

In aqueous solution, ammonia reacts as represented above. In 0.0180 M $\text{NH}_3(\text{aq})$ at 25°C, the hydroxide ion concentration, $[\text{OH}^-]$, is 5.60×10^{-4} M. In answering the following, assume that temperature is constant at 25°C and that volumes are additive.

Write the equilibrium-constant expression for the reaction represented above.

Determine the pH of 0.0180 M $\text{NH}_3(\text{aq})$.

Determine the value of the base ionization constant, K_b , for $\text{NH}_3(\text{aq})$.

Determine the percent ionization of NH_3 in 0.0180 M $\text{NH}_3(\text{aq})$.

In an experiment, a 20.0 mL sample of 0.0180 M $\text{NH}_3(\text{aq})$ was placed in a flask and titrated to the equivalence point and beyond using 0.0120 M $\text{HCl}(\text{aq})$.

Determine the volume of 0.0120 M $\text{HCl}(\text{aq})$ that was added to reach the equivalence point.

Determine the pH of the solution in the flask after a total of 15.0 mL of 0.0120 M $\text{HCl}(\text{aq})$ was added.

Determine the pH of the solution in the flask after a total of 40.0 mL of 0.0120 M $\text{HCl}(\text{aq})$ was added.

ANSWER:

9 points:

One point deduction for mathematical error (maximum once per question)

One point deduction for error in significant figures* (maximum once per question)

*number of significant figures must be correct within +/- one digit. (except for pH: +/- two digits)

1 point

$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

1 point

$$[\text{OH}^-] = 5.60 \times 10^{-4} \Rightarrow \{ \quad \text{pOH} = 3.252 \text{ or } [\text{H}^+] = 1.79 \times 10^{-11} \quad \} \Rightarrow \text{pH} = 10.748$$

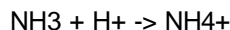
2 points

$$K_b = \frac{(5.60 \times 10^{-4})^2}{0.0180 - 5.60 \times 10^{-4}} = 1.74 \times 10^{-5} \text{ or } (1.80 \times 10^{-5})$$

Note: 1st point for the $[\text{NH}_4^+] = [\text{OH}^-] = 5.60 \times 10^{-4}$; 2nd point for the correct answer.

1 point

$$\% \text{ ionization} = \frac{5.60 \times 10^{-4}}{0.0180} \times 100\% = 3.11\% \text{ (or } 0.0311)$$



1 point

$$\begin{aligned} \text{mol NH}_3 &= 0.0180 \text{ M} \times 0.0200 \text{ L} = 3.60 \times 10^{-4} \text{ mol} = \text{mol H}^+ \text{ needed} \\ \text{vol HCl solution} &= \frac{3.60 \times 10^{-4} \text{ mol}}{0.0120 \text{ M}} = 0.0300 \text{ L} = 30.0 \text{ mL} \end{aligned}$$

1 point

$$\begin{aligned} \text{mol H}^+ \text{ added} &= \text{mol } 0.0120 \text{ M} \times 0.0150 \text{ L} = 1.80 \times 10^{-4} \text{ mol H}^+ \text{ added} \\ &= 1.80 \times 10^{-4} \text{ mol NH}_4^+ \text{ produced} \end{aligned}$$

$$[\text{NH}_4^+] = \frac{1.80 \times 10^{-4} \text{ mol}}{0.0350 \text{ L}} = 0.00514 \text{ M} = [\text{NH}_3]$$

Note: Points earned for 1.80×10^{-4} mol, or $0.00514 \text{ M} [\text{NH}_3]$ or $[\text{NH}_4^+]$, or statement "halfway to equivalence point".

1 point

$$K_b = 1.80 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{OH}^-] \Rightarrow \text{pOH} = 4.745 \Rightarrow \text{pH} = 9.255$$

(= 1.74 x 10⁻⁵) (= 4.759) (= 9.241)

1 point

10.0 mL past equivalence point
 0.0100 L x 0.0120 M = 1.20 x 10⁻⁴ mol H⁺ in 60.0 mL
 [H⁺] = $\frac{0.000120 \text{ mol}}{0.0600 \text{ L}} = 0.00200 \text{ M}$
 pH = -log(2.00 x 10⁻³) = 2.700

2. The overall dissociation of oxalic acid, H₂C₂O₄ is represented below. The overall dissociation constant is also indicated.

