Exercise-1

Marked Questions may have for Revision Questions.

OBJECTIVE QUESTIONS

Section (A) : Carbanions

A-6. Sol. (i) > (ii) > (iii) > (iv)







(+M) destabilising factor for carbanion [+M > +1]

Section (B) : Carbon free radicals & carbocations

- **B-2.** Sol. More electronegative atom release H⁺ ion easily.
- **B-3.** Sol. The geometry of a methyl carbocation and methyl carbanion is likely to be respectively planar & tetrahedral

>

OCH (+M)

- B-4. Sol. Combine effect of + I effect and hyperconjugation.
- **B-6.** Sol. $(1^*) \operatorname{CH}_3 \overset{\circ}{C} \operatorname{H}_2 1^\circ$ carbocation
 - (2) $CH_3 \overset{+}{C} H C_2 H_5$ 2° carbocation
 - (3) $(CH_3)_2 \overset{\circ}{C} H 2^\circ$ carbocation
 - (4) $(CH_3)_3 \stackrel{\prime}{C} 3^\circ$ carbocation
- B-8. Sol. Carbocation stability is depends upon +I effect and hyperconjugation.

B-10. Sol. Allyl carbocation ($H_2C=CH-CH_2$) is more stable than propyl carbocation due to resonance.

B-12. Sol. Aromatic carbocation is more stable than resonance stabilised carbocation and generally simple carbocation is less stable than resonance stabilised carbocation.

Section (C) : Tautomerism

 $\begin{array}{ccc} & & & & \\ & & & \\ R-CH-N & & \\ & & \\ & & \\ & & \\ C-3. & Sol. & H \end{array} \xrightarrow{OH} R-CH=N \xrightarrow{OH} OH$

 α –H atom is present which undergo enolisation.

C-4.

C-6.



9 σ bonds; 1 π bonds and 2 lonepairs.

Section (D) : Acidic strength

Sol.

- **D-1.** Sol. $K_a \propto$ stability of conjugate base \propto (–I, –m groups).
- **D-5.** Sol. $CH_3-CH_2-CH_2$ COOH > CH_3CH_2COOH > $CH_2=CH_-COOH$ > HC=C-COOH. (order of pKa)
- **D-6.** Sol. $K_a \text{ order } : (1) > (2) > (3) > (4)$
- **D-8.** Sol. $PhSO_3H > PhCO_2H > PhOH > PhCH_2OH$.
- D-9. The correct order of relative acidic strength of phenol, ethtyl alcohol and water is-
- **D-11.** Sol. I effect depends upon distance.
- **D-12.** Sol. + I effect increases, acidic strength of alcohol decreases. So, order is CH₃OH > CH₃CH₂OH > (CH₃)₂CHCH₂OH > (CH₃)₃COH
- **D-13.** Sol. Due to ortho effect ortho substituted benzoic acid is stronger acid than its other isomers as well as benzoic acid.
- **D-14.** Sol. $K_a \propto$ stability of conjugate base
 - \propto (–I, –m groups).

In the (iii) option ortho effect operates thus acidic nature increases

K_a ∝ la;qXeh {kkj dk LFkkf;Ro

 \propto (–I, –m lewg)

- (iii) fodYi esa vkWFkksZ izHkko dh mifLFkfr ds dkj.k vEyh;rk c<+ tkrh gSA
- D-15. Sol. Acid which has more than one –COOH groups.
- D-20. Sol. On the basis of stability of conjugate base due to electronic effects.
- D-21. Sol. Acidic strength is directly related to stability of conjugate base.

D-23.

0.N





Sol.

(Strong -I, -M effect of -NO2 group)

Section (E) : Basic strength

E-1. Sol. This is fact.

E-4. Sol. $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

In gas phase only I effect (electronic effect) operates.

- **E-5.** Sol. $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ In aqueous phase both I effect & sterric Hindrence (Due to solvation of conjugate acid) operates.
- **E-6.** Sol. $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ In aqueous phase both I effect & sterric Hindrence (Due to solvation of conjugate acid) operates.
- E-7. Sol. Basicity is inversely related to stability of anions.
- E-8. Sol. -I effect increases, basic strength decreases.
- E-10. Sol. Guanidine is strongest nitrogeneous base.



E-16. Sol. (1) Anionic bases are stronger than neutral bases and (2° Amine > 1° Amine > 3° Amine > NH₃)



E-17. Sol.

It does not have any lone pair of electrons to donate to H^o ion. blds ikl H^o dks nsus ds fy;s dksbZ ,dkdh bySDV^akWu ;qXe ugha gSA

Exercise-2

Marked Questions may have for Revision Questions.

