

IONIC EQUILIBRIUM-I



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: H₃PO₂, H₃PO₃, H₃BO₃, HCOOH, (COOH)₂.

(b) Write conjugate acids of SO₄²⁻, RNH₂, NH₂⁻, C₂H₅OC₂ H₅, F⁻

(c) Write conjugate base of HNO₂, OH⁻, H₂CO₃, HClO₄.

- (d) Write conjugate acid and conjugate base of following amphoteric species : HS-, NH₃, C₂H₅OH, H₂O
- (e) Classify the following into Lewis acid & Lewis base: H+, FeCl₃, (CH₃)₃N, F-, CH₂
- A-2. Classify the following into acid, base and amphiprotic species on the basis of protonic concept:

(i) H₂PO₂⁻

(ii) H₂PO₃-

(iii) H₂PO₄-

(iv) HPO₃2-

(v) HPO₄²-

(vi) NH₄+

(vii) CH₃COOH₂+

A-3. Comment upon H₂O as an Arrhenius acid/base, Bronsted–Lowry acid/base and Lewis acid/base.

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

Commit to memory:

 $K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25^{\circ}C$

 $[H^+] = [OH^-]$ (in water / a neutral solution)

 $pH = -log[H^+]; pOH = -log[OH^-]$

For H₂O, pH & pOH ↓ with ↑ in temperature

pH + pOH = pK_w = 14 (for an aqueous solution at 25°C)

Kself ionisation of $HA = [A^-][H_2A^+]$

B-1. At -50° C, liquid NH₃ has ionic product is 10^{-30} . How many amide (NH₂⁻) ions are present per mm³ in pure liquid NH₃? (Take N_A = 6 × 10^{23})

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

Commit to memory:

Ka (acid) × Kb (conjugate base) = Kw

 $pK_{a (acid)} + pK_{b (conjugate base)} = pK_{w} = 14 (at 25°C)$

- **C-1.** What is ionisation constant of HOCl, if K_b of OCl⁻ = 4×10^{-10} ? Also find its p K_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 HPO₄²⁻?
 - (ii) What is K_b of HPO₄²⁻?
 - (iii) What is K_b of H₂PO₄-?
 - (iv) What is order of K_b of $PO_4^{3-}(K_{b_3})$, $HPO_4^{2-}(K_{b_2})$ and $H_2PO_4^{-}(K_{b_1})$?



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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

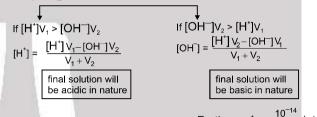
Commit to memory:

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.

$$\label{eq:mixture of two strong acids:} \qquad [H^+]_f = \frac{[H^+]_1 V_1 + [H^+]_2 V_2}{V_1 + V_2}$$

Mixture of two strong bases :
$$[OH^-]_f = \frac{[OH^-]_1 V_1 + [OH^-]_2 V_2}{V_1 + V_2}$$

Mixture of a strong acid and a strong base:



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

- **D-1.** Calculate pH of following solutions:
 - (i) 0.001 M HNO₃,
- (ii) 0.005 M H₂SO₄,
- (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 TℓOH dissolved in water to give 2 litre of solution. (Assume TℓOH to be a strong base)
 - (ii) 0.49% w/v H₂SO₄ solution
 - (iii) $\frac{M}{1000}$ 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 H₂SO₄.
- 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 HCI
 - (b) 2 mL of 0.1 M HCI + 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:

$$\mathsf{AB}\;(\mathsf{aq}) \ \Longleftrightarrow \ \mathsf{A^+}\;(\mathsf{aq})\; +\; \mathsf{B^-}\;(\mathsf{aq})\; ;\; \mathsf{K}_{\mathsf{eq}} = \ \frac{[\mathsf{A}^+][\mathsf{B}^-]}{[\mathsf{AB}]} = \frac{\mathsf{C}\alpha \quad .\quad \mathsf{C}\alpha}{\mathsf{C}(\mathsf{1}-\alpha)} = \frac{\mathsf{C}\alpha^2}{(\mathsf{1}-\alpha)}$$

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

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

$$\frac{\text{Acid strength of HA}_1}{\text{Acid strength of HA}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} \; ; \; \frac{\text{Basic strength of BOH}_1}{\text{Basic strength of BOH}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} \; ; \; \frac{K_{b_2}}{K_{b_2}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \sqrt{\frac{K_{b_2}}{K_{b_2}}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \sqrt{\frac{K_{b_2}}{K_{b_2}}} = \sqrt{\frac{K_{b_2}}{K_{b_2}}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \sqrt{\frac{K_{b_2}}{K_{b_2}}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \sqrt{\frac{K_{b_2}}{K_{b_2}}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \sqrt{\frac{K_{b_2}}{K_{b_2}}} = \sqrt{\frac{K_{b_2}}{K_{b_2}$$