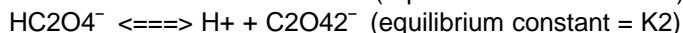
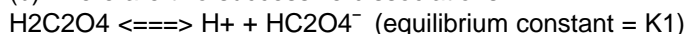


- a) What volume of 0.400-molar NaOH is required to neutralize completely a 5.00 x 10⁻³-mole sample of pure oxalic acid?**
- b) Give the equations representing the first and second dissociations of oxalic acid. Calculate the value of the first dissociation constant, K₁, for oxalic acid if the value of the second dissociation constant, K₂, is 6.40 x 10⁻⁵**
- c) To a 0.015-molar solution of oxalic acid, a strong acid is added until the pH is 0.5. Calculate the [C₂O₄²⁻] in the resulting solution. (Assume the change in volume is negligible.)**
- d) Calculate the value of the equilibrium constant, K_b, for the reaction that occurs when solid Na₂C₂O₄ is dissolved in water.**

ANSWER:

(a) 5.00 x 10⁻³ mol H₂C₂O₄ = 1.00 x 10⁻² mol H⁺ = 1.00 x 10⁻² mol OH⁻
 1.00 x 10⁻² mol OH⁻ / 0.400 M = 0.0250 L (25.0 mL).
 Calculation from moles to volume; use of incorrect moles still earns point.

(b) There are two successive dissociations:



Acceptable alternatives are the use of H₂O as reactant and H₃O⁺ as product or writing of correct equilibrium constant expressions. Consistent errors (such as missing atoms or charges) are only penalized once.

K₁₂ = K₁ times K₂, thus

$$K_1 = K_{12} / K_2 = 3.78 \times 10^{-4} / 6.40 \times 10^{-5} = 5.91 \times 10^{-2}; \text{ one point}$$

c)

pH = 0.5 therefore H⁺ = 0.32M (pH controls 1 sig. fig. in answer)

(This point also earned if conversion of K to pK is correct.)

K small therefore amount of dissociation small therefore assume [H₂C₂O₄] = 0.015

$$K_{12} = \frac{[\text{H}^+]^2 [\text{C}_2\text{O}_4^{2-}]}{[\text{H}_2\text{C}_2\text{O}_4]}$$

$$\text{then } [\text{C}_2\text{O}_4^{2-}] = \frac{(3.78 \times 10^{-6})(0.015)}{(0.32)^2} = 6 \times 10^{-7}$$

(Here 1, 2, or 3 sig. fig.'s accepted) Two points for correct set-up with substitution and final calculation (-1 point for each error).

Alternative methods, included proper use of Henderson-Hasselbalch equation, can earn credit.

(d)

C₂O₄²⁻ + H₂O \rightleftharpoons HC₂O₄⁻ + OH⁻ is the only significant reaction,

$$\text{so } K_b = \frac{K_w}{K_2} = \frac{1.00 \times 10^{-14}}{6.40 \times 10^{-5}} = 1.56 \times 10^{-10}$$

No credit earned if K₁ or K₁₂ used; 1, 2, or 3 sig. fig.'s accepted since number of significant figures for value of K_w not indicated in table on examination.

3. The acid ionization constant, K_a, for propanoic acid, C₂H₅COOH, is 1.3 x 10⁻⁵.

(a) Calculate the hydrogen ion concentration, [H⁺], in a 0.20-molar solution of propanoic acid.

(b) Calculate the percentage of propanoic acid molecules that are ionized in the solution in (a).

(c) What is the ratio of the concentration of propanoate ion, $\text{C}_2\text{H}_5\text{COO}^-$, to that of propanoic acid in a buffer solution with a pH of 5.20 ?

(d) In a 100-milliliter sample of a different buffer solution, the propanoic acid concentration is 0.50-molar and the sodium propanoate concentration is 0.50-molar. To this buffer solution, 0.0040 mole of solid NaOH is added. Calculate the pH of the resulting solution.