PART-I OBJECTIVE QUESTIONS (TOUGH LEVEL)

- 1. Sol. Free radical is a paramagnetic in nature.
- 2. Sol. (1) Have not stabilization effect
 - (2) Only stabilized by resonance.
 - (3) Only stabilized by hyperconjugation.
 - (4) Stabilized by resonance and hyperconjugation.



General Organic Chemistry



Charge will disperse over maximum number of carbon.

- 11. Sol. $\overline{C}F_{3} < \overline{C}CI_{3}$ (due to $p\pi$ - $d\pi$ back bonding). $HC = \overline{C} > CH_{2} = CH^{\oplus}$ sp^{2} sp^{2} sp^{2} sp^{2} $sp^{2} > CH_{2} = CH^{\oplus}$ $sp^{2} > CH_{2} = CH^{\oplus}$ $sp^{2} > Sp^{3}$ $ch^{2} > CH_{2} = CH^{\oplus}$ $sp^{2} > Sp^{3}$ $ch^{2} > CH^{2} = CH^{\oplus}$ $sp^{2} > CH^{2} = CH^{\oplus}$ $sp^{2} > CH^{2} = CH^{\oplus}$ $sp^{2} > Sp^{3}$ $ch^{2} = CH^{2}$ $sp^{2} > Sp^{3}$ $ch^{2} = CH^{2}$ $sp^{2} > Sp^{3}$ $ch^{2} = CH^{2}$ $ch^{2} = CH^{2}$ $ch^{2} = CH^{2}$ $sp^{2} > Sp^{3}$ $ch^{2} = CH^{2}$ $sp^{2} > Sp^{3}$ $ch^{2} = CH^{2}$ $ch^{2} = CH^{2}$ $sp^{2} > Sp^{3}$ $ch^{2} = CH^{2}$ $sp^{2} > Sp^{3}$ $ch^{2} = CH^{2}$ $sp^{2} > Sp^{3}$ $ch^{2} = CH^{2}$ $sp^{2} = Sp^{3}$ $sp^{2} = Sp^{3}$ $sp^{2} =$
- **12. Sol.** $sp^3 \alpha$ -H absent.

16. Sol.
$$|V > || > | > ||$$

Structure IV is most acidic as the conjugate base is aromatic.

18.



Sol.

acidic order is 1 > 11. due to the presence of ortho effect on – COOH group

- Sol. -I; -M group increases acidic strength of phenol.
 While +I; +M group decreases acidic strength of phenol.
- **21. Sol.** I effect depends upon distance.
- 24. Sol. Salicylic acid is more acidic than p-hydroxy benzoic acid.
- **26. Sol.** On the basis of stability of conjugate base due to electronegativity.





Stability order of conjugate acids is P > R > Q > S. Hence basicity order is I > III > II > IV.

28. Sol. Aniline > m-nitroaniline > p-nitroaniline > o-nitroaniline



- **31. Sol.** Only in (4) the ℓ .p of N atom is not involved in resonance with benzene ring.
- A-1. Ans. (1)

30.

- **A-2. Ans.** (4)
- **Sol.** Conjugate base of maleic acid is stabilised by intramolecular H-bonding. No intramolecular H-bonding in conjugate base of fumaric acid.
- **A-3. Ans.** (1)



(due to H-bonding)

(gkbMªkstu ca/k ds dkj.k)

- **A-4. Ans.** (1)
- Sol. Self explanatory.
- **A-5. Ans.** (4)
- **Sol.** In (I) lone pair of N is delocalised but not in (II). After protonation of (I) positive charge cannot participate in resonance (follow octet rule)

Section (B) : dkWye dks lqesfyr dhft, (MATCH THE COLUMN)

B-1.

Sol.

Ans (A - r) ; (B - p) ; (C - s) ; (D - q)

B-2. (B)		(q)	4 × 10 ⁻⁴
(C)	NH ₃	(r)	4.6 × 10⁻ ᠀

	(D)	CH3 –CH2 – CH3	NH – (s)	10 × 10 ⁻⁴
Ans.	A→p	B→r	C→a	D→s

Section (C) : ONE OR MORE THAN ONE OPTIONS CORRECT

C-7. Sol.
$$(+I)$$
 $>$ $H - C - O$ $H = O$
 $CH_2 = CH^{\odot} sp^2 > H - C = C$ sp

Exercise-3

PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE-MAIN OFFLINE

- 1. Sol. Acetylene reacts with the other three as : $CH = CNa \xleftarrow{Na} CH = CH \xrightarrow{HCI} CH_2 \xrightarrow{HCI} CH_3$ ĊHCI, CHCI (AgNO₃+NH₄OH) $AgC \equiv CAg$ white ppt.
- 2. Sol. Except the amines containing tertiary butyl group, all lower aliphatic amines are stronger bases than ammonia because of + I (inductive). The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen there by increasing the availability of the lone pair of electrons to proton or lewis acids and making the amine more basic. Thus the relative strength is in order $(CH_3)_2 NH > CH_3NH_2 > NH_3$.
- Lone pairs of N are not taking part in conjugation whereas in other options lone pairs are taking 3. Sol. part in conjugation.
- 4. СООН СООН СООН СООН ·NO₂ NO. Sol.

