# Answer Key to Acid/Base Problem Set

**1.** This is a strong base problem.

 Ba(OH)2 (aq) → Ba2+(aq) + 2 OH‾(aq)

 

 pOH = - log[OH‾] = - log(0.040) = 1.40

 pH = 14 – pOH = 14 – 1.40 = 12.60

**2.** This is an acidic buffer problem because a weak acid and a salt of the weak acid are present in appreciable quantities. From Table 16.3, the Ka of HCN = 4.9 x 10-10.

 HCN(aq) + H2O (l) ⮀ CN‾(aq) + H3O+(aq)

 init 0.30 0.40 0

 change -x x x

 equil 0.30 – x 0.40 + x x

 

Simplifies to:

 

 

 [HCN] = 0.30 – (3.7 x 10-10 ) = 0.30 M

 [CN‾] = 0.40 + x = 0.40 + (3.7 x 10-10 ) = 0.40 M

 [Na+] = 0.40 M

 

 [H2O] = 55.5 M

**3.** This is a strong acid problem.

 HNO3(aq) + H2O(l) ⮀ NO3‾(aq) + H3O+(aq)

 [HNO3] = 0 M

 [NO3‾] = [H3O+] = 0.45 M

 [H2O] = 55.5 M

 

**4.** This is a weak acid problem. The Ka of HNO2 is 4.5 x 10-4.

 HNO2(aq) + H2O(l) ⮀ NO2‾(aq) + H3O+(aq)

init 0.45 0 0

change -x +x +x

equil. 0.45 – x x x

 

Simplifies to:

 

 x2 = 4.5 x 10-4(0.45) = 2.0 x 10-4

 

 [HNO2] = 0.45 – x = 0.45 – 1.4 x 10-2  = 0.44 M

 

 [H2O] = 55.5 M

**5.** This is a hydrolysis problem. The salt is the salt of a strong acid and strong base, so neither Na+ (weak conjugate acid) nor NO3‾ (weak conjugate base) will hydrolyze. Both these ions are spectator ions. Thus, the only [H3O+] or [OH‾] is from the dissociation of water.

 [Na+] = [NO3‾] = 0.45 M

 [H3O+] = [OH‾] = 1.0 x 10-7 M

 [H2O] = 55.5 M

**6.** This is also a hydrolysis problem. The K+ is a spectator because it is the weak conjugate acid of a strong base. Nitrite ion will hydrolyze:

 NO2‾(aq) + H2O(l) ⮀ HNO2(aq) + OH‾(aq)

init 0.45 0 0

change -x x x

equil 0.45 – x x x

Need to find Kb: 

 

Simplifies to:

 

 x2 = 2.2 x 10-11(0.45) = 1.0 x 10-11

 

 [NO2ˉ] = 0.45 – x = 0.45 – (3.2 x 10-6) = 0.45 M

 [K+] = 0.45 M

 [H2O] = 55.5 M

**7.** This is a weak base problem. The Kb for CH3NH2 is found on Table 16.5 and has a value of 4.4 x 10-4.

 CH3NH2 (aq) + H2O(l) ⮀ CH3NH3+ (aq) + OHˉ(aq)

init. 0.35 0 0

change -x x x

equil. 0.35 – x x x

 

Simplifies to:

 

 x2 = 4.4 x 10-4(0.35) = 1.5 x 10-4

 

 [CH3NH2] = 0.35 – x = 0.35 – 0.012 = 0.34 M

 

 [H2O] = 55.5 M

**8.**  This is an alkaline buffer problem.

 CH3NH2 (aq) + H2O(l) ⮀ CH3NH3+ (aq) + OHˉ(aq)

init. 0.45 0.30 0

change -x x x

equil. 0.45 – x 0.30 + x x

 

Simplifies to:

 

 

 [CH3NH3+] = 0.30 + x = 0.30 - 6.6 x 10-4 = 0.30 M

 [CH3NH2] = 0.45 – x = 0.45 - 6.6 x 10-4 = 0.45 M

 

**9 a.** HBr is a strong acid, thus it dissociates completely:

 HBr(aq) + H2O(l) → Br¯(aq) + H3O+(aq)

$$ [H\_{3}O^{+}] = \frac{ 0.010 mol HBr}{1 L soln} x \frac{1 mol H\_{3}O^{+}}{1 mol HBr} = 0.010 M $$

 Using the Kw of water, find the [OH¯]:

 Kw = [H3O+][OH¯] = 1.0 x 10-14

$$[OH^{-}] = \frac{K\_{w}}{[H\_{3}O^{+}]} = \frac{1.0 x 10^{-14}}{0.010 } = 1.0 x 10^{-12} M$$

 pH = - log[H3O+] = - log(0.010) = 2.00

 pOH = - log[OH¯] = - log(1.0 x 10-12) = 12.00

 or

 pH + pOH = 14, so

 pOH = 14 – pH = 14 – 2.00 = 12.00

**9 b.** Ca(OH)2 is a strong base, thus it dissociates completely:

 Ca(OH)2(aq) → Ca2+(aq) + 2 OH¯(aq)

$$[OH^{-}] = \frac{0.30 mol Ca(OH)\_{2}}{1 L soln} x \frac{2 mol OH^{-}}{1 mol Ca(OH)\_{2}} = 0.60 M OH^{-} $$

$$[H\_{3}O^{+}] = \frac{K\_{w}}{[OH^{-}]} = \frac{1.0 x 10^{-14}}{0.60} = 1.7 x 10^{-14} M$$

 pH = - log[H3O+] = - log(1.7 x 10-14) = 13.78

 pOH = - log[OH¯] = - log(0.60) = 0.22

 or

 pH + pOH = 14, so

 pOH = 14 – pH = 14 – 13.78 = 0.22

**9 c.** Benzoic acid, C6H5COOH, is a weak acid with a Ka = 6.2 x 10-5. Write the equilibrium reaction and determine the expressions for the equilibrium amounts, starting with an initial amount of 0.20 M C6H5COOH. We are assuming that initially, there isn’t any acetate or hydronium ion present. An x amount of benzoic acid has to be lost to form an x amount of both benzoate ion and hydronium ion. Thus, at equilibrium, an amount of 0.20 – x of benzoic acid is present, and x amount of both benzoate ion and hydronium ion are present. This can be conveniently summarized in the table shown below:

 C6H5COOH(aq) + H2O (l) ⮀ C6H5COO¯(aq) + H3O+(aq)

 initial 0.20 M 0 0

 change -x +x +x

 equil. 0.20 – x x x

The equilibrium constant expression for the above equilibrium is:

$$K\_{a} = \frac{[C\_{6}H\_{5}COO^{-}][H\_{3}O^{+}]}{[C\_{6}H\_{5}COOH]} = 6.2 x 10^{-5}$$

Substituting the equilibrium amounts into the above expression gives:

$$\frac{(x)(x)}{0.20 - x} = 6.2 x 10^{-5}$$

The above expression may be simplified by making an assumption that the “x” in denominator expression, 0.20 – x is negligibly small. If the magnitude of the constant is more than 100 times smaller than the magnitude of the known initial concentration, this assumption is valid. In this problem, the magnitude of the constant (10-5) is 1000 times smaller than the certainty of the known concentration, 0.20 M (10-2 or second decimal place), so the x in 0.20 – x can be neglected. One caveat is that a 0.1% error in the result is acceptable when this assumption is made.

This simplifies the algebraic expression to:

$$\frac{x^{2}}{0.20} = 6.2 x 10^{-5}$$

Solve for x: x2 = 6.2 x 10-5(0.20) = 1.2 x 10-5

$$x = \sqrt{1.2 x 10^{-5}} = 3.5x 10^{-3} M = [C\_{6}H\_{5}COO^{-}] = [H\_{3}O^{+}]$$

Now that x is known, solve for [C6H5COOH] = 0.20 – x = 0.20 – 0.0035 = 0.20. Notice that our assumption that x was negligibly small relative to the benzoic acid concentration was valid.

Use the Kw of water to find the [OH¯]:

$$\frac{K\_{w}}{[H\_{3}O^{+}]} = [OH^{-}] = \frac{1.0 x 10^{-14}}{3.5 x 10^{-3}} = 2.8 x 10^{-12} M $$

To find the pH and pOH: pH = -log[H3O+] = -log(3.5 x 10-3) = 2.45

 pOH = 14 – pH = 14 – 2.72 = 11.55

**9 d.** Morphine is a weak organic base, as indicated by the Kb = 1.6 x 10-6. Write the equilibrium reaction and determine the expressions for the equilibrium amounts, starting with an initial amount of 0.050 M C17H19NO3. We are assuming that initially, there isn’t any conjugate acid of morphine (C17H19NO3H+) or any hydroxide (OH¯) present. To establish an equilibrium and x amount of morphine has be lost to from an x amount of the conjugate acid and x amount of hydroxide. The resulting equilibrium amounts are then deduced. Once again, this is most easily shown by the table below:

