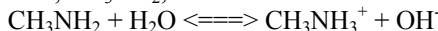


Chapters 14 & 15 Collected AP Exam Essays - 1980 – 2010 Answers

1980 - #1

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 .

$[\text{OH}^-]$, $[\text{CH}_3\text{NH}_3^+] = 0.00752 \text{ M}$, $[\text{CH}_3\text{NH}_2] = 0.160 \text{ M}$, $[\text{H}_3\text{O}^+] = 1.3 \times 10^{-12} \text{ M}$, **pH = 11.88**

(b) Calculate the value for K_b , the ionization constant for CH_3NH_2 , at 25°C . **$K_b = 3.5 \times 10^{-4}$**

(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 .)

$$K_b = 3.5 \times 10^{-4} = \frac{(0.20)(x)}{(0.20)} = x = [\text{OH}^-]$$

$$Q = [\text{La}^{3+}][\text{OH}^-]^3 = (0.050)(3.5 \times 10^{-4})^3 = 2.2 \times 10^{-12}$$

$Q > K_{sp}$, therefore $\text{La}(\text{OH})_3$ precipitation occurs.

1981 - #7



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

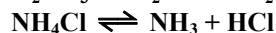
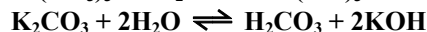
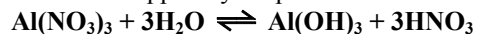
a solution of $\text{Al}(\text{NO}_3)_3$ is acidic

a solution of K_2CO_3 is basic

a solution of NaHSO_4 is neutral

a solution of NH_4Cl is acidic

(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, 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. **pH = 3.92**

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

(c) A 5.00-milliliter sample of 1.00-molar HCl is added to 100. milliliters of the original buffer solution.

Calculate the $[\text{H}_3\text{O}^+]$ of the resulting solution. **$[\text{H}_3\text{O}^+] = 1.5 \times 10^{-4} \text{ M}$**

(d) A 800-milliliter sample of 2.00-molar formic acid is mixed with 200. milliliters of 4.80-molar NaOH . Calculate the $[\text{H}_3\text{O}^+]$ of the resulting solution. **$[\text{H}_3\text{O}^+] = 1.2 \times 10^{-4}$**

1983 - #3

The molecular weight of a monoprotic acid HX was to be determined. A sample of 15.126 grams of 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 NaOH solution, requiring an average of 38.21 milliliters of NaOH . The 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 g mol^{-1}). The volume of NaOH solution required to neutralize 1.2596 grams of oxalic acid dihydrate was 41.24 milliliters.

(a) Calculate the molarity of the NaOH solution. **$\text{M} = 0.4846 \text{ M}$**

(b) Calculate the number of moles of HX in a 50.00-milliliter portion used for titration. **moles = 0.01852 mol HX**

(c) Calculate the molecular weight of HX . **$\text{MW} = 163.3 \text{ g/mol}$**

(d) Discuss the effect on the calculated molecular weight of HX if the sample of oxalic acid dihydrate contained a nonacidic impurity.

The calculated molecular weight is smaller than true value, because of the following:

Measured g $\text{H}_2\text{C}_2\text{O}_4$ is larger than true value.

Calculated mol $\text{H}_2\text{C}_2\text{O}_4$ is larger than true value.

Calculated mol NaOH is larger than true value.

Calculated M NaOH is larger than true value.

Calculated mol HX is larger than true value.

Therefore: $\text{MW} = \text{gHX (true value)} / \text{mol HX (calculated, and too large)}$

1983 - #6

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

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) 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^+ , $K_a = 5.6 \times 10^{-10}$)

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.

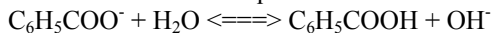
Dexter does not have a buffer solution, since his solution consists of a weak base plus a strong base.

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.

(a) Calculate the $[\text{OH}^-]$ in the sodium benzoate solution described above. **$[\text{OH}^-] = 4.0 \times 10^{-6} \text{ M}$**

(b) Calculate the value for the equilibrium constant for the reaction **$K_b = 1.6 \times 10^{-10}$**



(c) Calculate the value of K_a , the acid dissociation constant for benzoic acid. **$K_a = 6.3 \times 10^{-5}$**

(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. **$2.8 \times 10^{-2} \text{ M}$**

1985 - #1

At 25°C the solubility product constant, K_{sp} , for strontium sulfate, SrSO_4 , is 7.6×10^{-7} . The solubility product constant for strontium fluoride, SrF_2 , is 7.9×10^{-10}

(a) What is the molar solubility of SrSO_4 in pure water at 25°C ? **$8.7 \times 10^{-4} \text{ mol / liter}$**

(b) What is the molar solubility of SrF_2 in pure water at 25°C ? **$5.8 \times 10^{-4} \text{ mol / liter}$**

(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 F^- and 0.10 mole 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, Sr^{2+} , in the solution when the first precipitate begins to form? **When SrF_2 precipitates, $[\text{Sr}^{2+}] = 2.0 \times 10^{-6} \text{ M}$**

(d) 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?

The second precipitate to form is SrSO_4 , which appears when $[\text{Sr}^{2+}] = 7.6 \times 10^{-6} \text{ M}$.

$\% \text{F}^- \text{ still in solution} = 1.0 \times 10^{-2} / 2.0 \times 10^{-2} \times 100 = 50. \%$

1986 - #1 – Average Score: 3.14

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. **$K_a = \frac{[\text{H}^+][\text{N}_3^-]}{[\text{HN}_3]}$**
 (b) Calculate the pH of this solution at 25°C . **pH = 2.93**
 (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. **pH = 4.77**
 (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 . **$[\text{OH}^-] = 3.4 \times 10^{-6} \text{ M}$**

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.

- (a) Discuss the factors that are often used to predict correctly the strengths of the oxyacids listed above.

As number of lone oxygen atoms (oxygen atoms not bonded to hydrogen) increases, acid strength increases.

AND

As electronegativity of central atom increases, acid strength increases.

AND

Loss H^+ by neutral acid molecules reduces acid strength.

AND

K_a of $\text{H}_2\text{SO}_3 > K_a$ of HSO_3^-

- (b) Arrange the examples above in the order of increasing acid strength.

