**1970**

(a) What is the pH of a 2.0 molar solution of acetic acid. K_a acetic acid $= 1.8 \times 10^{-5}$

(b) A buffer solution is prepared by adding 0.10 liter of 2.0 molar acetic acid solution to 0.1 liter of a 1.0 molar sodium hydroxide solution. Compute the hydrogen ion concentration of the buffer solution.

(c) Suppose that 0.10 liter of 0.50 molar hydrochloric acid is added to 0.040 liter of the buffer prepared in (b). Compute the hydrogen ion concentration of the resulting solution.
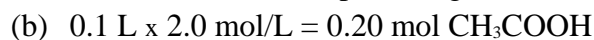
Answer:

(a) $CH_3COOH_{(aq)} \Longleftrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$
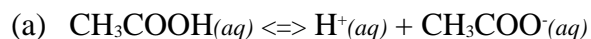
$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$[H^+] = [CH_3COO^-] = X$
$[CH_3COOH] = 2.0 - X, X \ll 2.0, (2.0 - X) = 2.0$

$$1.8 \times 10^{-5} = \frac{X^2}{2.0}$$

$X = 6.0 \times 10^{-3} = [H^+]; \quad pH = -\log[H^+] = 2.22$

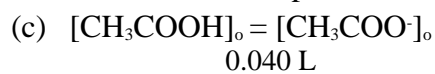(b) $0.1 \text{ L} \times 2.0 \text{ mol/L} = 0.20 \text{ mol } CH_3COOH$

$0.1 \text{ L} \times 1.0 \text{ mol/L} = 0.10 \text{ mol NaOH}$

the 0.10 mol of hydroxide neutralizes 0.10 mol CH_3COOH with 0.10 mol remaining with a concentration of 0.10 mol/0.20 L = 0.5 M. This also produces 0.10 mol of acetate ion in 0.20 L, therefore, $[CH_3COO^-] = 0.50$ M.

$$1.8 \times 10^{-5} = \frac{[H^+][0.50]}{[0.50]}$$

$[H^+] = 1.8 \times 10^{-5} = pH$ of 4.74

(c) $[CH_3COOH]_o = [CH_3COO^-]_o$

$$= 0.50 \text{ M} \times \frac{0.040 \text{ L}}{0.14 \text{ L}} = 0.143 \text{ M}$$

$$[H^+]_o = 0.50 \text{ M} \times \frac{0.10 \text{ L}}{0.14 \text{ L}} = 0.357 \text{ M}$$

the equilibrium will be pushed nearly totally to the left resulting in a decrease of the hydrogen ion by 0.143M. Therefore, the $[H^+]_{eq} = 0.357M - 0.143M = 0.214M$.
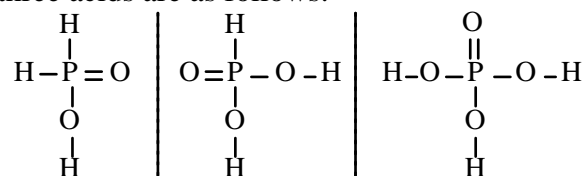

1970

H_3PO_2, H_3PO_3, and H_3PO_4 are monoprotic, diprotic and triprotic acids, respectively, and they are about equal strong acids.

$HClO_2$, $HClO_3$, and $HClO_4$ are all monoprotic acids, but $HClO_2$ is a weaker acid than $HClO_3$ which is weaker than $HClO_4$. Account for:

(a) The fact that the molecules of the three phosphorus acids can provide different numbers of protons.

(b) The fact that the three chlorine acids differ in strengths.

Answer:

(a) the structure for the three acids are as follows:

$$\overset{\displaystyle H}{\underset{\displaystyle O \atop \displaystyle |\; H}{|\atop H-P=O}} \qquad \overset{\displaystyle H}{\underset{\displaystyle O \atop \displaystyle |\; H}{|\atop O=P-O-H}} \qquad \overset{\displaystyle O}{\underset{\displaystyle O \atop \displaystyle |\; H}{\|\atop H-O-P-O-H}}$$

The hydrogen atom(s) bonded directly to the phosphorus atom is/are not acidic in aqueous solution; only those hydrogen atoms bonded to the oxygen atoms can be released as protons.

(b) The acid strength is successively greater as the number of oxygen atoms increases because the very electronegative oxygen atoms are able to draw electrons away from the chlorine atom and the O-H bond. This effect is more important as the number of attached oxygen atoms increases. This means that a proton is most readily produced by the molecule with the largest number of attached oxygen atoms.

1970

A comparison of the theories Arrhenius, Bronsted and Lewis shows a progressive generalization of the acid base concept. Outline the essential ideas in each of these theories and select three reactions, one that can be interpreted by all three theories, one that can be interpreted by two of them, and one that can be interpreted by only one of the theories. Provide these six interpretations.

Answer:

Arrhenius

 acid = produce H^+ ions in aqueous solution

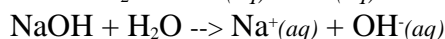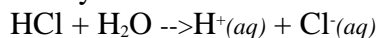 base = produce OH^- ions in aqueous solution

Bronsted-Lowry

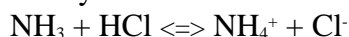 acid = proton (H^+) donor; base = proton acceptor

Lewis

 acid = e- pair acceptor; base = e- pair donor

Examples:

Interpreted by all three

  $HCl + H_2O \rightarrow H^+(aq) + Cl^-(aq)$

  $NaOH + H_2O \rightarrow Na^+(aq) + OH^-(aq)$

Interpreted by two

  $NH_3 + HCl \Longleftrightarrow NH_4^+ + Cl^-$

Interpreted by only one

 $BF_3 + NH_3 \rightarrow F_3B{:}NH_3$
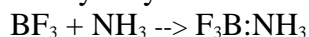
1972 *(repeated in gases topic)*

A 5.00 gram sample of a dry mixture of potassium hydroxide, potassium carbonate, and potassium chloride is reacted with 0.100 liter of 2.00 molar HCl solution

(a) A 249 milliliter sample of dry CO_2 gas, measured at 22°C and 740 torr, is obtained from this reaction. What is the percentage of potassium carbonate in the mixture?

(b) The excess HCl is found by titration to be chemically equivalent to 86.6 milliliters of 1.50 molar NaOH. Calculate the percentages of potassium hydroxide and of potassium chloride in the original mixture.

Answer:

(a) $K_2CO_3 + 2\ HCl \rightarrow CO_2 + 2\ KCl + H_2O$
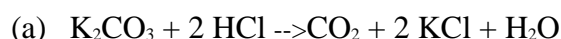
$$\text{mol } CO_2 = \frac{PV}{RT} = \frac{(740\,\text{torr})(249\,\text{mL})}{(62400\,\frac{\text{mL\_torr}}{\text{mol\_K}})(295K)} =$$

$$= 0.0100 \text{ mol } CO_2$$

0.10 mol CO_2 × 1 mol K_2CO_3 / 1mol CO_2 × 138.2 g K_2CO_3 /1 mol K_2CO_3 =
=1.38 g K_2CO_3

1.38 g K_2CO_3/5.00 g mixture × 100% = 27.6% K_2CO_3

(b) orig. mol HCl = 0.100 L × 2.00M   = 0.200 mol
   reacted with K_2CO_3 = 0.020 mol
   excess HCl = 0.0866L × 1.50M   = 0.130 mol
   mol HCl that reacted w/KOH   = 0.050 mol
   0.050 mol KOH = 2.81 g = 56.1% of sample
   the remaining KCl amounts to 16.3%

1972

Given a solution of ammonium chloride. What additional reagent or reagents are needed to prepare a buffer from the ammonium chloride solution?

Explain how this buffer solution resists a change in pH when:

(a) Moderate amounts of strong acid are added.

(b) Moderate amounts of strong base are added.

(c) A portion of the buffer solution is diluted with an equal volume of water.

Answer:

Since ammonium chloride is a salt of a weak base, the weak base is needed, ammonia, NH_3.

(a) When moderate amounts of a strong acid, H^+, are added, the ammonia reacts with it. The concentration of the hydrogen ion remains essentially the same and therefore only a very small change in pH.

$$NH_3 + H^+ <=> NH_4^+$$
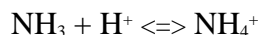
(b) When moderate amounts of a strong base, OH^-, are added, the ammonium ion reacts with it. The concentration of the hydrogen ion remains essentially the same and therefore only a very small change in pH.

$$NH_4^+ + OH^- <=> NH_3 + H_2O$$
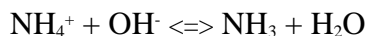
(c) By diluting with water the relative concentration ratio of $[NH_4^+]/[NH_3]$ does not change, therefore there should be no change in pH.

1973

A sample of 40.0 milliliters of a 0.100 molar $HC_2H_3O_2$ solution is titrated with a 0.150 molar NaOH solution. K_a for acetic acid = 1.8×10^{-5}

(a) What volume of NaOH is used in the titration in order to reach the equivalence point?

(b) What is the molar concentration of $C_2H_3O_2^-$ at the equivalence point?

(c) What is the pH of the solution at the equivalence point?

