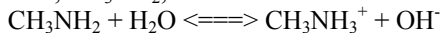


## Chapters 14 &amp; 15 Collected AP Exam Essays - 1980 – 2010

## 1980 - #1

Methylamine,  $\text{CH}_3\text{NH}_2$ , is a weak base that ionizes in solution as shown by the following equation.



- (a) At  $25^\circ\text{C}$ , the percentage ionization in a 0.160-molar solution of  $\text{CH}_3\text{NH}_2$  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  $\text{CH}_3\text{NH}_2$  at  $25^\circ\text{C}$ .
- (b) Calculate the value for  $K_b$ , the ionization constant for  $\text{CH}_3\text{NH}_2$ , at  $25^\circ\text{C}$ .
- (c) If 0.050 mole of crystalline lanthanum nitrate is added to 1.00 liter of a solution containing 0.20 mole of  $\text{CH}_3\text{NH}_2$  and 0.20 mole of its salt  $\text{CH}_3\text{NH}_3\text{Cl}$  at  $25^\circ\text{C}$ , 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  $1 \times 10^{-19}$  at  $25^\circ\text{C}$ .)

## 1981 - #7



- (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.

## 1982 - #1

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

- (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  $\text{HCl}$  is added to 100. milliliters of the original buffer solution. Calculate the  $[\text{H}_3\text{O}^+]$  of the resulting solution.
- (d) A 800-milliliter sample of 2.00-molar formic acid is mixed with 200. milliliters of 4.80-molar  $\text{NaOH}$ . Calculate the  $[\text{H}_3\text{O}^+]$  of the resulting solution.

## 1983 - #3

The molecular weight of a monoprotic acid  $\text{HX}$  was to be determined. A sample of 15.126 grams of  $\text{HX}$  was dissolved in distilled water and the volume brought to exactly 250.00 milliliters in a volumetric flask. Several 50.00-milliliter portions of this solution were titrated against  $\text{NaOH}$  solution, requiring an average of 38.21 milliliters of  $\text{NaOH}$ . The  $\text{NaOH}$  solution was standardized against oxalic acid dihydrate,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$  (molecular weight: 126.066  $\text{g mol}^{-1}$ ). The volume of  $\text{NaOH}$  solution required to neutralize 1.2596 grams of oxalic acid dihydrate was 41.24 milliliters.

- (a) Calculate the molarity of the  $\text{NaOH}$  solution.
- (b) Calculate the number of moles of  $\text{HX}$  in a 50.00-milliliter portion used for titration.
- (c) Calculate the molecular weight of  $\text{HX}$ .
- (d) Discuss the effect on the calculated molecular weight of  $\text{HX}$  if the sample of oxalic acid dihydrate contained a nonacidic impurity.

## 1983 - #6

- (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  $\text{NH}_4\text{Cl}$  and  $\text{HCl}$  solutions.
- Carla C. says she would mix  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3$  solutions.
- Dexter D. says he would mix  $\text{NH}_3$  and  $\text{NaOH}$  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,  $K_a = 1.8 \times 10^{-5}$ ,  $\text{NH}_4^+$ ,  $K_a = 5.6 \times 10^{-10}$ )

**1984 - #1**

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.

- Calculate the  $[\text{OH}^-]$  in the sodium benzoate solution described above.
- Calculate the value for the equilibrium constant for the reaction
$$\text{C}_6\text{H}_5\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{COOH} + \text{OH}^-$$
- Calculate the value of  $K_a$ , the acid dissociation constant for benzoic acid.
- 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.

**1985 - #1**

At 25°C the solubility product constant,  $K_{sp}$ , for strontium sulfate,  $\text{SrSO}_4$ , is  $7.6 \times 10^{-7}$ . The solubility product constant for strontium fluoride,  $\text{SrF}_2$ , is  $7.9 \times 10^{-10}$

- What is the molar solubility of  $\text{SrSO}_4$  in pure water at 25°C?
- What is the molar solubility of  $\text{SrF}_2$  in pure water at 25°C?
- An aqueous solution of  $\text{Sr}(\text{NO}_3)_2$  is added slowly to 1.0 liter of a well-stirred solution containing 0.020 mole  $\text{F}^-$  and 0.10 mole  $\text{SO}_4^{2-}$  at 25°C. (You may assume that the added  $\text{Sr}(\text{NO}_3)_2$  solution does not materially affect the total volume of the system.) Which salt precipitates first? What is the concentration of strontium ion,  $\text{Sr}^{2+}$ , in the solution when the first precipitate begins to form?
- As more  $\text{Sr}(\text{NO}_3)_2$  is added to the mixture in (c) a second precipitate begins to form. At that stage, what percent of the anion of the first precipitate remains in solution?

**1986 - #1 – Average Score: 3.14**

In water, hydrazoic acid,  $\text{HN}_3$ , is a weak acid that has an equilibrium constant,  $K_a$ , equal to  $2.8 \times 10^{-5}$  at 25°C. A 0.300-liter sample of a 0.050-molar solution of the acid is prepared.

- Write the expression for the equilibrium constant,  $K_a$ , for hydrazoic acid.
- Calculate the pH of this solution at 25°C.
- To 0.150 liter of this solution, 0.80 gram of sodium azide,  $\text{NaN}_3$ , is added. The salt dissolves completely. Calculate the pH of the resulting solution at 25°C if the volume of the solution remains unchanged.
- To the remaining 0.150 liter of the original solution, 0.075 liter of 0.100-molar  $\text{NaOH}$  solution is added. Calculate the  $[\text{OH}^-]$  for the resulting solution at 25°C.

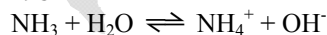
**1986 - #7**



Oxyacids, such as those above, contain an atom bonded to one or more oxygen atoms; one or more of these oxygen atoms may also be bonded to hydrogen.

- Discuss the factors that are often used to predict correctly the strengths of the oxyacids listed above.
- Arrange the examples above in the order of increasing acid strength.

**1987 - #1**



Ammonia is a weak base that dissociates in water as shown above. At 25°C, the base dissociation constant,  $K_b$ , for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .

- Determine the hydroxide ion concentration and the percentage dissociation of a 0.150-molar solution of ammonia at 25°C.
- 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.
- If 0.0800 mole of solid magnesium chloride,  $\text{MgCl}_2$ , 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  $1.5 \times 10^{-11}$ ).

