Chapter 10: Ionic Equilibrium

Review Questions

1. Astatine, atomic number 85, is radioactive and does not occur in appreciable amounts in nature. On the basis of what you have learned in this chapter, answer the following.

(a) How would the acidity of HAt compare to HI?

(b) How would the acidity of $HAtO_3$ compare with $HBrO_3$?

Solution

(a) The relative strength of the binary acids increases from top to bottom in a group of the periodic table, so we expect HAt to be a stronger acid than HI.

(b) The relative strength of oxoacids increases from bottom to top in a group of the periodic table, so we expect $HAtO_4$ to be a weaker acid that $HBrO_3$.

2. $HClO_4$ is a stronger proton donor than HNO_3, but in water both acids appear to be of equal strength; they are both 100% ionized. Why is this so? What solvent property would be necessary in order to distinguish between the acidities of these two Brönsted acids?

Solution

Both $HClO_4$ and HNO_3 are 100% ionized in water and, therefore, appear to be the same strength. To distinguish between these two, we would need a solvent that is a weaker proton acceptor than H_2O.

3. Explain why the oxide ion, O^{2-}, can function as a Lewis base but not as a Lewis acid.

Solution

The O^{2-} ion has a complete valence shell. It can donate electron pairs functioning as a Lewis base. It cannot accept additional electrons and, therefore, cannot serve as a Lewis acid.

4. In the reaction of calcium with oxygen to form calcium oxide, each calcium gives a pair of electrons to an oxygen atom. Why this is not viewed as a Lewis acid-base reaction?

Solution

In the reaction of calcium with oxygen, there is a complete transfer of the electron pair from the calcium to the oxygen, and then the electrostatic attractions bind the two ions together. In a Lewis acid-base reaction, a covalent bond is formed between the two atoms and the electrons are shared.

5. Explain why

(a) If the oxide of an element dissolves in water to give an acidic solution, the element is more likely to be a non-metal?

(b) Many chromium salts crystallize as hydrates containing the ion $Cr(H_2O)_6^{3+}$. Solutions of these salts tend to be acidic.

(c) Fe^{3+} is expected to give the more acidic solution than Fe^{2+}.

(d) Ions of the alkali metals have little effect on the acidity of a solution.

Solution

(a) Metal oxides are typically basic so this must be a non-metal oxide.

(b) This is due to the equilibrium: $Cr(H_2O)_6^{3+} + H_2O \rightleftharpoons Cr(H_2O)_5OH^{2+} + H_3O^+$

(c) The charge density on the Fe^{3+} is higher, so it is more acidic.

(d) This is because they have such a small charge density, so the metal ions have little impact and essentially zero interaction with H_2O in an acid-base sense.

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6. How are acidic, basic, and neutral solutions in water defined (a) in terms of $[H^+]$ and $[OH^-]$ and (b) in terms of pH?

Solution

(a) Neutral solution: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}\ M$; pH = 7.00

(b) Acidic solution: $[H_3O^+] > [OH^-]$; $pH < 7.00$

(c) Basic solution: $[H_3O^+] < [OH^-]$; $pH > 7.00$

7. Explain how acids and bases suppress the ionization of water, often called the common ion effect.

Solution

The product of H^+ and OH^- is a constant, 1×10^{-14}. By adding an acid to water the acid provides the H^+ ions, this forces the water to decrease the amount of OH^- in solution, thus suppressing the ionization of the water. The same effect occurs with the OH^-, but it is the base that is forcing the water to not ionize.

8. Explain the leveling effect of water.

Solution

The leveling effect of water is a result of the strength of water as an acid or a base. If it is the weaker acid or base in solution, then the other substance will ionize completely.

9. Identify the conjugate acid-base pairs in the following reactions.

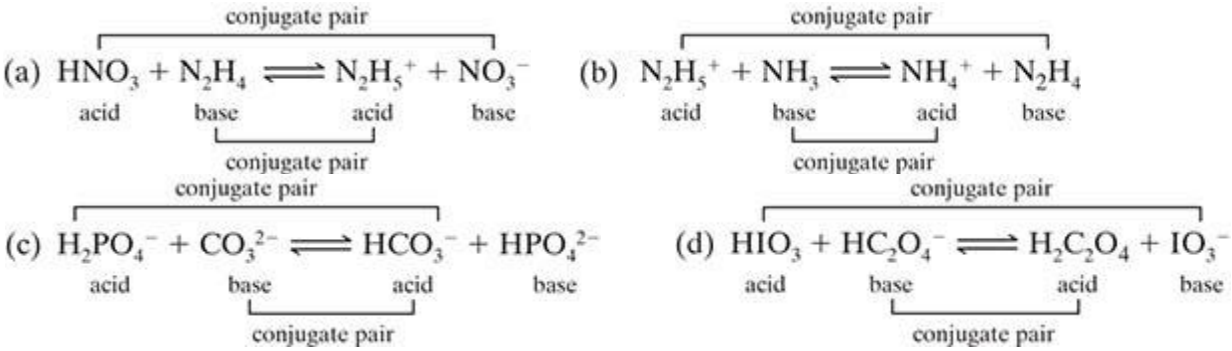
(a) $HNO_3 + N_2H_4 \rightleftharpoons NO_3^- + N_2H_5^+$

(b) $NH_3 + N_2H_5^+ \rightleftharpoons NH_4^+ + N_2H_4$

(c) $H_2PO_4^- + CO_3^{2-} \rightleftharpoons HPO_4^{2-} + HCO_3^-$

(d) $HIO_3 + HC_2O_4^- \rightleftharpoons IO_3^- + H_2C_2O_4$

Solution



10. Use Lewis structures to diagram the reaction

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Identify the Lewis acid and Lewis base in this reaction.

Solution

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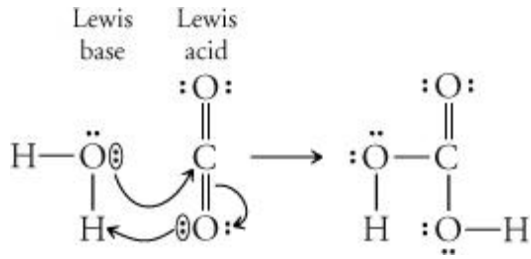

11. (a) Hydrazine, N_2H_4, is a weaker Brönsted base than ammonia. In the following reaction, would the position of equilibrium lie to the left or to the right? Justify your answer.

$$N_2H_5^+ + NH_3 \rightleftharpoons N_2H_4 + NH_4^+$$

(b) Identify the two Brönsted acids and two Brönsted bases in the reaction

$$NH_2OH + CH_3NH_3^+ \rightleftharpoons NH_3OH^+ + CH_3NH_2$$

Solution

(a) The equilibrium lies to the right since reactions favor the weaker acid and base.

(b) Acids: $CH_3NH_3^+$, NH_3OH^+; bases: NH_2OH, CH_3NH_2

12. Write the chemical equation for the ionization of each of the following weak bases in water. For each of the bases, write the appropriate K_b expression

(a) $(CH_3)_3N$ (b) AsO_4^{3-} (c) NO_2^- (d) $(CH_3)_2N_2H_2$

Solution

(a) $(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$, $K_b = \dfrac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$

(b) $AsO_4^{3-} + H_2O \rightleftharpoons HAsO_4^{2-} + OH^-$, $K_b = \dfrac{[HAsO_4^{2-}][OH^-]}{[AsO_4^{3-}]}$

(c) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$, $K_b = \dfrac{[HNO_2][OH^-]}{[NO_2^-]}$

(d) $(CH_3)_2N_2H_2 + H_2O \rightleftharpoons (CH_3)_2N_2H_3^+ + OH^-$, $K_b = \dfrac{[(CH_3)_2N_2H_3^+][OH^-]}{[(CH_3)_2N_2H_2]}$

13. What criterion do we use to determine whether or not the equilibrium concentration of an acid or base will be effectively the same as its initial concentration when we calculate the pH of the solution?

Solution

If $[HA]_{initial} < 400 \times K_a$ or if the percentage of ionization ≥5%, the initial concentration of the acid is not equal to the equilibrium concentration. The same argument holds true for bases.

14. A solution of hydrazinium acetate is slightly acidic. Without looking at the tables of equilibrium constants, is K_a for acetic acid larger or smaller than K_b for hydrazine? Justify your answer.

Solution

K_b for hydrazine is larger than K_a for acetic acid since the solution is acidic. The hydrazine reacts with water to form a weak acid. Since the solution is acidic, the more of the hydrazine has dissociated than the acetate ion has reacted, this occurs if K_b is larger than K_a.

15. Write ionic equations that illustrate how each pair of compounds can serve as a buffer pair.

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(a) H_2CO_3 and $NaHCO_3$ (the "carbonate" buffer in blood)
(b) NaH_2PO_4 and Na_2HPO_4 (the "phosphate" buffer inside body cells)
(c) NH_4Cl and NH_3

Solution

(a) $H_2CO_3 + OH^- \rightleftharpoons H_2O + HCO_3^-$

$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$

(b) $H_2PO_4^- + OH^- \rightleftharpoons H_2O + HPO_4^{2-}$

$H^+ + HPO_4^{2-} \rightleftharpoons H^+ + HPO_4^{2-}$

(c) $NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3$

$H^+ + NH_3 \rightleftharpoons NH_4^+$

16. Citric acid, found in citrus fruits, is a triprotic acid, $H_3C_6H_5O_7$. Write chemical equations for the three-step ionization of this acid in water and the corresponding K_a expressions.

Solution

$$H_3C_6H_5O_7 + H_2O \rightleftharpoons H_3O^+ + H_2C_6H_5O_7^-,\ K_{a_1} = \frac{[H_3O^+][H_2C_6H_5O_7^-]}{[H_3C_6H_5O_7]}$$

$$H_2C_6H_5O_7^- + H_2O \rightleftharpoons H_3O^+ + HC_6H_5O_7^{2-},\ K_{a_2} = \frac{[H_3O^+][HC_6H_5O_7^{2-}]}{[H_2C_6H_5O_7^-]}$$

$$HC_6H_5O_7^{2-} + H_2O \rightleftharpoons H_3O^+ + C_6H_5O_7^{3-},\ K_{a_3} = \frac{[H_3O^+][C_6H_5O_7^{3-}]}{[HC_6H_5O_7^{2-}]}$$

17. What simplifying assumptions do we usually make in working problems involving the ionization of polyprotic acids? Why are they usually valid? Under what conditions do they fail?

Solution

Nearly all of the H^+ in solution comes from the first ionization. The concentration of the conjugate base of a weak polyprotic acid once deprotonated is approximately equal to the value of the equilibrium constant. These approximations are usually valid because the value of the first ionization constant is much larger than the second ionization constant. If the two ionization constants are not very different, the approximation stated above will fail.

18. (a) When a formic acid solution is titrated with sodium hydroxide, will the solution be acidic, neutral, or basic at the equivalence point?
(b) When a solution of hydrazine is titrated by hydrochloric acid, will the solution be acidic, neutral, or basic at the equivalence point?
(c) If you use methyl orange in the titration of CH_3COOH with NaOH, will the end point of the titration correspond to the equivalence point? Justify your answer.

Solution

(a) Basic as weak acid and strong base are used.
(b) Acidic as weak base and strong acid are used.
(c) No, only phenopthalein is a suitable indicator.

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19. The conjugate acid of a molecular base has the hypothetical formula, BH^+, which has a pK_a of 5.00. A solution of a salt of this cation, BHY, tests slightly basic. Will the conjugate acid of Y^-, HY, have a pK_a greater than 5.00 or less than 5.00? Explain.

Solution

The conjugate acid BH^+ is acidic due to the following equilibrium:

$$BH^+ \rightleftharpoons H^+ + B$$

The base Y^- has the following equilibrium:

$$Y^- + H_2O \rightleftharpoons HY + OH^-$$

If a solution of the salt BHY is basic, it can only mean that Y^- is a stronger base than B:

$$BH^+ + Y^- \rightarrow HY + B$$

This can happen only if HY is a weaker acid than BH^+. We conclude that pK_a for HY is greater than 5.

20. Suppose a solution contains 0.0050 M Co^{2+} and is saturated with H_2S (with $[H_2S]$ = 0.1 M). Would CoS precipitate if the solution has a pH of 3.5? (Hint: What relationship do we use to determine whether a precipitate is going to form in a solution?)

Solution

CoS will precipitate if the H^+ concentration is too low. Solving for Q and then comparing Q to K_{spa}, we can determine whether or not CoS will precipitate.

$$K_{spa} = \frac{[Co^{2+}][H_2S]}{[H^+]^2} = 5\times10^{-1}$$

$$Q = \frac{[Co^{2+}][H_2S]}{[H^+]^2} = \frac{[0.005][0.10]}{[3.16\times10^{-4}]^2} = 5\times10^{3}$$

$Q > K_{spa}$. Since Q is greater than K_{spa}, then the reaction will move to reactants and CoS solid will form.

21. Use Le Châtelier's principle to explain how adjusting the pH enables the control of the concentration of $C_2O_4^{2-}$ in a solution of oxalic acid, $H_2C_2O_4$.

Solution

As the pH of an oxalic acid solution is decreased, the hydrogen ion concentration is increased, this shifts the equilibrium to the undissociated acid, thus increasing the $H_2C_2O_4$ concentration. The opposite is true as the pH of the solution is increased.

22. A solution of $MgBr_2$ can be changed to a solution of $MgCl_2$ by adding AgCl(s) and stirring the mixture well. In terms of the equilibria involved, explain how this happens.

Solution

AgCl and AgBr are both insoluble compounds. However, AgBr is less soluble than AgCl. When solid AgCl is added to an aqueous solution of $MgBr_2$, some of the AgCl dissociates. The Ag^+ ion reacts with the aqueous Br^- to form insoluble AgBr. This disrupts the AgCl/Ag^+ equilibrium and additional AgCl dissociates. With sufficient stirring, and perhaps a little heat, all of the AgCl will dissolve and AgBr will precipitate.

23. Using Le Châtelier's principle, explain how the addition of aqueous ammonia dissolves silver chloride. If HNO_3 is added after the AgCl has dissolved in the NH_3 solution, it causes AgCl to re-precipitate. Explain why.

Solution

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

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$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

Silver chloride is an insoluble solid. However, any Ag^+ ions present react with added NH_3 to form the $Ag(NH_3)_2^+$ complex ion. According to Le Châtelier's principle, as NH_3 is added to a solution containing Ag^+ ions, the complex ion forms using up the Ag^+ ions. This disrupts the equilibrium and forces AgCl to dissolve.

Upon addition of HNO_3, a strong acid, H^+ reacts with NH_3 to form NH_4^+. This disrupts the complex equilibria and causes the $Ag(NH_3)_2^+$ to dissociate and form free Ag^+ ions. Once again, the $[Ag^+]$ reaches a value sufficient in the presence of Cl^- to precipitate AgCl in accordance with Le Châtelier's principle.

24. For $PbCl_3^-$, $K_{form} = 2.5 \times 10^1$. If a solution containing this complex ion is diluted with water, $PbCl_2$ precipitates. Write the equations for the equilibria involved and use them together with Le Châtelier's principle to explain how this happens.

Solution

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$Pb^{2+}(aq) + 3Cl^-(aq) \rightleftharpoons PbCl_3^-(aq)$$

$$K_{form} = \frac{[PbCl_3^-]}{[Pb^{2+}][Cl^-]^3} = \frac{(\text{mol } PbCl_3^-/\text{volume})}{(\text{mol } Pb^{2+}/\text{volume})(\text{mol } Cl^-/\text{volume})^3}$$

$$K_{form} = \text{volume}^3 \times \frac{\text{mol } PbCl_3^-}{(\text{mol } Pb^{2+})(\text{mol } Cl^-)^3}$$

Notice that the above expression is the product of a ratio of mole amounts and a volume^3 term. The constant K_{form} does not change on dilution, but the volume term is changed by dilution. This means that the ratio of moles term in the above expression must change on dilution, in order to hold the product constant. If the volume is doubled, the ratio of moles would have to become smaller by a factor of 8 (= 2^3) in order for the entire argument to have a constant value, that is, in order for K_{form} to remain constant on dilution.

This means that the concentrations of Pb^{2+} and Cl^- must increase as the solution containing the complex ion is diluted. Eventually, the ion product for $PbCl_2$ will exceed the value of K_{sp} for $PbCl_2$, resulting in its precipitation.

25. Explain the buffering action in swimming pools.

Solution

The water in a swimming pool is a highly dilute solution of chemicals that prevent the growth of bacteria and help stabilize the pool lining. These substances can affect the pH of the pool water, making it unpleasant for swimmers. Therefore, the pH must be monitored and controlled with use of buffers.

Although most buffer systems consist of two separate species that react with H^+ or OH^-, the bicarbonate ion is an example of a single ion that is able to serve both functions. The reactions are

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

$$HCO_3^-(aq) + OH^-(aq) \rightarrow H_2O + CO_3^{2-}(aq)$$

Because sodium bicarbonate is non-toxic and because the pH of a solution of the salt is close to 7.0, there are many practical applications of the HCO_3^- buffer. For swimming pools, adding non-toxic $NaHCO_3$ is an effective way to keep the pool's pH at an acceptable value, preferably between 7.0 and 7.6.