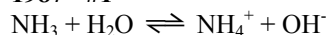
$\text{H}_3\text{BO}_3 < \text{HSO}_3^- < \text{H}_2\text{SO}_3 < \text{HClO}_3 < \text{HClO}_4$

H_3BO_3 or HSO_3^- weakest (must be together)

HClO_3 weaker than HClO_4

HSO_3^- weaker than H_2SO_3

Both S acid weaker than both Cl acids

1987 - #1

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 . **$[\text{OH}^-] = 1.6 \times 10^{-3} \text{ mol/L}$; % dissociation = 1.1%**
 (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. **pH = 8.73**
 (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}). **since $5.4 \times 10^{-6} > 4.3 \times 10^{-6} \text{ mol/L}$, then $\text{Mg}(\text{OH})_2$ precipitates**

1987 - #3

The percentage by weight of nitric acid, 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: $\text{KHC}_8\text{H}_4\text{O}_4 = 204.2$)

Molarity = 0.2764 M NaOH

- (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. **Molarity = 15.67 M HNO_3**

(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 HNO_3 in the original sample of concentrated nitric acid. **69.5% HNO_3**

1988 - #7 – Average Score: 1.76

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.

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.

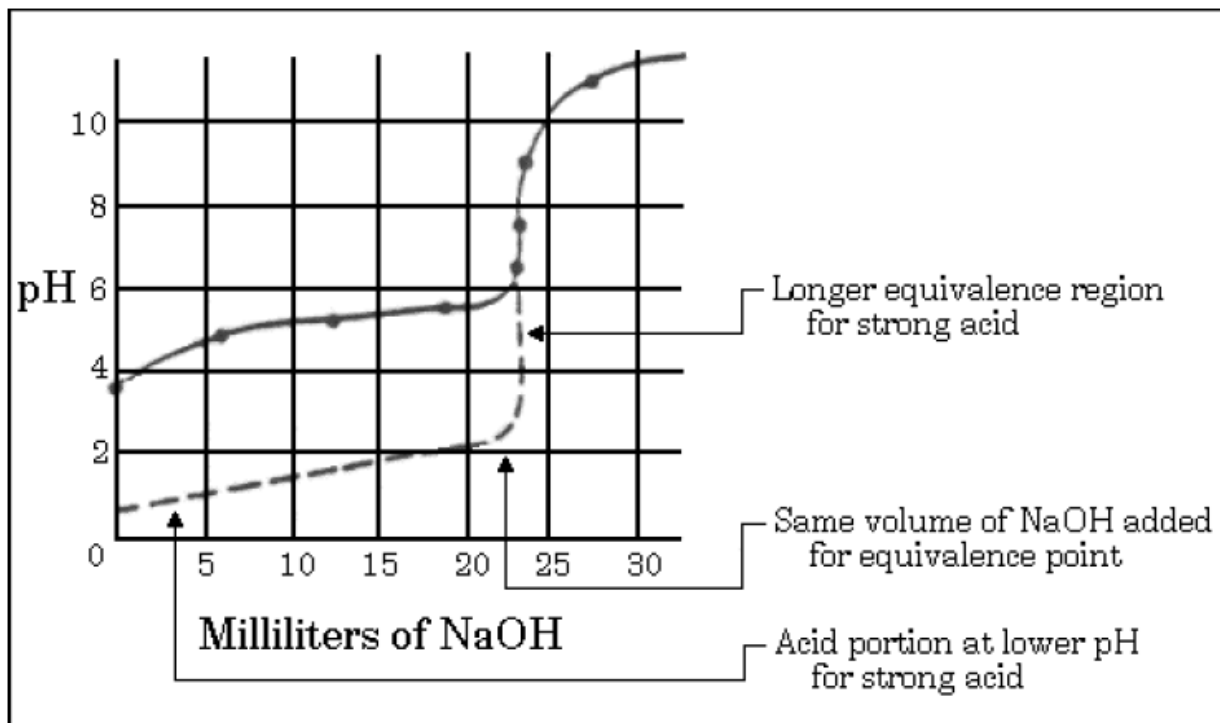
(b) Explain how this curve could be used to determine the acid dissociation constant K_a of the weak monoprotic acid. **At the half-equivalence point (where the volume of the base added is exactly half its volume at the equivalence point), the concentration $[\text{HX}]$ of the weak acid equals the concentration $[\text{X}^-]$ of its anion. Thus, in the equilibrium expression, $[\text{H}^+][\text{X}^-] / [\text{HX}] = K_a$. Therefore, pH at the half-equivalence point equals $\text{p}K_a$**

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

Cresol red is the best indicator because its $\text{p}K_a$ (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) 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. **176.1 grams/mol**
- (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. **$K_a = 7.7 \times 10^{-5}$**
- (c) Calculate the equilibrium constant for the reaction of the ascorbate ion, A^- , with water. **$K = 1.3 \times 10^{-10}$**
- (d) Calculate the pH of the solution at the equivalence point of the titration. **pH = 8.53**

1990 - #1

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

- (a) Write a balanced equation for the solubility equilibrium. **$Fe(OH)_2 \rightleftharpoons Fe^{2+} + 2OH^-$**
- (b) Write the expression for the solubility product constant, K_{sp} , and calculate its value.

$$K_{sp} = [Fe^{2+}][OH^-]^2$$

$$1.6 \times 10^{-14}$$

- (c) Calculate the pH of the saturated solution of $Fe(OH)_2$ at $25^\circ C$. **pH = 9.50**
- (d) A 50.0-milliliter sample of 3.00×10^{-3} molar $FeSO_4$ solution is added to 50.0 milliliters of 4.00×10^{-6} molar NaOH solution. Does a precipitate of $Fe(OH)_2$ form? Explain and show calculations to support your answer. **$Q (6.0 \times 10^{-15}) < K$ so no precipitate will form**

1990 - #8

Give a brief explanation for each of the following.