ANSWER:

a) three points

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]}$$

$$1.3 \times 10^{-5} = x \div 0.20$$

$$x = [\text{H}^+] = 1.6 \times 10^{-3}$$

b) one point

$$\% \text{ dissociation} = \frac{[\text{H}^+]}{[\text{HC}_3\text{H}_5\text{O}_2]}$$

$$= \frac{1.6 \times 10^{-3}}{0.20} = 0.80\%$$

c) two points

$$[\text{H}^+] = \text{antilog}(-5.20) = 6.3 \times 10^{-6}$$

$$1.3 \times 10^{-5} = (6.3 \times 10^{-6}) \times \left(\frac{[\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} \right)$$

$$\frac{[\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{1.3 \times 10^{-5}}{6.3 \times 10^{-6}} = 2.1$$

An alternate solution for (c) based on the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$$

$$5.20 = 4.89 + \log \left(\frac{[\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} \right)$$

$$\log \left(\frac{[\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} \right) = 0.31$$

$$\frac{[\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = 2.0$$

d) six points

$$0.10 \text{ L} \times 0.35 \text{ mol/L} = 0.035 \text{ mol HC}_3\text{H}_5\text{O}_2$$

$$0.10 \text{ L} \times 0.50 \text{ mol/L} = 0.050 \text{ mol C}_3\text{H}_5\text{O}_2^-$$

$$0.035 \text{ mol} - 0.004 \text{ mol} = 0.031 \text{ mol HC}_3\text{H}_5\text{O}_2$$

$$0.050 \text{ mol} + 0.004 \text{ mol} = 0.054 \text{ mol C}_3\text{H}_5\text{O}_2^-$$

$$1.3 \times 10^{-5} = [\text{H}^+] \times \left(\frac{0.054 \text{ mol}/0.1 \text{ L}}{0.031 \text{ mol}/0.1 \text{ L}} \right)$$

Can use 0.54 and 0.31 instead.

$$[\text{H}^+] = 7.5 \times 10^{-6}$$

$$\text{pH} = 5.13$$

An alternate solution for (d) based on the Henderson-Hasselbalch equation.

use []s or moles of $\text{HC}_3\text{H}_5\text{O}_2$ and $\text{C}_3\text{H}_5\text{O}_2^-$

$$\text{pH} = \text{p}K_a + \log \left(\frac{0.054}{0.031} \right)$$

$$= 4.89 + 0.24 = 5.13$$

4. In an experiment to determine the molecular weight and the ionization constant for ascorbic acid (vitamin C), a student dissolved 1.3717 grams of the acid in water to make 50.00 milliliters of solution. The entire solution was titrated with a 0.2211-molar NaOH solution. The pH was monitored throughout the titration. The equivalence point was reached when 35.23 milliliters of the base had been added. Under the conditions of this experiment, ascorbic acid acts as a monoprotic acid that can be represented as HA.

(a) From the information above, calculate the molecular weight of ascorbic acid.

(b) When 20.00 milliliters of NaOH had been added during the titration, the pH of the solution was 4.23. Calculate the acid ionization constant for ascorbic acid.

(c) Calculate the equilibrium constant for the reaction of the ascorbate ion, A^- , with water.

(d) Calculate the pH of the solution at the equivalence point of the titration.

ANSWER:

a) two points

$$\text{Mol. wt.} = (1.3717 \text{ grams} / (0.2211 \text{ mol/L}) \times (0.0523 \text{ L})) \\ = 1.3717 \text{ grams} / 7.789 \times 10^{-5} \text{ mole} = 176.1 \text{ grams/mol}$$

b) three points

$$\text{pH} = 4.23 \text{ therefore } [\text{H}^+] = 5.9 \times 10^{-5} \text{ M}$$

$$[\text{A}^-] = [(0.01523 \text{ L}) (0.2211 \text{ mol/L})] / (0.07000 \text{ L})$$

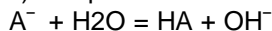
$$= 0.004422 \text{ mol} / 0.07000 \text{ L} = 0.06317 \text{ M}$$

$$[\text{HA}] = [(0.01523 \text{ L}) (0.2211 \text{ mol/L})] / (0.07000 \text{ L})$$

$$= 0.00367 \text{ mol} / 0.07000 \text{ L} = 0.04810 \text{ M}$$

$$K = ([\text{H}^+][\text{A}^-]) / [\text{HA}] = [(5.9 \times 10^{-5})(0.06317)] / (0.04810) = 7.7 \times 10^{-5}$$

c) one point



$$K = ([\text{HA}][\text{OH}^-]) / [\text{A}^-] = K_w / K_a$$

$$= (1.0 \times 10^{-14}) / (7.7 \times 10^{-5}) = 1.3 \times 10^{-10}$$

d) three points

$$[\text{A}^-] \text{ at equiv. point} = 7.789 \times 10^{-3} \text{ mol} / 0.08523 \text{ L} = 9.14 \times 10^{-2} \text{ M}$$

$$[\text{OH}^-]^2 = (1.3 \times 10^{-10})(9.14 \times 10^{-2}) = 1.2 \times 10^{-11}$$

$$[\text{OH}^-] = 3.4 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(3.4 \times 10^{-6}) = 5.47$$

$$\text{pH} = 14 - 5.47 = 8.53$$

5. See Picture

A 30.00-milliliter sample of a weak monoprotic acid was titrated with a standardized solution of NaOH. A pH meter was used to measure the pH after each increment of NaOH was added, and the curve above was constructed.

