13 Ionic Equilibrium

Ostwald dilution law : The dissociation of weak electrolyte obeys law of mass action. The application of law of mass action to weak electrolyte is known as Ostwald dilution law. **It is to be noted here, that either acids or bases are weak electrolytes but salts are usually strong electrolytes.**

Consider a weak electrolyte say HA (an acid)

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

	HA	H^+	A^-
Before dissociation	1	0	0
After dissociation	$1-\alpha$	α	α

Where α is degree of dissociation.

Let C be the concentration of HA in mol litre^{-1} before its dissociation then, $[HA] = C(1-\alpha)$; $[H^+] = C\alpha$; $[A^-] = C\alpha$

According to law of mass action

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(C\alpha \cdot C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If α is small, then $1-\alpha \approx 1$.

$$K_a = C\alpha^2 \quad \text{...(1)}$$

or

$$\alpha = \sqrt{\left(\frac{K_a}{C}\right)} \quad \text{...(2)}$$

where K_a is dissociation constant of acid.

Similarly, for a weak base

$$BOH \rightleftharpoons B^+ + OH^-$$

$$K_b = C\alpha^2 \quad \text{...(3)}$$

$$\therefore \quad \alpha = \sqrt{\left(\frac{K_b}{C}\right)} \quad \text{...(4)}$$

where K_b is dissociation constant of base.

Note: 1. K_a and K_b are just the equilibrium constants and hence depend only on temperature.

2. Greater are the values of K_a or K_b more is the strength of acid or base respectively.

3. Relations 1 to 4 are valid for mono basic acid and mono acid base.

4. Different expressions have to be derived for dibasic or tribasic acids and diacidic or triacidic base.

Acid and base

Arrhenius concept

(1) An acid furnishes H^+ ions in solution and a base furnishes OH^- ions in solutions

(2) The strength of acid depends upon its tendency to furnish H^+ ions.

Bronsted concept

(1) An acid is a proton donor; a base is a proton acceptor.

(2) The strength of an acid depends upon its tendency to donate proton. More is the tendency to donate proton, more is acidic nature.

(3) Water is amphoteric as it donates as well as accepts proton.

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

(4) Each cation is acid and each anion is base.

(5) A pair of acid and base which differ by a proton is known as conjugate pair of acid and base.

$$\text{Acid } (H_2S) \xrightarrow[\text{or } -H^+]{\text{Take out one proton}} \text{Conjugate base } (HS^-)$$

$$\text{Base } (NH_3) \xrightarrow[\text{or } +H^+]{\text{Add one proton}} \text{Conjugated base } (NH_4^+)$$

Lewis concept

(1) Acids are electron pair acceptor, *e.g.*, BF_3, $AlCl_3$.

(2) Bases are electron pair donor, *e.g.*, NH_3, PCl_3.

Relative strength of Acids and Bases :

For weak acids :

$$\text{Relative strength} = \frac{\text{Strength of I acid}}{\text{Strength II acid}}$$

$$= \frac{[H^+]\text{furnished by I acid}}{[H^+]\text{furnished by II acid}} = \frac{C_1\alpha_1}{C_2\alpha_2}$$

$$= \frac{C_1}{C_2} \times \sqrt{\left(\frac{K_{a_1}C_2}{K_{a_2}C_1}\right)} = \sqrt{\left(\frac{K_{a_1}C_1}{K_{a_2}C_2}\right)} \quad \text{...(5)}$$

$$= \sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)} (\text{if } C_1 = C_2) \quad \text{...(6)}$$

For strong acids :

$$\text{Relative strength} = \frac{K_1}{K_2}$$

$$= \frac{\text{rate constant for a reaction catalysed by I acid}}{\text{rate constant for a reaction catalysed by II acid}}$$

Note : For rate constant of acid catalysed reactions, see ester hydrolysis and sugar hydrolysis in **chemical kinetics.**

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Ionic product of water : Pure water, a weak electrolyte dissociates as

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

$$\therefore \quad K = \frac{[H^+][OH^-]}{[H_2O]} \quad \text{(According to law of mass action)}$$

or $\quad K_w = K[H_2O] = [H^+][OH^-] \quad \ldots(7)$

$\because$ $[H_2O]$ is constant since only one molecule out of 550 million molecules of H_2O dissociates, *i.e.*, $\alpha_{H_2O} = \frac{1}{550 \times 10^6}$

$$\alpha_{H_2O} = 1.8 \times 10^{-9} = 1.8 \times 10^{-7}\%$$

here K_w is a characteristic constant for water, known as ionic product of water. The numerical value of K_w is 10^{-14} mol^2 litre^{-2} at 25°C. The value of K_w however increases with increase in temperature.

pH and pOH values : Sorenson used a new term to express $[H^+]$ as pH defined as the negative power raised on 10 in order to express $[H^+]$.

i.e., $\quad [H^+] = 10^{-pH} \quad \ldots(8)$

or $\quad pH = -\log[H^+] \quad \ldots(9)$

(*i.e.*, negative logarithm of **magnitude of $[H^+]$**)

Thus, for pure water
- pH = 7 *i.e.*, Neutral solution
- pH = 0 to 7 *i.e.*, Acidic solution
- pH = 7 to 14 *i.e.*, Alkaline solution

Also $\because \quad [H^+][OH^-] = 10^{-14}$

$\therefore \quad (-\log H^+) + (-\log OH^-) = 14$

$\therefore \quad \mathbf{pH + pOH = 14} \quad \ldots(10)$

Common ion effect : The phenomenon in which degree of dissociation of a **weak electrolyte** is suppressed due to the presence of **common ion** present in it.

Consider a weak electrolyte along with common ion, *e.g.*,

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

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

$$\text{For acetic acid } K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Thus, $[CH_3COO^-]$ in solution becomes more in presence of CH_3COONa. However K_a is constant. Thus, in order to have K_a constant, $[H^+]$ in solution must decrease or $[CH_3COOH]$, *i.e.*, undissociated acid must increase or in other words degree of dissociation of CH_3COOH decreases.

Note : In presence of a common ion (from strong electrolyte) present with weak electrolyte, the concentration of common ion is derived from strong electrolyte.

Buffer solutions : Solutions which possess reserve acidic nature or alkaline nature or solutions which resist change or do not show significant change in pH due to dilution or addition of small quantities of acid or alkali are known as buffer solutions.

Types of buffer solutions :

(1) Simple buffer : Salts of weak acid and weak base,
e.g., $\quad CH_3COONH_4$, NH_4CN, etc.

(2) Mixed buffers : These are of two types.

(a) Acidic buffer mixtures : A weak acid + its salts or its conjugate base
e.g., $\quad CH_3COOH + CH_3COONa$

(b) Basic buffer mixtures : A weak base + its salt or its conjugate acid
e.g., $\quad NH_4OH + NH_4Cl$

Handerson equation for pH and pOH of mixed buffers

Acidic buffer mixtures : Consider a buffer mixture of weak acid + its conjugate base *i.e.*, $CH_3COOH + CH_3COONa$

Then $\quad CH_3COONa \longrightarrow CH_3COO^- + Na^+ \quad \ldots(A)$

$\quad CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \ldots(B)$

Applying law of mass action to Eq. (B)

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

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

or $$pH = -\log K_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]} \quad \ldots(11)$$

$$pH = pK_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]} \quad \ldots(12)$$

Similarly for basic buffers *i.e.*, A weak base + its conjugate acid

$$pOH = -\log K_b + \log\frac{[\text{Conjugate acid}]}{[\text{Base}]} \quad \ldots(13)$$

or $$pOH = pK_b + \log\frac{[\text{Conjugate acid}]}{[\text{Base}]} \quad \ldots(14)$$

Addition of acid or base to a buffer : The anion of salt consumes H^+ given by acid and thus, [anion] in buffer decreases and [acid] in buffer increases and pH changes slightly.

$$H^+ + \text{Anion} \longrightarrow \text{Acid}$$

The undissociated acid consumes OH^- given by alkali and thus, [anion] in buffer increases and [acid] in buffer decreases which results a change in pH slightly.

$$OH^- + \text{Acid} \longrightarrow \text{Anion}$$

Similarly, acid or alkali addition brings in following changes in basic buffer solutions.

$$H^+ + \text{Base} \longrightarrow \text{Cation}$$

$$OH^- + \text{Cation} \longrightarrow \text{Base}$$

Note: No doubt pH of buffer solutions experimentally remains unchanged on addition of small amount of acid or base but it change theoretically to a very small extent which however cannot be detected by pH meters.

Buffer capacity : The property of a buffer solution to which it resist the change in pH on addition of acid or alkali. It is expressed as :

$$\phi = \frac{d(b)}{d\text{pH}} \quad ...(15)$$

where b is no. of mole of acid or base added to one litre solution and dpH is change in pH.

e.g., suppose pH of buffer changes from 4.745 to 4.832 when 0.01 mole of KOH is added to 0.5 litre buffer.

$$\phi = \frac{0.01 \times 2}{0.087} = 0.230$$

pK_a and pK_b for a conjugate acid-base pair

$$pK_a + pK_b = pK_w = 14 \quad ...(16)$$

Note : 1. Stronger is acid, weaker is its conjugate base.

2. Higher is the value of pK_a of an acid, lower is acid strength and higher is basic strength of its conjugate base.

Solubility product : Consider a sparingly soluble salts in water. Let solubility of it be s mol litre^{-1}.

$$A_xB_y(s) + aq. \rightleftharpoons A_xB_y(aq.)$$

$$\text{or } A_xB_y(s) + aq. \rightleftharpoons \underset{xs}{xA^{+y}} + \underset{ys}{yB^{-x}} \quad \text{ions furnished after dissociation}$$

According to law of mass action,

$$K = \frac{[A^{+y}]^x[B^{-x}]^y}{[A_xB_y]} \text{ or } K[A_xB_y] = [A^{+y}]^x[B^{-x}]^y$$

$$K_{sp} = [A^{+y}]^x[B^{-x}]^y \quad ...(17)$$

where K_{sp} is a characteristic constant for a given solute known as solubility product and defined as the product of ionic concentrations with suitable powers. K_{sp} however changes with temperature.

Putting $[A^{+y}] = xs$ and $[B^{-x}] = ys$ in Eq. (17);

$$K_{sp} = (xs)^x(ys)^y = x^x \cdot y^y (s)^{x+y} \quad ...(18)$$

e.g., For AgCl

$$\therefore AgCl(s) + aq. \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{Cl^-}; K_{sp} = s^2$$

For Ag_2CrO_4

$$\because Ag_2CrO_4(s) + aq. \rightleftharpoons \underset{2s}{2Ag} + \underset{s}{CrO_4^{2-}}; K_{sp} = 4s^3$$

Now if

$[A^{+y}]^x[B^{-x}]^y > K_{sp}$; The solid A_xB_y will precipitate out

$[A^{+y}]^x[B^{-x}]^y < K_{sp}$; No precipitation

$[A^{+y}]^x[B^{-x}]^y = K_{sp}$; No precipitation upto this limit or precipitation will just start at this condition. This is a limiting case.

Effect of common ion on solubility

Consider saturated solution of AgCl. If a salt having either of the ion common to AgCl say KCl is added to it, then

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

$$KCl + aq. \longrightarrow K^+ + Cl^-$$

For AgCl : $K_{sp} = [Ag^+][Cl^-]$

$[Cl^-]$ increases in solution due to presence of KCl and thus to have K_{sp} constant, $[Ag^+]$ will decrease or AgCl will precipitate out from solution, *i.e.*, solubility of AgCl will decrease with increasing concentration of KCl in solution.

Let 0.1 M KCl($aq.$) solution with AgCl($aq.$). If solubility of AgCl is s mol litre^{-1}, then

For AgCl : $K_{sp} = [Ag^+][Cl^-]$

$$K_{sp} = s(s + 0.1)$$

s being small in comparison to 0.1 and thus may be neglected therefore,

$$K_{sp} = s \times 0.1 \text{ or } s_{AgCl} = \frac{K_{sp}}{0.1}$$

where s is solubility of AgCl in presence of 0.1 M KCl($aq.$).

Note: 1. A solute on addition if undergoes complex formation with ions of sparingly soluble salt, the solubility of salt increases.

2. The solubility of sparingly soluble salt say AgCN is also influenced if the salt undergoes hydrolysis. Normally solubility of salts increases with hydrolysis.

Simultaneous solubility : The phenomenon when two or more sparingly soluble salts having one ion common (either cation AgCl and AgBr or anion $BaSO_4$ and $CaSO_4$) leads to simultaneous solubility equilibria. For example.

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$AgBr \rightleftharpoons Ag^+ + Br^-$$

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

$$K_{sp}\ AgBr = [Ag^+][Br^-]$$

Thus if both are present $[Ag^+]$ should be same

or $$\frac{K_{sp}AgCl}{K_{sp}AgBr} = \frac{[Cl^-]}{[Br^-]}$$

Hydrolysis : The phenomenon in which anion or cation furnished by a salt interacts with H_2O to produce acidic nature or alkaline nature is known as salt hydrolysis.

The nature of aqueous solution of salt to be acidic or alkaline depends upon the nature of salt.

Salts of strong acid and weak base : *e.g.*, NH_4Cl, NH_4NO_3, $CuSO_4$, $ZnCl_2$, $FeCl_3$, etc.

$$NH_4Cl + H_2O \rightleftharpoons \underset{\text{weak}}{NH_4OH} + \underset{\text{Strong electrolyte}}{HCl}$$

or $$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

or $$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

NH_4Cl on dissolution in water furnish NH_4^+ and Cl^- ion. Cl^- with H^+ gives HCl, a strong acid which returns back all the H^+ to solution. On the other hand NH_4^+ interacts with OH^- to give NH_4OH, a weak electrolyte having low degree of dissociation. Also due to common ion effect of unhydrolysed NH_4^+, the degree of dissociation of NH_4OH is further suppressed and thus in solution the $[H^+]$ becomes more and it acquires acidic character. It is thus suggested that acidic character of NH_4Cl solution is due to hydrolysis of NH_4^+ ion or the hydrolysis of weak component of salt.

Hydrolysis constant and degree of hydrolysis : Consider a salt say NH_4Cl in water. Let C mol litre^{-1} be the concentration of salt and h the degree of hydrolysis of salt.

	NH_4Cl	+ H_2O ⇌	NH_4OH	+ HCl
Before hydrolysis	1	0	0	0
After hydrolysis	$(1-h)$	h	h	h

or $$\underset{(1-h)}{NH_4^+} + \underset{(1-h)}{Cl^-} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+} + \underset{h}{Cl^-}$$

or $$\underset{(1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+}$$

∴ According to law of mass action,

$$K = \frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]} \quad \text{or} \quad K[H_2O] = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

or $$K_H = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad ...(19)$$

Now for weak base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad ...(20)$$

By Eqs. (19) and (20), $K_H \times K_b = [H^+][OH^-] = K_w$

or $$K_H = \frac{K_w}{K_b} \quad ...(21)$$

Further, $[NH_4^+] = C(1-h)$

$[NH_4OH] = Ch$

$[H^+] = Ch$

∴ By Eqs. (19), $$K_H = \frac{Ch \cdot Ch}{C(1-h)} = \frac{Ch^2}{(1-h)} \quad ...(22)$$

∵ h is small ∴ $1-h \approx 1$ or $K_H = Ch^2$

or $$h = \sqrt{\left(\frac{K_H}{C}\right)} \quad ...(23)$$

Also pH is derived by $[H^+]$

$[H^+] = Ch$

By Eq. (23), $$[H^+] = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)} \quad ...(24)$$

By Eqs. (21) and (24), $$[H^+] = \sqrt{\left(\frac{K_w}{K_b} \cdot C\right)}$$

∴ $$-\log H^+ = \frac{1}{2}[\log K_b - \log K_w - \log C]$$

∴ $$pH = \frac{1}{2}[\log K_b - \log K_w - \log C] \quad ...(25)$$

Thus, following results can be written for case I and similar derivations can be made for case II and case III.

Case I : Salt of strong acid and weak base : *e.g.*, NH_4Cl

$$K_H = \frac{K_w}{K_b}; h = \sqrt{\left(\frac{K_H}{C}\right)} \text{ and } pH = \frac{1}{2}[\log K_b - \log K_w - \log C]$$
$$= \frac{1}{2}[pK_w - pK_b - \log C]$$

Case II : Salts of weak acid + Strong base : *e.g.*, CH_3COONa, KCN....., etc.

$$K_H = \frac{K_w}{K_a}; h = \sqrt{\left(\frac{K_H}{C}\right)} \text{ and } pOH = \frac{1}{2}[\log K_a - \log K_w - \log C]$$
$$= \frac{1}{2}[pK_w - pK_a - \log C]$$

Case III : Salts of weak acid + weak base : *e.g.*, CH_3COONH_4, NH_4CN,....., etc.

$$K_H = \frac{K_w}{K_a \cdot K_b}; h = \sqrt{K_H} \text{ (if } h \text{ is small) or } \frac{h}{1-h} = \sqrt{K_H}$$

$$pH = \frac{1}{2}[\log K_b - \log K_a - \log K_w] = \left[\frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b\right]$$

Case IV : Salts of strong acid + strong base : *e.g.*, NaCl, KNO_3,....., etc.

This category of salt does not undergo salt hydrolysis.

NOTE : (i) Eq. (21) and analogous equation for other category should be used only when the degree of hydrolysis is negligible.

(ii) All the derivations made for salt hydrolysis are for uni-univalent salts. For other types of salts (say uni-bivalent, *e.g.*, $Na_2C_2O_4$ or bi-bivalent CaC_2O_4, one should derive the similar equations following the same above methods). The term 'C' in the above equations however represents the concentration of ion that undergoes hydrolysis.

(iii) The pH of acidic salts of polyprotic acids in water say NaHS is given by : $pH = \frac{[pK_{a_1} = pK_{a_2}]}{2}$

• NUMERICAL PROBLEMS •

1. Calculate the amount of acetic acid present in one litre of its solution having $\alpha = 1\%$ and $K_a = 1.8 \times 10^{-5}$.
2. 0.16 g of N_2H_4 are dissolved in water and the total volume made upto 500 mL. Calculate the percentage of N_2H_4 that has reacted with water in this solution. The K_b for N_2H_4 is 4.0×10^{-6} M. **(Roorkee 1998)**
3. Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNiC. Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2.0 litre of solution. **(Roorkee 1993)**
4. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula HSaC. 4×10^{-4} mole of saccharin is dissolved in 200 cm^3 water of pH 3. Assuming no change in volume, calculate the concentration of SaC^- ions in the resulting solution at equilibrium. **(Roorkee 1994)**
5. Acetyl salicylic acid, *i.e.*, aspirin ionises in water as :
$$HC_9H_7O_4 + H_2O \rightleftharpoons H_3O^+ + C_9H_7O_4^-;$$
$$K_a = 2.75 \times 10^{-9}$$
If two tablets of aspirin each of 0.32 g is dissolved in water to produce 250 mL solution, calculate $[H^+]$, $[OH^-]$ and $[C_9H_7O_4^-]$ in solution.
6. The ionisation 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} litre mol^{-1} sec^{-1}. Calculate the rate constant for proton transfer from water to NH_3. **(IIT 1996)**
7. Calculate the concentration of fluoroacetic acid which is required to get $[H^+] = 1.50 \times 10^{-3}$ M. K_a of acid $= 2.6 \times 10^{-3}$.
8. An aqueous solution contains 10% ammonia by mass and has a density of 0.99 $g\,cm^{-3}$. Calculate hydroxyl and hydrogen ion concentration in this solution. K_a for $NH_4^+ = 5.0 \times 10^{-10}$ M. **(Roorkee 1995)**
9. Liquid ammonia ionises to a slight extent. At −50°C, its ionisation constant, $K_{NH_3} = [NH_4^+][NH_2^-] = 10^{-30}$. How many amide ions are present per cm^3 of pure liquid ammonia ? Assume $N = 6.0 \times 10^{23}$.
10. The ionisation constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid are converted to formate ion? The density of formic acid is 1.22g/cm^3.
11. Calculate the dissociation constant of NH_4OH at 25°C, if $\Delta H°$ and $\Delta S°$ for the given changes are as follows :
$$NH_3 + H^+ \rightleftharpoons NH_4^+; \quad \Delta H° = -52.2 \text{ kJ mol}^{-1}$$
$$H_2O \rightleftharpoons H^+ + OH^-; \quad \Delta H° = 56.6 \text{ kJ mol}^{-1}$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-; \quad \Delta S° = -76.53 \text{ JK}^{-1} \text{ mol}^{-1}$$
12. Prove that degree of dissociation of a weak acid is given by:
$$\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$
where K_a is its dissociation constant.
13. Determine degree of dissociation of 0.05 M NH_3 at 25°C in a solution of pH = 11.
14. In the qualitative analysis, Bi^{3+} is detected by the appearance of the precipitates of bismuthyl hydroxide $[BiO(OH)_S]$. Calculate the pH when the following equilibrium exists K_b for $BiO(OH) = 4 \times 10^{-10}$.
15. Calculate the concentration of all species of significant concentrations present in 0.1 M H_3PO_4 solution. $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 3.6 \times 10^{-13}$. Also calculate pH of solution.
16. Calculate the $[OH^-]$ of $[NH_2 \cdot C_2H_4NH_3]^+$ and $[H_3N - C_2H_4NH_3]^{2+}$ in 0.15 M ethylene diamine (*aq*.); if
$$NH_2C_2H_4NH_2 + H_2O \rightleftharpoons NH_2C_2H_4NH_3^+ + OH^-; \quad K_1 = 8.5 \times 10^{-5}$$
$$NH_2C_2H_4NH_3^+ + H_2O \rightleftharpoons [NH_3C_2H_4NH_3]^{2+} + OH^-; \quad K_2 = 2.7 \times 10^{-8}$$
17. Calculate pH of (1) 10^{-3} N HNO_3, (2) 10^{-3} M H_2SO_4, (3) 10^{-3} N H_2SO_4, (4) 0.01 N HCl, (5) 10^{-8} N HCl, (6) 10^2 M HCl.
18. Calculate pH for acid solutions having $[H^+]$ as (a) $[H^+] = 0.05$ M, (b) $[H^+] = 5.0$ M, (c) $[H^+] = 10^{-8}$ M.
19. Calculate pH for.
(a) 0.001 N NaOH (b) 0.01 N $Ca(OH)_2$
(c) 0.01 M $Ca(OH)_2$ (d) 10^{-8} M NaOH
(e) 10^2 M NaOH (f) 0.0008 M $Mg(OH)_2$
Assume complete ionisation of each. **(Roorkee 1992)**
20. Calculate pH of basic solutions having $[OH^-]$ as
(a) $[OH^-] = 0.05$ M, (b) $[OH^-] = 5.0$ M,
(c) $[OH^-] = 10^{-8}$ M.
21. Calculate pH of (Given K_a CH_3COOH = K_a NH_4OH = 2.0×10^{-3})
(a) 0.002 N acetic acid having 2.3% dissociation.
(b) 0.002 N NH_4OH having 2.3% dissociation.

22. 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 litre^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **(IIT 2000)**

23. Calculate $[H^+]$ and $[CHCl_2COO^-]$ in a solution that is 0.01 M HCl and 0.01 M in $CHCl_2COOH$. K_a for $CHCl_2COOH$ is 5×10^{-2}.

24. A solution contains 0.09 M $CHCl_2COOH$ and 0.1 M CH_3COOH. The pH of this solution is 1. If K_a for acetic acid is 10^{-5}, calculate K_a for $CHCl_2COOH$.

25. What is $[H^+]$ for a solution in which
(*i*) pH = 3 (*ii*) pH = 4.75 ?

26. The pH of 0.05 M aqueous solution of diethyl amine is 12.0. Calculate K_b. **(Roorkee 1993)**

27. The K_w for $2H_2O \rightleftharpoons H_3O^+ + OH^-$ changes from 10^{-14} at 25°C to 9.62×10^{-14} at 60°C. What is pH of water at 60°C? What happens to its neutrality?

28. Ionic product of water $(K_w) = 1 \times 10^{-14}$ at 25° C. What are dissociation constant of water and autoprotonation constant of water?

29. Will the pH of water be same at 4° C and 25° C? Explain. **(IIT 2003)**

30. The pH of pure water at 25°C and 35°C are 7 and 6 respectively. Calculate the heat of formation of water from H^+ and OH^-.

31. A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be pH of resulting solution?

32. 2.0 g of diborane (B_2H_6) reacts with water to produce 100 mL solution. If K_a for H_3BO_3 is 7.3×10^{-10}, calculate pH of solution.

33. 100 mL of HCl gas at 25°C and 740 mm pressure were dissolved in one litre of water. Calculate the pH of solution. Given, V.P. of H_2O at 25°C is 23.7 mm.

34. Find the concentrations of H^+, HCO_3^- and CO_3^{2-} in a 0.01 M solution of carbonic acid if the pH of solution is 4.18. $K_1 = 4.45 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$.

35. Calculate the $[Cl^-]$, $[Na^+]$, $[H^+]$, $[OH^-]$ and pH of resulting solution obtained by mixing 50 mL of 0.6 N HCl and 50 mL of 0.3 N NaOH.

36. Calculate the pH of solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4.

37. What is the pH of 1 M solution of acetic acid? To what volume one litre of this solution be diluted so that pH of the resulting solution will be twice of the original value? $K_a = 1.8 \times 10^{-5}$. **(IIT 1990)**

38. Calculate the pH of a solution which contains 100 mL of 0.1 M HCl and 9.9 mL of 1.0 M NaOH.

39. 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 1998)**

40. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M 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. [Assume there is no change in volume on mixing; K_a of acetic acid is 1.75×10^{-5} mol L^{-1}.] **(IIT 2002)**

41. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M? K_a for $C_6H_5NH_3^+$ is 2.4×10^{-5} M. **(Roorkee 1996)**

42. Calculate $[H^+]$ in a solution containing 0.1 M HCOOH and 0.1 M HOCN. K_a for HCOOH and HOCN are 1.8×10^{-4} and 3.3×10^{-4}.

43. What is the concentration of acetic acid which has same pH as 0.5 M HCOOH solution. K_a HCOOH $= 2.4 \times 10^{-4}$ and K_a $CH_3COOH = 1.8 \times 10^{-5}$

44. What are $[H^+]$, $[A^-]$ and $[B^-]$ in a solution that is 0.03 M HA and 0.1 M HB ? K_a for HA and HB are 1.38×10^{-4} and 1.05×10^{-10} respectively.

45. Calculate $[H^+]$, pH, $[CH_3COO^-]$ and $[C_7H_5O_2^-]$ in a solution containing 0.02 M CH_3COOH and 0.01 M C_6H_5COOH. $K_{CH_3COOH} = 1.8 \times 10^{-5}$ and $K_{C_6H_5COOH} = 6.4 \times 10^{-5}$.

46. What concentration of $HCOO^-$ is present in a solution of 0.015 M HCOOH and 0.02 M HCl. K_aHCOOH $= 1.8 \times 10^{-4}$

47. A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively. **(Roorkee 1992)**

48. The K_a for formic acid and acetic acid are 2.1×10^{-4} and 1.1×10^{-5} respectively. Calculate relative strength of acids.

49. Calculate the pH of a solution of given mixtures:
(a) $(2g\ CH_3COOH + 3g\ CH_3COONa)$ in 100 mL of mixture; $K_a = 1.8 \times 10^{-5}$
(b) 5 mL of 0.1 M NH_4OH + 250 mL of 0.1 M NH_4Cl; $K_b = 1.8 \times 10^{-5}$
(c) (0.25 mole of acid + 0.35 mole of salt) in 500 mL mixture; $K_a = 3.6 \times 10^{-4}$

50. Calculate the pH of a buffer solution prepared by dissolving 30 g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1 M HCl. K_a for $HCO_3^- = 5.63 \times 10^{-11}$.

51. 0.15 mole of pyridinium chloride has been added into $500 cm^3$ of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in volume.
(K_b for pyridine $= 1.5 \times 10^{-9} M$) **(Roorkee 1995)**

52. Calculate the mass of $(NH_4)_2SO_4$ in g which must be added to 500 mL of 0.2 M NH_3 to yield a solution of pH = 9.35. K_b for $NH_3 = 1.78 \times 10^{-5}$.

53. What volume of 0.1 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH = 4.0; pK_a of formic acid = 3.80? **(Roorkee 1990)**

54. How many mole of HCl will be required to prepare one litre of buffer solution (containing NaCN + HCl) of pH 8.5 using 0.01 g formula mass of NaCN ? $K_{HCN} = 4.1 \times 10^{-10}$.

55. A 40 mL solution of weak base BOH is titrated with $0.1N$ HCl solution. The pH of solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20.0 mL of acid respectively. Find out K_b for weak base. **(IIT 1991)**

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

57. A solution of weak acid was titrated with base NaOH. The equivalence point was reached when 36.12 mL of 0.1 M NaOH have been added. Now 18.06 mL 0.1 M HCl were added to titrated solution, the pH was found to be 4.92. What is K_a of acid?

58. Calculate $[H^+]$ in a 0.20 M solution of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) that also contains 0.1 M sodium dichloroacetate. Neglect hydrolysis of sodium salt.

59. Calculate the change in pH of 1 litre buffer solution containing 0.1 mole each of NH_3 and NH_4Cl up on addition of:
(i) 0.02 mole of dissolved gaseous HCl.
(ii) 0.02 mole of dissolved NaOH. **(Roorkee 1992)**
Assume no change in volume. $K_{NH_3} = 1.8 \times 10^{-5}$

60. 20 mL of 0.2 M NaOH are added to 50 mL of 0.2 M acetic acid ($K_a = 1.8 \times 10^{-5}$).
(1) What is pH of solution ?
(2) Calculate volume of 0.2 M NaOH required to make the pH of solution 4.74.

61. Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre and of other solution containing 1 mole CH_3COONa + 1 mole of acetic acid per litre.

62. A 0.1 M solution of weak acid HA is 1% dissociated at 25°C. What is its K_a? If this solution is *w.r.t.* NaA 0.2 M, what will be the new degree of dissociation of HA and pH ?

63. The $[H^+]$ in 0.2 M solution of formic acid is 6.4×10^{-3} mol litre^{-1}. To this solution formate is added so as to adjust the conc. of sodium formate to one mol per litre. What will be pH of this solution? K_a for HCOOH is 2.4×10^{-4} and degree of dissociation of HCOONa is 0.75.

64. What is the pH of a solution when 0.20 mole of HCl is added to one litre solution containing.
(a) 1 M each of acetic acid and acetate ion ?
(b) 0.1 M each of acetic acid and acetate ion?
Given K_a for acetic acid is 1.8×10^{-5}.

65. Calculate the composition of an acidic buffer solution made up of HA and NaA of total molarity 0.29 having pH = 4.4 and $K_a = 1.8 \times 10^{-5}$.

66. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagents is 0.6 mol litre^{-1}. **(Roorkee 1997)**

67. Calculate the pH of a solution obtained by mixing 100 mL of 0.3 M HCl with 100 mL of 0.4 M NH_3. pK_a for $NH_4^+ = 9.2552$.

68. Calculate the pH of a solution obtained by mixing 50 mL of 0.2 M NH_4Cl and 75 mL of 0.1 M NaOH. pK_a for $NH_4^+ = 9.2552$.

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

70. Two buffer, (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? ($K_{HA} = 1.0 \times 10^{-5}$) **(Roorkee 1999)**

71. A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base. **(IIT 1991)**

72. 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 10 mL sample of blood which is 2 M in 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 1993)**

73. 0.1 M CH_3COOH solution is titrated against 0.05 M NaOH solution. Calculate pH at 1/4th and 3/4th stages of neutralization of acid. The pH for 0.1 M CH_3COOH is 3.

74. K_{sp} of AgCl is 1.5×10^{-10} at 25°C. Calculate solubility of AgCl in; (a) Pure water, (b) 0.1 M $AgNO_3$, (c) 0.1 M NaCl. **(Roorkee 1995)**

75. How many grams of potassium bromide (molar mass 120) can be added to 0.5 litre of 0.05 M solution of silver nitrate just to start the precipitation of silver bromide? K_{sp} of AgBr is 5.0×10^{-13}.

76. The solubility of AgCl in water at 25°C is 1.79×10^{-3} g/litre. Calculate K_{sp} of AgCl at 25°C.

77. K_{sp} of AgBr is 4×10^{-13} and $[Ag^+]$ in a solution is 1×10^{-6} mol litre^{-1}. What is the $[Br^-]$ in that solution?

78. The $[Ag^+]$ ion in a saturated solution of Ag_2CrO_4 at 25°C is 1.5×10^{-4} M. Determine K_{sp} of Ag_2CrO_4 at 25°C.

79. 25 mL of a sample of clear saturated solution of PbI_2 requires 10 mL of a certain $AgNO_3(aq.)$ for its titration. What is the molarity of this $AgNO_3(aq.)$? K_{sp} for $PbI_2 = 4 \times 10^{-9}$.

80. Equal volumes of 0.02 M $CaCl_2$ and 0.0004 M Na_2SO_4 are mixed. Will a precipitate form?
(K_{sp} of $CaSO_4 = 2.4 \times 10^{-5}$).

81. What (H_3O^+) must be maintained in a saturated H_2S solution to precipitate Pb^{2+}, but not Zn^{2+} from a solution in which each ion is present at a concentration of 0.01 M?
($K_{sp} H_2S = 1.1 \times 10^{-22}$; $K_{sp} ZnS = 1.0 \times 10^{-21}$) **(Roorkee 2000)**

82. K_{sp} of $PbCl_2$ is 10^{-13}. What will be $[Pb^{2+}]$ in a solution prepared by mixing 100 mL of 0.1 M $Pb(NO_3)_2$ and 1 mL of 1 M HCl?

83. K_{sp} of $PbBr_2$ is 8×10^{-5}. If the salt is 80% dissociated in solution, calculate the solubility of salt in g per litre.

84. 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 1999)**

85. The ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for C_6H_5COOAg is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 as compared to pure water.

86. Calculate the solubility of CaF_2 in a solution buffered at pH = 3.0. K_a for HF is 6.3×10^{-4} and K_{sp} of $CaF_2 = 3.45 \times 10^{-11}$.

87. Will a precipitate of $Mg(OH)_2$ be formed in a 0.001 M solution of $Mg(NO_3)_2$, if the pH of solution is adjusted to 9? K_{sp} of $Mg(OH)_2 = 8.9 \times 10^{-12}$.

88. Calculate pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{2+} ions. K_{sp} of $Mg(OH)_2 = 1 \times 10^{-11}$. **(Roorkee 1992)**

89. Calculate the $[OH^-]$ of a solution after 100 mL of 0.1 M $MgCl_2$ is added to 100 mL of 0.2 M NaOH. K_{sp} of $Mg(OH)_2$ is 1.2×10^{-11}

90. 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^- per litre. Calculate the solubility product of AgCl (K_{sp} $Ag_2CO_3 = 8.2 \times 10^{-12}$). **(IIT 1997)**

91. Calculate simultaneous solubility of AgCNS and AgBr in a solution of water K_{sp} of AgBr $= 5 \times 10^{-13}$ and K_{sp} of AgCNS $= 1 \times 10^{-12}$. **(UPSEAT 1995)**

92. 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 % of that metal ion is precipitated?
(K_{sp} of AgI $= 8.5 \times 10^{-17}$ and K_{sp} of $Hg_2I_2 = 2.5 \times 10^{-26}$)

93. 0.01 mole of $AgNO_3$ is added to 1 litre of a solution which is 0.1 M in Na_2CrO_4 and 0.005 M in $NaIO_3$. Calculate the mole of precipitate formed at equilibrium and the concentrations of Ag^+, IO_3^- and CrO_4^{2-}. (K_{sp} values of Ag_2CrO_4 and $AgIO_3$ are 10^{-8} and 10^{-13} respectively). **(Roorkee 2001)**

94. The K_{sp} of $Ca(OH)_2$ is 4.42×10^{-5} at 25°C. 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 mg is precipitated? **(IIT 1992)**

95. A sample of hard water contains 0.005 mole of $CaCl_2$ per litre. What is the minimum concentration of Na_2SO_4 which must be added for removing Ca^{2+} ions from this water sample? K_{sp} for $CaSO_4$ is 2.4×10^{-5} at 25°C.

96. 1.75 g of solid NaOH are added to 0.25 dm^3 of 0.1 M $NiCl_2$ solution. Calculate:
(a) mass of $Ni(OH)_2$ formed; (b) pH of final solution
Given, K_{sp} of $Ni(OH)_2 = 1.6 \times 10^{-14}$

97. A mixture of water and AgCl is shaken until a saturated solution is obtained. Now the solution is filtered and 100 mL of clear solution of filtrate is mixed with 100 mL

of 0.03 M NaBr. Should a precipitate form? K_{sp} of AgCl and AgBr are 1×10^{-10} and 5×10^{-13}.

98. Calculate pH of a saturated solution of $Mg(OH)_2$. K_{sp} for $Mg(OH)_2$ is 8.9×10^{-12}.

99. 0.1 mili mole of $CdSO_4$ are present in 10 mL acid solution of 0.08 N HCl. Now H_2S is passed to precipitate all the Cd^{2+} ions. What would be the pH of solution after filtering off precipitate, boiling of H_2S and making the solution 100 mL by adding H_2O?

100. Zn salt is mixed with $(NH_4)_2S$ of molarity 0.021 M. What mass of Zn^{2+} will remain unprecipitated in 12 mL of the solution? K_{sp} of $ZnS = 4.51\times10^{-24}$.

