting. Thus, use the millimoles of acid to determine the millimoles of $\mathrm{NH_4{}^+}$.

ANSWER:

11.5 mmol

Hint 3. Calculate the amount of $\mathrm{NH_3}$ left

Initially, 15.0 mmol $\mathrm{NH_3}$ was present, and 11.5mmol reacted with the acid. How much $\mathrm{NH_3}$ is left over?

Express your answer numerically in millimoles.

ANSWER:

3.50 mmol

Hint 4. Calculate pK_a for $\mathrm{NH_4{}^+}$

This form of the Henderson-Hasselbalch equation calls for the $\mathrm{p}K_a$ value rather than $\mathrm{p}K_b$:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{NH_3}]}{[\mathrm{NH_4{}^+}]}$$

Given that K_b for $\mathrm{NH_3}$ is 1.8×10^{-5}, calculate $\mathrm{p}K_a$ for $\mathrm{NH_4{}^+}$.

Express your answer numerically.

Hint 1. How to approach the problem

For any conjugate acid-base pair, $K_a \times K_b = K_w$. Therefore,

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{K_b}$$

and

$$pK_a = -\log K_a$$

ANSWER:

pK_a = 9.26

ANSWER:

pH = 8.74

Correct

In case of a weak base-strong acid titration, the buffer solution accounts for the leveling of the titration curve in the buffer region between the start of the titration and the equivalence point.

Part D

A 52.0-mL volume of 0.35 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) is titrated with 0.40 M $NaOH$. Calculate the pH after the addition of 17.0mL of $NaOH$.

Express your answer numerically.

Hint 1. How to approach the problem

First, calculate the molar amounts of the reactants. Next, consider that an acid and a base will react to completion until one of the reactants is used up:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

If there is leftover CH_3COOH, you will have an CH_3COOH/CH_3COO^- buffer system. The pH of a buffer can be calculated using the Henderson-Hasselbalch equation

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

Since both species of the conjugate acid-base pair coexist in the same volume, we can use the ratio of the millimoles instead of the concentration ratio.

Hint 2. Calculate the amount of CH_3COO^- produced

When 17.0mL of 0.40 M $NaOH$ is added to 52.0 mL of 0.35 M CH_3COOH, how much CH_3COOH is converted to CH_3COO^-?

Express your answer numerically in millimoles.

Hint 1. Limiting reactant

If you calculate the number of millimoles of acid and base, you will see that the base is a limiting reactant. Thus, use the number of millimoles of base to determine the millimoles of CH_3COO^-.

ANSWER:

6.80 mmol

Hint 3. Calculate the amount of CH_3COOH left

Initially 18.2 mmol of CH_3COOH was present, and 6.8mmol was neutralized by the base. How much CH_3COOH is left over?

Express your answer numerically in millimoles.

ANSWER:

11.4 mmol

Hint 4. Calculate the p*K* a of CH_3COOH

Given that K_a for CH_3COOH is 1.8×10^{-5}, calculate its pK_a.

Express your answer numerically using three significant figures.

ANSWER:

pK_a = 4.74

ANSWER:

pH = 4.52

Correct

Calculating pH at the Equivalence Point

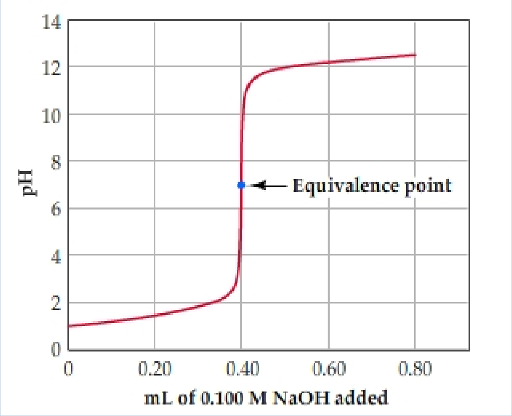
Learning Goal:

To calculate the pH at the equivalence point for various types of titrations.

The *equivalence point* in an acid-base titration is the point at which stoichiometrically equivalent quantities of acid and base have been mixed together. At this point the reaction is complete because all analyte has been consumed by titrant.

On a titration curve, the equivalence point is represented by the point of inflection (where the curve changes concavity).

