# IONIC EQUILIBRIUM-I

## Exercise-1

✍ **Marked questions are recommended for Revision.**

## PART - I : SUBJECTIVE QUESTIONS

### Section (A) : Acid-Base Concepts

**Commit to memory :**

Polyprotic Arrhenius acid : 2 or more replaceable H per acid molecule.
Polyprotic Arrhenius base : 2 or more replaceable OH per base molecule.
Acid – 1 $H^+$ = its Conjugate Base
Base + 1 $H^+$ = its Conjugate Acid
Amphiprotic species : $H^+$ donor as well as acceptor.
Lewis acid : Lone pair acceptor
Lewis base : Lone pair donor

**A-1.** (a) Select Polyprotic Arrhenius acids from the following : $H_3PO_2$, $H_3PO_3$, $H_3BO_3$, HCOOH, $(COOH)_2$.
(b) Write conjugate acids of $SO_4^{2-}$, $RNH_2$, $NH_2^-$, $C_2H_5OC_2H_5$, $F^-$
(c) Write conjugate base of $HNO_2$, $OH^-$, $H_2CO_3$, $HClO_4$.
(d) Write conjugate acid and conjugate base of following amphoteric species :
$HS^-$, $NH_3$, $C_2H_5OH$, $H_2O$

(e) Classify the following into Lewis acid & Lewis base : $H^+$, $FeCl_3$, $(CH_3)_3N$, $F^-$, $\ddot{C}H_2$

**A-2.** Classify the following into acid, base and amphiprotic species on the basis of protonic concept :
(i) $H_2PO_2^-$ (ii) $H_2PO_3^-$ (iii) $H_2PO_4^-$ (iv) $HPO_3^{2-}$
(v) $HPO_4^{2-}$ (vi) $NH_4^+$ (vii) $CH_3COOH_2^+$

**A-3.** Comment upon $H_2O$ as an Arrhenius acid/base, Bronsted–Lowry acid/base and Lewis acid/base.

### Section (B) : Properties of water, pH scale, Autoprotolysis

**Commit to memory :**

$K_w = [H^+][OH^-] = 10^{-14}$ at 25°C
$[H^+] = [OH^-]$ (in water / a neutral solution)
$pH = -\log[H^+]$ ; $pOH = -\log[OH^-]$
For $H_2O$, pH & pOH ↓ with ↑ in temperature
$pH + pOH = pK_w = 14$ (for an aqueous solution at 25°C)
$K_{\text{self ionisation}}$ of HA = $[A^-][H_2A^+]$

**B-1.** At –50°C, liquid $NH_3$ has ionic product is $10^{-30}$. How many amide ($NH_2^-$) ions are present per $mm^3$ in pure liquid $NH_3$ ? (Take $N_A = 6 \times 10^{23}$)

### Section (C) : Relation between $K_a$ and $K_b$ for conjugate acid - base pair

**Commit to memory :**

$K_{a\,(\text{acid})} \times K_{b\,(\text{conjugate base})} = K_w$
$pK_{a\,(\text{acid})} + pK_{b\,(\text{conjugate base})} = pK_w = 14$ (at 25°C)

**C-1.** What is ionisation constant of HOCl, if $K_b$ of $OCl^- = 4 \times 10^{-10}$ ? Also find its $pK_a$.

**C-2.** $K_{a_1}$, $K_{a_2}$ and $K_{a_3}$ values for $H_3PO_4$ are $10^{-3}$, $10^{-8}$ and $10^{-12}$ respectively. If $K_w$ ($H_2O$) = $10^{-14}$, then :
(i) What is dissociation constant of $HPO_4^{2-}$ ?
(ii) What is $K_b$ of $HPO_4^{2-}$ ?
(iii) What is $K_b$ of $H_2PO_4^-$ ?
(iv) What is order of $K_b$ of $PO_4^{3-}$ ($K_{b_3}$), $HPO_4^{2-}$($K_{b_2}$) and $H_2PO_4^-$($K_{b_1}$) ?

## Section (D) : pH calculation : Strong acid solutions, Strong base solutions, Solutions containing mixture of two or more strong acids, Solutions containing mixture of two or more strong bases, Solutions containing mixture of strong acid and strong base

**Commit to memory :**

Strong acid solution: $[H^+]$ = Molarity of strong acid solution × number of $H^+$ ions per acid molecule.

Strong base solution: $[OH^-]$ = Molarity of strong base solution × number of $OH^-$ ions per base molecule.

Mixture of two strong acids : $[H^+]_f = \dfrac{[H^+]_1V_1 + [H^+]_2V_2}{V_1 + V_2}$

Mixture of two strong bases : $[OH^-]_f = \dfrac{[OH^-]_1V_1 + [OH^-]_2V_2}{V_1 + V_2}$

Mixture of a strong acid and a strong base :

If $[H^+]V_1 > [OH^-]V_2$

$[H^+] = \dfrac{[H^+]V_1 - [OH^-]V_2}{V_1 + V_2}$

final solution will be acidic in nature

If $[OH^-]V_2 > [H^+]V_1$

$[OH^-] = \dfrac{[H^+]V_2 - [OH^-]V_1}{V_1 + V_2}$

final solution will be basic in nature

Further, $[H^+]_f = \dfrac{10^{-14}}{[OH^-]_f}$ (at 25ºC)

**D-1.** Calculate pH of following solutions :

(i) 0.001 M $HNO_3$, (ii) 0.005 M $H_2SO_4$ , (iii) 0.01 M KOH

(iv) $10^{-8}$ M NaOH, (v) 0.0008 M $Ba(OH)_2$ .

