

Chemistry 192
Problem Set 5
Spring, 2018
Solutions

1. In a titration experiment varying amounts of a 0.0100 M sodium hydroxide solution are added to 100. mL of 0.053 M hydrochloric acid. Determine the following:

- (a) the volume of the sodium hydroxide solution required to produce a solution of pH=7.0;

Answer:

$$\text{moles of H}_3\text{O}^+ = (0.053 \text{ mol L}^{-1})(0.100 \text{ L}) = 0.0053 \text{ mol}$$

$$V = \frac{0.0053 \text{ mol}}{0.0100 \text{ mol L}^{-1}} = 0.53 \text{ L} \equiv 530. \text{ mL}$$

- (b) the pH of the solution if the amount of sodium hydroxide solution added is 10.0 mL less than the volume found in problem 1a;

Answer:

$$\text{number of moles of H}_3\text{O}^+ \text{ remaining} = 0.0053 \text{ mol} - (0.52 \text{ L})(0.0100 \text{ mol L}^{-1})$$

$$= 0.00010 \text{ mol}$$

$$[\text{H}_3\text{O}^+] = \frac{0.00010 \text{ mol}}{0.620 \text{ L}} = 1.6 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log_{10}(1.6 \times 10^{-4}) = 3.79$$

- (c) the pH of the solution if the amount of sodium hydroxide solution added is 10.0 mL more than the volume found in problem 1a.

Answer:

$$[\text{OH}^-] = \frac{(0.010 \text{ L})(0.0100 \text{ mol L}^{-1})}{0.640 \text{ L}} = 1.6 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log_{10}(1.6 \times 10^{-4}) = 3.81 \quad \text{pH} = 14.00 - \text{pOH} = 10.19$$

2. In a titration experiment varying amounts of a 0.0100 M sodium hydroxide solution are added to 100. mL of 0.046 M benzoic acid (the pK_a of benzoic acid is found on page 745 of your textbooks). Determine the following:

- (a) the volume of the sodium hydroxide solution required to reach the equivalence point;

Answer:

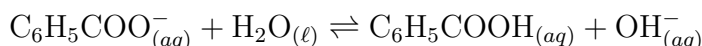
number moles benzoic acid = $(0.046 \text{ mol L}^{-1})(0.100 \text{ L}) = 0.0046 \text{ mol} = \text{moles OH}^- \text{ needed}$

$$V = \frac{0.0046 \text{ mol}}{0.0100 \text{ mol L}^{-1}} = 0.46 \text{ L}$$

- (b) the pH of the solution at the equivalence point;

Answer:

At the equivalence point, all benzoate is in the form of sodium benzoate. We need the dissociation constant for the reaction



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.6 \times 10^{-10}$$

$$[\text{C}_6\text{H}_5\text{COONa}] = \frac{0.0046 \text{ mol}}{0.56 \text{ L}} = 8.2 \times 10^{-3} \text{ M}$$

	$[\text{C}_6\text{H}_5\text{COO}^-]$	$[\text{C}_6\text{H}_5\text{COOH}]$	$[\text{OH}^-]$
initial	$8.2 \times 10^{-3} \text{ M}$	0 M	0 M
change	$-x \text{ M}$	$x \text{ M}$	$x \text{ M}$
equilibrium	$8.2 \times 10^{-3} - x \text{ M}$	$x \text{ M}$	$x \text{ M}$

$$\frac{x^2}{8.2 \times 10^{-3} - x} \cong \frac{x^2}{8.2 \times 10^{-3}} = 1.6 \times 10^{-10}$$

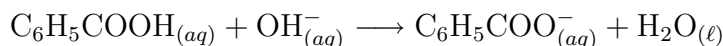
$$x = [\text{OH}^-] = \sqrt{1.3 \times 10^{-12}} = 1.1 \times 10^{-6}$$

$$\text{pOH} = -\log_{10}(1.1 \times 10^{-6}) = 5.94 \quad \text{pH} = 14.00 - \text{pOH} = 8.06$$

- (c) the pH of the solution if the amount of sodium hydroxide solution added is 10.0 mL less than the volume found in problem 2a;