101. Freshly precipitated Al and Mg hydroxides are stirred vigorously in a buffer solution containing 0.25 M of NH_4Cl and 0.05 M of NH_4OH.
Calculate $[Al^{3+}]$ and $[Mg^{2+}]$ in solution. K_b for $NH_4OH = 1.8\times10^{-5}$. K_{sp} of $Al(OH)_3 = 6\times10^{-32}$ and K_{sp} of $Mg(OH)_2 = 8.9\times10^{-12}$.

102. A solution has 0.05 M Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in solution. K_{sp} of $Mg(OH)_2 = 9.0\times10^{-12}$ and ionisation constant of NH_3 is 1.8×10^{-5}. **(Roorkee 1993)**

103. A particular water sample has 131 ppm $CaSO_4$. What fraction of the water must be evaporated in a container before solid $CaSO_4$ begins to deposit K_{sp} of $CaSO_4 = 9.0\times10^{-6}$?

104. To a solution of 0.1 M Mg^{2+} and 0.8 M NH_4Cl, an equal volume of NH_3 is added which just gives precipitate. Calculate $[NH_3]$ in solution. K_{sp} of $Mg(OH)_2 = 1.4\times10^{-11}$ and K_b of $NH_4OH = 1.8\times10^{-5}$.

105. 10 mL of 0.3 M Na_2SO_4 are mixed with 20 mL solution having initially 0.1 M Ca^{2+} and 0.1 M Sr^{2+} in it. What are the final concentrations of Ca^{2+}, Sr^{2+} and SO_4^{2-} in solution? Given K_{sp} of $SrSO_4 = 7.6\times10^{-7}$ and K_{sp} of $CaSO_4 = 2.4\times10^{-5}$.

106. The solubility of $CaCO_3$ is 7 mg/litre. Calculate the solubility product of $BaCO_3$ from this information and from the fact that when Na_2CO_3 is added slowly to a solution containing equimolar concentration of Ca^{2+} and Ba^{2+}, no precipitate is formed until 90% of Ba^{2+} has been precipitated as $BaCO_3$.

107. The solubility of $Mg(OH)_2$ is increased by the addition of NH_4^+ ion. Calculate.

(a) K_C for,

$$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons 2NH_3 + 2H_2O + Mg^{2+}$$

K_{sp} of $Mg(OH)_2 = 6\times10^{-12}$, K_b of $NH_3 = 1.8\times10^{-5}$

(b) Find solubility of $Mg(OH)_2$ in a solution containing 0.5 M NH_4Cl before addition of $Mg(OH)_2$.

108. The K_{sp} 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 0.152 mole in 500 mL water is shaken at 25°C with excess of Ag_2CO_3 till the 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 degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be same, calculate K_{sp} of Ag_2CO_3. **(IIT 1991)**

109. Calculate the solubility of AgCN in a buffer solution of pH = 3. Given K_{sp} of $AgCN = 1.2\times10^{-16}$ and K_a for $HCN = 4.8\times10^{-10}$.

110. Determine the concentration of NH_3 solution whose one litre can dissolve 0.10 mole AgCl. K_{sp} of AgCl and K_f of $Ag(NH_3)_2^+$ are 1.0×10^{-10} M^2 and 1.6×10^{7} M^{-2} respectively. **(Roorkee 1999)**

111. Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in $K[Ag(CN)_2]^-$. Given $K_{\text{instability constant}}$ for $[Ag(CN)_2]^- = 4.0\times10^{-19}$ and K_{sp} $AgCl = 2.8\times10^{-10}$.

112. Given: $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3, K_C = 6.2\times10^{-8}$ and K_{sp} of $AgCl = 1.8\times10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia. **(IIT 1998)**

113. Equal volumes of 0.02 M $AgNO_3$ and 0.02 M HCN are mixed. What is $[Ag^+]$ in solution after attaining equilibrium? Given K_a $HCN = 6.2\times10^{-10}$ and K_{sp} $AgCN = 2.2\times10^{-16}$.

114. Determine the mole of AgI which may be dissolved in 1.0 litre of 1.0 M CN^- solution. K_{sp} for AgI and K_C for $[Ag(CN)_2]^-$ are 1.2×10^{-17} M^2 and 7.1×10^{19} M^{-2} respectively. **(Roorkee 1998)**

115. 100.0 mL of a clear saturated solution of Ag_2SO_4 is added to 250.0 mL of a clear saturated solution of $PbCrO_4$. Will any precipitate form and if so what? Given, K_{sp} values for Ag_2SO_4, Ag_2CrO_4, $PbCrO_4$ and $PbSO_4$ are 1.4×10^{-5}, 2.4×10^{-12}, 2.8×10^{-13} and 1.6×10^{-8} respectively.

116. 2 M solution of Na_2CO_3 is boiled in a closed container with excess of CaF_2. Very little amount of $CaCO_3$ and

NaF are formed. If the solubility product of $CaCO_3$ is x and molar solubility of CaF_2 is y, find the molar concentration of F^- in the resulting solution after equilibrium is attained.

117. 25.0 mL clear saturated solution of $PbI_2(aq.)$ requires 13.3 mL of $AgNO_3(aq.)$ solution for complete precipitation. What is molarity of $AgNO_3$ solution? K_{sp} of PbI_2 is 7.1×10^{-9}.

118. 250.0 mL of saturated clear solution of $CaC_2O_4(aq.)$ requires 6.3 mL of 0.00102 M $KMnO_4(aq.)$ in acid medium for complete oxidation of $C_2O_4^{2-}$ ions. Calculate the K_{sp} of CaC_2O_4.

119. K_{sp} for $SrF_2 = 2.8\times10^{-9}$ at 25°C. How much NaF should be added to 100 mL of solution having 0.016 M in Sr^{2+} ions to reduce its concentration to 2.5×10^{-3} M?

120. An aqueous solution of a metal bromide MBr_2 (0.05M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? K_{sp} for $MS = 6.0\times10^{-21}$. Concentration of saturated $H_2S = 0.1\,M$; $K_1 = 10^{-7}$ and $K_2 = 1.3\times10^{-13}$ for H_2S. **(IIT 1993)**

121. H_2S is bubbled into a 0.02 M NaCN solution which is 0.02 M each in $Ag(CN)_2^-$ and $Cd(CN)_4^{-2}$. If K_{sp} of Ag_2S and K_{sp} of CdS are 1.0×10^{-50} and 7.1×10^{-28} and $K_{instability}$ for $[Ag(CN)_2^-]$ and $[Cd(CN)_4]^{2-}$ are 1.0×10^{-20} and 7.8×10^{-18}, which sulphide will precipitate first.

122. Calculate the pH at which an acid indicator with $K_a = 1\times10^{-5}$ changes colour when the indicator concentration is 1×10^{-3} M. Also report the pH at which coloured ion is 80% present.

123. 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 ($K_a = 1.0\times10^{-5}$)? **(IIT 1997)**

124. Bromophenol blue is an indicator with a value of $K_a = 5.84\times10^{-5}$. At what pH it will work as an indicator? Also report the % of this indicator in its basic form at a pH of 4.84.

125. Calculate the percentage hydrolysis in 0.003 M aqueous solution of NaOCN. K_a for $HOCN = 3.33\times10^{-4}$. **(Roorkee 1996)**

126. What is the pH of a 0.5 M aqueous NaCN solution? pK_b of $CN^- = 4.70$. **(IIT 1996)**

127. Calculate degree of hydrolysis and pH of 0.2 M solution of NH_4Cl. Given K_b for NH_4OH is 1.8×10^{-5}.

128. Find out the mass of NH_4Cl dissolved in 500 mL to have pH = 4.5 K_b for NH_4OH is 1.8×10^{-5}.

129. (a) K_a for butyric acid is 2.0×10^{-5}. Calculate pH and hydroxyl ion concentration in 0.2 M aqueous solution of sodium butyrate. **(Roorkee 1994)**

(b) The dissociation constant of a substituted benzoic acid at 25°C is 1×10^{-4}. Calculate the pH of 0.01 M solution of its sodium salt. **(IIT 2009)**

130. K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage of hydrolysis in an aqueous solution in which the concentration of Asc^- ions is 0.02 M. **(Roorkee 1997)**

131. Calculate the pH at the equivalence point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for acid $= 1.9\times10^{-5}$. **(Roorkee 1990)**

132. 0.1 M NaOH is titrated with 0.1 M HA till the end point. K_a of HA is 5.6×10^{-6} and degree of dissociation is less compared to 1. Calculate the pH of the resulting solution at the end point. **(IIT 2004)**

133. Calcium lactate is a salt of weak acid and represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.13 mole of salt in 0.50 litre solution. The pOH of this is 5.60. Assuming complete dissociation of salt, calculate K_a of lactic acid. **(Roorkee 1991)**

134. Calculate the pH of 0.1 M K_3PO_4 solution. The third dissociation constant of orthophosphoric acid is 1.3×10^{-12}. Assume that the hydrolysis proceeds only in the first step.

135. Equilibrium constant for the acid ionisation of Fe^{3+} to $Fe(OH)^{2+}$ and H^+ is 6.5×10^{-3}. What is the maximum pH which could be used so that at least 95% of the total Fe^{3+} in a dilute solution exists as Fe^{3+}?

136. The acid ionisation constant for

$$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+$$

is 1.0×10^{-9}. Calculate the pH of 0.0010 M solution of $ZnCl_2$. Also calculate basic dissociation constant of $Zn(OH)^+$.

137. The dissociation constants for aniline, acetic acid and water at 25°C are 3.83×10^{-10}, 1.75×10^{-5} and 1.008×10^{-14} respectively. Calculate degree of hydrolysis of aniline acetate in a deci normal solution. Also report the pH.

138. 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_b of ammonia = 4.8) **(IIT 1995)**

139. Calculate pH of the following mixtures. Given that $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$.

(a) 50 mL of 0.10 *M* NaOH + 50 mL of 0.05 *M* CH_3COOH.

(b) 50 mL of 0.05 *M* NaOH + 50 mL of 0.10 *M* CH_3COOH.

(c) 50 mL of 0.10 *M* NaOH + 50 mL of 0.10 *M* CH_3COOH.

(d) 50 mL of 0.10 *M* NH_4OH + 50 mL of 0.05 *M* HCl.

(e) 50 mL of 0.05 *M* NH_4OH + 50 mL of 0.10 *M* HCl.

(f) 50 mL of 0.10 *M* NH_4OH + 50 mL of 0.10 *M* HCl.

(g) 50 mL of 0.05 *M* NH_4OH + 50 mL of 0.05 *M* CH_3COOH.

140. The vapour pressure of 0.01 molal solution of weak base *B*OH in water at 20°C is 17.536 mm. Calculate K_b for base. Aqueous tension at 20°C is 17.540 mm. Assume molality and molarity same.

141. A 0.01 *M* aqueous solution of weak acid H*A* has an osmotic pressure 0.293 atm 25°C. Another 0.01 *M* aqueous solution of other weak acid H*B* has an osmotic pressure of 0.345 atm under the same conditions. Calculate equilibrium constants of two acids for their dissociation.

142. The salt $Zn(OH)_2$ is involved in the following two equilibria :

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq.) + 2OH^-(aq.) \qquad K_{sp} = 1.2 \times 10^{-17}$$

$$Zn(OH)_2(s) + 2OH^- \rightleftharpoons Zn(OH)_4^{2-}(aq.) \quad K_f = 0.12$$

Calculate the $[OH^-]$ at which solubility of $Zn(OH)_2$ be a minimum. Also find the solubility of $Zn(OH)_2$ at this pH.

143. A 500 mL sample of an equilibrium mixture of gaseous N_2O_4 and NO_2 at 25°C and 753 mm of Hg was allowed to react with enough water to make 250.0 mL of solution at 25°C. Assume that all the dissolved N_2O_4 is converted to NO_2 which disproportionates in water yielding a solution of nitrous acid and nitric acid. Assume further that disproportionation reaction goes to completion and that none of the nitrous acid disproportionates. The equilibrium constant (K_p) for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.113 at 25°C. K_a for HNO_2 is 4.5×10^{-4} at 25°C.

(a) Write balanced equation for disproportionation.

(b) What is molar concentration of NO_2^- and pH of the solution?

(c) What is osmotic pressure of solution?

(d) How many grams of lime (CaO) would be required to neutralize the solution?

144. K_a for HCN and CH_3COOH are 4.9×10^{-10} and 1.8×10^{-5} respectively. Calculate the equilibrium constant for the reaction:

$$CH_3COOH + NaCN \rightleftharpoons CH_3COONa + HCN$$

145. It is found that 0.1 *M* solution of three sodium salts Na*X*, Na*Y* and Na*Z* have pH 7.0, 9.0 and 11.0 respectively. Arrange the acids (H*X*, H*Y* and H*Z*) in order of increasing acidic character. Where possible calculate dissociation constant of acid.

146. Calculate the pH of 0.05 *M* $KHC_8H_4O_4$

$$H_2C_8H_4O_4 + H_2O \rightleftharpoons H_3O^+ + HC_8H_4O_4^-; \ pK_{a_1} = 2.94$$

$$HC_8H_4O_4^- + H_2O \rightleftharpoons H_3O^+ + C_8H_4O_4^{2-}; \ pK_{a_2} = 5.44$$

147. A buffer solution of 0.080 *M* Na_2HPO_4 and 0.020 *M* Na_3PO_4 is prepared. The electrolytic oxidation of 1.0 m mole *R*NHOH is carried out in 100 mL buffer to give.

$$RNHOH + H_2O \longrightarrow RNO_2 + 4H^+ + 4e$$

Calculate approximate pH of the solution after oxidation is complete. pK_{a_1}, pK_{a_2} and pK_{a_3} of H_3PO_4 are 2.12, 7.20 and 12.0 respectively.

148. Calculate the difference in pH for 1/3 and 2/3 stages of neutralisation of 0.10 *M* CH_3COOH and with 0.10 *M* NaOH.

149. The molar conductivity of a solution of a weak acid H*X* (0.01 *M*) is 10 times smaller than the molar conductivity of a solution of a weak acid H*Y* (0.1 *M*). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$, the difference in their pK_a values $pK_a(HX) - pK_a(HY)$, is (consider degree of ionization of both acids to be << 1) **[JEE (Advanced II) 2015]**

SOLUTIONS (Numerical Problems)

1. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$1 \quad 0 \quad 0$

$1-\alpha \quad \alpha \quad \alpha$

where α is degree of dissociation of acid, if C mol/litre is concentration of acid, then

$[H^+] = C\alpha\,;[CH_3COO^-] = C\alpha\,;[CH_3COOH] = C(1-\alpha)$

Also $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = C\alpha^2$

$[\because K_a$ is small $\therefore \alpha$ will also be small and thus $1-\alpha \simeq 1]$

or $1.8\times10^{-5} = C\times\left(\frac{1}{100}\right)^2 \quad \therefore C = 0.18$

$\because$ 1 litre solution contains = 0.18 mole of CH_3COOH

$\therefore$ 1 litre solution contains = $0.18\times60 =$ **10.8 g CH_3COOH**

2. $N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$

Before dissociation $1 \quad 0 \quad 0$

After dissociation $1-\alpha \quad \alpha \quad \alpha$

Also $K_b = \frac{C\alpha^2}{(1-\alpha)}$

Assuming $1-\alpha \simeq 1$

$K_b = C\alpha^2$

$[N_2H_4] = C = \frac{0.16\times1000}{32\times500} = 0.01$

Given $K_b = 4\times10^{-6}M \;\therefore\; \alpha^2 = \frac{4\times10^{-6}}{0.01} = 4\times10^{-4}$

$\alpha = 2\times10^{-2}$ *i.e.*, $\alpha =$ **0.02 or 2%**

3. Given, $HNiC \rightleftharpoons H^+ + NiC^-$

$1 \quad 0 \quad 0$

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

Also, $C = \frac{0.1}{2} = 5\times10^{-2}$ mol litre^{-1}; $\quad K_a = 1.4\times10^{-5}$

$\therefore \quad K_a = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad (\because 1-\alpha \simeq 1)$

$\therefore \quad \alpha = \sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{\left(\frac{1.4\times10^{-5}}{5\times10^{-2}}\right)}$

$= \mathbf{1.67\times10^{-2}}$ or **1.67%**

4. $[HSaC] = \frac{\text{mole}}{\text{litre}} = \frac{4\times10^{-4}}{200/1000} = 2\times10^{-3}M$

The dissociation of HSaC takes place in presence of $[H^+] = 10^{-3}$

$HSaC \rightleftharpoons H^+ + SaC^-$

Conc. before dissociation $2\times10^{-3} \quad 10^{-3} \quad 0$

In presence of H^+ the dissociation of HSaC is almost negligible because of common ion effect. Thus, at equilibrium

$[HSaC] = 2\times10^{-3}; [H^+] = 10^{-3}$

$\because K_a = \frac{[H^+][SaC^-]}{[HSaC]} \quad \therefore 2\times10^{-12} = \frac{[10^{-3}][SaC^-]}{2\times10^{-3}}$

$\therefore \; [SaC^-] = \mathbf{4\times10^{-12}}\, M$

5. $[HC_9H_7O_4] = \frac{0.32\times2\times1000}{180\times250} = 0.014\,M$

$\because \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.75\times10^{-9}}{0.014}} = 4.43\times10^{-4}$

$\therefore \quad [H^+] = C\cdot\alpha = 0.014\times4.43\times10^{-4} = \mathbf{6.21\times10^{-6}}\,M$

$[C_9H_7O_4^-] = C\cdot\alpha = \mathbf{6.21\times10^{-9}}\,M$

$[OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{6.21\times10^{-6}} = \mathbf{1.61\times10^{-9}}\,M$

6. $NH_3 + H_2O \underset{K_b}{\overset{K_f}{\rightleftharpoons}} NH_4^+ + OH^-; \qquad K_b = 3.4\times10^{10}$

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+; \qquad K_a = 5.6\times10^{-10}$

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

or $\frac{K_f}{3.4\times10^{10}} = \frac{10^{-14}}{5.6\times10^{-10}} \qquad \therefore K_f = \mathbf{6.07\times10^5}$

7. $CH_2FCOOH \rightleftharpoons CH_2FCOO^- + H^+$

Mole before dissociation $1 \quad 0 \quad 0$

Mole after dissociation $(1-\alpha) \quad \alpha \quad \alpha$

Given, $[H^+] = C\cdot\alpha = 1.5\times10^{-3}$ mole litre^{-1}

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

$2.6\times10^{-3} = \frac{1.5\times10^{-3}\times\alpha}{(1-\alpha)} \quad \therefore \alpha = 0.634$

Now, $C\cdot\alpha = 1.50\times10^{-3}$

$\therefore \quad C = \frac{1.50\times10^{-3}}{0.634} = \mathbf{2.37\times10^{-3}}\,M$

Note : Since K_a is of the order of $10^{-3}M$ and thus it is not advisable to use $K_a = C\alpha^2$. Because $(1-\alpha)$ is not equal to 1 since α is not small.

8. Given, $\frac{\text{mass of } NH_3}{\text{mass of solution}} = \frac{10}{100}$

$\because$ 100 g solution contains 10 g NH_3

$\therefore \quad M_{NH_3} = (10\times1000)/[(17\times(100/0.99)] = 5.82$

$(\because V = \text{mass}/\text{density})$

Now $NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Before dissociation $1 \quad 0 \quad 0$

After dissociation $(1-\alpha) \quad \alpha \quad \alpha$

$\therefore [OH^-] = C\cdot\alpha = C\sqrt{(K_b/C)} = \sqrt{(K_b\cdot C)}$

$[\because C = 5.82M$ and $K_b = K_w/K_a$

$= 10^{-14}/(5\times10^{-10}) = 2\times10^{-5}]$

$\therefore \quad [OH^-] = \sqrt{[2\times10^{-5}\times5.82]} = 1.07\times10^{-2}\,M$

$\therefore \quad [H^+] = 10^{-14}/1.07\times10^{-2} = 0.9268\times10^{-12}\,M$

$\therefore \quad pH = -\log[H^+] = -\log 0.9268\times10^{-12} = \mathbf{12.0330}$

9. $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ (self ionisation)

and $K = [NH_4^+][NH_2^-]$ $\therefore$ $[NH_4^+] = [NH_2^-]$

$\therefore$ $[NH_2^-] = \sqrt{K} = \sqrt{10^{-30}} = 10^{-15}\ M$

Number of amide ions in 10^3 cm^3 $= 10^{-15} \times 6 \times 10^{23}$

$\therefore$ Number of amide ions in one cm^3

$$= \frac{10^{-15} \times 6 \times 10^{23}}{10^3} = \mathbf{6 \times 10^5\ ions}$$

10. Given density of formic acid $= 1.22 g / cm^3$

$\therefore$ Mass of formic acid in 1 litre solution $= 1.22 \times 10^3$ g

Thus, $[HCOOH] = \frac{1.22 \times 10^3}{46} = 26.5 M$

Since in case of auto ionisation $[HCOOH_2^+] = [HCOO^-]$

and $[HCOO^-][HCOOH_2^+] = 10^{-6}$ $\therefore$ $[HCOO^-] = 10^{-3}$

Now % dissociation of

$$HCOOH = \frac{[HCOO^-] \times 100}{[HCOOH]} = \frac{10^{-3}}{26.5} \times 100$$

$$\left[\alpha = \frac{C\alpha}{C(1-\alpha)}\right] \qquad = \mathbf{0.004\%}$$

11. $NH_3 + H^+ \rightleftharpoons NH_4^+$; $\Delta H° = -52.2$

Adding, $H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H° = 56.6$

$\therefore$ $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$: $\Delta H° = 4.4$ kJ mol^{-1}

Similarly, $\Delta S°$ for the change $= -76.53$ JK^{-1} mol^{-1}

or for the change :

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$; $\Delta H° = 4.4$ kJ mol^{-1}

and $\Delta S° = -76.53$ JK^{-1} mol^{-1}

Now we have $\Delta G° = \Delta H° - T\Delta S°$

$\therefore$ $\Delta G° = 4.4 - (-76.53 \times 10^{-3}) \times 298 = 27.21$ KJ mol^{-1}

Also, $\Delta G° = -2.303 RT \log K_b$

$27.21 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log K_b$

$\therefore$ $\mathbf{K_b = 1.7 \times 10^{-5}}$

12. For a weak monoprotic acid

	HA	$\rightleftharpoons H^+$	$+ A^-$
Before dissociation	1	0	0
After dissociation	$1-\alpha$	α	α

$[H^+] = C\alpha$ ...(i)

and $K_a = \frac{C\alpha^2}{(1-\alpha)}$ ...(ii)

By substituting value of C from Eq. (ii) in Eq. (i)

$$[H^+] = \frac{K_a \cdot (1-\alpha) \cdot \alpha}{\alpha^2} = \frac{K_a(1-\alpha)}{\alpha} \quad ...(iii)$$

Thus, $-\log[H^+] = -[\log K_a + \log(1-\alpha) - \log \alpha]$

or $pH = \log \frac{1}{K_a} + \log \frac{\alpha}{(1-\alpha)}$ ...(iv)

Also, $pH = pK_a - \log\left[\frac{1-\alpha}{\alpha}\right]$ or $\log \frac{1-\alpha}{\alpha} = [pK_a - pH]$

$\frac{1-\alpha}{\alpha} = 10^{(pK_a - pH)}$ or $\frac{1}{\alpha} - 1 = 10^{(pK_a - pH)}$

or $\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$

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

NH_4OH	NH_4^+	OH^-
1	0	0
$(1-\alpha)$	α	α

Given, $pH = 11$

$\therefore$ $[H^+] = 10^{-11}$ $\therefore$ $[OH^-] = 10^{-3} = C\alpha$

Since, $C = 0.05$

$\therefore$ $\alpha = \frac{10^{-3}}{C} = \frac{10^{-3}}{0.05} = 2 \times 10^{-2}$ or **2%**

14. $[OH^-] \times [BiO^+] = 4 \times 10^{-10}$

$\therefore$ $[OH^-]^2 = 4 \times 10^{-10}$ $\therefore$ $[OH^-] = 2 \times 10^{-5}$

$\therefore$ $pOH = 4.6989$

$\therefore$ $pH = \mathbf{9.3010}$

15. **I Step** $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_1 = 7.5 \times 10^{-3}$

II Step $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_2 = 6.2 \times 10^{-8}$

III Step $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_3 = 3.6 \times 10^{-13}$

For I Step : $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

H_3PO_4	H^+	$H_2PO_4^-$
0.1	0	0
$0.1 - C$	C	C

$$K_1 = \frac{[H^+][H_2PO_4^{2-}]}{[H_3PO_4]} = \frac{C \cdot C}{(0.1 - C)}$$

$$7.5 \times 10^{-3} = \frac{C^3}{(0.1 - C)} \quad \therefore \ C = 0.024$$

$\therefore$ $[H^+] = \mathbf{0.024\ M}$ $\therefore$ $pH = \mathbf{1.6198}$

$[H_2PO_4^-] = \mathbf{0.024\ M}$

$[H_3PO_4] = 0.1 - 0.024 = \mathbf{0.076\ M}$

The value of K_1 is much larger than K_2 and K_3. Also dissociation of II and III steps occurs in presence of H^+ furnished in I step and thus, dissociation of II and III steps is further suppressed due to common ion effect.

For II step : $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

$H_2PO_4^-$	H^+	HPO_4^{2-}
0.024	0.024	0
$(0.024 - y)$	$(0.024 + y)$	y

The dissociation of $H_2PO_4^-$ occurs in presence of $[H^+]$ furnished in step I.

Thus, $K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$ or $6.2 \times 10^{-8} = \frac{(0.024 + y)y}{(0.024 - y)}$

$\because$ y is small $\therefore$ $0.024 - y \approx 0.024$ and neglecting y^2.

$\therefore$ $6.2 \times 10^{-8} = \frac{0.024 y}{0.024}$ $\therefore$ $y = 6.2 \times 10^{-8}$

or $[HPO_4^{2-}] = K_2 = \mathbf{6.2 \times 10^{-8}}$ **(Insignificant)**

For III Step : $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

HPO_4^{2-}	H^+	PO_4^{3-}
$(6.2 \times 10^{-8} - x)$	$(0.024 + x)$	x

$\therefore \quad K_3 = \dfrac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \dfrac{(0.024+x)\cdot x}{(6.2\times10^{-8}-x)}$

Again neglecting x^2 and assuming, $6.2\times10^{-8}-x = 6.2\times10^{-8}$

$\therefore \quad 3.6\times10^{-13} = \dfrac{0.024x}{6.2\times10^{-8}}$

$\therefore \quad x = \dfrac{3.6\times10^{-13}\times6.2\times10^{-8}}{0.024} = \mathbf{9.3\times10^{-19}}$

(Insignificant)

Note: For weak polyprotic acid having no other electrolyte, the anion concentration produced in II step of dissociation is always equal to K_2 if concentration is reasonable.

16. Case I: $[OH^-] = [NH_2C_2H_4NH_3]^+$

$= C\times\sqrt{\dfrac{K_{b_1}}{C}} = \sqrt{0.15\times8.5\times10^{-5}}$

$= \mathbf{3.57\times10^{-3}}\ M$

Case II: $NH_2C_2H_4NH_3^+ + H_2O \rightleftharpoons [NH_3C_2H_4NH_3]^{2+} + OH^-$

3.57×10^{-3}	0	3.57×10^{-3}
$[3.57\times10^{-3}-X]$	X	$(X+3.57\times10^{-3})$

$\therefore \quad 2.7\times10^{-8} = \dfrac{X\cdot(X+3.57\times10^{-3})}{(3.57\times10^{-3}-X)}$

Neglecting X^2, also $3.57\times10^{-3}-X = 3.57\times10^{-3}$;

(X is very small)

$2.7\times10^{-8} = \dfrac{3.57\times10^{-3}\cdot X}{3.57\times10^{-3}}$

$\therefore \quad X = 2.7\times10^{-8}$

$\therefore \quad [NH_2C_2H_4NH_3]^{2+} = \mathbf{2.7\times10^{-8}}\ M = K_{b_2}$

17. Strong acids ionise completely at normal dilutions.

(1) $10^{-3}\ N\ HNO_3$: $HNO_3 \longrightarrow H^+ + NO_3^-$

Conc. before ionisation	$10^{-3}\ N$	0	0
Conc. after ionisation	0	10^{-3}	10^{-3}

$\therefore \quad [H^+] = 10^{-3}$ mol/litre or Eq./litre ($\because H^+$ is monovalent)

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

$pH = \mathbf{3}$

(2) $10^{-3}\ M\ H_2SO_4$: $H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

Conc. before ionisation	$10^{-3}\ M$	0	0
Conc. after ionisation	0	2×10^{-3}	10^{-3}

$\because$ Mole ratio of $H_2SO_4 : H^+ : SO_4^{2-} :: 1 : 2 : 1$

$\therefore \quad [H^+] = 2\times10^{-3}\ M$

$\because \quad pH = -\log[H^+] = -\log 2\times10^{-3}$

$\therefore \quad pH = \mathbf{2.6989}$

(3) $10^{-3}\ N\ H_2SO_4$: $H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

Conc. before ionisation	$10^{-3}\ N$	0	0
Conc. after ionisation	0	10^{-3}	10^{-3}

$\because$ **Equal equivalent of a substance gives equal equivalent of its components.**

$\therefore \quad [H^+] = 10^{-3}\ M$

$\because \quad pH = -\log[H^+] \quad \therefore \quad pH = \mathbf{3}$

(4) $0.01\ N$ HCl: $HCl \longrightarrow H^+ + Cl^-$

Conc. before ionisation	$10^{-2}\ N$	0	0
Conc. after ionisation	0	10^{-2}	10^{-2}

$\therefore \quad [H^+] = 10^{-2}\ M$

$\because \quad pH = -\log[H^+] \quad \therefore \quad pH = \mathbf{2}$

(5) $10^{-8}\ N$ HCl:

Solution 1 : $HCl \longrightarrow H^+ + Cl^-$

Conc. before ionisation	$10^{-8}\ N$	0	0
Conc. after ionisation	0	10^{-8}	10^{-8}

$\therefore$ $[H^+] = 10^{-8}\ M$ but **pH = 8 is not possible because it is** acid. Now $[H^+] = 10^{-7}\ M$ are already present in solution and since $10^{-8} < 10^{-7}$ and thus, it should not be neglected.

$\therefore \quad [H^+] = 10^{-8} + 10^{-7} = 10^{-7}(1.1)M = 1.1\times10^{-7}\ M$

$\therefore \quad pH = \mathbf{6.9586}$

Solution II The above solution lacks with discrepancy that dissociation of H_2O, a weak electrolyte is also suppressed in presence of HCl due to common ion effect and thus, $[H^+]_{H_2O} \neq 10^{-7}$ but will be lesser than this.

Therefore, dissociation of H_2O in presence of $10^{-8}\ H^+$.

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

$(10^{-8}+a) \qquad a$

$\therefore \quad K_w = (10^{-8}+a)a \quad \therefore \quad a = 0.95\times10^{-7}$

$\therefore \quad [H^+] = 10^{-8} + 0.95\times10^{-7} = 10^{-7}\times1.05 = 1.05\times10^{-7}$

$\therefore \quad pH = \mathbf{6.9788}$

(6) $10^2\ M$ HCl: $HCl \longrightarrow H^+ + Cl^-$

Conc. before dissociation	10^2	0	0
Conc. after dissociation	0	10^2	10^2

$\therefore \quad [H^+] = 10^2\ M \quad \therefore \quad pH = \mathbf{-2}$

Students are often under the illusion that it is impossible to have a negative pH. There is no theoretical basis for this. A negative pH only means that the hydrogen ion concentration is greater than 1 M. However in actual practice, a negative pH is uncommon because of two reasons. First, even strong acids (say 100% H_2SO_4) becomes partially dissociated at high concentrations. The second reason has to do with activity.

Sorensons originally intended pH to be related to $[H^+]$, but his fundamental method of measurement—the hydrogen electrode—is now known to depend on thermodynamics activities rather than $[H^+]$, *i.e.*, on a_{H^+} and $a_{H^+} = [H^+]f_{H^+}$. In dilute solutions activity coefficient, f_{H^+} is near enough to unity and thus, $a_{H^+} = [H^+]$. At high concentrations, the activity coefficient is less than unity. Thus, pH defined by

$-\log[H^+]$ is not only of little theoretical significance, but in fact cannot be measured directly. It has therefore, come to be accepted that $pH = -\log_{10} a_{H^+}$ (this is what a pH meter reading is a measure of), *i.e.*, pH of 10^2 *M* HCl cannot be calculated until f_{H^+} is known. Nevertheless, there is mathematically no basis for not having a negative pH.

18. (a) $[H^+] = 0.05 = 5\times10^{-2}$

$\therefore$ $pH = -\log[H^+] = -\log 5\times10^{-2}$

$pH = \mathbf{1.3010}$

(b) $[H^+] = 5.0M$ but $pH \neq -\log 5 \neq -0.6989$

See Problem 17 part 6.

(c) $[H^+] = 10^{-8}$ $\therefore$ $pH \neq -\log 10^{-8} \neq 8$

See Problem 17 part 5.

19. (a) 0.001 *N* NaOH :

$$NaOH \longrightarrow Na^+ + OH^-$$
$$10^{-3}N \quad 0 \quad 0$$
$$0 \quad 10^{-3} \quad 10^{-3}$$

$\therefore$ $[OH^-] = 10^{-3}M$ $(\because N_{NaOH} = M_{NaOH})$

$\therefore$ $pOH = -\log[OH^-] = -\log 10^{-3} = 3$

$\therefore$ $pH = 14 - pOH = 14 - 3 = 11$ $\therefore$ $pH = \mathbf{11}$

(b) 0.01 *N* $Ca(OH)_2$:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$
$$10^{-2}N \quad 0 \quad 0$$
$$0 \quad 10^{-2} \quad 10^{-2}$$

$\therefore$ Equivalent litre^{-1} are given equation ratio $Ca(OH)_2 : Ca^{2+} : OH^- :: 1:1:1$

$\therefore$ $[OH^-] = 10^{-2}M$ $\therefore$ $pOH = 2$ $\therefore$ $pH = \mathbf{12}$

(c) 0.01 *M* $Ca(OH)_2$:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$
$$10^{-2}M \quad 0 \quad 0$$
$$0 \quad 10^{-2} \quad 2\times10^{-2}$$

$\therefore$ Mole ratio of $Ca(OH)_2$ $Ca^{2+} : OH^- :: 1:1:2$

$\therefore$ $[OH^-] = 2\times10^{-2}M$ $\therefore$ $pOH = 1.6989$

$\therefore$ $pH = 14 - 1.6989 = \mathbf{12.3010}$

(d) 10^{-8} *M* NaOH: $NaOH \longrightarrow Na^+ + OH^-$

$$10^{-8}N \quad 0 \quad 0$$
$$0 \quad 10^{-8} \quad 10^{-8}$$

$\therefore$ $[OH^-] = 10^{-8}M$

Now proceed for OH^- as in problem 17 part 5.

(e) 10^2 *M* NaOH:

$$NaOH \longrightarrow Na^+ + OH^-$$
$$10^2M \quad 0 \quad 0$$
$$0 \quad 10^2 \quad 10^2$$

$[OH^-] = 10^2M$

Now proceed as in problem 17 part 6.

(f) 0.0008 *M* $Mg(OH)_2$:

$$Mg(OH)_2 \longrightarrow Mg^{2+} + 2OH^-$$
$$8\times10^{-4}M \quad 0 \quad 0$$
$$0 \quad 8\times10^{-4} \quad 2\times8\times10^{-4}$$

$\therefore$ $[OH^-] = 16\times10^{-4}M$ $\therefore$ $pOH = 2.7958$

$\therefore$ $pH = \mathbf{11.2041}$

20. (a) $[OH^-] = 0.05M = 5\times10^{-2}$

$\therefore$ $pOH = -\log[OH^-]$ $\therefore$ $pOH = 1.3010$

$\therefore$ $pH = \mathbf{12.6989}$

(b) $[OH^-] = 5$

Proceed as in problem 17 part 6.

(c) $[OH^-] = 10^{-8}$

Proceed as in problem 17 part 5.

21. (a) 0.002 *N* CH_3COOH: Acetic acid is weak electrolyte and partially dissociated.

	$CH_3COOH \rightleftharpoons$	CH_3COO^-	$+H^+$
Conc. before dissociation	1	0	0
Conc. after dissociation	$1-\alpha$	α	α

$\therefore$ $[H^+] = C\alpha = 2\times10^{-3}\times\frac{2.3}{100} = 4.6\times10^{-5}M$

$\therefore$ $pH = -\log[H^+] = -\log 4.6\times10^{-5}$

$pH = \mathbf{4.3372}$

(b) 0.002 *N* NH_4OH: NH_4OH is weak base and partially dissociated.

	$NH_4OH \rightleftharpoons$	NH_4^+	$+OH^-$
Conc. before dissociation	1	0	0
Conc. after dissociation	$1-\alpha$	α	α

$\therefore$ $[OH^-] = C\alpha = 2\times10^{-3}\times\frac{2.3}{100} = 4.6\times10^{-5}M$

$\because$ $pOH = -\log[OH^-] = -\log 4.6\times10^{-5}$

$\therefore$ $pOH = 4.3372$ $\therefore$ $pH = 14 - 4.3372$

$pH = \mathbf{9.6628}$

22. Concentration of SO_2 in air is 10 ppm or 10 mole in 10^6 mole air or 10^{-5} mole SO_2 per mole of air. The concentration of SO_2 in air being substantial and since rain water is falling from enormously great height so, each drop of rain water will get saturated with SO_2 before it reaches earth.

Now the given concentration or solubility of SO_2 at 298 K is 1.3653 *M*. This value of solubility corresponds when $P_{SO_2} = 1\,atm$.

Thus according to Henry's law.