 C17H19NO3(aq) + H2O(l) ⮀ C17H19NO3H+(aq) + OH¯(aq)

 initial 0.050 0 0

 change - x +x +x

 equil. 0.050 – x x x

The equilibrium constant expression for the above equilibrium is:

$$K\_{b} = \frac{[C\_{17}H\_{19}NO\_{3}H^{+}][OH^{-}]}{[C\_{17}H\_{19}NO\_{3}]} = 1.6 x 10^{-6}$$

Substituting the equilibrium amounts into the above expression gives:

$$\frac{(x)(x)}{0.050 - x} = 1.6 x 10^{-6}$$

The above expression may be simplified by making an assumption that the “x” in denominator expression, 0.050 – x is negligibly small. If the magnitude of the constant is more than 100 times smaller than the magnitude of the known initial concentration, this assumption is valid. In this problem, the magnitude of the constant (10-6) is 1000 times smaller than the certainty of the known concentration, 0.050M (10-3 or third decimal place), so the x in 0.050 – x can be neglected. One caveat is that a 0.1% error in the result is acceptable when this assumption is made.

This simplifies the algebraic expression to:

$$\frac{x^{2}}{0.050} = 1.6 x 10^{-6}$$

Solve for x: x2 = 1.6 x 10-6(0.050) = 8.0 x 10-8

 $x = \sqrt{8.0 x 10^{-8}}$ = 2.8 x 10-4 = [C17H19NO3H+] = [OH¯]

Now that x is known, solve for [C17H19NO3] = 0.050 – x = 0.050 – (2.8 x 10-4) = 0.050 M

Notice that our assumption that x was negligibly small relative to the benzoic acid concentration was valid.

Use the Kw of water to find the [H3O+]:

$$[H\_{3}O^{+}] = \frac{K\_{w}}{[OH^{-}]} = \frac{1.0 x 10^{-14}}{2.8 x 10^{-4}} = 3.6 x 10^{-11}$$

To find the pH and pOH: pH = -log[H3O+] = -log(3.6 x 10-11) = 10.45

 pOH = 14 – pH = 14 – 10.45 = 3.55

**10.** In general, an acid and a base will form a salt and water. The **c**ation of the salt always comes from the **b**ase and the **a**nion of the salt always comes from the **a**cid (as a memory aid, keep the consonants and vowels together). Not all salts are neutral. The acid or base properties of a salt are determined by the relative strengths of the acid and base from which the salt originated. HCl, HBr, HI, HNO3, HClO4 and the first dissociation of H2SO4 are strong acids. All other acids are weak. Organic acids are always weak. An easy way to recognize and organic acid is to look for carbon in the formula. For example, acetic acid, CH3CO2**H**, is a weak organic acid. The acidic hydrogen is shown in bold font. This organic acid is often referred to, in general, as a carboxylic acid. The carboxylic acid group is often written in a formula as –CO2H or COOH. Group IA metal hydroxides, LiOH, NaOH, KOH, RbOH, CsOH, and in Group 2A, Ca(OH)2, Sr(OH)2 and Ba(OH)2 are typical strong bases. Ammonia, NH3, is a weak base and organic compounds called amines are weak bases. Amines are derivatives of ammonia. One or more of the hydrogens on ammonia have been replaced with a carbon group. For example, methyl amine is CH3NH2. Once again, the presence of carbon in the formula is a clear indication the base is weak. A strong acid produces a weak conjugate base; a strong base produces a weak conjugate acid. A weak acid produces a strong conjugate base; a weak base produces a strong conjugate acid. If a weak conjugate acid or weak conjugate base is produced, it means that that species is too weak to behave as an acid or base, respectively. On the other hand, if a strong conjugate acid or strong conjugate base is produced, then that species will behave as an acid or base, respectively. This process is called hydrolysis.

**10 a.** KBr is the salt of KOH and HBr. KOH is a strong base. Thus, K+ cation is a weak conjugate acid because it originated from a strong base (KOH). It will not behave as an acid, hence it does not hydrolyze and will solely be a spectator ion in solution. Similarly, Br¯ anion is a weak conjugate base because it originated from a strong acid (HBr). It will not behave as a base; hence it does not hydrolyze and will solely be a spectator ion in solution. Since neither the potassium ion nor the bromide ion is contributing to the hydronium ion or hydroxide ion concentration in solution, the only source for H3O+ or OH¯ in solution is from the dissociation of water. Thus, the concentration of hydronium ion will be 10-7, and the resulting pH of the solution will be 7. This is why KBr is a neutral salt.