Answer:

The neutralization reaction is



If 0.45 L of hydroxide solution are added, the number of moles of added hydroxide are

$$n_{\text{OH}^-} = (0.45 \text{ L})(0.0100 \text{ mol L}^{-1}) = 4.5 \times 10^{-3} \text{ mol}$$

The number of moles of benzoic acid (BA) after the addition of the hydroxide is given by

$$n_{BA} = 0.0046 \text{ mol} - 4.5 \times 10^{-3} \text{ mol} = 1.0 \times 10^{-4} \text{ mol.}$$

and

$$[\text{C}_6\text{H}_5\text{COOH}] = \frac{1.0 \times 10^{-4} \text{ mol}}{0.55 \text{ L}} = 1.8 \times 10^{-4} \text{ M}$$

The number of moles of benzoate ions is the same as the number of moles of added hydroxide, and

$$[\text{C}_6\text{H}_5\text{COO}^-] = \frac{4.5 \times 10^{-3} \text{ mol}}{0.55 \text{ L}} = 8.25 \times 10^{-3} \text{ M}$$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} \\ &= -\log_{10}(6.3 \times 10^{-5}) + \log_{10} \frac{8.2 \times 10^{-3}}{1.8 \times 10^{-4}} = 5.86 \end{aligned}$$

- (d) the pH of the solution if the amount of sodium hydroxide solution added is 10.0 mL more than the volume found in problem 2a.

Answer:

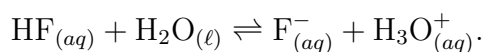
Excess number of moles of hydroxide added

$$n_{\text{OH}^-} = (0.0100 \text{ L})(0.0100 \text{ mol L}^{-1}) = 1.00 \times 10^{-4} \text{ mol}$$

$$[\text{OH}^-] = \frac{1.00 \times 10^{-4} \text{ mol}}{0.47 \text{ L}} = 2.1 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log_{10}(2.1 \times 10^{-4}) = 3.67 \quad \text{pH} = 14.00 - \text{pOH} = 10.32$$

3. Hydrofluoric acid (HF) is a weak acid that ionizes with water according to the reaction

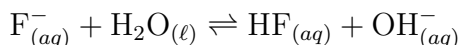


The equilibrium constant for the reaction is $K_a = 6.6 \times 10^{-4}$. When 0.0273 L of a sample of hydrofluoric acid are titrated with 0.0250 M aqueous potassium hydroxide (KOH, a strong base), the equivalence point is reached after the addition of 0.127 L of the KOH. Find the concentration of the original HF solution and the pH at the equivalence point.

Answer:

$$n_{\text{OH}^-} = (0.0250 \text{ mol L}^{-1})(0.127 \text{ L}) = 3.18 \times 10^{-3} \text{ mol}$$

$$[\text{HF}] = \frac{3.18 \times 10^{-3} \text{ mol}}{0.0273 \text{ L}} = 0.116 \text{ M}$$



$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.6 \times 10^{-4}} = 1.5 \times 10^{-11}$$

$$[\text{F}^-] = \frac{3.18 \times 10^{-3} \text{ mol}}{0.127 \text{ L} + 0.0273 \text{ L}} = 2.06 \times 10^{-2} \text{ M}$$

	$[\text{F}^-]$	$[\text{HF}]$	$[\text{OH}^-]$
initial	$2.06 \times 10^{-2} \text{ M}$	0 M	0 M
change	$-x$	x	x
equilibrium	$(2.06 \times 10^{-2} - x) \text{ M}$	$x \text{ M}$	$x \text{ M}$

$$\frac{x^2}{2.06 \times 10^{-2} - x} \approx \frac{x^2}{2.06 \times 10^{-2}} = 1.5 \times 10^{-11}$$

$$x = [\text{OH}^-] = 5.6 \times 10^{-7} \text{ M}$$

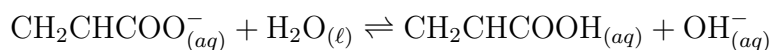
$$\text{pOH} = -\log_{10}(5.6 \times 10^{-7}) = 6.26 \quad \text{pH} = 14.00 - \text{pOH} = 7.74$$

4. Acrylic acid (CH_2CHCOOH) has $\text{p}K_a = 4.25$. When a 0.13 L sample of aqueous acrylic acid of unknown concentration are titrated with 0.0150 M potassium hydroxide (KOH), the equivalence point is reached after the addition of 0.251 L of the strong base. Find the concentration of the original acrylic acid solution and the pH of the solution at the equivalence point. Approximations work for this problem.