$[SO_2]$ dissolved in water $\propto P_{SO_2}$ in gas phase

Thus solubility of SO_2 at the condition of P_{SO_2} of 10^{-5} atm as $P \propto$ mole and therefore since solubility is reported at 1 atm

$\therefore [SO_2]$ dissolved at pressure 1 atm = 1.3653 *M*

$\therefore [SO_2]_2$ dissolved at pressure 10^{-5} atm

$= 1.3653\times10^{-5}M = C$

i.e., $[H_2SO_3] = [SO_2] = 1.3653\times10^{-5}M$

Now, $SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$

$$1 \quad 0 \quad 0$$
$$(1-\alpha) \quad \alpha \quad \alpha$$

$\therefore$ $$K_a = \frac{C\alpha\cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

or $0.012 = \dfrac{1.3653\times10^{-5}\times\alpha^2}{(1-\alpha)}$

$(\because pK_b = 1.92 \text{ and thus } K_b = 0.012)$

$1.3653\times10^{-5}\alpha^2 + 0.012\alpha - 0.012 = 0$

$$\alpha = \frac{-0.012\pm\sqrt{1.44\times10^{-5}+4\times1.44\times10^{-5}}}{2}$$

$= 1$

$\therefore$ $[H^+] = C\times\alpha = 1.3653\times10^{-5}$

$\therefore$ pH = **4.8648**

23. $CHCl_2COOH \rightleftharpoons CHCl_2COO^- + H^+$

C	0	0.01
$C(1-\alpha)$	$C\alpha$	$C\alpha + 0.01$

$\therefore$ $K_a = \dfrac{C\alpha\times(C\alpha+0.01)}{C(1-\alpha)} = \dfrac{\alpha(0.01\alpha+0.01)}{(1-\alpha)} = 5\times10^{-2}$

or $\dfrac{0.01\alpha(1+\alpha)}{(1-\alpha)} = 5\times10^{-2}$ or $\alpha^2 + 6\alpha - 5 = 0$

$\therefore$ $\alpha = 0.7416$

$\therefore$ $[CHCl_2COO^-] = 0.01\times0.7416 = \mathbf{7.416\times10^{-3}}$ ***M***

$[H^+] = 7.416\times10^{-3} + 0.01 = \mathbf{0.0174}$ ***M***

24. pH will be decided by $[H^+]$ furnished by HCl and $CHCl_2COOH$.

$CHCl_2COOH \rightleftharpoons CHCl_2COO^- + H^+$

Initial conc.	0.09	0	0.09 (From HCl)
Final conc.	$(0.09-x)$	x	$(0.09+x)$

$\therefore$ $[H^+] = 0.09 + x$;

but pH = 1, $\therefore$ $[H^+] = 10^{-1} = 0.1$

$\therefore$ $0.09 + x = 0.1$ $\therefore$ $x = 0.01$

K_a for $CHCl_2COOH$ can be given as

$$K_a = \frac{[H^+][CHCl_2COO^-]}{[CHCl_2COOH]} = \frac{0.1\times0.01}{(0.09-0.01)} = \mathbf{1.25\times10^{-2}}$$

25. (i) pH = 3 or $-\log[H^+] = 3$ $\therefore$ $[H^+] = \mathbf{10^{-3}}$ ***M***

(ii) pH = 4.75 $\therefore$ $-\log[H^+] = 4.75$

$\therefore$ $[H^+] = \mathbf{1.7782\times10^{-5}}$ ***M***

26. Diethyl amine is base and give OH^- as,

$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$

Initial conc.	1	0	0
Equilibrium	$(1-\alpha)$	α	α

$\therefore$ $[OH^-] = C\alpha$

where C is conc. of base and $C = 0.05M$

$\because$ pH = 12 $\therefore$ pOH = 2

or $[OH^-] = 10^{-2}$ *M* $\therefore$ $C\alpha = 10^{-2}$

or $0.05\times\alpha = 10^{-2}$ $(\because C = 0.05)$

$\therefore$ $\alpha = 0.2$

Now for a base, $K_b = \dfrac{C\alpha^2}{(1-\alpha)} = \dfrac{0.05\times(0.2)^2}{(1-0.2)}$

$= \dfrac{0.05\times0.04}{0.8} = \mathbf{2.5\times10^{-3}}$

Note: Do not use $K_b = C\alpha^2$ since $\alpha = 0.2$ and $1-\alpha = 0.8$.

27. K_w for H_2O at 25° C = 10^{-14}

$\therefore$ $[H^+][OH^-] = 10^{-14}$ $(\because K_w = [H^+][OH^-])$

$\therefore$ $[H^+] = 10^{-7}$ *M* $\therefore$ pH = 7

Now K_w for H_2O at 60°C = 9.62×10^{-14}

$\therefore$ $[H^+][OH^-] = 9.62\times10^{-14}$

For pure water $[H^+] = [OH^-]$

$\therefore$ $[H^+]^2 = 9.62\times10^{-14}$

$\therefore$ $[H^+] = \sqrt{(9.62\times10^{-14})} = 3.10\times10^{-7}$ *M*

$\therefore$ pH = $-\log H^+ = -\log 3.10\times10^{-7}$

pH = **6.51**

Thus, pH of water becomes 6.51 at 60°C but the nature is neutral since calculation for pure water has been made, *i.e.* **pH scale at 60°C becomes in between 0 to 13.02.**

28. $H_2O \rightleftharpoons H^+ + OH^-$ (molarity of water = 55.6 *M*)

$\therefore$ $K_b = \dfrac{[H^+][OH^-]}{[H_2O]} = \dfrac{K_w}{[H_2O]} = \dfrac{10^{-14}}{55.6} = \mathbf{1.8\times10^{-16}}$

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

$$K_{a\cdot p} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} = \frac{K_w}{[H_2O]^2}$$

$$= \frac{10^{-14}}{(55.6)^2} = \mathbf{3.24\times10^{-18}}$$

29. At 25°C, K_w for $H_2O = 10^{-14}$. Thus $[H^+] = [OH^-] = 10^{-7}$ or pH of water = 7. Also as the temperature decreases K_w for H_2O decrease (*i.e.*, $K_w < 10^{-14}$) because of low dissociation of water ($H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H = +ve$) following Le Chatelier's principle. This leads to lower concentrations of H^+ and OH^- ions. Thus pH of water is more at 4°C than at 25°C, however H_2O remains neutral.

30. At 25°C; $[H^+] = 10^{-7}$ $\therefore$ $K_w = 10^{-14}$

At 35°C; $[H^+] = 10^{-6}$ $\therefore$ $K_w = 10^{-12}$

Now using $2.303\log_{10}\dfrac{K_{w_2}}{K_{w_1}} = \dfrac{\Delta H}{R}\left[\dfrac{T_2-T_1}{T_1\times T_2}\right]$

$$2.303\log_{10}\frac{10^{-12}}{10^{-14}} = \frac{\Delta H}{2}\left[\frac{10}{298\times308}\right]$$

$\therefore$ $\Delta H = 84551.4$ cal / mol = **84.551 kcal / mol**

Thus, $H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H = 84.551$ **kcal / mol**

$\therefore$ $H^+ + OH^- \rightleftharpoons H_2O$; $\Delta H = -84.551$ **kcal / mol**

31. $HCl_I = 10^{-5}$ *M* since pH = 5

Meq. of HCl_I in 1 mL = $10^{-5}\times1$

Meq. of HCl_{II} in 1000 mL = $N\times1000$

Since II is prepared by diluting I and Meq. does not change on dilution.

i.e., Meq. of HCl (concentrated) = Meq. of HCl (dilute)

$\therefore\ 10^{-5} \times 1 = N \times 1000 \quad \therefore\ N_{HCl_{II}} = 10^{-8}$

Now, proceed as in problem 17 part 5.

$\therefore$ pH = **6.9788**

32. $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2$

1 mole (=27.6 g) of B_2H_6 = 2 mole H_3BO_3

$\therefore$ 2.0 g of $B_2H_6 = \frac{2\times2}{27.6} = 0.145$ mole H_3BO_3

$\therefore\ [H_3BO_3] = \frac{0.145\times1000}{100} = 1.45M$

Now $H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$

$$K_a = \frac{C\alpha^2}{1-\alpha} \qquad (\because 1-\alpha \simeq 1)$$

or $7.3\times10^{-10} = 1.45\times\alpha^2 \quad \therefore\ \alpha = 2.24\times10^{-5}$

$\therefore\ [H^+] = C\alpha = 1.45\times2.24\times10^{-5} = 3.25\times10^{-5}$

$\therefore$ pH = **4.4881**

33. For HCl gas $PV = nRT$

$\because\ P_{HCl_{dry}} = \frac{740-23.7}{760}$ atm $\quad V = \frac{100}{1000}$ litre

$T = 25+273 = 298$ K

$\therefore$ Mole of HCl, *i.e.*, $n_{HCl} = \frac{PV}{RT}$

$$= \frac{(740-23.7)\times100}{760\times1000\times0.0821\times298}$$

$\therefore\ n = 3.85\times10^{-3}$

Now, Molarity of HCl $= \frac{n}{V_{solution}} = \frac{3.85\times10^{-3}}{1}$ (V in litre)

$\therefore\ [H^+] = 3.85\times10^{-3}\ M$

$\therefore$ pH = $-\log H^+ = -\log 3.85\times10^{-3}$

pH = **2.4142**

34. Given, pH = 4.18 = $-\log[H^+]$

$\therefore\ [H^+] = \mathbf{6.61\times10^{-5}}$ **mol litre^{-1}**

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

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

or $4.45\times10^{-7} = \frac{[6.61\times10^{-5}][HCO_3^-]}{[0.01]}$

or $[HCO_3^-] = \mathbf{6.73\times10^{-5}}$ **mol litre^{-1}**

Again for dissociation of HCO_3^-, we have

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

or $4.69\times10^{-11} = \frac{[6.61\times10^{-5}][CO_3^{2-}]}{[6.73\times10^{-5}]}$

$\therefore\ [CO_3^{2-}] = \mathbf{4.78\times10^{-11}}$ **mol litre^{-1}**

35. $HCl + NaOH \longrightarrow NaCl + H_2O$

	HCl	NaOH	NaCl	H_2O
Meq. before reaction	50×0.6 = 30	50×0.3 = 15	0	0
Meq. after reaction	15	0	15	15

For monovalent electrolytes

Molarity = Normality = $\frac{\text{milli equivalent}}{\text{total volume}}$

$\therefore\ [Cl^-] = \frac{15+15}{100} = \mathbf{0.3}\ M$ (Cl^- proved by HCl and NaCl)

$[Na^+] = \frac{15}{100} = \mathbf{0.15}\ M$

$[H^+] = \frac{15}{100} = \mathbf{0.15}\ M$

$[OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{0.15} = \mathbf{6.6\times10^{-14}}\ M$

Also pH = $-\log[H^+] = -\log 0.15$

pH = **0.8239**

36. Milli equivalent of H^+ from HCl = 10×0.1 = 1

Milli equivalent of H^+ from H_2SO_4 = 40×0.2×2 = 16

$\therefore$ Total Meq. of H^+ in solution = 1+16 = 17

$\therefore\ [H^+] = \frac{17}{50} = 3.4\times10^{-1} \qquad \left(\because [H^+] = \frac{\text{Meq.}}{V_{\text{in mL}}}\right)$

$\therefore$ pH = $-\log[H^+] = -\log 0.34$

pH = **0.4685**

37. Case I : $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

	CH_3COOH	CH_3COO^-	H^+
Conc. before dissociation	1	0	0
Conc. after dissociation	1 − α	α	α

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

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

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

pH = 2.3724

Case II : New pH is given as = 2.3724×2 = 4.7448

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

$\therefore\ -\log[H^+] = 4.7448 \quad \therefore\ [H^+] = 1.8\times10^{-5}$

or $C_1\alpha_1 = 1.8\times10^{-5}$

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

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

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

$\alpha_1 = 0.5$

Now $C_1\alpha_1 = 1.8\times10^{-5}$

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

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

Eq. of dilute solution = Eq. of concentration solution

$3.6\times10^{-5}\times V = 1\times1$

$\therefore \quad V = \frac{1}{3.6\times10^{-5}} = \mathbf{2.77\times10^4}$ **litre**

Note : In II case α_1 comes 0.5 by $K_a = \frac{C_1\alpha_1^2}{(1-\alpha_1)}$ and thus, it is not advisable to assume $(1-\alpha_1)\approx 1$.

38. $HCl + NaOH \longrightarrow NaCl + H_2O$

	HCl	NaOH	NaCl	H_2O
Meq. before reaction	100×0.1 = 10	9.9×1 = 9.9	0	0
Meq. after reaction	0.1	0	9.9	9.9

$\therefore$ $[H^+]$ left from $HCl = \frac{0.1}{109.9} = 9.099\times10^{-4}\ M$

$\therefore \quad pH = -\log H^+ = -\log 9.099\times10^{-4}$

$pH = \mathbf{3.0409}$

39. pH of HCl = 2 $\quad\therefore\ [HCl] = 10^{-2}\ M$

pH of NaOH = 12 $\quad\therefore\ [NaOH] = 10^{-2}\ M$

$HCl + NaOH \longrightarrow NaCl + H_2O$

	HCl	NaOH	NaCl	H_2O
Meq. before reaction	200×10^{-2} = 2	300×10^{-2} = 3	0	0
Meq. after reaction	0	1	2	2

$\therefore$ $[OH^-]$ left from $NaOH = \frac{1}{500} = 2\times10^{-3}\ M$

$\therefore\ pOH = -\log OH^- = -\log 2\times10^{-3}$

$\therefore\ pOH = 2.6989 \quad \therefore \quad pH = \mathbf{11.3010}$

40. (i) Meq. of $CH_3COOH = 500\times0.2 = 100$

Meq. of $HCl = 500\times0.2 = 100$

$\therefore \quad [HCl] = \frac{100}{1000} = 0.1; [CH_3COOH] = \frac{100}{1000} = 0.1$

For CH_3COOH : $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

	CH_3COOH	CH_3COO^-	H^+
Before dissociation	0.1	0	0.1 (from HCl)
After dissociation	$(0.1-x)$	x	$(0.1+x)$

$\therefore \quad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x(0.1+x)}{(0.1-x)}$

Due to common ion effect dissociation of CH_3COOH is very small in presence of HCl. Therefore, $(0.1+x) = 0.1$ and $(0.1-x) = 0.1$.

$\therefore\ K_a = \frac{x\times0.1}{0.1} \quad \therefore \quad x = K_a = 1.75\times10^{-5}$

Thus, degree of dissociation

$\alpha = \frac{x}{0.1} = \frac{1.75\times10^{-5}}{0.1} = 1.75\times10^{-4} = \mathbf{0.000175 = 0.0175\%}$

Also, $\quad [H^+] = 0.1 + x = 0.1 \quad (x << 0.1)$

$\therefore \quad pH = -\log[H^+] = -\log[0.1] = \mathbf{1}$

(ii) Eq. of NaOH or mole of NaOH added $= \frac{6}{40} = 0.15$

Therefore, new equilibrium will have

$CH_3COOH + HCl + NaOH \rightarrow CH_3COONa + NaCl + H_2O$

CH_3COOH	HCl	NaOH	CH_3COONa	NaCl	H_2O
0.1	0.1	0.15	0	0	0
0.05	0	0	0.05	0	0

Thus, the solution will act as acidic buffer having $[CH_3COOH] = \frac{0.05}{1000}$ and $[CH_3COONa] = \frac{0.05}{1000}$

Thus, $\quad pH = -\log K_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$

$= -\log 1.75\times10^{-5} + \log\frac{[0.05/1000]}{[0.05/1000]}$

$pH = \mathbf{4.757}$

41. $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

Thus, $\quad K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$ ...(1)

Also K_b for $C_6H_5NH_2 = \frac{K_w}{K_a \text{ for } C_6H_5NH_3^+}$

$= \frac{1\times10^{-14}}{2.4\times10^{-5}}$ ...(2)

Since dissociation of $C_6H_5NH_2$ occurs in presence of NaOH and thus dissociation of $C_6H_5NH_2$ will suppress.

Thus, $\quad [OH^-] = ?; \quad [C_6H_5NH_2] = 0.24;$

$[C_6H_5NH_3^+] = 10^{-8}$

Therefore, $\quad \frac{1\times10^{-14}}{2.4\times10^{-5}} = \frac{10^{-8}\times[OH^-]}{0.24}$

$\therefore \quad [OH^-] = \frac{0.24\times10^{-14}}{2.4\times10^{-5}\times10^{-8}} = 0.01$

$\therefore \quad [NaOH] = \mathbf{0.01}\ \boldsymbol{M}$

42. In this problem both the acids contribute for $[H^+]$ due to appreciable dissociation. Thus,

$HCOOH \rightleftharpoons \underset{x+y}{H^+} + \underset{x}{HCOO^-}$

$HOCN \rightleftharpoons \underset{x+y}{H^+} + \underset{y}{OCN^-}$

Because $[H^+]$ will remain common in solution. Thus,

$K_{HCOOH} = \frac{[H^+][HCOO^-]}{[HCOOH]} = 1.8\times10^{-4}$ ...(1)

$K_{HOCN} = \frac{[H^+][OCN^-]}{[HOCN]} = 3.3\times10^{-4}$ ...(2)

or $\quad K_{HCOOH} = \frac{(x+y)x}{0.1} = 1.8\times10^{-4}$ ...(3)

$K_{HOCN} = \frac{(x+y)y}{0.1} = 3.3\times10^{-4}$ ...(4)

Thus, by Eqs. (3) and (4) $\frac{x}{y} = \frac{1.8}{3.3}$

or $\quad y = 1.83x$ ...(5)

From Eq. (3) $(x + 1.83x)\cdot x = 1.8\times10^{-5} \quad \therefore x = 2.52\times10^{-3}$

Therefore, $\quad y = 4.61\times10^{-3}$

Thus, $\quad [H^+] = x + y = 2.52\times10^{-3} + 4.61\times10^{-3}$

$= \mathbf{7.13\times10^{-3}}\ \boldsymbol{M}$

43. $HCOOH \rightleftharpoons H^+ + HCOO^-$

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

Since both have same pH and therefore.

$[H^+]$ by HCOOH = $[H^+]$ by CH_3COOH

$$C_1\alpha_1 = C_2\alpha_2$$

$$\sqrt{K_{a_1}C_1} = \sqrt{(K_{a_2}C_2)}$$

$$\therefore \sqrt{(2.4\times10^{-4}\times0.5)} = \sqrt{(1.8\times10^{-5}\times C)}$$

$$\therefore C_{CH_3COOH} = \mathbf{6.666}\ M$$

44. $HA \rightleftharpoons H^+ + A^-;\quad K_a = 1.38\times10^{-4}$

$HB \rightleftharpoons H^+ + B^-;\quad K_a = 1.05\times10^{-10}$

It is thus evident on account of low K_a values for HB, $[H^+]$ from HB is appreciably small in comparison to $[H^+]$ from HA and thus may be neglected.

For HA: $K_a = \dfrac{[H^+][A^-]}{[HA]}$

$$1.38\times10^{-4} = \frac{[H^+]^2}{[HA]}$$

$$[H^+]^2 = 1.38\times10^{-4}\times[HA]$$

$$= 1.38\times10^{-4}\times0.03$$

Therefore, $[H^+] = [A^-] = \mathbf{2.04\times10^{-3}}\ M$

Now for HB: $K_a = \dfrac{[H^+][B^-]}{[HB]}$

$$1.05\times10^{-10} = \frac{2.04\times10^{-3}\times[B^-]}{0.1}$$

(Since $[H^+]$ is provided by acid HA and HB is almost undissociated)

or $[B^-] = \mathbf{5.15\times10^{-9}}\ M$

45. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$

$$[H^+] = \sqrt{K_{a_1}\cdot C_1 + K_{a_2}\cdot C_2}$$

$$= \sqrt{1.8\times10^{-5}\times0.02 + 6.4\times10^{-5}\times0.01} = 1\times10^{-3}$$

$\therefore$ **pH = 3**

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

$$\therefore 1.8\times10^{-5} = \frac{[CH_3COO^-][1\times10^{-3}]}{0.02}$$

$$\therefore [CH_3COO^-] = \mathbf{3.6\times10^{-4}}$$

Similarly, $[C_6H_5COO^-] = \mathbf{6.4\times10^{-4}}$

46. Given, $[HCOOH] = 0.015M$

$[HCl] = 0.02M$

$\therefore$ $[H^+]$ in solution = 0.02 M

The dissociation of HCOOH is suppressed due to common ion effect in presence of HCl. The $[H^+]$ is provided by HCl in solution.

$HCOOH \rightleftharpoons HCOO^- + H^+$

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$1.8\times10^{-4} = \frac{[0.02][HCOO^-]}{[0.015]}$$

$$\therefore [HCOO^-] = \mathbf{1.35\times10^{-4}}\ M$$

47. $H_2S \rightleftharpoons H^+ + HS^-;\quad K_{a_1} = 10^{-7}$

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

$HCl \longrightarrow H^+ + Cl^-$

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

$$\therefore K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$10^{-7} = \frac{[0.3][HS^-]}{[0.1]}\quad [\because [H^+] \text{ from HCl} = 0.3]$$

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

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

$$1.3\times10^{-13} = \frac{[0.3][S^{2-}]}{3.3\times10^{-8}}$$

$$\therefore [S^{2-}] = \frac{1.3\times10^{-13}\times3.3\times10^{-8}}{0.3} = \mathbf{1.43\times10^{-20}}\ M$$

48. $\because$ Relative strength of weak acids $= \sqrt{\left(\dfrac{K_{a_1}}{K_{a_2}}\times\dfrac{C_1}{C_2}\right)}$

Assume C_1 and C_2 are same (Although not given)

$$\therefore \text{Relative strength} = \sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)} = \sqrt{\left(\frac{2.1\times10^{-4}}{1.1\times10^{-5}}\right)}$$

Relative strength for HCOOH to CH_3COOH = **4.36:1**

49. (a) We have $pH = -\log K_a + \log\dfrac{[\text{Conjugate base}]}{[\text{Acid}]}$

$\because$ $[\text{Conjugate base}] = \dfrac{3\times1000}{82\times100}M$ and $[\text{Acid}] = \dfrac{2\times1000}{60\times100}M$

$$\therefore pH = -\log 1.8\times10^{-5} + \log\frac{\dfrac{3\times1000}{82\times100}}{\dfrac{2\times1000}{60\times100}}\quad \therefore pH = \mathbf{4.7851}$$

(b) $pOH = -\log K_b + \log\dfrac{[\text{Conjugate acid}]}{[\text{Base}]}$

$\because$ Total volume after mixing = 250 + 5 = 255 mL

Meq. of conjugate acid = 250×0.1 = 25

Meq. of base = 5×0.1 = 0.5

$\therefore$ $[\text{Conjugate acid}] = \dfrac{25}{255}$ and $[\text{Base}] = \dfrac{0.5}{255}$

$$\therefore pOH = -\log 1.8\times10^{-5} + \log\frac{25/225}{0.5/255}$$

$pOH = 6.4437$ $\therefore$ $pH = 14 - pOH = \mathbf{7.5563}$

(c) $pH = -\log K_a + \log \frac{[Anion]}{[Acid]}$

$= -\log 3.6\times10^{-4} + \log \frac{0.35/500}{0.25/500}$

$pH = \mathbf{3.5898}$

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

	Na_2CO_3	HCl	NaCl	$NaHCO_3$
Meq. before reaction	$\frac{30}{106}\times1000$ = 283	150×1 = 150	0	0
Meq. after reaction	133	0	150	150

The solution contains Na_2CO_3 and HCO_3^- and thus, acts as buffer.

$\therefore\ pH = -\log K_a + \log \frac{[CO_3^{2-}]}{[HCO_3^-]}$

$pH = -\log K_a + \log \frac{133}{150} = -\log 5.63\times10^{-11} + \log \frac{133}{150}$

$= 10.249 - 0.052$

$pH = \mathbf{10.197}$

51. [Pyridinium chloride] = (0.15/500)×1000 = 0.3 *M*

[Pyridine] = 0.2 *M*

∴ A mixture of pyridine and its salt pyridinium chloride forms a basic buffer and therefore,

$pOH = -\log K_b + \log [\text{Conjugate acid}]/[\text{Base}]$

or $pOH = -\log 1.5\times10^{-9} + \log (0.30/0.20)$

$= -\log 1.5 + 9\log 10 + \log 1.5 = 9$

∴ $[OH^-] = 10^{-9}$

and $[H^+] = 10^{-5}$ So $pH = \mathbf{5}$

52. $pOH = -\log K_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]}$

or $pOH = -\log K_b + \log \frac{[NH_4^+]}{[NH_4OH]}$

∵ $[NH_4^+]$ is obtained from salt $(NH_4)_2SO_4$

∵ $pH = 9.35$ ∴ $pOH = 14 - 9.35 = 4.65$

∴ Millimole of NH_4OH in solution = 0.2×500 = 100

Let millimole of NH_4^+ added in solution = *a*

∴ $[NH_4^+] = \frac{a}{500}$; $[NH_4OH] = \frac{100}{500}$

$4.65 = -\log 1.78\times10^{-5} + \log \frac{a/500}{100/500}$

$4.65 = 4.7496 + \log \frac{a}{100}$ ∴ $a = 79.51$

∴ Millimole of $(NH_4)_2SO_4$ added $= \frac{a}{2} = \frac{79.51}{2} = 39.755$

∴ $\frac{w}{132}\times1000 = 39.755$ ∴ $w_{(NH_4)_2SO_4} = \mathbf{5.248\ g}$

53. Let *V* mL of 0.1 *M* HCOONa be mixed to 50 mL of 0.05 *M* HCOOH.

∵ $[\text{Molarity}] = \frac{\text{Total millimole}}{\text{Total volume}}$

∴ In mixture $[HCOONa] = \frac{0.1\times V}{(V+50)}$

$[HCOOH] = \frac{50\times0.05}{V+50}$

∵ $pH = -\log K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$

∴ $4.0 = 3.80 + \log \frac{(0.1\times V)/(V+50)}{2.5/(V+50)}$

∴ $V = \mathbf{39.62\ mL}$

54. NaCN + HCl is not a buffer but if HCl is in less mass then, it gives a buffer as it produces HCN.

$NaCN + HCl \longrightarrow NaCl + HCN$

	NaCN	HCl	NaCl	HCN
Mole added	0.01	*a*	0	0
Mole after reaction	(0.01 − *a*)	0	*a*	*a*

This is buffer of HCN + NaCN

Let *a* mole of HCl be used for this purpose

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

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

∴ $a = \mathbf{8.85\times10^{-3}}$ **mol of HCl**

55. Case I : $BOH + HCl \longrightarrow BCl + H_2O$

	BOH	HCl	BCl	H_2O
Millimole before reaction	*a*	1.0 × 5 = 0.5	0	0
Millimole after reaction	(*a* − 0.5)	0	0.5	0.5

∵ $pH = 10.04$ ∴ $pOH = -\log K_b + \log \frac{[B^+]}{[BOH]}$ ...(1)

∴ $pOH = 3.96$ ∴ $3.96 = -\log K_b + \log \frac{0.5}{(a-0.5)}$ ...(2)

Case II : $BOH + HCl \longrightarrow BCl + H_2O$

	BOH	HCl	BCl	H_2O
Millimole before reaction	*a*	0.1 × 20 = 2		
Millimole after reaction	(*a* − 0.2)	0	2	2

∵ $pH = 9.14$ ∴ $pOH = -\log K_b + \log \frac{[B^+]}{[BOH]}$ ...(3)

∴ $pOH = 4.86$ ∴ $4.86 = -\log K_b + \log \frac{2}{a-2}$ ...(4)

Solving Eqs. (2) and (4), $K_b = \mathbf{1.81\times10^{-5}}$

56. For neutralization :

Total Meq. of acid = Meq. of base = 26.6×0.1 = 2.66

Now for partial neutralization of acid

$HA + BOH \longrightarrow BA + H_2O$

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

The resultant mixture acts as a buffer and [*HA*] and [*BA*] may be placed in terms of Meq. since volume of mixture is constant.

∴ $pH = -\log K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$

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

$K_a = \mathbf{8.219\times10^{-6}}$

57. For complete neutralization,

Meq. of acid = Meq. of NaOH = 36.12×0.1 = 3.612

∴ $HA + NaOH \longrightarrow NaA + H_2O$

HA	NaOH	Na*A*	H_2O
3.612	3.612	0	0
0	0	3.612	3.612

Now 1.806 Meq. of HCl (18.06×0.1) are added to this solution containing 3.612 Meq. of Na*A*.

	NaA + HCl ⟶		NaCl + HA	
Meq. before reaction	3.612	1.806	0	0
Meq. after reaction	1.806	0	1.806	1.806

The solution has H*A* and Na*A* and thus, acts as buffer

$$\therefore \quad pH = -\log K_a + \log \frac{1.806}{1.806}$$

$$4.92 = -\log K_a$$

$$\therefore \quad K_a = \mathbf{1.2 \times 10^{-5}}$$

58. $CHCl_2 \cdot COOH \rightleftharpoons CHCl_2 \cdot COO^- + H^+$

	$CHCl_2 \cdot COOH$	$CHCl_2 \cdot COO^-$	H^+
Before dissociation	0.2	–	–
After dissociation	(0.2 – x)	x	x

$$CHCl_2 \cdot COONa \longrightarrow CHCl_2COO^- + Na^+$$
(0.1, 0.1)

For the dissociation of acid

$$K_a = 5 \times 10^{-2} = \frac{[CHCl_2COO^-][H^+]}{[CHCl_2 \cdot COOH]}$$

or $$0.05 = \frac{[0.1 + x][x]}{[0.2 - x]}$$

$$\therefore \quad x = 0.05 \quad \text{or} \quad [H^+] = \mathbf{0.05}$$

59. Initial pH of solution when,

$$[NH_3] = \frac{0.1}{1} \text{ and } [NH_4Cl] = \frac{0.1}{1}$$

$$pOH = -\log 1.8 \times 10^{-5} + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1}$$

$$pOH = 4.7447 \quad \therefore \quad pH = \mathbf{9.2553}$$

(i) Now 0.02 mole of HCl are added, then

	HCl + NH_4OH ⟶		$NH_4Cl + H_2O$
Mole before reaction	0.02	0.1	0.1
Mole after reaction	0	0.08	(0.1 + 0.02)

$\because$ Volume = 1 litre

$$\therefore \quad [NH_4OH] = \frac{0.08}{1} \quad \text{and} \quad [NH_4Cl] = \frac{0.12}{1}$$

$$\therefore \quad pOH_I = -\log 1.8 \times 10^{-5} + \log \frac{0.12}{0.08}$$

$$\therefore \quad pOH_I = 4.9208 \quad \therefore \quad pH_I = \mathbf{9.0792}$$

Change in pH = pH – pH_I = 9.2553 – 9.0792 = + 0.1761

$\therefore$ Change in pH = **0.1761 unit, *i.e.*, pH decreases**

(ii) Now 0.02 mole of NaOH are added

	NaOH + NH_4Cl ⟶		NaCl + NH_4OH	
Mole before reaction	0.02	0.1	0	0.1
Mole after reaction	0	0.08	0.02	0.12

$$\therefore \quad pOH_2 = -\log 1.8 \times 10^{-5} + \log \frac{0.08}{0.12}$$

$$pOH_2 = 4.5686 \quad \therefore \quad pH_2 = \mathbf{9.4314}$$

Change in pH = pH – pH_2 = 9.2553 – 9.4314 = –0.1761

$\therefore$ Change in pH = **0.1761 unit, *i.e.*, pH increases**

60. (1) $NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$

	NaOH	CH_3COOH	CH_3COONa	H_2O
Millimole added	20 × 0.2 = 4	50 × 0.2 = 10	0	0
Millimole after reaction	0	6	4	4

$$\because \quad [\text{Molarity}] = \frac{\text{Millimole}}{\text{Total volume}}$$

$$\therefore \quad [CH_3COOH] = \frac{6}{70} \; [CH_3COONa] = \frac{4}{70}$$

$$\therefore \quad pH = -\log 1.8 \times 10^{-5} + \log \frac{4/70}{6/70}$$

$$pH = \mathbf{4.5686}$$

(2) Let *V* mL of 0.2 *M* NaOH is required to make pH 4.74 then,

	NaOH + CH_3COOH →		CH_3COONa + H_2O	
Millimole added	0.2 × *V* = 0.2*V*	50 × 0.2 = 10	0	0
Millimole after reaction	0	(10 – 0.2*V*)	0.2*V*	0.2*V*

$$\therefore \quad [\text{Acid}] = \frac{10 - 0.2V}{50 + V}; \; [\text{Conjugate base}] = \frac{0.2V}{50 + V}$$

$$\therefore \quad 4.74 = -\log 1.8 \times 10^{-5} + \log \frac{(0.2V)/(50 + V)}{(10 - 0.2V)/(50 + V)}$$

(take $\log 1.8 \times 10^{-5}$ = 4.7447 = 4.74)

$$\therefore \quad V = \mathbf{25\ mL}$$

61. Case I : pH when 1 mole CH_3COONa and 1 mole HCl are present.

	CH_3COONa + HCl ⟶		CH_3COOH + NaCl	
Before reaction	1	1	0	0
After reaction	0	0	1	1

$$\therefore \quad [CH_3COOH] = 1M$$

$$\therefore \quad [H^+] = C \cdot \alpha = C\sqrt{\left(\frac{K_a}{C}\right)} = \sqrt{(K_a \cdot C)} = \sqrt{(K_a)} \; \because C = 1$$

$$\therefore \quad pH_I = \frac{1}{2} \log K_a$$

Case II : pH when 1 mole CH_3COONa and 1 mole of CH_3COOH; a buffer solution

$$\therefore \quad pH_2 = -\log K_a + \log \frac{\left[\begin{matrix}\text{Conjugate} \\ \text{base}\end{matrix}\right]}{[\text{Acid}]}$$

$\because$ [Salt] = [Anion] = 1 *M*

$\because$ [Acid] = 1 *M*

$$pH_2 = -\log K_a$$

$$\therefore \quad \frac{pH_1}{pH_2} = \mathbf{\frac{1}{2}}$$

62. For weak acid $HA : \alpha_{HA} = \frac{1}{100} = 0.01, [HA] = 0.1M$

$$\therefore \quad K_a = C\alpha^2 = 0.1 \times (0.01)^2 = 10^{-5}$$

Now 0.2 *M* Na*A*, a salt of H*A*, is added to it resulting a buffer solution of [H*A*] = 0.1*M* and [Na*A*] = 0.2*M*

$$\therefore \quad pH = -\log 10^{-5} + \log \frac{0.2}{0.1}$$

$$pH = \mathbf{5.3010}$$

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

HA	H^+	A^-
1	0	0
(1 – α)	α	α

$\because$ $[A^-]$ is provided by Na*A* since dissociation of H*A* in presence of Na*A* is suppressed due to a common ion effect

$$\therefore \quad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(C \cdot \alpha) \times 0.2}{C(1 - \alpha)} = 10^{-5}$$

$$\therefore \quad \alpha = \mathbf{5 \times 10^{-5}}$$

63. In 0.2 M HCOOH $[H^+] = 6.4 \times 10^{-3}$

$$C\alpha = 6.4 \times 10^{-3} \quad \therefore \ \alpha = 3.2 \times 10^{-2}$$

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

$$HCOONa \rightleftharpoons HCOO^- + Na^+$$

	$HCOONa$	$HCOO^-$	Na^+
Conc. before dissociation	1	0	0
Conc. after dissociation	(1 – 0.75)	0.75	0.75

So [HCOOH] = 0.2 $\therefore$ $[HCOO^-] = 0.75$

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

64. (a) Initially [Acetic acid] = 1 M

[Acetate] = 1 M

Now 0.2 mole of HCl are added to it.

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

	HCl	CH_3COO^-	CH_3COOH	Cl^-
Mole before reaction	0.2	1	1	0
Mole after reaction	0	0.8	1.2	0.2

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

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

(b) In II case initially [Acetic acid] = 0.1 M

[Acetate] = 0.1 M

Now 0.2 mole of HCl are added to it

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

	HCl	CH_3COO^-	CH_3COOH	Cl^-
Mole of before reaction	0.2	0.1	0.1	0
Mole after reaction	0.1	0	0.2	0.1

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

Note : CH_3COOH no doubt gives H^+ but being weak acid as well as in presence of HCl does not dissociate appreciably and thus, H^+ from CH_3COOH may be neglected.

