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Problem 15.29. (a) Calculate the pH of a 0.20 M solution of benzoic acid at 25°C.
(b) How many moles of acetic acid must be dissolved per liter of water to obtain the same pH as that from part (a)?

Solution:

(a) Suppose the change of concentration of benzoic acid is $-x$ M, then

	$\text{C}_6\text{H}_5\text{COOH}(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	+	$\text{C}_6\text{H}_5\text{COO}^-(\text{aq})$
Initial, M	0.20				0		0
Change, M	$-x$				x		x
Equilibrium, M	$0.20 - x$				x		x

The ionization constant of benzoic acid is $K_a = 6.46 \times 10^{-5}$, so

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{x^2}{0.20 - x} = 6.46 \times 10^{-5}$$

Because the ionization constant of benzoic acid, K_a is very small, the change of the concentration of $\text{C}_6\text{H}_5\text{COOH}$, $-x$, is much smaller than its initial concentration. In this way, we have the following approximation

$$K_a = 6.46 \times 10^{-5} \approx \frac{x^2}{0.20} \implies x = 3.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

So the equilibrium concentration of H_3O^+ is

$$[\text{H}_3\text{O}^+] = x \text{ mol} \cdot \text{L}^{-1} = 3.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

Therefore, the pH of the benzoic acid solution is

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(3.6 \times 10^{-3}) = \underline{2.44}$$

(b) To obtain the same pH as that from part (a), the concentration of H_3O^+ need to be $3.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

Suppose n mol acetic acid is dissolved per liter of water, then

	$\text{CH}_3\text{COOH}(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	+	$\text{CH}_3\text{COO}^-(\text{aq})$
Initial, M	n				0		0
Change, M	-3.6×10^{-3}				3.6×10^{-3}		3.6×10^{-3}
Equilibrium, M	$n - 3.6 \times 10^{-3}$				3.6×10^{-3}		3.6×10^{-3}

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The ionization constant of acetic acid is $K_a = 1.76 \times 10^{-5}$, so

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(3.6 \times 10^{-3})^2}{n - 3.6 \times 10^{-3}} = 1.76 \times 10^{-5} \implies n = 0.74$$

Therefore, 0.74 mol of acetic acid must be dissolved per liter of water. □

Problem 15.42. Suppose a 0.100 M solution of each of the following substances is prepared. Rank the pH of the resulting solutions from lowest to highest: KF, NH₄I, HBr, NaCl, LiOH.

Solution: KF is a salt of the weak acid HF and the strong base KOH, so the pH of its solution is little more than 7.

NH₄I is a salt of the strong acid HI and the weak base NH₃, so the pH of its solution is little less than 7.

HBr is a strong acid, so the pH of its solution is much less than 7.

NaCl is a salt of the strong acid HCl and strong base NaOH, so the pH of its solution is 7.

LiOH is a strong base, so the pH of its solution is much more than 7.

Therefore, rank of the resulting solution's pH from lowest to highest is:

$$\underline{\text{pH}(\text{HBr}) < \text{pH}(\text{NH}_4\text{I}) < \text{pH}(\text{NaCl}) < \text{pH}(\text{KF}) < \text{pH}(\text{LiOH})}.$$

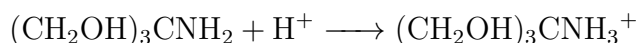
□

Problem 15.43. “Tris” is short for tris(hydroxymethyl)aminomethane. This weak base is widely used in biochemical research for the preparation of buffers. It offers low toxicity and a pK_b (5.92 at 25°C) that is convenient for the control of pH in clinical applications. A buffer is prepared by mixing 0.050 mol of tris with 0.025 mol of HCl in a volume of 2.00 L. Compute the pH of the solution.

