IONIC EQUILIBRIUM

PROBLEM 391 Addition of 100 mL 0.1 M HCl to certain volume of a slightly weak monobasic (0.1 M) acid solution decreases its pH from 2.0 to 1.7. Determine ionization constant of the weak acid and its volume.

PROBLEM 392 Calculate pH of 0.02 M succinnic acid solution taking into account both ionization. $K_{a_1} = 7 \times 10^{-5}, K_{a_2} = 3 \times 10^{-6}$.

PROBLEM 393 K_a of formic acid at 27°C is 1.7×10^{-4}. What will be the pH of a 0.1 M aqueous solution of formic acid at 47°C. Standard enthalpy of neutralization of formic acid and HCl versus NaOH are -42 kJ and -57 kJ respectively.

PROBLEM 394 Determine exact pD of a 10^{-7} M DCl solution is D_2O. Ionic product of D_2O is 1.35×10^{-15}.

PROBLEM 395 Calcium hypochlorite $[Ca(OCl)_2]$ is used as a disinfectant for swimming pools. The recommended pH of a swimming pool is 7.8. Calculate the percentage of HClO and ClO^- in the swimming pool. K_a for HOCl is 3×10^{-8}.

PROBLEM 396 In the vapour phase acetic acid molecule associate to the some extent to form dimmers. At 50°C, the pressure of a certain acetic acid vapour is 0.0342 atm in a 360 mL flask. The vapour is condensed and neutralized with 13.8 mL 0.0568 M NaOH. Calculate the degree of dissociation of the dimmer.

PROBLEM 397 Henery's law constant for CO_2 at 38°C is 2.28×10^{-3} mol/L. Determine pH of a solution of CO_2 at 38°C in equilibrium with the gas at a partial pressure of 3.2.
For $CO_2 : K_1 = 4.2 \times 10^{-7}, K_2 = 4.8 \times 10^{-11}$.

PROBLEM 398 Determine pH of a 5% aqueous solution of NaOCl (by weight). Density of the solution is 1.0 g/cc. $K_a = 3 \times 10^{-8}$.

PROBLEM 399 An ammonia-ammonium chloride buffer has a pH value of 9 with $[NH_3] = 0.25$. By how much the pH will change if 75 mL of 0.1 M KOH be added to 200 mL buffer solution. $K_b = 2 \times 10^{-5}$.

PROBLEM 400 A solution is prepared by dissolving 15 g of acetic acid and 25 g sodium acetate in 750 mL of water.

(a) What is the pH of this solution?
(b) What would the pH of the solution be after 25.00 mL 0.25 M NaOH is added?
(c) What would be the pH is 25 mL 0.4 M HCl is added into (b)?
$K_a = 2 \times 10^{-5}$.

PROBLEM 401 Determine freezing point of a 0.5 M solution of dichloroacetic acid ($K_a = 0.05$). Assume density of the solution to be 1 g/cc and K_f for water $= 1.86$.

PROBLEM 402 pK_w of heavy water at 20°C and 30°C are 15.05 and 14.7 respectively. Determine pD of a pure heavy water at 50°C.

PROBLEM 403 Suppose that two hydroxides MOH and $M'(\text{OH})_2$, both have $K_{sp} = 10^{-12}$ and that initially both cations are present in a solution at concentrations of 0.001 M. Which hydroxide precipitate first and at what pH when a NaOH solution is added dropwise?

PROBLEM 404 Determine molar solubility of Fe(OH)_2 at $\text{pH} - 8$ and at $\text{pH} = 6$. $K_{sp} = 1.6 \times 10^{-14}$.

PROBLEM 405 Determine solubility of CaF_2 ($K_{sp} = 4 \times 10^{-11}$)

(a) at pH = 7, (b) at pH = 5. $K_a = 3.45 \times 10^{-4}$.

PROBLEM 406 Determine the molar solubility of BaF_2 ($K_{sp} = 1.7 \times 10^{-6}$) at

(a) pH = 7, (b) pH = 4.

PROBLEM 407 When 10 mg sodium barbiturate are dissolved in 250 mL of water to form a solution, the resulting pH was found to be 7.71. The molar mass of the salt is 150. Determine percentage protonation of barbiturate ion and K_a of the acid.

PROBLEM 408 Determine pH of a 0.024 M hydroxyl amine hydrochloride solution. K_b of hydroxyl amine $= 10^{-8}$.

PROBLEM 409 A 25 mL 0.2 M oxalic acid is titrated with 0.2 M NaOH solution. Determine pH at the first and second equivalence point. $K_{a_1} = 6 \times 10^{-2}$ and $K_{a_2} = 6.5 \times 10^{-5}$.

PROBLEM 410 Determine molar solubility of ZnS ($K_{sp} = 1.6 \times 10^{-24}$) in a saturated solution of H_2S (0.1 M) buffered at pH = 7. What would be the solubility in a saturated H_2S solution buffered at pH = 10. For H_2S $K_1 = 10^{-7}$ and $K_2 = 10^{-14}$.

PROBLEM 411 Determine simultaneous solubility of Ag_2CO_3 and Ag_2CrO_4. $K_{sp}(\text{Ag}_2\text{CO}_3) = 8.1 \times 10^{-12}$ and $K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.2 \times 10^{-12}$.

PROBLEM 412 To a certain volume of a weak monobasic acid, when 20 mL of NaOH solution is added, pH of the resulting solution was found to be 3.7 whereas when 30 mL of the same NaOH is added to the same volume of the acid from same stock, pH was found to be 4.18. Determine K_a of the acid.

PROBLEM 413 Determine mass of sodium dihydrogen phosphate and volume of 1.5 M HCl solution required for preparation of a 100 mL buffer solution of pH 2.42 with concentration of H_2PO_4^- be 0.15 M. $K_1 = 7.6 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$ and $K_3 = 2 \times 10^{-13}$.

PROBLEM 414 Carbondioxide gas from a steel cylinder is bubbled for some time through pure water placed in a jar. When the supply of gas is terminated, pH of the solution was found to be 3.83. What is the pressure of gas in the cylinder if Henery's constant of CO_2 is 2.3×10^{-2}. For CO_2, $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$.

PROBLEM 415 Determine pH of a 0.1 M $Fe(NO_3)_2$ solution. Given

$$Fe(OH)_2 \rightleftharpoons Fe(OH)^+ + OH^- \qquad K_1 = 10^{-4}$$

$$Fe(OH)^+ \rightleftharpoons Fe^{2+} + OH^- \qquad K_2 = 2.5 \times 10^{-6}$$

PROBLEM 416 H_2S is bubbled into a 0.2 M NaCN solution which is 0.02 M in each $Ag(CN)_2^-$ and $Cd(CN)_4^{2-}$. Determine which sulphide precipitate first. K_{sp} $(Ag_2S) = 10^{-50}$, K_{sp} of CdS $= 7.1 \times 10^{-28}$. K_d $Ag(CN)_2^- = 10^{-20}$ and $Kd(Cd(CN)_4^{2-}) = 7.8 \times 10^{-18}$.

PROBLEM 417 Over what range of concentration of hydrogen ion concentration (pH) is it possible to separate Cu^{2+} from Ni^{2+} when both metal ions are present at 0.01 M concentration and solution is made saturated with 0.1 M H_2S? K_{sp} of CuS and NiS are 6×10^{-37} and 4×10^{-20} respectively.

PROBLEM 418 A solution contains calcium nitrate and nickel nitrate, each at concentration of 0.1 M. CO_2 is bubbled into make its concentration equal to 0.03 M. What pH range would make possible for the selective precipitation of metal carbonates? K_{sp} of $CaCO_3$ and $NiCO_3$ are 4.5×10^{-9} and 1.3×10^{-7} respectively.

PROBLEM 419 How many moles AgBr can dissolve in 1.0 L of 1.0 M NH_3 solution. K_{sp} of AgBr is 5×10^{-13} and K_f for $Ag(NH_3)_2^+$ is 1.5×10^7.

PROBLEM 420 A salt whose formula is of the form MX has a value of K_{sp} equal to 3.2×10^{-10}. Another sparingly soluble salt MX_3 must have what value of K_{sp} if the molar solubilities of the two salts are to be identical?

PROBLEM 421 A salt having formula of the type M_2X_3 has $K_{sp} = 2.2 \times 10^{-20}$. Another salt, M_2X, has to have what K_{sp} value if M_2X has twice the molar solubility of M_2X_3?

PROBLEM 422 Suppose Na_2SO_4 is gradually added to 100 mL of a solution that contains both Ca^{2+} and Sr^{2+} ions each at 0.15 M concentrations.

(a) What will the Sr^{2+} ion concentration be when $CaSO_4$ just begin to precipitate.

(b) What percentage of Sr^{2+} ion has precipitated when $CaSO_4$ just begin to precipitate? $K_{sp}(CaSO_4) = 2.4 \times 10^{-5}$, $K_{sp}(SrSO_4) = 3.2 \times 10^{-7}$.

PROBLEM 423 How many grams of solid NaCN have to be added to 1.2 L of water to dissolve 0.11 mole of $Fe(OH)_3$ in the form of $[Fe(CN)_6]^{3-}$?
$[K_{sp}$ of $Fe(OH)_3 = 1.6 \times 10^{-39}$, $K_f = 10^{31}]$

PROBLEM 424 Silver ion forms a complex with thiosulphate ion with their formula $[Ag(S_2O_3)_2]^{3-}$. K_f for this complex is 2×10^{13}. How many grams of AgBr ($K_{sp} = 5 \times 10^{-13}$) will dissolve in 125 mL of a 1.20 M $Na_2S_2O_3$ solution.

PROBLEM 425 A sample of hard water was found to contain 278 ppm of calcium ion. Into 1.00 L of this water, 1.06 g of Na_2CO_3 was added. What is the new concentration of Ca^{2+} ion in ppm. Density of all solution be 1.0 g/cc and K_{sp} of $CaCO_3$ is 4.5×10^{-9}.

PROBLEM 426 What are the concentration of Pb^{2+}, Br^- and I^- in an aqueous solution that is in contact with both PbI_2 and $PbBr_2$? K_{sp} $(PbBr_2) = 2 \times 10^{-6}$, $K_{sp}(PbI_2) = 8 \times 10^{-9}$.

PROBLEM 427 An indicator has its standard ionization constant 9×10^{-9}. The acid colour of the indicator is yellow while its basic colour is red. The yellow colour is visible when the ratio yellow/red is 30 and red colour becomes visible when the ratio red/yellow is 2. What is the working pH range of this indicator?

PROBLEM 428 (a) At what maximum concentration of hydroxide ion, 1.0 *m* mole $Zn(OH)_2$ will go into 1.0 L solution as $Zn(OH)_4^{2-}$? $K_{sp} = 3 \times 10^{-16}$ and $K_f = 2 \times 10^{20}$.

(b) At what maximum concentration of hydroxide ion will 1.0 *m* mole $Zn(OH)_2$ will go into 1.0 L solution as Zn^{2+}?

PROBLEM 429 Determine the simultaneous solubility of AgCN $(K_{sp} = 2.2 \times 10^{-16})$ and $AgCl(K_{sp} = 1.6 \times 10^{-10})$ in 1.0 M ammonia solution. $K_f[Ag(NH_3)_2^+] = 1.5 \times 10^7$.

PROBLEM 430 What must be the minimum concentration of acetic acid in a one litre buffer solution of acetic acid acetate (pH = 4.74) if the pH changes by not more than 0.1 unit on addition of 50 mL 1 M HCl. $K_a = 1.8 \times 10^{-5}$.

PROBLEM 431 How much 1.0 M HCl must be added to 1.00 L of 0.10 M sodium lactate $(NaC_3H_5O_3)$ to make a buffer of $pH = 3.77$. $K_a = 1.4 \times 10^{-4}$.

PROBLEM 432 Potas alum is $KAl(SO_4)_2 \cdot 12 \cdot H_2O$. As a strong electrolyte, it is considered to be 100% ionized into K^+, Al^{3+} and SO_4^{2-}. The solution is acidic because of the hydrolysis of Al^{3+}, but not so acidic as might be expected, because the sulphate ion can spong-up some of the H^+ by forming HSO_4^-. Given a solution is made by dissolving 11.4 g of alum in enough water to make 100 mL of the solution. Calculate pH considering the following hydrolysis reactions:

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+; \qquad K_h = 1.4 \times 10^{-5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}; \qquad K_{a_2} = 1.26 \times 10^{-2}$$

PROBLEM 433 Determine molar solubility of AgCN in water considering hydrolysis of CN^- ion. Given $K_{sp}(AgCN) = 2.3 \times 10^{-16}$ and $K_a(HCN) = 5 \times 10^{-10}$.

PROBLEM 434 To what volume a 50 mL 6.0 M ammonia solution be diluted to double the degree of protonation? $K_b = 2 \times 10^{-5}$.

PROBLEM 435 Molar solubility of PbS is 6.7×10^{-10}. Sulphide ion hydrolysis completely into HS^- but the further hydrolysis of HS^- is insignificant. Determine K_{sp} of PbS. $K_{a_1}(H_2S) = 10^{-7}$ and $K_{a_2}(H_2S) = 10^{-14}$.

PROBLEM 436 Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate. Lactic acid written HL is monoprotic, and the acid dissociation constant is $K(\text{HL}) = 1.4 \times 10^{-4}$.

The acid dissociation constants for carbonic acid are: $K_{a_1} = 4.5 \times 10^{-7}$ and $K_{a_2} = 4.7 \times 10^{-11}$. All carbon dioxide remains dissolved during the reactions.

(a) Calculate pH in a 3.00×10^{-3} M solution of HL.

(b) Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate.

(c) 3.00×10^{-3} mol lactic acid (HL) is added to 1.00 L of 0.024 M solution of $NaHCO_3$ (no change in volume, HL completely neutralized).

(i) Calculate the value of pH in the solution of $NaHCO_3$ before HL is added.

(ii) Calculate the value of pH in the solution after the addition of HL.

(d) pH in the blood of a person changed from 7.40 to 7.00 due to lactic acid formed during physical activity. Let an aqueous solution having pH $= 7.40$ and $[HCO_3^-] = 0.022$ M represent blood in the following calculation. How many moles of lactic acid have been added to 1.00 L of this solution when its pH has become 7.00?

