

## Chapter 18 Problem Set Solutions

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1. Benzoic Acid (C<sub>6</sub>H<sub>5</sub>COOH) is a solid. 15.000 grams is dissolved in 200.00 mL of distilled water.
- a) Benzoic acid is a weak acid that will dissociate to in water to form benzoate ions and hydronium ions.
- b)  $\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^{1-} + \text{H}_3\text{O}^{1+}$
- c) benzoic acid is the proton donor (It is an acid)
- d) water is the proton acceptor (It is the only available base)
- e) After the reaction has reached equilibrium:

$$M := \frac{\text{mole}}{\text{liter}} \quad K_a := 6.46 \cdot 10^{-5} \quad K_w := 1.0 \cdot 10^{-14}$$

$$\text{Mass}_{\text{benzoic}} := 15.000 \cdot \text{gm} \quad V_{\text{benzoic}} := 200 \cdot \text{mL}$$

$$\text{MW}_{\text{benzoic}} := ((7 \cdot 12.001) + (2 \cdot 15.9994) + (6 \cdot 1.00794)) \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{MW}_{\text{benzoic}} = 122.05344 \cdot \text{gm}$$

$$\text{mole}_{\text{benzoic}} := \frac{\text{Mass}_{\text{benzoic}}}{\text{MW}_{\text{benzoic}}}$$

$$\text{mole}_{\text{benzoic}} = 0.1229 \cdot \text{mole}$$

$$C_{\text{benzoic}} := \frac{\text{mole}_{\text{benzoic}}}{V_{\text{benzoic}}}$$

$$C_{\text{benzoic}} = 0.61448 \cdot \text{M}$$

	$\text{C}_6\text{H}_5\text{COOH}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{C}_6\text{H}_5\text{COO}^{1-}$	+	$\text{H}_3\text{O}^{1+}$
Start	$C_{\text{benzoic}} = 0.61448 \cdot \text{M}$				0		0
Change	-X				X		X
Equilibrium	$C_{\text{benzoic}} - X$				X		X

Start with the Equilibrium Expression

$$K_a = \frac{X \cdot X}{C_{\text{benzoic}} - X}$$

Substitute in known values

$$6.46 \cdot 10^{-5} = \frac{X \cdot X}{0.614 - X}$$

Solve

Using the Quadratic  $X = \left( \begin{array}{l} 6.2657507532092816567 \cdot 10^{-3} \\ -6.3303507532092816567 \cdot 10^{-3} \end{array} \right)$

Assuming X is small in the denominator  $X = 6.2979679262441468867 \cdot 10^{-3}$

These two answers are essentially identical.

Select the appropriate root:

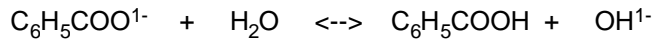
$$X := 6.2657507532092816567 \cdot 10^{-3} \cdot \text{M}$$

Concentrations of species present

Benzoic Acid	$C_{\text{benzoic}} := C_{\text{benzoic}} - X$	$C_{\text{benzoic}} = 0.60822 \cdot \text{M}$
Benzoate	$C_{\text{benzoate}} := X$	$C_{\text{benzoate}} = 0.00627 \cdot \text{M}$
Hydronium Ion	$C_{\text{H}_3\text{O}} := X$	$C_{\text{H}_3\text{O}} = 0.00627 \cdot \text{M}$
	$\text{pH} := -\log(X \cdot \text{M}^{-1})$	$\text{pH} = 2.20303$
Hydroxide Ion	$C_{\text{OH}} := \frac{1 \cdot 10^{-14}}{X}$	$C_{\text{OH}} = 0 \cdot \text{m}^6 \cdot \text{M}$
	$\text{pOH} := 14 - \text{pH}$	$\text{pOH} = 11.79697$

2. Sodium benzoate ( $\text{NaC}_6\text{H}_5\text{COO}$ ) is a solid. Used as a preservative in most pop (soda back east). 10.000 grams is dissolved in 100.00 mL of distilled water?

a) Sodium benzoate is a salt that will dissociate completely in water. The benzoate ion will then act as a weak base and undergo hydrolysis with water to form benzoic acid and hydroxide ions.



