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UNIT V--ACID-BASE EQUILIBRIUM

A) IONIZATION OF WEAK ACIDS

The extent to which an acid ionizes in aqueous medium can be expressed by the equilibrium constant, K_a, for the ionization reaction:

$$HC_2H_3O_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_2H_3O_2^-\ (aq)$$

$$K_a = \frac{[H_3O^+]\ [C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

The smaller the value of K_a, the weaker the acid. From the value of K_a, it is possible to calculate the concentration of the hydronium ion , $[H_3O^+]$, in a solution of a weak acid.

Example: K_a for acetic acid is 1.8×10^{-5}. Find the concentration of the $[H_3O^+]$ in a 0.10 M solution of acetic acid.

$$HC_2H_3O_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_2H_3O_2^-\ (aq)$$

Initial concentration

Change in concentration

Equilibrium concentration

$[H_3O^+]$ = __________M

Because the value of K_a is small, we might guess that '***x***' is quite small. If we solve the problem using a quadratic formula, we find that ***x*** = 1.3×10^{-3} M. We can make the approximation by ignoring '***x***' in the denominator. This type of approximation is used whenever a small fraction of acid ionizes. If the quantity 'x' which is subtracted from the original concentration is more than 5% of the initial value, it is best to use quadratic formula. In our example, ***x*** = 1.3×10^{-3} M.

$$\%\ \text{ionization} = \frac{x}{C}(100) = \frac{1.3 \times 10^{-3}}{0.10}(100) = 1.3\ \%$$

B) IONIZATION OF WEAK BASES (NITROGENOUS BASES)

Nitrogenous bases have a nonbonding pair of electrons on a nitrogen atom much like that found in ammonia, NH_3. Like ammonia, these nitrogenous bases can react with water to produce OH^- ions.

$$NH_3\ (aq) + H_2O(l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

$$K_b = \frac{[NH_4^+]\ [OH^-]}{[NH_3]}$$

(K_b is the base ionization constant.)

Example:

K_b for NH_3 (aq) is 1.8×10^{-5}. Calculate the concentration of OH^- in a 0.15 M NH_3 solution.

$$NH_3 (aq) + H_2O(l) \rightleftharpoons NH_4^+ (aq) + OH^- (aq)$$

Initial concentration

Change in concentration

Equilibrium concentration

$[OH^-]$ = ____ M

C) THE EFFECT OF DILUTION ON THE PERCENT IONIZATION OF A WEAK ACID

The extent of ionization depends on the initial concentration of the acid. The more dilute the solution, the higher the percent ionization. A qualitative explanation: When the acid is diluted, the number of particles per unit volume is reduced. According to Le Chatelier's principle, to counteract this stress (that is the dilution) the equilibrium is shifted to the right to produce more particles. Although the percent ionization of the acid increases , yet the H^+ ion concentration becomes lower by dilution.

Example: Compare the percent ionization of HF(aq) at the following concentrations:

i) 0.10 M
ii) 0.010 M

K_a for HF (aq) i s 7.1×10^{-4} .

i) $$HF (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq) + F^- (aq)$$

Initial concentration

Change in concentration

Equilibrium concentration

$$\% \text{ ionization} = \frac{x}{C} (100)$$

$[H_3O^+]$ = _____M

% ionization= _________ %

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ii) $HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + F^-\ (aq)$

Initial concentration

Change in concentration

Equilibrium concentration

% ionization $= \frac{x}{C} \times 100$

$[H_3O^+]$ = _____M

% ionization= _________ %

Compare the results.

Example: A 0.10 M solution of a weak monoprotic acid was found to have a pH= 5.37. What is K_a for this acid ?

$HX\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + X^-\ (aq)$

Initial concentration

Change in concentration

Equilibrium concentration

K_a = ________

D) THE COMMON ION EFFECT

The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance is called the common ion effect. For example , the addition of $C_2H_3O_2^-$ from $NaC_2H_3O_2$ to a solution of $HC_2H_3O_2$ will suppress the ionization of $HC_2H_3O_2$ (shift the equilibrium to the left), hence decreasing the $[H^+]$ concentration.

