Question 7.61:

The ionization constant of nitrous acid is 4.5 × 10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

Answer 7.61:

$NaNO_2$ is the salt of a strong base (NaOH) and a weak acid (HNO_2).

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

$$K_h = \frac{[HNO_2]\left[OH^-\right]}{\left[NO_2^-\right]}$$

$$\Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5\times10^{-4}} = .22\times10^{-10}$$

Now, If x moles of the salt undergo hydrolysis, then the concentration of various species present in the solution will be:

$$\left[NO_2^-\right] = .04 - x\ ;\ 0.04$$

$$\left[HNO_2\right] = x$$

$$\left[OH^-\right] = x$$

$$K_h = \frac{x^2}{0.04} = 0.22\times10^{-10}$$

$$x^2 = .0088\times10^{-10}$$

$$x = .093\times10^{-5}$$

$$\therefore \left[OH^-\right] = 0.093\times10^{-5}\ M$$

$$\left[H_3O^+\right] = \frac{10^{-14}}{.093\times10^{-5}} = 10.75\times10^{-9}\ M$$

$$\Rightarrow pH = -\log\left(10.75\times10^{-9}\right)$$

$$= 7.96$$

Therefore, degree of hydrolysis

$$= \frac{x}{0.04} = \frac{.093\times10^{-5}}{.04}$$

$$= 2.325 \times 10^{-5}$$

Question 7.62:

A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine

Answer 7.62:

pH = 3.44

We know that,
pH = – log [H⁺]

$$\therefore \left[\mathrm{H}^{+}\right] = 3.63\times10^{-4}$$

$$\text{Then, } K_h = \frac{\left(3.63\times10^{-4}\right)^2}{0.02} \qquad (\because \text{concentration} = 0.02\ \mathrm{M})$$

$$\Rightarrow K_h = 6.6\times10^{-6}$$

$$\text{Now, } K_h = \frac{K_w}{K_a}$$

$$\Rightarrow K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{6.6\times10^{-6}}$$

$$= 1.51\times10^{-9}$$

Question 7.63:

Predict if the solutions of the following salts are neutral, acidic or basic:

NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF

Answer 7.63:

(i) NaCl:

$$\underset{}{\mathrm{NaCl}} + \mathrm{H_2O} \longleftrightarrow \underset{\text{Strong base}}{\mathrm{NaOH}} + \underset{\text{Strong acid}}{\mathrm{HCl}}$$

Therefore, it is a neutral solution.

(ii) KBr:

$$\mathrm{KBr} + \mathrm{H_2O} \longleftrightarrow \underset{\text{Strong base}}{\mathrm{KOH}} + \underset{\text{Strong acid}}{\mathrm{HBr}}$$

Therefore, it is a neutral solution.

(iii) NaCN:

$$NaCN + H_2O \longleftrightarrow \underset{\text{Weak acid}}{HCN} + \underset{\text{Strong base}}{NaOH}$$

Therefore, it is a basic solution.

(iv) NH_4NO_3

$$NH_4NO_3 + H_2O \longleftrightarrow \underset{\text{Weak base}}{NH_4OH} + \underset{\text{Strong acid}}{HNO_3}$$

Therefore, it is an acidic solution.

(v) $NaNO_2$

$$NaNO_2 + H_2O \longleftrightarrow \underset{\text{Strong base}}{NaOH} + \underset{\text{Weak acid}}{HNO_2}$$

Therefore, it is a basic solution.

(vi) KF

$$KF + H_2O \longleftrightarrow \underset{\text{Strong base}}{KOH} + \underset{\text{Weak acid}}{HF}$$

Therefore, it is a basic solution.

Question 7.64:

The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1M acid and its 0.1M sodium salt solution?