Answer:

(a) $M_aV_a=M_bV_b$
   $(0.100M)(40.0 \text{ mL}) = (0.150M)(V_b)$

$V_b = 26.7$ mL

(b) acetate ion is a weak base with

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

$$[CH_3COO^-]_0 = \frac{4.00 \text{ mmol}}{(40.0 \text{mL} + 26.7 \text{mL})} = 0.0600 \text{ M}$$

$[CH_3COO^-]_{eq} = 0.600M - X$

$[OH^-] = [CH_3COOH] = X$

$5.6 \times 10^{-10} = \dfrac{X^2}{(0.0600 - X)}; \quad X = 9.66 \times 10^{-5} M$

$0.0600M - 9.66 \times 10^{-5}M = 0.0599M \; [CH_3COO^-]_{eq}$

$[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.0 \times 10^{-14}}{9.66 \times 10^{-5}} = 1.04 \times 10^{-10} \text{ M}$
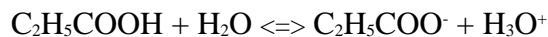
(c)

$pH = -\log [H^+] = -\log(1.04 \times 10^{-10}) = 9.98$

1974 A

A solution is prepared from 0.0250 mole of HCl, 0.10 mole propionic acid, C_2H_5COOH, and enough water to make 0.365 liter of solution. Determine the concentrations of H_3O^+, C_2H_5COOH, $C_2H_5COO^-$, and OH^- in this solution. K_a for propionic acid = 1.3×10^{-5}

Answer:

$C_2H_5COOH + H_2O \Longleftrightarrow C_2H_5COO^- + H_3O^+$

$[C_2H_5COO^-] = X$

$[C_2H_5COOH] = (0.10 mol/0.365L) - X$

$[H_3O^+] = (0.0250 mol/0.365L) + X$

$K_a = \dfrac{(X)(0.0685 + X)}{0.274 - X} = 1.3 \times 10^{-5}; \quad X = 5.2 \times 10^{-5}$

$[C_2H_5COO^-] = 5.2 \times 10^{-5}M; \; [C_2H_5COOH] = 0.274M$

$[H_3O^+] = 0.0685M;$

$[OH^-] = \dfrac{K_w}{0.0685} = 1.46 \times 10^{-13} \text{ M}$

1975 A

(a) A 4.00 gram sample of $NaOH_{(s)}$ is dissolved in enough water to make 0.50 liter of solution. Calculate the pH of the solution.

(b) Suppose that 4.00 grams of $NaOH_{(s)}$ is dissolved in 1.00 liter of a solution that is 0.50 molar in NH_3 and 0.50 molar in NH_4^+. Assuming that there is no change in volume and no loss of NH_3 to the atmosphere, calculate the concentration of hydroxide ion, after a chemical reaction has occurred. [Ionization constant at 25°C for the reaction $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$; K = 1.8×10^{-5}]

Answer:

$\dfrac{4.00 \text{gNaOH}}{0.50L} \times \dfrac{1 \text{ mol}}{40.0 \text{g}} = 0.20M$

(a)

$$[H^+] = \frac{K_w}{0.20} = 5 \times 10^{-14}; \ pH = -\log[H^+] = 13.3$$

(b)
$$[OH^-] = \frac{0.100 \ mol}{1.00 \ L} - X$$

$[NH_4^+] = 0.50M - X; \ [NH_3] = 0.50M + X$

$$1.8 \times 10^{-5} = \frac{(0.50 - X)(0.100 - X)}{(0.50 + X)}; \ X = 0.100 \ M$$

using the Henderson-Hasselbalch equation

$$pH = pK_a + \log\left[\frac{[NH_4^+]}{[NH_3]}\right] = 4.74 + \log\left(\frac{0.40}{0.60}\right) = 4.57$$
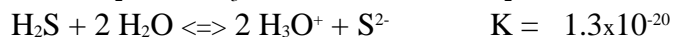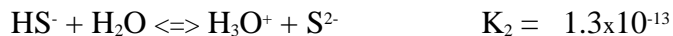
1975

Reactions requiring either an extremely strong acid or an extremely strong base are carried out in solvents other than water. Explain why this is necessary for both cases.

Answer:

Water is amphoteric and can behave either as an acid in the presence of a strong base or as a base in the presence of strong acid.

Water also undergoes autoionization.

1976

$H_2S + H_2O \Longleftrightarrow H_3O^+ + HS^-$	$K_1 =$	1.0×10^{-7}
$HS^- + H_2O \Longleftrightarrow H_3O^+ + S^{2-}$	$K_2 =$	1.3×10^{-13}
$H_2S + 2 H_2O \Longleftrightarrow 2 H_3O^+ + S^{2-}$	$K =$	1.3×10^{-20}
$Ag_2S_{(s)} \Longleftrightarrow 2 Ag^+ + S^{2-}$	$K_{sp} =$	5.5×10^{-51}

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

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

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

Answer:

(a) $H_2S + H_2O \Longleftrightarrow H_3O^+ + HS^-$
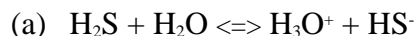
$$\frac{[H_3O^+][HS^-]}{[H_2S]} = 1.0 \times 10^{-7}$$

let $X = [H_3O^+] = [HS^-]$

$$\frac{X^2}{0.10 - X} = 1.0 \times 10^{-7}$$

$X \ll 0.10; \ X = 1.0 \times 10^{-4} \ M = [H_3O^+]$

(b) $H_2S + 2 H_2O \Longleftrightarrow 2 H_3O^+ + S^{2-}$
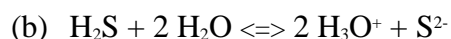
$$\frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} = 1.3 \times 10^{-20}$$

$$\frac{[0.40]^2[S^{2-}]}{[0.10]} = 1.3 \times 10^{-20} \qquad ; [S^{2-}] = 8.1 \times 10^{-21}M$$

(c) $Ag_2S_{(s)} \iff 2\,Ag^+ + S^{2-}$; $[Ag^+]^2[S^{2-}] = 5.5 \times 10^{-51}$
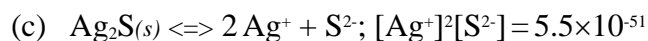
$$[Ag^+] = \sqrt{\frac{5.5 \times 10^{-51}}{1.5 \times 10^{-17}}} = 1.9 \times 10^{-17}\,M$$

1977

The value of the ionization constant, K_a, for hypochlorous acid, HOCl, is 3.1×10^{-8}.
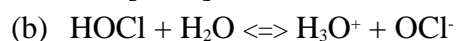
(a) Calculate the hydronium ion concentration of a 0.050 molar solution of HOCl.

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

(c) A solution is prepared by the disproportionation reaction below. $Cl_2 + H_2O \longrightarrow HCl + HOCl$
Calculate the pH of the solution if enough chlorine is added to water to make the concentration of HOCl equal to 0.0040 molar.
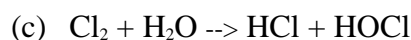
Answer:

(a) $HOCl + H_2O \iff H_3O^+ + OCl^-$
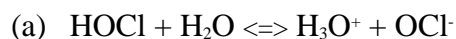
$$3.2 \times 10^{-8} = \frac{[H_3O^+][OCl^-]}{[HOCl]} = \frac{X^2}{(0.050 - X)}$$

$X = [H_3O^+] = 4.0 \times 10^{-5}M$

(b) $HOCl + H_2O \iff H_3O^+ + OCl^-$

$$\frac{[H_3O^+][0.010 + X]}{[0.0250 - X]} = 3.2 \times 10^{-8} \qquad ; \ X \ll 0.010$$

$X = [H_3O^+] = 8.0 \times 10^{-8}M$

(c) $Cl_2 + H_2O \longrightarrow HCl + HOCl$

[HOCl] = [HCl] = 0.0040M

HCl as principal source of H_3O^+

pH = -log$[H_3O^+]$ = 2.40

1978 A

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

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

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

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

(d) Calculate the $[H_3O^+]$ at pH = 5.65

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

Answer:

(a) at equivalence point, moles HA = moles NaOH

$= M_bV_b = (0.0274 \text{ L})(0.135 \text{ M}) = 3.70\times10^{-3} \text{ mol HA}$

(b) $\text{molec.wt.} = \dfrac{\text{mass HA}}{\text{mol HA}} = \dfrac{0.682 \text{ g}}{3.70 \infty10^{-3} \text{ mol}} = 184 \text{ g/mol}$

(c) $\text{HA} + \text{OH}^- \text{ --> } \text{A}^- + \text{H}_2\text{O}$

    initial: 0.00370 mol

    added: $(0.0106\text{L})(0.135\text{M}) = 0.00143$ mole

    remaining: $(0.00370 - 0.00143) = 0.00227$ mol

(d) $\text{pH} = -\log[\text{H}_3\text{O}^+];\ [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.65}$

    $= 2.2\times10^{-6}\text{M}$

(e) $K_a = \dfrac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \dfrac{(2.2\infty10^{-6})(0.00143\ /\ v)}{(0.00227\ /\ v)}$

    $= 1.4\times10^{-6}$

1978 D

Predict whether solutions of each of the following salts are acidic, basic, or neutral. Explain your prediction in each case

(a) $\text{Al(NO}_3)_3$ (b) K_2CO_3 (c) NaBr

Answer:

(a) acidic; $\text{Al}^{3+} + \text{H}_2\text{O} <=> \text{AlOH}^{2+} + \text{H}^+$;

    hydrolysis of Al^{3+};

    $\text{Al(OH}_2)_n^{3+}$ as Bronsted acid, etc.

(b) basic; $\text{CO}_3^{2-} + \text{H}_2\text{O} <=> \text{HCO}_3^- + \text{OH}^-$; or

    hydrolysis of CO_3^{2-} as conjugate to a weak acid, etc.

(c) neutral; Na^+ from strong base; Br^- from strong acid


1979 B

A solution of hydrochloric acid has a density of 1.15 grams per milliliter and is 30.0% by weight HCl.

(a) What is the molarity of this solution of HCl?

(b) What volume of this solution should be taken in order to prepare 5.0 liters of 0.20 molar hydrochloric acid by dilution with water?