**1987 - #3**

The percentage by weight of nitric acid,  $\text{HNO}_3$ , in a sample of concentrated nitric acid is to be determined.

- (a) Initially, a NaOH solution was standardized by titration with a sample of potassium hydrogen phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ , a monoprotic acid often used as a primary standard. A sample of pure  $\text{KHC}_8\text{H}_4\text{O}_4$  weighing 1.518 grams was dissolved in water and titrated with NaOH solution. To reach the equivalence point, 26.90 milliliters of base required. Calculate the molarity of the NaOH solution. (Molecular weight:  $\text{KHC}_8\text{H}_4\text{O}_4 = 204.2$ )
- (b) A 10.00-milliliter sample of the concentrated nitric acid was diluted with water to a total volume of 500.0 milliliters. Then 25.00 milliliters of the diluted acid solution was titrated with the standardized NaOH prepared in part (a). The equivalence point was reached after 28.35 milliliters of the base had been added. Calculate the molarity of the concentrated nitric acid.
- (c) The density of the concentrated nitric used in this experiment was determined to be 1.42 grams per milliliter. Determine percentage by weight of  $\text{HNO}_3$  in the original sample of concentrated nitric acid.

**1988 - #7**

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.

**1989 - #1 Average Score: 2.3**

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,  $\text{A}^-$ , with water.
- (d) Calculate the pH of the solution at the equivalence point of the titration.

**1990 - #1**

The solubility of iron(II) hydroxide,  $\text{Fe}(\text{OH})_2$ , is  $1.43 \times 10^{-3}$  gram per liter at  $25^\circ\text{C}$ .

- (a) Write a balanced equation for the solubility equilibrium.
- (b) Write the expression for the solubility product constant,  $K_{sp}$ , and calculate its value.
- (c) Calculate the pH of the saturated solution of  $\text{Fe}(\text{OH})_2$  at  $25^\circ\text{C}$ .
- (d) A 50.0-milliliter sample of  $3.00 \times 10^{-3}$  molar  $\text{FeSO}_4$  solution is added to 50.0 milliliters of  $4.00 \times 10^{-6}$  molar NaOH solution. Does a precipitate of  $\text{Fe}(\text{OH})_2$  form? Explain and show calculations to support your answer.

**1990 - #8**

Give a brief explanation for each of the following.

- (a) For the diprotic acid  $\text{H}_2\text{S}$ , the first dissociation constant is larger than the second dissociation constant by about  $10^5$  ( $K_1 = 10^5 K_2$ ).
- (b) In water, NaOH is a base, but HOCl is an acid.
- (c) HCl and HI are equally strong acids in water but, in pure acetic acid, HI is a stronger acid than HCl.
- (d) When each is dissolved in water, HCl is a much stronger acid than HF.

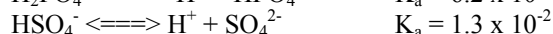
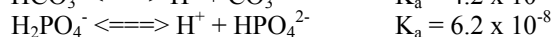
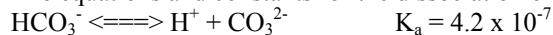
**1991 - #1**

The acid ionization constant,  $K_a$ , for propanoic acid,  $C_2H_5COOH$ , is  $1.3 \times 10^{-5}$ .

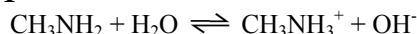
- Calculate the hydrogen ion concentration,  $[H^+]$ , in a 0.20-molar solution of propanoic acid.
- Calculate the percentage of propanoic acid molecules that are ionized in the solution in (a).
- What is the ratio of the concentration of propanoate ion,  $C_2H_5COO^-$ , to that of propanoic acid in a buffer solution with a pH of 5.20?
- 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.

**1992 - #6**

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

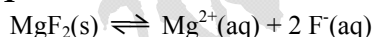


- From the systems above, identify the conjugate pair that is best for preparing a buffer with a pH of 7.2.
- Explain briefly how you would prepare the buffer solution described in (a) with the conjugate pair you have chosen.
- If the concentrations of both the acid and the conjugate base you have chosen 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.
- 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.

**1993 - #1**

Methylamine,  $CH_3NH_2$ , is a weak base that reacts according to the equation above. The value of the ionization constant,  $K_b$ , is  $5.25 \times 10^{-4}$ . Methylamine forms salts such as methylammonium nitrate,  $(CH_3NH_3^+)(NO_3^-)$ .

- Calculate the hydroxide ion concentration,  $[OH^-]$ , of a 0.225-molar solution of methylamine.
- Calculate the pH of a solution made by adding 0.0100 mole of a solid methylammonium nitrate to 120.0 milliliters of a 0.225-molar solution of methylamine. Assume that no volume change occurs.
- How many moles of either NaOH or HCl (state clearly which you choose) should be added to the solution in (b) to produce a solution that has a pH of 11.00? Assume that no volume change occurs.
- A volume of 100. milliliters of distilled water is added to the solution in (c). How is the pH of the solution affected? Explain.

**1994 - #1**

In a saturated solution of  $MgF_2$  at  $18^\circ C$ , the concentration of  $Mg^{2+}$  is  $1.21 \times 10^{-3}$  molar. The equilibrium is represented by the equation above.