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Maintaining the level of bicarbonate ion between 80 and 120 ppm produces the optimal results. Concentrations above this tend to cause the pool water to become cloudy and cause chlorine to lose its effectiveness. When the bicarbonate ion concentration is too low, wide swings in pH can occur, plaster walls become etched, metals can corrode, the pool's walls and floor can stain, the water can turn green, and the water can cause eyes to burn.

26. Acetic acid, CH_3COOH, and sodium acetate, CH_3COONa (this provides the acetate ion, CH_3COO^-), can be used to make an "acetate" buffer. Does the acetate ion or the acetic acid concentration increase when a strong acid is added to the buffer? Is it the acetate ion or acetic acid that decreases when a strong base is added to the buffer? Explain your answers.
In the acetate buffer, there are CH_3COOH and CH_3COO^- present. Upon addition of a strong acid, the concentration of CH_3COOH will increase:

$$H^+ + CH_3COO^- \rightarrow CH_3COOH$$

When a strong base is added, it reacts with the acid to form more of the acetate ion; therefore, the concentration of the acetic acid will decrease:

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

Numerical Problems
1. A soft drink was put on the market with $[H^+] = 1.4 \times 10^{-5}$ mol L^{-1}. What is its pH?
Solution

$$pH = -\log[H^+] = -\log(1.4\times10^{-5}) = 4.85$$

2. The interaction of water droplets in rain with carbon dioxide that is naturally present in the atmosphere causes rainwater to be slightly acidic because CO_2 is an acidic anhydride. As a result, pure clean rain has a pH of about 5.7. What are the hydrogen ion and hydroxide ion concentrations in this rainwater?
Solution

$$[H^+] = 10 - pH = 10 - 5.7 = 2.0\times10^{-6}\ M$$
$$pOH = 14.00 - pH = 14.00 - 5.7 = 8.3$$
$$[OH^-] = 10 - pOH = 10 - 8.3 = 5.0\times10^{-9}\ M$$

3. A solution was made by dissolving 0.837 g $Ba(OH)_2$ in 100 mL final volume. What is the molar concentration of OH^- in the solution? What are the pOH and the pH? What is the hydrogen ion concentration in the solution?
Solution

$$M\,OH^- = \frac{\text{moles } OH^-}{\text{L solution}}$$
$$= \left(\frac{0.837\text{ g } Ba(OH)_2}{0.100\text{ L solution}}\right)\left(\frac{1\text{ mol } Ba(OH)_2}{171.3\text{ g } Ba(OH)_2}\right)\left(\frac{2\text{ mol } OH^-}{1\text{ mol } Ba(OH)_2}\right)$$
$$= 0.0977\ M\,OH^-$$

$$pOH = -\log[OH^-] = -\log(9.77\times10^{-2}) = 1.01$$
$$pH = 14.00 - pOH = 14.00 - 1.01 = 12.99$$

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$$[H^+] = 10 - pH = 10 - 12.99 = 1.02 \times 10^{-13}\ M$$

4. A solution of HCl has a pH of 2.50. How many grams of HCl are there in 250 mL of this solution? How many grams of HCl are in 250 mL of an HCl solution that has twice the pH?

Solution

$$[H^+] = 10^{-pH} = 10^{-2.50} = 3.2 \times 10^{-3}\ M$$

$$g\ HCl = (0.250\ L)\left(\frac{3.2 \times 10^{-3}\ mol\ H^+}{1\ L\ solution}\right)\left(\frac{1\ mol\ HCl}{1\ mol\ H^+}\right)\left(\frac{36.46\ g\ HCl}{1\ mol\ HCl}\right)$$

$$= 2.9 \times 10^{-2}\ g\ HCl$$

$$pH = 2.50 \times 2 = 5.00$$

$$[H^+] = 10^{-pH} = 10^{-5.00} = 1 \times 10^{-5}\ M$$

$$g\ HCl = (0.250\ L)\left(\frac{1.0 \times 10^{-5}\ mol\ H^+}{1\ L\ solution}\right)\left(\frac{1\ mol\ HCl}{1\ mol\ H^+}\right)\left(\frac{36.46\ g\ HCl}{1\ mol\ HCl}\right)$$

$$= 9.1 \times 10^{-5}\ g\ HCl$$

5. How many milliliters of 0.0100 M KOH are needed to completely neutralize the HCl in 300 mL of a hydrochloric acid solution that has a pH of 2.25?

Solution

First, we must find the concentration of the HCl solution. Since HCl is a strong acid, we know that [HCl] = $[H^+]$. We can find $[H^+]$ from the pH:

$$[H^+] = 10 - pH = 10 - 2.25 = 5.6 \times 10^{-3}\ M\ H^+$$

Now we can solve the problem using the given conversion factors:

$$\text{Volume of } 0.0100\ M\ KOH = 300\ mL\left(\frac{5.6 \times 10^{-3}\ mol\ H^+}{1000\ mL\ solution}\right)\left(\frac{1\ mol\ OH^-}{1\ mol\ H^+}\right)\left(\frac{1000\ mL\ OH^-}{0.0100\ mol\ OH^-}\right)$$

$$= 168\ mL\ 0.0100\ M\ KOH$$

6. Suppose 38.0 mL of 0.000200 M HCl is added to 40.0 mL of 0.000180 M NaOH. What will be the pH of the final mixture?

Solution

$$\text{Moles } H^+ = (38.0\ mL)\left(\frac{0.000200\ mol}{1000\ mL}\right) = 7.60 \times 10^{-6}\ mol\ H^+$$

$$\text{Moles } OH^- = (40.0\ mL)\left(\frac{0.00018\ mol}{1000\ mL}\right) = 7.20 \times 10^{-6}\ mol\ OH^-$$

$$\text{Excess } H^+ = 4.0 \times 10^{-7}\ mol\ H^+$$

$$[H^+] = \frac{4.0 \times 10^{-7}\ mol}{(38\ mL + 40\ mL)(1\ L/1000\ mL)} = 5.13 \times 10^{-6}\ M$$

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We need to add in the concentration of H^+ from the autoionization of water, 1×10^{-7} M:

$$[H^+] = (5.13\times10^{-6}) + (1\times10^{-7}) = 5.23\times10^{-6}\ \text{M}$$

$$\text{pH} = -\log 5.23\times10^{-6} = 5.28$$

7. What is the pH of a 3.0×10^{-7} M solution of HCl?

Solution

The total $[H^+]$ is from the HCl and from the dissociation of H_2O. Since HCl is a strong acid, it will contribute 3.0×10^{-7} mol of H^+ per liter of solution. We need to use the equilibrium expression to determine the amount of H^+ contributed by the water.

$$K_w = [H^+][OH^-] = (3.0\times10^{-7} + x)(x) = 1.0\times10^{-14}$$

$$x^2 + 3.0\times10^{-7}x - 1.0\times10^{-14} = 0$$

$$x = \frac{-3.0\times10^{-7} \pm \sqrt{(3.0\times10^{-7})^2 - 4(1)(-1.0\times10^{-14})}}{2(1)} = 3.03\times10^{-8}$$

Solving a quadratic equation we see that $x = 3.03\times10^{-8} = [OH^-] = [H^+]$ from water dissociation.

So, $[H^+]_{total} = 3.0\times10^{-7} + 3.03\times10^{-8} = 3.30\times10^{-7}$ M and pH = –log (3.3) + 7 = 6.48.

8. How many milliliters of 0.10 M NaOH must be added to 200 mL of 0.010 M HCl to give a mixture with a pH of 3.00?

Solution

A solution with pH = 3.00 would have

$$[H^+] = 10^{-\text{pH}} = 10^{-3.00} = 1.00\times10^{-3}\ \text{M}$$

$$= 1.00\times10^{-3}\ \frac{\text{mol}[H^+]}{\text{L solution}} = 0.00100\ \frac{\text{mol}[H^+]}{\text{L solution}}$$

We begin with:

$$\text{mol HCl} = 200\ \text{mL HCl solution}\left(\frac{1\ \text{L HCl solution}}{1000\ \text{mL HCl solution}}\right)\left(\frac{0.010\ \text{mol HCl}}{1\ \text{L HCl solution}}\right)$$

$$= 0.002\ \text{mol HCl}$$

$$= 0.002\ \text{mol}\ H^+$$

Our final molarity will be: M = mol $[H^+]$/L solution. This can be written as

$$M = \frac{0.002 - n_{NaOH}}{0.200 + x}$$

where n_{NaOH} = moles of NaOH added and, x = volume of 0.10 M NaOH added.

But n_{NaOH} is simply $M_{NaOH} \cdot V_{NaOH}$, so

$$M = \frac{0.002 - 0.10x}{0.200 + x}$$

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$$0.00100 = \frac{0.002 - 0.10x}{0.200 + x}$$
$$(0.200 + x)\,0.00100 = (0.002 - 0.10x)$$
$$0.000200 + 0.00100x = 0.002 - 0.10x$$
$$0.101x = 0.0018 \Rightarrow x = 0.018 \text{ L or } 18 \text{ mL}$$

18 mL of 0.10 M NaOH should be added to 200 mL of 0.010 M HCl.

9. Milk of magnesia is a suspension of magnesium hydroxide in water. Although $Mg(OH)_2$ is relatively insoluble, a small amount does dissolve in the water, which makes the mixture slightly basic and gives it a pH of 10.08. How many grams of $Mg(OH)_2$ are actually dissolved in 100 mL of milk of magnesia?

Solution

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.08 = 3.92$$
$$\text{pOH} = -\log[\text{OH}^-]$$
$$[\text{OH}^-] = 10 - \text{pOH} = 10 - 3.92 = 1.2 \times 10^{-4}\ \text{M}$$
$$\text{Grams Mg(OH)}_2 = (100\,\text{mL})\left(\frac{1.2 \times 10^{-4}\ \text{mol}}{1000\,\text{mL}}\right)\left(\frac{1\,\text{mol Mg(OH)}_2}{2\,\text{mol OH}^-}\right)\left(\frac{58.32\,\text{g Mg(OH)}_2}{1\,\text{mol Mg(OH)}_2}\right)$$
$$= 3.5 \times 10^{-4}\ \text{g Mg(OH)}_2$$

10. A 1.0 M solution of acetic acid has a pH of 2.37. What percentage of the acetic acid is ionized in the solution?

Solution

$$[\text{H}^+] = 10 - \text{pH} = 10 - 2.37 = 4.27 \times 10^{-3}\ \text{M}$$
$$\text{Percentage ionization} = \frac{4.27 \times 10^{-3}}{1.0} \times 100\% = 0.43\%$$

11. A 0.20 M solution of a weak acid, HA, has a pH of 3.22. What is the percentage ionization of the acid? What is the value of K_a for the acid?

Solution

$$\text{pH} = 3.22 [\text{H}^+] = 10 - 3.22 = 6.03 \times 10^{-4}\ \text{M}$$
$$\text{Percentage ionization} = \frac{\text{Moles ionized per liter}}{\text{Moles available per liter}} \times 100\%$$
$$\text{Percentage ionization} = \frac{6.03 \times 10^{-4}\ \text{M}}{0.20\,\text{M}} \times 100\% = 0.30\%$$

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

	[HA]	**[H$^+$]**	**[A$^-$]**
I	0.20	–	–
C	-6.03×10^{-4}	$+6.03 \times 10^{-4}$	$+6.03 \times 10^{-4}$
E	0.20	6.03×10^{-4}	6.03×10^{-4}

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$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[6.03\times10^{-4}][6.03\times10^{-4}]}{[0.20]} = 1.82\times10^{-6}$$

12. Periodic acid, HIO_4, is an important oxidizing agent and a moderately strong acid. In a 0.10 M solution, $[H^+] = 3.8 \times 10^{-2}$ mol L^{-1}. Calculate the K_a and pK_a for periodic acid.

Solution

$$HIO_4 \rightleftharpoons H^+ + IO_4^-;\ K_a = \frac{[H^+][IO_4^-]}{[HIO_4]}$$

	[HIO_4]	**[H^+]**	**[IO_4^-]**
I	0.10	–	–
C	$-x$	$+x$	$+x$
E	$0.10 - x$	$+x$	$+x$

We know that at equilibrium $[H^+] = 0.038$ M = x. The equilibrium concentrations of the other components of the mixture are:

$$[HIO_4] = 0.10 - x = 0.062\,\text{M and}\,[IO_4^-] = x = 0.038\,\text{M}$$

Substituting the above values for equilibrium concentrations into the mass action expression gives

$$K_a = \frac{(0.038)(0.038)}{0.062} = 2.3\times10^{-2}$$

$$pK_a = -\log(K_a) = -\log(2.3\times10^{-2}) = 1.6$$

13. How many moles of NH_3 must be dissolved in water to give 500 mL of solution with a pH of 11.22?

Solution

Let Z = initial concentration of NH_3.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8\times10^{-5}$$

	[NH_3]	**[NH_4^+]**	**[OH^-]**
I	Z	–	–
C	$-x$	$+x$	$+x$
E	$Z - x$	$+x$	$+x$

Assume $x \ll Z$, we have

$$K_b = \frac{(x)(x)}{Z} = 1.8\times10^{-5} \quad Z = \frac{(x)(x)}{1.8\ \times\ 10^{-5}}$$

$$pOH = 14 - pH = 14 - 11.22 = 2.7$$

$$x = [OH^-] = 10^{-pOH} = 10^{-2.7} = 1.7\times10^{-3}\ \text{M and}\ Z = 0.15\,\text{M}$$

Therefore,

$$\text{mol}\,NH_3 = (500\,\text{mL})\left(\frac{0.15\,\text{mol}}{1000\,\text{mL}}\right) = 0.075\,\text{mol}\,NH_3$$

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14. Barbituric acid, $HC_4H_3N_2O_3$ (which we will abbreviate H-Bar), was discovered by the Nobel prize-winning organic chemist Adolph von Baeyer and named after his friend, Barbara. It is the parent compound of widely used sleeping drugs, the barbiturates. Its pK_a is 4.01. What is the $[H^+]$ and pH of a 0.020 M solution of H-Bar?

Solution

$$K_a = 10^{-pK_a} = 10^{-4.01} = 9.8\times10^{-5}$$

$$\text{H-Bar} \rightleftharpoons H^+ + Bar^-$$

$$K_a = \frac{[H^+][Bar^-]}{[\text{H-Bar}]} = 9.8\times10^{-5}$$

	[H-Bar]	**[H^+]**	**[Bar^-]**
I	0.020	–	–
C	$-x$	$+x$	$+x$
E	$0.020 - x$	$+x$	$+x$

Substituting the above values for equilibrium concentrations into the mass action expression, we get

$$K_a = \frac{(x)(x)}{0.020 - 0.0014} = 9.8\times10^{-5} \Rightarrow x = 1.35\times10^{-3}$$

So, $x = 1.35\times10^{-3} = [H^+]$. Hence, $pH = 2.87$.

15. Calculate the pH of 0.40 M KNO_2. What is the concentration of HNO_2 in the solution?

Solution

KNO_2 will be basic in solution since NO_2^- is a basic ion and K^+ is neutral.

$$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$$

For HNO_2, $K_a = 7.1 \times 10^{-4}$, we need K_b for NO_2^-;

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{7.1\times10^{-4}} = 1.4\times10^{-11}$$

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} = 1.4\times10^{-11}$$

	[NO_2^-]	**[HNO_2]**	**[OH^-]**
I	0.40	–	–
C	$-x$	$+x$	$+x$
E	$0.40 - x$	$+x$	$+x$

Substituting these values into the mass action expression gives

$$K_b = \frac{(x)(x)}{0.40 - x} = 1.4\times10^{-11}$$

Assuming that $x \ll 0.40$ we can solve for x and determine the equilibrium concentrations;

$$x = 2.4\times10^{-6}\ M = [OH^-] = [HNO_2]$$

$$pOH = -\log[OH^-] = -\log(2.4\times10^{-6}) = 5.63$$

$$pH = 14.00 - pOH = 14.00 - 5.63 = 8.37$$

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16. A weak base B forms the salt BHCl, composed of the ions BH^+ and Cl^-. A 0.15 M solution of the salt has a pH of 4.28. What is the value of K_b for the base B?

Solution

The reaction of the weak base in water is: $B + H_2O \rightleftharpoons BH^+ + OH^-$

The salt will react as: $BH^+ \rightleftharpoons H^+ + B$

$$K_a = \frac{[H^+][B]}{[BH^+]}$$

	[BH⁺]	**[H⁺]**	**[B]**
I	0.15	–	–
C	$-x$	$+x$	$+x$
E	$0.15 - x$	$+x$	$+x$

At equilibrium, the pH = 4.28 and $[H^+] = 5.2 \times 10^{-5}$ M = x. Substituting these values into the mass action expression gives

$$K_a = \frac{(x)(x)}{0.15 - x} = \frac{(5.2\times10^{-5})(5.2\times10^{-5})}{0.15-(5.2\times10^{-5})} = 1.8\times10^{-8}$$

Recall that

$$K_a \times K_b = K_w, \text{so } K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.8\times10^{-8}} = 5.6\times10^{-7}$$

17. A student added 100 mL of 0.10 M NaOH to 250 mL of a buffer that contained 0.15 M CH_3COOH and 0.25 M CH_3COO^-. By how much did the concentrations of CH_3COOH and CH_3COO^- change after the addition of the strong base? Use $K_a = 1.8 \times 10^{-5}$ for CH_3COOH.