(e) In a saturated aqueous solution of $CaCO_3\,(s)$, pH is measured to 9.95. Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant K_{sp} is 5×10^{-9}.

(f) Blood contains calcium. Determine the maximum concentration of “free” calcium ions in the solution (pH = 7.40, $[HCO_3^-] = 0.022$ M) given in *d*).

PROBLEM 437 The pH recorded when 1.7 g of a monoprotic acid ($K_a = 2 \times 10^{-10}$) was added to 100 mL of NaOH of 0.1 M strength was 10.2. Determine molar mass of the acid.

PROBLEM 438 A saturated solution of $Mg(OH)_2$ has pH value 10.5. A mixture of 10.0 g of $Mg(OH)_2$ and 100 mL 0.1 M HCl is stirred magnetically for some time at 25°C. Calculate pH of the liquid phase when equilibrium is reached.

PROBLEM 439 The concentration of CO_2 is expected to rise 440 ppm in year 2020. What would be the pH of rainwater in the year 2020 if molar solubility of CO_2 is $0.0343\ \text{L}^{-1}\,\text{bar}^{-1}$. K_{a_1} of $CO_2 = 4.2 \times 10^{-7}$.

PROBLEM 440 Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulphuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

(a) 0.2515 g of a grain sample was treated with sulphuric acid, sodium hydroxide was then added and the ammonia distilled into 50.00 mL of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 mL of 0.1050 M sodium hydroxide.
Calculate the concentration of nitrogen in the sample, in per cent by mass.

(b) Calculate the pH of the solution which is titrated in (a), when 0 mL, 9.65 mL, 19.30 mL and 28.95 mL of sodium hydroxide has been added. Disregard any volume change during the reaction of ammonia gas with hydrochloric acid. K_a for ammonium ion is 5.7×10^{-10}.

(c) Draw the titration curve based on the calculations in (b).

(d) What is the pH transition range of the indicator which could be used for the back titration.

(e) The Kjeldahl method can also be used to determine the molecular weight of amino acids. In a given experiment, the molecular weight of a naturally occuring amino acid was determined by digesting. 0.2345 g of the pure acid, and distilling the ammonia into 50.00 mL of 0.1010 M hydrochloric acid. A titration volume of 17.50 mL was obtained for the back titration with 0.1050 M sodium hydroxide.

Calculate the molecular weight of the amino acid based on one and two nitrogen groups in the molecule, respectively.

PROBLEM 441 In the precipitation titration of KCl against $AgNO_3$, K_2CrO_4 is used as an indicator since, AgCl is white coloured. End point is detected by appearance of deep yellow coloured precipitate of Ag_2CrO_4. Determine the minimum concentration of chromate ion required for detection of end point. K_{sp} of $AgCl = 2.5\times10^{-10}$ and K_{sp} of $Ag_2CrO_4 = 1.8\times10^{-12}$.

PROBLEM 442 50 mL of a 10^{-4} M aqueous solution of $La(NO_3)_3$ is mixed with 50 mL of an NH_4^+/NH_3 buffer that is originally 0.2 M in NH_4^+ and 0.4 M in NH_3. What percentage of La^{3+} has been precipitated at equilibrium. K_{sp} of $La(OH)_3 = 10^{-19}$ and K_b of $NH_3 = 2\times10^{-5}$.

PROBLEM 443 Aluminium phosphate is more soluble than its expected solubility due to hydrolysis of both Al^{3+} and PO_4^{3-} as:

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+ \qquad K_a = 10^{-5}$$

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \qquad K_b = 5\times10^{-2}$$

Determine the actual solubility of $AlPO_4$. K_{sp} of $AlPO_4 = 10^{-20}$.

PROBLEM 444 0.2 moles of $MgCl_2$ is mixed with 0.2 moles of NaOH in a total volume of 1.0 litre.

(a) Calculate pH of this solution. K_{sp} of $Mg(OH)_2$ is 1.6×10^{-12}.

(b) Also determine pH when 0.04 moles of NaOH is added in the solution (a).

(c) Also determine pH of solution obtained after adding 0.04 mole of HCl to solution (a).

PROBLEM 445 How many grams of PbS will precipitate from a 1.0 L saturated $PbSO_4$ solution if the solution is made saturated with H_2S (0.1 M) and pH adjusted to 0. K_{sp} of $PbSO_4 = 1.6\times10^{-8}$ and K_{sp} of $PbS = 2.5\times10^{-27}$. Also for H_2S; $K_{a_1} = 10^{-7}$ and $K_{a_2} = 10^{-14}$.

PROBLEM 446 A typical wine sample contain 2.3% by mass of the base urea. K_b for urea is 1.5×10^{-14}. If the density of urea solution is 1.06 g/mL and it is buffered at pH 6.35, determine the equilibrium concentration of protonated urea.

PROBLEM 447 At 25°C K_{sp} of AgCl is 2×10^{-10}. Using the following standard molar Gibb's free energies of formations: $AgCl(s) = -110$ kJ/mol, $Ag_2SO_4(s) = -618.5$ kJ/mol, $Cl^-(aq) = -131$ kJ/mol and $SO_4^{2-}(aq) = -742$ kJ/mol determine solubility of Ag_2SO_4 in a 1.0 m M Na_2SO_4 solution at 25°C.

PROBLEM 448 pH of a 100 mL HOCN solution is 2.75. Addition of 100 mL 0.05 M HOCN to the above solution lowers the pH to 2.5. Determine concentration of the original acid solution (assume degree of ionization to be negligible in comparison to one).

PROBLEM 449 1.0 metric ton coal containing 2.5% sulphur is burned and SO_2 produced in the combustion was dissolved in rainwater of volume equivalent to 2.0 cm rain fall over $2.6\ \text{km}^2$ area. Determine pH of rainwater if K_a of $H_2SO_3 = 1.5 \times 10^{-2}$.

PROBLEM 450 1.0 g impure sample of Mg is burnt completely in N_2 atmosphere and nitride is dissolved in 1.0 litre of water. pH of the resulting solution was found to be 10.75. Determine percentage purity of the sample ignoring solubility of $Mg(OH)_2$. K_b of $NH_3 = 2 \times 10^{-5}$.

PROBLEM 451 Bromine in excess is added drop wise to a 0.01 M solution of SO_2. All SO_2 is oxidized to sulphuric acid. Excess of bromine is removed by flushing with gaseous N_2. Determine pH of the resulting solution assuming K_{a_1} of H_2SO_4 to be very large and $K_{a_2} = 10^{-2}$.

PROBLEM 452 In laboratory class, a student is given three flasks that are labeled *Q*, *R* and *S*. Each flask contains one of the following solutions : 1.0 M $Pb(NO_3)_2$, 1.0 M NaCl and 1.0 M K_2CO_3. The student is also given two flasks that are labeled *X* and *Y*. One of these flasks contains 1.0 M $AgNO_3$ and other contains 1.0 M $BaCl_2$.

(a) When the student combined a sample of solution *Q* with a sample of solution *X*, a precipitate formed. A precipitate also formed when samples of solution *Q* and *Y* were combined. Identify *Q*.

(b) When solution *Q* is mixed with solution *R*, a precipitate forms. However, no precipitate forms when solution *Q* is mixed with solution *S*. Identify *R* and *S*.

(c) After knowing the identity of *Q*, *R* and *S*, employ them to identify *X* and *Y*.

PROBLEM 453 You are given two burettes. One is filled with 0.15 M acetic acid and other is filled with 0.10 M sodium acetate. How much of each would you mix together to produce a total of 20 mL of solution with a pH of 4.7. You may not add any water to solution. K_a of acetic acid is 2×10^{-5}.

PROBLEM 454 You are given two burettes. One is filled with 0.15 M acetic acid and other with 0.1 M NaOH solution. How much of each would you mix together to produce a total volume of 50 mL with a $\text{pH} = 4.7$ K_a of acetic acid $= 2 \times 10^{-5}$.

PROBLEM 455 1.6 g solid $Ba(NO_3)_2$ and 0.3 g H_3PO_4 are taken in a flask and volume made up to 2.0 litre by adding sufficient water. Determine pH of the final solution assuming $Ba_3(PO_4)_2$ to be insoluble in water.

PROBLEM 456 A solution contains the cations Mn^{2+}, Co^{2+} and Ag^+ at an original concentration of 0.01 M each. Determine the pH range of this precipitation when the solution is saturated in H_2S(0.1 M). K_{a_1} and K_{a_2} of H_2S are 10^{-7} and 10^{-14} respectively. MnS $K_{sp} = 2.5 \times 10^{-10}$, $CoS : K_{sp} = 4 \times 10^{-21}$, $Ag_2S : K_{sp} = 6.3 \times 10^{-50}$.

PROBLEM 457 A saturated hydrogen electrode (SHE) with $[H^+] = 1.0$ M is connected to a silver electrode placed in a saturated solution of silver oxalate $Ag_2C_2O_4$ via a salt bridge and e.m.f was found to be 0.589 V. Calculate solubility product constant K_{sp} for given oxalate. $E^\circ_{Ag^+/Ag} = 0.80$ V.

PROBLEM 458 If 150 mg of zinc hydroxide crystals are mixed with 250 mL of a 0.1 M NaOH solution, what mass of $Zn(OH)_2$ crystals will remain undissolved? $K_{sp} = 2.1 \times 10^{-16}$ and K_f for $Zn(OH)_4^{2-} = 2.8 \times 10^{15}$.

PROBLEM 459 K_{sp} for AgCl $= 2\times10^{-10}$ and K_f for $Ag(NH_3)_2^+ = 2\times10^7$. Calculate molar solubility of AgCl in an aqueous solution that is 0.1 M in KCl and 0.1 M in NH_3.

PROBLEM 460 K_{sp} values of silver halides are : $AgCl = 1.8\times10^{-10}$, $AgBr = 5\times10^{-13}$, $AgI = 8.4\times10^{-17}$. State the order in which halide ions should be added to a concentration of 0.1 M so that each precipitate will form from the $[Ag^+]$ in equilibrium with the previous precipitate. Support your answer with appropriate calculations.

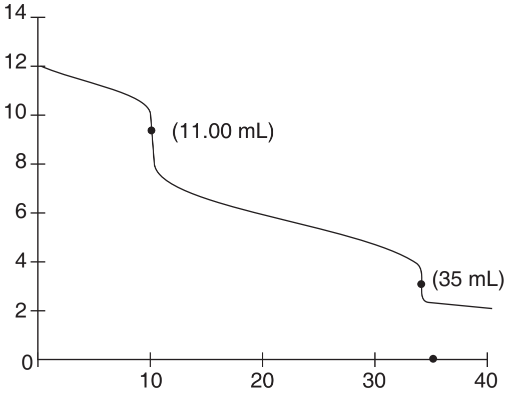
PROBLEM 461 Phosphoric acid ionizes according to the equations :

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \quad K_1 = 7\times10^{-3}$$
$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \quad K_2 = 6\times10^{-8}$$
$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \quad K_3 = 4.5\times10^{-13}$$

(a) If you are asked to prepare a buffer with a pH = 7.00, identify the species that should be used in the solution and calculate their ratio.

(b) Assume 50 mL of the buffer prepared in part ‘a’ is available in which more abundant species has a concentration of 0.10 M. If to this solution 20 mL 0.1 M NaOH is added further, what will be the new pH?

PROBLEM 462 A 0.50 gram mixture containing $NaHCO_3$, Na_2CO_3 and KCl was dissolved in 50.00 mL water and titrated with 0.115 M HCl resulting in the following titration curve.



Determine weight percentage of $NaHCO_3$, Na_2CO_3 and KCl in the mixture.

PROBLEM 463 K_{sp} of $Ca(H_2PO_4)_2 = 10^{-3}$. What minimum pH must be maintained in a 0.25 M H_3PO_4 solution to prevent precipitation of $Ca(H_2PO_4)_2$ if the solution is 0.15 M in calcium ion? K_{a_1} of H_3PO_4 is 7×10^{-3}.

PROBLEM 464 Fe^{3+} ion forms a blood red complexes with thiocyanate ion, SCN^-. Following equilibria exist on adding SCN^- to an aqueous solution of Fe^{3+} ion :

(i) $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^- \quad K_{sp} = 4\times10^{-38}$

(ii) $Fe^{3+} + 2SCN^- \rightleftharpoons Fe(SCN)_2^+ \quad K_f = 2.3\times10^3$

(iii) $SCN^- + H_2O \rightleftharpoons HSCN + OH^- \quad K_a = 71$

Discuss the effect of followings on concentration of Fe^{3+} ion in solution :
(a) Addition of HNO_3, (b) Addition of NaOH,
(c) Addition of NaSCN, (d) Addition of $Fe(OH)_3$.

PROBLEM 465 What will be the effect of adding a strong acid to an aqueous solution of $Cu(CN)_4^{2-}$, HCN is a weak acid with $K_a = 6 \times 10^{-10}$?

PROBLEM 466 What concentration of NH_3 must be present in a 0.1 M $AgNO_3$ solution to prevent AgCl from precipitating when 4.0 g of NaCl are added to a 250 mL of this solution. $K_{sp} = 2 \times 10^{-10}$, $K_f\ [Ag(NH_3)_2^+] = 10^7$.

PROBLEM 467 It is possible to keep $Co(OH)_3$ from precipitating from a 0.01 M $CoCl_3$ solution by buffering the solution at pH 9.1 with a buffer that contain NH_3 and NH_4^+ ion. How much of 6 M NH_3 and 6 M HCl must be added per litre of this solution to prevent $Co(OH)_3$ from precipitating? $[NH_3 : K_b = 2 \times 10^{-5}, Co(OH)_3(s) : K_{sp} = 10^{-43}, Co(NH_3)_6^{3+} : K_f = 2 \times 10^{35}]$

PROBLEM 468 Will $Co(OH)_3$ precipitate from a solution that is initially 0.1 M in Co^{3+} and 1M in SCN^- if this solution is buffered at pH = 7. K_{sp} of $Co(OH)_3 = 1.6 \times 10^{-44}$ and $K_f[Co(SCN)_4^-] = 10^3$?

