IONIC EQUILIBRIUM [JEE ADVANCED PREVIOUS YEAR SOLVED PAPER]

JEE Advanced

Single Correct Answer Type

1. An acidic buffer solution can be prepared by mixing the solutions of

a. ammonium acetate and acetic acid
b. ammonium chloride and ammonioum hydroxide
c. sulphuric acid and sodium sulphate
d. sodium chloride and sodium hydroxide.

(IIT-JEE 1981)

2. The pH of a 10^{-8} molar solution of HCl in water is

a. 8 **b.** −8
c. between 7 and 8 **d.** between 6 and 7

(IIT-JEE 1981)

3. Of the given anions, the strongest Bronsted base is

a. ClO^- **b.** ClO_2^- **c.** ClO_3^- **d.** ClO_4^-

(IIT-JEE 1981)

4. At 90°C, pure water has $[H_3O^+]$ 10^{-6} mole $litre^{-1}$. What is the value of K_w at 90°C?

a. 10^{-6} **b.** 10^{-12} **c.** 10^{-14} **d.** 10^{-8}

(IIT-JEF 1981)

5. The precipitate of

$CaF_2(K_{sp} = 1.7 \times 10^{-10})$

is obtained equal volume of the following are mixed

a. 10^{-4} M Ca^{2+} + 10^{-4} M F^-
b. 10^{-2} M Ca^{2+} + 10^{-3} M F^-
c. 10^{-5} M Ca^{2+} + 10^{-3} M F^-
d. 10^{-3} M Ca^{2+} + 10^{-5} M F^-

(IIT-JEE 1982)

6. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of the buffer is

a. 4 **b.** 7 **c.** 10 **d.** 14

(IIT-JEE 1984)

7. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is
   a. 1.0×10^{-4} **b.** 1.0×10^{-10}
   c. 1.0×10^{10} **d.** 1.0×10^{14}
(IIT-JEE 1984)

8. The best indicator for detection of end point in titration of a weak acid and a strong base is
   a. methyl orange (3 to 4)
   b. methyl red (5 to 6)
   c. bromothymol blue (6 to 7.5)
   d. phenolphthalein (8 to 9.6) **(IIT-JEE 1985)**

9. The conjugate acid of NH_2^- is
   a. NH_3 **b.** NH_2OH **c.** NH_4^+ **d.** N_2H_4
(IIT-JEE 1985)

10. The compound that is not a Lewis acid is
   a. BF_3 **b.** $AlCl_3$ **c.** $BeCl_2$ **d.** $SnCl_4$
(IIT-JEE 1985)

11. The compound insoluble in acetic acid is
   a. calcium oxide **b.** calcium carbonate
   c. calcium oxalate **d.** calcium hydroxide
(IIT-JEE 1986)

12. The compound whose 0.1 M solution is basic is
   a. ammonium acetate **b.** ammonium chloride
   c. ammonium sulphate **d.** sodium acetate
(IIT-JEE 1986)

13. The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be
   a. unionized in the small intestine and in the stomach
   b. completely ionized in the small intestine and in the stomach
   c. ionized in the stomach and almost unionized in the small intestine
   d. ionized in the small intestine and almost unionized in the stomach **(IIT-JEE 1988)**

14. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occurs only with
   a. 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
   b. 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
   c. 10^{-16} M (Ag^+) and 10^{-6} M (Cl^-)
   d. 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-) **(IIT-JEE 1988)**

15. Which of the following is the strongest acid?
   a. $ClO_3(OH)$ **b.** $ClO_2(OH)$
   c. $SO(OH)_2$ **d.** $SO_2(OH)_2$
(IIT-JEE 1989)

16. Among the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is
   a. $Mg(OH)_2$ **b.** $Ca(OH)_2$
   c. $Ba(OH)_2$ **d.** $Be(OH)_2$
(IIT-JEE 1990)

17. Which of the following solution will have pH close to 1.0?
   a. 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH
   b. 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH
   c. 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH
   d. 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH
(IIT-JEE 1992)

18. The following equilibrium in established when hydrogen chloride is dissolved in acetic acid.

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characterises the conjugate acid–base pairs is
   a. (HCl, CH_3COOH) and ($CH_2COOH_2^+$, Cl^-)
   b. (HCl, $CH_3COOH_2^+$) and (CH_3COOH, Cl^-)
   c. ($CH_3COOH_2^+$, HCl) and (Cl^-, CH_3COOH)
   d. (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)
(IIT-JEE 1992)

19. The degree of dissociation of water at 25°C is 1.9×10^{-7} % and density is 1.0 g cm^{-3}. The ionic constant for water is
   a. 1.0×10^{-10} **b.** 1.0×10^{-14}
   c. 1.0×10^{-16} **d.** 1.0×10^{-8}
(IIT-JEE 1995)

20. Which one is more acidic in aqueous solution?
   a. $NiCl_2$ **b.** $FeCl_3$ **c.** $AlCl_3$ **d.** $BeCl_2$
(IIT-JEE 1995)

21. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.
ClOH (I), BrOH (II), IOH (III)
   a. I > II > III **b.** II > I > III
   c. III > II > I **d.** I > III > II
(IIT-JEE 1996)

22. If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is
   a. 1.74×10^{-5} **b.** 3.52×10^{-3}
   c. 6.75×10^{-4} **d.** 5.38×10^{-2}
(IIT-JEE 1997)

23. The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is
   a. $6y^4$ **b.** $64y^4$ **c.** $36y^5$ **d.** $108y^5$
(IIT-JEE 1997)

24. The pH of 0.1 M solution of the following salts increases in the order:
   a. $NaCl < NH_4Cl < NaCN < HCl$
   b. $HCl < NH_4Cl < NaCl < NaCN$
   c. $NaCN < NH_4Cl < NaCl < HCl$
   d. $HCl < NaCl < NaCN < NH_4Cl$ **(IIT-JEE 1999)**

25. For a sparingly soluble salt, A_pB_q, the relationship of its solubility product (L_s) with its solubility (s) is
   a. $L_s = S^{p+q} \cdot P^p \cdot q^q$ **b.** $L_s = s^{p+q} \cdot P^q \cdot q^p$
   c. $L_s = S^{pq} \cdot P^p \cdot q^q$ **d.** $L_s = S^{pq} \cdot (P \cdot q)^{(p+q)}$
(IIT-JEE, 2001)

26. Which of the following acids has the smallest dissociation constant?

a. $CH_3CHFCOOH$
b. FCH_2CH_2COOH
c. $BrCH_2CH_2COOH$
d. $CH_3CHBrCOOH$

(IIT-JEE 2002)

27. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first.

a. FeS
b. MnS
c. HgS
d. ZnS

(IIT-JEE 2003)

28. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.01 M) on reacting with caustic soda. The degree of hydrolysis of NaX is

a. 0.01%
b. 0.0001%
c. 0.1%
d. 0.5%

(IIT-JEE, 2004)

29. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution?

a. 8×10^{-2} M
b. 8×10^{-11} M
c. 1.6×10^{-11} M
d. 8×10^{-5} M

(IIT-JEE 2005)

30. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $k_1 = 3.5 \times 10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $k_2 = 1.7 \times 10^{-3}$

Then the formation constant of $[Ag(NH_3)_2]^+$ is

a. 6.08×10^{-6}
b. 6.08×10^{6}
c. 6.08×10^{-9}
d. none of these

(IIT-JEE 2006)

31. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order

a. $MX > MX_2 > M_3X$
b. $M_3X > MX_2 > MX$
c. $MX_2 > M_3X > MX$
d. $MX > M_3X > MX_2$

(IIT-JEE 2008)

32. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates.

a. CuS and HgS
b. MnS and CuS
c. MnS and NiS
d. NiS and HgS

(IIT-JEE 2011)

33. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is

a. 1×10^{-4}
b. 1×10^{-5}
c. 1×10^{-6}
d. 1×10^{-3}

(JEE Advanced 2013)

34. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is

a. 1.1×10^{-11}
b. 1.1×10^{-10}
c. 1.1×10^{-12}
d. 1.1×10^{-9}

(JEE Advanced 2013)

Multiple Correct Answers Type

1. Which of the following statement(s) is (are) correct?

a. The pH of 1.0×10^{-8} M solution of HCl is 8
b. The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
c. Autoprotolysis constant of water increases with temperature
d. When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point

$$pH = \left(\frac{1}{2}\right)pK_a$$

(IIT-JEE 1998)

2. A buffer solution can be prepared from a mixture of

a. sodium acetate and acetic acid in water
b. sodium acetate and HCl in water
c. ammonia and ammonium chloride in water
d. ammonia and sodium hydroxide in water

(IIT-JEE 1999)

3. Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is (are)

a. HNO_3 and CH_3COOH
b. KOH and CH_3COONa
c. HNO_3 and CH_3COONa
d. CH_3COOH and CH_3COONa

(IIT-JEE 2010)

Linked Comprehension Type

When 100 mL of 1.0 M HCl was mixed 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

(Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1}) **(JEE Advanced 2015)**

1. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from Expt. 2 is

a. 1.0
b. 10.0
c. 24.5
d. 51.4

2. The pH of the solution after Expt. 2 is

a. 2.8
b. 4.7
c. 5.0
d. 7.0

Integer Answer Type

1. 0.1 M NaOH is titrated with 0.1 M HA till the end point; K_a for HA is 5.6×10^{-6} and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point. **(IIT-JEE 2004)**

2. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.1 M solution of its sodium salt is **(IIT-JEE 2009)**

3. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is

KCN K_2SO_4
$(NH_4)_2C_2O_4$ $NaClZn(NO_3)_2$
$FeCl_3$ K_2CO_3
NH_4NO_3 $LiCN$ **(IIT-JEE 2010)**

4. The total number of diprotic acids among the following is

H_3PO_4 H_2SO_4 H_3PO_3 H_2CO_3 $H_2S_2O_7$
H_3BO_3 H_3PO_2 H_2CrO_4 H_2SO_3
(IIT-JEE 2010)

5. In 1 L saturated solution of AgCl [$K_{sp}(AgCl) = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{sp}(CuCl) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of "x" is **(IIT-JEE 2011)**

Fill in the Blanks Type

1. The conjugate base of HSO_4^- in aqueous solutions is ______ **(IIT-JEE 1982)**
2. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be ______ **(IIT-JEE 1984)**
3. In the reaction $I^- + I_2 \rightarrow I_3^-$, the Lewis acid is ______. **(IIT-JEE 1996)**
4. $(CH_3OH_2)^+$ is ______ acidic than ($CH_3NH_3^+$). **(IIT-JEE 1997)**

True / False Type

1. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons. **(IIT-JEE 1982)**
2. Solubility of sodium hydroxide increases with increase in temperature. **(IIT-JEE 1985)**

Subjective Type

1. A solution contains Na_2CO_3 and $NaHCO_3$. 10 ml of solution requires 2.5 ml of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as an indicator. Methyl orange is then added when a further 2.5 ml of 0.2 M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in one litre of the solution. **(IIT-JEE 1979)**
2. How many moles of sodium propionate should be added to one litre of an aqueous solution containing 0.020 mole of propionic acid to obtain a buffer solution of pH 4.75? What will be the pH if 0.010 mole of hydrogen chloride is dissolved in the above buffer solution. Compare the last pH value with the pH of 0.010 molar HCl solution. Dissociation constant of propionic acid, K_a at 25°C = 1.34×10^{-5}. **(IIT-JEE 1981)**
3. 20 ml of 0.2 sodium hydroxide is added to 50 ml of 0.2 M acetic acid to give 70 ml of the solution. What is the pH of this solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. The ionization constant of acetic acid is 1.8×10^{-5}. **(IIT-JEE 1982)**
4. Given reasons for the statement that "The pH of an aqueous solution of sodium acetate is more than seven." **(IIT-JEE 1982)**
5. The dissociation constant of a weak acid HA is 4.9×10^{-8}. After making the necessary approximations, calculate:
   - **i.** percentage ionization
   - **ii.** pH
   - **iii.** OH^- concentration in a decimolar solution of the acid. Water has a pH of 7. **(IIT-JEE 1983)**
6. A solution contains a mixture of Ag^+ (0.10 M) and Hg_2^{2+} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated?