c) water is the proton donor (It acts as an acid)

d) benzoate ion is the proton acceptor (It is the only available base)

e) After the reaction has reached equilibrium:

$$\text{Mass}_{\text{Na\_benzoate}} := 10.00 \cdot \text{gm} \quad \text{V}_{\text{Na\_benzoate}} := 100 \cdot \text{mL}$$

$$\text{MW}_{\text{Na\_benzoate}} := (22.989768 + (7 \cdot 12.001) + (2 \cdot 15.9994) + (5 \cdot 1.00794)) \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{MW}_{\text{Na\_benzoate}} = 144.03527 \cdot \text{gm}$$

$$\text{mole}_{\text{Na\_benzoate}} := \frac{\text{Mass}_{\text{Na\_benzoate}}}{\text{MW}_{\text{Na\_benzoate}}}$$

$$\text{mole}_{\text{Na\_benzoate}} = 0.06943 \cdot \text{mole}$$

$$\text{C}_{\text{Na\_benzoate}} := \frac{\text{mole}_{\text{Na\_benzoate}}}{\text{V}_{\text{Na\_benzoate}}}$$

$$\text{C}_{\text{Na\_benzoate}} = 0.69427 \cdot \text{M}$$



Start	$\text{C}_{\text{Na\_benzoate}} = 0.69427 \cdot \text{M}$	0	0
Change	- X	X	X
Equilibrium	$\text{C}_{\text{Na\_benzoate}} - \text{X}$	X	X

Start with the Equilibrium Expression

$$K_b = \frac{X \cdot X}{C_{\text{Na\_benzoate}} - X} \quad K_b := \frac{K_w}{K_a} \quad K_b = 1.54799 \cdot 10^{-10}$$

Substitute in known values

$$1.548 \cdot 10^{-10} = \frac{X \cdot X}{0.694 - X}$$

Solve

Using the Quadratic  $X = \begin{pmatrix} 1.0364824915313481043 \cdot 10^{-5} \\ -1.0364979715313481043 \cdot 10^{-5} \end{pmatrix}$

Assuming X is small in the denominator  $X = 1.036490231502448845 \cdot 10^{-5}$

These two answers are essentially identical.

Select the appropriate root:

$$X := 1.036490231502448845 \cdot 10^{-5} \cdot \text{M}$$

Concentrations of species present

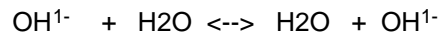
Benzoic Acid	$C_{\text{benzoate}} := C_{\text{Na\_benzoate}} - X$	$C_{\text{benzoate}} = 0.69426 \cdot \text{M}$
Benzoate	$C_{\text{benzoic}} := X$	$C_{\text{benzoic}} = 1.03649 \cdot 10^{-5} \cdot \text{M}$
Hydroxide Ion	$C_{\text{OH}} := X$	$C_{\text{OH}} = 1.03649 \cdot 10^{-5} \cdot \text{M}$
	$\text{pOH} := -\log(C_{\text{OH}} \cdot \text{M}^{-1})$	$\text{pOH} = 4.98443$
Hydronium Ion	$C_{\text{H3O}} := \frac{K_w \cdot \text{M}^2}{C_{\text{OH}}}$	$C_{\text{H3O}} = 9.64794 \cdot 10^{-10} \cdot \text{M}$
	$\text{pH} := -\log(C_{\text{H3O}} \cdot \text{M}^{-1})$	$\text{pH} = 9.01557$

3. Sodium Hydroxide (NaOH) is a solid. 5.000 grams is dissolved in 50.00 mL of distilled water?

a) Sodium hydroxide is a salt and a strong base. It will completely dissociate in water to form hydroxide ions and sodium ions



c) NaOH is an Arrhenius base so it is not typically thought of in terms of proton donors and acceptors. One way to do this is that after the NaOH dissociates the hydroxide undergoes the following acid/base reaction.