**D-2.** Calculate the pH of the following solutions :

(i) 2.21 g of T□OH dissolved in water to give 2 litre of solution. (Assume T□OH to be a strong base)

(ii) 0.49% w/v $H_2SO_4$ solution

(iii) $\dfrac{M}{1000}$ $Sr(OH)_2$ solution is diluted to quadruple volume.

(iv) 1 mL of 12 M HCl is diluted with water to obtain 1 litre of solution.

**D-3.** Calculate the pH of solution obtained by mixing 10 mL of 0.2 M HCl and 40 mL of 0.1 M $H_2SO_4$.

**D-4.** Calculate the pH of the resulting solution formed by mixing the following solutions :

(a) 20 mL of 0.2 M $Ba(OH)_2$ + 30 mL of 0.1 M HCl

(b) 2 mL of 0.1 M HCl + 10 mL of 0.01 M $Sr(OH)_2$

(c) 10 mL of 0.1 M $H_2SO_4$ + 10 mL of 0.1 M KOH.

## Section (E) : Ostwald dilution law, pH calculation : Solutions of weak monoprotic acid, Solutions of weak monoacidic base

**Commit to memory :**

AB (aq) $\rightleftharpoons$ $A^+$ (aq) + $B^-$ (aq) ; $K_{eq} = \dfrac{[A^+][B^-]}{[AB]} = \dfrac{C\alpha \;.\; C\alpha}{C(1-\alpha)} = \dfrac{C\alpha^2}{(1-\alpha)}$

$\alpha = \sqrt{\dfrac{K_{eq}}{C}}$ ; $[A^+] = [B^-] = C\,\alpha = \sqrt{CK_{eq}}$ (both valid if $\alpha$ < 0.1 or 10%)

Weak Acid (monoprotic) solution : $\alpha = \sqrt{\dfrac{K_a}{C}}$ ; $pH = \dfrac{1}{2}(pK_a - \log C)$ (both valid if $\alpha$ < 0.1 or 10%)

Weak base (monoacidic) solution : $\alpha = \sqrt{\dfrac{K_b}{C}}$ ; $pOH = \dfrac{1}{2}(pK_b - \log C)$ (both valid if $\alpha$ < 0.1 or 10%)

$\dfrac{\text{Acid strength of } HA_1}{\text{Acid strength of } HA_2} = \dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}}$ ; $\dfrac{\text{Basic strength of } BOH_1}{\text{Basic strength of } BOH_2} = \dfrac{\alpha_1}{\alpha_2} = \sqrt{\dfrac{K_{b_1}}{K_{b_2}}}$

**E-1.** Acetic acid gets 1.3% ionised in its decimolar solution. What is be the ionisation constant of acetic acid?

**E-2.** Prove that degree of dissociation of a weak monoprotic acid is given by :

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

where $K_a$ is its dissociation constant.

**E-3.** Calculate the pH of a 500 mL solution of 1 M BOH. ($K_b = 2.5 \times 10^{-5}$)

**E-4.** Whose pH increases by greater value on dilution from initial pH = 2 ?
(a) $CH_3COOH$ solution (b) HCl solution.

## Section (F) : Salt hydrolysis, pH calculation : Solutions of salt of monoprotic acid and monoacidic base

**Commit to memory :**

Salt of strong acid and weak base : $K_h \times K_b = K_w$ ; $h = \sqrt{\frac{K_h}{c}}$ ; $pH = \frac{1}{2}[pK_w - pK_b - \log c]$ (valid if h < 0.1 or 10%)

Salt of strong base and weak acid : $K_h \times K_a = K_w$ ; $h = \sqrt{\frac{K_h}{c}}$ ; $pH = \frac{1}{2}[pK_w + pK_a + \log c]$ (valid if h < 0.1 or 10%)

Salt of weak acid and weak base : $K_h \times K_a \times K_b = K_w$ ; $\left(\frac{h}{1-h}\right) = \sqrt{K_h}$ ; $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

**F-1.** Which of the following ions or compounds in a solution tend to produce an acidic, a basic or a neutral solution ?
(a) $C_2H_5O^-$ (b) $Cu^{+2}$ (c) $SO_3^{2-}$ (d) $F^-$ (e) $NH_4^+$ (f) $CH_3COONa$
(g) $KNO_3$ (h) NaOCl (i) $Na_2CO_3$ (j) $ZnCl_2$

**F-2.** Calculate pH of 0.2 M aqueous solution of sodium butyrate. Given : $K_a$ of butyric acid = $2 \times 10^{-5}$.

**F-3.** A 0.25 M solution of pyridinium chloride $C_5H_5NH^+Cl^-$ was found to have a pH of 2.75. What is $K_b$ for pyridine, $C_5H_5N$ ?

**F-4.** Calculate the percentage hydrolysis & the pH of 0.02 M $CH_3COONH_4$. $K_b(NH_3) = 1.6 \times 10^{-5}$, $K_a(CH_3COOH) = 1.6 \times 10^{-5}$.