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- 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 Ka 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) CH₃COOH 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 : $K_h \times K_a = K_w$; $h = \sqrt{\frac{K_h}{c}}$; $pH = \frac{1}{2} \left[pK_w + pK_a + \log c \right]$ (valid if h < 0.1 or 10%)

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

- F-1. Which of the following ions or compounds in a solution tend to produce an acidic, a basic or a neutral solution?
 - (a) C₂H₅O[−]
- (b) Cu⁺²

- (e) NH₄+
- (f) CH₃COONa

- (g) KNO₃
- (h) NaOCI
- (c) SO₃²⁻ (i) Na₂CO₃
- (d) F-(j) ZnCl₂
- Calculate pH of 0.2 M aqueous solution of sodium butyrate. Given: K_a of butyric acid = 2×10^{-5} . F-2.
- A 0.25 M solution of pyridinium chloride C₅H₅NH+Cl⁻ was found to have a pH of 2.75. What is K₀ for F-3. pyridine, C₅H₅N?
- Calculate the percentage hydrolysis & the pH of 0.02 M CH₃COONH₄. K_b(NH₃) = 1.6 × 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

- An acid with molelcular formula C₇H₆O₃ forms three types of sodium salts. i.e. C₇H₅O₃Na, C₇H₄O₃Na₂ and C₇H₃O₃Na₃. The basicity of the acid is :
 - (A) One
- (B) Two
- (C) Three
- (D) Six

- Select the incorrect option: A-2.
 - (A) H₃PO₄ is a tribasic acid.

- (B) H₃BO₃ is not an Arhenius acid.
- (C) Sr(OH)₂ is a strong diacidic base.
- (D) NH₃.H₂O is a strong monoacidic base.

Ionic Equilibrium (Elementary)



- 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 A-3. 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) PO₄³⁻ and C₂O₄²⁻
- The following equilibrium is established when HClO₄ is dissolved in weak acid HF solvent: A-4.

$$HF + HCIO_4 \rightleftharpoons CIO_4^- + H_2F^+$$

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

- (A) HF and HCIO₄
- (B) HF and ClO₄-
- (C) HF and H₂F⁺
- (D) HCIO₄ & H₂F⁺
- Which of the following correctly explains the nature of boric acid in aqueous medium? A-5.
 - (A) $H_3BO_3 \xrightarrow{H_2O} H_3O^+ + H_2BO_3^-$
- (B) $H_3BO_3 \xrightarrow{2H_2O} 2H_3O^+ + HBO_2^2$
- (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:

 $K_w = [H^+][OH^-] = 10^{-14} \text{ at } 25^{\circ}C$

[H+] = [OH-] (in water / a neutral solution)

 $pH = -log [H^+]$; $pOH = -log [OH^-]$

For H₂O, 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 H₂O 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).
- K_w of H₂O at 373 K is 1 × 10⁻¹². Identify, which of the following is incorrect: B-3.
 - (A) pH + pOH = 12, for every aqueous solutions.
 - (B) pH of H₂O is 6.
 - (C) $\alpha_{H,O}$ has increased from its value at 298 K.
 - (D) H₂O is acidic.
- B-4. In pure HCOOH liquid, concentration of HCOO⁻ = 10⁻³ M at 27°C. What is the self ionisation constant at 27° C (K = [HCOOH₂+] [HCOO-]) ?
 - (A) 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:

Ka (acid) × Kb (conjugate base) = Kw

 $pK_{a \text{ (acid)}} + pK_{b \text{ (conjugate base)}} = pK_w = 14 \text{ (at } 25^{\circ}C)$

C-1. Given:

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

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

Which relation is correct.