- (a) For the diprotic acid H_2S , the first dissociation constant is larger than the second dissociation constant by about 10^5 ($K_1 = 10^5 K_2$). **After the first H^+ is lost from H_2S , the remaining species, HS^- , has a negative charge. This increases the attraction of the S atom for the bonding electrons in HS^- . The bond is therefore stronger, H^+ is harder to remove, and K_2 is lower.**
- (b) In water, NaOH is a base, but HOCl is an acid. **Polar H_2O can separate ionic NaOH into Na^+ (aq) and OH^- (aq) giving a basic solution. In HOCl, chlorine has a high attraction for electrons due to its greater charge density. This draws electrons in the H-O bond towards it and weakens the bond. H^+ can be removed, making an acid solution.**
- (c) HCl and HI are equally strong acids in water but, in pure acetic acid, HI is a stronger acid than HCl. **Water is a more basic solvent (greater attraction for H^+) and removes H^+ from Cl $^-$ and I $^-$ equally. Acetic acid has little attraction for H^+ but the H^+ separates from the larger I $^-$ easier than from the smaller Cl $^-$.**
- (d) When each is dissolved in water, HCl is a much stronger acid than HF. **The bond between H and Cl is weaker than the bond between H and F. HCl is therefore a stronger acid.**

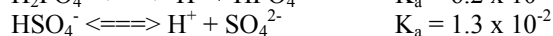
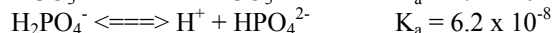
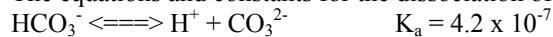
1991 - #1

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

- (a) Calculate the hydrogen ion concentration, $[H^+]$, in a 0.20-molar solution of propanoic acid. **1.6×10^{-3}**
- (b) Calculate the percentage of propanoic acid molecules that are ionized in the solution in (a). **0.80%**
- (c) 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? **2.0: 1.0**
- (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. **pH = 4.96**

1992 - #6

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

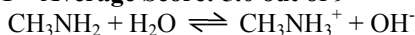


- (a) From the systems above, identify the conjugate pair that is best for preparing a buffer with a pH of 7.2. **best conjugate pair = $H_2PO_4^-$ and HPO_4^{2-} $K_a = 7.2$.**
- (b) Explain briefly how you would prepare the buffer solution described in (a) with the conjugate pair you have chosen. **Dissolve equal number of moles of a $H_2PO_4^-$ salt and a HPO_4^{2-} salt.**
- (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.

The pH would not change. The ratio [salt]/[acid] in the Henderson-Hasselbalch equation would remain the same if the concentrations were doubled. There is now more of each ion to react when an acid or a base is added.

(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. **Add one mole of conjugate acid to 0.5 mole of strong base or one mole of conjugate base to 0.5 mole strong acid.**

1993 - #1 – Average Score: 5.0 out of 9



Methylamine, CH_3NH_2 , is a weak base that reacts according to the equation above. The value of the ionization constant, K_b , is 5.25×10^{-4} . Methylamine forms salts such as methylammonium nitrate, $(\text{CH}_3\text{NH}_3^+)(\text{NO}_3^-)$.

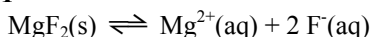
(a) Calculate the hydroxide ion concentration, $[\text{OH}^-]$, of a 0.225-molar solution of methylamine. **$[\text{OH}^-] = 1.09 \times 10^{-2}$**

(b) 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. **pH = 11.15**

(c) 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. **2.73×10^{-3} mol HCl**

(d) A volume of 100. milliliters of distilled water is added to the solution in (c). How is the pH of the solution affected? Explain. **The $[\text{CH}_3\text{NH}_3^+] / [\text{CH}_3\text{NH}_2]$ ratio does not change in the buffer solution with dilution. Therefore, no effect on pH.**

1994 - #1



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

(a) Write the expression for the solubility-product constant, K_{sp} , and calculate its value at 18°C .

$$K_{sp} = [\text{Mg}^{2+}] [\text{F}^-]^2 \text{ \& } 7.09 \times 10^{-9}$$

(b) Calculate the equilibrium concentration of Mg^{2+} in 1.000 liter of saturated MgF_2 solution at 18°C to which 0.100 mole of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.

$$7.09 \times 10^{-7} \text{ M}$$

(c) Predict whether a precipitate of MgF_2 will form when 100.0 milliliters of a 3.00×10^{-3} molar $\text{Mg}(\text{NO}_3)_2$ solution is mixed with 200.0 milliliters of a 2.00×10^{-3} molar NaF solution at 18°C . Calculations to support your prediction must be shown. **$Q = 1.77 \times 10^{-9}$ Since $Q < K_{sp}$, no precipitate will form.**

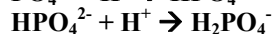
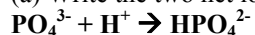
(d) At 27°C the concentration of Mg^{2+} in a saturated solution of MgF_2 is 1.17×10^{-3} molar. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

Increased temperature puts a stress on the system (LeChâtelier). The system will reduce the stress by shifting the equilibrium in the endothermic (left) direction.

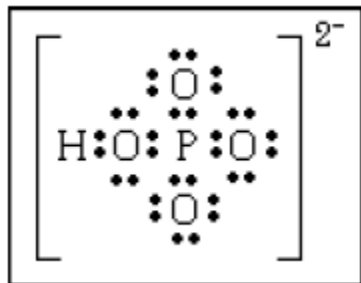
1994 - #7

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.

(a) Write the two net ionic equations for the formation of the major species.



(b) 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. **HPO_4^{2-}**



(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 Na₃PO₄ solution. Account for the shape of the curve.

Graph goes from upper left to the lower right. (pH decreases)

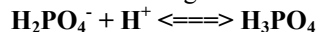
Two protons transferred

Two "buffers"

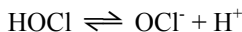
Two "equivalences"

Explain/correctly label at least one "buffer" or "equivalence" region

(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).



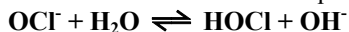
1996 - #2



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 x 10⁻⁸.

(a) Calculate the [H⁺] of a 0.14-molar solution of HOCl. **6.7 x 10⁻⁵ M**

(b) 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.



$$\mathbf{K_b = 3.1 \times 10^{-7}}$$

(c) 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. **pH = 10.27**

(d) 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.

5.00 mmoles

(e) Household bleach is made by dissolving chlorine gas in water, as represented below.

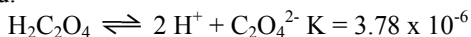


Calculate the pH of such a solution if the concentration of HOCl in the solution is 0.065 molar.

$$\mathbf{pH = 1.19}$$

1997 - #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? **25.0 mL**

(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

$$\mathbf{K_1 = 5.91 \times 10^{-2}}$$

(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.) **6 x 10⁻⁷**

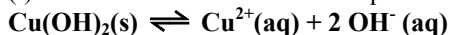
(d) Calculate the value of the equilibrium constant, K_b, for the reaction that occurs when solid Na₂C₂O₄ is dissolved in water. **K_b = 1.56 x 10⁻¹⁰**

1998 - #1

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

(a) The solubility of Cu(OH)₂ is 1.72 x 10⁻⁶ gram per 100. milliliters of solution at 25 °C.