PROBLEM 469 Calculate the concentration of CO_3^{2-} in a 0.1 M HCO_3^- solution buffered with equal number of moles of NH_3 and NH_4^+. Is this CO_3^{2-} concentration large enough to precipitate $BaCO_3$ when the solution is mixed with equal volume of 0.1 M Ba^{2+} ion. $[K_{sp} = 5 \times 10^{-9}, H_2CO_3 : K_{a_1} = 4.5 \times 10^{-7}$, $K_{a_2} = 4.7 \times 10^{-11}, NH_3 : K_b = 2 \times 10^{-5}]$

PROBLEM 470 Enough carbonate ion CO_3^{2-} can be leached out of clay to buffer ground water at pH = 8. Assume that total concentration of HCO_3^- and CO_3^{2-} ions in this solution is 0.10 M. Calculate the maximum concentration of ^{60}Co-isotope that could leach into ground water if clay were used as a barrier to store this radioactive isotope. K_{sp} of $CoCO_3$ and $Co(OH)_3$ are 1.4×10^{-13} and 1.6×10^{-44} respectively. For H_2CO_3 $K_{a_1} = 4.5 \times 10^{-7}$ and $K_{a_2} = 4.7 \times 10^{-11}$.

PROBLEM 471 Determine pH and degree of hydrolysis of a 10^{-3} M $C_6H_5NH_3Cl$ solution. $K_b = 5 \times 10^{-10}$.

PROBLEM 472 A solution is made by dissolving 0.001 mol $Ca(OI)_2$ in 100 mL of water and to this solution 100 mL 0.01 M acetic acid solution was added. Determine pH of this solution. K_a (acetic acid) $= 2 \times 10^{-5}$, K_a (HOI) $= 2 \times 10^{-11}$.

PROBLEM 473 Determine pH of a 0.01 M $ClC_6H_4NH_3Cl$, $K_b = 4 \times 10^{-12}$.

PROBLEM 474 The indicator dinitrophenol has $K_a = 1.1 \times 10^{-4}$. In a 10^{-4} M solution, it is colourless in acid medium and yellow in basic medium. Calculate pH range over which it goes from 25% (ionized) to 75% (ionized).

PROBLEM 475 Determine concentration of ammonium ion that is required to prevent the precipitation of $Mg(OH)_2$ in a solution with $[Mg^{2+}] = 0.1\,M$ and $[NH_3] = 0.1\,M$. $K_{sp}[Mg(OH)_2] = 1.5 \times 10^{-11}$ and $K_b(NH_3) = 2 \times 10^{-5}$.

PROBLEM 476 Determine molar solubility of $BaSO_4$ in a 0.25 M solution of $NaHSO_4$. K_a for $HSO_4^- = 1.2 \times 10^{-2}$. Also determine the factor by which solubility is decreased as compared to solubility in pure water $K_{sp} = 10^{-10}$.

PROBLEM 477 If the final volume is to be 1 litre, how many mL of $\frac{1}{3}$ M HCl will have to be added to 500 c.c. of 0.1 M Na_2CO_3 solution in order to adjust the pH to 10? K_{a_1} of $CO_2 = 4 \times 10^{-7}$ and $K_{a_2} = 5 \times 10^{-11}$.

PROBLEM 478 Formation constant of $[Ag(CN)_2]^-$ is 2.5×10^{18}. Determine concentration of $Ag^+(aq)$ in a solution which was originally 0.1 M in KCN and 0.03 M in $AgNO_3$.

PROBLEM 479 The solubility product of CaF_2 at 18°C is 3.4×10^{-11} while that of $CaCO_3$ is 9.5×10^{-9}. (a) What will be the nature of 1st precipitate when a solution of $CaCl_2$ is added to a solution which is 0.05 M in NaF and 0.02 M in Na_2CO_3. (b) In a 0.02 M solution of Na_2CO_3, what is the minimum concentration of NaF at which both CaF_2 and $CaCO_3$ will precipitate simultaneously?

PROBLEM 480 The solubility product of PbI_2 is 7.47×10^{-9} at 17°C and 1.4×10^{-8} at 27°C. Calculate (a) the molar heat of solution of PbI_2 (b) the solubility of PbI_2 at 77°C.

PROBLEM 481 The equivalence conductivity of a solution containing 2.54 g $CuSO_4$/L is 91 $cm^2\Omega^{-1}$ equ^{-1}. Calculate the specific conductivity of a solution. Also determine the resistance of a cm^3 of this solution when placed between two electrodes 1.00 cm apart, each having an area of 1.00 cm^2?

PROBLEM 482 The equivalent conductance of a 0.01 M ammonia solution is $10\,cm^2\Omega^{-1}equ^{-1}$. The equivalent conductance of ammonia at infinite dilution is $238\,cm^2\Omega^{-1}equ^{-1}$. Determine ionization constant K_b of ammonia.

PROBLEM 483 Equivalent conductance at infinite dilution for acetic acid is $390\,cm^2\Omega^{-1}$ at 25°C. Determine specific conductance and equivalent conductance of a 0.01 M acetic acid solution if K_a of acetic acid $= 2 \times 10^{-5}$.

PROBLEM 484 A conductivity cell is filled with 0.1 M KCl solution at 27°C. The measured resistance $R = 25\,\Omega$. Calculate cell constant if specific conductance of 0.1 M KCl solution is $0.0116\,\Omega^{-1}cm^{-1}$. If the same cell is filled with acetic acid, the cell resistance is 1982 Ω. Determine molar conductance of 0.1 M acetic acid solution.

PROBLEM 485 The conductivity of a 0.1 M NaOH solution is $0.022\,\Omega^{-1}cm^{-1}$. When an equal volume of 0.1 M HCl solution is added, the conductivity decreases to $0.0056\,\Omega^{-1}cm^{-1}$. A further addition of HCl solution, the volume of which is equal to that of first portion added, conductivity increases to $0.017\,\Omega^{-1}cm^{-1}$. Calculate molar conductance of NaOH, NaCl and HCl solutions in the given conditions.

PROBLEM 486 A sample of water from a large swimming pool has a resistance of 9200 Ω at 25°C when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85 Ω at 25°C. Five hundred grams of NaCl was then dissolved in swimming pool, stirred throughly and a sample of this solution gave a resistance of 7600 Ω. Calculate the volume of water in the pool. Given molar conductivity of NaCl solution at that concentration is $126.5\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and molar conductivity of KCl solution at 0.02 M is $138.3\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

PROBLEM 487 The molar conductivity of a 0.05 M aqueous solution of $MgCl_2$ is $195\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 27°C. A cell whose electrodes are of $1.5\ \text{cm}^2$ surface area and placed at a distance of 0.5 cm, is filled with 0.05 M $MgCl_2$ solution. How much current will flow if the potential difference across the electrodes is 5 V?

PROBLEM 488 A conductivity cell when filled with 0.02 M KCl gives resistance of 85 Ω. The same conductivity cell, when filled with a saturated solution of $PbCl_2$, gives resistance of 70 Ω. If the equivalent conductance of 0.02 N KCl solution and saturated solution of $PbCl_2$, under identical conditions are 138.3 and 106 $\text{cm}^2\Omega^{-1}\text{eq}^{-1}$ respectively, determine solubility product of $PbCl_2$.

Solutions

IONIC EQUILIBRIUM

391. For weak acid H*A*, the ionization equilibrium is :

$$\underset{C(1-\alpha)}{\mathrm{H}A} \rightleftharpoons \underset{C\alpha}{\mathrm{H}^+} + \underset{C\alpha}{A^-}$$

Also, $$[\mathrm{H}^+] = 10^{-2} = C\alpha = 0.1\,\alpha \quad \Rightarrow \quad \alpha = 0.1$$

$\Rightarrow$ $$K_a = \frac{C\alpha^2}{1-\alpha} = \mathbf{1.1 \times 10^{-3}}$$

Now, let us assume that 100 mL 0.1 M HCl is added to V mL of the above weak acid.

$$\text{m mol of HCl added} = 100 \times 0.1 = 10$$

$$\text{m mol of } A^- \text{ in the solution} = x$$

$$\text{m mol of H}A = 0.1\,\mathrm{V}$$

If, in presence of HCl, x m mol of H*A* is ionized,

$$\text{m mol of H}^+ \text{ in the solution} = x + 10$$

$$\text{m mol of } A^- \text{ in the solution} = x$$

$$\text{m mol of unionized H}A = 0.1V - x$$

$\Rightarrow$ $$K_a = \frac{[\mathrm{H}^+][A^-]}{[\mathrm{H}A]} = \frac{(x+10)(x)}{(100+V)(0.1V - x)} = 1.1 \times 10^{-3}$$

and $$[\mathrm{H}^+] = 2 \times 10^{-2} = \frac{x+10}{100+V}$$

$\Rightarrow$ $$\frac{2 \times 10^{-2}\, x}{(0.1\,\mathrm{V} - x)} = 1.1 \times 10^{-3} \quad \Rightarrow \quad V = 192\,x$$

Substituting in $[H^+]$ expression : $2\times10^{-2} = \dfrac{V+1920}{192(100+V)}$

$\Rightarrow \qquad V = \mathbf{540\ mL}$

392. Let dibasic acid be H_2A :

$$H_2A \rightleftharpoons H^+ + HA^-$$

$$HA^- \rightleftharpoons H^+ + A^{2-}$$

$\Rightarrow \qquad [A^{2-}] = Ka_2 = 3\times10^{-6}$

and $\qquad [H^+] = [HA^-] + [A^{2-}] = \dfrac{Ka_1[H_2A]}{[H^+]} + [A^{2-}]$

$\Rightarrow \qquad [H^+] = \dfrac{1.4\times10^{-6}}{[H^+]} + 3\times10^{-6} \quad \Rightarrow \quad [H^+] = 1.18\times10^{-3}$

$$pH = \mathbf{2.926}$$

393. Enthalpy of ionization of formic acid is 15 kJ/mol

$\Rightarrow \qquad \ln\dfrac{K(47°C)}{K(27°C)} = \dfrac{15\times10^3}{8.314}\left(\dfrac{20}{300\times320}\right) = 0.376$

$\Rightarrow \qquad K_a(47°C) = 2.47\times10^{-4}$

$$[H^+] = \sqrt{K_aC} = 4.97\times10^{-3} \quad \Rightarrow \quad pH = \mathbf{2.3}$$

394. $[D^+] = 10^{-7} + \dfrac{1.35\times10^{-15}}{[D^+]} \quad \Rightarrow \quad [D^+] = 1.12\times10^{-7} \quad \Rightarrow \quad pD = \mathbf{6.95}$

395. The hydrolysis equilibrium is :

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{3\times10^{-8}} = 3.33\times10^{-7}$$

$$= \frac{[HO^-][HOCl]}{[OCl^-]} = \frac{[HOCl]}{[OCl^-]} = \frac{3.33\times10^{-7}}{[HO^-]} = 0.528$$

$\Rightarrow$ % (by mole) HOCl = **34.55,** OCl^- = **65.45.**

396. $\qquad n(\text{dimer}) = \dfrac{PV}{RT} = 4.64\times10^{-4}$

moles of NaOH used up = moles of CH_3COOH produced from decomposition = 7.8×10^{-4}

$\Rightarrow$ Moles of dimer dissociated = $\dfrac{7.8\times10^{-4}}{2} = 3.9\times10^{-4} \quad \Rightarrow \quad \alpha = \dfrac{3.9\times10^{-4}}{4.64\times10^{-4}} = \mathbf{0.84}$

397. $\qquad [CO_2] = 2.28\times10^{-3}\times3.2 = 7.296\times10^{-3}$ M

$$[H^+] = \sqrt{K_1[CO_2]} = 5.53\times10^{-5} \quad \Rightarrow \quad pH = \mathbf{4.25}$$

398. $[\text{OCl}^-] = 0.67:$ $\qquad \text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$

$$[\text{OH}^-] = \sqrt{K_h C} = 4.72 \times 10^{-4}$$

$\Rightarrow \qquad \text{pOH} = 3.325 \quad \text{and} \quad \text{pH} = \mathbf{10.675}$

399. $$\text{pOH} = \text{p}K_b + \log \frac{[S]}{[B]} \Rightarrow [S] = 0.5$$

$$m \text{ mol of NH}_4\text{Cl} = 100$$

$$m \text{ mol of NH}_3 = 50$$

After adding 7.5 mmol KOH; m mol of $\text{NH}_4\text{Cl} = 92.5$

$$m \text{ mol of NH}_3 = 57.5$$

$\Rightarrow \qquad \text{pOH} = \text{p}K_b + \log \frac{92.5}{57.5} = 4.9$

$\Rightarrow \qquad \text{pH} = 9.1 \quad \text{and} \quad \Delta\,\text{pH} = \mathbf{0.1.}$

400. mol of $\text{CH}_3\text{COOH} = 0.25$, mol of $\text{CH}_3\text{COONa} = 0.30$

(a) $\qquad \text{pH} = \text{p}K_a + \log \frac{0.3}{0.25} = \mathbf{4.78}$

(b) $\qquad \text{pH} = \text{p}K_a + \log \frac{306.25}{243.75} = \mathbf{4.799}$

(c) $\qquad \text{pH} = \text{p}K_a + \log \frac{290}{260} = \mathbf{4.745}$

401. $K_a = \frac{C\alpha^2}{1-\alpha}$; Solving gives $\alpha = 0.27$

$\Rightarrow$ van't Hoff factor $(i) = 1 + \alpha = \mathbf{1.27}$

$$-\Delta T_f = iK_f m = 1.27 \times 1.86 \times \frac{0.5}{935.5} \times 1000 = \mathbf{1.26}$$

402. $$\ln \frac{1.99 \times 10^{-15}}{3.16 \times 10^{-16}} = \frac{\Delta H}{8.314}\left(\frac{10}{293 \times 303}\right) \Rightarrow \Delta H = 136.2 \text{ kJ}$$

$\Rightarrow \qquad \ln \frac{K_w(50°\text{C})}{3.16 \times 10^{-16}} = \frac{136.2 \times 10^3}{8.314}\left(\frac{30}{293 \times 323}\right)$

$\Rightarrow \qquad K_w(50°\text{C}) = 5.7 \times 10^{-14}$

$$\text{pD} = \mathbf{6.62}$$

403. MOH has lower solubility ($S = 10^{-6}$) and will precipitate first of pH = **8**

404. $K_{sp} = 1.6 \times 10^{-14} = [\text{Fe}^{2+}][\text{OH}^-]^2$

(i) At pH = 8, $[\text{OH}^-] = 10^{-6}$, $[\text{Fe}^{2+}] = \text{Solubility} = 1.6 \times 10^{-2}$

(ii) At pH = 6, $[\text{OH}^-] = 10^{-8}$, $[\text{Fe}^{2+}] = 160$ indicates very high solubility.