Solution: The pK_a of the conjugate acid of tris, $(\text{CH}_2\text{OH})_3\text{CNH}_3^+$, is

$$pK_a = 14 - pK_b = 14 - 5.92 = 8.08$$

The reaction equation of tris with HCl is



After mixing 0.050 mol of tris with 0.025 mol of HCl, the initial number of moles of tris and $(\text{CH}_2\text{OH})_3\text{CNH}_3^+$ are

$$n((\text{CH}_2\text{OH})_3\text{CNH}_2) = 0.025\text{mol}, \quad n((\text{CH}_2\text{OH})_3\text{CNH}_3^+) = 0.025\text{mol}$$

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so their initial concentration after mixing are

$$[(CH_2OH)_3CNH_2] = \frac{n((CH_2OH)_3CNH_2)}{V} = \frac{0.025mol}{2L} = 0.0125mol \cdot L^{-1}$$
$$[(CH_2OH)_3CNH_3^+] = \frac{n((CH_2OH)_3CNH_3^+)}{V} = \frac{0.025mol}{2L} = 0.0125mol \cdot L^{-1}$$

Therefore, the pH of the solution is

$$pH = pK_a - \log_{10} \frac{[(CH_2OH)_3CNH_3^+]_0}{[(CH_2OH)_3CNH_2]_0} = 8.08 - \log_{10} \frac{0.0125mol \cdot L^{-1}}{0.0125mol \cdot L^{-1}} = \underline{8.08}$$

□

Problem 15.49. You have at your disposal an ample quantity of a solution of 0.0500 M NaOH and 500 mL of a solution of 0.100 M formic acid (HCOOH). How much of the NaOH solution should be added to the acid solution to produce a buffer of pH 4.00?

Solution: The ionization constant of HCOOH is $pK_a = 1.77 \times 10^{-4}$. The pH of the buffer is

$$4.00 = pH = pK_a - \log_{10} \frac{[HCOOH]}{[HCOO^-]} = -\log_{10}(1.77 \times 10^{-4}) - \log_{10} \frac{[HCOOH]}{[HCOO^-]}$$

so the ratio of the initial concentration of HCOOH and $HCOO^-$ after reaction should be

$$\frac{[HCOOH]}{[HCOO^-]} = 0.565$$

The initial number of moles of HCOOH is

$$n_0(HCOOH) = c_0(HCOOH)V_0 = 0.100mol \cdot L^{-1} \times 0.500L = 0.0500mol$$

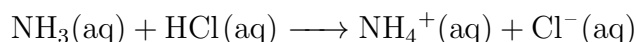
Suppose the volume of the NaOH solution added is $V(NaOH)$ and the volume of the buffer solution is V after the reaction is V , the ratio of the initial concentration of HCOOH and $HCOO^-$ after reaction is

$$\begin{aligned} \frac{[HCOOH]}{[HCOO^-]} &= \frac{\frac{n_0(HCOOH) - c(NaOH)V(NaOH)}{V}}{\frac{c(NaOH)V(NaOH)}{V}} \\ &= \frac{n_0(HCOOH) - c(NaOH)V(NaOH)}{c(NaOH)V(NaOH)} \\ &= \frac{0.0500mol - 0.0500mol \cdot L^{-1} \times V(NaOH)}{0.0500mol \cdot L^{-1} \times V(NaOH)} = 0.565 \\ &\implies V(NaOH) = 0.639L = 639mL \end{aligned}$$

Therefore, 639 mol of the NaOH solution should be added to the acid solution to produce a buffer of pH 4.00. □

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Problem 15.56. Ammonia is a weak base with a K_b of 1.8×10^{-5} . A 140.0 mL sample of a 0.175 M solution of aqueous ammonia is titrated with a 0.106 M solution of the strong acid HCl. The reaction is



Compute the pH of the titration solution before any acid is added, when the titration is at the half-equivalence point, when the titration is at the equivalence point, and when the titration is 1.00 mL past the equivalence point.