E.W.G. increases the acidity of benzoic acid, o-isomer will have higher acidity than corresponding m and p isomer due to ortho effect.

6. Sol. Due to resonance of electron pair in aniline, basic strength decreases. In benzylamine electron pair is not involved in resonance.



Decreasing order of basic strength is 4 > 3 > 2 > 1.

- **Sol.** The order of stability of free radical is as follows:
- tertiary > secondary > primary.

Benzyl free radicals are stabilised by resonance and hence are more stable than alkyl free radicals. Further as the number of phenyl group attached to the carbon atom holding the odd electron increases, the stability of a free radical increases accordingly i.e.

 $(CH_3)_2 \dot{C}H < (CH_3)_3 \dot{C} < (C_6H_5)_2 \dot{C}H < (C_6H_5)_3 \dot{C}$

8. Sol. Effect of substituent on the acid strength of aliphatic acids.

(i) Acidity decreases as the + I - effect of the alkyl group increases.

(ii) Acidity decreases as the - I-effect decreases.

(iii) On the basis of given information the relative order of increasing acid strength of the given compounds:

(CH₃)₂ COOH < CH₃ COOH < CH₃ OCH₂COOH < CF₃COOH

9.

7.

Sol. The increasing order of basicity of the given compounds is

 $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$

Due to the +I effect of alkyl groups the electron density on nitrogen increases and thus the availability of the lone pair of electrons to proton increases and hence the basicity of amines also increases. So aliphatic amines are more basic than aniline.

In case of tertiary amine $(CH_3)_3$ N, the covering of alkyl groups over nitrogen atom from all sides makes the approach and bonding by a proton relatively difficult, hence the basicity decreases. Electron withdrawing (C_6H_5-) groups decreases electron density on nitrogen atom and thereby decreasing basicity.

Sol.

°c€

€c

ө Сн₂—





+I effect of 2 CH₃

+I effect of 3 CH₃

Strong –I effect of CI and bonding with vacant d-orbital -m effect of phenyl



11. Sol. Basicity \propto Electronegativity (In period)

If lone pair of electron takes part in conjugation then availability of lone pair of electron decrease and basic strength decrease.

12. Sol. α -chlorobutyric acid is more stronger acid than others due to – I effect of Cl.

13. Sol.
$$CH_3 - C - CH_2 - CH_3 \longrightarrow CH_3 - C = CH - CH_2 - CH_3$$



Therefore acidity order is :
$$D > C > A > B$$
.

15. Sol.

Cyclopentadiene does not obey Huckel's Rule, as it has sp3 carbon in the ring.

Sol.

$$\begin{array}{c|c} OH \\ \hline O \\ H \\ \hline O \\ NO_2 \end{array} > \begin{array}{c} OH \\ \hline O \\ CI \\ CI \end{array} > \begin{array}{c} OH \\ \hline O \\ CH_3 \\ CH_3 \end{array} > \begin{array}{c} OH \\ \hline O \\ OCH_3 \\ OCH_3 \end{array}$$

$$(-m, -I) \quad (-I) \quad (+I, +HC) \quad (+m) \end{array}$$

electron releasing group decreases and electron withdrawing group increases acidic strength.

17. Sol. The order of stability of carbocation will be $CH_{2}^{\oplus} > CH_{2}=CH-CH_{2} > CH_{3}-CH_{2}-CH_{2}$

18.

Sol. Order of basic strength of aliphatic amine in aqueous solution is as follows. order of K_b : $(CH_3)_2 \ddot{N}H > CH_3 \ddot{N}H_2 > (CH_3)_3 \ddot{N} > C_6 H_5 \ddot{N}H_2$ As we know $pK_b = -\log K_b$ so $(CH_3)_2 \ddot{N}H$ will have smallest pK_b value.

JEE-MAIN ONLINE





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

* Marked Questions may have more than one correct option.

