Chemistry 192
Problem Set 4
Spring, 2018
Solutions

1. The ionization constant of benzoic acid in water associated with the reaction

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

is $K_a = 6.3 \times 10^{-5}$. Calculate the value of K_b associated with the reaction

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

Answer:

$$K_aK_b = \frac{[H_3O^+][C_6H_5COO^-]}{[C_6H_5COOH]}\frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]} = K_w$$

$$6.3 \times 10^{-5} K_b = 1.0 \times 10^{-14}$$

$$K_b = 1.6 \times 10^{-10}$$

2. Use the data and/or results from problem 1 to calculate the pH of a 0.100 M solution of sodium benzoate, NaC_6H_5COO.
Answer:

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

	$[C_6H_5COO^-]$	$[C_6H_5COOH]$	$[OH^-]$
initial	0.100 M	0 M	0 M
change	-x	x	x
equilibrium	(0.100 -x) M	x M	x M

$$K_b = \frac{x^2}{0.100 - x} = 1.6 \times 10^{-10}$$

$$x^2 = 1.6 \times 10^{-11} \qquad x = [OH^-] = 4.0 \times 10^{-6}$$

$$pOH = -\log_{10}[OH^-] = 5.40 \qquad pH = 14.00 - pOH = 8.60$$

3. The ionization constant of hydroxylamine producing the hydroxylammonium ion via the reaction

$$\mathrm{HONH}_{2(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{HONH}^{+}_{3(aq)} + \mathrm{OH}^{-}_{(aq)}$$

is $K_b = 9.1 \times 10^{-9}$. Calculate the pH of a 0.0100 M solution of hydroxylammonium chloride.
Answer:

$$\mathrm{HONH}^{+}_{3(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{H_3O}^{+}_{(aq)} + \mathrm{HONH}_{2(aq)}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{9.1 \times 10^{-9}} = 1.1 \times 10^{-6}$$

	$[\mathrm{HONH}_3^+]$	$[\mathrm{HONH}_2]$	$[\mathrm{H_3O^+}]$
initial	0.0100 M	0 M	0 M
change	-x	x	x
equilibrium	(0.0100 -x) M	x M	x M

$$\frac{x^2}{0.0100 - x} \cong \frac{x^2}{0.0100} = 1.1 \times 10^{-6}$$

$$x = [\mathrm{H_3O^+}] = \sqrt{1.1 \times 10^{-8}} = 1.1 \times 10^{-4}$$

$$\mathrm{pH} = -\log_{10}[\mathrm{H_3O^+}] = 3.96$$

4. Using the ionization constant of acetic acid

$$\mathrm{CH_3COOH}_{(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{CH_3COO}^{-}_{(aq)} + \mathrm{H_3O}^{+}_{(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

calculate the mass of sodium acetate that must be added to 100. mL of water to produce a solution with pH=8.00.
Answer:

$$\mathrm{CH_3COO}^{-}_{(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{CH_3COOH}_{(aq)} + \mathrm{OH}^{-}_{(aq)}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$[\mathrm{OH^-}] = [\mathrm{CH_3COOH}] = 10.^{-14+8} = 1.0 \times 10^{-6}$$

$$\frac{(1.0 \times 10^{-6})^2}{[\mathrm{CH_3COO^-}]} = 5.6 \times 10^{-10}$$

$$[\mathrm{CH_3COO^-}] = 0.0018 \text{ M}$$

$$n_{sodium\ acetate} = (0.0018 \text{ mol L}^{-1})(0.100 \text{ L}) = 0.00018 \text{ mol}$$

$$m = (82. \text{ g mol}^{-1})(0.00018 \text{ mol}) = 0.015 \text{ g}$$

5. The ionization reaction of hypochlorous acid with water

$$\mathrm{HOCl}_{(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{OCl}^-_{(aq)} + \mathrm{H_3O}^+_{(aq)}$$

has a $\mathrm{p}K_a = 7.54$. Consider a 0.100 M NaOCl (sodium hypochlorite) solution.

(a) Do you expect the pH of the NaOCl solution to be less than or greater than 7.00? Explain your reasoning.
Answer: NaOCl is the salt of a weak acid and a strong base. The pH should be greater than 7.00.

(b) Calculate the pH of a 0.100 M NaOCl solution given sodium hypochlorite is completely ionized in water.

$$\mathrm{OCl}^-_{(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{HOCl}_{(aq)} + \mathrm{OH}^-_{(aq)}$$

$$K_b = \frac{[\mathrm{HOCl}][\mathrm{OH}^-]}{[\mathrm{OCl}^-]} = 10^{-(14.00-7.54)} = 3.5 \times 10^{-7}$$