1) A solution containing both $HC_2H_3O_2$ and $NaC_2H_3O_2$ will be less acidic than a solution containing only $HC_2H_3O_2$ at the same concentration.

2) The shift in equilibrium of the acetic acid ionization is caused by the common ion, $C_2H_3O_2^-$.

Example: K_a for $HC_2H_3O_2$ = 1.8×10^{-5} .

a) Calculate the pH of a 0.20 M $HC_2H_3O_2$ solution without any $NaC_2H_3O_2$ added .

$$HC_2H_3O_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_2H_3O_2^-\ (aq)$$

Initial concentration

Change in concentration

Equilibrium concentration

Answer: $[H_3O^+]$ = ________M

pH = _________

b) Calculate the pH of a solution containing 0.20 M $HC_2H_3O_2$ and 0.30 M $NaC_2H_3O_2$.

$$HC_2H_3O_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_2H_3O_2^-\ (aq)$$

Initial concentration

Change in concentration

Equilibrium concentration

Answer: $[H_3O^+]$ = ________M

pH = _________

Example: What is the pH of a solution containing 0.015 M NH_3 (aq) and 0.0050 M NH_4Cl ? K_b for NH_3 (aq) = 1.6×10^{-5}.

$$NH\ (aq) + H_2O(l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

Initial concentration

Change in concentration

Equilibrium concentration

Answer: $[OH^-]$ = ________M

pH = _________

BUFFERS

A **buffer** is a solution that maintains a constant pH (resists the change in pH) upon the addition of a small amount of H^+ from a strong acid or OH^- from a strong base, or upon dilution. A buffer solution must contain components that are capable of reacting with added acid or added base in order to resist a change in pH.

Some Buffer Systems:

1) Weak acid and its salt (salt that contains conjugate base of the acid).
Example: $HC_2H_3O_2$ (aq) and $NaC_2H_3O_2$ (aq).

2) Weak base and its salt (salt that contains conjugate acid of the base).
Example: NH_3 (aq) and NH_4Cl(aq).

3) Acid salts (Salt containing ion with acidic H).
Example:

4) Salt of a weak acid and a weak base.
Example:

Example:
Consider a buffer solution that is 0.010 M in each of formic acid, HCO_2H, and sodium formate, $NaCO_2H$. K_a for formic acid is 1.77×10^{-4}.

a) Calculate the pH of the buffer solution.

Equilibrium equation: $HCO_2H\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CO_2H^-\ (aq)$

Initial concentration

Change in concentration

Equilibrium concentration

$[H_3O^+]=$ ___________M
pH= _______

b) Calculate the pH after the addition of a 0.0020 mole NaOH(s) to a 1.00 liter of the above buffer solution. (Assume the change in volume is negligible upon the addition of the NaOH (s))

Reaction going to completion:

OH^- (aq)***from added NaOH*** + HCO_2H(aq) ***present in buffer solution*** $\longrightarrow$ CO_2H^-(aq)+ H_2O(l)

The concentration of HCO_2H will **decrease** due to the above reaction .

Number of moles $_{HCO_2H}$ *reacted* = number of moles $_{HCO2H}$ *initial* - Number of moles $_{HCO2H}$

= 0.010 mole *initial* - 0.0020 mole *reacted*

= 0.008 mole $_{HCO_2H}$

The concentration of CO_2H^- will **increase** due to the above reaction.

Number of moles $_{CO2H^-}$ = number of moles $_{CO2H^-}$ *initial* + Number of moles $_{CO2H^-}$ *formed*

= 0.010 mole *initial* + .0020 mole *formed*

= 0.012 mole CO_2H^-

Equilibrium equation: $HCO_2H\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CO_2H^-\ (aq)$

Initial concentration

Change in concentration

Equilibrium concentration

$[H_3O^+]=$ ___________M
pH= _______

c) Calculate the pH after the adding 0.0020 mole NaOH(s) to a 1.00 liter of pure water . (No buffer is present.) [Assume the change in volume is negligible upon the addition of the NaOH (s).]