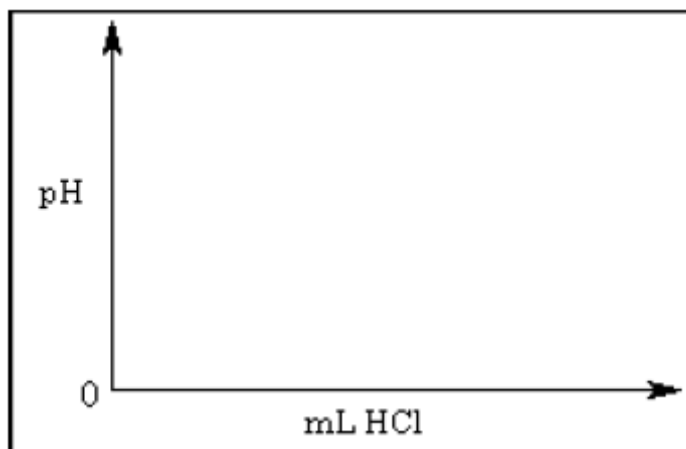
- Write the expression for the solubility-product constant,  $K_{sp}$ , and calculate its value at  $18^\circ C$ .
- Calculate the equilibrium concentration of  $Mg^{2+}$  in 1.000 liter of saturated  $MgF_2$  solution at  $18^\circ C$  to which 0.100 mole of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
- Predict whether a precipitate of  $MgF_2$  will form when 100.0 milliliters of a  $3.00 \times 10^{-3}$  molar  $Mg(NO_3)_2$  solution is mixed with 200.0 milliliters of a  $2.00 \times 10^{-3}$  molar NaF solution at  $18^\circ C$ . Calculations to support your prediction must be shown.
- At  $27^\circ C$  the concentration of  $Mg^{2+}$  in a saturated solution of  $MgF_2$  is  $1.17 \times 10^{-3}$  molar. Is the dissolving of  $MgF_2$  in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

**1994 - #7**

A chemical reaction occurs when 100. milliliters of 0.2000-molar HCl is added dropwise to 100. milliliters of 0.100-molar  $Na_3PO_4$  solution.

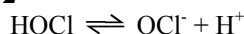
- Write the two net ionic equations for the formation of the major species.
- Identify the species that acts as both a Brønsted acid and as a Brønsted base in the equations in (a). Draw the Lewis electron-dot diagram for this species.

(c) Sketch a graph using the axis provided, showing the shape of the titration curve that results when 100. milliliters of the HCl solution is added slowly from a buret to the  $\text{Na}_3\text{PO}_4$  solution. Account for the shape of the curve.



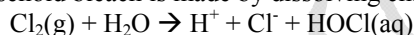
(d) Write the equation for the reaction that occurs if a few additional milliliters of HCl solution are added to the solution resulting from the titration in (c).

**1996 - #2**



Hypochlorous acid, HOCl, is a weak acid commonly used as a bleaching agent. The acid-dissociation constant,  $K_a$ , for the reaction represented above is  $3.2 \times 10^{-8}$ .

- Calculate the  $[\text{H}^+]$  of a 0.14-molar solution of HOCl.
- Write the correctly balanced net ionic equation for the reaction that occurs NaOCl is dissolved in water and calculate the numerical value of the equilibrium constant for the reaction.
- Calculate the pH of a solution made by combining 40.0 milliliters of 0.14-molar HOCl and 10.0 milliliters of 0.56-molar NaOH.
- How many millimoles of solid NaOH must be added to 50.0 milliliters of 0.20-molar HOCl to obtain a buffer solution that has a pH of 7.49? Assume that the addition of the solid NaOH results in a negligible change in volume.
- Household bleach is made by dissolving chlorine gas in water, as represented below.



Calculate the pH of such a solution if the concentration of HOCl in the solution is 0.065 molar.

**1997 - #2**

The overall dissociation of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$  is represented below. The overall dissociation constant is also indicated.



- What volume of 0.400-molar NaOH is required to neutralize completely a  $5.00 \times 10^{-3}$ -mole sample of pure oxalic acid?
- Give the equations representing the first and second dissociations of oxalic acid. Calculate the value of the first dissociation constant,  $K_1$ , for oxalic acid if the value of the second dissociation constant,  $K_2$ , is  $6.40 \times 10^{-5}$ .
- To a 0.015-molar solution of oxalic acid, a strong acid is added until the pH is 0.5. Calculate the  $[\text{C}_2\text{O}_4^{2-}]$  in the resulting solution. (Assume the change in volume is negligible.)
- Calculate the value of the equilibrium constant,  $K_b$ , for the reaction that occurs when solid  $\text{Na}_2\text{C}_2\text{O}_4$  is dissolved in water.

**1998 - #1**

Solve the following problem related to the solubility equilibria of some metal hydroxides in aqueous solution.

- The solubility of  $\text{Cu}(\text{OH})_2$  is  $1.72 \times 10^{-6}$  gram per 100. milliliters of solution at  $25^\circ\text{C}$ .
  - Write the balanced chemical equation for the dissociation of  $\text{Cu}(\text{OH})_2(\text{s})$  in aqueous solution.
  - Calculate the solubility (in moles per liter) of  $\text{Cu}(\text{OH})_2$  at  $25^\circ\text{C}$ .
  - Calculate the value of the solubility-product constant,  $K_{\text{sp}}$ , for  $\text{Cu}(\text{OH})_2$  at  $25^\circ\text{C}$ .
- The value of the solubility-product constant,  $K_{\text{sp}}$ , for  $\text{Zn}(\text{OH})_2$  is  $7.7 \times 10^{-17}$  at  $25^\circ\text{C}$ .
  - Calculate the solubility (in moles per liter) of  $\text{Zn}(\text{OH})_2$  at  $25^\circ\text{C}$  in a solution with a pH of 9.35.

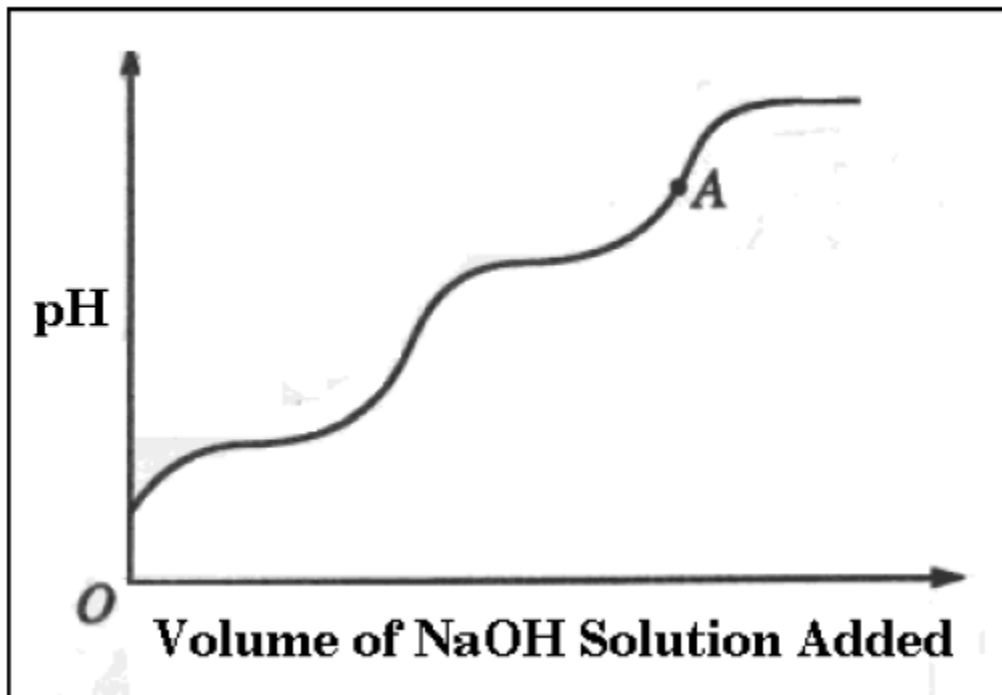
(ii) At 25°C, 50.0 milliliters of 0.100-molar  $\text{Zn}(\text{NO}_3)_2$  is mixed with 50.0 milliliters of 0.300-molar NaOH. Calculate the molar concentration of  $\text{Zn}^{2+}(\text{aq})$  in the resulting solution once equilibrium has been established. Assume that volumes are additive.

