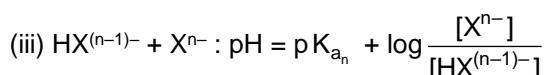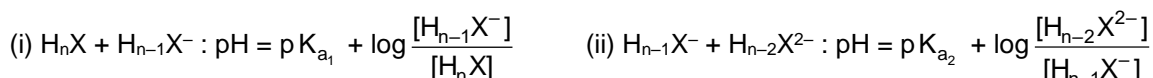# IONIC EQUILIBRIUM-II

Exercise-1

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

PART - I : SUBJECTIVE QUESTIONS

Section (A) : pH calculation : Buffer solutions generated from Polybasic acid / Polyacidic base, Buffer capacity

Commit to memory :

pH calculation : Buffer solutions generated from Polybasic acid (H_nX) :

(i) $H_nX + H_{n-1}X^-$: $pH = pK_{a_1} + \log \dfrac{[H_{n-1}X^-]}{[H_nX]}$ (ii) $H_{n-1}X^- + H_{n-2}X^{2-}$: $pH = pK_{a_2} + \log \dfrac{[H_{n-2}X^{2-}]}{[H_{n-1}X^-]}$

(iii) $HX^{(n-1)-} + X^{n-}$: $pH = pK_{a_n} + \log \dfrac{[X^{n-}]}{[HX^{(n-1)-}]}$

Buffer capacity : Moles of a strong acid or strong base required to change the pH of 1 L of a buffer by one unit.

Let there be a buffer solution of volume 1 L with 'b' mole of anion (coming from salt) and 'a' mole of weak acid.

B.C. $= \dfrac{dx}{d\Delta pH} = 2.303 \dfrac{(a+x)(b-x)}{a+b} \approx 2.303 \dfrac{ab}{a+b}$

Condition for maximum buffer capacity : [Acid] = [Anion of salt]

A-1. An enviromental chemist needs a carbonate buffer of pH 10 to study the effects of the acidification of limestone–rich soils. How many grams of Na_2CO_3 must be added to 1.5 L of freshly prepared 0.2 M $NaHCO_3$ to make the buffer ? For H_2CO_3, $K_{a_1} = 4.7 \times 10^{-7}$; $K_{a_2} = 4.7 \times 10^{-11}$.

Section (B) : pH calculation : Monobasic acid - Monoacidic base Titrations

Commit to memory :

pH calculation : Monobasic acid-Monoacidic base Titrations :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of WA by SB :

At half equivalence point : $pH = pK_a$; $pH_{x\ \%\ neutralisation} = pK_a + \dfrac{x}{100 - x}$

In titration of WB and SA :

At half equivalence point : $pOH = pK_b$; $pOH_{x\ \%\ neutralisation} = pK_b + \dfrac{x}{100 - x}$

B-1. Calculate pH of the following mixtures. Given : K_a of $CH_3COOH = 2 \times 10^{-5}$ and K_b of $NH_4OH = 2 \times 10^{-5}$.
(a) 50 mL of 0.10 M NaOH + 50 mL of 0.10 M HCl.
(b) 50 mL of 0.10 M NaOH + 50 mL of 0.05 M CH_3COOH.
(c) 50 mL of 0.05 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 0.10 M NH_4OH + 50 mL of 0.10 M HCl.
(f) 50 mL of 0.05 M NH_4OH + 50 mL of 0.05 M CH_3COOH.

B-2. 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. Given : pH of 0.1 M CH_3COOH solution is 3.

Section (C) : pH calculation : Titration of Salts, Polyprotic acid, Polyacidic base

Commit to memory :

pH calculation : Titration of Polyprotic acid, Polyacidic base :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of H_nX by strong base :

At half equivalence point w.r.t 1st neutralisation : pH = pK_{a_1} ;

At equivalence point w.r.t 1st neutralisation : pH = $\dfrac{pK_{a_2} + pK_{a_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : pH = pK_{a_2} ;

At equivalence point w.r.t 2nd neutralisation : pH = $\dfrac{pK_{a_3} + pK_{a_2}}{2}$;

At equivalence point w.r.t last neutralisation : pH = $\dfrac{1}{2}(pK_w + pK_{a_n} + \log C)$.

In titration of Polyacidic base B by strong acid :

At half equivalence point w.r.t 1st neutralisation : pOH = pK_{b_1} ;

At equivalence point w.r.t 1st neutralisation : pOH = $\dfrac{pK_{b_2} + pK_{b_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : pOH = pK_{b_2} ;

At equivalence point w.r.t 2nd neutralisation : pH = $\dfrac{pK_{b_3} + pK_{b_2}}{2}$;

At equivalence point w.r.t last neutralisation : pH = $\dfrac{1}{2}(pK_w - pK_{b_n} - \log C)$.