	$[\mathrm{OCl}^-]$	$[\mathrm{HOCl}]$	$[\mathrm{OH}^-]$
initial	0.100 M	0 M	0 M
change	-x	x	x
equilibrium	(0.100 -x) M	x M	x M

$$\frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} = 3.5 \times 10^{-7}$$

$$x = [\mathrm{OH}^-] = \sqrt{3.5 \times 10^{-8}} = 1.9 \times 10^{-4}\ \mathrm{M}$$

$$\mathrm{pOH} = -\log_{10}(1.9 \times 10^{-4}) = 3.73 \qquad \mathrm{pH} = 14.00 - \mathrm{pOH} = 10.27$$

6. The ionization constant for hydrofluoric acid via the reaction

$$\mathrm{HF}_{(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{H_3O}^+_{(aq)} + \mathrm{F}^-_{(aq)}$$

is $K_a = 6.6 \times 10^{-4}$. Calculate the concentration of fluoride ion in a 0.100 M hydrofluoric acid solution and an aqueous mixture 0.100 M aqueous HF and 0.0100 M HCl. Recall that HCl is completely ionized in water.
Answer:

$$\frac{[\mathrm{H_3O^+}][\mathrm{F}^-]}{[\mathrm{HF}]} = 6.6 \times 10^{-4}$$

Without HCl

	$[\mathrm{HF}]$	$[\mathrm{F}^-]$	$[\mathrm{H_3O^+}]$
initial	0.100 M	0 M	0 M
change	-x	x	x
equilibrium	(0.100 -x) M	x M	x M

$$\frac{x^2}{0.100 - x} = 6.6 \times 10^{-4}$$

$$x^2 + 6.6 \times 10^{-4}x - 6.6 \times 10^{-5} = 0$$

$$x = \frac{-6.6 \times 10^{-4} \pm \sqrt{(6.6 \times 10^{-4})^2 + 4(6.6 \times 10^{-5})}}{2} = 7.8 \times 10^{-3}$$

where only the positive solution is physical.
With HCl

	[HF]	[F^-]	[H_3O^+]
initial	0.100 M	0 M	0.0100 M
change	-x	x	x
equilibrium	(0.100 -x) M	x M	(0.0100 + x) M

$$\frac{x(0.0100 + x)}{0.100 - x} = 6.6 \times 10^{-4}$$

$$x^2 + 0.01066x - 6.6 \times 10^{-5} = 0$$

$$x = \frac{-0.01066 \pm \sqrt{(0.01066)^2 + 4(6.6 \times 10^{-5})}}{2} = 4.4 \times 10^{-3}$$

7. Aqueous methylamine is a weak base with the reaction

$$CH_3NH_{2(aq)} + H_2O_{(\ell)} \rightleftharpoons OH^-_{(aq)} + CH_3NH^+_{3(aq)}$$

having ionization constant $K_b = 4.2 \times 10^{-4}$. A 0.0100 M solution of mehtylamine is mixed with sufficient sodium hydroxide to yield a solution having pH=9.30. Calculate the concentration of the methylammonium ions and methylamine in the solution.
Answer:

$$\frac{[OH^-][CH_3NH_3^+]}{[CH_3NH_2]} = 4.2 \times 10^{-4}$$

$$[OH^-] = 10.^{-(14.00-9.30)} = 2.0 \times 10^{-5}$$

	[CH_3NH_2]	[$CH_3NH_3^+$]	[OH^-]
initial	0.0100 M	0 M	0 M
change	-x	x	2.0 $\times 10^{-5}$ M
equilibrium	(0.0100 -x) M	x M	2.0 $\times 10^{-5}$ M

$$\frac{x(2.0\times 10^{-5})}{0.0100-x} = 4.2\times 10^{-4}$$

$$2.0\times 10^{-5}x = 4.2\times 10^{-6} - 4.2\times 10^{-4}x$$

$$x = [\mathrm{CH_3NH_3^+}] = 9.5\times 10^{-3}\ \mathrm{M}$$

$$[\mathrm{CH_3NH_2}] = 0.0100 - x = 5.0\times 10^{-4}\ \mathrm{M}$$

Note: The Hendersen-Hasselbalch equation would fail for this problem, because the full quadratic equation is required for the solution.

8. The value of K_a for the dissociation of benzoic acid

$$\mathrm{C_6H_5COOH}_{(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{H_3O}^+_{(aq)} + \mathrm{C_6H_5COO}^-_{(aq)}$$

is 6.3×10^{-5}. Calculate the pH of a solution that is 0.0100 M in benzoic acid and 0.0100 M in sodium benzoate.