   (K_{sp}:AgI = 8.5×10^{-17}, $Hg_2I_2 = 2.5 \times 10^{-26}$) **(IIT-JEE 1984)**
7. The concentration of hydrogen ions in a 0.2 molar solution of formic acid is 6.4×10^{-3} mol/L. To this solution, sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre. What will be the pH of this solution? The dissociation constant of formic acid is 2.4×10^{-4} and the degree of dissociation of sodium formate is 0.75. **(IIT-JEE 1985)**
8. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g/L. Calculate its solubility (in g/L) in 0.02 M $Mg(NO_3)_2$ solution. **(IIT-JEE 1986)**
9. Given reasons for the statement "Acetic acid is less acidic in sodium acetate solution than in sodium chloride solution" **(IIT-JEE 1986)**
10. What is the pH of the solution when 0.20 moles of HCl is added to one litre of a solution containing:
    - **i.** 1 M each of acetic acid and acetate ion
    - **ii.** 0.1 M each of acetic acid and acetate ion

    Assume the total volume is one litre. K_a for acetic acid = 1.8×10^{-5}. **(IIT-JEE 1987)**
11. How many gram-mole of HCl will be required to prepare one litre buffer solution (containing NaCN and HCl) of pH 8.5 using 0.01 gram formula weight of NaCN?

    $K_{HCN} = 4.1 \times 10^{-10}$ **(IIT-JEE 1988)**
12. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/L of NH_4Cl and 0.05 M of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution

    $K_b\,[NH_4OH] = 1.8 \times 10^{-5}$
    $K_{sp}\,[Mg(OH)_2] = 8.9 \times 10^{-12}$
    $K_{sp}\,[Al(OH)_3] = 6 \times 10^{-32}$ **(IIT-JEE 1989)**
13. What is the pH of a 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value?

    Given: $K_a = 1.8 \times 10^{-5}$ **(IIT-JEE 1990)**

14. The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} $mol^3 L^{-3}$. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 mL water is shaken at 25°C with excess of Ag_2CO_3 till the following equilibrium is reached:

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3. **(IIT-JEE 1991)**

15. A 40.0 mL solution of a weak base, BOH is titrated with 0.1 N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20.0 mL of the acid respectively. Find out the dissociation constant of the base. **(IIT-JEE 1991)**

16. The solubilty product (K_{sp}) of $Ca(OH)_2$ at 25°C is 4.42×10^{-5}. A 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in milligrams is precipitated? **(IIT-JEE 1992)**

17. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M H_2CO_3, in order to maintain a pH of 7.4?
K_a for H_2CO_3 in blood is 7.8×10^{-7} **(IIT-JEE 1993)**

18. An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH which MS will precipitate?
K_{sp} for MS = 6.0×10^{-21}, conc. of saturated H_2S = 0.1 M and $K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$, for H_2S
(IIT-JEE 1993)

19. For the reaction,

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

The equilibrium constant, at 25°C, is 4.0×10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in $AgNO_3$.

20. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation (pK_a of formic acid = 3.8 and pK_a of ammonia = 4.8).
(IIT-JEE 1995)

21. What is the pH of a 0.50 M aqueous NaCN solution?
pK_b of CN^- = 4.70 **(IIT-JEE 1996)**

22. The ionization constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L/mol/sec. Calculate the rate constant per proton transfer from water to NH_3. **(IIT-JEE 1996)**

23. Given reasons for the following:
"Between Na^+ and Ag^+, which is a stronger Lewis acid and why?" **(IIT-JEE 1997)**

24. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- ions per litre. Calculate the solubility product of AgCl.

[K_{sp} (Ag_2CO_3) = 8.2×10^{-12}] **(IIT-JEE 1997)**

25. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change? ($K_a = 1.0 \times 10^{-5}$) **(IIT-JEE 1997)**

26. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^- with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions? (Assume $CaCO_3$ to be completely insoluble in water). If the Ca^{2+} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH? (One ppm means one part of the substance in one million part of water, weight/weight). **(IIT-JEE 1997)**

27. Given, $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$,

$K_c = 6.2 \times 10^{-8}$ and K_{sp} of AgCl = 1.8×10^{-10} at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, calculate the concentration of the complex in 1.0 M aqueous ammonia.
(IIT-JEE 1998)

28. What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0)?
(IIT-JEE 1998)

29. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8 **(IIT-JEE 1999)**

30. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mol/L and pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **(IIT-JEE 2000)**

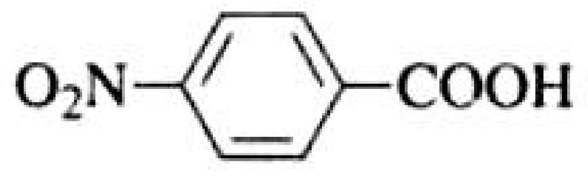
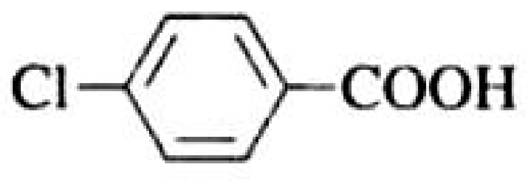
31. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 HCl at 25°C.

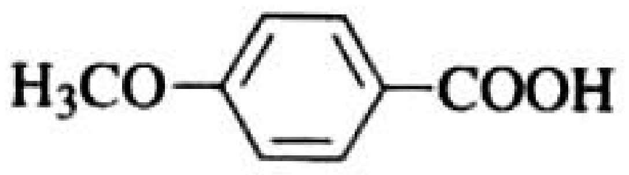
i. Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

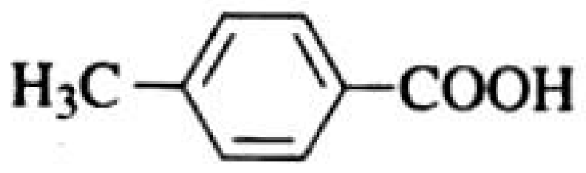
ii. If 6 g of NaOH is added to the above solution, determine the final pH (assuming there is no change in volume on mixing, K_a of acetic acid is 1.75×10^{-5} mol/L). **(IIT-JEE 2002)**

32. Give reasons for the following:
"Will the pH of water be same at 4°C and 25°C? Explain"
(IIT-JEE 2003)

33. Match the K_a values

	Compound	K_a
a.	Benzoic acid	3.3×10^{-5}
b.		6.3×10^{-5}
c.		30.6×10^{-5}

d.  6.4×10^{-5}

e.  4.2×10^{-5}

(IIT-JEE 2003)

34. In an experiment, 0.1 M NaOH is titrated with 0.1 M HA till the end point. K_a for HA is 5.6×10^{-5} and the degree of hydrolysis is less compared to 1. Calculate the pH of the resulting solution at the end point. **(IIT-JEE 2004)**

Answer Key

JEE Advanced

Single Correct Answer Type

1. a. **2.** d. **3.** a. **4.** b. **5.** b.
6. a. **7.** c. **8.** d. **9.** a. **10.** d.
11. c. **12.** d. **13.** d. **14.** a. **15.** a.
16. d. **17.** d. **18.** d. **19.** b. **20.** c.
21. a. **22.** c. **23.** d. **24.** b. **25.** a.
26. c. **27.** c. **28.** a. **29.** b. **30.** a.
31. d. **32.** a. **33.** a. **34.** b.

True/False Type

1. False **2.** False

Multiple Correct Answers Type

1. b., c. **2.** a., c. **3.** c., d.

Linked Comprehension Type

1. a. **2.** b.

Integer Answer Type

1. (9) **2.** (8) **3.** (3) **4.** (6) **5.** (7)

Fill in the Blanks Type

1. $\underset{\text{acid}}{HSO_4^-} \rightleftharpoons H^+ + \underset{\text{conjugate base}}{SO_4^{2-}}$

2. amphoteric **3.** I_2 **4.** more

Hints and Solutions

JEE Advaced

Single Correct Answer type

1. a. Acidic buffer is a mixture of weak acid and its salt with common anion.

- **a.** $CH_3COOH + CH_3COONH_4$ is acidic buffer.
- **b.** $NH_4Cl + NH_4OH$ is basic buffer.
- **c.** $H_2SO_4 + Na_2SO_4$ is not buffer because both the compounds are strong electrolytes.
- **d.** NaCl + NaOH is not strong buffer solution because both compounds are strong electrolytes.

2. d.

- **i.** pH of acid cannot be more than 7.
- **ii.** The neutral water has $[H^+] = 1 \times 10^{-7}$ M

By adding 1.0×10^{-8} M HCl, a concentration of 1.0×10^{-8} M H^+ ions have increased in solution.

Thus, total $[H^+] = (1 \times 10^{-7} + 1 \times 10^{-8})\ M = (1 \times 10^{-7} + 0.1 \times 10^{-7})\ M = 1.1 \times 10^{-7}$ M

$$pH = -\log(1.1 \times 10^{-7}) = -[\log 1.1 + \log 10^{-7}]$$
$$= -\log 1.1 + 7 \log 10 = -0.0414 + 7 = 6.9586$$

3. a.

- **i.** Lower the oxidation state of central atom, weaker will be oxy acid.
- **ii.** Weaker the acid, stronger will be its conjugate base. Oxidation state of Cl in HClO is +1, in $HClO_2$ is +3, in $HClO_3$ is +5, and in $HClO_4$ is +7.

  ∴ HClO is the weakest acid and so its conjugate base ClO^- is the strongest Bronsted base.

4. b. For pure water, $[H_3O^+] = [OH^-]$

$$\Rightarrow \quad K_w = 10^{-6} \times 10^{-6} = 10^{-12}$$

5. b. For precipitation to occur ionic product > solubility products

Given, $K_{sp}CaF_2 = 1.7 \times 10^{-10}$

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

Ionic product of $CaF_2 = [Ca^{2+}]\,[F^-]^2$

Calculate I.P. in each case

- **a.** I.P. of $CaF_2 = (10^{-4}) \times (10^{-4})^2 = 10^{-12}$
- **b.** I.P. of $CaF_2 = (10^{-2}) \times (10^{-3})^2 = 10^{-8}$
- **c.** I.P. of $CaF_2 = (10^{-5}) \times (10^{-3})^2 = 10^{-11}$
- **d.** I.P. of $CaF_2 = (10^{-3}) \times (10^{-5})^2 = 10^{-13}$

∵ I.P. > solubility in choice (b) only.