**10 b.** RbNO2 is the salt of RbOH and HNO2. RbOH is a strong base. Thus, Rb+ cation is a weak conjugate acid and will not hydrolyze. It will behave as a spectator ion in solution and not affect the pH of the solution. Nitrite ion, NO2¯, is the strong conjugate base of the weak acid, HNO2. Thus it will behave as a base in solution by accepting a proton from water:

 NO2¯ (aq) + H2O(l) ⮀ HNO2(aq) + OH¯(aq)

Since hydroxide ion is generated in solution, the solution will be alkaline with a pH > 7.

10. c. NH4NO3 is the salt of NH3 and HNO3. The nitrate ion, NO3¯, is the weak conjugate base of the strong acid, HNO3, thus it will not hydrolyze. It will behave as a spectator ion in solution. On the other hand, NH3 is a weak base. Thus, NH4+ is the strong conjugate acid of a weak base, NH3. Thus, the NH4+ cation will undergo hydrolysis and behave as an acid:

 NH4+(aq) + H2O(l) ⮀ NH3(aq) + H3O+(aq)

Since hydronium ion is being generated, the solution is acidic with a pH < 7.

**10 d.** NH4C6H5CO2 is the salt of ammonia, NH3, a weak base, and benzoic acid, C6H5CO2H, a weak acid. Thus, the ammonium cation, NH4+, is a strong conjugate acid and will hydrolyze behaving as an acid and the benzoate ion, C6H5CO2¯ is a strong conjugate base and will hydrolyze behaving as a base:

 NH4+(aq) + H2O(l) ⮀ NH3(aq) + H3O+(aq)

 C6H5CO2¯(aq) + H2O(l) ⮀ C6H5CO2H(aq) + OH¯(aq)

There are competing equilibria present and the pH will be decided by whichever equilibrium lies further towards products. This will be determined by comparing the magnitude of each of the equilibrium constants. The constants may be calculated from the fact that the KaKb = Kw for any acid/conjugate base pair or base/conjugate acid pair.

Calculate the Ka for NH4+ using the Kw for water and Kb for ammonia:

$$K\_{a} = \frac{K\_{w}}{K\_{b}} = \frac{1.0 x 10^{-14}}{1.8 x 10^{-5}} = 5.6 x 10^{-10}$$

Calculate the Kb for C6H5CO2¯ using the Kw of water and the Ka for C6H5CO2H:

$$K\_{b} = \frac{K\_{w}}{K\_{a}} = \frac{1.0 x 10^{-14}}{6.5 x 10^{-5}} = 1.5 x 10^{-10}$$

Comparison of the Ka and the Kb shows that the Ka for ammonium ion is slightly larger than the Kb for benzoate ion. Thus the hydrolysis of ammonium lies further towards products than the hydrolysis of benzoate ion. More hydronium ion is produced in solution that hydroxide ion, so the solution is acidic with a pH < 7.

**11.** One must do a stoichiometry problem to determine the moles of H3O+ present after each addition of NaOH and then calculate the concentration of H3O+ based on the total volume of the solution.

**11 a.** The initial concentration of H3O+ will be 0.10 M because HCl is a strong acid and dissociates completely into H3O+ and Cl¯:

 HCl(aq) + H2O(l) → H3O+(aq) + Cl¯(aq)

initial 0.10 M 0 M 0 M

change -0.10 M +0.10 M +0.10 M

“equil.” 0 M +0.10 M +0.10 M

From the [H3O+], calculate the pH:

 pH = -log[H3O+] = -log(0.10) = 1.00

To determine the [H3O+] once OH¯ have been introduced, one must use stoichiometry. First find the total moles of HCl available, calculate the moles of OH¯ introduced and determine which ion is in excess. Whichever ion is in excess will determine the pH.

First find the total moles of HCl. This will be used repeatedly throughout the problem.

$$25.0 mL HCl soln x \frac{1 x 10^{-3} L soln}{1 mL HCl soln} x \frac{0.10 mol HCl}{1 L soln} = 0.0025 mol HCl$$

**11 b.**  Next find the moles of hydroxide after the addition of 10.0 mL of NaOH:

$$10.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.10 mol NaOH}{1 L soln} = 0.0010 mol NaOH$$

The moles of NaOH added equals the moles of HCl that reacts. The moles of HCl remaining is determined by:

 0.0025 total moles HCl – 0.0010 mol HCl reacted = 0.0015 mol HCl remaining

The new total volume of the solution is: 10.0 mL soln + 25.0 mL soln = 35.0 mL soln.