Answer: We solve this problem two ways. First, we apply the Hendersen-Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{C_6H_5COO^-}]}{[\mathrm{C_6H_5COOH}]}$$

$$\frac{[\mathrm{C_6H_5COO^-}][\mathrm{H_3O^+}]}{[\mathrm{C_6H_5COOH}]} = K_a = 6.3\times 10^{-5}$$

$$\mathrm{p}K_a = -\log_{10}(6.3\times 10^{-5}) = 4.20$$

$$\mathrm{pH} = 4.20 + \log_{10}\frac{0.0100}{0.0100} = 4.20$$

Alternatively, we can solve the problem with an ICE table:

	$[\mathrm{C_6H_5COOH}]$	$[\mathrm{C_6H_5COO^-}]$	$[\mathrm{H_3O^+}]$
initial	0.0100 M	0.0100 M	0 M
change	-x	x	x
equilibrium	(0.0100 - x) M	$0.0100 + x$ M	x M

$$\frac{x(0.0100+x)}{0.0100-x} \approx x = 6.3\times 10^{-5}$$

$$\mathrm{pH} = -\log_{10} 6.3\times 10^{-5} = 4.20$$

9. For benzoic acid as in problem 8, calculate the pH of a solution that is 0.0100 M in benzoic acid and 0.0500 M in sodium benzoate.
Answer: Again, we can either use the Hendersen-Hasselbalch equation or an ICE table. Using the Hendersen-Hasselbalch equation first

$$\mathrm{pH} = 4.20 + \log_{10} \frac{0.0500}{0.0100} = 4.87$$

Using an ICE table

	$[C_6H_5COOH]$	$[C_6H_5COO^-]$	$[H_3O^+]$
initial	0.0100 M	0.0500 M	0 M
change	$-x$	x	x
equilibrium	0.0100 - x M	$0.0500 + x$ M	x M

$$\frac{x(0.0500+x)}{0.0100-x} = 6.3 \times 10^{-5}$$

$$x = [H_3O^+] \cong \left(\frac{.01}{.05}\right) 6.3 \times 10^{-5} = 1.3 \times 10^{-5}$$

$$\mathrm{pH} = -\log_{10} 1.3 \times 10^{-5} = 4.87$$

10. Sodium azide (NaN_3) is a highly toxic and highly water soluble salt made from sodium hydroxide (NaOH, a strong base) and hydrazoic acid (HN_3, a weak acid). Sodium azide solutions are completely ionized in water. It is found that a 0.100 M aqueous solution of sodium azide has a pH=8.80. Calculate the pK_a of the reaction

$$HN_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons N^-_{3(aq)} + H_3O^+_{(aq)}.$$

Answer:

$$N^-_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons HN_{3(aq)} + OH^-_{(aq)}$$

$$\mathrm{pOH} = 14.00 - 8.80 = 5.20 \qquad [OH^-] = 10^{-5.20} = 6.3 \times 10^{-6}$$

	$[N_3^-]$	$[HN_3]$	$[OH^-]$
initial	0.100 M	0 M	0 M
change	-6.3×10^{-6}	6.3×10^{-6}	6.3×10^{-6}
equilibrium	0.100 M	6.3×10^{-6} M	6.3×10^{-6} M

$$K_b = \frac{[HN_3][OH^-]}{[N_3^-]} = \frac{(6.3 \times 10^{-6})^2}{0.100} = 4.0 \times 10^{-10}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5} \qquad \mathrm{p}K_a = -\log_{10}(2.5 \times 10^{-5}) = 4.60$$

11. For aqueous ammonia using the reaction

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \qquad K_b = 1.8 \times 10^{-5}$$

calculate the pH of a solution that is 0.0100 M in ammonia and 0.0500 M in ammonium chloride.
Answer: Once again, we have the choice of solving this problem using the Hendersen-Hasselbalch equation or an ICE table. For the Hendersen-Hasselbalch equation,

$$NH^+_{4(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \qquad pK_a = -\log_{10}(5.6 \times 10^{-10}) = 9.26$$

$$\begin{aligned} pH &= pK_a + \log_{10}\frac{[NH_3]}{[NH_4^+]} \\ &= 9.26 + \log_{10}\frac{0.0100}{0.0500} = 8.56 \end{aligned}$$

Using an ICE table

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

	$[NH_3]$	$[NH_4^+]]$	$[OH^-]$
initial	0.0100 M	0.0500 M	0 M
change	-x	x	x
equilibrium	(0.0100 - x) M	$0.0500 + x$ M	x M

$$\frac{x(0.0500 + x)}{.0100 - x} = 1.8 \times 10^{-5}$$

$$[OH^-] \cong \left(\frac{.0100}{.0500}\right) 1.8 \times 10^{-5} = 3.6 \times 10^{-6}$$

$$pOH = -\log_{10} 3.6 \times 10^{-6} = 5.44 \qquad pH = 14.00 - pOH = 8.56$$

12. Calculate the pH when 100. mL of the solution discussed in problem 8 is combined with 20.0 mL of 0.0100 M hydrochloric acid.
Answer:
From problem 8 before the addition of the hydrochloric acid, the concentrations of all species are

$$[H_3O^+] = 6.3 \times 10^{-5} \qquad [C_6H_5COO^-] \cong [C_6H_5COOH] \approx 0.0100 \text{ M}$$

The initial number of moles of benzoic acid and the benzoate ion are

$$n_{C_6H_5COOH} = n_{C_6H_5COO^-} = (0.0100 \text{ mol L}^{-1})(0.100 \text{ L}) = 0.00100 \text{ mol}$$