C-1. 50 mL of 0.05 M Propane-1,2-diamine solution is titrated with 0.1 M HCl solution at 25°C. Determine the pH of solutions obtained by adding following volumes of HCl solution :
(a) 12.5 mL   (b) 25 mL   (c) 30 mL
Given : pK_{b_1} and pK_{b_2} of weak base are 4.18 and 7.39 respectively.

C-2. Determine the [H$^+$] at half-equivalence point and pH at equivalence point during the titration of a 50 mL, 0.1 M NH$_4$Cl solution with 0.1 M NaOH solution at 25°C. Given : K_b of NH$_3$ = 2 × 10^{-5}.

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : pH calculation : Buffer solutions generated from Polybasic acid / Polyacidic base, Buffer capacity

Commit to memory :

pH calculation : Buffer solutions generated from Polybasic acid (H_nX) :

(i) $H_nX + H_{n-1}X^- : pH = pK_{a_1} + \log \dfrac{[H_{n-1}X^-]}{[H_nX]}$ (ii) $H_{n-1}X^- + H_{n-2}X^{2-} : pH = pK_{a_2} + \log \dfrac{[H_{n-2}X^{2-}]}{[H_{n-1}X^-]}$

(iii) $HX^{(n-1)-} + X^{n-} : pH = pK_{a_n} + \log \dfrac{[X^{n-}]}{[HX^{(n-1)-}]}$

Buffer capacity : Moles of a strong acid or strong base required to change the pH of 1 L of a buffer by one unit.

Let there be a buffer solution of volume 1 L with 'b' mole of anion (coming from salt) and 'a' mole of weak acid.

B.C. = $\dfrac{dx}{d\Delta pH} = 2.303 \dfrac{(a+x)(b-x)}{a+b} \approx 2.303 \dfrac{ab}{a+b}$

Condition for maximum buffer capacity : [Acid] = [Anion of salt]

A-1. The pH of a solution resulting from the addition of 12.5 ml of 0.1 M HCl to 50 ml of a solution containing 0.15 M CH_3COOH & 0.2 M CH_3COONa will be : (Given : pK_a of CH_3COOH = 4.74)
(A) 4.74   (B) < 4.74   (C) > 4.74   (D) > 9.26

A-2. What % of the carbon in the $H_2CO_3 - HCO_3^-$ buffer should be in the form of HCO_3^-, so as to have a neutral solution ? (K_{a_1} of H_2CO_3 = 4×10^{-7})

(A) 20 %   (B) 40 %   (C) 60 %   (D) 80%

A-3. Buffer capacity of a buffer solution is x. The volume of 1 M NaOH solution added to 100 mL of this solution if change the pH by 1 is :
(A) 0.1 x mL   (B) 10 x mL   (C) 100 x mL   (D) x mL

Section (B) : pH calculation : Monobasic acid - Monoacidic base Titrations

Commit to memory :

pH calculation : Monobasic acid - Monoacidic base Titrations :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of WA by SB :

At half equivalence point : $pH = pK_a$; $pH_{x \% \text{ neutralisation}} = pK_a + \dfrac{x}{100 - x}$

In titration of WB and SA :

At half equivalence point : $pOH = pK_b$; $pOH_{x \% \text{ neutralisation}} = pK_b + \dfrac{x}{100 - x}$

B-1. Upon titrating 50 mL of 1.96% (w/v) H_2SO_4 with a KOH solution (containing 11.2 g KOH per litre of solution), on adding 50 mL KOH solution :
(A) Equivalence point has been just reached.   (B) Equivalence point has been crossed.
(C) pH of resulting solution = 1   (D) pH of resulting solution = 7

B-2. 100 mL of 0.02 M benzoic acid (pK_a = 4.2) is titrated using 0.02 M NaOH. pH after 50 mL and 100 mL of NaOH have been added are :

(A) 2.1, 8.1   (B) 4.2, 7   (C) 4.2, 8.1   (D) 4.2, 8.25

B-3. In the above question, upon 75% neutralisation of Benzoic acid, select the INCORRECT statement :

(A) Resulting solution will be a buffer solution.   (B) pH = 4.2 + log 3

(C) Both (A) & (B)   (D) None of these

B-4. Which of the following solutions have different pH ?