- Sol. Acidic strength ∝ Dissociation constant of acid. In given acids order of acidic strength CH₃ CHFCOOH > CH₃CHBrCOOH > FCH₂CH₂COOH > BrCH₂CH₂COOH Hence in these smallest dissociation constant for BrCH₂ —CH₂COOH
- **2.** Ans. (a) (ii) (b) (iii) (c) (iv) (d) (i)(e) (v)
- Sol. As we know that acid strength of acid ∝ K_a. So higher the value of K_a, higher the acidic strength of acid.
 Strength of acid ∝ Rate of formation of proton or stability of conjugate base.
 In carboxylic acid, acidic character is due to resonance stabilization of their carboxylate ion, like in benzoic acid.

$$C_{6H_{5}-C} \overset{\bigcirc}{\underset{I}{\overset{\bigcirc}{\overset{\bigcirc}{}}}} \overset{\bigcirc}{\underset{C_{6}H_{5}-C}{\overset{\bigcirc}{\overset{\bigcirc}{}}}} \overset{\bigcirc}{\underset{H_{5}}{\overset{\bigcirc}{}}} \overset{\bigcirc}{\underset{H_{5}}{\overset{\bigcirc}{}}} \overset{\bigcirc}{\underset{H_{5}}{\overset{\bigcirc}{}}} \overset{\bigcirc}{\underset{H_{5}}{\overset{\bigcirc}{}}} \overset{\bigcirc}{\underset{H_{5}}{\overset{\bigcirc}{}}} \overset{\bigcirc}{\underset{H_{5}}{\overset{\frown}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\frown}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}{}}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}{}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}}} \overset{\frown}{\underset{H_{5}}{\overset{\bullet}}} \overset{\bullet}{\underset{H_{5}}{\overset{\bullet}}} \overset{\bullet}{\underset{H_{5}}} \overset{\bullet}{\underset{H_{5}}{\overset{\bullet}}} \overset{\bullet}{\underset{H_{5}}{\overset{\bullet}}} \overset{\bullet}{\underset{H_{5}}{\overset{\bullet}}} \overset{\bullet}{\underset{H_{5}}{\overset{\bullet}}} \overset{\bullet}}{\underset{H_{5}}{\overset{\bullet}}} \overset{\bullet}{\underset{H_{5}}}}$$

So, acidic strength order of the following acid is :

$$O_2N$$
 COOH>CI COOH> COOH>H₃C COOH>H₃CO COOH>H₃CO (+m)

- **3.** Sol. Acidity of hydrogens $-COOH > PhOH > -C \equiv C-H$ (also NO₂ group increases acidic strength) hence if only two moles of base is taken then H[⊕] will come out from -COOH and PhOH.
- **4. Sol.** –COOH is stronger acid than $-\widetilde{NH}_3$ and –I group increases acidic strength.





- **Sol.** (I) +m effect of 'O' and hyperconjugative effect of 2-CH_3 groups. (II) is a simple 2° -carbocation
 - (III) +m effect of 'O' and hyperconjugation of one –CH₃ groups.
 - (IV) is a simple 1º-carbocation.



8.

Sol.

7.

More stable conjugate base (carboxylate anion, -ve charge always on oxygen atom).



More stable conjugate base (carboxylate anion, -ve charge always on oxygen atom). + I and hyperconjugative effect of $-CH_3$ group decreases stability of benzoate anion.



Less stable conjugate base (phenoxide ion is less resonance stabilized than benzoate anion). –Cl group exhibits – I effect.



Less stable conjugate base (phenoxide ion is less resonance stabilized than benzoate anion).

9.

Sol.



(More stable carbocation due to +m effect of - OH group and + I and hyperconjugative effect of -CH₃ group)

10. Ans. 2

Sol. – NH₂ and $-COO^{\Theta}$ are two basic groups.





Due to intramolecular hydrogen bonding in conjugate base of o-Hydroxybenzoic acid, it is strongest acid.

14.

Ans. (A)

Sol. Due to ortho effect, ortho substituted benzoic acid is more acidic than meta & para isomers.

Due to strong hydrogen bond in conjugate base of ortho hydroxybenzoic acid, it is more acidic than its meta & para isomers.

or





(III) Least basic, as the LP is used in aromaticity.

APSP Solutions

PART I

- **1.** I effect increases the K_a value or H⁺ ion concentration.
- 2. Order of radical stability : Resonance > Hyperconjugation > +Inductive effect
- $\textbf{5.} \qquad \textbf{K}_{b} \, order: II > I > III$
- 6. On the basis of stability of conjugate base due to electronic effects.



- **17.** 1,2–Deuterium shift forms most stable carbocation intermediate by increase in distance with –I and –m group.
- 20. K_a order is : I < II < III Hence, pK_a order is : III < II < I
- **22.** III > II > I

The basicity order is inversaly related to delocalisation of lone pair.

- 24. On heterolysis of propane carbocation and carbanion is formed.
- **25.** H_3N^{\oplus} (CH₂)₂ COOH has strongest acid due to strong –I effect of $-NH_3$.