Chemistry 192 Problem Set 3 Spring, 2018 Solutions

- 1. Problem 3, page 782, textbook Answer
  - (a)

$$\begin{array}{c} \text{HOBr} & \text{H}_2\text{O} & \text{H}_3\text{O}^+ & \text{OBr}^-\\ (\text{acid 1}) + (\text{base 2}) \rightleftharpoons (\text{acid 2}) + (\text{base 1}) \end{array}$$

(b)

$$\begin{array}{ccc} \mathrm{HSO}_{4}^{-} & \mathrm{H}_{2}\mathrm{O} & \mathrm{H}_{3}\mathrm{O}^{+} & \mathrm{SO}_{4}^{2-} \\ (\mathrm{acid}\ 1) + (\mathrm{base}\ 2) \rightleftharpoons (\mathrm{acid}\ 2) + (\mathrm{base}\ 1) \end{array}$$

(c)

$$\begin{array}{ccc} HS^{-} & H_2O & H_2S & OH^{-} \\ (\text{base 1}) + (\text{acid 2}) \rightleftharpoons (\text{acid 1}) + (\text{base 2}) \end{array}$$

(d)

$$\begin{array}{ccc} C_6H_5NH_3^+ & OH^- & C_6H_5NH_2 & H_2O\\ (acid 1) & + (base 2) \rightleftharpoons (base 1) + (acid 2) \end{array}$$

## 2. Calculate the pH and pOH of the following solutions of strong acids or bases:

(a) 0.0125 M HCl<sub>(aq)</sub> **Answer:**   $[H_3O^+] = 1.25 \times 10^{-2}$  $pH = -\log_{10}(1.25 \times 10^{-2}) = 1.903$  pOH = 14.00 - pH = 12.10 (b) 0.0460 M NaOH<sub>(aq)</sub> Answer:

$$[OH^{-}] = 4.60 \times 10^{-2}$$

$$pOH = -\log_{10}(4.60 \times 10^{-2}) = 1.337$$
  $pH = 14.00 - pOH = 12.66$ 

(c)  $1.75 \times 10^{-8}$  M HCl<sub>(aq)</sub>

## Answer:

There are two equilibrium processes to consider

$$\mathrm{HCl}_{(aq)} + \mathrm{H}_{2}\mathrm{O}_{(\ell)} \rightleftharpoons \mathrm{H}_{3}\mathrm{O}_{(aq)}^{+} + \mathrm{Cl}_{(aq)}^{-}$$

and

$$\mathrm{H}_{2}\mathrm{O}_{(\ell)} + \mathrm{H}_{2}\mathrm{O}_{(\ell)} \rightleftharpoons \mathrm{H}_{3}\mathrm{O}_{(aq)}^{+} + \mathrm{OH}_{(aq)}^{-}$$

All the  $OH_{(aq)}^-$  results from the self dissociation of water. We let  $x = [OH^-]$ . The H<sub>3</sub>O<sup>+</sup> concentration has contributions from both equilibria. Then  $[H_3O^+] = x + 1.75 \times 10^{-8}$ . Using the ion product of water

$$[H_3O^+][OH^-] = x(x + 1.75 \times 10^{-8}) = 1.00 \times 10^{-14}$$

or

$$x^2 + 1.75 \times 10^{-8}x - 1.00 \times 10^{-14} = 0$$

Using the quadratic formula

$$x = \frac{-1.75 \times 10^{-8} \pm \sqrt{(1.75 \times 10^{-8})^2 + 4 \times 10^{-14}}}{2} = 9.20 \times 10^{-8}, -1.10 \times 10^{-7}.$$

Only the positive solution for x is physical and

$$pOH = -\log_{10}(9.20 \times 10^{-8}) = 7.04$$
  $pH = 14.00 - pOH = 6.96$ 

(d)  $1.75 \times 10^{-8}$  M NaOH<sub>(aq)</sub>

## Answer:

The method of solution is identical to the solution to problem 2c, except that we set  $x = [H_3O^+]$ . Then using similar algebra

$$pH = -\log_{10}(9.20 \times 10^{-8}) = 7.04$$
  $pOH = 14.00 - pH = 6.96$ 

3. Problem 14, page 782, textbook Answer:

$$n_{OH^-} = (0.125 \text{ L})(0.606 \text{ mol } \text{L}^{-1}) = 0.0758 \text{ mol}$$
  