# PART - II : ONLY ONE OPTION CORRECT TYPE

## Section (A) : Acid-Base Concepts

**Commit to memory :**

Polyprotic Arrhenius acid : 2 or more replaceable H per acid molecule.
Polyprotic Arrhenius base : 2 or more replaceable OH per base molecule.
Acid – 1 $H^+$ = its Conjugate Base
Base + 1 $H^+$ = its Conjugate Acid
Amphiprotic species : $H^+$ donor as well as acceptor.
Lewis acid : Lone pair acceptor
Lewis base : Lone pair donor

**A-1.** An acid with molelcular formula $C_7H_6O_3$ forms three types of sodium salts. i.e. $C_7H_5O_3Na$, $C_7H_4O_3Na_2$ and $C_7H_3O_3Na_3$. The basicity of the acid is :
(A) One (B) Two (C) Three (D) Six

**A-2.** Select the incorrect option :
(A) $H_3PO_4$ is a tribasic acid. (B) $H_3BO_3$ is not an Arhenius acid.
(C) $Sr(OH)_2$ is a strong diacidic base. (D) $NH_3.H_2O$ is a strong monoacidic base.

**A-3.** In the reaction $HC_2O_4^-$ (aq) + $PO_4^{3-}$(aq) $\rightleftharpoons$ $HPO_4^{2-}$(aq) + $C_2O_4^{2-}$(aq), which are the two Bronsted bases ?

(A) $HC_2O_4^-$ and $PO_4^{3-}$ (B) $HPO_4^{2-}$ and $C_2O_4^{2-}$
(C) $HC_2O_4^-$ and $HPO_4^{2-}$ (D) $PO_4^{3-}$ and $C_2O_4^{2-}$

**A-4.** The following equilibrium is established when $HClO_4$ is dissolved in weak acid HF solvent :

$$HF + HClO_4 \rightleftharpoons ClO_4^- + H_2F^+$$

Which of the following is correct set of conjugate acid base pair ?

(A) HF and $HClO_4$ (B) HF and $ClO_4^-$ (C) HF and $H_2F^+$ (D) $HClO_4$ & $H_2F^+$

**A-5.** Which of the following correctly explains the nature of boric acid in aqueous medium ?

(A) $H_3BO_3 \xrightarrow{H_2O} H_3O^+ + H_2BO_3^-$ (B) $H_3BO_3 \xrightarrow{2H_2O} 2H_3O^+ + HBO_3^{2-}$

(C) $H_3BO_3 \xrightarrow{3H_2O} 3H_3O^+ + BO_3^{3-}$ (D) $H_3BO_3 \xrightarrow{H_2O} B(OH)_4^- + H^+$

## Section (B) : Properties of water, pH scale, Autoprotolysis

**Commit to memory :**

$K_w = [H^+] [OH^-] = 10^{-14}$ at 25°C
$[H^+] = [OH^-]$ (in water / a neutral solution)
pH = –log $[H^+]$ ; pOH = –log $[OH^-]$
For $H_2O$, pH & pOH ↓ with ↑ in temperature
pH + pOH = $pK_w$ = 14 (for an aqueous solution at 25°C)
$K_{\text{self ionisation}}$ of HA = $[A^-] [H_2A^+]$

**B-1.** ✍ Which of the following expression is not true ?

(A) $[H^+] = [OH^-] = \sqrt{K_w}$ for a neutral solution at all temperatures.

(B) $[H^+] > \sqrt{K_w}$ & $[OH^-] < \sqrt{K_w}$ for an acidic solution.

(C) $[H^+] < \sqrt{K_w}$ & $[OH^-] > \sqrt{K_w}$ for an alkaline solution.

(D) $[H^+] = [OH^-] = 10^{-7}$ M for a neutral solution at all temperatures .

**B-2.** pOH of $H_2O$ is 7 at 298 K. If water is heated to 350 K, which of the following statement should be true ?

(A) pOH will decrease. (B) pH will increase.
(C) pOH will remain 7. (D) Both (A) and (B).

**B-3.** $K_w$ of $H_2O$ at 373 K is $1 \times 10^{-12}$. Identify, which of the following is incorrect :

(A) pH + pOH = 12, for every aqueous solutions.
(B) pH of $H_2O$ is 6.
(C) $\alpha_{H_2O}$ has increased from its value at 298 K.
(D) $H_2O$ is acidic.

**B-4.** In pure HCOOH liquid, concentration of $HCOO^- = 10^{-3}$ M at 27ºC. What is the self ionisation constant at 27ºC ($K = [HCOOH_2^+] [HCOO^-]$) ?

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

## Section (C) : Relation between $K_a$ and $K_b$ for conjugate acid-base pair

**Commit to memory :**

$K_{a\,(\text{acid})} \times K_{b\,(\text{conjugate base})} = K_w$
$pK_{a\,(\text{acid})} + pK_{b\,(\text{conjugate base})} = pK_w = 14$ (at 25°C)

**C-1.** Given %

$$HF + H_2O \overset{K_a}{\rightleftharpoons} H_3O^+ + F^-$$

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

Which relation is correct.