This volume in liters is:

$$35.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln } = 0.0350 L soln$$

Calculate the new hydronium ion concentration:

$$\frac{0.0015 mol HCl}{0.0350 L soln} x \frac{1 mol H\_{3}O^{+}}{1 mol HCl} = [H\_{3}O^{+}] = 0.043 M ^{}$$

Calculate the new pH: pH = -log[H3O+] = -log(0.043) = 1.34

**11 c.** Find the moles of hydroxide after the addition of 25.0 mL of NaOH:

$$25.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.10 mol NaOH}{1 L soln} = 0.0025 mol NaOH$$

The moles of NaOH added equals the moles of HCl that reacts. The moles of HCl remaining is determined by:

 0.0025 total moles HCl – 0.0025 mol HCl reacted = 0 mol HCl remaining

The equivalence point of the titration has been reached. The equivalence point is where the moles of acid equal the moles of base. The salt formed from this reaction is sodium chloride. Neither the sodium ion nor the chloride ion undergoes hydrolysis and are spectator ions. As a result, the only source of hydronium ion in solution is from the dissociation of water. Water produces 1.0 x 10-7 M H3O+ in solution. Use this concentration to calculate the pH:

 pH = -log[H3O+] = -log(1.0 x 10-7) = 7.00

**11 d.** Find the moles of hydroxide after the addition of 30.0 mL of NaOH:

$$30.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.10 mol NaOH}{1 L soln} = 0.0030 mol NaOH$$

Notice the moles of hydroxide is in excess as the equivalence point has been exceeded.

Find the moles of excess hydroxide:

 0.0030 mol OH¯ - 0.0025 mol OH¯ reacted = 0.0005 mol OH¯ in excess

The total volume of solution is: 30.0 mL + 25.0 mL = 55.0 mL

Convert this volume into liters:

$$55.0 mL soln x \frac{1 x 10^{-3}L soln}{1 mL soln} = 0.0550 L soln$$

Find the concentration of hydroxide ion:

$$\frac{0.0005 mol OH^{-}}{0.0550 L soln} = [OH^{-}] = 9.0 x 10^{-3} M$$

Solve for pOH first, then convert to pH:

 pOH = -log[OH¯] = -log(9.0 x 10-3) = 2.04

 pH = 14 – pOH = 14 – 2.04 = 11.96

**12 a.** Initially, the weak acid, benzoic acid is dissociating and we solve the pH as if the question read: “What is the pH of a 0.10 M benzoic acid solution?” Thus, the problem is worked similar to Problem 9c:

Benzoic acid, C6H5COOH, is a weak acid with a Ka = 6.2 x 10-5. Write the equilibrium reaction and determine the expressions for the equilibrium amounts, starting with an initial amount of 0.20 M C6H5COOH. We are assuming that initially, there isn’t any acetate or hydronium ion present. An x amount of benzoic acid has to be lost to form an x amount of both benzoate ion and hydronium ion. Thus, at equilibrium, an amount of 0.20 – x of benzoic acid is present, and x amount of both benzoate ion and hydronium ion are present. This can be conveniently summarized in the table shown below:

 C6H5COOH(aq) + H2O (l) ⮀ C6H5COO¯(aq) + H3O+(aq)

 initial 0.20 M 0 0

 change -x +x +x

 equil. 0.20 – x x x

The equilibrium constant expression for the above equilibrium is:

$$K\_{a} = \frac{[C\_{6}H\_{5}COO^{-}][H\_{3}O^{+}]}{[C\_{6}H\_{5}COOH]} = 6.2 x 10^{-5}$$

Substituting the equilibrium amounts into the above expression gives:

$$\frac{(x)(x)}{0.20 - x} = 6.2 x 10^{-5}$$

The above expression may be simplified by making an assumption that the “x” in denominator expression, 0.20 – x is negligibly small. If the magnitude of the constant is more than 100 times smaller than the magnitude of the known initial concentration, this assumption is valid. In this problem, the magnitude of the constant (10-5) is 1000 times smaller than the certainty of the known concentration, 0.20 M (10-2 or second decimal place), so the x in 0.20 – x can be neglected. One caveat is that a 0.1% error in the result is acceptable when this assumption is made.