The number of added moles of hydronium ion is given by

$$n_{H_3O^+} = (0.0100 \text{ mol L}^{-1})(0.0200 \text{ L}) = 2.00 \times 10^{-4} \text{ mol}$$

From the reaction given in Problem 8 and LeChâtelier's principle, the addition of acid shifts the equilibrium to the left. Then

	C_6H_5COOH	$C_6H_5COO^-$	H_3O^+
initial	0.00100 mol	0.00100 mol	0 mol
change	2.00×10^{-4} mol	-2.00×10^{-4} mol	x
equilibrium	0.00120 mol	0.00080 mol	x mol

Letting $y = [H_3O^+]$

$$\frac{y\left(\dfrac{0.00080 \text{ mol}}{0.120 \text{ L}}\right)}{\left(\dfrac{0.00120 \text{ mol}}{0.120 \text{ L}}\right)} = 6.3 \times 10^{-5}$$

$$y = [H_3O^+] = 9.5 \times 10^{-5} \text{ M} \qquad \text{pH} = 4.02$$

13. Calculate the pH when 100. mL of the solution discussed in problem 11 is combined with 20.0 mL of 0.0100 M hydrochloric acid.

Answer:

Initially

$$n_{NH_4^+} = (0.0500 \text{ mol L}^{-1})(0.100 \text{ L}) = 0.00500 \text{ mol}$$

$$n_{NH_3} = (0.0100 \text{ mol L}^{-1})(0.100 \text{ L}) = 0.00100 \text{ mol}$$

The amount of added hydronium ion is

$$n_{H_3O^+} = (0.0200 \text{ L})(0.0100 \text{ mol L}^{-1}) = 2.00 \times 10^{-4} \text{ mol}$$

From the reaction given in Problem 11 and LeChâtelier's principle, the addition of acid shifts the equilibrium to the right. Then

	NH_3	NH_4^+	OH^-
initial	0.00100 mol	0.00500 mol	0 mol
change	-2.00 × 10^{-4} mol	2.00×10^{-4} mol	x mol
equilibrium	8.0×10^{-4} mol	5.20×10^{-3} mol	x mol

Let $y = [\mathrm{OH}^-]$. Then

$$\frac{y\left(\dfrac{5.20 \times 10^{-3}\ \mathrm{mol}}{0.120\ \mathrm{L}}\right)}{\left(\dfrac{8.0 \times 10^{-4}\ \mathrm{mol}}{0.120\ \mathrm{L}}\right)} = 1.8 \times 10^{-5}$$

$$y = [\mathrm{OH}^-] = 2.8 \times 10^{-6}\ \mathrm{M}$$

$$\mathrm{pOH} = -\log_{10}(2.8 \times 10^{-6}) = 5.56 \qquad \mathrm{pH} = 14.00 - \mathrm{pOH} = 8.44$$

14. Calculate the pH when 100. mL of the solution discussed in problem 8 is combined with 20.0 mL of a 0.0100 M aqueous sodium hydroxide solution.
Answer:
Initially

$$n_{C_6H_5COOH} = n_{C_6H_5COO^-} = (0.0100\ \mathrm{mol\ L}^{-1})(0.100\ \mathrm{L}) = 1.00 \times 10^{-3}\ \mathrm{mol}$$

Hydroxide ion added

$$n_{OH^-} = (0.0100\ \mathrm{mol\ L}^{-1})(0.0200\ \mathrm{L}) = 2.00 \times 10^{-4}\ \mathrm{mol}$$

	C_6H_5COOH	$C_6H_5COO^-$	H_3O^+
initial	1.00×10^{-3} mol	1.00×10^{-3} mol	0 mol
change	-2.00×10^{-4} mol	2.00×10^{-4} mol	x
equilibrium	8.0×10^{-4} mol	1.20×10^{-3} mol	x mol

Let $y = [\mathrm{H_3O}^+]$. Then

$$\frac{y\left(\dfrac{1.2 \times 10^{-3}\ \mathrm{mol}}{0.120\ \mathrm{L}}\right)}{\left(\dfrac{8.0 \times 10^{-4}\ \mathrm{mol}}{0.120\ \mathrm{L}}\right)} = 6.3 \times 10^{-5}$$

$$y = [\mathrm{H_3O}^+] = 4.2 \times 10^{-5}\ \mathrm{M} \qquad \mathrm{pH} = 4.37$$

15. From the dissociation constant of benzoic acid given in problem 8, calculate the number of grams of sodium benzoate that must be added to 100. mL of 0.0100 M benzoic acid to produce a solution buffered to pH = 4.00.
Answer:

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{C_6H_5COO^-}]}{[\mathrm{C_6H_5COOH}]}$$

$$4.00 = -\log_{10}(6.3 \times 10^{-5}) + \log_{10}\frac{[\mathrm{C_6H_5COO^-}]}{0.0100}$$

$$[C_6H_5COO^-] = 6.3 \times 10^{-3} \text{ M}$$

Assuming negligible volume change by the addition of the sodium benzoate

$$\text{number of moles} = (6.3 \times 10^{-3} \text{ mol L}^{-1})(0.100 \text{ L}) = 6.3 \times 10^{-3} \text{ mol}$$

$$\text{mass} = (144 \text{ g mol}^{-1})(6.3 \times 10^{-3} \text{ mol}) = 0.91 \text{ g}$$