$[H_3O^+]=$ ___________M
pH= _______

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d) Calculate the pH after the addition of a 0.0020 mole HCl to a 1.00 liter of the buffer solution in part (a). (Assume the change in volume is negligible upon the addition of the HCl)

Reaction going to completion:

H^+ (aq) ***from added HCl*** + CO_2H^-(aq) ***from NaCO2H*** ⟶ HCO_2H (aq)

The concentration of CO_2H^- will decrease due to the above reaction .

Number of moles $_{CO2H^-}$ = number of moles $_{CO2H^-}$ *initial* - Number of moles $_{CO2H^-}$ *reacted*

= 0.010 mole *initial* - 0.0020 mole *reacted*

= 0.008 mole CO_2H^-

The concentration of HCO_2H will increase due to the above reaction.

Number of moles $_{HCO2H}$ = number of moles $_{HCO2H}$ *initial* + Number of moles $_{HCO2H}$ *formed*

= 0.010 mole *initial* + .0020 mole *formed*

= 0.012 mole HCO2H

Equilibrium equation: HCO_2H (aq) + H_2O (l) ⇌ H_3O^+ (aq) + CO_2H^- (aq)

Initial concentration

Change in concentration

Equilibrium concentration

$[H_3O^+]$= ___________M

pH= _______

e) Calculate the pH after the adding 0.0020 mole HCl to a 1.00 liter of pure water. (No buffer is present.) [Assume the change in volume is negligible upon the addition of the HCl.]

$[H_3O^+]$= ___________M

pH= _______

Example:

a) How many moles of NH_4Cl must be added to a 1.00 liter of 0.10 M NH_3 solution to adjust the pH to 9.00 ? K_b for NH_3 (aq) = 1.8×10^{-5}.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

Initial concentration

Change in concentration

Equilibrium concentration

Answer = __________moles NH_4Cl

b) How would you prepare 100. ml buffer solution of pH =9.00 , using 0.10 M NH_3 (aq) stock solution and solid NH_4Cl? Specify the exact volumes and/or weights you should use.

K_b for NH_3 (aq)= 1.8×10^{-5}

Answer: _________________________

Example:

What must be the ratio of[NH_3]to [NH_4^+] (aq) to have a buffer of pH of 10.00 ?

K_b for NH_3 (aq)= 1.8×10^{-5}

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

Answer: ______________

Example:
What ratio of lactic acid (a monoprotic acid) to sodium lactate is required to give a solution having pH=4.25 ?
K_a for lactic acid = 1.38×10^{-4}

Answer: ____________

A STRONG ACID IS ADDED TO A SALT TO FORM A BUFFER SOLUTION :
Example:
How many moles of a strong monoprotic acid should be added to 1.00 liter of 0.40 M sodium formate solution, $NaCO_2H$ (aq), to prepare a buffer of pH= 4.35 ? K_a for formic acid = 1.77×10^{-4}

Molecular equation for a ' reaction going to completion':

$$HCl + NaCO_2H \rightleftharpoons HCO_2H\ (aq) + NaCl\ (aq)$$

Reaction going to completion -written in the net-ionic equation form:

H^+ (aq) ***from added strong acid*** + CO_2H^-(aq) ***from NaCO2H*** $\longrightarrow$ HCO_2H (aq)

Equilibrium equation: $HCO_2H\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CO_2H^-\ (aq)$

Initial concentration

Change in concentration

Equilibrium concentration

Answer: _______moles strong monoprotic acid

POLYPROTIC ACID (A MULTI-STAGE EQUILIBRIUM)

H_2CO_3 (aq) + H_2O (l) ⇌ H_3O^+ (aq) + HCO_3^- (aq) $K_{a1} = 4.2 \times 10^{-7}$

HCO_3^- (aq) + H_2O (l) ⇌ H_3O^+ (aq) + CO_3^{2-} (aq) $K_{a2} = 4.28 \times 10^{-11}$

Bicarbonate, HCO_3^- (aq) , is a much weaker acid than carbonic acid itself. It is more difficult to remove H^+ from the anion than from a neutral species. Because there are two stages of ionization, the species present in solution at equilibrium are:

H_2CO_3 (aq) , HCO_3^- (aq) , H_3O^+ (aq) , CO_3^{2-} (aq)

Example:

Calculate the concentration of all species in a 0.040 M H_2CO_3 solution at equilibrium.