(i) Write the balanced chemical equation for the dissociation of Cu(OH)₂(s) in aqueous solution.



(ii) Calculate the solubility (in moles per liter) of Cu(OH)₂ at 25 °C.

1.76 x 10⁻⁷ moles per liter

(iii) Calculate the value of the solubility-product constant, K_{sp}, for Cu(OH)₂ at 25°C.

$$\mathbf{K_{sp} = 2.18 \times 10^{-20}}$$

(b) The value of the solubility-product constant, K_{sp}, for Zn(OH)₂ is 7.7 x 10⁻¹⁷ at 25°C.

(i) Calculate the solubility (in moles per liter) of Zn(OH)₂ at 25°C in a solution with a pH of 9.35.

$$1.5 \times 10^{-7} \text{ M}$$

(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.

$$[\text{Zn}^{2+}] = 3.1 \times 10^{-14} \text{ M}$$

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

250 mL Erlenmeyer flask

Wash bottle filled with distilled water

Analytical balance

Phenolphthalein indicator solution

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.

(a) **4 essential steps**

1) weigh KHP

2) fill buret with NaOH solution

3) add indicator (phenolphthalein)

4) titrate to endpoint (color change)

(b) Describe (i.e., set up) the calculations necessary to determine the concentration of the NaOH solution.

moles KHP = Mass KHP / molar mass KHP

moles KHP = moles OH^- at equivalence and (moles OH^- / liters NaOH) = $[\text{OH}^-]$

(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.

Curve should have 3 important features:

1) curve begins above pH 1, but below pH 7

2) equivalence point at 25 mL

3) equivalence point above pH 7

3) equivalence point above pH 7

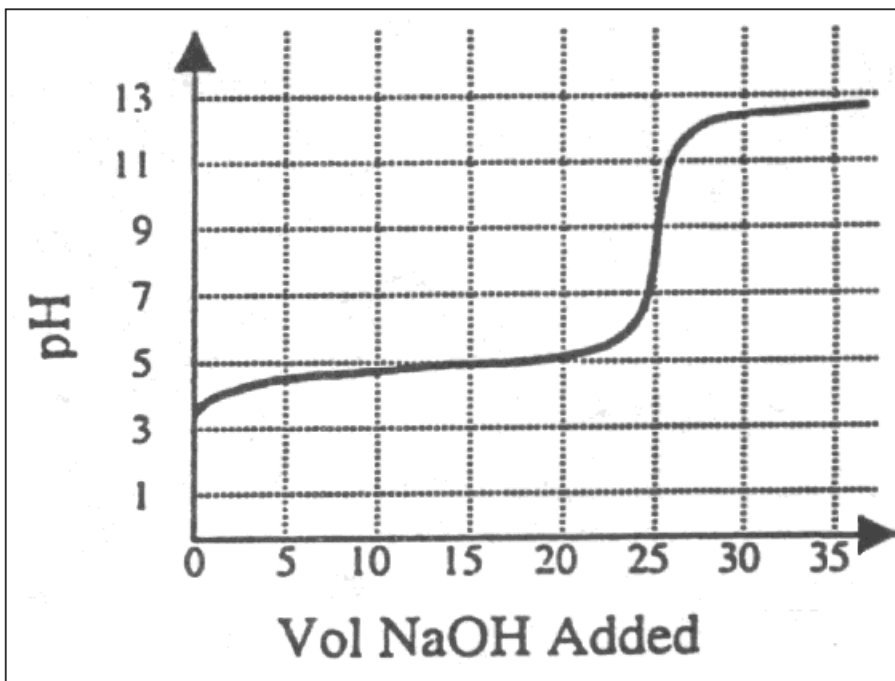
(d) Describe how the value of the acid-dissociation constant, K_a ,

for the weak acid HX could be determined from the titration curve in part (c).

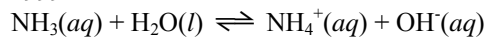
for the weak acid HX could be determined from the titration curve in part (c).

At the halfway point in the titration, $\text{pH} = \text{p}K_a$.

(e) The graph below shows the results obtained by titrating a different weak acid, H_2Y , 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. **At point A in the titration, the anion in highest concentration is Y^{2-} .**



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 5.60×10^{-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.

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

(b) Determine the pH of 0.0180 M $\text{NH}_3(\text{aq})$. **pH = 10.748**

(c) Determine the value of the base ionization constant, K_b , for $\text{NH}_3(\text{aq})$. **$K_b = 1.74 \times 10^{-5}$**

(d) Determine the percent ionization of NH_3 in 0.0180 M $\text{NH}_3(\text{aq})$. **3.11%**

(e) 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 $\text{HCl}(\text{aq})$.

(i) Determine the volume of 0.0120 M $\text{HCl}(\text{aq})$ that was added to reach the equivalence point. **30.0 mL**

(ii) 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. **pH = 9.255**

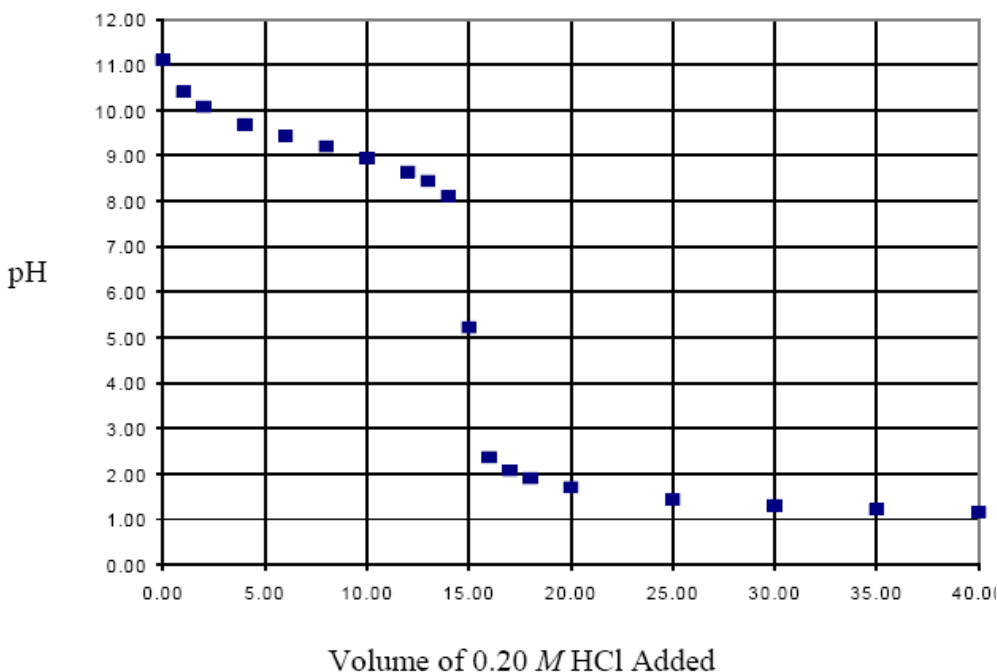
(iii) Determine the pH of the solution in the flask after a total of 40.0 mL of 0.0120 M $\text{HCl}(\text{aq})$ was added. **pH = 2.700**