Solution: The number of moles of the ammonia before titration is

$$n_0(\text{NH}_3) = c_0(\text{NH}_3)V_0(\text{NH}_3) = 0.175 \text{ mol} \cdot \text{L}^{-1} \times 0.1400 \text{ L} = 0.0245 \text{ mol}$$

and the ionization constant of its conjugate acid, NH_4^+ is

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Before any acid is added: suppose the change of the concentration of ammonia is $-x$ M, then

	$\text{NH}_3(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{OH}^-(\text{aq})$	+	$\text{NH}_4^+(\text{aq})$
Initial, M	0.175				0		0
Change, M	$-x$				x		x
Equilibrium, M	$0.175 - x$				x		x

The ionization of ammonia is

$$K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} = \frac{x^2}{0.175 - x} = 1.8 \times 10^{-5}$$

Because the ionization constant of ammonia, K_b , is very small, the change of the concentration of NH_3 , $-x$, is much smaller than its initial concentration. In this way, we have the following approximation

$$K_b = 1.8 \times 10^{-5} \approx \frac{x^2}{0.175} \implies x = 1.77 \times 10^{-3}$$

So the equilibrium concentration of OH^- is

$$[\text{OH}^-] = x \text{ mol} \cdot \text{L}^{-1} = 1.77 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

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Therefore, the pH of the titration solution before any acid is added is

$$pH = -\log_{10}[H^+] = -\log_{10} \frac{K_w}{[OH^-]} = -\log_{10} \frac{10^{-14}}{1.77 \times 10^{-3}} = \underline{11.25}$$

When the titration is at the half: the ratio of the NH_4^+ and its conjugate, NH_3 is 1, so the pH of the titration solution is

$$pH = pK_a - \log_{10} \frac{[NH_4^+]}{[NH_3]} = -\log_{10} 5.5 \times 10^{-10} - \log_{10} 1 = \underline{9.26}$$

When the titration is at the equivalence point: the volume of HCl solution added is

$$V_{eq}(HCl) = \frac{n(NH_3)}{c_0(HCl)} = \frac{0.0245 mol}{0.106 mol \cdot L^{-1}} = 0.231 L$$

Suppose the volume of the titration solution at the equivalence point is the sum of the initial volume of the ammonia solution and the volume of the HCl solution added

$$V_{eq} = V_0(NH_3) + V_{eq}(HCl) = 0.1400 L + 0.231 L = 0.371 L$$

At the equivalence point, the initial concentration of NH_4^+ is

$$c_{eq}(NH_4^+) = \frac{n_{eq}(NH_4^+)}{V_{eq}} = \frac{n_0(NH_3)}{V_{eq}} = \frac{0.0245 mol}{0.371 L} = 0.0660 mol \cdot L^{-1}$$

suppose the change of the concentration of NH_4^+ is $-y$ M, then

	$NH_4^+(aq)$	+	$H_2O(l)$	\rightleftharpoons	$H^+(aq)$	+	$NH_3 \cdot H_2O(aq)$
Initial, M	0.0660				0		0
Change, M	$-y$				y		y
Equilibrium, M	$0.0660 - y$				y		y

The ionization constant of NH_4^+ is

$$K_a = \frac{[H^+][NH_3 \cdot H_2O]}{[NH_4^+]} = \frac{y^2}{0.0660 - y} = 5.6 \times 10^{-10}$$

Because the ionization constant of NH_4^+ , K_a , is very small, the change of the concentration of NH_4^+ , $-y$, is much smaller than its initial concentration. In this way, we have the following approximation

$$K_a = 5.6 \times 10^{-10} \approx \frac{y^2}{0.0660} \Rightarrow y = 6.08 \times 10^{-6} mol$$

So the equilibrium concentration of H^+ is

$$[H^+] = y mol = 6.08 \times 10^{-6} mol$$

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Therefore, the pH of the titration solution at the equivalence point is

$$pH = -\log_{10}[H^+] = -\log_{10}(6.08 \times 10^{-6}) = \underline{5.22}$$

When the titration is 1.00 mL past the equivalence point: The volume of the HCl solution added is

$$V_1(HCl) = V_{eq}(HCl) + 1.00 \times 10^{-3}L = 0.232mL$$

The volume of the titration solution is

$$V_1 = V_0(NH_3) + V_1(HCl) = 0.1400L + 0.232L = 0.372L$$

So the concentration of H^+ is approximately

$$c_1(H^+) \approx \frac{c_0(HCl) \times 1.00 \times 10^{-3}L}{V_1} = \frac{0.106mol \cdot L^{-1} \times 1.00 \times 10^{-3}L}{0.372L} = 2.85 \times 10^{-4}mol \cdot L^{-1}$$