Now the hydroxide can be considered the proton acceptor (base) and the water is considered the proton donor (acid)

e) After the reaction has reached equilibrium: (Note since NaOH is a strong base, it is not necessary to work the equilibrium calculations. This reaction goes to completion.

$$\text{Mass}_{\text{NaOH}} := 5.00 \cdot \text{gm}$$

$$V_{\text{NaOH}} := 50 \cdot \text{mL}$$

$$\text{MW}_{\text{NaOH}} := (22.989768 + 15.9994 + 1.00794) \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{MW}_{\text{NaOH}} = 39.99711 \cdot \text{gm}$$

$$\text{mole}_{\text{NaOH}} := \frac{\text{Mass}_{\text{NaOH}}}{\text{MW}_{\text{NaOH}}}$$

$$\text{mole}_{\text{NaOH}} = 0.12501 \cdot \text{mole}$$

$$C_{\text{NaOH}} := \frac{\text{mole}_{\text{NaOH}}}{V_{\text{NaOH}}}$$

$$C_{\text{NaOH}} = 2.50018 \cdot \text{M}$$

Concentrations of species present

Hydroxide Ion

$$C_{\text{OH}} := C_{\text{NaOH}}$$

$$C_{\text{OH}} = 2.50018 \cdot \text{M}$$

$$\text{pOH} := -\log(C_{\text{OH}} \cdot \text{M}^{-1})$$

$$\text{pOH} = -0.39797$$

Hydronium Ion

$$C_{\text{H}_3\text{O}} := \frac{K_w \cdot \text{M}^2}{C_{\text{OH}}}$$

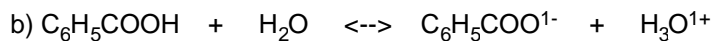
$$C_{\text{H}_3\text{O}} = 3.99971 \cdot 10^{-15} \cdot \text{M}$$

$$\text{pH} := -\log(C_{\text{H}_3\text{O}} \cdot \text{M}^{-1})$$

$$\text{pH} = 14.39797$$

4. The benzoic acid solution and the sodium benzoate solution are mixed together in a large flask.

a) Benzoic acid is a weak acid and benzoate is the conjugate base so this system will form a buffer solution.



c) benzoic acid is the proton donor (It is an acid)

d) water is the proton acceptor (It is the only available base)

e) After the reaction has reached equilibrium:

First determine the concentration of the acid and the base after dilution:

$$V_{\text{total}} := V_{\text{benzoic}} + V_{\text{Na_benzoate}} \quad V_{\text{total}} = 300 \cdot \text{mL}$$

$$C_{\text{acid}} := \frac{\text{mole benzoic}}{V_{\text{total}}} \quad C_{\text{acid}} = 0.40966 \cdot \text{M}$$

$$C_{\text{base}} := \frac{\text{mole Na_benzoate}}{V_{\text{total}}} \quad C_{\text{base}} = 0.23142 \cdot \text{M}$$

Next look at the equilibrium

	$\text{C}_6\text{H}_5\text{COOH}$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{C}_6\text{H}_5\text{COO}^{1-}$	+	$\text{H}_3\text{O}^{1+}$
Start	$C_{\text{acid}} = 0.40966 \cdot \text{M}$				$C_{\text{base}} = 0.23142 \cdot \text{M}$		0
Change	- X				X		X
Equilibrium	$C_{\text{acid}} - X$				$C_{\text{base}} + X$		X

Start with the Equilibrium Expression

$$K_a = \frac{(C_{\text{base}} + X) \cdot X}{C_{\text{acid}} - X}$$

Substitute in known values

$$6.49 \cdot 10^{-5} = \frac{(0.23142 + X) \cdot X}{0.40966 - X}$$

Solve

Using the Quadratic

$$X = \left( \begin{array}{l} 1.147969291519977 \cdot 10^{-4} \\ -.2315996969291519977 \end{array} \right)$$

Assuming X is small compared to the concentration of the acid or the base

$$X = 1.1488606861982542563 \cdot 10^{-4}$$

These two answers are essentially identical.