(c) In order to obtain a precise concentration, the 0.20 molar hydrochloric acid is standardized against pure HgO (molecular weight = 216.59) by titrating the OH- produced according to the following quantitative reaction.

$$\text{HgO}_{(s)} + 4\ \text{I}^- + \text{H}_2\text{O} \text{ --> } \text{HgI}_4^{2-} + 2\ \text{OH}^-$$
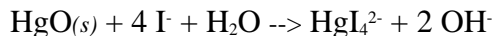
In a typical experiment 0.7147 grams of HgO required 31.67 milliliters of the hydrochloric acid solution for titration. Based on these data what is the molarity of the HCl solution expressed to four significant figures.
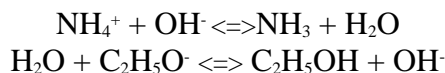
Answer:

(a) $\dfrac{1.15\text{g}}{1\,\text{mL}} \infty \dfrac{1000\,\text{mL}}{1\,\text{L}} \infty \dfrac{30.0\text{gHCl}}{100\,\text{g}} \infty \dfrac{1\,\text{mol}}{35.5\text{g}} = 9.5\text{M}$

(b) $M_fV_f = M_iV_i$

$(0.20M)(5.0L) = (9.5M)(V)$

$V = 0.11$ L

$\dfrac{0.7147\ g}{216.59\ g/mol} = 0.003300$ mol HgO

(c)

mol OH⁻ prod. = 2 (mol HgO) = 0.006600 mol

mol HCl req. = mol OH⁻ prod. = 0.006600 mol

$M_{HCl} = \dfrac{0.006600\ mol}{0.03167\ L} = 0.2084$ M

1979 D

$$NH_4^+ + OH^- <=> NH_3 + H_2O$$
$$H_2O + C_2H_5O^- <=> C_2H_5OH + OH^-$$

The equations for two acid-base reactions are given above. Each of these reactions proceeds essentially to completion to the right when carried out in aqueous solution.

(a) Give the Bronsted-Lowry definition of an acid and a base.

(b) List each acid and its conjugate base for each of the reactions above.

(c) Which is the stronger base, ammonia or the ethoxide ion. $C_2H_5O^-$? Explain your answer.

Answer:

(a) acid = proton donor; base = proton acceptor

(b)

	Acid	Conjugate base
1ˢᵗ reaction	NH_4^+	NH_3
	H_2O	OH^-
2ⁿᵈ reaction	H_2O	OH^-
	C_2H_5OH	$C_2H_5O^-$

(c) ethoxide is a stronger base than ammonia.

A stronger base is always capable of displacing a weaker base. Since both reactions are quantitative, in terms of base strength, $OH^- > NH_3$ in 1ˢᵗ reaction; $C_2H_5O^- > OH^-$ in 2ⁿᵈ rxn.

1980 A

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

$$CH_3NH_2 + H_2O <=> CH_3NH_3^+ + OH^-$$
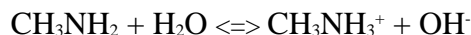
(a) At 25°C the percentage ionization in a 0.160 molar solution of CH_3NH_2 is 4.7%. Calculate $[OH^-]$, $[CH_3NH_3^+]$, $[CH_3NH_2]$, $[H_3O^+]$, and the pH of a 0.160 molar solution of CH_3NH_2 at 25°C

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

(c) If 0.050 mole of crystalline lanthanum nitrate is added to 1.00 liter of a solution containing 0.20 mole of CH_3NH_2 and 0.20 mole of its salt CH_3NH_3Cl at 25°C, and the solution is stirred until equilibrium is attained, will any $La(OH)_3$ precipitate? Show the calculations that prove your answer. (The solubility constant for $La(OH)_3$, $K_{sp} = 1\times10^{-19}$ at 25°C)

Answer:

(a) CH_3NH_2; 0.160M x 4.7% = 7.5×10^{-3} M ionizing

$(0.160M - 0.0075M) = 0.0152M$ @ equilibrium

$[CH_3NH_3{}^+] = [OH^-] = 7.5 \times 10^{-3}$ M

$[H_3O^+] = \dfrac{K_w}{7.5 \times 10^{-3}} = 1.3 \times 10^{-12}$ M

pH = -log $[H_3O^+]$ = 11.89

(b) $K_b = \dfrac{[CH_3NH_3{}^+][OH^-]}{[CH_3NH_2]} = \dfrac{(7.5 \times 10^{-3})^2}{0.152}$

$= 3.7 \times 10^{-4}$

(c) $K_b = 3.7 \times 10^{-4} = \dfrac{(0.20 + X)(X)}{(.020 - X)} \approx X$

$= [OH^-]$

$Q = [La^{3+}][OH^-]^3 = (0.050)(3.7 \times 10^{-4})^3$

$= 2.5 \times 10^{-12}$

$Q > K_{sp}$, therefore, $La(OH)_3$ precipitates

1981 D

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

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

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

Answer:

(a) $Al(NO_3)_3$ - acidic K_2CO_3 - basic

 $NaHSO_4$ - acidic NH_4Cl - acidic

(b) $Al^{3+} + H_2O \longrightarrow Al(OH)^{2+} + H^+$

 $Al(H_2O)_6{}^{3+} + H_2O \longrightarrow [Al(H_2O)_5OH]^{2+} + H_3O^+$

 $Al^{3+} + 3\ H_2O \longrightarrow Al(OH)_3 + 3\ H^+$

 $CO_3{}^{2-} + H_2O \longrightarrow HCO_3{}^- + OH^-$

 $HSO_4{}^- + H_2O \longrightarrow SO_4{}^{2-} + H_3O^+$

 $NH_4{}^+ + H_2O \longrightarrow NH_3 + H_3O^+$

1982 A

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

(a) Calculate the pH of this solution.

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

(c) A 5.00 millilitre sample of 1.00 molar HCl is added to 100. millilitres of the <u>original</u> buffer solution. Calculate the $[H_3O^+]$ of the resulting solution.

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

Answer:

(a) using the Henderson-Hasselbalch equation

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

$$= -\log(1.8 \times 10^{-4}) + \log\left[\frac{0.60}{0.40}\right]$$

$$= 3.92 \qquad \{\text{other approaches possible}\}$$

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

(c) initial concentrations

$$1.00\,M\ HCl\ \times \frac{5.00\,mL}{105\,mL} = 0.0476\ M$$

$$0.40\ M\ HCOOH\ \times \frac{100\,mL}{105\,mL} = 0.38\,M$$

$$0.60\,M\ HCOO^-\ \times \frac{100\,mL}{105\,mL} = 0.57\,M$$

concentrations after H^+ reacts with $HCOO^-$

$0.38M + 0.05M = 0.43M\ HCOOH$

$0.57M - 0.05M = 0.52M\ HCOO^-$

$$[H_3O^+] = 1.8 \times 10^{-4} \times \frac{0.43\,M}{0.52\,M} = 1.5 \times 10^{-4}\ M$$

(d) $0.800L \times 2.00M\ HCOOH = 1.60\ mol$

$0.200L \times 4.80M\ NaOH = 0.96\ mol\ OH^-$

at equil., $(1.60 - 0.96) = 0.64\ mol\ HCOOH$ and $0.96\ mol\ HCOO^-$

$$[H_3O^+] = 1.8 \times 10^{-4} \times \frac{0.64\,M}{0.96\,M} = 1.2 \times 10^{-4}\ M$$

1982 D

A solution of barium hydroxide is titrated with 0.1-M sulfuric acid and the electrical conductivity of the solution is measured as the titration proceeds. The data obtained are plotted on the graph below.
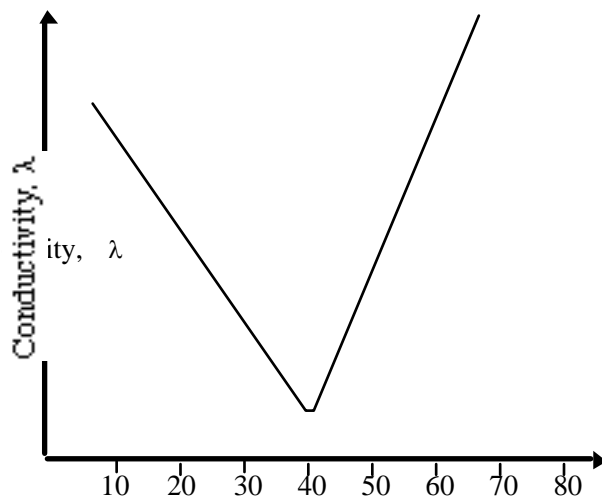
(a) For the reaction that occurs during the titration described above, write a balanced net ionic equation.

(b) Explain why the conductivity decreases, passes through a minimum, and then increases as the volume of H_2SO_4 added to the barium hydroxide is increased.

(c) Calculate the number of moles of barium hydroxide originally present in the solution that is titrated.

(d) Explain why the conductivity does not fall to zero at the equivalence point of this titration.

Answer:

(a) $Ba^{2+} + 2\,OH^- + 2\,H^+ + SO_4^{2-} \longrightarrow BaSO_{4(s)} + 2\,H_2O$

(b) The initial conductivity is high because of the presence of Ba^{2+} and OH^- ions. The conductivity decreases because Ba^{2+} forms insoluble $BaSO_4$ with the addition of SO_4^{2-}. The conductivity also decreases because OH^- combines with the addition of H^+ ions by forming H_2O. Beyond the equivalence point conductivity increases as H^+ and SO_4^{2-} ions are added.

(c) # mol $Ba(OH)_2$ = # mol H_2SO_4

=0.1M × 0.04L = 0.004 mol

(d) $BaSO_{4(s)}$ dissociates slightly to form Ba^{2+} and SO_4^{2-}, while the water ionizes slightly to form H^+ and OH^-.

1983 B

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 millilitres in a volumetric flask. Several 50.00 millilitre portions of this solution were titrated against NaOH solution, requiring an average of 38.21 millilitres of NaOH.

The NaOH solution was standardized against oxalic acid dihydrate, $H_2C_2O_4{\cdot}2H_2O$ (molecular weight: 126.066 gram mol^{-1}). The volume of NaOH solution required to neutralize 1.2596 grams of oxalic acid dihydrate was 41.24 millilitres.

(a) Calculate the molarity of the NaOH solution.

(b) Calculate the number of moles of HX in a 50.00 millilitre portion used for titration.

(c) Calculate the molecular weight of HX.