(a) Explain how this curve could be used to determine the molarity of the acid.

(b) Explain how this curve could be used to determine the acid dissociation constant K_a of the weak monoprotic acid.

(c) If you were to repeat the titration using an indicator in the acid to signal the endpoint, which of the following indicators should you select. Give the reason for your choice.

Methyl red $K_a = 1 \times 10^{-5}$

Cresol red $K_a = 1 \times 10^{-8}$

Alizarin yellow $K_a = 1 \times 10^{-11}$

(d) Sketch the titration curve that would result if the weak monoprotic acid were replaced by a strong monoprotic acid, such as HCl of the same molarity. Identify differences between this titration curve and the curve shown above.

ANSWER:

a) two points

The sharp vertical rise in the pH on the pH-volume curve appears at the equivalence point (about 23 mL). Because the acid is monoprotic, the number of moles of acid equals the number of moles of NaOH. That number is the product of the exact volume and the molarity of the NaOH. The molarity of the acid is the number of moles of the acid divided by 0.030 L, the volume of the acid.

b) two points

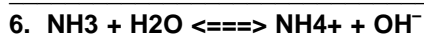
At the half-equivalence point (where the volume of the base added is exactly half its volume at the equivalence point), the concentration $[\text{HX}]$ of the weak acid equals the concentration $[\text{X}^-]$ of its anion. Thus, in the equilibrium expression, $[\text{H}^+][\text{X}^-] / [\text{HX}] = K_a$. Therefore, pH at the half-equivalence point equals pKa

c) one point

Cresol red is the best indicator because its pKa (about 8) appears midway in the steep equivalence region. This insures that at the equivalence point the maximum color change for the minimal change in the volume of NaOH added is observed.

d) three points

See Picture



Ammonia is a weak base that dissociates in water as shown above. At 25 °C, the base dissociation constant, K_b , for NH_3 is 1.8×10^{-5} .

(a) Determine the hydroxide ion concentration and the percentage dissociation of a 0.150-molar solution of ammonia at 25 °C.

(b) Determine the pH of a solution prepared by adding 0.0500 mole of solid ammonium chloride to 100. milliliters of a 0.150-molar solution of ammonia.

(c) If 0.0800 mole of solid magnesium chloride, MgCl_2 , is dissolved in the solution prepared in part (b) and the resulting solution is well-stirred, will a precipitate of $\text{Mg}(\text{OH})_2$ form? Show calculation to support your answer. (Assume the volume of the solution is unchanged. The solubility product constant for $\text{Mg}(\text{OH})_2$ is 1.5×10^{-11}).

ANSWER:

a) three points

$$[\text{NH}_4^+] = [\text{OH}^-] = x$$

$$[\text{NH}_3] = 0.150 \text{ mol/L} - x$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.150 - x)}$$

approximately equals $x^2 \div 0.150$

$$x = [\text{OH}^-] = 1.6 \times 10^{-3} \text{ mol/L}$$

$$\% \text{ diss} = \frac{(1.6 \times 10^{-3})}{(0.150)} \times 100\% = 1.1\%$$

b) three points

$$[\text{NH}_4^+] = 0.0500 \text{ mol} / 0.100 \text{ L} = 0.500 \text{ mol/L NH}_4^+$$

$$[\text{NH}_3] = 0.150 \text{ mol/L}$$

OR

$$\text{mol NH}_4^+ = 0.0500 \text{ mol NH}_4^+$$

$$\text{mol NH}_3 = 0.150 \text{ mol/L} \times 0.100 \text{ L} = 0.0150 \text{ mol}$$