The figure shows the titration of 40.0 mL of 0.100 M HCl with 0.100 M $NaOH$. When 40.0 mL of the $NaOH$ solution is added, the acid-base neutralization reaction is complete.



Part A

Match each type of titration to its pH at the equivalence point.

Drag each item to the appropriate bin.

Hint 1. How to approach the problem

Consider three examples:

- $HBr + KOH \rightarrow H_2O + KBr$ (strong acid + strong base),
- $HNO_3 + NH_3 \rightarrow NH_4NO_3$ (strong acid + weak base), and
- $CH_3COOH + NaOH \rightarrow H_2O + NaCH_3COO$ (weak acid + strong base).

At the equivalence point, the reaction has gone to completion and so only products remain. Look at each product and determine how it affects the pH.

Hint 2. Classify the products as acidic, basic, or neutral

Classify each of the following as acidic, basic, or neutral.

Drag each item to the appropriate bin.

Hint 1. How to identify acid, basic, and neutral salts

The anions of monoprotic strong acids, Cl^-, Br^-, I^-, $NO_3{}^-$, $ClO_4{}^-$, and $ClO_3{}^-$, are neutral.

The cations of strong bases, Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}, are neutral.

The combination of two neutral ions makes a neutral salt. One example is $LiCl$.

All other anions are basic because they are conjugates of a weak acid. All other cations are acidic because they are derived from weak bases. The combination of a neutral cation and a basic anion makes a basic salt (e.g., $LiCN$). The combination of an acidic cation and a neutral anion makes an acidic salt (e.g., NH_4Cl).

ANSWER:

ANSWER:

Correct

Part B

A 96.0mL volume of 0.25 M HBr is titrated with 0.50 M KOH. Calculate the pH after addition of 48.0mL of KOH.

Express the pH numerically.

Hint 1. How to approach the problem

The balanced equation for the titration reaction is

$$\mathrm{HBr(aq)} + \mathrm{KOH(aq)} \rightarrow \mathrm{KBr(aq)} + \mathrm{H_2O(l)}$$

Calculate the number of moles (or millimoles) of each reactant, then use stoichiometry to determine whether there is any reactant left over. If there is acid left over, the solution will be acidic. If there is base left over, the solution will be basic. If only products are left over (water and a neutral salt) the solution will be neutral.

Hint 2. Calculate the amount of HBr

Calculate the amount of HBr in millimoles in 96.0mL of a 0.25 M solution.

Express your answer numerically in millimoles.

Hint 1. Molarity formula

Recall that

$$\mathrm{molarity} = \frac{\mathrm{mol\ of\ solute}}{\mathrm{L\ of\ solution}} = \frac{\mathrm{mmol\ of\ solute}}{\mathrm{mL\ of\ solution}}$$

Thus, $\mathrm{mmol\ of\ solute} = \mathrm{molarity} \times \mathrm{mL\ of\ solution}$.

ANSWER:

amount of HBr = 24 mmol

Hint 3. Calculate the amount of KOH added

Calculate the amount of KOH in millimoles in 48.0mL of a 0.50 M solution.

Express your answer numerically in millimoles.

Hint 1. Molarity formula

Recall that

$$\mathrm{molarity} = \frac{\mathrm{mol\ of\ solute}}{\mathrm{L\ of\ solution}} = \frac{\mathrm{mmol\ of\ solute}}{\mathrm{mL\ of\ solution}}$$

Thus, $\mathrm{mmol\ of\ solute} = \mathrm{molarity} \times \mathrm{mL\ of\ solution}$.

ANSWER:

amount of KOH = 24 mmol

Hint 4. $\mathrm{HBr}-\mathrm{KOH}$ titration at the equivalence point

At the equivalence point of the titration of HBr (a strong acid) with KOH (a strong base), the solution contains only water and salt, KBr. K^+ and Br^- ions are neither acidic nor basic. Thus we can assume the $\mathrm{H_3O^+}$ concentration to be $1.0 \times 10^{-7}\ M$.

ANSWER:

pH = 7.00

Correct

In case of a strong acid-strong base titration, the salt produced is neutral. Therefore, the solution at the equivalence point has a pH of 7.00.