2000 - #8

A volume of 30.0 mL of 0.10 M $\text{NH}_3(\text{aq})$ is titrated with 0.20 M $\text{HCl}(\text{aq})$. The value of the base-dissociation constant, K_b , for NH_3 in water is 1.8×10^{-5} at 25°C.

(a) Write the net-ionic equation for the reaction of $\text{NH}_3(\text{aq})$ with $\text{HCl}(\text{aq})$. **$\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq})$**

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



- initial pH must be > 7 (calculated pH ≈ 11)
- equivalence point occurs at 15.0 mL of HCl added (equivalence point must be detectable from the shape of the curve or a mark on the curve)
- pH at equivalence point must be < 7 (calculated pH ≈ 5).

(c) 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

Methyl Red would be the best choice of indicator because the pK_a for Methyl Red is closest to the pH at the equivalence point.

(d) If equal volumes of 0.10 M $NH_3(aq)$ and 0.10 M $NH_4Cl(aq)$ are mixed, is the resulting solution acidic, neutral, or basic? Explain.

The resulting solution is basic.

K_b for NH_3 (1.8×10^{-5}) and K_a for NH_4^+ (5.6×10^{-10}) indicate that NH_3 is a stronger base than NH_4^+ is an acid

2001 - #1 – Average Score 3.94 out of 10

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

(a) At 10°C, 8.9×10^{-5} g of $AgCl(s)$ will dissolve in 100. mL of water.

(i) Write the equation for the dissociation of $AgCl(s)$ in water. **$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$**

(ii) Calculate the solubility, in $mol\ L^{-1}$, of $AgCl(s)$ in water at 10°C. **$6.2 \times 10^{-6}\ mol/L$**

(iii) Calculate the value of the solubility-product constant, K_{sp} , for $AgCl(s)$ at 10°C. **$K_{sp} = 3.8 \times 10^{-11}$**

(b) At 25°C, the value of K_{sp} for $PbCl_2(s)$ is 1.6×10^{-5} and the value of K_{sp} for $AgCl(s)$ is 1.8×10^{-10} .

(i) If 60.0 mL of 0.0400 M $NaCl(aq)$ is added to 60.0 mL of 0.0300 M $Pb(NO_3)_2(aq)$, will a precipitate form? Assume that volumes are additive. Show calculations to support your answer.

$Q = 6.0 \times 10^{-6}$ $Q < K$ so no precipitate forms

(ii) Calculate the equilibrium value of $[Pb^{2+}(aq)]$ in 1.00 L of saturated $PbCl_2$ solution to which 0.250 mole of $NaCl(s)$ has been added. Assume that no volume change occurs. **$2.6 \times 10^{-4}\ M$**

(iii) If 0.100 M $NaCl(aq)$ is added slowly to a beaker containing both 0.120 M $AgNO_3(aq)$ and 0.150 M $Pb(NO_3)_2(aq)$ at 25°C, which will precipitate first, $AgCl(s)$ or $PbCl_2(s)$? Show calculations to support your answer. **$AgCl(s)$ will precipitate first because at precipitation $[Cl^-]$ in $AgCl$ is $1.5 \times 10^{-9}\ M$. In $PbCl_2$ $[Cl^-]$ is $1.0 \times 10^{-2}\ M$**

2001 - #3d

A 2.00×10^{-3} mole sample of pure acetylsalicylic acid was dissolved in 15.00 mL of water and then titrated with 0.100 M $NaOH(aq)$. The equivalence point was reached after 20.00 mL of the $NaOH$ 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 **$K_a = 3.6 \times 10^{-4}$**

(ii) the pH of the solution after a total volume of 25.00 mL of the $NaOH$ solution had been added (assume that volumes are additive).

pH = 12.10

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

$HOBr(aq) \rightleftharpoons H^+(aq) + OBr^-(aq)$ $K_a = 2.3 \times 10^{-9}$

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

(a) Calculate the value of $[H^+]$ in an $HOBr$ solution that has a pH of 4.95. **$1.1 \times 10^{-5}\ M$**

(b) Write the equilibrium constant expression for the ionization of $HOBr$ in water, then calculate the concentration of $HOBr(aq)$ in an $HOBr$ solution that has $[H^+]$ equal to $1.8 \times 10^{-5}\ M$.

$$K_a = \frac{[H^+][OBr^-]}{[HOBr]}$$

$[HOBr] = 0.14\ M$

(c) A solution of $Ba(OH)_2$ is titrated into a solution of $HOBr$.

(i) Calculate the volume of 0.115 M $Ba(OH)_2(aq)$ needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 M $HOBr(aq)$. **41.3 mL**

(ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.

The pH will be greater than 7 (pH = 10.79) because $HOBr$ is a weak acid and $Ba(OH)_2$ is a strong base.