Solution

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$; $K_a = 1.8\times10^{-5}$

From the reaction, we have:

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$[H^+] = 1.8\times10^{-5}\frac{[0.15]}{[0.25]} = 1.1\times10^{-5}$$

Therefore, the initial pH of the buffer = $-\log(1.1 \times 10^{-5}) = 5.0$

Initial amounts in the solution are

$$\text{mol } CH_3COO^- = (0.25 \text{ mol L}^{-1})(0.25 \text{ L}) = 0.063 \text{ mol } CH_3COO^-$$

$$\text{mol } CH_3COOH = (0.15 \text{ mol L}^{-1})(0.25 \text{ L}) = 0.038 \text{ mol } CH_3COOH$$

The added base (0.100 L)(0.10 mol L^{-1}) = 0.010 mol NaOH) will react with the acetic acid present in the buffer solution. Assume the added base reacts completely. For each mole of base added, one mole of CH_3COOH is converted to CH_3COO^-. Since 0.010 mol of base is added;

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$$\text{mol}\,CH_3COOH_{final} = (0.038 - 0.010)\,\text{mol} = 0.028\,\text{mol}$$
$$\text{mol}\,CH_3COO_{initial} = (0.063 + 0.010)\,\text{mol} = 0.073\,\text{mol}$$

The final volume of solution is 250 mL + 100 mL = 350 mL.

The final concentrations are

$$[CH_3COOH]_{final} = \frac{0.028\,\text{mol}}{0.350\,\text{L}} = 0.08\,\text{M}\,CH_3COOH$$
$$[CH_3COO^-]_{final} = \frac{0.073\,\text{mol}}{0.350\,\text{L}} = 0.21\,\text{M}\,CH_3COO^-$$

So the *changes* in concentrations are
$$\Delta[CH_3COOH] = [CH_3COOH]_{final} - [CH_3COOH]_{initial} = 0.08\,\text{M} - 0.15\,\text{M} = -0.07\,\text{M}$$
$$\Delta[CH_3COO^-] = [CH_3COO^-]_{final} - [CH_3COO^-]_{initial} = 0.21\,\text{M} - 0.25\,\text{M} = -0.04\,\text{M}$$

18. (a) What is the pH of a solution that contains 0.15 M CH_3COOH and 0.25 M CH_3COO^-? Use $K_a = 1.8 \times 10^{-5}$ for CH_3COOH.
(b) By how much will the pH change if 25.0 mL of 0.20 M NaOH is added to 500 mL of the buffer in the above case?
Solution
(a) $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

	[CH_3COOH]	**[H^+]**	**[CH_3COO^-]**
I	0.15	–	0.25
C	$-x$	$+x$	$+x$
E	$0.15 - x$	$+x$	$0.25 + x$

Substituting these values into the mass action expression gives
$$K_a = \frac{(x)(0.25 + x)}{0.15 - x} = 1.8 \times 10^{-5}$$

Assume that $x \ll 0.15$ M and $x \ll 0.25$ M, then;
$$x \times \left(\frac{0.25}{0.15}\right) \approx 1.8 \times 10^{-5}$$
$$x \approx \left(\frac{0.15}{0.25}\right) \times 1.8 \times 10^{-5}$$
$$x \approx 1.1 \times 10^{-5}\,\text{M} = [H^+]$$

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Therefore, $pH = -\log[H^+] = 4.97$

(b) The initial pH of the buffer is 4.97 as determined above. The added base, 0.0250 L × 0.20 mol L^{-1} = 0.0050 mol, will react with the acetic acid present in the buffer solution. Assume the added base reacts completely. For each mole of base added, one mole of CH_3COOH is converted to CH_3COO^-. Since 0.0050 mol of base is added;

$$[CH_3COOH]_{final} = (0.075 - 0.0050)\,mol = 0.070\,mol$$

$$[CH_3COO^-]_{final} = (0.125 + 0.0050)\,mol = 0.130\,mol$$

(*Note:* The amount of acid and base present in the solution is half the stated molarity since we only have 500 mL. Additionally, we have carried one additional significant figure when calculating the number of moles of acetate ion in order to make the calculation more meaningful.)

Now, substitute these values into the mass action expression to calculate the final $[H^+]$ in solution (remember to convert back to molarity accounting for the new volume of 550 mL);

$$\frac{[H^+](0.24)}{(0.13)} = 1.8 \times 10^{-5}$$

$$[H^+] = 9.8 \times 10^{-6}\ mol\,L^{-1}\ \text{and the}\ pH = 5.01$$

The pH of the solution rises but does not change significantly upon addition of the base.

$4.97 - 5.01 = -0.04\,pH\,units$

19. How many grams of sodium formate, $NaCHO_2$, would have to be dissolved in 1.0 L of 0.12 M formic acid (pK_a 3.74) to make the solution a buffer for pH 3.50?

Solution

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

$$3.50 = 3.74 + \log\left(\frac{NaCHO_2}{HCHO_2}\right)$$

Therefore, $\frac{NaCHO_2}{HCHO_2} = 0.575$

$$NaCHO_2 = 0.575 \times HCHO_2 = 0.575 \times 0.12 = 0.069\,M$$

Thus, to the 1 L of formic acid solution we add: 0.069 mol $NaCHO_2$ × 68.0 g mol^{-1} = 4.7 g $NaCHO_2$, assuming no increase in volume upon addition of the sodium formate.

20. How many milliliters of 0.15 M HCl would have to be added to the original 100 mL of the buffer described in Problem (16.72) to make the pH decrease by 0.05 pH unit? How many milliliters of the same HCl solution would, if added to 100 mL of pure water, make the pH decrease by 0.05 pH unit?

Solution

The initial pH is 4.785. We want to lower the pH to 4.735, a decrease of 0.050 pH units. First we will calculate the ratio of acid and its conjugate base:

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$$\text{pH} = \text{p}K_a + \log\frac{[\text{anion}]}{[\text{acid}]} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$

$$4.735 = 4.745 + \log\left(\frac{NaC_2H_3O_2}{CH_3COOH}\right)$$

$$\frac{NaC_2H_3O_2}{CH_3COOH} = 0.977$$

We need a final ratio of conjugate base to acid of 0.977. Initially, there are 0.110 mol of acetate ion and 0.100 mol of acetic acid. We will add a strong acid using up some of the acetate ion and forming additional acetic acid. For every mole of acetate that reacts, one mole of acetic acid will be formed. We can solve the following equation:

$$\frac{0.110\,\text{mol acetate} - x\,\text{mol H}^+}{0.100\,\text{mol acetic acid} + x\,\text{mol H}^+} = 0.977$$

Solving we determine $x = 6.21 \times 10^{-3}$ mol H^+. This is the number of moles of HCl needed to change the pH by 0.05 pH units.

$$\text{mL} = (6.21\times10^{-3}\,\text{mol H}^+)\left(\frac{1\,\text{mol HCl}}{1\,\text{mol H}^+}\right)\left(\frac{1000\,\text{mL}}{0.15\,\text{mol HCl}}\right) = 41\,\text{mL}$$

Thus, we need to add only 41 mL to the 100 mL of buffer.
If we added 41 mL of 0.15 M HCl directly to 100 mL of pure water, we would find the pH = 1.36. Thus, the pH of pure water would change by 5.64 pH units as opposed to the 0.05 pH unit change in the buffer solution.

21. A solution contains calcium nitrate and nickel nitrate, each at a concentration of 0.10 M. Carbon dioxide is to be bubbled in to make its concentration equal to 0.030 M. What pH range would make it possible for the carbonate of one cation to precipitate but not that of the other? Given that K_{sp} of $CaCO_3$ is 4.5×10^{-9} and K_{sp} of $NiCO_3$ is 1.3×10^{-7}.

Solution

Given that $K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.5\times10^{-9}$ and $K_{sp} = [Ni^{2+}][CO_3^{2-}] = 1.3\times10^{-7}$

$NiCO_3$ is more soluble and will precipitate when:

$$[CO_3^{2-}] = \frac{K_{sp}}{[Ni^{2+}]} = \frac{1.3\times10^{-7}}{0.10} = 1.3\times10^{-6}$$

$CaCO_3$ will precipitate when:

$$[CO_3^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{4.5\times10^{-9}}{0.10} = 4.5\times10^{-8}$$

$CaCO_3$ will precipitate and $NiCO_3$ will not precipitate if $[CO_3^{2-}] > 4.5 \times 10^{-8}$ and $[CO_3^{2-}] < 1.3 \times 10^{-6}$. Now, using the equation

$$[H^+]^2 = K_a \times \frac{[H_2CO_3]}{[CO_3^{2-}]} = (2.4\times10^{-17})\left(\frac{0.030}{[CO_3^{2-}]}\right)$$

$NiCO_3$ will precipitate if:

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$$[H^+]^2 = (2.4\times10^{-17})\left(\frac{0.030}{1.3\times10^{-6}}\right) = 5.5\times10^{-13}$$

$$[H^+] = 7.4\times10^{-7} \quad pH = 6.13$$

$CaCO_3$ will precipitate

$$[H^+]^2 = (2.4\times10^{-17})\left(\frac{0.030}{4.5\times10^{-8}}\right) = 1.6\times10^{-11}$$

$$[H^+] = 4.0\times10^{-6} \quad pH = 5.40$$

22. Gold(III) chloride has $K_{sp} = 3.2 \times 10^{-25}$. Calculate the molar solubility of gold(III) chloride in (a) pure water, (b) 0.010 M HCl solution, (c) 0.010 M $MgCl_2$ solution, and (d) 0.010 M $Au(NO_3)_3$ solution.

$$AuCl_3(s) \rightleftharpoons Au^{3+} + 3Cl^-, \quad K_{sp} = [Au^{3+}][Cl^-]^3 = 3.2\times10^{-25}$$

Solution

(a) Let $x = [Au^{3+}]$; then $[Cl^-] = 3x$

$$K_{sp} = (x)(3x)^3 = 27x^4$$

$$x = \sqrt[4]{\frac{3.2\times10^{-25}}{27}} = 3.3\times10^{-7}\ M$$

The molar solubility of $AuCl_3$ is 3.3×10^{-7} M in H_2O.

(b) $[Au^{3+}] = x; [Cl^-] = 0.010 + 3x$

$K_{sp} = (x)(0.010+3x)^3$: Assume $3x \ll 0.010$, then $K_{sp} = (x)(0.010)^3$

Substituting $K_{sp} = 3.2 \times 10^{-25}$ and solving, we get $x = 3.2\times10^{-19}$ M.

The molar solubility of $AuCl_3$ is 3.2×10^{-19} M in 0.010 M HCl.

(c) $[Au^{3+}] = x$; $[Cl^-] = 0.020 + 3x$

$K_{sp} = (x)(0.020+3x)^3$: Assume $3x \ll 0.020$, then $K_{sp} = (x)(0.020)^3$

Substituting $K_{sp} = 3.2 \times 10^{-25}$ and solving, we get $x = 4.0\times10^{-20}$ M.

The molar solubility of $AuCl_3$ is 4.0×10^{-20} M in 0.010 M $MgCl_2$.

(d) $[Au^{3+}] = 0.010 + x; [Cl^-] = 3x$

$K_{sp} = (0.010+x)(3x)^3$: Assume $x \ll 0.010$ then $K_{sp} = (0.010)(3x)^3$

Substituting $K_{sp} = 3.2 \times 10^{-25}$ and solving, we get $x = \sqrt[3]{\frac{3.2\times10^{-25}}{0.27}} = 1.1\times10^{-8}$ M

The molar solubility of $AuCl_3$ is 1.1×10^{-8} M in 0.010 M $Au(NO_3)_3$.

23. In an experiment 2.20 g of NaOH(s) is added to 250 mL of 0.10 M $FeCl_2$ solution. What mass of $Fe(OH)_2$ will be formed? What will the molar concentration of Fe^{2+} be in the final solution?

Solution

$$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)\ K_{sp} = [Fe^{2+}][OH^-]^2$$

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$$\text{mol OH}^- = 2.20\,\text{g NaOH}\left(\frac{1\,\text{mol}}{40.01\,\text{g NaOH}}\right) = 0.0550\,\text{mol NaOH}$$

$$[\text{OH}^-] = \frac{\text{mol OH}^-}{\text{L solution}} = \frac{0.0550\,\text{mol}}{0.250\,\text{L}} = 0.22\,\text{M}$$

	[Fe^{2+}]	**[OH^-]**
I	–	0.22
C	$+x$	$+2x$
E	x	$0.22 + 2x$

We assume that $x \ll 0.22$, so that $0.22 + 2x \approx 0.22$, then we enter the equilibrium values of the above table into the K_{sp} expression:

$$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2$$
$$7.9\times10^{-16} = x(0.22)^2$$
$$x = \text{molar solubility} = 1.6\times10^{-14}\,\text{M}$$

Next, we must determine how many moles of $Fe(OH)_2$ are formed in the reaction. This is a limiting reactant problem.

The number of moles of OH^- is 0.0550 (see above).
The number of moles of Fe^{2+} is (0.250 L) (0.10 mol L^{-1}) = 0.025 mol

From the balanced equation at the top, we need two OH^- for every one Fe^{2+}.
This would be 2(0.025 mol) = 0.050 mol OH^-. Looking at the molar quantities above, we have more than enough OH^- so, Fe^{2+} is our limiting reactant:

0.025 mol $Fe(OH)_2$ will form in 0.25 L solution. If dissolved, this would be a concentration of 0.025 mol/0.25 L = 0.10 M. But from above, the maximum molar solubility of is 1.6×10^{-14} M.

This means that remainder of $Fe(OH)_2$ in excess of this value precipitates:

$$0.10 - 1.6\times10^{-14} \approx 0.10\,\text{M}$$

This works out to 0.25 L (0.10 mol L^{-1}) = 0.025 mol $Fe(OH)_2$(89.8 g mol^{-1})
= 2.2 g solid $Fe(OH)_2$ (essentially all of it).
The remaining OH^-, 0.005 mol, gives a concentration of OH^- of

$$\frac{0.005\,\text{mol OH}^-}{0.250\,\text{L}} = 0.02\,\text{M OH}^-$$

$$7.9\times10^{-16} = [\text{Fe}^{2+}][0.02]^2 \Rightarrow [\text{Fe}^{2+}] = 2.0\times10^{-12}\,\text{M}$$

24. Suppose 50.0 mL each of 0.0100 M solutions of NaBr and $Pb(NO_3)_2$ are poured together. Does a precipitate form? If so, calculate the molar concentrations of the ions at equilibrium.
Solution

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The precipitate that may form is $PbBr_2(s)$. To determine if a precipitate will form, a value for the reaction quotient, Q, must be calculated: $Q = [Pb^{2+}][Br^-]^2$. In performing this calculation, the dilution of the ions must be considered:

$$[Pb^{2+}] = [Br^-] = 0.00500\,M; \quad Q = [0.00500][0.00500]^2 = 1.3\times10^{-7}$$

If $Q > K_{sp}$, a precipitate will form. K_{sp} for $PbBr_2(s)$ is 2.1×10^{-6}. Therefore, a precipitate will not form. Hence, the concentrations calculated are the diluted concentrations. Since no precipitate forms, the concentrations are not equilibrium values.

25. Calculate the pH at equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH solution. (Given that K_a for acetic acid = 1.9×10^{-5}.)

Solution

At equivalence point the concentration of sodium acetate would 0.05 M. Sodium acetate is a salt of a strong base and a weak acid. For such salts we have

$$pH = \frac{1}{2}\left[pK_w + pK_a + \log C\right] = \frac{1}{2}[14 - \log(1.9\times10^{-5}) + \log(0.5)]$$

$$= \frac{1}{2}[14 + 4.72 - 1.3] = \frac{1}{2}[17.42] = 8.71$$

Additional Objective Questions

Single Correct Choice Type

1. In the hydrolytic equilibrium $A^- + H_2O \rightleftharpoons HA + OH^-$, $K_a = 1.0\times10^{-5}$ the degree of hydrolysis of 0.001 M solution of the salt is

(A) 10^{-3} (B) 10^{-4} (C) 10^{-5} (D) 10^{-6}

Solution

(A) $h = \sqrt{\left[\frac{K_h}{C}\right]} = \sqrt{\left[\frac{K_w}{K_a \times C}\right]} = \sqrt{\left[\frac{10^{-14}}{10^{-5}\times0.001}\right]} = 10^{-3}$

2. If S is the solubility of a sparingly soluble salt M_2X_3, its solubility product is equal to

(A) $9S^4$ (B) $27S^3$ (C) $6S^2$ (D) $108S^5$

Solution

(D) The solubility equilibrium for the salt is $M_2X_3 \rightleftharpoons 2M^{3+} + 3X^{2-}$. Using the equation

$$K_{sp} = [M^{3+}]^2[X^{2-}]^3$$

we get $K_{sp} = [M^{3+}]^2[X^{2-}]^3 = (2S)^2 \times (3S)^3 = 108S^5$.