Answer:

$$n_{\text{OH}^-} = (0.0150 \text{ mol L}^{-1})(0.251 \text{ L}) = 3.77 \times 10^{-3} \text{ mol} = n_{\text{CH}_2\text{CHCOOH}}$$

$$[\text{CH}_2\text{CHCOOH}] = \frac{3.77 \times 10^{-3} \text{ mol}}{0.13 \text{ L}} = 2.9 \times 10^{-2} \text{ M}$$



$$\text{p}K_b = 14.00 - \text{p}K_a = 9.75 \quad K_b = 10^{-\text{p}K_b} = 1.8 \times 10^{-10}$$

$$[\text{CH}_2\text{CHCOO}^-] = \frac{3.77 \times 10^{-3} \text{ mol}}{0.13 \text{ L} + 0.251 \text{ L}} = 0.0099 \text{ M}$$

	$[\text{CH}_2\text{CHCOO}^-]$	$[\text{CH}_2\text{CHCOOH}]$	$[\text{OH}^-]$
initial	0.0099 M	0 M	0 M
change	$-y$	y	y
equilibrium	$(0.0099 - y) \text{ M}$	$y \text{ M}$	$y \text{ M}$

$$1.8 \times 10^{-10} = \frac{[\text{CH}_2\text{CHCOO}^-][\text{OH}^-]}{[\text{CH}_2\text{CHCOOH}]} = \frac{y^2}{0.0099 - y} \approx \frac{y^2}{0.0099}$$

$$y = [\text{OH}^-] = 1.3 \times 10^{-6} \text{ M} \quad \text{pOH} = -\log_{10}(1.3 \times 10^{-6}) = 5.87 \quad \text{pH} = 14.00 - \text{pOH} = 8.12$$

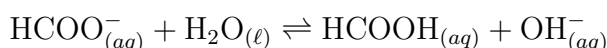
5. A 0.200 L sample of formic acid (HCOOH , $\text{p}K_a=3.74$) of unknown concentration is titrated with 0.130 M aqueous KOH (a strong base), and the equivalence point is reached after the addition of 0.454 L of KOH. Find the pH at the equivalence point.

Answer:

$$n_{\text{OH}^-} = (0.130 \text{ mol L}^{-1})(0.454 \text{ L}) = 5.90 \times 10^{-2} \text{ mol} = n_{\text{HCOOH}}$$

Benzoate concentration at equivalence point

$$[\text{HCOO}^-] = \frac{5.90 \times 10^{-2} \text{ mol}}{0.654 \text{ L}} = 9.02 \times 10^{-2} \text{ M}$$



$$K_a = 10^{-3.74} = 1.8 \times 10^{-4} \quad K_b = \frac{1.0 \times 10^{-14}}{K_a} = 5.6 \times 10^{-11}$$

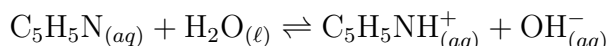
	$[\text{HCOO}^-]$	$[\text{HCOOH}]$	$[\text{OH}^-]$
initial	$9.02 \times 10^{-2} \text{ M}$	0 M	0 M
change	$-y \text{ M}$	$y \text{ M}$	$y \text{ M}$
equilibrium	$9.02 \times 10^{-2} - y \text{ M}$	$y \text{ M}$	$y \text{ M}$

$$\frac{y^2}{9.02 \times 10^{-2} - y} \approx \frac{y^2}{9.02 \times 10^{-2}} = 5.6 \times 10^{-11}$$

$$y = [\text{OH}^-] = 2.2 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log_{10}(2.2 \times 10^{-6}) = 5.65 \quad \text{pH} = 14.00 - \text{pOH} = 8.35$$

6. The base ionization constant of pyridine according to the reaction

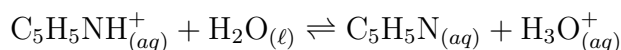


is $K_b = 1.5 \times 10^{-9}$. In an experiment 0.100 L of a pyridine solution of unknown concentration is titrated with 0.100 M hydrochloric acid (HCl, a strong acid), and the equivalence point is reached after the addition of 0.043 L of HCl. Find the concentration of the original pyridine solution and the pH at the equivalence point.