 $[\text{OH}^-] = \frac{0.0758 \text{ mol}}{15.0 \text{ L}} = 00.00505 \text{ M}$   
 $\text{pOH} = -\log_{10}(0.00505) = 2.297 \text{ pH} = 14.00 - \text{pOH} = 11.70$ 

4. Problem 19, page 782, textbook Answer:

Before mixing

$$n_{H^+} = (0.05000 \text{ L})(0.0155 \text{ mol } \text{L}^{-1}) = 0.000775 \text{ mol}$$

$$n_{OH^-} = (0.07500 \text{ L})(0.0106 \text{ mol } \text{L}^{-1}) = 0.000795 \text{ mol}$$

After mixing

$$n_{OH^-} = 0.000795 \text{ mol} - 0.000775 \text{ mol} = 0.0000200 \text{ mol}$$
  
 $[OH^-] = \frac{0.0000200 \text{mol}}{0.125 \text{ L}} = 0.000160 \text{ M}$   
 $pOH = -\log_{10}(0.000160) = 3.796 \text{ pH} = 14.00 - pOH = 10.20$ 

5. Problem 20, Page 782, textbook Answer:

$$[H_3O^+] = 10^{-2.12} = 7.58 \times 10^{-3} M$$
  

$$n_{H_3O^+} = (7.58 \times 10^{-3} \text{ mol } L^{-1})(0.02500 \text{ L}) = 1.94 \times 10^{-4} \text{ mol}$$
  

$$[OH^-] = 10^{-(14-12.65)} = 4.47 \times 10^{-2} M$$
  

$$n_{OH^-} = (0.02500 \text{ L})(4.47 \times 10^{-2} \text{ mol } L^{-1}) = 1.17 \times 10^{-3} \text{ mol}$$

After mixing

$$n_{OH^{-}} = 1.17 \times 10^{-3} \text{ mol} - 1.94 \times 10^{-4} \text{ mol} = 9.76 \times 10^{-4} \text{ mol}$$
$$[OH^{-}] = \frac{9.76 \times 10^{-4} \text{ mol}}{0.0500 \text{ L}} = 1.95 \times 10^{-2} \text{ M}$$
$$pOH = -\log_{10}(1.95 \times 10^{-2}) = 1.71 \quad \text{pH} = 14.00 - \text{pOH} = 12.29$$

6. Calculate the volume of a 0.100 M aqueous KOH solution that must be added to 100. ml of a 0.100 M aqueous HCl solution to obtain a solution having a pH=2.000. Answer:

Before mixing

 $n_{H_3O^+} = (0.100 \text{ mol } \text{L}^{-1})(0.100 \text{ L}) = 0.0100 \text{ mol}$ 

Let V = volume of the KOH solution to be added. Then the final  $H_3O^+$  concentration is

$$\frac{n_{H_3O^+}}{V_{final}} = \frac{(0.0100 \text{ mol} - (0.100 \text{ mol } \text{L}^{-1})V}{V + 0.100 \text{ L}} = 10^{-2} \text{ mol } \text{L}^{-1}$$

$$(10^{-2} \text{ mol } \text{L}^{-1})V + 1.00 \times 10^{-3} \text{ mol} = 0.0100 \text{ mol} - (0.100 \text{ mol } \text{L}^{-1})V$$

$$(0.110 \text{ mol } \text{L}^{-1})V = 0.00900 \text{ mol}$$

$$V = 0.0818 \text{ L} = 81.8 \text{ mL}$$

7. Given that sodium hydroxide is a strong base, calculate the pH of an aqueous  $7.5 \times 10^{-8}$  M sodium hydroxide solution. Approximations do not work for this problem. Answer:

$$[H_{3}O^{+}][OH^{-}] = 1.0 \times 10^{-14}$$
  
Let  $y = [H_{3}O^{+}]$   $[OH^{-}] = y + 7.5 \times 10^{-8}$   
 $y(y + 7.5 \times 10^{-8}) = 1.0 \times 10^{-14}$   
 $y^{2} + 7.5 \times 10^{-8}y - 1.0 \times 10^{-14} = 0$   
 $y = \frac{-7.5 \times 10^{-8} \pm [(7.5 \times 10^{-8})^{2} + 4.0 \times 10^{-14}]^{1/2}}{2}$ 