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

Answer:

(a) mol $H_2C_2O_4{\cdot}2H_2O = \dfrac{1.2596\ g}{126.066\ \sfrac{g}{mol}} =$

9.9916x10⁻³ mol

$H_2C_2O_4 + 2\,NaOH \longrightarrow Na_2C_2O_4 + 2\,H_2O$

$9.9916 \times 10^{-3}\,mol \times \dfrac{2\,mol\,NaOH}{1\,mol\,H_2C_2O_4} = 1.9983 \times 10^{-2}\,mol$ $M_{NaOH} = \dfrac{1.9983 \times 10^{-2}\,mol}{0.04124\ L} = 0.4846\ M$

(b) mol HX = mol NaOH

0.03821 L x 0.4846 M = 0.01852 mol HX

(c) $\dfrac{0.01852\ \text{mol}}{50.00\,\text{mL}} \infty\, 250.00\,\text{mL} = 0.09260\ \text{mol HX}$

$\text{MW} = \dfrac{15.126\ \text{g}}{0.09260\ \text{mol}} = 163.3\ \text{g}\!\!\Big/\!\!\text{mol}$

(d) The calculated molecular weight is smaller than true value, because:

measured g $H_2C_2O_4$ is larger than true value,

calculated mol $H_2C_2O_4$ 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,

$\text{MW} = \dfrac{\text{g HX \ (true value)}}{\text{mol HX \ (calculated , and too large)}}$

1983 C

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

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

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

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

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

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

Which of these applicants has given an appropriate procedure? Explain your answer, referring to your discussion in part (a). Explain what is wrong with the erroneous procedures.

(No calculations are necessary, but the following acidity constants may be helpful: acetic acid, $K_a = 1.8 \times 10^{-5}$; NH_4^+, $K_a = 5.6 \times 10^{-10}$)

Answer:

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

Preparation of a buffer: (1) mix a weak acid + a salt of a weak acid; or (2) mix a weak base + salt of a weak base; or (3) mix a weak acid with about half as many moles of strong base; or (4) mix a weak base with about half as many moles of strong acid; or (5) mix a weak acid and a weak base.

(b) Carla has the correct procedure, she has mixed a weak base, NH_3, with the salt of a weak base, NH_4Cl.

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

Beula doesn't have a buffer solution, 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 A

Sodium benzoate, C_6H_5COONa, is the salt of a the weak acid, benzoic acid, C_6H_5COOH. A 0.10 molar solution of sodium benzoate has a pH of 8.60 at room temperature.

(a) Calculate the [OH⁻] in the sodium benzoate solution described above.

(b) Calculate the value for the equilibrium constant for the reaction:
$$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$$

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

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

Answer:

(a) $pH = 8.6, pOH = 5.4$

$[OH^-] = 10^{-pOH} = 3.98 \times 10^{-6} M$

(b) $[C_6H_5COOH] = [OH^-]$

$$K_b = \frac{[C_6H_5COH][OH^-]}{[C_6H_5CO_2^-]} = \frac{(3.98 \times 10^{-6})^2}{(0.1 - 3.98 \times 10^{-6})}$$

$= 1.58 \times 10^{-10}$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.58 \times 10^{-10})} = 6.33 \times 10^{-5}$$

(c)

(d) $pH\ 2.88 = 1.32 \times 10^{-3} M\ [H^+] = [C_6H_5COO^-]$

$$[C_6H_5CO_2H] = \frac{[H^+][C_6H_5CO_2^-]}{K_a} = \frac{(1.32 \times 10^{-3})^2}{6.33 \times 10^{-5}}$$

$= 2.75 \times 10^{-2} M\ [C_6H_5COOH]$

total dissolved $= (2.75 \times 10^{-2} M + 1.32 \times 10^{-3} M$ as ions$)$

$= 2.88 \times 10^{-2} M$

1984 C

Discuss the roles of indicators in the titration of acids and bases. Explain the basis of their operation and the factors to be considered in selecting an appropriate indicator for a particular titration.

Answer:

An indicator signals the end point of a titration by changing color.

An indicator is a weak acid or weak base where the acid form and basic form of the indicators are of different colors.

An indicator changes color when the pH of the solution equals the pKa of the indicator. In selecting an indicator, the pH at which the indicator changes color should be equal to (or bracket) the pH of the solution at the equivalence point.

For example, when a strong acid is titrated with a strong base, the pH at the equivalence point is 7, so we would choose an indicator that changes color at a pH = 7. {Many other examples possible.}

1986 A

In water, hydrazoic acid, HN_3, is a weak acid that has an equilibrium constant, K_a, equal to 2.8x10⁻⁵ at 25°C. A 0.300 litre sample of a 0.050 molar solution of the acid is prepared.

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

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

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

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

Answer:

(a) $HN_3 \rightleftharpoons H^+ + N_3^-$

$$K_a = \frac{[H^+][N_3^-]}{[HN_3]}$$

(b) $[H^+] = [N_3^-] = X$
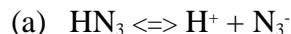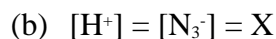
$$2.8 \times 10^{-5} = \frac{X^2}{0.050}; \quad X = 1.2 \times 10^{-3}\,M$$

pH = -log[H$^+$] = 2.93

(c)
$$[N_3^-] = \frac{0.80\,g}{0.150\,L} \times \frac{1\,mol}{65\,g} = 0.082\,M$$

$$2.8 \times 10^{-5} = \frac{[H^+](0.082)}{0.050}; \quad [H^+] = 1.7 \times 10^{-5}\,M$$

pH = 4.77

(d) (0.075L)(0.100M) = 0.0075 mol NaOH

(0.150L)(0.050M) = 0.0075 mol HN_3

$OH^- + HN_3 \longrightarrow H_2O + N_3^-$; neut. complete

$$K_b = \frac{K_w}{K_a}$$

$N_3^- + H_2O \rightleftharpoons HN_3 + OH^-$;
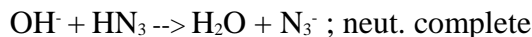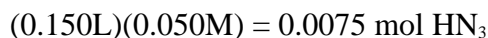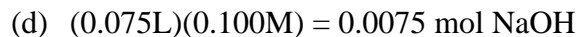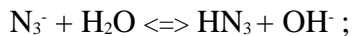
$$\frac{1.0 \times 10^{-14}}{2.8 \times 10^{-5}} = \frac{[HN_3][OH^-]}{[N_3^-]} = \frac{X^2}{0.0075 \big/ 0.225}$$

$X = [OH^-] = 3.5 \times 10^{-6}\,M$

1986 D

H_2SO_3 HSO_3^- $HClO_4$ $HClO_3$ H_3BO_3

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.

(b) Arrange the examples above in the order of <u>increasing</u> acid strength.

Answer:

(a) 1) As effective nuclear charge on central atom increases, acid strength increases. **OR**

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

As electronegativity of central atom increases, acid strength increases.

2) Loss of H^+ by a neutral acid molecule reduces acid strength. **OR**
K_a of $H_2SO_3 > K_a$ of HSO_3^-

(b) $H_3BO_3 < HSO_3^- < H_2SO_3 < HClO_3 < HClO_4$
H_3BO_3 or HSO_3^- weakest (must be together)

1987 A

$NH_3 + H_2O \Longleftrightarrow NH_4^+ + OH^-$ Ammonia is a weak base that dissociates in water as shown above. At 25°C, the base dissociation constant, K_b, for NH_3 is 1.8×10^{-5}.

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

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

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

Answer:

(a) $[NH_4^+] = [OH^-] = X$; $[NH_3] = (0.150 - X)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \quad ; \quad 1.8 \times 10^{-5} = \frac{X^2}{0.150 - X}$$

$X = [OH^-] = 1.6 \times 10^{-3} M$

% diss. $= \dfrac{1.6 \times 10^3}{0.150}$ x 100% = 1.1%

(b) $[NH_4^+] = 0.0500$ mol/0.100L = 0.500M
$[NH_3] = 0.150M$

$$1.8 \times 10^{-5} = \frac{(0.500)(X)}{0.150} \quad ; \quad X = [OH^-] = 5.4 \times 10^{-6} M$$

pOH = 5.27; pH = (14 - 5.27) = 8.73

(c) $Mg(OH)_2 \Longleftrightarrow Mg^{2+} + 2 OH^-$
$[Mg^{2+}] = (0.0800 mol/0.100L) = 0.800M$
$[OH^-] = 5.4 \times 10^{-6} M$
$Q = [Mg^{2+}][OH^-]^2 = (0.800)(5.4 \times 10^{-6})^2$
$= 2.3 \times 10^{-11}$
$Q > K_{sp}$ so $Mg(OH)_2$ precipitates

1987 B

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, $KHC_8H_4O_4$, a monoprotic acid often used as a primary standard. A sample of pure $KHC_8H_4O_4$ weighing 1.518 grams was dissolved in water and titrated with the NaOH solution.

To reach the equivalence point, 26.90 millilitres of base was required. Calculate the molarity of the NaOH solution. (Molecular weight: $KHC_8H_4O_4 = 204.2$)

(b) A 10.00 millilitre sample of the concentrated nitric acid was diluted with water to a total volume of 500.00 millilitres. Then 25.00 millilitres of the diluted acid solution was titrated with the standardized NaOH solution prepared in part (a). The equivalence point was reached after 28.35 millilitres of the base had been added. Calculate the molarity of the concentrated nitric acid.

(c) The density of the concentrated nitric acid used in this experiment was determined to be 1.42 grams per millilitre. Determine the percentage by weight of HNO_3 in the original sample of concentrated nitric acid.