Answer:

$$n_{\text{H}_3\text{O}^+} = n_{\text{C}_5\text{H}_5\text{N}} = (0.100 \text{ mol L}^{-1})(0.043 \text{ L}) = 4.3 \times 10^{-3} \text{ mol}$$

$$[\text{C}_5\text{H}_5\text{N}] = \frac{4.3 \times 10^{-3} \text{ mol}}{0.100 \text{ L}} = 4.3 \times 10^{-2} \text{ M}$$



$$K_a = \frac{[\text{C}_5\text{H}_5\text{N}][\text{H}_3\text{O}^+]}{[\text{C}_5\text{H}_5\text{NH}^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6}$$

$$[\text{C}_5\text{H}_5\text{NH}^+] = \frac{4.3 \times 10^{-3} \text{ mol}}{(0.100 \text{ L} + 0.043 \text{ L})} = 3.0 \times 10^{-2} \text{ M}$$

	$[\text{C}_5\text{H}_5\text{NH}^+]$	$[\text{C}_5\text{H}_5\text{N}]$	$[\text{H}_3\text{O}^+]$
initial	$3.0 \times 10^{-2} \text{ M}$	0 M	0 M
change	$-y \text{ M}$	$y \text{ M}$	$y \text{ M}$
equilibrium	$3.0 \times 10^{-2} - y \text{ M}$	$y \text{ M}$	$y \text{ M}$

$$\frac{y^2}{3.0 \times 10^{-2} - y} \approx \frac{y^2}{3.0 \times 10^{-2}} = 6.7 \times 10^{-6}$$

$$y = [\text{H}_3\text{O}^+] = 4.5 \times 10^{-4} \text{ M}$$

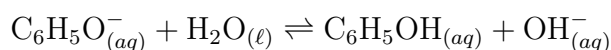
$$\text{pH} = -\log_{10}(4.5 \times 10^{-4}) = 3.35$$

7. Phenol ($\text{C}_6\text{H}_5\text{OH}$) is a weak acid with a $\text{p}K_a = 10.00$. When 0.100 L of phenol of unknown concentration are titrated with 0.150 M sodium hydroxide (a strong base), the equivalence point is reached after 0.0531 L of the base. Calculate the concentration of the original phenol solution and the pH at the equivalence point. Approximations do **not** work for this problem.

Answer:

$$n_{\text{OH}^-} = (0.150 \text{ mol L}^{-1})(0.0531 \text{ L}) = 7.97 \times 10^{-3} \text{ mol}$$

$$[\text{C}_6\text{H}_5\text{OH}] = \frac{0.797 \times 10^{-3} \text{ mol}}{0.100 \text{ L}} = 7.97 \times 10^{-2} \text{ M}$$



$$\text{p}K_b = 14.00 - \text{p}K_a = 4.00 \quad K_b = 1.0 \times 10^{-4}$$

$$[\text{C}_6\text{H}_5\text{O}^-] = \frac{7.97 \times 10^{-3} \text{ mol}}{0.1531 \text{ L}} = 5.20 \times 10^{-2} \text{ M}$$