Answer 7.64:

It is given that K_a for $ClCH_2COOH$ is 1.35×10^{-3}.

$$\Rightarrow K_a = c\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K_a}{c}}$$

$$= \sqrt{\frac{1.35\times10^{-3}}{0.1}} \qquad (\therefore \text{ concentration of acid } = 0.1\text{m})$$

$$\alpha = \sqrt{1.35\times10^{-2}}$$

$$= 0.116$$

$$\therefore \left[\text{H}^+\right] = c\alpha = 0.1\times0.116$$

$$= .0116$$

$$\Rightarrow \text{pH} = -\log\left[\text{H}^+\right] = 1.94$$

$ClCH_2COONa$ is the salt of a weak acid i.e., $ClCH_2COOH$ and a strong base i.e., NaOH.

$$\text{ClCH}_2\text{COO}^- + \text{H}_2\text{O} \longleftrightarrow \text{ClCH}_2\text{COOH} + \text{OH}^-$$

$$K_h = \frac{[\text{ClCH}_2\text{COOH}][\text{OH}^-]}{[\text{ClCH}_2\text{COO}^-]}$$

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

$$K_h = \frac{10^{-14}}{1.35\times10^{-3}}$$

$$= 0.740\times10^{-11}$$

$$\text{Also, } K_h = \frac{x^2}{0.1} \qquad (\text{where } x \text{ is the concentration of OH}^- \text{and ClCH}_2\text{COOH})$$

$$0.740\times10^{-11} = \frac{x^2}{0.1}$$

$$0.074\times10^{-11} = x^2$$

$$\Rightarrow x^2 = 0.74\times10^{-12}$$

$$x = 0.86\times10^{-6}$$

$$\left[\text{OH}^-\right] = 0.86\times10^{-6}$$

$$\therefore \left[\text{H}^+\right] = \frac{K_w}{0.86\times10^{-6}}$$

$$= \frac{10^{-14}}{0.86\times10^{-6}}$$

$$\left[\text{H}^+\right] = 1.162\times10^{-8}$$

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

$$= 7.94$$

Question 7.65:

Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

Answer 7.65:

Ionic product,

$$K_w = [H^+][OH^-]$$
$$\text{Let}[H^+] = x.$$
$$\text{Since}[H^+] = [OH^-], K_w = x^2.$$
$$\Rightarrow K_w \text{ at } 310\text{K is } 2.7 \times 10^{-14}.$$
$$\therefore 2.7 \times 10^{-14} = x^2$$
$$\Rightarrow x = 1.64 \times 10^{-7}$$
$$\Rightarrow [H^+] = 1.64 \times 10^{-7}$$
$$\Rightarrow pH = -\log[H^+]$$
$$= -\log[1.64 \times 10^{-7}]$$
$$= 6.78$$

Hence, the pH of neutral water is 6.78.

Question 7.66:

Calculate the pH of the resultant mixtures:

a) 10 mL of 0.2M $Ca(OH)_2$ + 25 mL of 0.1M HCl

b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $Ca(OH)_2$

c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

Answer 7.66:

(a) $\text{Moles of } H_3O^+ = \frac{25 \times 0.1}{1000} = .0025\,\text{mol}$

$$\text{Moles of OH}^- = \frac{10\times0.2\times2}{1000} = .0040\,\text{mol}$$

Thus, excess of OH^- = .0015 mol

$$\left[OH^-\right] = \frac{.0015}{35\times10^{-3}}\,\text{mol/L} = .0428$$
$$pOH = -\log[OH]$$
$$= 1.36$$
$$pH = 14 - 1.36$$
$$= 12.63 \qquad (\text{not matched})$$

(b) $$\text{Moles of H}_3\text{O}^+ = \frac{2\times10\times0.01}{1000} = .0002\,\text{mol}$$

$$\text{Moles of OH}^- = \frac{2\times10\times.01}{1000} = .0002\,\text{mol}$$

Since there is neither an excess of H_3O^+ or OH^-

(c) $$\text{Moles of H}_3\text{O}^+ = \frac{2\times10\times0.1}{1000} = .002\,\text{mol}$$

$$\text{Moles of OH}^- = \frac{10\times0.1}{1000} = 0.001\,\text{mol}$$

Excess of H_3O^+ = .001 mol

$$\text{Thus, } \left[H_3O^+\right] = \frac{.001}{20\times10^{-3}} = \frac{10^{-3}}{20\times10^{-3}} = .05$$
$$\therefore\ pH = -\log(0.05)$$

= 1.30

The solution is neutral. Hence, pH = 7.