16. The weak base diethylamine reacts with water according to the reaction

$$(C_2H_5)_2NH_{(aq)} + H_2O_{(\ell)} \rightleftharpoons (C_2H_5)_2NH^+_{2(aq)} + OH^-_{(aq)},$$

and the equilibrium constant for the reaction is $K_b = 6.9 \times 10^{-4}$. A buffer solution is formed by mixing diethylamine and diethylammonium chloride having concentrations $[(C_2H_5)_2NH]$=0.124 M and $[(C_2H_5)_2NH_2^+]$=0.224 M. Calculate the pH of the final solution when 0.400 L of the buffer are mixed with 0.1500 L of 0.0150 M NaOH (a strong base).

Answer:

$$n_{(C_2H_5)_2NH} = (0.124 \text{ mol L}^{-1})(0.400 \text{ L}) = 0.0496 \text{ mol}$$

$$n_{(C_2H_5)_2NH_2^+} = (0.224 \text{ mol L}^{-1})(0.400 \text{ L}) = 0.0896 \text{ mol}$$

$$n_{OH^-} = (0.0150 \text{ mol L}^{-1})(0.1500 \text{ L}) = 0.00225 \text{ mol}$$

Method 1: Hendersen-Hasselbalch:

$$(C_2H_5)_2NH^+_{2(aq)} + H_2O_{(\ell)} \rightleftharpoons (C_2H_5)_2NH_{(aq)} + H_3O^+_{(aq)}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.9 \times 10^{-4}} = 1.4 \times 10^{-11} \qquad \text{p}K_a = -\log_{10}(1.4 \times 10^{-11}) = 10.84$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[(C_2H_5)_2NH]}{[(C_2H_5)_2NH_2^+]}$$

$$= 10.84 + \log_{10} \frac{[(0.0496 + 0.0023)]/0.550}{[(0.0896 - 0.0023)]/0.550} = 10.61$$

Method 2: ICE Table:

	$n_{(C_2H_5)_2NH}$	$n_{(C_2H_5)_2NH^+}$	n_{OH^-}
initial	0.0496 mol	0.0896 mol	0 mol
change	0.0023 mol M	-0.0023 mol	y mol
equilibrium	0.0519 mol	0.0873 mol	y mol

$$6.9 \times 10^{-4} = \frac{[\mathrm{OH}^-](0.0873/0.550)}{(0.0519/0.550)}$$

$$[\mathrm{OH}^-] = 4.1 \times 10^{-4}\ \mathrm{M}$$

$$\mathrm{pOH} = -\log_{10}(4.1 \times 10^{-4}) = 3.39 \qquad \mathrm{pH} = 14.00 - 3.39 = 10.61$$

17. Pyridine (C_5H_5N) reacts with water as a weak base according to the reaction

$$\mathrm{C_5H_5N}_{(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{C_5H_5NH}^+_{(aq)} + \mathrm{HO}^-_{(aq)}$$

with associate base ionization constant $K_b = 1.5 \times 10^{-9}$. A buffer is made by combining aqueous pyridine and pyridinium chloride (C_5H_5NHCl) of concentrations [C_5H_5N]=0.200 M and [$C_5H_5NH^+$]=0.300 M. A 0.100 L sample of the buffer is then mixed with 0.0100 L of 0.235 M aqueous hydrochloric acid (HCl, a strong acid). Calculate the pH of the mixture of the buffer and hydrochloric acid.

Answer:

Methd 1, Hendersen-Hasselbalch

$$\mathrm{C_5H_5NH}^+_{(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{C_5H_5N}_{(aq)} + \mathrm{H_3O}^+_{(aq)}$$

$$K_a = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6} \qquad \mathrm{p}K_a = -\log_{10}(6.7 \times 10^{-6}) = 5.18$$

Before mixing

$$n_{C_5H_5N} = (0.200\ \mathrm{mol\ L^{-1}})(0.100\ \mathrm{L}) = 2.00 \times 10^{-2}\ \mathrm{mol}$$

$$n_{C_5H_5NH^+} = (0.300\ \mathrm{mol\ L^{-1}})(0.100\ \mathrm{L}) = 3.00 \times 10^{-2}\ \mathrm{mol}$$

$$n_{H_3O^+} = (0.235\ \mathrm{mol\ L^{-1}})(0.0100\ \mathrm{L}) = 2.35 \times 10^{-3}\ \mathrm{mol}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{C_5H_5N}]}{[\mathrm{C_5H_5NH^+}]}$$

$$= 5.18 + \log_{10}\left(\frac{\dfrac{2.00 \times 10^{-2} - 2.35 \times 10^{-3}}{0.110}}{\dfrac{3.00 \times 10^{-2} + 2.35 \times 10^{-3}}{0.110}}\right) = 4.92$$