(A)
$$K_b = \frac{1}{K_a}$$

(C)
$$K_a.K_b.K_w = 1$$

(B)
$$K_a \cdot K_b = K_w$$
 (C) $K_a \cdot K_b \cdot K_w = 1$ (D) $\frac{K_a}{K_b} = K_w$



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- **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) Ka (weak acid). Kb (weak base) = Kw
 - (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

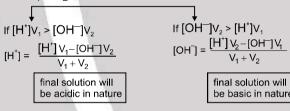
Commit to memory:

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 : $[H^{+}]_{f} = \frac{[H^{+}]_{1}V_{1} + [H^{+}]_{2}V_{2}}{V_{1} + V_{2}}$

Mixture of two strong bases : $[OH^{-}]_{f} = \frac{[OH^{-}]_{1}V_{1} + [OH^{-}]_{2}V_{2}}{V_{1} + V_{2}}$

Mixture of a strong acid and a strong base :



Further, $[H^{\dagger}]_f = \frac{10^{-14}}{[OH^{-}]_f}$ (at 25°C)

D-1. The $[OH^-]$ in 100 mL of 0.016 M HCl (aq) is :

(A) 6.25×10^{-12} M

- (B) $3 \times 10^{-10} \,\mathrm{M}$
- (C) 6.25×10^{-13} M
- (D) $1.6 \times 10^{-3} \text{ M}$
- 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 HNO₃, 0.1M HCl, 0.1M HI at 25°C is not equal.
 - (B) For a dilute solution, pH = $-\log \frac{1}{[H^+]}$
 - (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, $\frac{M}{200}$ 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)



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- **D-7.** Which of the following solutions will have pH close to 1?
 - (A) 100 mL of M/10 HCI + 100 mL of M/10 NaOH
 - (B) 55 mL of M/10 HCI + 45 mL of M/10 NaOH
 - (C) 10 mL of M/10 HCI + 90 mL of M/10 NaOH
 - (D) 75 mL of M/5 HCI + 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:

$$\mathsf{AB}\;(\mathsf{aq}) \ \ \, \stackrel{}{\longleftarrow} \; \; \mathsf{A}^{\scriptscriptstyle +}\;(\mathsf{aq})\; +\; \mathsf{B}^{\scriptscriptstyle -}\;(\mathsf{aq})\; ;\; \mathsf{K}_{\mathsf{eq}} = \frac{[\mathsf{A}^{\scriptscriptstyle +}][\mathsf{B}^{\scriptscriptstyle -}]}{[\mathsf{AB}]} = \frac{\mathsf{C}\alpha \quad . \quad \mathsf{C}\alpha}{\mathsf{C}(\mathsf{1}-\alpha)} = \frac{\mathsf{C}\alpha^2}{(\mathsf{1}-\alpha)}$$

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

Weak Acid (monoprotic) solution :
$$\alpha = \sqrt{\frac{K_a}{C}}$$
; pH = $\frac{1}{2}$ (pK_a – log C) (both valid if α < 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 α < 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 NH₃
- (B) 0.001 M NH₃
- (C) 0.1 M NH₃
- (D) 0.0001 M NH₃.
- K_a for formic acid and acetic acid are 1.8×10^{-4} and 1.8×10^{-5} respectively. The relative strength of E-2. acids is:
 - (A) 10:1
- (B) 1:10
- (C) 1 : √10
 - (D) √10 : 1
- K_a for a monobasic acid, whose 0.1 M solution has pH of 4.5, is : $(C) \sqrt{10} \times 10^{-4} \qquad (D) \sqrt{10} \times 10^{-6}$ E-3.

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

- F-1. Aqueous solution of NH₄Cl is in nature due to behaviour of ____ ion in solution :
 - (A) acidic: NH₄+
- (B) alkalline; NH₄+
- (C) acidic ; CI-
- (D) alkalline; CI-
- 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 25°C. Given that the ionic product of water is 10⁻¹⁴ at this temperature, what is the dissociation constant of the base?
 - (A) $\approx 1 \times 10^{-10}$
- (B) $\approx 1 \times 10^{-9}$
- (C) 3.33×10^{-9}
- (D) 3.33×10^{-10}
- F-3. The pH of 0.1 M solution of the following salts increases in the order:
 - (A) NaCl < NH₄Cl < NaCN < HCl
- (B) HCI < NH₄CI < NaCI < NaCN
- (C) NaCN < NH₄CI < NaCl < HCl
- (D) HCI < NaCI < NaCN < NH₄CI



- **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. (Single matching)

	Column-l		Column-II
(A)	HCI	(p)	Lewis acid
(B)	KOH	(q)	Arrhenius acid
(C)	NH₃	(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/cm³. 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) 1×10^{-6}
- (B) 1×10^8
- (C) 1×10^{-8}
- (D) 1×10^6

- 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) 2×10^{-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.
- % dissociation of a 0.024 M solution of a weak acid HA ($K_a = 2 \times 10^{-3}$) is :
 - (A) 0.25%
- (B) $\approx 29\%$
- (C) 25%
- (D) $\approx 0.29\%$
- 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
- 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
 - (iii) HA and HB have the same acidic strength
 - (v) A- is stronger base than B-
 - (vii) A- is the conjugate base of acid HA.
 - (ix) A- can be F- and B- can be CN-.
- (ii) HA is stronger acid than HB
- (iv) B- is stronger base than A-
- (vi) B- and HB are conjugate acid-base pair
- (viii) HA can be HSO₄- and HB can be HCOOH.