(A) $K_b = \dfrac{1}{K_a}$ (B) $K_a \,.\, K_b = K_w$ (C) $K_a.K_b.K_w = 1$ (D) $\dfrac{K_a}{K_b} = K_w$

**C-2.** Which of the following is incorrect ?
(A) $K_a$ (weak acid). $K_b$ (conjugate weak base) = $K_w$
(B) $K_a$ (strong acid). $K_b$ (conjugate weak base) = $K_w$
(C) $K_a$ (weak acid). $K_b$ (weak base) = $K_w$
(D) $K_a$ (weak acid). $K_b$ (conjugate strong base) = $K_w$

## Section (D) : pH calculation : Strong acid solutions, Strong base solutions, Solutions containing mixture of two or more strong acids, Solutions containing mixture of two or more strong bases, Solutions containing mixture of strong acid and strong base

**Commit to memory :**

Strong acid solution : $[H^+]$ = Molarity of strong acid solution × number of $H^+$ ions per acid molecule.

Strong base solution : $[OH^-]$ = Molarity of strong base solution × number of $OH^-$ ions per base molecule.

Mixture of two strong acids : $[H^+]_f = \dfrac{[H^+]_1V_1 + [H^+]_2V_2}{V_1 + V_2}$

Mixture of two strong bases : $[OH^-]_f = \dfrac{[OH^-]_1V_1 + [OH^-]_2V_2}{V_1 + V_2}$

Mixture of a strong acid and a strong base :

If $[H^+]V_1 > [OH^-]V_2$

$[H^+] = \dfrac{[H^+]V_1 - [OH^-]V_2}{V_1 + V_2}$

final solution will be acidic in nature

If $[OH^-]V_2 > [H^+]V_1$

$[OH^-] = \dfrac{[H^+]V_2 - [OH^-]V_1}{V_1 + V_2}$

final solution will be basic in nature

Further, $[H^+]_f = \dfrac{10^{-14}}{[OH^-]_f}$ (at 25ºC)

**D-1.** The $[OH^-]$ in 100 mL of 0.016 M HCl (aq) is :
(A) $6.25 \times 10^{-12}$ M (B) $3 \times 10^{-10}$ M (C) $6.25 \times 10^{-13}$ M (D) $1.6 \times 10^{-3}$ M

**D-2.** How many moles of NaOH must be removed from one litre of its aqueous solution to change its pH from 12 to 11 ?
(A) 0.009 (B) 0.01 (C) 0.09 (D) 0.1

**D-3.** Which statement/relationship is correct ?
(A) pH of aqueous solutions of 0.1 M $HNO_3$, 0.1M HCl, 0.1M HI at 25ºC is not equal.
(B) For a dilute solution, pH $= -\log \dfrac{1}{[H^+]}$
(C) At 25°C, the pH of pure water is 7.
(D) The value of $pK_w$ at 25°C is 7.

**D-4.** Upon mixing equal volume of two solutions of strong acids having pH values 2 & 4, resulting solution will have pH :
(A) equal to 3 (B) closer to 2 than 4
(C) closer to 4 than 2 (D) closer to 3 than 2

**D-5.** On adding 0.04 g solid NaOH to a 100 mL, $\dfrac{M}{200}$ $Ba(OH)_2$ solution, determine change in pH :
(A) 0 (B) +0.3 (C) –0.3 (D) +0.7

**D-6.** Upon mixing equal volume of a strong acid solution (HA) and a strong base (BOH) solution, pH of resulting solution :
(A) may be less than 7 (B) may be greater than 7
(C) will be equal to 7 (D) Both (A) & (B)

**D-7.** Which of the following solutions will have pH close to 1 ?
(A) 100 mL of M/10 HCl + 100 mL of M/10 NaOH
(B) 55 mL of M/10 HCl + 45 mL of M/10 NaOH

(C) 10 mL of M/10 HCl + 90 mL of M/10 NaOH
(D) 75 mL of M/5 HCl + 25 mL of M/5 NaOH.

## Section (E) : Ostwald dilution law, pH calculation : Solutions of weak monoprotic acid, Solutions of weak monoacidic base

**Commit to memory :**

$$AB\,(aq) \rightleftharpoons A^+\,(aq) + B^-\,(aq)\ ;\ K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha\ .\ C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\alpha = \sqrt{\frac{K_{eq}}{C}}\ ;\ [A^+] = [B^-] = C\,\alpha = \sqrt{CK_{eq}}\ \text{(both valid if } \alpha < 0.1 \text{ or } 10\%)$$

Weak Acid (monoprotic) solution : $\alpha = \sqrt{\frac{K_a}{C}}$ ; pH = $\frac{1}{2}$ ($pK_a$ – log C) (both valid if $\alpha$ < 0.1 or 10%)

Weak base (monoacidic) solution : $\alpha = \sqrt{\frac{K_b}{C}}$ ; pOH = $\frac{1}{2}$ ($pK_b$ – log C) (both valid if $\alpha$ < 0.1 or 10%)

$$\frac{\text{Acid strength of } HA_1}{\text{Acid strength of } HA_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}\ ;\ \frac{\text{Basic strength of } BOH_1}{\text{Basic strength of } BOH_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

**E-1.** Which of the following has the maximum degree of ionisation ?
(A) 1 M $NH_3$ (B) 0.001 M $NH_3$ (C) 0.1 M $NH_3$ (D) 0.0001 M $NH_3$.