Part C

Consider the titration of 50.0 mL of 0.20 M $\mathrm{NH_3}$ ($K_\mathrm{b} = 1.8 \times 10^{-5}$) with 0.20 M $\mathrm{HNO_3}$. Calculate the pH after addition of 50.0 mL of the titrant.

Express the pH numerically.

Hint 1. How to approach the problem

When a weak base such as $\mathrm{NH_3}$ reacts with an equal amount of the strong acid, the reaction

$$\mathrm{NH_3 + HNO_3 \rightarrow NH_4NO_3}$$

goes to completion. The product is an acidic salt with the following equilibrium:

$$\mathrm{NH_4{}^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)}$$

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{NH_3}]}{[\mathrm{NH_4{}^+}]}$$

Calculate the salt concentration at the equivalence point and use it as the initial concentration of $\mathrm{NH_4{}^+}$ when figuring out the equilibrium concentrations. Use the equilibrium H_3O^+ concentration to find the pH.

Hint 2. Calculate K_a for $NH_4{}^+$

Given that K_b for NH_3 is 1.8×10^{-5}, calculate K_a for $NH_4{}^+$.

Express your answer numerically using three significant figures.

Hint 1. How to approach the problem

For any conjugate acid-base pair, $K_a \times K_b = K_w$.

Therefore, $K_a = K_w/K_b = (1.0 \times 10^{-14})/K_b$.

ANSWER:

K_a = 5.56×10^{-10}

Hint 3. Calculate the salt concentration

When 50.0 mL of 0.20 M NH_3 is mixed with 50.0 mL of 0.20 M HNO_3, what is the concentration of NH_4NO_3 in the resulting solution?

Express the molar concentration numerically.

Hint 1. Calculate the number of millimoles of the salt formed

When 50.0 mL of 0.20 M NH_3 is mixed with 50.0 mL of 0.20 M HNO_3, how many millimoles of NH_4NO_3 are formed?

Express your answer numerically in millimoles.

Hint 1. The reaction equation

The reaction equation is

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Thus the reaction between one mole of NH_3 and one mole of HNO_3 produces one mole of NH_4NO_3.

ANSWER:

amount of salt formed = 10. $mmol$

Hint 2. Calculate the final volume

When 50.0 mL of 0.20 M NH_3 is mixed with 50.0 mL of 0.20 M HNO_3, what is the final volume?

Express your answer numerically in milliliters.

ANSWER:

volume = 100.0 mL

ANSWER:

salt concentration = 0.10 M

Hint 4. Calculate the hydrogen-ion concentration

Calculate the concentration of H_3O^+ in a 0.10 M solution of NH_4NO_3. K_a for $NH_4{}^+$ is 5.56×10^{-10}.

Express the molar concentration numerically using three significant figures.

Hint 1. Express K_a in terms of x

The following table expresses the equilibrium concentrations in terms of the variable x.

Concentrations	NH_4^+	$+\ H_2O \rightleftharpoons$	NH_3	$+\ H_3O^+$
initial (M):	0.10		0	0
change (M):	$-x$		$+x$	$+x$
final (M):	$0.10-x$		x	x

In terms of equilibrium concentrations,

$$K_a = \frac{[NH_3][H_3O^+]}{NH_4{}^+}.$$

What is K_a in terms of x?

Express K_a in terms of x.

ANSWER:

$$\frac{x^2}{0.10-x}$$

ANSWER:

$[H_3O^+]$ = 7.46×10^{-6} M

ANSWER:

pH = 5.13

Correct

In a weak base-strong acid titration, the pH at the equivalence point is less than 7 because the salt produced is acidic.

Part D

A 30.0-mL volume of 0.50 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) was titrated with 0.50 M NaOH. Calculate the pH after addition of 30.0 mL of NaOH.

Express the pH numerically.

Hint 1. How to approach the problem

When a weak acid such as CH_3COOH reacts with an equal amount of the strong base, the reaction

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

goes to completion. The product is a basic salt with the following equilibrium:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Calculate the salt concentration and use it as the initial concentration of CH_3COO^- when figuring out equilibrium concentrations. Then use the equilibrium OH^- concentration to calculate $[H_3O^+]$ and the pH.