(i) 100 mL of 0.2 M HCl + 100 mL of 0.4 M NH_3

(ii) 50 mL of 0.1 M HCl + 50 mL of 0.2 M NH_3

(iii) 100 mL of 0.3 M HCl + 100 mL of 0.6 M NH_3

(A) i & ii   (B) ii & iii   (C) i & iii   (D) All will have same pH.

B-5. Upon titrating a solution of weak monoprotic acid with a weak monoacidic base solution, at equivalence point :

(A) pH in general would increase if both solutions are first diluted to 10 times the original volume & then titration is carried out.

(B) pH in general would decrease if both solutions are first diluted to 10 times the original volume & then titration is carried out.

(C) pH in general would remain same (= 7) if both solutions are first diluted to 10 times the original volume & then titration is carried out.

(D) pH in general could be less than, greater than or equal to 7 if both solutions are first diluted to 10 times the original volume & then titration is carried out.

Section (C) : pH calculation : Titration of Salts, Polyprotic acid, Polyacidic base

Commit to memory :

pH calculation : Titration of Polyprotic acid, Polyacidic base :

Carry out chemical reaction between the two components, apply mole concept, observe the final composition of the mixture and then calculate pH accordingly (using different cases dealt in Ionic Equilibrium-I).

In titration of H_nX by strong base :

At half equivalence point w.r.t 1st neutralisation : pH = pK_{a_1} ;

At equivalence point w.r.t 1st neutralisation : pH = $\dfrac{pK_{a_2} + pK_{a_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : pH = pK_{a_2} ;

At equivalence point w.r.t 2nd neutralisation : pH = $\dfrac{pK_{a_3} + pK_{a_2}}{2}$;

At equivalence point w.r.t last neutralisation : pH = $\dfrac{1}{2}(pK_w + pK_{a_n} + \log C)$.

In titration of Polyacidic base B by strong acid:

At half equivalence point w.r.t 1st neutralisation : pOH = pK_{b_1} ;

At equivalence point w.r.t 1st neutralisation : pOH = $\dfrac{pK_{b_2} + pK_{b_1}}{2}$;

At half equivalence point w.r.t 2nd neutralisation : pOH = pK_{b_2} ;

At equivalence point w.r.t 2nd neutralisation : pH = $\dfrac{pK_{b_3} + pK_{b_2}}{2}$;

At equivalence point w.r.t last neutralisation : pH = $\dfrac{1}{2}(pK_w - pK_{b_n} - \log C)$.

C-1. The total number of different kind of buffers obtained during the titration of H_3PO_4 with NaOH are :
(A) 3   (B) 1   (C) 2   (D) Zero

C-2 Upon titration a solution of Ethylene diamine $\left(K_{b_1} = 8 \times 10^{-5}; K_{b_2} = 2.7 \times 10^{-8}\right)$ with HCl solution, pH value of solution at Ist equivalence point depends upon :
(A) Initial concentration of weak base solution   (B) Initial concentration of strong acid solution
(C) Both (A) & (B)   (D) None of these

C-3. What will be the pH at the equivalence point during the titration of a 100 mL 0.2 M solution of CH_3COONa with 0.2 M solution of HCl ? $K_a = 2 \times 10^{-5}$.
(A) $3 - \log \sqrt{2}$ (B) $3 + \log \sqrt{2}$ (C) $3 - \log 2$ (D) $3 + \log 2$

■ Exercise-2

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

PART - I : SINGLE AND DOUBLE VALUE INTEGER TYPE

1.✎ 15 mL sample of 0.15 M NH_3(aq) is titrated against 0.1M HCl(aq). What is the pH at the end point ? K_b of NH_3(aq) = 1.8×10^{-5}. Report the answer rounding it off to the nearest whole number.

2.✎ A 0.252 g sample of unknown organic base is dissolved in water and titrated with a 0.14 M HCl solution. After the addition of 20 mL of acid, a pH of 10.7 is recorded. The equivalence point is reached when a total of 40 mL of HCl is added. If the base and acid combine in a 1 : 1 molar ratio, then 'a' g is the molar mass of the organic base and 'b' is the ionisation constant of base. Report your answer as $\left(\dfrac{a}{1000\,b}\right)$.

PART - II : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Aniline behaves as a weak base. When 0.1 M, 50 mL solution sample of aniline was mixed with 0.2 M, 12.5 mL solution of HCl, the pH of resulting solution was 8. Then :
(A) pH of 0.01 M solution of anilinium chloride is 5.
(B) pH of original solution of aniline is 3.5.
(C) Upon adding the same aniline sample to the above mixture, pH of resulting solution becomes 8.48.
(D) Upon adding the same HCl sample to the above mixture, pH of resulting solution becomes 4.59.