**1998 - #5**

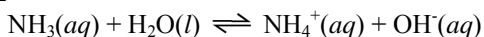
An approximately 0.1-molar solution of NaOH is to be standardized by titration. Assume that the following materials are available.

Clean, dry 50 mL buret	Analytical balance
250 mL Erlenmeyer flask	Phenolphthalein indicator solution
Wash bottle filled with distilled water	Potassium hydrogen phthalate, KHP, a pure solid monoprotic acid (to be used as the primary standard)

- (a) Briefly describe the steps you would take, using materials listed above, to standardize the NaOH solution.
- (b) Describe (i.e., set up) the calculations necessary to determine the concentration of the NaOH solution.
- (c) After the NaOH solution has been standardized, it is used to titrate a weak monoprotic acid, HX. The equivalence point is reached when 25.0 mL of NaOH solution has been added. In the space provided at the right, sketch the titration curve, showing the pH changes that occur as the volume of NaOH solution added increases from 0 to 35.0 mL. Clearly label the equivalence point on the curve.
- (d) Describe how the value of the acid-dissociation constant,  $K_a$ , for the weak acid HX could be determined from the titration curve in part (c).
- (e) The graph below shows the results obtained by titrating a different weak acid,  $\text{H}_2\text{Y}$ , with the standardized NaOH solution. Identify the negative ion that is present in the highest concentration at the point in the titration represented by the letter A on the curve.



**1999 -#1**



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  $5.60 \times 10^{-4}$  M. In answering the following, assume that temperature is constant at 25°C and that volumes are additive.

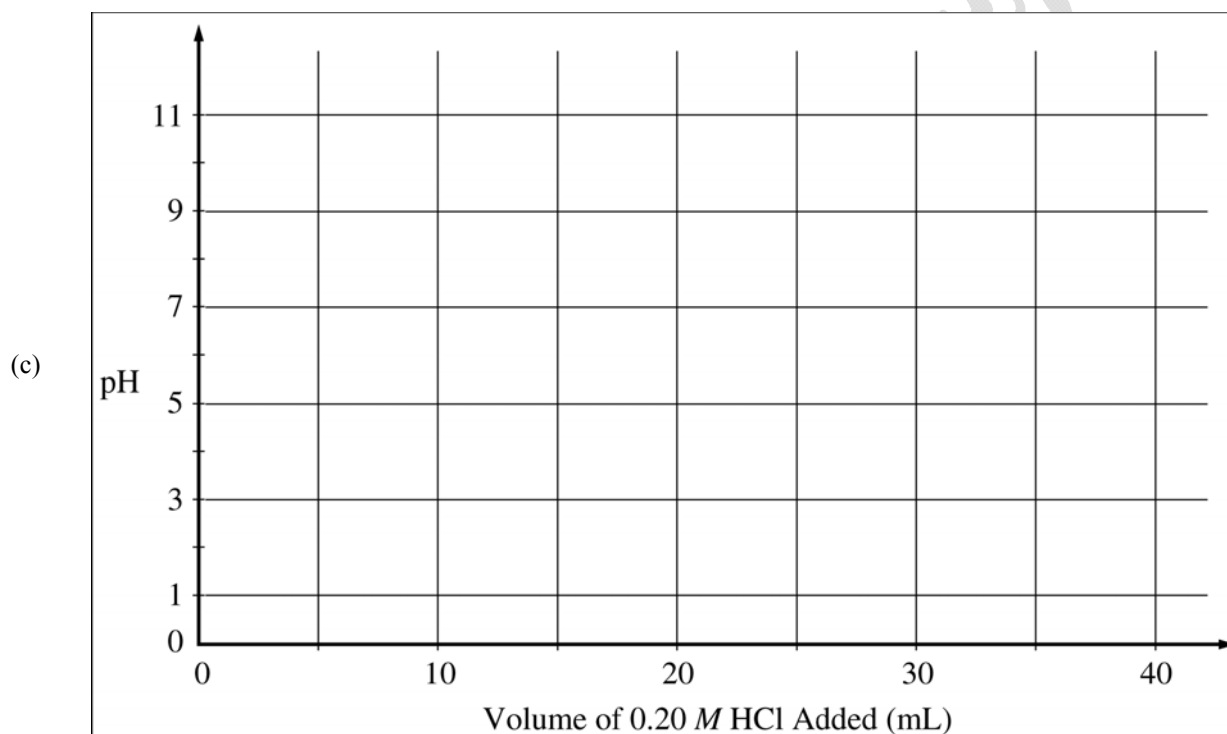
- (a) Write the equilibrium-constant expression for the reaction represented above.
- (b) Determine the pH of 0.0180 M  $\text{NH}_3(\text{aq})$ .
- (c) Determine the value of the base ionization constant,  $K_b$ , for  $\text{NH}_3(\text{aq})$ .
- (d) Determine the percent ionization of  $\text{NH}_3$  in 0.0180 M  $\text{NH}_3(\text{aq})$ .