Select the appropriate root:

$$X := 1.147969291519977 \cdot 10^{-4} \cdot \text{M}$$

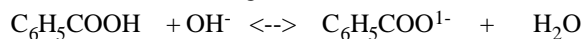
Concentrations of species present

Benzoic Acid	$C_{\text{benzoic}} := C_{\text{acid}} - X$	$C_{\text{benzoic}} = 0.40954 \cdot \text{M}$
Benzoate	$C_{\text{benzoate}} := C_{\text{base}} + X$	$C_{\text{benzoate}} = 0.23154 \cdot \text{M}$
Hydronium Ion	$C_{\text{H}_3\text{O}^+} := X$ $\text{pH} := -\log(X \cdot \text{M}^{-1})$	$C_{\text{H}_3\text{O}^+} = 1.14797 \cdot 10^{-4} \cdot \text{M}$ $\text{pH} = 3.94007$
Hydroxide Ion	$C_{\text{OH}^-} := \frac{1 \cdot 10^{-14} \cdot \text{M}^2}{X}$ $\text{pOH} := 14 - \text{pH}$	$C_{\text{OH}^-} = 8.71103 \cdot 10^{-11} \cdot \text{M}$ $\text{pOH} = 10.05993$

5. 1.00 mL of the sodium hydroxide solution is added to the buffer.

Adding NaOH shifts the equilibrium from the above system. To solve for the new equilibrium conditions, two steps are required.

First since  $\text{OH}^-$  is a strong base, and benzoic acid is the strongest acid available,



This reaction will go to completion so that for:

$$\begin{aligned} C_{\text{NaOH}} &= 2.50018 \cdot \text{M} & V_{\text{NaOH}} &:= 1 \cdot \text{mL} \\ \text{mole}_{\text{NaOH}} &:= C_{\text{NaOH}} \cdot V_{\text{NaOH}} & \text{mole}_{\text{NaOH}} &= 0.0025 \cdot \text{mole} \\ V_{\text{total}} &:= V_{\text{benzoic}} + V_{\text{Na_benzoate}} + V_{\text{NaOH}} & V_{\text{total}} &= 0.301 \cdot \text{liter} \end{aligned}$$

The new initial, NON-EQUILIBRIUM, conditions for benzoic acid and benzoate ion are:

Benzoic Acid	Benzoate
$\text{mole}_{\text{acid}} := \text{mole}_{\text{benzoic}}$	$\text{mole}_{\text{base}} := \text{mole}_{\text{Na_benzoate}}$
$\text{mole}_{\text{acid}} = 0.1229$	$\text{mole}_{\text{base}} = 0.06943$
$\text{mole}_{\text{benzoic}} := \text{mole}_{\text{acid}} - \text{mole}_{\text{NaOH}}$	$\text{mole}_{\text{benzoate}} := \text{mole}_{\text{base}} + \text{mole}_{\text{NaOH}}$
$C_{\text{benzoic}} := \frac{(\text{mole}_{\text{benzoic}})}{V_{\text{total}}}$	$C_{\text{benzoate}} := \frac{(\text{mole}_{\text{benzoate}})}{V_{\text{total}}}$
$C_{\text{benzoic}} = 0.4 \cdot \text{M}$	$C_{\text{benzoate}} = 0.23896 \cdot \text{M}$

Based upon these initial concentrations, solve for the equilibrium values, assuming X reacts:

$$K_a = \frac{(C_{\text{benzoate}} + X) \cdot X}{C_{\text{benzoic}} - X}$$



Substitute in known values

$$6.49 \cdot 10^{-5} = \frac{(0.23896 + X) \cdot X}{0.4 - X}$$

Solve

Using the Quadratic  $X = \left( \begin{array}{l} 1.0855862725786263 \cdot 10^{-4} \\ -.23913345862725786263 \end{array} \right)$

Assuming X is small compared to the concentration of the acid or the base  $X = 1.0863742885838634081 \cdot 10^{-4}$

These two answers are essentially identical.