	$[\text{C}_6\text{H}_5\text{O}^-]$	$[\text{C}_6\text{H}_5\text{OH}]$	$[\text{OH}^-]$
initial	$5.20 \times 10^{-2} \text{ M}$	0 M	0 M
change	$-y$	y	y
equilibrium	$(5.20 \times 10^{-2} - y) \text{ M}$	$y \text{ M}$	$y \text{ M}$

$$1.0 \times 10^{-4} = \frac{[\text{C}_6\text{H}_5\text{OH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{O}^-]} = \frac{y^2}{5.20 \times 10^{-2} - y}$$

$$y^2 + 1.0 \times 10^{-4}y - 5.20 \times 10^{-6} = 0$$

$$y = \frac{-1.0 \times 10^{-4} \pm [(1.0 \times 10^{-4})^2 + 4(5.20 \times 10^{-6})]^{1/2}}{2} = 2.2 \times 10^{-3} \quad \text{negative solution ignored}$$

$$[\text{OH}^-] = 2.2 \times 10^{-3} \text{ M} \quad \text{pOH} = -\log_{10}(2.2 \times 10^{-3}) = 2.65 \quad \text{pH} = 14.00 - \text{pOH} = 11.34$$

8. Allylamine ($\text{C}_3\text{H}_5\text{NH}_2$) is a weak base with $\text{p}K_b=9.49$. A 0.250 L sample of allylamine is titrated with 0.100 M nitric acid (HNO_3 , a strong acid), and the equivalence point is reached after 0.037 L of the strong acid are added to the allylamine solution. Calculate a) the initial allylamine concentration, b) the pH at the equivalence point, and c) the pH prior to the equivalence point after only 0.010 L of the strong acid have been added to the allylamine solution.

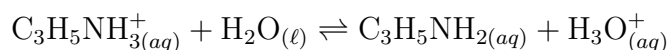
Answer:

a)

$$n_{\text{H}_3\text{O}^+} = n_{\text{C}_3\text{H}_5\text{NH}_2} = (0.100 \text{ mol L}^{-1})(0.037 \text{ L}) = 3.7 \times 10^{-3} \text{ mol}$$

$$[\text{C}_3\text{H}_5\text{NH}_2]_i = \frac{3.7 \times 10^{-3} \text{ mol}}{0.250 \text{ L}} = 0.015 \text{ M}$$

b)



$$\text{p}K_a = 14.00 - 9.49 = 4.51 \quad K_a = 10^{-4.51} = 3.1 \times 10^{-5}$$

$$[\text{C}_3\text{H}_5\text{NH}_3^+] = \frac{3.7 \times 10^{-3} \text{ mol}}{0.250 \text{ L} + 0.037 \text{ L}} = 1.3 \times 10^{-2} \text{ M}$$

	$[\text{C}_3\text{H}_5\text{NH}_3^+]$	$[\text{C}_3\text{H}_5\text{NH}_2]$	$[\text{H}_3\text{O}^+]$
initial	$1.3 \times 10^{-2} \text{ M}$	0 M	0 M
change	$-y$	y	y
equilibrium	$(1.3 \times 10^{-2} - y) \text{ M}$	$y \text{ M}$	$y \text{ M}$

$$3.1 \times 10^{-5} = \frac{y^2}{1.3 \times 10^{-2} - y} \approx \frac{y^2}{1.3 \times 10^{-2}}$$

$$y = [\text{H}_3\text{O}^+] = 6.3 \times 10^{-4} \quad \text{pH} = -\log_{10}(6.3 \times 10^{-4}) = 3.20$$

c)

$$n_{\text{C}_3\text{H}_5\text{NH}_3^+} = (0.100 \text{ mol L}^{-1})(0.010 \text{ L}) = 1.0 \times 10^{-3} \text{ mol}$$

$$n_{\text{C}_3\text{H}_5\text{NH}_2} = 3.7 \times 10^{-3} \text{ mol} - 1.0 \times 10^{-3} \text{ mol} = 2.7 \times 10^{-3} \text{ mol}$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{C}_3\text{H}_5\text{NH}_2]}{[\text{C}_3\text{H}_5\text{NH}_3^+]} = 4.51 + \log_{10} \frac{2.7 \times 10^{-3}}{1.0 \times 10^{-3}} = 4.94$$

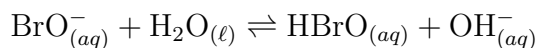
9. Hypobromous acid, HBrO , is a weak acid with $\text{p}K_a = 8.55$. A 0.10 L sample of hypobromous acid of unknown concentration is titrated with 0.12 M sodium hydroxide, and the equivalence point is reached after the addition of $4.2 \times 10^{-2} \text{ L}$ of the base. Determine the concentration of the original hypobromous acid solution and the pH of the solution at the equivalence point. Approximations work for this problem.