This simplifies the algebraic expression to:

$$\frac{x^{2}}{0.20} = 6.2 x 10^{-5}$$

Solve for x: x2 = 6.2 x 10-5(0.20) = 1.2 x 10-5

$$x = \sqrt{1.2 x 10^{-5}} = 3.5 x 10^{-3} M = [C\_{6}H\_{5}COO^{-}] = [H\_{3}O^{+}]$$

Now that x is known, solve for [C6H5COOH] = 0.20 – x = 0.20 – 0.0035 = 0.20. Notice that our assumption that x was negligibly small relative to the benzoic acid concentration was valid.

To find the pH: pH = -log[H3O+] = -log(3.5 x 10-3) = 2.45

**12 b.** Finding the pH upon the addition of 10.0 mL of strong base is a more complicated problem. One has to do a stoichiometry problem first. The balanced chemical reaction taking places is:

 C6H5COOH(aq) + OH¯ (aq) → C6H5COO¯(aq) + H2O(l)

Find the total moles of benzoic acid present and the C6H5COOH(aq):

$$25.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.20 mol C\_{6}H\_{5}CO\_{2}H}{1 L soln} = 5.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}H$$

Find the moles of hydroxide added:

$$10.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.10 mol NaOH}{1 L soln } x \frac{1 mol OH^{-}}{1 mol NaOH} = 1.0 x 10^{-3} mol OH^{-}$$

From the balanced reaction, the moles of hydroxide added are equal to the moles of benzoate ion formed and the moles of benzoic acid that has reacted.

$$1.0 x 10^{-3} mol OH^{-} x \frac{1 mol C\_{6}H\_{5}CO\_{2}^{-}}{1 mol OH^{-}} = 1.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}^{-} formed$$

$$1.0 x 10^{-3} mol OH^{-} x \frac{1 mol C\_{6}H\_{5}CO\_{2}H}{1 mol OH^{-}} = 1.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}H reacted$$

So far, the moles of hydroxide added are less than the total moles of benzoic acid, thus some of the benzoic acid remains unreacted. Since some benzoic acid, a weak acid, is present and some benzoate ion, the conjugate base of the weak acid, is also present, a buffer solution has been formed.

Find the moles of unreacted benzoic acid:

5.0 x 10-3 mol C6H5CO2H – 1.0 x 10-3 mol C6H5CO2H reacted = 4.0 x 10-3 mol unreacted

 C6H5CO2H

The total volume of the solution at this point is the sum of the volumes of benzoic acid solution and sodium hydroxide solutions:

 25.0 mL soln + 10.0 mL soln = 35.0 mL soln

Convert this volume into liters in preparation to calculate the new initial concentrations of benzoic acid and benzoate ion:

$$35.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} = 0.0350 L soln$$

Find the new initial concentrations of benzoic acid and benzoate ion:

$$[C\_{6}H\_{5}CO\_{2}H] = \frac{ 4.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}H}{0.0350 L soln} = 0.11 M C\_{6}H\_{5}CO\_{2}H$$

$$[C\_{6}H\_{5}CO\_{2}^{-}] = \frac{1.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}^{-}}{0.0350 L soln} = 0.029 M C\_{6}H\_{5}CO\_{2}^{-}$$

Use these new initial concentrations to set up the calculation for the buffer equilibrium shown below:

 C6H5COOH(aq) + H2O (l) ⮀ C6H5COO¯(aq) + H3O+(aq)

 initial 0.11 M 0.029 M 0

 change -x +x +x

 equil. 0.11 – x 0.029 + x x

The equilibrium constant expression for the above equilibrium is:

$$K\_{a} = \frac{[C\_{6}H\_{5}COO^{-}][H\_{3}O^{+}]}{[C\_{6}H\_{5}COOH]} = 6.2 x 10^{-5}$$

Substituting the equilibrium amounts into the above expression gives:

$$\frac{(0.029 + x)(x)}{0.11 - x} = 6.2 x 10^{-5}$$

The above expression may be simplified by making an assumption that the “x” in both the numerator expression, 0.029 + x and the denominator expression, 0.11 – x are negligibly small. If the magnitude of the constant is more than 100 times smaller than the magnitude of the known initial concentration, this assumption is valid. In this problem, the magnitude of the constant (10-5) is 1000 times smaller than the certainty of the known concentrations, One caveat is that a 0.1% error in the result is acceptable when this assumption is made.