THEN

$$1.8 \times 10^{-5} = \frac{(0.500)(x)}{(0.150)}$$

OR

$$\text{pOH} = 4.74 + \log(0.500 / 0.150)$$

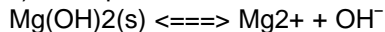
THEN

$$x = [\text{OH}^-] = 5.4 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} = 5.27$$

$$\text{pH} = 14.00 - 5.27 = 8.73$$

c) three points



$$[\text{Mg}^{2+}] = 0.0800 \text{ mol} / 0.100 \text{ L} = 0.800 \text{ mol/L} \quad (0.800 \pm x = \text{no credit})$$

$$([\text{OH}^-] = 5.4 \times 10^{-6} \text{ mol/L from b.})$$

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.800)(5.4 \times 10^{-6})^2$$

$$Q = 2.3 \times 10^{-11}$$

$$K_{sp} = 1.5 \times 10^{-11}$$

since $Q > K_{sp}$, $\text{Mg}(\text{OH})_2$ precipitates

(Q must be defined in the same way as K_{sp})

OR

$$K_{sp} = 1.5 \times 10^{-11} = (0.800)[\text{OH}^-]^2$$

$$[\text{OH}^-] = 4.3 \times 10^{-6} \text{ mol/L}$$

since $5.4 \times 10^{-6} > 4.3 \times 10^{-6} \text{ mol/L}$, then $\text{Mg}(\text{OH})_2$ precipitates

7. In water, hydrazoic acid, HN_3 , is a weak acid that has an equilibrium constant, K_a , equal to 2.8×10^{-5} at 25 °C. A 0.300-liter sample of a 0.050-molar solution of the acid is prepared.

(a) Write the expression for the equilibrium constant, K_a , for hydrazoic acid.

(b) Calculate the pH of this solution at 25 °C.

(c) To 0.150 liter of this solution, 0.80 gram of sodium azide, NaN_3 , is added. The salt dissolves completely. Calculate the pH of the resulting solution at 25 °C if the volume of the solution remains unchanged.

(d) To the remaining 0.150 liter of the original solution, 0.075 liter of 0.100-molar NaOH solution is added. Calculate the $[\text{OH}^-]$ for the resulting solution at 25 °C.

ANSWER:

a) one point

$$K_a = \frac{[\text{H}^+][\text{N}_3^-]}{[\text{HN}_3]}$$

b) three points

$$2.8 \times 10^{-5} = x^2 \div 0.050$$

$$x = [\text{H}^+] = \sqrt{(1.4 \times 10^{-6})} = 1.2 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = 2.93$$

c) two points

$$[\text{N}_3^-] = (0.80 \text{ grams} \times (1 \text{ mole}/65 \text{ grams})) / 0.150 \text{ liters} = 0.082 \text{ M}$$

$$2.8 \times 10^{-5} = \frac{[\text{H}^+](0.082)}{(0.050)}$$

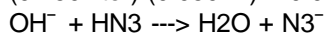
$$[\text{H}^+] = 1.7 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.77$$

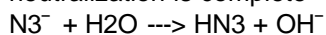
d) three points

$$(0.075 \text{ liter})(0.100 \text{ M}) = 0.0075 \text{ mole NaOH}$$

$$(0.150 \text{ liter})(0.050 \text{ M}) = 0.0075 \text{ mole HN}_3$$



neutralization is complete



$$K_b = K_w / K_a$$

$$1 \times 10^{-14} \div 2.8 \times 10^{-5} = \frac{[\text{HN}_3][\text{OH}^-]}{[\text{N}_3^-]}$$

$$= x^2 \div (0.0075 / 0.225)$$

$$x = [\text{OH}^-] = 3.4 \times 10^{-6} \text{ M}$$

Notes related to (d)

1) Neutralization of only H^+ in solution to get only excess OH^- , and division of moles of OH^- by total volume receives only one point

2) Neutralization of HN_3 and $[\text{OH}^-] = 10^{-7}$ received one point

8. Sodium benzoate, $\text{C}_6\text{H}_5\text{COONa}$, is a salt of the weak acid, benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$. A 0.10-molar solution of sodium benzoate has a pH of 8.60 at room temperature.

(a) Calculate the $[\text{OH}^-]$ in the sodium benzoate solution described above.

(b) Calculate the value for the equilibrium constant for the reaction



(c) Calculate the value of K_a , the acid dissociation constant for benzoic acid.

(d) A saturated solution of benzoic acid is prepared by adding excess solid benzoic acid to pure water at room temperature. Since this saturated solution has a pH of 2.88, calculate the molar solubility of benzoic acid at room temperature.