Therefore, the pH of the titration solution when the titration is 1.00 mL past the equivalence point is

$$pH = -\log_{10}[H^+] = -\log_{10}(2.85 \times 10^{-4}) = \underline{3.55}$$

□

Problem 15.58. An antacid tablet (such as Tums or Rolaids) weighs 1.3259 g. The only acid-neutralizing ingredient in this brand of antacid is $CaCO_3$. When placed in 12.07 mL of 1.070 M HCl, the tablet fizzes merrily as $CO_2(g)$ is given off. After all of the CO_2 has left the solution, an indicator is added, followed by 11.74 mL of 0.5310 M NaOH. The indicator shows that at this point the solution is definitely basic. Addition of 5.12 mL of 1.070 M HCl makes the solution acidic again. Then 3.17 mL of the 0.5310 M NaOH brings the titration exactly to an endpoint, as signaled by the indicator. Compute the percentage by mass of $CaCO_3$ in the tablet.

Solution: The total number of moles of HCl added is

$$\begin{aligned} n(HCl) &= c(HCl)(V_1(HCl) + V_2(HCl)) = 1.070mol \cdot L^{-1} \times (0.01207L + 0.00512L) \\ &= 0.01839mol \end{aligned}$$

The total number of moles of NaOH added is

$$\begin{aligned} n(NaOH) &= c(NaOH)(V_1(NaOH) + V_2(NaOH)) \\ &= 0.5310mol \cdot L^{-1} \times (0.01174L + 0.00317L) = 7.917 \times 10^{-3}mol \end{aligned}$$

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So the number of moles of CaCO_3 in the tablet is

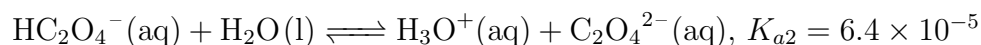
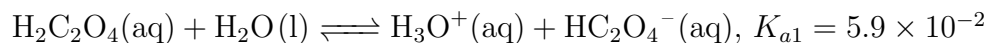
$$n(\text{CaCO}_3) = \frac{n(\text{HCl}) - n(\text{NaOH})}{2} = \frac{0.01839\text{mol} - 7.917 \times 10^{-3}\text{mol}}{2} = 0.0052365\text{mol}$$

Therefore, the mass percentage of CaCO_3 in the tablet is

$$\begin{aligned}\alpha(\text{CaCO}_3) &= \frac{n(\text{CaCO}_3)M(\text{CaCO}_3)}{m(\text{tablet})} \times 100\% = \frac{0.0052365\text{mol} \times 100.1\text{g} \cdot \text{mol}^{-1}}{1.3259\text{g}} \times 100\% \\ &= \underline{39.53\%}\end{aligned}$$

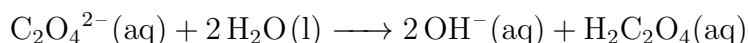
□

Problem 15.66. Oxalic acid ionizes in two stages in aqueous solution:



Calculate the equilibrium concentrations of $\text{C}_2\text{O}_4^{2-}$, HC_2O_4^- , $\text{H}_2\text{C}_2\text{O}_4$, and OH^- in a 0.10 M solution of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$).

Solution: Sodium oxalate is a salt of weak acid and strong weak, so we assume it hydrolyzes completely at first and then ionizes a little. The equation of hydrolyzation is



So the concentration of OH^- is

$$[\text{OH}^-] = c_0(\text{Na}_2\text{C}_2\text{O}_4) = 2 \times 0.10\text{mol} \cdot \text{L}^{-1} = \underline{0.20\text{mol} \cdot \text{L}^{-1}}$$

Suppose the change of the concentration of $\text{H}_2\text{C}_2\text{O}_4$ at first step of ionization is $-x$ M, then

	$\text{H}_2\text{C}_2\text{O}_4(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq})$	+	$\text{HC}_2\text{O}_4^-(\text{aq})$
Initial, M	0.10				0		0
Change, M	$-x$				x		x
Equilibrium, M	$0.10 - x$				x		x