Keeping the positive solution

$$y = [H_3O^+] = 6.9 \times 10^{-8} M$$
  $pH = -\log_{10}(6.9 \times 10^{-8}) = 7.16$ 

8. Calculate the pH and percent ionization of a 2.00 M aqueous HCN solution given that for the reaction

$$\mathrm{HCN}_{(aq)} + \mathrm{H}_2\mathrm{O}_{(\ell)} \rightleftharpoons \mathrm{H}_3\mathrm{O}_{(aq)}^+ + \mathrm{CN}_{(aq)}^-,$$

 $K_a = 4.1 \times 10^{-10}.$  Answer

$$K_a = \frac{[\mathrm{H}_3\mathrm{O}^+][\mathrm{CN}^-]}{[\mathrm{HCN}]}$$

	[HCN]	$[H_3O^+]$	$[CN^{-}]$
initial	2.00 M	0 M	0 M
change	- <i>x</i> M	x M	x M
equilibrium	(2.00-x) M	x M	x M

$$\frac{x^2}{2.00 - x} = 4.1 \times 10^{-10}$$
$$x^2 \approx 8.2 \times 10^{-10}$$
$$x = 2.9 \times 10^{-5}$$
% ionized = 
$$\frac{2.9 \times 10^{-5}}{2.00} \times 100. = 1.4 \times 10^{-3}\%$$
$$pH = -\log_{10}(2.9 \times 10^{-5}) = 4.54$$

9. The  $pK_a$  of phenol (C<sub>6</sub>H<sub>5</sub>OH) when acting as a weak acid in aqueous solution is 9.99. Calculate the pH of a 2.0 M phenol solution. Approximations work for this system. **Answer**:

$$K_a = 10^{-9.99} = 1.0 \times 10^{-10}$$

$$C_6H_5OH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons C_6H_5O_{(aq)} + H_3O_{(aq)}^+$$

	$[C_6H_5OH]$	$[C_6H_5O^-]$	$[H_3O^+]$
initial	2.0 M	0 M	0 M
change	- <i>y</i>	y	y
equilibrium	(2.0 - y) M	y M	y M

$$\frac{y^2}{2.0 - y} \approx \frac{y^2}{2.0} = 1.0 \times 10^{-10}$$
$$y = \sqrt{2.0 \times 10^{-10}} = 1.4 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$
$$\text{pH} = -\log_{10}(1.4 \times 10^{-5}) = 4.84$$

10. When a 0.072 M aqueous solution of benzoic acid reacts

$$C_6H_5COOH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + C_6H_5COO^-_{(aq)}$$

the pH is found to be 2.68. Calculate the  $pK_a$  for the reaction. Answer

Let  $BA \equiv C_6H_5COOH$  and  $A^- \equiv C_6H_5COO^-$ . Then

$$[H_3O^+] = 10^{-2.68} = 2.1 \times 10^{-3} = [A^-]$$

	[BA]	$[\mathrm{H}_{3}\mathrm{O}^{+}]$	$[A^-]$
initial	$0.072 {\rm M}$	0 M	0 M
change	- <i>x</i> M	x M	x M
equilibrium	(0.072-x) M	x M	x M

$$x = 2.1 \times 10^{-3}$$

$$K_a = \frac{[\mathrm{H}_3\mathrm{O}^+][\mathrm{A}^-]}{[\mathrm{BA}]} = \frac{x^2}{0.072 - x} = \frac{(2.1 \times 10^{-3})^2}{0.072 - 2.1 \times 10^{-3}} = 6.3 \times 10^{-5}$$
$$\mathrm{p}K_a = -\log_{10}(6.3 \times 10^{-5}) = 4.20$$

11. Formic acid (HCOOH) is a monoprotic acid with acid dissociation reaction

$$\text{HCOOH}_{(aq)} + \text{H}_2\text{O}_{(\ell)} \rightleftharpoons \text{HCOO}_{(aq)}^- + \text{H}_3\text{O}_{(aq)}^+.$$

The pH of a  $1.20 \times 10^{-3}$  M formic acid solution is found to be 3.41. Calculate  $K_a$  and p $K_a$  for formic acid.