Question 7.67:

Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9 (page 221). Determine also the molarities of individual ions.

Answer 7.67:

(1) Silver chromate:

$Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^{2-}$

Then,

$K_{sp} = \left[Ag^+\right]^2\left[CrO_4^{2-}\right]$

Let the solubility of Ag_2CrO_4 be s.

$\Rightarrow \left[Ag^+\right]2s \text{ and} \left[CrO_4^{2-}\right] = s$

Then,

$K_{sp} = (2s)^2 . s = 4s^3$

$\Rightarrow 1.1 \times 10^{-12} = 4s^3$

$.275 \times 10^{-12} = s^3$

$s = 0.65 \times 10^{-4}$ M

Molarity of Ag^+ = 2s = 2 × 0.65 × 10^{-4} = 1.30 × 10^{-4} M

Molarity of CrO_4^{2-} = s = 0.65 × 10^{-4} M

(2) Barium chromate:

$BaCrO_4 \longrightarrow Ba^{2+} + CrO_4^{2-}$

$\text{Then, } K_{sp} = \left[Ba^{2+}\right]\left[CrO_4^{2-}\right]$

Let the solubility of $BaCrO_4$. be s.

So, $\left[Ba^{2+}\right]$ = s and $\left[CrO_4^{2-}\right]$ = s

$\Rightarrow K_{SP} = s^2$

$\Rightarrow 1.2 \times 10^{-10} = s^2$

$\Rightarrow s = 1.09 \times 10^{-5}$ M

Molarity of Ba^{2+} = Molarity of $CrO_4^{2-} = s = 1.09\times10^{-5}\ M$

(3) Ferric hydroxide:

$$Fe(OH)_3 \longrightarrow Fe^{2+} + 3OH^-$$

$$K_{sp} = \left[Fe^{2+}\right]\left[OH^-\right]^3$$

Let s be the solubility of $Fe(OH)_3$.

$$\text{Thus,}\left[Fe^{3+}\right] = s \text{ and } \left[OH^-\right] = 3s \qquad \Rightarrow K_{sp} = s.(3s)^3$$

$$= s.27s^3$$

$$K_{sp} = 27s^4$$

$$1.0\times10^{-38} = 27s^4$$

$$.037\times10^{-38} = s^4$$

$$.00037\times10^{-36} = s^4 \qquad \Rightarrow 1.39\times10^{-10}\ M = S$$

Molarity of $Fe^{3+} = s = 1.39\times10^{-10}\ M$

Molarity of $OH^- = 3s = 4.17\times10^{-10}\ M$

(4) Lead chloride:

$$PbCl_2 \longrightarrow Pb^{2+} + 2Cl^-$$

$$K_{SP} = \left[Pb^{2+}\right]\left[Cl^-\right]^2$$

Let K_{SP} be the solubility of $PbCl_2$.

$$\left[PB^{2+}\right] = s \text{ and } \left[Cl^-\right] = 2s$$

$$\text{Thus, } K_{sp} = s.(2s)^2$$

$$= 4s^3$$

$$\Rightarrow 1.6\times10^{-5} = 4s^3$$

$$\Rightarrow 0.4\times10^{-5} = s^3$$

$$4\times10^{-6} = s^3 \Rightarrow 1.58\times10^{-2} M = S.1$$

Molarity of $PB^{2+} = s = 1.58\times10^{-2} M$

Molarity of chloride = $2s = 3.16\times10^{-2} M$

(5) Mercurous iodide:

$$Hg_2I_2 \longrightarrow Hg^{2+} + 2I^-$$
$$K_{sp} = \left[Hg_2^{2+}\right]^2\left[I^-\right]^2$$

Let s be the solubility of Hg_2I_2.