- (e) In an experiment, a 20.0 mL sample of 0.0180 M  $\text{NH}_3(aq)$  was placed in a flask and titrated to the equivalence point and beyond using 0.0120 M  $\text{HCl}(aq)$ .
- Determine the volume of 0.0120 M  $\text{HCl}(aq)$  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  $\text{HCl}(aq)$  was added.
  - Determine the pH of the solution in the flask after a total of 40.0 mL of 0.0120 M  $\text{HCl}(aq)$  was added.

**2000 - #8**

A volume of 30.0 mL of 0.10 M  $\text{NH}_3(aq)$  is titrated with 0.20 M  $\text{HCl}(aq)$ . The value of the base-dissociation constant,  $K_b$ , for  $\text{NH}_3$  in water is  $1.8 \times 10^{-5}$  at 25°C.

- Write the net-ionic equation for the reaction of  $\text{NH}_3(aq)$  with  $\text{HCl}(aq)$ .
- Using the axes provided below, sketch the titration curve that results when a total of 40.0 mL of 0.20 M  $\text{HCl}(aq)$  is added dropwise to the 30.0 mL volume of 0.10 M  $\text{NH}_3(aq)$ .



From the table below, select the most appropriate indicator for the titration. Justify your choice.

Indicator	pKa
Methyl Red	5.5
Bromothymol Blue	7.1
Phenolphthalein	8.7

- If equal volumes of 0.10 M  $\text{NH}_3(aq)$  and 0.10 M  $\text{NH}_4\text{Cl}(aq)$  are mixed, is the resulting solution acidic, neutral, or basic? Explain.

**2001 - #1**

Answer the following questions relating to the solubility of the chlorides of silver and lead.

- At 10°C,  $8.9 \times 10^{-5}$  g of  $\text{AgCl}(s)$  will dissolve in 100. mL of water.
  - Write the equation for the dissociation of  $\text{AgCl}(s)$  in water.
  - Calculate the solubility, in  $\text{mol L}^{-1}$ , of  $\text{AgCl}(s)$  in water at 10°C.
  - Calculate the value of the solubility-product constant,  $K_{sp}$ , for  $\text{AgCl}(s)$  at 10°C.
- At 25°C, the value of  $K_{sp}$  for  $\text{PbCl}_2(s)$  is  $1.6 \times 10^{-5}$  and the value of  $K_{sp}$  for  $\text{AgCl}(s)$  is  $1.8 \times 10^{-10}$ .
  - If 60.0 mL of 0.0400 M  $\text{NaCl}(aq)$  is added to 60.0 mL of 0.0300 M  $\text{Pb}(\text{NO}_3)_2(aq)$ , will a precipitate form? Assume that volumes are additive. Show calculations to support your answer.

- (ii) Calculate the equilibrium value of  $[\text{Pb}^{2+}(aq)]$  in 1.00 L of saturated  $\text{PbCl}_2$  solution to which 0.250 mole of  $\text{NaCl}(s)$  has been added. Assume that no volume change occurs.
- (iii) If 0.100 M  $\text{NaCl}(aq)$  is added slowly to a beaker containing both 0.120 M  $\text{AgNO}_3(aq)$  and 0.150 M  $\text{Pb}(\text{NO}_3)_2(aq)$  at 25°C, which will precipitate first,  $\text{AgCl}(s)$  or  $\text{PbCl}_2(s)$ ? Show calculations to support your answer.

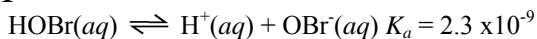
**2001 - #3d**

A  $2.00 \times 10^{-3}$  mole sample of pure acetylsalicylic acid was dissolved in 15.00 mL of water and then titrated with 0.100 M  $\text{NaOH}(aq)$ . The equivalence point was reached after 20.00 mL of the  $\text{NaOH}$  solution had been added. Using the data from the titration, shown in the table below, determine

- (i) the value of the acid dissociation constant,  $K_a$ , for acetylsalicylic acid and
- (ii) the pH of the solution after a total volume of 25.00 mL of the  $\text{NaOH}$  solution had been added (assume that volumes are additive).

Volume of 0.100 M NaOH Added (mL)	pH
0.00	2.22
5.00	2.97
10.00	3.44
15.00	3.92
20.00	8.13
25.00	?

**2002 - #1**



Hypobromous acid,  $\text{HOBr}$ , is a weak acid that dissociates in water, as represented by the equation above.

- (a) Calculate the value of  $[\text{H}^+]$  in an  $\text{HOBr}$  solution that has a pH of 4.95.
- (b) Write the equilibrium constant expression for the ionization of  $\text{HOBr}$  in water, then calculate the concentration of  $\text{HOBr}(aq)$  in an  $\text{HOBr}$  solution that has  $[\text{H}^+]$  equal to  $1.8 \times 10^{-5} M$ .
- (c) A solution of  $\text{Ba}(\text{OH})_2$  is titrated into a solution of  $\text{HOBr}$ .
- (i) Calculate the volume of 0.115 M  $\text{Ba}(\text{OH})_2(aq)$  needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 M  $\text{HOBr}(aq)$ .
- (ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.
- (d) Calculate the number of moles of  $\text{NaOBr}(s)$  that would have to be added to 125 mL of 0.160 M  $\text{HOBr}$  to produce a buffer solution with  $[\text{H}^+] = 5.00 \times 10^{-9} M$ . Assume that volume change is negligible.
- (e)  $\text{HOBr}$  is a weaker acid than  $\text{HBrO}_3$ . Account for this fact in terms of molecular structure.