∴ ppt of CaF_2 is obtained in case of choice (b) only.

6. a. $K_a \times K_b = 10^{-14}$

Thus, $K_a \times 10^{-10} = 10^{-14}$ or $K_a = 10^{-4}$

$$\text{Now,}\quad pH = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$
$$= -\log 10^{-4} + \log 1 = 4, \text{ (As [Salt] = [Acid])}$$

7. c. $\underset{\text{weak}}{HA} + \underset{\text{strong}}{BOH} \rightleftharpoons BA + H_2O$

$$\therefore \quad HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$$

$$\text{or} \quad HA + OH^- \rightleftharpoons A^- + H_2O$$

$$\therefore \quad K = \frac{[A^-]}{[HA][OH^-]} \qquad (1)$$

Also for weak acid, HA:

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

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (2)$$

By equations (1) and (2)

$$\frac{K_a}{K} = K_w \quad \text{or} \quad \frac{K_a}{K_w} = \frac{1 \times 10^{-4}}{1 \times 10^{-14}}$$

$$K = 1 \times 10^{10}$$

8. d. Phenolphthalein is an indicator if the base is strong, because strong base immediately changes the pH at end point.

9. a. $\underset{}{NH_2^-} + H^+ \rightarrow \underset{\text{conjugate acid}}{NH_3}$

Conjugate acid and base pair differ in proton.

10. d. As we know that electron acceptors or elements having incomplete octet are Lewis acids

In $BF_3 \rightarrow$ B has $6e^-$ in valence shell
In $BeCl_2 \rightarrow$ B has $4e^-$ in valence shell
In $AlCl_3 \rightarrow$ Al has $6e^-$ in valence shell

Only $SnCl_4$ has complete octet so it is Lewis base.

11. c. CaO, $CaCO_3$ and $Ca(OH)_2$ dissolve in CH_3COOH due to formation of $(CH_3COO)_2Ca$. But CaC_2O_4 does not dissolve as CH_3COO^- is a stronger conjugate base than $C_2O_4^{2-}$.

12. d.

a. Option (a) is a neutral solution due to both cationic and anionic hydrolysis ($K_a = K_b = 1.8 \times 10^{-5}$)
b. Option (b) is acidic solution due to cationic hydrolysis
c. Option (c) is acidic solution due to cationic hydrolysis
d. Option (d) is basic solution due to anionic hydrolysis.

13. d. Aspirin, being a weak acid is unionized in acid medium (common ion effect) and completely ionized in alkaline medium.

14. a. $AgCl \rightleftharpoons [Ag^+] + [Cl^-]$

$$= \left(\frac{10^{-4} \times V}{2V}\right)\left(\frac{10^{-4} \times V}{2V}\right) = 2.5 \times 10^{-9}$$

This value is greater than $K_{sp} = 1.8 \times 10^{-10}$

15. a. $ClO_3(OH)$ or $HClO_4$ is the strongest acid.
In oxy acids of halogens, the higher the oxidation state of the halogen, the stronger the acid.

16. d. $Ba(OH)_2 > Ca(OH)_2 > Mg(OH)_2 > Be(OH)_2$
In alkaline earth metal hydroxides, the solubility increases down the group.

17. d.

a. $HCl = 100 \times \frac{1}{10} = 10$ mEq

$NaOH = 100 \times \frac{1}{10} = 10$ mEq

Salt of S_A/S_B is formed, pH = 7

b. $HCl = 55 \times \frac{1}{10} = 5.5$ mEq

$NaOH = 45 \times \frac{1}{10} = 4.5$ mEq

1.0 mEq of HCl is left. So pH will be in acidic range but not equal to one, since concentration of HCl is very low.

c. $HCl = 10 \times \frac{1}{10} = 1$ mEq

$NaOH = 90 \times \frac{1}{10} = 9$ mEq

8 mEq of NaOH is left and pH > 7

d. $HCl = 75 \times \frac{1}{5} = 15$ mEq

$NaOH = 25 \times \frac{1}{5} = 5$ mEq

15 – 5 = 10 mEq of HCl is left

$$\therefore\ [HCl] = [H_3O^{\oplus}] = \frac{10\text{ mEq}}{(75+25)\text{ mL}} = \frac{10}{100} = 0.1\text{ M}$$

pH = –log (10^{-1}) = 1

18. d. Since HCl is stronger than CH_3COOH hence acts as acid. On the other hand Cl^- is a stronger base than $CH_3COOH_2^+$ and is the conjugate base of HCl.

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{CH_3COOH} \rightleftharpoons \underset{\text{base}_1}{Cl^-} + \underset{\text{acid}_2}{CH_3COOH_2^+}$$

19. b. $\underset{(1-\alpha)c}{H_2O} \rightleftharpoons \underset{\alpha c}{H^+} + \underset{\alpha c}{OH^-}$

$\alpha = 1.9 \times 10^{-7}$; Density of water $= \frac{1.0\text{ g}}{\text{cm}^3}$

$\therefore\quad c = \frac{1}{18} \times 1000 = 55.56$ moles/l

$\therefore\quad [H^+] = 55.56 \times 1.9 \times 10^{-9} = 1.055 \times 10^{-7}$

$\therefore\quad K_w = [H^+][OH^-] = (1.055 \times 10^{-7})^2 = 1.0 \times 10^{-14}$

20. c. Salts of weak base and strong acid get hydrolysed in aqueous solution forming an acidic solution.

$$\underset{\text{(weak)}}{AlCl_3} + 3H_2O \rightarrow \underset{\text{(strong)}}{Al(OH)_3} + \underset{\text{(acidic)}}{3HCl}$$

21. a. Among oxyacids of the same type formed by different elements, acidic nature increases with increasing electronegativity. In general, the strength of oxyacids decreases as we go down the family in the periodic table.

HOCl (I) > HOBr (II) > HOI (III)

[In halogen groups Cl is above Br and I]

22. c. $HF + H_2O \xrightarrow{K_a} H_3O^+ + F^-$

$$\therefore\quad K_a = \frac{[H_3O^+][F^-]}{[HF][H_2O]} \qquad \text{(i)}$$

$F^- + H_2O \xrightarrow{K_b} HF + OH^-$

$$\therefore\quad K_b = \frac{[HF][OH^-]}{[F^-][H_2O]} \qquad \text{(ii)}$$

$\therefore\quad K_a \times K_b = [H_3O^+][OH^-] = K_w = 10^{-14}$

Given, $\quad pK_b = 10.83 \Rightarrow K_b - 1.48 \times 10^{-11}$

$$\therefore\quad K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.48 \times 10^{-11}} = 6.75 \times 10^{-4}$$

23. d. $A_2X_3 \rightleftharpoons \underset{2y}{2A^{3+}} + \underset{3y}{3X^{2-}}$

$K_{sp} = [A^{3+}]^2[X^{2-}]^3 = (2y)^2(3y)^3$ or $K_{sp} = 108\ y^5$

24. b. $\Rightarrow$ Aqueous NH_4Cl solution is slightly acidic (pH is lowest)

$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl, [H^+] > [OH^-]$

$\Rightarrow$ Aqueous NaCN solution is basic

$NaCN + H_2O \rightleftharpoons NaOH + HCN, [OH^-] > [H^+]$

NaCN is salt of W.A. and S.B.
$\Rightarrow$ Aqueous NaCl solution is neutral.
In these HCl is stronger acid, so its pH is lowest.
Hence, increasing order of pH.

HCl < NH_4Cl < NaCl < NaCN

25. a. $A_pB_q \rightleftharpoons pA^+ + qB^-$

Solubility S, pS, qS (on 100% ionization)

K_{sp} of $A_pB_q = [A^+]^p \times [B^-]^q$
$= (pS)^p \times (qS)^q = S^{p+q}(p^p \cdot q^q)$
$K_{sp} = p^p\, q^q\, s^{p+q}$

26. c. Acidic strength ∝ dissociation constant of acid. In given acids order of acidic strength:

$CH_3CHFCOOH > CH_3CHBrCOOH > FCH_2CH_2COOH > BrCH_2CH_2COOH$

Acidic strength ∝ $-I$ nature of group

$$\propto \frac{1}{\text{distance of } -I \text{ group}}$$

Hence, in these smallest dissociation constant will be for

$$BrCH_2-CH_2-COOH$$

27. c. $\text{I.P} = \frac{10^{-3}}{2} \times \frac{10^{-16}}{2} = 0.25 \times 10^{-19}$

⇒ An electrolyte will be precipitated first whose ionic product is exceeded to its solubility product.

⇒ In similar ionic conc. of cations/an electrolyte is precipitated firstly for which K_{sp} is lower. In these electrolytes MnS, FeS, ZnS and HgS, HgS is precipitate firstly.

28. a. $NaX + H_2O \rightleftharpoons NaOH + HX$

In it HX is weak acid, so NaX is a salt of weak acid and strong base.

∴ Hydrolysis constant of NaX

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-5}} = 1 \times 10^{-9}$$

For this type of salt $K_h = \frac{\alpha^2}{V} = C\alpha^2$

α = degree of hydrolysis

∴ $1 \times 10^{-9} = 0.1 \times \alpha^2$

or $\alpha^2 = \frac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8}$

$\alpha = 1 \times 10^{-4}$

∴ % of degree of hydrolysis of NaX salt $= 1 \times 10^{-4} \times 100 = 1 \times 10^{-2} = 0.01\%$

29. b. For basic buffer pH is more than 7.

$$\begin{array}{llll} & CH_3NH_2 & + HCl \rightarrow & CH_3NH_3^+Cl^- \\ \text{Inital moles} & 0.1 & 0.08 & 0 \\ \text{Moles after mixing} & 0.02 & 0 & 0.08 \end{array}$$

As it is a basic buffer solution,

$$\text{pOH} = pK_b + \log\frac{0.08}{0.02} = -\log 5 \times 10^{-4} + \log 4$$

$$= 3.30 + 0.602 = 3.902$$

$$\text{pH} = 14 - 3.902 = 10.09; [H^+]$$

$$= 7.99 \times 10^{-11} \approx 8 \times 10^{-11}\ \text{M}$$

30. a.

i. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+;$ $k_1 = 3.5 \times 10^{-3}$

ii. $[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+;$ $k_2 = 1.7 \times 10^{-3}$

On the basis of above reaction

$$k_1 = \frac{[Ag(NH_3)]^+}{[Ag^+][NH_3]} \quad \text{(i)}$$

$$k_2 = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+[NH_3]} \quad \text{(ii)}$$

For the formation of $[Ag(NH_3)_2]^+$

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$\text{Formation constant } (K) = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \quad \text{(iii)}$$

When two equations are added their equilibrium constants are multiplied.