Answer:

$$n_{\text{OH}^-} = (0.12 \text{ mol L}^{-1})(4.2 \times 10^{-2} \text{ L}) = 5.0 \times 10^{-3} \text{ mol}$$

$$[\text{HBrO}] = \frac{5.0 \times 10^{-3} \text{ mol}}{0.10 \text{ L}} = 5.0 \times 10^{-2} \text{ M}$$

$$[\text{BrO}^-] = \frac{5.0 \times 10^{-3} \text{ mol}}{(0.10 \text{ L} + 4.2 \times 10^{-2} \text{ L})} = 3.5 \times 10^{-2} \text{ M}$$



	$[\text{BrO}^-]$	$[\text{HBrO}]$	$[\text{OH}^-]$
initial	$3.5 \times 10^{-2} \text{ M}$	0 M	0 M
change	$-y \text{ M}$	$y \text{ M}$	$y \text{ M}$
equilibrium	$(3.5 \times 10^{-2} - y) \text{ M}$	$y \text{ M}$	$y \text{ M}$

$$K_a = 10^{-8.55} = 2.8 \times 10^{-9} \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.8 \times 10^{-9}} = 3.6 \times 10^{-6}$$

$$3.6 \times 10^{-6} = \frac{[\text{HBrO}][\text{OH}^-]}{[\text{BrO}^-]} = \frac{y^2}{3.5 \times 10^{-2} - y} \approx \frac{y^2}{3.5 \times 10^{-2}}$$

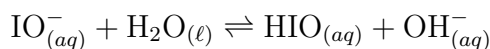
$$y = [\text{OH}^-] = 3.5 \times 10^{-4} \text{ M} \quad \text{pOH} = 3.45 \quad \text{pH} = 10.55$$

10. Hypoiodous acid (HIO) has a $\text{p}K_a = 10.50$. When 0.38 L of hypoiodous acid of unknown concentration are titrated with 0.20 M potassium hydroxide (a strong base), the equivalence point is reached after the addition of 0.019 L of the base. Calculate the concentration of the original hypoiodous acid solution, and the pH at the equivalence point. Approximations do not work for this problem.

Answer:

$$n_{\text{OH}^-} = (0.20 \text{ mol L}^{-1})(0.019 \text{ L}) = 0.0038 \text{ mol} = n_{\text{HIO}}$$

$$[\text{HIO}] = \frac{0.0038 \text{ mol}}{0.38 \text{ L}} = 0.010 \text{ M}$$



$$\text{p}K_b = 14.00 - \text{p}K_a = 3.50 \quad K_b = 10^{-3.50} = 3.2 \times 10^{-4}$$

$$[\text{IO}^-] = \frac{0.0038 \text{ mol}}{0.38 \text{ L} + 0.019 \text{ L}} = 9.5 \times 10^{-3} \text{ M}$$

	$[\text{IO}^-]$	$[\text{HIO}]$	$[\text{OH}^-]$
initial	$9.5 \times 10^{-3} \text{ M}$	0 M	0 M
change	$-y \text{ M}$	$y \text{ M}$	$y \text{ M}$
equilibrium	$(9.5 \times 10^{-3} - y) \text{ M}$	$y \text{ M}$	$y \text{ M}$

$$3.2 \times 10^{-4} = \frac{[\text{HIO}][\text{OH}^-]}{[\text{IO}^-]} = \frac{y^2}{9.5 \times 10^{-3} - y}$$

$$y^2 + 3.2 \times 10^{-4}y - 3.0 \times 10^{-6} = 0 \quad y = \frac{-3.2 \times 10^{-4} \pm [(3.2 \times 10^{-4})^2 + 4(3.0 \times 10^{-6})]^{1/2}}{2}$$

$$y = [\text{OH}^-] = 1.6 \times 10^{-3} \text{ M} \quad \text{pOH} = 2.80 \quad \text{pH} = 11.20$$