405.
$$\mathrm{CaF_2 \rightleftharpoons Ca^{2+} + 2F^-}$$
$$\mathrm{F^- + H^+ \rightleftharpoons HF}$$

Let 'α' be the fraction of total fluoride ion produced in $\mathrm{F^-}$ form

$$\alpha = \frac{[\mathrm{F^-}]}{2S} = \frac{[\mathrm{F^-}]}{[\mathrm{F^-}]+[\mathrm{H^+}]} = \frac{K_a}{K_a+[\mathrm{H^+}]}$$ where S is solubility.

(a) At $\mathrm{pH}=7, [\mathrm{H^+}]=10^{-7} << K_a \quad \Rightarrow \quad \alpha \approx 1$ and $K_{sp} = 4S^3$

$\Rightarrow$ $$S = \mathbf{2.15 \times 10^{-4}}$$

(b) At $\mathrm{pH}=5, \alpha = \dfrac{3.45\times10^{-4}}{3.45\times10^{-4}+10^{-5}} = 0.97$ and $[\mathrm{F^-}] = 25\alpha$

$\Rightarrow$ $$K_{sp} = 4S^3\cdot\alpha^2 \quad \Rightarrow \quad S = \mathbf{2.2 \times 10^{-4}}$$

406. Proceeding as in problem no. 405.

(a) $\alpha \approx 1$ and $S = \mathbf{7.5 \times 10^{-3}}$

(b) At $\mathrm{pH}=4; \alpha = \dfrac{3.45\times10^{-4}}{3.45\times10^{-4}+10^{-4}} = 0.775$

$\Rightarrow$ $$K_{sp} = 4S^3\alpha^2 \quad \text{and} \quad S = \mathbf{8.9 \times 10^{-3}}$$

407. $[\mathrm{Salt}] = \dfrac{10^{-2}}{150} = 6.67\times10^{-5}\ \mathrm{M}$

$$K_h = \frac{[\mathrm{OH^-}]^2}{C} = \frac{(5.12\times10^{-7})^2}{6.67\times10^{-5}} = 3.94\times10^{-9} = \frac{K_w}{K_a}$$

$\Rightarrow$ $$K_a = 2.53\times10^{-6}, \quad \alpha = \frac{5.12\times10^{-7}}{6.67\times10^{-5}} = 7.67\times10^{-3}$$

$\Rightarrow$ % protonation = **0.76**

408. $K_h = \dfrac{K_w}{K_b} = \dfrac{[\mathrm{H^+}]^2}{C} \quad \Rightarrow \quad [\mathrm{H^+}] = \sqrt{2.4\times10^{-8}} = 1.55\times10^{-4} \quad \Rightarrow \quad \mathrm{pH} = \mathbf{3.8}$

409. At first equivalence point, 5 mmol of $\mathrm{NaHC_2O_4}$ will be formed.

Hence, $$K_h = \frac{K_w}{K_{a_1}} = \frac{[\mathrm{OH^-}]^2}{C} \quad \Rightarrow \quad [\mathrm{OH^-}] = 1.3\times10^{-7}$$

$\Rightarrow$ $$\mathrm{pOH} = 6.89 \quad \mathrm{pH} = \mathbf{7.11}$$

At second end point, m mol of $\mathrm{Na_2C_2O_4} = 5$

Now, $$K_h = \frac{K_w}{K_{a_2}} = \frac{[\mathrm{OH^-}]^2}{C} \quad \Rightarrow \quad [\mathrm{OH^-}] = 3.92\times10^{-6}$$

$\Rightarrow$ $$\mathrm{pOH} = 5.4 \quad \mathrm{pH} = \mathbf{8.6}$$

410. For $H_2S : K_a = K_{a_1} \times K_{a_2} = 10^{-21} = \dfrac{[H^+]^2[S^{2-}]}{[H_2S]}$

At $pH = 7, [S^{2-}] = 10^{-8}$ and solubility $= [Zn^{2+}] = \dfrac{1.6 \times 10^{-24}}{10^{-8}} = \mathbf{1.6 \times 10^{-16}}$

At $pH = 10, [S^{2-}] = 10^{-2}$ and solubility $= \mathbf{1.6 \times 10^{-22}}$

411.
$$\frac{K_{sp}(Ag_2CO_3)}{K_{sp}(Ag_2CrO_4)} = \frac{[CO_3^{2-}]}{[CrO_4^{2-}]} = 6.75$$

Also, $$[Ag^+] = 2[CO_3^{2-}] + 2[CrO_4^{2-}]$$

$\Rightarrow$ $$\frac{[Ag^+]}{[CO_3^{2-}]} = 2 + \frac{2}{6.75} = 2.296$$

Also, $K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12} = [Ag^+]^2[CO_3^{2-}] = (2.296[CO_3^{2-}])^2[CO_3^{2-}]$

$\Rightarrow$ $$[CO_3^{2-}] = \mathbf{1.15 \times 10^{-4}} = \text{Solubility of } Ag_2CO_3$$

Similarly, $$[CrO_4^{2-}] = \mathbf{1.7 \times 10^{-5}} = \text{Solubility of } Ag_2CrO_4$$

412. In both case, solution is an acid-buffer. Let x m mol of acid be present in the given volume and y m mol of NaOH in 20 mL solution.

Then $$3.7 = pK_a + \log\frac{y}{x-y} \quad \text{and} \quad 4.18 = pK_a + \log\frac{1.5y}{x-1.5y}$$

Solving, $$pK_a = 3.7 \;\Rightarrow\; K_a = \mathbf{2 \times 10^{-4}}.$$

413. The buffer pair in this case is H_3PO_4 and NaH_2PO_4.

$\Rightarrow$ $$pH = pK_{a_1} + \log\frac{0.15}{[H_3PO_4]} \qquad \Rightarrow \; [H_3PO_4] = 0.3 \text{ M}$$

Also, m mol of HCl needed $= 0.3 \times 100 = 30 \;\Rightarrow\; V(HCl) = 20$ mL.

$$m \text{ mol of } NaH_2PO_4 = 0.15 \times 100 + 30 = 45$$

$\Rightarrow$ $$m(NaH_2PO_4) = \mathbf{5.4\ g}$$

414. $[H^+] = 1.48 \times 10^{-4}$ M $\Rightarrow$ $[CO_2] = \dfrac{[H^+]^2}{K_{a_1}} = 0.052$ M

$\Rightarrow$ $$0.052 = 2.3 \times 10^{-2}\, P = \mathbf{2.26\ atmosphere}$$

415. $Fe^{2+} + H_2O \rightleftharpoons Fe(OH)^+ + H^+ \quad K = \dfrac{K_w}{K_2} = \dfrac{[H^+]^2}{C} \;\Rightarrow\; pH = \mathbf{4.7}$

416. For Ag_2S: $2Ag(CN)_2^- + S^{2-} \rightleftharpoons Ag_2S + 4CN^-$;

$$K = \frac{K_d^2}{K_{sp}} = 10^{10} = \frac{[CN^-]^4}{[Ag(CN)_2^-][S^{2-}]}$$

$\Rightarrow$ $$[S^{2-}] = 4 \times 10^{-10}$$

Similarly, for CdS : $\quad Cd(CN)_4^{2-} + S^{2-} \rightleftharpoons CdS + 4CN^-$;

$$K = \frac{K_d}{K_{sp}} = \frac{[CN^-]^4}{[Cd(CN)_4^{2-}][S^{2-}]} \quad \Rightarrow \quad [S^{2-}] = 7.28\times10^{-12}$$

$\because$ Lower $[S^{2-}]$ is required for CdS, it will precipitate first.

417. $[S^{2-}]$ (required for precipitation of CuS) $= K_{sp}\,(CuS)/[Cu^{2+}] = 6\times10^{-35}$

$[S^{2-}]$ (required for precipitation of NiS) $= 4\times10^{-18}$

Now, $\quad K(H_2S) = K_1 \cdot K_2 = 10^{-21} = \dfrac{[H^+]^2[S^{2-}]}{[H_2S]}$

For NiS; $[H^+]^2 = \dfrac{10^{-22}}{4\times10^{-18}} = 2.5\times10^{-5} \quad \Rightarrow \quad [H^+] = 5\times10^{-3}$

Hence, if $[H^+]$ is greater than 5×10^{-3} (pH = 2.3), $[S^{2-}]$ will be less than 4×10^{-18} and NiS will not precipitate, only CuS will be precipitated.

418. Minimum carbonate ion concentration required for precipitation of carbonates are:

For $CaCO_3$, $[CO_3^{2-}] = 4.5\times10^{-8}$ and for $NiCO_3$, $[CO_3^{2-}] = 1.3\times10^{-6}$

For H_2CO_3; $K = K_1K_2 = 2\times10^{-16} = \dfrac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]}$

$[H^+]$ for precipitation of $CaCO_3 = \left[\dfrac{2\times10^{-16}\times0.03}{4.5\times10^{-8}}\right]^{1/2} = 1.15\times10^{-5} \quad \Rightarrow \quad pH = \mathbf{4.93}$

$[H^+]$ for precipitation of $NiCO_3 = \left[\dfrac{2\times10^{-16}\times0.03}{1.3\times10^{-6}}\right]^{1/2} = 2.1\times10^{-6} \quad \Rightarrow \quad pH = \mathbf{5.66}$

$\Rightarrow$ At pH 4.93, $CaCO_3$ will start precipitating but $NiCO_3$ will remain in solution and at pH = 5.66, $NiCO_3$ will start precipitating.

419. For the dissolution equilibrium :

$$\underset{-x}{AgBr} + \underset{1-2x}{2NH_3} \rightleftharpoons \underset{x}{Ag(NH_3)_2^+} + \underset{x}{Br^-}$$

$$K = K_{sp}\cdot K_f = 7.5\times10^{-6} = \left(\frac{x}{1-2x}\right)^2 \quad \Rightarrow \quad x = \mathbf{2.7\times10^{-3}}$$

420. For MX, solubility $= \sqrt{K_{sp}} = 1.78\times10^{-5}$

For $\quad MX_3, \rightleftharpoons K_{sp} = 27S^4 = \mathbf{2.76\times10^{-18}}$

421. For M_2X_3; $S = \left(\dfrac{K_{sp}}{108}\right)^{1/5} = 4.58\times10^{-5}$.

$\Rightarrow \quad$ Solubility of $M_2X = 2S = 9.16\times10^{-5} \quad \Rightarrow \quad K_{sp} = \mathbf{3\times10^{-12}}$

422. When $CaSO_4$ start to precipitate $[SO_4^{2-}] = \dfrac{K_{sp}}{[Ca^{2+}]} = 1.6 \times 10^{-4}$ M

(a) $[Sr^{2+}]$ when $CaSO_4$ start to precipitate $= \dfrac{K_{sp}(SrSO_4)}{[SO_4^{2-}]} = \mathbf{2 \times 10^{-3}}$

(b) % Sr^{2+} ion precipitated when $CaSO_4$ begin to precipitate $= \dfrac{0.15 - 2 \times 10^{-3}}{0.15} \times 100 = \mathbf{98.67}$

423. The dissolution equilibrium is :

$$Fe(OH)_3 + 6CN^- \rightleftharpoons Fe(CN)_6^{3-} + 3OH^- : K = K_{sp} \cdot K_f = 1.6 \times 10^{-8}$$

Let the initial concentration of $CN^- = x$ M

$$\Rightarrow \qquad 1.6 \times 10^{-8} = \frac{(0.092)(0.275)^3}{(x - 0.55)^6} \quad \Rightarrow \quad x = 7.57\text{ M}$$

$\Rightarrow$ Moles of NaCN dissolved $= 7.57 \times 1.2 = 9.084$

Mass of NaCN = **445 g.**

424. $$\underset{x}{AgBr} + \underset{1.2 - 2x}{2S_2O_3^{2-}} \rightleftharpoons \underset{x}{Ag(S_2O_3)^{3-}} + \underset{x}{Br^-} \qquad K = K_{sp} \cdot K_f = 10 = \left(\frac{x}{1.2 - 2x}\right)^2$$

$\Rightarrow \quad x = 0.52\ M \quad \Rightarrow$ mol of AgBr dissolved $= 0.065$

mass of AgBr dissolved = **12.22 g**

425. Initial concentration of $Ca^{2+} = \dfrac{0.278}{40}\text{ M} = 6.95 \times 10^{-3}$ M

Moles of Na_2CO_3 added $= \dfrac{1.06}{106} = 0.01$

Moles of CO_3^{2-} left unreacted after precipitation of

$$CaCO_3 = 0.01 - 6.95 \times 10^{-3} = 3.05 \times 10^{-3}$$

$$\Rightarrow \quad [Ca^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{4.5 \times 10^{-9}}{3.05 \times 10^{-3}} = 1.475 \times 10^{-6}\text{ M} = \mathbf{0.059\ ppm\ Ca^{2+}}.$$

426. $2 \times 10^{-6} = 4S^3$, where $S =$ solubility of $PbBr_2$

$\Rightarrow S = 7.93 \times 10^{-3}$ M $= [Pb^{2+}]$; $[Br^-] = 2S = 1.586 \times 10^{-2}$ M

$$8 \times 10^{-9} = [Pb^{2+}][I^-]^2 \quad \Rightarrow \quad [I^-] = 10^{-3}\text{ M.}$$

427. $$\underset{Y}{HIn} \rightleftharpoons H^+ + \underset{R}{In^-} \qquad pH = pK_{In} + \log\frac{R}{Y}$$

$$pH(\text{yellow}) = 8.045 - \log 30 = 6.57$$

$$pH(\text{red}) = 8.045 + \log 2 = 8.35 \quad \Rightarrow \quad \text{pH range} = \mathbf{6.57 \longleftrightarrow 8.35.}$$

428. (a) $$Zn(OH)_2 + \underset{x - 2 \times 10^{-3}}{2OH^-} \rightleftharpoons \underset{2 \times 10^{-3}}{Zn(OH)_4^{2-}}$$

$$K = K_{sp} \cdot K_f = 6 \times 10^4 = \frac{2 \times 10^{-3}}{(x - 2 \times 10^{-3})^2}$$

$\Rightarrow$ $$x = \mathbf{2.18 \times 10^{-3}\ M.}$$

(b) $$3 \times 10^{-16} = [\mathrm{Zn}^{2+}][\mathrm{OH}^-]^2 \quad \Rightarrow \quad [\mathrm{OH}^-] = \mathbf{5.47 \times 10^{-7}.}$$

429. $$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^- \qquad K_1 = 2.4 \times 10^{-3} = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

$$AgCN + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + CN^- \qquad K_2 = 3.3 \times 10^{-9} = \frac{[Ag(NH_3)_2^+][CN^-]}{[NH_3]^2}$$

$\Rightarrow$ $$\frac{K_1}{K_2} = 7.27 \times 10^5 = \frac{[Cl^-]}{[CN^-]} = \frac{\text{Solubility of AgCl}}{\text{Solubility of AgCN}}$$

The above ratio indicates that AgCl has very high solubility than AgCN.