**2002B - #1**



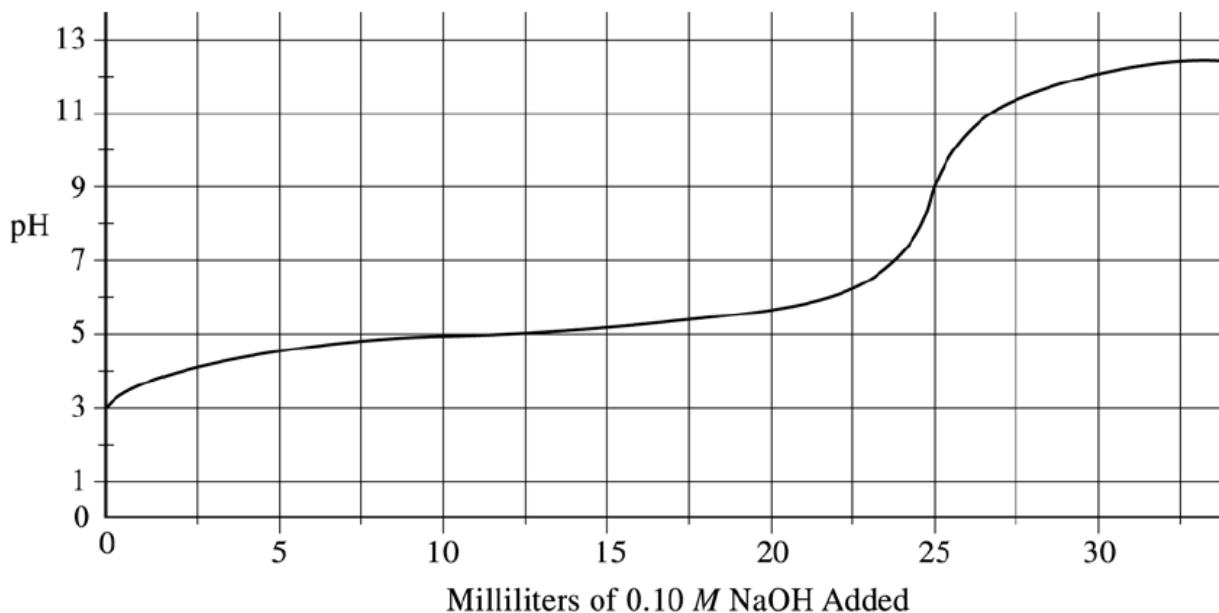
Lactic acid,  $\text{HC}_3\text{H}_5\text{O}_3$ , is a monoprotic acid that dissociates in aqueous solution, as represented by the equation above. Lactic acid is 1.66 percent dissociated in 0.50 M  $\text{HC}_3\text{H}_5\text{O}_3(aq)$  at 298 K. For parts (a) through (d) below, assume the temperature remains at 298 K.

- (a) Write the expression for the acid-dissociation constant,  $K_a$ , for lactic acid and calculate its value.
- (b) Calculate the pH of 0.50 M  $\text{HC}_3\text{H}_5\text{O}_3$ .
- (c) Calculate the pH of a solution formed by dissolving 0.045 mole of solid sodium lactate,  $\text{NaC}_3\text{H}_5\text{O}_3$ , in 250. mL of 0.50 M  $\text{HC}_3\text{H}_5\text{O}_3$ . Assume that volume change is negligible.
- (d) A 100. mL sample of 0.10 M  $\text{HCl}$  is added to 100. mL of 0.50 M  $\text{HC}_3\text{H}_5\text{O}_3$ . Calculate the molar concentration of lactate ion,  $\text{C}_3\text{H}_5\text{O}_3^-$ , in the resulting solution.

**2002B - #8**

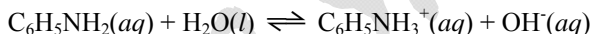
The graph below shows the result of the titration of a 25 mL sample of a 0.10 M solution of a weak acid,  $\text{HA}$ , with a strong base, 0.10 M  $\text{NaOH}$ .





- (a) Describe two features of the graph above that identify HA as a weak acid.
- (b) Describe one method by which the value of the acid-dissociation constant for HA can be determined using the graph above.
- (c) On the graph above, sketch the titration curve that would result if 25 mL of 0.10 M HCl were used instead of 0.10 M HA.
- (d) A 25 mL sample of 0.10 M HA is titrated with 0.20 M NaOH.
- What volume of base must be added to reach the equivalence point?
  - The pH at the equivalence point for this titration is slightly higher than the pH at the equivalence point in the titration using 0.10 M NaOH. Explain.

### 2003 - #1



Aniline, a weak base, reacts with water according to the reaction represented above.

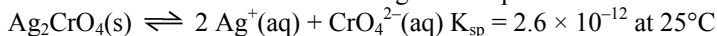
- Write the equilibrium constant expression,  $K_b$ , for the reaction represented above.
- A sample of aniline is dissolved in water to produce 25.0 mL of a 0.10 M solution. The pH of the solution is 8.82. Calculate the equilibrium constant,  $K_b$ , for this reaction.
- The solution prepared in part (b) is titrated with 0.10 M HCl. Calculate the pH of the solution when 5.0 mL of the acid has been added.
- Calculate the pH at the equivalence point of the titration in part (c).
- The  $\text{p}K_a$  values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

Indicator	$\text{p}K_a$
Erythrosine	3
Litmus	7
Thymolphthalein	10

### 2004 - #1

Answer the following questions relating to the solubilities of two silver compounds,  $\text{Ag}_2\text{CrO}_4$  and  $\text{Ag}_3\text{PO}_4$ .

Silver chromate dissociates in water according to the equation shown below.



- Write the equilibrium-constant expression for the dissolving of  $\text{Ag}_2\text{CrO}_4(\text{s})$ .
- Calculate the concentration, in  $\text{mol L}^{-1}$ , of  $\text{Ag}^+(\text{aq})$  in a saturated solution of  $\text{Ag}_2\text{CrO}_4$  at  $25^\circ\text{C}$ .
- Calculate the maximum mass, in grams, of  $\text{Ag}_2\text{CrO}_4$  that can dissolve in 100. mL of water at  $25^\circ\text{C}$ .

(d) A 0.100 mol sample of solid  $\text{AgNO}_3$  is added to a 1.00 L saturated solution of  $\text{Ag}_2\text{CrO}_4$ . Assuming no volume change, does  $[\text{CrO}_4^{2-}]$  increase, decrease, or remain the same? Justify your answer.

In a saturated solution of  $\text{Ag}_3\text{PO}_4$  at  $25^\circ\text{C}$ , the concentration of  $\text{Ag}^+(\text{aq})$  is  $5.3 \times 10^{-5} \text{ M}$ . The equilibrium constant expression for the dissolving of  $\text{Ag}_3\text{PO}_4(\text{s})$  in water is shown below.

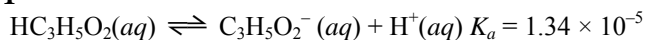
$$K_{\text{sp}} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$$

(e) Write the balanced equation for the dissolving of  $\text{Ag}_3\text{PO}_4$  in water.