**E-2.** $K_a$ for formic acid and acetic acid are $1.8 \times 10^{-4}$ and $1.8 \times 10^{-5}$ respectively. The relative strength of acids is :
(A) 10 : 1 (B) 1 : 10 (C) 1 : $\sqrt{10}$ (D) $\sqrt{10}$ : 1

**E-3.** $K_a$ for a monobasic acid, whose 0.1 M solution has pH of 4.5, is :
(A) $10^{-10}$ (B) $10^{-8}$ (C) $\sqrt{10} \times 10^{-4}$ (D) $\sqrt{10} \times 10^{-6}$

## Section (F) : Salt hydrolysis, pH calculation : Solutions of salt of monoprotic acid and monoacidic base.

**Commit to memory :**

Salt of strong acid and weak base : $K_h \times K_b = K_w$ ; $h = \sqrt{\frac{K_h}{c}}$ ; pH = $\frac{1}{2}$ [$pK_w$–$pK_b$–log c] (valid if h < 0.1 or 10%)

Salt of strong base and weak acid : $K_h \times K_a = K_w$ ; $h = \sqrt{\frac{K_h}{c}}$ ; pH = $\frac{1}{2}$ [$pK_w$+$pK_a$+log c] (valid if h < 0.1 or 10%)

Salt of weak acid and weak base : $K_h \times K_a \times K_b = K_w$ ; $\left(\frac{h}{1-h}\right) = \sqrt{K_h}$ ; pH = $\frac{1}{2}$ [$pK_w$+$pK_a$–$pK_b$]

**F-1.** Aqueous solution of $NH_4Cl$ is ____ in nature due to behaviour of ____ ion in solution :
(A) acidic ; $NH_4^+$ (B) alkalline ; $NH_4^+$ (C) acidic ; $Cl^-$ (D) alkalline ; $Cl^-$

**F-2.**✍ The chloride salt of a certain weak monoacidic organic base is hydrolysed to an extent of 3% in its 0.1M solution at 25ºC. Given that the ionic product of water is $10^{-14}$ at this temperature, what is the dissociation constant of the base?
(A) ≈ 1 x $10^{-10}$ (B) ≈ 1 x $10^{-9}$ (C) 3.33 x $10^{-9}$ (D) 3.33 x $10^{-10}$

**F-3.** 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 < $NH_4Cl$

**F-4.** The degree of hydrolysis of a salt of weak monobasic acid and weak monoacidic base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be :
(A) 100 % (B) 50 % (C) 25 % (D) None of these

## PART - III : MATCH THE COLUMN

**1.** Match the Column.

| | **Column-I** | | **Column-II** |
|---|---|---|---|
| (A) | HCl | (p) | Lewis acid |
| (B) | KOH | (q) | Arrhenius acid |
| (C) | $NH_3$ | (r) | Lewis base |
| (D) | $BF_3$ | (s) | Arrhenius base |

# Exercise-2

✍ **Marked questions are recommended for Revision.**

## PART - I : ONLY ONE OPTION CORRECT TYPE

**1.** The self ionisation constant for pure formic acid, K = $[HCOOH_2^+][HCOO^-]$ has been estimated as $10^{-6}$ at room temperature. The density of formic acid is 1.15 g/cm$^3$. What percentage of formic acid molecules in pure fomic acid are converted to formate ion ?
(A) 0.002% (B) 0.004% (C) 0.006% (D) 0.008%

**2.** $pK_a$ for an acid HA is 6. The value of K for the reaction $A^- + H_3O^+ \rightleftharpoons HA + H_2O$ is :
(A) $1 \times 10^{-6}$ (B) $1 \times 10^{8}$ (C) $1 \times 10^{-8}$ (D) $1 \times 10^{6}$

**3.** $10^{-6}$ M HCl is diluted to 100 times. Its pH is :
(A) 6 (B) 8 (C) 6.98 (D) 7.02

**4.** Which of the following solutions has a pH exactly equal to 8 ?
(A) $10^{-8}$ M HCl solution (B) Solution containing $10^{-8}$ M $H^+$
(C) $2 \times 10^{-6}$ M $Ba(OH)_2$ solution (D) $10^{-8}$ M NaOH solution

**5.**✍ 10 mL of a strong acid solution of pH = 2 are mixed with 990 mL of another strong acid solution of pH = 4. The pH of the resulting solution will be :
(A) 3 (B) 3.3 (C) 3.7
(D) Molecular formula of both strong acids should be known to answer above question.

**6.** % dissociation of a 0.024 M solution of a weak acid HA ($K_a = 2 \times 10^{-3}$) is :
(A) 0.25% (B) ≈ 29% (C) 25% (D) ≈ 0.29%

**7.** For a weak base BOH, $K_b = 10^{-4}$. Calculate pH of $10^{-4}$ M BOH solution. (Take log 6.2 = 0.79)
(A) 10 (B) 9.79 (C) 8 (D) None of these

**8.**✍ Four separate solutions of sodium salts NaW, NaX, NaY and NaZ have pH 7, 9, 10 and 11 respectively, when each solution has concentration 0.1 M. Then the strongest acid is :
(A) HW (B) HX (C) HY (D) HZ

## PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

**1.**✍ If an acid-base reaction $HA(aq) + B^-(aq) \rightleftharpoons HB(aq) + A^-(aq)$ has $K_{eq} = 10^{-4}$, how many of the following statements are true ?
(i) HB is stronger acid than HA (ii) HA is stronger acid than HB
(iii) HA and HB have the same acidic strength (iv) $B^-$ is stronger base than $A^-$
(v) $A^-$ is stronger base than $B^-$ (vi) $B^-$ and HB are conjugate acid-base pair
(vii) $A^-$ is the conjugate base of acid HA. (viii) HA can be $HSO_4^-$ and HB can be HCOOH.
(ix) $A^-$ can be $F^-$ and $B^-$ can be $CN^-$.