$\Rightarrow$ $$K_1 = 2.4 \times 10^{-3} \left[\frac{S}{1 - 2S}\right]^2 \quad \Rightarrow \quad S = [Cl^-] = 0.045$$

$\Rightarrow$ $$[CN^-] = \mathbf{6.13 \times 10^{-8}.}$$

430. $4.64 = 4.74 + \log \dfrac{x - 50}{x + 50} \quad \Rightarrow \quad x = 450 \quad \Rightarrow \quad [\text{Acid}] = 0.45\ \text{M}.$

431. Let x mol of HCl is added. Then moles of $C_3H_6O_3 = x$ and moles of

$$NaC_3H_5O_3 = 0.1 - x$$

$\Rightarrow$ $$3.77 = pK_a + \log \frac{0.1 - x}{x}$$

Solving, $x = 0.55$ mol

$\Rightarrow$ 55 mL of 1.0 M HCl will give the desired buffer.

432. $$\underset{c-x}{Al^{3+}} + H_2O \rightleftharpoons \underset{x}{Al(OH)^{2+}} + \underset{y}{H^+}$$

$$\Rightarrow \quad K_h = \frac{xy}{c - x} \qquad \ldots\text{(i)}$$

$$\underset{x-y}{HSO_4^-} \rightleftharpoons \underset{y}{H^+} + \underset{y}{SO_4^{2-}}$$

$$K_a = \frac{y^2}{x - y} \qquad \ldots\text{(ii)}$$

$\Rightarrow$ Solving for x and y gives $\text{pH} = -\log y = 3.53$

433. $$AgCN \rightleftharpoons Ag^+ + CN^-$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

Applying material balance $= [\mathrm{Ag}^+] = [\mathrm{CN}^-] + [\mathrm{HCN}] = \dfrac{K_{sp}}{[\mathrm{Ag}^+]} + \sqrt{\dfrac{K_w\,K_{sp}}{K_a[\mathrm{Ag}^+]}}$

Also 1st term on the right hand of the material balance is negligible in comparison to the second term.

$$\Rightarrow \qquad [\mathrm{Ag}^+] = \sqrt{\frac{K_w K_{sp}}{K_a[\mathrm{Ag}^+]}} \quad \Rightarrow \quad [\mathrm{Ag}^+] = \mathbf{1.66 \times 10^{-7}}$$

434. $\because\ \alpha = \sqrt{\dfrac{K_b}{C}} \quad \Rightarrow \quad \dfrac{\alpha_2}{\alpha_1} = \sqrt{\dfrac{C_1}{C_2}} = 2 \quad \Rightarrow \quad \dfrac{C_1}{C_2} = 4 = \dfrac{V_2}{V_1} \quad \Rightarrow V_2 = 4V_1 = \mathbf{200\ mL}$

435. $\because\ \mathrm{S}^{2-}$ hydrolysed completely into HS^- : $\mathrm{S}^{2-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HS}^- + \mathrm{OH}^-$

$$K_h = \frac{K_w}{K_{a_2}} = 1 = \frac{[\mathrm{HS}^-]^2}{[\mathrm{S}^{2-}]}$$

$$\Rightarrow \qquad [\mathrm{S}^{2-}] = [\mathrm{HS}^-]^2 = (6.7 \times 10^{-10})^2 = 4.489 \times 10^{-19}$$

$$\Rightarrow \qquad K_{sp} = [\mathrm{Pb}^{2+}][\mathrm{S}^{2-}] = \mathbf{3 \times 10^{-28}}$$

436. (a) $K_a = \dfrac{C\alpha^2}{1-\alpha} \quad \Rightarrow \quad \alpha = 0.19$ and $[\mathrm{H}^+] = 3 \times 10^{-3}\,\alpha \quad \Rightarrow \quad \mathrm{pH} = \mathbf{3.235}$

(b) $K = \dfrac{K_a(\mathrm{HL})}{K_{a_1}(\mathrm{H_2CO_3})} = \dfrac{1.4 \times 10^{-4}}{4.5 \times 10^{-7}} = \mathbf{311.11}$

(c) (i) $\mathrm{HCO_3^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2CO_3} + \mathrm{OH}^-$: $\mathrm{K}_h = \dfrac{K_w}{K_{a_1}} = \dfrac{[\mathrm{OH}^-]^2}{C} \qquad \Rightarrow \quad \mathrm{pH} = 11.35$

(ii) $\mathrm{HL} + \underset{0.024\,-\,3\times10^{-3}}{\mathrm{HCO_3^-}} \rightleftharpoons \underset{3\times10^{-3}}{\mathrm{H_2CO_3}} + \mathrm{L}^-$

$\because$ K is very high, all HL will be neutralized.

$$\Rightarrow \qquad K_{a_1} = 4.5 \times 10^{-7} = \frac{[\mathrm{H}^+][\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]}$$

$$\Rightarrow \qquad [\mathrm{H}^+] = 6.428 \times 10^{-8} \quad \text{and} \quad \mathrm{pH} = \mathbf{7.2.}$$

(d) $$K_{a_1} = 4.5 \times 10^{-7} = 10^{-7}\,\frac{(0.022 - x)}{x} \quad \Rightarrow \quad x = \mathbf{4 \times 10^{-3}}$$

(e) $$\mathrm{CaCO_3}(s) \rightleftharpoons \underset{S}{\mathrm{Ca}^{2+}} + \underset{S}{\mathrm{CO_3^{2-}}}$$

$$\mathrm{H_2O} + \underset{S\,-\,x}{\mathrm{CO_3^{2-}}} \rightleftharpoons \underset{x}{\mathrm{HCO_3^-}} + \underset{x}{\mathrm{OH}^-}$$

$$K_h = \frac{K_w}{K_{a_2}} = 2.12 \times 10^{-4} = \frac{x^2}{S - x} \qquad \Rightarrow \qquad S - x = 3.73 \times 10^{-5}$$

Also, $x = \mathbf{8.91 \times 10^{-5}}$

$\Rightarrow$ $K_{sp} = S(S-x) = 1.265 \times 10^{-4} \times 3.73 \times 10^{-5} = \mathbf{4.7 \times 10^{-9}}$

(f) For $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

$$K_h = \frac{K_w}{K_{a_2}} = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = 2.12 \times 10^{-4}$$

Substituting $[OH^-]$ and $[HCO_3^-]$, $[CO_3^{2-}] = 2.6 \times 10^{-5}$

$\Rightarrow$ $K_{sp} = 4.7 \times 10^{-9} = [Ca^{2+}][CO_3^{2-}] \Rightarrow [Ca^{2+}] = \mathbf{1.8 \times 10^{-4}\ M}$

437. Let x m mol acid (HA) is present in its 1.7 g.

$\Rightarrow$ m mol of salt $= x$ m mol NaA

m mol of NaOH left unreacted $= 10 - x$

Now,
$$\begin{array}{lcccc} & A^- + H_2O & \rightleftharpoons & HA + & OH^- \\ \text{m mols} & x-y & & y & 10-x+y \end{array}$$

$$K_h = \frac{K_w}{K_a} = 5 \times 10^{-5} = \frac{y(10-x+y)}{x-y} \qquad \ldots\text{(i)}$$

Given, $[OH^-] = 1.58 \times 10^{-4} = \dfrac{10-(x-y)}{100} \Rightarrow x - y = 9.9842$

Substituting in Eq. (i) yields $y = 3.16 \Rightarrow x = 13.144$

$$M = \frac{1.7}{13.144 \times 10^{-3}} = \mathbf{129.33}$$

438. $K_{sp} = 4S^3 = 1.58 \times 10^{-11}$. Also HCl is limiting reagent.

$\Rightarrow$ $[Mg^{2+}] = \frac{1}{2}[HCl] = 0.05$

$\Rightarrow$ $K_{sp} = [Mg^+][OH^-]^2 \Rightarrow [OH^-] = 1.76 \times 10^{-5}$

$pOH = 4.75 \Rightarrow pH = \mathbf{9.25}$

439. $[H_2CO_3] = 0.0343 \times \dfrac{440}{10^6} = 1.5 \times 10^{-5}$

Also, $K_a = \dfrac{C\alpha^2}{1-\alpha}$

Solving; $\alpha = 0.154 \Rightarrow [H^+] = C\alpha \Rightarrow pH = \mathbf{5.63}$

440. (a) m mol of HCl consumed $= 5 - 2.0265 = 2.9735 = m$ mol of NH_3

$\Rightarrow$ $m\%\ N = \dfrac{2.9735 \times 14 \times 10^{-3}}{0.2515} \times 100 = \mathbf{16.55}$

(b) 0.00 mL NaOH : $[H^+] = \dfrac{2.0265}{50} \Rightarrow pH = 1.39$

9.65 mL NaOH : m mol of HCl left $= 2.0265 - 9.65 \times 0.1050 = 1.01325$

$$[H^+] = \frac{1.01325}{50} \quad \Rightarrow \quad pH = 1.69$$

19.3 mL NaOH : No HCl left.

Now, $$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

$$K_h = \frac{K_w}{K_b} = \frac{[H^+]^2}{C}$$

$$\Rightarrow \qquad [H^+] = \sqrt{K_h C} = 5.8 \times 10^{-6} \quad \Rightarrow \quad pH = 5.23$$

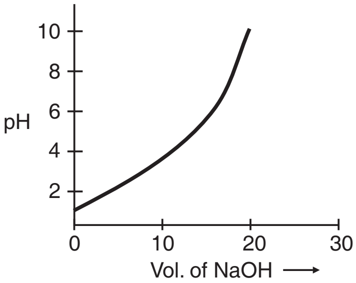
On adding 28.95 mL NaOH : m mol of $NH_4^+ = 2.9735 - 1.01325 = 1.96$

$$m \text{ mol of } NH_4OH = 1.01325$$

$$pOH = pK_b + \log \frac{1.96}{1.01325} = 5.04$$

$$\Rightarrow \qquad pH = \mathbf{8.96}$$

(c)



(d) pH range = 4.23 − 6.23

(e) $$m \text{ mol of N} = 32.5 \times 0.101 = 3.2825$$

$$M = \frac{0.2345}{3.2825} \times 1000 = 71.44$$

441. At end point, $[Ag^+] = \sqrt{K_{sp}\,(AgCl)} = 1.58 \times 10^{-5}$

$$[CrO_4^{2-}] = \frac{1.8 \times 10^{-12}}{(1.58 \times 10^{-5})^2} = \mathbf{7.3 \times 10^{-3}\ M}$$

442. $pOH = 5 - \log 2 + \log \frac{0.2}{0.4} = 4.4 \qquad \Rightarrow \quad [OH^-] = 4 \times 10^{-5}$ M

After adding Ca^{3+}, total volume = 100 mL $\Rightarrow$ $[OH^-] = 2 \times 10^{-5}$ M

$$K_{sp} = 10^{-19} = [La^{3+}][OH^-]^3 \qquad \Rightarrow \quad [La^{3+}] = 1.25 \times 10^{-5}$$

$\Rightarrow$ m mol of La^{3+} in solution $= 1.25 \times 10^{-3}$

m mol of La^{3+} precipitated $= 50 \times 10^{-4} - 1.25 \times 10^{-3} = 3.75 \times 10^{-3}$ % La^{3+} precipitated = 75.

443.

$$\underset{S-x}{\mathrm{Al^{3+}}} + \mathrm{H_2O} \rightleftharpoons \underset{x}{\mathrm{Al(OH)^{2+}}} + \mathrm{H^+} \qquad K_a = \frac{x[\mathrm{H^+}]}{S-x} \qquad \ldots\text{(i)}$$

$$\underset{S-y}{\mathrm{PO_4^{3-}}} + \mathrm{H_2O} \rightleftharpoons \mathrm{HPO_4^{2-}} + \mathrm{OH^-} \qquad K_b = \frac{y[\mathrm{OH^-}]}{S-y} \qquad \ldots\text{(ii)}$$

Also, $K_{sp} = (S-x)(S-y) = 10^{-20}$ …(iii)

Multiplying Eqs. (i) and (ii)

$$\frac{xy([\mathrm{H^+}][\mathrm{OH^-}])}{(S-x)(S-y)} = K_aK_b = 5\times10^{-7} \qquad \Rightarrow \qquad xy = 5\times10^{-13}$$

Now, solving for S: $S = \mathbf{7\times 10^{-7}}$.