3. Lewis base among the following can be

(A) NO_2 (B) SiO_2 (C) GeO_2 (D) None of these

Solution

(D) Lewis base is an electron acceptor. Since the

4. Which of the following is the strongest acid?

(A) $HClO_4$ dissolved in glacial CH_3COOH (B) $HClO_4$ dissolved in H_2O

(C) H_2SO_4 dissolved in H_2O (D) Glacial CH_3COOH dissolved in H_2O.

Solution

(B) As oxidation no of chlorine is +7.

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5. Neutralization reaction according to Lewis concept is a formation of
(A) salt and water. (B) acid-base adduct.
(C) coordinate compound. (D) zwitter ion.
Solution
(B)

6. Liquid ammonia ionizes to a slight extent. At –50°C, its ionic product is $K_{NH_3} = [NH_4^+][NH_2^-] = 10^{-30}$. How many amide ions, NH_2^- are present per mm^3 of pure liquid ammonia?
(A) 6.023×10^{23} (B) 6.023×10^{14}(C) 6.023×10^{15}(D) 6.023×10^{-15}.
Solution
(B) $[NH_2^-] = \sqrt{K_{NH_3}} = \sqrt{10^{-30}} = 10^{-15}$

$n_{NH_2^-} = MV = 10^{-15} \times 10^6 = 10^{-9}$

Number of NH_2^- ions = $6.023 \times 10^{23} \times 10^{-9}$ ions = 6.023×10^{14} ions

7. The degree of dissociation of pure water at 25°C is found to be 1.8×10^{-9}. Find K_w and K_d at 25°C.
(A) 3.24×10^{-18}; 5.83×10^{-20} (B) 1×10^{-14}; 1.8×10^{-16}
(C) 1.8×10^{-16}; 1×10^{-14} (D) 1×10^{-14}; 1×10^{-14}
Solution
(B) Since $\alpha = 1.8 \times 10^{-9}$ and for water $c = \frac{1000}{18} = 55.56$

$[H^+] = [OH^-] = c\alpha = 55.56 \times 1.8 \times 10^{-9} = 1 \times 10^{-14}$

$K_w = (1 \times 10^{-7})^2 = 10^{-14}$

$K_d = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{55.56} = 1.8 \times 10^{-16}$

8. How much water must be added to 300 mL of 0.2 M solution of CH_3COOH for the degree of dissociation of the acid to double? K_a for the acetic acid = 1.8×10^{-5}.
(A) 900 mL (B) 1000 mL (C) 500 mL (D) 300 mL
Solution
(A) $C_1\alpha_1^2 = C_2\alpha_2^2$ or $C_2 = C_1\left(\frac{\alpha_1}{\alpha_2}\right)^2 = \frac{C_1}{4}$

$M_1 = 0.2\,\text{M}; M_2 = \frac{0.2}{4}, V_1 = 300\,\text{mL}, V_2 = ?$

$M_1V_1 = M_2V_2$ or $V_2 = \frac{M_1V_1}{M_2} = \frac{0.2 \times 300 \times 4}{0.2} = 1200\,\text{mL}$

9. To a 100 mL solution of 0.1 M CH_3COONa and 0.1 M CH_3COOH, 0.4 g of solid NaOH was added. Assuming volume remains constant, calculate the change in pH value? Given that pK_a (CH_3COOH) = 4.74.
(A) 0.125 (B) 0.225 (C) 0.01 (D) 0.872
Solution

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(D) Before NaOH addition, $\text{pH} = \text{p}K_a = 4.74[\text{Since} \mid CH_3COOC^-] = [CHCOOH]]$

The following reaction occurs due to NaOH addition.

$$H_3CCOOH + NaOH\ I \rightarrow H_3CCOONa + H_2O$$

$t = 0$	$0.01\,\text{mol}$	$0.001\,\text{mol}$	0
	$-0.001\,\text{mol}$	$-0.001\,\text{mol}$	$0.001\,\text{mol}$
	$(0.01 - 0.001)\,\text{mol}$	$0.001\,\text{mol}$	

$n_{CH_3COONa} = 0.01\,\text{mol}$. After reaction $n_{CH_3COONa} = 0.009\ \text{mol}$.

$n_{CH_3COO^-} = (0.01 + 0.001)\ \text{mol} = 0.011\ \text{mol}$

$$\text{pH} = \text{p}K_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log\frac{0.011/V}{0.009/V} = 4.74 + \log\frac{11}{9} = 4.74 + 0.0872$$

Change in $\text{pH} = \log\frac{11}{9} = 0.872$

10. In the hydrolytic equilibrium $B^+ + H_2O \rightleftharpoons BOH + H^+, K_b = 1\times10^{-5}$. The hydrolysis constant is:

(A) 10^{-5} (B) 10^{-19} (C) 10^{-10} (D) 10^{-9}

Solution

(B) $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1\times10^{-5}} = 10^{-19}$

11. The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 M Ba^{2+} ions solution will start on adding H_2SO_4 of concentration:

(A) 10^{-9} M (B) 10^{-8} M (C) 10^{-7} M (D) 10^{-6} M

Solution

(D) $[Ba^{2+}][SO_4^{2-}] = 1.5\times10^{-9}(K_{sp})$ and $[Ba^{2+}] = 0.01\text{M}$

So, required $[SO_4^{2-}] = \frac{1.5\times10^{-9}}{0.01} = 1.5\times10^{-7}$

So, $[H_2SO_4] > 1.5 \times 10^{-7}$ for precipitation of $BaSO_4$.

12. Let the solubilities of AgCl in H_2O, 0.01 M $CaCl_2$; 0.01 M NaCl and 0.05M $AgNO_3$ be S_1, S_2, S_3, S_4, respectively. What is the correct relationship between these quantities?

(A) $S_1 > S_2 > S_3 > S_4$ (B) $S_1 > S_2 = S_3 > S_4$ (C) $S_3 > S_2 > S_4 > S_1$ (D) $S_4 > S_2 > S_3 > S_1$

Solution

(C) Solubility of AgCl in water $= \sqrt{K_{sp}} = S_1$

In 0.01 M $CaCl_2$ it is given by

$$K_{sp} = S \times (0.01 \times 2 + S) \text{ therefore } S_2 = \frac{K_{sp}}{0.02}$$

In 0.01 M NaCl it is given by

$$K_{sp} = S \times (0.01 + S) \text{ therefore } S_3 = \frac{K_{sp}}{0.01}$$

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In 0.05 M $AgNO_3$ it is given by

$$K_{sp} = S \times (0.05 + S) \text{ therefore } S_4 = \frac{K_{sp}}{0.05}$$

The solubilities are derived by neglecting S in comparison to 0.02, 0.0l, and 0.05.
Hence, the correct order is $S_3 > S_2 > S_4 > S_1$

13. pH of a mixture of HA and A^- buffer is 5. K_b of A^- = 10^{-10}. Hence [HA]/[A^-] will be:
(A) 1 (B) 10 (C) 0.1 (B) 100

Solution

(C) For conjugate acid–base pair $K_a K_b = K_w$

$$K_a = \frac{10^{-14}}{10^{-10}} = 10^{-4}$$

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$5 = 4 + \log\frac{[A^-]}{[HA]} \Rightarrow 1 = \log\frac{[A^-]}{[HA]} \Rightarrow 10 = \frac{[A^-]}{[HA]} \Rightarrow \frac{[HA]}{[A^-]} = 0.1$$

14. Calculate the [H_3O^+] of blood, the pH of which is 7.3 (slightly basic)
(A) 5×10^{-8} M (B) 6×10^{-8} M (C) 5×10^{-9} M (D) 4×10^{-7} M

Solution

(A) As pH = 7.3, so [H_3O^+] = antilog (–7.3) = 5×10^{-8} M

15. How many grams of CaC_2O_4 will dissolve in one liter of saturated solution? K_{sp} of CaC_2O_4 is 2.5×10^{-9} mol^{-2} and its molecular weight is 128.
(A) 0.0064 g (B) 0.0128 g (C) 0.0032 g (D) 0.0640 g

Solution

(A) $CaC_2O_4 \rightleftharpoons Ca^{++} + C_2O_4^-$; $K_{sp} = s \times s = s^2$

$$s = \sqrt{K_{sp}} = (2.5 \times 10^{-9})^{1/2} = 5 \times 10^{-5} \text{ mol L}^{-1}$$

Therefore , $\frac{w}{128} = 5 \times 10^{-5}$ Therefore $w = 6.4 \times 10^{-3}$ g

16. A solution of HCl is diluted so that its pH changes by 0.3. How does concentration of H^+ ion change?
(A) 0.5 times to the initial value (B) 0.3 times to the initial value
(C) 10^{-3} times increases (D) None of these

Solution

(A) Let H^+ ion concentration changes by x factor.

Since $\text{pH} = -\log\ [H_3O^+]$

Therefore, $\text{pH} + \Delta\text{pH} = -\log\ \{x[H_3O^+]\} = -\log x - \log[H_3O^+]$

or $\text{pH} = -\log x = 0.3 \Rightarrow x = 0.5$.

17. The pH of a 0.01 M solution of acetic acid is
(A) 2. (B) less than 2. (C) greater than 2. (D) cannot be predicted.

Solution

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(C) Acetic acid is incompletely dissociated and therefore, pH cannot be calculated from its stoichiometric concentration.

18. One drop of which of the following solution will give pink color with potassium hydroxide solution?
(A) Methyl orange (B) Methyl red (C) Bromothymol blue (D) Phenolphthalein
Solution
(D)
19. The pH of 0.1 M solution of the following salts increases in the order of: [IIT-JEE 1999]
(A) NaCl < NH_4Cl < NaCN < HCl (B) HCl < NH_4Cl < NaCl < NaCN
(C) NaCN < NH_4Cl < NaCl < HCl (D) HC < NaCl < NaCN < NH_4Cl
Solution
(B)

20. Arrhenius theory of acid-base is not applicable in
(A) aqueous solution. (B) presence of water. (C) non-aqueous solutions. (D) none of these.
Solution
(C) Since Arrhenius theory is only applicable to aqueous media.

21. Which of the following is not Brönsted acid?
(A) NH_4^+ (B) HPO_4^{2-} (C) $AlCl_3$ (D) CH_3COOH
Solution
(C) A Brönsted acid is one which is capable of donating protons to another species.

22. Which of the following is not the characteristic of an acid?
(A) Turns blue litmus to red. (B) Turns phenolpthalein pink from colorless.
(C) Decomposes carbonates (D) Forms oxy compounds of non-metals.
Solution
(B) Option (B) indicates characteristic of bases.

23. The compound which is not a Lewis acid is
(A) BF_3 (B) $AlCl_3$ (C) $SnCl_4$ (D) $BeCl_2$
Solution
(D) $BeCl_2$ exists in polymeric form and so cannot act as a Lewis acid.

24. The pH of 0.1 M CH_3COOH is 2.873. What is pH of 0.1 M NH_4OH? [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$ and $K_b(NH_4OH) = 1.8 \times 10^{-5}$]
(A) 11.127 (B) 2.873 (C) 7 (D) 9.53.
Solution
(A) Since $K_a(CH_3COOH) = K_b(NH_4OH)$ and concentration are equal so pH (CH_3COOH) = pOH (NH_4OH). Given that $\text{pH} = 2.873$. Therefore, $\text{pH} = 14 - \text{pOH} = 14 - 2.873 = 11.127$.

25. If the K_b value in the hydrolysis reaction, $B + H_2O \rightleftharpoons BOH + H^+$; is 1.0×10^{-6}, then the hydrolysis constant of the salt would be [IIT-JEE 1998]
(A) 1.0×10^{-6} (B) 1.0×10^{-7} (C) 1×10^{-8} (D) 1.0×10^{-9}
Solution

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(C) $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

26. The solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5×10^{-23} and 1.8×10^{-14}, respectively. If NH_4OH is added to a solution containing Al^{3+} and Zn^{2+} ions, then substance precipitated first is

(A) $Al(OH)_3$ (B) $Zn(OH)_2$ (C) Both (A) and (B) (D) None of these.

Solution

(A) Solubility of $Al(OH)_3$ is lesser than $Zn(OH)_2$.

27. The solubility product of AgCl in water at 25°C is 1.6×10^{-10}. Its solubility in the presence of 0.1 M HCl is

(A) 1.26×10^{-5} (B) 2.52×10^{-7} (C) 1.6×10^{-9} (D) 1.6×10^{-8}

Solution

(C) $K_{sp} = [Ag^+][Cl^-]$. If S' is the solubility in presence of 0.1 M HCl.

$K_{sp} = [S'][S' + 0.1] \approx S' \times 0.1$. (Neglecting S' compared to 0.1 in the second term).

28. Strength of an acid can be explained on the basis of

(A) its concentration in solution. (B) its degree of ionization.

(C) both (A) and (B) are required. (D) It is an inherent property of acid.

Solution

(C) Since for strong acids (completely ionized) only concentration is the measure of strength but for weak (incompletely ionized) acids both degree of ionization (or K_a) and concentration will be required.

29. Which of the following indicates the correct order of acidic strength of the following acids?

(I) HCOOH ($K_a = 1.8 \times 10^{-4}$) (II) CH_3COOH ($K_a = 1.8 \times 10^{-5}$)

(III) HCN ($K_a = 4.8 \times 10^{-10}$) (IV) HS^- ($K_a = 1 \times 10^{-14}$)

(A) I > II > III > IV (B) IV > III > II > I (C) I > III > II > IV (D) II > UK KIV

Solution

(A) As one can conclude from the increasing values of K_a.

30. In a saturated solution of silver chromate in pure water at 25°C, the concentration of chromate ion is 2×10^{-4} mol L^{-1}. The solubility product of silver chromate is

(A) 2×10^{-8} (B) 4×10^{-8} (C) 3.2×10^{-12} (D) 3.2×10^{-11}

Solution

(D) $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$ $K_{sp} = (2 \times 2 \times 10^{-14})^2 (2 \times 10^{-4}) = 32 \times 10^{-12} = 3.2 \times 10^{-11}$.

31. Calculate the pOH and pH of a 0.1 M CH_3COOH solution ($K_a = 1.8 \times 10^{-5}$). There is 7.5×10^{-3}% yield of OH^- ions in the given reaction $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

(A) 6.12, 7.88 (B) 4.12, 9.88 (C) 5.13, 8.87 (D) None of these

Solution

(C) $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C = 7 + \frac{1}{2} \times 4.74 + \frac{1}{2}\log(0.1)$

$pH = 8.87$ and $pOH = 14 - 8.87 = 5.13$

32. pH of 0.01 MHS^- will be

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(A) $\text{pH} = 7 + \frac{\text{p}K_a}{2} + \frac{\log C}{2}$ (B) $\text{pH} = 7 - \frac{\text{p}K_a}{2} + \frac{\log C}{2}$

(C) $\text{pH} = \frac{\text{p}K_1 + \text{p}K_2}{2}$ (D) $\text{pH} = 7 + \left(\frac{\text{p}K_a + \text{p}K_b}{2}\right)$

Solution

(A) $HS^- + H_2O \rightleftharpoons OH$

33. A sample of 100 mL of 0.10 M acid HA ($K_a = 1 \times 10^{-5}$) is titrated with standard 0.10 M KOH. How many ml of KOH will have to be added when the pH in the titration flask will be 5.00?

(A) 0 (B) 10 (C) 100 (D) 50

Solution

(D) $\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$

$$5 = 5 + \log\left[\frac{N_2V_2}{N_1V_1 - N_2V_2}\right]$$

$$1 = \frac{0.1 \times V_2}{0.1 \times 100 - 0.1 \times V_2} \Rightarrow 10 - 0.1V_2 = 0.1V_2 \text{ or } V_2 = 50\,\text{mL}$$

34. 1.458 g of Mg reacts with 80.0 mL HCl solution whose pH is –0.477. The change in pH after all Mg has reacted. (Assume constant volume. Mg = 24.3 g mol^{-1} and log 3 = 0.477.)

(A) –0.176 (B) + 0.477 (C) –0.2385 (D) 0.3

Solution

(D) $\text{Mg(aq)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2$

Moles of Mg = $\frac{1.458}{24.3}$ mol

$$\text{Millimoles of HCl} = \frac{10^{-0.477}}{0.08\,\text{L}} \times 1000\,\text{mol} = 240\,\text{mM}$$

Moles of HCl after reaction = 240 – 60 × 2 = 120

$$\text{New molarity} = \frac{120}{80} = 1.5\text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 1.5 = -0.176$$

Change is $\text{pH} = -0.176(-0.477) = 0.3$

35. 0.1 mol of $CH_3NH_3 (K_b = 5 \times 10^{-4})$ is mixed with 0.08 mol of HCl and diluted to 1 L. What will be the H^+ ion concentration in the solution?