Answer:

$$[\mathrm{H}_{3}\mathrm{O}^{+}] = 10^{-3.41} = 3.9 \times 10^{-4}$$

	[HCOOH]	$[H_3O^+]$	[HCOO <sup>-</sup> ]
initial	$1.20 \times 10^{-3} { m M}$	0 M	0 M
change	$-3.9 \times 10^{-4} \mathrm{M}$	$3.9 \times 10^{-4} \mathrm{M}$	$3.9 \times 10^{-4} \mathrm{~M}$
equilibrium	$8.1 \times 10^{-4} \mathrm{M}$	$3.9 \times 10^{-4} \mathrm{M}$	$3.9 \times 10^{-4} \mathrm{M}$

 $K_a = \frac{[\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{HCOOH}]} = \frac{(3.9 \times 10^{-4})^2}{8.1 \times 10^{-4}} = 1.9 \times 10^{-4}$  $pK_a = -\log_{10} K_a = -\log_{10} (1.9 \times 10^{-4}) = 3.73$ 

12. Dimethylamine ionizes according to the reaction

$$(\mathrm{CH}_3)_2\mathrm{NH}_{(aq)} + \mathrm{H}_2\mathrm{O}_{(\ell)} \rightleftharpoons (\mathrm{CH}_3)_2\mathrm{NH}_{2(aq)}^+ + \mathrm{OH}_{(aq)}^-$$

A 0.95 M solution of dimethylamine is found to have a pH of 12.32. Calculate the p $K_b$  of the reaction.

Answer:

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$
  
pOH = 14.00 - pH = 1.68 [OH<sup>-</sup>] = 10<sup>-1.68</sup> = 2.1 × 10<sup>-2</sup>

	$[(CH_3)_2NH]$	$[(\mathrm{CH}_3)_2\mathrm{NH}_2^+]$	$[OH^{-}]$
initial	$0.95 \mathrm{M}$	0 M	0 M
change	- <i>x</i> M	x M	x M
equilibrium	(0.95-x) M	x M	x M

$$\frac{x^2}{0.95 - x} = \frac{(2.1 \times 10^{-2})^2}{0.95 - 2.1 \times 10^{-2}} = 4.7 \times 10^{-4}$$
$$pK_b = -\log_{10}(4.7 \times 10^{-4}) = 3.32$$

13. Hydrofluoric acid  $(HF_{(aq)})$  is formed when gas-phase hydrogen fluoride  $(HF_{(g)})$  is dissolved in water according to the reaction

$$\mathrm{HF}_{(aq)} + \mathrm{H}_{2}\mathrm{O}_{(\ell)} \rightleftharpoons \mathrm{F}_{(aq)}^{-} + \mathrm{H}_{3}\mathrm{O}_{(aq)}^{+}$$

The  $pK_a$  of hydrofluoric acid is 3.18. Calculate the pH of a solution that forms when 0.25 grams of gas-phase HF are dissolved in water to make 1.2 L of solution. Approximations do not work for this problem.

Answer:

$$K_a = 10^{-3.18} = 6.6 \times 10^{-4}$$

Initially

[HF] = 
$$\frac{(0.25 \text{ g})\left(\frac{\text{mol}}{(19.0 + 1.0) \text{ g}}\right)}{1.2 \text{ L}} = 1.0 \times 10^{-2} \text{ M}$$

	[HF]	$[H_3O^+]$	$[F^{-}]$
initial	$1.0 \times 10^{-2} \mathrm{M}$	0 M	0 M
change	- <i>y</i> M	y M	y M
equilibrium	$(1.0 \times 10^{-2} - y) \text{ M}$	y M	y M

$$6.6 \times 10^{-4} = \frac{[\mathrm{F}^{-}][\mathrm{H}_{3}\mathrm{O}^{+}]}{[\mathrm{HF}]} = \frac{y^{2}}{1.0 \times 10^{-2} - y}$$
$$y^{2} + 6.6 \times 10^{-4}y - 6.6 \times 10^{-6} = 0$$

Ignoring the negative solution

$$y = \frac{-6.6 \times 10^{-4} + [(6.6 \times 10^{-4})^2 + 4(6.6 \times 10^{-6})]^{1/2}}{2} = 2.2 \times 10^{-3}$$
$$[H_3O^+] = 2.2 \times 10^{-3} \text{ M} \qquad \text{pH} = -\log_{10}(2.2 \times 10^{-3}) = 2.66$$