- (d) Calculate the number of moles of $\text{NaOBr}(s)$ that would have to be added to 125 mL of 0.160 M HOBr to produce a buffer solution with $[\text{H}^+] = 5.00 \times 10^{-9} \text{ M}$. Assume that volume change is negligible. **9.2×10^{-3} moles**
- (e) HOBr is a weaker acid than HBrO_3 . Account for this fact in terms of molecular structure. **The H-O bond is weakened or increasingly polarized by the additional oxygen atoms bonded to the central bromine atom in HBrO_3 .**

2002 B - #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.

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

$$K_a = 1.4 \times 10^{-4}$$

- (b) Calculate the pH of 0.50 M $\text{HC}_3\text{H}_5\text{O}_3$. **pH = 2.08**
- (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. **pH = 3.41**
- (d) A 100. mL sample of 0.10 M 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. **$[\text{C}_3\text{H}_5\text{O}_3^-] = 7.0 \times 10^{-4}$**

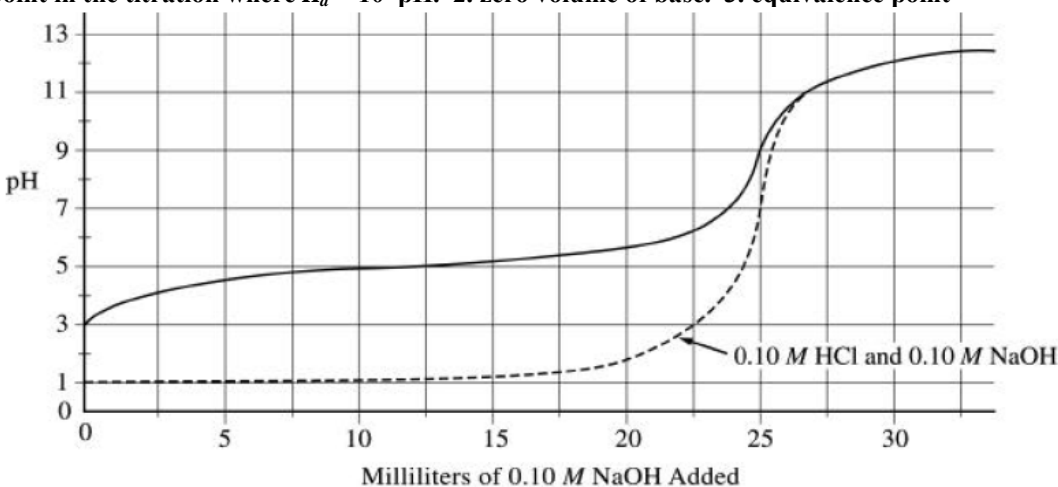
2002 B #8

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

- (a) Describe two features of the graph above that identify HA as a weak acid.

Initial pH > 1; at equivalence point pH > 7

- (b) Describe one method by which the value of the acid-dissociation constant for HA can be determined using the graph above. **The K_a for the weak acid can be obtained by determining the pH at the: 1. half-equivalence point in the titration where $K_a = 10^{-\text{pH}}$. 2. zero volume of base. 3. equivalence point**



- (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. **The graph should have the following features: 1. The pH before adding any base is 1. 2. The equivalence point pH is 7 at 25 mL. 3. The titration curve beyond the equivalence point is nearly identical to the original curve**

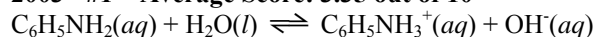
- (d) A 25 mL sample of 0.10 M HA is titrated with 0.20 M NaOH .

(i) What volume of base must be added to reach the equivalence point? **13 mL**

(ii) 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. **In the titration with 0.1 M NaOH , the total volume at the equivalence point is 50 mL. In the titration with 0.20 M NaOH the total volume at the equivalence point is 37.5 mL. The smaller volume in the titration with 0.2 M NaOH means the $[\text{A}^-]$, the molar concentration of**

the conjugate base of HA, is larger compared to the [A⁻] at the equivalence point with 0.1 M NaOH. Therefore, the pH is slightly higher.

2003 - #1 – Average Score: 3.35 out of 10



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

(a) Write the equilibrium constant expression, K_b , for the reaction represented above.

$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

(b) 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. **$K_b = 4.4 \times 10^{-10}$**

(c) 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. **pH = 5.24**

(d) Calculate the pH at the equivalence point of the titration in part (c). **pH = 2.96**

(e) 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.

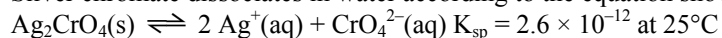
Indicator	$\text{p}K_a$
Erythrosine	3
Litmus	7
Thymolphthalein	10

The pH at the equivalence point is acidic. The best indicator is erythrosine, for which the value of $\text{p}K_a$ is closest to the pH at the equivalence point.

2004 - #1 – Average Score: 4.7 out of 10

Answer the following questions relating to the solubilities of two silver compounds, Ag_2CrO_4 and Ag_3PO_4 .

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



(a) Write the equilibrium-constant expression for the dissolving of $\text{Ag}_2\text{CrO}_4(s)$.

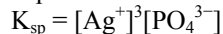
$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

(b) Calculate the concentration, in mol L^{-1} , of $\text{Ag}^+(aq)$ in a saturated solution of Ag_2CrO_4 at 25°C . **$[\text{Ag}^+] = 1.7 \times 10^{-4}$**

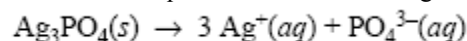
(c) Calculate the maximum mass, in grams, of Ag_2CrO_4 that can dissolve in 100. mL of water at 25°C . **0.0029 g**

(d) A 0.100 mol sample of solid AgNO_3 is added to a 1.00 L saturated solution of Ag_2CrO_4 . Assuming no volume change, does $[\text{CrO}_4^{2-}]$ increase, decrease, or remain the same? Justify your answer. **The $[\text{CrO}_4^{2-}]$ will decrease. Adding $[\text{Ag}^+]$ will make $Q > K$. To re-establish equilibrium, the reaction goes from right to left, decreasing the quotient to return to equilibrium.**

In a saturated solution of Ag_3PO_4 at 25°C , the concentration of $\text{Ag}^+(aq)$ is 5.3×10^{-5} M. The equilibrium constant expression for the dissolving of $\text{Ag}_3\text{PO}_4(s)$ in water is shown below.



(e) Write the balanced equation for the dissolving of Ag_3PO_4 in water.

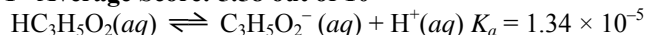


(f) Calculate the value of K_{sp} for Ag_3PO_4 at 25°C . **$K_{sp} = 2.6 \times 10^{-18}$**

(g) A 1.00 L sample of saturated Ag_3PO_4 solution is allowed to evaporate at 25°C to a final volume of 500. mL. What is $[\text{Ag}^+]$ in the solution? Justify your answer. **$[\text{Ag}^+] = 5.3 \times 10^{-5}$ M**

The $[\text{Ag}^+]$ in a saturated solution of Ag_3PO_4 is independent of the volume of the solution.