$$\Rightarrow \left[Hg_2^{2+}\right] = s \text{ and} \left[I^-\right] = 2s$$

$$\text{Thus, } K_{sp} = s(2s)^2 \Rightarrow K_{sp} = 4s^3$$
$$4.5\times10^{-29} = 4s^3$$
$$1.125\times10^{-29} = s^3$$
$$\Rightarrow s = 2.24\times10^{-10} \text{ M}$$

Molarity of $Hg_2^{2+} = s = 2.24\times10^{-10}$ M

Molarity of $I^- = 2s = 4.48\times10^{-10}$ M

Question 7.68:

The solubility product constant of Ag_2CrO_4 and AgBr are 1.1 × 10^{-12} and 5.0 × 10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

Answer 7.68:

Let *s* be the solubility of Ag_2CrO_4.

$$\text{Then, } Ag_2CrO_4 \longleftrightarrow Ag^{2+} + 2CrO_4^-$$
$$K_{sp} = (2s)^2 .s = 4s^3$$
$$1.1\times10^{-12} = 4s^3$$
$$s = 6.5\times10^{-5} \text{ M}$$

Let *s*´ be the solubility of AgBr.

$$AgBr_{(s)} \longleftrightarrow Ag^+ + Br^-$$
$$K_{sp} = s'^2 = 5.0\times10^{-13}$$
$$\therefore s' = 7.07\times10^{-7} \text{ M}$$

Therefore, the ratio of the molarities of their saturated solution is

$$\frac{s}{s'} = \frac{6.5\times10^{-5}\text{M}}{7.07\times10^{-7}\text{M}} = 91.9.$$

Question 7.69:

Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate?

(For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

Answer 7.69:

When equal volumes of sodium iodate and cupric chlorate solutions are mixed together, then the molar concentrations of both solutions are reduced to half i.e., 0.001 M. Then,

$$\begin{array}{lllll} Na10_3 & \rightarrow & Na^+ & + & 10_3^- \\ 0.001M & & & & 0.001M \end{array}$$

$$\begin{array}{lllll} Cu(ClO_3)_2 & \rightarrow & Cu^{2+} & + & 2ClO_3^- \\ 0.001M & & & & 0.001M \end{array}$$

Now, the solubility equilibrium for copper iodate can be written as:

$$Cu(10_3)_2 \rightarrow Cu^{2+}_{(aq)} + 210^-_{3(aq)}$$

Ionic product of copper iodate:

$$= [Cu^{2+}][10_3^-]^2$$

$$= (0.001)(0.001)^2$$

$$= 1 \times 10^{-9}$$

Since the ionic product (1×10^{-9}) is less than K_{sp} (7.4×10^{-8}), precipitation will not occur.

Question 7.70:

The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

Answer 7.70:

Since pH = 3.19,

$$\left[H_3O^+\right] = 6.46 \times 10^{-4}\ M$$

$$C_6H_5COOH + H_2O \longleftrightarrow C_6H_5COO^- + H_3O$$

$$K_a \frac{\left[C_6H_5COO^-\right]\left[H_3O^+\right]}{\left[C_6H_5COOH\right]}$$

$$\frac{\left[C_6H_5COOH\right]}{\left[C_6H_5COO^-\right]} = \frac{\left[H_3O^+\right]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Let the solubility of C_6H_5COOAg be x mol/L.

Then,

$$\left[Ag^+\right] = x$$

$$\left[C_6H_5COOH\right] + \left[C_6H_5COO^-\right] = x$$

$$10\left[C_6H_5COO^-\right] + \left[C_6H_5COO^-\right] = x$$

$$\left[C_6H_5COO^-\right] = \frac{x}{11}$$

$$K_{sp}\left[Ag^+\right]\left[C_6H_5COO^-\right]$$

$$2.5 \times 10^{-13} = x\left(\frac{x}{11}\right)$$

$$x = 1.66 \times 10^{-6}\ \text{mol/L}$$

Thus, the solubility of silver benzoate in a pH 3.19 solution is 1.66×10^{-6} mol/L.