**2.** What is pOH of an aqueous solution with $[H^+] = 10^{-2}$ M and $K_w = 2 \times 10^{-12}$ ? Report your answer after dividing by 2 and round it off to the nearest whole number.

**3.** Percentage ionisation of water as follows at certain temperature is $3.6 \times 10^{-7}$ %. Calculate $K_w$ and pH of water at this temperature. $2H_2O \rightleftharpoons H_3O^+ + OH^-$

**4.** 0.1 mole HCl is dissolved in distilled water of volume V. Then, at $\lim\limits_{V \to \infty}$, $(pH)_{solution}$ is equal to .....

**5.**✍ Determine $pK_a(H_2O) + pK_a(H_3O^+)$.

**6.** What volume (in L) of water must be added to 1 L of 0.1 M solution of B (weak organic monoacidic base; ionisation constant = $10^{-5}$) to triple the % ionisation of base ?

**7.**✍ If $pH_{x\%}$ is the pH of a 1 M weak monoprotic acid which is x % ionised, then find the value of $\left[\frac{pH_{50\%}}{pH_{10\%}}\right] \times 100$.

**8.** If the equilibrium constant for the reaction of weak acid HA with a strong base is $10^9$, then determine pH of 0.1 M NaA solution.

**9.**✍ What is the concentration of $CH_3COOH(aq)$ in a solution prepared by dissolving 0.01 mole of $NH_4^+CH_3COO^-$ in 1 L $H_2O$ ? Report your answer after multiplying by $9 \times 10^5$.
$[K_a(CH_3COOH) = 1.8 \times 10^{-5};\ K_b(NH_3.H_2O) = 1.8 \times 10^{-5}]$

## PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

**1.** Which statement(s) is/are correct ?
(A) All Bronsted bases are also Lewis bases.
(B) All Bronsted acids are not Lewis acids.
(C) Most cations are acids and most anions are bases.
(D) All Bronsted bases are also Arrhenius bases.

**2.** Select the incorrect statement(s) :
(A) $NH_4^+$ (aq) is a strong acid.
(B) $CH_3COO^-$ (aq) is a weak base.
(C) $H^-$ is a weak base.
(D) $HS^-$ is a weak acid as well as a weak base.

**3.** For pure water :
(A) $pK_w$ increases with decrease in temperature.
(B) Absolute dissociation constant decreases with decrease in temperature.
(C) $\alpha_{H_2O}$ increases with decrease in temperature.
(D) Both pH and pOH decrease with rise in temperature.

**4.**✍ One litre of a strong acid solution contains $10^{-5}$ moles of $H^+$ ions. Then :
(A) pOH = 9.
(B) Percentage ionisation of water in solution is $1.8 \times 10^{-9}$ %.
(C) Number of $OH^-$ ions per mL of solution = $6.022 \times 10^{15}$.
(D) $[H^+]_{\text{from } H_2O} = 10^{-9}$ M

**5.**✍ Equal volumes of 0.2 M HCl and 0.2 M $Sr(OH)_2$ are mixed. Which of the following statement is/are correct ?
(A) $[Sr^{2+}] = 0.1$ M
(B) $[Cl^-] = 0.1$ M
(C) pH of resulting solution = 13
(D) Solution is neutral.

**6.** If 0.1 M $CH_3COOH$ ($K_a = 1.8 \times 10^{-5}$) is diluted at 25°C, then which of the following will be correct ?
(A) $[H^+]$ will increase.
(B) pH will increase.
(C) number of $H^+$ ions will increase.
(D) $K_a$ will increase.

**7.** Degree of hydrolysis for a salt of strong acid and weak base :
(A) is independent of dilution
(B) increases with dilution
(C) increases with decrease in $K_b$ of the bases
(D) decreases with decrease in temperature.

**8.**✍ Equal volumes of following solutions are mixed, in which case the pH of resulting solution will be average value of pH of two solutions.
(A) Aqueous HCl of pH = 2, aqueous NaOH of pH = 12
(B) Aqueous HCl of pH = 2, aqueous HCl of pH = 4
(C) Aqueous NaOH of pH = 12, aqueous NaOH of pH = 10
(D) Aqueous $CH_3COOH$ of pH = 5, aqueous $NH_3$ of pH = 9. $[K_a(CH_3COOH) = K_b(NH_3)]$

## PART - IV : COMPREHENSION

**Read the following passages carefully and answer the questions.**

**Comprehension # 1**

pH calculation upon dilution of a strong acid solution is generally done by equating $n_{H^+}$ in original solution & diluted solution. However, if strong acid solution is very dilute, then $H^+$ from water are also to be considered.

Take log 3.7 = 0.568 and answer the following questions.

**1.**✍ A 1 litre solution of pH = 4 (solution of a strong acid) is added to the 7/3 litre of water. What is the pH of resulting solution ?

(A) 4.52 (B) 4.365 (C) 4.4 (D) 4.432

**2.**✍ A 1 litre solution of pH = 6 (solution of a strong acid) is added to the 7/3 litre of water. What is the pH of resulting solution ? Neglect the common ion effect on $H_2O$.