(A) 8×10^{-2} M (B) 8×10^{-11} M (C) 1.6×10^{-11} M (D) 8×10^{-5} M

Solution

(B) 0.08 mol of HCl will react with 0.08 mol CH_3NH_2 and 0.02 mol CH_3NH_2 is left over, producing 0.08 mol salt $CH_3^+NH_3Cl^-$

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$$\text{pOH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pOH} = -\log 5\times10^{-4} + \log\frac{0.08}{0.02} = 3.3010 + 0.6021 = +3.9031$$

$$\text{pH} = \text{pOH} = 14 - 3.9031 = 11.0969$$

$$(\text{H}^+) = 10^{-\text{pH}} = 10^{-11.0969} = 10^{-11.0969}\times10^{-12}$$

$$= 0.8019\times10^{-12} = 8.019\times10^{-11}\ \text{mol L}^{-1}$$

36. A buffer solution contains 100 mL of 0.01 M CH_3COOH and 200 mL of 0.02 M CH_3COONa 700 mL of water is added. The values of pH before and after dilution are (pK_a = 4.74)

(A) 5.04, 5.04 (B) 5.04, 0.504 (C) 5.04, 1.54 (D) 5.34, 5.34

Solution

(D) $\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$

$$\text{pH} = 4.74 + \log\left[\frac{0.02\times200}{0.01\times100}\right] = 4.74 + \log 4$$

$$= 4.74 + 0.6 = 5.34$$

pH of buffer solution remain same after dilution.

37. A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13}, respectively.

(A) $1.44\times10^{-19}, 3.3\times10^{-7}$ (B) $1.44\times10^{-20}, 3.3\times10^{-8}$

(C) $1.44\times10^{-22}, 3.3\times10^{-3}$ (D) $1.44\times10^{-18}, 3.3\times10^{-5}$

Solution

(B) $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-;\ K_{a_1} = 10^{-7}$

$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-};\ K_{a_2} = 1.3\times10^{-13}$

$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}$

Due to common ion effect the dissociation of H_2S is suppressed and the $[\text{H}^+]$ in solution is due to HCl.

$$K_{a_1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$10^{-7} = \frac{[0.3][\text{HS}^-]}{[-01]}[\text{Since}[\text{H}^+]\text{ from HCl} = 0.3]$$

$$[\text{HS}^-] = \frac{10^{-7}\times0.1}{0.3} = 3.3\times10^{-8}\ \text{M}$$

$$K_{a_2} = \frac{[\text{H}^+][\text{S}^{-2}]}{[\text{HS}^-]}$$

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Further $1.3\times10^{-13} = \dfrac{[0.3][S^{-2}]}{3.3\times10^{-R}}$

$$[S^{-2}] = \frac{1.3\times10^{-13}\times3.3\times10^{-8}}{0.03} = 1.43\times10^{-20}\ \text{M}$$

38. To a 100 mL solution of 0.1 M CH_3COONa and 0.1 M CH_3COOH, 0.4 g of solid NaOH was added. Assuming volume remains constant, the change in pH value will be (pK_a of CH_3COOH = 4.74)

(A) 0.125 (B) 0.225 (C) 0.01 (D) 0.0872

Solution

(D) Before NaOH addition,

$$\text{pH} = \text{p}K_a = 4.74\ [\text{Since } [CH_3COO^-] = [CH_3COOH]]$$

The following reaction occurs due to NaOH addition.

$$H_3CCOOH + NaOH \rightarrow H_3CCOONa + H_2O$$

Initially	0.01 mol	0.01 mol	0 mol	0
Finally	(0.01 − 0.001) mol		0 mol	0.001 mol

$n_{H_3CCOONa} = 0.01$ mol

After reaction, $n_{CH_3COOH} = 0.009$ mol

$n_{CH_3COOH} = (0.01 + 0.001)\ \text{mol} = 0.011\ \text{mol}$

$$\text{pH} = \text{p}K_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log\frac{0.011/V}{0.009/V} = 4.74 + \log\frac{11}{9} = 4.74 + 0.872$$

Change in $\text{pH} = \log\dfrac{11}{9} = 0.0872$

39. What is the pH of the solution when 0.2 mol of hydrochloric acid is added to 1 L of a solution containing (a) 1 M each of acetic acid and acetate ion and (b) 0.1 M each of acetic acid and acetate ion? Assume that the total volume is 1 L. K_a for acetic acid = 1.8×10^{-5}.

(A) 4.57, 2 (B) 4.57, 1 (C) 5.57, 1 (D) 5.57, 2

Solution

(B)

(a) The reaction is

$$CH_3COO^- + HCl \rightarrow CH_3COOH + Cl^-$$

1	0.2	1
0.8	0	0.2

Total concentration of $CH_3COOH = 1 + 0.2 = 1.2$

$$\text{pH} = \text{p}K_s + \log\left(\frac{\text{salt}}{\text{acid}}\right) = -\log 1.8\times10^{-5} + \log\frac{[0.8]}{[1.2]}$$

$$= 4.7447 - 0.1761 = 4.5686 \approx 4.57$$

(b) Now for the reaction

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$$CH_3COO^- + HCl \rightarrow CH_3COOH + Cl^-$$

	0.1	0.2	0.1
	0	0.1	0.2

Hence the concentration of $[H^+]$ arises only from free HCl = 0.1M = 10^{-1}. Hence pH = 1. <

40. Two buffers, (X) and (Y) of pH 4.0 and 6.0, respectively, are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? ($K_{HA} = 1.0 \times 10^{-5}$).

(A) 4.7033 (B) 5.7033 (C) 6.7033 (D) 8.7033

Solution

(B) pH of buffer is given by

$$\text{pH} = -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{Case I}: 4 = -\log 1.0\times10^{-5} + \log\frac{[\text{salt}]}{(0.5)}$$

$$\text{or} \quad [\text{salt}] = 0.1\times0.5 = 0.05\,\text{M}$$

$$\text{Case II}: 6 = -\log 1.0\times10^{-5} + \log\frac{[\text{salt}]}{(0.5)}$$

As $\log\frac{[\text{salt}]}{(0.5)} = 1$, $[\text{salt}] = 10\times0.5 = 5\,\text{M}$

Now the two buffer [(I. NaA = 0.05 M and HA = 0.5 M) and (II. NaA = 5 M and HA = 0.5 M)] are mixed in equal proportion.

Thus, new cone to concentration of NaA is mixed buffer = $\frac{0.05\times V + 5\times V}{2V} = \frac{5.05}{2}$

New concentration of HA in mixed buffer = $\frac{0.5\times V + 0.5\times V}{2V} = 0.5\text{ M}$

$$\text{pH} = -\log(1.0\times10^{-5}) + \log\frac{[5.05/2]}{[0.5]}$$

Thus, $\text{pH} = 5 + 0.7033 = 5.7033.$

41. To what volume must one liter of 1 M CH_3COOH solution be diluted so that the pH of resulting solution becomes twice the original value. [Given: $K_a = 1.8 \times 10^{-5}$]

(A) 2.78×10^5 (B) 2.78×10^4 (C) 2.78×10^3 (D) 2.78×10^2

Solution

(B) The reaction is

	H_3CCOOH +	$H_2O \rightleftharpoons$	H_3CCOO +	H_3O^+
at $t = 0$	1.0 M		0	0
at $t = t_{eq}$	$(-x)$ M		x	
$t = t_{eq}$	$(1-x)$M		x	

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$$K_a = \frac{x^2}{1-x} \approx \frac{x^2}{1}$$

$$x = \sqrt{K_a} = 4.2\times10^{-3} = [H_3O^+]$$

$$pH = -\log[H_3O^+] = -\log\{4.2\times10^{-3}\} = 3 - \log 4.2 = 2.37$$

Now, let 1 L of 1 M ACOH solution be diluted to VL to double the pH and the concentration of diluted solution be *C*.

	H_3CCOOH	+ H_2O	$\rightleftharpoons$ H_3CCOO^-	+ H_3O^+
$t = 0$	C	0	0	
	-1.8×10^{-5}	1.8×10^{-5}	1.8×10^{-5}	
$t = t_{eq}$	$C - 1.8\times10^{-5}$	1.8×10^{-5}	1.8×10^{-5}	

New $pH = 2\times \text{old } pH = 2\times 2.37 = 4.74$

$pH = -\log[H_3O^+] = 4.74 \Rightarrow [H_3O^+] = 1.8\times10^{-5}$

$$K_a = \frac{[CH_3COO^-]\times[H_3O^+]}{[CH_3COOH]}$$

$$1.8\times10^{-5} = \frac{1.8\times10^{-5}\times1.8\times10^{-5}}{C - 1.8\times10^{-5}}$$

$$C = 3.6\times10^{-5}\ \text{L}$$

On dilution, $M_1V_1 = M_2V_2$

$$1\text{M}\times1\text{L} = 3.6\times10^{-5}\ \text{L}\times V_2$$

or $$V_2 = 2.78\times10^4\ \text{L}$$

Formula of calcium lactate suggests that lactic acid is dibasic acid. Each mole of salt furnishes two moles of lactate ion

$$Ca(Lac)_2 \rightleftharpoons Ca^{2+} + 2\,Lac$$

0.50 L solution contains = 0.13 mol of salt = 0.26 mol of lactate ion
1 L of solution contains = 0.52 mol of lactate ion
So, [lactate] = 0.52 M
Given pOH = 5.6, so pH = 14 – 5.6 = 8.4
Using equation of pH for salt of weak acid and strong base

$$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$$

$$8.4 = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$$

$$8.4 = 7 + \frac{pK_a}{2} + \frac{\log 0.52}{2} = 7 + \frac{pK_a}{2} - 0.14$$

Solving, we get $pK_a = 3.08$, so $K_a = 10^{-3.08} = 8.3\times10^{-4}$.

42. An acid-base indicator has K_a of 3×10^{-5}. The acid form of the indicator is red and the basic form is blue. By how much must the pH change in order to change the indicator from 75% red to 75% blue?

(A) 1.95 (B) 2.95 (C) 0.95 (D) 3.95

Solution

(C) $HIn \rightleftharpoons H^+ + In^-$

$$K_{ln} = K_a = \frac{[H^+][In^-]}{[HIn]} = \frac{[H^+][base]}{[acid]}$$

$$[H^+] = K_a \frac{[acid]}{[base]}$$

$$\text{For 75% red}: \ [H^+] = \frac{(3\times10^{-5})(75)}{25} = 9\times10^{-5}. \text{ Therefore, pH} = 4.05$$

$$\text{For 75% blue}: [H^+] = \frac{(3\times10^{-5})(75)}{75} = 1\times10^{-5}. \text{ Therefore, pH} = 5$$

The change in pH = 5 – 4.05 = 0.95

43. The indicator used for the titration of a weak base and strong acid is

(A) methyl orange. (B) phenolphthalein. (C) phenol red. (D) litmus paper.

Solution

(A)

44. Ammonium ion is a

(A) Lewis acid. (B) Lewis base. (C) Brönsted acid. (D) Brönsted base.

Solution

(C) NH_4^+ is a proton donor.

45. When a 0.1 N solution of an acid at 25°C has a degree of ionization of 8%, the concentration of OH^- present is

(A) 1.25×10^{-3} (B) 1.25×10^{-11} (C) 1.25×10^{-12} (D) 1.25×10^{-13}

Solution

(C) $[H^+] = C\alpha = 0.1\times8\times10^{-2}$

$$[OH^-] = \frac{10^{-14}}{[H^+]} = 1.25\times10^{-12}$$

46. A solution has 0.05 M $Mg^{2+}$and 0.05 M NH_3. Calculate the concentration of NH_4CI required to prevent the formation of $Mg(OH)_2$ in solution. $K_{sp[Mg(OH)_2]} = 9.0\times10^{-12}$ and ionization constant of NH_3 is 1.8×10^{-5}.

(A) 4.123 M (B) 0.67 M (C) 5.267 M (D) 0.067 M

Solution

(D) The minimum $[OH^-]$ at which there will be no precipitation of $Mg(OH)_2$ can be obtained by

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 9.0\times10^{-12} = (0.05)\times[OH^-]^2 \Rightarrow [OH^-] = 1.34\times10^{-5} \text{ M}$$

Thus, solution having $[OH^-] = 1.34 \times 10^{-5}$ M will not show precipitation of $Mg(OH)_2$ in 0.05 M Mg^{2+}. These hydroxyl ions are to be derived by basic buffer of NH_4Cl and NH_4OH.

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$$\text{pOH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{acid}]} = \text{p}K_b + \log\frac{[NH_4^+]}{[NH_4OH]}$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

In presence of [NH_4CI], all the NH_4^+ are provided by NH_4Cl as due to common ion effect, dissociation of NH_4OH will decrease.

$$-\log[OH^-] = -\log 1.8\times10^{-5} + \log\frac{[NH_4^+]}{[0.05]}$$

$$\text{Therefore } NH_4^+ = 0.067\text{M} \text{ or } [NH_4Cl] = 0.067\text{ M}$$

47. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K = 1.8 \times 10^{-10}$) will occur only with

(A) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-) (B) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)

(C) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-) (D) 10^{-10}M (Ag^+) and 10^{-10} M (Cl^-)

Solution

(A) One can calculate ionic product from given data and for precipitation, ionic product > K_{sp}.

For part (A), ionic product = $(10^{-4}) \times (10^{-4}) = 10^{-8}$ M which is greater than K_{sp}.

48. The correct order of increasing [H_3O^+] in the following aqueous solution is

(A) 0.001 M H_2S < 0.01 M H_2SO_4 < 0.01 M NaCl < 0.01 M $NaNO_2$

(B) 0.01 M NaCl < 0.01 M $NaNO_2$ < 0.01 M H_2S < 0.01 M H_2SO_4

(C) 0.01 M $NaNO_2$ < 0.01 M NaCl 0.01 M H_2S < 0.01 M H_2SO_4

(D) 0.01 M H_2S < 0.01 M NaCl < 0.0 l M $NaNO_2$ < 0.01 M H_2SO_4

Solution

(C)

H_2SO_4 is a strong acid, so it will completely dissociate and have the highest concentration of [H^+]. H_2S is a weak acid, so will have lower [H^+]. NaCl is a salt of strong acid and strong base so will give rise to neutral solution. $NaNO_2$ will alkaline solution on hydrolysis, so[H^+] is the least.

49. To a 50 mL of 0.1 M HCl solution, 10 mL of 0.1 M NaOH is added and the resulting solution is diluted to 100 mL. What is change in pH of the HCl solution?

(A) 4.398 (B) 0.398 (C) 0.1 (D) None of these

Solution

(B) Before adding HCl solution

$$\text{pH} = 1\ [\text{Since}[\text{HCl}] = [H_3O]^+ = 10^{-1}\text{ M}]$$

$$n_{\text{HCl}}\ (\text{initially}) = MV = 0.1\text{M}\times0.05\text{L} = 5\times10^{-3}\text{ mol}$$

$$n_{\text{HCl}}\ \text{added} = MV = 0.1\text{M}\times0.01\text{L} = 1\times10^{-3}\text{ mol}$$

The reaction involved is

$$\begin{array}{lccc} & \text{HCl} + \text{NaOH} & \rightarrow & \text{NaCl} + H_2O \\ t = 0 & 5\times10^{-3}\text{ mol} & 1\times10^{-3}\text{ mol} & 0 \\ & 4\times10^{-3}\text{ mol} & & 0 \end{array}$$

$$V_{\text{final}} = 100\text{ mL} = 0.1\text{L}$$

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$$[\text{HCl}] = \frac{n}{V} = \frac{4\times10^{-3}\text{ mol}}{0.1\text{L}} = 4\times10^{-2}\text{ M}$$

$$\text{pH} = -\log\ [\text{H}_3\text{O}^+] = 2-\log 4 = 2-2\log 2 = 2-2\times0.301 = 2-0.602 = 1.398$$

So, Increase in pH = (1.398 – 1) = 0.398

50. What amount of solid sodium acetate be added into 1 L of the 0.1 M CH_3COOH solution so that the resulting solution has pH almost equal to pK_a (CH_3COOH) = 4.74?

(A) 12 g (B) 5 g (C) 10 g (D) 15 g

Solution

(D) Since the resulting solution be the acidic buffer, one may use Henderson equation

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Let n mol of CH_3COONa be added to do so

or
$$\text{pH} = 4.74 + \log\frac{n\,\text{mol L}^{-1}}{0.1\,\text{mol L}^{-1}}$$

$$5 = 4.74 + \log\frac{n}{0.1} \Rightarrow \log\frac{n}{0.1} = 0.26$$

$$\frac{n}{0.1} = \text{antilog}\ 0.26 = 1.8197$$

Therefore, $n = 0.18197\ \text{mol} \cong 0.182\ \text{mol}$. Amount of sodium acetate = 0.182 × 82 g = 14.924 g.

51. Which of the following sulphides has maximum solubility in water?

(A) CdS (K_{sp} = 36 × 10^{-30}) (B) FeS (K_{sp} = 11 × 10^{-20})

(C) HgS (K_{sp} = 32× 10^{-54}) (D) ZnS (K_{sp} = 11 × 10^{-22})

Solution

(B) All salt are AB type so solubility will be $\sqrt{K_{sp}}$

52. Law of mass action can be applied to aqueous solutions of weak electrolyte since

(A) reaction is always carried out in a closed vessel.