2005 - #1 – Average Score: 5.58 out of 10



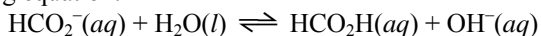
Propanoic acid, $\text{HC}_3\text{H}_5\text{O}_2$, ionizes in water according to the equation above.

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

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

- (b) Calculate the pH of a 0.265 M solution of propanoic acid. **pH = 2.725**
- (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.
- The concentration of the propanoate ion, $\text{C}_3\text{H}_5\text{O}_2^- (aq)$, in the solution **0.103**
 - The concentration of the $\text{H}^+(aq)$ ion in the solution **$3.45 \times 10^{-5} M$**

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



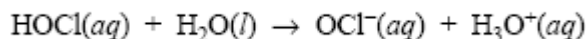
- (d) Given that $[\text{OH}^-]$ is $4.18 \times 10^{-6} M$ in a 0.309 M solution of sodium methanoate, calculate each of the following.
- The value of K_b for the methanoate ion, $\text{HCO}_2^-(aq)$ **$K_b = 5.65 \times 10^{-11}$**
 - The value of K_a for methanoic acid, HCO_2H **$K_a = 1.77 \times 10^{-4}$**
- (e) Which acid is stronger, propanoic acid or methanoic acid? Justify your answer.
 K_a for propanoic acid is 1.34×10^{-5} , and K_a for methanoic acid is 1.77×10^{-4} . For acids, the larger the value of K_a , the greater the strength; therefore methanoic acid is the stronger acid because $1.77 \times 10^{-4} > 1.34 \times 10^{-5}$.

2005 B - #1

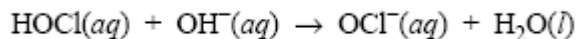
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = 3.2 \times 10^{-8}$$

Hypochlorous acid, HOCl, is a weak acid in water. The K_a expression for HOCl is shown above.

- (a) Write a chemical equation showing how HOCl behaves as an acid in water.



- (b) Calculate the pH of a 0.175 M solution of HOCl. **pH = 4.13**
- (c) Write the net ionic equation for the reaction between the weak acid $\text{HOCl}(aq)$ and the strong base $\text{NaOH}(aq)$.

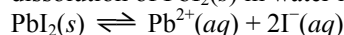


- (d) In an experiment, 20.00 mL of 0.175 M $\text{HOCl}(aq)$ is placed in a flask and titrated with 6.55 mL of 0.435 M $\text{NaOH}(aq)$.
- Calculate the number of moles of $\text{NaOH}(aq)$ added. **$2.85 \times 10^{-3} \text{ mol NaOH}$**
 - Calculate $[\text{H}_3\text{O}^+]$ in the flask after the $\text{NaOH}(aq)$ has been added. **$[\text{H}_3\text{O}^+] = 7.3 \times 10^{-9} M$**
 - Calculate $[\text{OH}^-]$ in the flask after the $\text{NaOH}(aq)$ has been added. **$[\text{OH}^-] = 1.4 \times 10^{-6}$**

2006 - #1 – National Average Score: 4.19 out of 9, Petras Average: 3.6 out of 9

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

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



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

$$K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2$$

- (ii) Calculate the molar concentration of $\text{I}^-(aq)$ in the solution. **$[\text{I}^-] = 2.6 \times 10^{-3}$**

- (iii) Calculate the value of the equilibrium constant, K_{sp} . **$K_{sp} = 8.8 \times 10^{-9}$**

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

The concentrations would be the same as above. The concentration of solute particles in a saturated solution is a function of K_{sp} and independent of the volume.

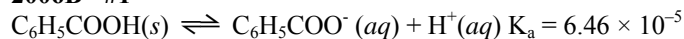
- (c) Solid NaI is added to a saturated solution of PbI_2 at 25°C. Assuming that the volume of the solution does not change, does the molar concentration of $\text{Pb}^{2+}(aq)$ in the solution increase, decrease, or remain the same? Justify your answer. **$[\text{Pb}^{2+}]$ will decrease. Adding NaI adds I^- to the solution and causes the reaction to shift left.**

- (d) The value of K_{sp} for the salt BaCrO_4 is 1.2×10^{-10} . When a 500. mL sample of $8.2 \times 10^{-6} M \text{Ba}(\text{NO}_3)_2$ is added to 500. mL of $8.2 \times 10^{-6} M \text{Na}_2\text{CrO}_4$, no precipitate is observed.

(i) Assuming that volumes are additive, calculate the molar concentrations of $\text{Ba}^{2+}(aq)$ and $\text{CrO}_4^{2-}(aq)$ in the 1.00 L of solution. $[\text{Ba}^{2+}] = 4.1 \times 10^{-6} \text{ M}$, $[\text{CrO}_4^{2-}] = 4.1 \times 10^{-6}$

(ii) Use the molar concentrations of $\text{Ba}^{2+}(aq)$ ions and $\text{CrO}_4^{2-}(aq)$ ions as determined above to show why a precipitate does not form. You must include a calculation as part of your answer. $Q = 1.7 \times 10^{-11}$ **Since $Q < K$ no precipitate will form.**

2006B - #1



Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, 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.

(i) $[\text{H}^+]$ in the solution **$[\text{H}^+] = 4.3 \times 10^{-5} \text{ M}$**

(ii) $[\text{OH}^-]$ in the solution **$[\text{OH}^-] = 2.3 \times 10^{-10} \text{ M}$**

(iii) The number of moles of NaOH added **2.25×10^{-3} moles**

(iv) The number of moles of $\text{C}_6\text{H}_5\text{COO}^-(aq)$ in the solution **2.25×10^{-3} moles**

(v) The number of moles of $\text{C}_6\text{H}_5\text{COOH}$ in the solution **1.5×10^{-3} moles**

(b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning. **At the equivalence point the solution is basic because a weak acid is being titrated with a strong base.**

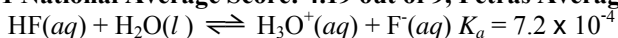
In a different titration, a 0.7529 g sample of a mixture of solid $\text{C}_6\text{H}_5\text{COOH}$ and solid NaCl is dissolved in water and titrated with 0.150 M NaOH. The equivalence point is reached when 24.78 mL of the base solution is added.

(c) Calculate each of the following.