First stage: H_2CO_3 (aq) + H_2O (l) ⇌ H_3O^+ (aq) + HCO_3^- (aq)

Initial concentration

Change in concentration

Equilibrium concentration

Answer: [H_2CO_3] = _______M_____

[HCO_3^-] = _______M

[H_3O^+]= _______M

Second stage: HCO_3^- (aq) + H_2O (l) ⇌ _ H_3O^+ (aq) + CO_3^{2-} (aq)

Initial concentration

Change in concentration

Equilibrium concentration

Answer: [HCO_3^-] = _______M

[H_3O^+]= _______M

[CO_3^{2-}] = _______M

Conclusion:1) For any solution containing only a polyprotic acid where $K_{a2} << K_{a1}$, the concentration of the anion formed in the second ionization will always equal to K_{a2}, provided that the acid is the only solute.
2) From the first ionization step, the concentration of HCO_3^-, H_3O^+, and H_2CO_3 are found. The pH of the solution is essentially due to the first ionization.

Example:

Suppose that we wish the sulfide ion concentration, [S^{2-}] to be 8.4×10^{-15} M in a saturated 0.10 M solution of H_2S. What hydrogen ion concentration must be maintained by a buffer to give this S^{2-} concentration?

$$H_2S\ (aq) + H_2O\ (l) \rightleftharpoons HS^-\ (aq) + H_3O^+(aq) \quad K_{a1}= 1.1 \times 10^{-7}$$
$$HS^-\ (aq) + H_2O\ (l) \rightleftharpoons S^{2-}\ (aq) + H_3O^+(aq) \quad K_{a2}= 1.0 \times 10^{-14}$$

Add:

$$H_2S\ (aq)+H_2O\ (l) +HS^-\ (aq)+H_2O\ (l) \rightleftharpoons HS^-\ (aq) + H_3O^+(aq) +S^{2-}\ (aq)+ H_3O^+(aq)$$

$$H_2S\ (aq) + 2\ H_2O\ (l) \rightleftharpoons S^{2-}\ (aq) + 2\ H_3O^+(aq) \qquad K_{overall}= K_{a1} \cdot K_{a2}$$

<u>Caution</u>: The above condensed method can be used ***<u>only</u>*** *when two of the three equilibrium concentrations are given and we wish to calculate the third. It cannot be used to determine, for example, both H_3O^+ and S^{2-} concentrations in solutions of known H_2S concentration.*

HYDROLYSIS

The hydrolysis of an ion is the reaction of an ion of a weak acid or a weak base with water to produce either a H_3O^+ or OH^- ion.

a) Anions of weak acids hydrolyze to give basic solutions.

b) Cations of weak bases hydrolyze to give acidic solutions.

c) Hydration (not hydrolysis) will take place when ions of strong acids and strong bases are dissolved in water.

Hydrolysis of a salt:
If one of the ions of the salt is hydrolyzed to a greater extent than the other, the pH of the solution will be different from 7.
a) Salt of a strong acid and a strong base.

Neither ion is hydrolyzed. Only hydration of ions occur. The solution is neutral.

b) Salt of a strong base and a weak acid.

The anion is hydrolyzed. The solution is basic.

c) Salt of a weak base and strong acid.

The cation is hydrolyzed. The solution is acidic.

d) Salt of a weak base and a weak acid.
Hydrolysis of both ions occurs. The solution could be either basic or acidic, depending on the extent of hydrolysis of each ion.