(B) pressure, temperature of surroundings remain constant.

(C) state of equilibrium exists between the ionized and unionized molecules.

(D) nothing can be predicted.

Solution

(C)

53. Given that $[\text{Ag(NH}_3)_2]^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$, $K_\text{C} = 6.2\times10^{-8}$ and $K_{\text{sp(AgCl)}} = 1.8\times10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.

(A) 0.539 (B) 0.239 (C) 1.539 (D) 0.812

Solution

(A)

Let the solubility of AgCl and $[\text{Ag(NH}_3)_2]^-$ be x and y, then

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$$AgCl(s) \rightleftharpoons \underset{x+y}{Ag^+}(aq) + \underset{y}{Cl^-}(aq)$$

$$K_{sp} = [Ag^+][Cl^-] = (x+y)y$$

$$[Ag(NH_3)_2]^+ \rightleftharpoons \underset{x+y}{Ag^+} + \underset{2x}{2NH_3}$$

Given that

$$K_c = \frac{[Ag^+]\,[NH_3]^2}{[Ag(NH_3)_2]^+} = 6.2\times10^{-8}$$

In case of simultaneous solubility, Ag^+ remains same in both the equilibrium

$$K_c = \frac{(x+y)\times(2x)}{[Ag(NH_3)_2]^+}$$

$$K_{sp} = (x+y)y$$

Therefore, $$\frac{K_c}{K_{sp}} = \frac{2x}{[Ag(NH_3)_2]^+\,y}$$

Given that $[NH_3] = 2x = 1M$.

$[Ag(NH_3)^+] = [Cl^-] = y$ because Ag^+ obtained from AgCl passes in $[Ag(NH_3)_2]^+$ state

$$\frac{K_c}{K_{sp}} = \frac{1}{y\times y} \text{ or } y^2 = \frac{1.8\times10^{-10}}{6.2\times10^{-8}} = 0.29\times10^{-2}$$

Therefore $y = 0.539\times10^{-1} = 0.0539$, that is, $[Ag(NH_3)_2]^+ = 0.539$.

54. pH of a buffer containing 6.0 g of CH_3COOH and 8.2 g of CH_3COONa in 1 L of water is (pK_a = 4.5)
(A) 7.5 (B) 4.5 (C) 5.5 (D) 6.5
Solution
(B) $[CH_3COOH] = \frac{6.0}{60}\times1 = 0.1\text{ M}$ and $[CH_3COONa] = \frac{8.2}{82}\times1 = 0.1M$

So, $$pH = pK_a + \log\frac{[salt]}{[acid]} = 4.5 + \log\left(\frac{0.1}{0.1}\right) = 4.5$$

55. After the dissolution of a sparingly soluble salt, if hydrolysis of any one of the ions will occur, then
(A) solubility of salt decreases. (B) solubility of salt increases
(C) there will be no effect on solubility. (D) cannot be predicted.
Solution
(B) Dissolution equilibria shift toward right side due to hydrolysis of cation or anion.

56. The compound whose 0.1 M solution basic is
(A) ammonium chloride. (B) ammonium acetate.
(C) ammonium sulphate. (D) sodium acetate.
Solution

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(D) Since sodium acetate is salt of (WA + SB) and its pH > 7.

57. Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to

(A) 1.0 (B) 100.0 (C) 10.0 (D) 0.1

Solution

(A) The buffer action of a buffer mixture is effective in the pH range pK_a ± 1. It is maximum when pH = pK_a.

58. Weak acid HX has the dissociation constant 1×10^{-5}. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX is

(A) 0.0001 (B) 0.01 (C) 0.1 (D) 0.15

Solution

(B) $K_a = 1\times10^{-5} \quad K_w = 1\times10^{-14} \quad c = 0.1$

$$h = \sqrt{\frac{K_w}{K_b \times c}} = \sqrt{\frac{10^{-14}}{10^{-5}\times10^{-1}}} = \sqrt{10^{-8}} = 10^{-4} = 0.0001$$

Percentage of hydrolysis = 0.0001 × 100 = 0.01%

59. The pOH of 10^{-8} M HCl is

(A) 8. (B) 6. (C) between 6 and 7. (B) between 7 and 8.

Solution

(D) $[H^+]\text{from HCl} = 10^{-8}$

$[H^+]\text{from } H_2O = 10^{-7}$

$$\text{Total}[H^+] = 10^{-8} + 10^{-7} = 10^{-7}[0.1+1] = 1.1\times10^{-7}\text{ g ions L}^{-1}$$

$$\text{pH} = -\log_{10}[H^+] = -\log_{10}(1.1\times10^{-7}) = -\log_{10}1.1 + 7\log_{10}10 = 7 - 0.0414 = 6.9$$

$\text{pOH} = 14 - 6.9 = 7.1$ which is between 7 and 8.

60. For preparing a buffer solution of pH = 6 by mixing sodium acetate and acetic acid, the ratio of concentration of salt and acid ($K_a = 10^{-5}$) should be

(A) 1:10 (B) 10:1 (C) 100:1 (B) 1:100

Solution

(B) Given that pH = 6, $K_a = 10^{-5}$. So,

$pK_a = -\log K_a = -\log_{10}10^{-5} = 5\times\log_{10}10 = 5$

Now, $\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$. Therefore,

$$6 = 5 + \log\frac{[\text{salt}]}{[\text{acid}]}$$

or

$$\frac{[\text{salt}]}{[\text{acid}]} = \frac{10}{1} = 10:1$$

61. pH of a saturated solution of $Ba(OH)_2$ is 12. Hence, K_{sp} of $Ba(OH)_2$ is

(A) $5\times10^{-7}\text{ M}^3$ (B) $5\times10^{-4}\text{ M}^2$ (C) $1\times10^{-6}\text{ M}^3$ (B) $4\times10^{-6}\text{ M}^3$

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Solution

(A) $\text{pH of } Ba(OH)_2 = 12$ and $\text{pOH of } Ba(OH)_2 = 2$

$[OH^-] = 10^{-2}$ and $[OH^-] = 2[Ba^{2+}] \Rightarrow [Ba^{2+}] = \frac{1}{2}[OH^-]$

Therefore, $$K_{sp} = \left[\frac{10^{-2}}{2}\right][10^{-2}]^2 = \frac{10^{-6}}{2} = 5\times10^{-7}\ M^3$$

62. An acid solution of pH = 6 is diluted thousand times. The pH of solution becomes approximately.

(A) 6.99 (B) 6 (C) 4 (B) 9

Solution

(A) pH of acid solution = 6. When acid solution is diluted thousand times, $[H^+] = 10^{-9}$ M

When H^+ concentration less than 10^{-6}, in that case we also take the H^+ concentration from water.

Therefore, total H^+ concentration $= [10^{-9}] + [10^{-7}] = 1.01\times10^{-7}$

Hence, pH of diluted acid is = $-\log 1.01\times10^{-7} = 6.99$.

63. Calculate the pH at the equivalence point of the titration between 0.1 M CH_3COOH and 0.05 M NaOH [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$).]

(A) 4.75 (B) 5.63 (C) 6.63 (B) 3.63

Solution

(A) The reaction involved is

$$CH_3CHOOH + NaOH \rightarrow CH_3COONa + H_2O$$

Initial	0.1	0.05	0	0
At equillibrium point	0.05	0	0.05	0.05

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

But $[salt] = [acid]$, therefore,

$$pH = -\log K_a = -\log 1.8\times10^{-5} = 5 - \log 1.8 = 5 - 0.2553 = 4.7447$$

64. The self-ionization constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperate. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is 1.22 g cm^{-3}.

(A) 0.0037 (B) 0.037 (C) 0.37 (D) 1.037

Solution

(A) Given density of formic acid = 1.22 g cm^{-3}

Weight of formic acid in 1 L solution = 1.22×10^3 g

$$\text{Since}[HCOOH] = a\frac{1.22\times10^3}{46} = 26.5\,M$$

In the case of autoionization, $[HCOOH_2^+] = [HCOO^-]$

So, $[HCOOH_2^+][HCOO^-] = 10^{-6} \Rightarrow [HCOO^-] = 10^{-3}$

Now percentage dissociation of

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$$\text{HCOOH} = \frac{[\text{HCOO}^-]\times 100}{[\text{HCOOH}]} = \frac{10^{-3}\times 100}{265} = 0.00377$$

65. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm. What is the pH when the average temperate is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mol L^{-1} and the pK_a of H_2SO_3 is 1.92, the pH of rain on that day is

(A) 4.865 (B) 3.865 (C) 5.865 (D) 6.865

Solution

(A) Amount of SO_2 in atmosphere = $\frac{10}{10^6} = 10^{-5}$

Molar concentration of SO_2 in presence of water $= (\text{Amount of } SO_2 \times \text{ solubility of } SO_2 \text{ in water})$

$$[SO_2] = 10 - 5\times 1.5653\,\text{mol}\,L^{-1} = 1.3653\times 10^{-5}\ \text{M}$$

Now,

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

At equilibrium $[1.3653\times 10^{-5}] - x$ $\quad x \quad x$

So, $K_a = \frac{x^2}{(1.3653\times 10^{-5} - x)} = 10^{-1.92}$

Solving, we get $x = 1.364 \times 10^{-5}$. hence, $\text{pH} = -\log(1.364\times 10^{-5}) = 4.865$.

66. How much Ag^+ would remain is solution after mixing equal volumes of 0.080 M $AgNO_3$ and 0.08 N HOCN. Given that K_{sp} of AgOCN = 2.3×10^{-7} and K_a of HOCN = 3.3×10^{-4}.

(A) 5×10^{-5} M (B) 5×10^{-4} M (C) 5×10^{-3} M (D) 5×10^{-2} M

Solution

(C) Due to two-fold dilution

$$\text{HOCN} \rightleftharpoons H^+ + {}^-\text{OCN}$$

$$Ag^+ + {}^-\text{OCN} \rightleftharpoons \text{AgOCN(s)}$$

Let $[Ag^+] = x$. The amount of Ag^+ precipitated = $(0.04 - x)$ M

Amount of $^-$OCN precipitated = $(0.04 - x)$ N

$[\text{HOCN}] = x - [{}^-\text{OCN}] = x$ M

$[H^+] = 0.04 - x$

Then, $$\frac{[{}^-\text{OCN}]}{[\text{HOCN}]} = \frac{K_a}{[H^+]} = \frac{3.3\times 10^{-4}}{0.04 - x} \text{ or } [\text{OCN}] = \frac{3.3\times 10^{-4}\times x}{0.04 - x}$$

and $$[Ag^+][{}^-\text{OCN}] = \frac{3.3\times 10^{-4}x^2}{0.04 - x} = K_{sp} = 2.3\times 10^{-7}$$

or $$x = [Ag^+] = 5\times 10^{-3}\ \text{M}.$$

67. A solution of HCl is diluted so that its pH changes by 0.3. How does the concentration of H^+ ion change?

(A) 0.5 times to the initial value (B) 0.6 times to the initial value

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(C) 10^{-3} times increases (D) 0.2 times to the initial value

Solution

(A) Let H^+ ion concentration changes by x factor. Since, $\text{pH} = -\log[H^+]$. Therefore,

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

or $$\Delta\text{pH} = -\log x = 0.3 \Rightarrow x = 0.5$$

68. A weak base (BOH) with $K_b = 10^{-5}$ is titrated with a strong acid, HCl. At three-fourth of the equivalence point, pH of the solution is

(A) 5 + log3 (B) 14 – 5 – log3 (C) 14 – 5 + log3 (D) 9.523

Solution

(B) Let the initial equivalent of BOH be x

	BOH	+	HCl	→	BCl	+	H_2O
Initial equivalent	x		$\frac{3}{4x}$		0		0
At $\frac{3}{4}$th equivalence point	$x - \frac{3x}{4} = \frac{x}{4}$		0		$\frac{3}{4}x$		$\frac{3}{4}x$

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]} = 5 + \log\frac{3x \times 4}{4 \times x} = 5 + \log 3$$

Hence, pH = 14 – 5 – log3.

69. An aqueous solution .contains 10% ammonia by mass and has density of 0.99 g cm^{-3}. The pH of this solution is [K_a for =5 × 10^{-10} M].

(A) 11.033 (B) 12.033 (C) 9.033 (D) 7.2033

Solution

(B) Given that

$$\frac{\text{Weight of } NH_2}{\text{Weight of solution}} = \frac{10}{100}$$

100 g solution contain 10 gNH_3

$$M_{NH_3} = \frac{(10 \times 1000)}{[17 \times (100/0.99)]} = 5.82 \quad \left(\text{Since } V = \frac{\text{mass}}{\text{density}}\right)$$

Now	$NH_2 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$			
Before dissociation	1		0	0
After dissociation	$(1-\alpha)$		α	α

$$\left[OH^-\right] = C\alpha = C\sqrt{\left(\frac{K_b}{C}\right)} = \sqrt{(K_b \times C)}$$

where $C = 5.82\,\text{M}$ and $K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5 \times 10^{-10}} = 2 \times 10^{-5}$. Substituting, we get

$$[OH^-] = \sqrt{[2 \times 10^{-5} \times 5.82]} = 1.07 \times 10^{-2}\ \text{M}$$

$$[H^+] = \frac{10^{-14}}{1.07} \times 10^{-2} = 0.9268 \times 10^{-12}\ \text{M}$$

Hence, $pH = -\log[H^+] = -\log 0.9268 \times 10^{-12} = 12.0330$

70. A solution of 0.010 M $CdCl_2$ containing 0.010 M NH_3. What concentration of NH_4^+ ion from NH_4Cl is necessary to prevent the precipitation of $Cd(OH)_2$? ($K_{sp} = 2 \times 10^{-14}$ and K_b for $NH_4OH = 1.8 \times 10^{-5}$)

(A) 0.13 M (B) 0.23 M (C) 0.33 M (D) 1.13 M

Solution

(A) The reaction involved is

$$Cd^{2+} + 2OH^- \rightleftharpoons Cd(OH)_2, \quad K_{sp} = 2 \times 10^{-14}$$

NH_3 in aqueous solution will exist as ($NH_3 + H_2O \rightarrow NH_4OH$)

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad K_b = 1.8 \times 10^{-5}$$

$[Cd^{2+}] = 0.01\text{M}$ and $[NH_4OH] = [NH_3] = 0.01\text{M}$

$$K_{sp} = [Cd^{2+}][OH^-]^2 = 2 \times 10^{-14} = [0.01][OH^-]^2$$

$$[OH^-]^2 = 2 \times 10^{-12}[OH^-] = 1.414 \times 10^{-6}$$

$$[NH_4^+] = \frac{1.8 \times 10^{-7}}{1.414 \times 10^{-6}} = 1.28 \times 10^{-1} = 0.13\text{M}$$

71. A weak acid HA after treatment with 12 mL of 0.1 M strong base BOH has a pH of 5. At the end point, the volume of same base required is 26.6 mL. The K_a of acid is

(A) 8.219×1^{-5} (B) 8.219×10^{-7} (C) 8.219×10^{-6} (D) 8.219×10^{-4}

Solution

(C) Total Meq. of acid = Meq. of base $= 26.6 \times 0.1 = 2.66$

Now for partial neutralization of acid

	HA +	BOH →	BA +	H_2O
Meq. before reaction	2.66	1.2	0	0
Meq. after reaction	1.46	0	1.2	1.2

The resultant mixture acts as a buffer or

$$pH = -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$5 = -\log K_a + \log\frac{1.2}{1.46}$$

Solving, we get $K_a = 8.219 \times 10^{-6}$.

72. Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNiC. Calculate its percent dissociation in a solution which contains 0.10 mol of nicotinic acid per 2.0 L of solution.

(A) 2.67 (B) 1.87 (C) 1.67 (D) 1.37

Solution

(C) The reaction involved is

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$$\begin{array}{lcccc} & HNiC & \rightleftharpoons & H^+ & + & NiC^- \\ & 1 & & 0 & & 0 \\ & (1-\alpha) & & \alpha & & \alpha \end{array}$$

Also, $C = \frac{0.1}{2} = 5\times10^{-2}$ mol L^{-1}; $K_s = 1.4\times10^{-5}$

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \quad (\text{Since} 1-\alpha = 1)$$

Therefore, $\alpha = \sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{\left(\frac{1.4\times10^{-5}}{5\times10^{-2}}\right)} = 1.67\times10^{-2}$ or 1.67%

73. The ratio of pH of a solution containing 1 mol of CH_3COONa + 1 mol of HCl per liter and of other solution: containing 1 mol CH_3COONa + 1 mol of acetic acid per liter will be

(A) 1:2 (B) 2:1 (C) 1:3 (D) 3:1

Solution

(A) Case I: pH when 1 mol of CH_3COONa and 1 mol of HCl are present.

$$CH_3COONA + HCl \rightarrow CH_3COOH + NaCl$$

Before reaction	1	1	0	0
After reaction	0	0	1	1

Given that $[CH_3COOH] = 1M$

Therefore, $[H^+] = C\alpha = C\sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_a C)} = \sqrt{(K_a)}$ therefore $C = 1$

or $pH_I = -\frac{1}{2}\log K_a$

Case II: pH when 1 mol of CH_3COONa and 1 mol of CH_3COOH; a acidic buffer solution forms.