This simplifies the algebraic expression to:

$$\frac{(0.029)(x)}{0.11 } = 6.2 x 10^{-5}$$

Rearrange the algebraic expression to solve for x:

$$x = \frac{(6.2 x 10^{-5})(0.11)}{0.029} = 2.4 x 10^{-4} = [H\_{3}O^{+}]$$

Since x = [H3O+], the pH can be calculated as:

 pH = -log[H3O+] = -log(2.4 x 10-4) =3.63

**12 c.** Finding the pH upon the addition of 25.0 mL of strong base is very similar to the previous problem. One has to do a stoichiometry problem first. The balanced chemical reaction taking places is:

 C6H5COOH(aq) + OH¯ (aq) → C6H5COO¯(aq) + H2O(l)

Find the total moles of benzoic acid present and the C6H5COOH(aq):

$$25.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.20 mol C\_{6}H\_{5}CO\_{2}H}{1 L soln} = 5.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}H$$

Find the moles of hydroxide added:

$$25.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.10 mol NaOH}{1 L soln } x \frac{1 mol OH^{-}}{1 mol NaOH} = 2.5 x 10^{-3} mol OH^{-}$$

From the balanced reaction, the moles of hydroxide added are equal to the moles of benzoate ion formed and the moles of benzoic acid that has reacted.

$$2.5 x 10^{-3} mol OH^{-} x \frac{1 mol C\_{6}H\_{5}CO\_{2}^{-}}{1 mol OH^{-}} = 2.5 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}^{-} formed$$

$$2.5 x 10^{-3} mol OH^{-} x \frac{1 mol C\_{6}H\_{5}CO\_{2}H}{1 mol OH^{-}} = 2.5 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}H reacted$$

So far, the moles of hydroxide added are still less than the total moles of benzoic acid, thus some of the benzoic acid remains unreacted. Since some benzoic acid, a weak acid, is present and some benzoate ion, the conjugate base of the weak acid, is also present, a buffer solution has been formed.

Find the moles of unreacted benzoic acid:

5.0 x 10-3 mol C6H5CO2H – 2.5 x 10-3 mol C6H5CO2H reacted = 2.5 x 10-3 mol unreacted

 C6H5CO2H

The total volume of the solution at this point is the sum of the volumes of benzoic acid solution and sodium hydroxide solutions:

 25.0 mL soln + 25.0 mL soln = 50.0 mL soln

Convert this volume into liters in preparation to calculate the new initial concentrations of benzoic acid and benzoate ion:

$$50.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} = 0.0500 L soln$$

Find the new initial concentrations of benzoic acid and benzoate ion:

$$[C\_{6}H\_{5}CO\_{2}H] = \frac{ 2.5 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}H}{0.0500 L soln} = 0.050 M C\_{6}H\_{5}CO\_{2}H$$

$$[C\_{6}H\_{5}CO\_{2}^{-}] = \frac{2.5 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}^{-}}{0.0500 L soln} = 0.050 M C\_{6}H\_{5}CO\_{2}^{-}$$

Use these new initial concentrations to set up the calculation for the buffer equilibrium shown below:

 C6H5COOH(aq) + H2O (l) ⮀ C6H5COO¯(aq) + H3O+(aq)

 initial 0.050 M 0.050 M 0

 change -x +x +x

 equil. 0.050 – x 0.050 + x x

The equilibrium constant expression for the above equilibrium is:

$$K\_{a} = \frac{[C\_{6}H\_{5}COO^{-}][H\_{3}O^{+}]}{[C\_{6}H\_{5}COOH]} = 6.2 x 10^{-5}$$

Substituting the equilibrium amounts into the above expression gives:

$$\frac{(0.050 + x)(x)}{0.050 - x} = 6.2 x 10^{-5}$$

The above expression may be simplified by making an assumption that the “x” in both the numerator expression, 0.050 + x and the denominator expression, 0.050 – x are negligibly small. If the magnitude of the constant is more than 100 times smaller than the magnitude of the known initial concentration, this assumption is valid. In this problem, the magnitude of the constant (10-5) is 100 times smaller than the certainty of the known concentrations, One caveat is that a 0.1% error in the result is acceptable when this assumption is made.

This simplifies the algebraic expression to:

$$\frac{(0.050)(x)}{0.050 } = 6.2 x 10^{-5}$$

The above expression simplifies to x = [H3O+] = 6.2 x 10-5

Since x = [H3O+], the pH can be calculated as:

 pH = -log[H3O+] = -log(6.2 x 10-5) = 4.21

Notice how [C6H5CO2H] = [C6H5CO2¯]. This unique point is often referred to as the half equivalence point. At the half equivalence point, pH = pKa.