Hint 2. Calculate K_b for the acetate anion

Given that K_a for CH_3COOH is 1.8×10^{-5}, calculate K_b for CH_3COO^-.

Express your answer numerically using three significant figures.

Hint 1. How to approach the problem

For any conjugate acid-base pair, $K_a \times K_b = K_w$.

Therefore, $K_b = K_w/K_a = (1.0 \times 10^{-14})/K_a$.

ANSWER:

K_b = 5.56×10^{-10}

Hint 3. Calculate the salt concentration

When 30.0 mL of 0.50 M CH_3COOH and 30.0 mL of 0.50 M $NaOH$ are mixed together, calculate the concentration of the salt, CH_3COONa, in the final solution.

Express the molar concentration numerically.

Hint 1. Calculate the number of millimoles of each reactant

Calculate the number of millimoles of solute present in 30.0 mL of 0.50 M solution.

Express your answer numerically in millimoles.

ANSWER:

15 $mmol$

ANSWER:

salt concentration = 0.25 M

Hint 4. Calculate the concentration of OH^-

Calculate the concentration of the OH^- ion in a 0.25 M solution of CH_3COONa. K_b for CH_3COO^- is 5.56×10^{-10}.

Express the molar concentration numerically using three significant figures.

Hint 1. Express K_b in terms of x

The following table expresses the equilibrium concentrations in terms of the variable x.

Concentrations	CH_3COO^-	$+$	H_2O	$\rightleftharpoons$	CH_3COOH	$+$	OH^-
initial (M):	0.25				0		0
change (M):	$-x$				$+x$		$+x$
final (M):	$0.25-x$				x		x

In terms of equilibrium concentrations,

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

What is K_b in terms of x?

Express K_b in terms of x.

ANSWER:

K_b = $\frac{x^2}{0.25-x}$

ANSWER:

$[OH^-]$ = 1.18×10^{-5} M

Hint 5. Calculate the concentration of H_3O^+

The concentration of the OH^- ion in the solution is 1.18×10^{-5} M. Calculate the concentration of H_3O^+.

Express the molar concentration numerically.

Hint 1. How to approach the problem

Recall that $[H_3O^+][OH^-]=K_w=1.0\times10^{-14}$.

ANSWER:

$[H_3O^+]$ = 8.48×10^{-10} M

ANSWER:

pH = 9.07

Correct

For a weak monoprotic acid titrated with strong base, the pH at the equivalence point is always greater than 7 because the anion of the weak acid is a base.

± Creating a Buffer Solution

Buffer solutions can be produced by mixing a weak acid with its conjugate base or by mixing a weak base with its conjugate acid. The Henderson-Hasselbalch equation,

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

allows you to calculate the pH of a buffer. Note that molarity, moles, and millimoles are all proportional, so you can substitute the number moles, or millimoles, for the concentration terms in this formula.

Part A

You need to produce a buffer solution that has a pH of 5.10. You already have a solution that contains 10 mmol (millimoles) of acetic acid. How many millimoles of acetate (the conjugate base of acetic acid) will you need to add to this solution? The $\mathrm{p}K_\mathrm{a}$ of acetic acid is 4.74.

Express your answer numerically in millimoles to three significant figures.

Hint 1. Find the ratio of conjugate base to acid

What is the concentration ratio of acetate to acetic acid if the pH is 5.10?

Express your answer numerically to three significant figures.

Hint 1. How to determine the ratio

The Henderson-Hasselbalch equation relating the pH of a buffer to the $\mathrm{p}K_\mathrm{a}$ is

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

We want to find the quantity $[\mathrm{base}]/[\mathrm{acid}]$. Let's call that x, so

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log(x)$$

By rearranging the equation, we can solve for x, the concentration ratio:

$$\begin{aligned} \mathrm{pH} - \mathrm{p}K_\mathrm{a} &= \log(x) \\ 10^{(\mathrm{pH}-\mathrm{p}K_\mathrm{a})} &= x \end{aligned}$$

ANSWER:

$\frac{[\mathrm{base}]}{[\mathrm{acid}]}$ = 2.29

ANSWER:

22.9 $\mathrm{mmol\ acetate}$

Correct

Score Summary:

Your score on this assignment is 108.3%.
You received 21.65 out of a possible total of 20 points.