(f) Calculate the value of  $K_{\text{sp}}$  for  $\text{Ag}_3\text{PO}_4$  at  $25^\circ\text{C}$ .

(g) A 1.00 L sample of saturated  $\text{Ag}_3\text{PO}_4$  solution is allowed to evaporate at  $25^\circ\text{C}$  to a final volume of 500. mL. What is  $[\text{Ag}^+]$  in the solution? Justify your answer.

### 2005 - #1



Propanoic acid,  $\text{HC}_3\text{H}_5\text{O}_2$ , ionizes in water according to the equation above.

(a) Write the equilibrium-constant expression for the reaction.

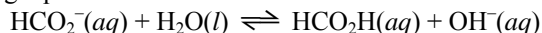
(b) Calculate the pH of a 0.265 M solution of propanoic acid.

(c) A 0.496 g sample of sodium propanoate,  $\text{NaC}_3\text{H}_5\text{O}_2$ , is added to a 50.0 mL sample of a 0.265 M solution of propanoic acid. Assuming that no change in the volume of the solution occurs, calculate each of the following.

(i) The concentration of the propanoate ion,  $\text{C}_3\text{H}_5\text{O}_2^-(\text{aq})$ , in the solution

(ii) The concentration of the  $\text{H}^+(\text{aq})$  ion in the solution

The methanoate ion,  $\text{HCO}_2^-(\text{aq})$ , reacts with water to form methanoic acid and hydroxide ion, as shown in the following equation.



(d) Given that  $[\text{OH}^-]$  is  $4.18 \times 10^{-6} \text{ M}$  in a 0.309 M solution of sodium methanoate, calculate each of the following.

(i) The value of  $K_b$  for the methanoate ion,  $\text{HCO}_2^-(\text{aq})$

(ii) The value of  $K_a$  for methanoic acid,  $\text{HCO}_2\text{H}$

(e) Which acid is stronger, propanoic acid or methanoic acid? Justify your answer.

### 2005B - #1

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = 3.2 \times 10^{-8}$$

Hypochlorous acid,  $\text{HOCl}$ , is a weak acid in water. The  $K_a$  expression for  $\text{HOCl}$  is shown above.

(a) Write a chemical equation showing how  $\text{HOCl}$  behaves as an acid in water.

(b) Calculate the pH of a 0.175 M solution of  $\text{HOCl}$ .

(c) Write the net ionic equation for the reaction between the weak acid  $\text{HOCl}(\text{aq})$  and the strong base  $\text{NaOH}(\text{aq})$ .

(d) In an experiment, 20.00 mL of 0.175 M  $\text{HOCl}(\text{aq})$  is placed in a flask and titrated with 6.55 mL of 0.435 M  $\text{NaOH}(\text{aq})$ .

(i) Calculate the number of moles of  $\text{NaOH}(\text{aq})$  added.

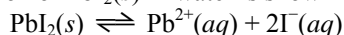
(ii) Calculate  $[\text{H}_3\text{O}^+]$  in the flask after the  $\text{NaOH}(\text{aq})$  has been added.

(iii) Calculate  $[\text{OH}^-]$  in the flask after the  $\text{NaOH}(\text{aq})$  has been added.

### 2006 - #1

Answer the following questions that relate to solubility of salts of lead and barium.

(a) A saturated solution is prepared by adding excess  $\text{PbI}_2(\text{s})$  to distilled water to form 1.0 L of solution at  $25^\circ\text{C}$ . The concentration of  $\text{Pb}^{2+}(\text{aq})$  in the saturated solution is found to be  $1.3 \times 10^{-3} \text{ M}$ . The chemical equation for the dissolution of  $\text{PbI}_2(\text{s})$  in water is shown below.



(i) Write the equilibrium-constant expression for the equation.

(ii) Calculate the molar concentration of  $\text{I}^-(\text{aq})$  in the solution.

(iii) Calculate the value of the equilibrium constant,  $K_{\text{sp}}$ .

(b) A saturated solution is prepared by adding  $\text{PbI}_2(\text{s})$  to distilled water to form 2.0 L of solution at  $25^\circ\text{C}$ . What are the molar concentrations of  $\text{Pb}^{2+}(\text{aq})$  and  $\text{I}^-(\text{aq})$  in the solution? Justify your answer.

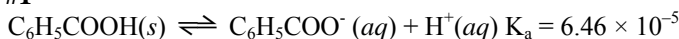
(c) Solid  $\text{NaI}$  is added to a saturated solution of  $\text{PbI}_2$  at  $25^\circ\text{C}$ . Assuming that the volume of the solution does not change, does the molar concentration of  $\text{Pb}^{2+}(\text{aq})$  in the solution increase, decrease, or remain the same? Justify your answer.

(d) The value of  $K_{sp}$  for the salt  $BaCrO_4$  is  $1.2 \times 10^{-10}$ . When a 500. mL sample of  $8.2 \times 10^{-6} M Ba(NO_3)_2$  is added to 500. mL of  $8.2 \times 10^{-6} M Na_2CrO_4$ , no precipitate is observed.

(i) Assuming that volumes are additive, calculate the molar concentrations of  $Ba^{2+}(aq)$  and  $CrO_4^{2-}(aq)$  in the 1.00 L of solution.

(ii) Use the molar concentrations of  $Ba^{2+}(aq)$  ions and  $CrO_4^{2-}(aq)$  ions as determined above to show why a precipitate does not form. You must include a calculation as part of your answer.

### 2006B - #1



Benzoic acid,  $C_6H_5COOH$ , dissociates in water as shown in the equation above. A 25.0 mL sample of an aqueous solution of pure benzoic acid is titrated using standardized 0.150 M NaOH.

(a) After addition of 15.0 mL of the 0.150 M NaOH, the pH of the resulting solution is 4.37. Calculate each of the following.

- $[H^+]$  in the solution
- $[OH^-]$  in the solution
- The number of moles of NaOH added
- The number of moles of  $C_6H_5COO^-(aq)$  in the solution
- The number of moles of  $C_6H_5COOH$  in the solution

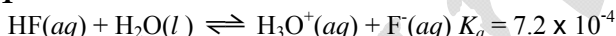
(b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning.