ANSWER:

Average score 4.36

a) two points

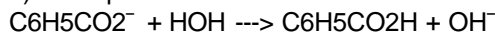
$$\text{pH} = 8.60$$

$$[\text{H}^+] = 1 \times 10^{-8.60} \text{ M} = 2.5 \times 10^{-9} \text{ M}$$

$$[\text{OH}^-] = (1 \times 10^{-14}) / (2.5 \times 10^{-9}) \text{ M}$$

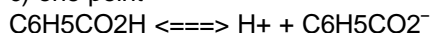
$$= 4.0 \times 10^{-6} \text{ M}$$

b) three points



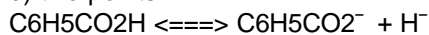
$$\begin{aligned} K &= \frac{[\text{C}_6\text{H}_5\text{CO}_2\text{H}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{CO}_2^-]} \\ &= \frac{(4.0 \times 10^{-8})(4.0 \times 10^{-6})}{(0.10 - 4.0 \times 10^{-6})} \\ &= 1.6 \times 10^{-10} \end{aligned}$$

c) one point



$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{CO}_2\text{H}]} \\ &= \frac{(2.5 \times 10^{-9})(0.10)}{(4.0 \times 10^{-6})} \\ &= 6.3 \times 10^{-5} \end{aligned}$$

d) two points



$$\text{pH} = 2.88$$

$$[\text{H}^+] = 1 \times 10^{-2.88} \text{M} = 1.3 \times 10^{-3}$$

$$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{CO}_2\text{H}]}$$

$$6.3 \times 10^{-5} = \frac{(1.3 \times 10^{-3})(1.3 \times 10^{-3})}{x}$$

$$x = 2.8 \times 10^{-2} \text{M}$$

Total $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ in solution =

$$(2.8 \times 10^{-2} + 1.3 \times 10^{-3}) \text{M} =$$

$$2.9 \times 10^{-2} \text{M}$$

9. (a) Specify the properties of a buffer solution. Describe the components and the composition of effective buffer solutions.

(b) An employer is interviewing four applicants for a job as a laboratory technician and asks each how to prepare a buffer solution with a pH close to 9.

Archie A. says he would mix acetic acid and sodium acetate solutions.

Beula B. says she would mix NH_4Cl and HCl solutions.

Carla C. says she would mix NH_4Cl and NH_3 solutions.

Dexter D. says he would mix NH_3 and NaOH solutions.

Which of these applicants has given an appropriate procedure? Explain your answer, referring to your discussion in part (a). Explain what is wrong with the erroneous procedures. (No calculations are necessary, but the following acidity constants may be helpful: acetic acid, $K_a = 1.8 \times 10^{-5}$, NH_4^+ , $K_a = 5.6 \times 10^{-10}$)

ANSWER:

(a) three points

A buffer solution resists changes in pH upon the addition of an acid or base.

Preparation:

- Mix a weak acid + a salt of a weak acid.
- Or mix a weak base + a salt of a weak base.
- Or mix a weak acid with about half as many moles of strong base.
- Or mix a weak base with about half as many moles of strong acid.
- Or mix a weak acid and a weak base.

(b) five points

Carla has the correct procedure. She has mixed a weak base, NH_3 , with the salt of a weak base, NH_4Cl .

Archie has buffer solution but it has a pH around 5.

Beula does not have a buffer solution, since her solution consists of a strong acid and a salt of a weak base.

Dexter does not have a buffer solution, since his solution consists of a weak base plus a strong base.

10. A buffer solution contains 0.40 mole of formic acid, HCOOH , and 0.60 mole of sodium formate, HCOONa , in 1.00 liter of solution. The ionization constant, K_a , of formic acid is 1.8×10^{-4}

(a) Calculate the pH of this solution.

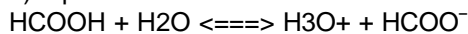
(b) If 100. milliliters of this buffer solution is diluted to a volume of 1.00 liter with pure water, the pH does not change. Discuss why the pH remains constant on dilution.

(c) A 5.00-milliliter sample of 1.00-molar HCl is added to 100. milliliters of the original buffer solution. Calculate the $[H_3O^+]$ of the resulting solution.

(d) A 800-milliliter sample of 2.00-molar formic acid is mixed with 200. milliliters of 4.80-molar NaOH. Calculate the $[H_3O^+]$ of the resulting solution.