From equations (i) and (ii), we get

$$k = k_1 \times k_2$$

$$= 3.5 \times 10^{-3} \times 1.7 \times 10^{-3} = 5.95 \times 10^{-6} \approx 6.08 \times 10^{-6}$$

31. d. $\underset{}{MX} \rightarrow \underset{s}{M^+} + \underset{s}{X^-}$ (where s is the solubility)

Then $K_{sp} = s^2$ or $s = \sqrt{K_{sp}}$

Similarly for $MX_2 \rightarrow M^{2+} + 2X^-$

$$K_{sp} = s \times (2s)^2 = 4s^3 \text{ or } s = \left[\frac{K_{sp}}{4}\right]^{1/3}$$

and for $M_3X \rightarrow \underset{3s}{3M^+} + \underset{s}{X^{-3}}$

$$K_{sp} = (3s)^3 \times s = 27s^4 \text{ or } s = \left[\frac{K_{sp}}{27}\right]^{1/4}$$

From the given values of K_{sp} for MX, MX_2 and M_3X, we can find the solubilities of those salts at temperature, T

Solubility of $MX = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$

$$\text{Solubility of } MX_2 = \left[\frac{3.2 \times 10^{-14}}{4}\right]^{1/3} \text{ or } \left[\frac{32}{4} \times 10^{-15}\right]^{1/3}$$

$$= [8 \times 10^{-15}]^{1/3} \text{ or } 2 \times 10^{-15}$$

$$\text{Solubility of } M_3X = \left[\frac{2.7 \times 10^{-15}}{27}\right]^{1/4} = [10^{-16}]^{1/4} \text{ or } 10^{-4}$$

Thus the solubilities are in the order $MX > M_3X > MX_2$, i.e., the correct answer is (d).

32. a. In acidic solution $[S^{2-}]$ is low. So CuS and HgS (IInd group cations) will be precipitated more easily due to low K_{sp} value. NiS and MnS (IV group cation) will precipitate if H_2S is passed in basic medium.

33. a. Rate in weak acid $= \frac{1}{100}$ (rate in strong acid)

$$\therefore \quad [H^+]_{\text{weak acid}} = \frac{1}{100}[H^+]_{\text{strong acid}}$$

$$\therefore \quad [H^+]_{\text{weak acid}} = \frac{1}{100} M = 10^{-2}\ \text{M}$$

∴ $C\alpha = 10^{-2}$

∴ $K_a = 10^{-4}$

Hence (a) is correct.

34. b. $K_{sp} = 1.1 \times 10^{-12} = [Ag^+]^2[CrO_4^{-2}]$

$1.1 \times 10^{-12} = [0.1]^2 [s]$

$S = 1.1 \times 10^{-10}$

Multiple Correct Answers Type

1. **b., c.**

⇒ pH of 1×10^{-7} M is below to 7 but near 7

$$\Rightarrow \quad H_2PO_4^- + H_2O \rightleftharpoons \underset{\text{conjugate base of } H_2PO_4^- \text{ acid}}{HPO_4^{2-}} + H_3O^+$$

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

⇒ K (Auto protolysis constant of water i.e., with ionic product of water) increases with temperature due to increase in ionization.

⇒ For half neutralization of a weak acid by a weak base

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

[Salt] = [Acid] $\therefore\ pH = pK_a$

2. **a., c.**

Because a buffer solution is prepared by mixing a weak acid/base with salt of its conjugate base/acid.

3. **c., d.**

a. Not buffer since it is a mixture of strong acid and weak acid.

b. Not buffer since it is a mixture of strong base and salt of weak acid/strong base.

c. It is an acidic buffer since some of HNO_3 will react with CH_3COONa to produce weak acid and some CH_3COONa to produce weak acid and some CH_3COONa will be left. So buffer is formed.

$$\begin{array}{lcccc} & HNO_3 & + CH_3COONa & \rightarrow NaNO_3 & + CH_3COOH \\ \text{Initial} & x & y & 0 & 0 \\ \text{Final} & — & (y-x) & (y-x) & (y-x) \end{array}$$

d. It is an acidic buffer (mixture of weak acid and salt of weak acid/strong base)

Linked Comprehension Type

1. a. Let the heat capacity of insulated beaker be C.

Mass of aqueous content in expt. 1 = (100 + 100) × 1 = 200 g

⇒ ± Total heat capacity = $(C + 200 \times 4.2)$ J/K

Mole of acid, base neutralised in Expt. 1

$= 0.1 \times 1 = 0.1$

⇒ Heat released in Expt. 1 = 0.1 × 5.7 = 5.7 KJ

$= 5.7 \times 1000$ J

⇒ $5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T$

$5.7 \times 1000 = (C + 200 \times 4.2) \times 5.7$

⇒ $(C + 200 \times 4.2) = 1000$

In second experiment,

$$N_{CH_3COOH} = 0.2,\ N_{NaOH} = -0.1$$

Total mass of aqueous content = 200 g

⇒ Total heat capacity = $(C + 200 \times 4.2) = 1000$

⇒ Heat released = 1000 × 5.6 = 5600 J

Overall, only 0.1 mol of CH_3COOH undergo neutralization.

$$\Rightarrow \Delta H_{neutralization} \text{ of } CH_3COOH = \frac{-5600}{0.1}$$

$$= -56000 \text{ J/mol} = 56 \text{ KJ/mol.}$$

⇒ $\Delta H_{neutralization}$ of CH_3COOH = 57 – 56 = 1 KJ/mol

2. b. Final solution contains 0.1 mole of CH_3COOH and CH_3COONa each.

Hence it is a buffer solution.

$$pH = pK_a \log\frac{[CH_3COO^-]}{[CH_3COOH]} = 5 - \log 2 + \log\frac{0.1}{0.1} = 4.7$$

Integer Answer Type

1. (9) $HA + NaOH \rightarrow NaA + H_2O$

At the end point, the solution contains only NaA whose concentration is 0.1/2 = 0.05 M

Since the salt NaA is formed by strong alkali (NaOH) and weak acid HA (indicated by its low K_a value), its pH can be evaluated by the following relation.

$$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

$$= \frac{1}{2}[14 + 5.3010 + (-1.3010)] = 9$$

2. (8) $K_a(C_6H_5COOH) = 1 \times 10^{-4}$

pH of 0.01 M C_6H_5COONa

$$\underset{0.01(1-h)}{C_6H_5COO^-} + H_2O \rightleftharpoons \underset{0.01h}{C_6H_5COOH} + \underset{0.01h}{OH^{-1}}$$

$$K_h = \frac{K_w}{K_a} = \frac{0.01h^2}{1-h}$$

$$\frac{10^{-14}}{10^{-4}} = \frac{10^{-2}h^2}{1-h} \qquad (1 - h \approx 1)$$

$[OH^-] = 0.01\,h = 0.01 \times 10^{-4} = 10^{-6}$

$[H^+] = 10^{-8}$

pH = 8

3. (3) KCN, K_2CO_3 and LiCN are the salts of weak acid and strong base. So, their aqueous solution turns red litmus paper blue.

4. (6) Diprotic acids are H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2CrO_4 and H_2SO_3.

5. (7) Let the solubility of AgCl is x mol litre^{-1} $AgCl \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-}$

and that of CuCl is y mol litre^{-1} $CuCl \rightleftharpoons \underset{y}{Cu^+} + \underset{y}{Cl^-}$

$\therefore$ K_{sp} of AgCl = $[Ag^+][Cl^{-1}]$

$1.6 \times 10^{-10} = x(x + y)$ (i)

Similarly K_{sp} of CuCl = $[Cu^+][Cl^-]$

$1.6 \times 10^{-6} = y(x + y)$ (ii)

On solving (i) and (ii)

$[Ag^+] = 1.6 \times 10^{-7}$

$\therefore$ $x = 7$

Fill in the Blanks Type

1. $\underset{acid}{HSO_4^-} \rightleftharpoons H^+ + \underset{conjugate\ base}{SO_4^{2-}}$

   Conjugate acid base pairs deffer in proton.
2. amphoteric
3. I_2. Lewis acid is which accepts electron pairs.
4. more.

   Conjugate base of $(CH_3OH_2)^+$ i.e., CH_3OH is less basic than the conjugate base of $(CH_3NH_3)^+$ i.e., CH_3NH_2.

True / False Type

1. **False:**

   $AlCl_3$ is a Lewis acid (although they do not have a proton, aprotic) because it accepts electrons (octet being incomplete).
2. **False:**

   Sodium hydroxide is a strong base. It is completely ionized and its solubility in water is an exothermic reaction.

Subjective Type

1. Phenolphthalein indicates half neutralization.

$$Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+ \qquad \text{(i)}$$

Methyl orange indicates complete neutralisation

$$NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2 \qquad \text{(ii)}$$

$\therefore$ Volume of 0.1 M H_2SO_4 required for complete neutralisation = $2 \times 2.5 = 5.0$ ml

$0.1 \text{ M } H_2SO_4 \equiv 0.2 \text{ N} H_2SO_4$

[For H_2SO_4 molarity = 2 × normality]

($\because$ Mol. wt. of $H_2SO_4 = 98$, and Eq. wt. of $H_2SO_4 = 49$)

$\therefore$ $0.2 \text{ M } H_2SO_4 \equiv 0.4 \text{ N} H_2SO_4$

N_1 = normality of Na_2CO_3
V_1 = volume of Na_2CO_3 = 10 ml
N_2 = normality of H_2SO_4 = 0.2
V_2 = volume of H_2SO_4 = 5.0 ml

$$\therefore \quad N_1V_1 = N_2V_2$$
$$N_1 \times 10 = 0.2 \times 5$$
$$\therefore \quad N_1 = \frac{0.2 \times 5}{10} = 0.1 \text{ N}$$

$\therefore$ Eq. wt. of $Na_2CO_3 = \frac{1}{2} \times$ molecular weight $= \frac{106}{2} = 53$

Strength of $Na_2CO_3 = 53 \times 0.1 = 5.3$ g/l

[$\because$ strength = normality × Eq. wt.]

For neutralization with methyl orange, volume of 0.2 M H_2SO_4 used = 2.5 ml = 2.5 ml of 0.4 N H_2SO_4

= 5 ml of 0.2 N H_2SO_4 [$\because N_1V_1 = N_2V_2$]

From 5 ml of 0.2 N H_2SO_4, 2.5 ml is used for neutralizing $NaHCO_3$ formed during first half neutralization Na_2CO_3

$\therefore$ Volume of 0.2 N H_2SO_4 used for neutralization of $NaHCO_3$ present in original solution = 5.0 – 2.5 = 2.5 ml

$$\therefore \quad N_1V_1 = N_2V_2$$

where N_1 = Normality of $NaHCO_3$
N_2 = Normality of H_2SO_4 = 0.2
V_1 = Volume of $NaHCO_3$ = 10 ml
V_2 = Volume of H_2SO_4 = 2.5 ml

$$N_1V_1 = N_2V_2$$
$$N_1 \times 10 = 0.2 \times 2.5$$
$$N_1 = \frac{0.2 \times 2.5}{10} = 0.05 \text{ N}$$

Eq. wt. of $NaHCO_3$ = 84

$\therefore$ Strength of $NaHCO_3 = 84 \times 0.05 = 4.2$ g/l

2. Suppose the number of moles of sodium propionate = x

Then $\text{pH} = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$$4.75 = -\log(1.34 \times 10^{-5}) + \log\left(\frac{x}{0.02}\right)$$

or $$4.75 = 5 - 0.1271 + \log\frac{x}{0.02}$$

or $$4.75 = 4.8729 + \log\frac{x}{0.02}$$

$$\log\frac{x}{0.02} = -0.1229$$

or $$\frac{x}{0.02} = \text{Antilog}\,[-0.1229]$$

or $$\frac{x}{0.02} = 0.7536$$

$$x = 0.7536 \times 0.02 = 1.5072 \times 10^{-2} \text{ mol}$$

$$\underset{0.01\text{ mol}}{HCl} \rightleftharpoons \underset{0.01\text{ mole}}{H^+} + Cl^-$$

When 0.01 mole of HCl is added, there is (0.01 + 0.02) M of propionic acid and (0.015 – 0.010) M of propionate. Therefore

$$\text{pH} = -\log(1.34 \times 10^{-5}) + \log\frac{0.005}{0.03} = 4.09$$

The pH of a 0.010 molar HCl solution = $-\log 10^{-2} = 2$.