Given that $[\text{salt}] = 1M$, $[\text{acid}] = 1M$. Therefore,

$$pH_{II} = -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]} = -\log K_a$$

Therefore $\frac{pH_I}{pH_{II}} = \frac{1}{2}$

74. An acid type indicator, Hln, differs in color from its conjugate base (In^-). The human eye is sensitive to color differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in pH of the solution to observe a complete color change? ($K_a = 1.0 \times 10^{-5}$).

(A) 3 (B) 2 (C) 1 (D) 4

Solution

(B) The reaction involved is

$$HIn \rightleftharpoons H^+ + In^- \qquad K_a = \frac{[H^+][In^-]}{[HIn]}$$

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When $\frac{[\text{In}]}{[\text{HIn}]} = 10,$ we have

$$K_a = [H^+] \times 10 \Rightarrow [H^+] = \frac{1 \times 10^{-5}}{10} = 10^{-6}$$

or pH = 6

When $\frac{[\text{In}]}{[\text{HIn}]} = \frac{1}{10},$ we have

$$K_a = [H^+] \times \frac{1}{10} \Rightarrow [H^+] = 1 \times 10^{-5} \times 10 = 10^{-4}$$

or pH = 4

Therefore minimum change in $\text{pH} = 6 - 4 = 2$

75. Solid $AgNO_3$ is added to a solution which is 0.1 M in Cl^- and 0.1 M in CrO_4^{2-}. K_{sp} values for AgCl and Ag_2CrO_4 are 1.7×10^{-10} and 1.9×10^{-12}, respectively. The concentration of Cl^- when Ag_2CrO_4 starts precipitating will be

(A) 3.9×10^{-5} M (B) 2.9×10^{-5} M (C) 3.9×10^{-3} M (D) 1.9×10^{-2} M

Solution

(A) Since $K_{sp}(\text{AgCl}) = [Ag^+][Cl^-]$

To precipitate AgCl, $[Ag^+] = \sqrt{\frac{1.7 \times 10^{-10}}{0.1}} = 4.12 \times 10^{-5}\text{M}$

Since $K_{sp}(Ag_2CrO_4) = [Ag^-]^2[CrO_2^{2-}]$

To precipitate Ag_2CrO_4, $[Ag^+] = \sqrt{\frac{1.9 \times 10^{-12}}{0.1}} = 4.34 \times 10^{-6}\text{M}$

Since $[Ag^+]$ required to precipitate AgCl is less than that required to precipitateAg_2CrO_4, AgCl will precipitate first. Nowm since $[Ag^+] = 4.34 \times 10^{-6}$ when Ag_2CrO_4 starts precipitating, $[Cl^-]$ at this stage can be calculated as $K_{sp}[\text{AgCl}] = [Ag^+][Cr^-]$

or $1.7 \times 10^{-10} = (4.34 \times 10^{-6})[Cl^-] \Rightarrow [Cl^-] = 3.9 \times 10^{-5}$ M

Multiple Correct Choice Type

1. Correct options for the following reaction is $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

(A) $K_{a(NH_4^+)} + K_{b(NH_3)} = 10^{-14}$ (B) $K_{a(NH_4^+)} \times K_{b(NH_3)} = \frac{1}{K_w}$

(C) $K_{a(NH_4^+)} \times K_{b(NH_3)} = K_w$ (D) $pK_{a(NH_4^+)} + pK_{b(NH_3)} = 14$

Solution

(C, D) For weak acids and weak bases $K_a \times K_b = K_w$ of $pK_a + pK_b = pK_w$.

2. The ionization constant of acetic acid is 1.74×10^{-5} [Given log 9.3 = 0.97]. The correct options are

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(A) The degree of dissociation of acetic acid in its 0.05 M solution is 1.86×10^{-2}.
(B) The concentration of acetate ion in the solution is 9.3×10^{-4} mol L^{-1}.
(C) pH of acetate ion in the solution is 3.03.
(D) pH of acetate ion in the solution is 5.12.

Solution

(A, B, C) $K_a\ (CH_3COOH) = 1.74 \times 10^{-5}$. If α is the degree of ionization of the acid and C its concentration in the solution, then for equilibrium state, we can write

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$
$$C(1-\alpha) \qquad C\alpha \qquad C\alpha$$

We have $K_a = \dfrac{C\alpha \times C\alpha}{C(1-\alpha)} = \dfrac{C\alpha^2}{(1-\alpha)}$. Substituting values, we get

$$1.74 \times 10^{-5} = \frac{0.05 \times \alpha^{-5}}{(1-\alpha)} = 0.05\,\alpha^2 \quad (\alpha \ll 1)$$

Solving, we get $\alpha = \sqrt{\dfrac{1.74 \times 10^{-5}}{0.05}} = 1.86 \times 10^{-2}$.

$[CH_3COO^-] = [H^+] = C\alpha = 0.05 \times 1.86 \times 10^{-2}\ \text{mol}\,L^{-1} = 9.3 \times 10^{-4}\ \text{mol}\,L^{-1}$

Therefore, $pH = -\log(9.3 \times 10^{-4}) = 3.03$.

3. A 1 L solution of pH = 1 diluted up to 10 times. What volume of a solution with pH = 2 is to be added in diluted solution so that pH does not change

(A) 1 L (B) 10 L (C) 100 L (D) 25 L

Solution

(A, B, C, D) After dilution $[H^+] = 10^{-2}$ or $pH = 2$

Let V liter solution of pH = 2 is added in original solution so that pH remains fixed.

Therefore, $$[H^+] = \frac{10^{-2}x + V \times 10^{-2}}{X + V} = 10^{-2}$$

This result is independent of volume taken.

4. When HCl(g) is passed through a saturated solution of common salt, pure NaCl is precipitated because

(A) HCl is highly soluble in water.
(B) The ionic product $[Na^+]\,[Cl^-]$ exceeds its solubility product (K_{sp})
(C) The K_{sp} of NaCl is lowered by the presence of Cl^- ions
(D) HCl causes precipitation.

Solution

(B, D)

5. Identify the correct statement(s)

(A) The solubility of HCN exceeds the square root of its K_{sp}.
(B) When 1 mol of HCl is reacted with 1 mol of aniline in aqueous solution, the resulting solution has a pH of 7.
(C) Titration curves for the titration of 0.1 M oxalic acid with 0.1 M NaOH and 0.2 M oxalic acid with 0.2 M NaOH both pass through the same pH at the first equivalence point.

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(D) A solution prepared by dissolving 0.1 mol of H_3PO_4 in 250 mL solution will have $[H_3PO_4]+[H_2PO_4^-]+[HPO_4^{2-}]+[PO_4^{3-}]0.4\,M$.

Solution

(A, C, D) (A) CH^- is strong conjugate base and undergoes hydrolysis so S is not equal to $\sqrt{K_{sp}}$ but more than that

(B) Weak base strong acid salt is not neutral.

(C) At fist equivalence $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$ not depend upon concentration

(D) $[H_3PO_4]_{initial} = \frac{0.1}{250} \times 1000 = 0.4\,M$. The reaction is

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \rightleftharpoons HPO_4^- + H^+ \rightleftharpoons PO_4^{3-} + H^+$$
$$0.4 - x \qquad x - y \qquad y - z$$

6. Which of the following is the correct expression of degree of dissociation for weak acid? (Assume $\alpha \ll 1$).

(A) $\sqrt{\frac{K_a}{C}}$

(B) $\sqrt{\frac{K_a \times C}{K_a}}$

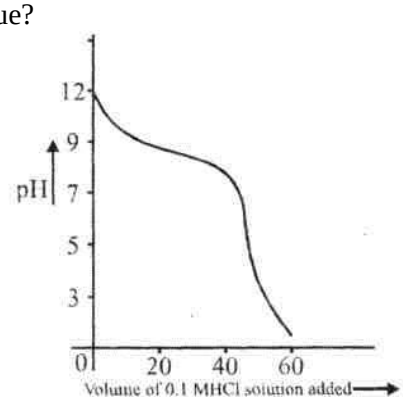
(C) $\sqrt{\frac{K_w}{K_b \text{ of conjugate base}} \times \frac{1}{C}}$

(D) $\sqrt{K_b \text{ of conjugate base} \times C}$

Solution

(A, C) $\alpha = \sqrt{\frac{K_a}{C}}$ for weak acids; and $K_a = \frac{K_w}{K_b}$

7. When weak base solution (50 mL of 0.1 N NH_4OH) is titrated with strong acid 0.1 N HCl, the pH of solution initially decreases fast and then decreases slowly till near equivalence point in the following figure. Which of the following is true?



(A) The slow decrease of pH is due to formation of an acidic buffer solution after addition of some HCl.

(B) The slope of shown pH graph will be minimum when 25 mL of 0.1 N HCl is added.

(C) The slow decrease of pH is due to formation of a basic buffer solution.

(D) The initial fast decrement in pH is due to fast consumption of free OH^- ions by HCl.

Solution

(B, C, D)

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(A) Basic buffer is formed
(B) Slope will be minimum at pH = pK_a (maximum) buffer capacity.
(C, D) Initial decrement is due to consumption of free OH^- ions, then slow decrement in pH is due to basic buffer solution and minimum slope will be there when there is best buffer action ([salt]/[base] = 1)

8. At what pH at 100°C, the solution will be basic (K_w at 100°C is 5.6×10^{-13})
(A) 7 (B) 6.125 (C) 6.9 (D) 7.1
Solution
(A, C, D) $K_w = [H_3O^+][^-OH]$

$$\text{In water, } [H_3O^+] = [^-OH] \quad K_w = [H_3O^+]^2$$

$$\log K_w = 2\log[H_3O^+]$$

$$pH = -\log[H_3O^+] = -\frac{1}{2}\log K_w = -\frac{1}{2}\log\{5.6\times10^{-13}\} = 6.1259 \text{ (for neutral solution)}$$

9. Let the color of the indicator HIn (colorless) will be visible only when its ionized form (pink) is 25% or more in a solution. Suppose HIn (pK_a = 9.0) is added to a solution of pH = 9.6 predict what will happen? (Take log 2 = 0.3)
(A) Pink color will be visible.
(B) Pink color will not be visible.
(C) Percentage of ionized form will be less than 25%.
(D) Percentage of ionized form will be more than 25%.
Solution
(B, C) For an indication

$$HIn \rightleftharpoons H^+ + In^- \qquad K_a = \frac{[H^+][In^-]}{[HIn]}$$

$$[H^+] = K_a\frac{[HIn]}{[In^-]} \Rightarrow pH = pK_a + \log\frac{[In^-]}{[HIn]}$$

Substituting values, we get $$9.6 = 9.0 + \log\frac{[In^-]}{[HIn]}$$

Hence, $$\log 4 = \log\frac{[In^-]}{[HIn]} \Rightarrow \frac{[In^-]}{[HIn]} = 4$$

So, percentage of $[In^-] = 80\%$; percentage of $[HIn] = 20\%$.

10. The pH values of 0.1 M and 0.01 MNH_4Cl are 5.128 and 5.628, respectively. Choose the correct statement(s) from the following:
(A) If dilution is the only factor, the pH should be 6.128 instead of 5.628.
(B) The given value suggests that NH_4^+ ion dissociates more in a more dilute solution.
(C) The degree of hydrolysis of NH_4^+ ion is about 1000 times less for the dilute solution.
(D) A 0.01 M solution of NH_4CI is less acidic than 0.1 M solution.
Solution
(A, B) Between 0.1 M and 0.01 M there is a dilution factor of 10. If this is the only change that happens, then the $[H^+]$ should have gone down by a factor of 10 and pH would go up by one unit, that is, 5.128–6.128. Actually, it is of 5.628 which is less and would thus correspond to a more acidic solution than expected. This means that the acid NH_4^+ ion dissociates more in a more dilute solution.

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The degree of hydrolysis for 0.1 M and 0.01 M solution can be shown to be 7.5×10^{-5} and 2.4×10^{-4}, respectively.

11. For $K_{sp}(\text{AgCl}) = 2.8 \times 10^{-10}$. Choose the correct statements.

(A) Solubility of AgCl(s) in pure water is 1.673×10^{-5} mol L^{-1}.
(B) Solubility of AgCl(s) in a solution of 0.1 M NaCl at 25°C is 2.8×10^{-9} mol L^{-1}.
(C) Solubility of AgCl(s) in pure water is 1.256×10^{-5} mol L^{-1}.
(D) Solubility of AgCl(s) in a solution of 0.1 M NaCl at 25°C is 1.4×10^{-9} mol L^{-1}.

Solution

(A, B) The reaction is

$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$

Inital	0	0
At equilibrium	x	x

$$K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})] = (x)(x) \Rightarrow 2.8 \times 10^{-10} = x^2$$

Solving, we get $x = 1.673 \times 10^{-5}$ mol L^{-1}.

NaCl(s) → Na+(aq) + Cl–(aq)
The concentrations of sodium and chloride ions are equal to the concentration of the NaCl(aq) solution.
$[Na^+(aq)]$ = 0.10 mol/L before adding AgCl(s)
$[Cl^-(aq)]$ = 0.10 mol/L before adding AgCl(s)
Now,

$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$$

Inital	0	0.1
At equilibrium	x	$x + 0.1$

$$K_{sp} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})] = (x)(x + 0.1) \Rightarrow \frac{2.8 \times 10^{-10}}{x + 0.1} = x$$

AgCl(s) has a very low solubility, so $x + 0.1 \cong 0.1$. Solving, we get $x = 2.8 \times 10^{-9}$ mol L^{-1}.

12. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with

(A) 10^{-4} M $[Ag^+]$ and 10^{-4} M $[HCl]$
(B) 10^{-3} M $[Ag^+]$ and 10^{-3} M $[Cl^-]$
(C) 10^{-6} M $[Ag^+]$ and 10^{-6} M $[Cl^-]$
(D) 10^{-2} M $[Ag^+]$ and 10^{-2} M $[Cl^-]$

Solution

(A, B, D) For A, B, D ionic product > solubility product.

13. Which of the following will suppress the ionization of phthalic acid in an aqueous solution?

(A) KCl (B) H_2SO_4 (C) HNO_3 (D) NaOH

Solution

(B, C)These being strong acids would dissociate more readily thus increasing H+ ion concentration. The ionization of phthalic acid will be suppressed due to common ion effect.

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14. Buffer solution A of a weak monoprotic acid and its sodium salt in the concentration ratio x:y has pH = $(pH)_1$. Buffer solution B of the same acid and its sodium salt in the concentration ratio y:x has pH = $(pH)_2$. If $(pH)_2 - (pH)_1 = 1$ unit and $(pH)_1 + (pH)_2 = 9.5$ units, then
(A) $pK_a = 4.75$ (b) $x/y = 2.36$ (c) $x/y = 3.162$ (d) $pK_a = 5.25$
Solution

(A, C) $(pH)_1 = pK_a + \log\left(\frac{y}{x}\right)$ and $(pH)_2 = pK_a + \log\left(\frac{x}{y}\right)$

$$(pH)_2 + (pH)_1 = \log\left(\frac{x}{y}\right) - \log\left(\frac{y}{x}\right) = 1 \text{ or } \log\left(\frac{x^2}{y^2}\right) = 1$$

$$\text{so } \frac{x^2}{y^2} = 10 \text{ or } \frac{x}{y} = 3.162$$

$$(pH)_2 + (pH)_1 = 2pK_a + \log\left(\frac{y}{x}\right) + \left(\frac{x}{y}\right) = 2pK_a = 9.5$$

$$\text{so } pK_a = \frac{9.5}{2} = 4.75$$

Assertion–Reasoning Type
Choose the correct option from the following:
(A) Statement 1 is True; Statement 2 is True; Statement 2 is a correct explanation for Statement 1.
(B) Statement 1 is True; Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1.
(C) Statement 1 is True; Statement 2 is False.
(D) Statement 1 is False, Statement 2 is True.
1. Statement 1: If equal volumes of 0.002 M solutions of sodium iodate and copper chlorate are mixed together then copper iodate will precipitate. [K_{sp} $(Cu(IO_3)_2) = 7.4 \times 10^{-8}$].
Statement 2: The ionic product in the solution relative to $Cu(IO_3)_2$ is less than the K_{sp} for copper iodate.
Solution
(D) When equal volumes of the 0.002 M solutions of sodium iodate and copper sulphate are mixed, their effective concentration in the mixture becomes 0.001 M. Thus in the solution,
[iodate ion] = $[IO_3^-]$ = 0.001 M
[copper ion] = $[Cu^{2+}]$ = 0.001 M
Then, the ionic product of Cu^{2+} and 10_3^- ions in the solution relative to $Cu(IO_3)_2$ is given by,
Ionic product in solution $= [Cu^{2+}][IO_3^-]^2 = (0.001) \times (0.001)^2 = 4 \times 10^{-9}$
But $K_{sp}(Cu(IO_3)_2) = 7.4 \times 10^{-8}$
Since the ionic product in the solution relative to $Cu(IO_3)_2$ is less than the K for copper iodate, no precipitation will occur in the solution.