Answer:

(a)
$$1.518 \text{ g} \times \frac{1\text{mol}}{204.2\text{g}} = 7.434 \times 10^{-3} \text{ mol acid}$$

$= \text{mol NaOH required to neut.}$

$$\frac{7.434 \times 10^{-3}\text{mol}}{0.02690 \text{ L}} = 0.2764 \text{ M NaOH}$$

(b)
$$\frac{28.35\,\text{mLNaOH}}{25.00\,\text{mLHNO}_3} \times \frac{0.2764 \text{ mol}}{1\text{L}} \times \frac{1\text{molHNO}_3}{1\text{molNaOH}} =$$

$= 0.3134\text{M HNO}_3$

$M_fV_f = M_iV_i; (0.3134\text{M})(500\text{mL}) = (M)(10.00\text{mL})$

$M = 15.67\text{M HNO}_3$

(c)
$$\% \text{ HNO}_3 \text{ in conc . sol'n} = \frac{g/\text{L HNO}_3}{g/\text{L sol'n}} \times 100\%$$

grams HNO_3 in 1 L conc. sol'n =
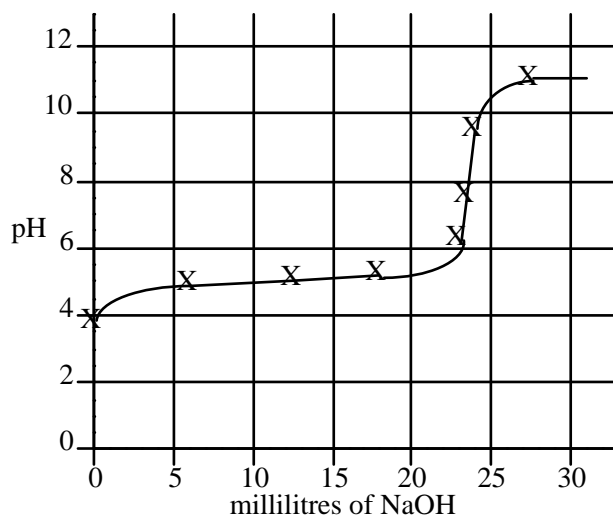$$\frac{15.67\,\text{molHNO}_3}{1 \text{ L}} \times \frac{63.02\text{g}}{1 \text{ mol}} = 987.5\,{}^g\!/_L$$

grams sol'n in 1 L conc. Sol'n
$$\frac{1.42\text{g sol'n}}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1420\,{}^g\!/_L$$

$$[HA] = \frac{(0.0152\,3\text{ L})(0.2211\,{}^{mol}\!/_L)}{0.0700\,0 \text{ L}} = 0.04810 \text{ M}$$

$$K = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a} = \frac{1.\times10^{-14}}{7.7\times10^{-5}} = 1.3\times10^{-10}$$

$$[A^-] = \frac{7.789\times10^{-3}\text{mol}}{0.0852\,3 \text{ L}} = 0.0914 \text{ M}$$
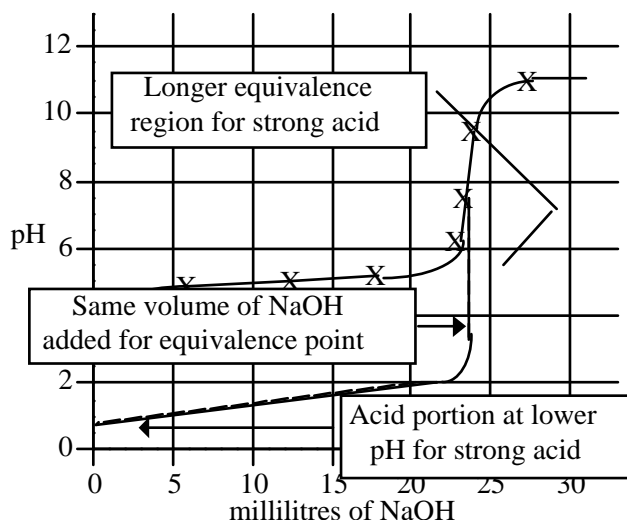
1988 D

A 30.00 millilitre 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 dissociation constant K_a of the weak monoprotic acid.

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

    Methyl red $K_a = 1\times10^{-5}$
    Cresol red $K_a = 1\times10^{-8}$
    Alizarin yellow $K_a = 1\times10^{-11}$

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

Answer:

(a) The sharp vertical rise in 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 0.30L, the volume of the acid.

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

(c) Cresol red is the best indicator because its pK_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)

12 —

Longer equivalence
region for strong acid

10 —

8 —

pH 6 —

Same volume of NaOH
added for equivalence point

2 —

Acid portion at lower
pH for strong acid

0 —

0   5   10   15   20   25   30

millilitres of NaOH

1989 A

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 millilitres 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 millilitres of the base has 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 millilitres of NaOH had been added during the titration, the pH of the solution was 4.23. Calculate the acid ionization constant for ascorbic acid.

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

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

Answer:

(a) $(0.2211M)(0.03523L) = 7.789 \times 10^{-3}$ mol

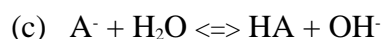$1.3717g / 7.789 \times 10^{-3}$ mol $= 176.1$ g/mol

(b) at pH 4.23, $[H^+] = 8.0 \times 10^{-8}$ M

$$[A^-] = \frac{(0.02000 \text{ L})(0.2211 \text{ mol}\_L^{-1})}{0.07000 \text{ L}} = 0.06317 \text{ M}$$

$$[HA] = \frac{(0.01523 \text{ L})(0.2211 \text{ mol}\_L^{-1})}{0.07000 \text{ L}} = 0.04810 \text{ M}$$

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

(c) A⁻ + H₂O <=> HA + OH⁻

$$K = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a} = \frac{1.\infty 10^{-14}}{7.7 \infty 10^{-5}} = 1.3 \infty 10^{-10}$$

(d) at equiv. pt.

$$[A^-] = \frac{7.789 \times 10^{-3} \, \text{mol}}{0.08523 \, \text{L}} = 0.0914 \, M$$

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

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

$pOH = -\log(3.4 \times 10^{-6}) = 5.47; \; pH = (14 - 5.47) = 8.53$

1990 D

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 ($K_1 \sim 10^5 K_2$).

(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.

Answer:

(a) 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^-. Therefore, the bond is stronger, H^+ is harder to remove, and K_2 is lower.

(b) 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 acidic solution.

(c) Water is a more basic solvent (greater attraction for H^+) and removes H^+ from HCl and HI equally.

Acetic acid has little attraction for H^+, but the H^+ separates from the larger I^- more easily than from the smaller Cl^-.

(d) The bond between H and Cl is weaker than the bond between H and F. Therefore, HCl is a stronger acid.

1991 A

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.

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

(c) What is the ratio of the concentration of propanoate ion, $C_2H_5COO^-$, to that of propanoic acid in a buffer solution with a pH of 5.20?

(d) In a 100.-milliliter sample of a different buffer solution, the propanoic acid concentration is 0.35-molar and the sodium propanoate concentration is 0.50-molar. To this buffer solution, 0.0040 mole of solid NaOH is added. Calculate the pH of the resulting solution.

Answer:

(a) $\dfrac{[H^+][C_2H_5COO]}{[C_2H_5COOH]} = K_a$

$[H^+] = [C_2H_5COO^-] = X$

$[C_2H_5COOH] = 0.20$ M - X

assume X is small, $\therefore$, 0.20 - X ~ 0.20

$$\frac{X^2}{0.20} = 1.3 \times 10^{-5}; X = 1.6 \times 10^{-3} \text{ M} = [H^+]$$

(b) from (a), X = amount of acid that ionized, therefore,

$$\frac{1.6 \times 10^3}{0.20} \text{ x } 100\% = 0.81\% \text{ ionized}$$

(c) @ pH 5.20, $[H^+] = $ antilog $(-5.20) = 6.31 \times 10^{-6}$ M

$$\frac{(6.3 \times 10^{-6})[C_2H_5COO^-]}{[C_2H_5COOH]} = K_a = 1.3 \times 10^{-5}$$

$$\frac{[C_2H_5COO]}{[C_2H_5COOH]} = \frac{2.1}{1}$$

OR

(c) Henderson-Hasselbalch

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

$$5.20 = 4.89 + \log\frac{[C_3H_5O_2^-]}{[HC_3H_5O_2]}$$

$$\log\frac{[C_3H_5O_2^-]}{[HC_3H_5O_2]} = 0.31 = 2.1$$

(d) $[C_2H_5COO^-] = 0.50$ M; $[C_2H_5COOH] = 0.35$ M

$[OH-] = 0.0040$ mol/0.100 L $= 0.040$ M

this neutralizes 0.04 M of the acid, giving $[C_2H_5COOH] = 0.31$ M and the propanoate ion increases by a similar amount to 0.54 M.

$$\frac{[H^+](0.54)}{0.31} = 1.3 \text{ x } 10^{-5}, \ [H^+] = 7.5 \text{ x } 10^{-6}M$$

pH = - log $[H^+] = 5.13$

OR
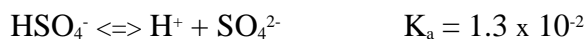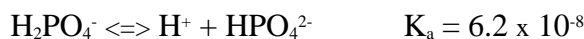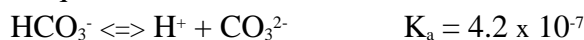
(d) using [ ]'s or moles of propanoic acid and propanoate ion...

$$pH = pK_a + \log\frac{0.54}{0.31}$$

$$= 4.89 + 0.24 = 5.13$$

1992 D

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

$HCO_3^- \Longleftrightarrow H^+ + CO_3^{2-}$ $\qquad K_a = 4.2$ x 10^{-7}

$H_2PO_4^- \Longleftrightarrow H^+ + HPO_4^{2-}$ $\qquad K_a = 6.2$ x 10^{-8}

$HSO_4^- \Longleftrightarrow H^+ + SO_4^{2-}$ $\qquad K_a = 1.3$ x 10^{-2}

(a) From the systems above, identify the conjugate pair that is best for preparing a buffer with a pH of 7.2. Explain your choice.

(b) Explain briefly how you would prepare the buffer solution described in (a) with the conjugate pair you have chosen.