2. Which of the following mixtures will act as buffer ?
(A) H_2CO_3 + NaOH (1.5 : 1 molar ratio)   (B) H_2CO_3 + NaOH (1.5 : 2 molar ratio)
(C) NH_4OH + HCl (5 : 4 molar ratio)   (D) NH_4OH + HCl (4 : 5 molar ratio)

3.✎ Titration curves for 0.1M solutions of three weak acids HA_1, HA_2 and HA_3 with ionization constants K_1, K_2 and K_3 respectively with a strong base are plotted as shown in the figure. Which of the following options is/are true ?
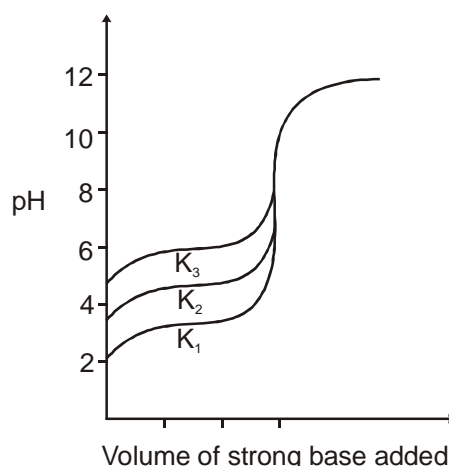
(A) $K_2 = (K_1 + K_3)/2$ (B) $pK_1 < pK_3$ (C) $K_1 > K_2$ (D) $K_2 > K_3$

PART - III : COMPREHENSION

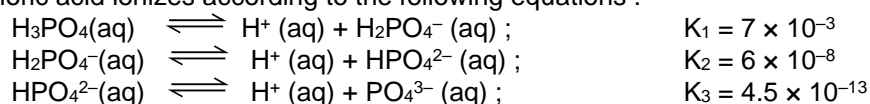**Read the following passage carefully and answer the questions.**

Comprehension # 1

The pH of basic buffer mixtures is given by : $pH = pK_a + \log\dfrac{[\text{Base}]}{[\text{Salt}]}$, whereas pH of acidic buffer

mixtures is given by : $pH = pK_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]}$. Addition of little acid or base although shows no

appreciable change in pH for all practical purposes, but since the ratio $\dfrac{[\text{Base}]}{[\text{Salt}]}$ for $\dfrac{[\text{Salt}]}{[\text{Acid}]}$ changes, a

slight decrease or increase in pH results.

1. A solution containing 0.2 mole of dichloroacetic acid ($K_a = 5 \times 10^{-2}$) and 0.1 mole sodium dichloroacetate in one litre solution has $[H^+]$:
(A) 0.05 M   (B) 0.025 M   (C) 0.10 M   (D) 0.005 M

2. The volume of 0.2 M NaOH needed to prepare a buffer of pH 4.74 with 50 mL of 0.2 M acetic acid is :
(pK_b of CH_3COO^- = 9.26)
(A) 50 mL   (B) 25 mL   (C) 20 mL   (D) 10 mL

3. The ratio of pH of solution (I) containing 1 mole of CH_3COONa and 1 mole of HCl and solution (II) containing 1 mole of CH_3COONa and 1 mole of acetic acid in one litre is :
(A) 1 : 2   (B) 2 : 1   (C) 1 : 3   (D) 3 : 1

Comprehension # 2

Phosphoric acid ionizes according to the following equations :

$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$; $K_1 = 7 \times 10^{-3}$
$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$; $K_2 = 6 \times 10^{-8}$
$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$; $K_3 = 4.5 \times 10^{-13}$

4. If you are asked to prepare a buffer with a pH = 7.00, what may be the molar ratio of the species that should be used in the solution ?
(A) 0.6   (B) 0.8   (C) 2   (D) 4

5. Assume 50 mL of the buffer prepared in the previous part is available in which more abundant species has a concentration of 0.1 M. If to this solution, 20 mL 0.1 M NaOH is added further, what will be the new pH ?
(A) 6.56   (B) 7.44
(C) 7.78   (D) Same as before as it's a buffer

Exercise-3

* Marked questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1.   500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.
(a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
(b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in
volume on mixing. K_a of acetic acid is 1.75×10^{-5}.   **[JEE-2002, 5/60]**

2.   0.1 M NaOH is titrated with 0.1 M HA till the end point. K_a for HA is 5.6×10^{-6} and degree of hydrolysis
is less compared to 1. Calculate pH of the resulting solution at the end point.   **[JEE-2004, 2/60]**