2. Statement 1: Upon dilution, degree of hydrolysis of a salt increases except in case of salt of weak acid and weak base.
Statement 2: Upon dilution, K_h of a salt increases.
Solution
(C) Upon dilution, K_h of a salt decreases.

3. Statement 1: Weak acid + Salt of this acid with a strong base will behave like a buffer.

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Statement 2: Weak base + Salt of this base with a strong acid behave like a buffer.
Solution
(B) The buffer consists of two solutes, one providing a weak Brönsted acid and the other a weak Brönsted base. Usually, the acid and base represent a conjugate pair.

4. Statement 1: Ammonium chloride is acidic in liquid ammonia solvent.
Statement 2: The strongest acid and base that can exist in self-ionizing solvent are the characteristic cation and anion, respectively.
Solution
(A) Liquid NH_3 undergoes self-ionization according to the reaction,

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

According to the solvent system concept of acid and base, the strongest acid and base that can exist in a self-ionizing solvent are the characteristic cation and anion respectively. Thus, in liquid ammonia the strongest acid is NH_4^+ and the strongest base is NH_2^-.
Thus, all ammonium salts act as acids, and amides act as bases in liquid NH_3.

5. Statement 1: The solubilities of AgCl in water (S_1), 0.01 M (S_2) $CaCl_2$, 0.01 M (S_3) NaCl are $S_1 > S_2 > S_3$.
Statement 2: Solubility decreases with increasing common ion concentration.
Solution
(A)

6. Statement 1: pH of buffer changes with temperature.
Statement 2: Ionic product of water (K_w) changes with temperature.
Solution
(A)

7. Statement 1: A solution of 2:1 molar ratio of CH_3COONa and HCl results an acidic buffer.
Statement 2: An acidic buffer is a mixture of weak acid and its salt with strong base.
Solution
(A)

8. Statement 1: The addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution, will first precipitate AgBr rather than AgCl.
Statement 2: The value of K_{sp} of AgCl < K_{sp} of AgBr.
Solution
(C) The value of K_{sp} of AgCl > K_{sp} of AgBr, that is why AgCl is more soluble.
Comprehension Type
Read the paragraphs and answer the questions that follow.
Paragraph I
A buffer solution is resistant to change of pH on the addition of a small amount of acid or base. These solutions usually consist of a mixture of a weak acid and salt of its conjugate base, for example, acidic buffers such as CH_3COOH and CH_3COONa or mixture of a weak base and salt of its conjugate acid, for example, basic buffers such as NH_4OH and NH_4Cl. A salt of a weak acid and a weak base like CH_3COONH_4 also has a buffering action. The pH of an acidic buffer and basic buffer is expressed by Henderson–Hasselbach equations as

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$$\text{pH} = \text{p}K_a + \log\frac{\text{conjugate base}}{\text{weak acid}}$$

$$\text{pOH} = \text{p}K_b + \log\frac{\text{conjugate base}}{\text{weak acid}}$$

But limitations of the above equations is that these equations are applicable for buffer solutions that fit the following criteria

(a) The ratio of [conjugate base] to [weak acid] has a value between 0.1 and 10.

(b) Both [conjugate base] and [weak acid] > K_a by a factor of 100 or more.

The resistance to the change in pH on the addition of an acid or alkali is called buffer action and is measured by buffer index (BI)

$$\text{BI} = \frac{\text{Moles of base added to 1 L buffer solution}}{\text{Change in pH}}$$

BI is maximum when the acid and the salt are present in equal concentrations.

1. The acetate–acetic acid buffer is suitable in the pH (assume K_b of CH_3COO^- = 10^{-9})

(A) 8–10 (B) 4–6 (C) 5–7 (D) 5.5–7.5

Solution

(B) A solution of sodium acetate and acetic acid acts as a buffer solution around pH = 4.75.

2. A solution of pH = 6 will be maintained by acidic buffer. Below are the few options given to a chemist. Which option will the chemist choose?

(A) HA (0.1 M), NaA (1 M) K_b of A^- = 10^{-9}

(B) HB (0.01 M), NaB (1 M) K_b of B^- = 10^{-10}

(C) HC (1 M), NaX (0.01 M) K_b of X^- = 10^{-6}

(D) Any one of the above

Solution

(A) As $[H^+]$ ion concentration does not changes

3. pH of a mixture is 1 M benzoic acid (pK_a = 4.20) and 1 M C_6H_5COONa is 4.5. What is the volume of benzoic acid required to prepare a 300 mL buffer [log 2 = 0.3]?

(A) 200 mL (B) 150 mL (C) 100 mL (D) 50 mL

Solution

(C) $\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]} \Rightarrow 4.5 = 4.20 + \log\frac{[\text{salt}]}{[\text{acid}]}$

$$\text{Antilog}\,0.3 = \frac{[\text{salt}]}{[\text{acid}]} \Rightarrow \frac{\text{Moles of salt}}{\text{Moles of acid}} = 2$$

Now, $\frac{(1/1000)\times 300}{(1/1000)\times V} = 2 \Rightarrow V = 150\,\text{mL}$

Paragraph II

A solution of weak acid HA was titrated with base NaOH. The equivalence point was reached when 20 mL of 0.1 M NaOH has been added. K_a of HA = 10^{-5}.

4. pH when 10 mL of 0.1 M HCl is added in the titrated solution:

(A) 3 (B) 7 (C) 5 (D) 10

Solution

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(C) At the equivalence pH = 7 on adding HCl, pH decreases to 5.

5. pH of the solution obtained by mixing 10 mL 0.2 M NaOH and 10 mL of 0.2 M HA.
(A) 7 (B) 9 (C) 11 (D) 5
Solution
(B)
For titration of weak acid with strong base,

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

	NaOH	+ HA	$\rightleftharpoons$ NaA	+ H_2O
Initial	0.2×10	0.2×10	0	0
After hydrolysis	0	0	2	2

So $[\text{NaA}] = \frac{0.2}{20} = 0.1\text{M}$

and given that $\text{p}K_\text{a} = 5$.

The pH of the solution will be determined by hydrolysis of salt of strong base and weak acid and is given by

$$\text{pH} = \frac{1}{2}\left[\text{p}K_\text{w} + \text{p}K_\text{a} + \log C\right] = \frac{1}{2}\ [14+5-1] = 9$$

6. 18.25 g of HCl, 41 g of CH_3COONa, and 30 g of CH_3COOH are mixed in a container and volume made up to 10 L. Final pH of solution is [K_a of CH_3COOH at 25°C = 1.8×10^{-5}]
(A) 2.37 (B) 1.3 (C) 0.3 (D) 2.87
Solution
(D) Given that [Acetic acid] = 0.5 M, [Acetate ion]= 0.5 M. Addition of 0. 5 M of HCl to this buffer will lead to the following changes:

	$HCl + CH_3COONa$	$\rightleftharpoons$	CH_3COOH	$+ NaCl$
Initial	0.5	0.5	0.5	0
After hydrolysis	0	0	1.0	0.5

The concentration of the salt in the solution is 0.5/10 = 0.05M. Therefore,

$$\text{pH} = 7 + \frac{1}{2}\text{p}K_\text{a} + \frac{1}{2}\log C = 7 + \frac{1}{2}[-\log(1.8\times10^{-5})] + \frac{1}{2}\log(0.05)$$

$$= 7 - \frac{1}{2}(4.7448 - 1.3010) = 7 - 1.7219 = 5.27$$

Paragraph III

K_sp of $\text{CdS} = 8\times10^{-27}$, K_sp of $\text{ZnS} = 1\times10^{-21}$, K_a of $\text{H}_2\text{S} = 1\times10^{-21}$

7. Which metal sulphide is precipitated first when H_2S is added?
(A) ZnS (B) CdS (C) Both at same time (D) Both do not form ppt.
Solution
(B)

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For ZnS: $K_{sp} = [Zn^{2+}][S^{2-}] = 1\times10^{-21}$

For CdS: $K_{sp} = [Cd^{2+}][S^{2-}] = 8\times10^{-27}$

For the same concentration of sulphide ions, cadmium ions require lower concentration of sulphide ions for precipitation; hence CdS will precipitate first.

8. What $[H^+]$ must be maintained in a saturated HS (0.1 M) to precipitate CdS but not ZnS, if $[Cd^{+2}]$ = $[Zn^{+2}]$ = 0.1 M initially

(A) >0.1 M (B) >0.01 M (C) >0.2 M (D) >0.02 M

Solution

(A) $[H^+]$ must be greater than $[Cd^{+2}]$.

9. When ZnS starts precipitating, what is the concentration of Cd^{2+} is left?

(A) 8×10^{-7} (B) 0.1 (C) 4×10^{-10} (D) 2×10^{-9}

Solution

(A) ZnS starts precipitating when concentration of sulphide ion concentration reaches

$$[S^{2-}] = \frac{1\times10^{-21}}{[Zn^{2+}]}$$

The concentration of Cd^{2+} remaining when ZnS starts to precipitate is

$$= \frac{K_{sp}\text{CdS}}{\text{sulphide concentration at which ZnS precipitates}}$$

$$= \frac{8\times10^{-27}}{1\times10^{-21}} \times [Zn^{2+}]$$

$$= 8\times10^{-7}$$

Paragraph IV

The degree of dissociation of weak electrolyte is inversely proportional to the square root of concentration. It is called Ostwald dilution law

$$\alpha = \sqrt{\frac{K_a}{C}}$$

As the temperature increases degree of dissociation will increase.

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} \text{ if concentration is same}$$

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{C_2}{C_1}} \text{ if acid is same}$$

10. 0.01 M CH_3COOH has 4.24% degree of dissociation. The degree of dissociation of 0.1 M CH_3COOH will be

(A) 1.33% (B) 4.24% (C) 5.24% (D) 0.33%

Solution

(A) $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{C_2}{C_1}} \Rightarrow (\alpha_2)^2 = \frac{C_1(\alpha_1)^2}{C_2} = \frac{0.01\times(0.0424)\times(0.0424)}{0.1}$

Solving, we get α_2 = 0.0134 or 1.34%.

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11. pH of 0.005 M HCOOH $[K_a = 2\times10^{-4}]$ is equal to

(A) 3 (B) 2 (C) 4 (D) 5

Solution

(A) $[H^+] = \sqrt{K_a \times C} = \sqrt{2\times10^{-4}\times0.005} = 10^{-3}$ M. So, pH = 3.

12. Which of the following is strongest acidic solution?

(A) pH = 1 (B) pH = 2 (C) pH = 3 (D) pH = 4

Solution

(A) Less is pH, stronger is the acid.

13. α_1 and α_2 are in ratio of 1:2 where $K_{a_1} = 2\times10^{-4}$. What will be the value of K_{a_2}

(A) 8×10^{-4} (B) 2×10^{-4} (C) 4×10^{-4} (D) 1×10^{-4}

Solution

(A) $\dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}} \Rightarrow K_{a_2} = 4\times2\times10^{-4} = 8\times10^{-4}$.

Integer Answer Type

1. What will be pH of the resulting solution obtained by mixing 10 mL of 0.1 N HCl and 990 mL solution o NaCl?

Solution

(3) $[HCl] = \dfrac{10\times0.1}{10+990} = \dfrac{1}{1000} = 10^{-3}$. So, pH = 3

2. The pH of an aqueous solution of a sparingly soluble metal hydroxide $M(OH)_2$ with $[M^{2+}]$ = 0.05 M and solubility product 5×10^{-16} mol^3 dm^{-9} at 298 K is ____.

Solution

(7) $K_{sp} = [M^{2+}][OH^-]^2 = [0.05]\times[OH^-]^2 = 5\times10^{-16}$

$[OH^-] = (5\times10^{-14}\ M)^{1/2} = 10^{-7}$

$pOH = -\log[OH^-] = 7$

$pH = 14 - 7 = 7$

3. What will be the pH of 1 L of a buffer solution containing 0.01 M NH_4Cl and 0.01 M NH_4OH having pK_b = 5?

Solution

(9) $pOH = pK_b + \log\dfrac{[NH_4Cl]}{[NH_4OH]}$

$5 + \log\dfrac{0.01}{0.01} = 5$

$pH = 14 - pOH = 14 - 5 = 9$

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4. For the reaction involving oxidation of ammonia by oxygen to form nitric oxide and water vapor, the equilibrium constant has the units $(\text{bar})^n$. Then n is ____.

Solution

(1)

$$2NH_3 + \tfrac{5}{2}O_2 \rightarrow 2NO + 3H_2O$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$K = \frac{(\text{bar})^4(\text{bar})^6}{(\text{bar})^4(\text{bar})^5} = (\text{bar})^1 \Rightarrow n = 1$$

5. What will be pH of the solution of the salt of weak acid and weak base? ($K_b = 1 \times 10^{-6}$ and $K_a = 1 \times 10^{-4}$).

Solution

(6) $\text{pH} = \frac{1}{2}\left(14 + \text{p}K_a - \text{p}K_b\right)$

$$\frac{1}{2}(14 + 4 - 6) = 6$$

Matrix–Match Type

1. K_1 and K_2 are first and second ionization constant of H_2CrO_4. K_3 is dissociation constant for NH_3. Match the following:

Column I	**Column II**
(A) 0.1 M H_2CrO_4	(p) $\text{pH} = 7 + \frac{1}{2}\text{p}K_2 - \frac{1}{2}\text{p}K_3$
(B) 0.1 M $KHCrO_4$	(q) $\text{pH} = 7 + \frac{1}{2}\text{p}K_2 + \frac{1}{2}\log C$
(C) 0.1 M $(NH_4)_2CrO_4$	(r) $\text{pH} = \frac{1}{2}\text{p}K_1 - \frac{1}{2}\log C$
(D) 0.1 M K_2CrO_4	(s) $\text{pH} = \frac{1}{2}\left(\text{p}K_1 + \text{p}K_2\right)$

Solution

(A) → (r); (B) → (s); (C) → (p); (D) → (q)

(A) Diprotic weak acid, H^+ only comes from first ionization (K_1).

(B) $HCrO_4$ is amphiprotic anion.

(C) $(NH_4)_2$ it is salt of weak base and weak acid.

(D) Hydrolysis of CrO_4^{2-} (polyvalent anion), but only first hydrolysis is appreciable.

2. Match the salt with the pH expression

Column I	**Column II**
(A) Salt of strong acid and strong base	(p) $\frac{1}{2}\left[\text{p}K_w + \text{p}K_a - \text{p}K_b\right]$
(B) Salts of weak acid and strong base	(q) $\frac{1}{2}\left[\text{p}K_w + \text{p}K_a - \log C\right]$

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(C) Salt of weak base and strong acid	(r) $\frac{1}{2}\left[\mathrm{p}K_{\mathrm{w}} - \mathrm{p}K_{\mathrm{b}} - \log C\right]$
(D) Salt of weak acid and weak base	(s) $\frac{1}{2}\mathrm{p}K_{\mathrm{w}}$

Solution

(A) → (s); (B) → (q); (C) → (r); (D) → (p)

3. Match the substance with degree of hydrolysis

Column I	**Column II**
(A) NH_4Cl	(p) No hydrolysis
(B) NaCl	(q) $h = \sqrt{\frac{K_{\mathrm{h}}}{C}}$
(C) CH_3COONa	(r) $h = \sqrt{\frac{K_{\mathrm{w}}}{CK_{\mathrm{b}}}}$
(D) CH_3COONH_4	(s) $h = K_{\mathrm{h}}$ (t) $\mathrm{pH} < 7$ at $25°\mathrm{C}$

Solution

(A) → (q), (r), (t); (B) → (p); (C) → (q); (D) → (s)

NH_4Cl which is a salt of a strong acid (HCl) and a weak base (NH_4OH). It undergoes complete dissociation in aqueous medium. The hydrolysis constant is $K_{\mathrm{h}} = K_{\mathrm{w}}/K_{\mathrm{b}}$, and so $h = \sqrt{\frac{K_{\mathrm{h}}}{C}} = \sqrt{\frac{K_{\mathrm{w}}}{CK_{\mathrm{b}}}}$

The salt is acidic so $\mathrm{pH} < 7$ at $25°\mathrm{C}$.

NaCl is salt of strong acid and strong base, so it does not undergo hydrolysis.

CH_3COONa which is a salt of weak acid (CH_3COOH) and a strong base (NaOH). It undergoes complete dissociation in aqueous solution. The degree of hydrolysis is $h = \sqrt{\frac{K_{\mathrm{h}}}{C}} = \sqrt{\frac{K_{\mathrm{w}}}{K_{\mathrm{a}}C}}$

CH_3COONH_4 is a salt of a weak acid (CH_3COOH) and a weak base (NH_4OH). The salt will be partially dissociated in aqueous medium. The degree of hydrolysis is $h = \sqrt{\frac{K_{\mathrm{w}}}{K_{\mathrm{a}} \times K_b}} = K_{\mathrm{h}}$.

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