Select the appropriate root:

$$X := 1.0855862725786263 \cdot 10^{-4} \cdot \text{M}$$

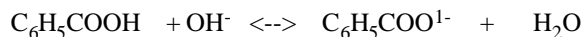
Concentrations of species present

Benzoic Acid	$C_{\text{benzoic}} := C_{\text{benzoic}} - X$	$C_{\text{benzoic}} = 0.39988 \cdot \text{M}$
Benzoate	$C_{\text{benzoate}} := C_{\text{benzoate}} + X$	$C_{\text{benzoate}} = 0.23907 \cdot \text{M}$
Hydronium Ion	$C_{\text{H}_3\text{O}^+} := X$	$C_{\text{H}_3\text{O}^+} = 1.08559 \cdot 10^{-4} \cdot \text{M}$
	$\text{pH} := -\log(X \cdot \text{M}^{-1})$	$\text{pH} = 3.96434$
Hydroxide Ion	$C_{\text{OH}^-} := \frac{1 \cdot 10^{-14} \cdot \text{M}^2}{X}$	$C_{\text{OH}^-} = 9.21161 \cdot 10^{-11} \cdot \text{M}$
	$\text{pOH} := 14 - \text{pH}$	$\text{pOH} = 10.03566$

6. 10.00 mL of the sodium hydroxide solution is added to the buffer.

Adding NaOH shifts the equilibrium from the above system. To solve for the new equilibrium conditions, two steps are required.

First since OH<sup>-</sup> is a strong base, and benzoic acid is the strongest acid available,



This reaction will go to completion so that for:

$$\begin{aligned} C_{\text{NaOH}} &= 2.50018 \cdot \text{M} & V_{\text{NaOH}} &:= 10 \cdot \text{mL} \\ \text{mole}_{\text{NaOH}} &:= C_{\text{NaOH}} \cdot V_{\text{NaOH}} & \text{mole}_{\text{NaOH}} &= 0.025 \cdot \text{mole} \\ V_{\text{total}} &:= V_{\text{benzoic}} + V_{\text{Na_benzoate}} + V_{\text{NaOH}} & V_{\text{total}} &= 0.31 \cdot \text{liter} \end{aligned}$$

The new initial, NON-EQUILIBRIUM, conditions for benzoic acid and benzoate ion are:

Benzoic Acid	Benzoate
$\text{mole}_{\text{acid}} = 0.1229$	$\text{mole}_{\text{base}} = 0.06943$
$\text{mole}_{\text{benzoic}} := \text{mole}_{\text{acid}} - \text{mole}_{\text{NaOH}}$	$\text{mole}_{\text{benzoate}} := \text{mole}_{\text{base}} + \text{mole}_{\text{NaOH}}$
$C_{\text{benzoic}} := \frac{(\text{mole}_{\text{benzoic}})}{V_{\text{total}}}$	$C_{\text{benzoate}} := \frac{(\text{mole}_{\text{benzoate}})}{V_{\text{total}}}$
$C_{\text{benzoic}} = 0.3158 \cdot \text{M}$	$C_{\text{benzoate}} = 0.30461 \cdot \text{M}$

Based upon these initial concentrations, solve for the equilibrium values, assuming X reacts:

$$K_a = \frac{(C_{\text{benzoate}} + X) \cdot X}{C_{\text{benzoic}} - X}$$

Substitute in known values

$$6.49 \cdot 10^{-5} = \frac{(0.30461 + X) \cdot X}{0.3158 - X}$$

Solve

Using the Quadratic  $X = \left( \begin{array}{l} 6.72549552686874 \cdot 10^{-5} \\ -.3047421549552686874 \end{array} \right)$

Assuming X is small compared to the concentration of the acid or the base  $X = 6.728413381044614425 \cdot 10^{-5}$

These two answers are essentially identical.

Select the appropriate root:

$$X := 6.728413381044614425 \cdot 10^{-5} \cdot \text{M}$$

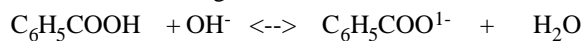
Concentrations of species present

Benzoic Acid	$C_{\text{benzoic}} := C_{\text{benzoic}} - X$	$C_{\text{benzoic}} = 0.31572 \cdot \text{M}$
Benzoate	$C_{\text{benzoate}} := C_{\text{benzoate}} + X$	$C_{\text{benzoate}} = 0.30468 \cdot \text{M}$
Hydronium Ion	$C_{\text{H}_3\text{O}^+} := X$	$C_{\text{H}_3\text{O}^+} = 6.72841 \cdot 10^{-5} \cdot \text{M}$
	$\text{pH} := -\log(X \cdot \text{M}^{-1})$	$\text{pH} = 4.17209$
Hydroxide Ion	$C_{\text{OH}^-} := \frac{1 \cdot 10^{-14} \cdot \text{M}^2}{X}$	$C_{\text{OH}^-} = 1.48623 \cdot 10^{-10} \cdot \text{M}$
	$\text{pOH} := 14 - \text{pH}$	$\text{pOH} = 9.82791$

7. 25.00 mL of the sodium hydroxide solution is added to the buffer.