3. **i.** Find the moles of each species after reaction.

ii. $\text{pH} = -\log K_a + \log\left[\frac{\text{Salt}}{\text{Acid}}\right]$

Given, NaOH 0.2 M, 20 ml
CH_3COOH 0.2 M, 50 ml

$$K_a = 1.8 \times 10^{-5}$$

V of 0.2 M NaOH required to make pH = 4.74 = ?

From the chemical reaction

$$\underset{50\text{ ml}}{CH_3COOH} + \underset{20\text{ ml}}{NaOH} \longrightarrow \underbrace{CH_3COONa + H_2O}_{20\text{ ml}}$$

It is evident that 70 ml of the product will contain

i. 30 ml of 0.2 M unused CH_3COOH
[unused CH_3COOH = 50 – 20 = 30 ml]

ii. 20 ml of CH_3COONa

$\therefore$ No. of moles of CH_3COOH in solution

$$= \frac{0.2}{1000} \times 30 = 0.006 \text{ mole}$$

Similarly, no. of moles of CH_3COONa solution

$$= \frac{0.2}{1000} \times 20 = 0.004 \text{ moles}$$

$$\text{pH} = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

Substituting the values of the various values

$$\text{pH} = -\log 1.8 \times 10^{-5} + \log\frac{0.004}{0.006}$$
$$= 4.7447 - 0.1761 = 4.5686$$

Calculation of the addition volume of 0.2 M NaOH required to make pH of solution 4.74.

$$\text{pH} = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

or $$4.74 = -\log 1.8 \times 10^{-5} + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

or $$4.74 = 4.7447 + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore \quad \log\frac{[\text{Salt}]}{[\text{Acid}]} = 0.0047 \text{ or } \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{1.011}$$

Let x ml be the volume of additional 0.2 M NaOH added to make the pH of the solution 4.74. This will further neutralize x ml of 0.2 M CH_3COOH and produce x ml of 0.2 sodium acetate. The resulting solution $(70 + x)$ will now contain

i. $(30 - x)$ ml of 0.2 M acetic acid.
ii. $(20 + x)$ ml of 0.2 M sodium acetate.
Number of moles of acetic acid in $(70 + x)$ ml solution

$$= \frac{0.2}{1000} \times (30 - x) = 2 \times 10^{-4}(30 - x)$$

Number of moles of CH_3COONa in $(70 + x)$ ml solution

$$= \frac{0.2}{1000} \times (20 + x) = 2 \times 10^{-4}(20 + x)$$

$$\text{Therefore, } \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{2 \times 10^{-4}(20 + x)}{2 \times 10^{-4}(30 - x)} = \frac{20 + x}{30 - x}$$

$$\frac{1}{1.011} = \frac{20 + x}{30 - x}$$

or $1.001\,x + x = 30 - 20.22$
$2.011\,x = 9.78$ or $x = 4.86$
Therefore, the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74 is 4.86 ml.

4. The pH of an aqueous solution of sodium acetate is more than 7 because sodium acetate is a salt of a weak acid and strong base, therefore it gets hydrolysed to yield an alkaline solution. The pH of alkaline solution is always more than 7.

5. **i.** $$\alpha = \sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{\left(\frac{4.9 \times 10^{-8}}{1/10}\right)}$$

$$\left(\because C = \frac{1}{10}M,\ K_a = 4.9 \times 10^{-8}\right)$$

$$= 7 \times 10^{-4} = 0.07\%$$

ii. $$H^+ = C\alpha = \frac{1}{10} \times 7 \times 10^{-4} = 7 \times 10^{-5}$$

$$\therefore \quad pH = -\log[H^+] = -\log 7 \times 10^{-5}$$
$$= -\log 7 - \log 10^{-5} = 4.15$$

iii. $[OH^-][H^+] = 10^{-14}$

$$\therefore \quad [OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{7 \times 10^{-5}} = 1.43 \times 10^{-10}$$

6. The $[I^-]$ needed for precipitation of Ag^+ and Hg_2^{2+} are derived as precipitation takes place if ionic product exceeds solubility product.

For AgI: $[Ag^+][I^-] = K_{sp(AgI)}$
$(0.1)[I^-] = 8.5 \times 10^{-17}$
$\therefore \quad [I^-] = 8.5 \times 10^{-16}$ M (1)

For Hg_2I_2: $[Hg_2^{2+}][I^-]^2 = K_{sp(Hg_2I_2)}$
$(0.1)[I^-]^2 = 2.5 \times 10^{-26}$
$\therefore \quad [I^-] = 5 \times 10^{-13}$ M (2)

Since $[I^-]$ required for precipitation of AgI is less and thus AgI begins to precipitate first. Also, it will continue up to addition of $[I^-] = 5 \times 10^{-13}$ M when Hg_2I_2 begins to precipitate and thus, maximum $[I^-]$ for AgI precipitation $= 5 \times 10^{-13}$ M.
Now, at this concentration of I^-,
$[Ag^+]$ left in solution is $[Ag^+]_{left}\,[I^-] = K_{sp(AgI)} = K_{sp}(Ag^+)$

$$\therefore \quad [Ag^+]_{left} = \frac{8.5 \times 10^{-17}}{5.0 \times 10^{-13}} = 1.7 \times 10^{-4}\,M$$

$\because$ 0.1 M Ag^+ will be left $= 1.7 \times 10^{-4}$ M Ag^+ in solution

$\therefore$ 100 M Ag^+ will be left = 0.17% M Ag^+
$\therefore$ % of Ag precipitated = 99.83%

7. In 0.2 M HCOOH, $= 6.4 \times 10^{-3}$

$$C\alpha = 6.4 \times 10^{-3} \Rightarrow \alpha = \frac{6.4 \times 10^{-3}}{0.2} \qquad [\text{As } C = 0.2\text{ M}]$$

$\therefore \quad \alpha = 3.2 \times 10^{-2}$
Now, sodium formate is added and the dissociation will further be suppressed and therefore, new degree of dissociation (α_1) for HCOOH in presence of HCOONa is so small that it may be neglected, i.e.
$\therefore$ [HCOOH] after dissociation = [HCOOH] before dissociation
$\therefore$ [HCOOH] = 0.2

$$\begin{array}{lcccc} & HCOONa & \rightleftharpoons & HCOO^- & + Na^+ \\ \text{before dissociation} & 1 & & 0 & 0 \\ \text{after dissociation} & (1 - 0.75) & & 0.75 & 0.75 \end{array}$$

$\therefore \ [HCOO^-] = 0.75$

$$\text{For acidic buffer pH} = -\log Ka + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore \quad pH = -\log 2.4 \times 10^{-4} + \log\frac{0.75}{0.2} = 4.19$$

8. Solubility of $Mg(OH)_2(s) = 9.57 \times 10^{-3}$ g/L

$$\therefore \text{ Solubility of } Mg(OH)_2(s) = \frac{9.57 \times 10^{-3}}{58}\text{ mol/L}$$
$$= 1.65 \times 10^{-4}\text{ mol/L}$$

$\therefore \quad K_{sp} = (s)(2s)^2 = 4s^3 = 4(1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11}$ approximately
$K_{sp} = [Mg^{2+}][OH^-]^2$

$$\therefore \quad [OH^-]^2 = \frac{1.8 \times 10^{-11}}{0.02} \quad (\text{in } 0.02\text{ M } Mg(NO_3)_2)$$
$$= 9 \times 10^{-10}$$

or $\quad [OH^-] = 3 \times 10^{-5}$

$$\therefore \quad [Mg^{2+}] = \frac{1}{2}[OH^-] = \frac{1}{2} \times 3 \times 10^{-5} = 1.5 \times 10^{-5}\text{ mol/L}$$

$$\therefore \quad [Mg^{2+}] = 1.5 \times 10^{-5} \times 58\text{ g/L} = 8.7 \times 10^{-4}\text{ g/L}$$

9. Due to common ion effect, acetate ions (from sodium acetate) suppress the ionization of acetic acid, so the acetic acid becomes less acidic.

10. **i.** Initially,
$[CH_3COOH] = 1M$
$[CH_3COO^-] = 1M$
Now, 0.2 moles of HCl are added to it.

$$\begin{array}{lcccc} & HCl & + CH_3COO^- & \rightarrow CH_3COOH & + Cl^- \\ \text{before reaction} & 0.2 & 1 & 1 & 0 \\ \text{after reaction} & 0 & 0.8 & 1.2 & 0.2 \end{array}$$

$\therefore$ Now, $[CH_3COOH] = 1.2$ and $[CH_3COO^-] = 0.8$

$$\therefore \quad pH = -\log 1.8 \times 10^{-5} + \log\frac{0.8}{1.2} = 4.5686$$

ii. In second case, initially,
$[CH_3COOH] = 0.1$ M
$[CH_3COO^-] = 0.1$ M
Now, 0.2 moles of HCl are added to it.

$$\therefore \quad \begin{array}{lcccc} & HCl & + CH_3COO^- & \rightarrow CH_3COOH & + Cl^- \\ \text{before reaction} & 0.2 & 0.1 & 0.1 & 0 \\ \text{after reaction} & 0.1 & 0 & 0.2 & 0.1 \end{array}$$

$\therefore$ $[H^+]$ from free $[HCl = 0.1] = 10^{-1}$

$\therefore$ $pH = -\log[H^+] = \log 10^{-1} = 1.$

(CH_3COOH no doubt gives H^+ but being weak acid as well as in presence of HCl does not dissociate appreciable and thus, H^+ from CH_3COOH may be neglected)

11. NaCN + HCl is not a buffer if HCl is in less amount then, it given a buffer as it produces HCN.

	NaCN +	HCl →	NaCl +	HCN
moles added	0.01	a	0	0
after reaction	$(0.01 - a)$	0	a	a

This is buffer of HCN + NaCN.