**12 d.** Once again, one must do the stoichiometry problem first to solve for the pH upon addition of 50.0 mL of strong base. The balanced chemical reaction taking places is:

 C6H5COOH(aq) + OH¯ (aq) → C6H5COO¯(aq) + H2O(l)

Find the total moles of benzoic acid present and the C6H5COOH(aq):

$$25.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.20 mol C\_{6}H\_{5}CO\_{2}H}{1 L soln} = 5.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}H$$

Find the moles of hydroxide added:

$$50.0 mL soln x \frac{1 x 10^{-3} L soln}{1 mL soln} x \frac{0.10 mol NaOH}{1 L soln } x \frac{1 mol OH^{-}}{1 mol NaOH} = 5.0 x 10^{-3} mol OH^{-}$$

The moles of acid equal the moles of base. The benzoic acid has been neutralized and only sodium benzoate and water are present in solution. The moles of benzoate ion equal the moles of benzoic acid neutralized:

$$5.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}H x \frac{1 mol C\_{6}H\_{5}CO\_{2}^{-}}{1 mol C\_{6}H\_{5}CO\_{2}H} = 5.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}^{-}$$

The total volume of the solution is: 25.0 mL + 50.0 mL = 75.0 mL. Convert this volume to liters in preparation for finding the concentration of benzoate ion:

$$75.0 ml soln x \frac{1 x 10^{-3} L soln}{1 mL soln} = 0.070 L soln$$

Find the concentration of benzoate ion in solution:

$$[C\_{6}H\_{5}CO\_{2}^{-}] = \frac{5.0 x 10^{-3} mol C\_{6}H\_{5}CO\_{2}^{-}}{0.0750 soln} = 0.067 M C\_{6}H\_{5}CO\_{2}^{-}$$

Recall at the equivalence point, only the salt is moving around in aqueous solution. In this case the salt is sodium benzoate. The sodium ion is the weak conjugate acid of a strong base, and thus will not undergo hydrolysis. It will be a spectator ion. On the other hand, the benzoate ion is the strong conjugate base of a weak acid and will undergo hydrolysis and behave as a base:

 C6H5CO2¯(aq) + H2O(l) ⮀ C6H5CO2H(aq) + OH¯(aq)

To evaluate the pH, we need to do a hydrolysis equilibrium problem. First, calculate the equilibrium constant, Kb, for this reaction from the fact that the KaKb = Kw for any acid/conjugate base pair (or in other instances, for any base/conjugate acid pair).

$$K\_{b} = \frac{K\_{w}}{K\_{a}} = \frac{1.0 x 10^{-14}}{6.2 x 10^{-5}} = 1.6 x 10^{-10}$$

Set up a table to determine the equilibrium concentrations in solution. Initially, 0.067 M benzoate is present in solution, to establish equilibrium an “x” amount of benzoate must be used to form an “x” amount of benzoic acid and “x” amount of hydroxide. Combining these quantities gives us the equilibrium quantities:

 C6H5CO2¯(aq) + H2O(l) ⮀ C6H5CO2H(aq) + OH¯(aq)

 initial 0.067 M 0 0

 change -x + x + x

 equil. 0.067 – x x x

Substitute these quantities into the equilibrium constant expression:

$$K\_{b} = \frac{[C6H5CO2H][OH^{-}]}{[C\_{6}H\_{5}CO\_{2}^{-}]} = \frac{(x)(x)}{0.067 - x} = 1.6 x 10^{-10}$$

The “x” in the denominator term, 0.067 – x can be neglected because the magnitude of the constant is 107 times smaller than the last certain digit of the known concentration, hence the expression will simplify to:

$$\frac{x^{2}}{0.067} = 1.6 x 10^{-10}$$

Solve for x: x2 = (1.6 x 10-10)(0.067) = 1.1 x 10-11

$$x = \sqrt{1.1 x 10^{-11}} = 3.3 x 10^{-6} = [OH^{-}]$$

There are two common methods for finding the pH. One method would be to find the pOH and then convert to pH:

pOH = -log[OH¯] = -log[3.3 x 10-6] = 5.48

 pH = 14 – pOH = 14 – 5.48 = 8.52

Alternatively, one could first calculate the [H3O+] using the Kw expression for water and then find the pH:

$$[H\_{3}O^{+}] = \frac{K\_{w}}{[OH^{-}]} = \frac{1.0 x 10^{-14}}{3.3 x 10^{-6} } = 3.04 x 10^{-9} M$$

 pH = -log[H3O+] = -log(3.04 x 10-9) = 8.52