The ionization constant of the first step of ionization is

$$\begin{aligned}K_{a2} &= \frac{[\text{H}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = \frac{x^2}{0.10 - x} = 5.9 \times 10^{-2} \\ &\implies x = 0.53 \text{ or } -0.11 \text{ (unphysical!)}\end{aligned}$$

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So the concentration of $H_2C_2O_4$ is

$$[H_2C_2O_4] = 0.10 \text{ mol} \cdot L^{-1} - x \text{ mol} \cdot L^{-1} = 0.10 \text{ mol} \cdot L^{-1} - 0.53 \text{ mol} \cdot L^{-1} = \underline{0.047 \text{ mol} \cdot L^{-1}}$$

and the concentration of $HC_2O_4^-$ and H^+ after the first step of ionization is

$$[HC_2O_4^-] = [H^+]_1 = x \text{ mol} \cdot L^{-1} = \underline{0.053 \text{ mol} \cdot L^{-1}}$$

Suppose the change of the concentration of $HC_2O_4^-$ is $-y$ M, then The ionization constant

	$HC_2O_4^-(aq)$	+	$H_2O(l)$	\rightleftharpoons	$H_3O^+(aq)$	+	$C_2O_4^{2-}(aq)$
Initial, M	0.047				0.053		0
Change, M	$-y$				y		y
Equilibrium, M	$0.047 - y$				$0.053 + y$		y

of the second step of the ionization is

$$K_{a2} = \frac{[H_3O^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = \frac{(0.053 + y)y}{0.047 - y} = 6.4 \times 10^{-5} \text{ mol} \cdot L^{-1}$$

Because the ionization constant, K_{a2} , is very small, the change of the concentration of $HC_2O_4^-$, y , is much smaller than $[HC_2O_4^-]$ and $[H^+]_1$. In this way, we have the following approximation

$$K_{a2} = 6.4 \times 10^{-5} \text{ mol} \cdot L^{-1} = \frac{0.053x}{0.047} \Rightarrow y = 5.7 \times 10^{-5} \text{ mol} \cdot L^{-1}$$

So the concentration of $C_2O_4^{2-}$ is

$$[C_2O_4^{2-}] = y \text{ mol} = \underline{6.4 \times 10^{-5} \text{ mol} \cdot L^{-1}}$$

Therefore,

$$\begin{aligned}[C_2O_4^{2-}] &= 6.4 \times 10^{-5} \text{ mol} \cdot L^{-1} \\ [HC_2O_4^-] &= 0.053 \text{ mol} \cdot L^{-1} \\ [H_2C_2O_4] &= 0.047 \text{ mol} \cdot L^{-1} \\ [OH^-] &= 0.20 \text{ mol} \cdot L^{-1}\end{aligned}$$

□

Problem 15.73. Which will be the stronger acid: benzene (C_6H_6) or cyclohexane (C_6H_{12})? Explain by using resonance Lewis structures.

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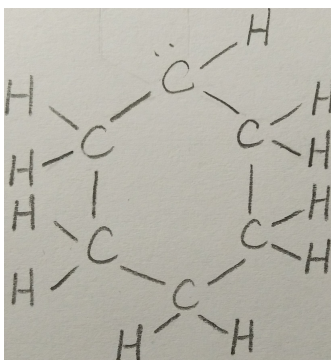


图 1: Problem 15.73 Lewis diagram for the conjugate base of cyclohexane

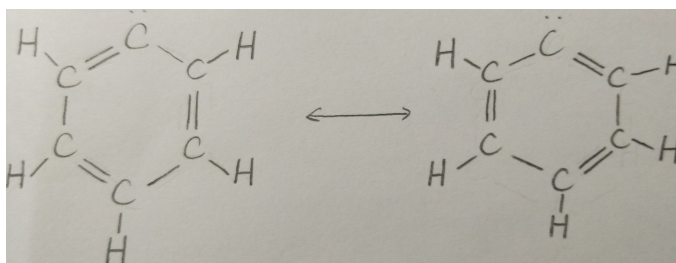


图 2: Problem 15.73 Resonance diagrams for the conjugate base of benzene

Solution: We can write only one Lewis diagram for the conjugate base of cyclohexane as shown in Figure 1.

while we can write two resonance diagrams for the conjugate base of benzene as shown in Figure 2 which is very stable. Therefore, C_6H_6 is the stronger acid. \square

Problem 15.75. For each of the following pairs of molecules, predict which is the stronger acid.