65.
$$pH = -\log K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

Let a mol litre^{-1} be concentration of salt, then concentration of acid = $(0.29 - a)$.

$$4.4 = -\log 1.8 \times 10^{-5} + \log \frac{a}{(0.29 - a)} \quad \therefore \ a = 0.09$$

$\therefore$ [Salt] = **0.09 M**

[Acid] = 0.29 – 0.09 = **0.20 M**

66.
$$pOH = -\log K_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

$$5 = 4.7 + \log \frac{a}{b}$$

$$\frac{a}{b} = 2 \quad \therefore \ a = 2b$$

Given $a + b = 0.6$

$2b + b = 0.6$

$3b = 0.6$

$\therefore$

or $b = 0.2$ mole or $0.2 \times 17 = \mathbf{3.4\ g/L}$

$\therefore$ $a = 0.4$ mole or $0.4 \times 53.5 = \mathbf{21.4\ g/L}$

Thus, [Salt] = **0.4 M** and [Base] = **0.2 M**

67.
$$HCl + NH_3 \longrightarrow NH_4Cl$$

	HCl	NH_3	NH_4Cl
mm at $t = 0$	30	40	0
mm after reaction	0	10	30

$$\therefore \ pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]} \qquad (pK_a + pK_b = 14)$$

$$= 4.7448 + \log \frac{30}{10} = 5.2218$$

$$\therefore \ pH = 14 - 5.2218 = \mathbf{8.7782}$$

68.
$$NH_4Cl + NaOH \rightleftharpoons NH_4OH + NaCl$$

NH_4Cl	$NaOH$	NH_4OH	$NaCl$
50×0.2 = 10	75×0.1 = 7.5	0	0
2.5	0	7.5	7.5

$(pK_a + pK_b = 14)$

$$\therefore \ pOH = 4.7448 + \log \frac{2.5}{7.5} = 4.2676$$

$$\therefore \ pH = \mathbf{9.7324}$$

69.
$$K_{b(x^{-1})} = 10^{-10}$$

Also for conjugate acid – base pair

$$K_{a(HX)} \times K_{b(x^{-1})} = 10^{-14} \quad \therefore \ K_{a(HX)} = 10^{-4}$$

Now $[HX] = [X^-]$ (acid) (anion)

$$\therefore \ pH = -\log K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]} = -\log 10^{-4}$$

pH = 4

70. pH of buffer is given by:

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

Case I : $4 = -\log 1.0 \times 10^{-5} + \log \frac{[\text{Conjugate base}]}{(0.5)}$

$$\therefore \ \log \frac{[\text{Conjugate base}]}{0.5} = -1$$

[Conjugate base] = 0.1 × 0.5 = 0.05 M

Case II : $6 = -\log 1.0 \times 10^{-5} + \log \frac{[\text{Conjugate base}]}{0.5}$

$$\therefore \ \log \frac{[\text{Conjugate base}]}{0.5} = 1$$

$\therefore$ [Conjugate base] = [Salt] = 10 × 0.5 = 5M

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

Thus, new conc. of NaA is mixed buffer

$$= \frac{0.05 \times V + 5 \times V}{2V} = \frac{5.05}{2}$$

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

Thus, $pH = -\log 1.0 \times 10^{-5} + \log \frac{[5.05/2]}{[0.5]}$

$$pH = 5 + 0.7033 = \mathbf{5.7033}$$

71. $\underset{\text{Weak}}{HA} + \underset{\text{Strong}}{BOH} \rightleftharpoons BA + H_2O$

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

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

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

Also for weak acid HA: $HA \rightleftharpoons H^+ + A^-$

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

By Eqs. (2) and (1), $\dfrac{K_a}{K} = K_w$

$$\therefore \quad K = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = \mathbf{10^{10}}$$

72. $[H_2CO_3]$ in blood $= 2M$

Volume of blood $= 10$ mL

$[NaHCO_3] = 5M$

Let volume of $NaHCO_3$ used $= V$ mL

$\therefore \quad [H_2CO_3]$ in mixture $= \dfrac{2\times 10}{(V+10)}$

$[NaHCO_3]$ in mixture $= \dfrac{(5\times V)}{(V+10)}$

$$\therefore \quad pH = pK_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$$7.4 = -\log 7.8\times 10^{-7} + \log\frac{(5\times V)/(V+10)}{(2\times 10)/(V+10)}$$

$\therefore \quad V = \mathbf{78.36\ mL}$

73. K_a for CH_3COOH can be derived by $[H^+] = 10^{-3}$

$$C\alpha = 10^{-3} \quad \therefore \quad \alpha = \frac{10^{-3}}{0.1} = 10^{-2}$$

Now $\quad K_a = C\alpha^2 = 0.1\times(10^{-2})^2 = 10^{-5}$

Case I : $\quad CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Before addition NaOH $\quad 0.1$

After addition of NaOH $\quad 0.1\times\frac{3}{4} \qquad\qquad 0.1\times\frac{1}{4}$

when $\frac{1}{4}$ acid neutralizes

$$\because \quad pH = -\log K_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$$pH = -\log 10^{-5} + \log\frac{0.1/4}{0.3/4} \quad \therefore \quad pH = \mathbf{4.5228}$$

Case II : $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

After addition of NaOH $\quad 0.1\times 1/4 \qquad\qquad 0.1\times 3/4$

For 3/4 neutralization

$$\therefore \quad pH = -\log 10^{-5} + \log\frac{0.3/4}{0.1/4} \quad \therefore \quad pH = \mathbf{5.4771}$$

74. (a) In pure water :

Let solubility of AgCl be s mol litre^{-1}

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

$$K_{sp} = [Ag^+][Cl^-] = s\times s$$

$$\therefore \quad s = \sqrt{(K_{sp})} = \sqrt{(1.5\times 10^{-10})}$$

$$= \mathbf{1.224\times 10^{-5}\ mol\ litre^{-1}}$$

(b) In 0.1 M $AgNO_3$:

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

$$AgNO_3 \longrightarrow \underset{0.1}{Ag^+} + \underset{0.1}{NO_3^-}$$

$$\therefore \quad K_{sp} = [Ag^+][Cl^-] = (0.1+s)(s)$$

($\because s <<< 0.1$, presence of common ion decreases solubility)

$\therefore \quad s(0.1) = 1.5\times 10^{-10}$

$\therefore \quad s = \mathbf{1.5\times 10^{-9}\ mol\ litre^{-1}}$

(c) Solubility of AgCl is more in (*aq.*) NaCl than $AgNO_3$ due to complex formation.

$$AgCl(s) + NaCl \rightleftharpoons [AgCl_2]^- + Na^+$$

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

In saturated solution $K_{sp} = [Ag^+][Cl^-] \quad ...(i)$

$$Ag^+ + 2Cl^- \rightleftharpoons [AgCl_2]^-$$

In NaCl(*aq.*) $\quad K_f = \dfrac{[AgCl_2]^-}{[Ag^+][Cl^-]^2} \quad ...(ii)$

By (i) and (ii) $\quad K_{sp}\times K_f = \dfrac{[AgCl_2]^-}{[Cl^-]} \quad ...(iii)$

Solubility of AgCl in pure water :

$$K_{sp} = [Ag^+][Cl^-] = [Ag^+]^2$$

$$\therefore \quad [Ag^+] = \sqrt{K_{SP}} = \sqrt{1.0\times 10^{-10}}$$

$$= 10^{-5}\,M$$

In 0.01 M NaCl : By (iii)

$$[AgCl_2]^- = K_{sp}\times K_f\times Cl^-$$

$$= 1\times 10^{-10}\times 3\times 10^{+5}\times 0.01$$

$$= 3\times 10^{-7}\,M$$

75. $\quad KBr + AgNO_3 \longrightarrow AgBr + KNO_3$

Let a mole of KBr be added into 1 litre of 0.05 M $AgNO_3$ to bring in precipitation.

Thus, $\quad [KBr] = \frac{a}{1}; \quad [AgNO_3] = 0.05$

or $\quad [Br^-] = a \quad$ and $\quad [Ag^+] = 0.05$

$\therefore \quad [Ag^+][Br^-] = K_{sp}$

$$0.05\times a = 5.0\times 10^{-13}$$

$\therefore \quad a = 5\times 10^{-11}\,M = 5\times 10^{-11}\times 120$

$$= \mathbf{6.00\times 10^{-9}\ g/1000\ mL}$$

Thus, mass of KBr needed for precipitation of AgBr from 500 mL 0.05 M are $\mathbf{3.0\times 10^{-9}\ g}$

76. Solubility (s) of AgCl $= 1.79\times 10^{-3}$ g / litre

$$= \frac{1.79\times 10^{-3}}{143.5}\ \text{mol litre}^{-1}$$

$$= 1.247\times 10^{-5}\ \text{mol litre}^{-1}$$

$\therefore \quad K_{sp} = [Ag^+][Cl^-] = s \times s$

$= [1.247 \times 10^{-5}][1.247 \times 10^{-5}]$

$K_{sp} = \mathbf{1.55 \times 10^{-10}\ mol^2\ litre^{-2}}$

77. $AgBr(s) \rightleftharpoons Ag^+(aq.) + Br^-(aq.)$

$K_{sp} = [Ag^+][Br^-]$

$4 \times 10^{-13} = [1 \times 10^{-6}][Br^-]$

$\therefore \quad [Br^-] = \frac{4 \times 10^{-13}}{1 \times 10^{-6}} = \mathbf{4 \times 10^{-7}\ mol\ litre^{-1}}$

78. For saturated solution of Ag_2CrO_4, if solubility is s mol litre^{-1}. Then,

$$Ag_2CrO_4(s) \rightleftharpoons \underset{2s}{2Ag^+(aq.)} + \underset{s}{CrO_4^{2-}(aq.)}$$

$K_{sp} = (2s)^2(s) = 4s^3 \qquad [\because [Ag^+] = 2s = 1.5 \times 10^{-4}$

$= 4 \times (0.75 \times 10^{-4})^3 \qquad \therefore s = 0.75 \times 10^{-4}]$

$K_{sp} = \mathbf{1.688 \times 10^{-12}\ mol^3\ litre^{-3}}$

79. For PbI_2, $\quad PbI_2 \rightleftharpoons \underset{s}{Pb^{2+}} + \underset{2s}{2I^-}$

where s is solubility of PbI_2

$\therefore \quad K_{sp} = 4s^3 \qquad \therefore s^3 = \frac{K_{sp}}{4}$

or $\quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4 \times 10^{-9}}{4}} = 10^{-3}$

$\therefore \quad [I^-] = 2s = 2 \times 10^{-3}$ mol/litre

Now, for $\quad Ag^+ + I^- \longrightarrow AgI$

Meq. of Ag^+ = Meq. of I^-

$N \times 10 = 2 \times 10^{-3} \times 25$

$\therefore \quad N$ or M of $AgNO_3 = \mathbf{5 \times 10^{-3}}$

80. $CaCl_2 + Na_2SO_4 \longrightarrow CaSO_4 + 2NaCl$

Millimole added $\quad 0.02V \quad 0.0004 \times V \quad 0 \quad 0$

Suppose V mL of both are mixed

$\therefore \quad [Ca^{2+}] = \frac{0.02V}{2V} \qquad [SO_4^{2-}] = \frac{0.0004V}{2V}$

Thus, $[Ca^{2+}][SO_4^{2-}]$ in solution $< K_{sp}$

$2 \times 10^{-6} < 2.4 \times 10^{-5}$

$\therefore$ **$CaSO_4$ will not precipitate.**

81. For ZnS not to be precipitated from a solution of Zn^{2+} and Pb^{2+}

$[Zn^{2+}][S^{2-}] < K_{sp}$ of ZnS

$[10^{-2}][S^{2-}] < 1.0 \times 10^{-21}$

or the maximum $[S^{2-}] = 10^{-19}$ at which ZnS will begin to precipitate or upto this concentration, no precipitation will occur.

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

$\therefore \quad [H^+]^2[S^{2-}] = 1.1 \times 10^{-22}$

$\therefore \quad [H^+]^2[10^{-19}] = 1.1 \times 10^{-22}$

$\therefore \quad [H^+]^2 = 11 \times 10^{-4} \quad \therefore [H^+] = \mathbf{3.3 \times 10^{-2}\ M}$

Thus, if $[H^+] = 3.3 \times 10^{-2}$ or **slightly higher, the precipitation of ZnS will not take place and only PbS will precipitate.**

82. $Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$

	$Pb(NO_3)_2$	$2HCl$	$PbCl_2$	$2HNO_3$
Millimole added	$100 \times 0.1 = 10$	$1 \times 1 = 1$	0	0
Millimole left	9.5	0	0.5	1

$\because$ Concentration in $M = \frac{m\text{mole}}{\text{Total volume}}$

$\therefore \quad [Pb^{2+}] = \frac{9.5 + 0.5}{101}$

Now if $PbCl_2$ is precipitated, then contribution 0.5 of $[Pb^{2+}]$ from $PbCl_2$ should be left.

To see precipitation, ionic concentration product $> K_{sp}$

Ionic conc. product

$= [Pb^{2+}][Cl^-]^2 = \left[\frac{10}{101}\right]\left[\frac{1}{101}\right]^2 = 9.70 \times 10^{-6}$

which is greater than K_{sp} of $PbCl_2$ and thus, precipitation of $PbCl_2$ occurs.

$\therefore \quad [Pb^{2+}] = \frac{9.5}{101} = \mathbf{9.4 \times 10^{-2}\ mol\ litre^{-1}}$

83. Let solubility of $PbBr_2$ be s mol litre^{-1}

$$PbBr_2(s) \rightleftharpoons PbBr_2(aq.) \rightleftharpoons \underset{\frac{s \times 80}{100}}{Pb^{2+}} + \underset{\frac{2s \times 80}{100}}{2Br^-}$$

$\because$ Ionisation of $PbBr_2(s) = 80\%$

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

$8 \times 10^{-5} = \left[\frac{s \times 80}{100}\right]\left[\frac{2s \times 80}{100}\right]^2$

$\therefore \quad s = 0.034$ mol litre^{-1} ($\because$ M. mass of $PbBr_2 = 367$)

$s = 0.034 \times 367$ litre^{-1}

$s = \mathbf{12.48\ g\ litre^{-1}}$

84. K_{sp} of $Pb(OH)_2 = 4s^3 = 4 \times (6.7 \times 10^{-6})^3 = 1.203 \times 10^{-15}$

The buffer contains pH = 8 $\therefore$ pOH = 6 or $[OH^-] = 10^{-6}$

Now left solubility of $Pb(OH)_2$ be s mol litre^{-1} in it.

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

$[Pb^{2+}][10^{-6}]^2 = 1.203 \times 10^{-15}$

[Buffer has pH = 8; $\therefore$ pOH = 6 and $[OH^-] = 10^{-6}$]

$\therefore \quad [Pb^{2+}] = \frac{1.203 \times 10^{-15}}{10^{-12}} = \mathbf{1.203 \times 10^{-3}\ mol\ litre^{-1}}$

85. K_{sp} of $C_6H_5COOAg = [C_6H_5COO^-][Ag^+]$

$= 2.5 \times 10^{-13}$

In pure water $\quad S^2 = 25 \times 10^{-14}$

$S = 5 \times 10^{-7}$

In pH = 3.19 ; pOH = 10.81 or $[OH^-] = 1.55\times10^{-11}$,
$C_6H_5COO^-$ undergoes hydrolysis to form C_6H_5COOH.

$$C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$$

$$\therefore \quad K_H = \frac{K_w}{K_a} = \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]}$$

$$\therefore \quad \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{K_w}{K_a[OH^-]}$$

$$= \frac{10^{-14}}{6.46\times10^{-5}\times1.55\times10^{-11}} = 10$$

$[Ag^+]$ dissolved in pH 3.19 = $[C_6H_5COO^-]$ left after hydrolysis + $[C_6H_5COOH]$ formed due to hydrolysis
$= [C_6H_5COO^-] + 10[C_6H_5COO^-] = 11[C_6H_5COO^-]$

$$\therefore \quad [C_6H_5COO^-] = \frac{[Ag^+]}{11}$$

$$[Ag^+][C_6H_5COO^-] = [Ag^+]\frac{[Ag^+]}{11} = 2.5\times10^{-13}$$

$$\therefore \quad [Ag^+] = 1.658\times10^{-6}$$

i.e., solubility is $\frac{1.658\times10^{-6}}{5\times10^{-7}}$ = **3.316** times greater then pure water.

86. $[Ca^{2+}][F^-]^2 = 3.45\times10^{-11}$

The F^- reacts with H^+ (pH = 3.0) to produce HF

$$K_{a_{HF}} = \frac{[H^+][F^-]}{[HF]}$$

or $$6.3\times10^{-4} = \frac{10^{-3}\times[F^-]}{[HF]}$$

$$\therefore \quad HF = 1.58\times[F^-]$$

Also the solution contains $[HF] + [F^-] = 2\times[Ca^{2+}]$

or $1.58\times[F^-] + [F^-] = 2\times[Ca^{2+}]$

$$\therefore \quad [F^-] = \frac{2}{2.58}\times[Ca^{2+}] = 0.775[Ca^{2+}]$$

Let solubility of CaF_2 be S mol litre^{-1} $\therefore$ $[Ca^{2+}] = S$

$$\therefore \quad [F^-] = 0.775\times S$$

Thus $$S\times(0.775\times S)^2 = 3.45\times10^{-11}$$

$$\therefore \quad S = \mathbf{3.86\times10^{-4}}\ M$$

87. pH = 9 $\therefore$ $[H^+] = 10^{-9}\,M$ or $[OH^-] = 10^{-5}\,M$

Now if $Mg(NO_3)_2$ is present in a solution of $[OH^-] = 10^{-5}\,M$, then,

Product of ionic conc.

$$= [Mg^{2+}][OH^-]^2 = [0.001][10^{-5}]^2$$

$= 10^{-13}$ lesser than K_{sp} of $Mg(OH)_2$ *i.e.*, 8.9×10^{-12}

$\therefore$ **$Mg(OH)_2$ will not precipitate.**

88. When $Mg(OH)_2$ starts precipitation, then,

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

$$[0.1][OH^-]^2 = 1\times10^{-11}$$

$\therefore$ $[OH^-] = 10^{-5}\,M$ $\quad\therefore$ pOH = 5

$\therefore$ pH = 14 − pOH $\quad\therefore$ **pH = 14 − 5 = 9**

89. $$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 + 2NaCl$$

	$MgCl_2$	$2NaOH$	$Mg(OH)_2$	$2NaCl$
mm before reaction	10	20	0	0
	0	0	10	20

Thus, 10 *m* mole of $Mg(OH)_2$ are formed. The product of $[Mg^{2+}][OH^-]^2$ is therefore $\left[\frac{10}{200}\right]\times\left[\frac{20}{200}\right]^2 = 5\times10^{-4}$

which is more than K_{sp} of $Mg(OH)_2$. Now solubility (s) of $Mg(OH)_2$ can be derived by

$$K_{sp} = 4s^3$$

$$\therefore \quad s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.2\times10^{-11}}{4}} = 1.4\times10^{-4}$$

$$\therefore \quad [OH^-] = 2s = \mathbf{2.8\times10^{-4}}$$

90. $$Na_2CO_3 + 2AgCl \rightleftharpoons 2NaCl + Ag_2CO_3$$

	Na_2CO_3	$2AgCl$	$2NaCl$	Ag_2CO_3
mm added	7.5	excess	0	0
mm left	(7.5 − a)	excess	2a	a

Given $$[Cl^-] = \frac{0.0026}{35.5} = 7.32\times10^{-5}$$

Also, conc. of Cl^- formed = $\frac{\text{Millimole}}{\text{Volume in mL}} = \frac{2a}{5}$

$\therefore$ $\frac{2a}{5} = \frac{0.0026}{35.5}$ $\quad\therefore$ $a = 1.83\times10^{-4}$ millimole

$\therefore$ *m* mole of Na_2CO_3 left in 5 mL = $7.5 - 1.83\times10^{-4} = 7.5$

or $$[CO_3^{2-}] = \frac{7.5}{5}$$

Now $$K_{sp_{Ag_2CO_3}} = [Ag^+]^2[CO_3^{2-}]$$

$$\therefore \quad [Ag^+]^2 = \frac{8.2\times10^{-12}}{7.5/5} = 5.46\times10^{-12}$$

$$\therefore \quad [Ag^+] = 2.34\times10^{-6}$$

$$\therefore \quad K_{sp} \text{ of } AgCl = [Ag^+][Cl^-] = 2.34\times10^{-6}\times\frac{0.0026}{35.5}$$

$$K_{sp} = \mathbf{1.71\times10^{-19}}$$

91. Let solubility of AgCNS and AgBr in a solution be a and b mol litre^{-1} respectively.

$$AgCNS(s) \rightleftharpoons Ag^+ + CNS^-$$

[Ion] furnished on dissolution $\quad a \quad a$

$$AgBr(s) \rightleftharpoons Ag^+ + Br^-$$

[Ion] furnished on dissolution $\quad b \quad b$

$\therefore$ $[Ag^+] = a + b;$ $[CNS^-] = a;$ $[Br^-] = b$

$\therefore$ For AgCNS $K_{sp_{AgCNS}} = [Ag^+][CNS^-]$

$$1\times10^{-12} = (a+b)(a) \quad ...(1)$$

For AgBr $K_{sp_{AgBr}} = [Ag^+][Br^-]$

$$5\times10^{-13} = (a+b)(b) \quad ...(2)$$

By Eqs. (1) and (2),

$$\therefore \quad \frac{a}{b} = \frac{10^{-12}}{5\times10^{-13}} = 2 \quad \text{or} \quad a = 2b$$

$\therefore$ By Eq. (1), $(2b+b)(2b) = 1\times10^{-12}$ $\therefore$ $6b^2 = 1\times10^{-12}$

$b = \mathbf{4\times10^{-7}}$ **mol litre^{-1}**

By Eq. (1), $(a + a/2)(a) = 1\times10^{-12}$

$\therefore$ $a = \mathbf{8.16\times10^{-7}}$ **mol litre^{-1}**

92. The $[I^-]$ needed for precipitation of Ag^+ and Hg_2^{2+} are derived as:

For AgI : $[Ag^+][I^-] = K_{sp_{AgI}}$

$(0.1)[I^-] = 8.5\times10^{-17}$

$\therefore$ $[I^-] = 8.5\times10^{-16}\,M$ ...(1)

For Hg_2I_2 : $[Hg_2^{2+}][I^-]^2 = 2.5\times10^{-26}$

$(0.1)[I^-]^2 = 2.5\times10^{-26}$

$\therefore$ $[I^-] = 5\times10^{-13}\,M$ ...(2)

Since, $[I^-]$ required for precipitation of AgI is less and thus **AgI begins to precipitate first.** Also it will continue upto addition of $[I^-] = 5\times10^{-13}$ when Hg_2I_2 begins to precipitate and thus,

Maximum $[I^-]$ for AgI precipitation = $\mathbf{5\times10^{-13}\,M}$

Now at this concentration of I^-, $[Ag^+]$ left in solution is

$[Ag^+]_{left}[I^-] = K_{sp_{AgI}}$

$\therefore$ $[Ag^+]_{left} = \dfrac{8.5\times10^{-17}}{5.0\times10^{-13}} = \mathbf{1.7\times10^{-4}\,M}$

$\because$ $0.1M\,Ag^+$ will be left = $1.7\times10^{-4}\,M\,Ag^+$ in solution

$\therefore$ 100 " " = **0.17% M Ag^+**

$\therefore$ % of Ag precipitated = **99.83%**

93. The K_{sp} values of Ag_2CrO_4 and $AgIO_3$ reveals that CrO_4^{2-} and IO_3^- will be precipitated on addition of $AgNO_3$ as :

$[Ag^+][IO_3^-] = 10^{-13}$

$[Ag^+]_{needed} = \dfrac{10^{-13}}{[0.005]} = 2\times10^{-11}$

$[Ag^+]^2[CrO_4^{2-}] = 10^{-8}$

$[Ag^+]_{needed} = \sqrt{\dfrac{10^{-8}}{0.1}} = 3.16\times10^{-4}$

Thus, $AgIO_3$ will be precipitated first.

Now, in order to precipitate $AgIO_3$, one can show :

$AgNO_3$ +	$NaIO_3$ $\longrightarrow$	$AgIO_3$ +	$NaNO_3$
0.01	0.005	0	0
0.005	0	0.005	0.005

The left mole of $AgNO_3$ are now used to precipitate Ag_2CrO_4

$2AgNO_3$ +	Na_2CrO_4 $\longrightarrow$	Ag_2CrO_4 +	$2NaNO_3$
0.005	0.1	0	0
0	0.0975	0.0025	0.005

Thus, $[CrO_4^{2-}]$ left in solution = **0.0975**

Now, solution has $AgIO_3\,(s) + Ag_2CrO_4\,(s) + CrO_4^{2-}$ ions

0.005 0.0025 0.0975

$\therefore$ $[Ag^+]_{left} = \dfrac{K_{sp}Ag_2CrO_4}{[CrO_4^{2-}]} = \sqrt{\dfrac{10^{-8}}{0.0975}} = \mathbf{3.2\times10^{-4}\,M}$

$\therefore$ $[IO_3^-]_{left} = \dfrac{K_{sp}AgIO_3}{[Ag^+]} = \dfrac{10^{-13}}{3.2\times10^{-4}} = \mathbf{3.2\times10^{-10}\,M}$

94. 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 $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

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

Then, $4s^3 = 4.42\times10^{-5}$

$\therefore$ $s = \sqrt[3]{\left(\dfrac{4.42\times10^{-5}}{4}\right)} = 0.0223\,M$

Now $Ca(OH)_2$ + NaOH are mixed

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

On mixing, $[Ca^{2+}] = \dfrac{0.0223\times500}{1000}$

$= 0.01115 = 111.5\times10^{-4}\,M$

$[OH^-] = \dfrac{0.0223\times2\times500}{1000} + \dfrac{500\times0.4}{1000}$

(from $Ca(OH)_2$) (from NaOH)

$= 0.2223\,M$

$\therefore$ $[Ca^{2+}][OH^-]^2 = K_{sp}$

$[Ca^{2+}]_{left}[0.2223]^2 = 4.42\times10^{-5}$

$[Ca^{2+}]_{left} = \dfrac{4.42\times10^{-5}}{[0.2223]^2} = 8.94\times10^{-4}$ mol litre^{-1}

$\because$ Mole of $Ca(OH)_2$ precipitated = Mole of $[Ca^{2+}]$ precipitated

$= 111.5\times10^{-4} - 8.94\times10^{-4} = 102.46\times10^{-4}$

$\therefore$ Mass of $Ca(OH)_2$ precipitated from $Ca(OH)_2$ solution $= 102.46\times10^{-4}\times74 = 7582.04\times10^{-4}\,g$ = **758.2 mg**

95. For $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$

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

Let $[SO_4^{2-}] = a$, just sufficient to precipitate $CaSO_4$ from a solution having $[Ca^{2+}] = 0.005\,M$

Then, $[0.005][a] = 2.4\times10^{-5}$ $\therefore$ $a = \dfrac{2.4\times10^{-5}}{0.005}$

$[SO_4^{2-}] = \mathbf{4.8\times10^{-3}}$ **mol litre^{-1}**

96. (a)

	2NaOH +	$NiCl_2$ $\longrightarrow$	$Ni(OH)_2$ +	2NaCl
Mole before reaction	$\frac{1.75}{40}$ = 0.0438	0.25×0.1 = 0.025		
Mole left	0	$\left(0.025 - \frac{0.0438}{2}\right)$	$\frac{0.0438}{2}$	0.0438

$\therefore$ Mole of $Ni(OH)_2$ formed $= \frac{0.0438}{2}$

$\therefore$ mass of $Ni(OH)_2$ formed $= \frac{0.0438}{2} \times 92.6 = 2.0279$g

(b) Also for $Ni(OH)_2$ solution, $Ni(OH)_2 \rightleftharpoons Ni + 2OH^-$

$$[Ni^{2+}][OH^-]^2 = K_{sp}$$

$$\left[\frac{0.025 - \frac{0.0438}{2}}{0.25}\right][OH^-]^2 = 1.6 \times 10^{-14}$$

$\therefore$ $[OH^-] = 11.35 \times 10^{-7}$ $\therefore$ pOH = 5.94 $\therefore$ pH = **8.06**

Note: $Ni(OH)_2$ formed will be precipitated out since maximum solubility of $Ni(OH)_2$ is 1.58×10^{-5} M.

97. $[Ag^+]$ in solution $= \sqrt{K_{sp_{AgCl}}} = \sqrt{1 \times 10^{-10}} = 10^{-5} M$

Now the solution after mixing with NaBr has $[Ag^+] = \frac{10^{-5} \times 100}{200}$

and $[Br^-] = \frac{100 \times 0.03}{200}$

Thus, $[Ag^+][Br^-] = \left[\frac{10^{-5} \times 100}{200}\right] \times \left[\frac{100 \times 0.03}{200}\right]$

$$= \mathbf{7.5 \times 10^{-8}}$$

The product of ionic concentration is greater than K_{sp} and thus AgBr will be precipitated.

98. Let solubility of $Mg(OH)_2$ be s mol litre^{-1}

$$Mg(OH)_2 \rightleftharpoons \underset{s}{Mg^{2+}} + \underset{2s}{2OH^-}$$

$\therefore$ $[Mg^{2+}][OH^-]^2 = K_{sp}$

$$4s^3 = 8.9 \times 10^{-12}$$

$\therefore$ $s = 1.305 \times 10^{-4} M$; $OH^- = 2 \times 1.305 \times 10^{-4} M$

$\therefore$ pOH = 3.5832

pH = **10.4168**

99. $CdSO_4 + HCl + H_2S \longrightarrow CdS + H_2SO_4$

	$CdSO_4$	HCl	CdS	H_2SO_4
Millimole added	0.1	10 × 0.08 = 0.8		
Millimole after reaction	0	0.8	0.1	0.1

$\therefore$ Millimole of H^+ left = 0.8 (from HCl) + 0.1 × 2 (from H_2SO_4) = 1.0

Total volume = 100 mL

$\therefore$ $[H^+] = \frac{1}{100} = 10^{-2} M$

$\therefore$ pH = **2**

100. $[(NH_4)_2S] = 0.021M$

$\therefore$ $[S^{2-}] = 0.021M$

$\therefore$ At equilibrium, $[Zn^{2+}][S^{2-}] = K_{sp}$ of ZnS

$\therefore$ $[Zn^{2+}] = \frac{4.51 \times 10^{-24}}{0.021} = 2.15 \times 10^{-22} M$

$\therefore$ $[Zn^{2+}]$ left in solution $= 2.15 \times 10^{-22} \times 65$g / litre

$$= \frac{2.15 \times 10^{-22} \times 65 \times 12}{1000} \text{g / 12 mL}$$

$$= \mathbf{1.677 \times 10^{-22}} \textbf{ g / 12 mL}$$

101. For buffer solution,

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

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

$\therefore$ $pOH = -\log 1.8 \times 10^{-5} + \log \frac{0.25}{0.05}$

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

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

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

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

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

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

$$[Mg^{2+}][3.6 \times 10^{-6}]^2 = 8.9 \times 10^{-12}$$

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

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

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$9.0 \times 10^{-12} = [0.05][OH^-]^2$$

$\therefore$ $[OH^-] = 1.34 \times 10^{-5} M$

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

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

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

For NH_4OH $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

In presence of NH_4Cl; all the $[NH_4^+]$ are provided by NH_4Cl since common ion effect decreases dissociation of NH_4OH.

$\therefore$ $1.8 \times 10^{-5} = \frac{[NH_4^+][1.34 \times 10^{-5}]}{[0.05]}$

$\therefore$ $[NH_4^+] = 0.067M$ or $[NH_4Cl] = \mathbf{0.067}$ M

103. Maximum solubility of $CaSO_4$ in water

$$S = \sqrt{K_{sp}} = 3 \times 10^{-3} \text{ mol litre}^{-1}$$

Let V litre of sample is taken, then $CaSO_4$ present

$$= \frac{131 \times V \times 10^{-3}}{10^6} \text{g}$$

[$\because$ ppm = g of $CaSO_4$ in 10^6 g of sample]

$$= 131 \times 10^{-3} V \text{g} = \frac{131 \times 10^{-3} \times V}{136} \text{ mole in } V \text{ litre}$$

if water is evaporated on heating so that just deposition of $CaSO_4$ occurs. Let V_1 litre of water is left, then

$\frac{131\times10^{-3}\times V}{136}$ mole are present in V_1 litre solution are equal to $3\times10^{-3}\times V_1$ mole.

$$\therefore \quad \frac{131\times10^{-3}\times V}{136}=3\times10^{-3}\times V_1 \qquad \therefore \quad V_1=0.32V$$

Thus, volume evaporated $=V-0.32V=$ **0.68 V or 68% of water should be evaporated.**

104. Suppose V mL of solution contains $0.1\,M\ Mg^{2+}$ and $0.8\,M\ NH_4Cl$

Now V mL of 'a' molarity NH_3 is added which just gives precipitate of $Mg(OH)_2$, then

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

$$\left[\frac{0.1V}{2V}\right][OH^-]^2=1.4\times10^{-11}$$

$$\left([Mg^{2+}]=\frac{\text{Millimole}}{\text{Total volume}}\right)$$

$$\therefore \quad [OH^-]=1.67\times10^{-5}\,M$$

Now if the $[OH^-]=1.67\times10^{-5}$, on addition of NH_3 in NH_4Cl, then $Mg(OH)_2$ will precipitate. For buffer solution of NH_3 and NH_4Cl.

$$\therefore \quad -\log[OH^-]=-\log K_b+\log\frac{[NH_4Cl]}{[NH_3]}$$

$$-\log 1.67\times10^{-5}=-\log 1.8\times10^{-5}+\log\frac{(0.8\times V)/2V}{(a\times V)/2V}$$

$$\therefore \quad a=0.7421M$$

$$\therefore \quad [NH_3] \text{ in solution}=\frac{0.7421\times V}{2V}=\mathbf{0.3710\,M}$$

105.

$$[Ca^{2+}][SO_4^{2-}]=2.4\times10^{-5}$$

$$[Sr^{2+}][SO_4^{2-}]=7.6\times10^{-7}$$

$$\therefore \quad \frac{[Sr^{2+}]}{[Ca^{2+}]}=0.03167$$

Initial conc. of $SO_4^{2-}=\frac{10\times0.3}{30}=0.1M$

Initial conc. of Sr^{2+} = Initial conc. of Ca^{2+} $=\frac{0.1\times20}{30}=0.0667M$

Let final conc. of $Ca^{2+}=X$, $\therefore\ [Sr^{2+}]=0.03167X$

$\therefore$ Change in conc. of SO_4^{2-} = change in conc. of Ca^{2+} and Sr^{2+}

$$=0.0667-X+0.0667-0.03167X$$
$$=0.1334-1.03167X$$

$$\therefore \quad \text{Final } [SO_4^{2-}]=0.1-[0.1334-1.03167X]$$

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

$$\therefore \quad X\cdot[0.1-(0.1334-1.03167X)]=2.4\times10^{-5}$$

$$\therefore \quad 1.03167X^2-0.0334X=2.4\times10^{-5}$$

$$\therefore \quad \mathbf{X=3.3\times10^{-2}\,M} \text{ or } \mathbf{[Ca^{2+}]=3.3\times10^{-2}\,M}$$

$$\therefore \quad \mathbf{[Sr^{2+}]=1.05\times10^{-3}\,M} \quad \therefore \mathbf{[SO_4^{2-}]=7.17\times10^{-4}\,M}$$

106. K_{sp} of $CaCO_3=\left(\frac{7\times10^{-3}}{100}\right)^2=49\times10^{-10}$

When only Ba^{2+} is 90% precipitated then only $CaCO_3$ starts precipitation then if solution contains a mol litre^{-1} of Ca^{2+} and Ba^{2+} each,

$$[Ca^{2+}][CO_3^{2-}]=49\times10^{-10}$$

$$[CO_3^{2-}]=\frac{49\times10^{-10}}{a}$$

Now for $BaCO_3$;

$$K_{sp}=[Ba^{2+}][CO_3^{2-}]=\frac{a\times10}{100}\times\frac{49\times10^{-10}}{a}$$

$$=\mathbf{4.9\times10^{-10}}$$

107. (a) For $Mg(OH)_2+2NH_4^+ \rightleftharpoons 2NH_3+2H_2O+Mg^{2+}$

$$\therefore \quad K_C=\frac{[NH_3]^2[Mg^{2+}]}{[NH_4^+]^2}=\frac{[NH_4OH]^2[Mg^{2+}]}{[NH_4^+]^2} \quad \text{...(1)}$$

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

$$K_b=\frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{...(2)}$$

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

$$\therefore \quad K_C=\frac{K_{sp}}{K_b^2}=\frac{6\times10^{-12}}{(1.8\times10^{-5})^2}=\mathbf{1.85\times10^{-2}}$$

(b) Let a mol litre^{-1} of $Mg(OH)_2$ be dissolved in presence of $0.5\,M\ NH_4Cl$

	$Mg(OH)_2+2NH_4^+$	$\rightleftharpoons 2NH_3+2H_2O+$	Mg^{2+}
Mole before reaction	0.5	0	0
Mole after reaction	$(0.5-2a)$	$2a$	a

$$\therefore \quad K_C=\frac{a\times(2a)^2}{(0.5-2a)^2}$$

$$1.85\times10^{-2}=\frac{4a^3}{(0.5-2a)^2} \quad \text{...(3)}$$

Solving cubic equation,

$$\therefore \quad a=\mathbf{0.081\,M}$$

Note : Eq. (3) is cubic equation and its solution is not included in our subject. However if $2a$ is neglected in comparison to 0.5, then 'a' comes equal to $0.1049\,M$.

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

	Ag_2CO_3	$K_2C_2O_4$	$Ag_2C_2O_4$	K_2CO_3
Mole before reaction	excess	0.1520		
Mole at equilibrium		(0.1520 − 0.0358) = 0.1162	0.0358	0.0358

At equilibrium,

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

$\because [Ag^+]^2[C_2O_4^{2-}] = \left[\frac{2\times 0.0358}{0.5}\right]^2\left[\frac{0.1520}{0.5}\right] = 6.23\times10^{-3}$

Thus, $[Ag^+]^2[C_2O_4^{2-}] > K_{sp}$ of $Ag_2C_2O_4$ (1.29×10^{-11})

$\therefore$ $Ag_2C_2O_4$ will precipitate out.