(c) If the concentrations of both the acid and the conjugate base you have chosen were doubled, how would the pH be affected? Explain how the capacity of the buffer is affected by this change in concentrations of acid and base.

(d) Explain briefly how you could prepare the buffer solution in (a) if you had available the solid salt of the only one member of the conjugate pair and solution of a strong acid and a strong base.

Answer:

(a) Best conjugate pair: $H_2PO_4^-$, HPO_4^{2-}. When $7.2 = pH = pK_a$ for this pair when $[H_2PO_4^-] = [HPO_4^{2-}]$.

(b) Dissolve equal moles (or amounts) of $H_2PO_4^-$, and HPO_4^{2-} (or appropiate compounds) in water.

(c) pH not changed. Capacity of buffer would increase because there are more moles of conjugate acid and conjugate base to react with added base or acid.

(d) Add strong base to salt of conjugate acid **OR** add strong acid to salt of conjugate base.

Add 1 mole conjugate acid to 1/2 mole strong base **OR** 1 mole conjugate base to 1/2 mole strong acid.

OR

Use pH meter to monitor addition of strong base to conjugate acid **OR** strong acid to conjugate base.


1993 A

$$CH_3NH_2 + H_2O <=> CH_3NH_3^+ + OH^-$$
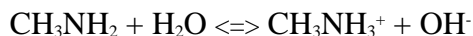
Methylamine, CH_3NH_2, is a weak base that reacts according to the equation above. The value of the ionization constant, K_b, is 5.25×10^{-4}. Methylamine forms salts such as methylammonium nitrate, $(CH_3NH_3^+)(NO_3^-)$.

(a) Calculate the hydroxide ion concentration, $[OH^-]$, of a 0.225-molar aqueous solution of methylamine.

(b) Calculate the pH of a solution made by adding 0.0100 mole of solid methylammonium nitrate to 120.0 milliliters of a 0.225-molar solution of methylamine. Assume no volume change occurs.

(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.

(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.

Answer:

(a)
$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

$$CH_3NH_2 + H_2O <=> CH_3NH_3^+ + OH^-$$

[ ]$_i$ 0.225   0   0
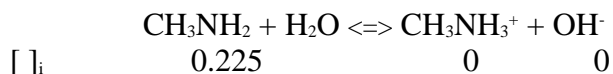
$$\Delta[\ ] \qquad\qquad -X \qquad\qquad +X \qquad +X$$
$$[\ ]_{eq} \qquad 0.225-X \qquad\qquad X \qquad X$$

$$K_b = 5.25 \times 10^{-4} = \frac{[X][X]}{[0.225 - X]} \cong \frac{X^2}{0.225}$$

$X = [OH^-] = 1.09 \times 10^{-2}$ M

solved using quadratic: $X = [OH^-] = 1.06 \times 10^{-2}$ M

(b) $[CH_3NH_3^+] = 0.0100$ mol $/ 0.1200$ L $= 0.0833$ M

or $CH_3NH_2 = 0.120$ L x 0.225 mol/L $= 0.0270$ mol

$$K_b = 5.25 \times 10^{-4} = \frac{[0.0833 + X][X]}{[0.225 - X]} \cong \frac{0.0833\,X}{0.225}$$

$X = [OH^-] = 1.42 \times 10^{-3}$ M; pOH $= 2.85$; pH $= 11.15$

OR

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

$$K_a = \frac{1 \times 10^{-14}}{5.25 \times 10^{-4}} = 1.91 \times 10^{-11}; \quad pK_a = 10.72$$

$$pH = 10.72 + \log \frac{(0.225)}{(0.0833)} = 11.15$$

OR

$$pOH = pK_b + \log \frac{[acid]}{[base]}; \quad pK_b = 3.28$$

$$pOH = 3.28 + \log \frac{(0.0833)}{(0.225)} = 2.85; \quad pH = 11.15$$

(c) HCl must be added.

$$K_b = 5.25 \times 10^{-4} = \frac{[0.0833 + X][0.0010]}{[0.225 - X]}$$

$X = 0.0228$ M

0.0228 mol/L x 0.120 L $= 2.74 \times 10^{-3}$ mol HCl

OR

$$11.00 = 10.72 + \log \frac{[base]}{[acid]}; \quad \log \frac{[base]}{[acid]} = 0.28$$

$$\frac{[base]}{[acid]} = 1.905 = \frac{(0.225 - X)}{(0.0833 + x)}; \quad X = 0.0227$ M$$

0.0227 M x 0.120 L $= 2.73 \times 10^{-3}$ mol HCl

(d) The $\dfrac{[CH_3NH_3^+]}{[CH_3NH_2]}$ ratio does not change in this buffer solution with dilution, therefore, no effect on pH.

1993 D (Required)

The following observations are made about reaction of sulfuric acid, H_2SO_4. Discuss the chemical processes involved in each case. Use principles from acid-base theory, oxidation-reduction, and bonding and/or intermolecular forces to support your answers.

(a) When zinc metal is added to a solution of dilute H_2SO_4, bubbles of gas are formed and the zinc disappears.

(b) As concentrated H_2SO_4 is added to water, the temperature of the resulting mixture rises.

(c) When a solution of $Ba(OH)_2$ is added to a dilute H_2SO_4 solution, the electrical conductivity decreases and a white precipitate forms.

(d) When 10 milliliters of 0.10-molar H_2SO_4 is added to 40 milliliters of 0.10-molar NaOH, the pH changes only by about 0.5 unit. After 10 more milliliters of 0.10-molar H_2SO_4 is added, the pH changes about 6 units.

Answer:

(a) Zn is oxidized to Zn^{2+} by H^+ which in turn is reduced by Zn to H_2. Identify $H_{2(g)}$ or Zn dissolving as Zn^{2+}.

$Zn_{(s)} + 2\ H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$
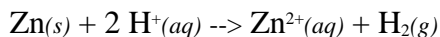
Explicit: Redox or e- transfer or correctly identify oxidizing agent or reducing agent.

(b) H_2SO_4 dissociates, forms ions or dydration ôeventö. Bonds form, therefore, energy given off (connection).

(c) $BaSO_4$ (ppt) forms or $H^+ + OH^-$ form water. Newly formed water and ppt remove ions lowering conductivity.

$Ba^{2+}_{(aq)} + OH^-_{(aq)} + H^+_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow$

$$BaSO_{4(s)} + H_2O_{(l)}$$
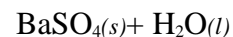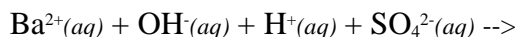
(d) First 10 mL produces solution of SO_4^{2-} and OH^- or excess OH^- or partial neutralization (pH 13.0 $\rightarrow$ 12.6). [presence of HSO_4^- in solution voids this point]

Second 10 mL produces equivalence where pH decreases (changes) rapidly (pH 12.6 $\rightarrow$ 7.0). [pH ôrisesö or wrong graph, if used, voids this point]
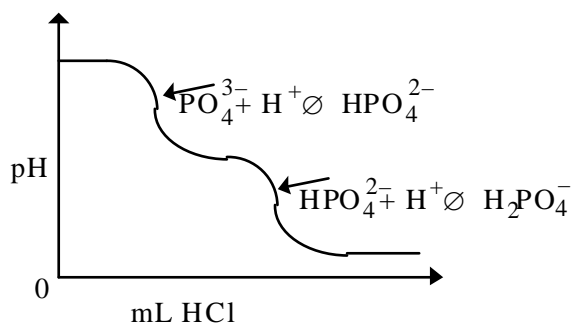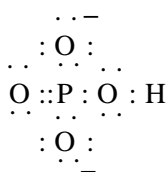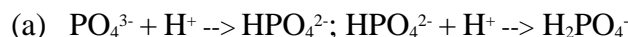

1994 D

A chemical reaction occurs when 100. milliliters of 0.200-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 products.

(b) Identify the species that acts as both a Bronsted acid and as a Bronsted base in the equation in (a), Draw the Lewis electron-dot diagram for this species.

(c) Sketch a graph using the axes 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 Na_3PO_4 solution. Account for the shape of the curve.
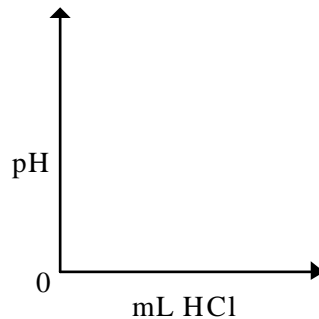
(d) Write the equation for the reaction that occurs if a few additional milliliters of the HCl solution are added to the solution resulting from the titration in (c).
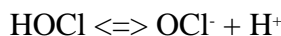
Answer:

(a) $PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$; $HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$

(b) HPO_4^{2-}

(c)

(d) $H^+ + H_2PO_4^- \rightarrow H_3PO_4$

1996 A

$$HOCl \Longleftrightarrow OCl^- + H^+$$

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 3.2×10^{-8}.

(a) Calculate the $[H^+]$ of a 0.14-molar solution of HOCl.

(b) Write the correctly balanced net ionic equation for the reaction that occurs when NaOCl is dissolved in water and calculate the numerical value of the equilibrium constant for the reaction.

(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.

(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.