- (a) CF_3COOH or CCl_3COOH
- (b) $CH_2FCH_2CH_2COOH$ or $CH_3CH_2CHFCH_2COOH$
- (c) $(C_6H_5)COOH$ or $(C(CH_3)_3)_2(C_6H_5)COOH$

Solution: (a) CF_3COOH is the stronger acid, because atoms F are more electronegative than atoms Cl and, therefore, have stronger attraction on the electrons in the carboxyl to make it easier for the atom H in the carboxyl to ionize.

(b) $CH_3CH_2CHFCH_2COOH$ is the stronger acid, because atom F in $CH_3CH_2CHFCH_2COOH$ is closer to the atom H in the carboxyl than it in $CH_2FCH_2CH_2COOH$ and, therefore have stronger attraction on the electrons in the carboxyl to make it easier for the atom H in the carboxyl to ionize.

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(c) (C₆H₅)COOH is the stronger acid, because the accessory groups on the second one have repulsion on the electrons in the carboxyl to make the atom H in the carboxyl not so easy to ionize. □

Problem 15.78. A sample of vinegar contains 40.0 g of acetic acid (CH₃COOH) per liter of solution. Suppose 1.00 mL is removed and diluted to 1.00 L, and 1.00 mL of that solution is removed and diluted to 1.00 L. Calculate the pH of the resulting solution. (Hint: This is a sufficiently dilute solution that the autoionization of water cannot be neglected.)

Solution: The concentration of acetic acid in the original solution is

$$c_1(\text{CH}_3\text{COOH}) = \frac{m(\text{CH}_3\text{COOH})/M(\text{CH}_3\text{COOH})}{V_0} = \frac{40.0\text{g}/60.1\text{g} \cdot \text{mol}^{-1}}{1\text{L}} = 0.666\text{mol}$$

The concentration of diluted acetic acid is

$$c_2(\text{CH}_3\text{COOH}) = \frac{c_1(\text{CH}_3\text{COOH})V_1}{V_2} \times \frac{V_3}{V_4} = \frac{0.666\text{mol} \cdot \text{L}^{-1} \times 0.00100\text{mL}}{1.00\text{L}} \times \frac{0.00100\text{mL}}{1.00\text{L}} = 6.66 \times 10^{-7}\text{mol} \cdot \text{L}^{-1}$$

Suppose the change of concentration of CH₃COOH during ionization is $-x$ M, then The

	CH ₃ COOH(aq)	+	H ₂ O(l)	\rightleftharpoons	H ₃ O ⁺ (aq)	+	CH ₃ COO ⁻ (aq)
Initial, M	6.66 × 10 ⁻⁷				10 ⁻⁷		0
Change, M	-x				x		x
Equilibrium, M	6.66 × 10 ⁻⁷ - x				10 ⁻⁷ + x		x

ionization constant of CH₃COOH is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(10^{-7} + x)x}{6.66 \times 10^{-7} - x} = 1.76 \times 10^{-5}$$
$$\implies x = 6.39 \times 10^{-7} \text{ or } -1.83 \times 10^{-5} \text{ (unphysical!)}$$

So the concentration of H⁺ in the resulting solution is

$$[\text{H}^+] = 10^{-7}\text{mol} \cdot \text{L}^{-1} + x\text{mol} \cdot \text{L}^{-1} = 10^{-7}\text{mol} \cdot \text{L}^{-1} + 6.39 \times 10^{-7}\text{mol} \cdot \text{L}^{-1} = 7.39 \times 10^{-7}\text{mol} \cdot \text{L}^{-1}$$

Therefore, the pH of the resulting solution is

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(7.39 \times 10^{-7}) = \underline{6.13}$$

□