Method 2, ICE Table

Before mixing

$$n_{C_5H_5N} = (0.200\ \mathrm{mol\ L^{-1}})(0.100\ \mathrm{L}) = 2.00 \times 10^{-2}\ \mathrm{mol}$$

$$n_{C_5H_5NH^+} = (0.300\ \mathrm{mol\ L^{-1}})(0.100\ \mathrm{L}) = 3.00 \times 10^{-2}\ \mathrm{mol}$$

$$n_{H_3O^+} = (0.235\ \mathrm{mol\ L^{-1}})(0.0100\ \mathrm{L}) = 2.35 \times 10^{-3}\ \mathrm{mol}$$

	$n_{C_5H_5N}$	$n_{C_5H_5NH^+}$	n_{OH^-}
initial	2.00×10^{-2}	3.00×10^{-2}	0
change	-2.35×10^{-3}	$+2.35 \times 10^{-3}$	y
equilibrium	1.77×10^{-2}	3.24×10^{-2}	y

$$K_b = \frac{[\mathrm{C_5H_5NH^+}][\mathrm{OH^-}]}{[\mathrm{C_5H_5N}]}$$

$$1.5 \times 10^{-9} = \frac{[\mathrm{OH^-}]\left(\dfrac{3.24 \times 10^{-2}}{0.110}\right)}{\left(\dfrac{1.77 \times 10^{-2}}{0.110}\right)}$$

$[\mathrm{OH^-}] = 8.2{\times}10^{-10}$ M $\quad$ pOH $= -\log_{10}(8.2{\times}10^{-10}) = 9.08$ $\quad$ pH $= 14.00 - 9.08 = 4.92$

18. The base dissociation constant of phenylamine ($C_6H_5NH_2$) is $K_b = 5.0 \times 10^{-10}$. A buffer is prepared that is 0.100 M in phenylamine and 0.200 M in phenylammonium cation ($C_6H_5NH_3^+$). A 0.100 L sample of the buffer is then mixed with 0.100 L of 0.0100 M sodium hydroxide (a stong base). Calculate a) the pH of the initial buffer solution, and 2) the pH of the buffer/sodium hydroxide mixture.
Answer:
Method 1 - ICE Table

$$\mathrm{C_6H_5NH_{2(\mathit{aq})}} + \mathrm{H_2O_{(\ell)}} \rightleftharpoons \mathrm{C_6H_5NH^+_{3(\mathit{aq})}} + \mathrm{OH^-_{(\mathit{aq})}}$$

Buffer

	$[\mathrm{C_6H_5NH_2}]$	$[\mathrm{C_6H_5NH_3^+}]$	$[\mathrm{OH^-}]$
initial	0.100 M	0.200 M	0 M
change	-y	y	y
equilibrium	(0.100 -y) M	(0.200 + y) M	y M

$$5.0 \times 10^{-10} = \frac{[\mathrm{C_6H_5NH_3^+}][\mathrm{OH^-}]}{[\mathrm{C_6H_5NH_2}]} = \frac{y(0.200 + y)}{0.100 - y} \approx 2y$$

$y = [\mathrm{OH^-}] = 2.5{\times}10^{-10}$ M $\quad$ pOH $= -\log_{10}(2.5{\times}10^{-10}) = 9.60$ $\quad$ pH $= 14.00 - $pOH $= 4.40$

Mixture

$$n_{C_6H_5NH_2} = (0.100 \text{ mol L}^{-1})(0.100 \text{ L}) = 1.00 \times 10^{-2} \text{ mol}$$

$$n_{C_6H_5NH_3^+} = (0.200 \text{ mol L}^{-1})(0.100 \text{ L}) = 2.00 \times 10^{-2} \text{ mol}$$

$$n_{OH^-} = (0.0.0100 \text{ mol L}^{-1})(0.100 \text{ L}) = 1.00 \times 10^{-3} \text{ mol}$$

	$n_{C_6H_5NH_2}$	$n_{C_6H_5NH_3^+}$	n_{OH}^{-}
initial	1.00×10^{-2}	2.00×10^{-2}	0
change	1.00×10^{-3}	-1.00×10^{-3}	y
equilibrium	1.1×10^{-2}	1.9×10^{-2}	y

$$5.0 \times 10^{-10} = \frac{[\mathrm{OH^-}]\left(\dfrac{1.9 \times 10^{-2}}{0.200}\right)}{\left(\dfrac{1.1 \times 10^{-2}}{0.200}\right)}$$

$[\mathrm{OH^-}] = 2.9 \times 10^{-10}$ M $\quad$ $\mathrm{pOH} = -\log_{10}(2.9 \times 10^{-10}) = 9.54$ $\quad$ $\mathrm{pH} = 14.00 - \mathrm{pOH} = 4.46$