444. (a) $\underset{0.2}{\mathrm{Mg^{2+}}} + \underset{0.2}{2\mathrm{OH^-}} \longrightarrow \mathrm{Mg(OH)_2}(s)$. At the end of reaction, $\mathrm{Mg^{2+}} = 0.1$ mol

$$K_{sp} = 1.6\times10^{-12} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 \quad \Rightarrow \quad [\mathrm{OH^-}] = 4\times10^{-6} \quad \Rightarrow \quad \mathrm{pH} = \mathbf{8.6}$$

(b) $\underset{0.1}{\mathrm{Mg^{2+}}} + \underset{0.04}{2\mathrm{OH^-}} \longrightarrow \mathrm{Mg(OH)_2}(s)$ At the end, $[\mathrm{Mg^{2+}}] = 0.1 - \dfrac{0.04}{2} = 0.08$

$\Rightarrow \quad 1.6\times10^{-12} = 0.08\times[\mathrm{OH^-}]^2 \quad \Rightarrow \quad [\mathrm{OH^-}] = 4.47\times10^{-6} \quad \Rightarrow \quad \mathrm{pH} = \mathbf{8.65}$

(c) $\underset{0.02}{\mathrm{Mg(OH)_2}} + \underset{0.04}{2\mathrm{HCl}} \longrightarrow \underset{0.02}{\mathrm{Mg^{2+}}} + 2\mathrm{Cl^-} + 2\mathrm{H_2O}$

$$[\mathrm{Mg^{2+}}] = 0.1 + 0.02 = 0.12\ \mathrm{M} \qquad \Rightarrow \quad 1.6\times10^{-12} = 0.12[\mathrm{OH^-}]^2$$

$$\Rightarrow \qquad [\mathrm{OH^-}] = 3.65\times10^{-6}$$

$$\mathrm{pH} = \mathbf{8.56}$$

445. The precipitate exchange equilibrium is:

$$\mathrm{PbSO_4} + \mathrm{S^{2-}} \rightleftharpoons \mathrm{PbS} + \mathrm{SO_4^{2-}} \qquad K = \frac{[\mathrm{SO_4^{2-}}]}{[\mathrm{S^{2-}}]} = 6.4\times10^{18}$$

Also for $\mathrm{H_2S}$: $K_a = 10^{-21} = \dfrac{[\mathrm{H^+}]^2[\mathrm{S^{2-}}]}{[\mathrm{H_2S}]} \quad \Rightarrow \quad [\mathrm{S^{2-}}] = 10^{-22} \quad \Rightarrow \quad [\mathrm{SO_4^{2-}}] = 6.4\times10^{-4}$

Hence, $[\mathrm{Pb^{2+}}]$ present $= 2.5\times10^{-5}$ M

Initial $[\mathrm{Pb^{2+}}] = 1.26\times10^{-4}$ M $\Rightarrow$ moles of PbS precipitated $= 10^{-4}$

$$m(\mathrm{PbS}) = \mathbf{23.8\ mg.}$$

446.

$$M(\text{urea}) = \frac{1060\times2.3}{6000} = 0.4$$

and

$$[\mathrm{H_2S{-}CO{-}NH_3^+}] = \frac{K_bC}{[\mathrm{OH^-}]} = \mathbf{2.68\times 10^{-7}}$$

447. Using K_{sp} (AgCl), $\Delta G°$ of $\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) = +55.33$ kJ

Now, $55.33\ \mathrm{kJ/mol} = G°_f\,(\mathrm{Ag^+}) - 131 + 110$

$\Rightarrow \qquad G°_f\,(\mathrm{Ag^+}) = +\ 76.33$ kJ

For Ag_2SO_4 : $$Ag_2SO_4(s) \rightleftharpoons 2Ag^+ + SO_4^{2-}$$

$$\Delta G^\circ\,(\text{ionization}) = 2\times 76.33 - 742 + 618.5 = 29.16 = -RT\ln K_{sp}.$$

$\Rightarrow$ $$K_{sp} = 7.73\times 10^{-6} = [Ag^+]^2[SO_4^{2-}]$$

$\Rightarrow$ $$[Ag^+] = \text{Solubility} = \mathbf{8.8\times 10^{-2}\ M}$$

448. $$HOCN \rightleftharpoons H^+ + OCN^- \qquad K_a = \frac{(1.77\times 10^{-3})^2}{C} = \frac{3.16\times 10^{-6}}{C}$$

After adding 100 mL 0.05 M HOCN, $[HOCN] = \dfrac{C+0.05}{2}$

$\Rightarrow$ $$K_a = \frac{2\times 10^{-5}}{C+0.05} = \frac{3.16\times 10^{-6}}{C};\quad \text{Solving}\quad C = \mathbf{0.009\ M.}$$

449. Mass of sulphur $= \dfrac{10^6\times 2.5}{100} = 2.5\times 10^4$ g

Moles of H_2SO_3 produced = 781.25

Volume of rain-water $= 5.2\times 10^7$ L. $\Rightarrow$ $[H_2SO_3] = 1.5\times 10^{-5}$ M

Such a low concentration of acid indicate $\alpha \approx 1$.

$\Rightarrow$ $$pH = -\log(1.0\times 10^{-5}) = \mathbf{4.8}$$

450. $$[NH_3] = \frac{[OH^-]^2}{K_b} = 0.0158 \;\Rightarrow\; \text{moles of Mg} = \frac{3}{2}\times 0.0158 = 0.0237$$

$$m = 0.5688\text{ g} \quad\text{and}\quad \%\text{ purity} = \mathbf{56.88}$$

451. The balanced equation for reaction between Br_2 and SO_2 is :

$$Br_2 + \underset{0.01}{SO_2} + 2H_2O \longrightarrow \underset{0.02}{2HBr} + \underset{0.01}{H_2SO_4}$$

Now, $$H_2SO_4 \longrightarrow \underset{0.03+x}{H^+} + \underset{0.01-x}{HSO_4^-}$$

$$\underset{0.01-x}{HSO_4^-} \rightleftharpoons \underset{0.03+x}{H^+} + \underset{x}{SO_4^{2-}}$$

$$K_{a_2} = 10^{-2} = \frac{x(0.03+x)}{0.01-x} \;\Rightarrow\; x = 2.36\times 10^{-3}$$

$$[H^+] = 3.236\times 10^{-2} \quad\text{and}\quad pH = \mathbf{1.49}$$

452. (a) Since, Q forms precipitate with both X and Y, it must be K_2CO_3 because Ag_2CO_3 and $BaCO_3$ are insoluble salts.

(b) K_2CO_3 on mixing with $Pb(NO_3)_2$ will give precipitate $PbCO_3$ but no precipitate will be formed if K_2CO_3 is combined with NaCl solution. Therefore, R is $Pb(NO_3)_2$ and S is NaCl.

(c) If X forms a precipitate with S(NaCl) but not with $R = [Pb(NO_3)_2]$, it must be $AgNO_3$. On the other hand if Y forms precipitate only with Q but not with R and S, it must be $BaCl_2$.

453. Let x mL of acid is taken, then volume of salt solution taken $= 20 - x$. Now, applying Henderson's equation:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} \quad\Rightarrow\quad 4.7 = 4.7 + \log\frac{0.1(20-x)}{0.15\,x}$$

$\Rightarrow$ $2 - 0.1\,x = 0.15\,x$ and $x = 8$ mL, volume of salt solution $= 12$ mL.

454. Let x mL of acetic acid taken, volume of base taken $= 50 - x$

m mol of acid $= 0.15\,x$, m mol of base $= (50 - x)\,0.1$

$\Rightarrow$ m mol of salt formed $= 0.1(50 - x)$, m mol of acid left unreacted $= 0.15\,x - 0.1(50 - x)$

Applying Henderson's equation:

$$4.7 = 4.7 + \log\frac{0.1(50-x)}{0.15\,x - 0.1(50-x)} \quad\Rightarrow\quad \frac{5 - 0.1\,x}{0.25\,x - 5} = 1 \quad\Rightarrow\quad x = 28.6\text{ mL}$$

Volume of base required = **21.4 mL**.

455. The balanced chemical reaction involved in precipitation reaction is:

	$3\text{Ba(NO}_3)_2(s)$	$+\,2\text{H}_3\text{PO}_4 \longrightarrow$	$\text{Ba}_3(\text{PO}_4)_2(s)$	$+\,6\text{HNO}_3(aq)$
m mol (Initial) :	6.13	3	0	0
m mol (Final) :	1.63	0	1.5	9

pH of solution will be mainly due to HNO_3.

$$\Rightarrow \quad [\text{HNO}_3] = \frac{9}{2000} = 4.5\times10^{-3} \quad\Rightarrow\quad \text{pH} = -\log(4.5\times10^{-3}) = \mathbf{2.35}$$

456. The minimum concentrations of sulphide ion required for precipitation of these metals are:

MnS : $[\text{S}^{2-}] = K_{sp}/[\text{Mn}^{2+}] = 2.5\times10^{-8}$ M

CoS : $[\text{S}^{2-}] = K_{sp}/[\text{Co}^{2+}] = 4\times10^{-19}$ M

Ag_2S : $[\text{S}^{2-}] = K_{sp}/[\text{Ag}^+]^2 = 6.3\times10^{-46}$ M

Now, for H_2S : $\quad \text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$

$$K_a = K_{a_1}\times K_{a_2} = 10^{-21} = \frac{[\text{H}^+]^2\,[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$$\Rightarrow \quad [\text{H}^+]^2\,[\text{S}^{2-}] = 10^{-22}.$$

Since, minimum S^{2-} ion is required for Ag^+, corresponding $[\text{H}^+]$:

$$[\text{H}^+]\text{(to begin precipitation of Ag}_2\text{S} = \sqrt{10^{-22}/6.3\times10^{-46}} = 3.98\times10^{11}$$

i.e., to prevent precipitation of Ag_2S, minimum $[\text{H}^+] = 3.98\times10^{11}$ and at a $[\text{H}^+]$ below to this value Ag_2S will precipitate. Such a large concentration of $[\text{H}^+]$ is unachievable, Ag_2S will precipitate at any practical concentration of H^+.

Limiting $[\text{H}^+]$ required to begin precipitation of CoS:

$$[\text{H}^+] = \sqrt{10^{-22}/4\times10^{-19}} = 1.58\times10^{-2}\text{ M} \quad\Rightarrow\quad \text{pH} = 1.8$$

i.e., at $[\text{H}^+]$ above 1.58×10^{-2} M $[\text{S}^{2-}]$ will be less than 4×10^{-19} M and CoS will not precipitate.

Limiting $[\text{H}^+]$ required to begin precipitation of MnS:

$$[H^+] = \sqrt{\frac{10^{-22}}{2.5 \times 10^{-8}}} = 6.32 \times 10^{-8} \quad \Rightarrow \quad pH = 7.2$$

i.e., at pH below 7.2, MnS will not precipitate.

pH range : At pH below 1.8, only Ag_2S will precipitate.

At $pH > 1.8$ but < 7.2, only CoS will precipitate.

At pH > 7.2, MnS will start precipitating.

457. The cell reactions are:

$$\begin{array}{lll} H_2 \longrightarrow 2H^+ + 2e & & \\ 2Ag^+ + 2e \longrightarrow 2Ag & & E^\circ = 0.8\text{ V} \\ \hline H_2 + 2Ag^+ \longrightarrow 2H^+ + 2Ag & & E^\circ = 0.8\text{ V} \end{array}$$

$$E = 0.589 = 0.8 - \frac{0.059}{2} \log \frac{[H^+]^2}{[Ag^+]^2} \quad \Rightarrow \quad [Ag^+] = 2.65 \times 10^{-4}$$

$$K_{sp} = [Ag^+]^2 [C_2O_4^{2-}] = 4S^3 \quad \text{and} \quad 2S = 2.65 \times 10^{-4}$$

$$\Rightarrow \quad S = 1.325 \times 10^{-4} \quad \Rightarrow \quad K_{sp} = 4S^3 = 9.3 \times 10^{-12}.$$

458. For the dissolution reaction:

$$\underset{x}{Zn(OH)_2} + \underset{0.1-2x}{2OH^-} \rightleftharpoons \underset{x}{Zn(OH)_4^{2-}} \qquad K = K_{sp} \cdot K_f = 0.588$$

$$K = 0.588 = \frac{x}{(0.1-2x)^2} = \frac{x}{10^{-2} - 4x^2 - 0.4x}$$

Solving: $x = 0.0048$ M, *i.e.,* $0.0048 \times 250 = 1.2$ m mol $Zn(OH)_2$ dissolved.

mmol of $Zn(OH)_2$ taken initially $= \frac{150}{99} = 1.515$

$\Rightarrow$ mmol $Zn(OH)_2$ left undissolved $= 1.515 - 1.2 = 0.315$

$\Rightarrow$ mass of $Zn(OH)_2$ left undissolved = **31.185 mg**

459. Reaction for dissolution of AgCl in ammonia is :

$$\underset{x}{AgCl} + \underset{0.1-2x}{2NH_3} \rightleftharpoons \underset{x}{Ag(NH_3)_2^+} + \underset{0.1+x}{Cl^-} \qquad K = K_{sp} \cdot K_f = 4 \times 10^{-3}$$

$$\Rightarrow \quad K = 4 \times 10^{-3} = \frac{x(0.1+x)}{(0.1-2x)^2} = \frac{0.1x + x^2}{10^{-2} + 4x^2 - 0.4x}$$

$$\Rightarrow \quad 0.1x + x^2 = 4 \times 10^{-5} + 1.6 \times 10^{-2} x^2 - 1.6x \times 10^{-3}$$

$$\text{or} \quad 0.984x^2 + 0.1016x - 4 \times 10^{-5} = 0$$

$$\Rightarrow \quad x = \frac{-0.1016 + \sqrt{(0.1016)^2 + 16 \times 10^{-5} (0.984)}}{2 \times 0.984} = 3.92 \times 10^{-4}\text{ M}$$

460. The order in which halide ions should be added is : Cl^- than Br^- than I^-.

When Cl^- is added to 0.1 M, $[Ag^+] = \dfrac{K_{sp}\,(AgCl)}{0.10} = 1.8 \times 10^{-9}$ M

When Br^- is added to 0.1 M, $[Ag^+] = \dfrac{K_{sp}\,(AgBr)}{0.10} = 5 \times 10^{-12}$ M

When I^- is added to 0.1 M, $[Ag^+] = \dfrac{K_{sp}\,(AgI)}{0.10} = 8.4 \times 10^{-16}$

The $[Ag^+]$ in equilibrium with AgCl in 0.1 M Cl^- is 1.8×10^{-9} M, which is more than 5×10^{-12} M ($[Ag^+]$ required to initiate precipitation of AgBr when $[Br^-] = 0.1$ M). Hence, the solution containing $[Ag^+] = 1.8 \times 10^{-9}$ in equilibrium with AgCl in 0.1 M Cl^-, will give precipitate of AgBr when Br^- is added to 0.1 M. Had we added Br^- to 0.1 M before Cl^-, $[Ag^+]$ would have been 5×10^{-12} M and on making this solution 0.1 M in Cl^- in the subsequent step would not have yielded AgCl precipitate. Hence the order.