$\because$ Ag_2CO_3 is solid and $Ag_2C_2O_4$ is almost precipitated 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

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

$$= \mathbf{3.97\times10^{-12}\ mol^3\ litre^{-3}}$$

109. Let solubility of AgCN be a mol litre^{-1}

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

$a \quad a$ (After reaction)

However the CN^- formed will react with H^+ to form HCN

$$CN^- + H^+ \longrightarrow HCN$$

$a \quad 10^{-3}$ (Before reaction)

$0 \quad 10^{-3}$ (buffer) $\quad a$ (After reaction)

$\therefore \quad [Ag^+] = a$ and $[HCN] = a$

Since HCN is weak acid and has low degree of dissociation. Also its dissociation is suppressed in presence of $[H^+]$. Thus

Now $\quad HCN \rightleftharpoons H^+ + CN^-$

$$\therefore \quad \frac{[CN^-][H^+]}{[HCN]} = K_a$$

or $$[CN^-] = \frac{K_a[HCN]}{[H^+]} = \frac{a\times(4.8\times10^{-10})}{10^{-3}}$$

Now for $AgCN(s) + aq. \rightleftharpoons Ag^+ + CN^-$

$$K_{sp} = [Ag^+][CN^-]$$

$$1.2\times10^{-16} = \frac{a\times a\times 4.8\times10^{-10}}{10^{-3}}$$

$$\therefore \quad a^2 = \frac{1.2\times10^{-16}\times10^{-3}}{4.8\times10^{-10}}$$

$$\therefore \quad a = \mathbf{1.58\times10^{-5}\ mol\ litre^{-1}}$$

110. $AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$

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

$$K_{sp} = [Ag^+][Cl^-] \quad ...(1)$$

Given $\quad Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

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

By Eqs. (1) and (2), $K_{sp}\times K_f = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$

or $$1\times10^{-10}\times1.6\times10^7 = \frac{a\times a}{[NH_3]^2}$$

Given $\quad$ solubility of AgCl = $0.1M$

$\therefore \quad a = 0.1M$ for $Ag(NH_3)_2^+$ and Cl^-

$$\therefore \quad [NH_3]^2 = \frac{0.1\times0.1}{1.6\times10^{-3}} = 6.25 \quad \therefore \quad [NH_3] = \mathbf{2.5\ M}$$

Also $0.2M$ NH_3 is needed to dissolve $0.1\ M$ Ag^+ ions, thus

$$[NH_3] = 2.5\times+0.2 = \mathbf{2.7\ M}$$

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

$$K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-} = 4\times10^{-19} \quad ...(1)$$

$$K_{sp}AgCl = [Ag^+][Cl^-] = 2.8\times10^{-10} \quad ...(2)$$

By Eq. (1) $4\times10^{-19} = \frac{x\cdot 4x^2}{0.05}$

$$\therefore \quad x = [Ag^+] = 1.70\times10^{-7}$$

$$\therefore \quad [Ag^+][Cl^-] = 1.70\times10^{-7}\times0.02 = 3.41\times10^{-9} > K_{sp}$$

Thus, precipitation of AgCl will take place.

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

$a+b \quad 2a$

$$K_C = \frac{[NH_3]^2[Ag^+]}{[Ag(NH_3)_2^+]} \quad ...(1)$$

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

$a+b \quad b$

$$K_{sp} = [Ag^+][Cl^-] \quad ...(2)$$

In case of simultaneous solubility Ag^+ remains same in solution.

Given $[NH_3] = 2a = 1M$; also $[Ag(NH_3)_2^+] = [Cl^-] = b$ because Ag^+ obtained from AgCl passes in $[Ag(NH_3)_2^+]$ state.

Thus, by Eqs. (1) and (2)

$$\frac{K_C}{K_{sp}} = \frac{[NH_3]^2}{[Cl^-][Ag(NH_3)_2^+]} = \frac{1}{b^2}$$

or $$b^2 = \frac{1.8\times10^{-10}}{62\times10^{-8}} = 0.29\times10^{-2}$$

$$\therefore \quad b = 0.539\times10^{-1} = \mathbf{0.0539}$$

or $$[Ag(NH_3)_2^+] = \mathbf{0.0539}$$

113. $Ag^+ + HCN \longrightarrow AgCN + H^+$

$\frac{0.02\times V}{2V} \quad \frac{0.02\times V}{2V} \quad 0 \quad 0$

$0 \quad 0 \quad 0.01 \quad 0.01 \quad \therefore [H^+] = 10^{-2}$

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

$$\therefore K_{sp} = 2.2\times10^{-16} = [Ag^+][CN^-]$$

$HCN \rightleftharpoons H^+ + CN^- \quad K_a = 6.2\times10^{-10} = \frac{[H^+][CN^-]}{[HCN]}$

Now, soluble CN^- formed will hydrolyse as

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

$\therefore$ $[Ag^+]$ of soluble AgCN = CN^- left after hydrolysis + HCN formed after hydrolysis.

$$\therefore \quad \left[\frac{2.2\times10^{-16}}{[CN^-]}\right] = [CN^-] + \frac{[H^+][CN^-]}{6.2\times10^{-10}}$$

$$= [CN^-] + \frac{10^{-2}[CN^-]}{6.2\times10^{-10}} \quad \left[\because CN^- <<< \frac{10^{-2}[CN^-]}{6.2\times10^{-10}}\right]$$

or $[CN^-]^2 = \frac{2.2\times10^{-16}\times6.2\times10^{-10}}{10^{-2}}$

$\therefore$ $[CN^-] = 3.7\times10^{-12}$

$\therefore$ $[Ag^+] = \frac{K_{sp}}{[CN^-]} = \frac{2.2\times10^{-16}}{3.7\times10^{-12}} = \mathbf{5.96\times10^{-5}}\ M$

114. Given, $AgI(s) \rightleftharpoons Ag^+(aq.) + I^-(aq.)$;

$$K_{sp} = [Ag^+][I^-] = 1.2\times10^{-17} \quad ...(1)$$

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

$$K_f = \frac{[Ag(CN)_2]^-}{[Ag^+][CN^-]^2} = 7.1\times10^{19} \quad ...(2)$$

Let x mole of AgI be dissolved in CN^- solution then,

Now, $AgI(s) + 2CN^- \rightleftharpoons [Ag(CN)_2]^- + I^-$

Mole before reaction	1	0	0
Mole after reaction	$(1-2x)$	x	x

By Eqs. (1) and (2), $K_{eq.} = K_{sp}\times K_f$

$$K_{eq.} = \frac{[Ag(CN)_2^-][I^-]}{[CN^-]^2} = 1.2\times10^{-17}\times7.1\times10^{19}$$

$$K_{eq.} = 8.52\times10^2 \quad ...(3)$$

$\therefore$ $K_{eq.} = 8.52\times10^2 = \frac{x\cdot x}{(1-2x)^2} = \frac{x^2}{(1-2x)^2}$

or $\frac{x}{1-2x} = 29.2$

Thus, $x = 29.2 - 58.4x$ or $x = \mathbf{0.49\ mol}$

115. For $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$
$\qquad\qquad 2s \qquad s$

$K_{sp} = 4s^3$ or $s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.4\times10^{-5}}{4}} = 1.52\times10^{-2}\ M$

For $PbCrO_4 \rightleftharpoons Pb^{2+} + CrO_4^{2-}$

$K_{sp} = s_1^2$ or $s_1 = \sqrt{K_{sp}} = \sqrt{2.8\times10^{-13}} = 5.29\times10^{-7}M$

In solution, conc. of each ion can be given as :

Thus, $[Ag^+] = \frac{2s\times100}{350} = \frac{2\times1.52\times100}{350} = 0.869\times10^{-2}\ M$

$$[SO_4^{2-}] = \frac{s\times100}{350} = \frac{1.52\times10^{-2}\times100}{350} = 0.43\times10^{-2}$$

$$[Pb^{2+}] = \frac{s_1\times250}{350} = \frac{5.29\times10^{-7}\times250}{350} = 3.78\times10^{-7}$$

$$[CrO_4^{2-}] = \frac{s_1\times250}{350} = \frac{5.29\times10^{-7}\times250}{350} = 3.78\times10^{-7}$$

It is thus evident that

$$[Ag^+]^2[CrO_4^{2-}] = (0.869\times10^{-2})^2\times(3.78\times10^{-7})$$

$$= \mathbf{2.85\times10^{-11}} > K_{sp}\ Ag_2CrO_4$$

The product is greater than K_{sp} of Ag_2CrO_4 and thus Ag_2CrO_4 will ppt.

116. $Na_2CO_3 + CaF_2(s) \longrightarrow CaCO_3 + 2NaF$

Mole taken	2		0	0
Mole left	$(2-a)$		a	$2a$

where a is very-very small and thus assume that $CaCO_3$ is in soluble form

Now, K_{sp} of $CaCO_3 = x = [Ca^{2+}][CO_3^{2-}]$

Also $[CO_3^{2-}] = 2 - a + a = 2 \quad \therefore \quad [Ca^{2+}] = \frac{x}{2}$

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

$$K_{sp_{CaF_2}} = [Ca^{2+}][F^-]^2$$

$$K_{sp_{CaF_2}} = [y][2y]^2 = 4y^3$$

Further for $[F^-]$, we can have

$$[F^-] = [F^-] \text{ from } CaF_2 + [F^-] \text{ from NaF}$$

$$[F^-] = \sqrt{\frac{K_{sp_{CaF_2}}}{[Ca^{2+}]}} + \text{Negligible value}$$

$\therefore$ $[F^-] = \sqrt{\frac{4y^3}{x/2}} = \sqrt{\frac{\mathbf{8y^3}}{x}}$

117. For PbI_2 saturated solution,

$PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$
$\qquad\qquad s \qquad 2s$

$\therefore$ $K_{sp} = 4s^3$

or $s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\left[\frac{7.1\times10^{-9}}{4}\right]} = 1.21\times10^{-3}\ M$

$\therefore$ $[I^-]$ in solution $= 2\times1.21\times10^{-3}\ M = 2.42\times10^{-3}\ M$

Now, if $AgNO_3$ is used to neutralise these I^- ions

Then, Meq. of $AgNO_3$ = Meq. of I^-

$$13.3\times N = 2.42\times10^{-3}\times25$$

$\therefore$ $N_{AgNO_3} = \mathbf{4.55\times10^{-3}} = M_{AgNO_3}$

For $AgNO_3$ normality = molarity

118. Meq. of $C_2O_4^{2-}$ = Meq. of $KMnO_4$

$$= 0.00102\times6.3\times5\,(Mn^{7+} + 5e \rightarrow Mn^{2+}) = 0.032$$

$\therefore$ Molarity of $C_2O_4^{2-} = \frac{\text{Meq.}}{\text{Volume in mL}\times\text{Valence factor}}$

or $s = \frac{0.032}{250\times2}M = 6.4\times10^{-5}\ M \qquad (C_2^{3+} \rightarrow 2C^{4+} + 2e)$

$\therefore\ K_{sp}$ of $CaC_2O_4 = s^2 = (6.4\times10^{-5})^2$

$= \mathbf{4.09\times10^{-9}}$

119. Initial $[Sr^{2+}] = 16\times10^{-3}\ M$

Left $[Sr^{2+}] = 2.5\times10^{-3}\ M$

$\therefore\ [Sr^{2+}]$ precipitated $= (16-2.5)\times10^{-3} = 13.5\times10^{-3}\ M$

$\therefore\ [F^-]$ needed for this precipitation $= 2\times13.5\times10^{-3}\ M$

$= 27.0\times10^{-3}\ M$

$(\because Sr^{2+} + 2F^- \longrightarrow SrF_2)$

Also $[Sr^{2+}][F^-]^2 = K_{sp_{SrF_2}} = 2.8\times10^{-9}$

$$\therefore\ [F^-]^2 = \frac{2.8\times10^{-9}}{2.5\times10^{-3}}$$

$\therefore\ [F^-] = 1.058\times10^{-3}\ M$, *i.e.*, the concentration of F^- which will also appear in solution state.

Thus, $[F^-]$ needed $= [27.0+1.058]\times10^{-3}\ M$

$= 28.058\times10^{-3}\ M$

$\therefore$ NaF needed for 1 litre $= 28.058\times10^{-3}\times42$ g

$$\therefore\ \text{NaF needed for 100 mL} = \frac{28.058\times10^{-3}\times42}{10}\text{g}$$

$= \mathbf{0.1178\ g}$

120. Given, $MBr_2(g) \rightleftharpoons MBr_2(aq.) \longrightarrow M^{2+} + 2Br^-$

$MBr_2 + H_2S \longrightarrow MS + 2HBr$

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

$6\times10^{-21} = [0.05][S^{2-}]$

$\therefore\ [S^{2-}] = 1.2\times10^{-19}\ M$

Thus, MS will be precipitated if H_2S provides $1.2\times10^{-19}\ M$ ions of S^{2-}.

Now for H_2S $\quad H_2S \rightleftharpoons 2H^+ + S^{2-}$

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

$$10^{-7}\times1.3\times10^{-13} = \frac{[H^+]^2[1.2\times10^{-19}]}{[0.1]}$$

$\therefore\ [H^+] = 1.04\times10^{-1}$ and $pH = \mathbf{0.9826}$

121. $H_2S \rightleftharpoons 2H^+ + S^{-2}$

$NaCN \longrightarrow Na^+ + CN^-$

	$NaCN$	Na^+	CN^-
	0.2	0	0
	0	0.2	0.2

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

$$K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-} = \frac{[Ag^+]\times(0.2)^2}{0.02} = 1.0\times10^{-20}$$

$[Ag^+] = 5\times10^{-21}\ M$

For $Cd(CN)_4^{2-} \rightleftharpoons Cd^{2+} + 4CN^-$

$$K = \frac{[Cd^{2+}][CN^-]^4}{[Cd(CN)_4]^{2-}}$$

$$7.8\times10^{-18} = \frac{[Cd^{2+}]\times(0.2)^4}{0.02}$$

$\therefore\ [Cd^{2+}] = 9.75\times10^{-17}$

Now, $[Ag^+]^2\times[S^{2-}] = 1.0\times10^{-50}$

$$\therefore\ [S^{2-}] \text{ needed to precipitate } Ag_2S = \frac{1.0\times10^{-50}}{(5\times10^{-21})^2}$$

$= 4\times10^{-10}\ M$

$$[S^{2-}] \text{ needed to precipitate CdS} = \frac{7.1\times10^{-28}}{9.75\times10^{-17}}$$

$= 7.28\times10^{-12}\ M$

Therefore, CdS will be precipitated first.

122. For indicator dissociation equilibrium; being an acid

$HIn \rightleftharpoons H^+ + In^-$

Colour *A* $\qquad$ Colour *B*

$$\therefore\ K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

The midpoint of the colour range of an indicator HIn is the point at which $[In^-] = [HIn]$.

$\therefore\ K_{In} = [H^+] = 1\times10^{-5}$

$\therefore\ [H^+] = 1\times10^{-5}$ or $pH = 5$

Thus, at pH = 5 of the solution, the indicator will change its colour.

Again $\quad K_{In} = \dfrac{[H^+][In^-]}{[HIn]}$

$$1\times10^{-5} = \frac{[H^+]\times80\times100}{100\times20}$$

$\therefore\ [H^+] = 0.25\times10^{-5}\ \therefore\ pH = \mathbf{5.6020}$

123. The two conditions when colour of indicator will be visible are derived by

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

(i) $pH = 5 + \log 10 = 6$

(ii) $pH = 5 + \log 0.1 = 4$

Thus, minimum change in pH = **2**

124. $HBPh \rightleftharpoons H^+ + BPh^-$

$K_a = \dfrac{[H^+][BPh^-]}{[HBPh]}$, when $BPh^- = HBPh$, indicator will work. Thus

$[H^+] = 5.84\times10^{-5}\ \therefore\ pH = 4.2336$

Also if $pH = 4.84$ or $[H^+] = 1.44\times10^{-5}$, then

$$K_a = \frac{[H^+][BPh^-]}{[HBPh]} \text{ or } 5.84\times10^{-5} = \frac{1.44\times10^{-5}\cdot C\alpha}{C(1-\alpha)}$$

$\alpha = \mathbf{0.8}$ or **80%**

125. $NaOCN + H_2O \rightleftharpoons NaOH + HCN$

$$h = \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w}{K_aC}\right)} = \sqrt{\frac{10^{-14}}{3.33\times10^{-4}\times0.003}}$$

$h = 10^{-4}$

$\therefore$ % hydrolysis $= 10^{-4} \times 100 = \mathbf{10^{-2}}$

126. pK_a for HCN $= 14 - 4.70 = 9.30$

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

	1	0	0
	$1-h$	h	h

$$\therefore \quad [OH^-] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{K_H \cdot C} = \sqrt{\left(\frac{K_w \cdot C}{K_a}\right)}$$

or $\quad pOH = \frac{1}{2}[pK_w - \log C - pK_a]$

$$= \frac{1}{2}[14 + 0.3010 - 9.30] = 2.5$$

$\therefore \quad pH = 14 - 2.5 = \mathbf{11.5}$

127.

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

where h is degree of hydrolysis

$$h = \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w}{K_b \cdot C}\right)}$$

$$= \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.2}} = \mathbf{5.27 \times 10^{-5}}$$

From HCl, a strong acid

$$\therefore \quad [H^+] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)} = \sqrt{\left(\frac{K_w}{K_b} \cdot C\right)}$$

$$= \sqrt{\left(\frac{10^{-14} \times 0.2}{1.8 \times 10^{-5}}\right)} = 1.054 \times 10^{-5}$$

$\therefore \quad pH = -\log[H^+] = -\log 1.054 \times 10^{-5} = \mathbf{4.9771}$

Let conc. of NH_4Cl be C mol litre^{-1}

128.

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

$$\therefore \quad [H^+] = \sqrt{(K_H \cdot C)} = \sqrt{\left(\frac{K_w}{K_b} \cdot C\right)} = \sqrt{\left(\frac{10^{-14} \times C}{1.8 \times 10^{-5}}\right)}$$

$$10^{-4.5} = \sqrt{\left(\frac{10^{-14} \times C}{1.8 \times 10^{-5}}\right)} \quad \therefore \; C = 1.8 \text{ mol litre}^{-1}$$

$\therefore$ Mass of $NH_4Cl = 1.8 \times 53.5$ g / litre^{-1}

$$= 1.8 \times 53.5 \times \frac{1}{2} \text{ g / 500 mL} = \mathbf{48.15 \text{ g}}$$

129. (a)

$$NaBu + H_2O \rightleftharpoons NaOH + BuH$$

Conc. before hydrolysis	1	0	0
Conc. after hydrolysis	$1-h$	h	h

$$\therefore [OH^-] = C \cdot h = C \cdot \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)} = \sqrt{\left(\frac{K_w}{K_a} \cdot C\right)}$$

$$[OH^-] = \frac{10^{-14} \times 0.2}{2 \times 10^{-5}} = \sqrt{10^{-10}} = \mathbf{10^{-5}}$$

$\therefore \quad pOH = 5$

Also $pH + pOH = 14 \quad \therefore \; pH = 14 - 5 = \mathbf{9}$

(b) **[Ans : 8]**

130.

$$Asc^- + H_2O \rightleftharpoons HAsc + OH^-$$

$$\therefore \quad [OH^-] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{K_H \cdot C} = \sqrt{\left(\frac{K_w}{K_a} \cdot C\right)}$$

$$= \sqrt{\left(\frac{10^{-14} \times 0.02}{5 \times 10^{-5}}\right)} = 2 \times 10^{-6}$$

$$\therefore \quad [H^+] = \frac{1 \times 10^{-14}}{2 \times 10^{-6}} = \mathbf{5 \times 10^{-9}}$$

Also $\quad h = \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w}{K_a \times C}\right)}$

$$= \sqrt{\left(\frac{10^{-14}}{5 \times 10^{-5} \times 0.02}\right)} = \mathbf{10^{-4}} \quad \text{or} \quad \mathbf{0.01\%}$$

131. Let V mL of acid and V mL of NaOH be used. Conc. of both acid and NaOH are same.

$$\therefore \quad CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

	CH_3COOH	$NaOH$	CH_3COONa	H_2O
Conc. before reaction	$\frac{0.1 \times V}{2V}$	$\frac{0.1 \times V}{2V}$	0	0
Conc. after reaction	0	0	$\frac{0.1 \times V}{2V}$	$\frac{0.1 \times V}{2V}$

$$\therefore \quad [CH_3COONa] = \frac{0.1}{2} = \mathbf{0.05\ M}$$

Now calculate pH by hydrolysis of CH_3COONa

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$[OH^-] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w \times C}{K_a}\right)}$$

$$= \sqrt{\left(\frac{10^{-14} \times 0.05}{1.9 \times 10^{-5}}\right)} = 5.12 \times 10^{-6}$$

$\therefore \quad pOH = 5.29 \quad \therefore \; pH = \mathbf{8.71}$

132. **[Ans : 8.975]**

133.

$$Ca(LaC)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HLaC$$

or

$$2LaC^- + 2H_2O \rightleftharpoons 2OH^- + 2HLaC$$

Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

$$\therefore \quad [Ca(LaC)_2] = \frac{0.13}{0.5} = 0.26\ M$$

$$\therefore \quad [LaC^-] = 0.26 \times 2 = 0.52\ M$$

$\because$ 1 mole $Ca(LaC)_2$ gives 2 moles (LaC)

Now $\quad [OH^-] = C \cdot h = C\sqrt{\left(\frac{K_H}{C}\right)}$

$$= \sqrt{(K_H \cdot C)} = \sqrt{\left(\frac{K_w \times C}{K_a}\right)}$$

where C is conc. of anion which undergoes hydrolysis

$$\therefore \quad 10^{-5.60} = \sqrt{\left(\frac{10^{-14} \times 0.52}{K_a}\right)} \quad \therefore \; K_a = \mathbf{8.25 \times 10^{-4}}$$

134.

$$K_3PO_4 + H_2O \rightleftharpoons K_2HPO_4 + KOH$$

or

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$$

Since hydrolysis proceeds only in I step

$\therefore \quad [OH^-] = C \cdot h = C\sqrt{\left(\frac{K_w}{K_a \cdot C}\right)} = \sqrt{\left(\frac{K_w \cdot C}{K_a}\right)}$

K_a is III dissociation constant of acid H_3PO_4

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad K_1$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \quad K_2$

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \quad K_3 = K_a = 1.3\times10^{-12}$

$\therefore \quad [OH^-] = \sqrt{\left(\frac{10^{-14}\times0.1}{1.3\times10^{-12}}\right)} \quad \therefore \ pOH = 1.5634$

$\therefore \quad$ **pH = 12.4366**

135. $Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+; \quad K_H = 6.5\times10^{-3}$

$(1-h) \qquad h \qquad h$

$[H^+] = Ch$

and $\quad K_H = \frac{C\cdot h^2}{1-h}$ and $h = \frac{5}{100}$

Thus, $\quad 6.5\times10^{-3} = \frac{C\times5\times5\times100}{100\times100\times95}$

$\therefore \ C = 2.47M \ \therefore \ [H^+] = 2.47\times\frac{5}{100} \ \therefore$ **pH = 0.9083**

136. $Zn^{2+} + H_2O \rightleftharpoons [Zn(OH)]^+ + H^+ \quad K_H = 1.0\times10^{-9}$

$\therefore \quad [H^+] = C\cdot h = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{(K_H \cdot C)}$

$= \sqrt{10^{-9}\times0.001} = 10^{-6} \quad \therefore \ pH = 6$

137. $\because \quad$ Aniline$^+$ + Acetate$^-$ + $H_2O \rightleftharpoons$ Aniline + Acetic acid

	Aniline$^+$	Acetate$^-$	Aniline	Acetic acid
Before hydrolysis	1	1	0	0
After hydrolysis	$1-h$	$1-h$	h	h

Let concentration of salt be C mol litre^{-1}

$\therefore \ K_H = \frac{[\text{Aniline}]\ [\text{Acetic acid}]}{[\text{Aniline}]^+\ [\text{Acetate}]^-} = \frac{C\cdot h\cdot C\cdot h}{C\cdot(1-h)\cdot C\cdot(1-h)}$

$\therefore \ K_H = \frac{h^2}{(1-h)^2} \quad \therefore \quad \frac{h}{1-h} = \sqrt{(K_H)}$

$\frac{h}{1-h} = \sqrt{\left(\frac{K_w}{K_a\cdot K_b}\right)} = \sqrt{\left(\frac{1.008\times10^{-14}}{1.75\times10^{-5}\times3.83\times10^{-10}}\right)}$

$\therefore \quad$ **h = 54.95%**

Note: If $K_H = h^2$ is used assuming $1-h \approx 1$ the value of h comes greater than 1 which is not possible and thus, it is always advised in all such cases, not to assume $1-h\approx1$ when h values are higher. Also the term dissociation constant of water is used here for ionic product of water. See the value.

138. The pH of salt $HCOONH_4$ (a salt of weak acid + weak base) is given by :

$HCOONH_4 + H_2O \rightleftharpoons HCOOH + NH_4OH$

$pH = \frac{1}{2}[\log K_b - \log K_a - \log K_w]$

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

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

139. (a) $\quad NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

	NaOH	CH_3COOH	CH_3COONa	H_2O
mM before reaction	$50\times0.1 = 5$	$50\times0.05 = 2.5$	0	0
mM after reaction	2.5	0	2.5	2.5

$\because$ Strong alkali is left free and thus, it will decide pH of solution.

$\therefore \quad [NaOH] = \frac{2.5}{100} = 2.5\times10^{-2}M$

$\therefore \quad [OH^-] = 2.5\times10^{-2}M \ \therefore \ pOH = 1.6021$

$\therefore \quad$ **pH = 12.3979**

(b) $\quad NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

	NaOH	CH_3COOH	CH_3COONa	H_2O
mM before reaction	$50\times0.05 = 2.5$	$50\times0.1 = 2.5$	0	0
mM after reaction	0	2.5	2.5	2.5

The solution consists CH_3COOH and CH_3COONa and thus, is a buffer

$\therefore \quad pH = -\log K_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$

$\because \ [CH_3COOH] = \frac{2.5}{100}M; \ [CH_3COONa] = \frac{2.5}{100}M$

$\therefore \ pH = -\log 1.8\times10^{-5} + \log\frac{2.5/100}{2.5/100} \ \therefore$ **pH = 4.7447**

(c) $\quad NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

	NaOH	CH_3COOH	CH_3COONa	H_2O
mM before reaction	$50\times0.1 = 5$	$50\times0.1 = 5$	0	0
mM after reaction	0	0	5	5

$\because \ CH_3COONa$ is left with concentration $= \frac{5}{100}M$ and thus, pH is decided by salt hydrolysis

$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

	CH_3COONa	CH_3COOH	NaOH
Before hydrolysis	1	0	0
After hydrolysis	$1-h$	h	h

$\therefore \quad [OH^-] = Ch = C\sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{K_w\cdot C}{K_a}\right)}$

$= \sqrt{\left(\frac{10^{-14}}{1.8\times10^{-5}}\times\frac{5}{100}\right)}$

$= 5.27\times10^{-6}M$

$\therefore \quad$ **pH = 8.7218**

(d) $\quad NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

	NH_4OH	HCl	NH_4Cl	H_2O
mM before reaction	$50\times0.1 = 5$	$50\times0.05 = 2.5$	0	0
mM after reaction	2.5	0	2.5	2.5

The solution contains NH_4OH and NH_4Cl and thus, acts as buffer

Thus, $\quad pOH = -\log K_b + \log\frac{[NH_4Cl]}{[NH_4OH]}$

$\because \quad [NH_4Cl] = \frac{2.5}{100}M; \ [NH_4OH] = \frac{2.5}{100}$

$\therefore \quad pOH = -\log 1.8\times10^{-5} + \log\frac{2.5/100}{2.5/100}$

$$pOH = 4.7447 \quad \therefore \quad pH = \mathbf{9.2553}$$

(e)

	NH_4OH	+ HCl ⟶	NH_4Cl	+ H_2O
mM before reaction	$50 \times 0.05 = 2.5$	$50 \times 0.1 = 5$	0	0
mM after reaction	0	2.5	2.5	2.5

$\because$ Strong acid is left and therefore, pH is decided by HCl.

$$[HCl] = [H^+] = \frac{2.5}{100} M \quad \therefore \quad pH = \mathbf{1.6021}$$

(f)

	NH_4OH	+ HCl ⟶	NH_4Cl	+ H_2O
mM before reaction	$50 \times 0.1 = 5$	$50 \times 0.1 = 5$		
mM after reaction	0	0	5	5

$\because$ Salt is left and thus, pH will be decided by salt hydrolysis.

$$[NH_4Cl] = \frac{5}{100} = 5 \times 10^{-2} M$$

Since NH_4Cl is salt of strong acid and weak base and therefore,

$$pH = \frac{1}{2}[\log K_b - \log C - \log K_w]$$

$$= \frac{1}{2}[\log 1.8 \times 10^{-5} - \log 5 \times 10^{-2} - \log 1 \times 10^{-14}]$$

$$\therefore \quad pH = \mathbf{5.2782}$$

(g)

	NH_4OH	+ CH_3COOH →	CH_3COONH_4	+ H_2O
mM before reaction	$50 \times 0.05 = 2.5$	$50 \times 0.05 = 2.5$	0	0
mM after reaction	0	0	2.5	2.5

$\because$ Salt is left and thus, pH will be decided by salt hydrolysis.

$$[CH_3COONH_4] = \frac{2.5}{100} = 2.5 \times 10^{-2} M$$

Now	$CH_3COONH_4 + H_2O$	⇌ CH_3COOH	+ NH_4OH
Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

$$CH_3COOH = Ch$$

Now for dissociation of CH_3COOH

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

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

$\because$ α is small and thus, $[CH_3COOH] = Ch$

Also $[CH_3COO^-]$ is provided from CH_3COONH_4 left unhydrolysed in solution, *i.e.*, $[CH_3COO^-] = C(1-h)$

$$\therefore \quad K_a = \frac{C(1-h)[H^+]}{Ch} \qquad \because h << 1$$

$$\text{or} \quad [H^+] = hK_a \qquad \therefore 1-h = 1$$

$$= \sqrt{\left(\frac{K_w}{K_a \cdot K_b}\right)} \times K_a = \sqrt{\left(\frac{K_w K_a}{K_b}\right)}$$

$$\therefore \quad pH = +\frac{1}{2}[\log K_b - \log K_w - \log K_a]$$

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

$$= +\frac{1}{2}[\log 1.8 \times 10^{-5} - \log 10^{-14} - \log 1.8 \times 10^{-5}]$$

$$pH = \mathbf{7}$$

140. We have from Raoult's law

$$\frac{P^o - P_s}{P_s} = \frac{w \times M}{m \times W}$$

$$\therefore \quad \frac{w}{m \times W} = \frac{17.540 - 17.536}{17.536 \times 18} = 1.267 \times 10^{-5}$$

$$\therefore \quad \text{Molality} = \frac{w}{m \times W} \times 1000 = 1.267 \times 10^{-5} \times 10^3$$

$$= 1.267 \times 10^{-2} = \text{Molarity} = \text{Conc. of } [BOH]$$

For	BOH	⇌ B^+	+ OH^-
	1	0	0
	$(1-\alpha)$	α	α

Molarity is also given as 1×10^{-2}

$$\therefore \quad \frac{\text{Exp. value of molarity}}{\text{Normal value of molarity}} = 1 + \alpha$$

$$\therefore \quad \frac{1.267 \times 10^{-2}}{1 \times 10^{-2}} = 1 + \alpha \quad \therefore \quad \alpha = 0.267$$

$$\text{Now,} \quad K_b = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.01 \times 0.267 \times 0.267}{(1-0.267)} = \mathbf{9.74 \times 10^{-4}}$$

141.

	HA	⇌ H^+	+ A^-
	1	0	0
	$1-\alpha$	α	α

$$\therefore \quad \pi V = nST(1+\alpha) \quad \text{or} \quad 1+\alpha = \frac{\pi \times V}{n \times S \times T}$$

$$\therefore \quad 1+\alpha = \frac{0.293}{0.01 \times 0.0821 \times 298} \qquad \left(\frac{n}{V} = 0.01\right)$$

$$\therefore \quad \alpha = 1.197 - 1 = 0.197$$

$$\therefore \quad K_a \text{ for } HA = \frac{C\alpha^2}{(1-\alpha)} = \frac{0.01 \times (0.197)^2}{(1-0.197)} = \mathbf{4.83 \times 10^{-4}}$$

Similarly, K_a for $HB = \mathbf{2.85 \times 10^{-3}}$

142. (i) $Zn(OH)_2(s) \rightleftharpoons Zn^{2+} + 2OH^- \quad K_{sp} = [Zn^{2+}][OH^-]^2$

(ii) $Zn(OH)_2(s) + 2OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$

$$K_f = \frac{[Zn(OH)_4)]^{2-}}{[OH^-]^2}$$

Let the solubility be s in change (i) and thus solubility will also be s in change (ii) By coupling (i) and (ii),

$$2Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq.) + [Zn(OH)_4]^{2-}(aq.)$$

$$\therefore \quad K_{sp} \times K_f = s \times s$$

$$\text{or} \quad s = \sqrt{K_{sp} \times K_f} = \sqrt{1.2 \times 10^{-17} \times 0.12} = 1.2 \times 10^{-9} M$$

Thus total solubility, will be $2s = 2 \times 1.2 \times 10^{-9}$

$$= 2.4 \times 10^{-9} M$$

This solubility is minimum when $[Zn^{2+}][OH^-]^2$

$$= 1.2 \times 10^{-17}$$

$$1.2 \times 10^{-9}[OH^-]^2 = 1.2 \times 10^{-17}$$

$$\therefore \quad [OH^-] = \mathbf{10^{-4} M}$$

Note : If only I change than solubility of

$$Zn(OH)_2 = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.2 \times 10^{-7}}{4}} = 1.44 \times 10^{-6} \text{ m}$$

and at this conc. $[OH^-] = 2\times 1.44\times 10^{-6} M = \mathbf{2.88\times 10^{-6} M}$

143. (a) $N_2O_4 \rightleftharpoons 2NO_2$

Let a mole of N_2O_4 and b mole of NO_2 were present in equilibrium mixture

$$\therefore \quad (a+b) = \frac{PV}{RT} = \frac{753\times 0.5}{760\times 0.0821\times 298} = 0.020 \quad ...(1)$$

$$K_p = \frac{(n_{NO_2})^2}{(n_{N_2O_4})}\times\left[\frac{P}{[n_{NO_2}+n_{N_2O_4}]}\right]^1$$

$$\therefore \quad 0.113 = \frac{b^2}{a}\times\left[\frac{753}{760\times(a+b)}\right]$$

$$\therefore \quad \frac{b^2}{a(a+b)} = 0.114 \quad ...(ii)$$

By Eqs. (i) and (ii)

$$\therefore \quad \frac{b^2}{a} = 0.114\times 0.020 = 2.3\times 10^{-3} \quad ...(iii)$$

$$b^2 = 2.3\times 10^{-3} a = 2.3\times 10^{-3}\times(0.02-b)$$

or $b^2 + 0.0023b - 4.6\times 10^{-5} = 0$

$$\therefore \quad b = -\frac{0.0023\pm\sqrt{(0.0023)^2+4\times 4.6\times 10^{-5}\times 1}}{2\times 1}$$

$$= \frac{-0.0023\pm\sqrt{1.90\times 10^{-4}}}{2}$$

$$b = 5.73\times 10^{-3}$$

$\therefore$ By Eq. (i) $a = 0.014$

(b) $2NO_2(aq.) + 2H_2O(l) \longrightarrow HNO_2(aq.) + H_3O^+(aq.) + NO_3^-(aq.)$

Total NO_2 mole $= 5.73\times 10^{-3} + 2\times$ moles of N_2O_4 from NO_2

$= 5.73\times 10^{-3} + 2\times 0.014$

$= 0.0337$

$2NO_2(aq.) + 2H_2O(l) \rightarrow HNO_2 + H_3O^+(aq.) + NO_3^-(aq.)$

0.0337	0	0	0
0	$\frac{0.0337}{2}$	$\frac{0.0337}{2}$	$\frac{0.0337}{2}$

$$\therefore \quad [HNO_2] = \frac{0.0337\times 1000}{2\times 250} = 0.0674\, M;$$

$$[H^+] = \frac{0.0337\times 1000}{2\times 250} = 0.0674\, M$$

Due to common ion effect (H_3O^+ furnished by HNO_3), the dissociation of HNO_2 is suppressed.

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{0.0674\times[NO_2^-]}{0.0674} = 4.5\times 10^{-4}$$

$\therefore$ $[NO_2^-] = \mathbf{4.5\times 10^{-4}}$

Also $pH = -\log[H^+] = -\log 0.0674 = \mathbf{1.17}$

(c) $\pi = C.S.T.\times$(No. of particles present in solution)

$= 0.0674\times 0.0821\times 298\times 3$

($2NO_2$ furnishes three particles)

$= \mathbf{4.95\ atm}$

(d) Eq. of CaO required = Eq. of HNO_2 + Eq. of HNO_3

$$= \frac{0.0337}{2}\times 1 + \frac{0.0337}{2}\times 1 = 0.0337$$

$\therefore$ Mole of CaO required $= \frac{0.0337}{2}$ or $\frac{w}{56} = \frac{0.0337}{2}$

$\therefore$ $w_{CaO} = \mathbf{0.924\ g}$

144. $CH_3COOH + Na^+ + CN^- \rightleftharpoons CH_3COO^- + Na^+ + HCN$

$$K_{eq} = \frac{[CH_3COO^-][HCN]}{[CH_3COOH][CN^-]} \quad ...(i)$$

For CH_3COOH and HCN in same solution

$$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad ...(ii)$$

$$K_2 = \frac{[CN^-][H^+]}{[HCN]} \quad ...(iii)$$

By Eqs. (ii) and (iii)

$$K_{eq} = \frac{K_1}{K_2} = \frac{1.8\times 10^{-5}}{4.9\times 10^{-10}} = \mathbf{3.674\times 10^4}$$

145. $NaX + H_2O \longrightarrow$ No hydrolysis because pH = 7.0

$NaY + H_2O \longrightarrow NaOH + HY$ pH = 9.0

$NaZ + H_2O \longrightarrow NaOH + HZ$ pH = 11.0

Thus acidic character order for acids is : $HX > HY > HZ$

Also for NaY: $[OH^-] = 10^{-5}$ $\because$ pH = 9 $\therefore$ pOH = 5

$$Ch = 10^{-5}$$

$$C\cdot\sqrt{\frac{K_H}{C}} = 10^{-5} \quad \text{or} \quad \sqrt{\frac{K_w\times C}{K_a}} = 10^{-5}$$

$\therefore$ $\frac{10^{-14}\times 0.1}{K_a} = 10^{-10}$ $\therefore$ K_a for $HY = 10^{-5}$

Similarly, K_a for $HZ = \mathbf{10^{-9}}$

146. The conjugate base (here $HC_8H_4O_4^-$) of polybasic acid (here $H_2C_8H_4O_4$), is amphioprotic and can act as either an acid or a base because it can donate its remaining acidic hydrogen atom or accept an acidic hydrogen atom and revert to the original acid.