Method 2 - Henderson-Hasselbalch

$$\mathrm{C_6H_5NH^+_{3(\mathit{aq})}} + \mathrm{H_2O_{(\ell)}} \rightleftharpoons \mathrm{C_6H_5NH_{2(\mathit{aq})}} + \mathrm{H_3O^+_{(\mathit{aq})}}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-10}} = 2.0 \times 10^{-5} \qquad \mathrm{p}K_a = -\log_{10}(2.0 \times 10^{-5}) = 4.70$$

Buffer

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{C_6H_5NH_2}]}{[\mathrm{C_6H_5NH_3^+}]}$$

$$= 4.70 + \log_{10}\frac{0.100}{0.200} = 4.40$$

Mixture

$$\mathrm{pH} = 4.70 + \log_{10}\frac{\dfrac{1.00 \times 10^{-2} + 1.00 \times 10^{-3}}{0.200}}{\dfrac{2.00 \times 10^{-2} - 1.00 \times 10^{-3}}{0.200}} = 4.46$$

19. A buffer of volume 0.400 L is 0.250 M in formic acid (HCOOH) and 0.350 M in the formate ($\mathrm{HCOO^-}$) anion. The buffer is then combined with 0.100 L of 0.0250 M sodium hydroxide. Given the pK_a of formic acid is 3.74, calculate the pH of the mixture of the buffer with the NaOH solution. Approximations work for this problem.
Answer:

$$\mathrm{HCOOH_{(\mathit{aq})}} + \mathrm{H_2O_{(\ell)}} \rightleftharpoons \mathrm{HCOO^-_{(\mathit{aq})}} + \mathrm{H_3O^+_{(\mathit{aq})}}$$

$$n_{HCOOH} = (0.250 \text{ mol L}^{-1})(0.400 \text{ L}) = 0.100 \text{ mol}$$

$$n_{HCOO^-} = (0.350 \text{ mol L}^{-1})(0.400 \text{ L}) = 0.140 \text{ mol}$$

$$n_{OH^-} \text{ added } = (0.0250 \text{ mol L}^{-1})(0.100 \text{ L}) = 2.50 \times 10^{-3} \text{ mol}$$

Method 1, Henderson-Hasselbalch

$$\mathrm{pH} = \mathrm{p}K_a + \frac{[\mathrm{HCOO^-}]}{[\mathrm{HCOOH}]}$$

$$= 3.74 + \frac{\frac{0.140 + 2.50 \times 10^{-3}}{0.500}}{\frac{0.100 - 2.50 \times 10^{-3}}{0.500}} = 3.90$$

Method 2, ICE table

$$K_a = 10^{-3.74} = 1.8 \times 10^{-4}$$

	n_{HCOOH}	n_{HCOO^-}	$n_{H_3O^+}$
initial	0.100 mol	0.140 mol	0 mol
change	-2.50×10^{-3} mol	2.50×10^{-3} mol	y mol
equilibrium	0.098 mol	0.143 mol	y mol

$$1.8 \times 10^{-4} = \frac{\frac{0.143}{0.500}[\mathrm{H_3O^+}]}{\frac{0.098}{0.500}}$$

$$[\mathrm{H_3O^+}] = 1.2 \times 10^{-4}\ \mathrm{M} \qquad \mathrm{pH} = -\log_{10}(1.2 \times 10^{-4}) = 3.90$$

20. Ethanolamine, $HO(CH_2)_2NH_2$ is a weak base in aqueous solutions, and its conjugate acid, $HO(CH_2)_2NH_3^+$ is called the ethanolammonium ion. The pK_b of ethanolamine is 4.50. A buffer is formed by mixing 0.10 moles of $HO(CH_2)_2NH_2$ with 0.20 moles of $HO(CH_2)_2NH_3^+$ to make an aqueous solution having a final total volume of 0.500 L. Calculate a) the pH of the buffer, and b) the pH if the buffer is mixed with 0.100 L of 0.050 M hydrochloric acid (a strong acid). Approximations work for this problem.
Answer:
Method I, Henderson-Hasselbalch

$$\mathrm{HO(CH_2)_2NH^+_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons HO(CH_2)_2NH_{2(aq)} + H_3O^+_{(aq)}}$$

$$\mathrm{p}K_a = 14.00 - \mathrm{p}K_b = 9.50$$

Original Buffer

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{HO(CH_2)_2NH_2}]}{[\mathrm{HO(CH_2)_2NH_3^+}]}$$

$$= 9.50 + \log_{10}\frac{0.10}{0.20} = 9.20$$

After mixing

$$n_{H_3O^+} = (0.050\ \mathrm{mol\ L^{-1}})(0.100\ \mathrm{L}) = 0.0050\ \mathrm{mol}$$

$$\mathrm{pH} = 9.50 + \log_{10}\frac{0.10 - 0.005}{0.20 + 0.005} = 9.17$$

Method II, ICE Table

$$\mathrm{HO(CH_2)_2NH}_{2(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{HO(CH_2)_2NH}^{+}_{3(aq)} + \mathrm{OH}^{-}_{(aq)}$$