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

$$Cl_2(g) + H_2O \longrightarrow H^+ + Cl^- + HOCl(aq)$$

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

Answer:

(a) $K_a = \dfrac{[OCl^-][H^+]}{[HOCl]} = 3.2\times10^{-8}$

X = amount of acid that ionizes = $[OCl^-] = [H^+]$

$(0.14 - X) = [HOCl]$ that remains unionized

$3.2\times10^{-8} = \dfrac{X^2}{0.14 - X}$; $X = 6.7\times10^{-5}\,M = [H^+]$

(b) $NaOCl(s) + H_2O \longrightarrow Na^+(aq) + HOCl(aq) + OH^-(aq)$

$K_b = \dfrac{K_w}{K_a} = \dfrac{1\times10^{-14}}{3.2\times10^{-8}} = 3.1\times10^{-7}$

(c) $[\ ]_o$ after dilution but prior to reaction:

$[HOCl] = 0.14\,M \times \dfrac{40\ mL}{50mL} = 0.11\,M$

$[OH^-] = 0.56\,M \times \dfrac{10\ mL}{50mL} = 0.11\,M$

Equivalence point reached. $[OH^-] \sim [HOCl]$

$K_b = \dfrac{[OH^-]^2}{0.11} = 3.1\times10^{-7}$

$[OH^-] = 1.8\times10^{-4}$; pOH = 3.7

pH = 14 - 3.7 = 10.3

(d) at pH 7.49, the $[H^+] = 10^{-7.49} = 3.24\times10^{-8}\,M$

when the solution is half-neutralized, pH = pK_a and $\dfrac{[OCl^-]}{[HOCl]} = 1$

$\dfrac{0.20\ mol\ HOCl}{1\ L}$ x 50.0 mL = 10.0 mmol HOCl

half this amount, or 5.0 mmol of NaOH added.

(e) 1 mol H+ for every 1 mole of HOCl produced

$[H^+] \sim [HOCl] = 0.065\,M$

pH = - log (0.065) = 1.2

1997 A

The overall dissociation of oxalic acid, $H_2C_2O_4$, is represented below. The overall dissociation constant is also indicated.

$H_2C_2O_4 \Longleftrightarrow 2\,H^+ + C_2O_4^{2-}$ $K = 3.78\times10^{-6}$

(a) What volume of 0.400-molar NaOH is required to neutralize completely a 5.00×10^{-3}-mole sample of pure oxalic acid?

(b) Give the equations representing the first and second dissociations of oxalic acid. Calculate the value of the first dissociation constant, K_1, for oxalic acid if the value of the second dissociation constant, K_2, is 6.40×10^{-5}.

(c) To a 0.015-molar solution of oxalic acid, a strong acid is added until the pH is 0.5. Calculate the $[C_2O_4^{2-}]$ in the resulting solution. (Assume the change in volume is negligible.)

(d) Calculate the value of the equilibrium constant, K_b, for the reaction that occurs when solid $Na_2C_2O_4$ is dissolved in water.

Answer:

(a) 5.00×10^{-3} mol oxalic acid $\times \dfrac{2 \text{ mol H}^+}{1 \text{ mol oxalic acid}} \times$

$\dfrac{1 \text{ mol OH}}{1 \text{ mol H}^+} \times \dfrac{1000. \text{ mL NaOH}}{0.400 \text{ mol NaOH}} =$

$= 25.0$ mL NaOH

(b) $H_2C_2O_4 \Longleftrightarrow H^+ + HC_2O_4^-$

$HC_2O_4^- \Longleftrightarrow H^+ + C_2O_4^{2-}$
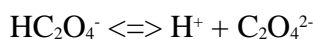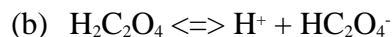
$K = K_1 \times K_2$

$K_1 = \dfrac{K}{K_2} = \dfrac{3.78 \times 10^{6}}{6.40 \times 10^{5}} = 5.91 \times 10^{-2}$

(c) $X =$ amt. ionized

$[H_2C_2O_4] = 0.015 - X$

$[H^+] = 10^{-pH} = 10^{-0.5} = 0.316\ M$

$[C_2O_4^{2-}] = X$

$K_a = \dfrac{[H^+]^2 [C_2O_{4^2}]}{[H_2C_2O_4]} = 3.78 \times 10^{-6}$

$3.78 \times 10^{-6} = \dfrac{[0.316]^2 [X]}{[0.015 - X]}$; $X = 5.67 \times 10^{-7}\ M$

(d) $K_b = \dfrac{K_w}{K_2} = \dfrac{1 \times 10^{14}}{6.40 \times 10^{6}} = 1.56 \times 10^{-10}$

**1998 D (Required)** [repeated in lab procedures section]

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 the 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.

Volume of NaOH Solution Added (mL)
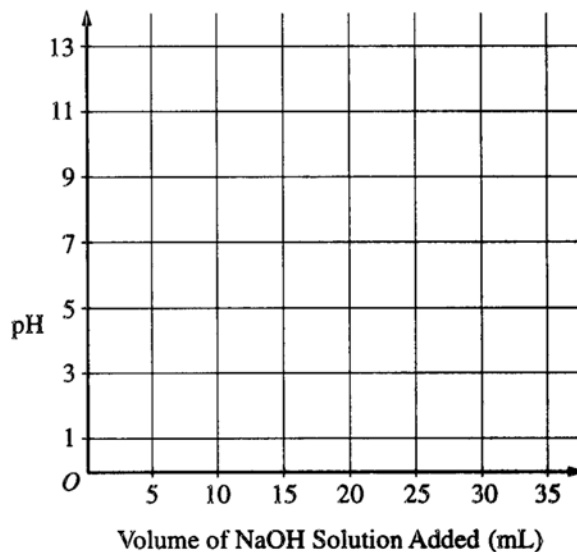
(d) Describe how the value of the acid-dissociation constant, K_a, for the weak acid HX could be determined from the titration curve in part (c).

(e) The graph below shows the results obtained by titrating a different weak acid, 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.

Volume of NaOH Solution Added
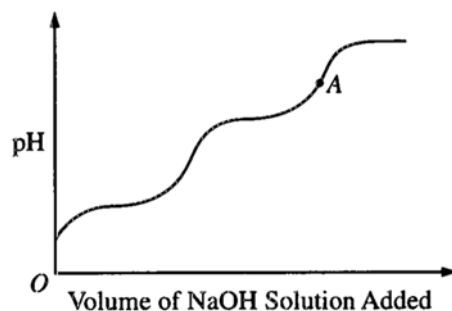
Answer

(a) · exactly mass a sample of KHP in the Erlenmeyer flask and add distilled water to dissolve the solid.
 · add a few drops of phenolphthalein to the flask.
 · rinse the buret with the NaOH solution and fill.
 · record starting volume of base in buret.
 · with mixing, titrate the KHP with the NaOH solution until it just turns slightly pink.
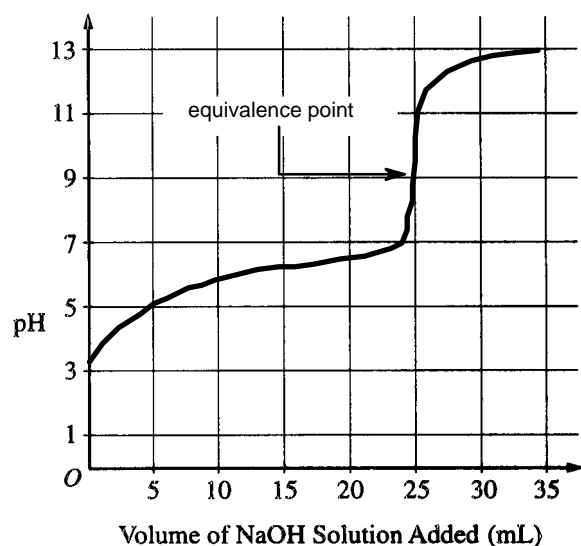
- record end volume of buret.
- repeat to check your results.

(b) $\dfrac{\text{mass of KHP}}{\text{molar mass KHP}}$ = moles of KHP

since KHP is monoprotic, this is the number of moles of NaOH

$\dfrac{\text{moles of NaOH}}{\text{L of titrant}}$ = molarity of NaOH

(c)

Volume of NaOH Solution Added (mL)

(d) from the titration curve, at the 12.5 mL volume point, the acid is half-neutralized and the pH = pK_a. $K_a = 10^{pKa}$

(e) Y^{2-} (could it be OH^- ?)

1998 D

Answer each of the following using appropriate chemical principles.

(b) When NH_3 gas is bubbled into an aqueous solution of $CuCl_2$, a precipitate forms initially. On further bubbling, the precipitate disappears. Explain these two observations.

In each case, justify your choice.

Answer

(b) A small amount of NH_3 in solution causes an increase in the $[OH^-]$.

$NH_3 + H_2O <=> NH_4^+ + OH^-$
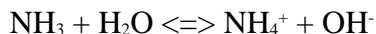
This, in turn, causes the K_{sp} of copper(II) hydroxide to be exceeded and the solution forms a precipitate of $Cu(OH)_2$.

With the addition of more NH_3, you form the soluble tetraamminecopper(II) complex ion, $[Cu(NH_3)_4]^{2+}$, which will cause the precipitate to dissolve.

2000 D

A volume of 30.0 mL of 0.10 M $NH_3(aq)$ is titrated with 0.20 M $HCl(aq)$. 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 $NH_3(aq)$ with $HCl(aq)$.

(b) Using the axes provided below, sketch the titration curve that results when a total of 40.0 mL of 0.20 M HCl$_{(aq)}$ is added dropwise to the 30.0 mL volume of 0. 10 M NH$_{3(aq)}$.


pH

11
9
7
5
3
1
0

0   10   20   30   40

Volume of 0.20M HCl Added (mL)
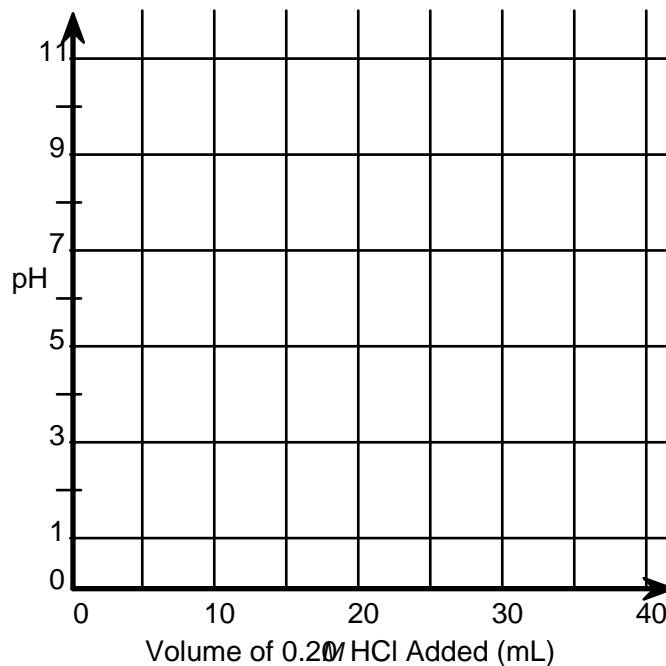
(c) From the table below, select the most appropriate indicator for the titration. Justify your choice.