Adding NaOH shifts the equilibrium from the above system. To solve for the new equilibrium conditions, two steps are required.

First since OH<sup>-</sup> is a strong base, and benzoic acid is the strongest acid available,



This reaction will go to completion so that for:

$$\begin{aligned} C_{\text{NaOH}} &= 2.50018 \cdot \text{M} & V_{\text{NaOH}} &:= 25 \cdot \text{mL} \\ \text{mole}_{\text{NaOH}} &:= C_{\text{NaOH}} \cdot V_{\text{NaOH}} & \text{mole}_{\text{NaOH}} &= 0.0625 \cdot \text{mole} \\ V_{\text{total}} &:= V_{\text{benzoic}} + V_{\text{Na_benzoate}} + V_{\text{NaOH}} & V_{\text{total}} &= 0.325 \cdot \text{liter} \end{aligned}$$

The new initial, NON-EQUILIBRIUM, conditions for benzoic acid and benzoate ion are:

Benzoic Acid	Benzoate
$\text{mole}_{\text{acid}} = 0.1229$	$\text{mole}_{\text{base}} = 0.06943$
$\text{mole}_{\text{benzoic}} := \text{mole}_{\text{acid}} - \text{mole}_{\text{NaOH}}$	$\text{mole}_{\text{benzoate}} := \text{mole}_{\text{base}} + \text{mole}_{\text{NaOH}}$
$C_{\text{benzoic}} := \frac{(\text{mole}_{\text{benzoic}})}{V_{\text{total}}}$	$C_{\text{benzoate}} := \frac{(\text{mole}_{\text{benzoate}})}{V_{\text{total}}}$
$C_{\text{benzoic}} = 0.1858 \cdot \text{M}$	$C_{\text{benzoate}} = 0.40594 \cdot \text{M}$

Based upon these initial concentrations, solve for the equilibrium values, assuming X reacts:

$$K_a = \frac{(C_{\text{benzoate}} + X) \cdot X}{C_{\text{benzoic}} - X}$$

Substitute in known values

$$6.49 \cdot 10^{-5} = \frac{(0.40594 + X) \cdot X}{0.1858 - X}$$

$$6.49 \cdot 10^{-5} = \frac{(0.40594) \cdot X}{0.1858}$$

Solve

Using the Quadratic

$$X = \left( \begin{array}{l} 2.969801110315791 \cdot 10^{-5} \\ -.40603459801110315791 \end{array} \right)$$

Assuming X is small compared to the concentration of the acid or the base

$$X = 2.9704931763314775583 \cdot 10^{-5}$$

These two answers are essentially identical.

Select the appropriate root:

$$X := 2.969801110315791 \cdot 10^{-5} \cdot \text{M}$$

Concentrations of species present

Benzoic Acid	$C_{\text{benzoic}} := C_{\text{benzoic}} - X$	$C_{\text{benzoic}} = 0.18579 \cdot \text{M}$
Benzoate	$C_{\text{benzoate}} := C_{\text{benzoate}} + X$	$C_{\text{benzoate}} = 0.40597 \cdot \text{M}$
Hydronium Ion	$C_{\text{H}_3\text{O}^+} := X$	$C_{\text{H}_3\text{O}^+} = 2.9698 \cdot 10^{-5} \cdot \text{M}$
	$\text{pH} := -\log(X \cdot \text{M}^{-1})$	$\text{pH} = 4.52727$
Hydroxide Ion	$C_{\text{OH}^-} := \frac{1 \cdot 10^{-14} \cdot \text{M}^2}{X}$	$C_{\text{OH}^-} = 3.36723 \cdot 10^{-10} \cdot \text{M}$
	$\text{pOH} := 14 - \text{pH}$	$\text{pOH} = 9.47273$