(A) 6.4 (B) 6.52 (C) 6.365 (D) 6.432

**Comprehension # 2**

Consider a solution of $CH_3COONH_4$ which is a salt of weak acid & weak base.

The equilibrium involved in the solutions are :

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ ..........(1)

$NH_4^- + H_2O \rightleftharpoons NH_3.H_2O + H^+$ ..........(2)

$H^+ + OH^- \rightleftharpoons H_2O$ ..........(3)

If we add these three reactions, then the net reaction is :

$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_3.H_2O$ ..........(4)

Both $CH_3COO^-$ and $NH_4^+$ get hydrolysed independently and their hydrolysis depends on :

(i) their initial concentration

(ii) the value of $K_h$ which is $\frac{K_w}{K_a}$ for $CH_3COO^-$ and $\frac{K_w}{K_b}$ for $NH_4^+$.

Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore unless & until the value of $\frac{K_w}{K_a}$ and $\frac{K_w}{K_b}$ or $K_a$ and $K_b$ is same, the degree of hydrolysis of ion can't be same.

To explain why we assume that degree of hydrolysis of cation and anion is same, we need to now look at the third reaction i.e., combination of $H^+$ and $OH^-$ ions. It is obvious that this reaction happens only because one reaction produced $H^+$ ion and the other produced $OH^-$ ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium constant is affected more by the common ion effect. For the same reason, if for any reason a reaction is made to occur to a greater extent by the comsumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.

Therefore we conclude that firstly the hydrolysis of both the ions ocurs more in the presence of each other (due to consumption of the product ions) than in each other's absence. Secondly, the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of $K_h$) is affected more than the one whose $K_h$ is greater. Hence, we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolysed in the presence of each other.

Now answer the following questions :

**3.**✍ In the hydrolysis of salt of weak acid & weak base :

(A) degree of hydrolysis of cation and anion is different

(B) degree of hydrolysis of cation and anion is same

(C) degree of hydrolysis of cation and anion is different and they can never be assumed same.

(D) degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolysed in the presence of each other.

**4.**✍ For 0.1 M $CH_3COONH_4$ salt solution given, $K_a$ ($CH_3COOH$) = $K_b$ ($NH_3.H_2O$) = $2 \times 10^{-5}$.
In this case, degree of hydrolysis of cation and anion are :
(A) exactly same
(B) slightly different
(C) can't say
(D) different but can be take approximatly same

# Exercise-3

## JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

### JEE(MAIN) OFFLINE PROBLEMS

**1.** The conjugate base of $H_2PO_4^-$ is : **[AIEEE-2004, 3/225]**
(1) $PO_4^{3-}$ (2) $P_2O_5$ (3) $H_3PO_4$ (4) $HPO_4^{2-}$

**2.** What is the conjugate base of $OH^-$ ? **[AIEEE-2005, 3/225]**
(1) $O_2$ (2) $H_2O$ (3) $O^-$ (4) $O^{2-}$

**3.** Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be : **[AIEEE-2005, 3/225]**
(1) $3.98 \times 10^8$ (2) $3.88 \times 10^6$ (3) $3.68 \times 10^{-6}$ (4) $3.98 \times 10^{-6}$

**4.** The first and second dissociation constants of an acid $H_2A$ are $1.0 \times 10^{-5}$ and $5.0 \times 10^{-10}$ respectively. The overall dissociation constant of the acid will be : **[AIEEE-2007, 3/120]**
(1) $5.0 \times 10^{-15}$ (2) $0.2 \times 10^5$ (3) $5.0 \times 10^{-5}$ (4) $5.0 \times 10^{15}$

**5.** The $pK_a$ of a weak acid, HA, is 4.80. The $pK_b$ of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be : **[AIEEE-2008, 3/105]**
(1) 4.79 (2) 7.01 (3) 9.22 (4) 9.58

**6.** Three reactions involving $H_2PO_4^-$ are given below : **[AIEEE-2010, 4/144]**
(i) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$
(ii) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$
(iii) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$
In which of the above, does $H_2PO_4^-$ act as an acid ?
(1) (ii) only (2) (i) and (ii) (3) (iii) only (4) (i) only

**7.** The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, $K_a$ of the acid is: **[AIEEE-2012, 4/120]**
(1) $3 \times 10^{-1}$ (2) $1 \times 10^{-3}$ (3) $1 \times 10^{-5}$ (4) $1 \times 10^{-7}$

**8.** How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? **[JEE(Main) 2013, 4/120]**
(1) 0.1 L (2) 0.9 L (3) 2.0 L (4) 9.0 L

**9.** $pK_a$ 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, 4/120]**
(1) 6.9 (2) 7.0 (3) 1.0 (4) 7.2

**10.** Which of the following salts is the most basic in aqueous solution? **[JEE(Main) 2018, 4/120]**
(1) $FeCl_3$ (2) $Pb(CH_3COO)_2$ (3) $Al(CN)_3$ (4) $CH_3COOK$

### JEE(MAIN) ONLINE PROBLEMS

**1.** Assuming that the degree of hydrolysis is small, the pH of 0.1 M solution of sodium acetate ($K_a = 1.0 \times 10^{-5}$) will be : **[JEE(Main) 2014 Online (11-04-14), 4/120]**
(1) 5.0 (2) 6.0 (3) 8.0 (4) 9.0

**2.** The conjugate base of hydrazoic acid is : **[JEE(Main) 2014 Online (12-04-14), 4/120]**
(1) $N^{-3}$ (2) $N_3^-$ (3) $N_2^-$ (4) $HN_3^-$

**3.** What quantity (in mL) of a 45% acid solution of a mono-protic strong acid must be mixed with a 20% solution of the same acid to produce 800 mL of a 29.875% acid solution ?