461. As we know, a buffer solution shows its best buffering action near to its ionization constant value. Therefore, the above buffer can best be prepared by taking $H_2PO_4^-$ and HPO_4^{2-}.

(a) $\mathrm{pH} = \mathrm{p}K_2 + \log \dfrac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7 \;\Rightarrow\; \log \dfrac{[HPO_4^{2-}]}{[H_2PO_4^-]} = -0.22$ and $\dfrac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.6$

(b) In 50 mL buffer, $[H_2PO_4^-] = 0.10\text{ M} = 5$ m mol $\Rightarrow$ $[HPO_4^{2-}] = 0.06\text{ M} = 3$ m mol

m mol of NaOH added $= 20 \times 0.1 = 2$

This added NaOH will neutralize 2.0 m mol of $H_2PO_4^-$

$$\Rightarrow \qquad \text{m mol of } H_2PO_4^- = 5 - 2 = 3$$

$$\text{m mol of } HPO_4^{2-} = 3 + 2 = 5$$

$$\mathrm{pH} = \mathrm{p}K_2 + \log \tfrac{5}{3} = 7.44$$

462. From the titration curve it is concluded that the 1st end point correspond to completion of the following reaction :

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

$\Rightarrow$ m mol of HCl consumed $= 11 \times 0.115 = 1.265 =$ m mol of Na_2CO_3

$\Rightarrow$ mass of $Na_2CO_3 = 1.265 \times 106 \times 10^{-3} = 0.134$ g

Second end point corresponds to the following reaction :

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

Volume of HCl consumed $= 35 - 11 = 24$ mL

Out of this 24 mL, 11 mL HCl would be consumed by $NaHCO_3$ produced from Na_2CO_3.

$\Rightarrow$ m mol of original $NaHCO_3 = (24 - 11)0.115 = 1.495$

$\Rightarrow$ mass of $NaHCO_3 = 1.495 \times 84 \times 10^{-3} = 0.1256$ g

$\Rightarrow$ *m*% of $Na_2CO_3 = \dfrac{0.134}{0.5} \times 100 = 26.8$

$\Rightarrow$ m% of $NaHCO_3 = \dfrac{0.1256}{0.5} \times 100 = 25.12$

m% of KCl = 48.08%.

463. $K_{sp} = 10^{-3} = [\mathrm{Ca}^{2+}][\mathrm{H_2PO_4^-}]^2 \quad \Rightarrow \quad [\mathrm{H_2PO_4^-}] = \sqrt{\dfrac{10^{-3}}{0.15}} = 8.165 \times 10^{-2}\ \mathrm{M}$

i.e., to prevent precipitation, $[\mathrm{H_2PO_4^-}]$ should be less than 8.165×10^{-2} M.

Also $$\mathrm{H_3PO_4} \rightleftharpoons \mathrm{H^+ + H_2PO_4^-}$$

$$K_{a_1} = \frac{[\mathrm{H^+}]\,[\mathrm{H_2PO_4^-}]}{[\mathrm{H_3PO_4}]} \quad \Rightarrow \quad [\mathrm{H^+}] = \frac{K_{a_1}[\mathrm{H_3PO_4}]}{[\mathrm{H_2PO_4^-}]} = \frac{7 \times 10^{-3} \times 0.25}{8.165 \times 10^{-2}}$$

$$= 2.14 \times 10^{-2}\ \mathrm{M}$$

i.e., to prevent precipitation, $[\mathrm{H^+}] > 2.14 \times 10^{-2}$, $\mathrm{pH} = 1.66$.

i.e., at pH below 1.66, no precipitation of $\mathrm{Ca(H_2PO_4)_2}$ will occur.

464. (a) Addition of $\mathrm{HNO_3}$ will neutralize $\mathrm{OH^-}$ in solution driving solubility equilibrium in forward direction and this will increase concentration of $\mathrm{Fe^{3+}}$ in solution. Also, as $\mathrm{Fe^{3+}}$ comes in solution due to neutralization of $\mathrm{OH^-}$ with $\mathrm{HNO_3}$, it will form complex with $\mathrm{SCN^-}$ present in solution due to high K_f value, but still, the overall effect will be increase in concentration of $\mathrm{Fe^{3+}}$ in solution.

(b) Addition of NaOH will drive both equilibrium (i) and (iii) in backward direction and it will decrease concentration of $\mathrm{Fe^{3+}}$ ion in solution.

(c) Addition of NaSCN will drive equilibrium (ii) in forward direction and concentration of $\mathrm{Fe^{3+}}(aq)$ will decrease.

(d) Addition of $\mathrm{Fe(OH)_3}(s)$ will have no effect on $\mathrm{Fe^{3+}}(aq)$ concentration since active mass of former is unity.

465. The dissociation equilibrium of the complex is:

$$[\mathrm{Cu(CN)_4}]^{2-} \rightleftharpoons \mathrm{Cu^{2+}}(aq) + 4\mathrm{CN^-}(aq)$$

As strong acid is added, following equilibrium will be established parallely :

$$\mathrm{H^+ + CN^-} \rightleftharpoons \mathrm{HCN} \quad K = \frac{1}{K_a} = 1.67 \times 10^9$$

The above equilibrium will lie predominantly to right, removing most of the cyanide ion from 1st equilibrium. This will increase concentration of $\mathrm{Cu^{2+}}$ in solution.

466. m mol of NaCl added $= \dfrac{4 \times 1000}{58.5} = 68.38$

m mol of $\mathrm{Ag^+}$ in solution $= 25$

Now: $$\underset{x-0.2}{\mathrm{AgCl}(s) + 2\mathrm{NH_3}(aq)} \rightleftharpoons \underset{0.1}{\mathrm{Ag(NH_3)_2^+}(aq)} + \underset{0.2735}{\mathrm{Cl^-}(aq)}$$

$$K = K_{sp} \cdot K_f = 2 \times 10^{-3} = \frac{2.735 \times 10^{-2}}{x - 0.2}$$

$\Rightarrow$ $$x = 13.875\ \mathrm{M}$$

468. The solubility equilibrium is:

$$K = K_{sp} \cdot K_f$$

$$\mathrm{Co(OH)_3 + 4SCN^- \rightleftharpoons Co(SCN)_4^- + 3OH^-} \quad K = 1.6\times10^{-41}$$

At the given conditions : $\quad 1-0.4 \qquad\qquad 0.1 \qquad 10^{-7}$

$$Q = \frac{(0.1)\,(10^{-7})^3}{(0.6)^4} = 7.716\times10^{-22} >> K(1.6\times10^{-41})$$

Therefore, precipitation must occur.

469. $[\mathrm{OH^-}]$ of buffer $= 2\times10^{-5} \quad\Rightarrow\quad [\mathrm{H^+}] = 5\times10^{-10}$

Now: $\quad \mathrm{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}} \qquad K_{a_2} = 4.7\times10^{-11} = \dfrac{5\times10^{-10}x}{0.1-x}$

$\quad 0.1-x \qquad 5\times10^{-10} \qquad x \qquad\qquad$ Solving : $x = 8.6\times10^{-3}$ M

Now, on adding equal volume of 0.1 M $\mathrm{Ba^{2+}}$ ion, concentration of $\mathrm{Ba^{2+}}$ ion in final solution will become 0.05 M and that of carbonate ion will become 4.3×10^{-3} M.

$\Rightarrow \qquad K_{\mathrm{IP}} = [\mathrm{Ba^{2+}}][\mathrm{CO_3^{2-}}] = 2.15\times10^{-4} >> K_{sp}$, precipitation will occur.

470. For the equilibrium : $\quad \mathrm{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}}$

$$K_{a_2} = 4.7\times10^{-11} = \frac{[\mathrm{H^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 10^{-8}\,\frac{[\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} \quad\Rightarrow\quad [\mathrm{HCO_3^-}] = 213\,[\mathrm{CO_3^{2-}}]$$

Also $\qquad [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] = 0.1 \quad\Rightarrow\quad [\mathrm{CO_3^{2-}}] = 4.67\times10^{-4}$

$$\Rightarrow \qquad [\mathrm{Co^{2+}}] = \frac{1.4\times10^{-13}}{4.67\times10^{-4}} = 3\times10^{-10}\ \mathrm{M}$$

$$[\mathrm{Co^{3+}}] = \frac{1.6\times10^{-44}}{4.67\times10^{-4}} = 3.4\times10^{-41}\ \mathrm{M}$$

471. The hydrolysis reaction is :

$$\mathrm{C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_3OH + H^+}$$

$$C(1-\alpha) \qquad\qquad\qquad C\alpha \qquad\quad C\alpha$$

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{5\times10^{-10}} = 2\times10^{-5}$$

Also $K_h = \dfrac{C\alpha^2}{1-\alpha} \quad\Rightarrow\quad 2\times10^{-5} = \dfrac{10^{-3}\alpha^2}{1-\alpha} \quad\Rightarrow\quad \alpha^2 + 2\times10^{-2}\,\alpha - 2\times10^{-2} = 0$

$$\alpha = \frac{-2\times10^{-2} + \sqrt{(2\times10^{-2})^2 + 8\times10^{-2}}}{2} = 0.13$$

$$\Rightarrow \qquad [\mathrm{H^+}] = C\alpha = 10^{-3}\times0.13 = 1.3\times10^{-4}$$

$$\mathrm{pH} = \mathbf{3.88}$$

472. As, acetic acid is added, it will react quantitatively with $\mathrm{OI^-}$ as:

$$\mathrm{CH_3COOH + OI^- \rightleftharpoons CH_3COO^- + HOI}$$

	$\mathrm{CH_3COOH}$	$\mathrm{OI^-}$	$\mathrm{CH_3COO^-}$	HOI
m moles:	1	2	0	0
	0	1	1	1

$$K = \frac{K_a\,[\text{acetic acid}]}{K_a\,(\text{HOI})} = 10^6 > \text{very large value.}$$

Now the conjugate base of weaker acid (HOI) will hydrolyze predominantly as :

$$\text{OH}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOI} + \text{OH}^- \qquad K_h = \frac{K_w}{K_a} = 5\times10^{-4}$$

Concentration of OI^- left unreacted after reaction with $\text{CH}_3\text{COOH} = 5\times10^{-3}$

Concentration of HOI produced by reaction of CH_3COOH with $\text{IO}^- = 5\times10^{-3}$

Now, if x MIO^- is hydrolyzed then :

$$\underset{5\times10^{-3}-x}{\text{IO}^-} + \text{H}_2\text{O} \rightleftharpoons \underset{5\times10^{-3}+x}{\text{HOI}} + \underset{x}{\text{OH}^-}$$

$$K_h = 5\times10^{-4} = \frac{(5\times10^{-3}+x)x}{5\times10^{-3}-x} = \frac{5\times10^{-3}x + x^2}{5\times10^{-3}-x}$$

$$\Rightarrow \qquad x^2 + 5.5\times10^{-3}x - 2.5\times10^{-6} = 0$$

$$\Rightarrow \qquad x = \frac{-5.5\times10^{-3} + \sqrt{3.025\times10^{-5} + 10^{-5}}}{2} = 4.22\times10^{-4}$$

$$\Rightarrow \qquad \text{pOH} = 3.37 \quad \text{and} \quad \text{pH} = \mathbf{10.63}$$

473. The hydrolysis reaction is :

$$\underset{C(1-\alpha)}{\text{ClC}_6\text{H}_4\text{NH}_3^+} + \text{H}_2\text{O} \rightleftharpoons \underset{C\alpha}{\text{ClC}_6\text{H}_4\text{NH}_3\text{OH}} + \underset{C\alpha}{\text{H}^+} \qquad K_h = \frac{K_w}{K_b} = 2.5\times10^{-3}$$

$$K_h = 2.5\times10^{-3} = \frac{C\alpha^2}{1-\alpha} = \frac{10^{-2}\alpha^2}{1-\alpha} \quad \Rightarrow \quad \alpha^2 + 0.25\,\alpha - 0.25 = 0$$

and $$\alpha = \frac{-0.25 + \sqrt{0.0625+1}}{2} = 0.39 \qquad \text{(not negligible)}$$

$$\Rightarrow \qquad [\text{H}^+] = C\alpha = 3.9\times10^{-3} \quad \text{and} \quad \mathbf{pH = 2.4}$$

474. $$K_a = \frac{[\text{H}^+][\text{dnp}^-]}{[\text{dnp}]} = \frac{[\text{H}^+][25]}{75} = \frac{[\text{H}^+]}{3} \quad \Rightarrow \quad \text{pH}_1 = 3.48$$

when 75% ionized $$\frac{[\text{H}^+][75]}{25} = 1.1\times10^{-4}$$

$$\Rightarrow \qquad [\text{H}^+] = \frac{1.1\times10^{-4}}{3} \quad \Rightarrow \quad \text{pH} = \mathbf{4.53}$$

475. For $$\text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$$

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 \quad \Rightarrow \quad 1.5\times10^{-11} = 0.1[\text{OH}^-]^2$$

$$\Rightarrow \qquad [\text{OH}^-] = 1.224\times10^{-5}$$

This is the minimum concentration of OH^- required to begin the precipitation of Mg(OH)_2. Therefore, $[\text{OH}^-] \le 1.224\times10^{-5}$ M.