14. Ethylamine,  $C_2H_5NH_2$ , is a weak base in aqueous solution. The pH of a 1.0 M aqueous ethylamine solution is measured to be 12.32. Calculate the p $K_b$  of ethylamine. Answer:

$$C_2H_5NH_{2(aq)} + H_2O_{(\ell)} \rightleftharpoons C_2H_5NH_{3(aq)}^+ + OH_{(aq)}^-$$
  
pOH = 14.00 - pH = 1.68 [OH<sup>-</sup>] = 10<sup>-1.68</sup> = 2.1 × 10<sup>-2</sup>

	$[C_2H_5NH_2]$	$[\mathrm{C_2H_5NH_3^+}]$	$[OH^{-}]$
initial	1.0 M	0 M	0 M
change	$-2.1 \times 10^{-2} { m M}$	$2.1 \times 10^{-2} \mathrm{M}$	$2.1 \times 10^{-2} \mathrm{M}$
equilibrium	0.98 M	$2.1 \times 10^{-2} \mathrm{M}$	$2.1 \times 10^{-2} \mathrm{M}$

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{(2.1 \times 10^{-2})^2}{0.98} = 4.5 \times 10^{-4}$$
$$pK_b = -\log_{10}(4.5 \times 10^{-4}) = 3.35$$

15. The two values for the  $pK_a$  of hydrosulfuric acid according to the reactions

$$H_{2}S_{(aq)} + H_{2}O_{(\ell)} \rightleftharpoons H_{3}O_{(aq)}^{+} + HS_{(aq)}^{-}$$
$$HS_{(aq)}^{-} + H_{2}O_{(\ell)} \rightleftharpoons H_{3}O_{(aq)}^{+} + S_{(aq)}^{2-}$$

are respectively 7.00 and 19.0. Calculate the concentrations of all species present in a 0.0100 and 0.00100 M aqueous solution of hydrosulfuric acid. **Answer**:

$$\frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{HS}^{-}]}{[\mathrm{H}_{2}\mathrm{S}]} = 1.00 \times 10^{-7}$$
$$\frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{S}^{2-}]}{[\mathrm{HS}^{-}]} = 1.00 \times 10^{-19}$$

(a) 0.0100 M

	$[H_2S]$	$[HS^-]$	$[H_3O^+]$
initial	$0.0100 {\rm M}$	0 M	0 M
change	- <i>x</i>	x	x
equilibrium	(0.0100 - x) M	x M	x M

$$\frac{x^2}{0.0100 - x} = 1.00 \times 10^{-7} \cong \frac{x^2}{0.0100}$$

 $x^{2} = 1.00 \times 10^{-9}$   $x = [H_{3}O^{+}] = [HS^{-}] = \sqrt{1.00 \times 10^{-9}} = 3.16 \times 10^{-5} \text{ M}$   $[H_{2}S] \approx 0.0100 \text{ M}$ 

	$[\mathrm{HS}^{-}]$	$[S^{2-}]$	$[H_3O^+]$
initial	$3.16 \times 10^{-5} { m M}$	0 M	$3.16 \times 10^{-5} \mathrm{M}$
change	-x	x	x
equilibrium	$(3.16 \times 10^{-5} - x) M$	x M	$(3.16 \times 10^{-5} + x) M$

$$\frac{x(3.16 \times 10^{-5} + x)}{3.16 \times 10^{-5} - x} \approx x = [S^{2-}] = 1.00 \times 10^{-19}$$

(b) 0.00100 M. In this case the approximations used in solving the previous case are a bit large, and full solution to the quadratic equations are needed.