The relationship between K_a or K_b and K_h

A) Consider a salt where one ion only is undergoing hydrolysis.

1) $NH_4^+ (aq) + H_2O (l) \rightleftharpoons NH_3 (aq) + H_3O^+ (aq)$

2) $C_2H_3O_2^- (aq) + H_2O (l) \rightleftharpoons HC_2H_3O_2 (aq) + OH^- (aq)$

B) Consider a salt where both ions are undergoing hydrolysis.

Example:

What is the hydrolysis equilibrium constant for NO_2^- ? K_a for $HNO_2 = 7.2 \times 10^{-4}$

Example:

What is the hydrolysis equilibrium constant for NH_4^+ ? K_b for $NH_3 = 1.6 \times 10^{-5}$

Example:

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral. You must justify your answer.

1) KCl

2) $NaC_2H_3O_2$

3) KCN

4) KNO_3

5) NaF

6) NH_4Cl

7) NH_4NO_3

8) $NaHSO_3$ Given : $K_{a\,1}$ for H_2SO_3 = 1.3×10^{-2}

$K_{a\,2}$ for HSO_3^- = 5.6×10^{-8}

Setup:

HYDROLYSIS OF METAL IONS:

The cations of the IA metals, as well as Ca^{2+}, Sr^{2+}, and Ba^{2+} do not react with water since they are derived from strong bases. Most other cations, however, do hydrolyze.

In the hydrolysis of a metal cation, a coordinated water molecule of the hydrated cation donates a proton to a free water molecule.

Example:

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral. You must justify your answer.

K_b for NH_3 = 1.8×10^{-5}

K_a for HCN = 4.0×10^{-10}

K_a for $Al(H2O)_6^{3+}$ = 1.4×10^{-5}

K_a for HNO_2 = 4.5×10^{-4}

$K_{a\,1}$ for H_2SO_3 = 1.3×10^{-14}

$K_{a\,2}$ for HSO_3^- = 5.6×10^{-8}

1) $FeCl_3$

2) NH_4CN

3) $Al_2(SO_3)_3$

4) NH_4NO_2

5) $BaCl_2$

DETERMINING THE pH OF SALT SOLUTIONS

A) SALTS THAT PRODUCE ACIDIC SOLUTIONS:

Example:

1) Calculate the pH of a 0.10 M NH_4Cl solution. K_b for NH_3 = 1.8×10^{-5}

Equilibrium equation:

Initial Concentration:

Change in concentration:

Equilibrium concentration:

pH= _______

2) Calculate the percent hydrolysis of the above salt.

Percent hydrolysis = ____________%

B) SALTS THAT PRODUCE BASIC SOLUTIONS:

Example:

1) Calculate the pH of a 0.30 M NaF solution. K_a for HF = 7.2×10^{-4}

Equilibrium equation:

Initial Concentration:

Change in concentration:

Equilibrium concentration:

pH= _______

2) Calculate the percent hydrolysis of the above salt.

Percent hydrolysis = ____________%

Example:

What is the pH of a solution of a 0.10 M $NaNO_2$? K_a for HNO_2 = 4.5×10^{-4}

Equilibrium equation:

Initial Concentration:

Change in concentration:

Equilibrium concentration:

SOME COMMON WEAK BASES:

NH_3 (aq) + H_2O (l) $\rightleftharpoons$ _ NH_4^+ (aq) + OH^- (aq)

CH_3NH_2 + H_2O (l) $\rightleftharpoons$

$C_2H_5NH_2$(aq) + H_2O (l) $\rightleftharpoons$

$C_6H_5NH_2$ (aq) + H_2O (l) $\rightleftharpoons$

C_6H_5N (aq) + H_2O (l) $\rightleftharpoons$

LIST OF STRONG ACIDS

LIST OF STRONG BASES

FINDING THE pH OF A SALT SOLUTION AFTER A SMALL AMOUNT OF STRONG ACID IS ADDED:

Example: The pH of a 0.50 M $NaHCO_3$ solution is 10.0 . What is the pH after adding 0.05 mole HCl to a 1.0 liter of the above solution? (Assume there is no volume change upon the addition of the HCl.) K_{a1} for H_2CO_3 = 4.3×10^{-7}

Equation for reaction going to completion:

Equilibrium equation:

Initial Concentration:

Change in concentration:

Equilibrium concentration:

pH= _____________

FINDING THE NUMBER OF MOLES OF A STRONG ACID THAT SHOULD BE ADDED TO A SALT SOLUTION TO ADJUST THE pH TO A CERTAIN VALUE:

Example:

How many moles of a strong monoprotic acid should be added to a 1.00 liter of 0.50 M NaCN solution to adjust the pH to 10.00 ? K_a for HCN = 4.9×10^{-10}

Equation for reaction going to completion:

Equilibrium equation:

Initial Concentration:

Change in concentration:

Equilibrium concentration:

Answer= _____________moles

Example:

25.00 ml of 0.010 M $HC_4H_3N_2O_3$ (barbituric acid) is titrated against 0.0200 M NaOH.

K_a for $HC_4H_3N_2O_3 = 1.0 \times 10^{-5}$

a) Calculate the pH after each of the following amounts of NaOH is added.

b) Identify the problem as: buffer, weak acid, hydrolysis, weak base, or strong base.

i) 0.00 ml of NaOH is added.

pH= __________

ii) 4.00 ml of NaOH are added.

Equation for reaction going to completion:

$HC_4H_3N_2O_3$ (aq) + NaOH (aq) $\rightleftharpoons$ H_2O (l) + $NaC_4H_3N_2O_3$ (aq)

Equilibrium equation:

Initial Concentration:

Change in concentration:

Equilibrium concentration:

pH= __________

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iii) 6.25 ml of NaOH are added.
Equation for reaction going to completion:

$HC_4H_3N_2O_3$ (aq) + NaOH (aq) $\rightleftharpoons$ H_2O (l) + $NaC_4H_3N_2O_3$ (aq)

Equilibrium equation:

Initial Concentration:

Change in concentration:

Equilibrium concentration:

pH= __________

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iv) 12.5 ml of NaOH are added .
Equation for reaction going to completion:

$HC_4H_3N_2O_3$ (aq) + NaOH (aq) $\rightleftharpoons$ H_2O (l) + $NaC_4H_3N_2O_3$ (aq)

Equilibrium equation:

Initial Concentration:

Change in concentration:

Equilibrium concentration:

(Continued next page)

v) 17.5 ml of NaOH are added.
Equation for reaction going to completion:

$HC_4H_3N_2O_3$ (aq) + NaOH (aq) $\rightleftharpoons$ H_2O (l) + $NaC_4H_3N_2O_3$ (aq

pH= ___________________

REVIEW PROBLEMS: BUFFER AND HYDROLYSIS:
Example:
1) How many ml of 0.350 M $HC_2H_3O_2$ must be added to 750. ml of 0.200 M $NaC_2H_3O_2$ to give a solution that has a pH= 5.00 ? K_a for $HC_2H_3O_2$ = 1.8×10^{-5} Answer: 238 ml

2) How many ml of 0.450 M $NaC_2H_3O_2$ must be added to 750. ml of 0.200 M $HC_2H_3O_2$ to give a solution that has a pH= 5.00 ? K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$ Answer: 600. ml

3) How many ml of 0.280 M $NaCHO_2$ must be added to 250. ml of 0.350 M $HCHO_2$ to give a solution that has a pH= 3.50 ? K_a for $HCHO_2 = 1.70 \times 10^{-4}$ Answer: 168 ml

4) A chemist wants to prepare a buffer with pH= 3.50. How many ml of 0.1350 M formic acid, $HCHO_2$, must be added to 275 ml of 0.0840 M NaOH solution to obtain such a buffer?

K_a for $HCHO_2 = 1.70x\ 10^{-4}$ <u>Answer:</u> 493 ml