**[JEE(Main) 2017 Online (09-04-17), 4/120]**

(1) 330 (2) 316 (3) 320 (4) 325

**4.** Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of the them will be equal to 1?

**[JEE(Main) 2018 Online (15-04-18), 4/120]**

(1) 100 mL $\frac{M}{10}$ HCl + 100 mL $\frac{M}{10}$ NaOH (2) 75 mL $\frac{M}{5}$ HCl + 25 mL $\frac{M}{5}$ NaOH

(3) 60 mL $\frac{M}{10}$ HCl + 40 mL $\frac{M}{10}$ NaOH (4) 55 mL $\frac{M}{10}$ HCl + 45 mL $\frac{M}{10}$ NaOH

# Answers

## EXERCISE - 1

### PART - I

**A-1.** (a) $H_3PO_3$, $(COOH)_2$
(b) $HSO_4^-$, $RNH_3^+$, $NH_3$, $(C_2H_5)_2OH^+$, HF
(c) $NO_2^-$, $O^{2-}$, $HCO_3^-$, $ClO_4^-$
(d) Conjugate acids: $H_2S$, $NH_4^+$, $C_2H_5OH_2^+$, $H_3O^+$
Conjugate base: $S^{2-}$, $NH_2^-$, $C_2H_5O^-$, $OH^-$
(e) Lewis acid: $H^+$, $FeCl_3$, $\ddot{C}H_2$
Lewis base: $(CH_3)_3N$, $F^-$

**A-2.** Acidic – (vi), (vii) ; Basic – (i), (iv) ; Amphiprotic – (ii), (iii), (v)

**A-3.** $H_2O$ – Arrhenius acid, Arrhenius base, Bronsted–Lowry acid, Bronsted–Lowry base, Lewis base but not Lewis acid.

**B-1.** 600 ions / $mm^3$ **C-1.** $2.5 \times 10^{-5}$ ; 4.6

**C-2.** (i) $10^{-12}$ (ii) $10^{-6}$ (iii) $10^{-11}$ (iv) $K_{b_1} < K_{b_2} < K_{b_3}$

**D-1.** (i) 3, (ii) 2, (iii) 12, (iv) 7.02, (v) 11.2

**D-2.** (i) 11.7, (ii) 1, (iii) 10.7, (iv) 1.92 **D-3.** 0.7 **D-4.** (a) 13 ; (b) 7 ; (c) 1.3.

**E-1.** $1.69 \times 10^{-5}$ **E-2.** Refer class notes / sheet theory.

**E-3.** 11.7 **E-4.** HCl

**F-1.** (a) Basic (b) acidic (c) basic (d) basic (e) acidic (f) basic
(g) neutral (h) basic (i) basic (j) acidic

**F-2.** 9 **F-3.** $K_b = 8 \times 10^{-10}$ **F-4.** 0.625%, pH = 7

### PART - II

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **A-1.** | (C) | **A-2.** | (D) | **A-3.** | (D) | **A-4.** | (C) | **A-5.** | (D) |
| **B-1.** | (D) | **B-2.** | (A) | **B-3.** | (D) | **B-4.** | (D) | **C-1.** | (B) |
| **C-2.** | (C) | **D-1.** | (C) | **D-2.** | (A) | **D-3.** | (C) | **D-4.** | (B) |
| **D-5.** | (B) | **D-6.** | (D) | **D-7.** | (D) | **E-1.** | (D) | **E-2.** | (D) |
| **E-3.** | (B) | **F-1.** | (A) | **F-2.** | (A) | **F-3.** | (B) | **F-4.** | (B) |

### PART - III

**1.** (A) → r; (B) → s; (C) → r; (D) → p

# EXERCISE – 2

## PART - I

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1.** | (B) | **2.** | (D) | **3.** | (C) | **4.** | (B) | **5.** | (C) |
| **6.** | (C) | **7.** | (B) | **8.** | (A) | | | | |

## PART - II

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** | 4 (i, v, vi, vii) | **2.** | 5 (Actual answer = 9.7) | | | **3.** | $K_w = 4 \times 10^{-14}$, pH = 6.7 |
| **4.** | 7 | **5.** | 14 | **6.** | 8 | **7.** | 30 |
| **8.** | 9 | **9.** | 50 | | | | |

## PART - III

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1.** | (ABC) | **2.** | (AC) | **3.** | (ABD) | **4.** | (ABD) | **5.** | (ABC) |
| **6.** | (BC) | **7.** | (BCD) | **8.** | (AD) | | | | |

## PART - IV

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** | (A) | **2.** | (D) | **3.** | (D) | **4.** | (A) |

# EXERCISE – 3

## JEE(MAIN) OFFLINE PROBLEMS

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1.** | (4) | **2.** | (4) | **3.** | (4) | **4.** | (1) | **5.** | (2) |
| **6.** | (1) | **7.** | (3) | **8.** | (4) | **9.** | (1) | **10.** | (4) |

## JEE(MAIN) ONLINE PROBLEMS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1.** | (4) | **2.** | (2) | **3.** | (2) | **4.** | (2) |