	$[H_2S]$	$[HS^{-}]$	$[H_3O^+]$
initial	0.00100 M	0 M	0 M
change	- <i>x</i>	x	x
equilibrium	(0.00100 - x) M	x M	x M

$$\frac{x^2}{0.00100 - x} = 1.00 \times 10^{-7}$$
$$x^2 + 1.00 \times 10^{-7} x - 1.00 \times 10^{-10} = 0$$
$$x = \frac{-1.00 \times 10^{-7} \pm \sqrt{(1.00 \times 10^{-7})^2 + 4 \times 1.00 \times 10^{-10}}}{2}$$

Keeping only the positive solution

$$x = [H_3O^+] = [HS^-] = 9.95 \times 10^{-6}$$
  $[H_2S] \approx 0.00100 \text{ M}$ 

	$[HS^{-}]$	$[S^{2-}]$	$[H_3O^+]$
initial	$9.95 \times 10^{-6} \mathrm{M}$	0 M	$9.95 \times 10^{-6} \mathrm{M}$
change	-x	x	x
equilibrium	$(9.95 \times 10^{-6} - x) \text{ M}$	x M	$(9.95 \times 10^{-6} + x) \text{ M}$

$$\frac{x(9.95 \times 10^{-6} + x)}{9.95 \times 10^{-6} - x} \approx x = [S^{2-}] = 1.00 \times 10^{-19}$$

16. When phthalic acid combines with water, two equilibrium reactions occur

$$H_2C_8H_4O_{4(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O_{(aq)}^+ + HC_8H_4O_{4(aq)}^- \qquad K_{a1} = 1.1 \times 10^{-3}$$

and

$$\mathrm{HC}_{8}\mathrm{H}_{4}\mathrm{O}_{4(aq)}^{-} + \mathrm{H}_{2}\mathrm{O}_{(\ell)} \rightleftharpoons \mathrm{H}_{3}\mathrm{O}_{(aq)}^{+} + \mathrm{C}_{8}\mathrm{H}_{4}\mathrm{O}_{4(aq)}^{2-} \qquad K_{a2} = 3.9 \times 10^{-6}$$

Calculate the pH and concentrations of all species present in a 0.010 M phthalic acid solution.

Answer:

$$K_{a1} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{H}\mathrm{C}_{8}\mathrm{H}_{4}\mathrm{O}_{4}^{-}]}{[\mathrm{H}_{2}\mathrm{C}_{8}\mathrm{H}_{4}\mathrm{O}_{4}]} = 1.1 \times 10^{-3}$$

	$[\mathrm{H}_{2}\mathrm{C}_{8}\mathrm{H}_{4}\mathrm{O}_{4}]$	$[\mathrm{HC}_{8}\mathrm{H}_{4}\mathrm{O}_{4}^{-}]$	$[H_3O^+]$
initial	0.010 M	0 M	0 M
change	- <i>x</i>	x	x
equilibrium	(0.010 - x) M	x M	x M

$\frac{x^2}{0.010 - x} = 1.1 \times 10^{-3}$
$x^2 + 1.1 \times 10^{-3}x - 1.1 \times 10^{-5} = 0$
$x = \frac{-1.1 \times 10^{-3} \pm \sqrt{(1.1 \times 10^{-3})^2 + 4 \times 1.1 \times 10^{-5}}}{-1.1 \times 10^{-5}}$
$x = \frac{2}{2}$
$x = [H_3O^+] = [HC_8H_4O_4^-] = 2.8 \times 10^{-3} M$
$K_{a2} = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{C}_{8}\mathrm{H}_{4}\mathrm{O}_{4}^{2-}]}{[\mathrm{H}\mathrm{C}_{8}\mathrm{H}_{4}\mathrm{O}_{4}^{-}]} = 3.9 \times 10^{-6}$
$[HC_8H_4O_4^-] \qquad [C_8H_4O_4^{2-}] \qquad [H_3O^+]$

	$[\mathrm{HC}_{8}\mathrm{H}_{4}\mathrm{O}_{4}^{-}]$	$[C_8H_4O_4^{2-}]$	$[H_3O^+]$
initial	$2.8 \times 10^{-3} \mathrm{M}$	0 M	$2.8 \times 10^{-3} \mathrm{M}$
change	-x	x	x
equilibrium	$(2.8 \times 10^{-3} - x)$ M	x M	$(2.8 \times 10^{-3} + x) \text{ M}$

$$\frac{x(2.8 \times 10^{-3} + x)}{2.8 \times 10^{-3} - x} \approx x = 3.9 \times 10^{-6} = [C_8 H_4 O_4^{2-}]$$