Acid :

$HC_8H_4O_4^-(aq.) + H_2O(l) \rightleftharpoons H_3O^+ + C_8H_4O_4^{2-}$; $pK_{a_2} = 5.44$

$$K_{a_2} = \frac{[H_3O^+][C_8H_4O_4^{2-}]}{[HC_8H_4O_4^-]} \quad ...(i)$$

Hydrolysis :

$HC_8H_4O_4^-(aq.) + H_2O(l) \rightleftharpoons H_2C_8H_4O_4 + OH^-$; $pK_H = 11.06$

$$K_H = \frac{[H_2C_8H_4O_4][OH^-]}{[HC_8H_4O_4^-]} \quad ...(ii)$$

Also for $H_2C_8H_4O_4$

$$H_2C_8H_4O_4 \rightleftharpoons H^+ + HC_8H_4O_4^-$$

$$K_{a_1} = \frac{[H^+][HC_8H_4O_4^-]}{[H_2C_8H_4O_4]} \quad ...(iii)$$

By Eqs. (ii) and (iii)

$$K_H \times K_{a_1} = [H^+][OH^-] = K_w \quad ...(iv)$$

Assuming $HC_8H_4O_4^-$ having low degree of dissociation as well as low degree of hydrolysis, acidic nature of $HC_8H_4O_4^-$ and hydrolysis of $HC_8H_4O_4^-$ producing $C_8H_4O_4^{2-}$ and $H_2C_8H_6O_4$ of almost equal conc.

$$[H_2C_8H_4O_4] = [C_8H_4O_4^{2-}] \quad ...(v)$$

From Eqs. (i), (ii) and (v) $\frac{K_H}{K_{a_2}} = \frac{[OH^-]}{[H^+]}$ ...(vi)

Also $K_w = [H^+][OH^-]$ ...(vii)

By Eqs. (vi) and (vii)

$$\therefore \quad K_w = \frac{[H^+] \times K_H \times [H^+]}{K_{a_2}} \quad ...(viii)$$

By Eqs. (iv) and (viii) $K_H \times K_{a_1} = \frac{[H^+]^2 \times K_H}{K_{a_2}}$

or $[H^+]^2 = K_{a_1} \times K_{a_2}$ or $[H^+] = \sqrt{K_{a_1} \times K_{a_2}}$

$$pH = \frac{1}{2}[pK_{a_1} + pK_{a_2}]$$

$$\frac{1}{2}[2.94 + 5.44] = 4.19$$

Note: 1. The pH is independent of salt concentration in case of acidic salt solution.

2. All polyprotic acids (except H_2SO_4) are weak acids and the relation $pH = \frac{1}{2}[pK_{a_1} + pK_{a_2}]$ holds good.

3. The relation $pH = \frac{1}{2}[pK_{a_1} + pK_{a_2}]$ is derived by using reasonable assumptions and doing some intricate algebra. The assumptions include that if pK_{a_2} is high HA^- is weak acid, the solution will have high pH. If pK_{a_1} is large HA^- is likely to act as 'strong' weak base. Thus, if both pK_{a_1} and pK_{a_2} are large, pH will be high.

147. $[H^+]$ formed due to electrolyte oxidation = 4 *m* moles

$$Na_2HPO_4 + Na_3PO_4$$

Initial mm $0.08 \times 100 = 8$ $\quad 0.02 \times 100$ = 2

$[H^+]$ will be used by PO_4^{3-} to give $H_2PO_4^-$

$$PO_4^{3-} + 2H^+ \longrightarrow H_2PO_4^-$$

PO_4^{3-}	$2H^+$	$H_2PO_4^-$
2	4	0
0	0	2

Thus, a new buffer containing Na_2HPO_4 (8 mm) and $H_2PO_4^-$ (2 mm) will remain in solution

$$\therefore pH = pK_{a_{H_2PO_4^-}} + \log\frac{[Na_2HPO_4]}{[H_2PO_4^-]} = 7.2 + \log\frac{8}{2} = \mathbf{7.81}$$

148. $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

at 1/3 neutralisation $\frac{2}{3}$ $\qquad \frac{1}{3}$

$\therefore$ [Conjugate base] = $[CH_3COO^-] = \frac{1}{3}$

[Acid] = $[CH_3COOH] = \frac{2}{3}$

$$\therefore \quad pH_1 = -\log K_a + \log\frac{1/3}{2/3} = -\log K_a - \log 2$$

at 2/3 neutralisation [conjugate base] $= \frac{2}{3}$

[Acid] $= \frac{1}{3}$

$$\therefore \quad pH_2 = -\log K_a + \log\frac{2/3}{1/3}$$

$$= -\log K_a + \log 2$$

$$\therefore \quad \Delta pH = pH_1 - pH_2 = \log\frac{1}{2} - \log 2$$

$$= \mathbf{-2\log 2}$$

149. (3)

$\Lambda_m(HX) = \frac{x}{10}$ $\quad \Lambda_m(HY) = x$. Also $\alpha = \frac{\Lambda_m}{\Lambda_0}$. Let α_1 and α_2 be degree of dissociation of 0,01 *M* HX and 0.1 *M* HY

$$\therefore \frac{\alpha_1}{\alpha_2} = \frac{\Lambda_m(HX)/\Lambda_m^0(HX)}{\Lambda_m(HY)/\Lambda_m^0(HY)} = \frac{(x/10)/\Lambda_m^0(HX)}{x/\Lambda_m^0(HY)} = \frac{1}{10}$$

$HX \rightleftharpoons$	H^+	+	X^-
0.01	–		–
$0.01(1-\alpha_1)$	$0.01\alpha_1$		$0.01\alpha_1$

$K_{a_1} = 0.01\alpha_1^2$ $\quad (\because \alpha_1 <<< 1)$

$HY \rightleftharpoons$	H^+	+	Y^-
0.1	–		–
$0.1(1-\alpha_2)$	$0.1\alpha_2$		$0.1\alpha_2$

$K_{a_2} = 0.1\alpha_2^2$ $\quad (\because \alpha_2 << 1)$

$$\frac{K_{a_1}}{K_{a_2}} = \frac{0.01\alpha_1^2}{0.1\alpha_2^2} = \frac{1}{10}\cdot\frac{\alpha_1^2}{\alpha_2^2} = \frac{1}{10}\times\left(\frac{1}{10}\right)^2 = \frac{1}{1000}$$

$\log K_{a_1} - \log K_{a_2} = -3$

$pK_{a_1} - pK_{a_2} = 3$

• SINGLE INTEGER ANSWER PROBLEMS •

1. 500 mL of HCl of pH 4.3010 is allowed to react with 500 mL of pH 9.6990 NaOH solution at 300 K. If temperature remains constant, approximate pH of resulting solution is....
2. 300 mL of 5×10^{-2} M HCl is allowed to react with 200 mL of 5×10^{-2} M NaOH at 300 K. The pH of resulting solution at 300 K is......
3. 500 mL of 0.01 M $CH_3COOH + 500$ mL of 0.02 M CH_3COONa gives a pH equal to 5.3010. The pK_b of CH_3COO^- is.......
4. K_b for MeOH an indicator is 10^{-9}. The pH at which it shows is a colour change is.......
5. K_{sp} of $M(OH)_2$ is 5×10^{-16} at 25°C. The pH of its saturated solution at 25°C is ....
6. The equilibrium constant of a strong acid (HA) with weak base BOH is 10^{11}. The pH of 0.10 M solution of BA is.......
7. 10 mL of 0.25 M H_2SO_4 is completely neutralised by 0.125 M solution of NH_3. The pH of the solution at the equivalence point is......., if K_b for $NH_3 = 10^{-5}$.
8. 100 mL of 0.20 M weak acid HA is completely neutralised by 0.20 M NaOH. K_b for A^- is 10^{-3}, the pOH at the equivalence point is.......
9. One litre of 1 M solution of an acid HA ($K_a = 10^{-4}$ at 25°C) has pH = 2. It is diluted by water so that new pH becomes double. The solution was diluted to 5×10^a mL. The value of a is.......
10. K of pure water is 10^{-12} at 60°C. The pH of pure water at 60°C is.......
11. An aqueous solution of 0.24 M aniline ($K_b = 4.166 \times 10^{-10}$) is mixed with NaOH solution to maintain anilinium ion concentration to 1×10^{-8} M. The pOH of NaOH solution used was ....
12. A certain buffer solution equals concentration of X^- and HX. K_b for X^- is 10^{-10}. The pH of buffer is.......
13. Two weak acids HA and HB have same pH when their concentration ratio is 3 : 1. The ratio of the dissociation constants of HB and HA is.......
14. Conjugate base of a weak acid has $K_b = 10^{-9}$. The equilibrium constant for the reaction of acid with strong base is.......
15. K_{sp} of SrF_2 is 1×10^{-10}. The solubility of SrF_2 in 0.1 M NaF is 1×10^{-a} M. The value of a is.......
16. pH of 0.1 M NaCl solution is.......
17. The solubility of $RNH_{2(g)}$ in water at 1 atm and 27°C is 24.63 litre per litre water. If pK_b of $RNH_2 = 4$, the maximum pOH of the resulting solution will be ....
18. If K_{sp} of $HgSO_4$ is 6.4×10^{-5} mole^2 litre^2, then solubility of $HgSO_4$ in mole/m^3 is ....
19. The dissociation constant of a monoprotic acid, morphine a pain killer is 10^{-a}. Its 0.01 M solution with its 0.01M sodium salt shows a pH 6, the value of pK_a is.....
20. The molar concentration of SO_4^{2-} required to precipitate $RaSO_4$ for 2×10^{-4} mole of Ra^{2+} in 500 mL is 10^{-a} M. If K_{sp} of $RaSO_4$ is 4×10^{-11} then value of a is.....
21. The A^{2+} left in solution when 50.0 mL of 0.20 M $A(NO_3)_2$ is added to 50mL of 1.5M NaCl is 9.95×10^{-a} M. If K_{sp} of ACl_2 is 5.6×10^{-4} then the value of a is.....
22. The solubility of CoS in 0.10M H_2S and 0.15M H^+ solution is $a \times 10^{-6}$ M. The value of a is..... Given K for $H_2S \rightleftharpoons 2H^+ + S^{2-}$ is 1×10^{-21} and K_{sp} CoS $= 3.11 \times 10^{-26}$
23. If K_{a_1} and K_{a_2} for H_2S are 1×10^{-7} and 1×10^{-14} respectively. Then hydrolysis constant for $S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$ is.......
24. The pK_{eq} for $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is –6, then pK_{eq} for HA is.....
25. pH of 0.1M NaCl solution is.....
26. A buffer mixture containing equal mole of HB and its conjugate base B^- ($K_b = 10^{-10}$) has pH equal to.....
27. The pH at which an indicator pK_b = 5.00 changes its colour is.....
28. Ethylenediamine $NH_2C_2H_4NH_2$ a base (B) can add 1 or 2 protons. The successive pK_b values are 4 and 7 respectively. The $p^{[BH_2^{2+}]}$ in 0.001M solution of ethylenediamine is.....
29. The per cent error in $[H_3O^+]$ made by neglecting the ionisation of water in a 1.0×10^{-6} M NaOH solution.
30. The pH of solution resulting when 50 mL of 0.20M HCl is mixed with 50 mL of 0.20M CH_3COOH (p$K_a = 1.8 \times 10^{-5}$)
31. The pK_{eq} for the reaction of Na_2A and HCl at exactly half neutralisation of Na_2A is 6, then pK_{eq} for $A^{2-} + H^+ \rightleftharpoons HA^-$ will be.....
32. If $K_{eq.}$ for $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is 10^6, then pK_a for acid HA is.....
33. The solubility of $M(OH)_X$ is 10^{-4} M. If its pK_{sp} is 4×10^{-12}, then the value of X is.....
34. An acid indicator ($K_a = 10^{-5}$) will have 50% its basic form at pOH.
35. The solubility product of AgCl is 10^{-10} M^2 at 25°C. The minimum volume of water (in m^3) required to dissolve 1.435 g AgCl at 25°C.

36. The molar solubility of Ag_2CO_3 ($K_{sp} = 4 \times 10^{-13}$) in 0.1 M Na_2CO_3 is 10^{-a} M. The value of a is ....

37. The pH of an aqueous solution of 0.1 M NH_4Cl and 0.01M NH_4OH ($pK_b = 5$) is ....

38. The pOH of resulting 500 mL solution by mixing 25 mL of 0.1 M NaOH and 25 mL 0.08 M HCl, finally diluted with water is ....

39. If aM solution of weak acid HA has same pH as bM solution of weak acid HB. Also if $\frac{a}{b} = 4$, then the ratio of dissociation constant of two acids HB and HA will be ....

40. The minimum pH required to prevent the precipitation of ZnS in a solution having 0.1M $ZnCl_2$ and 0.1M H_2S if $Ka_1 \times Ka_2$ for H_2S is 10^{-20} and K_{sp} of ZnS $= 10^{-21}$.

41. The per cent error in $[H^+]$ made by neglecting ionisation of water in 1.0×10^{-6} M NaOH is ....

42. 0.01 mole of NaOH in 10 litre water are added. How much the pH water changes?

43. The approximate pH of a solution of benzoic acid ($K_a = 6.4 \times 10^{-5}$) having density 2.06 g/dm^3 is ....

44. A mixture of KOH and $Ca(OH)_2$ weighing 6.13 g is completely neutralized by an acid. If mass percent of KOH in mixture is 45.68 and normality of acid is 20 N, then find the approximate volume (in mL) of acid used in neutralisation.

45. 50 mL of 0.2 N NaCN is mixed with 50 mL of 0.2 M HCl. Calculate approximate concentration of $[H^+]$ in molarity $\times 10^{-6}$ if K_b for CN^- is 2×10^{-5}.

46. The dissociation constant of a substituted benzoic acid at 25°C is 1×10^{-4}. The pH of a 0.01 M solution of its sodium salt is : **(IIT 2009)**

47. The total number of diprotic acids among the following is....... **(IIT 2010)**
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

48. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper to blue is....... **(IIT 2010)**
KCN, K_2SO_4, $(NH_4)_2C_2O_4$, NaCl, $Zn(NO_3)_2$
$FeCl_3$, K_2CO_3, NH_4NO_3, LiCN

49. In one litre saturated solution of AgCl [K_{sp} of AgCl $= 1.6 \times 10^{-10}$], 0.1 mole of CuCl [K_{sp} of 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 2011)**

ANSWERS

1. Seven 2. Two 3. Nine 4. Five 5. Nine 6. Six 7. Five 8. Two 9. Six 10. Six 11. Two 12. Four
13. Three 14. Nine 15. Eight 16. Seven 17. Two 18. Eight 19. Six 20. Seven 21. Four 22. Seven 23. One 24. Six
25. Seven 26. Four 27. Nine 28. Seven 29. One 30. One 31. Six 32. Six 33. Two 34. Nine 35. One 36. Six
37. Eight 38. Three 39. Four 40. One 41. One 42. Four 43. Three 44. Seven 45. Seven 46. Eight 47. Six 48. Three
49. Seven

OBJECTIVE PROBLEMS (One Answer Correct)

1. The equilibrium constant for :
$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ is :
(Given pK_b for $CN^- = 4.69$ and pH for $CH_3COO^- = 9.25$)
(a) 3.7×10^4 (b) 2.8×10^{-5}
(c) 1.97 (d) 0.5

2. The ionisation of codein in 0.01 M solution shows a $pH = 10.1$. The ionisation constant of codein is :
(a) 1.6×10^{-4} (b) 1.6×10^{-6}
(c) 1.6×10^{-8} (d) 1.6×10^{-3}

3. The solubility of a sparingly soluble salt $A(OH)_2$ (molar mass 192.3 g mol^{-1}) is 19.23 g/litre at 300 K. The pH of its saturated solution assuming 80% ionisation at 300 K is :
(a) 1.0970 (b) 12.9030
(c) 13.2041 (d) 12.0000

4. K_b for CH_2ClCOO^- is 7.41×10^{-12}. The pH of 0.1 M $CH_2ClCOONa$ in water is :
(a) 7.93 (b) 6.66
(c) 1.94 (d) 12.06

5. Equimolar solution of $CaCl_2$ and K_2SO_4 are mixed in equal volumes. If K_{sp} of $CaSO_4$ is 9.1×10^{-6}, the maximum molar concentrations of $CaCl_2$ and K_2SO_4 which will lead no precipitation of $CaSO_4$ is :
(a) 0.006 (b) 0.004
(c) 0.002 (d) 0.008

6. If K_{sp} of ZnS is 1.0×10^{-21}, the minimum volume of water is required for the dissolution of 0.097 g ZnS is :
(a) 3.16×10^5 litre (b) 3.16×10^7 litre
(c) 3.16×10^9 litre (d) 3.16×10^3 litre

7. K_{sp} of $M(OH)_x$ is 27×10^{-12} and its solubility in water is 10^{-3} mole $litre^{-1}$. The value of x is :
(a) 1 (b) 2
(c) 3 (d) 4

8. The dissociation constants for acetic acid are 1.8×10^{-5} and 1.805×10^{-5} at 300 and 310 K respectively. The enthalpy of deprotonation for acetic acid is :
(a) 50 cal (b) 52.8 cal
(c) 51.6 cal (d) 48.48 cal

9. Solubility product of $A_2X_3 \cdot 4H_2O$ is given by :
(a) $[A^{3+}]^2[X^{2-}]^3[H_2O]^4$
(b) $[2A^{3+}]^2[3X^{2-}]^3[H_2O]^4$
(c) $[2A^{2+}]^2[3X^{3-}]^3[H_2O]^4$
(d) $[A^{3+}]^2[X^{2-}]^3$

10. pH of some solutions is given by : $[H^+] = \frac{pK_{a_1} + pK_{a_2}}{2}$.
For which type of compounds this formula is not valid?
(a) NaHS (b) NaH_2PO_4
(c) NaH_2PO_3 (d) NaH_2BO_3

11. Which one is not correct statement about buffer mixture ?
(a) NH_4OH + its conjugate acid
(b) CH_3COONa + its conjugate base
(c) 1 millimole of NaCN + 0.5 millimole of HCl in 1 litre
(d) 0.5 millimole of NaCN + 1 millimole of HCl in 1 litre

12. A buffer solution is prepared by dissolving 1 mole of CH_3COOH and 'a' mole of Zn acetate. The pH of solution is 4.7447 and pK_a for $CH_3COOH = 4.7447$. The number of mole of zinc acetate are :
(a) 1 (b) 2
(c) 0.5 (d) 0.25

13. The percentage error in H^+ concentration provided by 10^{-8} M HCl if ionisation of water is not neglected is :
(a) 3% (b) 2%
(c) 5% (d) 4%

14. The degree of dissociation of water is 1.8×10^{-9} at 300 K. The self ionisation constant for water is :
(a) 1.0×10^{-14} (b) 1.8×10^{-16}
(c) 3.23×10^{-18} (d) none of these

15. The change in pH of water when 0.01 mole of NaOH are added in 10 litre water is :
(a) 11 units (b) 3 units
(c) 4 units (d) 2 units

16. Which of the following has concentration dependent pH?
(a) CH_3COONa (b) CH_2NH_2COOH
(c) CH_3COONH_4 (d) NaHS

17. An acid-base indicator ($pK_a = 4.5271$) has the acid form red and basic form blue. If we need 75% red to be converted into 75% blue form in solution, the change in pH of solution should be :
(a) 4.05 (b) 5.0
(c) 0.95 (d) 0.80

18. 0.1 mole of CH_3NH_2 ($pK_b = 3.3010$) is mixed with 0.08 mol of HCl and volume is made to 1 litre. The pH of solution is :
(a) 7.32 (b) 11.4642
(c) 10.097 (d) 11.5020

19. 0.08 mole of CH_3NH_2 ($pK_b = 3.3010$) is mixed with 1.0 mole of HCl and volume is made to 1 litre. The pH of solution is :
(a) 1.699 (b) 2.699
(c) 10.097 (d) 7.32

20. 0.04 M solution of CH_3NH_2 ($pK_b = 3.3010$) is diluted to reduce its molar concentration to half. The change in pH during dilution is :

(a) +0.1615 (b) −0.1615
(c) + 0.2615 (d) −0.2615

21. The enthalpy change for first proton neutralisation of H_2S is $-33.7 \text{ kJ mol}^{-1}$. What is enthalpy change for first ionisation of H_2S?
(a) 23.6 (b) 33.7
(c) 20.8 (d) 10.4

22. Which will have pH closer to 1.0?
(a) 100 mL of 0.1 M HCl + 100 mL 0.1 M NaOH
(b) 55 mL of 0.1 M HCl + 45 mL of 0.1 M NaOH
(c) 10 mL of 0.1 M HCl + 90 mL 0.1 M NaOH
(d) 75 mL of 0.2 M HCl + 25 mL 0.2 M NaOH

23. 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

24. The conjugate acid of NH_2^- is:
(a) NH_3 (b) NH_2OH
(c) NH_4^+ (d) N_2H_4

25. The compound that is not Lewis acid is:
(a) BF_3 (b) $AlCl_3$
(c) $SnCl_4$ (d) CCl_4

26. 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) unionised in small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

27. Which of the following is the strongest acid?
(a) $ClO_3(OH)$ (b) $ClO_2(OH)$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

28. pK_b of NH_4OH is 5. The pH of a mixture containing 10mL of 0.3M NH_4OH and 200 mL of 0.1M $(NH_4)_3PO_4$ is:
(a) 5 (b) 5.3010
(c) 6.3010 (d) 7.6987

29. K_w for water is $9.5 \times 10^{-14} m^2$ at 60°C. An aqueous solution of a salt at 60°C has pH = 7, it is:
(a) acidic (b) basic
(c) neutral (d) none of these

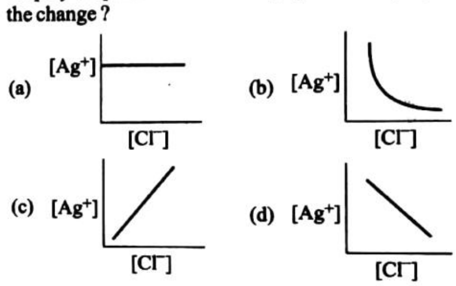
30. 100 mL of 0.005 M H_2SO_4 is diluted to one litre. The pH of resulting solution is:
(a) 3 (b) 4
(c) 5 (d) 2

31. How much water should be added to 300 mL of 0.2 M solution of acetic acid ($K_a = 1.8 \times 10^{-5}$) to increase its degree of dissociation two times?
(a) 1.2 litre (b) 1.5 litre
(c) 0.9 litre (d) 0.7 litre

32. If pK_b for $C_6H_5O^-$ is 4, what is the pH of 0.1M $C_6H_5O^-$ in solution at 25°C?
(a) 13.0 (b) 12.5
(c) 11.5 (d) 10.5

33. 2, 4-dinitrophenol (pK_a = 4) acts as buffer and if pH of this buffer is adjusted to 5, the ratio of concentration of dissociated and undissociated molecules of 2, 4-di nitrophenol is:
(a) 1 (b) 10
(c) 0.1 (d) 0.01

34. In a saturated solution of AgCl, addition of NaCl is made drop by drop in excess. Which graph correctly represents the change?



35. Solubility of Ag_2CrO_4 in 0.2 M K_2CrO_4 is 'a' and solubility of Ag_2CrO_4 in 0.4 M $AgNO_3$ is 'b', then:
(a) $a = b$
(b) $a > b$
(c) $a < b$
(d) cannot be predicted in absence of K_{sp} of Ag_2CrO_4

36. 0.1 M solution of H_3A being a weak tribasic acid having K_{a_1}, K_{a_2} and K_{a_3} as $10^{-5}, 10^{-9}$ and 10^{-13} respectively. If pX represents $-\log \frac{[A^{3-}]}{[HA^{2-}]}$, then the value of p$X$ is:
(a) 7 (b) 8
(c) 10 (d) 9

37. pH of mixture having 0.1 M NH_4OH and 0.1 M NH_4Cl is equal to pK_w − pK_b. If 0.1 M NH_4OH and 0.1 M $(NH_4)_2SO_4$ are taken, the pH will be:
(a) pK_w − pK_b (b) pK_w + pK_b
(c) pK_w − pK_b + log 2 (d) pK_w − pK_b − log 2

38. In the equilibrium: $BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$ if $[Ba^{2+}]$ is increase two times, then $[F^-]$ in solution will:
(a) increase two times (b) increase four times
(c) decrease two times (d) decrease to $1/\sqrt{2}$ times

39. The pH of 100 mL solution containing 0.3 M NH_4^+, 0.2M NH_4OH (K_b = 4.74) and 0.01 M HCl in it is :
(a) 9.05 (b) 8.66
(c) 7.46 (d) 8.05

40. The pH of a 100 mL solution containing 0.3 mole of NH_4^+, 0.2 M NH_4OH and 0.01 M NaOH in it is :
(a) 10.12 (b) 9.12
(c) 8.12 (d) 8.5

41. A weak acid has pH = 4, then :
(a) $C = 10^{-3}, \alpha = 10\%$ (b) $C = 10^{-3}, \alpha = 10^{-6}$
(c) $[A^-] = 10^{-5}$ (d) $K_a = 10^{-2}, \alpha = 10$

42. An acidic buffer solution can be prepared by mixing the solution of :
(a) ammonium acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium sulphate
(d) sodium chloride and sodium hydroxide

43. 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

44. Of the given anions, the strongest Bronsted base is :
(a) ClO^- (b) ClO_2^-
(c) ClO_3^- (d) ClO_4^-

45. 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}

46. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes 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) $10^{-3}\,M\,Ca^{2+} + 10^{-5}\,M\,F^-$

47. A certain buffer solution contains equal concentration X^- and HX. Then K_b for X^- is 10^{-10}. The pH of the buffer is :
(a) 4 (b) 7
(c) 10 (d) 14

48. 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}

49. 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)

50. The following equilibrium is 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 ($CH_3COOH_2^+, CH_3COOH$)

51. The compound insoluble in acetic acid is :
(a) calcium oxide (b) calcium carbonate
(c) calcium oxalate (d) calcium hydroxide

52. The compound whose 0.1 M solution is basic is :
(a) ammonium acetate (b) ammonium chloride
(c) ammonium sulphate (d) sodium acetate

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

54. The degree of dissociation of water at 25°C is 1.9×10^{-7}% and density is 1.0 g cm^{-3}. The equilibrium constant for water is :
(a) 1.0×10^{-14} (b) 2.0×10^{-14}
(c) 2.0×10^{-16} (d) 1.0×10^{-8}

55. Which one is more acidic in aqueous solution ?
(a) $NiCl_2$ (b) $FeCl_3$
(c) $AlCl_3$ (d) $BeCl_2$

56. 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

57. 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}

58. 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) $108y^5$

59. Among the following the one having lowest K_{sp} is :

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

60. Which of the following is correct for 1.0 M solution of strong acid HA and 1.0 M solution of weak acid HB ?

(a) HA : pH = 0; HB : pH < 1
(b) $HA : [H^+] = [A^-]$; $HB ; [H^+] = [A^-]$
(c) $HA ; [HA] = 0$; $HB : [HB] = (1-\alpha)$
(d) All of these

61. Which order is not correct for basic nature ?

(a) $NH_3 > PH_3$ (b) $H_2O > H_2S$
(c) $NH_3 > NCl_3$ (d) $NF_3 > NH_3$

62. Which of the following acid-base neutralisation does not form water with salt ?

(a) $Al_2O_3(s) + NaOH(aq.)$ (b) $Al_2O_3 + HCl(aq.)$
(c) $SiO_2 + NaOH(aq.)$ (d) $ZnO + NaOH(aq.)$

63. How many mole of HCl must be added to 1 litre aqueous solution of HCl of pH = 3, in order to decrease its pH to 2?

(a) 0.009 (b) 0.001
(c) 1 (d) 0.1

64. Which one is correct decreasing order of solubility of AgCl ?

(i) in water (ii) in 0.1 M NaCl
(iii) in 0.1 M $BaCl_2$ (iv) in 0.1 M NH_3

(a) (iv > iii > ii > i) (b) (iv > i > ii > iii)
(c) (iv > ii > iii > i) (d) (i > ii > iii > iv)

65. 0.1 M aqueous solution of BOH (a weak base) has pH equal to 12 at 27°C. Assuming K_w at 27°C 1.0×10^{-14}, calculate the osmotic pressure of 0.1 M BOH(aq.)

(a) 2.71 atm (b) 2.46 atm
(c) 0.246 atm (d) 24.6 atm

66. 300 mL of saturated, clear solution of $CaC_2O_4(aq.)$ is completely oxidised by 6 mL of 0.001 M $KMnO_4$ in acid medium. The K_{sp} of CaC_2O_4 is :

(a) 25×10^{-8} (b) 25×10^{-9}
(c) 25×10^{-10} (d) 25×10^{-11}

67. Solubility of AgCl (in mole/litre) in a mixture of 1 litre solution containing 0.05M NaCl and 0.05 M $BaCl_2$ is : (Given K_{sp} of AgCl = 1.0×10^{-10})

(a) 6.6×10^{-8} (b) 6.6×10^{-10}
(c) 1.0×10^{-9} (d) 1.0×10^{-8}

68. Select the correct choice when 100 mL of 0.5 M hydrazoic acid (N_3H having $K_a = 3.6 \times 10^{-4}$) and 400 mL of 0.1 M cyanic acid (HOCN having $K_a = 8 \times 10^{-4}$) are mixed :

(a) pH = 2 (b) $[N_3^-] = 3.6 \times 10^{-3}$
(c) $[OCN^-] = 6.4 \times 10^{-3}$ (d) all of these

69. Autoprotonation constant for liquid NH_3 is 3.46×10^{-27} at −50°C. The number of anions present in 1 mL of pure NH_3 at −50°C is :

(a) 2.08×10^9 (b) 1×10^{-15}
(c) 6.023×10^{-5} (d) 1×10^{15}

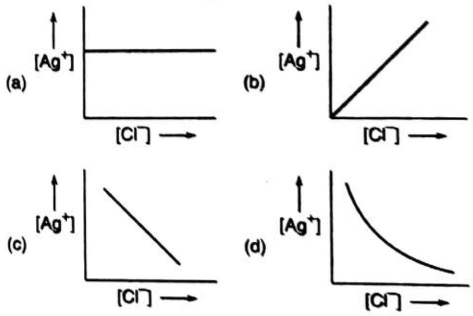
70. Solubility product of AgCl is 1.0×10^{-10}. What minimum volume of water in litre is required to dissolve 4.305 mg of AgCl?

(a) 1 (b) 2
(c) 3 (d) 4

71. How many mixed buffers can be obtained using KOH and H_3PO_4 ?

(a) 1 (b) 2
(c) 3 (d) 4

72. Which graph correctly represents addition of NaCl to a saturated solution of AgCl?



73. Which reagent can be used to separate one of ions as precipitate from a solution containing Cu^{2+} and Pb^{2+} ions ?

(a) $H_2S(g)$ (b) NH_4NO_3
(c) HNO_3 (d) H_2SO_4

74. Which can be used to separate F^- ion from a solution of F^- and Cl^- in solution ?

(a) $AgNO_3$ (b) $Pb(NO_3)_3$
(c) HNO_3 (d) H_2SO_4

75. Except one in rest all cases, K_2CO_3 solution on addition gives a precipitate :

(a) $BaCl_2(aq.)$ (b) $CaBr_2(aq.)$
(c) $(NH_4)_2SO_4$ (d) $Pb(NO_3)_2$

76. Arrange the following in increasing order of pH :

1. 0.1 M CH_3COONa + 0.1 M CH_3COOH
2. 0.1 M CH_3COOH + 0.1 M HCl
3. 0.1 M CH_3COOH
4. 0.1 M HCl

(a) 2 < 4 < 3 < 1 (b) 1 < 2 < 3 < 4
(c) 2 < 3 < 4 < 1 (d) 4 < 3 < 2 < 1

77. A solution has pH = 4. It is 1000 times less acidic than another solution of same species of pH :

(a) 1 (b) 2
(c) 3 (d) 4

78. pOH of 0.003 M HCl is :
(a) 11 + log 3 (b) 11 − log 3
(c) 7 + log 3 (d) 7 − log 3

79. 10 mL of 10^{-4} N H_2SO_4 is diluted with water to have 1 dm^3 solution : The pH of this solution is :
(a) 6 (b) slightly more than 6
(c) slightly less than 6 (d) 7

80. The pH of a solution obtained by mixing 10 mL of 0.1 M HCl and 10 mL of 0.01 M $Sr(OH)_2$.
(a) 1.40 (b) 1.50
(c) 11.70 (d) 7.00

81. If heat of ionisation $\Delta_i H°$ for HCN and $\Delta_i H°$ for CH_3COOH are 45.2 kJ mol^{-1} and 2.1 kJ mol^{-1}, then which one is not correct ?
(a) $pK_{a_{HCN}} > pK_{a_{CH_3COOH}}$
(b) K_a of HCN < K_a of CH_3COOH
(c) acetic acid is stronger than HCN
(d) $pK_{a_{HCN}} < pK_{a_{CH_3COOH}}$

82. The ratio of degree of dissociation of HCN ($K_a = 10^{-9}$) in its 0.1 M and 0.001 M solution :
(a) 0.1 (b) 0.2
(c) 0.3 (d) 0.4

83. Which of the following ions can exist in solution ?
(a) H_3O^+ (b) $H_3O_2^-$
(c) $H_5O_2^+$ (d) all of these

84. What will be degree of hydrolysis and pH respectively of an aqueous solution of ammonium formate : $pK_a = 4$, $pK_b = 5$; $pK_w = 14$:
(a) 3.16×10^{-3}, 7 (b) 4.16×10^{-3}, 6.5
(c) 3.16×10^{-3}, 6.5 (d) 4.16×10^{-3}, 7.0

85. The solubility product of AgCl is 10^{-10}. Applying Debye Huckel limiting law, the correct solubility order of AgCl is different solutions of 0.1 M concentration is :
(a) NaCl < H_2O < $NaNO_3$ < $Ca(NO_3)_2$
(b) H_2O < NaCl < $NaNO_3$ < $Ca(NO_3)_2$
(c) $NaNO_3$ < $Ca(NO_3)_2$ < H_2O < NaCl
(d) $Ca(NO_3)_2$ < $NaNO_3$ < H_2O < NaCl

86. For, $Ag(CN^-)_2 \rightleftharpoons Ag^+ + 2CN^-$
$K_C = 4 \times 10^{-19}$ at 25°C
Calculate Ag^+ concentration in a solution which is originally 0.1 M in KCN and 0.03 M in $AgNO_3$.
(a) 7.5×10^{-18} M (b) 7.5×10^{-15} M
(c) 6.2×10^{-15} M (d) 3.4×10^{-15} M

87. The solubility product of PbI_2 is 7.47×10^{-9} and 1.39×10^{-8} at 15°C and 25°C respectively. The molar heat of solution of PbI_2 is :
(a) 9.969 k cal (b) 10.66 k cal
(c) 8.88 k cal (d) 11.11 k cal

88. A solution of a weak monobasic acid has $\wedge_M$ for 0.1 N solution and $\wedge_\infty$ equal to 60 S $cm^2 mol^{-1}$ and 400 S $cm^2 mol^{-1}$ respectively. The pH of this solution and K_a of acid is :
(a) 1.82, 2.65×10^{-3} (b) 2.82, 2.65×10^{-3}
(c) 1.82, 2.25×10^{-3} (d) 2.82, 2.25×10^{-3}

89. The dissociation constant of HA and A^- are equal. The pH of 0.001 HA solution is :
(a) 3 (b) 4
(c) 5 (d) 6

90. pK_a of acetic acid is 4.74. What mass of KOH is required to be added in 500 mL of 1 M acid in order to prepare a buffer solution of maximum capacity.
(a) 28 g (b) 14 g
(c) 7 g (d) 10 g

91. K_a of HCOOH is 10^{-5} and solubility of HCOOAg is 10^{-2} M. The solubility of HCOOAg in a buffer solution of pH = 3 is ....
(a) 0.01 M (b) 0.1 M
(c) 0.2 M (d) 0.02 M

92. From the following informations, select the strongest base :

Acid	$H_2PO_4^-$	HPO_4^{2-}	HCO_3^-	HSO_3^-
K_a	6.0×10^{-8}	4.8×10^{-13}	4.7×10^{-11}	6.3×10^{-8}

(a) PO_4^{3-} (b) HPO_4^{2-}
(c) CO_3^{2-} (d) SO_3^{2-}

93. 0.125 mole of CaA_2 are present in 0.5 litre solution. If K_a of HA is 8.0×10^{-4} and salt CaA_2 is completely ionised, the pH of solution is :
(a) 5.60 (b) 5.75
(c) 8.40 (d) 8.25

94. At what $\frac{[Br^-]}{\sqrt{[CO_3^{2-}]}}$, the following cell shows equilibrium :
$Ag(s) | Ag_2CO_3(s), Na_2CO_3(aq.) || AgBr(aq.) | Ag(s)$
K_{SP} of $Ag_2CO_3 = 8 \times 10^{-12}$ and
K_{SP} of $AgBr = 4 \times 10^{-13}$
(a) 2×10^{-7} (b) $\sqrt{2} \times 10^{-7}$
(c) $\sqrt{3} \times 10^{-7}$ (d) 2

95. Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol L^{-1}. Solubility product of $Ag_2C_2O_4$ is :
(a) 2.42×10^{-8} (b) 2.66×10^{-12}
(c) 4.5×10^{-11} (d) 5.3×10^{-12}

SOLUTIONS (One Answer Correct)

1. (a) $K_{eq.} = \frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$;

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

$K_{HCN} = \frac{[H^+][CN^-]}{[HCN]}$

$pK_{bCN^-} = 4.69 \therefore pK_{HCN} = 9.31$;

$pK_{CH_3COOH} = 4.75$

$\therefore K_{eq.} = \frac{K_{CH_3COOH}}{K_{HCN}} = \frac{1.77\times10^{-5}}{4.9\times10^{-10}} = 3.7\times10^4$

2. (b) pH of Codein = 10.1 $\therefore$ it is a base.