ANSWER

a) 3 points



$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

$$\text{Initial: } 0.40 \quad 0.60$$

$$\text{Equil: } 0.40 - y \quad y \quad 0.60 + y$$

$$K_a = 1.8 \times 10^{-4} = \frac{(y)(0.60 + y)}{(0.40 - y)}$$

neglect the +y and the -y

$$[H_3O^+] = y = 1.2 \times 10^{-4}$$

$$pH = -\log(1.2 \times 10^{-4}) = 3.92$$

Alternative Approach:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$= -\log(1.8 \times 10^{-4}) + \log(0.60 / 0.40)$$

$$= 3.92$$

b) 1 point

The pH remains unchanged because the ratio of the formate and formic acid stays the same

c) 3 points

Initial amounts of concentrations:

$$1.00 \text{ M HCl} \times 0.00500 \text{ L} = 0.00500 \text{ mole HCl}$$

$$0.40 \text{ M HCOOH} \times 0.100 \text{ L} = 0.040 \text{ mole HCOOH}$$

$$0.60 \text{ M HCOO}^- \times 0.100 = 0.060 \text{ mole HCOO}^-$$

or

$$1.00 \text{ M HCl} \times (5.00 \text{ ml} / 105 \text{ ml}) = 0.0476 \text{ M HCl}$$

$$0.40 \text{ M HCOOH} \times (100 \text{ ml} / 105 \text{ ml}) = 0.38 \text{ M HCOOH}$$

$$0.60 \text{ M HCOO}^- \times (100 \text{ ml} / 105 \text{ ml}) = 0.57 \text{ M HCOO}^-$$

Amounts or concentrations after H^+ reacts with $HCOO^-$:

$$0.040 + 0.005 = 0.045 \text{ mole HCOOH}$$

$$0.060 - 0.005 = 0.055 \text{ mole HCOO}^-$$

or

$$0.43 \text{ M HCOOH and } 0.52 \text{ M HCOO}^-$$

$$[H_3O^+] = 1.8 \times 10^{-4} \times \left(\frac{0.045/\text{vol.}}{0.055/\text{vol.}} \right) = 1.5 \times 10^{-4} \text{ M}$$

d) 2 points

$$0.800 \text{ liter} \times 2.00 \text{ M HCOOH} = 1.60 \text{ moles HCOOH}$$

$$0.200 \text{ liter} \times 4.80 \text{ M NaOH} = 0.96 \text{ mole OH}^-$$

$$1.60 \text{ moles HCOOH} + 0.96 \text{ mole OH}^- \text{ yields } 0.64 \text{ mole HCOOH and } 0.96 \text{ mole HCOO}^-$$

$$[H_3O^+] = 1.8 \times 10^{-4} \times \frac{(0.64 \text{ mole/liter})}{(0.96 \text{ mole/liter})} = 1.2 \times 10^{-4}$$

The alternative approach in part (a) can also be used in part (d)

11. $Al(NO_3)_3$ K_2CO_3 $NaHSO_4$ NH_4Cl

(a) Predict whether a 0.10-molar solution of each of the salts above is acidic, neutral, or basic.

(b) For each of the solutions that is not neutral, write a balanced chemical equation for a reaction occurring with water that supports your prediction.

ANSWER:

a) 4 points

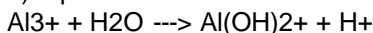
a solution of $Al(NO_3)_3$ is acidic

a solution of K_2CO_3 is basic

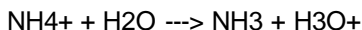
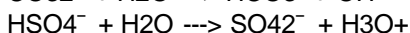
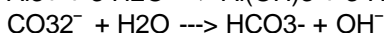
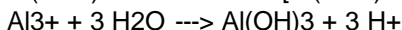
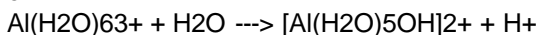
a solution of $NaHSO_4^-$ is acidic

a solution of NH_4Cl is acidic

b) 4 points



or



Equations needed to be balanced and ions must show correct charges. Molecular formulas were acceptable if acids and bases formed were marked strong and weak.

12. 1) A 0.682-gram sample of an unknown weak monoprotic organic acid, HA, was dissolved in sufficient water to make 50 milliliters of solution and was titrated with a 0.135-molar NaOH solution. After the addition of 10.6 milliliters of base, a pH of 5.65 was recorded. The equivalence point (end point) was reached after the addition of 27.4 milliliters of the 0.135-molar NaOH.

(a) Calculate the number of moles of acid in the original sample.