Let a moles of HCl be used for this purpose

$$\therefore \quad pH = -\log K_a + \log\frac{0.01-a}{a}$$

$$8.5 = -\log 4.1\times10^{-10} + \log\frac{0.01-a}{a}$$

$\therefore$ $a = 8.85 \times 10^{-3}$ mole of HCl

12. For buffer solution,

$NH_4Cl = 0.25$ M and $NH_4OH = 0.05$ M

$$pOH = -\log K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$\therefore \quad pOH = -\log 1.8\times10^{-5} + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$\therefore$ $[OH]^- = 3.6 \times 10^{-6}$ M

Now, $Al(OH)_3$ and $Mg(OH)_2$ are stirred vigorously in it,

$\therefore$ $[Al^{3+}][OH^-]^3 = K_{sp}$ of $Al(OH)_3$

$[Al^{3+}][3.6 \times 10^{-6}]^3 = 6 \times 10^{-32}$

$\therefore$ $[Al^{3+}] = 1.28 \times 10^{-15}$ M

Also, $[Mg^{2+}][OH^-]^2 = K_{sp}$ of $Mg(OH)_2$

$[Mg^{2+}][3.6\times10^{-6}]^2 = 8.9\times10^{-12}$

$[Mg^{2+}] = 0.686$ M

13. **Case I**

	$CH_3COOH \rightleftharpoons$	$CH_3COO^- +$	H^+
Before dissociation	1	0	0
After dissociation	$1-\alpha$	α	α

$$[H^+] = (C\alpha) = C\sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_aC)} = \sqrt{(1.8\times10^{-5}\times1)}$$

$$= \sqrt{(18\times10^{-6})} = 4.24\times10^{-3}\text{ M}$$

$$\therefore \quad pH = -\log[H^+] = -\log(4.24\times10^{-3}) = 2.3724$$

Case II

New pH is given as $= 2.3724 \times 2 = 4.7448$

Let new conc. be C_1 and degree of dissociation be α_1

$\therefore$ $-\log[H^+] = 4.7448$

$\therefore$ $[H^+] = 1.8 \times 10^{-5}$ or $C_1\alpha_1 = 1.8 \times 10^{-5}$

Now, again

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

$$K_a = \frac{C_1\alpha_1 \times C_1\alpha_1}{C_1(1-\alpha_1)} = \frac{C_1\alpha_1\cdot\alpha_1}{(1-\alpha_1)}$$

$$\therefore \quad 1.8\times10^{-5} = \frac{1.8\times10^{-5}\times\alpha_1}{(1-\alpha_1)}$$

$$\therefore \quad \alpha_1 = 0.5$$

Now, $C_1\alpha_1 = 1.8 \times 10^{-5}$

$$\therefore \quad C_1 = \frac{1.8\times10^{-5}}{\alpha_1} = \frac{1.8\times10^{-5}}{0.5} = 3.6\times10^{-5}\text{ M}$$

Let 1 L of conc. solution be diluted to V litre.

Equivalent of dilute solution = equivalent of conc. solution

$3.6 \times 10^{-5} \times V = 1 \times 1$

$$\therefore \quad V = \frac{1}{3.6\times10^{-5}} = 2.77\times10^4\text{ L}$$

$\left(\text{In case II, } \alpha \text{ come 0.5 by } K_a = \frac{C_1\alpha_1^2}{(1-\alpha_1)} \text{ and thus, it is not advisable to assume } (1-\alpha_1) \approx 1\right).$

14.

	Ag_2CO_3 +	$K_2C_2O_4 \rightleftharpoons$	$Ag_2C_2O_4$ +	K_2CO_3
Before reaction	Excess	0.1520	—	—
After reaction	—	(0.1520– 0.0358) = 0.1162	0.0358	0.0358

At equilibrium,

$$\therefore \quad [C_2O_4^{2-}] = \frac{0.1162}{0.5}, [CO_3^{2-}] = \frac{0.0358}{0.5} = 0.2324\text{ M} = 0.0716\text{ M}$$

$$\therefore \quad [Ag^+]^2[C_2O_4^{2-}] = \left(\frac{2\times0.0358}{0.5}\right)^2\left[\frac{0.1520}{0.5}\right] = 6.23\times10^{-3}$$

Thus, $[Ag^+]^2[C_2O_4^{2-}] > \underset{(1.29\times10^{-11})}{K_{sp} \text{ of } Ag_2C_2O_4}$

$\therefore$ $Ag_2C_2O_4$ will precipitate out

For $Ag_2C_2O_4$ precipitation.

$$[Ag^+]^2[C_2O_4^{2-}] = K_{sp}(Ag_2C_2O_4)$$

$$[Ag^+]^2[0.2324] = 1.29\times10^{-11}$$

$$\therefore \quad [Ag^+]^2 = \frac{1.29\times10^{-11}}{0.2324} = 5.55\times10^{-11}$$

Now, for Ag_2CO_3

$$K_{sp} = [Ag^+]^2[CO_3^{2-}] = [5.55\times10^{-11}][0.0716]$$

$$= 3.94\times10^{-12}\text{ mol}^3/\text{L}^3$$

15. **Case I**

	BOH +	HCl →	BCl +	H_2O
before reaction	a	0.1×5=0.5	0	0
after reaction	$(a-0.5)$	0	0.5	0.5

$\because$ pH = 10.04

$\because$ pOH = 3.96

$$\text{Now,} \quad pOH = -\log K_b + \log\frac{[BCl]}{[BOH]} \qquad (1)$$

$$\therefore \quad 3.96 = -\log K_b + \log\frac{0.5}{(a-0.5)} \qquad (2)$$

Case II

	BOH +	HCl →	BCl +	H_2O
before reaction	a	0.1×20=2		
after reaction	$(a-2)$	0	2	2

$\because$ pH = 9.14

$\therefore$ pOH = 4.86

$$\text{Now,} \quad pOH = -\log K_b + \log\frac{[BCl]}{[BOH]} \qquad (3)$$

$$\therefore \quad 4.86 = -\log K_b + \log\frac{2}{(a-2)} \qquad (4)$$

Solving equations (2) and (4)

$$K_b = 1.81 \times 10^{-5}$$

16. 500 mL of 0.4 M NaOH are mixed with 500 mL of $Ca(OH)_2$, a saturated solution having $Ca(OH)_2$ solubility as sM. For

$$\begin{array}{ccc} Ca(OH)_2 & \rightleftharpoons & Ca^{2+} + 2OH^- \\ \text{sM} & & \text{sM} \quad \text{2sM} \end{array}$$

$$\therefore \quad K_{sp} \text{ of } Ca(OH)_2 = [Ca^{2+}][OH^-]^2$$

$$4.42 \times 10^{-5} = s \times (2s)^2 = 4s^3$$

$$\therefore \quad s = \left(\frac{4.42 \times 10^{-5}}{5}\right)^{1/3} = 0.0223 \text{ M}$$

Now $Ca(OH)_2$ and NaOH are mixed.

$\therefore$ Solution has Ca^{2+} and OH^-, out of which some Ca^{2+} are precipitated,

$$\text{On mixing } [Ca^{2+}] = \frac{0.0223 \times 500}{1000} = 0.0115 = 111.5 \times 10^{-4} \text{ M}$$

$$[OH^-] = \underset{\text{From } Ca(OH)_2}{\frac{0.0223 \times 2 \times 500}{1000}} + \underset{\text{From NaOH}}{\frac{500 \times 0.4}{100}} = 0.2223 \text{ M}$$

$$\therefore \quad K_{sp} \text{ of } Ca(OH)_2 = [Ca^{2+}][OH^-]^2$$

$$4.42 \times 10^{-5} = [Ca^{2+}][0.2223]^2$$

$$[Ca^{2+}] = \frac{4.42 \times 10^{-5}}{(0.2223)^2} = 8.94 \times 10^{-4} \text{ M}$$

$\because$ Moles of $Ca(OH)_2$ precipitated

= moles of Ca^{2+} precipitated

$= 111.5 \times 10^{-4} - 8.94 \times 10^{-4}$

$= 102.46 \times 10^{-4}$

$\therefore$ Weight of $Ca(OH)_2$ precipitated = moles × mol. wt.

$= 102.46 \times 10^{-4} \times 74$

$= 7.582$ g

17. Let the volume of 5 M $NaHCO_3$ be x mL millimoles of $NaHCO_3 = 5 \times V = 5V$

($\because$ millimoles = molarity × V in mL)

Millimoles of $H_2CO_3 = 10 \times 2 = 20$

These are present in $(10 + V)$ mL of mixture by Henderson's equation:

$$pH = -\log K_a + \log \frac{[NaHCO_3]}{[H_2CO_3]}$$

$$7.4 = -\log 7.8 \times 10^{-7} + \log \frac{5V}{20}$$

$$7.4 = 6.1079 + \log \frac{5V}{20}$$

By solving, $V = 78.36$ mL

18. In MBr_2, M^{2+} conc. = 0.05 M

$$MBr_2 \rightleftharpoons M^{2+} + 2Br^-$$

$\therefore$ H_2S is diprotonic acid which is ionized as follows:

$$H_2S \underset{}{\overset{k_1}{\rightleftharpoons}} H^+ + HS^-$$

$$K_1 = \frac{[H^+] \times [HS^-]}{[H_2S]} \qquad \text{(i)}$$

$$HS^- \overset{k_2}{\rightleftharpoons} S^{2-} + H^+$$

$$K_2 = \frac{[S^{2-}][H^+]}{[HS^-]} \qquad \text{(ii)}$$

From equations (i) and (ii)

$$K_1 \times K_2 = \frac{[H^+] \times [HS^-]}{[H_2S]} \times \frac{[S^{2-}][H^+]}{[HS^-]}$$

$$K_1 \times K_2 = \frac{[H^+]^2 \times [S^{2-}]}{[H_2S]}$$

$$\text{or} \quad 1 \times 10^{-7} \times 1.3 \times 10^{-13} = \frac{[H^+]^2[S^{2-}]}{0.1} \qquad \text{(iii)}$$

MS ionizes on follows:

$$MS \rightleftharpoons M^{2+} + S^{2-}$$

$$K_{sp} \text{ of MS} = [M^{2+}][S^{2-}]$$

From given data,

$$6.0 \times 10^{-21} = [0.05][S^{2-}]$$

$$[S^{2-}] = \frac{(6.0 \times 10^{-21})}{(0.05)} \qquad \text{(iv)}$$

Substituting the value of $[S^{2-}]$ in equation (iii)

$$1 \times 10^{-7} \times 1.3 \times 10^{-13} = \frac{[H^+]^2}{(0.1)} \times \frac{[6.0 \times 10^{-21}]}{(0.05)}$$

$\therefore$ On solving $[H^+] = 10.4 \times 10^{-2}$ M

$$pH = -\log H^+$$

$$= -\log_{10}(10.4 \times 10^{-2})$$

$$= -\log_{10} 10.4 + 2\log_{10} 10$$

$$= -1.0170 + 2 = 0.983$$

19.

$$\begin{array}{lccc} & 2CN^- & + Ag^+ \rightleftharpoons & [Ag(CN)_2]^+ \\ \text{At } t = 0 & 0.1\text{M} & 0.03\text{M} & 0 \\ \text{At equilibrium} & (0.1-0.06)\text{M} & 0.0\text{M} & 0.03\text{M} \\ & =0.04\text{M} & & \end{array}$$

In this reaction, concentration of Ag^+ is zero, so this equilibrium is shifted towards left.