Now Codein + $H_2O \rightleftharpoons$ Codein$^+$ + OH^-

$K_b = \frac{[Codein^+][OH^-]}{[Codein]}$;

Also, $[OH^-] = c\alpha = 0.01\times\alpha$

$-\log 3.9 = 0.01\alpha$

$\therefore \alpha = \frac{1.259\times10^{-4}}{0.01} = 0.0125$

$K_a = \frac{c\alpha^2}{(1-\alpha)}$

$K_a = \frac{0.01\times(0.0125)^2}{(1-0.0125)} = 1.6\times10^{-6}$

3. (c) $S = \frac{19.23}{192.3}$ mol/litre = 0.1 M

$A(OH)_2 \rightleftharpoons A + \underset{2S}{2OH^-}$

$\therefore [OH^-] = \frac{0.1\times2\times80}{100} = 0.16$

$\therefore$ pOH = 0.7958

$\therefore$ pH = 13.2041

4. (a) $CH_2ClCOO^- + H_2O \rightleftharpoons CH_2ClCOOH + OH^-$

$[OH^-] = ch = c\sqrt{\frac{K_H}{c}} = \sqrt{K_H\cdot c} = \sqrt{\frac{K_w\times c}{K_a}}$

$= \sqrt{K_b\times c} = \sqrt{7.41\times10^{-12}\times0.1}$

$= 8.606\times10^{-7}$

$\therefore$ pOH = 6.065

pH = 7.93

5. (a) Let molar concentration of salts be a M

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

$\left[\frac{a\times V}{2V}\right]\left[\frac{a\times V}{2V}\right] = 9.1\times10^{-6}$

$\therefore a^2 = 4\times9.1\times10^{-6} \quad \therefore a = 6.033\times10^{-3}$

6. (b) Solubility of ZnS = $S = \sqrt{K_{sp}} = \sqrt{1\times10^{-21}}$

$= 3.16\times10^{-11}$ mol/litre

$= 3.16\times10^{-11}\times97$ g/L

$= 3.065\times10^{-9}$ g/L

$\therefore$ Volume of water in litre required $= \frac{0.097}{3.065\times10^{-9}}$

$= 3.16\times10^7$ litre

7. (c) K_{sp} of $M(OH)_X = X^X\cdot(S)^{X+1} = 27\times10^{-12}$

$\therefore X^X\cdot(10^{-3})^{X+1} = 27\times10^{-12}$

By putting X = 1, 2, 3........

$\therefore X = 3$

8. (c) $2.303\log\frac{K_2}{K_1} = \frac{\Delta H}{R}\frac{[T_2-T_1]}{T_1T_2}$

$2.303\log\frac{1.805\times10^{-5}}{1.8\times10^{-5}} = \frac{\Delta H}{R}\times\frac{10}{300\times310}$

$\therefore \Delta H = 51.6$ cal

9. (d) Hydrated water molecules do not interfere in K_{sp}.

10. (d) The formula is valid for acidic salts as well as for zwitter ionic molecules. NaH_2BO_3 is neither an acid salt nor it exists.

11. (d) NaCN + HCl → NaCl + HCN

NaCN	HCl	NaCl	HCN
1	0.5	0	0
0.5	0	0.5	0.5

i.e., 0.5 NaCN+0.5 HCN, buffer

NaCN + HCl ⟶ NaCl + HCN

NaCN	HCl	NaCl	HCN	
0.5	1	0	0	Not a buffer
0	0.5	0.5	0.5	

12. (c) $pH = pK_a + \log\frac{2a}{1}$

$(CH_3COO)_2Zn$ gives 2 mol CH_3COO^-

$4.7447 = 4.7447 + \log\frac{2a}{1} \quad \therefore a = 1/2$

13. (c) $10^{-8}M$ HCl $\therefore [H^+] = 10^{-8} = 10\times10^{-9}$ if dissociation of water is neglected

if not neglected then : $H_2O \rightleftharpoons \underset{a+10^{-8}}{H^+} + \underset{a}{OH^-}$

$\therefore a\times(a+10^{-8}) = 10^{-14}$

$a = 0.95\times10^{-7}$

$\therefore$ % error $= \frac{(10\times10^{-9} - 9.5\times10^{-9})}{10\times10^{-9}}\times100 = 5\%$

14. (c) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$[H_3^+O] = C\alpha = 10^{-7} = [OH^-]$

$\therefore C = \frac{10^{-7}}{1.8\times10^{-9}} = 55.6$

$K_{s.i.} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} = \frac{10^{-14}}{(55.6)^2} = 3.23\times10^{-18}$

15. (c) $[OH^-] = \frac{0.01}{10} = 10^{-3}$ ∴ pOH = 3 or pH = 11

Thus, pH changes from 7 to 11 by 4 units.

16. (a) pH of acidic salts, salts of weak-acid + weak-base and zwitter ionic species is independent of concentration.

17. (c) For 75% red from $\underset{\substack{(Red)\\75}}{HI_n} \rightleftharpoons \underset{25}{H^+} + \underset{\substack{(Blue)\\25}}{I_n^-}$

$$K_a = \frac{[H^+][I_n^-]}{[HI_n]}$$

$$pH = pK_a + \log\frac{25}{75} = 4.5271 - 0.4771 = 4.05$$

For 75% blue form $pH = 4.5271 + \log\frac{75}{25}$

$$= 4.5271 + 0.4771 = 5.0$$

∴ $\Delta pH = 5.0 - 4.05 = 0.95$

18. (c) $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+ + Cl^-$

0.1	0.08	0	0
0.02	0	0.08	0.08

$[CH_3NH_2] = \frac{0.02}{1}$, $[CH_3NH_3^+] = 0.08$

This acts as basic buffer.

$$pOH = pK_b + \log\frac{0.08}{0.02} = 3.3010 + 0.6020$$

$$pOH = 3.903$$

∴ $pH = 10.097$

19. (a) $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+ + Cl^-$

0.08	1	0	0
0	0.02	0.08	0.08

∴ $[H^+] = 0.02 = 2\times10^{-2}$; ∴ pH = 1.699

20. (a) $I: [CH_3NH_2] = 0.04$

$$K_b = \frac{c\alpha^2}{(1-\alpha)} = 5\times10^{-4} = \frac{0.04\times\alpha^2}{(1-\alpha)} \quad (1-\alpha \neq 1)$$

∴ $\alpha = 0.1056$

$[OH^-] = c\alpha = 0.04\times0.1056 = 4.224\times10^{-3}$

$pOH = 2.3743$

$II: [CH_3NH_2] = 0.02$

$$K_b = \frac{c\alpha^2}{(1-\alpha)} = 5\times10^{-4} = \frac{0.02\times\alpha^2}{(1-\alpha)} (1-\alpha \neq 1)$$

∴ $\alpha = 0.1456$

∴ $[OH^-] = c\alpha = 0.02\times0.1456 = 2.912\times10^{-3}$

$pOH = 2.5358$

∴ $-\Delta pOH = \Delta pH = +0.1615$, *i.e.*, pOH increases on dilution or pH decreases.

21. (a) $H_2S + OH^- \longrightarrow H_2O + HS^-$; $\Delta H = -33.7\,kJ$

$H^+ + OH^- \longrightarrow H_2O$; $\Delta H = -57.3\,kJ$

∴ $H_2S \rightleftharpoons H^+ + HS^-$; $\Delta H = +57.3 - 33.7 = +23.6\,kJ$

22. (d)

HCl	+ NaOH	⟶ NaCl	+ H_2O
75×0.2	25×0.2		
= 15	5	0	0
10	0	5	5

$[H^+] = \frac{10}{100} = 0.1$

∴ pH = 1

23. (b) HCl is an acid having lowest pH, $NaCN_{aq.}$ is alkaline and NH_4Cl is acidic due to hydrolysis.

24. (a) $\underset{base}{NH_2^-} + H^+ \longrightarrow \underset{conjugate\ acid}{NH_3}$

25. (d) CCl_4 has complete octet and can not expand its octet.

26. (d) Aspirin an acid will be completely ionised in alkaline medium.

27. (a) $HClO_4$ is strongest acid among these because of higher oxidation number of Cl (*i.e.*, +7).

28. (d) mM of $NH_4OH = 10\times0.3 = 3$

mM of $[NH_4^+]$ from $(NH_4)_3PO_4 = 200\times0.1\times3 = 60$

∴ $pOH = 5 + \log\frac{60}{3} = 5 + \log 20 = 6.3010$

∴ $pH = 14 - 6.3010 = 7.6987$

29. (b) $K_w = [H^+]^2 = 9.65\times10^{-14}$ for pure water

∴ $[H^+] = 3.1\times10^{-7}$

If $[H^+] > 3.1\times10^{-7}$ acidic

$< 3.1\times10^{-7}$ basic

Thus, if $[H^+] = 10^{-7}$ *i.e.*, $< 3.1\times10^{-7}$, solution is basic.

30. (a) Meq. of H_2SO_4 present initially = Meq. of H_2SO_4 after dilution.

$0.005\times2\times100 = 1000\times N$

∴ $[H^+] = 1\times10^{-3}$

∴ pH = 3

31. (c) Initially, $\alpha_1 = \sqrt{\frac{K_a}{c_1}} = \sqrt{\frac{1.8\times10^{-5}}{0.2}} = 9.49\times10^{-3}$

If α is doubled, then new $\alpha_2 = 1.898\times10^{-2}$

Since α remains negligible in both cases, therefore

$$c_1\alpha_1^2 = c_2\alpha_2^2$$

∴ $c_2 = 0.2\times\left(\frac{1}{2}\right)^2 = 0.05$

On dilution $c_1V_1 = c_2V_2$ (or $M_1V_1 = M_2V_2$)

$300\times0.2 = 0.05\times V_2$

∴ $V_2 = 1200\,mL$

∴ Volume of water added = 900 mL

32. (c) $C_6H_5O^- + H_2O \longrightarrow C_6H_5OH + OH^-$

$$[OH^-] = c\cdot h = c\cdot\sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w}{K_a}\cdot c}$$

$$= \sqrt{K_b\cdot c} = \sqrt{10^{-4}\times0.1} = 3.16\times10^{-3}$$

∴ $pOH = -2.5$

∴ $pH = 11.5$

33. (b) $pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$

$$5 = 4 + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\log \frac{[\text{conjugate base}]}{[\text{acid}]} = 1$$

$$\therefore \quad \frac{[\text{conjugate base}]}{[\text{acid}]} = \frac{[\text{dissociated ions}]}{[\text{undissociated acid}]} = 10$$

34. (b) $[Ag^+][Cl^-] = K_{sp}$ or $[Ag^+] = \frac{K_{sp}}{[Cl^-]}$

if $[Cl^-]$ increases, then to have K_{sp} constant and thus $[Ag^+]$ decreases. Also after sufficient addition of $[Cl^-]$, $[Ag^+]$ will become almost constant.

35. (d) $K_{sp} Ag_2CrO_4 = [Ag^+]^2[CrO_4^{2-}]$

$= (2s)^2 \times s = 4s^3$

Now in 0.2 M K_2CrO_4	In 0.4 M $AgNO_3$
$K_{sp} = [Ag^+]^2 \times 0.2$	$K_{sp} = [0.4 + S]^2 \times S$
$\therefore [Ag^+] = \sqrt{\frac{K_{sp}}{0.2}}$	$\therefore s = \frac{K_{sp}}{0.16}$
or $a = \sqrt{\frac{K_{sp}}{0.2}}$	$b = \frac{K_{sp}}{0.16}$
$= 2.23 \times \sqrt{K_{sp}}$	$= 6.25 \times K_{sp}$

36. (c) $[H^+]$ are obtained in dissociation of H_3A in all the three steps, but the $[H^+]$ obtained in II & III steps are too low. Thus $[H^+]$ can be obtained from 1 step

$$[H^+] = \sqrt{Ka_1 \times c} \qquad (1-\alpha \simeq 1)$$

$$= \sqrt{10^{-5} \times 0.1} = 10^{-3}$$

Now, $K_3 = \frac{[H^+][A^{3-}]}{[HA^{2-}]}$

$(HA^{2-} \rightleftharpoons H^+ + A^{3-}$ II Step)

$$10^{-13} = \frac{10^{-3} \times [A^{3-}]}{[HA^{2-}]}$$

$$\therefore \quad \frac{[A^{3-}]}{[HA^{2-}]} = 10^{-10} \quad \therefore \quad pX = 10$$

37. (d) **In I Case :**

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_4OH]} = pK_b$$

$\therefore \quad pH = pK_w - pK_b \quad [\because [NH_4^+] = [NH_4OH] = 0.1]$

In II Case :

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_4OH]} = pK_b + \log 2$$

$\therefore \quad pH = pK_w - pK_b - \log 2 \quad [\because [NH_4^+] = 0.1 \times 2]$

38. (d) $BaF_{2(s)} \rightleftharpoons Ba^{2+} + 2F^-$

$K_{sp} = [Ba^{2+}][F^-]^2$

$$\therefore \quad [F^-] = \sqrt{\frac{K_{sp}}{Ba^{2+}}}$$

Again $K_{sp} = 2 \times [Ba^{2+}][F^-]^2$

[Ba^{2+} is increased two times]

$$[F^-]^2 = \frac{K_{sp}}{2 \times [Ba^{2+}]}$$

or $[F^-] = \sqrt{\frac{K_{sp}}{2[Ba^{2+}]}}$

39. (a) $NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$

0.2   0.01   0s

0.19   0   0.01

$\therefore \quad [NH_4^+] = 0.30 + 0.01 = 0.31$

$[NH_4OH] = 0.19$

$\therefore \quad pOH = 4.74 + \log \frac{0.31}{0.19}$

$= 4.95$

$\therefore \quad pH = 14 - 4.95 = 9.05$

40. (b) $NH_4^+ + NaOH \longrightarrow NH_4OH + Na^+$

0.3   0.01   0   0

0.29   0   0.01

$\therefore \quad [NH_4^+] = 0.29$

$[NH_4OH] = 0.2 + 0.01 = 0.21$

$\therefore \quad pOH = 4.74 + \log \frac{0.29}{0.21}$

$= 4.880$

$\therefore \quad pH = 14 - 4.880 = 9.12$

41. (a) $HA \rightleftharpoons H^+ + A^-$

$[H^+] = [A^-] = \alpha \cdot c = \frac{10}{100} \times 10^{-3} = 10^{-4}$

$\therefore \quad pH = 4$

42. (a) Weak acid (CH_3COOH) and its conjugate base CH_3COO^- and this buffer is an acidic buffer.

43. (d) HCl is an acid.

44. (a) Stronger is the acid, weaker is its conjugate base.

45. (b) $K_w = [H_3O^-][OH^-]$. Also $[H_3O^+] = [OH^-]$

$10^{-6} \times 10^{-6} = 10^{-12}$

46. (b) Q for $CaF_2 = [Ca^{2+}][F^-]^2$

$$= \left[\frac{10^{-2} \times V}{2V}\right]\left[\frac{10^{-3} \times V}{2V}\right]^2 = \frac{1}{8} \times 10^{-8} = 1.2 \times 10^{-9}$$

$Q > K_{sp}$

47. (a) $pH = -\log K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} = 10^{-4} + \log \frac{1}{1} = 4$

$[\because pK_a + pK_a = 14]$

48. (c) $HX \rightleftharpoons H^+ + X^-$

$$K_a = 10^{-4} = \frac{[H^+][X^-]}{[HX]} \qquad ...(i)$$

$HX + NaOH \rightleftharpoons NaX + H_2O$

$$K_{eq} = \frac{[Na^+][X^-][H_2O]}{[HX][Na^+][OH^-]} = \frac{[X^-][H_2O]}{[HX][OH^-]} \quad ...(ii)$$

By Eqns. (i) and (ii)

$$\frac{K_{eq}}{K_a} = \frac{1}{K_w} \quad \therefore \quad K_{eq} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

49. (d) Phenolphthalein is good indicator for strong alkali titrations.

50. (d) $\underset{\text{Acid}}{HCl} \longrightarrow \underset{\text{C-base}}{Cl^-}$

51. (c) Calcium oxalate is weaker base.

52. (d) $CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

53. (a) Q for AgCl $= [Ag^+][Cl^-] = \left[\frac{10^{-4} \times V}{2V}\right]\left[\frac{10^{-4} \times V}{2V}\right]$

$= 2.5 \times 10^{-9}$

$\because$ $Q > K_{sp}$, precipitation will occur.

54. (c) $K_{eq.} = \frac{[H^+][OH^-]}{[H_2O]}$

for $\underset{1-\alpha}{H_2O} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{OH^-}$

$\therefore$ $[H^+] = c\alpha$ and $c_{H_2O} = \frac{1000}{18} = 55.6$

$$K_{eq.} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} \quad (1-\alpha = 1)$$

$$\therefore \quad K_{eq.} = \frac{(55.6 \times 1.9 \times 10^{-9})^2}{55.6} = 2 \times 10^{-16}$$

55. (b) Both $FeCl_3$ and $AlCl_3$ will furnish $3OH^-$ ions and $Fe(OH)_3$ is relatively stronger base than others.

56. (a) HOCl > HOBr > HOI due to more electronegative nature of halogen.

57. (c) $HF \rightleftharpoons H^+ + F^-$

$pK_a + pK_b = 14$

$pK_a + 10.83 = 14$

$\therefore$ $pK_a = 3.17$

$K_a = 6.76 \times 10^{-4}$

58. (d) K_{sp} of $A_2X_3 = 2^2 \cdot (S)^2 \times 3^3 \times S^3$

$= 108\,(S)^5 = 108y^5$

59. (d) The solubility of alkaline earth metal hydroxides increases down the gp. more is solubility, more is K_{sp}.

60. (d) $HA \longrightarrow H^+ + A^-$

$HB \rightleftharpoons H^+ + B^-$

61. (d) F is more electronegative than H and thus it reduces electron pair donation nature in NF_3.

62. (a) $Al_2O_3 + 2NaOH(aq.) + 3H_2O(l) \longrightarrow 2NaAl(OH)_4$

63. (a) $[H^+] = [HCl]$ or mole of HCl of pH = 3 in 1 litre is 10^{-3} = 0.001

$[H^+] = [HCl]$ or mole of HCl of pH = 2 in 1 litre is 10^{-2} = 0.01

$\therefore$ Mole of HCl to be added in HCl of pH = 3 are 0.01 − 0.001 = 0.009

64. (b) AgCl forms complex with NH_3 and thus more soluble. Also solubility of a salt decreases in presence of common ion.

65. (a)

$$\underset{\substack{C \\ C(1-\alpha)}}{BOH} \rightleftharpoons \underset{\substack{0 \\ C\alpha}}{B^+} + \underset{\substack{0 \\ C\alpha}}{OH^-}$$

$[OH^-] = C\alpha = 10^{-2}$

[For BOH, pH = 12 $\therefore$ $[OH^-] = 10^{-2}$]

$$\therefore \quad \alpha = \frac{10^{-2}}{0.1} = 10^{-1} = 0.1$$

$\therefore$ Total number of particles present are $(1-\alpha+\alpha+\alpha) = 1+\alpha = 1.1$

Now $\pi = CST(1+\alpha)$

$= 0.1 \times 0.0821 \times 300 \times 1.1$

$= 2.71$ atm

66. (c) $Mn^{7+} + 5e \longrightarrow Mn^{2+}$

$(C^{3+})_2 \longrightarrow 2C^{4+} + 2e$

meq. of $C_2O_4^{2-}$ = meq. of $KMnO_4$

$M \times 2 \times 300 = 0.001 \times 5 \times 6$

$\therefore$ $M_{C_2O_4^{2-}} = 5 \times 10^{-5}$

For $CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$

$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 5 \times 10^{-5} \times 5 \times 10^{-5}$

$= 25 \times 10^{-10}$

67. (b) $[Cl^-]$ in mixture $= \underset{\text{from NaCl}}{0.05} + \underset{\text{from } BaCl_2}{2 \times 0.05} = 0.15\,M$

For $AgCl \rightleftharpoons Ag^+ + Cl^-$

$K_{sp} = [Ag^+][Cl^-] = S \times 0.15 = 1.0 \times 10^{-10}$

$S = 6.6 \times 10^{-10}$

68. (d) After mixing the two $[N_3H] = \frac{100 \times 0.5}{500} = 10^{-1}$

$[HOCN] = \frac{400 \times 0.1}{500} = 8 \times 10^{-2}$

$N_3H \rightleftharpoons N_3^- + H^+$

at eq. $(0.1-x)$ $\quad x \quad x+y$

$$K_{N_3H} = \frac{x(x+y)}{(0.1-x)}$$

$HOCN \rightleftharpoons OCN^- + H^+$

$(0.08-y)$ $\quad y \quad x+y$

$$K_{HOCN} = \frac{y(x+y)}{0.08-y}$$

[Both are weak, thus $0.1-x \approx 0.1$, $0.08-y \approx 0.08$]

$$\therefore \quad \frac{K_{N_3H}}{K_{HOCN}} = \frac{x(x+y)/0.1}{y(x+y)/0.08}$$

or

$$\frac{3.6 \times 10^{-4}}{8 \times 10^{-4}} = \frac{0.08x}{0.1y}$$

or $\frac{x}{y} = \frac{3.6\times10^{-5}}{6.4\times10^{-5}} = 0.5625$

Also, $8\times10^{-4} = \frac{y(x+y)}{0.08} = \frac{y(0.5625y+y)}{0.08}$

or $1.5625\,y^2 = 8\times10^{-4}\times0.08$

or $y = \sqrt{\frac{8\times10^{-4}\times0.08}{1.5625}} = 6.4\times10^{-3} = [OCN^-]$

$\therefore$ $x = 0.5625\times6.4\times10^{-3} = 3.6\times10^{-3} = [N_3^-]$

$H^+ = 6.4\times10^{-3} + 3.6\times10^{-3} = 10\times10^{-3} = 10^{-2}$

$\therefore$ pH = 2

69. (a) Given $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

$$K = \frac{[NH_4^+][NH_2^-]}{[NH_3]^2(l)}$$

or $3.46\times10^{-27} = \frac{[NH_4^+][NH_2^-]}{(58.82)^2}$

$[NH_3] = \frac{1000}{17} = 58.82\,M$

$\therefore$ $[NH_4^+] = [NH_2^-] = 3.46\times10^{-12}\,M$

$= 6.023\times10^{23}\times3.46\times10^{-12}$

$= 2.08\times10^{12}$ anions / litre

$= 2.08\times10^{9}$ anions / mL

70. (c) K_{sp} of AgCl $= 1\times10^{-10} = S^2$

$\therefore$ $S = 10^{-5}$ mole/l $= 10^{-5}\times143.5$ g/l

$= 1.435\times10^{-3}$ g/l $= 1.435$ mg/l

$\because$ 1.435 g of AgCl requires 1 litre

$\therefore$ 4.305 g of AgCl requires $\frac{1\times4.305}{1.435} = 3$ litre

71. (c) $KH_2PO_4 + H_3PO_4$, $KH_2PO_4 + K_2HPO_4$ and $K_2HPO_4 + K_3PO_4$

72. (d) $[Ag^+] = \frac{K_{sp}}{[Cl^-]}$,

Addition of Cl^- shows a decrease in $[Ag^+]$.

or $[Ag^+] \propto \frac{1}{[Cl^-]}$ (K_{sp} is constant)

73. (d) $PbSO_4$ is insoluble. H_2S precipitates both CuS and PbS.

74. (a) AgF is soluble in water.

75. (c) K_2SO_4 and $(NH_4)_2CO_3$ both are water soluble

$K_2CO_3 + (NH_4)_2SO_4 \longrightarrow K_2SO_4 + (NH_4)_2CO_3$

76. (a) pH of 0.1 M HCl + 0.1 M CH_3COOH is lowest as it has strong acid and CH_3COOH

77. (a) $[H^+] = 10^{-4}$

$[H^+] = 10^{-1}$

10^3 times more acidic than $[H^+] = 10^{-4}$

78. (a) $[H^+] = 3\times10^{-3}$

$\therefore$ pH $= 3 - \log 3$

pOH $= 14 - 3 + \log 3 = 11 + \log 3$

79. (b) meq. of dil solution = meq. of conc. solution

$N\times1000 = 10\times10^{-4}$

$\therefore$ $N = \frac{10^{-3}}{1000} = 10^{-6}$

$H^+ \approx 10^{-6} + 10^{-7} = 1.01\times10^{-7}$

$\therefore$ pH > 6

80. (a) meq. of HCl = 10 × 0.1 = 1

meq. of $Sr(OH)_2$ = 10 × 0.01 × 2 = 0.2

meq. of HCl left = 1 − 0.2 = 0.8

$\therefore$ $N_{HCl} = \frac{0.8}{10+10} = \frac{0.8}{20} = 0.04$

$\therefore$ pH $= -\log\frac{4}{100} = -\log 4 + \log 100$

$= 2 - 0.6020 = 1.3979$

81. (d) Lesser amount of energy is required for dissociation of acetic acid or acetic acid is stronger than HCN.

82. (a) $\alpha = \sqrt{\frac{K_a}{C}}$

$\therefore$ $\alpha_1 = \sqrt{\frac{K_a}{0.1}}$

$\alpha_2 = \sqrt{\frac{K_a}{0.001}}$

or $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{0.001}{0.1}} = 10^{-1} = 0.1$

83. (d) $H_2O + H^+ \longrightarrow H_3O^+$

$H_3O^+ + H_2O \longrightarrow H_5O_2^+$

$H_2O + OH^- \longrightarrow H_3O_2^-$

84. (c) $h = \sqrt{\frac{k_w}{k_a\cdot k_b}} = \sqrt{\frac{10^{-14}}{10^{-5}\times10^{-4}}} = \sqrt{10^{-5}}$

$= 3.16\times10^{-3}$

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

$= \frac{14}{2} + \frac{4}{2} - \frac{5}{2}$

$= 9 - 2.5 = 6.5$

85. (a) Solubility of AgCl in NaCl is lower than H_2O. Also other orders are derived by Debye-Huckel limiting law.

86. (a) $AgNO_3 + KCN \longrightarrow AgCN\downarrow + KNO_3$

$AgCN + KCN \longrightarrow KAg(CN)_2$

or $\underset{\substack{0.03\\0.0}}{AgNO_3} + \underset{\substack{0.1\\0.04}}{2KCN} \longrightarrow \underset{\substack{0\\0.03}}{K[Ag(CN)_2]} + \underset{\substack{0\\0.03}}{KNO_3}$

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

$\therefore$ $K_C = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-} = \frac{[Ag^+][0.04]^2}{[0.03]}$

$= 4\times10^{-19}$

$[Ag^+] = 7.5\times10^{-18}$ M

87. (b)
$$2.303\log\frac{K_{sp_2}}{K_{sp1}}=\frac{\Delta H}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$
$$2.303\log\frac{1.39\times10^{-8}}{7.47\times10^{-9}}=\frac{\Delta H}{2}\times\left[\frac{298-288}{288\times298}\right]$$
$$\Delta H=10.66\text{ k cal mol}^{-1}$$

88. (a)
$$\alpha=\frac{\wedge m}{\wedge_\infty}=\frac{60}{400}=\frac{3}{20}=0.15$$

Now $[H^+]=C\alpha=0.1\times\frac{3}{20}$

$\therefore$ $pH=-\log H^+$
$$=-\log\frac{3}{200}=-0.4771+2.3010$$
$$=1.8239$$

Also $K_a=\frac{C\alpha^2}{(1-\alpha)}=\frac{0.1\times(0.15)^2}{(1-0.15)}$
$$=2.65\times10^{-3}$$

89. (c) $HA \rightleftharpoons H^+ + A^-$

Acid Conjugate base

$pKa_{HA}+pKb_{A^-}=14$

$\therefore$ $pKa_{HA}=\frac{14}{2}=7$ ($\because$ $pKa_{HA}+pKb_{A^-}$)

$\therefore$ $K_a=10^{-7}$

$[H^+]=\sqrt{Ka\times C}=\sqrt{10^{-7}\times0.001}=10^{-5}$

$\therefore$ pH = 5

90. (b) Maximum buffer capacity = $pKa\pm1$

This is possible when $\frac{[\text{conjugate base}]}{[\text{acid}]}=1$

Thus milli mole of acetic acid taken = 500 × 1 = 500

milli mole of acetic acid to be neutralised = 250

$\because$ milli mole of KOH required = 250
$$\frac{w}{56}\times1000=250$$
$$w_{KOH}=14g$$

91. (b) Let solubility of HCOOAg be a mol/litre

$$H^+ + HCOO^- \rightleftharpoons HCOOH$$

10^{3-} a —

10^{3-} — a

(buffer)

Since HCOOH is a weak acid and has low degree of dissociation. Also its dissociation is suppressed in presence of H^+. Thus,

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

or $Ka=\frac{[H^+][HCOO^-]}{[HCOOH]}$

$$[HCOO^-]=\frac{K_a\times[HCOOH]}{[H^+]}=\frac{10^{-5}\times a}{10^{-3}}$$
$$=a\times10^{-2}$$

Also for HCOOAg:

$HCOOAg(s) \rightleftharpoons HCOO^-(aq.)+Ag^+(aq.)$

$$K_{SP}=S^2=(10^{-2})^2=10^{-4}$$

Also $K_{SP}=[HCOO^-][Ag^+]$
$$10^{-4}=a\times10^{-2}\times a$$

$\therefore$ $a=10^{-1}=0.1M$

92. (a) Lesser is Ka, weaker is acid (HPO_4^{2-}), stronger is its conjugate base (PO_4^{3-})

93. (c)
$$[CaA_2]=\frac{0.125}{0.5}=0.25\text{ M}$$
$$[A^-]=2\times0.25=0.50M$$
$$A^-+H_2O \rightleftharpoons HA+OH^-$$
$$[OH^-]=C\cdot h=C\sqrt{\frac{K_H}{C}}$$
$$=\sqrt{\frac{K_w\cdot C}{K_a}}=\sqrt{\frac{10^{-14}\times0.5}{8\times10^{-4}}}$$
$$=\sqrt{6.25\times10^{-12}}=2.5\times10^{-6}$$
$$pOH=5.60$$

or $pH=14-5.60=8.40$

94. (b) $E_{Cell}=E^\circ_{OP_{Ag/Ag^+}}-\frac{0.059}{2}\log[Ag^+]_{LHS}+E^\circ_{RP_{Ag^+/Ag}}$
$$+\frac{0.059}{1}\log[Ag^+]_{RHS}$$

$\because$ at equilibrium $E_{Cell}=0$ and $E^\circ_{OP_{Ag/Ag^+}}=-E^\circ_{RP_{Ag^+/Ag}}$
$$0=\frac{0.059}{2}\log\frac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}}$$

or $\frac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}}=1$ or $[Ag^+]_{RHS}=[Ag^+]_{LHS}$

At LHS:
$$[Ag^+]^2[CO_3^{2-}]=K_{SP}\ Ag_2CO_3=8\times10^{-12}$$

$\therefore$ $[Ag^+]=\sqrt{\frac{8\times10^{-12}}{[CO_3^{2-}]}}=\frac{2\sqrt{2}\times10^{-6}}{\sqrt{[CO_3^{2-}]}}$

At RHS : $[Ag^+][Br^-]=K_{SP\ AgBr}=4\times10^{-13}$

$\therefore$ $[Ag^+]=\frac{4\times10^{-13}}{[Br^-]}$

$\therefore$ $\frac{4\times10^{-13}}{[Br^-]}=\frac{2\sqrt{2}\times10^{-6}}{\sqrt{[CO_3^{2-}]}}$

or $\frac{[Br^-]}{\sqrt{[CO_3^{2-}]}}=\sqrt{2}\times10^{-7}$

95. (d)
$$Ag_2C_2O_4(s) \rightleftharpoons \underset{2s}{2Ag^+}+\underset{s}{C_2O_4^{2-}}$$

Given $[Ag^+]=2s=2.2\times10^{-4}$
$$s=1.1\times10^{-4}$$
$$K_{sp}=(2s)^2\times s=4s^3$$
$$=4(1.1\times10^{-4})^3=5.3\times10^{-12}$$

• PREVIOUS YEARS PROBLEMS •

1. The correct acidic strength order is : **(IIT 2001)**
(a) $HClO < HClO_2 < HClO_3 < HClO_4$
(b) $HClO_4 < HClO_3 < HClO_2 < HClO$
(c) $HClO < HClO_4 < HClO_3 < HClO_2$
(d) $HClO_4 < HClO_2 < HClO_3 < HClO$

2. For a sparingly soluble salt A_pB_q, the relationship of its solubility product L_s with its solubility (S) is : **(IIT 2001)**
(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) $L_S = S^{pq} \cdot (pq)^{p+q}$

3. The correct order of acidic strength is : **(IIT 2002)**
(a) $CaO < CuO < H_2O < CO_2$
(b) $H_2O < CuO < CaO < CO_2$
(c) $CaO < H_2O < CuO < CO_2$
(d) $H_2O < CO_2 < CaO < CuO$

4. H_3BO_3 is : **(IIT 2003)**
(a) monobasic and weak Lewis acid
(b) monobasic and weak Bronsted acid
(c) monobasic and strong Lewis acid
(d) tribasic and weak Bronsted acid

5. 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^{-45} respectively which one will precipitate first? **(IIT 2003)**
(a) FeS (b) MgS
(c) HgS (d) ZnS

6. A weak-acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is : **(IIT 2004)**
(a) 0.0001% (b) 0.01%
(c) 0.1% (d) 0.15%

7. 0.1 mole of CH_3NH_2 ($K_b = 5\times10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. The $[H^+]$ in solution is : **(IIT 2005)**
(a) 8×10^{-2} M (b) 8×10^{-11} M
(c) 1.6×10^{-11} M (d) 8×10^{-5} M

8. The species present in solution when CO_2 is dissolved in water : **(IIT 2006)**
(a) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$
(b) H_2CO_3, CO_3^{2-}
(c) CO_3^{2-}, HCO_3^-
(d) CO_2, H_2CO_3

9. 2.5 mL of $\frac{2M}{5}$ weak monoacidic base ($K_b = 1\times10^{-12}$ at 25°C) is titrated with $\frac{2M}{15}$ HCl in water at 25°C. The concentration of H^+ at equivalence point is : **(IIT 2008)**
(a) 3.7×10^{-13} M (b) 3.2×10^{7} M
(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M

10. Solubility product K_{sp} of salt of type 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 of these salts in mol dm^{-3} at temperature T are in the order : **(IIT 2008)**
(a) $MX > MX_2 > M_3X$ (b) $M_3X < MX_2 > MX$
(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

11. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01M solution of its sodium salt is : **(IIT 2009)**
(a) 10 (b) 8
(c) 12 (d) 6

12. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **[JEE (Main) 2013]**
(a) 2.0 L (b) 9.0 L
(c) 0.1 L (d) 0.9 L

13. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is : **[JEE (Advanced) I 2013]**
(a) 1.1×10^{-11} (b) 1.1×10^{-10}
(c) 1.1×10^{-12} (d) 1.1×10^{-9}

14. The initial rate of hydrolysis of methyl acetate (1M) 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 : **[JEE (Advanced) II 2013]**
(a) 1×10^{-4} (b) 1×10^{-5}
(c) 1×10^{-6} (d) 1×10^{-3}

15. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is : **[JEE (Main) 2017]**
(a) 7.2 (b) 6.9
(c) 7.0 (d) 1.0

16. In the following reactions, ZnO is respectively acting as a/an : **[JEE (Main) 2017]**
(1) $ZnO + Na_2O \longrightarrow Na_2ZnO_2$
(2) $ZnO + CO_2 \longrightarrow ZnCO_3$
(a) base and acid (b) base and base
(c) acid and acid (d) acid and base

SOLUTIONS (Previous Years Problems)

1. (a) Higher is the oxidation number of central non-metal, more is acidic nature.

2. (a) $A_pB_q \rightleftharpoons pA^{q+} + qB^{p-}$

$pS \quad qS$

$\therefore \quad K_{sp} = (pS)^p (qS)^q$

$= p^p \cdot q^q \cdot (S)^{p+q}$

3. (a) CaO is strongest base, CO_2 is acidic. Also, CuO is strong base than H_2O.

4. (a) $H_3BO_3 + OH^- \longrightarrow B(OH)_4^- + H^+$

Accepts lone pair of electron thus Lewis acid but weak.