Now, let the solubility of C_6H_5COOAg be x' mol/L.

$$\text{Then, } \left[Ag^+\right] = x'M \text{ and } \left[CH_3COO^-\right] = x'M.$$

$$K_{sp} = \left[Ag^+\right]\left[CH_3COO^-\right]$$

$$K_{sp} = (x')^2$$

$$x' = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7}\ \text{mol/L}$$

$$\therefore \frac{x}{x'} = \frac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = 3.32$$

Hence, C_6H_5COOAg is approximately 3.317 times more soluble in a low pH solution.

Question 7.71:

What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, K_{sp} = 6.3 × 10^{-18}).

Answer 7.71:

Let the maximum concentration of each solution be *x* mol/L. After mixing, the volume of the concentrations of each solution will be reduced to half i.e., x/2 .

$$\therefore [FeSO_4] = [Na_2S] = \frac{x}{2}M$$

$$\text{Then, } [Fe^{2+}] = [FeSO_4] = \frac{x}{2}M$$

$$\text{Also, } [S^{2-}] = [Na_2S] = \frac{x}{2}M$$

$$FeS_{(s)} \longleftrightarrow Fe^{2+}{}_{(aq)} + S^{2-}{}_{(aq)}$$

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

$$6.3\times10^{-18} = \left(\frac{x}{2}\right)\left(\frac{x}{2}\right)$$

$$\frac{x^2}{4} = 6.3\times10^{-18}$$

$$\Rightarrow x = 5.02\times10^{-9}$$

If the concentrations of both solutions are equal to or less than 5.02 × 10^{-9} M, then there will be no precipitation of iron sulphide.

Question 7.72:

What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is 9.1 × 10^{-6}).

Answer 7.72:

$$CaSO_{4(s)} \longleftrightarrow Ca^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

Let the solubility of $CaSO_4$ be *s*.

$\text{Then, } K_{sp} = s^2$

$9.1 \times 10^{-6} = s^2$

$s = 3.02 \times 10^{-3} \text{ mol/L}$

Molecular mass of $CaSO_4$ = 136 g/mol

Solubility of $CaSO_4$ in gram/L

= 3.02 × 10^{-3} × 136

= 0.41 g/L

This means that we need 1L of water to dissolve 0.41g of $CaSO_4$

Therefore, to dissolve 1g of $CaSO_4$ we require $= \frac{1}{0.41} \text{L} = 2.44 \text{L}$ of water.

Question 7.73:

The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is 1.0 × 10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions precipitation will take place?

Given K_{sp} for $FeS = 6.3 \times 10^{-18}$, $MnS = 2.5 \times 10^{-13}$, $ZnS = 1.6 \times 10^{-24}$, $CdS = 8.0 \times 10^{-27}$

Answer 7.73:

For precipitation to take place, it is required that the calculated ionic product exceeds the K_{sp} value.

Before mixing:

$\left[S^{2-}\right] = 1.0 \times 10^{-19} \text{ M} \quad \left[M^{2+}\right] = 0.04\text{M}$

$\text{volume} = 10 \text{ mL} \qquad \text{volume} = 5 \text{ mL}$

After mixing:

$$\left[S^{2-}\right]=? \qquad \left[M^{2+}\right]=?$$

$$\text{volume}=(10+5)=15\text{ mL} \qquad \text{volume}=15\text{ mL}$$

$$\left[S^{2-}\right]=\frac{1.0\times10^{-19}\times10}{15}=6.67\times10^{-20}\text{ M}$$

$$\left[M^{2+}\right]=\frac{0.04\times5}{15}=1.33\times10^{-2}\text{ M}$$

$$\begin{aligned}\text{Ionic product} &= \left[M^{2+}\right]\left[S^{2-}\right]\\ &=\left(1.33\times10^{-2}\right)\left(6.67\times10^{-20}\right)\\ &=8.87\times10^{-22}\end{aligned}$$

This ionic product exceeds the K_{sp} of Zns and CdS. Therefore, precipitation will occur in $CdCl_2$ and $ZnCl_2$ solutions.