(b) Calculate the molecular weight of the acid HA.

(c) Calculate the number of moles of unreacted HA remaining in solution when the pH was 5.65.

(d) Calculate the $[\text{H}_3\text{O}^+]$ at pH = 5.65.

(e) Calculate the value of the ionization constant, K_a , of the acid HA.

13. 1) The value of the ionization constant, K_a , for hypochlorous acid, HOCl, is 3.2×10^{-8} .

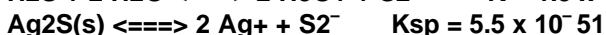
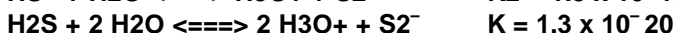
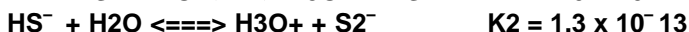
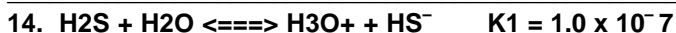
(a) Calculate the hydronium ion concentration of a 0.050-molar solution of HOCl.

(b) Calculate the concentration of hydronium ion in a solution prepared by mixing equal volumes of 0.050-molar HOCl and 0.020-molar sodium hypochlorite, NaOCl.

(c) A solution is prepared by the disproportionation reaction below.



Calculate the pH of the solution if enough chlorine is added to water to make the concentration of HOCl equal to 0.0040-molar.



(a) Calculate the concentration of H_3O^+ of a solution which is 0.10-molar in H_2S .

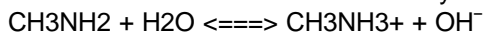
(b) Calculate the concentration of the sulfide ion, S^{2-} , in a solution that is 0.10-molar in H_2S and 0.40-molar in H_3O^+ .

(c) Calculate the maximum concentration of silver ion, Ag^+ , that can exist in a solution that is 1.5×10^{-17} -molar in sulfide ion, S^{2-} .

15. (a) A 4.00 gram sample of NaOH(s) is dissolved in enough water to make 0.50 liter of solution. Calculate the pH of the solution.

(b) Suppose that 4.00 grams of NaOH(s) is dissolved in 1.00 liter of solution that is 0.50 molar in NH_3 and 0.50 molar in NH_4^+ . Assuming there is no change in volume and no loss of NH_3 to the atmosphere, calculate the concentration of hydroxide ion, after chemical reaction has occurred. The K_b for ammonia is 1.8×10^{-5}

16. Methylamine, CH_3NH_2 , is a weak base that ionizes in solution as shown by the following equation.

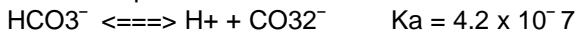


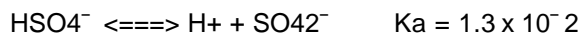
(a) At 25 °C, the percentage ionization in a 0.160-molar solution of CH_3NH_2 is 4.7%. Calculate $[\text{OH}^-]$, $[\text{CH}_3\text{NH}_3^+]$, $[\text{CH}_3\text{NH}_2]$, $[\text{H}_3\text{O}^+]$, and the pH of a 0.160-molar solution of CH_3NH_2 at 25 °C.

(b) Calculate the value for K_b , the ionization constant for CH_3NH_2 , at 25 °C.

(c) If 0.050 mole of crystalline lanthanum nitrate is added to 1.00 liter of a solution containing 0.20 mole of CH_3NH_2 and 0.20 mole of its salt $\text{CH}_3\text{NH}_3\text{Cl}$ at 25 °C, and the solution is stirred until equilibrium is attained, will any $\text{La}(\text{OH})_3$ precipitate? Show the calculations that prove your answer. (The solubility product constant for $\text{La}(\text{OH})_3$, K_{sp} , is 1×10^{-19} at 25 °C.)

17. The equations and constants for the dissociation of three different acids are given below.





- (a) From the systems above, identify the conjugate pair that is best for preparing a buffer with a pH of 7.2.
- (b) Explain briefly how you would prepare the buffer solution described in (a) with the conjugate pair you have chosen.
- (c) If the concentrations of both the acid and the conjugate base you have chosen were doubled, how would the pH be affected? Explain how the capacity of the buffer is affected by this change in concentrations of acid and base.
- (d) Explain briefly how you would prepare the buffer solution in (a) if you had available the solid salt of only one member of the conjugate pair and solutions of a strong acid and a strong base.