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ADVIEQ(M) - 26

Ionic Equilibrium (Elementary),



- What is pOH of an aqueous solution with $[H^+] = 10^{-2} \,\text{M}$ 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 x 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 $\lim_{V \to \infty}$, (pH)_{solution} is equal to
- 5. Determine $pK_a(H_2O) + pK_a(H_3O^+)$.
- 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?
- 7.2. If $pH_{x\%}$ is the pH of a 1 M weak monoprotic acid which is x % ionised, then find the value of $\left\lceil \frac{pH_{50\%}}{pH_{10\%}} \right\rceil \times 100.$
- 8. If the equilibrium constant for the reaction of weak acid HA with a strong base is 10⁹, then determine pH of 0.1 M NaA solution.
- 9.3 What is the concentration of CH₃COOH(aq) in a solution prepared by dissolving 0.01 mole of NH₄⁺CH₃COO⁻ in 1 L H₂O ? Report your answer after multiplying by 9×10^5 . [K_a(CH₃COOH) = 1.8×10^{-5} ; K_b(NH₃.H₂O) = 1.8×10^{-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) NH₄⁺ (aq) is a strong acid.
- (B) CH₃COO⁻ (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) α_{Ho} 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 1.8×10^{-9} %.
 - (C) Number of OH⁻ ions per mL of solution = 6.022×10^{15} .
 - (D) $[H^+]_{from H_2O} = 10^{-9} M$
- **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) $[Sr^{2+}] = 0.1 \text{ M}$

- (B) $[CI^-] = 0.1 \text{ M}$
- (C) pH of resulting solution = 13
- (D) Solution is neutral.
- 6. If 0.1 M CH₃COOH (Ka = 1.8 × 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) Ka will increase.



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- **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 Kb 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 CH₃COOH of pH = 5, aqueous NH₃ of pH = 9. [K_a (CH₃COOH) = K_b (NH₃)]

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 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
- 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 H₂O.
 - (A) 6.4
- (B) 6.52
- (C) 6.365
- (D) 6.432

Comprehension # 2

Consider a solution of CH₃COONH₄ 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:

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

Both CH₃COO⁻ and NH₄+ 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 $\frac{K_w}{K_h}$ 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.



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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.
- For 0.1 M CH₃COONH₄ salt solution given, K_a (CH₃COOH) = K_b (NH₃.H₂O) = 2 x 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

 $(2) 1 \times 10^{-3}$

(2) 0.9 L

Exercise-3

JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

		JEE(MAIN) OFFL	INE PROBLEMS			
1.	The conjugate base of to 1) PO ₄ 3-	H ₂ PO ₄ ⁻ is : (2) P ₂ O ₅	(3) H ₃ PO ₄	(4) HPC	[AIEEE-2004, 0 ₄ 2-	3/225]
2.	What is the conjugate b (1) O ₂	ase of OH⁻? (2) H₂O	(3) O-	(4) O ²⁻	[AIEEE-2005,	3/225]
3.	Hydrogen ion concentra (1) 3.98 × 10 ⁸	ation in mol/L in a solution (2) 3.88×10^6	on of pH = 5.4 will be : (3) 3.68×10^{-6}	(4) 3.98	[AIEEE-2005 , × 10 ⁻⁶	3/225]
4.		ssociation constants of a constant of the acid will (2) 0.2 × 10 ⁵			[AIEEE-2007,	
5.	The pK _a of a weak acid solution of the correspo (1) 4.79	d, HA, is 4.80. The pK_b nding salt, BA, will be : (2) 7.01	of a weak base, BOH, i (3) 9.22		[AIEEE-2008,	
6.	(i) $H_3PO_4 + H_2O \rightarrow H_3O$ (ii) $H_2PO_4^- + H_2O \rightarrow HP$ (iii) $H_2PO_4^- + OH^- \rightarrow H_3$	O ₄ ²⁻ + H ₃ O ⁺			[AIEEE-2010,	4/144]
	(1) (ii) only	(2) (i) and (ii)	(3) (iii) only	(4) (i) or	nly	
	The pH of a 0.1 molar sis:	solution of the acid HQ is	s 3. The value of the ion	ization c	onstant, K _a of	



an aqueous solution with pH of 2?