$$K_b = 10^{-4.50} = 3.2 \times 10^{-5}$$

Before Mixing

	$[\mathrm{HO(CH_2)_2NH_2}]$	$[\mathrm{HO(CH_2)_2NH_3^+}]$	$[\mathrm{OH^-}]$
initial	0.10/0.50 M	0.20/0.50 M	0 M
change	-y	y	y
equilibrium	0.20-y M	$0.40 + y$ M	y M

$$\frac{y(0.40+y)}{0.20-y} \approx \frac{0.40y}{0.20} = 3.2 \times 10^{-5}$$

$$y = [\mathrm{OH^-}] = 1.6 \times 10^{-5}$$

$$\mathrm{pOH} = -\log_{10}(1.6 \times 10^{-5}) = 4.80 \qquad \mathrm{pH} = 14.00 - \mathrm{pOH} = 9.20$$

After Mixing

	$n_{HO(CH_2)_2NH_2}$	$n_{HO(CH_2)_2NH_3^+}$	n_{OH^-}
initial	0.10	0.20	0
change	-0.0050	0.0050	y
equilibrium	0.095	0.205	y

$$\frac{[\mathrm{OH^-}]0.205}{0.095} = 3.2 \times 10^{-5}$$

$$[\mathrm{OH^-}] = 1.5 \times 10^{-6} \qquad \mathrm{pOH} = 4.83 \qquad \mathrm{pH} = 9.17$$

21. Ethyl amine ($C_2H_5NH_2$) is a weak base with p$K_b = 3.37$. A buffer is made by combining 0.025 moles of ethyl amine and 0.050 moles of an ethyl ammonium salt ($C_2H_5NH_3^+$) with water so that the total volume is 0.25 L. The buffer is then combined with 0.020 L of 0.100 M hydrochloric acid (HCl). Calculate 1) the initial pH of the buffer, and 2) the pH of the buffer after the addition of the hydrochloric acid. Approximations work for this problem.
Answer:
Method 1, Henderson-Hasselbalch

$$\mathrm{C_2H_5NH}^{+}_{3(aq)} + \mathrm{H_2O}_{(\ell)} \rightleftharpoons \mathrm{C_2H_5NH}_{2(aq)} + \mathrm{H_3O}^{+}_{(aq)}$$

---

[0] Name:

$$\mathrm{p}K_a = 14.00 - \mathrm{p}K_b = 10.63$$

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{C_2H_5NH_2}]}{[\mathrm{C_2H_5NH_3^+}]}$$

Before the addition of HCl

$$\mathrm{pH} = 10.63 + \log_{10}\frac{0.025/0.25}{0.050/0.25} = 10.33$$

After the addition of HCl

$$n_{H_3O^+} = (0.100 \text{ mol L}^{-1})(0.020 \text{ L}) = 0.0020 \text{ mol}$$

$$\mathrm{pH} = 10.63 + \log_{10}\frac{(0.025 - 0.0020)/0.27}{(0.050 + 0.0020)/0.27} = 10.28$$

Method 2, ICE table

$$\mathrm{C_2H_5NH_{2(\mathit{aq})}} + \mathrm{H_2O_{(\ell)}} \rightleftharpoons \mathrm{C_2H_5NH^+_{3(\mathit{aq})}} + \mathrm{OH^-}(aq)$$

$$K_b = 10^{-3.37} = 4.3 \times 10^{-4}$$

Before mixing

	$[\mathrm{C_2H_5NH_2}]$	$[\mathrm{C_2H_5NH_3^+}]$	$[\mathrm{OH^-}]$
initial	0.025/0.25 M	0.050/0.25 M	0 M
change	-y	y	y
equilibrium	0.10-y M	$0.20 + y$ M	y M

$$4.3 \times 10^{-4} = \frac{y(0.20 + y)}{0.10 - y} \approx \frac{y(0.20)}{0.10} \qquad y = [\mathrm{OH^-}] = 2.2 \times 10^{-4}$$

$$\mathrm{pOH} = -\log_{10}(2.2 \times 10^{-4}) = 3.68 \qquad \mathrm{pH} = 14.00 - \mathrm{pOH} = 10.33$$

After mixing

$$n_{H_3O^+} = (0.100 \text{ mol L}^{-1})(0.020 \text{ L}) = 0.0020 \text{ mol}$$

	$n_{C_2H_5NH_2}$	$n_{C_2H_5NH_3^+}$	n_{OH^-}
initial	0.025	0.050	0 M
change	-0.0020	0.0020	y
equilibrium	0.023	0.052	y

$$4.3 \times 10^{-4} = \frac{[\mathrm{OH^-}](0.052)}{0.023} \qquad [\mathrm{OH^-}] = 1.9 \times 10^{-4} \text{ M}$$

$$\mathrm{pOH} = -\log_{10}(1.9 \times 10^{-4}) = 3.72 \qquad \mathrm{pH} = 14.00 - \mathrm{pOH} = 10.28$$