Hence by dissociation some Ag^+ is formed.

$$\begin{array}{lccc} & [Ag(CN)_2]^+ \rightleftharpoons & Ag^+ + & 2CN^- \\ \text{At equilibrium} & 0.03\text{M} & 0 & 0.04\text{M} \\ \text{At new equilibrium} & (0.03-x)\text{M} & x\text{M} & (0.04+2x)\text{M} \end{array}$$

$$K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^+}$$

$$\text{Hence, } 4 \times 10^{-19} = \frac{x \times (0.04 + 2x)^2}{(0.03 - x)} \text{ or } 0.03 - x \sim 0.03$$

$$\text{So, } \quad 4 \times 0.03 \times 10^{-19} = x \times (0.04 + 2x)^2$$

$$1.2 \times 10^{-20} = x \times (16 \times 10^{-4} + 4x^2 + 0.16x)$$

$$= 16 \times 10^{-4}x + 4x^3 + 0.16x^2$$

On neglecting the higher power of x

$$\therefore \quad 16 \times 10^{-4} x = 1.2 \times 10^{-20}$$

$$x = 7.5 \times 10^{-18} \text{ M}$$

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

20. CH_3COONH_4 is a salt of weak acid and weak base. So, for calculating pH of the aqueous solution of ammonium formate, following formula is applicable:

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$

$$\therefore \quad pH = \frac{1}{2}[14 + 3.8 - 4.8] = 6.5$$

21. NaCN is hydrolysed according to following equation:

$$NaCN + H_2O \rightleftharpoons NaOH + HCN$$

$$\begin{array}{lccccc} \text{or} & CN^- & + H_2O & \rightleftharpoons & HCN & + OH^- \\ \text{At equilibrium} & \frac{1-h}{V} & — & & \frac{h}{V} & \frac{h}{V} \end{array}$$

$$[OH^-] = \frac{h}{V} = C \cdot h$$

h = Degree of hydrolysis of this type of salt $= \sqrt{\dfrac{K_w}{K_a \times C}}$

C = conc. of salt

So $\quad [OH^-] = C\sqrt{\dfrac{K_w}{K_a \times C}} = \dfrac{\sqrt{C \times K_w}}{K_a}$

$$-\log_{10}[OH^-] = -\frac{1}{2}\log_{10}K_w - \frac{1}{2}\log_{10}C + \frac{1}{2}\log_{10}K_a$$

$$pOH = 7 - \frac{1}{2}\log_{10}C + \frac{1}{2}\log_{10}K_a$$

$$= 7 - \frac{1}{2}\log_{10}C - \frac{1}{2}pK_a$$

$\therefore \quad pK_a + pK_b = 14$

(For base and its conjugated acid)

$\therefore \quad pK_a = 14 - 4.70 = 9.3$

$\therefore \quad pOH = 7 - \dfrac{1}{2}\log 0.50 - \dfrac{1}{2} \times 9.30 = 7 + \dfrac{1}{2} \times 0.301 - 4.65$

$\quad pOH = 7 + 0.1505 - 4.65 = 2.50$

$\therefore \quad pH = 14 - pOH = 14 - 2.50 = 11.5$

22. $NH_3 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_4^+ + OH^-, K_b = 3.4 \times 10^{10}$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+, K_a = 5.6 \times 10^{-10}$$

$$K_{(base)}NH_3 = \frac{K_f}{K_b} = \frac{K_w}{K_{acid(NH_4^+)}} \quad (\because K_{acid} \times K_{base} = K_w)$$

or $\quad \dfrac{K_f}{3.4 \times 10^{10}} = \dfrac{10^{-14}}{5.6 \times 10^{-10}}$

$\therefore \quad K_f = 6.07 \times 10^5$

23. Electron acceptors are Lewis acids.

In Ag^+ ion ($1s^2$, $2s^2\,p^6$, $3s^2\,p^6\,d^{10}$, $4s^2\,p^6\,d^8$, $5s^2$) in the outermost shell is incomplete, so it can accommodate electrons more in valence shell and is electron acceptor. In case of Na^+, ($1s^2$, $2s^2\,p^6$) 8 electrons are present in outermost shell, i.e., its outermost orbit is complete, so it can't accommodate more electrons. Thus Ag^+ is a strong Lewis acid.

24. The concerned chemical reaction is:

$$2AgCl + Na_2CO_3 \rightarrow Ag_2CO_3 + 2\,NaCl$$

Calculation of $[Ag^+]$ left in the solution:

$$K_{sp}(Ag_2CO_3) = [Ag^+]^2\,[CO_3^{2-}]$$

$$[Ag^+] = \sqrt{\frac{8.2 \times 10^{-12}}{1.5}} = 2.34 \times 10^{-6}\,M$$

Concentration of Cl^- left = 0.0026 g/L

$$= \frac{0.0026}{35.5}\,\text{mol l l} = 7.33 \times 10^{-5}\,M$$

$\therefore \quad K_{sp}(AgCl) = [Ag^+]\,[Cl^-] \quad = (2.34 \times 10^{-6})\,(7.33 \times 10^{-5})$

$\qquad\qquad\qquad\qquad = 1.71 = \times 10^{-10}$

25. $pH = -\log K_a + \log\dfrac{[I_n^-]}{[HI_n]}$

$$pH_{(1)} = -\log(1 \times 10^{-5}) + \log\frac{1}{10} = 5 - 1 = 4$$

$$pH_2 = -\log(1 \times 10^{-5}) + \log\frac{1}{0.1} = 5 + 1 = 6$$

Thus, the pH of the solution should change from 4 to 6.

26. The given sample contains 183 ppm of HCO_3^-

$$\equiv 183 \times 10^{-6} \times 1000\,kg \equiv 183\,g \equiv \frac{183}{61} \equiv 3\text{ moles}$$

Removal of HCO_3^- by CaO

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 + 2H_2O$$

i.e., 2 moles of HCO_3^- are removed by 1 mole of CaO

$\therefore$ moles of HCO_3^- will be removed by $\dfrac{1}{2} \times 3 = 1.5$ moles of CaO

By now $Ca(HCO_3)_2$ has been completely neutralized and what remains is 96 ppm of $CaSO_4$.

So Ca^{2+} ions remaining

$= 96$ ppm of Ca^{2+}

$\equiv 96 \times 10^{-6} \times 1000 \times 1000 = 96$ g

$= \dfrac{96}{40} = 2.4$ moles of Ca^{2+} in 1000 kg of water

$= 2.4$ moles in 1000 l of water $= 2.4 \times 10^{-3}$ moles/l

Note: $CaSO_4$ is salt of weak base and strong acid. It will dissociate completely.

$$CaSO_4 + 2H_2O \rightarrow Ca(OH)_2 + H_2SO_4$$

$\therefore \quad [H^+]$ = conc. of $Ca^{2+} = 2.4 \times 10^{-3}$

$\therefore \quad pH = -\log[H^+] = -\log(2.4 \times 10^{-3})$

$\therefore \quad pH = -(-2.62) = 2.62.$

27. $[Ag(NH_3)_2]^+(aq) \rightleftharpoons Ag^+(aq) + 2NH_3(aq)$

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

Multiply and divide by Cl^-

or $\quad K_c = \dfrac{[Ag^+][Cl^-][NH_3]^2}{[Ag(NH_3)_2][Cl^-]} \qquad$ (i)

$$K_{sp}\text{ of }AgCl = [Ag^+][Cl^-] = 1.8 \times 10^{-10}\,M^2$$

Equation (i) is written as follows:

$$6.2 \times 10^{-8} = \frac{K_{sp}\text{ of }AgCl \times [NH_3]^2}{[Ag(NH_3)_2]^+[Cl^-]}$$

$$6.2 \times 10^{-8} = \frac{1.8 \times 10^{-10} \times [NH_3]^2}{[Ag(NH_3)_2]^+[Cl^-]} \qquad \text{(ii)}$$

$$\begin{array}{lcccccc} & AgCl_{(s)} & + & 2NH_{3(l)} & \rightleftharpoons & [Ag(NH_3)_2]^+_{(aq)} & + & Cl^-_{(aq)} \\ \text{At } t=0 & & & 1M & & 0 & & 0 \\ \text{At equilibrium} & & & (1-x)M & & xM & & xM \end{array}$$

Substituting the values of equation (ii)

$$6.2 \times 10^{-8} = \frac{1.8 \times 10^{-10} \times 1(1-x)^2}{x \times x}$$

Here, we assumed as $1 - x \sim 1$

$$6.2 \times 10^{-8} = \frac{1.8 \times 10^{-10}}{x^2}$$

$\therefore \quad x = \sqrt{\dfrac{1.8 \times 10^{-10}}{6.2 \times 10^{-8}}} = 0.0538\,M$

Conc. of $[Ag(NH_3)_3]^+ = 0.0538\,M$

28.

$$\begin{array}{lcccccccc} & \text{HCl} & + & \text{NaOH} & \rightarrow & \text{NaCl} & + & \text{H}_2\text{O} \\ \text{meq. before reaction} & 200\times10^{-2} & & 300\times10^{-2} & & 0 & & 0 \\ \text{meq. after reaction} & & & 100\times10^{-2} & & 200\times10^{-2} & & 200\times10^{-2} \end{array}$$

$$\text{Conc. of NaOH} = \frac{100\times10^{-2}}{500} = 2\times10^{-3}\,\text{M}$$

$$[\text{OH}^-] = 2\times10^{-3}\,\text{M}$$

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

$$\therefore \quad \text{pOH} = -\log 2\times10^{-3} = -\log 2 + 3\log 10$$

$$= -0.3010 + 3 = 2.6999$$

$$\therefore \quad \text{pH} = 14 - \text{pOH} = 14 - 2.6999 = 11.3010$$

29. pH of buffer solution = 8

$\therefore$ $[\text{H}^+]$ in buffer solution = 10^{-8} M

or $[\text{OH}^-]$ in buffer solution = 10^{-6} M

The solubility of Pb(OH)_2 in water is 6.7×10^{-6} M

$$\therefore \quad \underset{6.7\times10^{-6}\,\text{M}}{\text{Pb(OH)}_2} \rightleftharpoons \underset{6.7\times10^{-6}\,\text{M}}{\text{Pb}^{2+}} + \underset{2\times6.7\times10^{-6}\,\text{M}}{2\,^-\text{OH}}$$

$$\therefore \quad K_{sp} \text{ of } \text{Pb(OH)}_2 = [\text{Pb}^{2+}][\text{OH}^-]^2$$

$$= 6.7\times10^{-6}\times(13.4\times10^{-6})^2$$

$$= 1203.05\times10^{-18}\,(\text{mol/L})^3$$

Suppose the solubility of Pb(OH)_2 in pH = 8, buffer solution is x M

$$\therefore \quad \underset{x\text{M}}{\text{Pb(OH)}_2} \rightleftharpoons \underset{x\text{M}}{\text{Pb}^{2+}} + \underset{2x\text{M}}{2\text{OH}^-}$$

In buffer solution, total $[\text{Pb}^{2+}] = (6.7\times10^{-6} + x)$M

$[\text{OH}^-] = 10^{-6}$ M (given data i.e., pH = 8)

$$\therefore \quad K_{sp} = [\text{Pb}^{2+}][\text{OH}^-]^2$$

$$1203.05\times10^{-18} = (6.7\times10^{-6} + x)(10^{-6})^2$$

or

$$1203.05\times10^{-18} = 6.7\times10^{-6}\times10^{-12} + x\times10^{-12}$$

$$x\times10^{-12} = (1203.05 - 6.7)\times10^{-18}$$

$$x = \frac{1196.35\times10^{-18}}{10^{-12}} = 1196.35\times10^{-6}\,\text{M}$$

30. Average concentration of SO_2 in atmosphere is 10 ppm, i.e $\frac{10}{10^6} = 10^{-5}\,\text{mol L}^{-1}$

Molar concentration of SO_2 in water is the product of concentration of SO_2 in atmosphere and solubility of SO_2 in water, i.e $= 1\times10^{-5}\times1.3653 = 1.3653\times10^{-5}\,\text{mol L}^{-1}$

$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$$

$$\therefore \quad [\text{SO}_2] = [\text{H}_2\text{SO}_3] = 1.3653\times10^{-5}\,\text{M}$$