 $(1) \ 3 \times 10^{-1}$

(1) 0.1 L

8.

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 $(3) 1 \times 10^{-5}$

How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create

(3) 2.0 L

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[JEE(Main) 2013, 4/120]

(4) 1×10^{-7}

(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

10. Which of the following salts is the most basic in aqueous solution? [JEE(Main) 2018, 4/120]

(1) FeCl₃ (2) Pb(CH₃COO)₂ (3) AI(CN)₃

(4) CH₃COOK

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]

(3) 8.0

(4) 9.0

2.

[JEE(Main) 2014 Online (12-04-14), 4/120]

The conjugate base of hydrazoic acid is: $(1) N^{-3}$

(2) N_3^-

 $(3) N_2^-$

What quantity (in mL) of a 45% acid solution of a mono-protic strong acid must be mixed with a 20% 3. 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

(1) 5.0

(2)316

(2) 6.0

(3)320

Following four solutions are prepared by mixing different volumes of NaOH and HCl of different 4. 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) H₃PO₃, (COOH)₂
 - (b) HSO₄-, RNH₃+, NH₃, (C₂H₅)₂OH+, HF
 - (c) NO₂-, O²-, HCO₃-, ClO₄-
 - (d) Conjugate acids: H₂S, NH₄+, C₂H₅OH₂+, H₃O+ Conjugate base: S²-, NH₂-, C₂H₅O-, OH-
 - (e) Lewis acid: H+, FeCl₃, CH₂

Lewis base: (CH₃)₃N, F-

- A-2. Acidic (vi), (vii); Basic (i), (iv); Amphiprotic (ii), (iii), (v)
- **A-3.** H₂O Arrhenius acid, Arrhenius base, Bronsted–Lowry acid, Bronsted–Lowry base, Lewis base but not Lewis acid.
- **B-1.** 600 ions / mm³

C-1. 2.5×10^{-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,

D-2.

(ii) 2,

(i) 11.7, (ii) 1, (iii) 10.7, (iv) 1.92

- (iii) 12,
- (iv) 7.02,
- (v) 11.2

- **D-3.** 0.7
- **D-4.** (a) 13; (b) 7; (c) 1.3.

E-1. 1.69×10^{-5}

E-2. Refer class notes / sheet theory.

E-3. 11.7

E-4. HCI

F-1. (a) Basic

- (c) basic
- (d) basic
- (e) acidic
- (f) basic

(g) neutral

(D)

(B)

- (i) basic
- (i) acidic
- . .

F-2. 9

F-3. $K_b = 8 \times 10^{-10}$

(D)

F-4. 0.625%, pH = 7

(C)

PART - II

- **A-1**. (C)
- **A-2.** (D)

(b) acidic

(h) basic

- A-3.
- A-4.
- A-5.

- B-1.
- B-2.
- (A)

(C)

- **B-3.** (D)
- **B-4.** (D)
- **C-1**. (B)

(D)

- **C-2.** (C)
- D-1.
- D-2.
- **5** 7.
- **D-4.** (B)

- **D-5**. (B)
- D-6.
- (D)
- **D-2.** (A)
- **D-3.** (C)
- (-

- D-3. (L
- D-0.
- **D-7.** (D)
- **E-1.** (D)
- **E-2.** (D)

- E-3.
- **F-1.** (A)
- **F-2.** (A)
- **F-3.** (B)
- **F-4.** (B)

PART - III

1. (A) \rightarrow q; (B) \rightarrow s; (C) \rightarrow r; (D) \rightarrow p

EXERCISE – 2

PART - I

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

- **6.** (C)
- 7.
- (B)

(D)

- 8.
 - (A)



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ADVIEQ(M) - 31

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.
- **6.** 8
- **7.** 30

- **8.** 9
- 9.
- **PART III**

- **1.** (ABC)
- 2.
- (AC)

14

50

- (ABD)
- **4.** (ABD)
- **5.** (ABC)

- **6.** (BC)
- 7.
- (BCD)
- (AD)
- (._ ,
- **PART-IV**

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

EXERCISE - 3

JEE(MAIN) OFFLINE PROBLEMS

1. (4)

(1)

2.

7.

- (4) (3)
- 3. 8.
- (4)

(4)

(2)

- 4. 9.
- (1)

(1)

- 5.
- **10.** (4)

(2)

JEE(MAIN) ONLINE PROBLEMS

1. (4)

6.

- 2.
- (2)
- 3.
- 4
- (2)