$$pH = -\log_{10} 2.8 \times 10^{-3} = 2.55$$

17. Germanic acid (H<sub>2</sub>GeO<sub>3</sub>) is a diprotic acid with  $pK_a$ 's for the two protons in aqueous solution given by  $pK_{a,1} = 9.01$  and  $pK_{a,2} = 12.30$ . Calculate the equilibrium concentrations of  $\text{HGeO}_{3(aq)}^{-}$ ,  $\text{GeO}_{3(aq)}^{2-}$  and  $\text{H}_3\text{O}_{(aq)}^{+}$  and the pH for a 1.50 M aqueous solution of germanic acid. Approximations work for this problem. Answer:

$$K_{a1} = 10^{-9.01} = 9.8 \times 10^{-10} \qquad K_{a2} = 10^{-12.30} = 5.0 \times 10^{-13}$$
$$H_2 \text{GeO}_{3(aq)} + H_2 \text{O}_{(\ell)} \rightleftharpoons \text{HGeO}_{3(aq)}^- + H_3 \text{O}_{(aq)}^+$$

	$[H_2GeO_3]$	$[HGeO_3^-]$	$[H_3O^+]$
initial	$1.50 \mathrm{~M}$	0 M	0 M
change	- <i>y</i>	y	y
equilibrium	(1.50 - y) M	y M	y M

$$9.8 \times 10^{-10} = \frac{[\text{HGeO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{GeO}_3]} = \frac{y^2}{1.50} \approx \frac{y^2}{1.50}$$
$$y = [\text{H}_3\text{O}^+] = [\text{HGeO}_3^-] = 3.8 \times 10^{-5} \text{ M} \qquad \text{pH} = -\log_{10}(3.8 \times 10^{-5}) = 4.42$$
$$\text{HGeO}_{3(aq)}^- + \text{H}_2\text{O}_{(\ell)} \rightleftharpoons \text{GeO}_{3(aq)}^{2-} + \text{H}_3\text{O}_{(aq)}^+$$

	$[\mathrm{HGeO}_3^-]$	$[\text{GeO}_3^{2-}]$	$[H_3O^+]$
initial	$3.8 \times 10^{-5} \mathrm{M}$	0 M	$3.8 \times 10^{-5} \mathrm{M}$
change	-y	y	y
equilibrium	$(3.8 \times 10^{-5} - y) M$	y M	$(3.8 \times 10^{-5} + y) \text{ M}$

$$5.0 \times 10^{-13} = \frac{[\text{GeO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HGeO}_3^-]} = \frac{y(3.8 \times 10^{-5} + y)}{3.8 \times 10^{-5} - y} \approx y$$
$$[\text{GeO}_3^{2-}] = 5.0 \times 10^{-13} \text{ M}$$

18. Selenic acid  $(H_2SeO_4)$  is a diprotic acid. Like sulfuric acid, the first proton is essentially 100% ionized in aqueous solution. The second proton dissociates according to the reaction

$$\text{HSeO}_{4(aq)}^- + \text{H}_2\text{O}_{(\ell)} \rightleftharpoons \text{SeO}_{4(aq)}^{2-} + \text{H}_3\text{O}_{(aq)}^+$$

with a  $pK_a = 1.92$ . Consider a 0.10 M solution of selenic acid. Calculate the equilibrium concentrations of  $HSeO_4^-$  and  $SeO_4^{2-}$ , and the pH of the solution at equilibrium. Approximations work for the dissociation equilibrium. **Answer**:

	$[HSeO_4^-]$	$[\mathrm{SeO}_4^{2-}]$	$[H_3O^+]$
initial	0.10 M	0 M	0.10 M
change	- <i>y</i>	y	y
equilibrium	(0.10 - y) M	y M	(0.10+y) M

$$K_a = 10^{-1.92} = 1.2 \times 10^{-2} = \frac{[\text{SeO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSeO}_4^{-}]}$$

$$\begin{split} &= \frac{y(0.10+y)}{0.10-y} \approx y \\ & [\mathrm{SeO}_4^{2-}] = 1.2 \times 10^{-2} \\ [\mathrm{HSeO}_4^{-}] &= 0.10 - 1.2 \times 10^{-2} = 0.10 \text{ (to two significant figures)} \\ & [\mathrm{H}_3\mathrm{O}^+] = 0.10 + 1.2 \times 10^{-2} = 0.11 \text{ M} \\ & \mathrm{pH} = -\log_{10}(0.11) = 0.96 \end{split}$$