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \quad \Rightarrow \quad [NH_4^+] = \frac{2 \times 10^{-5} \times 0.1}{1.224 \times 10^{-5}} = 0.16\ \text{M}$$

i.e., to maintain $[OH^-]$ equal to 1.224×10^{-5} M or less, the concentration of ammonium ion in solution must be greater than or equal to 0.16 M.

476. The equilibria existing are:

$$\underset{}{BaSO_4(s)} \rightleftharpoons \underset{y}{Ba^{2+}(aq)} + \underset{x+y}{SO_4^{2-}(aq)}$$

$$SO_4^{2-} + H_2O \rightleftharpoons HSO_4^- + OH^- \quad K_b = \frac{K_w}{K_a} = 8.33 \times 10^{-13}$$

The above K_b value indicates that tendency of hydrolysis of SO_4^{2-} is very less.

Also, $$\underset{0.25-x}{HSO_4^-} \rightleftharpoons \underset{x}{H^+} + \underset{x+y}{SO_4^{2-}}$$

Here x M HSO_4^- is ionized and y M $BaSO_4$ dissolved.

$$\Rightarrow \quad K_{sp} = 10^{-10} = y(x+y) \quad \ldots(1)$$

$$K_a = 1.2 \times 10^{-2} = \frac{x(x+y)}{0.25-x} \quad \ldots(2)$$

$$\Rightarrow \quad 8.3 \times 10^{-9} = \frac{y(0.25-x)}{x} \quad \Rightarrow \quad x >> y \quad \text{and} \quad 1.2 \times 10^{-2} = \frac{x^2}{0.25-x}$$

Solving $x = 4.46 \times 10^{-3} \quad \Rightarrow \quad y = \frac{10^{-10}}{x+y} \approx \frac{10^{-10}}{x} = 2.24 \times 10^{-8}$ M

Solubility in water $= \sqrt{K_{sp}} = 10^{-5} \quad \Rightarrow \quad$ factor $= \frac{10^{-5}}{2.24 \times 10^{-8}} = \mathbf{446}$

477. Initial mmol of $Na_2CO_3 = 500 \times 0.1 = 50$

Now, let us assume that x mmol of HCl is added to adjust the desired pH. Then

$$\underset{50-x}{Na_2CO_3} + \underset{0}{HCl} \longrightarrow \underset{x}{NaHCO_3} + \underset{x}{NaCl}$$

The leftover Na_2CO_3 will hydrolyze to give the desired pH as :

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

$$K_h = \frac{K_w}{K_{a_2}} = 2 \times 10^{-4} = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = \frac{10^{-4}x}{50-x}$$

$$\Rightarrow \quad x = \frac{100}{3} = \frac{1}{3} \times V$$

$$\Rightarrow \quad V = 100\ \text{mL}$$

i.e., to prepare the desired solution, 100 mL of the given HCl will have to be added and finally solution will be diluted to 1000 mL.

478. $$Ag^{+} + 2CN^{-} \rightleftharpoons Ag(CN)_2^{-}$$

Initial (M) : 0.03 0.1

Final (M) : ≈ 0 $0.1 - 0.06$ 0.03

$$\Rightarrow \quad K_f = 2.5 \times 10^{18} = \frac{[Ag(CN)_2]^{-}}{[Ag^{+}][CN^{-}]^2} = \frac{0.03}{[Ag^{+}]\,[0.04]^2}$$

$$\Rightarrow \quad [Ag^{+}] = 7.5 \times 10^{-18}\ M$$

479. (a) For CaF_2 : $3.4 \times 10^{-11} = [Ca^{2+}][F^{-}]^2 = [Ca^{2+}](0.05)^2$

$\Rightarrow$ $[Ca^{2+}]$ required to begin precipitation of $CaF_2 = 13.6 \times 10^{-9}$ M

For $CaCO_3$: $9.5 \times 10^{-9} = [Ca^{2+}][CO_3^{2-}] = [Ca^{2+}][0.02]$

$\Rightarrow$ $[Ca^{2+}]$ required to begin precipitation of $CaCO_3 = 4.75 \times 10^{-7}$ N

i.e., higher concentration of Ca^{2+} is required to start precipitation of $CaCO_3$, CaF_2 will precipitate first.

(b) When $CaCO_3$ start precipitating, the required $[Ca^{2+}]$ is 4.75×10^{-7}. To commence simultaneous precipitation of CaF_2 and $CaCO_3$ at this stage, the minimum $[F^{-}]$ can be evaluated as:

$$3.4 \times 10^{-11} = 4.75 \times 10^{-7}\,[F^{-}]^2$$

$$\Rightarrow \quad [F^{-}] = 8.46 \times 10^{-3}\ M.$$

480. (a) For $$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq)$$

$$\Delta G^\circ\ (\text{at } 17^\circ C) = -RT \ln K_{sp} = -8.314 \times 290 \ln(7.47 \times 10^{-9}) = 45.1166\ kJ$$

and $$\Delta G^\circ\ (\text{at } 27^\circ C) = -RT \ln K_{sp} = -8.314 \times 300 \ln(1.4 \times 10^{-8}) = 45.1056\ kJ$$

Now $$\Delta G^\circ\ (\text{at } 17^\circ C) = 45116.6 = \Delta H^\circ - 290\,\Delta S^\circ \quad \ldots(i)$$

$$\Delta G^\circ\ (\text{at } 27^\circ C) = 45105.6 = \Delta H^\circ - 300\,\Delta S^\circ \quad \ldots(ii)$$

From Eqs. (i) and (ii), $11 = 10\,\Delta S^\circ \Rightarrow \Delta S^\circ = 1.1\ JK^{-1}$

Substituting, $\Delta S^\circ = 1.1$ in Eq. (i):

$$\Delta H^\circ = 45116.6 + 290 \times 1.1 = 45.4356\ kJ\ mol^{-1}$$

(b) $\Delta G^\circ\ (\text{at } 77^\circ C) = \Delta H^\circ - 350 \times 1.1 = 45.8206\ kJ = -RT \ln K_{sp}$

$$\Rightarrow \quad K_{sp} = 1.45 \times 10^{-7} = 4S^3 \quad \Rightarrow \quad S = \mathbf{3.3 \times 10^{-3}\ M}$$

481. Normality of solution $= \dfrac{2.54 \times 2}{159.5} = 0.0318$ N

$$\because \quad \Lambda_{eq} = \frac{K \times 1000}{N} \quad \Rightarrow \quad k \text{ (specific conductance)}$$

$$= \frac{91 \times 0.0318}{1000} = 2.89 \times 10^{-3}\ \Omega^{-1}cm^{-1}$$

Also $$\frac{1}{R} = k\left(\frac{A}{l}\right) \Rightarrow R = \frac{1}{k}\left(\frac{l}{A}\right) = \frac{1}{2.89 \times 10^{-3}}\left(\frac{1}{1}\right) = 346\ \Omega.$$

482. For a weak electrolyte:

$$\frac{\Lambda_c}{\Lambda_\infty} = \alpha = \frac{10}{238} = 0.042$$

For NH_3 :

$$\underset{C(1-\alpha)}{NH_3} + H_2O \rightleftharpoons \underset{C\alpha}{NH_4^+} + \underset{C\alpha}{OH^-}$$

$$K_b = \frac{C\alpha^2}{1-\alpha} = \frac{10^{-2}\ (0.042)^2}{1-0.042} = \mathbf{1.8 \times 10^{-5}}$$

483. The ionization reaction of acetic acid is:

$$\underset{C(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{C\alpha}{CH_3COO^-} + \underset{C\alpha}{H^+}$$

$$K_a = 2\times 10^{-5} = \frac{C\alpha^2}{1-\alpha} = \frac{10^{-2}\alpha^2}{1-\alpha}$$

$$\Rightarrow \quad \alpha^2 + 2\times 10^{-3}\alpha - 2\times 10^{-3} = 0$$

$$\Rightarrow \quad \alpha = \frac{-2\times 10^{-3} + \sqrt{4\times 10^{-6} + 8\times 10^{-3}}}{2} = 0.0437$$

Now $$\frac{\Lambda_c}{\Lambda_\infty} = 0.0437$$

$$\Rightarrow \quad \Lambda_c = 17.043\ \text{cm}^2\Omega^{-1}\text{eq}^{-1}$$

Also $$\Lambda_c = \frac{k \times 1000}{C}$$

$$\Rightarrow \quad k = \frac{\Lambda_c C}{1000} = \frac{17.043\times 0.01}{1000} = 1.704\times 10^{-4}\ \Omega^{-1}\text{cm}^{-1}.$$

484. $G = \frac{1}{R} = k\left(\frac{A}{l}\right) = k\cdot\frac{1}{K}$, where K is cell constant (l/A).

$$\Rightarrow \quad K = Rk = 25\times 0.0116 = 0.29\ \text{cm}^{-1}$$

For acetic, acid solution, $K = 0.29\ \text{cm}^{-1} = kR$

$$\Rightarrow \quad k(CH_3COOH) = \frac{0.29\ \text{cm}^{-1}}{1982\ \Omega} = 1.463\times 10^{-4}\ \Omega^{-1}\text{cm}^{-1}$$

$$\Rightarrow \quad \Lambda_m = \frac{k\times 1000}{C} = \frac{1.463\times 10^{-4}}{0.1}\times 1000 = 1.463\ \text{cm}^2\text{mol}^{-1}\Omega^{-1}.$$

485. Initially, only NaOH was present at 0.1 M.

$$\Rightarrow \quad \Lambda_m(\text{NaOH}) = \frac{k\times 1000}{C} = \frac{0.022\times 1000}{0.1} = 220\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}.$$

After adding equal volume of HCl, NaOH will be neutralized completely giving NaCl of concentration 0.05 (since volume is doubled, concentration of salt will be halved).

$$\Rightarrow \quad \Lambda_{\text{NaCl}} = \frac{0.0056 \times 1000}{0.05} = 112\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}.$$

On further adding HCl, no neutralization will occur and conductivity will be due to NaCl and HCl together. Now the concentrations of NaCl $= \frac{2}{3} \times 0.05$ and concentration of HCl $= \frac{2}{3} \times 0.05$ M.

Now :
$$k = k(\text{NaCl}) + k(\text{HCl}) = (\Lambda_{\text{NaCl}} + \Lambda_{\text{HCl}}) \times \frac{C}{1000}$$

$$\Rightarrow \quad \frac{1000 \times 0.017}{2 \times 0.05} \times 3 = 112 + \Lambda_{\text{HCl}}$$

$$\Rightarrow \quad \Lambda_{\text{HCl}} = 510 - 112 = 398\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

486. For NaCl solution :

$$\Lambda_m = \frac{k \times 1000}{C} = 126.5 \qquad \ldots\text{(i)}$$

Here the 1st objective is to determine k (specific conductance) of NaCl and then C(NaCl).

Also; conductance
$$G = \frac{1}{R} = k\left(\frac{A}{l}\right) = \frac{k}{K} \qquad \ldots\text{(ii)}$$

For KCl solution :
$$\Lambda_m = \frac{k \times 1000}{C}$$

$$\Rightarrow \quad k(\text{KCl}) = \frac{138.3 \times 0.02}{1000} = 2.766 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$$

Now from Eq. (ii),

$$K \text{ (cell constant)} = kR = 2.766 \times 10^{-3} \times 85 = 0.235\ \text{cm}^{-1}$$

Now; conductance of water

$$\Rightarrow \quad G_{\text{H}_2\text{O}} = \frac{1}{9200}$$

Conductance of
$$\text{NaCl}(aq) = G_{\text{NaCl}(aq)} = \frac{1}{7600}$$

$$\Rightarrow \text{Conductance due to NaCl alone} = \frac{1}{7600} - \frac{1}{9200} = 22.88 \times 10^{-6}\ \Omega^{-1}$$

$$\Rightarrow \quad k(\text{NaCl}) = GK = 22.88 \times 10^{-6}\ \Omega^{-1} \times 0.235\ \text{cm}^{-1} = 5.38 \times 10^{-6}\ \Omega^{-1}\text{cm}^{-1}$$

Substituting, in Eq. (i) :

$$126.5 = \frac{5.38 \times 10^{-6} \times 1000}{C}$$

$$\Rightarrow \quad C(\text{NaCl}) = 4.25 \times 10^{-5}\ \text{M}$$

$$\Rightarrow \quad \text{Volume of swimming pool} = \frac{\text{Number of moles of NaCl}}{\text{Molarity}} = \frac{500}{58.5 \times 4.25 \times 10^{-5}}$$

$$= \mathbf{2.011 \times 10^5\ L}$$

487. k (specific conductance) $= \dfrac{\Lambda C}{1000} = \dfrac{195 \times 0.05}{1000} = 9.7 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$

Conductance $(G) = \dfrac{1}{R} = k\left(\dfrac{A}{l}\right) = 9.7 \times 10^{-3} \times \dfrac{1.5}{0.5} = 0.0291\,\Omega^{-1}$

$\Rightarrow \quad R = 34.36\ \Omega = \dfrac{V}{I}$

$\Rightarrow \quad I = \dfrac{V}{R} = \dfrac{5}{34.36} = \mathbf{0.1455\ A.}$

488. Since, $\Lambda_{eq} = \dfrac{k \times 1000}{N} = \dfrac{K \times 1000}{RN}$ where K is cell constant.

$\Rightarrow \quad \Lambda_{\text{eq}}\,(\text{KCl}) = \dfrac{K \times 1000}{85 \times 0.02} = 138.3$

$\Lambda_{\text{eq}}\,(\text{PbCl}_2) = \dfrac{K \times 1000}{70\ N} = 106$

$\Rightarrow \quad \dfrac{138.3}{106} = \dfrac{70\ N}{85 \times 0.02} \quad \Rightarrow \quad N = 3.168 \times 10^{-2}$

$\Rightarrow$ Molarity of PbCl_2 in its saturated solution $= \dfrac{N}{2} = 1.58 \times 10^{-2}$

$\Rightarrow \quad K_{sp} = 4\,M^3 = 1.6 \times 10^{-6}.$