H_2SO_3 ionises as follows:

$$\begin{array}{lcccc} & \text{H}_2\text{SO}_3 & \rightleftharpoons & \text{H}^+ + & \text{HSO}_3^- \\ \text{At } t=0 & 1.3653\times10^{-5}\,\text{M} & & 0 & 0 \\ \text{After ionisation} & (1.3653\times10^{-5} - x)\text{M} & & xM & xM \end{array}$$

$$K_a = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]}$$

$$pK_a = 1.92$$

$$-\log K_a = 1.92$$

$$K_a = -\text{antilog } 1.92$$

$$= \frac{x^2}{(1.3653\times10^{-5} - x)}$$

$$-\text{antilog } 1.92 = \frac{x^2}{(1.3653\times10^{-5} - x)}$$

Take negative log on both sides

$$1.92 = -2\log x + \log(1.3653\times10^{-5} - x)$$

Neglecting x,

$$1.92 = -2\log[\text{H}^+] + \log 1.3653\times10^{-5}$$

$$= 2\,\text{pH} + \log 1.3653\times10^{-5}$$

$$\text{pH} \approx 3.3925.$$

31. **i.** 500 mL of 0.2 M CH_3COOH solution is mixed with 500 mL of 0.2 M HCl at 25°C, therefore in mixture the conc. of CH_3COOH is 0.1 M and conc. of H^+ of HCl is also 0.1 M. CH_3COOH is ionized as follows:

$$\begin{array}{lccccc} & \text{CH}_3\text{COOH} & \rightleftharpoons & \text{CH}_3\text{COO}^- & + & \text{H}^+ \\ \text{At } t=0 & 0.1\text{M} & & 0 & & 0 \\ \text{At equilibrium} & (0.1-x)\text{M} & & x\text{M} & & (0.1+x)\text{M} \end{array}$$

$$\text{Total } [\text{H}^+] = \underset{\substack{\uparrow \\ \text{Coming from HCl}}}{0.1} + x$$

$$\text{Thus, } K_a \text{ of } \text{CH}_3\text{COOH} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$K_a \text{ of } \text{CH}_3\text{COOH} = 1.75\times10^{-5}\,\text{mol/L}$$

$$\text{Thus,} \quad 1.75\times10^{-5} = \frac{x\times(0.1+x)}{(0.1-x)}$$

CH_3COOH is weak acid, so for it $0.1 - x \sim 0.1$ M and $0.1 + x \sim 0.1$ M

$$\text{Hence, } 1.75\times10^{-5} = \frac{x\times0.1}{0.1}$$

On solving we get $x = 1.75\times10^{-5}$

$$\text{Degree of dissociation of CH}_3\text{COOH} = \frac{1.75\times10^{-5}}{0.1} = 1$$

$$= 1.75\times10^{-4}$$

% degree of dissociation = 1.75×10^{-2} %

$$\text{pH} = -\log_{10}(\text{H}^+) = -\log_{10}0.1 = -1\log 10 = -1$$

ii. 6 g of NaOH is added in above solution, thus the concentration of NaOH $\frac{6}{40}$ M = 0.15 M

($\because$ solution is 1000 ml)

From it 0.1 M is neutralized with 0.1 M HCl and rest 0.05 M NaOH reacts with CH_3COOH to give CH_3COONa. Thus,

$$\begin{array}{lccccccc} & \text{CH}_3\text{COOH} & + & \text{NaOH} & \rightleftharpoons & \text{CH}_3\text{COONa} & + & \text{H}_2\text{O} \\ \text{Initial moles} & 0.1\text{M} & & 0.05\text{M} & & 0 & & 0 \\ \text{At equilibrium} & (0.1-0.05)\text{M} & & 0\text{M} & & 0.05\text{M} & & 0.0.5\text{M} \end{array}$$

By Henderson's equation

$$\text{pH} = -\log_{10}K_a + \log_{10}\frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$= -\log_{10}1.75\times10^{-5} + \log_{10}\frac{(0.05)}{0.05}$$

$$= -\log_{10}1.75 + 5\log_{10}10 + \log_{10}1$$

$$= -0.2430 + 5 + 0 = 4.757$$

32. pH of solution depends upon H^+ ion concentration, which depends on K_w which is a function of temperature. Therefore, change in temperature brings a change in pH value for given sample of water. So pH of water will not be same at 4°C and 25°C.

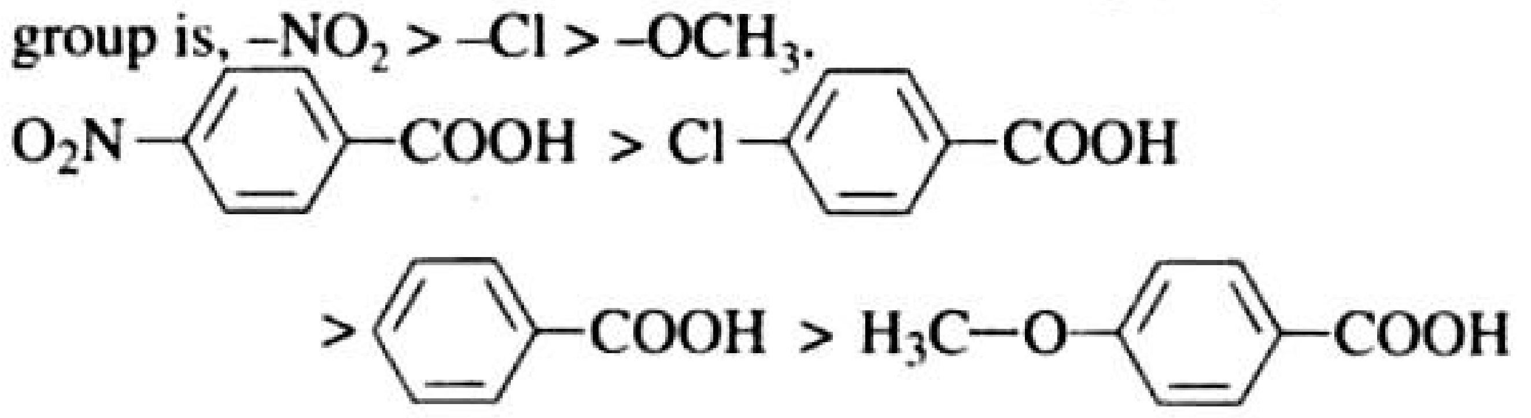
33. ⇒ As we know that acid strength of acid ∝ K_a. So higher the value of K_a higher the acidic strength of acid.

⇒ Strength of acid ∝ Stability of benzoate ion.

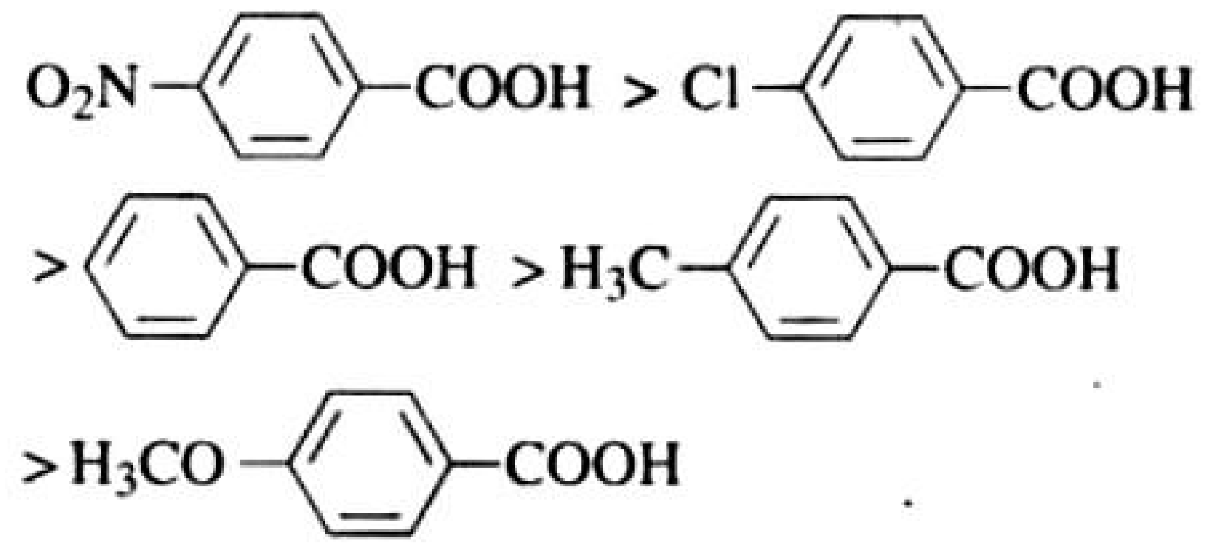
Resonance stabilization of benzoate ion

–I group stabilizes benzoate ion.

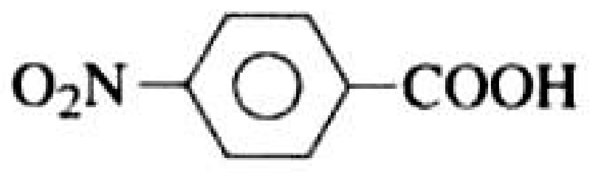
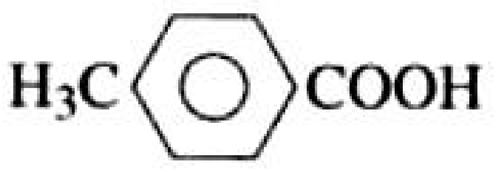
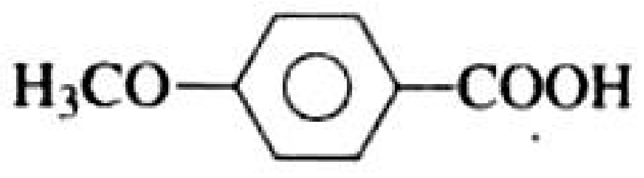
⇒ Order of $-I$ effect in –Cl atom, $-OCH_3$ group and $-NO_2$ group is, $-NO_2 > -Cl > -OCH_3$.



While on attachment of electron donating group or atoms ($+I$) effect showing group, acidic strength decreases due to decreasing the stability of caroxylate ion. So, p-methyl benzoic acid is weak acid in comparison of benzoic acid. Hence, the order of acidic strength in given acids.



For matching their K_a value acidic strength ∝ K_a. Hence,

Acid	K_a
	30.6×10^{-5}
	6.4×10^{-5}
	6.3×10^{-5}
	4.2×10^{-5}
	3.3×10^{-5}

34. $\underset{\substack{0.1\\0}}{NaOH} + \underset{\substack{0.1\\0}}{HA} \rightarrow \underset{\substack{0\\0.1}}{NaA} + \underset{\substack{0\\0.1}}{H_2O}$

$[NaA] = \frac{0.1}{2}$ because volume is double on mixing.

NaA is a salt of weak acid HA and strong base NaOH. For such salt solution:

$$\begin{aligned}
pH &= 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C \\
&= 7 + \frac{1}{2}(-\log 5.6 \times 10^{-5}) + \frac{1}{2}\log\left(\frac{0.1}{2}\right) \\
&= 7 + \frac{1}{2}(5 - \log 5.6) + (-0.65) \\
&= 7 + \frac{5.25}{2} = 8.975
\end{aligned}$$