In a different titration, a 0.7529 g sample of a mixture of solid  $C_6H_5COOH$  and solid NaCl is dissolved in water and titrated with 0.150 M NaOH. The equivalence point is reached when 24.78 mL of the base solution is added.

(c) Calculate each of the following.

- The mass, in grams, of benzoic acid in the solid sample
- The mass percentage of benzoic acid in the solid sample

### 2007 - #1

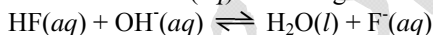


Hydrofluoric acid,  $HF(aq)$ , dissociates in water as represented by the equation above.

(a) Write the equilibrium-constant expression for the dissociation of  $HF(aq)$  in water.

(b) Calculate the molar concentration of  $H_3O^+$  in a 0.40 M  $HF(aq)$  solution.

$HF(aq)$  reacts with  $NaOH(aq)$  according to the reaction represented below.



A volume of 15 mL of 0.40 M  $NaOH(aq)$  is added to 25 mL of 0.40 M  $HF(aq)$  solution. Assume that volumes are additive.

(c) Calculate the number of moles of  $HF(aq)$  remaining in the solution.

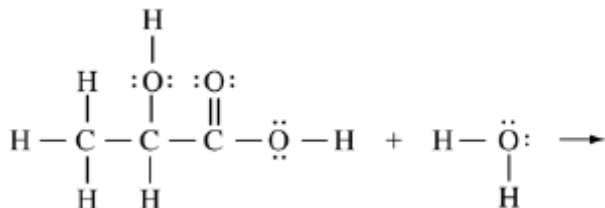
(d) Calculate the molar concentration of  $F^-(aq)$  in the solution.

(e) Calculate the pH of the solution.

### 2007B - #5

Answer the following questions about laboratory situations involving acids, bases, and buffer solutions.

(a) Lactic acid,  $HC_3H_5O_3$ , reacts with water to produce an acidic solution. Shown below are the complete Lewis structures of the reactants.



In the space provided above, complete the equation by drawing the complete Lewis structures of the reaction products.

(b) Choosing from the chemicals and equipment listed below, describe how to prepare 100.00 mL of a 1.00 M aqueous solution of  $NH_4Cl$  (molar mass  $53.5 \text{ g mol}^{-1}$ ). Include specific amounts and equipment where appropriate.

$\text{NH}_4\text{Cl}(s)$       50 mL buret                      100 mL graduated cylinder                      100 mL pipet  
 Distilled water    100 mL beaker                      100 mL volumetric flask                      Balance

(c) Two buffer solutions, each containing acetic acid and sodium acetate, are prepared. A student adds 0.10 mol of HCl to 1.0 L of each of these buffer solutions and to 1.0 L of distilled water. The table below shows the pH measurements made before and after the 0.10 mol of HCl is added.

	pH Before HCl Added	pH After HCl Added
Distilled water	7.0	1.0
Buffer 1	4.7	2.7
Buffer 2	4.7	4.3

- (i) Write the balanced net-ionic equation for the reaction that takes place when the HCl is added to buffer 1 or buffer 2.  
 (ii) Explain why the pH of buffer 1 is different from the pH of buffer 2 after 0.10 mol of HCl is added.  
 (iii) Explain why the pH of buffer 1 is the same as the pH of buffer 2 before 0.10 mol of HCl is added.

### 2009 - #1

Answer the following questions that relate to the chemistry of halogen oxoacids.

(a) Use the information in the table below to answer part (a)(i).

Acid	$K_a$ at 298 K
HOCl	$2.9 \times 10^{-8}$
HOBr	$2.4 \times 10^{-9}$

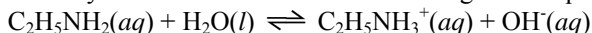
- (i) Which of the two acids is stronger, HOCl or HOBr? Justify your answer in terms of  $K_a$ .  
 (ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).  
 (iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.
- (b) Write the equation for the reaction that occurs between hypochlorous acid and water.
- (c) A 1.2 M NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction  $\text{OCl}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOCl}(aq) + \text{OH}^-(aq)$  occurs.
- (i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between  $\text{OCl}^-(aq)$  and  $\text{H}_2\text{O}(l)$ .  
 (ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.  
 (iii) Calculate the value of  $[\text{OH}^-]$  in the 1.2 M NaOCl solution at 298 K.
- (d) A buffer solution is prepared by dissolving some solid NaOCl in a solution of HOCl at 298 K. The pH of the buffer solution is determined to be 6.48.
- (i) Calculate the value of  $[\text{H}_3\text{O}^+]$  in the buffer solution.  
 (ii) Indicate which of  $\text{HOCl}(aq)$  or  $\text{OCl}^-(aq)$  is present at the higher concentration in the buffer solution. Support your answer with a calculation.

### 2009B - #1

A pure 14.85 g sample of the weak base ethylamine,  $\text{C}_2\text{H}_5\text{NH}_2$ , is dissolved in enough distilled water to make 500. mL of solution.

(a) Calculate the molar concentration of the  $\text{C}_2\text{H}_5\text{NH}_2$  in the solution.

The aqueous ethylamine reacts with water according to the equation below.



(b) Write the equilibrium-constant expression for the reaction between  $\text{C}_2\text{H}_5\text{NH}_2(aq)$  and water.

(c) Of  $\text{C}_2\text{H}_5\text{NH}_2(aq)$  and  $\text{C}_2\text{H}_5\text{NH}_3^+(aq)$ , which is present in the solution at the higher concentration at equilibrium? Justify your answer.

(d) A different solution is made by mixing 500. mL of 0.500 M  $\text{C}_2\text{H}_5\text{NH}_2$  with 500. mL of 0.200 M HCl.

Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.

(i) Calculate the concentration of  $\text{OH}^-(aq)$  in the solution.

- (ii) Write the net-ionic equation that represents the reaction that occurs when the  $\text{C}_2\text{H}_5\text{NH}_2$  solution is mixed with the  $\text{HCl}$  solution.
- (iii) Calculate the molar concentration of the  $\text{C}_2\text{H}_5\text{NH}_3^+(aq)$  that is formed in the reaction.
- (iv) Calculate the value of  $K_b$  for  $\text{C}_2\text{H}_5\text{NH}_2$ .

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