5. (c) K_{sp} of HgS is minimum and thus possesses less solubility. Note all salts are AB type.

6. (b) $h = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}}$

$= \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}} = \sqrt{10^{-8}}$

$= 10^{-4}$

or $\quad h = 10^{-4} \times 100 = 10^{-2} = 0.01\%$

7. (b) $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+Cl$

0.1	0.08	0
0.02	0	0.08

This is basic buffer solution.

$[OH^-] = K_b \times \frac{[\text{base}]}{[\text{conjugate acid}]}$

$= 5 \times 10^{-4} \times \frac{0.02}{0.08} = 1.25 \times 10^{-4}$

$\therefore \quad [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{1.25 \times 10^{-4}} = 8 \times 10^{-11} M$

8. (a) All the following equilibrium exist together

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

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

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

9. (d) $BOH + HCl \longrightarrow BCl + H_2O$

Meq. of BOH = Meq. of HCl = Meq. of BCl

$2.5 \times \frac{2}{5} \times 1 = V \times \frac{2}{15} \times 1 = 1$

$\therefore \quad V = 7.5 \text{ mL}$

$\therefore$ Total volume = 2.5 + 7.5 = 10 mL

Thus, $\quad [BCl] = \frac{1}{10} = 0.1$

Now for hydrolysis of BCl; $K_H = \frac{Ch^2}{1-h} = \frac{K_w}{K_b}$

$\therefore \quad h = 0.27$

or $\quad [H^+] = c \cdot h = 0.27 \times 0.1 = 2.7 \times 10^{-2} M$

10. (d) Solubility of MX, MX_2 and M_3X are respectively

$S = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4} M$

$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.2 \times 10^{-14}}{4}} = 2 \times 10^{-5} M$

$S = \sqrt[4]{\frac{K_{sp}}{27}} = \sqrt[4]{\frac{2.7 \times 10^{-15}}{27}} = 1 \times 10^{-4} M$

11. (b) $C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + OH^-$

$\therefore \quad [OH^-] = ch = c\sqrt{\frac{K_H}{c}} = \sqrt{\frac{K_w \cdot c}{K_a}}$

$= \sqrt{\frac{10^{-14} \times 0.01}{1 \times 10^{-4}}} = 10^{-6}$

$\therefore \quad [H^+] = 10^{-8}$ or pH = 8

12. (b) meq. of I HCl = meq of II HCl

$1 \times 10^{-1} = V \times 10^{-2}$

$\therefore \quad V = 10$ litre

$\therefore$ volume of water added = (10 – 1) = 9L

13. (b) Ionic product of $Ag_2CrO_4 = [Ag^+]^2[CrO_4^{-2}]$

$= (2S + 0.1)^2 \times S = 1.1 \times 10^{-12}$

neglecting S as compared to 0.1

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

14. (a) Rate = K[Ester] $[H^+]$

For strong acid $[H^+] = 1 M$

For weak acid $[H^+] = \sqrt{K_a.C}$

$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[H^+]_1 \text{ for strong acid}}{[H^+]_2 \text{ for weak acid}}$

$\frac{1}{1/100} = \frac{1}{\sqrt{K_a \times 1}}$ $\quad$ ($C = 1M$ for weak acid)

$K_a = 10^{-4} M$

15. (b) $pH = 7 + \frac{1}{2}(pK_a - pK_b)$

$= 7 + \frac{1}{2}(3.2 - 3.4)$

$= 6.9$

16. (d) In (a), Na_2O is basic oxide and thus ZnO acts as acidic oxide.

In (b), CO_2 is acidic oxide and thus ZnO acts as basic oxide.

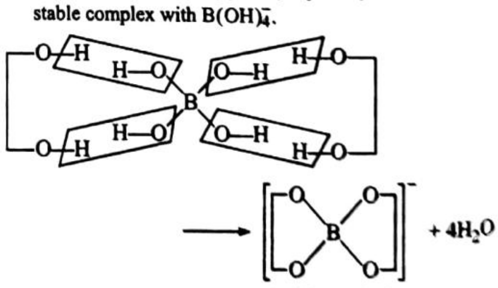
OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. Which one is not acidic salts ?
   (a) Na_2HPO_4 (b) NaH_2PO_2
   (c) Na_2HPO_3 (d) NaH_2PO_4
2. The resulting mixtures which act buffer are :
   (a) 10 mL 0.1 M HCl + 20 mL 0.1 M NaCN
   (b) 10 mL 0.1 M NaOH + 20 mL 0.1 M NH_4CN
   (c) 10 mL 0.1 M NH_4OH + 20 mL 0.1 M CH_3COONH_4
   (d) 10 mL 0.1 M CH_3COOH + 20 mL 0.1 M CH_3COONH_4
3. Which one is correct for the saturated solution of $Ca_3(PO_4)_2$ salt if its K_{sp} is 2.05×10^{-33} ?
   (a) Solubility of Ca_3PO_4 is $1.63 \times 10^{-6} M$
   (b) $[Ca^{2+}]_{eq.} = 4.9 \times 10^{-6}\ M$
   (c) $[PO_4^{3-}]_{eq.} = 3.26 \times 10^{-6}\ M$
   (d) $[Ca_3PO_4]_{eq.}$ = Zero
4. Which of the following are correct ?
   (a) Aniline is a weak-acid in acetic acid
   (b) Ammonium salts act as acid in liquid NH_3
   (c) The reaction CsF + LiI $\longrightarrow$ CsI + LiF is acid-base reaction
   (d) HCl acts as base in HF.
5. Which of the following acid-base reactions are possible?
   (a) $PH_3 + NH_4^+ \longrightarrow PH_4^+ + NH_3$
   (b) $NH_3 + PH_4^+ \longrightarrow NH_4^+ + PH_3$
   (c) $(CH_3)_3P + NH_4^+ \longrightarrow (CH_3)_3P^+H + NH_3$
   (d) $(CH_3)_3N + PH_4^+ \longrightarrow (CH_3)_3NH^+ + PH_3$
6. Select the correct statements :
   (a) All Bronsted bases are Lewis bases
   (b) All Bronsted acids are Lewis acids
   (c) All Arrhenius acids are Bronsted acids
   (d) All Arrhenius bases are Bronsted bases
7. The correct acidic orders are :
   (a) $Li^+ > Na^+ > K^+$ (b) $Li^+ < Be^{2+} < B^{3+}$
   (c) $Fe^{3+} > Fe^{2+} > Fe^+$ (d) $NF_3 < NCl_3 < NBr_3$
8. Select the correct statements :
   (a) HCN is weak acid
   (b) Reaction of $HCl_{(g)}$ and $NH_{3(l)}$ is Arrhenius acid-base reaction
   (c) Pure H_2SO_4 and $HClO_4$ do not conduct current but in presence of each other they are good conductor
   (d) Mn_2O_7 is acidic oxide.
9. The oxo acids of P_2O_5 are :
   (a) H_3PO_4 (b) $H_4P_2O_7$
   (c) HPO_3 (d) H_3PO_3
10. Which of the following statement(s) is (are) correct?
   (a) pH of $1.0 \times 10^{-18}\ M$ 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 $pH = (1/2)\ pK_a$
11. A buffer solution can be prepared from a mixture of:
   (a) sodium acetate and acetic acid in water
   (b) sodium acetate and hydrochloric acid in water
   (c) ammonia and ammonium chloride in water
   (d) ammonia and sodium hydroxide in water
12. In a buffer solution of NaH_2PO_4 and Na_2HPO_4 :
   (a) NaH_2PO_4 is acid and Na_2HPO_4 is salt
   (b) $pH = pK_2$ of $H_3PO_4 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$
   (c) Na_2HPO_4 is acid and NaH_2PO_4 is salt
   (d) $pH = pK_3$ of $H_3PO_4 + \log \frac{[H_2PO_4^-]}{[HPO_4^{2-}]}$
13. Select the correct statments :
   (a) The K_{a_1} values for H_2SO_3 is 1.3×10^{-2}
   (b) H_2SO_3 exist in only minute concentration in aqueous solution of SO_2
   (c) The K_{a_1}, values of H_2SO_3 refers for the process $H_2SO_3 \rightleftharpoons H^+ + SO_3^{2-}$
   (d) The K_a, value of H_2SO_3 refers for the process $\underset{(g)}{SO_2} + \underset{(l)}{H_2O} \rightleftharpoons \underset{(aq.)}{H^+} + \underset{(aq.)}{HSO_3^-}$
14. Select the correct statements :
   (a) HF is a weak acid
   (b) The strength of weak acids increases with dilution ($HA \rightleftharpoons H^+ + A^-$)
   (c) The strength of HF increases with concentration ($HF \rightleftharpoons H^+ + F^-$)
   (d) The F^- furnished by HF reacts with HF to give HF_2^- and thereby shifting the reaction to right
15. An aqueous solution of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pairs of solution which form a buffer upon mixing is/are : **(IIT 2010)**
   (a) HNO_3 and CH_3COOH
   (b) KOH and CH_3COONa
   (c) HNO_3 and CH_3COONa
   (d) CH_3COOH and CH_3COONa

16. The correct statement(s) for orthoboric acid is/are : **[JEE (Advanced) 2014]**
(a) It behaves as a weak acid in water due to self ionization.
(b) Acidity of its aqueous solution increases upon addition of ethylene glycol.
(c) It has a three dimensional structure due to hydrogen bonding.
(d) It is a weak electrolyte in water.

SOLUTIONS (More Than One Answer Correct)

1. (b,c) H_3PO_2 is monobasic and H_3PO_3 is dibasic.
2. (a,b,c,d)
$$\begin{array}{cccc} HCl & + \; NaCN \longrightarrow & NaCl & + \; HCN \\ 10\times0.1 & 20\times0.1 & & \\ =1 & =2 & 0 & 0 \\ 0 & 1 & 1 & 1 \end{array}$$
$$[HCN]=\frac{1}{30} \text{ and } [NaCN]=\frac{1}{30}$$
3. (a,b,c,d) $Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$
$$\quad\quad 3s \quad\quad 2s$$
$\therefore$ $K_{sp}=2.05\times10^{-33}=108s^5$
$\therefore$ $s=1.63\times10^{-6}\,M$
$\therefore$ $[Ca^{2+}]=3\times1.63\times10^{-6}=4.9\times10^{-6}\,M$
$[PO_4^{3-}]=2\times1.63\times10^{-6}=3.26\times10^{-6}\,M$
$[Ca_3PO_4]_{eq.}=0$, because all the salt is in ionic state.
4. (b,c,d) Aniline is strong base in acetic acid. $NH_{3(l)}$ ionises as :
$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-;$$
$$\underset{\text{Soft-hard}}{CsF} + \underset{\text{Hard-soft}}{LiI} \longrightarrow \underset{\text{Soft-soft}}{CsI} + \underset{\text{Hard-hard}}{LiF}$$
This reaction is an interesting example of soft acid-hard base and hard acid-soft base combination
$$HF + HCl \longrightarrow F^- + H_2Cl^+$$
5. (b,c) Proton affinity of NH_3 is greater than PH_3. Proton affinity of $(CH_3)_3P$ is greater than NH_3.
6. (a,c) NaOH is Arrhenius base but not Bronsted base. HCl is Bronsted acid but not Lewis acid.
7. (a,b,c,d) Higher is effective nuclear charge more is acidic nature of Lewis acid cations. The increasing electronegativity from I to F in NX_3 give rise to lesser tendency for N to donate electron pair as it acquires more +ve charge on N-atom.
8. (a,b,c,d) Arrhenius concept is in aqueous medium
$$HClO_4 + H_2SO_4 \longrightarrow H_3SO_4^+ + ClO_4^-$$
$$Mn_2O_7 + H_2O \longrightarrow \underset{\text{Acid}}{2HMnO_4}$$
9. (a,b,c) Each has P^{5+} state.
10. (b,c) HCl is acid; for (d) $pH = pK_a$
11. (a,b,c) For (b) $\underset{\text{more}}{CH_3COONa} + \underset{\text{less}}{HCl} \rightarrow CH_3COOH + NaCl$
12. (a,b) HPO_4^{2-} is conjugate base of $H_2PO_4^-$ and thus.
13. (a,b,d) Choice (b) is correct explanation for H_2SO_3.
14. (a,b,c,d) All are facts. Choice (d) is correct explanation for HF in aqueous medium.
15. (c,d) CH_3COONa (in more amount) than HNO_3 forms a buffer mixture of $(CH_3COONa + CH_3COOH)$ in solution.
16. (b,d) Orthoboric acid H_3BO_3 is a weak monobasic Lewis acid as it accepts OH^- ions
$$H_3BO_3 + H{-}OH \rightleftharpoons B(OH)_4^- + H^+$$
The equilibrium is shifted in forward direction by the addition of ethylene glycol (a syndiol) which forms a stable complex with $B(OH)_4^-$.



(stable complex)

It has a planar sheet like structure due to sp^2 hybridization of B atom as well as hydrogen bonding.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Solubility of a substance in its saturated solution can be derived from its K_{sp} values. Higher is the K_{sp} for same type of compound more is the solubility. If S is the solubility in mol/litre then K_{sp} of a compound A_xB_y is expressed as

$$K_{sp} = x^x \cdot y^y [S]^{x+y}$$

Consider a compound $M(OH)_x$ having $= K_{sp} = 27 \times 10^{-12}$ and solubility in pure water is 10^{-3} mol litre^{-1}.

[1] The value of x is :
(a) 1 (b) 2
(c) 3 (d) 4

[2] The solubility (in M) of $M(OH)_x$ in 0.1 M NaOH solution is :
(a) 2.7×10^{-10} (b) 2.7×10^{-3}
(c) 2.7×10^{-8} (d) 2.7×10^{-4}

[3] The solubility (in M) of $M(OH)_x$ in 0.1 $Ca(OH)_2$ solution is :
(a) 6.46×10^{-4} (b) 2.7×10^{-8}
(c) 2.7×10^{-4} (d) 3.375×10^{-9}

[4] The solubility (in mole/litre) of $M(OH)_x$ in $0.1\,M(NO_3)_x$ solution is :
(a) 2.15×10^{-4} (b) 2.15×10^{-5}
(c) 2.15×10^{-6} (d) 2.15×10^{-7}

Comprehension 2: K_b of CH_3COO^- is 5.26×10^{-10}. Calculate for 0.01 N solution of sodium acetate.

[1] Hydrolysis constant of CH_3COO^- is :
(a) 5.26×10^{-10} (b) 5.26×10^{-11}
(c) 5.26×10^{-12} (d) 5.26×10^{-9}

[2] Degree of hydrolysis of CH_3COO^- is :
(a) 2.29×10^{-6} (b) 2.29×10^{-4}
(c) 2.29×10^{-3} (d) 2.29×10^{-5}

[3] pH of solution is :
(a) 8.56 (b) 5.44
(c) 8.36 (d) 9.56

Comprehension 3: Oxides of metals are usually basic and oxides of non metals are usually acidic. However some acidic oxides of metals and neutral oxides of non metals such as N_2O, NO, CO, H_2O are known.

[1] Which of the following oxide is acidic ?
(a) Cr_2O_3 (b) CrO_3
(c) MnO_2 (d) MnO

[2] In the reaction of CO with NaOH at high P and T to give sodium formate, CO acts as :
(a) acid (b) base
(c) neutral (d) amphoteric

[3] Number of OH gp present in H_3PO_2 are :
(a) 1 (b) 2
(c) 3 (d) none of these

Comprehension 4 : The dissolution of ammonia gas in water does not obey Henry's law. On dissolving, a major portion of ammonia, molecules unite with H_2O to form NH_4OH molecules. NH_4OH again dissociates into NH_4^+ and OH^- ions. In solution therefore, we have NH_3 molecules, NH_4OH molecules and NH_4^+ ions and the following equilibrium exist :

$NH_3(g)$ (pressure P and concentration C) initially $\rightleftharpoons$ $NH_3(l) + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Let C_1 mol/L of NH_3 pass in solution state a part of which on dissolution in water forms C_2 mol/L of NH_4OH. The solution contains C_3 mol/L of NH_4^+ ions.

[1] Total concentration of ammonia, which can be determined by volumetric analysis is equal to :
(a) $C_1 + C_2$ (b) $C_1 + C_2 + C_3$
(c) $C_1 + C_3$ (d) $C_2 + C_3$

[2] Concentration of undissociated ammonium hydroxide is :
(a) $C_1 + C_2$ (b) $C_2 - C_3$
(c) $C_1 + C_3$ (d) $C_1 - C_2$

[3] Degree of dissociation of ammonium hydroxide is :
(a) C_1 (b) C_3 / C_1
(c) C_3 / C (d) C_3 / C_2

[4] If p is the partial pressure of ammonia at equilibrium, then which of the following is constant? α is degree of dissociation of NH_3.
(a) $\frac{p}{C_1}$ (b) $\frac{p}{C}$
(c) $\frac{p}{C_2}$ (d) $\frac{p}{C_3}$

[5] The dissociation constant of NH_4OH can be given as :
(a) $K_b = \frac{(C_3)^2}{(C_2 - C_3)}$ (b) $K_b = \frac{(C_3)^2}{C_2}$
(c) $K_b = \frac{C_3}{(C_2 - C_1)}$ (d) $K_b = \frac{C_3}{C_1 - C_2}$

[6] The pH of solution can be given by :
(a) $pK_w + \log C_3$
(b) $pK_w - \frac{1}{2} pK_b + \frac{1}{2} \log C_2$
(c) $pK_a + \frac{1}{2} \log C_2 + \frac{1}{2} pK_b$
(d) either of these

Comprehension 5 : The pH of pure water at 25°C and 60°C are 7 and 6.5 respectively. HCl gas is passed through water at 25°C till the resulting 1 litre solution acquires a pH of 3. Now 4×10^{-3} mole of NaCN are added into this solution. Also a fresh 0.1 *M*HCN solution has pH 5.1936. Now in the one part of solution obtained after addition of NaCN, one millimole of NaOH are added and in the second part of this solution 0.5 millimole of HCl are added.

[1] The heat of formation of water from H^+ and OH^- is :
(a) 13.06 kcal (b) – 13.06 kcal
(c) 16.32 kcal (d) – 16.32 kcal

[2] The volume of HCl passed through the solution at 25°C and 1 atm is :
(a) 24.46 mL (b) 2.446 mL
(c) 244.6 mL (d) 0.2446 mL

[3] The dissociation constant of HCN is :
(a) 4.1×10^{-10} (b) 4.1×10^{-6}
(c) 4.1×10^{-3} (d) 4.1×10^{-8}

[4] The degree of dissociation of 0.1 *M* HCN solution is :
(a) 6.4×10^{-5} (b) 6.4×10^{-3}
(c) 6.4×10^{-2} (d) 6.4×10^{-6}

[5] The pH of resulting solution after addition of NaCN is :
(a) 9.86 (b) 8.86
(c) 6.86 (d) 5.86

[6] The pH of resulting solution after addition of 0.1 millimole of HCl is :
(a) 9.68 (b) 9.39
(c) 9.21 (d) 9.98

[7] The pH of resulting solution after addition of 0.05 millimole of NaOH is :
(a) 10.23 (b) 11.23
(c) 9.23 (d) 8.23

SOLUTIONS

Comprehension 1

[1] (c) $M(OH)_x \rightleftharpoons \underset{S}{M^{+x}} + \underset{x_s}{xOH^-}$

$$K_{sp} = x^x \cdot (S)^{1+x} = 27\times10^{-12}$$

$\therefore \quad x = 3$

[2] (c) $K_{sp} = [M^{+x}][OH^-]^x = [M^{+3}][OH^-]^3$

$$27\times10^{-12} = S\times[3S+0.1]^3 \; [3S <<< 0.1]$$

$$\therefore \quad S = \frac{27\times10^{-12}}{(0.1)^3} = \mathbf{2.7\times10^{-8}}$$

[3] (d) $K_{sp} = [M^{+3}][OH^-]^3$

$$27\times10^{-12} = S\times[3S+0.2]^3 \; [3S <<< 0.2]$$

$$S = \frac{27\times10^{-12}}{(0.2)^3} = \mathbf{3.375\times10^{-9}}$$

[4] (a) $K_{sp} = [M^{+3}][OH^-]^3$

$$= [S+0.1][3S]^3 \; [S <<< 0.1]$$

$$27S^3 = \frac{27\times10^{-12}}{0.1}$$

$$S = 2.15\times10^{-4}$$

Comprehension 2

For $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

Before hydrolysis	1	0	0
After hydrolysis	$(1-h)$	h	h

K_b for $CH_3COO^- = 5.26\times10^{-10}$

$\therefore$ K_a for $CH_3COOH = 1.9\times10^{-5}$

[1] (a) $K_H = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9\times10^{-5}} = \mathbf{5.26\times10^{-10}}$

[2] (b) $h = \sqrt{\left(\frac{K_H}{C}\right)} = \sqrt{\left(\frac{5.26\times10^{-10}}{0.01}\right)} = \mathbf{2.29\times10^{-4}}$

[3] (c) $[OH^-]$ from NaOH, a strong alkali $= Ch$

$$= 0.01\times2.29\times10^{-4}$$

$$= 2.29\times10^{-6}\,M$$

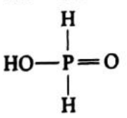
$\therefore \quad pOH = 5.64 \quad \therefore\ pH = \mathbf{8.36}$

Comprehension 3

[1] (b) Some metal oxides in their highest oxidation state are acidic.

[2] (a) $\underset{\text{acid}}{CO} + \underset{\text{base}}{NaOH} \xrightarrow{P.T.} \underset{\text{(salt)}}{HCOONa}$

[3] (a)



Comprehension 4

[1] (b) The intermediate solution of acid will react with all the NH_3 present in solution.

[2] (b) NH_4OH left undissociated $= C_2 - C_3$.

[3] (d) $\alpha = \frac{\text{Mole of } NH_4OH \text{ dissociated}}{\text{Total mole}} = \frac{C_3}{C_2}$.

[4] (a) Acc. to Henry's law $a \propto P_{NH_3}$

Where a is the amount of gas dissolved per unit volume of solvent.

or $\quad C_{NH_3} \propto P_{NH_3}$

$$\therefore \quad K = \frac{P_{NH_3}}{C_{NH_3}} = \frac{P}{C_1}$$

[5] (a) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

C_2	0	0
(C_2-C_3)	C_3	C_3

$$\therefore \quad K_b = \frac{C_3^2}{C_2 - C_3}$$

[6] (d) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$t=0$	C_2	0	0
At eq.	$C_2(1-\alpha)$	$C_2\alpha$	$C_2\alpha$

Also $C_2\alpha = C_3$

$\therefore [OH^-] = C_3$

or $pOH = -\log C_3$

$\therefore pH = pK_w - pOH = pK_w + \log C_3$

Also $[OH^-] = C_2\alpha = C_2\sqrt{\frac{K_b}{C_2}} = \sqrt{K_b \cdot C_2}$

$$\therefore\ pOH = -\frac{1}{2}\log K_b - \log C_2$$

$$= \frac{1}{2}pK_b - \frac{1}{2}\log C_2$$

$$\therefore\ pH = pK_w - pOH = pK_w - \frac{1}{2}pK_b + \frac{1}{2}\log C_2$$

$$= pK_a + \frac{1}{2}pK_b + \frac{1}{2}\log C_2$$

Comprehension 5

[1] (b) At 25°C pH = 7 $\quad \therefore\ K_w = 10^{-14}$;

At 60°C, pH = 6.5 $\quad K_w = 10^{-13}$

$H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H = ?$

$$2.303\log\frac{10^{-13}}{10^{-14}} = \frac{\Delta H}{R}\left[\frac{35}{333\times298}\right]$$

$\therefore \quad \Delta H = 13.06$ kcal

$\therefore \quad H^+ + OH^- \rightarrow H_2O; \quad \Delta H = -13.06$ kcal

[2] (a) pH of solution after passage of HCl = 3

$\therefore \quad [H^+] = 10^{-3}\,M$ or $[HCl] = 10^{-3}\,M$

From $\quad PV = nRT$

$$1\times V = 10^{-3}\times0.0821\times298$$

$$V = 24.46 \text{ mL}$$

[3] (a) $\underset{\substack{1\\1-\alpha}}{HCN} \rightleftharpoons \underset{\substack{0\\\alpha}}{H^+} + \underset{\substack{0\\\alpha}}{CN^-}$

Also $[H^+] = c\cdot\alpha = c\sqrt{\frac{K_a}{c}} = \sqrt{K_a c}$

or $-\log H^+ = -\frac{1}{2}[\log K_a + \log c]$

$$5.1936 = -\frac{1}{2}[\log K_a + \log 0.1]$$

$\therefore$ $K_a = 4.1\times10^{-10}$

[4] (a) $K_a = C\cdot\alpha^2$ for HCN

$$4.1\times10^{-10} = 0.1\times\alpha^2$$

$\therefore$ $\alpha = 6.4\times10^{-5}$

[5] (a) $\underset{\substack{10^{-3}\\0}}{HCl} + \underset{\substack{4\times10^{-3}\\0.003}}{NaCN} \longrightarrow \underset{\substack{0\\0.001}}{NaCl} + \underset{\substack{0\\0.001}}{HCN}$

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

$= 9.3872 + \log\frac{0.003}{0.001} = 9.8643$

[6] (b) $\underset{\substack{0.001\\0}}{H^+} + \underset{\substack{0.003\\0.002}}{NaCN} \longrightarrow \underset{\substack{0.001\\0.002}}{HCN}$

$\therefore$ $pH = 9.3872 + \log\frac{0.002}{0.002} = 9.3872$

[7] (a) $\underset{\substack{0.0005\\0}}{NaOH} + \underset{\substack{0.001\\0.0005}}{HCN} \longrightarrow \underset{\substack{0.003\\0.0035}}{NaCN}$

$\therefore$ $pH = 9.3872 + \log\frac{0.0035}{0.0005} = 10.2323$

In each sub question given below a statement **S** and explanation **E** is given. Choose the correct answers from the codes a, b, c and d given for each question :

(a) S is correct but E is wrong

(b) S is wrong but E is correct

(c) Both S and E are correct and E is correct explanation for S

(d) Both S and E are correct but E is not correct explanation for S

1. S : The pH of a basic buffer mixture is given by :
$$pH = pK_a + \log\frac{[\text{base}]}{[\text{conjugate acid}]}$$
E : The pH of an acidic buffer mixture is given by :
$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

2. S : On passing $HCl(g)$ through a saturated solution of $BaCl_2$, a white turbidity appears.
E : The common ion effect is responsible for white turbidity.

3. S : Degree of hydrolysis and pH of a salt say NH_4CN is independent of concentration of NH_4CN.
E : The solution of NH_4CN in water has pH slightly greater than 7.

4. S : In a pair of two electrolytes one having higher value of K_{sp} is more soluble in water than the other having lower value of K_{sp}.
E : Solubility of electrolyte depends upon K_{sp} as well as on the nature of electrolyte.

5. S : $HgCl_2$ and $SnCl_2$ cannot coexist in a solution.
E : Increase in concentration of Cl^- in solution brings in precipitation of either of them.

6. S : The solubility of HgI_2 in water decreases in presence of KI.
E : HgI_2 is insoluble in water but it becomes soluble in $KI(aq)$.

7. S : The pH of $NH_4OH(aq)$ decreases on addition of little NH_4Cl in it.
E : The pH of NH_4Cl brings in decrease in degree of dissociation of NH_4OH due to common ion effect.

8. S : The $[H^+]$ in $10^{-8}\,N$ HCl is $1.05 \times 10^{-7}\,M$.
E : The H^+ is obtained from HCl and H_2O ; the later furnishes less H^+ than 10^{-7} due to common ion effect.

9. S : HCl acts as weak base in liquid HF but weak acid in acetic acid.
E : The tendency to act as acid or base also depends upon the nature of other substance to accept or donate a proton.

10. S : Cu^+, Ag^+ are soft acids whereas CN^-, H^- are soft bases.
E : Soft acids do not possess noble gas configuration whereas soft bases have donor atom of easily polarised nature.

11. S : Metal oxides are usually either acidic or amphoteric but Mn_2O_7 is acidic.
E : On dissolution in water, Mn_2O_7 forms per manganic acid.

12. S : The dissociation constants of polyprotic acid are in the order $K_1 > K_2 > K_3$.
E : The $[H^+]$ furnished in first step of dissociation exerts common ion effect to reduce the second dissociation so on.

13. S : All strong acid in water show almost same acidic nature.
E : This is due to levelling effect of water on account of its high dielectric constant and strong proton accepting tendency.

14. S : CCl_4, C_6H_6 and liquid SO_2 are aprotic solvents.
E : Aprotic solvents do not influence the acidic or basic nature of solute.

15. S : The acidic nature of some cations is :
$$Al^{3+} > Be^{2+} > Na^+ > K^+$$
E : More is the effective nuclear charge on cation more is its acidic nature.

16. S : Acidic nature of boron trihalides is in the order :
$$BF_3 < BCl_3 < BBr_3 < BI_3$$
E : Basic nature of nitrogen trihalides is in the order :
$$NF_3 > NCl_3 > NBr_3 > NI_3$$

17. S : $CO + NaOH \xrightarrow[\text{High } T]{\text{High } P} HCOONa$.
E : CO although being neutral can acts as acid in the given reaction.

18. S : The dissociation constant of water at 60°C is 10^{-13}.
E : The pH of water is 6.5 and that it behaves as acid at 60°C.

19. S : Salting out action of sodium soap in presence of NaCl is based on common ion effect.
E : Salting out action of soap is based on the fact that as the concentration of Na^+ increases, the $RCOONa$ shows precipitation because $[RCOO^-][Na^+] > K_{sp}$.

20. S : Hydrolysis of salt is an exothermic phenomenon.
E : It involves breaking up of water molecule of produce acid and base respectively.

21. S : 0.1 *M* NaCN + 0.05 *M* HCl solution on mixing in equal volume form a buffer solution.

E : The solution after mixing contains a weak acid and its conjugate base and thus act as buffer.

22. S : The pH of NH_4OH remains unchanged on addition of NH_4Cl.

E : Addition of NH_4Cl suppresses the dissociation of NH_4OH due to common ion effect.

23. S : Heat given out during neutralisation of NaOH and HF is –13.7 kcal/eq.

E : F^- ion is more easily hydrated and thus heat of neutralisation of HF and NaOH is more.

24. S : The pH of pure water is less than 7 at 60°C.

E : As the temperature increases, pure water becomes slightly acidic.

25. S : The pH of human blood at body temperature is found to be 6.9.

E : Blood is alkaline in nature.

26. S : Solubility of AgCl is more in conc. HCl than in water.

E : AgCl form a complex with conc. HCl and thus solubility of AgCl increases in conc. HCl.

27. S : All Arrhenius acids are also Bronsted acids.

E : All Bronsted bases are also Lewis bases.

28. S : Cl^- is weak base than $C_2H_5O^-$.

E : Stronger is acid, weaker is its conjugate base.

29. S : H_3BO_3 in water behaves as monobasic acid.

E : The ionisation reaction is :

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

30. S : Solubility of AgCl is less in 0.1 *M* NaCl than in water.

E : In presence of NaCl, the solubility of AgCl is lowered on account of common ion effect.

31. S : In water orthoboric acid behaves as a weak monobasic acid.

E : In water orthoboric acid behaves as a proton donor.

32. S : HNO_3 is a stronger acid than HNO_2.

E : In HNO_3 there are two nitrogen-to-oxygen bonds whereas in HNO_2 there is only one.

ANSWERS (Statement Explanation Problems)

1. (d) For basic buffer $pOH = pK_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]}$

   $\therefore pH = pK_w - pOH$

2. (a) This is not common ion effect (At least one should be weak electrolyte). Here product of ionic concentration exceeds K_{sp} of $BaCl_2$.
3. (d) NH_4OH is relatively stronger than HCN.
4. (b) $K_{sp} = p^p \cdot q^q \cdot s^{(p+q)}$ for A_pB_q.
5. (a) $SnCl_2 + 2HgCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2\downarrow$

   $Hg_2Cl_2 + SnCl_2 \longrightarrow SnCl_4 + 2Hg\downarrow$

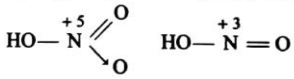
   This is redox change.
6. (b) HgI_2 forms soluble complex with KI

   $2KI + HgI_2 \longrightarrow K_2HgI_4$
7. (c) Explanation is correct reason for statement.
8. (c) —do—
9. (c) —do—
10. (c) —do—
11. (c) —do—
12. (c) Explanation is correct reason for statement.
13. (c) Explanation is correct reason for statement.
14. (c) Explanation is correct reason for statement.
15. (c) Explanation is correct reason for statement.
16. (a) Statement is correct due to back bonding in boron. In nitrogen halides the order is $NF_3 < NCl_3 < NBr_3 < NI_3$. On account of decreasing electronegativity of halogens, in NF_3, the lone pair is not released easily, due to more +ve charge on N.
17. (c) CO is acid, NaOH is base and salt formed is HCOONa.
18. (a) $K_w = 10^{-13}$ at 60°C $\therefore$ pH = 6.5; but water is neutral because pH scale contracts to 0 to 13.
19. (b) $RCOONa \rightarrow RCOO^- + Na^+$; In presence of NaCl, $[Na^+]$ increases and $[RCOO^-][Na^+]$ exceeds than K_{sp} of *R*COONa.
20. (b) Breaking up of bonds is endothermic.
21. (c) $NaCN + HCl \longrightarrow NaCl + HCN$

NaCN	HCl	NaCl	HCN
0.1	0.05	0	0
0.05	0	0.05	0.05

   The solution contains a weak acid HCN and its conjugate base CN^- and thus acts as buffer.
22. (b) The dissociation of NH_4OH is suppressed in presence of NH_4Cl and thus pH of NH_4OH decreases.
23. (b) Heat given out during complete neutralisation of HF and NaOH is – 16.4 kcal/eq. due to extensive hydration of F^- on NaF account of its smaller size.
24. (a) The scale of pH (0 to 14 at 25°C) changes to (0 to less than 14) as the temperature rises because K_w of water increases with temperature. Note that $[H^+] = [OH^-]$ and thus water remains neutral.
25. (d) Blood is alkaline and at body temperature (98°F) scale of pH lies between 0 to 13.6.
26. (c) Explanation is correct reason for statement.
27. (a) All Bronsted bases are not Lewis bases.
28. (c) Explanation is correct reason for statement.
29. (c) Explanation is correct reason for statement.
30. (a) The equilibrium $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

   $$K_{sp} = [Ag^+][Cl^-]$$

   if $[Cl^-]$ increases, the equilibrium is shifted in the backward direction, *i.e.*, solubility of AgCl decreases in presence of NaCl. Note this is Le Chatelier's principle application to solubility product. In common ion effect, there must be a weak electrolyte.
31. (a) $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$
32. (a) 

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1.

List A	List B
(a) Adsorption indicator	(i) $K_3Fe(CN)_6$
(b) External indicator	(ii) Starch
(c) Self indicator	(iii) Methyl red
(d) Acid-base indicator	(iv) $KMnO_4$

2.

List A	List B
(a) pH of amphioprotic salt	1. $-\frac{1}{2}[\log(K_{a_1}c_1 + K_{a_2}c_2)$
(b) pH of mixtures of two weak acids	2. $\frac{1}{2}[pK_{a_1} + pK_{a_2}]$
(c) pH of a basic buffer mixture	3. $pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$
(d) pH of an acidic buffer mixture	4. $pK_a + \log\frac{[\text{base}]}{[\text{conjugate acid}]}$
(e) pH of a salt solution of weak acid + strong base	5. $\frac{1}{2}[pK_w + pK_a + \log c]$
(f) pH of a salt solution of strong acid + weak base	6. $\frac{1}{2}[pK_w - pK_b - \log c]$

3.

List A	List B
(a) K_{sp} of $BaCl_2 \cdot 2H_2O$	1. $[Ba^{2+}][Cl^-]^2[H_2O]^2$
(b) K_{a_2} of dibasic acid	2. $[Ba^{2+}][Cl^-]^2$
(c) Conjugate acid of RNH_2	3. $[A^{-2}]$
(d) Conjugate base of RNH_2	4. RNH^-
(e) Solubility of AgCl in NaCl	5. RNH_3^+
	6. $S = \frac{K_{sp}}{[Cl^-]}$

Type II : More Than One Match Possible

4.

List A	List B
(a) Solubility of PbS	1. Increases in dil. HCl. *aq.*
(b) Solubility of Ag_2S	2. Increases in dil. NaCN *aq.*
(c) Solubility of CuS	3. Increases in dil. NH_3 *aq.*
(d) Solubility of $BaSO_4$	4. Increases in conc. HCl

Type III : Only One Match From Each List

5.

List A	List B	List C
A. Melting of ice	1. Favoured with decrease in *P*	a. $pH = \frac{1}{2}[pK_{a_1} + pK_{a_2}]$
B. Freezing of water	2. Favoured with increase in *P*	b. $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$
C. 0.1 *M* NaHS (*aq.*)	3. Hydrolysis and protonation	c. Favoured by addition of ice
D. 0.1 *M* CH_3COONH_4 (*aq.*)	4. Hydrolysis	d. Not favoured by addition of ice
E. 0.1 *M* NH_4Cl (*aq.*)	5. Acidic	e. $pH = \frac{1}{2}[pK_a - \log C]$

ANSWERS

1. a–ii; b–i; c–iv; d-iii
2. a–2; b–1; c–4; d-3; e–5; f–6
3. a–2; b–3; c–5; d-4; e–6;
4. a–1,3,4; b–1,2,3,4; c–1,2,3,4; d-4
5. A–2–d; B–1–c; C–3–a; D–4–b; E–5–e