3.   0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be
the H^+ concentration in the solution ?   **[JEE-2005, 3/84]**
(A) 8×10^{-2} M   (B) 8×10^{-11} M   (C) 1.6×10^{-11} M   (D) 8×10^{-5} M

4.   2.5 mL of $\dfrac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\dfrac{2}{15}$ M HCl in water at

25°C. The concentration of H^+ at equivalence point is : ($K_w = 1 \times 10^{-14}$ at 25°C)   **[JEE-2008, 3/163]**
(A) 3.7×10^{-14} M   (B) 3.2×10^{-7} M   (C) 3.2×10^{-2} M   (D) 2.7×10^{-2} M

5.*   Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided.
The pair(s) of solutions which form a buffer upon mixing is (are) :   **[JEE-2010, 3/163]**
(A) HNO_3 and CH_3COOH (B) KOH and CH_3COONa
(C) HNO_3 and CH_3COONa (D) CH_3COOH and CH_3COONa

Comprehension #

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant
pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (**Expt. 1)**.
Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ
mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment
(**Expt. 2)**, 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under
identical conditions to **Expt. 1**) where a temperature rise of 5.6°C was measured.
(Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

6.   Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the **Expt. 2** is :
                                                                                    [JEE (Advance)2015, 4/168]
(A) 1.0   (B) 10.0   (C) 24.5   (D) 51.4

7.   The pH of the solution after **Expt. 2** is   **[JEE (Advance)2015, 4/168]**
(A) 2.8   (B) 4.7   (C) 5.0   (D) 7.0

8.   Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution
of the solution on $[H^+]$ are given in LIST-II.

(Note : degree of dissociation (α) of weak acid and weak base is <<1; degree of hydrolysis of salt <<1;
$[H^+]$ represents the concentration of H^+ ions)   **[JEE (Advance)2018, 3/120]**

LIST-I	LIST-II
(P) (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL	(1) the value of $[H^+]$ does not change on dilution
(Q) (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL	(2) the value of $[H^+]$ changes to half of its initial value on dilution
(R) (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL	(3) the value of $[H^+]$ changes to two times of its initial value on dilution
(S) 10 mL saturated solution of $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution).	(4) the value of $[H^+]$ changes to $\dfrac{1}{\sqrt{2}}$ times of its initial value on dilution
	(5) the value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in LIST-I with one or more effect(s) in LIST-II. the correct option is
(A) P → 4 ; Q → 2 ; R → 3 ; S → 1   (B) P → 4 ; Q → 3 ; R → 2 ; S → 3
(C) P → 1 ; Q → 4 ; R → 5 ; S → 3   (D) P → 1 ; Q → 5 ; R → 4 ; S → 1

PART - II : JEE (MAIN) (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. An alkali is titrated against an acid with methyl orange as indictor, which of the following is a correct combination? **[JEE(Main)-2018, 4/120]**

	Base	Acid	End point
(1)	Weak	Strong	Yellow to pinkish red
(2)	Strong	Strong	Pink to colourless
(3)	Weak	Strong	Colourless to pink
(4)	Strong	Strong	Pinkish red to yellow

Answers

EXERCISE - 1

PART - I

A-1. K **A-2.** 15 g Na_2CO_3 **B-1.** (a) 7, (b) 12.4, (c) 4.7, (d) 9.3, (e) 5.3, (f) 7

B-2. 4.52, 5.48 **C-1.** (a) 9.82 (b) 8.215 (c) 7.21 **C-2.** 5×10^{-10} M; 11

PART - II

A-1.	(A)	**A-2.**	(D)	**A-3.**	(C)	**B-1.**	(C)	**B-2.**	(C)
B-3.	(D)	**B-4.**	(D)	**B-5.**	(D)	**C-1.**	(A)	**C-2**	(D)
C-3.	(A)								

EXERCISE - 2

PART - I

1. 5 (exact answer = 5.24) **2.** 90 (a = 45 & b = 5×10^{-4})

PART - II

1. (ACD) **2.** (ABC) **3.** (BCD)

PART - III

1.	(A)	**2.**	(B)	**3.**	(A)	**4.**	(A)	**5.**	(B)

EXERCISE - 3

PART - I

1.	(a) 0.0175%, 1 (b) 4.757	**2.**	$8.98 \approx 9$	**3.**	(B)	**4.**	(D)
5.*	(CD)	**6.**	(A)	**7.**	(B)	**8.**	(D)

PART - II

JEE(MAIN) OFFLINE PROBLEMS

1. (1)