(i) The mass, in grams, of benzoic acid in the solid sample **0.453 grams**

(ii) The mass percentage of benzoic acid in the solid sample **60.2%**

2007 - #1 National Average Score: 4.19 out of 9, Petras Average: 5.6 out of 9



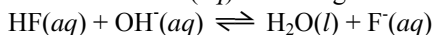
Hydrofluoric acid, $\text{HF}(aq)$, dissociates in water as represented by the equation above.

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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

(b) Calculate the molar concentration of H_3O^+ in a 0.40 M $\text{HF}(aq)$ solution. **0.017 M**

$\text{HF}(aq)$ reacts with $\text{NaOH}(aq)$ according to the reaction represented below.



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

(c) Calculate the number of moles of $\text{HF}(aq)$ remaining in the solution. **0.004 mol**

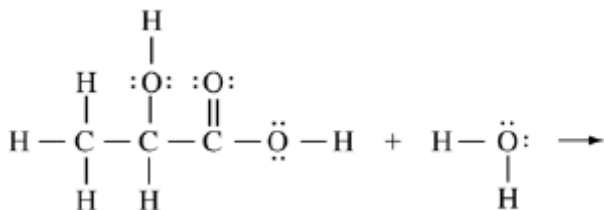
(d) Calculate the molar concentration of $\text{F}^-(aq)$ in the solution. **0.15 M $\text{F}^-(aq)$**

(e) Calculate the pH of the solution. **pH = 3.32**

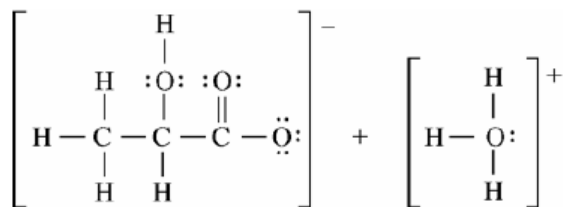
2007B - #5

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

(a) Lactic acid, $\text{HC}_3\text{H}_5\text{O}_3$, 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 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

mass of $\text{NH}_4\text{Cl} = (0.100 \text{ L})(1.00 \text{ mol L}^{-1})(53.5 \text{ g mol}^{-1}) = 5.35 \text{ g NH}_4\text{Cl}$

1. Measure out 5.35 g NH_4Cl using the balance.

2. Use the 100 mL graduated cylinder to transfer approximately 25 mL of distilled water to the 100 mL volumetric flask.

3. Transfer the 5.35 g NH_4Cl to the 100 mL volumetric flask.

4. Continue to add distilled water to the volumetric flask while swirling the flask to dissolve the NH_4Cl and remove all NH_4Cl particles adhered to the walls.

5. Carefully add distilled water to the 100 mL volumetric flask until the bottom of the meniscus of the solution reaches the etched mark on the flask.

(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. $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$

(ii) Explain why the pH of buffer 1 is different from the pH of buffer 2 after 0.10 mol of HCl is added.

Before the HCl was added, each buffer had the same pH and thus had the same $[\text{H}^+]$. Because K_a for acetic acid is a constant, the ratio of $[\text{H}^+]$ to K_a must also be constant; this means that the ratio of $[\text{HC}_2\text{H}_3\text{O}_2]$ to $[\text{C}_2\text{H}_3\text{O}_2^-]$ is the same for both buffers, as shown by the following equation, derived from the equilibrium-constant expression for the dissociation of acetic acid.

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

After the addition of the H^+ , the ratio in buffer 1 must have been greater than the corresponding ratio in buffer 2, as evidenced by their respective pH values. Thus a greater proportion of the $\text{C}_2\text{H}_3\text{O}_2^-$ in buffer 1 must have reacted with the added H^+ compared to the proportion that reacted in buffer 2. The difference between these proportions means that the original concentrations of $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{C}_2\text{H}_3\text{O}_2^-$ had to be smaller in buffer 1 than in buffer 2.

(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.

Both buffer solutions have the same acid to conjugate-base mole ratio in the formula below.

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

Therefore, the buffers have the same $[\text{H}^+]$ and pH.

2009 - #1 National Average Score: 4.5 out of 10, Petras Average: 4.5 out of 10

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

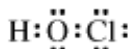
(a) Use the information in the table below to answer part (a)(i).

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

(i) Which of the two acids is stronger, HOCl or HOBr? Justify your answer in terms of K_a .

HOCl is the stronger acid because its K_a value is greater than the K_a value of HOBr.

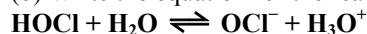
(ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).



(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.

HOI is a weaker acid than HOCl because the O–H bond in HOI is stronger than the O–H bond in HOCl. The lower electronegativity (electron-drawing ability) of I compared with that of Cl results in an electron density that is higher (hence a bond that is stronger) between the H and O atoms in HOI compared with the electron density between the H and O atoms in HOCl.

(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 $\text{H}_2\text{O}(l)$.

$$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$$

(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction. 3.4×10^{-7}

(iii) Calculate the value of $[\text{OH}^-]$ in the 1.2 M NaOCl solution at 298 K. $6.4 \times 10^{-4} M$

(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. $3.3 \times 10^{-7} M$

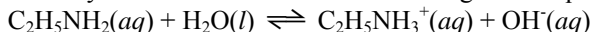
(ii) Indicate which of $\text{HOCl}(aq)$ or $\text{OCl}^-(aq)$ is present at the higher concentration in the buffer solution. Support your answer with a calculation. $[\text{OCl}^-] \div [\text{HOCl}] = 0.088$ so $[\text{HOCl}] > [\text{OCl}^-]$

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. **0.659 M**

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.

$$K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]}$$

(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. **$\text{C}_2\text{H}_5\text{NH}_2$ is present in the solution at the higher concentration at equilibrium. Ethylamine is a weak base, and thus it has a small K_b value. Therefore only partial dissociation of $\text{C}_2\text{H}_5\text{NH}_2$ occurs in water, and $[\text{C}_2\text{H}_5\text{NH}_3^+]$ is thus less than $[\text{C}_2\text{H}_5\text{NH}_2]$.**

(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. **$8.5 \times 10^{-4} M$**

(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 HCl solution. **$\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_3\text{O}^+ \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_3^+ + \text{H}_2\text{O}$**

(iii) Calculate the molar concentration of the $\text{C}_2\text{H}_5\text{NH}_3^+(aq)$ that is formed in the reaction. **0.100 M**

(iv) Calculate the value of K_b for $\text{C}_2\text{H}_5\text{NH}_2$. **5.67×10^{-4}**