Indicator	pK_a
Methyl Red	5.5
Bromothymol Blue	7.1
Phenolphthalein	8.7

(d) If equal volumes of 0.10 M NH$_{3(aq)}$ and 0.10 M NH$_4$Cl$_{(aq)}$ are mixed, is the resulting solution acidic, neutral, or basic? Explain.

Answer:

(a) NH$_3$ + H$^+$ → NH$_4{}^+$

Volume of 0.20 M HCl Added (mL)
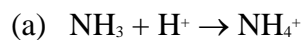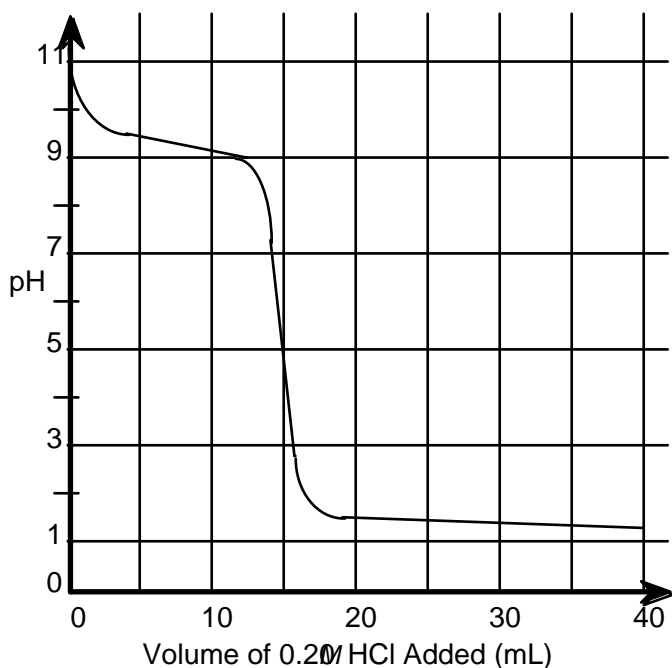
(b)

(c) methyl red. The pK_a of the indicator (where it changes color) should be close to the pH at the equivalence point. The equivalence point of a weak base and a strong acid will be slightly acidic.

(d) basic. If equivolumes of a weak base, ammonia, and the salt of a weak base, ammonium chloride, are mixed, it will create a basic buffer solution.

2001 B

Answer the following questions about acetylsalicylic acid, the active ingredient in aspirin.

(a) The amount of acetylsalicylic acid in a single aspirin tablet is 325 mg, yet the tablet has a mass of 2.00 g. Calculate the mass percent of acetylsalicylic acid in the tablet.

(b) The elements contained in acetylsalicylic acid are hydrogen, carbon, and oxygen. The combustion of 3.000 g of the pure compound yields 1.200 g of water and 3.72 L of dry carbon dioxide, measured at 750. mm Hg and 25°C. Calculate the mass, in g, of each element in the 3.000 g sample.

(c) A student dissolved 1.625 g of pure acetylsalicylic acid in distilled water and titrated the resulting solution to the equivalence point using 88.43 mL of 0.102 M NaOH$_{(aq)}$. Assuming that acetylsalicylic acid has only one ionizable hydrogen, calculate the molar mass of the acid.

(d) 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

   (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).

Volume of 0.100M 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	?

Answer:

(a) × 100% = 16.3%

(b) 1.200 g H_2O × + 16 g H_2O) = 0.134 g H

n = = = 0.150 mol CO_2

0.150 mol CO_2 × = 1.801 g C

3.000 g ASA – (1.801 g C + 0.134 g H) = 1.065 g O

(c) 0.08843 L × = 0.00902 mol base

1 mol base = 1 mol acid

 = 180 g/mol

(d) (i) HAsa ↔ Asa^- + H^+

 = 0.133 M

pH = –log[H^+]; 2.22 = –log[H^+]

[H^+] = M = [Asa^-]

[HAsa] = 0.133 M – 6.03 × 10^{-3} M = 0.127 M

K = = = 2.85× 10^{-4}

OR

when the solution is half-neutralized, pH = pK_a

at 10.00 mL, pH = 3.44; K = 10^{-pH}

= $10^{-3.44}$ = 3.63×10^{-4}

(ii) 0.025 L × 0.100 mol/L = 2.50 × 10^{-3} mol OH-

2.50 × 10^{-3} mol OH- - 2.00 × 10^{-3} mol neutralized = 5.0 × 10^{-4} mol OH- remaining in (25 + 15 mL) of solution; [OH-] = 5.0×10^{-4} mol/0.040 L = 0.0125 M

pH = 14 – pOH = 14 + log[OH-] = 14 – 1.9 = 12.1

2002 A Required

HOBr*(aq)* ⇔ H*+(aq)* + OBr*-(aq)* K_a = 2.3 × 10^{-9}
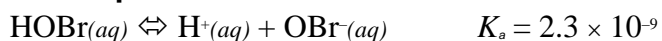
Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.

(a) Calculate the value of [H+] in an HOBr solution that has a pH of 4.95.

(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 1.8×10^{-5} 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 $HOBr_{(aq)}$.

(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 $NaOBr_{(s)}$ that would have to be added to 125 mL of 0.160 M HOBr to produce a buffer solution with [H$^+$] = 5.00×10^{-9} M. Assume that volume change is negligible.

(e) HOBr is a weaker acid than $HBrO_3$. Account for this fact in terms of molecular structure.

Answer:

(a) pH = -log[H$^+$]; 4.95 = -log[H$^+$]
[H$^+$] = 1.12×10^{-5}

(b) K_a = = 2.3×10^{-9}
[H$^+$] = [OBr$^-$] = 1.8×10^{-5} M
= 2.3×10^{-9}
X = [HOBr] = 0.14 M

(c) (i) 65.0 mL × ×

× ×

× = 41.3 mL

(ii) pH > 7; salt of a weak acid is a weak base

(d) pH = pK_a + log; [A$^-$] =
[OBr$^-$] = = 0.0736 M
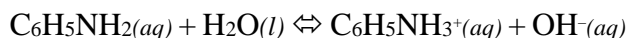125 mL × × =
= 0.00920 mol NaOBr

(e) very electronegative oxygen is able to draw electrons away from the bromine and weaken the O–H bond, making it easier for the hydrogen ion "to leave".

$$O\!\!\nwarrow\atop O\!\!\nearrow Br-O-H$$

2003 A Required

$$C_6H_5NH_{2(aq)} + H_2O_{(l)} \Leftrightarrow C_6H_5NH_3{}^+{}_{(aq)} + OH^-{}_{(aq)}$$
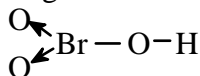
Aniline, a weak base, reacts with water according to the reaction represented above.

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

(b) A sample of aniline is dissolved in water to produce 25.0 mL of 0.10 M solution. The pH of

the solution is 8.82. Calculate the equilibrium constant, K_b, for this reaction.

(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 titrated.

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

(e) The pK_a values for several indicators are given below. Which of the indicators listed is most suitable for this titration? Justify your answer.

Indicator	pK_a
Erythrosine	3
Litmus	7
Thymolphthalein	10

Answer:

(a) $K_b = \dfrac{\left[C_6H_5NH_3^+\right]\left[OH^-\right]}{\left[C_6H_5NH_2\right]}$

(b) pOH = 14 – pH = 14 – 8.82 = 5.18

-log[OH$^-$] = 5.18; [OH$^-$] = 6.61×10^{-6} M

[OH–] = [C$_6$H$_5$NH$_3{}^+$]

$K_b = \dfrac{\left(6.61\times10^{-6}\right)^2}{0.10 - 6.61\times10^{-6}}$ = 4.4×10^{-10}

(c) 25 mL × = 2.5 mmol C$_6$H$_5$NH$_2$

5 mL × = 0.5 mmol H$^+$ added

2.0 mmol base remains in 30.0 mL solution

$4.4\times10^{-10} = \dfrac{[X]\left[X + \dfrac{0.50\ \text{mmol}}{30.0\ \text{mL}}\right]}{\left[\dfrac{20.0\ \text{mmol}}{30.0\ \text{mL}}\right]}$

$X = 1.80\times10^{-9} = [OH^-]$

$[H^+] = \dfrac{1\times10^{-14}}{1.8\times10^{-9}}$ = 5.6×10^{-6}; pH = 5.26

(d) when neutralized, there are 2.5 mmol of C$_6$H$_5$NH$_3{}^+$ in 50.0 mL of solution, giving a [C$_6$H$_5$NH$_3{}^+$] = 0.050 M

this cation will partially ionize according to the following equilibrium:

C$_6$H$_5$NH$_3{}^+{}_{(aq)}$ ⟺ C$_6$H$_5$NH$_2{}_{(aq)}$ + H$^+{}_{(aq)}$

at equilibrium, [C$_6$H$_5$NH$_2$] = [H$^+$] = X

[C$_6$H$_5$NH$_3{}^+$] = (0.050–X)

$\dfrac{X^2}{(0.050 - X)}$ = K_a = 2.3×10^{-5}

$X = 1.06\times10^{-3} = [H^+]$

$$pH = -\log[H^+] = 2.98$$

(e) erythrosine; the indicator will change color when the pH is near its pK_a, since the equivalence point is near pH 3, the indicator must have a pK_a near this value.